INTERACTIONS BETWEEN PLASTICISED PVC FILMS
AND CITRUS JUICE COMPONENTS

Thesis submitted for the degree of Doctor of Philosophy
in Advanced Food Science (& Food Packaging Science)
in the Centre for Advanced Food Research, University of Western Sydney,
Hawkesbury, Richmond, NSW, Australia.

By
STÉPHANE CLAUDE FAYOUX

December, 2004
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AND CITRUS JUICE COMPONENTS

A contribution to the comprehension of a new debittering process
for Navel orange juice
INTERACTIONS BETWEEN PLASTICISED PVC FILMS AND CITRUS JUICE COMPONENTS

STÉPHANE CLAUDE FAYOUX

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RICHMOND, NSW, AUSTRALIA.
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DECLARATION

This is to certify that the work presented in this thesis has not been submitted to any other university or institution for a higher degree.

Stéphane C. Fayoux
FOREWORD

(including a presentation of the papers associated with the research)
FOREWORD

Preliminary work for this Ph.D. started at the University of Burgundy’s ‘Higher’ National School of Food Engineering and Nutrition (ENS.BANA), Dijon, France – Prof. A. J. Voilley – in 1996. It consisted in reviewing the extensive literature on food and packaging interactions and studying the sorption of d-limonene (liquid phase) by packaging plastics (cf. Appendices for more information).

It continued then at the School of Packaging of Michigan State University, East-Lansing, MI, USA - Assoc. Prof. R. J. Hernandez and Late Prof. J. R. Giacin -. The aim was to study the debittering of Navel orange juice by sorption of limonin, the bitter principle; many packaging plastics were investigated (this project was initiated a year before by Late Dr. R. L. Johnson during my short research period in CSIRO, now Food Science Australia).

Finally, since 1998, the thesis could be finalized at the University of Western Sydney, Hawkesbury, Richmond NSW, Australia – Assoc. Prof. J. Hourigan and Dr. R. V. Holland from CSIRO –. More fundamentally, it was possible to screen the effect of the structural differences of many hydroxylated and aromatic compounds in particular on their mass transfer properties. Associated plasticiser migration issues were studied.

Such work should contribute to better understand the orange juice / plastic liner interactions that occur during debittering, but it is also believed to contribute in many ways to the scientific community interested in understanding such food or even non food packaging interactions.
PRESENTATIONS AND PAPERS ASSOCIATED WITH THE RESEARCH

The work concerning the sorption of d-limonene from an orange juice model solution by plasticised poly(vinyl chloride) films, and that is not included in the thesis, remains associated to it as an essential prior-investigation: it was presented orally in partial fulfillment of the Superior Diploma of Research Studies (D.S.E.R.), at the Superior National School of Food Process Engineering and Nutrition (ENS.BANA), Université de Bourgogne, 1996, Dijon, France. It was awarded higher distinctions (cf. summary Appendix A).

The literature review and food packaging interaction theories presented in Chapters 1a and 1b, have been received with congratulations from the editor Prof. Frank Paines and published in Packaging Technology and Science, Vol. 10, pp. 69-82 and 145-160 in 1997 (Fayoux, S.C., Seuvre, A.-M., and Voilley, A.J.).

In the meantime, a collaborative work was presented as poster for “Packaging Beyond 2000” at the 10th International Association of Packaging Research Institutes (IAPRI) World Conference on Packaging, between March, 24th and 27th, 1997, Melbourne, VIC, Australia. It was entitled “Active Packaging - Debittering Orange Juice” (Jiang, X., Fayoux, S., Holland, R.V., Johnson, R.L., and Santangelo, R.). It was published in the proceedings.

The results of the study as detailed in Chapter 2 were presented orally during the Food Packaging Technical Session 77 of the Institute of Food Technologists (IFT) Annual Meeting & Food Expo, on June, 18th, 1997, Orlando, FL, USA. It was entitled
“The use of plastic materials for debittering citrus juices” (Fayoux, S., Hernandez, R.J., and Giacin, J.R.). The abstract was published in the proceedings and audio recording is available.

Part of the results as detailed in Chapters 3, 4 and 5 was used and commented during the poster presentation at the Australian Institute of Food Science and Technology (AIFST) Annual Conference, on March, 29th, 1998, Melbourne, VIC, Australia. It was entitled “Lost your Flavours ? Study of the influence of various physico-chemical characteristics of vanillin and a homologous series of alcohols on their diffusion into plasticised poly(vinyl chloride) plastic films” (Fayoux, S., Holland, R.V., and Hourigan, J.).

Chapters 2, 3, 4, and 5 are subject to publication in various international refereed journals, respectively the Journal of Food Science, Packaging Technology and Science, International Journal of Food Science and Technology, and Food Additives and Contaminants, explaining their different writing styles.
ACKNOWLEDGEMENTS

I am grateful to Associate Professor Jim A. Hourigan, chairman of the thesis panel, who efficiently oriented the original raw debittering project into an attractive Ph.D. research piece of work.

I am indebted to three peers: Dr. Robert V. Holland (member of thesis panel) who patiently helped for the design of experiments & the (re)writing of the thesis, the late Dr Robert L. Johnson (initially * member of thesis panel) who gave me much advice on the overall citrus debittering issue as well as the initiator of this research, Dr Bruce Chandler.

Thanks also to Professor Andrée J. Voilley and her research team who taught me the basics of mass transfers and molecular interactions (in particular Dr. Frédéric Debeaufort). My gratefulness goes to the late * Professor Jack R. Giacin and Associate Professor Ruben J. Hernandez who gave me the opportunity to perfect my understanding of polymers and shared my willingness to investigate the solubility parameters theory for sorption prediction.

I really appreciated the scientific guidance of Dr. Alexandre Feigenbaum (LNSA, INRA, Reims, France) all along this project.

Finally, I would like to express my gratitude to a number of people who in one way or another made this study possible: there are the technical staff (Professors, lecturers, secretaries, etc) of all institutions and departments I have been during this work, for their valuable assistance, as well as all my friends for their great support.
(Flatmates, research team friends, from France, Australia and many others countries of all continents…).

I would like to express my appreciation to Sunkist Growers, Inc., Ontario, California, U.S.A. who generously donated many litres of concentrated bitter Navel orange juice for my study. Similarly Monsanto, St. Louis, Missouri, U.S.A., is acknowledged for generously supplying many plasticiser samples.

To my mother Geneviève Fayoux, my father Dr. Claude Fayoux and my brother Olivier Fayoux whom I dedicate this work for their courage and trust, patience and support, and especially for financing the totality of the living and travel expenses during five years spent in three different countries.

Special thanks are also due to DEETYA (Department of Education, Employment, Training and Youth Affairs of Australia) for giving me this chance and for contributing four years of OPRS Ph.D. enrollment fees (Overseas Postgraduate Research Scholarship Award).

* deceased before thesis completion.
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SUMMARY OF THESIS
SUMMARY OF THE THESIS

The study presented here consists in an original piece of work to better understand complex food packaging interactions.

The majority of investigations on food polymer interactions related to orange juice and this provided a good base to our study (Literature reviews: cf. Chapters 1a and b).

Additionally a rather remarkable finding in 1994 was that limonin, a trace bitter material found in some varieties of orange juice was rapidly absorbed by highly plasticised polyvinyl chloride (PVC plastisol) (Chapter 2).

Several commercial absorbants are available for debittering, relying on limonin absorption on the large surface area of the highly porous absorbant pellets. However, the absorptive properties of the smooth plastisols apparently relied on a different mechanism. Limonin is a very large (470.5 g/mol) compound, but some preliminary experiments with another much smaller orange juice constituent d-limonene (136.2 g/mol) indicated a similar rapid uptake.

Because of the uniquely rapid uptake of absorbates in plastisols, methods used earlier (Moisan 1980, Holland and Santangelo 1988) to measure solubilities and diffusion constants in packaging films could be advantageously used to survey these properties in a wide range of materials, including model compounds of various types,
and a number of compounds which may be found in citrus juices (Chapters 3, 4 and 5).

Experimentally, the method found most suitable was to use a ‘test film’ of pure plastisol which was wrapped tightly on both sides by a similar ‘supply film’ blended with 1 Molar test material (also called ‘absorbate’), setting up a concentration gradient. The inner test film was removed at regular intervals (minutes to hours) to measure (mainly by weighing) the uptake of the test reagent with time.

Rather unexpectedly, it was found in a number of cases that the test film lost weight, either from the beginning, or after a period of time. Three main types of behaviour were identified: Type A lost weight from the beginning and over a long period of time, Type B gained weight initially and then lost weight, and Type C gained weight until a steady state was reached. Often the maximum, or near maximum, mass increase occurred within around 100 minutes, indicating a very rapid, liquid-like diffusion mechanism, in harmony with the rapid uptake of d-limonene and limonin. The major parameters of interest with these compounds are their diffusion rates and their solubilities, and in the presence of aqueous media (orange juice and other foodstuffs) the partition coefficient between the plastisol and water, which is related to the hydrophobicity function LogP for the compound.

The major complicating factor in these measurements is the observation that the plasticiser materials themselves also migrate, in the reverse direction, because of the lower effective concentration in the supply film. This effect tends to be small, but is
one explanation for the mass loss observed above, and cannot be ignored over the long

term, nor in its practical applications to contamination in foods.

There are many possible applications for the techniques described above. The
removal or addition of compounds in food packaging itself is one. Upgrading foods,
such as orange juice, commercially, is another. In many cases ‘scalping’ off-flavours
or other minor components takes place exclusively through solid or liquid contact
with the packaging. The removal from the headspace measured by the current gas
permeation methods is irrelevant for the vast numbers of involatile, but easily
diffusible compounds. For such compounds these novel applications are simple and
rapid, require little specialised equipment, and fill a niche in the armoury of food and
packaging chemists.
INTRODUCTION
INTRODUCTION

The study presented here aims to improve a process to debitter Navel orange juice following the principle of the sorption on polymers, and to provide additional understanding of the process by studying the interactions between various polymeric - packaging - materials and a number of model food components.

The basics of food and packaging interactions is reviewed first (Chapters 1a and b) with a focus on d-limonene, a major aroma constituent of orange juice; emphasis is put on the type of polymer (from polyolefins to complex laminates) and on the analytical technique (eg. ‘headspace’ method). In Chapter 1a, d-limonene sorption, diffusion and permeation coefficients are tabulated but few cross-comparisons are possible because of the discrepancies in the experimental conditions of the literature. The development of off-flavours and flavour scalping are also discussed, as well as the influence of synergistic effects with other aroma compounds and with plasticisers. In Chapter 1b, many orange juice aroma compounds are reviewed: influence of chain length, boiling points, polarities of the absorbed compounds, of their functional groups, solute interaction, polymer types and degree of plasticisation, are discussed under a range of temperature, humidity and storage conditions. Attempted sorption predictions are presented together with the theoretical tools (eg. solubility parameters) and thermodynamical equations.

The experimental investigation begins in Chapter 2 with a comparison of the sorption of the bitter compound limonin by various materials (Limonin occurs
excessively in some commercial citrus products, and reducing its concentration is essential for customer acceptance.). It turns out that highly plasticised poly(vinyl chloride) (PVC) is more efficient than the styrene di-vinyl benzene resins currently used in the industry. The influence of the type of plasticiser on sorption is discussed. Its migration into Navel orange juice is described but more theoretical considerations on diffusion of plasticisers are needed: they are addressed in Chapters 4 and 5. Some reasonable but limited limonin sorption understanding, on the basis of Fick’s law, is proposed, and further discussed in Chapters 3 and 4.

Since limonin is a large molecule, with several functional groups, it was decided therefore in Chapters 3, 4, and 5, to simplify the study by using low molecular weight mono-functional compounds as models.

Consequently Chapter 3 is first devoted to the measurement of the sorption of a limited range of such compounds (eg. octanol and vanillin) by gravimetry and/or spectrophotometry in order to compare two sorption techniques: ‘headspace’ versus ‘laminate’. This Chapter is particularly focused on the assessment of the ‘laminate’ technique developed at CSIRO (Food Science Australia) for quickly measuring mass transfers in situ in ordinary packaging films. No work had been done on very plasticised polymers however (up to 40% of plasticiser in our case), and there were a number of problems to be overcome (plasticiser migration, calibration of techniques). In Chapter 3 a fresh theoretical basis for interpreting the data is then worked out as sorption were more complex but also more rich in information than expected. Finally, an attempt is made to calculate the sorption and diffusion coefficients.
In Chapters 4 and 5 a wider variety of permeants of various size and shape (also called ‘absorbates’), mostly of interest to the food industry (flavours, vitamins, antioxidants, solvents and other contaminants), was chosen to test, and possibly to confirm or refine the theories of the sorption in highly plasticised PVC which have emerged along the preceding study (Chapter 3).

On one hand (Chapter 4) a range of C$_6$ hydroxylated compounds (alcohols, phenols and isomers) is investigated as simple model systems by using the laminate technique. Three types of sorption kinetics are reported and discussed: vapour pressures (and boiling points) and calculated solubility parameters (estimating ‘absorbate’/plastisol molecular interactions) are used in an attempt to explain the three kinetic shapes. Prediction of those sorption patterns is also attempted.

On the other hand Chapter 5 is intended to provide a wider survey, leaving individual compounds to be examined more closely later: with a focus on citrus juice components, the sorption of ‘absorbates’ is monitored by the same laminate technique. In addition to the number of physico-chemical parameters selected in the previous Chapter, the better known octanol-water partition function (Log P$_{o/w}$) is introduced: the three sorption patterns are still observed and better interpreted, and the occurrence of the sorption anomalies is more precisely defined (eg. evaporation, plasticiser migration, over-plasticisation).

The relevance of such theoretical work (Chapters 3 to 5) to the early limonin work (Chapter 2) is to look for reasonable interpretation of the ‘mysterious’ debittering of Navel orange juice by plasticised plastics and of its contamination by the plasticiser. The prediction and optimization of that process strongly depends on this primary research stage.
CHAPTER 1.A

LITERATURE REVIEW

« The Effects of Packaging on the Organoleptic Quality of Citrus Juices »

AROMA TRANSFERS IN AND THROUGH PACKAGINGS:

ORANGE JUICE AND D-LIMONENE. A REVIEW.

PART I : ORANGE JUICE AROMA SORPTION
Aroma Transfers in and through Plastic Packagings: Orange Juice and \textit{d}-Limonene. A Review. Part I: Orange Juice Aroma Sorption

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Nowadays, the quality of foodstuffs has more than ever included the notion that packaging contact is not always wholesome. It can alter the packaged food product by flavour scalping and can also affect the food by off-flavour release. Much research has been carried out to better understand the mass transfers involved with various synthetic polymeric films.\textsuperscript{2}

Orange juice and one of its major volatile constituents, \textit{d}-limonene, were probably amongst the first food products to be thoroughly studied. Yet, no extensive literature review has been undertaken in order to obtain a general and accurate description of the sorption and diffusion phenomena.

This review underlines the effects of packaging on the organoleptic quality of citrus juices; it therefore presents a focused interest on \textit{d}-limonene mass transfer experimental results with a variety of plastic polymers.

Part I deals with first, loss of organoleptic quality of orange juice during storage and \textit{d}-limonene sorption is discussed. Second, generalities are presented concerning volatiles transfer measurements and two tables summarise the experimental \textit{d}-limonene sorption, diffusion and permeation results we could obtain easily, after which we offer our comments. © 1997 by John Wiley & Sons, Ltd.


Keywords: packaging; plastics; \textit{d}-limonene; sorption; diffusion; permeation; aroma compounds; citrus; thermodynamics

INTRODUCTION

It is well known in the food packaging industry that minimising plastic package/-
product interactions has become an unfilled need. The sorption of food constituents, especially aromatic compounds, by polymeric materials, can cause, firstly, the food to end up with an unbalanced flavour profile and, second, a further desorption of undesirable flavours from the polymer (LDPE, PET, PC, etc.) into the next product packaged may take place. The latter was observed with PET refillable bottles when sorbed aroma compounds were not totally removed during washing. The first phenomenon is called flavour scalping and can lead, by diffusion and desorption steps, to movement (migration) out of the container of organoleptically important aroma compounds (Figure 1).

Off-flavours also appear after any unwanted migration into the product because the packaging barrier properties are not adapted.

Most research has been focused on aroma compounds, especially d-limonene, which appeared to be the most common when the first packaging research interests were pointed out by the industry. Its wide occurrence in orange juice, one of the most world-wide commercialised products, has occupied many researchers in the understanding of mass transfers through polymeric films. Experience in mastering plastic technology and the arrival of plastic bottles and aseptic packs, such as BrikPak or Comibloc, have increased the need for knowledge of sorption of citrus compounds into the polymer in contact with the juice (polyethylene liner in both BrikPak and Comibloc). Accurate description of the mass transfer behaviour of limonene/barrier systems must also consider permeation mechanisms for the prediction of changes in the quality of the packaged product, i.e. both sorption and diffusion.

Loss of organoleptic characteristics during storage have been commonly observed: the retention of citrus aroma compounds during storage of orange juice was reported in 1971. Mannheim and Havkin and Gherardi et al. showed that the shelf-life of juices in plastic lined carton packs is half that in glass jars and is usually not more than 3–4 months at ambient storage temperature. Dürre et al. reported significant losses of d-limonene, neral, geranial, octanal and decanal from orange juice stored in carton packs. Moshonas and Shaw noticed significant reduced flavour scores using a sensory panel for a commercial orange juice stored for 6 weeks in flexible multilayer
cartons. Marshall et al.\textsuperscript{17} and Mannheim et al.\textsuperscript{18} reported agreeable results. Flavour changes were particularly noticeable in 100% orange juice.\textsuperscript{10,17} Pieper et al.\textsuperscript{20} however, observed that a reduction of up to 50% of d-limonene into the LDPE (low density polyethylene) inside coating of commercial cartons did not affect orange juice sensory characteristics. Also, orange juice semi-concentrates in PP (polypropylene) were stable for up to 6 months storage at 20–33°C as far as their physico-chemical characteristics are concerned.\textsuperscript{21} Finally, the overall impact of flavour–package interaction has also been assessed on orange juice quality by Sadler et al.,\textsuperscript{22} whereas the interaction impact on vitamin C, colour, iron and calcium have been measured by Kenawi et al.\textsuperscript{23}

Previous observations have sometimes been contradictory because flavour alteration depends on many parameters, in particular on the type of polymer in contact. Orange juice flavour change is noticed because of the unequal intensity of sorption of each aroma compound leading to an unbalanced flavour profile. To simplify, often only the organoleptically important aroma compounds have been investigated. For instance, it must be noted that, as aldehydes have been shown to have a very desirable effect on orange flavour\textsuperscript{24} and because d-limonene is a known solvent and can act as a carrier of other components into the amorphous regions of polymers,\textsuperscript{25} d-limonene mass transfer characteristics need more than ever to be compiled and during deterpenation\textsuperscript{26,27} the d-limonene may carry other aroma compounds with it.\textsuperscript{28}

The deterpenation of citrus oils is quite common because terpenes like d-limonene generally have no olfactive or taste value\textsuperscript{29} and they are reactive oxidisable compounds.\textsuperscript{30} The sorption or migration out of the package of d-limonene is comparable with deterpenation and it is believed to serve the consumer. Hence, several studies have shown loss of d-limonene to be of little importance on taste\textsuperscript{20,31} and many investigators have indicated that d-limonene sorption can be beneficial for the product since it can act as a precursor for off-flavours, forming α-terpineol in orange juice.\textsuperscript{9,16,32} Blair et al.\textsuperscript{33} suggested that d-limonene undergoes a series of hydration–dehydration reactions, producing α-terpineol, 1,4-cineole and other products, during storage at room or higher temperatures.\textsuperscript{34} For instance, α-terpineol contributes a stale, musty or piney aroma in aged canned orange juice.\textsuperscript{34} Indeed it has a typical lilac odour and a sweet taste reminiscent of peach on dilution.\textsuperscript{30}

\textit{Is d-limonene flavour scalping an advantage?} A certain amount of terpenes must be left in the oil to retain the characteristic freshness of citrus flavour;\textsuperscript{15} d-limonene at 120–200 p.p.m. is also required in orange juice for acceptable flavour and mouthfeel.\textsuperscript{32} Above its sensory threshold, d-limonene is considered as a flavour defect.\textsuperscript{36} In general, d-limonene flavour scalping is believed to be a rather wanted phenomenon, although limonene could also carry other organoleptically important citrus compounds with it and Kim et al.\textsuperscript{37} stressed that its antimicrobial potency was better conserved in d-limonene-impervious citrus juice cartons.\textsuperscript{38} It may also have cancer chemoprevention effects.\textsuperscript{39} However, being more easily oxidised in orange juice than when absorbed by a polyethylene polymer,\textsuperscript{32} efforts to hinder flavour scalping may be detrimental to final flavour quality.

Table 1 summarises the pros and the cons as far as d-limonene scalping from orange juice is concerned.
Table 1. Benefits and drawbacks of d-limonene scalping in orange juice

<table>
<thead>
<tr>
<th>Benefits of scalping</th>
<th>Drawbacks of scalping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-flavours (α-terpineol) removal\textsuperscript{9,16,32,34} due to oxidation (easy in orange juice, not in polyethylene\textsuperscript{32}) and other chemical reactions\textsuperscript{33}</td>
<td>Loss of the characteristic freshness of citrus flavour,\textsuperscript{35} of the typical orange flavour and mouthfeel\textsuperscript{32} as limonene is a possible flavour carrier and solvent\textsuperscript{38} and facilitates sorption of other volatiles</td>
</tr>
<tr>
<td>d-Limonene has no olfactory nor taste value (deterpenation)\textsuperscript{20,29-31}</td>
<td>Reduction of the natural orange juice antimicrobial activity\textsuperscript{37,38} and cancer chemoprevention potentialities\textsuperscript{39}</td>
</tr>
</tbody>
</table>

MASS TRANSFER OF VOLATILES

Measurement

In order to assess these transfers, many different common apparatus have been used depending on the data sought and on the laboratory facilities available. Back to basics, by combining Henry's law

\[ C = Sp \]  

(1)

with Fick's law

\[ J = -D \frac{\partial C}{\partial x} \]  

(2)

the steady state permeation flux \( J \) through a membrane of thickness \( l \) is given by equation 3

\[ J = SD\Delta p/l = P\Delta p/l \]  

(3)

So the general transfer equation arises

\[ P = DS \]  

(4)

the diffusion coefficient \( D \) being assumed independent of the concentration of the penetrant.

\( C \) is the penetrant concentration in the polymer, \( S \) the absorption coefficient, \( p \) the pressure of the volatile, \( D \) the diffusion coefficient, \( \partial C/\partial x \) the concentration gradient and \( \Delta p \) the pressure difference between the two faces of the membrane and \( P \) the steady state permeability. Permeation \( P \) is generally measured as such or via measurements of both the diffusion \( D \) and the sorption \( S \) coefficients. The latter is obtained either by directly assaying the polymer (weighing method,\textsuperscript{40,41} conventional solvent or supercritical carbon dioxide extraction, purge-and-trap method\textsuperscript{42,43}) or indirectly by measuring exhaustion of the compound from the surrounding...
environment (vapour or liquid) by gas$^{44-46}$ or liquid chromatography,$^{47,48}$ often coupled with mass spectrometry$^{49-51}$ or olfactometry.$^{11}$

Permeability parameters can then be calculated. However, as mentioned by Nielsen and Jägerstad,$^1$ it is paramount to define the subsequent way of expressing the extent of sorption of limonene by polymers as has been described many times by very different ratios. As for diffusion and permeation, units are generally coherent between investigators: the following two tables show how inhomogeneous are the units and experimental conditions used by investigators and compile all available data we could gather on limonene mass transfer. Table 2 concerns sorption of limonene in both the vapour and aqueous phases, whereas Table 3 presents some diffusion and permeation results obtained mostly in the vapour phase.

Before proceeding to comment on the mass transfer results of $d$-limonene through plastic packagings, it is useful to have a few data on the molecule itself:

- $d$-limonene, $C_{10}H_{16}$;
- molecular weight, 136.23;
- boiling point (d.l form): 176–178°C;
- volume, $22.8 \times 10^{-3}$ nm$^3$;
- insoluble in water but miscible with alcohol;
- its saturated vapour pressure at 25°C 3000 p.p.m.$^{52}$ or 1.5 mm Hg.$^{53}$

It is the most important and widespread unsaturated terpene hydrocarbon, at amounts up to 90–95% in lemon, orange and mandarin oils;$^{54}$ it has a typical lemon-like odour.$^{50}$

Because of the availability of $d$-limonene (hereafter referred to as limonene) it has become the most extensively studied aroma compound with respect to its sorption by polymers; its rather good hydrophobicity allows easy sorption by many synthetic polymeric materials, especially non-polar polyolefins. Packaging materials–limonene interactions were stressed as greatly affecting the quality aspects of fruit juice processing and packaging by Rysstad et al.$^{55}$

Amongst all experimental results presented (Table 2), those obtained with orange juice products should give a true view of the actual limonene sorption that takes place in bottles or packages during storage. Starting with polyolefins, for polyethylene polymers Charara et al.$^{56}$ measured a 54% loss of $d$-limonene at 23°C in spiked orange juice with terpeneless oil; sesquiterpene loss reached 40%, whereas aldehydes were only sorbed 1–30% for undecanal; LDPE had the highest absorption value, followed by Surlylon$^\text{TM}$, PP and HDPE (Table 2). Dürr et al.$^9$ also reported a rapid loss of $d$-limonene (40% over 90 days at 20°C) and other citrus aroma volatiles into the PE lining of flexible packages. Some other experiments show a decrease ranging from 25 to 80% in LDPE.$^{17,18,20,57,58}$

As far as other polymers are concerned [EVOH and PET, e.g. co-polymers of ethylene vinyl alcohol and poly(ethylene) terephthalate respectively], it was found that orange juice lost 41% of its total limonene content to LDPE but only 18% to EVOH$^{59}$ (Table 2), mostly because of its higher polarity; in PET, no detectable limonene was sorbed. However, in orange flavoured soft drinks, small amounts of limonene were effectively sorbed by PET.$^4$ Along the same lines, in PET bottles Nielsen$^5$ (Table 2)
<table>
<thead>
<tr>
<th>Name</th>
<th>Reference</th>
<th>Type</th>
<th>Weight</th>
<th>Penetrant characteristics</th>
<th>Quantity of juice or limonene vapour concentration and comments</th>
<th>T/°C</th>
<th>Time of contact</th>
<th>Sorption results</th>
<th>Respective units used</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE 18</td>
<td>Film, surface to volume ratio = 2.7:4</td>
<td>50 cm²</td>
<td>NA</td>
<td>Reconstituted orange juice and model solutions</td>
<td>NA</td>
<td>25</td>
<td>&gt;3 weeks</td>
<td>30-50%</td>
<td>mg/l at time t/mg/l at start</td>
</tr>
<tr>
<td>LDPE 41</td>
<td>Normal film; linear (LLDPE) film</td>
<td>50 cm²</td>
<td>NA</td>
<td>Saturated limonene vapour</td>
<td>0.719 mg/l in 17.8 ml tubes</td>
<td>25</td>
<td>24 h</td>
<td>3.46 × 10⁻³</td>
<td>(g limonene/g structure)/p.p.m. limonene</td>
</tr>
<tr>
<td>LDPE 56</td>
<td>Beads</td>
<td>3.4 g</td>
<td>500 ml</td>
<td>Reconstituted orange juice, added terpenes oil (12° Brix)</td>
<td>23</td>
<td>4 days</td>
<td>54%</td>
<td>(area sample − area control)/area original oil × 100</td>
<td></td>
</tr>
<tr>
<td>LDPE 59</td>
<td>Film, 41.9 μm</td>
<td>258.1 cm²</td>
<td>Orange juice and antioxidants</td>
<td>176 mg/l limonene, 260 mg/l juice</td>
<td>22 ± 2</td>
<td>24 days in contact (3-6 days for equilibrium)</td>
<td>61%</td>
<td>(Kp = 16.37)</td>
<td></td>
</tr>
<tr>
<td>LDPE 63</td>
<td>Powder</td>
<td>40 mg</td>
<td>Mixture of solutes in aqueous solution (including limonene)</td>
<td>1000 p.p.m. in 2 ml tubes</td>
<td>23</td>
<td>25 days (equilibrium)</td>
<td>61%</td>
<td>(Kp = 79)</td>
<td></td>
</tr>
<tr>
<td>LDPE 64</td>
<td>Disks, 650 μm</td>
<td>0.6-10 g</td>
<td>Aqueous solution of limonene in ethanol</td>
<td>12-100 p.p.m. in 125 ml liquid</td>
<td>6, 23 &amp; 38</td>
<td>12 to &gt;72 h</td>
<td>3400</td>
<td>Unitless</td>
<td></td>
</tr>
<tr>
<td>LDPE 60</td>
<td>Film, 20 μm, 0.923 g/ml</td>
<td>20-30 mg</td>
<td>Pure limonene vapour under nitrogen flow</td>
<td>0.5 cm³ flask</td>
<td>25</td>
<td>Equilibrium state attained?</td>
<td>0.0208</td>
<td>g flavour/g amorphous polymer</td>
<td></td>
</tr>
<tr>
<td>LDPE 65</td>
<td>Film</td>
<td>NA</td>
<td>Aqueous solution of limonene in methanol</td>
<td>35 ml vial</td>
<td>23 ± 0.5</td>
<td>NA</td>
<td>38</td>
<td>(value recalculated in water) in g/cm³ bar</td>
<td></td>
</tr>
<tr>
<td>HDPE 36,66</td>
<td>Film, 48 μm</td>
<td>93 cm²</td>
<td>Limonene into FEG400</td>
<td>Headspace vapour phase = 0.1 μm/l + 0.018 mbar</td>
<td>23</td>
<td>Up to 1000 h</td>
<td>43</td>
<td>g/cm³ bar, determined from permeation measurements (cell)</td>
<td></td>
</tr>
<tr>
<td>HDPE 41</td>
<td>Film</td>
<td>50 cm²</td>
<td>Saturated limonene vapour</td>
<td>0.719 mg/l in 17.8 ml tubes</td>
<td>25</td>
<td>24 h</td>
<td>2.7 × 10⁻³</td>
<td>(g limonene/g structure)/p.p.m. limonene</td>
<td></td>
</tr>
<tr>
<td>HDPE 56</td>
<td>Beads</td>
<td>3.4 g</td>
<td>Reconstituted orange juice, added terpenes oil (12° Brix)</td>
<td>500 ml (stirred)</td>
<td>23</td>
<td>4 days</td>
<td>22%</td>
<td>(area sample − area control)/area original oil × 100</td>
<td></td>
</tr>
<tr>
<td>HDPE 36</td>
<td>Powder</td>
<td>40 mg</td>
<td>Mixture of solutes in aqueous solution (including limonene)</td>
<td>1000 p.p.m. in 2 ml tubes</td>
<td>23</td>
<td>25 days (equilibrium)</td>
<td>43%</td>
<td>(Kp = 35)</td>
<td></td>
</tr>
<tr>
<td>HDPE 65</td>
<td>Film</td>
<td>NA</td>
<td>Aqueous solution of limonene in methanol</td>
<td>35 ml vial</td>
<td>23 ± 0.5</td>
<td>NA</td>
<td>26</td>
<td>(value recalculated in water) in g/cm³ bar</td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Reference</td>
<td>Type</td>
<td>Weight comments</td>
<td>Penetrant characteristics</td>
<td>Quantity of juice or limonene vapour concentration and comments</td>
<td>T/C</td>
<td>Time of contact</td>
<td>Sorption results</td>
<td>Respective units used</td>
</tr>
<tr>
<td>------</td>
<td>-----------</td>
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<td>--------------------------</td>
<td>---------------------------------------------------------------</td>
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<td>----------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>PP</td>
<td>52</td>
<td>Film 30 μm SCB= BOPP Beads</td>
<td>NA</td>
<td>Saturated limonene vapour</td>
<td>19 p.p.m.</td>
<td>25</td>
<td>NA</td>
<td>510</td>
<td>g m⁻¹ N⁻¹</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>Powder</td>
<td>3.4 g</td>
<td>Reconstituted orange juice, added terpeneless oil (12° Brix)</td>
<td>500 ml (stirred)</td>
<td>23</td>
<td>4 days</td>
<td>36%</td>
<td>(area sample – area control)/area original oil × 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Powder, d=0.9017 g/ml, d=0.9045 g/ml</td>
<td>40 mg</td>
<td>Mixture of solutes in aqueous solution (of which limonene)</td>
<td>200 p.p.m.</td>
<td>23</td>
<td>4 hours</td>
<td>92% (NA)</td>
<td>Per cent HPLC peak area (sorbed), (Kₛ) in conc. of solute in polymer/conc. of solute residual in solution</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>Film 20 μm 0.905 g/ml</td>
<td>20–30 mg</td>
<td>Pure limonene vapour under nitrogen flow</td>
<td>0.5 cm² flask</td>
<td>25</td>
<td>Equilibrium state attained</td>
<td>0.01</td>
<td>g flavour/g amorphous polymer</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td>Films &amp; ground films, d=0.9213 g/ml, d=0.9139 g/ml, d=0.8830 g/ml</td>
<td>40 mg</td>
<td>Model aqueous solution of limonene</td>
<td>2 ml total volume</td>
<td>23</td>
<td>125 days (5 days when ground)</td>
<td>0.00846</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72,73</td>
<td>Film 51 μm</td>
<td>93 cm²</td>
<td>Limonene into PEG400</td>
<td>Headspace vapour phase = 0.1 μl/ml = 0.018 mbar</td>
<td>23</td>
<td>Up to 1000 h</td>
<td>1</td>
<td>g/cm² bar</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>Film homopolymer</td>
<td>NA</td>
<td>Aqueous solution of limonene in methanol</td>
<td>35 ml vial</td>
<td>23 ± 0.5</td>
<td>NA</td>
<td>37</td>
<td>(cell) value recalculated in water in g/cm² bar</td>
</tr>
<tr>
<td>PET</td>
<td>5</td>
<td>Normal, bottle</td>
<td>41 g</td>
<td>Fanta® orange juice</td>
<td>500 ml juice, i.e. 30 mg limonene (60 p.p.m. w/w)</td>
<td>4</td>
<td>12 weeks storage (equilibrium probably not reached)</td>
<td>3.31 ± 0.16</td>
<td>μg/g plastic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Normal, bottle</td>
<td>41 g</td>
<td>Stripped PET</td>
<td></td>
<td>25</td>
<td>25</td>
<td>9.30 ± 0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strips, d=1.35 g/ml</td>
<td>250 mb</td>
<td>Crystaline PET strips, d=1.37 g/ml</td>
<td></td>
<td>25</td>
<td>25</td>
<td>21.6 ± 1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>Film, 12 μm</td>
<td>93 cm²</td>
<td>Limonene into PEG400</td>
<td>Headspace vapour phase = 0.1 μl/ml = 0.018 mbar</td>
<td>21</td>
<td>Well over 8000 hours</td>
<td>7.40 ± 0.59</td>
<td>g/cm² bar, determined from permeation measurements (cell)</td>
</tr>
<tr>
<td>EVDH</td>
<td>59</td>
<td>Film, 21.1 μm high ethylene content</td>
<td>258.1 cm²</td>
<td>Orange juice and antioxidants</td>
<td>176 mg/l limonene, 260 ml juice</td>
<td>22 ± 2</td>
<td>24 days in contact (3–6 days for equilibrium)</td>
<td>-18% (Kₛ = 7.58)</td>
<td>Per cent decrease in juice (mg/mg control)</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>Film, 20 μm, 1.19 g/ml</td>
<td>20–30 mg</td>
<td>Pure limonene vapour under nitrogen flow</td>
<td>0.5 cm² flask</td>
<td>25</td>
<td>Equilibrium state attained</td>
<td>0.00103</td>
<td>Kg (mg/g polymer)/(mg/g juice)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Strips, d=1.60 g/ml</td>
<td>250 mg</td>
<td>Fanta® orange juice</td>
<td>500 ml juice, i.e. 30 mg limonene (60 p.p.m. w/w)</td>
<td>25</td>
<td>12 weeks storage (equilibrium probably not reached)</td>
<td>93.2 ± 7.2</td>
<td>μg/g plastic</td>
</tr>
</tbody>
</table>
### Table 2. Continued

<table>
<thead>
<tr>
<th>Name</th>
<th>Polymer characteristics</th>
<th>Penetrant characteristics</th>
<th>T(°C)</th>
<th>Time of contact</th>
<th>Sorption results</th>
<th>Respective units used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-polymers 41</td>
<td>EVA 7% ethylene vinyl acetate films EVA 5% ethylene vinyl acetate</td>
<td>Saturated limonene vapour, 0.719 mg/l in 17.8 ml tubes</td>
<td>25</td>
<td>24 h</td>
<td>$3.74 \times 10^{-3}$</td>
<td>Ig limonene/g structure/p.p.m. limonene</td>
</tr>
<tr>
<td>Co-polyter film, 67.3 μm</td>
<td></td>
<td>Orange juice and antioxidants, 176 mg/l limonene, 260 ml juice</td>
<td>22 ± 2</td>
<td>24 days in contact (3-6 days for equilibrium)</td>
<td>$-\varepsilon % \ (K_r=0.03)$</td>
<td>Per cent decrease in juice (mg/mg control), K_r in (mg/g polymer)/(mg/g juice)</td>
</tr>
<tr>
<td>Co-polymer PP film</td>
<td>NA</td>
<td>Aqueous solution of limonene in methanol, 35 ml via</td>
<td>23 ± 0.5</td>
<td>NA</td>
<td>53</td>
<td>(value recalculated in water) in g/cm² bar</td>
</tr>
<tr>
<td>Multilayered polymers</td>
<td>Carton packs, strips</td>
<td>Reconstituted orange juice &amp; model solutions</td>
<td>35</td>
<td>14 days</td>
<td>25</td>
<td>Per cent mg/l at time t mg/l at start</td>
</tr>
<tr>
<td>20</td>
<td>Three different LDPE composite structures</td>
<td>Orange juice pasteurized in a TetraPak plant</td>
<td>4</td>
<td>24 weeks</td>
<td>40-80</td>
<td>Per cent limonene retention (v/v remaining in solution)</td>
</tr>
<tr>
<td>40</td>
<td>HDPE structure, film 48 μm Glassine structure (polyvinyl alcohol and wax coatings) film 56 μm</td>
<td>Limonene vapour in nitrogen, 1.5 and 6.3 p.p.m. limonene in the vapour phase</td>
<td>20.5</td>
<td>10 hours</td>
<td>7.3 $\times$ 10^{-3}$</td>
<td>(g limonene/g structure p.p.m. (w/v) limonene in the vapour phase</td>
</tr>
<tr>
<td>44</td>
<td>Aluminium foil MPET Saran Saran EVOH EVOH</td>
<td>Multilayered film of LDPE+ tie layer (+), 30 cm²</td>
<td>20.5</td>
<td>20 hours</td>
<td>1.5 $\times$ 10^{-3}$</td>
<td>Ratio: polymer to gas concentrations (for HDPE: 6.9-15.6 $\times$ 10⁶ ratio)</td>
</tr>
<tr>
<td>56</td>
<td>Surlyn™ beads (lipophilic zinc-ionomer between aluminium foil and PP/PE films)</td>
<td>Limonene vapour at 95% RH, 1 p.p.m. in 20 ml headspace vials</td>
<td>25</td>
<td>40 days at 25°C and 20 days at 40°C (equilibrium)</td>
<td>1600</td>
<td>Ratio of polymer and gas concentration (g/ml)</td>
</tr>
<tr>
<td>Tie layers</td>
<td></td>
<td>Reconstituted orange juice, added terpeneless oil (12°C Brix)</td>
<td>23</td>
<td>4 days</td>
<td>39%</td>
<td>larea sample / area control/area original oil x 100</td>
</tr>
<tr>
<td>64</td>
<td>Surlyn™ 1652</td>
<td>Aqueous solution of limonene in ethanol, 120-100 p.p.m. in 125 ml liquid</td>
<td>6.23</td>
<td>12-&gt;72 h</td>
<td>3400</td>
<td>Unitless</td>
</tr>
<tr>
<td>66</td>
<td>Pure acrylic layer, 2 μm</td>
<td>Limonene into PEG400, Headspace vapour phase = 0.1 μl/ml = 0.018 mbar</td>
<td>23</td>
<td>up to 1000 hours</td>
<td>14</td>
<td>g/cm³ bar determined from permeation measurements (cell)</td>
</tr>
</tbody>
</table>

NA, not available.
<table>
<thead>
<tr>
<th>Name</th>
<th>Reference</th>
<th>Type</th>
<th>Quantity &amp; comments</th>
<th>Material</th>
<th>Limonene concentration and comments</th>
<th>T (°C)</th>
<th>Diffusion coefficient (D) (m² s⁻¹)</th>
<th>Permeability coefficient (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>41</td>
<td>Normal film linear (LLDPE) film Film</td>
<td>18 cm²</td>
<td>Limonene vapour in nitrogen</td>
<td>0.719 mg/l</td>
<td>25</td>
<td>5.1 × 10⁻¹⁴</td>
<td>1.41 × 10⁻⁴ g/cm/cm² cm Hg s</td>
</tr>
<tr>
<td></td>
<td>74</td>
<td></td>
<td>NA</td>
<td>Limonene in methanol</td>
<td>NA</td>
<td>23</td>
<td>4.3 × 10⁻¹³</td>
<td>NA</td>
</tr>
<tr>
<td>HDPE</td>
<td>66</td>
<td>Film, 51 μm Film, 46 μm</td>
<td>79 cm²</td>
<td>Limonene into PEG400</td>
<td>Headspace vapour phase = 0.1 μ%/ml = 0.018 mbar</td>
<td>23 (350-1270 hours)</td>
<td>4.3 × 10⁻¹⁴</td>
<td>1.85 × 10⁻⁴ g/cm s bar</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>Film</td>
<td>18 cm²</td>
<td>Limonene vapour in nitrogen</td>
<td>0.719 mg/l</td>
<td>25</td>
<td>3.7 × 10⁻¹⁴</td>
<td>2.13 × 10⁻⁶ g/cm² cm Hg s</td>
</tr>
<tr>
<td>PP</td>
<td>52</td>
<td>Film, 30 μm 'SCB' + BOPP Film BOPP 2 mil</td>
<td>NA</td>
<td>Saturated limonene vapour</td>
<td>Vapour activity levels: 0.05-0.5 0.21 0.29 0.42 0.50</td>
<td>23 ± 1</td>
<td>0.65 × 10⁻¹³</td>
<td>0.33-6.0 × 10⁻¹⁰ g m⁻¹ N⁻¹ s⁻¹</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td></td>
<td>NA</td>
<td>Limonene vapour in nitrogen + binary mixture + ethyl acetate</td>
<td>3.5 ± 0.2 × 10⁻¹⁴</td>
<td>0.1 ± 0.2 0.11 ± 0.3 × 10⁻¹⁴</td>
<td>1.4 ± 0.2 0.24 ± 0.6 × 10⁻¹⁴</td>
<td>1.8 ± 0.3 2.3 ± 0.5 × 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td>66,76</td>
<td>Film, 12 μm Film BOPP 20 μm Film BOPP 20 μm Film BOPP 20 μm</td>
<td>79 cm²</td>
<td>Limonene into PEG400</td>
<td>Headspace vapour phase = 0.1 μ%/ml = 0.018 mbar</td>
<td>23 (350-1270 hours)</td>
<td>3.73 × 10⁻¹⁴</td>
<td>1.56 × 10⁻⁸ g/cm² cm Hg s</td>
</tr>
<tr>
<td>FET</td>
<td>68</td>
<td>Film, 12 μm</td>
<td>177 cm²</td>
<td>Limonene into PEG400</td>
<td>Headspace vapour phase = 2.2 μ%/ml = 0.4 mbar</td>
<td>23 (&gt;8000 hours)</td>
<td>6 × 10⁻¹⁴</td>
<td>1 × 10⁻¹⁴ g/cm s bar</td>
</tr>
<tr>
<td>Co-polymers</td>
<td>41</td>
<td>EVA 7% ethylene vinyl acetate films EVA 5% ethylene vinyl acetate films</td>
<td>18 cm²</td>
<td>Saturated limonene vapour</td>
<td>0.719 mg/l</td>
<td>25</td>
<td>8.1 × 10⁻¹⁴</td>
<td>2.56 × 10⁻⁴ g/cm² cm Hg s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.16 × 10⁻¹³</td>
<td>2.74 × 10⁻⁹</td>
</tr>
<tr>
<td>Multi-layered polymers</td>
<td>40</td>
<td>HDPE structure film 48 μm Glassine structure (polyvinyl alcohol and wax coatings) film 56 μm</td>
<td>NA</td>
<td>Limonene vapour, 0% RH, 1 atm 1.5-4.8 p.p.m. noted CV</td>
<td>0.4-3.6 p.p.m.</td>
<td>23</td>
<td>5-9 × 10⁻¹⁴</td>
<td>4.9 × 10⁻⁴ exp (0.7 Cv)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.3 × 10⁻³ exp (1.3 Cv)</td>
<td>4.9 × 10⁻⁴ exp (0.7 Cv)</td>
</tr>
</tbody>
</table>

Table 3. Experimental diffusion and permeability results for limonene into various plastic materials
<table>
<thead>
<tr>
<th>Name</th>
<th>Reference</th>
<th>Type</th>
<th>Quantity &amp; comments</th>
<th>Penetrant characteristics</th>
<th>T (°C)</th>
<th>Diffusion coefficient (D) (m² s⁻¹)</th>
<th>Permeability coefficient (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multilayered Polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(cont)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDPE/nylon</td>
<td>47</td>
<td>1.25 mm, 0% RH</td>
<td></td>
<td>Limonene vapour in nitrogen normalized to 100 p.p.m. (g/ml air)</td>
<td>23</td>
<td>NA</td>
<td>0.0409</td>
</tr>
<tr>
<td>HDPE/nylon</td>
<td></td>
<td>1.25 mm, 75% RH</td>
<td></td>
<td></td>
<td></td>
<td>0.0014</td>
<td>0.0009</td>
</tr>
<tr>
<td>HDPE/EVOH</td>
<td></td>
<td>1.25 mm, 0% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0012</td>
</tr>
<tr>
<td>HDPE/EVOH</td>
<td></td>
<td>1.25 mm, 75% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0037</td>
</tr>
<tr>
<td>HDPE/nylon/EVOH</td>
<td></td>
<td>1.40 mm, 0% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.0003</td>
</tr>
<tr>
<td>HDPE/nylon/EVOH</td>
<td></td>
<td>1.40 mm, 75% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.400</td>
</tr>
<tr>
<td>PP/EVOH orient.</td>
<td></td>
<td>1.00 mm, 0% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0061</td>
</tr>
<tr>
<td>PP/EVOH orient.</td>
<td></td>
<td>1.00 mm, 75% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.315</td>
</tr>
<tr>
<td>PP/PET glycol</td>
<td></td>
<td>1.00 mm, 0% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0071</td>
</tr>
<tr>
<td>PP/PET/glycol (all films)</td>
<td></td>
<td>1.00 mm, 75% RH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOPP-acrylic, film 21 μm b</td>
<td>66</td>
<td>79 cm²</td>
<td>Limonene into PEG400 Headspace vapour phase = 0.1 μl/ml = 0.018 mbar</td>
<td>23</td>
<td>NA</td>
<td>3.28 × 10⁻¹⁰</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(350–1270 hours)</td>
<td></td>
<td></td>
<td>g/cm s bar</td>
</tr>
<tr>
<td>Tie layers</td>
<td>66</td>
<td>Pure acrylic layer, 2 μm b</td>
<td>79 cm²</td>
<td>Limonene into PEG400 Headspace vapour phase = 0.1 μl/ml = 0.018 mbar</td>
<td>23</td>
<td>2 × 10⁻²⁰</td>
<td>1.56 × 10⁻¹⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(350–1270 hours)</td>
<td></td>
<td></td>
<td>g/cm s bar</td>
</tr>
</tbody>
</table>

* The first three diffusion coefficients are obtained with the time lag method, the cell permeation method and the pouch method respectively. BOPP means biaxially oriented polypropylene.

b BOPP-acrylic, two-side acrylic-coated BOPP.

