A STUDY OF OSMOTIC DISTILLATION IN HOLLOW FIBRE MODULE

A thesis submitted as fulfilment of the requirements for the Degree of Master of Science (Honours)

By

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JULY, 2002
PLEASE NOTE

The greatest amount of care has been taken while scanning this thesis,

and the best possible result has been obtained.
DECLARATION

It is to certify that the work presented in this thesis is original. It was completed at the Centre for Advanced Food Research, University of Western Sydney – Hawkesbury campus, Australia. Acknowledgements for any help and all other sources used in this thesis have been made.

I also certify that this work has not been submitted to any other University or Institution for any other degree or qualification.

Anh Viet Bui
July, 2002
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ABSTRACT

Osmotic distillation is a process of removing water from an aqueous solution, driven by water vapour pressure gradient across a hydrophobic membrane. The process occurs at or below ambient temperature and under atmospheric pressure.

This research project investigates the osmotic distillation process in hollow fibre modules using hollow fibres PP375, PV375 and PV660 supplied by Memcor Australia (South Windsor, New South Wales, Australia).

Laboratory and pilot scale osmotic distillation systems using hollow fibre modules were designed, constructed, and successfully operated at the University of Western Sydney, Hawkesbury campus, Australia.

Operating conditions such as temperature, feed concentration and brine cross flow velocity, but not the feed cross flow velocity, were found to have significant effect on the flux rate, which ranged from 1.67 to 4.73kg.m\(^{-2}\).h\(^{-1}\) for PV375 and PP375, and 1.00 to 2.87kg.m\(^{-2}\).h\(^{-1}\) for PV660.

Models for heat and mass transfers were used to study the polarisation phenomena in osmotic distillation. Temperature and concentration profiles at the membrane surfaces due to polarisation were quantified. Temperature and concentration polarisations were found to contribute to flux decrease of up to 7.0±0.13% and 10.6±1.04% respectively for module PV375; and 7.9±0.11% and 8.7±0.50% respectively for module PV660.

Scholfield and Ordinary Diffusion models were validated as the governing mechanism of water vapour transport across the hydrophobic membrane.

Mass transfer models for flux prediction based on the bulk conditions were developed and validated. Models for water activity and viscosity of aqueous glucose and calcium chloride solutions were also developed and validated in this work.

Pilot osmotic distillation with apple juice and grape juice up to 48°Brix and 65°Brix respectively resulted in consistent quality of the products at average flux of 1.58 to 1.88kg.m\(^{-2}\).h\(^{-1}\).
# NOMENCLATURES