* Pure acrylic layer is a theoretical film made of acrylic material only.

¹ NA, not available
observed only a 1–2% loss of the total content of myrcene and limonene from an orange flavoured soft drink; severe washing treatments after emptying did not remove much of the sorbed terpenes, so that off-flavours could arise at the next bottle filling. Part II of this review will comment on the sorption, diffusion and permeation of volatiles in general and of limonene in particular taking into account the particularities of both phases in contact, the liquid or vapour phase and the polymer phase. Current thermodynamic considerations will also be presented to better explain and further predict possible sorption.

**ABBREVIATIONS**

BOPP Bi-oriented polypropylene  
C Concentration  
CED Cohesive energy density in MPa  
Co-VDC Vinylidene chloride co-polymer (Saran®)  
D Diffusion coefficient  
EVAX Ethylene vinyl acetate with X% vinyl acetate  
EVOH Ethylene vinyl alcohol  
G Gibbs partial molar free energy in J mol⁻¹  
H Enthalpy in J mol⁻¹  
HDPE High density polyethylene  
J Steady state permeation flux  
Kₚ Partition coefficient between two phases (sorption)  
LDPE Low density polyethylene  
LLDPE Linear low density polyethylene  
MDPE Medium density polyethylene  
mm Hg Millimeters of mercury  
MPET Metallized polyester  
Nylon® Polyamide (Nylon® 6,6)  
P Permeability coefficient (permeation)  
p Pressure  
PA Polyamide  
PC Polycarbonate  
PE Polyethylene  
PEG400 Polyethyleneglycol 400  
PET Polyethylene terephthalate  
PP Polypropylene  
PS Polystyrene  
PVC Polyvinyl chloride  
R Gas law constant  
RH Relative humidity  
S Solubility coefficient (sorption)  
S₀, S', S'' Constants  
Saran® Co-VDC
Surlyn™ Slightly hydrophilic zinc ionomer
T Temperature in K
\( \nu_1 \) Partial molar volume of the penetrant

**Greek characters**

\( \alpha \) Percentage crystallinity
\( \alpha_t \) Volatility of the volatile in solution
\( \gamma + = \gamma \) Flory interaction parameter\(^{60}\)
\( \delta \) Hildebrand solubility parameter in MPa\(^{1/2}\)
\( \delta_c \) New parameter defined by Matsui et al.\(^{61}\)
\( \gamma \) Constant characteristic of the polymer
\( \pi \) Permachor value\(^{62}\)
\( \Pi_2 \) Volume fraction of the polymer in the mixture

**Subscripts**

0 Constant
1 Penetrant, flavour
2 Polymer
mix Mixing
np Non-polar
p Polar (except \( K_p \))
vap Vaporization
w Water

**REFERENCES**

CHAPTER 1.B

LITERATURE REVIEW

« The Effects of Packaging on the Organoleptic Quality of Citrus Juices »

AROMA TRANSFERS IN AND THROUGH PACKAGINGS :

ORANGE JUICE AND D-LIMONENE. A REVIEW.

PART II : OVERALL SORPTION MECHANISMS AND PARAMETERS – A LITERATURE SURVEY

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Nowadays, the quality of foodstuffs has more than ever included the notion that packaging contact is not always wholesome. It can alter the packaged food product by flavour scalping and can also affect the food by off-flavour release. Much research has been carried out to better understand the mass transfers involved with various synthetic polymeric films.

Orange juice and one of its major volatile constituents, \( d \)-limonene, were probably amongst the first food products to be thoroughly studied. Yet, no extensive literature review has been undertaken in order to obtain a general and accurate description of the sorption and diffusion phenomena.

This review underlines the effects of packaging on the organoleptic quality of citrus juices; it therefore presents a focused interest on \( d \)-limonen mass transfer experimental results with a variety of plastic polymers.

Part II deals with sorption mechanisms and parameters mentioned in the literature which are described to better understand the effect of the permeants and polymers physico-chemical characteristics as well as some external factors of \( d \)-limonene sorption.

Finally, current theoretical considerations for the prediction of \( d \)-limonene sorption are presented chronologically in order to keep investigators up-to-date with what has already been done. © 1997 by John Wiley & Sons, Ltd.


Keywords: packaging; plastics; \( d \)-limonene; sorption; diffusion; permeation; aroma compounds; citrus; thermodynamics

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INFLUENCE OF THE PERMEANT CHARACTERISTICS ON SORPTION

Effect of the carbon chain length or boiling point

The impact of the carbon chain length or boiling point of volatiles has been pointed out for homologous series of hydrocarbons, esters, aldehydes, alcohols and benzoates in the vapour phase;\(^1,2\) the solubility coefficients (S) and the permeation coefficients of the volatiles in various polymers increased 2- to 5-fold with each additional methylene group in the compound below 10 carbon atoms; diffusivity decreased because of steric hindrance. However, for molecules composed of 11 or more carbon atoms, the increments were either less or, in the case of aldehydes, negative. Sorption is thus a very determinant factor conditioning permeation \((P = D \times S)\).

Similar results were observed in PP, PE, VDC and EVOH for the sorption of alkyl esters \((C_5-C_{10})\), methyl ketones \((C_7-C_{10})\), aldehydes \((C_7-C_{10})\) and sulfur compounds.\(^3,5\) Compounds with eight or more carbon atoms were sorbed from yoghurt drinks by HDPE, while shorter molecules remained in the product.\(^6,7\) In the same study it was observed that highly branched molecules were sorbed to a greater extent than linear molecules. From thermodynamic data it was also calculated that the solubility of ethyl butyrate (a predominant orange aroma) in VDC co-polymers (co-VDC), was 10-fold less than that of longer esters such as hexyl butyrate; the solubility parameters (a notion developed later on) agreed favourably with calculated values.\(^8\) Even longer molecules are capable of being absorbed into plastic materials: recently, Pieper and Petersén\(^9\) observed the absorption of free fatty acids from orange juice into LDPE; these were molecules containing 16–18 carbon atoms that were able to delaminate multilayered flexible packagings.

The carbon chain length is closely related to the boiling point of a molecule, and several researchers have indicated a relationship between the solubility and the boiling points of sorbates. A linear relationship between the logarithm of the solubility coefficient in co-VDC and the boiling points of linear esters, alkanes and ketones (e.g. hexyl butyrate, \(n\)-decane or 3-octanone) was observed.\(^3,8\) Shimoda et al.\(^1\) noticed that the effect of the molecular weight or the boiling point was much larger than the functional group in the vapour phase.

These results were obtained for molecules in the vapour phase; this can only be explained if the solubility coefficient is dependent to a large extent on the energy required to keep the penetrant in the vapour phase.\(^8\)

Effect of the functional groups and polarity of permeants on sorption

As noted by Shimoda et al.,\(^1\) the effect of functional groups on the distribution ratios of flavour compounds between film and solution was greater in the liquid phase because of closer interactions; in the vapour phase, the molecular weight or the boiling point were more important. For instance, in aqueous model solutions an important split
was observed into two polarity groupings, the hydrocarbons and the oxygenated terpenes, which were not significantly absorbed by PP nor by LDPE; solute polarity was the predominant controlling factor to explain the tendency for sorption. Comparing carvone (C_{10}H_{14}O) and limonene (C_{10}H_{16}), both similar terpenes but with different polarities, some investigators have found that the less polar limonene was not only sorbed at a faster rate but diffused more rapidly, due to ‘lesser cohesive forces’. In a study of the sorption of citrus oil constituents by polyolefins, terpenes (such as limonene, C_{10} carbon length) showed the highest affinity for the polymers, followed by sesquiterpenes (C_{15}); larger amounts of esters and aldehydes were sorbed than alcohols, due to polarity. For the same reasons, saturated aldehydes were sorbed to a greater extent than those containing double bonds.

Orange juice aromas were also sorbed to different extents, starting with hydrocarbon compounds, which showed the highest affinity to LDPE, followed by ketones, then aldehydes and finally alcohols. Esters were ranked before aldehydes as previously reported. Such ranking was also observed for apple juice aroma compounds into LDPE, LLDPE, PP, PA and to PET. Finally, the pH was found to affect the polarity of the permeant and could therefore change sorption by a factor of 40 between pH 3 and pH 5 for 2-hexanal into polyethylene. Lowering the pH to 3 increased the sorption of alcohols into LDPE. For limonene in orange juice, pH has rarely been considered: although this molecule does not include any oxygen moiety for potential hydrogen bonding, Blain showed that limonene was sorbed 1.3 times more into LDPE at 22°C at pH 5.2 than at pH 2.6, results which were significant at the 95% level.

**Effect of solutes interaction (co-permeants)**

A greater sorption of limonene by LDPE from model solutions than in the juice was found due to the presence of other constituents in the juice, such as pulp, which increased the solubility of the limonene in the aqueous phase. Indeed, limonene is much more soluble in orange pulp and in PE than in the water phase. The extent of limonene sorption tended to be less when limonene was present in a mixture than when it acted as the sole permeant; it could be a result of competition for sorption sites. This has also been shown for PP, which gives 63–75% sorption for limonene in a model solution, whereas Charara et al. observed only 36% sorption in orange juice, under similar conditions.

The effect of synergy of a co-permeant on another permeant was first shown by Hensley et al. for the case of a BOPP (bi-axially oriented) film in the vapour phase. Similarly, Nielsen and Giacin observed that the permeability of ethyl acetate was increased exponentially up to 40 times when limonene was added to it (1:3 ethyl acetate:limonene mixture). Again, in a liquid mixture of limonene and carvone, Letinski and Halek showed that 5% less limonene was sorbed into ground PP films than when exposed to the same film alone; this result was attributed to competition between the two compounds for space on the surface and within the polymer.

In contrast, in the vapour phase Baner et al. did not observe any interaction between limonene and ethyl acetate, n-hexanal or α-terpineol on their sorption.
EFFECT OF POLYMER STRUCTURE

Limonene sorption by polymer films and ground polymers in aqueous solutions has been frequently studied as this terpene occurs naturally in such a liquid phase, e.g. citrus juices. However, some vapour permeation studies have also been carried out for polymeric materials such as LDPE, which is an important packaging material. Studies have also been carried out on MDPE, HDPE, PP, EVOH, co-VDC, PA, PC, PET and various other polymers (Table 1).

Polymeric materials present a wide range of structures and properties depending on their chemical structure (Table 1), method of preparation and processing conditions. Furthermore, a great number of structural parameters strongly affect barrier properties to numerous molecules (O₂, CO₂, N₂, solvents, aroma compounds, etc.)

For example, plastic packagings are generally semi-crystalline or amorphous materials; the polarity and crystallinity of the polymer was found to better explain the extent of sorption for a given compound with a known polarity.

Parameters most often reported are:

1. the free volume, of which only a part, called the hole-free volume, governs transport processes into a polymer as it is constantly redistributed by thermal fluctuations; it provides a fairly reasonable explanation for the concentration and temperature dependance of diffusion;
2. the crystallinity, because sorption generally does not occur in the crystalline but the amorphous phase;
3. the polarity;
4. the tacticity, which derives from the type of polymerization of the monomers; the isotactic form, where all substituent groups lie on one side of the backbone polymer chain (Table 1), allows a denser packing than other forms, so that permeability may be affected, depending on the type of substituent;
5. the cross-linking and grafting (degree of branching), which both influence the looseness of the polymer and decrease diffusion;
6. the orientation or stretching effect, which is induced by processing and which strongly modifies mechanical properties; it increases the crystallinity of semi-crystalline polymers such as PE and decreases their permeabilities and diffusivities (PE, PP, PVC, PC, PET);
7. the presence of additives; for example, plasticization lowers the glass transition temperature Tg and provokes an increase of free volume, therefore resulting in a greater permeability and diffusivity;
8. the polymer blends.

Observed effects of various polymer structures on limonene sorption and diffusion

Taking the above-mentioned considerations into account, the solubility of limonene in different polymers varies a great deal. Below are presented some observed results with the most common polymers, e.g. PP, LDPE and HDPE, and with some other plastic
polymers. Experiments relating to citrus juice are commented on first, leaving the more fundamental parts concerning model solutions and vapour transfers until later.

**Citrus products and their sorption onto common polyolefins.** Common results in cold-pressed orange oil in contact with LDPE usually give a 70–80% limonene

| Table 1. Molecular and spatial structures of common plastic polymers |
|---|---|
| Polymer name | Chemical formula |
| LDPE (d=0.910–0.925) | \([-\text{CH}_2\text{I}_{n1}-(\text{CH}-(\text{CH}_2)_{p1})\text{-CH}_3]_{q1}\) |
| MDPE (d=0.926–0.940) | \([-\text{CH}_2\text{I}_{n2}-(\text{CH}-(\text{CH}_2)_{p2})\text{-CH}_3]_{p2}\) |
| HDPE (d=0.941–0.959) | \([-\text{CH}_2\text{I}_{n3}]\) |
| PP | \([-\text{CH}_2-(\text{CH}-\text{CH}_3)]_n\) |
| EVOH \(^b\) | \([-\text{CH}_2\text{-CHOH}-\text{CH}_2\text{-CHOH}]_n\) |
| | \([-\text{CH}-\text{CHOH}-\text{CH}_2\text{-CHOH}]_p\) |
| PVC | \([-\text{CH}_2\text{-CHCl}]_n\) |
| co-VDC (Saran\(^TM\)) | \([-\text{CH}_2\text{-CCL}_2\text{-CHCl}]_n\) |
| Polyamide (Nylon\(^b\)) | \(\text{H}\text{-[NH-CO-(CH}_2\text{H}_4\text{-CO-NH-(CH}_2\text{H}_6]_n\text{-NH}_2}\) |
| | \(\text{H}_2\text{N-[(CH}_2\text{H}_4\text{-NH-CO-(CH}_2\text{H}_4\text{-CO-NH}]_p\text{-H}\)} |
| PC \(^c\) | \(\text{HO-[(benz-CH}_3\text{CCH}_3]_n\text{-benz-O-COO]}_n\) |
| | \(-\text{benz-(CH}_2\text{CCH}_3\text{-benz-OH]}_n\) |
| PET \(^c\) | \(\text{HO-[C}_2\text{H}_4\text{-OOC-benz-COO-CH}_2\text{H}_4\text{-OH]}_n\) |
| PS \(^c\) | \([-\text{[(CH}_2\text{-CH-benz]}_n\text{-CH}_2\text{-CH}]_n\text{-benz]}_n\) |

- \(^a\) Densities for PE homopolymers (g cm\(^{-3}\)) according to ASTM D 1248 (in International Plastics Handbook, p. 158).
- \(^b\) \(\text{f}\), hydrogen bonding.
- \(^c\) Benz, benzene ring.
Atactic, spatial conformation where the substituents, R, in the chains of poly–olefins (CH–CHR), show an irregular, random arrangement about the main chain, Syndiotactic, the substituents, R, alternate below and above the backbone chain.

NA, not available.
sorption whereas it often only attains 30% with HDPE and PP films at 23°C.\textsuperscript{10,42} However, greater solubilities were observed (and hence sorption), up to 92%, in PP within 4 hours (94% loss into LDPE and HDPE).\textsuperscript{20} Ackermann and Wartenberg\textsuperscript{43} observed 80% loss in LDPE, 60% loss in polyamide and 45% loss in polystyrene (PS) from a model solution. Imai \textit{et al.}\textsuperscript{44} only observed a 41% loss of limonene from orange juice into LDPE, 18% loss into EVOH and almost no loss into PET. A similar result has been given by Paik\textsuperscript{45} in the vapour phase.

**D-limonene sorption by common polyolefins.** Similarly, in model solutions limonene showed solubility (i.e. sorption, expressing the same phenomenon) differences between LDPE, polyamide and polystyrene; from a greater to a least extent in that order.\textsuperscript{15} The partition coefficient $K_p$ for limonene in model solutions was higher in stereoregular PP ($K_p=98$) than in branched LDPE ($K_p=79$) or unbranched HDPE ($K_p=35$) at 23°C.\textsuperscript{2} A partition coefficient of $K_p=3400$ for limonene into LDPE was obtained by Kwapon and Hotchkiss.\textsuperscript{17} As for results obtained in the vapour phase, limonene was greatly sorbed into loose structured polyolefins, i.e. more in LDPE, less in linear LDPE and less again in HDPE.\textsuperscript{46} The corresponding permeation and diffusion rates were both affected by the polymer structure.\textsuperscript{46} Paik and Writer\textsuperscript{47} agree, demonstrating that PP (unbranched) films also sorbed less limonene than LDPE films. The final example would be that of different types of PPS in contact with limonene in the liquid\textsuperscript{22} or the vapour phase.\textsuperscript{20,48} Tables 2 and 3 in Part I of this review show a similar behaviour: when the PP density increased or the PP was stretched during fabrication (bi-oriented polypropylene, BOPP), the sorption, diffusion and permeation coefficients of limonene decreased by up to 10-fold.

**Sorption abilities of other polymers.** (See Tables 2 & 3 in Part I) Limonene and myrcene have been reported to be sorbed to a much greater extent into PC, which is a totally amorphous polymer, than into PET, where crystallinity attained 30%;\textsuperscript{49} the author also mentioned the differences in polarity and solubility parameters. Franz\textsuperscript{50} needed well over 11 months to reach equilibrium for PET films to get to a 30-fold lower solubility, a 300-fold lower diffusivity and an estimated 10 000-fold lower permeability coefficient than after only 41 days with BOPP films; it is noticeable that PET films demonstrated high barrier properties to limonene. In an EVOH co-polymer, the distribution ratio of limonene increased with increasing ethylene content,\textsuperscript{36,51} as the polarity was lower: similarly, comparing with MDPE,\textsuperscript{51} sorption was 350 times lower in a 38% ethylene content EVOH co-polymer. In composite films, limonene permeation rates were 20–40 times smaller in all Nylon\textsuperscript{®}-EVOH structures than in PP structures at either 0 or 75% RH.\textsuperscript{52} Finally, in an acrylic tie layer, the sorption rate of citrus flavour compounds was correlated with the ethyl acrylate content\textsuperscript{53} so that, to sum up, the results for limonene all followed the same rule: non-polar molecules have affinity for non-polar polyolefin materials.

**The plasticization of the polymer by limonene; swelling and crystallinity incidences.** Absorption can have adverse effects on the packaging itself, causing either delamination of multiple layer films\textsuperscript{54,55} or swelling of the polymer giving rise
to higher permeabilities to many compounds. As Halek and Luttmann\textsuperscript{2} stressed, the diffusion step depends on the mobility of the solute, which can depend on its size and its interaction with the polymer to plasticize and relax the polymer chain segments for co-operative hole formation. Hence, effectively, sorption has an effect on subsequent diffusion. It was also reported that, because of similarities between the solubility parameters (\(\delta\)) of limonene and that of PP/PE polymers, much penetrant–polymer interaction could occur to yield plasticization and polymer segment relaxation; differences in the packing density of the unbranched HDPE, compared with that of LDPE with its short chain branches and with PP with its methyl groups on alternate carbons (Table 1), could result in a higher susceptibility to plasticization by limonene for the LDPE and PP; limonene was effectively better sorbed by PP and LDPE,\textsuperscript{2} (Table 2, Part I) as previously mentioned.

Terpene hydrocarbons are lipophilic and tend to diffuse into the amorphous part of polymers.\textsuperscript{56,57} The sorption of few micrograms of limonene per millilitre of polymer may swell LDPE and even HDPE films,\textsuperscript{25} (Table 2, Part I) thus increasing the oxygen permeability through the polymer\textsuperscript{57,58} and so accelerating both aerobic and anaerobic degradation of ascorbic acid and browning in orange juice at 25 and 35\textdegree{}C, as reported by Mannheim \textit{et al.}\textsuperscript{59} and Sizer \textit{et al.};\textsuperscript{15} furthermore, mechanical properties could be affected.\textsuperscript{38} However, at high limonene concentrations, a decrease in the partition coefficient has been observed,\textsuperscript{17,20} but permeability has been measured as higher in co-PP.\textsuperscript{60}

By biaxially drawing the polymer film, thereby increasing the crystallinity of the polymer, the extent of limonene sorption can be reduced.\textsuperscript{36} although Franz\textsuperscript{50} observed the reverse effect; he agreed however as far as diffusion and permeability are concerned (Table 3, Part I). In a similar manner, it was found that a PE film with decreased crystallinity resulted in increased solubility of various aromas.\textsuperscript{2} Other researchers came to the same conclusion when studying the sorption of citrus oils by polyolefins.\textsuperscript{10} Strandburg \textit{et al.}\textsuperscript{8} even suggested that calculation of the solubility coefficient \(S\) should be corrected for crystallinity by a factor, \(a\), using \(S_{\text{effective}} = S_{\text{amorphous}} \times (1 - a)\). Paik and Writer\textsuperscript{47} also normalized in the same way the sorption value for percent crystallinity.

**EFFECTS OF EXTERNAL FACTORS ON LIMONENE SORPTION**

**Temperature**

Contrary to the results obtained in the vapour phase,\textsuperscript{47,61–64} limonene sorption from model solutions and orange juice increases with temperature.\textsuperscript{17,28} as shown in Table 2 Part I of this Review. Also, Paik and Writer\textsuperscript{47} and Baner \textit{et al.}\textsuperscript{61} observed that limonene vapour solubility was halved when the temperature increased from 25 to 40\textdegree{}C, whereas in the liquid phase Nielsen\textsuperscript{49} measured a 3-fold greater sorption at 25\textdegree{}C compared with that at 4\textdegree{}C. Similarly, a 30–50\% sorption was reported at 25\textdegree{}C after 3 weeks as well as at 35\textdegree{}C within only 6 hours\textsuperscript{65} (Table 2, Part I) in reconstituted orange juice and model solutions. Still in the liquid phase, larger amounts of aldehydes, esters
and alcohols have been sorbed into LDPE at 75°C than at 5°C.\textsuperscript{11} As for permeability and diffusivity, it seems that no experimentation on temperature change has been made (Table 3, Part I). Comparisons between authors are difficult as film crystallinities are seldom mentioned even if the units used are more homogeneous than for solubility. However, De Lassus \textit{et al.}\textsuperscript{66} have reported that high temperatures caused a large increase in the permeability to limonene in a vinylidene chloride co-polymer and in an EVOH co-polymer.

**Humidity**

De Lassus \textit{et al.}\textsuperscript{66} noticed high humidity caused the permeability to limonene to increase by a factor of as much as 1000 in an EVOH co-polymer, due to a plasticizing effect of the sorbed water; in the vinylidene chloride co-polymer studied, no change was observed. However, Hatzidimitriu \textit{et al.}\textsuperscript{52} suggested that one of their HDPE/Nylon® composite films probably improved its barrier properties with increasing RH, owing to moisture sorption from the polyamide\textsuperscript{67} (Table 3, Part I). In a similar manner as De Lassus \textit{et al.},\textsuperscript{66} Johansson and Leufvén and Leufvén \textit{et al.}\textsuperscript{13} again observed that the plasticizing effect of water on the permeability parameters of both alcohols and aldehydes was higher in low crystallinity films. Debeaufort \textit{et al.}\textsuperscript{69} also reported the same effect with 1-octen-3-ol in methylcellulose-based films, but it is still to be studied in more depth for limonene sorption into hydrophilic polymers as results obtained often seem controversial.

**Other storage conditions**

Finally, other storage conditions may affect the solubility of the aroma compounds in the film;\textsuperscript{70} for example, static conditions create a monolayer barrier which slows down any sorption, whereas dynamic conditions, such as stirring of batches of orange juice, would eliminate the monolayer (Reynolds number >2000) and ease the sorption of selected compounds present in the juice.

**CURRENT THEORETICAL CONSIDERATIONS FOR THE PREDICTION OF LIMONENE SORPTION**

In the liquid phase, the value of the Gibbs partial molar free energy change ($\Delta G = -RT \ln K_p$) gives an estimate of the strength of the tendency for sorption; the more negative the value of $\Delta G$, the stronger the sorption tendency;\textsuperscript{2} at 23°C, $\Delta G$ ranged between $-8.8$ and $-11.3 \text{ KJ.g}^{-1}.\text{mol}^{-1}.\text{K}^{-1}$ for limonene into HDPE, LDPE and PP.

For permanent gases, Salame\textsuperscript{71} derived the empirical permeability equation as a Permachor value of the polymer ($\pi$), but a direct application to flavours for estimating the solubility properties of polymers was considered inadequate due to many interactions arising between the sorbant and the polymer.

Other investigators have chosen a theoretical thermodynamic approach that reflects
the overall relative forces of attraction for the solute between the solution and the polymer; these forces are affected by structural and polarity effects. The affinity of an aroma compound for a film greatly affects the magnitude of sorption so that more and more investigators have tried to predict the sorption behaviour of flavours for various packaging films on the basis of the solubility parameter concept; this consists of estimating the polymer–solvent compatibility via calculation of a solubility parameter \( \delta \) expressed in MPa\(^{1/2} \), i.e. Hildebrand’s units (H), or more often expressed in cal\(^{1/2} \) cm\(^{-3/2} \).

Strandburg et al. have measured the solubility parameters (herein \( \delta \) in MPa\(^{1/2} \), subscript 2 for polymers, 1 for sorbants) of many penetrant molecules as well as that of co-VDC (\( \delta_2 = 21 \)) and EVOH (\( \delta_2 = 23.9 \)) at 85°C, and PP (\( \delta_2 = 17 \)) at 30°C. The solubility parameters \( \delta \) used in the Hildebrand, or Regular Theory, approximation of the partial molar heat of mixing are the square root of the cohesive energy density (CED in MPa or cal cm\(^{-3} \)) for low molecular weight species. This value estimates the cohesive property of a compound for a polymer, i.e. sorption.

Halek and Luttmann measured the Hildebrand solubility parameters at 25°C of PP, \( \delta_2 = 16.6 \) and PE \( \delta_2 = 16.6 \); limonene \( \delta_1 = 16.8 \) and PP, and limonene and PE showed similar cohesive forces; they observed easier adsorption into the polymer because these similarities of cohesive energies improved the rate of interaction with the attractive centres of the polymer; penetrant–polymer attractions accelerated solubility into the polymer. They also observed that absorption, the second sorption phase, was greater, as well as diffusion. Amongst others, Rajulu et al. have continued to estimate the Hildebrand parameters of some polymers and many have been published thanks to Sears and Darby.

In the same manner as for polymers, it was possible to calculate the structural and polarity effects of seven citrus flavour compounds on the basis of cohesive energy density (CED) forces. A compilation was undertaken for the latter with solubility parameters ranging from \( \delta_1 = 16.2 \) for myrcene, an unsaturated acyclic terpene, to 20.7 MPa\(^{1/2} \) for citral a and b, both acyclic terpene aldehydes; the solubility of such compounds was calculated from physical constants or from tables of structural group molar cohesive energy factors for liquids; the method of calculation, after Small or Fedors, consists of summing the factors for molar vaporization energy or cohesive energy \( U \) in J m\(^{-3} \) and for molar volume \( \nu_1 \) in m\(^3\) mol\(^{-1} \) for each of the molecular structural elements: CED = \(-U/N\). By comparing the polymers CED values with the solutes’ CED values, it was possible to estimate the solubility coefficient:

\[
S = S_0 \exp[(\Delta H_{\text{vap}} - \Delta H_{\text{mix}})/RT]
\]

using the Hildebrand approximation for the heat of mixing:

\[
\Delta H_{\text{mix}} = \nu_1 \Phi_2 (\delta_1 - \delta_2)^2
\]

where \( \nu_1 \) is the partial molar volume of the penetrant, \( \Phi_2 \) is the volume fraction of the polymer in the mixture, subscript 1 standing for flavour and subscript 2 for polymer. The previous solubility parameters are also listed in S.I. units of MPa\(^{1/2} \) for a few polymers and for limonene in Table 2.

Prediction of flavour sorption was also carried out using the Flory–Huggins

equation\textsuperscript{85–87} in order to better take into account the entropic contribution in the phenomenon due to molecular size differences.\textsuperscript{88} According to Paik and Writer,\textsuperscript{47} the Flory interaction parameter ($\Psi$), a function of intermolecular forces, can be expressed as

$$\Psi = (\nu / RT) (\delta_1 - \delta_2)^2$$  \hspace{1cm} (7)

### Table 2. Solubility parameters for various polymers and for limonene

<table>
<thead>
<tr>
<th>Reference</th>
<th>Polymer name and conditions (+ limonene temperature)</th>
<th>Density (g/cm$^3$)</th>
<th>Crystallinity (%)</th>
<th>Solubility parameter ($\delta$)\textsuperscript{a} (MPa$^{1/2}$)</th>
<th>(cal/cc)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paik, 1992\textsuperscript{45}</td>
<td>LDPE</td>
<td>0.923</td>
<td>40.43</td>
<td>17.6</td>
<td>8.61</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td>0.905</td>
<td>36.59</td>
<td>17.1</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>EVOH</td>
<td>1.19</td>
<td>62.69</td>
<td>22.2</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Limonene, mol.wt 136.24 (25–70°C), 97% purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.840</td>
<td>Not relevant</td>
<td>16.8</td>
<td>8.21</td>
</tr>
<tr>
<td>Strandburg et al., 1991\textsuperscript{8}</td>
<td>EVOH at 85°C co-VDC at 85°C</td>
<td>ND</td>
<td>ND</td>
<td>23.9</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>PP at 30°C</td>
<td></td>
<td></td>
<td>21.0</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>LDPE at 30°C</td>
<td></td>
<td></td>
<td>16.9</td>
<td>8.3\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.3</td>
<td>8.0\textsuperscript{b}</td>
</tr>
<tr>
<td></td>
<td>Limonene, 85°C</td>
<td>NP</td>
<td>Not relevant</td>
<td>16.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Halek and Luttmann, 1991\textsuperscript{2}</td>
<td>PE</td>
<td>ND</td>
<td>ND</td>
<td>16.6</td>
<td>8.12</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td></td>
<td></td>
<td>16.6</td>
<td>8.12</td>
</tr>
<tr>
<td>Arora and Halek, 1994\textsuperscript{84}</td>
<td>Limonene, 25°C PP, = 23°C PET, = 23°C</td>
<td>NP</td>
<td>Not relevant</td>
<td>16.8</td>
<td>8.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.0\textsuperscript{c}</td>
<td>7.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.5\textsuperscript{c}</td>
<td>10.52</td>
</tr>
</tbody>
</table>

\textsuperscript{a} MPa$^{1/2}$ is equivalent to J$^{1/2}$ cm$^{-3/2}$; (cal/cc) stands for calory per cubic centimeter.

\textsuperscript{b} PP and LDPE solubility parameters at 30°C are accepted literature values from Burell.\textsuperscript{97}

\textsuperscript{c} From Barton.\textsuperscript{115}

ND, not determined.

NP, not precise.
If it assumed that $\Psi$ is only related to the heat of mixing and if the molecular interactions are dispersive in nature (in the case of limonene). Equation 7 in fact expresses the same interaction phenomenon as equation 6; the lower the difference of $\delta$ values, the greater the compatibility. However, good predictions of sorption of limonene into LDPE and EVOH were achieved in the vapour phase only.\textsuperscript{47}

Contrary to the vapour phase, as noted by Matsui \textit{et al.},\textsuperscript{89} the equation gave for the aqueous phase an adequate but insufficient relationship resulting from the influence of an interaction force from the solution on the magnitudes of physical adsorption and condensation of flavours on the film surface; the obtained equation can be written as follows:

\[
S = S'_0 \exp \gamma \nu_1 (\delta^2_1 - \delta^2_c)/(RT)
\]  \hspace{1cm} (8)

where $\gamma$ is a constant characteristic of the polymer and $\delta_c$ is a new parameter defined by Matsui \textit{et al.}\textsuperscript{51} this new parameter divides into polar $\delta_p$ and non-polar $\delta_{np}$ parts by application of the homomorph concept.\textsuperscript{90} For limonene, $\delta_p = 5.6$ and $\delta_{np} = 15.9$.\textsuperscript{51} According to Chen’s theory,\textsuperscript{91} polymer–aroma compound compatibility ($\delta_c$) represents the energy of mixing caused by dispersion forces and dipole forces: $\delta_c$ was therefore defined accordingly as the two-dimensional distance between the $\delta_{ip} + \delta_{in} = \delta_c$ values of the aroma compound and the $\delta_{2p} + \delta_{2np}$ values of the polymer

\[
\delta^2_c = (\delta_{ip} - \delta_{in})^2 + (\delta_{ip} - \delta_{2p})^2
\]

with $\delta_c = 5.6$ for limonene–MDPE (more affinity) and $\delta_c = 16.3$ for limonene–co–EVOH (less affinity). Concerning sorption, Matsui \textit{et al.}\textsuperscript{51} showed a very good negative linear relationship between log $S$ and $\delta_c$ in the aqueous phase. However, although Hansen\textsuperscript{92–94} had claimed its importance previously, hydrogen bonding induced by water molecules were not taken into account,\textsuperscript{91} so that hydrocarbon sorption values did not follow the same linear relationship as oxygen-containing compounds.\textsuperscript{35,51} This might be a reason for a recent return to the Hansen’s three-dimensional solubility parameters theory.\textsuperscript{95}

Following the results of Matsui \textit{et al.}, Fukamachi \textit{et al.}\textsuperscript{96} recently improved derivation of the sorption equation for aqueous phases by taking into account the solubility parameter of water ($\delta_w = 47.9$ MPa\textsuperscript{1/2})\textsuperscript{97} as well as the volatility $\alpha_1$ of the volatile in solution:

\[
S = \alpha_1 S'_0 \exp \gamma \nu_1 [\delta_w - \delta_1]^2 - \delta^2_c]/(RT)
\]  \hspace{1cm} (10)

A sufficient correlation ($r \approx 0.95$) could then be obtained for various polymers (PP, EVA and EVOH) and various volatile compounds, including limonene, in model aqueous solutions.

**PERSPECTIVES**

After compiling all available data on $d$-limonene it would be probable that, for example, the refined predictive models from Matsui \textit{et al.}\textsuperscript{89} and Fukamachi \textit{et al.}\textsuperscript{96} would serve for all investigators. However, more experimental data are required to
evaluate the validity of the model. Molecular modelling and molecular dynamics (MD) simulation are also advancing rapidly\textsuperscript{98–103} to confirm the observed mechanisms. In the more applied research field, active packaging seems promising,\textsuperscript{104–107} for which highly selective polymers are sought. As far as limonene and orange juice are concerned, a very limonene-impervious film has recently been developed\textsuperscript{108} to preserve inherent terpene antimicrobial activity,\textsuperscript{109} and a polymer liner which reduces the bitterness of orange juice,\textsuperscript{110} is currently being investigated; its major effect is to sorb limonin, $C_{26}H_{30}O_8$, a tetracyclic triterpenoid, the most intense bitter principle of citrus fruit, which appears to have antimutagenic properties.\textsuperscript{111–113} Thus, it is now possible to obtain value-added products from an evermore selective packaging technology. Consequently, the food packaging industry must pay attention to real advances in the understanding of all fundamental aspects of mass transfer characteristics of any compounds, especially in the knowledge of the overall interaction phenomena involved.

**ABBREVIATIONS**

BOPP Bi-oriented polypropylene  
$C$ Concentration  
CED Cohesive energy density in MPa  
Co-VDC Vinlylidene chloride copolymer (Saran\textsuperscript{®})  
$D$ Diffusion coefficient  
EVAX Ethylene vinyl acetate with X% vinyl acetate  
EVOH Ethylene vinyl alcohol  
$G$ Gibbs partial molar free energy in J mol\textsuperscript{−1}  
$H$ Enthalpy in J mol\textsuperscript{−1}  
HDPE High density polyethylene  
$J$ Steady state permeation flux  
$K_p$ Partition coefficient between two phases (sorption)  
LDPE Low density polyethylene  
LLDPE Linear low density polyethylene  
MDPE Medium density polyethylene  
mm Hg millimeters of mercury  
MPET Metallized polyester  
Nylon\textsuperscript{®} Polyamide (Nylon\textsuperscript{®} 6,6)  
$P$ Permeability coefficient (permeation)  
$p$ Pressure  
PA Polyamide  
PC Polycarbonate  
PE Polyethylene  
PEG400 Polyethyleneglycol 400  
PET Polyethylene terephthalate  
PP Polypropylene  
PS Polystyrene  
PVC Polyvinyl chloride
$R$ Gas law constant
$\text{RH}$ Relative humidity
$S$ Solubility coefficient (sorption)
$S'_0, S''_0$ Constants
Saran\textsuperscript{$\text{TM}$} Co-VDC
Surlyn\textsuperscript{$\text{TM}$} Slightly hydrophilic zinc ionomer
$T$ Temperature in K
$v_1$ Partial molar volume of the penetrant

Greek characters

$\alpha$ Percentage crystallinity
$\alpha_i$ Volatility of the volatile in solution
$\Psi$ Flory interaction parameter\textsuperscript{47}
$\delta$ Hildebrand solubility parameter in MPa\textsuperscript{1/2}
$\delta_c$ New parameter defined by Matsui et al.\textsuperscript{51}
$\gamma$ Constant characteristic of the polymer
$\pi$ Permachor value\textsuperscript{71}
$\Phi_2$ Volume fraction of the polymer in the mixture

Subscripts

0 Constant
1 Penetrant, flavour
2 Polymer
mix Mixing
np Non-polar
p Polar (except $K_p$)
vap Vaporization
w Water

REFERENCES


Recent Literature Searches (12/2004) have revealed little or no significant new work neither on food flavour (including citrus juice flavour) sorption nor on d-limonene sorption by plastic packagings, as well as no significant new theory on sorption and diffusion through polymers.

If needed one may still consult the new references (and comments) available in Appendix H at end of Thesis.
CHAPTER 2

EXPERIMENTAL RESEARCH

THE DEBITTERING OF NAVEL ORANGE JUICE

USING POLYMERIC FILMS
2.1 ABSTRACT

In order to better understand and optimize the sorption of limonin (the major Navel orange juice bitter principle) by various plasticized polymeric films, a sorption and plasticizer migration study was carried out using high performance liquid chromatography (HPLC) and gas chromatography (GC). Low molecular weight (LMW) poly(vinyl chloride) (PVC) plasticized with dioctyl adipate (DOA) gave the best results for both limonin sorption and low DOA migration. Thick films did not significantly sorb more limonin than thin films in the timeframe of our experiments, as the absorption involved rapid surface sorption followed by slow bulk diffusion. The debittering efficiency was a thousand fold greater than that obtained with current polystyrene divinylbenzene resin beads, with potential for industrial scale debittering.

**Key Words:** debittering, orange juice, sorption, migration, polymeric films.
2.2. INTRODUCTION

A major problem in the citrus industry worldwide is the formation of bitterness in some early-to-mid season citrus juice products within hours of extraction from the fruit, or, if heated, within a few minutes. The problem occurs in a variety of oranges (including mandarins), grapefruit and lemons. Washington Navel, Satsuma, Natsudaidai and Shamouti oranges are particularly prone to this problem.

The primary cause of this “delayed bitterness” are the triterpenoid dilactones (“limonoids”), limonin and nomilin. Limonin bitterness is by far the strongest and should be eliminated from the juice prior to consumption. Navel orange juice can reach a limonin concentration of up to 40 µg/g which corresponds to an intense bitter sensation in the back of the tongue, lingering up to one hour despite frequent rinsing (Chandler and Nicol, 1975). Such oranges require expensive debittering to produce fresh fruit juice with a limonin concentration below the critical sensory threshold of 4-6 µg/g limonin in single strength orange juice (Guadagni et al., 1973), thus raising the juice to USDA Grade A i.e. to the “premium standard of quality set by the United States Department of Agriculture for color, flavor and the absence of defects in citrus fruit or its juices”.

Although many different methods have been used since the early 1970s (Dekker, 1988), the current debittering technology uses adsorption onto cellulose acetate or macroporous resin beads (Chandler and Johnson, 1977) or cross-linked styrene divinylbenzene resins (Hicks, 1990), the surface to volume ratio of which reaches up to 900 m²/g for plastic polymers. Porous and ion exchange resins have also been tested for their absorption efficiency by many investigators (Chandler and Johnson, 1981).
Cellulose acetate beads do not affect very much the total soluble solid content, the acidity nor the ascorbic acid content of the juice (Johnson, 1982) but they do adsorb many other compounds such as hesperidin, pigments, flavoring constituents, sterols and non-phenolic flavonoids, which may participate in 'poisoning' the beads (Johnson, 1981). Similar drawbacks, such as flavor scalping and the production of off-flavors, have been reported when using resins such as Amberlite® XADs (Shaw, 1997, personal communication).

In addition, the use of heavy or expensive equipment (such as centrifuges) is required prior to industrial debittering due to the need to depulp the juice. Only clarified juice may be pumped through the resin column. Therefore, new, cost-effective and competitive methods are required, the end result hopefully being a better product at a lower cost.

Our proposal was to use polymeric films in order to avoid the need for clarification and to prevent membrane fouling. A highly plasticized PVC was proposed to debitter Navel orange juice (OJ); no prior research seems to have been carried out yet on this particular aspect. Only a debittering liquid-membrane-based process was proposed by the USDA in 1996: the use of a microporous polypropylene film containing Shell Sol 71 (Shell Chemical Company), that is a mixture of aliphatic solvents, and isohexadecyl alcohol, was proposed but not investigated (Internet http://www.sbir.dsu.edu / home / proposal_preparation / sample_proposals / usda_sample2.htm).

The only available data reported on PVC sorption in orange juice concerned flavors, and in particular d-limonene (Fayoux et al., 1996) as preliminary studies to this Ph.D. work. Sears and Darby (1982) have also accumulated detailed information on many other organic compounds, particularly as a function of the plasticizer content. As for plasticizer release from the PVC, French and Greek scientists have been particularly active in the field of phthalates and adipates release to foodstuffs and simulants (Messadi and Vergnaud, 1982; Cerbulis and Byler, 1986; Kondyli et al., 1990; Papasyrides and Duvis, 1990; Ducruet et al.,
1992; Kondyli et al., 1992; Riquet and Feigenbaum, 1997). It is of interest to note that citrus debittering could be achieved by vegetable oil extraction (Dekker, 1988).

Our objective was to investigate the sorption of limonin by plasticized PVC membranes, and selected commercial polymers, for comparison purposes. Plasticization levels should be high (40% w/w for instance) so as to prepare a liquidified oily membrane or gel. Di-(2-ethylhexyl) phthalate (DEHP) is was of the most commonly used plasticizers for PVC. It was selected as the reference plasticizer. Other plasticizers were tested. Dioctyl adipate (DOA) being more innocuous, although migrating fairly readily out of the polymer matrix, was selected as more appropriate for food contact purposes. Other synthetic plasticizers were tried in order to understand the importance of chemical group interactions. Their migration into the juice was monitored parallel to the limonin sorption. Juice and films were analyzed before and after sorption. Debittering results were compared to citrus literature data obtained with resins and cellulose acetate flakes and gel beads (Chandler and Johnson, 1981; Dekker, 1988; Hicks, 1990; Tseng et al., 1993).
2.3. MATERIAL & METHODS

2.3.1. Material

Early season Washington Navel OJ was made from 6-fold frozen concentrate generously supplied by Sunkist Growers Inc., Ontario CA, USA. It was produced on Dec., 31, 1996, via Brown extractors (Brown International Corp., Covina CA, USA) and concentrated with a TASTE (thermally accelerated short time evaporation) evaporator (Gulf Machinery Co., Safety Harbor FL, USA). After dilution, its limonin concentration was 20 ppm w/w (µg/g) and was checked by HPLC after dichloromethane extraction. The concentrate was 66.2°Brix and 4.49% acid w/w expressed as anhydrous citric acid (data from Sunkist Growers Inc.). Orange juice concentrate was stored at -18°C and only the required quantity was thawed and made up with purified water for daily experimentation.

Two PVC resins (Sigma-Aldrich Co., St. Louis MO, USA), molecular weights approx. 65,000 and 110, 000 g/moL, with respective 0.65 and 1.02 inherent viscosities, and with an average density of 1.4 g/cm³ were used. Four different plasticizers were used; di-(2-ethylhexyl)phthalate (DEHP, 391 g/moL) was supplied by Sigma and dioctyl adipate (DOA, 371 g/moL), butylbenzyl phthalate (SANTICIZER®160, or BBP, 312 g/moL) and (2-ethylhexyl)diphenyl phosphate (SANTICIZER®141, or 2EHDP, 362 g/moL) were supplied by Monsanto Co., St. Louis MO, USA.

All chemicals used were laboratory grade, except for HPLC applications where methanol, acetonitrile and water were HPLC-grade products (J.T. Baker, Phillipsburg NJ, USA). In particular, (over 98 %) pure limonin (C₂₆H₃₀O₈, 470.52 g/moL) was supplied by LKT Laboratories Inc., St. Paul MN, USA.
2.3.2. Preparation of plastic films

Plasticized PVC films were cast from organic solutions (organosols) in our Laboratories. All organosols were prepared from 14 g of PVC powder in 90 mL tetrahydrofuran (THF). Both high (HMW) and low molecular weight (LMW) PVC solutions were stirred all night with a magnetic stirrer until solutions were smooth and transparent without apparent lumps. Then the appropriate amount of plasticizer, e.g. 40% w/w (or g per 100g total), was added into the solution; one sample was unplasticized for reference (“pure” PVC film). Stirring was needed for an hour for complete homogenization. Solutions were left for another hour to de-aerate. Containers were always covered to limit evaporation during stirring and subsequent standing. The organosol was cast onto wide glass plates and the thickness was adjusted by drawing a stainless steel Mayer bar along two stainless steel cylindrical rails. Two different rail thicknesses were used (1.6 and 1.1 mm diameter) to provide two plastic films of distinct thicknesses (about 100 and 200 µm) after solvent evaporation at room temperature and ambient Relative Humidity. Evaporation took place in a fume hood for one day; while the fume extractor was on, the glass screen was left a quarter open to allow uniform and reproducible membrane formation. Films were cut, pulled off by hand and stored in aluminum foil for a month at room temperature before use. They were odorless, transparent and very deformable, without detectable residual THF.

Other commercial plastic films were tested for limonin sorption: they are low density polyethylene - LDPE - (broad molecular weight distribution, MSU SoP, East Lansing, Michigan), used as standard, metallocene “mpo” (polyolefin-HDPE copolymer) and metallocene “eva” (ethylvinyl acetate-HDPE copolymer) closed-cell cross-linked foams with narrow molecular weight distribution (Sentinel Products Corp., Hyannis MA, USA), poly(ethylene terephthalate) Mylar® - PET - (the polymer commonly used for orange juice
plastic bottles), poly(vinyl acetate) - PVA -, and styrene butadiene copolymer - SB - (K-Resin® KR10 grade, Phillips Chemical Co., Houston TX, USA). A macroporous polypropylene (PP) woven film was also tested: Tyvek® 1059B, DuPont – E.I. du Pont de Nemours & Co. -, Wilmington DE, USA.

Also, two KRAFT cellulose papers, bleached and unbleached, were tested because of their chemical similarity to fruit pulp (MSU SoP, East Lansing MI, USA): in citrus fruits in particular, the bitter principles are initially present in the tissues and the pulp (Maier et al., 1980) in the glucoside forms (Hasegawa et al., 1991). Consistently previous investigators also already noted some interesting debittering properties of lignin (up to 48% removal) derived from carob seed (Magnoloto, 1981).

Finally not only films were tested but resin beads: pure PVC resin was tried as a powder, as well as Amberlite® XAD-4 and XAD-7 resins (Supelco, Sigma-Aldrich Co., Bellefonte PA, USA) which debittering activities (unpublished) were checked in our Laboratories: as they were comparable to those given by former studies (Johnson and Chandler, 1982 & 1988), only the latter, including many other XAD resins, will be considered in the 'debittering power' section (2.4.5).

2.3.3. Methods

2.3.3.a) Characteristics of the plastics

Films thickness was measured with a micrometer gauge (Testing Machines Inc., Ronkonkoma NY, USA) over 20 samples, and a CD-6”BS Digimatic Caliper (Mitutoyo Corp., Japan) for the permeation-studies bags.
2.3.3.b) Limonin sorption study

40 mL amber borosilicate-glass vials (Supelco, Sigma-Aldrich Co., St. Louis MO, USA) were chosen to restrict the decomposition of some sorbents due to light. By keeping the ratio (volume of liquid) / (surface of the polymer) in the 2-10 mL/inch$^2$ range, we could comply with the ASTM (American Society for Testing and Materials, West Conshohocken PA, USA) D4754-87 standard test method concerning two-sided liquid extraction of plastic materials using FDA migration cells (although they were not 23 mL vials as normally required) (Food and Drug Administration, Rockville MD, USA). They were shaken occasionally during the experiment.

Each film was cut into disks, 23 mm diameter, with a cork borer tool. Then, 16 disks were threaded onto a stainless steel wire with pairs of glass beads as spacers and placed in the glass vial. After filling up the vial with 32 mL of pulpy orange juice, it was carefully teflon-capped and maintained at room temperature during the experiment. A blank without plastic material was also prepared. 2 mL aliquots of juice were removed at regular time intervals until equilibrium was reached (less than 72 hours to prevent microbiological spoilage from occurring). One disk was also removed and assayed via direct acetonitrile extraction: this kept the surface to volume ratio constant. Trials were done at least in duplicates.

2.3.3.c) Limonin permeation study

Permeation of limonin was measured after a DOA-plasticized PVC bag, made in our laboratory, and filled with orange juice, was immersed into a well-stirred water solution of sodium hydroxide pH12 (Mallinkrodt Inc., Paris KY, USA), where limonin was expected to dissolve as limonoate A-ring lactone - besides a non bitter compound - (Figure 2.1). The bag was made in a similar manner as the films except the organosol was poured onto a glass tube. Sodium metabisulfite (J.T. Baker, Phillipsburg NJ, USA), 2.5 g/L, was added to the orange
juice for preservation purposes. At regular time intervals, 2 mL samples of the basic solution were extracted with 2 mL of acetonitrile, separated with ammonium sulfate and re-acidified to pH3 with hydrochloric acid (Mallinckrodt) to lactonize the limonoate.

A flow-chart also summarizes the experiment (Figure 2.2).

![Diagram of limonin and limonoate](image)

**Fig. 2.1 - Limonin (bitter), in acidic conditions, turns to limonoate A-ring lactone (non bitter), in alkaline conditions.**
Frozen Concentrated Navel Orange Juice
Sunkist Growers, Ontario CA

**ORANGE JUICE MAKING**
(water dilution up to 11 Brix)
Single Strength pulpy Orange Juice
Bitterness: 25 ppm w/w LIMONIN

**SORPTION EXPERIMENT ASTM D-4754**
16 Disks with 32 mL juice in tefloned amber glass vials occasionally shaken

**PERMEATION EXPERIMENT**
Plasticized PVC 'bags' filled with juice, and immersed into a NaOH pH12 stirred solution

2 mL Juice (and NaOH Solution) **SAMPLING**
at 0, 20 min., 1h, 3h, 5h, 72h
1 Disk sampling to keep film/ juice ratio constant

Juice Integrity Check
Brix, pH, taste and color (by tongue and eye only), vitamin C (not done)

Acetonitrile (AcN) **EXTRACTION** 1:1 v/v of LIMONIN (5 min.) and PLASTICIZERS (15 min.)
Juice and NaOH solution re-acidified: ammonium sulfate separation 5 min.
Disks: checking limonin's uptake
(Limonin Extraction Yield >99%) (Plasticizers Extraction Yields >95%)

**Standard Limonin Solution in AcN for HPLC Calibration**
Column C18
Eluant MeOH:AcN:Water 26.5:21.5:52 v/v/v, Temperature 23°C, UV Detector @ 207 nm, Rt = 6 min.

**LIMONIN SORPTION ASSAY**
Take 1 mL of upper AcN layer and fill the tefloned vials on the HPLC carrousel
Autosampler set on 10 µL injections

**PLASTICIZERS MIGRATION ASSAY**
Take 1 µL of upper AcN layer: GC Injection

**FLAVOR SCALPING ASSAY**
(Flavor Profile) (not carried out here)

Quantitation with Calibration Curves and Kinetics Plots
Computer Calculations: Kp, Sorption/Migration and D Coefficients through Crank's Theoretical Equations

Fig. 2.2 - Flow-chart of limonin sorption and plasticizers migration study. Primary objective: high limonin sorption, low plasticizer migration.
2.3.3.d) Limonin extraction and analysis

Limonin in orange juice was best extracted (over 99%) by shaking equal volumes (2 mL each) of acetonitrile (AcN) and juice (1:1 v/v extraction) for 1 minute. After another 30 seconds, 150 mg (approx.) ammonium sulfate (CCI Inc., Columbus WI, USA) were added to speed up phase separation. After 5 minutes standing, 1 mL of the upper clear solvent layer was removed and put into a 1 mL glass vial, which formed the inner core of a much larger plastic vial (Supelco) that could adapt to our HPLC carousel. Vials were stored at 4°C when the HPLC was not available for injection assays.

A similar procedure was followed with acetonitrile extraction of the plastic disks. Each disk to be analyzed was cleaned with EX-L cellulose tissue (Kimberly-Clark Co., Roswell GA, USA) to remove the orange pulp on the surface, and then soaked in 2 mL acetonitrile for 15 minutes (over 95% extraction yield), giving quicker and more accurate results than Soxhlet extraction because of less handling losses. Limonin was assayed directly by HPLC with no plasticizer interferences at the selected wavelength (207 nanometers). The mass balance could then be checked.

High performance liquid chromatography was performed at 23°C with automated 10 μL duplicate injections, according to the Shaw and Wilson method (1984). The latter was adjusted to this study: the column used was a Delta-Pak™ C18 300Å, 3.9x150 mm; the mobile phase was 26.5:21.5:52, v/v/v, HPLC grade methanol(MeOH)-acetonitrile-water; the flow rate was 1 mL/min at 100 bars (Shaw, 1986). The eluate was monitored with a ultraviolet Waters™ 486 tunable absorbance detector at 207 nm. A degassing device was mounted before the injection port. Limonin eluated after 6 minutes (Retention time, Rt).

The weight of limonin was calculated from the peak areas of the limonin standards calibration curve ($r^2=0.9986$) (Eq. 1):
\[ [\text{Limonin}] \, \mu g/mL = \text{Area}_{\text{HPLC response}} \cdot (2.210 \pm 0.016) \times 10^{-5} \quad (\text{Eq. 1}) \]

One disk, \(W\) grams, contacted 2 mL of juice with 3.8 cm\(^2\), each side, so that (Eq. 2):

\[ \text{Limonin sorbed}_{\mu \text{mol/dm}^2} = (\left[ C_0 \right] - \left[ C_{\text{equilibrium}} \right]) \, \mu \text{g/mL} \cdot \frac{200}{(7.6 \, \text{cm}^2 \times 470 \, \text{g/mol})} \quad (\text{Eq. 2}). \]

The weight balance was controlled by solvent extraction and HPLC assay: the amount of limonin disappearing from the juice was equal to that up-taken by the polymer (approx. 90%). The limonin uptake per unit area of mass of polymer was plotted as a function of time. Diffusion coefficient values were subsequently estimated by using the appropriate solution of the second Fick’s Law (Crank, 1975) and an iterative solver tool from Lotus 1-2-3 IBM® spreadsheet software.

2.3.3.e) Plasticizer migration assays

Acetonitrile proved to be a very efficient extraction solvent for the four plasticizers studied: therefore, the acetonitrile extraction of orange juice that was used for limonin assay was also used for plasticizer migration studies.

Following the US EPA (United States Environmental Protection Agency, Washington DC, USA) method 606 for phthalate esters assay, a HP 5890 gas chromatograph equipped with a flame ionization detector and a SPB-5 fused silica capillary column (30 m length x 0.32 mm i.d.) with non-polar bounded stationary phase was used. Conditions were slightly changed: Helium, 1.5 mL/min. @ 40 psi, was utilized as carrier gas. Other conditions were: Nitrogen, 30 mL/min. @ 30 psi, Air, 300-320 mL/min. @ 36 psi, and Hydrogen, 30 mL/min.
@ 18 psi. Temperatures were programmed as follows: injection port, 220°C, oven, 200°C to 250°C at 10°C/min. (hold 8 min.), and detection port, 280°C. Sample injection into acetonitrile was 1 µL, splitless.

Results were expressed according to calibration curves obtained for each plasticizer. Diffusion coefficients (D) were estimated using the simple ‘square root’ equation, Eq. 3 (Chapter 3), which was used for sorption experiments but which is still valid in our desorption case for small times according to Crank (1975): the ‘infinite polymer slab’, ‘infinite solution’, and ‘constant plasticization concentration’ conditions were satisfied, especially the latter because of the very high plasticizer concentration in the polymer, without significant change in 6 hours migration experiments.

\[
\frac{\text{Total amount desorbed at time } t}{\text{Total amount desorbed at equilibrium}} \approx \frac{4}{\sqrt{\pi}} x \frac{\sqrt{D t}}{\text{film thickness}}
\]  
(Eq. 3).
2.4. RESULTS & DISCUSSION

2.4.1. Effect of the type of polymer film on limonin sorption

We monitored the limonin concentration decrease in orange juice over 72 hours for the selected polymer films. For practical purposes, since 90% at least of the equilibrium concentration was reached after 5 hours (Table 2.1), and since all plasticized LMW PVC films could decrease limonin concentration by 40 to 85% in this time, we did not consider longer durations for any other films (LDPE, HDPE, PET, PVA, SB) because of their lower debittering performance (hence their respective limonin diffusion coefficients were certainly overestimated since their de-sorption equilibriums were not reached with certainty).

Polyolefins were not efficient in removing limonin from the juice: neither LDPE, nor the metalloocene ‘mpo’ foam were useful debittering agents, although we hoped that the greater surface to volume ratio of such hydrophobic (HDPE) foams would increase the sorption of limonin, a rather hydrophobic molecule too; in fact foams contain enormous air cavities, but there is no real porous system to allow any mass transfer. On the other hand, we tested a macroporous spunbonded olefin, Tyvek®, that exhibited some debittering effect, 13 ± 1% limonin reduction in only 1 hour. This result shows that limonin can be sorbed whenever the surface to volume ratio of the plastic in contact increases, but that the type of polymer is critical. In our case, polyolefins are no use. They are probably too hydrophobic (cf. limonin chemical formula, Figure 2.1).
Table 2.1 - Percent limonin decrease in orange juice after 5 hours sorption at 23°C (All films), except otherwise stated

<table>
<thead>
<tr>
<th>Plastic films characteristics</th>
<th>Limonin sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Thickness (µm)</td>
</tr>
<tr>
<td>LDPE</td>
<td>32 ± n/a</td>
</tr>
<tr>
<td>Metallocene ‘mpo’</td>
<td>1000 ± n/a</td>
</tr>
<tr>
<td>Tyvek® 1059B</td>
<td>165 ± n/a</td>
</tr>
<tr>
<td>(Woven HDPE)</td>
<td></td>
</tr>
<tr>
<td>PET Mylar®</td>
<td>13 ± n/a</td>
</tr>
<tr>
<td>PVA</td>
<td>38 ± n/a</td>
</tr>
<tr>
<td>Metallocene ‘eva’</td>
<td>690 ± n/a</td>
</tr>
<tr>
<td>Styrene Butadiene</td>
<td>25 ± n/a</td>
</tr>
<tr>
<td>K-Resin® KR10</td>
<td></td>
</tr>
<tr>
<td>KRAFT (unbleached)</td>
<td>155 ± n/a</td>
</tr>
<tr>
<td>KRAFT (bleached)</td>
<td>124 ± n/a</td>
</tr>
<tr>
<td>PVC* (unplasticized)</td>
<td>127 ± n/a</td>
</tr>
<tr>
<td>PVC*-DOA</td>
<td>124 ± 8</td>
</tr>
<tr>
<td>PVC*-DEHP</td>
<td>137 ± 3</td>
</tr>
<tr>
<td>PVC*-2EHDPP</td>
<td>120 ± 5</td>
</tr>
<tr>
<td>PVC*-BBP</td>
<td>122 ± 15</td>
</tr>
</tbody>
</table>

NB: initial limonin concentration was 20.8 ± 2.6 µg/mL except for “pure” PVC and KRAFT papers experiments, 26.7 ± 1.0 µg/mL; *: LMW; n/a: not available.
PET and SB-copolymer scarcely sorbed any limonin whereas PVA, which has less tight chains, could sorb a lot more. Indeed, the higher the crystallinity of the polymer, the lower the sorption.

Unbleached KRAFT paper was very efficient (45 ± 3 % limonin removal) whereas bleached paper was totally inefficient. One interpretation would be that, in the paper industry, during the KRAFT process (sulfonation and bleaching), the water dissolution of lignin (a complex hydrophobic polymer with phenyl-propane units including methoxy- and phenol groups) requires the formation of hydrophilic groups in particular through chlorine oxidation (Nolan, 1970; Singh, 1970). The resulting hydrogen bonding cementing effect between processed lignin fibres further increases crystallinity; therefore bleached KRAFT paper is too hydrophilic for effectively sorbing the hydrophobic limonin (Table 2.1).

Finally, we observed (by smelling) that the use of unbleached paper gave strong off-flavors to the orange juice, preventing its potential commercial debittering utilization.

The use of unplasticized PVC appeared more promising for limonin removal from the juice: in 5 hours, we already reached 13 ± 1 % limonin reduction, similar to the value obtained with the macroporous Tyvek®. As the pure PVC film was not porous, and because PVC has a very tight chain structure, PVC’s affinity for limonin appeared greater. Remarkably both PVC and limonin are hydrophobic and slightly polar: our theory was that chlorine moieties might be involved in limonin affinity for PVC. Consistently, a study realized by physical chemists on the selective adsorption of furan rings (limonin has one) by some alkali halides (like NaCl) confirms its relevance (Guérin and Léard, 1982).

Consequently, in order to further improve limonin sorption, PVC chains would need to be more available, for instance by increasing the surface to volume ratio (beads or powder) or
by facilitating limonin diffusion with the addition of plasticizers. The latter case was experimented and results are shown in Figure 2.3.

Fig. 2.3 - Effect of the type of plasticizer on limonin sorption kinetics into plasticized PVC, "pure" PVC, and LDPE. % w/w Reductions in limonin may be obtained by multiplying the sorbed quantities in mg/dm$^2$ by 173, or by 141 (approx.) for pure PVC.
Figure 2.3 is a plot of the limonin sorption kinetics for the four different plasticized PVC films. For comparison, the effect of the standard LDPE is also indicated, the pure PVC behaving similarly with an equilibrium sorption of about $0.07 \pm 0.01 \text{ mg/dm}^2$ (about 13% limonin reduction). In only 5 hours, the equilibrium stage was nearly reached: the sorption phenomena involved are extremely quick.

Although the plasticizer quantity was 40% w/w for all four films, PVC chains were probably not as mobilized to sorb limonin, hence not as debittering-effective, for each type of plasticizer: the type of plasticizer seemed crucial, as noted by Sears and Darby (1982). For example it is shown that trilolyl or triphenyl phosphate gels the most rapidly with PVC (good plasticization) whereas DOA and paraffinic oils do it with difficulty (less good plasticization). Consistently, the phosphate plasticizer (2EHDP), which structure is very close to triphenyl phosphate, ended up to be the most efficient for limonin sorption, whereas the DOA and the BBP behave similarly as moderate debittering PVC additives, and DEHP was not as efficient as one might have thought (being commonly considered as one of the best plasticizer for PVC).

Therefore, specific interactions coming from the chemical structure of each plasticizer are very important. This is in agreement with Shailaja and Yaseen (1993): they mentioned for instance that phthalate alkyl chains’ hydrophobic repulsion could explain the loss of initial water barrier properties of their plasticized PVC membranes whereas, on the other hand, Chandler and Johnson (1977) could not explain limonin sorption in terms of hydrogen bonding or hydrophobic interactions, but a number of possibilities were addressed.
Nevertheless the first role of a plasticizer is of kinetic order: it enhances the local chain segmental mobilities, leading to an increase in the free volume, while also lowering the glass transition temperature, Tg (Sears and Darby, 1982). Diffusion wise, pure PVC and DEHP plasticized PVC appear to give the best results (Table 2.2), but not 2EHDPP films which are yet the best sorption wise.

**Table 2.2** - Estimated limonin partition coefficients $K_{90}$, at 90% (approx.) sorption equilibrium, and diffusion coefficients D (percents error between parentheses)

<table>
<thead>
<tr>
<th></th>
<th>PVC $^a$</th>
<th>40% w/w plasticized low molecular weight PVC films</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>PVC-DOA</td>
<td>PVC-DEHP</td>
</tr>
<tr>
<td>$K_{90}^b$</td>
<td>&lt;15</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>(n/a)</td>
<td>(66%)</td>
</tr>
<tr>
<td>D ($10^{-14}$ m$^2$/s)</td>
<td>&lt;17</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>(n/a)</td>
<td>(11%)</td>
</tr>
</tbody>
</table>

$^a$ “pure” PVC film in the “glassy” state, the other plastics being in the “rubbery” state.  
$^b$ (mg limonin sorbed / mL of sheet per mg limonin remaining in solution / mL orange juice).

n/a means “not available”.

Consequently, although kinetic considerations are commonly appropriate, and explanatory, for diffusion, our results showed that plasticization also has a thermodynamic role, meaning that in particular surface polymer segmental mobility is a condition for increased sorption. It results that a high plasticizer concentration, permitting a greater spatial movement, should give even better debittering results: agreeably in preliminary studies the author (Fayoux et al., 1996) showed that d-limonene was sorbed greater when increasing the
DOA and DEHP content of PVC. Similar results were later obtained with several compounds such as vanillin into 20, 30 and 40 % w/w acetyl tributylcitrate plasticized PVC films (Chapter 3). Pure plasticizers (100% w/w) should be tried for liquid / liquid extractions of limonin in orange juice, as it was done very early with olive oil with success, but with obvious organoleptic issues: this should demonstrate limonin's affinity for plasticizers.

Understanding the interactions involved is a difficult task but the differences observed in Fig. 2.3 stress the relevance of further studying molecular compatibility in order to optimize sorption (diffusion being already optimized, since PVC can not bear higher plasticizer levels at the risk of obtaining plasticizer exsudates). Therefore it is advisable to consider here, on top of common plasticizer-polymer compatibility, the dual affinity of limonin for a plasticizer and a for a polymer (conditions that seems fulfilled with our plasticized PVC films).

2.4.2. Effect of the PVC molecular weight

Figure 2.4 is an histogram representing the limonin concentration in our four plasticized film, made of lower (LMW) or higher molecular weight (HMW) PVC. We observed that LMW PVC films exhibited significantly greater limonin sorption. What could explain these results is that the chain lengths, being less for LMW PVC, more readily allow the penetrant to move and search for another free volume to hop into. Also, HMW PVC is believed to be more crystalline and more difficult to plasticize than LMW PVC: during the fabrication of organosols, plasticizers were probably mixing less homogeneously with HMW PVC powder than with LMW's. In agreement with this idea, for the same 40% w/w plasticization level, we observed that the LMW PVC film appeared more flexible to the touch.
Fig. 2.4 - Effect of PVC molecular weight on limonin sorption, after 72 hours (considered as equilibrium time) at 23°C. Values after 5 hours were given in Table 2.1 for LMW PVC films.
Differential Scanning Calorimetry plots were very difficult to interpret as many ‘jumps’ in the curve appeared: plasticized films may not be homogeneous (as mentioned earlier re. plastic crystallinity ratios), depending upon the particular compatibility of the plasticizer with the polymer. Accordingly it was not relevant to present such graphs in the paper; they are currently being studied in our Laboratories.

Eventually, when Figure 2.4 sorption results are compared to those obtained for KRAFT papers, where bleaching lowers the average molecular weight, we get the opposite effect because the ‘absorbate’-polymer compatibility end up to be more important (and critical) than the polymer structural characteristics. Nevertheless, it would be interesting to continue testing wider PVC molecular weight ranges in order to obtain more significant results.

### 2.4.3. Effect of the film thickness

As only macroporous resins or polymers have been used in the industry (Tseng et al., 1993), limonin has always been considered to be ad-sorbed. A competitive race for greater surface to volume ratios was concluded with cross-linked polystyrene divinylbenzene resins (like Amberlite® XADs) with incredible adsorption power. With 50,000-fold less surface to volume ratios (in our experiments, 0.01 m²/g of film), we still managed to decrease the limonin concentration from 20 down to 5 ppm w/v in only 5 hours, in orange juice. Supposing a more specific limonin-film compatibility was achieved so that limonin absorption kinetics were very quick, limonin sorption had to be still in the main a surface phenomenon.
Fig. 2.5 - Effect of the film thickness on limonin sorption, after 72 hours at 23°C. NB: "Thin" films were 126 ± 8 µm thick and “thick” films were 205 ± 35 µm thick.
Changing the film thickness was aimed at understanding the limonin sorption phenomena. Was it an ad-sorption or a complete ab-sorption? After less than 72 hours, the sorption curves plateaued. Figure 2.5 summarizes the equilibrium limonin concentrations in the film, in mg/g as a function of the film thicknesses at that stage. For thicker films, the concentration was lower, indicating a slower equilibration time or possibly a surface sorption phenomenon. We found that the amounts of limonin sorbed in mg/dm$^2$ were identical within experimental error (10%). Still it is possible that equilibrium was not reached due to the very slow migration of limonin through the film. Due to potential microbiological spoilage it was not possible to pursue the experiment for longer periods. With unprocessed fresh orange juice Figure 2.5 may not give the final definite total limonin sorption value.

Since limonin is at least three times bigger than the usual solvents or flavors, and is not flexible, it might be expected to have a much smaller diffusion coefficient. To support this idea, we decided to estimate an apparent diffusion coefficient by using the following solution of the second Fick’s Law (Crank, 1975) for a stirred solution of limited volume (Eq. 4): the (shaken) vials initially contained 32 mL of orange juice and about 1 mL of plastic films, resulting in a v/v ratio that was considered sufficiently high to follow this 'limited volume' hypothesis; besides it was unchanged all along the experiment:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-\frac{D q_n^2 t}{L^2}\right)$$  

(Eq. 4)

where $M_t$ is the total amount of limonin sorbed into the film (in µg) at time t, $M_\infty$ is the corresponding quantity after infinite time (equilibrium), $q_n$ are the non-zero positive roots of tan $q_n = -\alpha q_n$, and $\alpha$ times the partition coefficient $K$ equals the ratio of the volumes of orange juice and disks. $K_{90}$, i.e. when $M_t / M_\infty = 0.9$, was particularly used for convenient and
rapid estimation of the diffusion coefficient. Samplings were stopped after 5-6 h sorption, when 90% of the equilibrium was reached for all films (106 ± 29, 92 ± 16, 95 ± 20 and 90 ± 18 % respectively for DOA-, DEHP-, 2EHDPP- and BBP-plasticized films); in prior studies, they were resumed after 72 hours to reach equilibrium stages. Therefore diffusion calculations were carried out when $M_t / M_\infty = 0.9$. Five terms were needed ($n=5$) to get 89%, 91%, 78% and 86% accuracy (i.e. the sum of the exponential coefficients) - 95% for unplasticized PVC.

The results for our four plasticized membranes are given in Table 2.2. Diffusion coefficients of the order of $10^{-14}$ m$^2$/s are common in the rubbery state whereas $10^{-19}$ m$^2$/s values are common in the glassy state (eg. “pure” PVC).

First in pure PVC, limonin’s diffusion coefficient should hence be a lot lower than $10^{-19}$ m$^2$/s but Table 2.2’s estimate is one million more: this result is too far from a realistic figure and this may be attributed to the calculation procedures which needs to take into account a definite value for equilibrium. But this may be attributed more reasonably to a too short duration of the experiments, especially because glassy polymers need a lot more time to reach equilibrium, and although the sorption curve appeared flat after 72 hours.

Secondly, the plasticized PVC films exhibited limonin diffusion coefficients of a fair $10^{-14}$ m$^2$/s value, similar to that of the smaller citrus terpene d-limonene (Table 2.3) in a similar “rubbery” environment. Theoretically bigger molecules migrate slower than smaller ones but in a very plasticized polymer, this may not be applicable (Rogers, 1985), and especially with 40% w/w plasticization. Thus it is relevant to suggest that limonin, although bulkier, would diffuse easily under these particular conditions, at the rate of $10^{-14}$ m$^2$/s. It is
believed that at least a slow limonin transfer occurs in the plastic, and if this is so, our
equations would give an equilibrium time of about a month, not in about 3 days (72 hours).

**Table 2.3** - Literature data for d-limonene diffusion coefficients ($D$ in m$^2$/s) into glassy and rubbery
copolymers

<table>
<thead>
<tr>
<th></th>
<th>Glassy State ( $T &lt; T_g$ )</th>
<th>Rubbery State ( $T &gt; T_g$ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-limonene into polystyrene</td>
<td>$D_{C_1-C_{10}} &lt;&lt; 10^{-16}$ a</td>
<td>$D_{C_1-C_{10}} &gt; 10^{-14}$ a</td>
</tr>
<tr>
<td>d-limonene into poly(vinyl chloride)</td>
<td>$3 \times 10^{-18}$</td>
<td>$&lt; 10^{-19}$</td>
</tr>
<tr>
<td>d-limonene into high density polyethylene</td>
<td>$3 \times 10^{-14}$</td>
<td>$2.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>d-limonene into oriented polypropylene</td>
<td>$3 \times 10^{-14}$</td>
<td></td>
</tr>
</tbody>
</table>

a Crank and Park (1968); Berens and Hopfenberg (1982).

Previous results were obtained for LMW PVC films.

For HMW PVC films, diffusion coefficients were not significantly different ($6.4 \times 10^{-14}$
and $1.5 \times 10^{-13}$ m$^2$/s for the PVC-DOA and PVC-DEHP films respectively - % error n/a -).

Apparently, the change in molecular weight would affect sorption more than diffusion, for
plasticized PVC films: once sorbed, the limonin molecule would diffuse between the polymer
chains at the same rate, be they long or short. However, at the surface of the polymer, longer
chains might handicap limonin in the search for an “entry” site (Fig. 2.6): shortening polymer
chains when using plastic films should increase their “porosity”. Therefore the sorption
mechanism is critical for limonin.

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2.4.4. Permeation studies

In order to actually test limonin diffusion through the films, we measured the concentration of limonin in the NaOH solution, located on the other side of the 200 µm thick (<10% error) membrane. As far as plasticizers migration is concerned, after 15 days permeation at 23°C, no significant amount was observed into the alkaline solution (< 1 ppm) although DOA was being released into the orange juice, as observed during normal sorption studies (no extra peak, due for example to any hydrolysis, was observed on chromatograms.).
A calculation of the number of days needed to permeate such a thick membrane gave about a month. This result is in fact sufficient to explain why no limonin was assayed on the other side of the film after 15 days. A longer lasting experiment or a thinner film might have given a positive result, in agreement with the previous findings of Jiang et al. (1997). The use of a preservative into the juice is common and could interfere with limonin sorption, and pasteurization of the juice might also interfere with the sorption, and also increases the limonin content of the juice; this is preferably done before debittering (Shaw, 1994). The best option is to reduce the thickness of the film. Unless the area is increased thanks to other means, a new permeation technique to make thin films (eg. coating on perforated plate) would have to be developed as thinner films will become extremely difficult to handle.

2.4.5. Debittering power

A comparison between our optimized films and literature data was attempted, and especially with the current resins used in the industry, XAD-16 being the most used (Chandler and Johnson, 1981, 82, 88; Tseng et al., 1993) (Fig. 2.7).

The debittering power, $\xi$, was expressed as (Eq. 5):

$$\xi = \frac{Volume_{OJ}}{Volume_{Polymer}} \times \frac{[Limonin]_{initial} - [Limonin]_{equilibrium}}{[Limonin]_{initial}}$$  (Eq. 5)

This dimensionless ratio does not take into account the surface area of the polymer in contact with the juice. Commercially, the specific surface area, SSA in m$^2$/g resin, is the important factor. A ratio taking into account the surface area of the polymer in contact with
the orange juice (OJ) was better measuring the actual affinity of the polymer towards limonin: we called it surface debittering efficiency, \( \text{SDE} = \xi / \text{SSA} \), in g/m².

Plasticized PVC performed 1,000-fold better than all cross-linked polystyrene divinylbenzene resins (XADs or S-861), or cellulose acetate flakes or beads (Fig. 2.7 presents the results relatively to the greatest sorbent).

In fact the difference between macroporosity and nanoporosity is the core issue: macroporous polymers (resins) have important SSAs (from 25 for XAD-12 up to 860 m²/g for XAD-16) whereas unplasticized films have small SSAs (from 0.002 for Metallocenes to 0.15 m²/g for the PET film). Strictly speaking, all other sorbents' SSAs were inappropriate but they may not have been measured adequately (eg. by nitrogen gas adsorption): indeed, plasticized PVC films, KRAFT papers, cellulose acetate flakes (probably swollen by contacting the juice), and cellulose acetate beads (“plasticized” by water before manipulation), can be considered as gels. “Nano”-porosity is a property of gels: like pectin, which has been demonstrated to hold more limonin in aqueous solution (and in the orange juice), it comprises a 3-dimensional network of molecules holding together a great bulk of water with the appearance of an elastic solid (Johnson and Chandler, 1978). By using appropriate molecules as fillers between polymer chains, nanometric diffusion channels are created (probably about 1.5 nanometre, corresponding to the plasticizers / limonin size), allowing a better contact between the polymer and limonin than with usual industrial resins (which average pore diameters range from about 4 nm for XAD-4 to 20 nm for XAD-1) (Johnson and Chandler, 1988). Effectively debittering was improved thanks to the use of gels, or “liquid membranes”.
Fig. 2.7 - Relative surface debittering efficiencies (SDE): comparison of the PVC films with industrial polymers *. SDEs are normalized on PVC-2EHDP results. All limonin sorption uptakes taken into account correspond to over 90% of the equilibrium values; SSAs are in m²/g of dry matter for XADs, S-861 resins, and cellulose acetate sorbents, all being considered as porous materials; ** bleached KRAFT paper value is a maximum value; *** Tyvek(R) value idem, since its specific surface area (SSA) was underestimated for such a macroporous material.
On this criterion, when not plasticized, no membrane debittering technology is likely to supplant any macroporous resin bead techniques, excepting if a very limonin-specific membrane is developed. This has been developed but in that case the mass transfer was active as it involved some enzymatic treatment: cellulose acetate membranes with entrapped naringinase have recently been fabricated (Soares and Hotchkisss, 1998), for naringin (another bitter limonoid of similar chemical structure) removal from grapefruit juice, but limonin was not adequately sorbed. Indeed, cellulose acetate was not as compatible with limonin as plasticized PVC, as it is explained in the following paragraph and in next Fig. 2.8. In a future work cellulose acetate could be plasticized with similar plasticizers in order to get even better debittering efficiencies (phthalates, glycerides, etc).

An attempt to understand the plasticized PVCs/limonin compatibility was sought with the use of the solubility parameters (δ) (Grulke, 1989). Calculations were carried out following Hoy’s (van Krevelen, 1990) group contribution method (For KRAFT papers, an estimation was possible by considering the chemical structures presented in the Handbook of Pulp and Paper Technology - Nolan and Singh, 1970 ;-; the other chemical structures were known and approximations were made as far as their branching is concerned).

The difference between the polymer and the ‘absorbate’ solubility parameters, Δδ, should be as little as possible, and estimated lower than 5 MPa$^{1/2}$ - or (J.cm$^{-3}$)$^{1/2}$ - for actual solubility to occur, i.e. for sorption to occur. The surface debittering efficiencies are presented Fig. 2.8, in function of these compatibility indicators, Δδs, between limonin and each of the polymers.
Fig. 2.8 - SDEs (g/m²) vs. Δδs (MPa¹/²) - Hoy's method - of plasticized PVC films, commercial films and resins, and cellulose acetate flakes and gel beads. The dotted line at 5 MPa¹/² represents the solubility threshold (Sears and Darby, 1982). a water is indicated as a least efficient debittering agent; b cross-linked macroporous polyacrylate resin; c the uncertainties on Δδ calculations are due to the approximation of the chemical formulas to take into account (lignin and cellulose), in particular after 'kraft' and bleaching processes (eg. NaHSO₃ and H₂O₂ reactions); d non porous copolymer (closed-cell foam); e should have lower SDE because of its high specific surface area (not measured); (1) PVC-BBP; (2) PVC-DEHP; (3) PVC-DOA; (4) PVC-2EHDPP.
Sorption can therefore be predicted for a number of polymers, considering the number of points below the 5 MPa$^{1/2}$ threshold: for instance, poly-vinyl acetate and acrylate seem promising. During the $\Delta\delta$ calculation of KRAFT papers, lignin alone gave also good results but not cellulose, unless esterified.

This tool may serve to select a new better polymer for improved limonin sorption. However, the structure of the polymer still needs to be taken into account (molecular weight, crystallinity, tacticity, spatial conformation, macro/nano-porosity, etc).

2.4.6. Plasticizer migration

The presence of plasticizer in the PVC film lowers the glass transition temperature (Tg) of the film, enhancing the local chain segmental mobilities, leading to an increase in the free volume. Consequently, a high plasticizer concentration permits a greater mobility for penetrant molecules as well as for the plasticizer itself. Penetrant molecules (or ‘absorbates’) may also over-plasticize PVC in a similar way to d-limonene with polyethylene (Baner et al., 1986), and improve themselves their diffusion rate: this is often observed with initially unplasticized polymers through swelling.

In our case while limonin is sorbed, plasticizers may be released into the orange juice in the same time.

Figure 2.9(a, b, c, d) shows both the limonin sorption into the plastic films and the plasticizer migration into the orange juice. Results are indicated in $\mu$moL/dm$^2$ in order to test the existence of a sorption / migration synergy i.e. whether one molecule of limonin would replace one molecule of plasticizer (in our case, limonin and the other plasticizers have similar molecular weights):
Fig. 2.9 - Limonin sorption into the plastic films versus plasticizer migration into the orange juice, relative to the European Community (EC) Specific Migration Limits (SMLs), when available. The Global Migration Limit is about 30 µmol / dm² for all plasticizers; curves are drawn to fit to the 72 h 'equilibrium' sampling plots; n/a: not available. NB: y-axis scales differ; multiply by 38 to get µmol / litre of juice.
The graphs indicate that sorption and migration seem to be two independent phenomena. Still, plasticizer migration could rule out the commercial use of the films so that specific migration limits are indicated on Fig. 2.9. Only European Community limits are indicated (Council Directives 82/711/EEC, 85/572/EEC) as they are more drastic than the FDA US limits (FDA, 1988).

After 5 hours, DOA and DEHP were released at a lower rate than limonin was sorbed whereas 2EHDPP and especially BBP migrated too quickly into the juice. Two hours only sufficed for BBP to overtake the EC limit and, although it provides very good debittering, this drawback prevents its consideration for debittering purposes. The ratio, [limonin sorbed] divided by [plasticizer migrated] after 5 hours, gives a definite advantage to DOA and DEHP. The comparison of the four plasticizers’ diffusion coefficients (x 10^{-19} \text{ m}^2/\text{s}) also acknowledges this fact: 1.89 \pm 0.08, 0.7 \pm 0.1, 19.4 \pm 0.6 and 178 \pm 39, respectively for DOA-, DEHP-, 2EHDPP- and BBP-plasticized PVC films. DOA should be the preferred material because of the well-known phthalate suspected toxic effects (Markx, 1972; Elcombe and Mitchell, 1986; Lhuguenot et al., 1988; Anonym., 1995; Petersen et al., 1995).

Already new plasticizers have been proposed to replace the phthalates in PVC. However, DOA ends up to migrate faster and its safety has not yet been established for sure. More hopefully acetyl tributylcitrate (ATBC) which the author used in contact with food and non food molecules (Chapter 5), the use of polymeric plasticizers which barely migrate (Kalaoutzis and Demertzis, 1992) and the use of modified vegetable oils (Pryde and Rothfus, 1989) such as epoxidized soya oils (ESOs) might be preferred.
2.5. CONCLUSION

Amongst all films tested the plasticized PVCs were the best limonin removing materials, followed by KRAFT papers.

Different kinds of plasticizers exhibited different effects on the sorption of limonin in 40% w/w plasticized PVC films. The “phosphate” was the most efficient. However, for migration reasons, it could not be selected. The best compromise would be the DOA and DEHP of which only the adipate may be allowed in food contact. It realized over 60% limonin decrease in 5 hours, that being accompanied with a DOA migration into the orange juice of only one tenth of the EC Specific Migration limit.

The sorption phenomenon is believed to involve a fast ad-sorption followed by a slow ab-sorption, but further test need to be done. In any case, limonin sorption was increased by lowering the PVC molecular weight, thus permitting the absorbate to diffuse more freely into the polymer matrix. Sorption and migration occur simultaneously and probably synergistically, with one material triggering the other. By seeking the best limonin-plasticizer polymer compatibility with the help of the solubility parameter tool, it might be possible to design specific formulations for greater sorption with lower migration.

For example, cellulose acetate can also be highly plasticized (phthalates and glycerides) and appears to have a high affinity for limonin (Chandler and Johnson, 1977), and might form an efficient debittering “liquid membrane”, so any plasticized plant fibers material (in particular lignin); any “liquid membrane” such as this would yield the best Surface Debittering Efficiency, according to our findings (the commercial XAD resins end up to be extremely unspecific). Polymeric plasticizers, and food authorized (GRAS – “Generally
Recognized As Safe”) plasticizers might be compatible with EC regulations and environmental trends.

Pilot plant debittering could be initiated, but there may be some doubts about the recycling (and re-use) of the film. Additional data concerning limonin permeation is needed for the purpose; a thinner film needs to be tested with the same alkaline side-concentration setup as that proposed by the USDA in 1996. Fouling has to be assessed as well as the integrity of the organoleptic characteristics of the juice before and after the process (nutrition, flavors, colors).

As future work, it would be necessary to fundamentally understand the interactions occurring between such a liquid membrane and the adsorbed materials. At the moment, the mechanisms of limonin sorption by highly plasticized PVC films are still unclear, so that other important constituents of citrus juices may be unwillingly sorbed.

For these reasons, and to make relevant contributions to the juice and beverage industry, it is important to study the sorption of many other (simpler) “model” molecules by such plastics. The objective is therefore to tailor plasticized PVC films (change plastic formulas) for a specific task or to test one formula and screen the sorption of structurally close compounds, which also implies speeding up sorption kinetics assessments.

This work is currently being continued at UWSH, Australia, with a better food contact plasticizer. A range of chemicals with a wide variety of structures are being tested in contact with such a film, in an attempt to find a relationship between absorbate's physico-chemical characteristics and sorption activity. Hopefully this will give some insight into the limonin sorption enigma.
2.6. REFERENCES


• Magnoloto, 1981. Location of bitter principles of orange juice in the pulp.


• Shaw, P.E. 1994. Private communication, USDA ARS Citrus Research and Education Center, Lake Alfred, Florida.


2.7. LIST OF TABLES

**Table 2.1** - Percent limonin decrease in orange juice after 5 hours sorption at 23°C (All films), except otherwise stated

**Table 2.2** - Estimated limonin partition coefficients \( K_{90} \), at 90% (approx.) sorption equilibrium, and diffusion coefficients \( D \) (percents error between parentheses)

**Table 2.3** - Literature data for d-limonene diffusion coefficients (\( D \) in \( m^2/s \)) into glassy and rubbery polymers
2.8. LIST OF FIGURES

Fig. 2.1 - Limonin (bitter), in acidic conditions, turns to limonoate A-ring lactone (non bitter), in alkaline conditions.