1. **Upper case nomenclatures**

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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>A</td>
<td>Effective membrane area</td>
<td>( \text{m}^2 )</td>
</tr>
<tr>
<td>( A_F )</td>
<td>Cross-section flow area on the feed side</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( A_B )</td>
<td>Cross-section flow area on the brine side</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>C</td>
<td>Solute concentration of a solution</td>
<td>( % )</td>
</tr>
<tr>
<td>( C_{f,b} )</td>
<td>Feed concentration in the bulk</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( C_{f,m} )</td>
<td>Feed concentration at the membrane surface</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( C_{s,b} )</td>
<td>Brine concentration in the bulk</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( C_{s,m} )</td>
<td>Brine concentration at the membrane surface</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( \Delta C_{f,m} = C_{f,m} - C_{f,b} )</td>
<td></td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( \Delta C_{s,m} = C_{s,m} - C_{s,b} )</td>
<td></td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( D_{i,w} )</td>
<td>Diffusion coefficient of solute (i) in water</td>
<td>( \text{m}^2 \cdot \text{s}^{-1} )</td>
</tr>
<tr>
<td>( D_i )</td>
<td>Internal diameter of the shell of hollow fibre module</td>
<td>( \text{m} )</td>
</tr>
<tr>
<td>( G^E )</td>
<td>Excess Gibbs free energy of an aqueous solution</td>
<td>( \text{J} )</td>
</tr>
<tr>
<td>( H^E )</td>
<td>Excess enthalpy of an aqueous solution</td>
<td>( \text{---} )</td>
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<tr>
<td>( H )</td>
<td>Global heat transfer coefficient</td>
<td>( \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1} )</td>
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<td>( \Delta H_w )</td>
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<td>Mass transfer coefficient on the feed side on water vapour basis</td>
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<td>( K_s )</td>
<td>Mass transfer coefficient on the brine side on water vapour basis</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( K_n )</td>
<td>Knudsen number defined in equation (2-11)</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( K_1 )</td>
<td>Membrane parameter defined as ( K_1 = (\varepsilon / \tau) )</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( K_2 )</td>
<td>Constant in Norrish equation defined in equation (4-6)</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( L )</td>
<td>Effective length of heat and mass transfer</td>
<td>( \text{m} )</td>
</tr>
<tr>
<td>( L_T )</td>
<td>Total length of module</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( L_E )</td>
<td>Effective length of module</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( L_{HR} )</td>
<td>Length of velocity profile</td>
<td>( \text{---} )</td>
</tr>
<tr>
<td>( L_{CR} )</td>
<td>Length of concentration profile</td>
<td>( \text{---} )</td>
</tr>
</tbody>
</table>
### Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Molecular weight</td>
<td>[kg/kg mol]</td>
</tr>
<tr>
<td>P</td>
<td>Water vapour pressure of solution (in general)</td>
<td>[Pa]</td>
</tr>
<tr>
<td>( P_0 )</td>
<td>Water vapour pressure of pure water</td>
<td>[---]</td>
</tr>
<tr>
<td>( P_{f,m} )</td>
<td>Water vapour pressure at the membrane surface on the feed side</td>
<td>[---]</td>
</tr>
<tr>
<td>( P_{f,b} )</td>
<td>Water vapour pressure in the bulk on the feed side</td>
<td>[---]</td>
</tr>
<tr>
<td>( P_{s,m} )</td>
<td>Water vapour pressure at the membrane surface on the brine side</td>
<td>[---]</td>
</tr>
<tr>
<td>( P_{s,b} )</td>
<td>Water vapour pressure in the bulk on the brine side</td>
<td>[---]</td>
</tr>
<tr>
<td>( P_{bp} )</td>
<td>Bubble point of the fibres</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>Hydrodynamic pressure drop</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P_b )</td>
<td>Bulk water vapour pressure difference</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P_m )</td>
<td>Water vapour pressure difference across the membrane surfaces</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P_{m,T} )</td>
<td>Water vapour pressure difference across the membrane surfaces assessed at bulk temperature</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P_{m,C} )</td>
<td>Water vapour pressure difference across the membrane surfaces assessed at bulk concentrations</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta P_{m}^{initial} )</td>
<td>Hypothesised initial water vapour pressure difference to trigger mass transfer.</td>
<td>[---]</td>
</tr>
<tr>
<td>Q</td>
<td>Total heat transferred across the membrane</td>
<td>[J]</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>[J.kg mol(^{-1}).K(^{-1})]</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>Coefficient of determination (also ( r^2 ))</td>
<td></td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity of air</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>[K] or [°C]</td>
</tr>
<tr>
<td>( T_{f,b} )</td>
<td>Feed temperature in the bulk,</td>
<td>[---]</td>
</tr>
<tr>
<td>( T_{f,m} )</td>
<td>Feed temperature at the membrane surface</td>
<td>[---]</td>
</tr>
<tr>
<td>( T_{b} )</td>
<td>Brine temperature in the bulk</td>
<td>[---]</td>
</tr>
<tr>
<td>( T_{s,m} )</td>
<td>Feed temperature at the membrane surface</td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta T_b = T_{s,b} - T_{f,b} )</td>
<td></td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta T_m = T_{s,m} - T_{f,m} )</td>
<td></td>
<td>[---]</td>
</tr>
<tr>
<td>( \Delta T_{f,m} = T_{f,b} - T_{f,m} )</td>
<td></td>
<td>[---]</td>
</tr>
</tbody>
</table>
\[ \Delta T_{i,m} = T_{x,m} - T_{i,b} \]

\( V_i \)  Partial molar volume of solvent  \( [m^3/kg \text{ mol}] \)

\( V_i \)  Flow rate if liquid stream (i=f or s)  \( [m^3/s] \)

\( X \)  Mole fraction of a component in solution

2. Lower case nomenclature

\( a_w \)  Water activity of a solution

\( c_p \)  Specific heat of a solution  \( [J/kg \cdot K] \)

\( d_i \)  Internal diameter of fibres  \( [m] \)

\( d_o \)  External diameter of fibres  \( [---] \)

\( d_p \)  Nominal pore diameter  \( [---] \)

\( d_h \)  Characteristic diameter of a channel  \( [---] \)

\( g_i^e \)  Molar Gibbs free energy  \( [J/kg \text{ mol}^{-1}] \)

\( h \)  Heat transfer coefficient  \( [W/m^2 \cdot K] \)

\( h_f \)  Heat transfer coefficient at the feed side  \( [---] \)

\( h_t \)  Heat transfer coefficient at the brine side  \( [---] \)

\( h_m \)  Heat transfer coefficient of the membrane  \( [---] \)

\( h^E \)  Molar excess enthalpy  \( [J/kg \text{ mol}^{-1}] \)

\( k \)  Thermal conductivity  \( [W/m \cdot K] \)

\( k_{air} \)  Thermal conductivity of air  \( [---] \)

\( k_m \)  Thermal conductivity of the membrane  \( [---] \)

\( k_p \)  Thermal conductivity of the solid polymer (PVDF)  \( [---] \)

\( k_f \)  Mass transfer coefficient on the feed side on concentration basis  \( [m/s] \)

\( k_s \)  Mass transfer coefficient on the brine side on concentration basis  \( [---] \)

\( m \)  Solute molarity

\( n \)  number of fibres in a module

\( r_i \)  Internal diameter of fibre  \( [m] \)

\( r_o \)  External diameter of fibre  \( [---] \)

\( r_p \)  Pore radius  \( [---] \)
Nomenclature

\( \nu_f \) \hspace{1cm} \text{Cross flow velocity on the feed side} \hspace{1cm} [\text{m.s}^{-1}]

\( \nu_s \) \hspace{1cm} \text{Cross flow velocity on the brine side} \hspace{1cm} [\text{---}]