Fig. 2.2 - Flow-chart of limonin sorption and plasticizers migration study. Primary objective: high limonin sorption, low plasticizer migration.

Fig. 2.3 - Effect of the type of plasticizer on limonin sorption kinetics into plasticized PVC, “pure” PVC, and LDPE. % w/w Reductions in limonin may be obtained by multiplying the sorbed quantities in mg/dm$^2$ by 173, or by 141 (approx.) for pure PVC.

Fig. 2.4 - Effect of PVC molecular weight on limonin sorption.

Fig. 2.5 - Effect of the film thickness on limonin sorption. “Thin” films were 126 ± 8 µm thick and “thick” films were 205 ± 35 µm thick.

Fig. 2.6 - Schematic of limonin sorption in plasticized, high / low molecular weight PVC films. Limonin molecules (oval-shaped) are represented near to Aβ-sorption sites only, where their diffusion should begin.

Fig. 2.7 - Relative surface debittering efficiencies (SDE): comparison of the PVC films with industrial polymers. SDEs are normalized on PVC-2EHDP results. All limonin sorption uptakes taken into account correspond to over 90% of the equilibrium values.

Fig. 2.8 - SDEs (g/m$^2$) vs. $\Delta\delta$s (MPa$^{1/2}$) - Hoy’s method - of plasticized PVC films, commercial films and resins, and cellulose acetate flakes and gel beads. The dotted line at 5 MPa$^{1/2}$ represents the solubility threshold (Sears and Darby, 1982).

Fig. 2.9 - Limonin sorption into the plastic films versus plasticizer migration into the orange juice, relative to the European Community (EC) Specific Migration Limits (SMLs), when available. The Global Migration Limit is about 30 µmoL / dm$^2$ for all plasticizers.
CHAPTER 3

EXPERIMENTAL RESEARCH

SORPTION AND DIFFUSION EVALUATION
OF AROMA COMPOUNDS & FOOD ANTI-OXIDANTS
IN HIGHLY PLASTICISED PVC FILMS:
‘HEADSPACE’ TECHNIQUE V. LAMINATE
TECHNIQUE
3.1. ABSTRACT

It has been shown in Chapter 2 that whereas un-plasticised polymer films showed little effect in debittering orange juice by removing limonin, the major bitter component, highly plasticised PVC films (plastisols) were extremely efficient.

In this Chapter a variety of model compounds (alcohols and aromatic compounds) have been used to investigate both the sorption mechanism itself and also the desorption of the plasticiser from the film into the surrounding media (back-migration).

Two different techniques have been used and compared.

The first is the traditional ‘headspace technique’ in which strips of test films are suspended in a closed container over the saturated vapour of a volatile test reagent. In many cases the test reagent is quite compatible with the plasticiser, and a kind of ‘solvent extraction’ (desorption) of plasticiser occurred on the film surface, causing great practical difficulties in measuring, by weighing, the uptake of reagent, especially as the samples are wiped before each weighing.

In the second type, the test reagent is dissolved in a polymer film, which is placed firmly in contact on both sides of the polymer film to be tested for its sorption and diffusion properties. This ‘supply’ film provides a concentrated solution of the test reagent (‘absorbate’), thermodynamically but not kinetically equivalent to the ‘headspace’ method, and non-volatile ‘absorbates’ may also be used. This ‘3-layer laminate’ procedure is commonly used with liquid solvent systems (eg. orange juice),
but the advantage of a polymer-solvent is that diffusion of the polymer-solvent into the test material does not occur (a polymeric matrix acting as a ‘solid solvent system’).

There are also two types of measurement, corresponding to traditional sorption methods, as above, in which the test film is measured at time intervals for the uptake of ‘absorbate’, or by transmission through the test film and measured by another absorbing film on the other side, which is usually a slower technique, depending on the thickness of the test film (‘5-layer laminate technique’).

Both micro-gravimetric and spectrophotometric methods have been used to assay the film samples.

Attempts have been made to estimate diffusion coefficients and solubilities of the ‘absorbates’ in the plastisol, and useful guidelines on the likely sorption and back-migration behaviour of food and film additive components in food packages can be constructed. It is also possible to compare diffusion from the vapour phase in the ‘headspace’ with diffusion from and into the solid and liquid components in intimate contact with packaging.

**Keywords:** Laminate; Sorption; Diffusion; Plasticiser; Migration
3.2. INTRODUCTION

The interactions between packaging and foodstuffs or pharmaceuticals have been the subject of much research, because of intermittent scalping or off-flavour problems \(^1\) which are often difficult to monitor and expensive to measure (supercritical carbon dioxide coupled to gas chromatography for example). \(^2\)

Not only off-flavours but many additives can be released from the packaging \(^3\): such migrations have been assessed in the liquid phase (orange and other fruit juices \(^4\) - see Chapter 1A - olive oil and many liquid simulants \(^5,6\)) just like the sorption of aroma compounds.

Often, to simplify the interpretation of the sorption results obtained, the ‘solvent’ parameter (eg. water in orange juice) has been eliminated by measuring sorption kinetics in the vapour phase: the diffusion coefficient of an organic vapour sorbed by a plastic film can be determined by using the basic ‘headspace’ technique \(^7\). It involves measuring, at regular time intervals, the amount of ‘absorbate’ taken up by a piece of polymer film in a closed volume containing an excess of the absorbate vapour. Although results are accurate, it still often takes a long time to reach equilibrium. Furthermore the method is not sensitive for high molecular weight (eg. low vapour pressure or high boiling point) compounds.

However not all packaged items exchange material in the vapour phase.

In particular, this leaves unsolved the problem of migration to and from solid foods in contact with packaging films. Few recent experiments have been done \(^8\) but modelling is not easy.
The ‘laminate technique’ addresses this problem: it is actually similar in principle to the recent ‘sandwich’ functional barriers which have emerged for recycled packagings. In this case the sorption kinetics of any kind of ‘absorbate’ should be measurable. Similarly to the ‘headspace’, there is no solvent, except when large quantities of plastic additives are used in one of the films in contact, but proportions can be varied to model different kinds of foodstuffs/packagings.

We propose to use this technique, with for the first time highly plasticised PVC films composing the multiple sandwiched layers, in particular as a model of food matrix. This was developed in CSIRO, Australia, by R.V. Holland and R. Santangelo in order to measure odour transmission rates through food packaging films and now to model the sorption of orange juice components of organoleptic interest. We will also utilise the ‘headspace’ technique in order to discuss the advantages and the disadvantages of both techniques, depending on diverse parameters such as the type of compound to test, the plasticiser concentration (0, 20, 30, 40% w/w), the assay (gravimetric or spectrophotometric), the procedure used (3-layer sorption or 5-layer transmission mode); finally a ‘square root’ calculation method will estimate the diffusion coefficients of absorbates, before attempting to predict their sorption kinetics in plasticised environments.
Figure 3.1.(a). Schematic diagram of the ‘headspace’ experiment, at 22°C

- TEFLONned glass top
- Stainless steel hook
- Glass jar
- High vapour pressure compound
- Nylon thread
- Plastic films (ATBC20, 30, 40)
- Cellulose liner

Figure 3.1.(b). Schematic diagram of the experimental laminate assemblages before compacting: (a) ‘3-layer’ sorption, and (b) ‘5-layer’ transmission, at 22°C

- External Al foil preventing evaporation from Supply film
- Middle film
- Al foil & sticky tape for easy manipulation
- Test film
- Respective test film weight change in function of time
- Time lag
Figure 3.1.(c). Arrangements of films in the 3-layer laminate technique

Aluminium foil
Supply film ‘loaded’ with aroma compound
Test film ‘initially unloaded’ and taking up the aroma compound

Figure 3.1.(d). Arrangements of films in the 5-layer laminate technique

Aluminium foil
Supply film ‘loaded’ with aroma compound
Middle film ‘initially unloaded’
Test film ‘initially unloaded’ and taking up the aroma compound, after a certain ‘time-lag’
3.3. THEORETICAL CONSIDERATIONS

Figures 3.1.(a)(b)(c)(d) illustrate the three different arrangements of test films described above.

In all cases the standard version of Fick’s second law (\( \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \)) is chosen, and the partition coefficient \( K_p \) (the relative solubility \( S \) of the absorbate between the supply film containing the absorbate, and the test film, see Figure 3.1.(e) at the end of section) and the diffusion coefficient \( D \), which expresses the ease of transfer through the film, can be both estimated. \( S \) was obtained in equilibrium conditions between the saturated (1 Molar) supply film and the test film, when the test film absorbed no more material.

In the following section a solution to Fick's law for both the 3-layer laminate method and the ‘headspace’ technique is expressed by equation 3.1a (3.1b in approximate form for small times) for finding \( D \), and by equation 3.2 (the ‘time-lag’ method) in transmission experiments.

3.3.1. Determination of \( D \) by the ‘constant supply’ method

A constant supply of absorbate with uniform initial distribution \((C=C_0=c_{st}^{(saturation)}) \text{ at } x<L/2 \text{ and } x>L/2, \text{ } C_0=0 \text{ when } -L<2x<L\), and a constant film thickness are assumed. This means an homogeneous, continuous and saturated supply of absorbate is needed: in all cases a 1 M reagent level caused cloudiness or oiliness in the film, and as reagent was depleted, more dissolved.
The complex equation obtained by the use of the Laplace transform\textsuperscript{12} is shown below:

\[
\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{L^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \int_{nL/2\sqrt{Dt}}^\infty \text{erfc} \, \xi \, d\xi \right\} \quad (3.1a)
\]

where \text{erfc} is commonly referred to as the error-function complement (erfc = 1-\text{erf})\textsuperscript{12}. It has been reduced for small times to equation 3.1b:

\[
\frac{M_t}{M_\infty} \approx 4 \sqrt{\pi} \left( \frac{Dt}{L^2} \right)^{1/2} \quad (3.1b)
\]

with \(M_t\) the mass of absorbed material at time \(t\), \(M_\infty\) the equivalent at equilibrium, \(D\) the diffusion coefficient in m\(^2\).s\(^{-1}\), \(L\) the thickness of the test film in metres. This allows an average value for the diffusion coefficient to be rapidly calculated from the initial gradient of the sorption curve when plotted against the square root of time. Of course the final concentration in the test film is \(C_\infty = C_0\) (and \(K_p = 1\)).

This approximation was also called here the ‘square root I’ calculation method.

3.3.2. Determination of \(D\) by the ‘time-lag’ method

The time-lag method was used for transmission experiments using the 5-layer laminate technique. In this case too diffusion and thickness are assumed constant. The absorbate concentration in the external supply layers needs to be constant so that the following expression remains valid, although approximate because in our case the test
film concentration was not maintained at zero concentration. The solution to Fick’s second law has an intercept on the t-axis given by Equation 3.2 (as \( t \to +\infty \)):

\[
\tau = \frac{L^2}{6D} \quad (3.2)
\]

with \( \tau \), the ‘time-lag’ in seconds (corresponding approximately to the time for a permeant to go through a film of thickness \( L \), in metres), and \( D \), the diffusion coefficient in \( \text{m}^2\text{s}^{-1} \).

### 3.3.3. Determination of D by other calculation methods

Other versions of the diffusion equation could be used, following the lines of Mohney et al.\textsuperscript{13} and of several packaging research teams\textsuperscript{14}: in particular the ‘Tan Qn’ method (if the external supply layer is considered as a stirred solution of limited volume) or the ‘impermeable 3-layer method’ (used for calculations concerning recycled packaging films\textsuperscript{15} which sides have been coated by ‘clean’ plastic films) which does take into account the depletion of the supply film. They also have similar ‘square root II, and square root III’ approximations for small times. Nevertheless in prior studies we found that they did not lead to better results.
Figure 3.1.(e). Calculation of the partition coefficient $K_p$ of absorbates in the 3-layer laminate technique

<table>
<thead>
<tr>
<th>Initial composition of the laminate</th>
<th>Supply film</th>
<th>Test film</th>
<th>Supply film</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>ATBC</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Absorbate</td>
<td>$x$</td>
<td>0</td>
<td>$x$</td>
</tr>
</tbody>
</table>

100 g. initially

Initially ‘$x$’ grams of absorbate was added into the organosol of the supply film to get a 1 Molar concentration, assuming first that the totality of the absorbate is solubilised in the supply film (which may not always be the case, in particular when supply films were cloudy), and assuming secondly that $d_{\text{absorbate}} \approx 1 \text{ g/mL}$ and $d_{\text{ATBC}} \approx 1 \text{ g/mL}$ and approximating $d_{\text{PVC}} \approx 1.4 \text{ g/mL}$: then,

$$x = \frac{60}{d_{\text{PVC}}} + \frac{40}{d_{\text{ATBC}}} \approx \frac{83}{1000},$$

with $\text{MW}_{\text{absorbate}}$ the molecular weight of the absorbate studied in g/mol.

<table>
<thead>
<tr>
<th>Final composition of the laminate (sorption equilibrium)</th>
<th>Supply film</th>
<th>Test film</th>
<th>Supply film</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>ATBC</td>
<td>$c$</td>
<td>$b$</td>
<td>$c$</td>
</tr>
<tr>
<td>Absorbate</td>
<td>$x-a/2$</td>
<td>$a$</td>
<td>$x-a/2$</td>
</tr>
</tbody>
</table>

At equilibrium the main hypothesis taken was that ATBC and absorbate mass transfers were independent of each other. This is to simplify the calculation (Effectively the plasticiser migration may well depend on the absorbate diffusion).

Accordingly, $K'_{p(\text{ATBC})} = \frac{[\text{ATBC}]_{\text{supply}}}{[\text{ATBC}]_{\text{test}}} = 1$ for the plasticiser, $a$ is defined with the relation $\Delta m = a + b - 40$ (the mass uptake of the test film at equilibrium, measured experimentally, in g/100g of initial test film, or % w/w),

$$b = \frac{3.40 \left( a + \frac{60}{d_{\text{PVC}}} \right)}{2. x + 3. \frac{60}{d_{\text{PVC}}}} = \frac{3.40 \left( \Delta m + 40 + \frac{60}{d_{\text{PVC}}} \right)}{2. x + 3.40 + 3. \frac{60}{d_{\text{PVC}}}} \approx \frac{\Delta m + 83}{x + \frac{83}{60 + 40}}$$

(balance). The partition coefficient of the absorbate is therefore:

$$K_{p(\text{absorbate})} = \frac{[\text{absorbate}]_{\text{test}}}{[\text{absorbate}]_{\text{supply}}} = \frac{a \left( x-a/2 + \frac{3.40-b}{2. d_{\text{ATBC}} + d_{\text{PVC}}} + \frac{60}{d_{\text{absorbate}}} \right)}{(x-a/2) \left( \frac{a}{d_{\text{absorbate}}} + \frac{b}{d_{\text{ATBC}}} + \frac{60}{d_{\text{PVC}}} \right)}$$

with the concentration of the absorbate, noted $[\text{absorbate}]$, in mol/L of film.
3.4. MATERIALS AND METHODS

3.4.1. Chemicals

All chemicals were laboratory grade, generally over 98% purity. Concerning ‘absorbates’, 5 aromatics were used: vanillin, 2[3]-tert-butyl-4-hydroxyanisole (BHA), 2[6]-di-tert-butyl-p-cresol (BHT), anisole and chlorobenzene. 4 alcohols were chosen for comparison purposes: 1-butanol, 1-hexanol, cyclohexanol and 1-octanol. Finally β-carotene was sometimes used as a common food component. Compounds not containing double bonds (low UV extinction coefficients) were not assayed via spectrophotometry but gravimetry only.

Next page, Table 3.1 presents the compounds list, together with their principal physico-chemical characteristics.
### Table 3.1. Principal physico-chemical characteristics of selected compounds (sorted by boiling points and/or vapour pressures)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular Weight g/mol</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
<th>Density g/cm³</th>
<th>Vapour pressure* mmHg @25°C</th>
<th>Supplier information**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alcohols (gravimetric method)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butanol</td>
<td>C₄H₁₀O</td>
<td>74.12</td>
<td>-90</td>
<td>117.7</td>
<td>0.810</td>
<td>6.70</td>
<td>M&amp;B Aust Pty Ltd., ’AR’</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>C₆H₁₄O</td>
<td>102.18</td>
<td>-52</td>
<td>156.5</td>
<td>0.814</td>
<td>0.928</td>
<td>A, 98%</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>C₆H₁₂O</td>
<td>100.16</td>
<td>+21</td>
<td>160.5</td>
<td>0.963</td>
<td>0.8</td>
<td>A, 99%</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>C₈H₁₈O</td>
<td>130.23</td>
<td>-15</td>
<td>196</td>
<td>0.827</td>
<td>0.0794</td>
<td>Fluka AG Sw</td>
</tr>
<tr>
<td><strong>Aromatics and other unsaturated (spectrophotometry and gravimetry)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>C₆H₅Cl</td>
<td>112.56</td>
<td>-45.58</td>
<td>131.687</td>
<td>1.107</td>
<td>12.0</td>
<td>Ajax Chem. Aust S</td>
</tr>
<tr>
<td>Anisole</td>
<td>C₇H₈O</td>
<td>108.14</td>
<td>-37.3</td>
<td>155.5</td>
<td>0.9961(20/4)</td>
<td>3.54</td>
<td>S, &gt;90%, 3-isomers</td>
</tr>
<tr>
<td>BHA</td>
<td>C₁₁H₁₈O₂</td>
<td>180.25</td>
<td>+48-55</td>
<td>264-70(733)</td>
<td>n/a</td>
<td>n/a</td>
<td>S, &gt;99%</td>
</tr>
<tr>
<td>BHT</td>
<td>C₁₁H₁₈O₂</td>
<td>220.36</td>
<td>+70</td>
<td>265</td>
<td>1.048(20/4)</td>
<td>0.00516</td>
<td></td>
</tr>
<tr>
<td>Vanillin</td>
<td>C₈H₈O₃</td>
<td>152.15</td>
<td>+77-82#</td>
<td>285</td>
<td>1.056</td>
<td>0.000118</td>
<td>S</td>
</tr>
<tr>
<td>β-Carotene</td>
<td>C₄₀H₅₆</td>
<td>536.88</td>
<td>+184</td>
<td>n/a</td>
<td>1.00(20/20)</td>
<td>n/a</td>
<td></td>
</tr>
</tbody>
</table>


** A = Aldrich Chemical Co. Inc., Milwaukee, WI, USA; S = Sigma Chemical Co., St. Louis, MO, USA; Aust = Australia; Sw = Switzerland; with % purity when available.

# depending on crystalline form.

### Notes:

- # at 760 mm Hg otherwise stated between parentheses.
- ## at 760 mm Hg otherwise stated between parentheses.
- ### (x/y) means it was measured at x °C in reference to water at y °C, other values at 25°C.
3.4.2. The making of plastic films

The following method is in part similar to that described in Chapter 2: an organic solution (organosol) was prepared by dissolving 14 g of PVC powder (‘inherent viscosity 0.51’ re. Aldrich) in 90 ml tetrahydrofuran (THF, 99.9% anhydrous and inhibitor free; Aldrich), before adding the required amount of plasticiser, acetyl tributyl citrate (ATBC; Croda Surfactants, NSW, Australia) to get final 0, 20, 30 or 40% w/w total plasticised plastics. ATBC was chosen because it may be an acceptable replacement to phthalates in food applications. The plastic films that were obtained were called PVC, ATBC20, ATBC30 and ATBC40.

Before film casting, a smooth organosol without air bubbles was needed: overnight stirring and one hour standing were satisfactory: no visible air bubbles were detected.

Supply films were made from the same organosol batch by adding aroma compounds (1 Molar, and sometimes 0.1 M), stirring for ten minutes and another hour standing.

Films were cast directly onto a glass plate, or onto aluminium (Al) foil, followed by dragging a threaded cylinder across. The depth of the threading generated a specific thickness for the plastic film, generally between 50 and 100 µm (accurately determined later). Evaporation of THF took place in a fume cupboard at 22°C. The slower the evaporation process, the smoother the film, and the less the aroma loss (this problem was addressed by choosing a high absorbate concentration - 1 Molar - in the film, which in all cases provided the ‘supersaturation’ required by the use of equation 3.1a (Note that the term ‘supersaturation’ was used for a saturated solution with excess undissolved absorbate).
Usually, overnight evaporation, was required for THF to completely disappear (this state corresponded to no weight change for films without aroma loading). Films (plastisols) were easily released from their support (glass or foil) by hand, and stored in Al foil at 22°C and 75% humidity (laboratory conditions). No significant change in weight (<5%) was measured in the first month.

A 2109F dial thickness gauge (precision ± 1 µm) from Mitutoyo Corp., Japan, was used to measure film thicknesses at a number of points. Films with a homogeneous thickness (<5% difference in sample) were then cut into strips of 2 cm x 6 cm, and stored or immediately used for sorption experiments.

3.4.3. General experimental conditions

All films were handled with tweezers, in closed rooms at 22°C, with a minimum of air movement to limit evaporation of the absorbate and prevent dust from settling. Jars and laminates were in immediate proximity to the balance and the spectrophotometer.

Monitoring lasted until equilibrium was reached (i.e. no more mass transfer detected). The duration of the experiments was adjusted in preliminary trials.

3.4.4. The ‘headspace’ technique

500 mL glass jars (Verrerie d’Arques, France), equipped with lockable glass tops and rubber seals, were used. Seals were previously coated with Teflon™ tape to get the desired confinement. Then the inside of the jars were lined with cellulose tissue and filled with at least 5 ml of one of the liquid organic compounds. A saturated
vapour pressure (Table 3.1) was created at room temperature and kept constant because liquid was always present at the bottom of the jar. Jars were left 2 weeks at 22°C before sampling started.

The required number of ready-to-use films, tightly wrapped into Al foil during storage (see 3.4.2.), was removed before the experiment: then weights and thicknesses of the selected strips of plastic films were recorded (with a minimum of two measurements and replicates) before suspending them with hooks (from paper clips) on polyester threads (Figure 3.1.(a)) inside the jar sealed volume. Films’ weight was recorded to monitor sorption kinetics: at regular time intervals the jar was unlocked, opened rapidly, films were unhooked and removed from the jar with tweezers, before locking the jar again. Films were then carefully wiped with cellulose tissue to remove condensation, and carefully weighed. Such manipulation lasted an average of one minute. Films were immediately placed back into the jar.

When sorption mass uptakes were too strong too rapidly (anisole and chlorobenzene), strips were exposed to the vapour during only 10 seconds each time before quickly closing the jar, but this could lead to repeatability errors beyond 20%.

Sampling had to be done every 30 minutes at least in order to re-saturate the ‘headspace’: in preliminary studies this re-saturation was checked by comparing this type of sampling to another procedure consisting in using 6 jars with 1-octanol (which had the lowest vapour pressure), introducing films simultaneously at start, and sampling them at different times in different jars.
3.4.5. The laminate techniques

In section 3.3, this new experimental technique was described to facilitate the understanding of the mathematical expressions proposed. In this section we are giving more experimental details.

3.4.5.a) The 3-layer ‘sorption’ technique

A test film (not loaded with aroma compounds i.e. a ‘clean’ film) is sandwiched between two supply films (initially loaded with 1M of aroma compound). Experimentally it was more convenient to fold a 2 ½ cm x 13 cm strip of supply film over a central and smaller 2 cm x 6 cm strip of test film, to ensure a good contact between films. Films being generally sticky because of high plasticisation levels, this contact could be considered to be tight. Finally, the supply film was carefully covered with Al foil on its external face, adhering likewise (Figure 3.1.(b)), to limitate evaporation of the absorbate.

Test and supply films had the same plasticiser concentration (before addition of absorbate) in order to simplify the interpretation of the mass transfers involved.

At all times the central film was handled by a small strip of Al foil attached to a small strip of sticky tape at its extremity. The foil and tape allowed for more rapid attachment to the microbalance hook, reducing time of evaporation, but absorbed an insignificant amount of material. Tweezers were used to avoid contamination from gloves. At the beginning, the test film was thus placed in the centre of the supply films folder. At regular time intervals the folder was opened and the central test film was removed (still with tweezers), before closing the folder. It was placed either into the microbalance chamber or positioned on a specially made spectrophotometer cell. At
least two samples were assayed for each absorbate. The gravimetry procedure lasted about a minute whereas spectrophotometry measurements were often faster. Then as the test film was leaving some marks of its location inside the folder (because of pressing), it was placed back at the same position. Pressing was done first by hand. Then laminates were stored under a 5 mm glass plate (giving a constant pressure), as ‘sealing procedure’.

3.4.5.b) The 5-layer ‘transmission’ technique

Similarly to the 3-layer technique, the 5-layer ‘transmission’ technique consisted in a superposition of 5 plastic films: one, central, being unloaded, covered by a folded unloaded film (the middle film), covered itself by another folded, but loaded, film, this one being finally covered with Al foil to prevent the absorbate from evaporating. Contacting layers were also usually of the same plasticiser concentration.

The test film was 2 cm x 6 cm in size. Both the middle and supply films were 2 ½ cm x 13 cm to fully cover the test film. All thicknesses have been recorded in duplicate before starting the experiment.

Sorption monitoring was the same as in the 3-layer technique. The measurements were different because the weight change of the test film was zero all the while the absorbate was migrating through the middle film.

Whatever the laminate technique used here, there was no direct relation between the concentrations in the laminate film technique and the vapour pressures of the pure compounds in the ‘headspace’ technique: the latter technique gave the maximum permeation possible for very volatile materials, the former gave a standard gradient (≤1M permeant).
3.4.6. Sorption kinetics monitoring by mass and absorbance measurements

3.4.6.a) Gravimetry

Gravimetry was used for cases listed in Table 3.3. The measuring apparatus consisted in an electronic microbalance, precision $\pm 1 \mu g$ (Model 4503 MP6, Sartorius, Göttingen, Germany), kindly lent by Food Science Australia (DFST, North Ryde NSW, Australia).

For laminate techniques, test films were attached with sticky tape to an Al foil strip, for handling purposes (neither the tape nor the foil was contacting the supply films). In the ‘headspace’ technique, film strips could be weighed without taking such precautions as the amount of sorbed material was high.

During weighing, de-sorption occurred slowly and the highest initial value displayed by the electronic balance was recorded. Films were placed back to their initial positions as soon as possible. The balance was regularly re-calibrated at 300.000 mg.

In principle much larger samples could be weighed using a standard balance, but greater quantities of test materials might not always be available, and evaporation might be a critical issue.

3.4.6.b) Spectrophotometry

Spectrophotometry was used to monitor sorption kinetics of vanillin, BHA, BHT, and chlorobenzene. Some attempts were also carried out with $\beta$-carotene and a common PVC plasticiser, di-octyl phthalate (DOP).

Films were scanned from 200 to 350 nm using a UV-visible spectrophotometer (LKB Biochrom-4060, Pharmacia Biotech, Cambridge, U.K.). They were positioned
with sticky tape on a plastic absorbance cell with apertures for the scanning beam. Absorbance was recorded at several wavelengths (not obligatorily at $\lambda_{\text{max}}$). The best discriminative peak was chosen to express the sorption of the absorbate: Table 3.2 presents some wavelengths used for the compounds containing benzene rings: the best discriminating wavelength depended on the degree of plasticisation (for example 305 nm was chosen for vanillin in ATBC40, and 290 nm for BHA – see Figure 3.4.(a)).

<table>
<thead>
<tr>
<th>Name of compounds</th>
<th>Wavelength (nanometres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanillin</td>
<td>205, 230, 274$^{(1)}$, 305$^{(1)}$</td>
</tr>
<tr>
<td>BHA</td>
<td>204, 227, 290$^{(1)}$</td>
</tr>
<tr>
<td>BHT</td>
<td>204, 217$^{(2)}$, 277$^{(1)}$</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>288</td>
</tr>
<tr>
<td>DOP</td>
<td>206, 225$^{(3)}$, 274$^{(1)}$</td>
</tr>
</tbody>
</table>

(1) measured in ATBC40, (2) peak with shoulder, (3) wide peak

3.4.6.c) Analysis of raw experimental results

Films were assayed at least in duplicate: measurement averages ($<5\%$ standard deviation) of weight ($M_t$) or absorbance ($A_t$) values were used for plotting (for convenience). When using absorbance to evaluate mass transfers, no standard calibration curve was needed because only the ratio of the absorbance $A_t$ to that at equilibrium $A_\infty$ was used ($\frac{A_t}{A_\infty} = \frac{M_t}{M_\infty}$) according to Chapter 3.3.1.

Sorption was evaluated by the maximum weight uptake in g per 100 g of initial film (noted $\%$ w/w, or $\Delta m/100$), whereas diffusion needed solving the equations previously mentioned.
3.4.7. Objective of the study

A number of alcohols of differing types were used as model compounds, in order to try and determine the relative importance of MW, vapour pressure, and other physical characteristics on the sorption and diffusion of a similar group of compounds. In contrast, another group of compounds with quite different characteristics, but in most cases of some relevance in food applications, were also chosen for a preliminary survey in this field.

Through the analysis of the sorption kinetics of these absorbates, the objective was to get an idea of the adequacy of each technique for mass transfer characteristics determination in highly plasticised PVC, by comparing techniques and measurement methods.

| Table 3.3. Experimental plan showing the compounds and the parameters studied |
|---|---|---|
| Laminate technique | ‘Headspace’ technique |
| Sorption | Transmission | Sorption * |
| Gravimetry | All compounds studied except DOP (in ATBC40) | Vanillin, 1-Hexanol, Cyclohexanol, 1-Octanol, BHT, Chlorobenzene (in ATBC40) | 1-Butanol, 1-Hexanol, Cyclohexanol, 1-Octanol, Chlorobenzene, Anisole (in ATBC20/30/40) |
| Spectrophotometry | Vanillin (in ATBC20/40) DOP, BHA, BHT, Chlorobenzene & β-Carotene (in ATBC40) | Vanillin (in ATBC20/30/40) DOP (in ATBC20/40) BHA & Chlorobenzene (in ATBC40) | N/A |

* Transmission experiments were not performed in the vapour phase. N/A not available.
Laminate and ‘headspace’ techniques, gravimetry and spectrophotometry assays, sorption and transmission methods were not always tested with ‘universal’ compounds, as not all techniques were appropriate for any particular compound. Also comparisons of results were not all possible for experimental reasons (e.g. timing), as shown in Table 3.3.

However, some cross-correlations can be discussed:
Figure 3.2.(a). 3-layer laminate technique sorption curves, and (b) 'headspace' technique sorption curves, for 40% ATBC w/w plasticised films, at 22°C; same x-scales are used for comparison; note the y-scale difference; all plots are means of at least 2 replicates (max. 5% standard deviation).
Figure 3.2.(c). Sorption percentages observed in the 3-layer laminate and the 'headspace' techniques, for studied compounds (gravimetric assay), in 40% w/w ATBC plasticised PVC films, at 22°C (Equilibrium is always reached in the laminate technique; equilibrium flags indicate steady state in the 'headspace' technique, cf (b)).
3.5. RESULTS AND DISCUSSION

3.5.1. Three-layer laminate and sorption measurements by gravimetry

The following comparative sorption results concern four alcohols and two aromatic compounds (see Figures 3.2.(a)(b) and (c)).

The most obvious difference between the ‘headspace’ and sorption methods in the above graphs is the roughly tenfold greater weight changes observed in the ‘headspace’ method over time, though the relative rate of change over the same time scale appears much the same.

A second feature of interest is that similar kinetic anomalies in the form of negative weight changes occur in both methods.

Thirdly, there appears to be no great correlation between the weight changes measured by each method.

At first glance these differences might seem alarming, but are indeed mostly to be expected from analysis of the physical parameters involved.

3.5.1.a) Sorption kinetic anomalies in the ‘headspace’

In the ‘headspace’ technique, the supply of absorbate vapour is essentially unlimited, but the uptake rate must be kinetically limited at some stage when the vapour pressure is quite low (see vapour pressures in Table 3.1).
Secondly, any plasticiser in the film with a great affinity for the absorbate will tend to move into the surface condensed layer of absorbate (liquid/liquid extraction), and eventually be removed by wiping or dripping off the film. Absorbates with a lesser affinity will tend to remain absorbed in equilibrium with the vapour.

This extraction of ATBC by droplets on the film surface was similar to an experiment reported by Castle et al. during microwave-cooking of soup: the ATBC transfer was due to the condensation of water from the hot soup onto the inner surface of the plasticised PVC film wrapper. The extraction of the plasticiser was followed by condensate dripping into the soup.

In the case of the more volatile absorbates, the weighing procedure is also likely to lose material by evaporation.

With these principles in mind, we find that 1-octanol (boiling point 196°C) is absorbed slowly over a period of at least 240 minutes, cyclohexanol (b.p. 160°C) a little faster, 1-hexanol (b.p. 157°C) about the same with a tendency to decrease at 240 mins, anisole (b.p. 156°C) with obviously a great affinity for the plastisol is absorbed rapidly, and loses weight equally rapidly, chlorobenzene (b.p. 132°C), another strong absorber, disappears even faster. As regards 1-butanol (b.p. 118°C), it would appear to be too volatile to be measured satisfactorily.
Figure 3.3. Gravimetric results: 3-layer laminate sorption curves for vanillin (dotted lines), BHA, BHT (full line) and \( \beta \)-carotene (long dotted lines showing negative mass change after 4000 min i.e. 2.8 days), for 40% w/w ATBC plasticised films, at 22°C.
3.5.1.b) 3-layer laminate anomalous results

The laminate technique is not essentially dependent on the vapour pressure of the absorbate, but volatiles will still be lost, more from the test films when being weighed because of longer exposure to the atmosphere, but eventually from the supply films. This would gradually modify concentration gradients and affect sorption equilibria. The fact that the test films show weight changes over many minutes show that diffusion is still occurring after several hours, but the weight loss measured under these conditions is suspect (evaporation).

Secondly a (super)saturated solution in the supply film corresponds to the saturated vapour pressure of the ‘headspace’ method, but in this case there is a limited supply of absorbate (<1 M) in the supply film, and also a kinetic limitation in the diffusion rate between the supply and test films. This phenomenon would also decrease concentration gradients between films. However, the rates to the absorption peaks seem to be comparable in the two methods.

Finally, although the supply film and the test film both start with the same amount of plasticiser, there will always be a miss-match as soon as a soluble absorbate is added to the supply film, changing the relative concentrations, until equilibrium is reached, as the plasticiser will migrate in the opposite direction to the absorbate.

Along these lines, in Figure 3.2.(a), octanol is no longer the slowest, but the fastest migrating material, with an absorption peak followed by a lower plateau region. This is interpreted as a rapid migration of a reasonably soluble absorbate, followed by a slower back-migration of the larger plasticiser molecules, similarly with anisole, together (because of higher vapour pressure in this case) with a continuous loss of weight by evaporation. It also indicates that at the low vapour pressures above pure
octanol, the ‘headspace’ method is kinetically limited. Cyclohexanol appears to take longer to reach its maximum value and back-migration of plasticiser is not observed: both “apparently” migrate at about the same rate. The other compounds, including chlorobenzene, suffer a major loss of weight, probably due to high evaporation losses during weighings. It may be noted that chlorobenzene has a very high vapour pressure compared to octanol, and in this case the ‘headspace’ method appears superior, because of somewhat faster weighings (or of higher concentration gradients caused by condensation droplets).

In Figure 3.3, a number of non-volatile film additives are tested (in duplicate), including a re-used vanillin film to test how effective saturated vanillin films are after one run, and a 0.1 M vanillin film.

The conclusions are that the saturated vanillin films perform well throughout the first run, into the second. The duplicates agree well, indicating that a reproducible maximum transmission rate through the interface is likely, and the 0.1 M vanillin films show that less-than-saturated films may not give satisfactory results. It may not appear clear why this is the case, as the concentration gradients of the plasticiser and vanillin are similarly reduced, but in fact the vanillin molecules are rapidly depleted at the interface, are not replaced by dissolved materials in this particular case, and have progressively further to travel as the interface molecules are depleted.

To summarise, volatile materials (bp < 180°C, i.e. vp > 1 mmHg approx.) cause considerable practical problems with weighings, but their general affinity for plastisols can still be observed.
Kinetic anomalies can be explained: weight losses are due to absorbate loss, and to counter-diffusion (back-migration) of plasticiser into the supply film. Hence for low vapour pressure materials the laminate technique may help to quantify back-migration.

3.5.1.c) Improving the laminate technique

As with the 0.1 M vanillin experiment, a range of absorbate concentration trials (0.1, 0.2, 0.3 M, etc) could be tested to find the concentration threshold that initiates mass transfers for each particular absorbate, in the same fashion as sorption isotherms are usually obtained before undertaking ‘headspace’ experiments.

An example of the importance of knowing the saturation state of the supply film can be given with our results when 1 M of supply material is added in the plastic film, and this does not imply a high concentration gradient. The example of β-carotene showed that a significant weight loss was observed in the long term (5000 minutes, i.e. 3 ½ days), but not in the short term (left scale in Figure 3.3). This is consistent with the size difference between plasticiser (402 g/mol) and absorbate (537 g/mol). The slightly smaller plasticiser molecules now migrate, under a very slight concentration gradient presumably, more rapidly into the supply film than β-carotene into the test film. Unlike β-carotene, vanillin and probably BHA and BHT happened to be soluble enough in the plastisol to produce high enough gradients to outweigh ATBC migration.

A modified experimental procedure could be followed by stopping the plasticiser from migrating. A test film could be tailored with a specific plasticiser concentration, that would be identical to the concentration obtained initially in the supply film (eg. for a 100 MW absorbate, about 36.7 % w/w for 1 M and 39.7 % w/w
for 0.1 M absorbate concentration, see Figure 3.1(e)) for each absorbate. This procedure could be rather time consuming.

Obviously in our case the separation of absorbate sorption from ATBC migration, eg. by spectrophotometry, would help determine absorbate concentration changes.

### 3.5.2. Spectrophotometric results

Instead of gravimetry, spectrophotometry was used for a few absorbates with reasonable UV absorbances, including measuring diffusion of the plasticiser DOP into ATBC plasticised films. Only the initial stages could be measured, as the absorbance values soon went off scale (see Figure 3.4. and Table 3.4).

DOP appeared to equilibrate in four hours (same values after four days). The whole technique appears rather restrictive in that absorbance measurements go rapidly off scale in many systems, but in principle could answer many questions for which gravimetry is unsatisfactory, especially since ATBC has a low absorbance in much of its spectrum, and therefore does not interfere eg. with DOP desorption from plastisol during debittering (see Chapter 2), or with the migration studies considered here.

Finally with modified experimental conditions, sorption kinetics obtained by spectrophotometry, free from plasticiser back-migration, could allow the estimation of the effective diffusion coefficients more accurately (those indicated in Table 3.4. are only approximate): spectrophotometry should be restricted to compounds with low extinction coefficients, in order to keep absorbate concentration gradients high and still using the simple equations proposed (re. the constant supply condition).
Figure 3.4. Spectrophotometric results: (a). example of a BHA spectrophotogram versus time, for 40% ATBC w/w plasticised film, & (b). vanillin, BHA, BHT and DOP sorption curves, for 50 µm normalized thickness films, and for 20, 30, and 40% plasticised films, at 22°C. DOP concentration was 0.1M instead of 1M and was also tested after 4 days (*); error bars are indicated for some plots only: they are mainly due to film thickness errors; NB the effective comparison of the sorption curves should be done by weight, not absorbance values; the parentheses 'ATBC40>20' mean for example that the supply film is ATBC40 and the middle film is ATBC20 (the test film is always ATBC40)
Table 3.4. Transmission (5-layer laminate) versus Sorption (3-layer laminate): a comparison of some diffusion coefficients D estimated via two different methods.

<table>
<thead>
<tr>
<th>Absorbate names &amp; type of film *</th>
<th>Sorption ('Square root I' method)</th>
<th>Transmission (Time-lag method)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D ( \times 10^{-13} \text{ m}^2\text{s}^{-1} )</td>
<td>% Error</td>
</tr>
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<td>Vanillin20</td>
</tr>
<tr>
<td></td>
<td>Technique</td>
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</tr>
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<td></td>
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</tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>DOP40 ** +4days</td>
</tr>
<tr>
<td><strong>Gravimetry</strong></td>
<td>Laminate</td>
<td>Vanillin40</td>
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<td></td>
<td>Technique</td>
<td>Vanillin40 ****</td>
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<tr>
<td></td>
<td></td>
<td>Vanillin40 (re-use)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BHA40</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Anisole40</td>
</tr>
</tbody>
</table>

◊ for sorption results via spectrophotometry, the equilibrium phase was extrapolated graphically, causing really more error than indicated, especially with BHA; * the number immediately after the absorbate’s name is the % plasticisation in ATBC; ** DOP concentration in the film was 0.1M; *** experiment not followed long enough as the migration was extremely slow; **** experiment carried out 1 week after the previous one; # the migration of chlorobenzene was too fast for accurate determination of D with the ‘square root I’ calculation method; ## no sorption was observed with this method, but a negative weight change; n/a not available
3.5.3. **Diffusion coefficients results and discussion**

3.5.3.a) ‘Headspace’ v. laminate

In many cases there is a serious discrepancy between diffusion coefficients calculated for the ‘headspace’ technique and those calculated from laminate data (Table 3.4). The enormously fast ‘diffusion coefficients’ for butanol and chlorobenzene, for example, are suspect. The explanation appears to be as follows:

Many of the ‘headspace’ samples accumulate a liquid layer, and/or liquid drops, on the surface. This liquid appears to be a solution of plasticiser and absorbate, and is an example of phase separation. This liquid layer does not necessarily allow greatly accelerated diffusion, but the mobility of the surface layer (drop formation) plus frequent wiping down guarantees convective mixing of the two liquids and a vastly increased ‘diffusion rate’. These problems are not easily overcome.

In the laminate technique, the supply films are also phase-separated (inhomogeneous), but there is no apparent mechanism for transferring excess absorbate to the test film, when the concentration gradient is saturated, but not ‘supersaturated’, a thermodynamically unstable condition. ‘Supersaturation’ can be observed easily in a few cases, in the form of an oily exudation smelling the absorbate on the supply film’s surface (like for octanol) (‘over-plasticisation’) or when this surface is covered of powder (or crystals, like for β-carotene) of absorbate (possible ‘anti-plasticisation’). But in the majority of cases the test film has the added advantage of reaching the saturation solubility. Convection in the gel-like state is also very unlikely, and the values obtained, though erratic and variable between the various methods of measurement, are all consistent with purely diffusive transport.
3.5.3.b) Calculation of D using short term kinetics

The equation 3.1b was used to calculate values for Table 3.4, using only the initial slopes of the kinetics in the ‘headspace’ (see also Figure 3.6) and 3-layer techniques. Only ‘apparent initial diffusion coefficients’ are obtained this way; they are also summarised in Figure 3.7. The calculation of exact diffusion coefficients is obviously problematic because of evaporation problems in many cases, and counter-diffusion of plasticiser in all of them (see for instance the decreasing curves after 2 hour-sorption in Figure 3.6). Nevertheless by focusing on short times both disturbances can be minimised. These figures may be considered as minimum values only, but in the range of liquid diffusion rather than into normal polymer.

Figures 3.5.(a)(b) were useful for studying diffusion in the transmission manner, but not sorption, because of the much longer time-scale involved in reaching equilibrium with these comparatively thick films, using equation 3.2, with intercept obtained by linear regression. For vanillin, time-lags were about 30 and 50 minutes for spectrophotometry and gravimetry respectively, leading to very different D values (see Table 3.4.). Usually such differences could be attributed to film thickness differences but calculations were carried out to get normalized D values using a single film thickness. Simply it appears that spectrophotometry is more sensitive in detecting the first molecules that have diffused through the middle film.

A number of test materials are shown in Figure 3.5. Only vanillin was measured by spectrophotometry (in ATBC20, 30, 40 films). These results are less equivocal in illustrating diffusion, and probably give closer results to the ‘true’ diffusion values in the initial stages of penetration of the test films, before back-migration is problematic.
Figure 3.5. Transmission method: (a). spectrophotometric results (vanillin in ATBC20, ATBC30, and ATBC40 films*, versus (b). gravimetric results (1-Hexanol, cyclohexanol, vanillin, chlorobenzene, in ATBC40, and 1-octanol, in ATBC40 and pure PVC films - with a slight negative mass change due to experimental error -), at 22°C.

* Results have been normalized to 20 µm thickness films except for ATBC40 (100 µm thickness) as vanillin diffuses rapidly; errors in absorbance (< 22%) are due to film thickness discrepancies; errors in mass uptakes are less than 5%; '>' in legend indicates the mass transfer direction (eg. ‘from ATBC40 through ATBC30’).
Figure 3.6. ‘Headspace’ technique sorption curves (examples) of (a). 1-hexanol, in function of time, and of (b). cyclohexanol, in function of the square root of time, for a 50 µm normalized thickness film, for 20, 30, and 40% ATBC w/w plasticised films, at 22°C.
Figure 3.7. Comparison of the initial ‘apparent’ diffusion coefficients obtained with the ‘headspace’ and the 3-layer laminate technique; parentheses show the number of carbon atoms in linear alcohols; * compounds containing aromatic rings; data concern sorption experiments with gravimetric assay, at 22°C, and using 40% w/w ATBC plasticised PVC films.
It is clear, from the vanillin results (see Figure 3.5.(a)) that increased plasticisation corresponds to increased rates of diffusion. In contrast, there is no diffusion of octanol through un-plasticised PVC observed, even in one day. In Figure 3.2.(a) octanol appeared to diffuse fast, faster than vanillin, both with 8 carbon atoms, indicating the importance of molecular interactions in the mass transfer phenomenon studied, but on the whole, there seemed to be little correlation with size or other parameters.