\( x \) \hspace{1cm} \text{Mole fraction of a component in solution}

\textbf{Greek symbols}

\( \alpha \) \hspace{1cm} \text{Confidence level in statistic}

\( \alpha, \beta \) \hspace{1cm} \text{Exponents in equation (5-5)}

\( \delta \) \hspace{1cm} \text{Membrane thickness} \hspace{1cm} [\text{m}]

\( \delta_i \) \hspace{1cm} \text{Boundary layer thickness on (i) side.} \hspace{1cm} [\text{---}]

\( \varepsilon \) \hspace{1cm} \text{Membrane porosity}

\( \gamma \) \hspace{1cm} \text{Activity coefficient}

\( \mu_i \) \hspace{1cm} \text{Fluid viscosity} \hspace{1cm} [\text{Pa.s}]

\( \rho_i \) \hspace{1cm} \text{Fluid density} \hspace{1cm} [\text{kg.m}^{-3}]

\( \phi \) \hspace{1cm} \text{Packing density}

\( \Pi \) \hspace{1cm} \text{Osmotic pressure} \hspace{1cm} [\text{Pa}]

\( \tau \) \hspace{1cm} \text{Membrane tortuosity}

\textbf{3. The subscripts}

\( f \) \hspace{1cm} \text{For feed solution}

\( s \) \hspace{1cm} \text{For brine solution}

\( b \) \hspace{1cm} \text{In the bulk}

\( m \) \hspace{1cm} \text{At the membrane surface}

\( w \) \hspace{1cm} \text{For water, water vapour}

\textbf{4. The dimensionless numbers}

\( Sh \) \hspace{1cm} \text{Sherwood number}

\( Sh^{"} \) \hspace{1cm} \text{Sherwood number defined on water vapour basis}

\( Re \) \hspace{1cm} \text{Reynolds number}

\( Sc \) \hspace{1cm} \text{Schmidt number}

\( Nu \) \hspace{1cm} \text{Nusselt number}

\( Pr \) \hspace{1cm} \text{Prandtl number}

\( Gz \) \hspace{1cm} \text{Graetz number}

\( Gzm \) \hspace{1cm} \text{Defined in (5-12)}

\textit{Note: [---] indicates the same dimension as that of the previous one.}
CHAPTER 2: THE OSMOTIC DISTILLATION PROCESS - A LITERATURE REVIEW

2.1. INTRODUCTION

In recent years, a number of novel separation techniques at molecular level for clarification and concentration of solutions and suspensions have been developed. Amongst them, new membrane processes have been investigated and applied in the food industry. They include direct osmosis, membrane distillation and osmotic distillation.

In direct osmosis, water is removed from an aqueous solution with lower osmotic pressure to an aqueous solution with higher osmotic pressure in liquid state through a semi-permeable membrane due to osmosis (Wong & Winger, 1999).

Osmotic distillation (OD) or osmotic evaporation is a process for separating water from an aqueous solution. In the OD process, the solution to be concentrated (the feed) and the stripping solution (the brine) are isothermal and pumped over opposite sides of a microporous hydrophobic membrane in either co-current or counter-current flow as shown on figure 2-1. It occurs at or below ambient temperature and under atmospheric pressure.

![Diagram of Osmotic Distillation](image)

**Fig.2-1:** The schematic principle of osmotic distillation
The process involves water evaporation from the feed, water vapour diffusion through the membrane, water vapour condensation on the other side of the membrane and being swept away by the brine solution.

The *thermodynamic driving force* in the OD process is the *water vapour pressure difference* across the membrane, which is produced by the difference in *osmotic pressure* or *chemical potential* of the two solutions on both sides of the membrane due to the nature of their compositions and concentrations (Johnson, Valks & Lefebvre, 1989; Hogan et al, 1998).

*Membrane distillation* is similar to osmotic distillation. However, the driving force is created by heating up the feed solution rather than by the compositions and concentrations of the two streams (Scholfield, Fane & Fell, 1987).

As OD is operated at or below ambient temperature, it is able to reduce or eliminate the heat damage to flavour, colour and aromas of concentrated products, which are always associated with conventional evaporation process. In addition, the OD process has been reported to be able to concentrate liquid food up to 75-80%TS which is unachievable by freeze concentration (FC) and reverse osmosis (RO) (Johnson, Valks & Lefebvre, 1989; Nguyen, 2000), while an OD system does not require as high investment as FC and RO due to its simplicity. Thus, OD has been developed for concentrating liquid foods and pharmaceutical products to high concentration where high quality of concentrated products is required (Hogan et al, 1998).

The proposed arrangement of an OD system for the concentration of liquid foods is illustrated on figure 2-2. The dilute feed is pumped and circulated through the OD unit until a desired concentration is achieved while the brine is pumped on the other side of the membrane, and reconcentrated in the evaporator. In continuous operation, a series of OD units may be used to achieve the desired concentration.
2.2. OSMOTIC DISTILLATION THEORY

2.2.1. The driving force of OD process

As mentioned above, the thermodynamic driving force in osmotic distillation is the water vapour pressure difference across the membrane. As a rough estimation, it can be derived from the water vapour pressures of the two solutions at bulk condition as given in (2-1).

\[ \Delta P_b = P_{f,b} - P_{s,b} \]  

(2-1)

\( \Delta P_b \)  Bulk water pressure difference or bulk OD driving force

\( P_{f,b} \)  Water vapour pressure in the bulk on the feed side

\( P_{s,b} \)  Water vapour pressure in the bulk on the brine side

However, as in many membrane processes, polarisation phenomena also occur in OD (Hogan et al, 1998; Johnson, Valks & Lefebvre, 1989); hence the real driving force that actually governs the OD process is the water vapour
pressure difference across the membrane surfaces. Thus the real OD driving force is defined as:

$$\Delta P_m = P_{f,m} - P_{s,m}$$  \hspace{1cm} (2-2)$$

- $P_{f,m}$ - Water vapour pressure at the membrane surface on the feed side
- $P_{s,m}$ - Water vapour pressure at the membrane surface on the brine side

Details of the polarisation phenomena will be discussed later in section (2.2.3).

In general, the water vapour pressure of an aqueous solution depends on the solution composition and temperature, which is directly related to the osmotic pressure of that aqueous solution. According to Cheryan (1998), the osmotic pressure of a solution can be defined as:

$$\Pi = \frac{RT}{V_i} \cdot \ln \frac{P_0}{P}$$  \hspace{1cm} (2-3)$$

- $\Pi$ - osmotic pressure, \hspace{1cm} Pa;
- $T$ - temperature, \hspace{1cm} K;
- $R$ - universal gas constant, \hspace{1cm} J.kg mol\(^{-1}\).K\(^{-1}\);
- $V_i$ - partial molar volume of solvent \hspace{0.5cm} m\(^3\).kg mol\(^{-1}\).
- $P_0$, $P$ - vapour pressure of pure solvent, and solution, Pa; as in the case the solvent is water $P_0$, $P$ are water vapour pressure of pure water and of solution respectively.

Van’t Hoff (in Cheryan, 1998) has developed a correlation for osmotic pressure, which later was further developed by using the formula (2-3). The osmotic pressure is then defined as:

$$\Pi = n_2 RT = i \cdot \frac{C}{M} RT$$  \hspace{1cm} (2-4)$$

- $n_2$ - molar concentration of the solute \hspace{1cm} kg mol.m\(^{-3}\);
- $C$ - concentration of solute in solution \hspace{1cm} kg.m\(^{-3}\).
M-molecular weight of solute \( \text{kg.kg mol}^{-1} \); i-number of ions for ionised solutes (e.g., \( i=2 \) for NaCl; \( i=1 \) for sugars);

The vapour pressure of pure water is a function of temperature and can be determined by Antoine equation given in (2-5) (Fernández-Pineda, Izquierdo-Gil & Garcia-Payo, 2002).

\[
\ln(P_0) = 23.5377 - \frac{4016.3632}{T - 38.6339} \quad \text{{[Pa]}} \quad (2-5)
\]

Formula (2-3), (2-4) and (2-5) are the basic tools for calculating the water vapour pressure of the two solutions involved in the OD process once their osmotic pressures are known or measured by an osmometer.

Osmotic pressure or water vapour pressure of an aqueous solution can also be determined via its water activity, which is defined as:

\[
a_w = \frac{P}{P_0} \quad (2-6)
\]

Water activity of a solution, on the other hand, can be determined by different methods based on the vapour-liquid equilibrium principle as described in Labuza et al (1976), or based on freezing point depression and/or boiling elevation (Robison & Stokes, 1959; Fontan & Chirife, 1981; Lerici, Piva & Rosa, 1983).

There are also a number of models for water activity prediction of solutions (Leiras, Alzamora & Chirife, 1990; Chirife, Favetto & Fontan, 1982; Bell & Labuza, 2000). These models are useful for water activity determination. However, most of them are confined to determination of water activity at temperature of 25°C. Therefore, further development of models for water activity prediction for a wider temperature range is still needed.

Thus, once the solution composition and temperature are known, models for water activity prediction available in the literature may be applied, and/or using water activity meters, to determined the water vapour pressure of that solution. Then the bulk driving force in the OD process \( \Delta P_b \) can be identified.
For the real driving force $\Delta P_w$, it will require the knowledge of the polarisation layers at the membrane surfaces, which in turn depends on heat and mass transfer characteristics of the OD process.

### 2.2.2. Osmotic distillation flux model

The flux in osmotic distillation of an aqueous solution is defined as the rate of water vapour removal across a unit membrane area over a unit of time. OD flux ($J$) may have dimension in either $\text{kg.m}^{-2}.\text{h}^{-1}$, $\text{kg.m}^{-2}.\text{s}^{-1}$, $\text{l.m}^{-2}.\text{h}^{-1}$ or $\text{l.m}^{-2}.\text{s}^{-1}$.

The first model for describing the OD flux was based on the simple diffusion of water vapour through the immobilised air trapped in the membrane pores. According to Geankoplis (1983), if water vapour pressures are fixed on both sides of the membrane by the liquids' composition and the characteristics of the boundary layers, then the OD flux can be determined as given in (2-7).

$$J_D = \frac{1}{Y_{in}} \cdot \frac{D_{w-air}}{\tau \delta} \cdot \frac{M}{RT} (P_1 - P_2) = \frac{1}{Y_{in}} \cdot \frac{K1 \cdot D_{w-air}}{\delta} \cdot \frac{M}{RT} \cdot \Delta P_w$$  

(2-7)

$J_D$—OD flux based on diffusion model, $\text{kg.m}^{-2}.\text{s}^{-1}$;

$M$—molecular weight of solvent (water), $\text{kg.kg.mol}^{-1}$;

$Y_{in}$—log-mean molar fraction of air trapped in the pore;

$D_{w-air}$—diffusivity of water vapour through stagnant air $\text{m}^2.\text{s}^{-1}$;

$\varepsilon$—membrane porosity;

$\tau$—membrane tortuosity;

$\delta$—membrane thickness, m;

$P_1, P_2$—water vapour pressure at the membrane surfaces, Pa; $P_1 > P_2$;

$K1 = \varepsilon/\tau$ - a membrane parameter;

$\Delta P_w = P_1 - P_2$ — water vapour pressure difference across the membrane.