3.5.3.c) Improving the calculation of D when using laminates

In the present case a decreasing-with-time diffusion coefficient for absorbate (\(D_{\text{absorbate}}(t)\)) can usually be expected: as plasticiser migrates the test film becomes stiffer, all the more so absorbates such as vanillin might be considered as ‘anti-plasticisers’ (i.e. stiffening the film) rather than plasticisers. The equation could be modified accordingly.

More practically and still using the same equation, it should be possible, with some difficulty, to reduce the flow of plasticiser by using test and supply films of equal plasticiser activity initially, though this could be very demanding experimentally.

Finally, increasing the thickness of the middle film would give more precise measurements, but to avoid back-migration problems the plasticisation levels should not be changed. We did not need to do it but a few investigators mentioned the possibility of such a technique\textsuperscript{11,14}. 
3.6. CONCLUSION

- The traditional ‘headspace’ analysis of sorption kinetics has been complemented by a laminate technique whereby absorbate test material is dissolved in a polymer (to eliminate solvent migration) and used in contact with test plastic materials. These absorbate-containing films can be used as supply films in either of the traditional sorption or transmission modes to measure solubilities and diffusion rates of the absorbate in the test material.

- The 3-layer laminate technique coupled with gravimetric measurements had most advantages: it was simple, rapid (thanks to the use of highly plasticised polymer that speeded up the process), did not require expensive apparatus, and avoided the condensation issues linked to the ‘headspace’ technique (no ‘wiping’): it led to increased accuracy in the estimation of D. It also gave more accurate sorption results than the 5-layer transmission technique. Spectrophotometric readings went rapidly off-scale, thus preventing solubility measurements.

On the whole the laminate technique seemed well suited to non-volatile absorbates that are soluble in plastisols up to high concentrations, even though the rate of absorption may be slow or anomalous. To some extent though, the ‘headspace’ (for higher v.p. compounds) and the laminate (for lower v.p. compounds) techniques may be considered as complementary.
• As regards sorption, it has been shown that in highly plasticised films, the total quantity absorbed depends on the partition coefficient, and on the absorbate's concentration gradient between test and supply films.

• Diffusion of absorbates from solid or liquid substrates can be much more rapid than in un-plasticised films, and diffusion times much shorter than relevant storage times for foods. Except when absorbate evaporation was decreasing concentration gradients, diffusion appeared to be independent of absorbate vapour pressure, or size (because of the high plasticisation level used); nevertheless measurement of the diffusion rate in these systems was vitiated by the concurrent counter-diffusion (back-migration) of plasticiser out of the film. The obtained $D_{\text{absorbate}}$ was an ‘apparent’ diffusion coefficient; in general it was very high, and comparable with liquid or gel systems.

• The rate of plasticiser back-migration may be affected by the use of high initial concentrations of absorbate in the supply film: this could engender specific absorbate interactions, and vice-versa.

If the potential back-migration of the plasticiser is kept well in mind, this laminate technique appears appropriate to rapidly model liquid/solid-gel (food) contacts with plastic packagings containing food additives/antioxidants (β-carotene, BHA, BHT, etc), aroma compounds (vanillin, etc) or other lower v.p. compounds. For example a virgin plastisol (test film) might simulate a cling packaging film and a loaded plastisol (supply film), a flavoured solid fatty food product.
3.7. FUTURE WORK

- Many other food-related compounds can be measured by this technique. Possible effects by plasticisers contaminating foods can be investigated, especially with regard to partition coefficients between foodstuffs and packaging films.

- As regards the mathematical modelling of sorption curves various assumptions remain to be tried in refining the diffusion equations (see Appendices at end of thesis). Among the numerous modelling possibilities, equations could include the notions of ‘film depletion’, of ‘dual diffusion’, consider the diffusion coefficient of the plasticiser ($D_{ATBC}$), vary with time ($D(t)$) or/and concentration ($D(C)$)…: the latter case for instance was that of chlorobenzene in polystyrene films, or of ethyl acetate or d-limonene at high concentrations in polypropylene and polyethylene films (see Chapter 1); also ‘supersaturation’ may be modelled by considering the dissolution rate of the excess un-dissolved (aggregated/crystallised) absorbate (eg. β-carotene, vanillin) in the ‘supersaturated’ supply film.
3.8. ACKNOWLEDGMENTS

This work was supported by an Overseas Postgraduate Research Scholarship granted by the Department of Education, Employment and Training and Youth Affairs of the Commonwealth Government of Australia. Special thanks are forwarded to Dr Robert Holland, formerly from Food Research Australia (CSIRO/AFISC), and late Dr Robert Johnson from Food Research Australia (CSIRO/AFISC) who both dedicated a lot of time in the realisation of this Chapter.
3.9. REFERENCES


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Fig. 3.1 (b) – Schematic diagram of the experimental laminate assemblages before compacting: (a) 3-layer sorption and (b) 5-layer transmission, at 22°C.

Fig. 3.1 (c) – Arrangements of films in the 3-layer laminate technique.

Fig. 3.1 (d) – Arrangements of films in the 5-layer laminate technique.

Fig. 3.1 (e) – Calculation of the partition coefficient Kp of absorbates in the 3-layer laminate technique.

Fig. 3.2 (a)(b) – (a). 3-layer laminate technique sorption curves, and (b). ‘headspace’ technique sorption curves, for 40% ATBC w/w plasticised films, at 22°C; same x-scales are used for comparison; note the y-scale difference; all plots are means of at least 2 replicates (max. 5% standard deviation).

Fig. 3.2 (c) – Sorption percentages observed in the 3-layer laminate and the ‘headspace’ techniques, for studied compounds (gravimetric assay), in 40% w/w
ATBC plasticised PVC films, at 22°C (Equilibrium is always reached in the laminate technique; equilibrium flags indicate steady state in the ‘headspace’ technique, cf (b)).

**Fig. 3.3** – Gravimetric results: 3-layer laminate sorption curves for vanillin (dotted lines), BHA, BHT (full line) and β-carotene (long dotted lines showing negative mass change after 4000 min i.e. 2.8 days), for 40% w/w ATBC plasticised films, at 22°C.

**Fig. 3.4** – Spectrophotometric results: (a). example of a BHA spectrophotogram versus time, for 40% ATBC w/w plasticised film, and (b). vanillin, BHA, BHT and DOP sorption curves, for 50 mm normalized thickness films, and for 20, 30, and 40% plasticised films, at 22°C. DOP concentration was 0.1M instead of 1M and was also tested after 4 days (*); error bars are indicated for some plots only: they are mainly due to film thickness errors; NB the effective comparison of the sorption curves should be done by weight, not absorbance values; the parentheses 'ATBC40>20' mean for example that the supply film is ATBC40 and the middle film is ATBC20 (the test film is always ATBC40).

**Fig. 3.5 (a)(b)** – Transmission method: (a). spectrophotometric results (vanillin in ATBC20, ATBC30, and ATBC40 films*, versus (b). gravimetric results (1-Hexanol, cyclohexanol, vanillin, chlorobenzene, in ATBC40, and 1-octanol, in ATBC40 and pure PVC films - with a slight negative mass change due to experimental error -), at 22°C. * Results have been normalized to 20 mm thickness films except for ATBC40 (100 mm thickness) as vanillin diffuses rapidly; errors in absorbance (< 22%) are due to film thickness discrepancies; errors in mass uptakes are less than 5%; '>' in legend indicates the mass transfer direction (eg. 'from ATBC40 through ATBC30').

**Fig. 3.6** – ‘Headspace’ technique sorption curves (examples) of (a). 1-hexanol, in function of time, and of (b). cyclohexanol, in function of the square root of time, for a
50 mm normalized thickness film, for 20, 30, and 40% ATBC w/w plasticised films, at 22°C.

**Fig. 3.7** – Comparison of the initial ‘apparent’ diffusion coefficients obtained with the ‘headspace’ and the 3-layer laminate technique; parentheses show the number of carbon atoms in linear alcohols; * compounds containing aromatic rings; data concern sorption experiments with gravimetric assay, at 22°C, and using 40% w/w ATBC plasticised PVC films.
CHAPTER 4

EXPERIMENTAL RESEARCH

PREDICTING MASS TRANSFERS INTO HIGHLY PLASTICISED PVC FILMS WITH THE LAMINATE TECHNIQUE:

THE INFLUENCE OF PHYSICO-CHEMICAL CHARACTERISTICS OF SOME RELATED ALCOHOLS
4.1. ABSTRACT

Previous Chapters (2 & 3) have demonstrated the sorption efficiency of highly plasticised (40 % w/w) poly-(vinyl chloride) (PVC) (plastisols) for debittering Navel orange juice and shown that the ‘three-layer laminate technique’, although sometimes yielding anomalous sorption kinetics, was most appropriate to deepen plastisols sorption investigations notably through the more systematic screening of structurally close compounds: in this Chapter it was therefore used to calculate the ‘sorption percentage’ [SP] and diffusion [D] coefficients of 18 aliphatic and aromatic hydroxy-compounds in plastisol films:

- A sorption maximum occurred between C$_8$ (1-octanol) and C$_{12}$ (1-dodecanol); it corresponded to a range of molecular weights, boiling, melting points, and vapour pressures. C$_6$ primary, secondary and tertiary alcohols behaved similarly (SP $\approx$ 0.2 %, and D $\approx$ 8.10$^{-13}$ m$^2$s$^{-1}$).

- Double bonds, aromatic rings and multiple OH groups usually increased sorption (SP $> 2$ %), D being unaffected. Branched ‘bulky’ compounds sometimes sorbed better than linear ones. However D decreased with the molecule length, from C$_6$ to C$_{18}$ alcohols.

- Compounds were sorted into three ‘Types’, A, B and C according to their sorption curve shapes, respectively showing ‘mass loss’, ‘low sorption, followed by mass loss’, and ‘high sorption’.
• An attempt was made to explain these curves’ anomalous shapes: the ‘Types’
corresponded roughly to the order of hydrogen bonding interactions estimated by
K. L. Hoy’s solubility parameters $\delta$, but vapour pressures and the clustering
possibilities of the absorbates remained essential indicators to eventually get a
better sorption prediction.

• Finally, deplasticisation, i.e. plasticiser back-migration, induced by the absorbates,
was demonstrated (mass loss).

**Keywords**

Food/packaging interactions, laminate technique, mass transfers, alcohol sorption
prediction, plasticiser migration, solubility parameters, clustering.
4.2. INTRODUCTION

Flavour scalping has often been the focus of food packaging research (Leufvén and Stöllman, 1992). Therefore the sorption of many commercially significant flavour compounds has been investigated (Shimoda et al., 1988). Food model solutions have also been investigated (Mannheim et al., 1987; Halek and Luttmann, 1991). Major food wraps and commercial plastics contain additives (Robertson, 1993) and plasticisers, hence complicating the investigation.

During initial investigations, un-plasticised polymers containing additives or contaminants have been studied. For example, the behaviour of antioxidants in polyethylene was often reported (Miltz et al., 1988; Schabron and Fenska, 1990), and more recently the use of recycled polymers has brought forward the need for functional barriers. These work by ‘sandwiching’ a contaminated recycled plastic layer between two virgin plastic layers (Begley and Hollifield, 1993; Katan, 1996). Scientists have proposed general sorption rules related to the shape of the molecule, to specific physico-chemical characteristics of the absorbate and of the polymer, and usually only related to un-plasticised polymers (or laminates) (cf. Chapter 1b).

As for plasticised polymers containing additives or others molecules, they have been seldom studied (Riquet and Feigenbaum, 1997; Biedermann and Grob, 1998; Petersen and Breindahl, 1998), probably because of their complexity.
Since in Chapter 3 differences between the sorption behaviour of several alcohols were noted, a more systematic study using the ‘3-layer laminate technique’ with gravimetric analyses and the ‘square-root diffusion method’ was proposed:

Eighteen hydroxy compounds were chosen to measure sorption in plastisol to test the effects of chain length, branching and saturation. It was hoped to correlate these, along the lines of Baner and Piringer (1991), with solubility parameters ($\delta$ in $(J.cm^3)^{1/2}$), which measure molecular interactions, and other physico-chemical parameters (eg. vapour pressure, presence of double bonds, number of hydroxy/methyl groups), and possibly predict sorption in plastisols.

Eventually this may lead to a better understanding of the variety of sorption behaviours of many common food and non-food molecules when in contact with very plasticised polymers. This prior study was also needed before extending these tests to multiple-functional-groups (food) model molecules (such as orange juices), and in order to ‘model interactions’ as close as possible to actual food-packaging interactions for simulation purpose.
4.3. MATERIALS AND METHODS

4.3.1. Chemicals

All chemicals were laboratory grade, generally over 98% purity. Two classes of hydroxy compounds, alcohols and phenols have been assessed: they are 1-butanol (C₄OH), 1-hexanol (C₆OH), 2-hexanol (2C₆OH), 2-methyl-1-pentanol (2M1P), 2-methyl-2-pentanol (2M2P), 3,3-dimethyl-1-butanol (33dM1B), cis-3-hexen-1-ol (cisOH), trans-3-hexen-1-ol (transOH), cyclohexanol (cyclOH), 1-octanol (C₈OH), 1-decanol (C₁₀OH), 1-dodecanol (C₁₂OH), 1-octadecanol - or stearyl alcohol - (C₁₈OH), (trans-)geraniol (GER), 1,4-butane-diol (14BD), phenol (PhOH), resorcinol - or 3-hydroxy phenol - (Ph(OH)₂) and phloroglucinol - 1,3,5-trihydroxybenzene - (Ph(OH)₃). Abbreviations, including Me for methyl, will be used as little as possible to ease the reading.

As in the previous Chapter, Table 4.1 contains the essential data, molecular weights (MW), melting points (m.p.s), boiling points (b.p.s), vapour pressures (v.p.s), etc, for most of the compounds.
## Table 4.1 Principal physico-chemical characteristics of selected hydroxy compounds (sorted by boiling points and/or vapour pressures)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molecular Weight (g/mole)</th>
<th>Melting point(^\circ)(°)C</th>
<th>Boiling point(^\circ)(°)C</th>
<th>Density (g/cm(^3))</th>
<th>Vapour pressure* (mmHg @ 25°C)</th>
<th>Supplier information**</th>
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<tr>
<td>1-butanol</td>
<td>C(_4)H(_8)O</td>
<td>74.12</td>
<td>-90</td>
<td>117.73</td>
<td>0.810</td>
<td>6.70</td>
<td>M&amp;B, ‘AR’</td>
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<td>2-methyl-2-pentanol</td>
<td>C(<em>6)H(</em>{12})O</td>
<td>102.18</td>
<td>-108</td>
<td>121.1</td>
<td>0.835</td>
<td>8.60</td>
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<td>2-hexanol</td>
<td>idem</td>
<td>idem</td>
<td>n/a</td>
<td>136</td>
<td>n/a</td>
<td>2.49</td>
<td>A, 99%</td>
</tr>
<tr>
<td>3,3-di-Me-1-butanol</td>
<td>idem</td>
<td>idem</td>
<td>-60</td>
<td>143</td>
<td>0.844</td>
<td>2.45</td>
<td>A, 99%</td>
</tr>
<tr>
<td>2-methyl-1-pentanol</td>
<td>idem</td>
<td>idem</td>
<td>n/a</td>
<td>148</td>
<td>0.824</td>
<td>1.92</td>
<td>A, 99%</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>idem</td>
<td>idem</td>
<td>-52</td>
<td>156.5</td>
<td>0.814</td>
<td>0.928</td>
<td>A, 98%</td>
</tr>
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<td>Cis-3-hexen-1-ol</td>
<td>C(<em>6)H(</em>{12})O</td>
<td>100.16</td>
<td>n/a</td>
<td>156.5</td>
<td>0.846</td>
<td>0.554***</td>
<td>A, 98%</td>
</tr>
<tr>
<td>Trans-3-hexen-1-ol</td>
<td>idem</td>
<td>idem</td>
<td>n/a</td>
<td>61.5(^{(12)})</td>
<td>0.817</td>
<td>0.554***</td>
<td>A, 98%</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>idem</td>
<td>idem</td>
<td>+21</td>
<td>160.5</td>
<td>0.963</td>
<td>0.8</td>
<td>A, 99%</td>
</tr>
<tr>
<td>1-octanol</td>
<td>C(<em>8)H(</em>{18})O</td>
<td>130.23</td>
<td>-15</td>
<td>196</td>
<td>0.827</td>
<td>0.0794</td>
<td>Fluka AG Sw</td>
</tr>
<tr>
<td>Geraniol</td>
<td>C(<em>{10})H(</em>{18})O</td>
<td>154.25</td>
<td>n/a</td>
<td>229.5</td>
<td>0.889</td>
<td>0.0300</td>
<td>Fluka AG Sw</td>
</tr>
<tr>
<td>1,4-butane-diol</td>
<td>C(<em>8)H(</em>{16})O(_2)</td>
<td>90.12</td>
<td>+16</td>
<td>230</td>
<td>1.017</td>
<td>0.0105</td>
<td>A, &gt;99%</td>
</tr>
<tr>
<td>1-decanol</td>
<td>C(<em>{10})H(</em>{22})O</td>
<td>158.29</td>
<td>+7</td>
<td>231</td>
<td>0.829</td>
<td>0.00851</td>
<td>A, &gt;99%</td>
</tr>
<tr>
<td>1-dodecanol</td>
<td>C(<em>{12})H(</em>{26})O</td>
<td>186.34</td>
<td>+25.5</td>
<td>261</td>
<td>0.820</td>
<td>0.000848</td>
<td>S, ~99%</td>
</tr>
<tr>
<td>1-octadecanol</td>
<td>C(<em>{18})H(</em>{38})O</td>
<td>270.50</td>
<td>+60.5</td>
<td>170.5(^{(12)})</td>
<td>0.812[^{[50]}]</td>
<td>0.000003</td>
<td>AJAX</td>
</tr>
<tr>
<td><strong>Aromatic 'Hydroxy' Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>C(_6)H(_6)O</td>
<td>94.11</td>
<td>+41</td>
<td>182</td>
<td>1.071</td>
<td>0.350</td>
<td>A, &gt;99%</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>C(_6)H(_8)O(_2)</td>
<td>110.11</td>
<td>+111</td>
<td>178(^{(16)})</td>
<td>1.292</td>
<td>0.000489</td>
<td>AJAX</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>C(_6)H(_8)O(_3)</td>
<td>126.10</td>
<td>+219.5</td>
<td>n/a</td>
<td>1.460</td>
<td>0.00016</td>
<td>S, 97%</td>
</tr>
</tbody>
</table>

---

# Average when range was given.

### Upper script parentheses indicate vapour pressure in mm of Hg if otherwise than 760.

#### Upper script brackets indicate temperature in degree Celsius if otherwise than 25°C.


** M&B = M&B Australia Pty. Ltd.; A = Aldrich Chemical Co. Inc., Milwaukee, WI, USA; S = Sigma Chemical Co., St. Louis, MO, USA; AJAX = AJAX Chemicals, Auburn, Sydney, NSW, Australia; Sw = Switzerland; with % purity when available.

*** Not differentiated according to previous reference (*).

----- Above the 1 mm of Hg level, the volatility is considered too high for meaningful results. Below 0.1 mm of Hg, evaporation becomes an unimportant factor except over long time periods.

n/a Not available.
4.3.2. Plastic films

Films were prepared according to the method described in Chapters 2 & 3. Acetyl Tributyl Citrate (ATBC) - Croda Surfactants, NSW, Australia – was used as plasticiser. Films were all 40 % w/w plasticised (ATBC40) to increase diffusion and obtain rapid measurements, well suited to a survey program such as this.

4.3.3. Gravimetric 3-layer laminate method

This ‘sandwich’ method (Holland and Santangelo, 1988; Fig. 4.1) with microbalance has been described in Chapter 3. Its rapidity allowed the measurement of many less volatile absorbates with sufficient precision (± 10 %) to determine sorption and diffusion coefficients. Here experiments have been focused on sorption determination: basically a supply ‘loaded’ film, containing 40 % w/w ATBC and 1 Molar (M) in added absorbate (to obtain ‘supersaturation’ and constant supply), was folded onto a test ‘unloaded’ film containing only 40 % w/w [≈ 1 M] ATBC. The ‘sandwich’ was enclosed in aluminium foil to minimise evaporation, with a glass weight (5 mm thick pane) on top to obtain a tight adherence between layers, and the test film was weighed at regular time intervals (several minutes depending on the previous recorded mass change). Then sorption curves were plotted and compared with the physico-chemical characteristics of the absorbates. The maximum uptake (sorption percentage SP) and the diffusion coefficient D were the significant experimental parameters used in these comparisons.

The mass transfers involved are schematised in Fig. 4.2
Figure 4.1 Arrangement of the several film layers (a) for the sorption technique (b), and theoretical resulting sorption curve (c) - the supply film ('folder') is considered supersaturated by the 'absorbate' -.
Figure 4.2  Schematic representation of the mass transfers involving both ATBC and the ‘absorbate’ gradients*.

* The initial concentration gradient strength is indicated by the size of the arrow.
4.3.4. Theoretical considerations

4.3.4.a) Sorption coefficients of absorbates.

The maximum sorption percentage was defined as the sorption percentage \( SP \) (in mass change per 100 g of initial test film mass, hereafter noted 100\(\Delta\)w/w or simply % sorption, % SP or even % when there is no confusion). It could be obtained directly from the sorption curves’ highest points (peak or plateau).

However SP’s do not correspond to actual sorption/partition coefficients (relative solubility), that are normally recorded as \( S \) or \( K_p \). SP’s are only an approximation of \( S \)’s: in fact 1 M equivalent absorbate was added to the organosol but not all of it was actually dissolved; the un-dissolved part, in the form of some aggregates, could give a milky appearance to the film, or was simply evaporated. For these reasons, and because the initial and final dissolved parts of absorbates in ATBC40 supply films were not quantified, \( S \) should be slightly greater than the ratio \( C_{\infty}(\text{test film})/1M(\text{supply film}) \). Equation 1 shows the relationship between experimental SP and theoretical \( S \) (with \( S \) in (mole of absorbate sorbed per litre of test film) per (mole of absorbate remaining at equilibrium per litre of supply film), and with \( MW_{\text{absorbate}} \) the molecular weight of the absorbate in g/mole):

\[
S = \frac{C_{\infty}(\text{test film})}{C_{\infty}(\text{supply film})} \geq \frac{1}{\frac{100}{SP} - 1} \cdot \frac{1000}{MW_{\text{absorbate}}} \approx \frac{10 \cdot SP}{MW_{\text{absorbate}}} \quad (1)
\]

SP’s will be used for rapid comparative sorption results as well as an estimation of the solubility/compatibility of absorbates in ATBC40 (cf. Chapter 3): in principle then, the greater the SP in the test film, the greater the dissolved absorbate fraction in
the supply film, i.e. the closer to 1 M the concentration in that film (which can be ‘under-saturated’, just saturated, or ‘supersaturated’ depending on how much absorbate is dissolved).

$SP_\infty$, the sorption percentage at equilibrium, has a different meaning from that commonly used with pure polymers (the major investigative field over the past twenty years), as it is composed of both absorbate and plasticiser equilibria. Sometimes the maximum SP is greater than the final equilibrium value $SP_\infty$: this could be due to the different rates of sorption and of deplasticisation (i.e. of plasticiser back-migration, cf. Chapter 3). For clarity the Figures that are presented in this Chapter contain two time ranges: in general, the initial rate was measured before 1000 mins. (SP), and the ‘equilibrium’ sorption rate ($SP_\infty$) was often taken after 20,000 mins. (approximately 2 weeks). This $SP_\infty$ was also called final deplasticisation ratio (FDR) when negative (cf. Table 4.2.) i.e. when the test film mass ended up less than its initial value (NB: Table 4.2. will be explained in section 4.4.).
Table 4.2 Sorption and Diffusion \([D]\) results, at 22°C, sorted by ‘sorption Type’ and increasing sorption percentage \([SP]\) order; the initial deplasticisation rate (IDR) is shown in g lost per 100 g initial film per 100 minutes (-100Δ\(w/w\)/100mins. or % mins., positive number), as well as the final observed deplasticisation ratio (FDR) in g per 100 g initial film (negative).

<table>
<thead>
<tr>
<th>Name Structure</th>
<th>Film aspect²</th>
<th>SP* (± 0.02 max.)</th>
<th>IDR (% min)</th>
<th>FDR** (± 0.02 max.)</th>
<th>[D]**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A (no sorption but mass loss)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butanol I</td>
<td>Sm smell disappears fast</td>
<td>0.00</td>
<td>0.25 ± 0.08</td>
<td>&lt; -0.20</td>
<td>n/a</td>
</tr>
<tr>
<td>2-hexanol II</td>
<td>St Sm</td>
<td>0.00</td>
<td>0.10 ± 0.05</td>
<td>-0.45</td>
<td>n/a</td>
</tr>
<tr>
<td>Phloroglucinol Arom. Ring</td>
<td>M no-Sm no-St</td>
<td>0.00</td>
<td>0.20 ± 0.05</td>
<td>-0.40</td>
<td>n/a</td>
</tr>
<tr>
<td>Type B (very low to medium sorption, then mass loss)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Me-2-pentanol III</td>
<td>St Sm</td>
<td>0.05 (i)</td>
<td>0.20 ± 0.05</td>
<td>-0.60</td>
<td>8.0 ± 5.4</td>
</tr>
<tr>
<td>1-hexanol I</td>
<td>Sm Oil electrostatic</td>
<td>0.07 (i)</td>
<td>0.10 ± 0.05</td>
<td>&lt; -0.20</td>
<td>11.9 ± 6.3</td>
</tr>
<tr>
<td>2-Me-1-pentanol I</td>
<td>St Sm</td>
<td>0.15 (i)</td>
<td>0.20 ± 0.06</td>
<td>-0.45</td>
<td>7.0 ± 2.9</td>
</tr>
<tr>
<td>Trans OH I unsat.</td>
<td>St Sm IS</td>
<td>0.20 (i)</td>
<td>0.10 ± 0.03</td>
<td>&lt; -0.50</td>
<td>6.9 ± 2.0</td>
</tr>
<tr>
<td>3,3-di-Me-1-butanol I</td>
<td>St Sm IS</td>
<td>0.20 (i)</td>
<td>0.20 ± 0.06</td>
<td>-0.80</td>
<td>7.0 ± 0.8</td>
</tr>
<tr>
<td>Cyclohexanol II Cyclic</td>
<td>St Sm</td>
<td>0.30 (i)</td>
<td>0.15 ± 0.05</td>
<td>&lt; -0.20</td>
<td>9.5 ± 1.5</td>
</tr>
<tr>
<td>1-octadecanol (B(C)) I</td>
<td>M no-St no-Sm</td>
<td>0.60</td>
<td>n/a</td>
<td>&lt; 0.00</td>
<td>0.26 ± 0.04</td>
</tr>
<tr>
<td>Cis OH (B(C)) I unsat.</td>
<td>St Oil</td>
<td>1.10 (i)</td>
<td>0.20 ± 0.06</td>
<td>-0.60</td>
<td>10.5 ± 1.8</td>
</tr>
<tr>
<td>Type C (high sorption)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-octanol I</td>
<td>St Oil IS</td>
<td>2.20 (i)</td>
<td>0.3 ± 0.1</td>
<td>n/r</td>
<td>14.6 ± 0.7</td>
</tr>
<tr>
<td>1,4-butanediol I diol</td>
<td>M Oil Sm</td>
<td>2.40</td>
<td>&gt; 0.01 ± 0.01</td>
<td>n/r</td>
<td>0.036 ± 0.006</td>
</tr>
<tr>
<td>1-decanol I</td>
<td>v-Oil Sm</td>
<td>2.70 (i)</td>
<td>0.20 ± 0.06</td>
<td>n/r</td>
<td>5.7 ± 0.3</td>
</tr>
<tr>
<td>1-dodecanol (C(B)) I</td>
<td>St Sm Oil Syneresis</td>
<td>2.80</td>
<td>0.15 ± 0.05</td>
<td>n/r</td>
<td>2.4 ± 0.7</td>
</tr>
<tr>
<td>Phenol Arom. Ring</td>
<td>Oil Sm</td>
<td>3.20</td>
<td>0.20 ± 0.05</td>
<td>n/r</td>
<td>13.5 ± 1.1</td>
</tr>
<tr>
<td>Resorcinol (C(B)) Arom. Ring slippery v-Oil Sm IS</td>
<td>3.80</td>
<td>n/a</td>
<td>n/r</td>
<td>3.7 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>Geraniol (C(B)) I unsat.</td>
<td>Oil Sm IS</td>
<td>&gt; 4.60</td>
<td>n/a</td>
<td>n/r</td>
<td>6.1 ± 0.2</td>
</tr>
</tbody>
</table>

# I, II & III: primary, secondary and tertiary structures; unsat.: unsaturated; Arom.: aromatic.
## M, milky; St, sticky; Sm, smooth; Oil, oily; no-, not or non; IS, intense smell; v-, very.
* in g ‘absorbate’ gain / 100 g initial film; null for Type A; (i) when SP’s corresponded to initial sorption peaks.
** The error being always in the ± 0.02 range, the smallest the SP, the greatest the % error (thickness determination and weighing threshold were the major cause of error).
*** in g ‘absorbate’ loss / 100 g initial film; when > 0, sampling had stopped after 6 weeks, and sorption ratios were still positive without definite decrease in mass.
**** in 10\(^{-13}\) m\(^{-2}\) s\(^{-1}\), estimated with the square root I method (eqn 5); the precision of D as well as that of its standard deviation depend on the precision of the film thickness measurements.
/ not available.
/ not relevant.
4.3.4.b) Diffusion coefficients $D$ of absorbates.

As in the previous Chapter, to calculate $D$ the mass uptake data was analysed according to the method of Crank (1975) for the first hour or so, i.e. when the absorbate concentration gradient (Fig. 4.2) was initially the highest; this assumed that plasticiser back-migration was not interfering severely at that stage. Indeed ATBC is a larger molecule and its migration can be realistically considered slower than all absorbates’ (in Chapter 2 the plasticisers tested all diffused 1,000 to 100,000-fold slower).

This allowed an approximate/average diffusion coefficient to be easily calculated thanks to equation 5 (presented below) when the test film mass uptake was plotted against the square root of time, and by using only the initial kinetics plots. A linear regression gave an $R^2 > 0.97$, which showed satisfactory linearity. Of course when the very slow back migration becomes important, or even predominant, only then equation 5 becomes invalid. This equation was called ‘square root I approximation method’ in Chapter 3 and proved to be best suited to this laminate technique. Its derivation is recalled below.

Equation 5 approximates the solution of Fick’s second law in the first stages of the sorption curve. Fick’s second law (eqn 3) (for one-dimensional and constant diffusion [$D$] and for isotropic substances) assumes that “the rate of transfer [F] of diffusing absorbates through unit area of a section is proportional to the concentration [$C$] gradient [$\partial C/\partial x$] measured normal to the section” (eqn 2):

$$ F = -D \frac{\partial C}{\partial x} \quad (2) \quad \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3) $$
By using initial rates of sorption and/or desorption, and considering a uniform initial distribution, and equal surface concentrations, equation 3 can be solved (Crank, 1975) in the non-steady state to give equation 4:

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left\{ -D(2n+1)^2 \pi^2 t / L^2 \right\} \quad (4)
\]

which reduces for small times to equation 5 (or ‘square root I method’):

\[
\frac{M_t}{M_\infty} = 4 \sqrt{\frac{D}{\pi L}} \approx \left( 2.257 \frac{\sqrt{D}}{L} \right) \sqrt{t} \quad (5)
\]

with \( M_t \) the mass of absorbed material at time \( t \), \( M_\infty \) the equivalent mass at equilibrium, \( D \) the diffusion coefficient in m\(^2\)s\(^{-1}\), \( L \) the thickness of the (central) test film in metres.

**4.3.4.c) Permeability coefficients of absorbates.**

Usually the equation ‘Permeability equals Diffusivity times Solubility (P=D.S)’ is used to compare initial migration rates, assuming constant supply concentration gradients (thanks to ‘1 M supersaturation’) and no interaction between migrating species at the initial sorption stage. This was not undertaken here since neither \( S \) nor \( D \) would be sufficiently accurate, the errors in \( P \) being even greater.

All results were averages of at least two replicates with a coefficient of variation never exceeding ± 0.02 100Δw/w sorption (cf. graphs).
4.3.5. The use of solubility parameters to measure polymer/absorbate compatibility and predict sorption

In the pursuit of an eventual molecular_structure/sorption Behaviour relationship, many researchers have already used the solubility parameter $\delta$ (Baner and Piringer, 1991; Halek and Luttmann, 1991; Strandburg et al., 1991; Arora and Halek, 1994; Bressa et al., 1996) to predict the sorption of low molecular weight compounds, but only in un-plasticised polymers.

$\delta$s are also applicable to plasticised polymers. They have been used in Chapter 2 to evaluate the limonin sorption capacities of various plastisols, but here their purpose is to attempt to better predict and explain the observed sorption differences between absorbates than explanations based on the usual physico-chemical characteristics such as vapour pressures and molecular weights. Solubility parameters actually include in their definition all the latter characteristics in a global value $\delta_{\text{total}}$, sometimes further divided into two or three specific $\delta$s, not used in Chapter 2 but they are here to help differentiate the types of interaction involved.

$\delta$s, in (J.cm$^{-3}$)$^{1/2}$, were calculated following the method of Hoy (1985, 89) and a computer program developed by Fayoux (1997) according to van Krevelen's theory (1990): it consisted in “summing the factors for molar vaporisation energy per unit volume for each of the structural elements of the molecule”, similar to the Small method (1970). The unique characteristic of this method was that it gave an estimate of the three solubility parameters, respectively the $\delta_{\text{dispersive forces}}$, the $\delta_{\text{polar forces}}$, and the
hydrogen bonding forces. Then \( \delta_{\text{total}}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \), and the compatibility PVC/absorbate \( \Delta \delta \) was estimated by the quadratic deviation, according to equation 6:

\[
(\Delta \delta)^2 = (\delta_{\text{S}} - \delta_{\text{P}})^2 + (\delta_{\rho} - \delta_{\rho})^2 + (\delta_{\text{S}} - \delta_{\text{P}})^2
\] (6)

where the subscripts S and P stand for (ab)Sorbate and Polymer respectively (here PVC).

The comparison could have also been done with the plasticiser as it represented 40 % w/w of the bulk of the plastic sheet. However, both PVC and ATBC have very close \( \delta \) values: this explains their great compatibility [\( \Delta \delta \approx 1.1 \) is considered very small according to Sears and Darby (1982) who suggested ‘\( \Delta \delta < 5 \)’ as provisional interaction limit]. Both calculations, \( \Delta \delta_{\text{S/PVC}} \) and \( \Delta \delta_{\text{S/ATBC}} \), would lead to similar results and conclusions.

In addition a new parameter was calculated: \( \Delta \delta_{\text{H-d}} \), i.e. the difference between the \( \delta_{\text{hydrogen}} \) and the \( \delta_{\text{dispersive}} \). When this value was negative, then the van der Waals dispersive interaction forces would be the major solubility factor. This allowed testing for the hydrophobic character of a substance, and in particular here that of the absorbates (note that the polar parameter essentially contains the same information as \( \delta_{\text{hydrogen}} \); therefore it was not considered).

Table 4.3 lists the calculated \( \delta \) and \( \Delta \delta \) values which are discussed throughout the Chapter.
Table 4.3 Solubility parameters and absorbate-PVC compatibility estimations, at 25 °C #, in (J.cm\(^{-3}\))\(^{1/2}\), sorted by ‘sorption Type’ like in Table 4.2

<table>
<thead>
<tr>
<th>Name</th>
<th>(\delta_{\text{total}})</th>
<th>(\delta_{\text{dispersive}})</th>
<th>(\delta_{\text{polar}})</th>
<th>(\delta_{\text{hydrogen}})</th>
<th>(\Delta\delta_{\text{H-d}})</th>
<th>(\Delta\delta_{\text{S-PVC (or } \Delta\delta)})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type A</strong> (no sorption but mass loss)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butanol*</td>
<td>25.6 (23.8)</td>
<td>14.4 (14.0)</td>
<td>10.1 (8.2)</td>
<td>18.5 (17.4)</td>
<td>4.1</td>
<td>11.7 (11.0)</td>
</tr>
<tr>
<td>2-hexanol</td>
<td>22.0(^{(1)})</td>
<td>14.3</td>
<td>8.0(^{(1)})</td>
<td>14.7(^{(1)})</td>
<td>0.4(^{(1)})</td>
<td>8.5(^{(1)})</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>28.3</td>
<td>16.0</td>
<td>15.1</td>
<td>17.7</td>
<td>1.7</td>
<td>11.7</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td>27.0(^{(1)})</td>
<td>14.9</td>
<td>12.6(^{(1)})</td>
<td>18.1(^{(1)})</td>
<td>2.9(^{(1)})</td>
<td>11.7(^{(1)})</td>
</tr>
<tr>
<td><strong>Type B</strong> (very low to medium sorption, then mass loss)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Me-2-pentanol</td>
<td>20.5</td>
<td>13.8</td>
<td>7.3</td>
<td>13.3</td>
<td>-0.5</td>
<td>7.7</td>
</tr>
<tr>
<td>1-hexanol</td>
<td>23.3</td>
<td>14.7</td>
<td>8.7</td>
<td>15.8</td>
<td>1.1</td>
<td>9.2</td>
</tr>
<tr>
<td>2-Me-1-pentanol</td>
<td>22.8</td>
<td>14.5</td>
<td>8.7</td>
<td>15.2</td>
<td>0.7</td>
<td>8.7</td>
</tr>
<tr>
<td>TransOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,3-di-Me-1-butanol</td>
<td>22.1</td>
<td>14.3</td>
<td>8.8</td>
<td>14.4</td>
<td>0.1</td>
<td>9.7</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>23.5</td>
<td>14.2</td>
<td>8.8</td>
<td>16.5</td>
<td>2.3</td>
<td>9.9</td>
</tr>
<tr>
<td>1-octadecanol</td>
<td>19.5</td>
<td>15.9</td>
<td>5.8(^{(2)})</td>
<td>9.8(^{(2)})</td>
<td>-6.1(^{(2)})</td>
<td>6.2(^{(2)})</td>
</tr>
<tr>
<td>(B(^{C})) CisOH (B(^{C}))</td>
<td>23.8</td>
<td>14.4</td>
<td>9.6</td>
<td>16.4</td>
<td>2.0</td>
<td>9.6</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td>22.4</td>
<td>14.5</td>
<td>8.8(^{(2)})</td>
<td>15.4(^{(2)})</td>
<td>1.1(^{(2)})</td>
<td>8.9(^{(2)})</td>
</tr>
<tr>
<td><strong>Type C</strong> (high sorption)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-octanol **</td>
<td>22.0</td>
<td>14.8</td>
<td>7.8</td>
<td>14.2</td>
<td>-0.6</td>
<td>8.1</td>
</tr>
<tr>
<td>1,4-butane-diol</td>
<td>31.0(^{(3)})</td>
<td>13.1</td>
<td>13.1((10.5))</td>
<td>24.9(^{(3)})</td>
<td>11.8(^{(3)})</td>
<td>18.2(^{(3)})(15.9))</td>
</tr>
<tr>
<td>1-decanol</td>
<td>21.1</td>
<td>15.0</td>
<td>7.1</td>
<td>13.2</td>
<td>-1.8</td>
<td>7.5</td>
</tr>
<tr>
<td>1-dodecanol (C(^{B}))</td>
<td>20.6</td>
<td>15.0</td>
<td>6.6(^{(3)})</td>
<td>12.4</td>
<td>-2.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Phenol</td>
<td>25.0</td>
<td>18.1(^{(3)})</td>
<td>12.1</td>
<td>12.3</td>
<td>-5.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Resorcinol (C(^{B}))</td>
<td>26.8</td>
<td>17.0</td>
<td>13.9</td>
<td>15.3</td>
<td>-1.7</td>
<td>8.9</td>
</tr>
<tr>
<td>Geraniol (C(^{B}))</td>
<td>21.4</td>
<td>15.0</td>
<td>8.9</td>
<td>12.4</td>
<td>-2.6</td>
<td>5.9</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td>22.8(^{(3)})</td>
<td>15.0(^{(3)})</td>
<td>10.5(^{(3)})</td>
<td>13.3(^{(3)})</td>
<td>-2.5(^{(3)})</td>
<td>7.3(^{(3)})</td>
</tr>
<tr>
<td><strong>PVC</strong></td>
<td>20.3</td>
<td>15.4</td>
<td>11.3</td>
<td>7.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td><strong>ATBC</strong></td>
<td>19.9</td>
<td>15.6</td>
<td>10.1</td>
<td>7.2</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

* Figures in parentheses indicate that calculations took into account the possibility of hydrogen bonding between molecules, except for (1), (2) and (3) which indicate the ‘aberrations’ (an ‘aberration’ was defined here as the smallest, or highest value or that deviating more than 30% from the average): they were not taken into account when calculating averages.

** For example, \(8.1^2=(14.8-15.4)^2+(7.8-11.3)^2+(14.2-7.0)^2\), for 1-octanol’s \(\Delta\delta\) calculation.

# The laboratory temperature was slightly lower, at 22 °C, but this was not considered an issue because this study required relative not absolute parameters only.
4.4. RESULTS AND DISCUSSION

4.4.1. Overview

A wide range of sorption behaviours is observed, as in Chapter 3. The explanations given there (evaporation of absorbate and plasticiser migration) are re-examined, using calculated solubility parameters as well as boiling points and vapour pressures.

On the whole, equilibrium was often reached in about one week, but the maximum sorption (SP) was often attained in the first one to three hours, after which the test film mass decreased or increased towards a final equilibrium value (shown on the right-hand side of the graphs).

Sorption kinetics have been classified into three sorption Types as shown in Tables 4.2 and 4.3: Type A corresponded to no positive SP at all (1-butanol); Type B corresponded to a very low sorption, rapidly yielding a negative 100Δw/w ratio (taking SP < 1 % approx. as a definition); finally Type C represented only positive sorption. Sorption trends, deduced from the longer term kinetics, are also indicated in upper script, like in ‘B’ or ‘C’ which means very high sorption.

This classification of kinetic curves was chosen to simplify the interpretation of results. For the same reason four simple measurements have been extracted from the curves in order to describe them in a more quantitative manner: SP (the maximum sorption value), IDR (the so-called initial deplasticisation rate, i.e. the negative slope
that was observed just after SP, probably caused by absorbate evaporation and/or plasticiser migration, cf. Chapter 3), FDR (the final deplasticisation ratio, eg. the negative weight change of the test film due to ATBC migration at ‘equilibrium’), and D as an estimation of the initial diffusion coefficient of absorbates (Table 4.2 & Fig. 4.3).

At first sight categorizing sorption kinetics into three ‘Types’ seems highly empirical, but is based on the physical parameters of the plastisol and absorbates.
Figure 4.3 The three different shapes of kinetic curves observed, called Types A, B, and C, illustrating SP (\(\uparrow\)), IDR (\(\downarrow\)), and FDR (\(\downarrow\)), in relation to Table 4.2.
Figure 4.4  Sorption curves of linear aliphatic alcohols at 22°C (Test film mass change v. time); the legend indicates the boiling point in °C, the vapour pressure in mmHg x 100, and finally $\Delta \delta$, i.e. the solubility parameter that measures the compatibility ‘absorbate'-PVC in (J.cm$^{-3}$)$^{1/2}$.  

- 1-Butanol (118 / 670 / 11.7)
- 1-Hexanol (157 / 93 / 9.2)
- 1-Octanol (196 / 8 / 8.1)
- 1-Decanol (231 / 1 / 7.5)
- 1-Dodecanol (261 / 0.1 / 7.2)
- 1-Octadecanol (>>270/<<0.01/ 6.2)
4.4.2. Linear alcohols of increasing chain length

The first study compared the permeation parameters, SP and D, of linear alcohols of increasing chain length, in Fig. 4.4 and Table 4.2.

Butanol (highest v.p.) showed a typical Type A sorption kinetic (SP < 0.02 g/100g initial film = ‘0.02 % SP’) with a steady loss at about - 0.5 % FDR in the long term. As Type B, 1-hexanol evaporated less (lower v.p. at 0.93 mm of Hg) and retained a sufficiently high concentration gradient so that a small sorption maximum was still reached (SP < 0.1 %) before a negative weight change appeared (cf. Table 4.1). An empirical v.p. limit was set at about 1 mm of Hg (the ‘hexanol limit’) above which evaporation was assumed too strong to study sorption accurately with the laminate technique. In contrast below 0.1 mm of Hg of vapour pressure (the ‘octanol limit’), 1-octanol (2.2 % SP), 1-decanol (2.7 % SP), dodecanol (2.8 % SP), and octadecanol (0.6 % SP) sorption curves all continued to be positive in the long run (Type C). With little evaporation, one could then observe a sorption maximum between C$_8$ and C$_{12}$ for the short term sorption. This observation is consistent with the results obtained by Shimoda et al. (1988) for polyethylene films.