Model (2-7) is named Ordinary Diffusion Model.

If based on the kinetic theory of gases by Present (1958), the number ($n$) of moles of a gas confined in a volume ($V$) at pressure ($P$) and temperature ($T$)
can be determined as \( n = \frac{P_V}{R.T} \); then log-mean molar fraction of air in the pore can be approximated as given in (2-8).

\[
Y_{in} = \frac{x_{a2} - x_{a1}}{\ln \left( \frac{x_{a2}}{x_{a1}} \right)} = \frac{(1-x_{w2}) - (1-x_{w1})}{\ln \left( \frac{1-x_{w2}}{1-x_{w1}} \right)} = \ln \left( \frac{1 - \frac{P_2}{P_T}}{1 - \frac{P_1}{P_T}} \right)
\]

(2-8)

where \( x_{a1}, x_{a2} \) (with corresponding water vapour molar fractions \( x_{w1}, x_{w2} \)) are the molar fractions of air at the pore ends at vapour pressures \( P_1 \) and \( P_2 \) respectively. \( P_T \) is the total pressure in the within the pore.

The membrane structural parameter \( K_1 = \varepsilon / \tau \) is a quantity that is difficult to be precisely determined since membrane porosity and tortuosity are quantities with relative values. It is that because while the membrane porosity (\( \varepsilon \)) can be determined by Electronic Scanning Microscopy (ESM) with a relative accuracy, the tortuosity is a matter of acceptance for values ranging from 1.5 to 10 (Geankoplis, 1983).

Therefore, it is difficult to evaluate the accuracy of the model. In addition, the membrane pore size parameter is absent, or in other words, the model does not consider the interactions between the water vapour molecules and the membrane pores.

The model given in (2-7) has been derived for flat sheet membrane. For hollow fibres – the tubular membrane with diameter of tenths of millimetres or some millimetres, the derivation is based on diffusion of gaseous water molecules through stagnant film of air in a cylindrical porous body. Thus, for hollow fibre membrane, the model is modified to (2-9) (Geankoplis, 1993).

\[
J_{D_v} = \frac{1}{Y_{in}} \cdot \frac{K_1 D_{w-air}}{r_i \cdot \ln \left( \frac{r_0}{r_i} \right)} \cdot \frac{M}{RT} \cdot \Delta P_w
\]

(2-9)

\( J_{D_v} \) OD flux for hollow fibres based on the internal surface area.

\( r_i \) inner radius of fibres

\( r_0 \) outer radius of fibres
Taking into account the interactions between the vapour molecules and the membrane pores, Johnson, Valks and Lefebvre (1989) divided the vapour transport in the OD process into 2 types: Knudsen flow & Poiseuille flow.

Knudsen flow occurs in the regions where the pore size is less than the mean free path of the permeating molecules. The latter collide more frequently with the pore walls than with each other. Thus, the frictional forces between the permeating molecules and the pore walls are the main cause of the pressure drop across the membrane. The flux model $J_k$ in this case is:

$$J_k = \frac{4}{3} \frac{r_p}{\delta} K_1 \sqrt{\frac{2M}{\pi RT}} \Delta P_w$$

(2-10)

$J_k$-OD flux based on Knudsen model;

$r_p$ -pore radius, m;

other parameters are the same as in (2-7).

Poiseuille flow, on the other hand, is observed in the regions where the pore size is much greater than the mean free path of the permeating molecules. The latter collide more frequently with each other than with the pore walls. Thus, the shear stresses within the fluid are the main cause of the pressure drop across the membrane. The flux model $J_p$ in this case is:

$$J_p = \frac{1}{8} \frac{r_p^2}{\delta} K_1 \frac{M}{\mu_w RT} \Delta P_w$$

(2-11)

$J_p$-OD flux based on Poiseuille model;

$\mu_w$ -vapour viscosity, Pa.s;

$P_m=(P_2+P_f)/2$ -mean vapour pressure, Pa;

other parameters are the same as in (2-7), and (2-10)

Models (2-10) and (2-11) are valid for not only flat sheet membrane but also for hollow fibres since they have been derived on the basis of single cylindrical pores of the membrane.
Thus, the OD vapour flux is proportional to the pore radius $r_p$ in Knudsen flow or to the square of $r_p$ in Poiseuille flow, and inversely proportional to membrane thickness.

Considerations of the mechanism under which water vapour molecules travel across the membrane usually rely on the so-called Knudsen number $K_n$ which is defined as the ratio between the mean free path $\lambda$ of gaseous water molecule and the pore size of the membrane (Geankoplis, 1993).

$$K_n = \frac{\lambda}{2r_p} \quad (2-11)$$

The free path $\lambda$ of gaseous water molecule depends on the pressure and temperature, and can be estimated as given in (2-12) (Geankoplis, 1993; Present, 1958).

$$\lambda = \frac{3.2\mu}{P} \sqrt{\frac{RT}{2\pi M}} \quad (2-12)$$

In the formula, $\lambda$ is in m; the gas viscosity is in Pa.s; the pressure $P$ is in Pa; the temperature $T$ is in K; the molecular weight $M$ is in kg.kg mol$^{-1}$; and the universal gas constant $R$ is in J.kg mol$^{-1}$.K$^{-1}$.

If $K_n > 10/1$ then Knudsen mechanism will be predominant, if $K_n < 1/100$ the Poiseuille mechanism holds, or otherwise, the diffusion is in a transition regime.

Apparently, Knudsen and Poiseuille models show the interaction between the diffusing water molecules and the membrane pores, but the effect of stagnant trapped air in the pore, which is very probable, is missing. In addition, according to Kunz, Benhabiles and Ben-Aïm (1996), the pore size of OD membranes is typically and practically in order of some tenths of microns, which are comparable to the mean free path of vapour molecules under the conditions that OD is operated. Therefore, a semi-empirical model for the transition regime for OD flux prediction with air and without air trapped in the pores should be investigated.

Scholfield, Fane and Fell (1990$^a$, 1990$^b$) proposed a semi empirical model to describe the transport of gaseous molecules through membrane pores in the
transition regime during membrane distillation. The model was successfully applied by Fernández-Pineda, Izquierdo-Gil and García-Payo (2002) for gas permeation and membrane distillation. Since membrane distillation and osmotic distillation are governed by a similar driving force, the water vapour pressure gradient across the membrane, the model should also be applicable for osmotic distillation. The model was then named after the authors, the Scholfield Model, and is given in (2-13).

\[
J = \left( \frac{1}{a(1-b) + ab \left( \frac{P_n}{P_{ref}} \right)} + \frac{Y_{in}RT\delta}{K_1D_{w-air}\cdot M} \right)^{-1}\Delta P_w \tag{2-13}
\]

where \( a \) is the membrane permeation constant evaluated at reference pressure \( P_{ref} \); \( b \) is a constant indicating the extent of Poiseuille flow contribution. Other parameters are defined as in the previous models.

The constants \( a \) and \( b \) are to be obtained experimentally. The reference pressure is the pressure ranging within the pressures under which the gas transport process occurs.

Application of Scholfield model (2-13) requires the knowledge of constant \( a \) and \( b \) which are dependent on the membrane properties and the pressure range at which the process occurs. At different range of pressure, or different reference pressure, Fernández-Pineda, Izquierdo-Gil and García-Payo (2002) proposed the derivations as given in (2-14) and (2-15) to modify the constants \( a \) and \( b \).

\[
a^* = a \left[ (1-b) + b \frac{P_{ref}^*}{P_{ref}} \right] \tag{2-14}
\]

\[
b^* = \frac{b \left( \frac{P_{ref}^*}{P_{ref}} \right)}{1 - b + b \left( \frac{P_{ref}^*}{P_{ref}} \right)} \tag{2-15}
\]
Model (2-13) was derived for flat sheet membrane. For hollow fibre membrane, the flux model, based on the inner surface, can be modified as given in (2-16).

\[
J = \left( \frac{1}{a(1-b)+ab\left(\frac{P_m}{P_{ref}}\right)} \right) \cdot \frac{Y_{in}.RT.r_i\ln\left(\frac{r_0}{r_i}\right)}{K_1.D_{w-air}.M} \cdot \Delta P_w
\]  

Another model for gas transport in a porous body in the transition regime is the Dusty-Gas Model. In this model, the porous medium is considered as an array of dust particles positioned stationary in space. These dust particles are treated as gain molecules and the interactions between the gas molecules and the surface of the dust particles are taken into account (Mason & Malinouskas, 1983). The flux equation based on the Dusty-Gas model in direct contact membrane distillation (which is similar to OD in term of the driving force), taking into account the presence of ordinary diffusion, Knudsen flow and Poiseuille flow, was proposed by Fernández-Pineda, Izquierdo-Gil and Garcia-Payo (2002), and modified for hollow fibre membrane as given in (2-17).

\[
J = \frac{M}{r_i.\ln\left(\frac{r_0}{r_i}\right)} \cdot \frac{1}{1 + \bar{x}_a.\bar{v}_w.K_0/K1.D_{w-air}} \left( K_0.\bar{v}_w.\Delta \bar{n}_w + \frac{B_0.\bar{n}_w.P_T}{\mu_w} \right)
\]  

K_0 and B_0 are the parameters characterising the Knudsen and Poiseuille flows respectively. Those parameters are dependent on the membrane properties only, and can be determined by experiments of gas permeation.

\bar{x}_a, \bar{v}_w, and \bar{n}_w are the average mole faction of air, speed of gaseous water and mole concentration of gaseous water respectively.

\Delta \bar{n}_w is the mole concentration difference across the membrane of gaseous water.

\textit{P}_T is the total pressure in the porous medium.