Yet can physico-chemical characteristics explain such sorption kinetics differences? Butanol has already been considered ‘too highly volatile’ to be used with the laminate technique in Chapter 3. In fact the lower MW alcohols (MWs ≈ 100 or less) have the lowest b.p.s and highest v.p.s; they are also the most polar, which is reflected in the ratio of OH groups to hydrocarbon tail that accounts for the solubility parameter data where hydrogen bonding is essentially identical (single OH group)
(this singular agreement between $\delta$ and v.p. conclusions is in fact inherent to their thermodynamic relationships, cf. the ‘theoretical considerations’ section).

As regards ‘involatiles’, like dodecanol (m.p. 25.5 °C) and octadecanol (m.p. 60.5 °C), it is also possible that a melting point above the laboratory temperature (22 °C) could hinder the mass transfer, in particular because of the formation of oily/solid state aggregates, not due to hydrogen bonding; C$_4$ to C$_{10}$ alcohols appeared to be completely miscible in ATBC alone as no phase separation was observed, but this was not the case of dodecanol (syneresis/exudate) nor of octadecanol (milky film). This also corresponded to a MW above about 180 g/mole.

In the light of solubility parameters, the smaller the $\Delta\delta$s are (Fig. 4.4), the greater the compatibility (Types B and C) between the higher alcohols ($\geq$ C$_6$) and the plasticised PVC, corresponding to a $\Delta\delta$ value below the ‘hexanol limit’, at 9 (J.cm$^{-3}$)$^{1/2}$: however $\Delta\delta$s appeared to only work up to C$_{12}$ (approximately) and were not able to explain, nor to predict, the influence of the physical state of absorbates (eg. aggregation) inside the plastic during mass transfer.

The difference between C$_8$, C$_{10}$ and C$_{12}$ alcohols was also kinetic, and only noticeable after 100 hours: C$_8$OH sorption slowed down (more data would be desirable), C$_{10}$OH’s became steady whereas C$_{12}$OH’s seemed to continue increasing, as its large size slowed the attainment of sorption equilibrium. Accordingly the value for $D_{\text{dodecanol}}$ was far from accurate, generating a greater error than indicated in Table 4.2, which was basically related to imprecise thickness measurements. Still it appeared on the whole that the longer the carbon chain the slower the diffusion: butanol > hexanol [12 to 18] > octanol [15] > decanol [6] > dodecanol [3] >
octadecanol [0.3] \( \times 10^{-13} \text{ m}^2\text{s}^{-1} \), assuming that butanol would diffuse the fastest due to its smaller size (Rogers, 1985). Also it was observed that above 8 carbons, \( D \) seemed to be halved with each addition of a pair of carbon atoms.

To sum up, sorption appeared to go through a maximum value (between \( C_8 \) and \( C_{12} \) for the short term, and \( C_{12} \) and \( C_{18} \) for the longer term) with increasing chain length. Type A curves, with these examples, appear to be due solely to evaporation, and hence an artificial category due to measurement problems with volatile compounds, but other mechanisms are possible as well. Prediction of sorption Types B and C might be done for the most ‘compatible’ absorbates (\( C_8-C_{18} \) aliphatic alcohols), i.e. with a \( \Delta \delta \) value less than 9 \( (\text{J}\cdot\text{cm}^{-3})^{1/2} \) in a ‘validity range’ approximately determined by v.p. < 0.1 mm of Hg and m.p. < 22 °C (room temperature). In a nutshell the alcohols with low v.p.s and high MWs should all naturally belong in Type C, whatever the hydrogen bonding, providing the slowest ones are monitored long enough.

Finally, in plastisols, diffusion results could not reveal the 3 curves’ Types because Ds were only accurate for ‘meaningful kinetics’ such as Type C’s. They still were consistent with two well-established results: diffusion coefficients were high, around \( 10^{-13} \text{ m}^2\text{s}^{-1} \), because of the very plasticised environment, and they decreased with chain length, from 18 (\( C_2 \)) to 0.3 (\( C_{18} \)) \( \times 10^{-13} \text{ m}^2\text{s}^{-1} \) (cf. Table 4.2). However although sorption remains far more difficult to predict than diffusion (via the estimation of molecular size), what follows mainly focuses on sorption variations, in particular those that may be attributed to the spatial conformation of the alcohols:
from a practical packaging point of view, the variations in the diffusion coefficients are of little consequence compared to the much longer shelf-lives of food products.

4.4.3. Aliphatic Mono-hydroxy-alcohols of Similar Size

Our second comparative study concerned therefore the variation between a selection of C₆ hydroxy compounds of similar size: methyl isomers of primary (I) hexanols (Fig. 4.5), hydroxy isomers (primary, secondary, tertiary)(I, II, and III) of 1-hexanol (Fig. 4.6), and cis/trans-isomers of 3-hexen-1-ol (Fig. 4.7). Both absorbate sorption and ATBC migration are discussed:

4.4.3.a) Methyl isomers of primary hexanols.

On Fig. 4.5, 1-hexanol, 2-methyl-1-pentanol and 3,3-dimethyl-1-butanol (33dM1B) behave differently but all with extremely weak SP’s, lower than 0.2 % (all in about one hour) and, in the longer run (over a day) rather important FDR’s, below -0.5 %, SP’s and FDR’s being ranked in the reverse order (Type B).

What was singular in this experiment was that, firstly 33dM1B sorbs the most, even though the most volatile of the three, (all MWs, and presumably overall volumes, were the same and initial concentration gradients depended only on the relative solubilities.), so specific interactions with the plastisol (measured here with δs) were important and apparently outweighed the effect of the vapour pressures which would predict the opposite trend in SP’s. The long term reverse migration of ATBC also supports the order of solubilities, as it is greater the greater the absorbate solubility.
Figure 4.5 Sorption curves of C₆ methyl isomers of hexanol (primary alcohols) showing deplasticization, at 22°C (Type B); the legend indicates the boiling point in °C, the vapour pressure in mmHg x 100, and finally $\Delta \delta$, i.e. the solubility parameter that measures the compatibility 'absorbate'-PVC in $(J.cm^{-3})^{1/2}$. 
Two major observations: first, SP’s were small and agreed with the not particularly low $\Delta\delta$ values, at about 9 (J.cm$^{-3}$)$^{1/2}$; second, as expected the sorption curves showed that the lower the $\Delta\delta$, the greater the first sorption peak, and the more marked the negative weight change in the long term (FDR) in agreement with Chapter 3’s hypothesis that the more soluble the absorbate in the supply film, the greater the initial ATBC concentration gradient, and the greater the eventual plasticiser migration.

In the long term ATBC did appear to considerably migrate more when $\Delta\delta$ was below 8 (see 33dM1B), rather than 9 (J.cm$^{-3}$)$^{1/2}$ the threshold that was taken into account at the beginning.

As regards absorbate diffusion, grafting a methyl group at any position on a C$_5$ molecule does not change much its global size (this leads to equal MWs, and D values all about $7 \times 10^{-13}$ m$^2$.s$^{-1}$).

On the whole, the $\Delta\delta$ (and v.p.) tool remained useful for predicting both the sorption of such primary alcohols and the induced migration of the plasticiser; the latter seems higher for even lower $\Delta\delta$ values i.e. for greater absorbate/plastic compatibility, and for bulkier compounds (like 33dM1B).

To add to these findings and go further in the structure/sorption study of C$_6$ aliphatic alcohols of similar size, the results concerning I, II, and III isomers are presented below.
4.4.3.b) I, II, and III hydroxy isomers of 1-hexanol.

In Fig. 4.6, Type B sorption curves are represented by 2-methyl-1-pentanol (I) and 2-methyl-2-pentanol (III) and Type A by 2-hexanol (II).

Again small SP values were consistent with $\Delta\delta s \approx 9 \text{ (J.cm}^{-3} \text{)}^{1/2}$. In this case though, 2M2P although having the most favourable solubility parameter for a high SP, is relegated to second place. A very high vapour pressure can reasonably be held responsible for reducing the peak height (with significant short term evaporation), and the high solubility can be confirmed by the greater back-migration of ATBC.

A similar argument explains the order of the other two alcohols. Hence the ranking of the sorption peaks (SP’s) should have been 2M2P [$\Delta\delta = 7.7$] $> 2$-hexanol [$\Delta\delta = 8.5$] $\geq 2$M1P [$\Delta\delta = 8.7$] following the solubility theory, with 2M2P as Type A rather than Type B curve. This is also consistent with the fact that all three supply films were losing some odour intensity from start.

These absorbates are considered too volatile for accurate measurements (all well above the ‘hexanol limit’) to get a simple picture of the sorption in plastisols.

Whatever the absorbate, vapour pressures need to be taken into account in priority, before solubility parameters, to interpret the sorption curves (short term) anomalies. On the other hand $\Delta\delta s$ alone did seem more reliable in longer term predictions, more connected to ATBC slower migration: this is not surprising since equilibria are determined by thermodynamic indicators such as $\Delta\delta s$, whereas initial peaks are more conditioned by kinetic parameters, i.e. by the size of the absorbate, and by its evaporation from the supply and test films.
Figure 4.6 Hydroxy isomers of 1-hexanol; comparison of the sorption curves of 2-methyl-1-pentanol, 2-methyl-2-pentanol (Type B) and 2-hexanol (Type A) at 22°C, showing a definite mass loss; the legend indicates the boiling point in °C, the vapour pressure in mmHg x 100, and finally $\Delta\delta$, i.e. the solubility parameter that measures the compatibility 'absorbate'-PVC in (J.cm$^3$)$^{1/2}$. 
As regards absorbates’ diffusion, the values given in Table 4.2 have to be carefully thought about because of evaporation; \( D_{2-hexanol} \) could not be calculated but the diffusion coefficients of all the other aliphatic \( C_6 \) alcohols should be similar because of their similar size.

Finally, concerning the migration rate of ATBC, the IDR’s were still all the same at about 0.2 % per 100 mins., meaning again that this depression related to a single phenomenon, not to absorbate evaporation (which would depend on each absorbate’s v.p.) but to ATBC migration (observed after 200 mins.). IDR’s also appeared lower to initial sorption slopes in all cases, implying a smaller ATBC diffusion coefficient than absorbates’, in agreement with ATBC’s bigger size (cf. Chapter 2). Although slower to diffuse, ATBC, with a MW of about 400 g/mole, was able to generate eventually a greater - opposite - mass transfer than the lower MW absorbates (see the FDR’s): this also helps explain Types A and B (anomalous) curves.

4.4.3.c) Cis/trans conformations.

Fig. 4.7 shows the sorption curves of cis- and trans-3-hexen-1-ols. Both were definitely Type B compounds, but the cis-compound was sorbed a lot more than its isomer (respectively 1.1 and 0.2 % SP; cisOH was then classified Type B\(^C \) in Table 4.2 to emphasize the difference between the two isomers): the addition of one double bond onto 1-hexanol tripled the SP for transOH, and multiplied it by 16 for cisOH. This was not predicted by solubility parameters (of little use here since sorption curves should have been perfect duplicates). Only Type B sorption could be predicted, by \( \Delta \delta s \) just about 9 (J.cm\(^{-3}\))\(^{1/2} \) and v.p.s below 1 mm of Hg.
Figure 4.7 Comparing isomers: sorption curves of cis-3-hexen-1-ol and trans-3-hexen-1-ol, at 22°C (Type B); * separate v.p.'s and b.p.'s are not known (cf. Table 4.1); the legend indicates the boiling point in °C, the vapour pressure in mmHg x 100, and finally $\Delta \delta$, i.e. the solubility parameter that measures the compatibility 'absorbate'-PVC in $(J \cdot cm^{-3})^{1/2}$. 
Geometrical shape appears to be the only relevant factor, though there may conceivably be differences in vapour pressures. Part of the answer may be the more compact structure of the cis-isomer (consistent to its higher diffusion coefficient, at \(11 \times 10^{13} \text{ m}^2\text{s}^{-1}\)) or to specific interactions with the plastic.

As regards ATBC migration, it was estimated to be about twice as fast for the cis-compound (IDRs were respectively 0.2 and 0.1 % mins.) consistent with its greater SP value, but the data does not warrant firm conclusions about the effect of the two isomers.

4.4.3.d) Comparisons of two ‘trans’ compounds with two model compounds.

An attempt to test the combined influence of chain length and double bonds is presented Fig. 4.8. It compares two C\(_6\) and C\(_{10}\) aliphatic mono-hydroxy compounds to two of their trans-unsaturated counterparts in respectively 1-hexanol to 3-hexen-1-ol, and 1-decanol to 3,7-dimethyl-2,6-octadiene-1-ol (i.e. geraniol).

These compounds are not exact models, but do illustrate some significant factors of importance.

Firstly, the long chained compounds (plus double bonds) were 40-50 times more soluble than their short chain (saturated) counterparts (in SP terms). This is well demonstrated in their solubility constants: C\(_6\)’s were Type B (higher \(\Delta\delta\)s \(\approx 9\)) and C\(_{10}\)’s were Type C (lower \(\Delta\delta\)s). Geraniol (SP \(> 4.6\%\)), which has by far the lowest \(\Delta\delta\) value of any alcohol, appears to be absorbed indefinitely, the sign of great
compatibility, and can probably be considered as a plasticising agent ($\Delta \delta_{\text{geraniol}}$, at 5.9, had effectively the lowest value just after ATBC’s at 1.1 (J.cm$^{-3}$)$^{1/2}$).

The same may be said about decanol, but to a lesser extent. Indeed geraniol is non-linear and bulky (because both double bonds tend to fold the molecule), in contrast to decanol (linear molecule). Decanol has also different physico-chemical parameters.

As regards diffusion, geraniol and 1-decanol (both C$_{10}$), with nearly equal MWs, did sorb equally fast (same $D_s \approx 6 \times 10^{-13}$ m$^2$s$^{-1}$); the curves differed in the long term, in agreement with $\Delta \delta$ values. But D coefficients, calculated from the ‘peak’ positions might be overestimated due to absorbate exudation (visible on the film surface, and mentioned in Chapter 3 as ‘over-plasticisation’) *.

Any migration of ATBC cannot be determined, as there is no long term decrease in weight (the weight loss after the geraniol peak may be due to back-migration). An independent technique such as gas chromatography might be used to confirm the ‘high absorbate sorption/high ATBC migration’ theory (cf. Chapter 3), as Fig. 4.4 has already suggested.

Finally, these compounds are oily and tend to (over)-plasticise * the films, in contrast to the larger saturated alcohols such as octadecanol, where cloudy un-plasticised (less flexible) films occur, and Type C behaviour is not observed. So, a low $\Delta \delta$ value ($\Delta \delta_{\text{octadecanol}}$ was lower, at 6.2) does not necessarily imply a high sorption; for instance above a certain chain length, a lower melting point (as in unsaturated alcohols) is required.

* (great flexibility of the polymer, higher diffusion and oily exudates on the surface of the film can characterize this unstable physical state).
Figure 4.8  Sorption curves of two related C₆ and C₁₀ hydroxy-compounds (2 saturated, and 2 trans-isomers) showing the influence of diverse structural features (double bonds, branching, chain length) on sorption, at 22°C (All sorption Types, A, B, and C, represented); * no separate values with the cis-isomer (cf. Table 4.1); the legend indicates the boiling point in °C, the vapour pressure in mmHg x 100, and finally ∆δ, i.e. the solubility parameter that measures the compatibility 'absorbate'-PVC in (J cm⁻³)¹/².
On the whole, longer carbon chains, at least up to $C_{10}$, and more compact structures, might contribute to greater sorption. Also it seems that Type C$^D$ curves could be predicted through $\Delta\delta$ values lower than $7.5 \, (J\cdot cm^{-3})^{1/2}$ for involatile oily aliphatic mono-hydroxy compounds.

4.4.4. The ‘Clustering’ OH Group Effect: Mono-, Di-, and Tri- Hydroxy Compounds

4.4.4.a) Overview.

It was decided to study polyols separately because hydrogen bonding appeared to deeply affect the sorption behaviour of absorbates, as it is indicated in Fig. 4.9. All kinetics were very different: Fig. 4.9 compares 1-butanol (Type A) to 1,4-butane-diol (14BD, Type C) and presents three typical examples of mono-, di-, and tri-hydroxy aromatic compounds, i.e. phenol, resorcinol, and phloroglucinol (respectively Types C, C$^D$, and A). Interestingly all these Type C absorbates produced smooth films with a ‘tacky and slight oily feel’.

Table 4.3 attests to the much greater importance of hydrogen bonding interactions than other forms of interaction, especially for polyols (the more OH groups, the higher the $\delta_{\text{hydrogen}}$ values, and the higher the $\Delta\delta_{\text{hydrogen/dispersive}}$ values; the latter are noted $\Delta\delta_{\text{H-d}}$ and measure the relative importance of hydrogen bonding forces over dispersive van der Waals forces, i.e. approximately that of OH groups over that of the carbon chain). Empirically: ‘$\Delta\delta_{\text{H-d}}<0$’ could be Type C, ‘$>3$’ Type A, else Type B.
Figure 4.9 Poly-ols (mono-, di-, and tri-hydroxy compounds); effect of the OH group: sorption of 1-butanol (Type A), 1,4-butane-diol, phenol, resorcinol (all three Type C), and phloroglucinol (Type A) into ATBC40, at 22°C; the legend indicates between parentheses the boiling point in °C, the vapour pressure in mmHg x 100, and finally Δδ, i.e. the solubility parameter that measures the compatibility 'absorbate'-PVC in (J.cm\(^3\))\(^{1/2}\).
The increased melting and boiling points also confirm the importance of hydrogen bonding. However, because of the complexity of hydrogen bonding interactions in many cases, leading to preferential interactions between absorbate molecules (‘clustering’), solubility and diffusion properties are often not all well predicted; the fact that these films often had an oily feel indicates however that these clusters or aggregates have significant plasticisation effects.

At first sight the results presented in Fig. 4.9 were surprising because a lower $\Delta\delta$ value was not obligatorily implying a greater sorption (see for example 1,4-butanediol or resorcinol) as previously explained: on the basis of the OH bonding theory, hypotheses are then formulated below in an attempt to understand the failure of the $\Delta\delta$ prediction tool in the polyols case:

### 4.4.4.b) Butanediol (14BD), a linear hydroxy-compound.

First, Fig. 4.9 demonstrated that the addition of a second OH group on the butanol molecule greatly increased sorption (14BD was Type C). This was not predicted by usual solubility parameters ($\Delta\delta_{\text{butanol}} = 11.7 < \Delta\delta_{14\text{BD}} = 18.2$), but indirectly through very high values of $\Delta\delta_{\text{H-d}}$ and $\delta_{\text{hydrogen}}$ for14BD, which imply multiple hydrogen bonding (consistently to its high 230°C b.p. for a C$_6$ compound), and hence a strong hydrophilic character. This also reveals aggregation/plasticising possibilities, which are not exclusively due to van der Waals interactions (consistent with its higher $\delta_{\text{dispersive-forces}}$ a characteristics of compounds with long carbon chains) but to hydrogen bonding interactions (higher $\delta_{\text{H}}$; like in the 14BD case): possibly long chains of hydrogen bonded butanediol molecules (put ‘end to tail’) explain its very slow but steady absorption.
As for its plasticising capacity, it was probably related to molecular aggregation but the best evidences were (one) the oily feel and flexibility of the films, (two) the known use of diols such as glycols or glycerols as common industrial plasticising additives, and (three) the very low diffusion coefficient obtained (cf. Table 4.2).

4.4.4.c) Aromatic hydroxy-compounds.

Phenol v. resorcinol: diol’s over-plasticisation behaviour.

The use of phenols, with lower vapour pressures (<< 1 mm of Hg), gave a more reliable picture as evaporation was not considered critical. As predicted, phenol is very soluble, possibly because of the aromatic ring, but not as soluble as resorcinol over the long term. The $\Delta \delta$ theory gave ‘phenol (1 OH) > resorcinol (2 OHs) > phloroglucinol (3 OHs)’ for the long term SP ranking: the Type A behaviour of phloroglucinol is surprising and unpredicted, indicating again the uncertainty of the solubility theory in cases of complex interactions.

However the same theory can give an order of the intensity of the interactions involved: for instance, with a $\delta_{\text{hydrogen}}$ as high as 18, and a $\Delta \delta$ that is the second highest at 11.7 (J.cm$^{-3}$)$^{1/2}$), phloroglucinol is very likely to aggregate in such a hydrophobic medium ($\delta_{\text{hydrogen}}$ (PVC & ATBC) only reached 7 (J.cm$^{-3}$)$^{1/2}$).

Then, the simplest explanation of phloroglucinol’s behaviour (and to a lesser extent of resorcinol’s behaviour) would be that clustering occurs, leading to more hydrophobic surfaces in contact with the ATBC. If such aggregates were bigger that ATBC molecules, increased migration in the opposite direction might be expected.

This could also produce an ‘over-plasticisation’ phenomenon, as already suggested with the aliphatic diol 14BD (indeed resorcinol films were easily deformable by hand.).
**Clustering.**

In fact aggregations of absorbates have been already observed, and called ‘clustering’: as mentioned by Hernandez et al. (1992, 1994) clustering concerns the reorganisation of molecules inside the polymer matrix into bigger units; it can drastically hinder diffusion. For example, this phenomenon has been observed with water into polyurethane and polyamide polymers (Barrie *et al*., 1974; Hernandez *et al*., 1992; Hernandez, 1994). Following our investigations, it appears moreover that clustering, by modifying the plasticisation level of the film (higher or lower), hence its overall hydrophobicity, also affects sorption.

Sorption may be affected by clusters in two ways: they may (over)-plasticise the film or, when very large, may alternatively hinder diffusion. By comparing different D values (lower for bulky clusters), and perhaps also by comparison with larger molecules which model the cluster (like a biphenyl molecule replacing two phenyl molecules), the solubility parameter of the cluster may be ‘re-processed’ (for instance, two, three or more molecules could be considered, with relevant OH bonding between them, before calculating the $\delta_{\text{cluster}}$’), and some limited improvement in the $\delta$ value might be obtained.

The effect on back migration remains difficult to predict.
Figure 4.10 Sorption curves of cyclohexanol (saturated C₆ hydroxy ring) and phenol (unsaturated C₆ hydroxy ring), at 22°C; the legend indicates between parentheses the boiling point in °C, the vapour pressure in mmHg x 100, and finally Δδ, i.e. the solubility parameter that measures the compatibility ‘absorbate’-PVC in (J.cm⁻³)¹/₂.
4.4.5. Effect of Aromaticity: Phenol v. Cyclohexanol

Like double bonds in aliphatic molecules, \( \pi \) bonds in ring molecules (aromaticity) did increase sorption: Fig. 4.10 shows indeed that phenol (Type C) sorbed 10 times more than its saturated counterpart (Type B).

Compared to cyclohexanol, phenol was less volatile (lower v.p., m.p. = 41°C i.e. above laboratory temperature), explaining its higher SP (Type C predictable). Both compounds have higher vapour pressure than octanol, but in the case of phenol, evaporation was apparent only after a considerable period of time; at intermediate periods, there could even be a slight increase, compatible with the low \( \Delta \delta \) solubility constant (second only to geraniol, Table 4.3).

Clustering could not be demonstrated: films were not even slightly opaque for either of the ring molecules; as for any hint of clustering that might be obtained through the magnitude of the diffusion coefficients, \( D_{\text{cyclohexanol}} \) was slightly but significantly smaller \( (= 10^{-12} \text{ m}^2\text{s}^{-1}) \), as would be expected for its slightly greater molecular size. The diffusion coefficients averaging \( 10^{-12} \text{ m}^2\text{s}^{-1} \) for the \( C_6 \) compounds, it is probable that neither phenol nor cyclohexanol molecules have aggregated in the plastisol, even at that high concentration.


The Type behaviour of compounds can be first estimated from their v.p. data (or boiling points).
Type C behaviour might be usually (but not always) expected when the v.p. is below about 0.1 mm of Hg. Type B is typically (but not always) in the v.p. range between 0.1 and 1.0 mm of Hg, and Type A typically above this pressure range.

Also solubility parameters (Table 4.3) on average predict somewhat similar ranges based on the spread of ∆δ values. Corresponding Δδ\textsubscript{H-d} averages are -2.5 for Type C, 1.1 for Type B, and 2.9 (J.cm\textsuperscript{-3})\textsuperscript{1/2} for Type A. As the v.p. and solubility constants are both correlated with intermolecular adhesion, this is not altogether surprising. In general, the solubility data offers a good explanation of the compounds which fall outside the expected range based on v.p.s.

Also, visual clues such as opaque or cloudy film may imply clustering, and oily films indicating (over)-plasticised films generally give Type C sorption curves.

It should also be noted that alcohols, even though chosen as a typical but restricted class of compounds, are a challenge to the solubility theory described here. Also, they are not particularly compatible, in terms of solubility parameters, with the plastisol, and other classes of compounds could behave quite differently; it would therefore require considerable effort to correlate solubility parameters across the wide range of possible absorbates, and the predictive value could be quite low.

Nevertheless, the basic classification system has been tested and found to be useful, and the anomalies are usually explicable if not quantifiable in terms of solubility parameters and it should be possible to interpret a full range of model compounds and a range of absorbates found in orange juice with some confidence.
4.5. CONCLUSION

Some understanding of structure-sorption relationship has been gained through the use of a simple method which may be of interest for scalping or tainting problems, caused by additives or others compounds in contact with oily or fatty materials (herein simulated by a highly plasticised polymer), in particular in the food safety domain. Unlike the commonly studied cases with diluted solutions, here molecular interactions could deeply affect the general solubility of some absorbates in plastisols, as well as their diffusion coefficients.

Above all, the usual physico-chemical parameters of tested absorbates, like, on one hand, MW, size, length or electronic saturation, and on the other hand, v.p., b.p., or m.p. could be more or less correlated to a particular sorption behaviour in plastisols:

Firstly,

- MW has a direct influence on concentration gradients because of the experimental setup;
- the size of single absorbates did not seem to significantly distinguish between diffusion coefficients in so highly plasticised media, but the bigger size of absorbate clusters did seem to;
- aliphatic chain length, yielding dispersive-type interactions, gave optimum sorption between C₈ and C₁₂ (methyl graftings also improved sorption in various cases);
the presence of double bonds definitely increased sorption for both aliphatic and ring molecules (especially aromatics);

finally the presence of OH groups producing strong hydrogen bonding interactions could drastically increase sorption (1,4-butanediol was over-plasticising the original plastisol film) or decrease sorption (phloroglucinol was ‘solidifying’ the film – ‘anti-plasticising’ it), depending on the number of OH groups; D values could be smaller than expected because of the formation of bigger ‘migrating entities’.

Secondly, when v.p.s were reasonably low (high b.p.s), evaporation could not account for a decrease in the sorption curve but a greater opposite mass transfer of plasticiser, which, although small, did appear on the kinetics as ‘negative sorption’ (which could be sometimes anticipated from the opaque/milky aspect of supply films, due to the crystallisation/aggregation of absorbates: being larger diffusing entities, the latter would diffuse slower than ATBC).

The laminate/gravimetric approach still needs additional in-depth studies to better relate sorption/diffusion quantities to usual physico-chemical parameters and to confirm the existence of such molecular reorganisations in plastisols, which are certainly a consequence of the use of ‘supersaturated’ films.

More accurate prediction of sorption in plastisols can be envisaged: indeed, together with the earlier parameters, \( \Delta \delta \) parameters gave a rather good estimation of the interactions involved by classifying the alcohols’ anomalous sorption curves in three main Types. This can becomes more significant with \( \Delta \delta_{H-d} \) values which roughly
measure the low, medium, and high hydrophobic character of the absorbates. Hence empirical quantitative boundaries were proposed for each Type.

By experimenting on concentrated media/foods, this laminate technique can rapidly indicate the existence of complex interactions directly through the observed SP and D values, and appraise them through various experimental and theoretical physico-chemical quantities. Yet, strictly speaking, any sorption prediction using $\Delta\delta_{\text{single\_molecule}}$ may end up erroneous, and a new theory is required for more accurate sorption predictions.
4.6. ACKNOWLEDGMENTS

The principal author of this work was supported by an Overseas Postgraduate Research Scholarship from the Department of Employment, Education and Training and Youth Affairs of the Commonwealth Government of Australia.
4.7. REFERENCES


Fayoux, S.C. (1997). Solubility parameters computer calculation program. Michigan State University, School of Packaging, MI, USA.


4.8. LIST OF TABLES AND FIGURES (TITLES)

Table 4.1 Principal physico-chemical characteristics of selected hydroxy compounds (sorted by boiling points and/or vapour pressures).

Table 4.2 Sorption and Diffusion (D) results, at 22°C, sorted by ‘sorption Type’ and increasing sorption percentage (SP) order.

Table 4.3 Solubility parameters and ‘absorbate’-PVC compatibility estimation, at 25°C, in (J.cm\(^{-3}\))\(^{1/2}\), sorted by ‘sorption Type’, like in Table 4.2.

Figure 4.1 Arrangement of the several film layers (a) for the sorption technique (b), and resulting sorption curve (c).

Figure 4.2 Schematic representation of the mass transfers involving both ATBC and the ‘absorbate’ gradients.

Figure 4.3 The three different shapes of kinetic curves observed, called Types A, B, and C, illustrating SP (\(^\uparrow\)), IDR (\(^\Downarrow\)), and FDR (\(^\downarrow\)), in relation to Table 4.2.

Figure 4.4 Sorption curves of linear aliphatic alcohols at 22°C (Test film mass change v. time).

Figure 4.5 Sorption curves of C\textsubscript{6} methyl isomers of hexanol (primary alcohols) showing deplasticisation, at 22°C (Type B).

Figure 4.6 Hydroxy isomers of 1-hexanol; comparison of the sorption curves of 2M1P, 2M2P (Type B) and 2C\textsubscript{6}OH (Type A), at 22°C, showing a definite mass loss.

Figure 4.7 Comparing isomers: sorption curves of cis-3-hexen-1-ol and trans-3-hexen-1-ol, at 22°C (Type B).

Figure 4.8 Sorption curves of two related C\textsubscript{6} and C\textsubscript{10} hydroxy-compounds showing the influence of diverse structural features (double bonds, branching, chain length) on sorption, at 22°C (All sorption Types, A, B, and C, represented).

Figure 4.9 Mono-, Di-, and tri-hydroxy compounds; effect of the OH group: sorption of 1-butanol, 1,4-butane-diol, phenol, resorcinol and phloroglucinol into ATBC40, at 22°C.

Figure 4.10 Sorption curves of cyclohexanol (saturated C\textsubscript{6} hydroxy ring) and phenol (unsaturated C\textsubscript{6} hydroxy ring), at 22°C.
CHAPTER 5

EXPERIMENTAL RESEARCH
ACETYL TRIBUTYL CITRATE MIGRATION
FROM PLASTICISED PVC
TRIGGERED BY FOOD
AND NON FOOD COMPONENTS:
MEASUREMENT OF CONTAMINATION
WITH THE LAMINATE TECHNIQUE
&
APPLICATION
TO CITRUS JUICE DEBITTERING
5.1. Abstract.

The sorption potentialities of highly plasticised poly(vinyl chloride) (plastisol) have been demonstrated, notably as a debittering agent for Navel orange juice via limonin sorption (Chapters 2, 3 & 4), but not its food safety status: in this aim a wide range of food components/contaminants (‘absorbates’) is super-saturated into plastisol films as food models; the release of acetyl tributyl citrate (ATBC) from ‘virgin’ plastisol films is then measured using the ‘laminate technique’ whereby one film, sandwiched between two food model films, is regularly weighed. In agreement with Chapter 4, identical anomalous kinetic curves are observed and categorized in Types A/B (notably in function of ATBC back-migration through mass loss measurement), or C (where only mass gain is detected but back-migration is strongly suspected). Various interpretations are proposed, notably in function of the possibilities of evaporation of the absorbate, of film-swelling (over-plasticisation) and plasticiser exudation, of absorbate aggregation (clustering) and film-hardening (anti-plasticisation), and of ATBC/absorbate diffusion rate differences. These are consistent with various simple parameters, like vapour pressure (volatility), film-appearance, hydrophobic value (solubility), curves’ initial slope and absorbate size/flexibility (diffusion), but prediction of the absorbate’s sorption (Type) and of the plasticiser back-migration are rather poor. Back-migration can still be estimated by comparison to a ‘standard experiment’ that consists in a sandwich of ATBC 30% / 40% / 30% w/w plastisol films. The particular use of rotenone as limonin model leads to the reasonable estimation of a Specific Migration Limit (SML) for orange juice. This eventually indicates the need of re-thinking the SMLs set for different foods and packagings, and the need for more comprehensive test procedures, the laminate technique can help in this development.

**Keywords:** poly (vinyl chloride), plasticiser, contamination, food components, fatty food simulants.
5.2. INTRODUCTION

Concern in the packaging industry, environmental lobbies, and consumers have turned scientific focus increasingly away from monomer migration in plastics (Benfenati et al. 1991, Katan 1992; Fayoux et al. 1997a, b - cf. Chapters 1a, 1b -) to the additives contained in nearly all of them, especially phthalates and adipates (Kondyli et al. 1990, Petersen and Breindahl 1998) from plasticised poly (vinyl chloride) (PVC) food wraps (Startin et al. 1988, Petersen 1995, Lan and Wong 1996). Indeed the monomer issue can be currently avoided thanks to better quality industrial productions: for instance vinyl chloride monomers would not represent more than 0.001% w/w of the total PVC (cf. Chapter 3).

Much of the previous work concerned ‘contact’ liquids such as olive oil, orange juice, oily food simulants and diverse aqueous simulants (ethanol, tetrahydrofuran, iso-octane) (Charara et al. 1992, Vergnaud 1995/96, Fayoux et al. 1996, Riquet et al. 1998, cf. Chapter 2 & Appendix A). Solid contacts have been studied with real foods such as cheeses, fish or fresh meat, but specific migration models were not proposed.

The influence of the sorption of food simulants (penetration) on the back-migration of additives from the plastic has been frequently noted (Messadi and Vergnaud 1981, Papaspyrides and Duvis 1990, Riquet et al. 1991, Ducruet et al. 1992, Arora and Halek 1994; Hamdani and Feigenbaum 1996) but no extensive study has been performed. Only a few compounds were studied such as BHT and other food antioxidants with regards to their migration into solid materials (Bieber et al. 1985); also recently fatty foods in contact with can coatings were shown to extract various glycidyl ether contaminants (Bierdermann and Grob 1996); general migration rules have been set by Piringer (1990) which simply stated that very high molecular weight
absorbates, with little or no interaction with plastics (eg. sucrose with polypropylene films), should not have any influence on migration (no extraction was noted.).

A specific study of the back-migration of ATBC (a safer plasticiser, Robertson 1993) from a plastic film into poultry meat and model food systems was done during microwave cooking: the lipid portion tended to increase the amount of plasticiser found, especially when food was in direct contact with the liner or wrap (Castle et al. 1988). Such an ‘induced/triggered deplasticisation’ or ‘mobility enhancement’ was also investigated by Bieber et al. (1985) to measure the effect of food fat on the release of phenolic antioxidants from different types of plastic materials, and recently by Ducruet et al. (1992) who used methyl fatty esters in plasticised PVC to simulate fatty foods. In fact they all observed the effects of ‘over-plasticising’ a plastic packaging by the food’s fatty content (Berens 1990, Halek and Luttmann 1991).

More absorbates need testing since not only food fat or methyl fatty esters but other specific food constituents or additives may engender the contamination of the food by plastic packagings’ plasticisers.

The current article’s main objective is to measure, better interpret, and maybe predict these crossed contaminations, with a focus on the interpretation of orange juice debittering by plasticised plastic films (cf. Chapter 2).

Above all, by screening more compounds with more functional groups or spatial conformations than in Chapter 4, this study verifies that the theories developed to interpret the kinetics anomalies observed do still apply, in particular the negative sorption uptakes and slopes that may attest to the back-migration of plasticiser. The 3-layer laminate technique with ATBC-highly-plasticised PVC (plastisol) films is used because it was found particularly rapid for a screening work such as this, best suited to
non-volatile and low-volatility absorbates (cf. Chapter 3) (Moisan 1980, Holland and Santangelo 1988); it can also simulate fatty_food/packaging contacts.

The sorption of selected absorbates and induced back-migration behaviour is discussed using a range of physico-chemical parameters such as the usual boiling point and vapour pressure (b.p. and v.p.), and a ‘new’ and simple tool measuring absorbates’ hydrophobicity (LogP, unitless) (Rekker 1977) as a guide to their likely solubility in the plastisol material.

The migration of the plasticiser under a concentration gradient between two plastisols with different levels of plasticiser is demonstrated, thus confirming the importance of back-migration.

In a later section of this work, a model compound (rotenone) for limonin is examined and shown to behave as a slower migrant than ATBC, consistent with its large molecular weight. This Chapter should allow a better understanding of the various mass transfers involved during the debittering-by-plastisols of Navel orange juice.

In the last sections contamination is eventually assessed, leading to general comments on food/packaging regulation.
5.3. MATERIALS AND METHODS

5.3.1. Chemicals

Chemicals were all laboratory grade and above 98% purity: their list and some of their physico-chemical characteristics are given in table 5.1.

5.3.2. Film making

Plastisol films were prepared according to the method described in Chapter 4. When made of 60% PVC + 40% ATBC w/w, they are also called ATBC40 films.

5.3.3. The laminate technique

The 3-layer laminate technique was used to study the influence of the presence of a compound in a plasticised polymer matrix, as food model, on the extraction of the plasticiser from a food wrap: it is presented in figure 5.1 (details in Chapter 4).

5.3.4. Measurement of the absorbates’ sorption and of the suspected ATBC back-migration

Test films were weighed (by micro-gravimetry, cf. Chapter 4) at regular time intervals and the sorption percentage (SP, in g gained or lost per 100 g initial film, or %) was plotted versus time (x-axis). All measurements were done in duplicate at 22 ± 2 °C. ATBC being non volatile, the negative SPs were chosen as a very rapid and
convenient way to estimate the release of ATBC by the test film. When the sorption curve remained in the positive Y-axis (SP) region, the slight depression happening after the initial sorption peak was chosen provisionally instead (correlation was suspected), providing the absorbate did not evaporate.

5.3.5. Measuring absorbates’ solubility through LogP values

Basically LogP can be used to estimate the ‘extractability’ of absorbates from aqueous media into an oily medium such as plastisol.

By definition LogP is the octanol/water partition coefficient at 25 °C expressed as its logarithm (Rekker 1977, Sangster 1989). It is very convenient: the more positive the value the more hydrophobic the compound. For instance LogP<sub>sucrose</sub> = - 3.70 and LogP<sub>decanol</sub> = +4.57. It gives a measurement of solubility of a compound.

Here the use of the LogP function follows Castle et al. (1988)’s observation that ATBC migration was increased by contact with fatty (eg. hydrophobic) food surfaces, like ‘our’ plastisol.

Also, LogP values are more easily available than the complex δ/∆δ solubility parameters that were used in the previous studies (cf. Chapters 2, 3 and 4). Of course they are not expected to give as precise interaction measurements between absorbate and plastisol because they approximate plastisol for octanol.

However, it must be emphasized that the LogP<sub>octanol/water</sub> values are only a guide to solubility in the plastisol, and not a numerical estimate.

Values for each absorbate are indicated in the legend of all the following figures; they were taken from the literature (table 5.1).
5.3.6. *Rapid estimation of diffusion*

Instead of diffusion coefficients (Ds) which necessitate lengthy calculations (cf. previous Chapters) the initial slopes of sorption curves will be recorded as ‘weak, medium, or strong’ slopes, positive for $D_{\text{absorbtes}}$, negative for $D_{\text{ATBC}}$: these categories correspond approximately to rates of $\leq 1$, $\approx 3$, and $\geq 6 \%$SP per hour.
Table 5.1. Selected compounds & characteristics listed in decreasing boiling point or vapour pressure order (continues next page)

<table>
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<tr>
<th>Compound class, and name</th>
<th>Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>Boiling point (°C)</th>
<th>Vapour pressure (at 25°C)</th>
<th>Log P **</th>
<th>Supplier information ***</th>
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<td>Para-chlorotoluene</td>
<td>C₆H₅CH₂Cl</td>
<td>126.59</td>
<td>162.4</td>
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<td>Para-dichlorobenzene</td>
<td>C₆H₄Cl₂</td>
<td>147.00</td>
<td>174.1</td>
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<td>BHA (ortho- and meta-)</td>
<td>C₆H₄<a href="OCH%E2%82%83">C(CH₃)₃</a>(OH)</td>
<td>180.25</td>
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<td>BHT</td>
<td>C₆H₄<a href="CH%E2%82%83">C(CH₃)₃</a>(OH)</td>
<td>220.35</td>
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<td>Para-hydroxy-benzaldehyde</td>
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<td>122.12</td>
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<td>3-Phenyl-phenol</td>
<td>C₆H₂(C₆H₅OH)</td>
<td>170.21</td>
<td>&gt;300</td>
<td>6.14 10⁻⁵</td>
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Table 5.1. Selected compounds & characteristics listed in decreasing boiling point or vapour pressure order (continued)

<table>
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<tr>
<th>Compound class, and name</th>
<th>Formula</th>
<th>Molecular Weight g/mol</th>
<th>Boiling point °C</th>
<th>Vapour pressure * mmHg at 25°C</th>
<th>Log P **</th>
<th>Supplier information ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common food compounds (with a focus on orange juice constituents)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-Limonene</td>
<td>C_{10}H_{16}</td>
<td>136.24</td>
<td>176</td>
<td>1.98</td>
<td>4.83</td>
<td>Fluka AG Sw</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>C_{6}H_{5}CHO</td>
<td>106.13</td>
<td>179</td>
<td>0.127</td>
<td>1.48</td>
<td>UWS-H Storage</td>
</tr>
<tr>
<td>Geraniol</td>
<td>C_{10}H_{17}OH</td>
<td>154.25</td>
<td>229.5</td>
<td>0.0300</td>
<td>3.47</td>
<td>Fluka AG Sw</td>
</tr>
<tr>
<td>Coumarin</td>
<td>C_{6}H_{2}O</td>
<td>146.15</td>
<td>297-9</td>
<td>0.00339</td>
<td>1.39</td>
<td>BDH Ltd, Poole, E Sw</td>
</tr>
<tr>
<td>Vanillin</td>
<td>C_{6}H_{5}(OCH_{3})(CHO)(OH)</td>
<td>152.15</td>
<td>285</td>
<td>0.000118</td>
<td>1.21</td>
<td>Ajax Aust, ‘Univar’</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>C_{6}H_{12}O_{6}</td>
<td>180.16</td>
<td>n/a</td>
<td>1.82 10^{-8}</td>
<td>-1.88</td>
<td>UWS-H Storage</td>
</tr>
<tr>
<td>Citric acid</td>
<td>C_{6}H_{8}O_{7}(COOH)_{3}</td>
<td>192.13</td>
<td>(decomposes)</td>
<td>3.70 10^{-9}</td>
<td>-1.72</td>
<td>UWS-H Storage</td>
</tr>
<tr>
<td>β-Sitosterol ##</td>
<td>C_{29}H_{49}OH</td>
<td>414.72</td>
<td>n/a</td>
<td>&lt; 10^{-9}</td>
<td>9</td>
<td>UWS-H Storage S</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>C_{6}H_{8}O_{5}(COOH)_{2}</td>
<td>176.13</td>
<td>(decomposes)</td>
<td>2.49 10^{-10}</td>
<td>-1.64</td>
<td>S</td>
</tr>
<tr>
<td>Quercetin</td>
<td>C_{15}H_{11}O_{7}</td>
<td>302.24</td>
<td>314</td>
<td>2.81 10^{-14}</td>
<td>1.48</td>
<td>Food Science Aust</td>
</tr>
<tr>
<td>Sucrose</td>
<td>C_{12}H_{22}O_{11}</td>
<td>342.30</td>
<td>n/a</td>
<td>5.15 10^{-17}</td>
<td>-3.70</td>
<td>UWS-H Storage</td>
</tr>
<tr>
<td>β-Carotene</td>
<td>C_{40}H_{56}</td>
<td>536.88</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>Food Science Aust</td>
</tr>
</tbody>
</table>

Polyvinyl chloride films processing chemicals: solvent and plasticiser

| Tetrahydrofuran (THF) | C_{4}H_{8}O | 72.11 | 65-67 | 162 | 0.46 | A, 99.9% |
| Acetyl tributyl citrate (ATBC) | C_{20}H_{31}O_{8} | 402 ### | n/a | n/a | n/a | Croda Chem. Aust |
| | | | | | | Food Science Aust |


** Log P is the logarithm of the partition coefficient of the compound between 1-octanol and water at 25°C; the smaller, and a fortiori the more negative the Log P value, the more hydrophilic the compound.

*** A = Aldrich Chemical Co. Inc., Milwaukee, WI, USA; S = Sigma Chemical Co., St. Louis, MO, USA; Ajax = Ajax Chemicals, Auburn, Sydney; H & W = Hopkin & Williams Ltd, Chadwell Health; Gvt S Dpt = Gvt. Stores Dpt., Drug Branch; K-L Lab = Koch-Light Lab. Ltd, Colnbrook Bucks; Aust = Australia; E = England, Sw = Switzerland; with % purity when available.