Other parameters are defined as in the previous model.
The models described above have been successfully applied in direct contact membrane distillation (Fernández-Pineda, Izquierdo-Gil & García-Payo, 2002; Scholfield, Fane & Fell 1990). For hollow fibre membranes, models (2-9), (2-16), and (2-17) can be considered as the models for prediction of OD flux once the water vapour pressures at the membrane surfaces are known. However, their applicability and validity in osmotic distillation, especially with hollow fibres, has not so far been reported, and therefore must be validated.

Presentation of those models in an analogical circuit that combine different transport mechanisms is illustrated in figure 2-3. It can be seen that if the Poiseuille flow is negligible, then Scholfield and Dusty-Gas models are equivalent.

Fig.2-3: Analogical circuit of the combination of different transport mechanisms in Diffusion, Scholfield and Dusty-Gas models (Fernández-Pineda, Izquierdo-Gil & García-Payo, 2002).

2.2.3. The polarisation phenomena in osmotic distillation

In the OD process, removal of water from the feed, and its transfer into the brine creates concentration changes at the less mobile thin film layers at the membrane surfaces at both the feed side and brine side as shown on figure 2-4. The concentration is increasing at the feed side membrane surface, but
decreasing at the other side. This phenomenon is called *concentration polarisation* in OD (Hogan et al, 1998; Johnson, Valks & Lefebvre, 1989).

![Vapour Flux J](image)

**Fig.2-4:** Concentration profiles at the membrane surfaces due to polarisation in osmotic distillation.

Due to the concentration polarisation, the vapour pressures of the two solutions differ from that in the bulk, and the resulted water vapour pressure difference across the membrane that effectively governs the OD process is lower than the bulk values as indicated on figure 2-4.

Osmotic distillation involves not only mass transfer but also heat transfer processes. Water evaporation occurs at the feed side membrane surface, decreasing the temperature there. And at the other side, water condensation occurs, increasing the temperature at the brine side membrane surface. These changes of temperature at the membrane surfaces in OD is called *temperature polarisation*, and illustrated on figure 2-5 (Hogan et al, 1998; Johnson, Valks & Lefebvre, 1989).
Vapour Flux $J$

\[ T_{f,b} = T_{s,b}; \quad T_{f,m} < T_{s,m}; \quad \Delta P_b > \Delta P_m \]

**Fig.2-5:** Temperature profiles at the membrane surfaces due to polarisation in osmotic distillation.

Apparently, the temperature changes due to temperature polarisation negatively affect the performance of the OD process. In some cases, when water activities of the two solutions are comparable, this phenomenon may stop the process as well.

From the illustration above, polarisation phenomena in OD are undesirable, but not avoidable. Once, there is a flux ($J$), these phenomena occur.

The formation of the boundary layers, and the concentration and temperature profiles in these regions depend on the hydrodynamic conditions of the system as well as the physical properties of the solutions involved in the OD process. And as mass and heat transfer processes occur simultaneously in OD process, modelling of the process becomes even more complicated.

According to Mengual et al (1993), the concentration profiles at the membrane surfaces in OD could be determined based on Fick's law of mass transfer, while the temperature profiles could be estimated due to the heat transfer and the energy balance in those regions. However, the key points here lie on the determination of the heat and mass transfer coefficients. This matter,
however, has not yet been clearly indicated especially for hollow fibre modules. More details of clarification and quantification of the polarisation profiles will be discussed in chapter 5.

2.2.4. Factors affecting the OD flux

As indicated in the models, water vapour pressures at the membrane surfaces are the causes that govern the transport of water vapour through the membrane. Concentration and temperature polarisations, however, differ the water vapour pressures at the membrane surfaces from the ones in the bulk, and complicate the characteristics of the OD process; and according to Sheng, Johnson and Lefebvre (1991), the physico-chemical interactions between the solutions and the membrane do not pose any influence to the water vapour flux as in the case with reverse osmosis. Therefore, any factor that affects the water vapour pressures of the two solutions (feed and brine) and the polarisation profiles can be considered to have effect on flux rate of the OD process. They include the feed and brine cross flow velocities, the compositions and concentrations of the two solutions, and the process temperature. Another factor that affects the OD flux rate is the membrane configuration such as pore size, porosity, thickness, tortuosity and membrane material (related to heat conductivity).

Membrane hydrophobicity is an aspect that is critical for the OD process integrity. Therefore, the operating conditions applied in the OD process must be within the limits that do not pose any danger to the membrane hydrophobicity.

Studies on the effects of the operating conditions on the OD process have indicated that they have significant effect on the OD flux rate, especially the temperature (Vaillant et al, 2001; Courel et al, 2000b, Mengual et al, 1993).

In general, the solutions' velocities improve the performance of the OD process due to better heat and mass transfer in the boundary regions. The feed and the brine concentrations act in way of affecting the water vapour pressure difference across the membrane, and in the same way is the process temperature. However, little attention has been paid to the effect of solutions'
viscosity, which in turn is dependent on the solution concentration and the process temperature, on the OD flux.

Several attempts have been made to quantify the effect of operating conditions on the OD flux rate by the development of models for OD flux prediction.