# Boiling points and vapour pressures are indicated respectively for the ortho-, meta- and para-forms.

## Approximate values based on cholesterol values at 7.79 10^{-10} mmHg, and Log P = 8.74 at 25°C.

### Approximate value.
Figure 5.1. Experimental set-up for the laminate technique, in relation to its food applications (solid/liquid food contacts).

**MODEL:** (Fatty) solid food (matrix, fats, specific constituents)

**MODEL:** Food package, eg. “cling wrap” (plasticised polymer film)

Aluminium foil  Supply film  Test film  Supply film

PVC  ATBC  ‘absorbate’

The diagram represents a cut of the ‘sandwiched’ films. The acetyl tributyl citrate (ATBC) plasticiser is represented migrating to the supply film whereas the ‘absorbate’ is represented diffusing to the test film.

The use of plasticiser diminishes the duration of the experiment because diffusion is enhanced.

The above scheme represents a mushroom as typical example of packaged solid food.

1) shows the plastic additives’ migration,
2) the penetration of food ‘absorbates’ (non volatiles),
3) the evaporation of particular flavour compounds, water and other gases,
4) the condensate that may extract plastic additives and get food components to penetrate the plastic, and
5) the transport of the extracted additive to the food, which may also exude some liquid constituents (water, fats, etc) with extractive potentialities.

* this plastic may also contain other additives than plasticisers.
5.4. RESULTS AND DISCUSSION

Sorption and back-migration results are presented in table 5.2, and the corresponding kinetics in figures 5.2, 5.3, and 5.4. Their interpretation is summarized in figure 5.5 and table 5.3.

5.4.1. Interpreting the sorption curves

5.4.1a) Sorption Types

Up to the present, the sorption curves have been described purely empirically as Type A, in which mass loss occurs continuously (figure 5.2), Type B, where an initial weight gain is followed by a weight loss (figure 5.3), and Type C, where there is only weight gain (figure 5.4).

A gain in weight was expected in all cases as the absorbate migrated from the surrounding supply films, driven by the concentration gradient of the absorbate across the interface, but a loss in weight at whatever stage required an explanation:

Figure 5.5 and table 5.3 present various interpretations in 4 main categories. Basically they all agree with the theories developed in the previous Chapter 4, concerning the role of evaporation, back-migration, and diffusion of each species into ATBC40 plastisol, all depending on their own solubility:

- **Evaporation**: for most of the absorbates which suffer a weight loss, the explanation is simple; when the vapour pressure is higher than about 0.01 mmHg (decanol’s v.p.) a weight loss eventually occurs (see decreasing curves after a
sorption peak between 30 and 60 minutes in figure 5.4.b), or later on in figure 5.4.a)), but more slowly when there appears to be a great affinity (high solubility) of absorbate in plastisol, like for decanol (LogP = 4.57), geraniol (LogP = 3.47), paradichlorobenzene (LogP = 3.44), and phenol (LogP =1.46). This is exactly what one would expect in typical ‘headspace’ experiments where plastic films are put in contact with volatile absorbates in sealed jars (cf. Chapter 3): the greater the vapour pressure the stronger the sorption, and, the greater the plastic-affinity the stronger the sorption also. Inversely when plastic films previously loaded with absorbates are left to evaporate in the atmosphere, the greater the vapour pressure the stronger the evaporation, but, the greater the plastic-affinity the weaker the evaporation. This evaporation phenomenon must occur during the experimental procedure involved in weighing the samples, when test films are more exposed to the atmosphere than supply films (folded then to prevent evaporation). In agreement with this, one can see in the geraniol curve that when sampling is too frequent, weight loss occurs, whereas a significant mass uptake is observed at 60,000 minutes after a long period without sampling. This phenomenon can also lead to the observation of negative SPs when the increase in weight absorbate material no longer exceeds the weight of back-migrating ATBC (figures 5.2 and 5.3 when v.p.s are superior to about 1 mmHg, i.e. hexanol’s v.p.); the phenomenon is also enhanced by the diffusion differentials between absorbate and ATBC:

- **Back-migration**: there is a second mechanism whereby the test film can lose weight continuously, and that is when the absorbate diffuses more slowly (or indeed not at all) across the interface than the ATBC back-migrates, like rotenone (Type A).
\(\beta\)-carotene (537 g/mol) and \(\beta\)-sitosterol (415 g/mol) were also slower migrants, but their mass uptakes did counterbalance ATBC’s weight loss for a while (see beginning of Type B curves) because of their difference in M.Ws. with ATBC (402 g/mol). Note then that an absorbate can diffuse as much and as rapidly as ATBC (or even faster) but still produce a negative SP simply because its M.W. is much smaller than ATBC’s (402 g/mol): for instance, when one mole of 150 M.W. absorbate enters the test film, if one mole of ATBC leaves, then the test film loses 402-150=252 g, and if two moles of absorbate enter then the test film still loses 402-2x150=102 g… This theory remains to be studied further. Nevertheless it is consistent with phloroglucinol’s Type A curve: with a small molecular size (126 g/mol) and insignificant volatility (v.p.=0.00016 mmHg) phloroglucinol should migrate fast and sorb strongly, but it did not manage to eventually counterbalance ATBC’s mass loss (at least 4 moles of phloroglucinol per mole of ATBC would be necessary to do it, following this ‘mole transfer theory’).

Apart from this peculiarity, back-migration is believed to be generally caused by a difference of speed of diffusion: ‘\(D\text{_{absorbate}}\) versus \(D\text{_{ATBC}}\)’. This implies that the original peaks observed for Type C curves (less in Type B) are essentially due to the rapid saturation of the test film (in less than 1 hour): absorbates must have been ‘pulled’ by a proportionally greater concentration gradient than ATBC’s. This agrees with Chapter 3’s hypothesis for calculating diffusion coefficients from the initial part of the curve: ATBC back-migration was considered negligible then, and neglected.

- **Diffusion and molecular shape and size**: as mentioned above, it is interesting to remark that the Type B & C curves with peaks are essentially obtained for
moderate M.W., chlorinated aromatics and linear alcohols, with high plastisol-solubility (LogP are all above 3). One-ring aromatics, moderately substituted, are small diffusants indeed, just like octanol, decanol, dodecanol or geraniol which can be expected to ‘reptate’, move in a very rapid snake-like way when diffusing. Even octadecanol, although not very soluble, did equilibrate moderately quickly, presumably by this mechanism.

On the whole the consequence of rapid diffusion is a rapid sorption equilibrium for the absorbate, leaving back-migration to follow over a longer period of time, reducing the weight of the test film again.

A further increase over an even longer period of time (figure 5.4.b)) can be caused by a gradual increase of diffusion by over-plasticisation of the test film: this film can literally ‘swell’ by super-saturation. But another (much more complicated) interpretation can be suggested if the initial supply films were ‘only slightly super-saturated’ i.e. with a tiny amount of undissolved absorbate: a first equilibrium could be reached rapidly in the test film, below saturation, then a second equilibrium (higher) would occur slowly as the undissolved absorbate gets dissolved and is able to diffuse: this is like a saturated salt solution containing salt crystals being put suddenly in contact with water through a salt-permeable membrane. The kinetics of dissolution of the absorbate would be the critical factor (further investigation needed). Finally the ‘long term sorption increase’ could simply be an artefact of the experimental method, especially for the volatile compounds (see previous section on sampling frequency).

As for the consequence of a slow diffusion of the absorbate, it results in a slow sorption equilibrium, often masked here by a faster ATBC back-migration which rapidly reduces the weight of the test film (Type A & B curves): this concerns very
large and bulky species (like rotenone). But this may also involve small species becoming aggregated inside the plastisol (when they are less soluble: LogP close to zero or negative); they could form ‘big (slower) migrating entities’ (aggregates): for example there exists strong hydrogen-bonding possibilities for small aromatics like parahydroxybenzaldehyde (slowest Type C) and phloroglucinol (Type A), or for the aliphatic acids and sugars, some of them even forming (visible) crystals unable to move (sucrose)(table 5.3). This theory agrees with the earlier ‘mole transfer theory’: for instance parahydroxybenzaldehyde might diffuse by pairs (through OH-CHO bonding).

Finally there might exist slower transfers due to anti-plasticisation, like for β-carotene or β-sitosterol: these species, soluble but heavy and rigid (solid indeed at 22° C) are believed to stiffen the test film and decrease its diffusion characteristics as they penetrate inside the ATBC40 matrix. This hypothesis is consistent with the apparent stiffness (by touch) of the β-carotene supply films for instance (which would also restrain back-migration, cf. table 5.3).

It is thus possible from the graphs to get an idea of the importance of the various factors which explain the overall forms of the curves.
Figure 5.2. Sorption curves of ‘Type A’ compounds (showing mass losses), at 22°C; the ATBC blank experiment consists in a sandwich of ATBC40 with ATBC30 films; butanol, ascorbic and citric acids, sucrose, xylenes and toluene, and phenolphthalein all suffered small but insignificant losses (< 0.1% SP) and have been omitted from the graph; between parentheses are indicated the vapour pressure in mm of Hg and the LogP (unitless), both available at 25°C only (cf. Table 5.1). Abbreviation: E-n means $10^{-n}$; n/a: not available. Curves, in dotted lines, are not all represented for clarity reasons.
Figure 5.3. Sorption curves of ‘Type B’ compounds (showing mass uptakes, then mass losses), at 22°C; hexanol, glucose, benzene, and alizarin appeared to give slight weight increases initially (< 0.1 % SP) but all decreased to slightly negative values later, and have been omitted from the graph (these values correspond to the limits of reproducibility in this data; between parentheses are indicated the vapour pressure in mm of Hg and the LogP (unitless), both available at 25°C only (cf. Table 5.1). Abbreviation: E-n means $10^{-n}$; n/a: not available. Curves, in dotted lines, are not all represented for clarity reasons.
Figure 5.4. Sorption curves of ‘Type C’ compounds (showing the greatest mass uptakes), at 22°C; a) for curves that eventually drop, or appear steady (‘C or C°’, cf. Table 5.2) and b) for curves which continue to rise significantly even after 4 days (‘C°, cf. Table 5.2); between parentheses are indicated the vapour pressure in mm of Hg & the LogP (unitless), both available at 25°C only (Table 5.1). Abbreviation: E-n means x 10^(-n); n/a: not available. Curves (dotted lines) are approximate.
Table 5.2. Sorption percentage (SP), ATBC induced migration (estimating an ‘Individual Migration Limit’ - IML - for food safety), and sorption curve ‘Type’ at 22°C

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Sorption Percentage *</th>
<th>ATBC migration **</th>
<th>Sorption Type #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/100g initial film</td>
<td>mg.dm²/(100mins**)</td>
<td>A^(0) (limit case)</td>
</tr>
<tr>
<td>Quercetin</td>
<td>0.00</td>
<td>0.19 ± 0.04</td>
<td>A? (limit case)</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>= 0 ?</td>
<td>&gt; 3.8 ± 0.8</td>
<td>A</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>0.00</td>
<td>&gt; 4.6 ± 0.9</td>
<td>A</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.00</td>
<td>&gt; 6.3 ± 1.3</td>
<td>A</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.00</td>
<td>&gt; 7.2 ± 1.4</td>
<td>A</td>
</tr>
<tr>
<td><strong>Rotenone</strong></td>
<td>0.00</td>
<td>&gt; 23.3 ± 4.7</td>
<td>A</td>
</tr>
<tr>
<td>ATBC30/40/30</td>
<td>0.00</td>
<td>&gt; 40.4 ± 8.1</td>
<td>A</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.01</td>
<td>3.9 ± 0.8</td>
<td>A</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>0.03</td>
<td>&gt; 3.8 ± 0.8</td>
<td>A (limit case)</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.03</td>
<td>&gt; 4.2 ± 0.9</td>
<td>A (limit case)</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.04</td>
<td>&gt; 5.0 ± 1.0</td>
<td>A (limit case)</td>
</tr>
<tr>
<td>Phenol phthalain</td>
<td>0.04</td>
<td>&gt; 7.5 ± 1.5</td>
<td>A? (limit case)</td>
</tr>
<tr>
<td>Xylenes</td>
<td>0.07</td>
<td>5.1 ± 1.0</td>
<td>A</td>
</tr>
<tr>
<td>Hexanol</td>
<td>0.07</td>
<td>&gt; 9.4 ± 1.9</td>
<td>B</td>
</tr>
<tr>
<td>β-Sitosterol</td>
<td>0.08</td>
<td>&gt; 0.6 ± 0.1</td>
<td>B (limit case)</td>
</tr>
<tr>
<td>Alizarin</td>
<td>0.13</td>
<td>&gt; 3.8 ± 0.8</td>
<td>A</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>0.14</td>
<td>&gt; 8.8 ± 1.8</td>
<td>B</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.21</td>
<td>&gt; 7.5 ± 1.5</td>
<td>B</td>
</tr>
<tr>
<td>d-Limonene</td>
<td>0.36</td>
<td>&gt; 10 ± 2</td>
<td>B (limit case)</td>
</tr>
<tr>
<td>Octadecanol</td>
<td>0.58</td>
<td>Not calculable</td>
<td>B</td>
</tr>
<tr>
<td>β-Carotene</td>
<td>0.60</td>
<td>&gt; 6.3 ± 1.3</td>
<td>B (limit case)</td>
</tr>
<tr>
<td>p-Chlorotoluene</td>
<td>0.77</td>
<td>&gt; 13.8 ± 2.8</td>
<td>B</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.98</td>
<td>&gt; 0.8 ± 0.2</td>
<td>B</td>
</tr>
<tr>
<td>Anisole</td>
<td>1.05</td>
<td>&gt; 7.1 ± 1.4</td>
<td>B</td>
</tr>
<tr>
<td>p-Hydroxybenzaldehyde</td>
<td>1.25 (20,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>1.27</td>
<td>4.9 ± 1.6 **</td>
<td>C</td>
</tr>
<tr>
<td>Octanol</td>
<td>2.31</td>
<td>2.8 ± 0.1 **</td>
<td>C</td>
</tr>
<tr>
<td>Vanillin</td>
<td>2.59 (20,000)</td>
<td>0.019 ± 0.004 **</td>
<td>C</td>
</tr>
<tr>
<td>Decanol</td>
<td>2.72</td>
<td>3.7 ± 0.4 **</td>
<td>C</td>
</tr>
<tr>
<td>BHA</td>
<td>2.72 (20,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>Dodecanol</td>
<td>2.79 (20,000)</td>
<td>2.2 ± 0.2 **</td>
<td>C</td>
</tr>
<tr>
<td>p-diChlorobenzene</td>
<td>2.98 (20,000)</td>
<td>4.8 ± 0.4 **</td>
<td>C</td>
</tr>
<tr>
<td>Phenol</td>
<td>3.18</td>
<td>2.2 ± 2.2 ***</td>
<td>C</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>3.80</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>BHT</td>
<td>3.85 (20,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>Geraniol</td>
<td>4.60 (60,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>Coumarin</td>
<td>5.53 (60,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
<tr>
<td>3-Phenylphenol</td>
<td>5.59 (20,000)</td>
<td>Not calculable</td>
<td>C</td>
</tr>
</tbody>
</table>

* Value observed at 'pseudo-equilibrium' (peak) or at the time indicated between parentheses (in min) if the equilibrium is not reached yet (Error ± 0.02); it corresponds to the highest absorbate intake.
** Minimal values normally indicate a sorption time less than 2 weeks (20,000 mins), or, if a mass loss is still occurring after 2 weeks, the value represents the slight depression occurring after the initial sorption peak, believed to be due to back-migration (in g/100g per 100mins): the values are approximate and given for the reader’s guidance only.
*** The error is so high due to insufficient data.
# cf. Chapter 4 for details; ’0’ means that mass uptake barely existed.
Four factors in interpreting sorption curves (cf. figure 5.5):

- **1)** excessive evaporation of volatile absorbate during weighing. ATBC back-migration leads to continuous weight loss,
- **2)** very compatible absorbates increase plasticisation (cf. ‘over-plasticisation concept’, Halek and Luttmann 1991), and enhance diffusion, especially for smallest species,
- **3)** exudation, causing liquid layers on the surface, and increasing transfer rates, and
- **4)** formation of molecular aggregates, slowing migration rates, perhaps below the rate of ATBC.

The methodology using ‘super-saturated’ plastisols (Chapter 3) is the principal cause of the above anomalies; interactions between absorbate and plastisol affect both solubility and diffusion, on top of the usual diffusion rate distinction between the two species (called ‘kinetic interpretation’ in figure 5.5).
Figure 5.5. Possible interpretations of the sorption anomalies obtained with the use of initially supersaturated-plastisol supply films, the 3-layer laminate technique and micro-gravimetric measurements; * the magnitude of the mass transfer in either way should be proportional to the dissolution ratio of each absorbate i.e. to the mutual compatibility absorbate/plastisol; ** the shape of the curves depends on the kinetic differentials absorbate/ATBC and on various parameters *** (evaporation, exudation, and molecular interactions changing the physical characteristics of the film).
Table 5.3. Appearances of supply films and possible critical parameters to explain the kinetic anomalies, in function of sorption ‘Types’, and estimation of back-migration at equilibrium (***)

<table>
<thead>
<tr>
<th>Sorption Type *</th>
<th>Absorbate name</th>
<th>Film aspect and Critical parameter **</th>
<th>Back-migration of plasticiser ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Quercetin</td>
<td>opaque rigid films</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Ascorbic acid</td>
<td>flexible films (but H₂ bonding)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Phloroglucinol</td>
<td>cloudy rigid films (H₂ bonding)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Sucrose</td>
<td>visible crystals (strong H₂ bonding)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Butanol</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Rotenone ****</td>
<td>rather clear, still flexible films</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>ATBC30/40/30</td>
<td>oily flexible films (sticky)****</td>
<td>H****</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Anthraquinone</td>
<td>opaque rigid films</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Chlorobenzene</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Citric acid</td>
<td>flexible films (but H₂ bonding)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Phenol phthalein</td>
<td>very opaque films (but still flexible)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Xylenes</td>
<td>clear flexible films, fading smell</td>
<td>H</td>
</tr>
<tr>
<td>B</td>
<td>Hexanol</td>
<td>clear films, smell (v.p.=1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>β-Sitosterol</td>
<td>cloudy rigid films</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Alizarin</td>
<td>opaque rigid films</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>D-Glucose</td>
<td>visible crystals (H₂ bonding)</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>d-Limonene</td>
<td>clear films, smell citrus</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Octadecanol</td>
<td>opaque films, still rather flexible</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>β-Carotene</td>
<td>very opaque, rigid films</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>p-Chlorotoluene</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Anisole</td>
<td>clear films, smell (v.p.&gt;1 mmHg)</td>
<td>H</td>
</tr>
<tr>
<td>C</td>
<td>p-Hydroxybenzaldehyde</td>
<td>clear films (but strong H₂ bonding)</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>clear films (but H₂ bonding)</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Octanol</td>
<td>clear oily films (flexible), smell</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Vanillin</td>
<td>clear films, strong smell (H₂ bonding)</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Decanol</td>
<td>clear oily films (flexible)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>BHA</td>
<td>clear flexible films</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Dodecanol</td>
<td>clear oily films (flexible)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>p-diChlorobenzene</td>
<td>clear flexible films, strong smell</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>clear flexible films, smell</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Resorcinol</td>
<td>cloudy (hydrogen bonding)</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>BHT</td>
<td>cloudy flexible films</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Geraniol</td>
<td>clear, flexible, oily films, smell</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>Coumarin</td>
<td>cloudy flexible films, strong smell</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>3-Phenylphenol</td>
<td>clear flexible films</td>
<td>H</td>
</tr>
</tbody>
</table>

*: according to table 5.2.

**: in general hydrogen bonding and hydrophilicity explain the opacity of the film (the absorbate is less keen to dissolve in plastisol), indeed even its least flexibility (called ‘rigidity’) if an anti-plasticisation phenomenon takes place; opacity and flexibility were assessed by touch and sight.

***: Empirical estimation of ATBC’s back-migration at equilibrium (sorption monitoring requiring more than 15 days, the average duration of the experiments studied here): L for Low, M for Medium, H for High; this is mainly based on the negative SP’s and the compatibility of the compounds with plastisol (‘high compatibility for high back-migration’).

****: simulation of the highest back-migration (two different ATBC concentrations, 30% and 40% w/w, are put in contact until they equilibrate).
5.4.1b) Two Typical Numerical evaluations of the mass transfers

(N.B.: calculations do not take into account the density differences of the different species and mixtures, all generally close to 1.0, except that of PVC equal to 1.4; in the examples, unloaded plastisol films are made of 600 g PVC + 400 g ATBC).

Relying on the previous results and hypotheses, two typical numerical evaluations of the mass transfers involved with super-saturated plastisols are pictured as examples in figure 5.6: the first one concerns a fast-diffusing 100 M.W. non-volatile absorbate, and the second one a slow-diffusing 400 M.W. non-volatile absorbate.

These extreme examples were chosen because they are simple to understand, with only one species moving at a time basically.

In a way, the first example pictures strong Type C behaviours whereas the second represents strong Type A behaviours (Again Type B curves can be considered to be kinds of weighted combinations of Types A and B, where both migrating species move at a similar speed: Type B curves are therefore difficult to simulate by means of standard diffusion theory, cf. Chapter 3).
Above: initial situation for absorbate 100 M.W.; originally 1M concentration was sought, so 92 g was added (30 g dissolved + 62 g undissolved: saturation reached). This corresponds to a saturation peak at 3% SP observed on the curve (as example), that is a 30 g mass uptake (below). In this simulation ATBC is basically not moving.

Above: initial situation for absorbate 400 M.W.; originally 1M concentration was sought, so 552 g was added (52 g dissolved + 500 g undissolved: saturation reached). This corresponds to sorption equilibrium at -3% SP observed on the curve for ATBC (as example), i.e. a 30 g mass loss (below). Here the absorbate does not/barely move *.

Figure 5.6. Two quantified, and simplified, examples of the mass transfers occurring in the 3-layer laminate, and the expected sorption kinetics. In these simulations the supply films are considered effectively super-saturated by either a fast-diffusing 100 M.W. species(a) or a slow-diffusing 400 M.W. species(b) (non-volatile molecules); arrow length represents migration speed comparatively to ATBC, not concentration gradient intensity which is indicated inside boxes (in Molar); * presumably due to clustering, anti-plasticisation and/or molecular rigidity.
5.4.2. Orange juice debittering with plastisol: related issues

5.4.2a) ATBC migration: a superior limit sought via the ‘ATBC30/40/30’ standard experiment

Whatever the material (eg. food) in contact with plastisol, an upper limit to migration is required: the migration of ATBC is measured from a simple concentration gradient (figure 5.2). The concentration gradient that was created was about 40-30%=10 % w/w, or 1.20-0.93 = 0.27M from the test film to the supply films; eventually the concentration would be identical in all three films at about 1.02M, and ATBC w/w levels would be about 30% in the test film (PVC 60% unchanged) and 35% in the supply films (PVC 70% unchanged).

If the concentrations in the test and supply films were reversed, a similar positive curve would be expected, but of modest magnitude initially compared to the absorbates in figure 5.4, but one increasing steadily over a very long period of time. This calibration of the initial diffusion rate allows the initial migration rate to be estimated for any concentration gradient, at least over a small range where changes in plasticisation might not be great.

The volume change when absorbate is dissolved in the plastisol produces the ATBC concentration gradient in these experiments, and in principle would allow the migration rate to be calculated when the absorbate solubility is known (see examples in figure 5.6), and it is presumed there is no coupling between the two migrants; the magnitude of the measured effect in any case confirms that migration will not be large initially under most conditions.

Consequently one can expect that the back-migration obtained with the ATBC40/30/40 experiment constitutes an upper limit to migration; for food/packaging
regulation reasons, the negative SP obtained for ATBC (-3.2 %) at 20,000 mins (= half a month) was converted in mg.dm\(^{-2}\) (40 mg.dm\(^{-2}\), table 5.2). In theory this migration limit would reach about -10% SP (asymptotic line), but as far as orange juice debittering is concerned, the duration of contact with plastisol films would never exceed 15 days (5 hours already proved to be sufficient, cf. Chapter 2).

For comparison this migration value is well over that of 5.1 mg.dm\(^{-2}\) recorded by Castle et al. (1988) for its most oily product (peanut biscuits) after microwave cooking, but the copolymer of PVC and poly(vinylidene chloride) that was used contained 4.8% ATBC only: these results correspond in fact to a consistent 1/8\(^{th}\) ratio.

5.4.2b) **ATBC migration, when the concentration gradient is induced by ‘rotenone’, as model compound for limonin**

A majority of Type A compounds shows a slow rate of back-migration, assumed to be caused by slow dissolution of the excess undissolved absorbate or/and by increase in film rigidity caused by high melting point absorbates (anti-plasticisation). This is consistent with weak initial slopes on the curves (figure 5.2); rotenone would simply be present in more easily soluble form (steeper slope) and a larger amount of dissolved rotenone would create the strong back-gradient observed for ATBC (note that this phenomenon is similar to the absorption of water by saturated salt solutions.).

Nevertheless, in orange juice the release of ATBC would be small, and certainly even less than 40 mg.dm\(^{-2}\).

Effectively if one considers that limonin in orange juice is one of its most plastisol-compatible component (cf. Chapter 2), even more than rotenone (figure 5.7), and because the rotenone curve shows a lesser back-migration (within 15 days), at
about 23 mg.dm\(^{-2}\) (table 5.2), one can calculate an estimated migration of 28 mg.dm\(^{-2}\) with limonin (in proportion with the different intensities of back-migration, cf. figure 5.8 for details).

Sitosterol could have been included in this analysis (and in figure 5.7) because its sorption behaviour is similarly remarkable, with strong negative SPs. However, although shape and size were similar, its solubility parameters were very different from limonin’s: \(\Delta \delta_{\text{plastisol-sitosterol}} \approx 8.5\), \(\delta_h(\text{sitosterol})\) is zero... Because of that, it is expected that sitosterol induces far less ATBC migration in orange juice than limonin during debittering with plastisol.

\[
\begin{align*}
\text{Limonin} & \quad C_{26}H_{30}O_8, \text{ M.W. 470.52} \\
\delta_d & = 17.35 \quad \text{medium anti-plasticisation} \\
\delta_h & = 7.37 \quad \text{of plastisol expected} \\
(\Delta \delta_{\text{plastisol-limonin}} & \approx 3 \text{ to } 4 \text{ MPa}^{1/2}) \\
\text{Rotenone} & \quad C_{23}H_{22}O_6, \text{ M.W. 394.43} \\
\delta_d & = 17.5 \quad \text{strong anti-plasticisation} \\
\delta_h & = 11.1 \quad \text{of plastisol expected} \\
(\Delta \delta_{\text{plastisol-rotene}} & \approx 4.6 \text{ MPa}^{1/2})
\end{align*}
\]

*Figure 5.7. Limonin and rotenone chemical formulas and solubility parameters; \(\Delta \delta s\) are given as comparative solubility parameters only (cf. Chapter 4), in (J.cm\(^3\))\(^{1/2}\) or MPa\(^{1/2}\); the dispersive (hydrophobic) part of the interactions of each molecule is given by \(\delta_d\) and its hydrogen-bonding part (hydrophilic) by \(\delta_h\) (same units); * the plastisols used were 40% w/w plasticised by other plasticisers than ATBC, like di-octyl phthalate or di-octyl adipate (cf. Chapter 2).*
5.4.2c) ATBC migration: food/packaging regulation issues, citrus juice debittering & consumer acceptance

Three migration limit concepts are used in figure 5.8 and need to be explained:

- firstly the Global Migration Limit (GML), set to 10 mg.dm$^{-2}$ by the European Community (EC) Plastics Directive 90/128/EEC (other countries may regulate differently), whatever the plastic additive,
- secondly the usual Specific Migration Limit (SML) which looks at one plastic additive and is valid for a category of foods, like fatty or acidic foods (eg. orange juice),
- and thirdly an Individual Migration Limit (IML) which can be considered as a new concept specially suited to the study of the migration induced by one type of triggering agent (one absorbate), not by a mix of compounds like normal foods would be. In the current study, the IML$_{\text{rotenone}}$(ATBC) could be set to 23 mg.dm$^{-2}$ (15 day contact), corresponding to the most negative SP observed with rotenone-saturated plastisol.

During debittering, many orange juice components are sorbed by plastisol, in particular the bitter principle limonin. Testing all these components for measuring the induced ATBC migration is neither reasonable nor feasible.

Nevertheless it is possible to get an estimate of the SML for orange juice if limonin is considered as causing (one of) the strongest ‘ATBC-releases’: then the IML$_{\text{limonin}}$(ATBC), 28 mg.dm$^{-2}$, can be assumed equal to the SML-OJ.
Before the extrapolated value of 28 mg.dm\(^{-2}\) is used as SML for orange juice when in contact with plastisols, it must be cross-checked by independent research teams. But in the meantime, it is believed to be a reasonable estimate especially because it was obtained under drastic conditions of maximum concentration gradients (‘super-saturation’), though sorption equilibrium was not quite complete: in figure 5.8 theoretical equilibria are shown (exaggerated representation) for ATBC30/40/30 and for saturated rotenone and limonin, assuming all material is dissolved from the start; although standard migration limits are determined at steady state, after 15 days the sorption curves were closely approaching their asymptotic values at the end of the experiment to obtain significant migration limits values.

But it is not necessary to reach the steady state: only 5 hours would have been sufficient to measure ATBC migration with saturated rotenone plastisol, before a relevant estimation is done for the back-migration in orange juice during limonin sorption by plastisol.

Indeed, whereas limonin’s absorption by plastisols is demonstrated in Chapter 2, here there is no evidence for diffusion of rotenone at all (no positive SP is observed), but it must occur, and at a reduced rate to the back-migration of ATBC, assuming rotenone behaves similarly to limonin (at least size wise). Then diffusion being similarly slow for both compounds, and debittering being effective in 5 hours (limonin concentration in orange juice could drop below the human sensory threshold of 5 ppm w/v - US-FDA ‘Grade A’ citrus juices - with a very similar 40% w/w dioctyl adipate plasticised PVC film, cf. Chapter 2), a minimal amount of ATBC is expected to be released in the orange juice in the same time: on the rotenone curve this would make up less than 13 mg.dm\(^{-2}\), which is very close to the GML set by the European Community Directive, not to be exceeded by any of the SMLs (figure 5.8).
Figure 5.8. Simplified and deliberately exaggerated representation of the theoretical sorption curve of ATBC30/40/30, and of those that one would originally expect for rotenone and limonin: they all express ATBC back-migration only. The grey square represents the experimental region.

Legend:
* assuming they were totally dissolved in the supply films;
** displaying an initial slope that is less steep than limonin's, ATBC moving slower because of rotenone's stronger anti-plasticising effect on plastisol (figure 5.7);
*** a lower sorption equilibrium than rotenone's is predicted, considering its higher solubility (smaller $\Delta\delta$, cf. preceding Chapters);
IML means Individual Migration Limit;
SML means Specific Migration Limit;
GML (EC) is the General Migration Limit specified by the European Community.

N.B.: ATBC30/40/30 is similar to a laminate of (ATBC40+33%PVC / ATBC40 / ATBC40+33%PVC),
‘Rotenone’ is a laminate of (ATBC40+54%rotenone / ATBC40 / ATBC40+54%rotenone),
‘Limonin’ is a laminate of (ATBC40+54%rotenone / ATBC40 / ATBC40+54%rotenone).
The SML of di-octyl adipate, a preferred plasticiser for food contact over the more common (but suspect) phthalates (cf. Chapter 2), is a mere 3 mg.dm\(^{-2}\); ATBC’s SML not being established yet.

Assuming the GML to be unchanged (10 mg.dm\(^{-2}\)), it is hoped that the debittering process by sorption on the plastisol could be authorized. Starting with 13 mg.dm\(^{-2}\) in 5 hours, passing below the GML seems feasible, especially if:

- the composition of the plastisol is optimized (eg. with new, bigger and slower moving additives, or with ATBC38 or ATBC35 \((*)\) i.e. films with less plasticiser…),
- a high SML is accepted for the Generally Recognized As Safe (GRAS) ATBC.

\((*)\): 35% w/w is the maximum level of use in PVC for Australia (A.S. 1992).
Figure 5.9. Sorption curves of essential oils (mainly orange juice) and other components found in orange juice, at 22°C; ascorbic and citric acids, sucrose and glucose did not give but slight mass uptake results (< 0.1% SP), and have been omitted from the graph; between parentheses are indicated successively the vapour pressure in mm of Hg and the LogP (unitless).

All ‘sorption Types’ are thus expected to be present in orange juice; and depending on sorption duration, plastisol films could selectively extract one kind of orange juice molecules rather than another kind, which could favour a more or less important contamination of the juice by the plasticiser (here negative SPs are a measurement of it, expressing the fact that the plasticiser leaves the film faster than the absorbate enters).

A representation of the sorption curve of rotenone is added to show the possible behaviour of limonin in orange juice (cf. Figure 5.2).

Abbreviations: E-n means x 10^{-n}; n/a: not available. Curves, in dotted lines, are not all represented for clarity reasons, such as the chemical formulas of the absorbates.
5.4.3 Mass transfer of citrus juice components in ATBC40

Eight citrus juice components (table 5.1), and rotenone as limonin model, are gathered in one graph (figure 5.9). In order to point out the components that are suspected to significantly trigger back-migration (contamination) into orange juice, please refer to table 5.3.

It appears that whether solid or liquid, the hydrophobic compounds, eg. β-carotene or geraniol (or perhaps clustered hydrophilic compounds forming hydrophobic aggregates - Hernandez et al. 1992/94 -, eg. resorcinol or benzaldehyde, cf. Chapter 4) can often be tested by the laminate method, which involves only hydrophobic solvents.

The use of saturated hydrophobic plastisol to model an aqueous solution such as orange juice may be considered peculiar, but this choice is supported by the following reasons:

- high concentrations of citrus components can be achieved in order to amplify, and possibly reveal the molecular interactions involved inside the plastisol,
- plastisol films are known as ‘liquid films’ or ‘gels’, and can be good liquid models providing they are sufficiently plasticised (our case),
- the major solvent (PVC polymer in the plastisol) does not migrate itself, unlike normal sorption experiments in water-based solutions such as orange juice, for example, and
- orange juice is a micro-emulsion (Fayoux et al. 1996, cf. Appendix A).
This last point is probably significant for a number of hydrophobic compounds including limonin, which would be expected to migrate from oily micro-micelles into a plastisol, rather than from an aqueous solution, as it is extremely insoluble in water. This of course gives added significance to the laminate technique.

Figure 5.9 can be interpreted differently then, as if a particularly concentrated (and oily !) orange juice had been in contact with ATBC40 for 15 days at 22°C. If a single strength juice was debittered with ATBC40 it is probable that similar curves would be obtained, but in the period of weeks/months rather than the hours/days typically measured in this work, providing microbial spoilage is contained… Therefore the back-migration measured in this study being over-estimated for actual orange juice, the SML for ATBC should end up dropping well below the 13 mg.dm$^{-2}$ value (This is a drawback of using this laminate technique but, for the consumers’ safety, over-estimating the SML is better than under-estimating it).

Nevertheless, during actual limonin extraction, care would have to be taken not to allow sufficient time for significant extraction of ATBC into the juice; fortunately the extraction time can be short, but further experiments need to be done to optimise and guarantee regulatory compliance of the process.
5.5. CONCLUSION

The laminate sorption technique has been used to investigate the migration properties of a wide variety of absorbates, including orange juice components, into plastisol. The method appears suitable for rapid screening purposes, and may be a reasonable model for debittering investigations, but other supply systems will be needed for aqueous based systems.

This Chapter attempts to explain the debittering phenomenon by plastisol, and the juice contamination issue: providing the model is validated, it is probable that limonin dissolves readily in plastisol while anti-plasticising it. Limonin diffusion is judged to be extremely slow compared to back-migration of the plasticiser. Perhaps limonin forms clusters in plastisol, explaining its strong retention. Also, the fact that limonin is extracted efficiently from orange juice, presumably from micelles, means that the reverse process for ATBC or other plasticisers is also likely (cf. di-octyl adipate, cf. Chapter 2).

It was shown that contamination by ATBC is expected to be low due to the short duration of the debittering process, and thus regulatory migration limits may be achievable. It is probable that other citrus components, like flavour compounds, dissolve more intensely in plastisol and severely trigger back-migration, emphasizing the importance of the rapidity of the process (no flavour scalping has been noted, but see Chapter 2).

Consequently a safe orange juice debittering is feasible with ATBC-plastisols.
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5.7. LIST OF TABLES AND FIGURES

Table 5.1. Selected compounds & characteristics listed in decreasing boiling point or vapour pressure order

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Table 5.3. Appearances of Supply films and possible critical parameters to explain the kinetic anomalies, in function of sorption ‘Types’, and estimation of back-migration at equilibrium

Figure 5.1. Experimental set-up for the laminate technique, in relation to its food applications (solid/liquid food contacts)

Figure 5.2. Sorption curves of ‘Type A’ compounds (showing mass losses), at 22 °C

Figure 5.3. Sorption curves of ‘Type B’ compounds (showing mass uptakes, then mass losses), at 22 °C

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Figure 5.7. Limonin and rotenone chemical formulas and solubility parameters

Figure 5.8. Simplified and deliberately exaggerated representation of the theoretical sorption curve of ATBC30/40/30, and of those that one would originally expect for rotenone and limonin: they all express ATBC back-migration only.

Figure 5.9. Sorption curves of some citrus juice - and other plants - essential oils constituents, at 22 °C
GENERAL CONCLUSION
GENERAL CONCLUSION

This research program has developed Chapter by Chapter, depending on the research outcomes at each stage, until a reasonably comprehensive understanding of plastisol absorbents has been reached.

Following the initial observation of limonin extraction by a plastisol film, a very extensive literature review was initiated (Chapter 1).

In Chapter 2, a wide variety of plastisol films and other potential absorbents were investigated. Dioctyl adipate was considered to be the optimal plasticiser when safety concerns were taken into account as well as efficiency. Kraft paper was the best non-plasticised absorbent; possibly lignin-based absorbents could also be investigated.

However, the mechanism of the diffusion and sorption needed to be investigated, as highly plasticised absorbing films have received little scientific examination. And, the effect on the other components in foodstuffs such as orange juice also needs examination...perhaps they are strongly absorbed also.

Chapter 3 introduces two possible techniques for studying this problem: (1) the traditional ‘headspace’ technique, (2) new experimental techniques (‘laminate methods’) which have the considerable advantage of modelling extraction of materials from liquid or solid phases (as in orange juice itself, rather than just from the ‘headspace’). This also allows measurements of the extraction rates of non-volatiles. A careful selection of appropriate diffusion equations for these procedures allowed the calculation of diffusion and sorption parameters. Several model compounds were tested by these methods, and it was soon discovered that problems with the laminate methods included difficulties in...
measuring even moderately volatile absorbates, and problems with the back-migration of plasticisers into the supply medium. Nevertheless, this latter procedure was persevered with, as loss of plasticiser is also of considerable interest to the food packaging industry, and the technique looked promising for quick surveys of a vast array of migrants of concern, either into plastics from foods (‘scalping’) or out of the plastic (contamination).

In **Chapter 4**, model compounds (alcohols and phenols in particular) were investigated to test the limits of the method. It was found that rough measurements of diffusion rates and solubilities of most of these compounds could be found, but that it was hard to use solubility calculations for predictive purposes, especially when hydrogen bonding was an important factor. The classification of sorption Types into three classes proved empirically convenient, and was shown to have a basis in physical parameters.

Finally, in **Chapter 5**, a wide range of orange juice components and many other compounds chosen as models were investigated according to the above classification scheme, and using a simple solubility parameter. One large molecular-weight model compound (rotenone) was selected instead of the difficultly obtainable limonin. Its behaviour was surprising in several ways: rotenone proved to be both soluble and somewhat indifferent to migration, at least compared to the plasticiser.

If limonin, which is believed to occur predominantly in oily micelles in the orange juice behaved similarly, the ready extraction and retention could be readily understood.

Testing of packaging-food interactions might be expected to be tested by the methods used in this thesis; for lightly plasticised packaging materials much longer extraction times might be expected, but as the polymer solvent parameters would be similar, similar results might be expected.
FUTURE WORK
FUTURE WORK

a) New Materials.

Debittering projects need to be continued and optimised. More screening of promising ‘absorbates’ needs to be done (cf. Applications section). Many plasticisers and polymers can be tested:

First it is believed that the use of ATBC as plasticiser should be pursued because of its acceptability for food contact. ATBC could be tried with other compatible polymers such as poly(vinylidene chloride), poly(vinyl chloride-acetate), poly(vinyl acetate) (a promising limonin absorbent, cf. Chapter 2), polystyrene, cellulose nitrate or ethyl cellulose (another limonin absorbent re. Chandler and Johnson's early results). ATBC is also compatible with the following resins in a nitrocellulose film (acetophenone resin, toluene sulphonamide resin, maleic resins, urea resins, melamine resins, alkyd resins) (Croda Surfactants Australia).

Other plasticisers may also be used but it may be wise first to read the early work of Van Veersen and Meulenberg, (1972, The relation between the chemical structure of plasticizers and their performance in PVC, SPE Ann. Tech. Conf. Prepr. 18, 314-328). Also vegetable oils may be used as such or after epoxidisation and new formulations may be investigated; biodegradability studies may be included to meet current consumer demand. Because of their plasticising efficiencies for PVC, both diisobutyl adipate (DIBA) and dioctyl sebacate (DOS) (Croda) would be worth testing.
DIBA and DOS are also approved for use in regenerated cellulose intended for food contact in the EC.

In the industry, as blends of plasticisers are often used to get the optimum performance, the effect of blending might be investigated with regard to the global migration limit (GML) of these plastic additives.

Polymeric plasticisers could be tested as little work has been done on them; the main objective would be to reduce the plasticiser migration in the environment. The debittering yield may be affected.

All the polymers suggested above can be used as such or further processed with increased porosity (average pore diameters would need checking), variable cross-linking ratios or tacticity (other modifications of the physical state of the polymer are described in Chapter 1b). Before use the final material can be shaped as beads, strips, films, tubes, fibres, etc.

A last option is to apply literally that ‘like dissolves like’: sorbing limonin would become easy and selective if the polymeric sorbent was made of poly-limonin groups or analogues. Already a poly-limonene material exists but costs are prohibitive.

As regards the use of entrapped enzymes or microorganisms for example, it is beyond the scientific scope of this thesis, but it may be worth trying with adapted plasticisers.

Applications to other fruit juices are also possible (cf. Applications section).
b) New Analysis Methods.

Firstly the laminate technique still needs to be perfected, for example by improving the measurements of higher vapour pressure test compounds or by precisely monitoring each concentration gradient.

This will depend on the experimental conditions (temperature, pressure, humidity). Thickness may be varied, to reduce depletion of the supply films. The initial concentrations of the ‘absorbate’ can be changed and sorption isotherms can be drawn to measure limits to the Fickian diffusion, as well as supersaturation limits (highly recommended).

Handling may be improved by automating the weighing or the spectrophotometric readings. The order of the layers in the laminate may be changed as Test/Supply/Test, in the same fashion as the functional barriers for recycled packagings. Both the supply and the test films could be monitored. Also numerous layers can be assembled into a multi-laminate film to observe the diffusion progress at regular time intervals (cf. Reynier, A., Dole, P. and Feigenbaum, A., 1999. Food Add. Contam., 16(4), 137-152.). Eventually, supply films re-usability needs investigation.

Secondly new types of measurements are needed to improve accuracy in order to get deeper insights in the sorption and diffusion phenomena.

For example, contact angle measurements would give an idea of the surface tension on plastic films of at least non volatile liquids in order to study the formation of condensate, for example on the inside of food packagings. They will also contribute to experimentally estimate the solubility parameters of the ‘absorbates’ (Grulke, 1989, Polymer Handbook Third Ed., 519-526).
Induced deplasticisation could be quantified by in-depth studies of the shapes of the curves obtained from Differential Scanning Calorimetry (DSC), in particular the change in glass transition temperatures (Tg).

Very accurate mass transfer measurements would be obtained with radio-labeled plasticisers and/or ‘absorbates’. Fourier Transformed Infra Red Spectroscopy (FTIR) would be particularly suited to detect and measure polymer/absorbate/plasticiser interactions (NB: furan ring and chlorine interactions, cf. Guérin, R., and Léard, M., 1982, Infrared spectra of furan adsorbed on some alkali halides. Adsorption potential calculations, J. Phys. Chem., 86, 3338-45), and Nuclear Magnetic Resonance (NMR) apparatus could focus on the detection of clustering...

Naturally, High Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC), coupled or not to Mass Spectrometry (MS), would be needed for comparison and ‘standardisation’ of the laminate technique.

Thirdly, in addition to parameters already mentioned in this thesis, parameters to be taken into account should be the temperature, to check the Arrhenius equation, the pH of the product, in relation to hydrogen bonding and polarity, the viscosity of both the product and the organosol before solvent evaporation, and the strength of the plastic. Parameters should be quantified for single and combined constituents: interactions estimates between permeants (Analysis of Variance - ANOVA - needed) could be calculated. Particular experimental conditions would have to be adapted to the FDA and EC regulations: for example, a ‘40°C/10days’ plan would be required to follow the Plastics Directive 90/128/EEC.
By focusing on only one material in contact, more precision would be gained. Although direct application to packaged food products would not be possible, a database of results is first required to attempt to generalise any new mass transfer concepts that may arise, especially in concentrated media. Quantitative Structure/Activity Relationship (QSAR) studies should become a major objective in understanding mass transfers in a plasticised environment, in particular to elucidate the debittering issue. Then prediction and rational optimisation could follow:

c) Using Predictive Techniques.

Food Models. Prediction of food packaging interactions may be modelled experimentally. Already liquid simulants have been widely tested (FDA, EC) and regulations have mushroomed. ASTM and EPA methods have been developed accordingly. A common feature in all Regulations is that they principally use liquid contacts. By varying the temperature, the pH, the composition (aqueous or oily), the surface area, the sample volume and contact time, researchers have attempted to simulate common food packaging contacts.

However, foodstuffs are often heterogeneous and interact with the package either in the vapour, the liquid or/and the solid phase, and more generally in all of them simultaneously. All phases may not be correctly simulated by single liquid contacts.

As the headspace technique and liquid contacts have been studied well, more emphasis should be put on solid and ‘gel’ contacts, which are directly approachable via the laminate technique: a plasticised polymer can play the role of a typical food,
with better reproducibility. By changing the composition of the supply films in the laminate technique, new food simulants could be investigated: from very solid, eg. cheddar cheese, to rather liquid, eg. milk.

**Modelling Sorption Kinetics.** Sorption kinetics modelling could be done by using the relevant solutions of the second Fick’s Law (Crank, 1975, cf. Chapter 4 for complete reference). These solutions may be used for laminates with, for instance, two different diffusion coefficients ($D_{\text{absorbate}}$ and $D_{\text{additive}}$): for information, three modelling equations and their ‘approximations for short times’ have been proposed in Chapter 3 as well as diverse theoretical approaches to simulate sorption kinetics by plasticised polymers. Interactions could be revealed by comparing the experimental sorption curves, with one, two or more ‘absorbates’, and by varying the concentrations ‘absorbate’(s)/additive(s). Statistical analysis is required (ANOVA). Migration Limits could be calculated.

**Theoretical Prediction of Sorption / Diffusion.** Many theories have been developed and used over the years. Scientists have dreamt of developing a unifying theory that could predict all molecular interactions. Once again interactions are so diverse that this objective is far from accomplished. The results presented in this thesis witness this fact. However it is important to test available theories before to envisage of developing new ones.

Sorption wise, the regular solution theory has proved to be rather inaccurate; the tri-dimensional solubility parameter ($\delta_{\text{dispersive forces}}, \delta_{\text{polar forces}}, \delta_{\text{hydrogen_bonding forces}}$) theory seems more promising, especially with the latest refinements available (cf. Chapter 1b); also one could replace $\delta_{\text{Water}}$ by $\delta_{\text{Plasticiser}}$ when using these refinements. In
that prospect, it could be wise to consider a global parameter representing the entire plastic, not only the polymer itself: the law of mixture could be applied if minimal interactions exist between the polymer P and the additive A:

$$\delta_{PLASTIC} = V_P \cdot \delta_P + V_A \cdot \delta_A$$

where the solubility parameter of the plastic is a weighed sum average of each of the solubility parameters of its constituents (polymer, additives), the weights being the volume fractions of these constituents (unitless) (NB: an example follows next page with $\Delta \delta_{limonin-ATBC40}$ where $\delta_{ATBC40} = 0.6 \times \delta_{PVC} + 0.4 \times \delta_{ATBC}$, as approximation).

A semi-empirical method called UNIFAC (or another one called UNIQUAC) could be of interest to quantitatively predict aroma sorption by polymers (for example). Better agreement with experimental values, than solubility predictions made by the regular solution theory and the Flory-Huggins equation, can usually be made. Unfortunately the use of such methods is rather non-explanatory as they are based on several different theories in combination with experimentally obtained molecular interactions data for various ‘absorbate’/sorbant systems. They could be used in process optimisation, like neural networks.

As regards diffusion, the Flory-Huggins interaction parameter ($\chi$) could be a good start too. For experienced mathematicians, the ‘Zielinski-Duda’ free-volume theory has proved very accurate in predicting polymer solvent diffusion coefficients. More recently computer molecular dynamics (MD) simulations of diffusion were able to predict diffusivities within 30% of experimental diffusivities (Karlsson, G. E.,
Also a new empirical approach could be designed by comparing the vapour pressures of many related compounds and estimating the vapour pressure contribution of each of the substituents (or moieties) of the molecule, in a same fashion as the solubility parameters and the LogP group contribution methods. Any physico-chemical characteristics of the ‘absorbate’ could be analysed this way, and hopefully related to sorption, diffusion and deplasticisation.

Since molecular interactions can modify the physical states of both the ‘absorbate’ (causing so-called ‘clustering’ through molecular aggregation, crystallisation,…) and the plastic (via ‘over/anti-plasticisation’), mass transfer prediction is altered. Hence new empirical parameters could be defined in diffusion equations and in the calculation of solubility parameters: for example in a case of anti-plasticisation or dual, triple, etc, molecular associations (cf. resorcinol, 1,4-butane-diol results in Chapter 3), diffusion coefficients would have to be reduced by some factor, and compatibility parameters (\(\Delta \delta\), LogP, etc) could include a ‘plasticisation level indicator’. In fact this may express and generalise the water activity (\(A_w\)) concept: instead of water, any plastic additive could be studied through its activity (\(A_{pa}\)), which would be defined in direct relation to the sorption isotherms mentioned earlier. This is believed to constitute an important research area towards better sorption predictions.

Eventually, as mentioned earlier, structure/activity relationships could predict and optimise sorption properties; they could be tested further, with adequate QSAR computer software (Katan, L. L., 1992, Multiplicity of migrants. Nature, 358, 183).
For information, the following table lists some tri-dimensional solubility parameters in \((\text{J} \cdot \text{cm}^{-3})^{1/2}\), obtained by the method of Hoy (cf. thesis' previous Chapters) (and calculated thanks to a computer program developed by the author) for compounds found in (bitter) citrus juice. They could be used for a future work on the ‘debittering issue project’:

<table>
<thead>
<tr>
<th>Name</th>
<th>(\delta_{\text{TOTAL}})</th>
<th>(\delta_{\text{DISPERSE}})</th>
<th>(\delta_{\text{POLAR}})</th>
<th>(\delta_{\text{HYDROGEN}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limonin</td>
<td>22.96</td>
<td>17.35</td>
<td>13.12</td>
<td>7.37</td>
</tr>
<tr>
<td>Limonoate A ring lactone</td>
<td>22.87</td>
<td>17.92</td>
<td>14.08</td>
<td>1.95</td>
</tr>
<tr>
<td>Nomilin</td>
<td>22.12</td>
<td>17.64</td>
<td>13.34</td>
<td>0.00</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>26.32</td>
<td>13.26</td>
<td>12.00</td>
<td>19.31</td>
</tr>
<tr>
<td>Citral cis/trans</td>
<td>19.71</td>
<td>15.52</td>
<td>8.72</td>
<td>8.45</td>
</tr>
<tr>
<td>Ethyl butyrate</td>
<td>20.54</td>
<td>15.23</td>
<td>8.24</td>
<td>11.04</td>
</tr>
</tbody>
</table>

NB: \(\Delta\delta_{\text{limonin-PVC}} = 2.70\), \(\Delta\delta_{\text{limonin-ATBC}} = 3.49\), \(\Delta\delta_{\text{limonin-ATBC40}} = 2.99\), a theoretical demonstration of limonin's prior affinity for poly(vinyl chloride); however limonin's plasticisation activity (anti-plasticisation ?) can not be shown that way.

d) Applications for the Food Industry (and other sectors).

The possibility of using the laminate technique for food modelling has been proposed earlier. Many more applications arise. A few are mentioned below.

The debittering of citrus juices has some potential still, as noted by the USDA in their ‘liquid membrane’ proposal (cf. Chapter 2). The extraction of limonoids from other plants extracts using the laminate technique is worth having a look at; for example the limonoids of the Neem tree can be used as natural insecticides and anti-
mutagenic compounds. The wine industry could be interested, as it is believed that flavonoids can be easily sorbed in such plastics.

Many more compounds could be tested for academic and fundamental interests: for example, resorcinol *versus* mesitylene and other tri-substituted benzenes, many triterpenes, including steroids, sesquiterpenes, and diols like 1,4-butanediol *versus* other glycols, and triols like glycerol commonly used as plasticisers in the industry, …

The specific removal of contaminants could be envisaged (chlorophenols, dioxine, …) with plasticised PVC films. Finally as the ‘absorbates’ chosen in this thesis only contain C, H, O, and Cl elements, many more remain to test, such as phosphates, nitrates, organo-metallics (eg. hemes), etc.

Oppositely, the development of a ‘minimal interaction’ plastics could be foreseen: as multiple migrations occur, from the packaging to the food and from the food to the packaging, the study of the long term equilibrium may give rise to the development of new packagings. For instance, films pre-saturated with orange juice components such as odours, or colorants such as β-carotene, could be used to package fresh orange juice and reduce scalping losses.

This process is applicable for many packaged foods, but it would suffer microbiological spoilage if not used properly. As regards shelf-life, the water, oxygen, carbon dioxide, ethylene permeabilities would need further investigations. Such a package would be adapted to a particular food ONLY. It is another type of ‘smart packaging’. 
Finally, plasticised PVC (or other polymers) could be tailored to the specific release of drugs, medicines, food additives, preservatives, …, by optimising its composition and controlling external parameters like temperature or humidity.

e) Implications.

Immediate regulatory implications could emerge from this work. It appears that different types of ‘absorbate’ would trigger differently the plasticiser migration. The set up of a specific migration limit (SML) in mg per dm$^2$ needs to take into account the type of food in contact, as well as its physical state. Deplasticisation potentials could be measured and regulated. The interactions between multiple co-penetrants have to be taken into account for proper SML and GML to be definitively set. The making of a database for solid, ‘semi-solid’ and ‘gel-type’ food could be started, along with the respective toxicology data.

In any case each particular foodstuff ‘phase’ should be tested in direct contact with its commercial packaging, i.e. its solid, liquid, and vapour phases, at various temperatures (at least those corresponding to each production, processing, storage, and transportation stage), notably because of the condensation issues on the internal face of the packaging. This would produce at least 3 migration limits with more explicit and comprehensive knowledge on the mass transfer phenomena that take place, leading to sharper food regulations.

On the whole future assays will have to be directed to actual food products, be it in the solid, liquid or the vapour phase, to complete the theoretical investigation (cf.
following table) and find improved food simulators and food/packaging contact models.

<table>
<thead>
<tr>
<th>MODEL</th>
<th>VAPOUR</th>
<th>LIQUID</th>
<th>SOLID/'GEL’</th>
</tr>
</thead>
<tbody>
<tr>
<td>UWS-H (1) 1997-8</td>
<td>ENS.BANA (2) 1995</td>
<td>UWS-H 1997-8</td>
<td></td>
</tr>
<tr>
<td>(Headspace technique: condensation issue)</td>
<td>(d-limonene, water, emulsifier)</td>
<td>(Laminate technique: supersaturation issue)</td>
<td></td>
</tr>
<tr>
<td>A model for high water activity - A_w - foodstuffs, and products containing volatile compounds - flavours - …</td>
<td>A model for citrus juices in a packaging plastic containing additives</td>
<td>A model for typical solid foods (eg. animal fat, meat, fish, cheese …) containing additives or not with better reproducibility</td>
<td></td>
</tr>
<tr>
<td>Future work: try the laminate technique at lower temperatures to reduce evaporation of ‘absorbate’</td>
<td>Future work: use of the laminate technique with ATBC40 and limonin, try citrus oils as plasticisers, and common food additives and pollutants</td>
<td>Future work: use of other polymers and ‘absorbates’, and of lower ‘supply film’ saturation levels to simulate other products (mushroom, fruits…), multiple mass transfers study (incl. additives contamination)</td>
<td></td>
</tr>
<tr>
<td>ACTUAL PRODUCT</td>
<td>Sorption by plasticised PVC still to be done</td>
<td>MSU SoP (3) 1996</td>
<td>Some solid food has been tested</td>
</tr>
<tr>
<td>Future work: citrus or other flavour scalping (NB: this has limited importance as much impervious packaging exists for volatile compounds)</td>
<td>(Navel orange juice debittering by plasticised PVC films: contamination issue)</td>
<td>(cf. literature on PVC cling films)</td>
<td></td>
</tr>
<tr>
<td>Future work: other liquid foods, sewage treatment, recovering useful natural compounds (vitamins, colours, pharmaceuticals, etc.)</td>
<td>Future work: sorption still to be done for specific plastic formulations, on all solid food products with regard to current Regulations (safety, organoleptic quality)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) University of Western Sydney Hawkesbury, Australia
(2) Preliminary studies at the Ecole Nationale Supérieure de Biologie Appliquée à la Nutrition et à l’Alimentation, France (cf. Appendices)
(3) Michigan State University, School of Packaging, United States of America
APPENDIX A

SUMMARY OF PRELIMINARY STUDIES
(on the sorption of a typical citrus aroma compound in an orange juice model solution by plasticised PVC films)

Prior investigations (not included in the thesis) concerned the study of the sorption of d-limonene (C_{10}H_{16}, M.W. = 136.24 g/moL), the major flavour constituent of citrus essence, by plasticised PVC (Laboratory made): d-limonene was dissolved in water with 0.2 % Tween®80, a polyoxyethylenesorbitan monooleate ester authorised in the food industry for its emulsifying properties, and 2 % ethanol. The model solution was put in contact with 15, 30, 40 and 50 % w/w di-(2-ethylhexyl) phthalate (DEHP) plasticised PVC films. A rapid saturation of the available PVC-‘flavour sites’ was observed (within the first 2 hours) followed by a slower sorption. Optimum (maximum) sorption was observed for 30 % plasticiser content. A greater content did not improve significantly d-limonene sorption. The migration of plasticiser to the model solution was observed but not precisely quantified (>150 mg/L i.e. >21 mg/dm²). Additionally the octanol/water partition coefficient (LogP_{o/w}), the solubility parameters (δ), the contact angle measurements (θ), and the hydrophilic-lipophilic balance (HLB) were used in order to estimate the interactions between the molecules in contact; hence an oily micro-micellar structure was proposed, and checked by light-scattering analysis, to explain the transportation of d-limonene and the DEHP release.

This work is un-published, yet to be submitted (I.P. rights pending) for publication in Journal of Agriculture and Food Chemistry (Fayoux et al., 1996).
APPENDIX B

Acetyl Tributyl Citrate

The following information concerns Acetyl Tributyl Citrate (ATBC) characteristics and health regulations. It has been supplied by Croda Surfactants, Wetherill Park NSW, Australia.

"ATBC is a non-toxic plasticiser, ideally suited for food packaging applications. Polymers plasticised with ATBC display excellent heat stability, low temperature flexibility and low odour. It is recommended as an alternative to dioctyl phthalate (DOP) and dibutyl phthalate (DBP). ATBC is resistant to hydrolysis, does not support fungus growth in resins and gives improved light stability in cellulose acetate.

Because it is so outstanding as a food packaging plasticiser, it may be used with the most delicate foodstuffs without the risk of an odour being transmitted from the plasticiser to the food. ATBC is therefore suitable for dairy product cartons, soft drink bottle caps, preserved jar seals, meat packages and other applications which require odourless additives."
[ATBC] "is approved for direct food contact in the USA. It conforms to the requirements of the FDA with respect to food packaging. It is also permitted for specific indirect food contact applications in the USA in accordance with CFR21 (Code of Federal Regulation)."

"ATBC is approved for use in regenerated cellulose intended for food contact in the EEC. It is ‘not hazardous’ according to the current Dangerous Substances Directive (67/548/EEC)."

In Australia (Plastics materials for food contact use Part8: Miscellaneous additives), Australian Standard AS 2070.8-1992, North Sydney NSW, the maximum level of use of ATBC in PVC is 35%. For comparison, in PVC, restrictions apply for cetyl alcohol (14BD) at 3%, citric acid at 1%, BHA at 0.5%, BHT at 0.2%, DOA at 35% (max. total), DEHP (unsuitable for fatty food applications) at 40%, n-dodecanol at 2%, tocopherols at 0.1%.

ATBC’s LD50 (oral, rat) is less then 2000 mg/kg (‘non-toxic’).

NB: the overall migration limit given by the Plastics Directive 90/128/EEC is equal to 10 mg/dm² of plastic surface.
APPENDIX C

Limonin versus Limonoate

(in alkaline conditions, limonin becomes non-bitter: this is the principle of the USDA proposal for extracting limonin from Navel orange juice, cf. Chapter 2)

Limonin: Bitter  Limonoate A-ring lactone: Non Bitter
APPENDIX D

Limonin 17-O-β-glucopyranoside

It amounts to 180 ± 25 ppm in commercial orange juices, that is over 50 % of the total limonoid glucosides (about 320 ppm)(1). Limonin 17-O-β-D-glucopyranoside is also the major glucoside in flesh tissues of Navel orange (2).

Unlike limonin (aglycone), which is commonly extracted with solvents like dichloromethane (cf. Chapter 2), limonin glucosides are extracted (with methanol) from the remaining aqueous residue. Most of the 10 limonoid glucosides that have been isolated from grapefruit seeds (by Thin Layer Chromatography) appear to be present in orange juice. Orange juice contains the highest quantity of these glucosides in comparison to grapefruit (190 ± 36 ppm) or lemon (82 ± 9 ppm) juices (1).

Clearly the bulk of the limonoids present in citrus juices are glucosides. They accumulate in fruit tissues during late stages of growth and maturation as end products. The ratio of glucosides to aglycons in commercial orange juice reaches about 150:1 (1), whereas in the seeds the ratio is about 1:2 (3).

From such results and because limonin is extremely insoluble in water (2 to 3 ppm), limonin glucosides could strongly increase the potential limonin content in orange juice, and possibly increased further by the pectin, sugars and cellulose present in orange juice, so much that intensely bitter juices can be produced (up to 45 ppm of limonin in Navel orange juice)(4).


APPENDIX E - 1

Measuring Diffusion Coefficients:

Comparison of 3 Mathematical Simulations of Mass Transfers occurring in 3-Layer Laminates - THEORY

The three following approaches were obtained by solving the second Fick’s law

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

relative to mono-directional (x axis) mass transfers with constant diffusion coefficients (D) (C: concentration of the permeant; t: time), with three different theories, explained in Figure E-1.

Experimentally the ‘test’ film mass is monitored until equilibrium is reached between ‘supply’ and ‘test’ films, i.e. when the ‘test’ film absorbs no more material. The (unitless) partition coefficient \( K_p \) (also called relative solubility S of the permeant between the supply film and the test film) is measured before the diffusion coefficient D (characteristic parameter expressing the ease of the transfer through the plastic film) be evaluated (in m².s⁻¹) by the relevant equation.
Figure E-1 Concentration distributions v. time in the 3 ‘model’ compartments of the 3-layer laminate technique. Three hypotheses are tested by using: i) the “Constant supply” method, ii) the “Tan Qn” method, and iii) the “Impermeable surfaces” method.

\[ C_0 = C_\infty \]

\[ C_0 = C_\infty \text{ (test)} \]

\[ C_\infty \text{ (when } K_p = 1 \text{)} \]
Determination of D by the ‘constant supply’ method (*idem* Chapter 3)

It assumes a constant ‘absorbate’ (permeant) supply with uniform initial distribution: \( C = C_0 = c_{st} \) at \( x<–L/2 \) and \( x>L/2 \), \( C_0=0 \) when \( –L<2x<L; \) \( D = c_{st} \) and the ‘test’ film thickness \( L = c_{st} \). The solution to Fick’s second law is obtained by the use of the Laplace transform \(^1\) and is shown below:

\[
\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{L^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \int_0^\infty \text{erfc} \xi \frac{d\xi}{\sqrt{2\pi L}} \right\}
\]

where \( \text{erfc} \) is commonly referred to as the error-function complement (\( \text{erfc} = 1-\text{erf} \) \(^1\)).

Equation 1a can be easily reduced for small times to equation 1b:

\[
\frac{M_t}{M_\infty} \approx \frac{4}{\sqrt{\pi}} \left( \frac{Dt}{L^2} \right)^{1/2}
\]

with \( M_t \) the mass of absorbed material at time \( t \) (in seconds), \( M_\infty \) the equivalent at equilibrium, \( D \) in \( m^2.s^{-1} \), \( L \) in metre. This allows an average D value to be rapidly calculated from the initial gradient of the sorption curve when plotted against the square root of time. Of course the final concentration in the test film is \( C_\infty = C_0 \) (and \( K_p = 1 \)).

This approximation has been called in Chapter 3 the ‘square root I’ calculation method.
ii) Determination of D by the ‘Tan Qn’ method

By analogy to sorption in the liquid or vapour phase, the equation that follows may be used, if the external supply layer is considered as a stirred solution of limited volume. There the concentration of solute in the solution falls (but stays uniform) as solute enters the sheet at the same rate (boundary conditions) (see Figure E-1 ii)). Here D and the ‘test’ film thickness (L-2H) are also considered constant. With initial conditions such as C=C0 for –L<2x<–L+2H and L-2H<2x<L, C=0 for –L+2H<2x<L-2H, the solution to Fick’s second law (Laplace transform), is given by equation 2a:

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha (1+\alpha)}{1+\alpha + \alpha^2 q_n^2} \exp \left( -\frac{4 D q_n^2 t}{(L-2H)^2} \right)
\]  

(2a)

where the \(q_n\)s are the non-zero positive roots of equations (\(\tan q_n = -\alpha q_n\)), and \(\alpha = 2H/(L-2H)\), the ratio of the thickness of the ‘supply’ and ‘test’ films. If there is a partition factor \(K_p\) (or \(S\)) such that the concentration just within the ‘test’ film is \(K_p\) times that in the ‘supply’ film, then \(\alpha K_p = 2H/(L-2H)\). Here H is the thickness of the ‘supply’ film and L that of the entire stack (3 layers). The final concentration in the ‘test’ film is \(C_\infty = C_0 \alpha K_p/(1+\alpha)\). It is therefore \(C'_\infty = C_0 \alpha/(1+\alpha)\) in the supply film.

A ‘square root II’ approximation for small times may be estimated by using a formula proposed by Crank, and applying first-order asymptotic expansions:

\[
\frac{M_t}{M_\infty} \approx \frac{(1+\alpha)}{\alpha} \frac{4}{\sqrt{\pi}} \left( \frac{Dt}{(L-2H)^2} \right)^{1/2}
\]

(2b)
iii) Determination of D by the impermeable 3-layers method

The impermeable layers method has been used for calculations concerning recycled packaging films which sides had been coated by ‘clean’ plastic films. In this case, the difference with hypothesis ii) is that the ‘clean’ film is the central ‘test’ film, not the outside layer, and that the ‘solution is not stirred’ i.e. the concentration in the ‘supply’ film not only depends on time but on distance: it is not uniform (see Figure E-1 iii) for a representation of concentration distributions). Concentration decrease can be easily observed experimentally for multiple layer films.

Initial conditions are \( C = C_0 \) at \( 0 < x < H \) and \( L-H < x < L \), and \( C = 0 \) at \( H < x < L-H \), and with the relevant impermeable boundary conditions, the solution expressing the total amount of ‘absorbate’ \( M_t \) in the ‘test’ film at time \( t \) as a fraction of \( M_\infty \), the corresponding quantity after infinite time (equilibrium), is given by equation 3b. It was obtained by integrating the concentration equation (3a) (for the ‘test’ film) given by Crank:

\[
\frac{C}{C_\infty} = 1 + 2 \sum_{n=1}^{\infty} \frac{1}{(2\pi n \beta)} \sin(2\pi n \beta) \cos \left( \frac{2\pi nx}{L} \right) \exp \left( -\frac{(2\pi n)^2 D t}{L^2} \right) \quad (3a)
\]

\[
\frac{M_t}{M_\infty} = 1 - \frac{4}{\beta (1-2\beta)} \sum_{n=1}^{\infty} \frac{1}{(2\pi n)^2} \sin^2(2\pi n \beta) \exp \left( -\frac{(2\pi n)^2 D t}{L^2} \right) \quad (3b)
\]
with $\beta=H/L$ (unitless) the ratio of the thickness of the ‘supply’ film to that of the entire stack (3 layers) of films, $D$, assumed constant, in $m^2.s^{-1}$, and $H$ and $L$, constant, expressed in metre.

This method may need to include a partition coefficient $K_p$. It is given in the following mass balance: 

$$HC_0 = \left(\frac{L}{2}-H\right)C_\infty + \frac{HC_\infty}{K_p}.$$  

In this case $C'_\infty = C_\infty/K_p$ in the ‘supply’ film at equilibrium.

For comparison we have developed an approximation of equation 3b for small times (‘square root III’ method):

$$\frac{M_t}{M_\infty} \approx \frac{L}{H} \frac{1}{\sqrt{\pi}} \left[ \frac{Dt}{(L-2H)^2} \right]^{\frac{1}{2}}$$  \hspace{1cm} (3c)

where $(L-2H)$ is the thickness of the ‘test’ film.

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APPENDIX E - 2

Measuring Diffusion Coefficients:

Comparison of 3 Mathematical Simulations of Mass Transfers occurring in 3-Layer Laminates - EXPERIMENTAL RESULTS

The relevance and adaptability to the laminate technique of the 3 calculation methods explained in Appendix E - 1 can be discussed by comparing a few experimental results (in relation to Chapter 3): these are compiled in Table E.

In addition discrepancies between ‘complete models’ (equations 1a, 2a, 3b) and their approximations for short times (‘square root I, II, III’ methods) can be observed in Figure E-2:

One can easily see that ‘square root’ equations are good models for short times (yielding a 10% lower value), but two comments need to be made. Firstly the impermeable method leads to diffusion coefficients about twice the size as both other methods. Secondly the ‘square root II’ equation approximation is not as good as its ‘TanQn’ parent equation.
Nevertheless, none of these theoretical approaches can model with certainty what effectively goes on inside such plasticised PVC films: ‘real’ D values may not be constant but in any case, by choosing either calculation methods, ‘absorbates’ are ranked in the same order (see Table E). The ‘square root I’ method, although assuming more drastic approximations before solving Fick’s second law (eg. only one layer, the ‘test’ film, is taken into account !) ends up sufficient for a comparative study.

** A partition coefficient Kp=0.5 was chosen (close to experimental results): it was especially used for the ‘square root II’ and associated ‘tan Qn’ methods. When Kp was chosen closer to unity (common sorption studies), the estimation of D did not change much (Table E): for example, for 1-octanol D = 8.9 (±2%) with Kp=0.5, and D = 8.6 (±4%) (×10^-13 m^2.s^-1) with a Kp equal to unity.
Table E. Diffusion coefficients of ‘absorbates’: comparison of 3 calculation methods and their associated “square root” approximations.

<table>
<thead>
<tr>
<th>Absorbate Name (1)</th>
<th>Weight uptake (2)</th>
<th>Partition Coefficient (3)</th>
<th>Calculation methods (4)</th>
<th>Impermeable surfaces &amp; “square root III”**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>∆m g/100g of initial test film</td>
<td>Kp (unitless) (in “tan Q_n” method)</td>
<td>Constant supply &amp; “square root I”**</td>
<td>“tan Q_n” (5) &amp; “square root II”**</td>
</tr>
<tr>
<td>l-octanol</td>
<td>+2.2 (15*)</td>
<td>0.54</td>
<td>D= 15.6 (5%) 0.999^a</td>
<td>D= 13.1 (9%) 11.1 (11%) 0.998^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=13.7 (5%) 0.999^a</td>
<td>D*=8.9 (2%) 8.6 (4%) 0.999</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=32.8 (82%) 0.995^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=28.7 (57%) 0.999</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>+0.3 (120)</td>
<td>0.42</td>
<td>D=11.2 (7%) 0.996^a</td>
<td>D=9.9 (10%) 8.1 (13%) 0.996^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=9.5 (7%) 0.991^a</td>
<td>D*=6.8 (2%) 7.5 (9%) 0.991</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=27.1 (72%) 0.996^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=21.0 (61%) 0.991</td>
</tr>
<tr>
<td>Vanillin</td>
<td>+2.6 (18000)</td>
<td>0.54</td>
<td>D=1.0 (2%) 0.999^a</td>
<td>D=1.1 (26%) 0.8 (14%) 0.995</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=0.9 (2%) 0.996^a</td>
<td>D*=0.8 (5%) 0.6 (9%) 0.996</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=2.2 (32%) 0.981</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=1.7 (52%) 0.996^a</td>
</tr>
<tr>
<td>BHA</td>
<td>+2.7 (&gt;20000)</td>
<td>0.52</td>
<td>D=0.6 (2%) 0.999</td>
<td>D=0.5 (15%) 0.6 (7%) 0.999^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=0.6 (2%) 0.999</td>
<td>D*=0.4 (5%) 0.3 (9%) 0.999^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=1.1 (79%) 0.999</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=1.2 (52%) 0.999</td>
</tr>
<tr>
<td>BHT</td>
<td>+3.9 (&gt;20000)</td>
<td>0.54</td>
<td>D=0.5 (56%) 0.937</td>
<td>D=0.3 (41%) 0.3 (33%) 0.931</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=1.3 (2%) 0.946</td>
<td>D*=0.8 (5%) 0.4 (39%) 0.946^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=0.8 (28%) 0.929</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=2.5 (52%) 0.954^a</td>
</tr>
<tr>
<td>Anisole</td>
<td>+1.1 (15*)</td>
<td>0.48</td>
<td>D=8.7 (5%) 0.999^a</td>
<td>D=7.3 (8%) 6.1 (11%) 0.999^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D*=8.2 (5%) 0.958^a</td>
<td>D*=5.4 (2%) 3.7 (7%) 0.999^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D=15.4 (77%) 0.997^a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D*=16.2 (56%) 0.999</td>
</tr>
</tbody>
</table>

(1) in 40% w/w plasticised PVC supply films (ATBC40)
(2) at equilibrium: between parentheses is the time in minutes when ∆m was recorded; * indicates a peak sorption due to anomalous kinetics; error was less than 5%
(3) Kp=[Absorbate]_{test film}/[Absorbate]_{supply film} at equilibrium with concentrations in mol/L of test film volume: see Figure 3.1.(e) for Kp calculation
(4) D is in 10^{-13} m^2.s^{-1}; between parentheses are an indication of estimation errors; they are believed to be mainly due to thickness measurement errors; underlined is the correlation coefficient obtained between the experimental plots and the model (“a” is for automatic computerised fitting, else fitting was done by hand by trying various diffusion coefficient values to outline the kinetics by ±5% ∆m); ** indicates that D (then written D*) was calculated thanks to the associated “square root” method (I, II, or III); for ‘complete calculations’ using infinite sums, n=10 in equations 1a and 3b, n=4 in equation 2a, all allowing a minimum of 95% convergence
(5) between brackets are indicated diffusion coefficient values when Kp=1 (when the ‘absorbate’ concentrations would be equal in all three compartments – supply, test, supply – at equilibrium)
### APPENDIX F

**Solubility parameters of Chapter 5’s compounds (25 °C), following table 5.2 ‘SPs’ order**

<table>
<thead>
<tr>
<th>Absorbate name</th>
<th>$\delta_{\text{Hydrogen}}$</th>
<th>$\Delta\delta_{\text{H-d}} = \delta_{\text{Hydrogen}} - \delta_{\text{dispersive}}$</th>
<th>$\Delta\delta_{\text{(PVC-absorbate)}}$ or $\Delta\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quercetin</td>
<td>18.7</td>
<td>3.8</td>
<td>12.6</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>28.3</td>
<td>18.1</td>
<td>22.6</td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td>17.7</td>
<td>1.7</td>
<td>11.7</td>
</tr>
<tr>
<td>Sucrose *</td>
<td>29.9</td>
<td>18.2</td>
<td>23.9</td>
</tr>
<tr>
<td>Butanol</td>
<td>18.5</td>
<td>4.1</td>
<td>11.7</td>
</tr>
<tr>
<td>Rotenone</td>
<td>11.1</td>
<td>-6.4</td>
<td>4.6</td>
</tr>
<tr>
<td>ATBC30/40/30</td>
<td>7.2</td>
<td>-8.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.7</td>
<td>-11.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>11.2</td>
<td>-6.2</td>
<td>5.6</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>7.5</td>
<td>-12.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Citric acid</td>
<td>17.0</td>
<td>5.3</td>
<td>10.8</td>
</tr>
<tr>
<td>Phenol phthalein</td>
<td>9.8</td>
<td>-8.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Xylenes</td>
<td>7.4</td>
<td>-11.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Hexanol</td>
<td>15.8</td>
<td>1.1</td>
<td>9.2</td>
</tr>
<tr>
<td>β-Sitosterol</td>
<td>0.0</td>
<td>-16.7</td>
<td>8.5</td>
</tr>
<tr>
<td>Alizarin</td>
<td>15.4</td>
<td>-0.4</td>
<td>9.3</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>29.8</td>
<td>18.1</td>
<td>23.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>8.7</td>
<td>-10.8</td>
<td>5.1</td>
</tr>
<tr>
<td>d-Limonene</td>
<td>5.6</td>
<td>-11.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Octadecanol</td>
<td>9.8</td>
<td>-6.1</td>
<td>6.2</td>
</tr>
<tr>
<td>β-Carotene</td>
<td>0.0</td>
<td>-15.5</td>
<td>8.0</td>
</tr>
<tr>
<td>p-Chlorotoluene</td>
<td>7.2</td>
<td>-12.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Styrene</td>
<td>6.9</td>
<td>-11.8</td>
<td>3.9</td>
</tr>
<tr>
<td>Anisole</td>
<td>9.7</td>
<td>-8.7</td>
<td>4.3</td>
</tr>
<tr>
<td>p-Hydroxybenzaldehyde</td>
<td>15.2</td>
<td>-1.9</td>
<td>8.9</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>11.3</td>
<td>-4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Octanol</td>
<td>14.2</td>
<td>-0.6</td>
<td>8.1</td>
</tr>
<tr>
<td>Vanillin</td>
<td>15.4</td>
<td>-1.0</td>
<td>8.8</td>
</tr>
<tr>
<td>Decanol</td>
<td>13.2</td>
<td>-1.8</td>
<td>7.5</td>
</tr>
<tr>
<td>BHA</td>
<td>9.5</td>
<td>-7.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Dodecanol</td>
<td>12.4</td>
<td>-2.6</td>
<td>7.2</td>
</tr>
<tr>
<td>p-diChlorobenzene</td>
<td>6.7</td>
<td>-13.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Phenol</td>
<td>12.3</td>
<td>-5.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>15.3</td>
<td>-1.7</td>
<td>8.9</td>
</tr>
<tr>
<td>BHT</td>
<td>6.8</td>
<td>-10.2</td>
<td>4.8</td>
</tr>
<tr>
<td>Geraniol</td>
<td>12.4</td>
<td>-2.6</td>
<td>5.9</td>
</tr>
<tr>
<td>Coumarin</td>
<td>11.9</td>
<td>-5.1</td>
<td>5.3</td>
</tr>
<tr>
<td>3-Phenylphenol</td>
<td>6.6</td>
<td>-13.1</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* Sucrose solubility parameters were obtained as average of glucose and saccharose solubility parameters.
APPENDIX G

A Personal Representation of the Molecular Interactions Taking Place when a Plastisol Film Enters in Contact with Orange Juice (OJ) Constituents:

Laminate Modelling (with rotenone)  

versus

Actual Debittering (with limonin)

Plasticised PVC laminates are pictured next page: this is a personal representation of contacting molecules.

In the upper part (A), rotenone and d-limonene in ATBC plasticised PVC represent a model of bitter OJ.

In the lower part (B), limonin is shown in a ‘water/d-limonene’ plasticised polymer (‘gel’), made of cellulose and pectin, to represent actual OJ (*).
based on the following references: Chandler, B.V., 1970, Some solubility relationships of limonin and their importance in orange juice bitterness, Proceedings of Int. Fed. Fruit Juice Prod., Palermo, Italy, 41-52 (re. limonin's increased water solubility with 12 % sucrose and 0.1 % pectin); Fong, C.H., Hasegawa, S., Herman, Z., and Ou, P., 1989, Limonoid glucosides in commercial citrus juices, J. Food Sci., 54(6), 1505-6 (re. the possibility of solubilisation of limonin aglycone by its hydrophilic glucoside, respectively present in OJ in the 1:150 ratio); Guérin, R., and Léard, M., 1982, Infrared spectra of furan adsorbed on some alkali halides. Adsorption potential calculations, J. Phys. Chem., 86, 3338-45 (re. the most favourable adsorption sites for furan and 'π-electrons' [ring] molecules on polar media - such as PVC -)(\textsuperscript{2}).

This representation of an ATBC40 film contacting an OJ does not show neither ATBC back migration (except via serpentine arrow), nor citric acid (re. pH), nor amphiphilic molecules (limonin-17-O-β-D-glucopyranoside (\textsuperscript{1}), lecithins, β-sitosterol, acids, alcohols, aldehydes, etc), which hold in solution, for example the OJ essential oils, like terpenes, inside micro-micelles, nor β-carotene, etc. Nevertheless d-limonene, as the major constituent of citrus oils, is displayed close to a portion of molecule of pectin which degree of methylation (**), unlike cellulose, should encourage such adsorption; it is also shown close to a hydrophobic element of the limonin molecule, as 'solubilising agent'. The adsorptions of rotenone and limonin on PVC have been represented through their furan or phenyl moieties, as they exhibit similar interactions (\textsuperscript{2}).

\* based on the following references: Chandler, B.V., 1970, Some solubility relationships of limonin and their importance in orange juice bitterness, Proceedings of Int. Fed. Fruit Juice Prod., Palermo, Italy, 41-52 (re. limonin's increased water solubility with 12 % sucrose and 0.1 % pectin); Fong, C.H., Hasegawa, S., Herman, Z., and Ou, P., 1989, Limonoid glucosides in commercial citrus juices, J. Food Sci., 54(6), 1505-6 (re. the possibility of solubilisation of limonin aglycone by its hydrophilic glucoside, respectively present in OJ in the 1:150 ratio); Guérin, R., and Léard, M., 1982, Infrared spectra of furan adsorbed on some alkali halides. Adsorption potential calculations, J. Phys. Chem., 86, 3338-45 (re. the most favourable adsorption sites for furan and 'π-electrons' [ring] molecules on polar media - such as PVC -)(\textsuperscript{2}).

\* this is consistent with the extensive use of Cellulose Acetate or Cellulose Acetate Butyrate as debittering agents (cf. eg. Chandler and Johnson references at the end of Chapter 2).
APPENDIX H

Latest Relevant Literature Search and Comments


  *[another use of lipid membranes by Prof. Kiyoshi Toko research team.]*


  *[an excellent relevant paper comparable to Cava et al.’s use of ATR-FTIR to measure D in relation with multiple penetrants’ interactions - amyl acetate and limonene -: comparison with gravimetry is also performed. Again only volatiles can be studied.]*


  *http://www.chipsbooks.com/citrusli.htm.*

  [this novel and heavily mathematical work consisted in modelling water transport after obtaining time-dependent water concentration profiles in different solid matrices; it takes into account the shrinkage of the gel before solving the Diffusivity equation. NB: Concentration profiles were mentioned in the future work section of this Thesis in order to better model our sorption curves.]


  [another debittering trial using immobilized bacteria on polyurethane foam pads; 85% conversion was obtained after 200 hours.]


  [a very relevant paper to this Thesis, especially re. the future works: indeed an attempt to apply the technique in transmission mode, cf. Cotugno et al., was made to determine the transport coefficients of pure...]

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and mixed citric aroma compounds during desorption from polyethylene, and compared to a conventional gravimetric method. Sorbants were d/l-limonene, α-pinene, citral and linalool. The major issue was the concentration dependency of the absorbance coefficients: frequency shifts and change in band shape could result in a deficient correlation with gravimetry. On the other hand, a significant advantage of the FT-IR technique is the possibility of studying mixtures of aroma compounds and their interactions, which were shown to affect strongly the value of D, especially because d-limonene was plasticising the polymer. Nevertheless this technique requires desorption mode, which is usually described by Fick’s laws, whereas sorption often leads to anomalous sigmoidal shaped curves. The challenge is that FT-IR gathers both lack of detection and potentially overlapping of bands, making identification or analysis difficult, compared to GC. Its use with plastisols and limonin may not be possible then.


[FTIR spectroscopy in transmission mode has been developed to monitor sorption-desorption behaviour of small molecules in polymer films: different kinds of interactions can be differentiated such as the plasticising effect of water molecules and their evolution as a function of the penetrant concentration. H-bonding and dimers formation can be 'seen' on the spectra, and weak interactions are shown to play a stronger role as saturation of the polymer gets closer. Microgravimetric sorption curves are nearly same. It would be interesting to test the feasibility of such a technique on ‘our’ plastisols.]


concentrated solutions used as food flavourings, *Food Addit. Contam.*, 11, 1040-1045.


  *Dynamic thermal mechanical analysis - DTMA - and time domain nuclear magnetic resonance - TD-NMR - were used to study plasticisation and antiplasticisation.*


  *This review publication is similar to that presented in Chapter 1b.*


  *d-limonene’s efficacy in preclinical models of breast and colon cancers was investigated as dietary intake and potential protective effect in relation to skin SCC.*


[a totally automated electro-microbalance was used to determine \( S \) and \( D \) and theoretical sorption curves were obtained and commented upon re. deviation from Henry's law; this work only concerns vapour phase sorption and recalls that the use of simplified expressions of \( D \) may result in large errors in \( D \).]


['new' styrene / divinyl-benzene resin beads equivalent to XAD-16 cf. Chapter 2: it is a macroporous highly crosslinked polymer, with a surface area of 800 m\(^2\)/g, a pore volume of 1200 mm\(^3\)/g and pore size 50-100 nm.]


  [this important discovery may compete in the long run with polymer-debittering techniques since it may be possible to hinder the delayed formation of bitter limonoid aglycones and enhance that of tasteless limonin glucosides. Enzymatic glucosylation could be accessed through the creation of transgenic Citrus free from limonoid bitterness as well as for increasing specific limonoid glucoside molecules having anticancer properties.]


  [XAD-16 resins were used, some non-bitter flavonoids, vitamin C, and phenolics were also removed, and the colour of the debittered concentrate could be described as slightly paler than that of the control.]


[the liquid membrane was made of porous hydrophobic PTFE filled with n-undecane and di-n-hexyl ether and allowed the extraction of vanillin from an aqueous phase: the principle is similar to the current USDA project for debittering though the latter do not use porous but 'organosol' membranes like in this Thesis, cf. USDA sample proposal.]


[plasticisation was observed via $T_g$ and tensile strengths measurements.]


  [This reference is relevant since lignin was suggested to be a good debittering agent when testing KRAFT paper in Chapter 2; however d-limonene was not studied...]


  [The role of pulp can be determinant as various substituted cellulose polymers have proved successful in debittering citrus juices, cf. Chapter 2]


  [A more complex computer model has been developed in order to take into account limonene degradation rate in a model food system, after limonene]
has been sorbed and subsequently released back into the food, but same Fick's-based equations apply; the concept of regulating food aroma by packaging polymers is similar to that of the use of 'pre-saturated packagings' as it is mentioned at the end of the Thesis, Future work, page xiv line 16.]


[another use of lipid membranes by another team than Toko's.]


[the FTIR method was used cf. Cotugno et al.]


[Thesis Chapters 1a & 1b referenced.]


[BHA and BHT were leaching from PVC films into the oil during storage but oxidation seemed to depend more on oxygen permeability and vitamin E natural occurrence in the oil: polymer plasticisation was not investigated.]


[This novel and singular work shows that a PVC lipid/polymer membrane can be used to quantify taste interactions such as the suppression effect which occurs between bitterness and sweetness; various plasticisers were used such as n-decyl alcohol, oleic acid, dioctyl phosphate and trioctyl methyl ammonium chloride mixtures. Other polymers than PVC are also used as matrix to optimise the sensor selectivity.]


[Polyethylene ‘pouches’ were used, and filled with CO2. The pouch technique was already used in Chapter 2 in the liquid phase.]

• USDA (United States Department of Agriculture) sample proposal: Membrane-based process for debittering citrus juice, 2004, Robert C. Byrd National Technology Transfer Center (NTTC)1 & Small Business Innovation Research at Dakota State University (SBIR-DSU)2,

1: [http://www.nttc.edu/resources/funding/doag/01doag/usda_sample2.asp](http://www.nttc.edu/resources/funding/doag/01doag/usda_sample2.asp)
cf. Dr Melvin Ustad mel.ustad@dsu.edu.

This project has been going on for a long time and never been funded in Florida where it originates from; it is now still looking for funding through two Research Centers/Institutes and has been mentioned in this Thesis where PVC organosols end up cheaper and do not involve any pH differentials. Membranes used could be made of polytetrafluoroethylene, microporous polyethylene, polysulfone or polivinylidene difluoride, and candidate sorbed-liquids include high-molecular-weight even-numbered straight-chain alcohols. Interestingly this Thesis' project is not mentioned in their proposal's Related R&D section...!


  [san extensive work to improve laboratory analytical methods; for instance, headspace GC is discussed for orange juice off-flavour analysis.]