Mengual et al (1993) proposed a simple model as given in (2-18) to describe the effect of solute content and the stirring rate on the OD flux.

\[ J = K_m \Delta P_m = K_0 \Delta P_b \]  \hspace{1cm} (2-18)

Where \( K_m \) was a coefficient to be determined in (2-9), (2-16) and (2-17) for hollow fibre modules, and \( K_0 \) was as a function of concentration of the brine, the membrane properties, the temperature and the stirring rate. However, the model was developed for flat sheet membrane with pure water as feed, which means the study was focused on the brine side only. Moreover, it neglected the effect of the temperature polarisation, and even came to the conclusion that temperature polarisation contribution to flux decrease in OD was negligible. This statement was in contrast to Vahdati and Priestman (1994) and Gostoli (1999) who claimed that temperature differences at the membrane surfaces significantly reduced the OD flux rate.

In Mengual et al (1993) model, the net created temperature difference across the membrane was estimated on the foundation of the latent heat of water evaporation and an accepted heat transfer coefficient without accounting the apparent effect of the stirring rate on the phenomenon. It is not totally true and must be further investigated, especially when the feed is different from pure water.

Sheng, Johnson and Lefebvre (1991) developed an empirical model to describe the combination of the effect of the operating conditions on flux rate of OD in a plate-and-frame module. The model showed the relationship between the vapour flux and the time of the process, taking into account the effect of the membrane heat conductivity, the temperature of the aqueous solution to be concentrated, and the flow rate. However, the model is considered valid only for PTFE membrane with thickness 100\( \mu \)m and pore
size 0.2\,\mu m used in that particular module. Therefore, applicability of this model is limited and its accuracy should be clarified.

Temperature appeared to have exponential effect on the OD flux as indicated in many studies (Courel et al, 2000; Mengual et al, 1993). Mengual et al (1993) argued that the exponential effect of temperature on the OD flux rate was due to its exponential effect on the water vapour pressure as shown in equation (2-5) and (2-6). However, the conclusion is not complete as temperature also exponentially reduces the viscosity of the solutions participating in the OD process, which in turn improves the heat and mass transfer in the boundary layers, and reduces the magnitude of the polarisations.

To sum up, research and published information about the effect of operating conditions and the membrane properties are still very few and unsatisfactory. Moreover, reports of OD flux depending on different conditions show a big discrepancy as indicated in table 2-1. And that was the fact that raised the uncertainty and curiosity of the information provided (Kunz, Benhabiles & Ben-Aim, 1996). Therefore, further work will be necessary to clarify the effect of operating conditions on OD flux, to quantify the temperature and concentration polarisations and their contribution in the reduction of the OD flux.

The fluxes reported in table 2-1, however, demonstrate the ability of OD for concentration of liquid food. Thus, OD appears to be an attractive method for industrial concentration processes, but more detailed studies of relevant parameters are required for a better understanding and further optimising the process.
<table>
<thead>
<tr>
<th>References</th>
<th>Membrane configuration &amp; properties</th>
<th>Temperature °C</th>
<th>Feed</th>
<th>Brine</th>
<th>Flux obtained kg.m⁻².h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson, Valks &amp; Lefebvre, 1989</td>
<td>Spiral wound, other parameters-not specified.</td>
<td>Ambient</td>
<td>Orange, grape, pear, apple juice up to 75%TS</td>
<td>Saturated NaCl</td>
<td>5-10</td>
</tr>
<tr>
<td>Sheng, Johnson &amp; Lefebvre, 1991</td>
<td>Flat-and-frame, PTFE, dₚ=0.2μm, δ=100μm, A=0.7 m² area</td>
<td>29-40</td>
<td>Orange, apple and grape juice, 5-70°Brix</td>
<td>NaCl 28%</td>
<td>0-2.3</td>
</tr>
<tr>
<td>Durham, 1992</td>
<td>Tubular-shell PTFE, dₚ=0.2μm, dₚ=12mm, δ=8.5μm, A=0.03 m²; Plate-and-frame PP, A=19.63 cm² and 0.6 m², dₚ=0.2-0.45μm, [δ=6.4-20μm]</td>
<td>20-30</td>
<td>Tomato sauce and puree</td>
<td>NaCl 28%</td>
<td>0.7-1.4</td>
</tr>
<tr>
<td>Mengual et al, 1993</td>
<td>Flat sheet PVDF, dₚ=0.2, δ=125μm; Flat sheet PTFE, dₚ=0.2μm, δ=178μm; A=27.5cm² for all cases.</td>
<td>20-60</td>
<td>Water</td>
<td>NaCl 0.5-5M</td>
<td>0-0.5</td>
</tr>
<tr>
<td>Vahdati &amp; Priestman, 1994</td>
<td>Flat sheet, δ=60μm, others-not specified</td>
<td>20-33</td>
<td>Dilute liquid food and water</td>
<td>Saturated MgSO₄</td>
<td>0.2-3.3</td>
</tr>
<tr>
<td>Hogan et al, 1998</td>
<td>PP hollow fibre Liqui-Cell module, dₚ=0.03μm, dₚ=0.3mm, δ=30μm, A=19.2 m²</td>
<td>Ambient</td>
<td>Fruit and vegetable juices up to 70°Brix</td>
<td>K₂HPO₄</td>
<td>0.3-3.0</td>
</tr>
</tbody>
</table>

**Table 2-1 (continued)**

<table>
<thead>
<tr>
<th>References</th>
<th>Membrane configuration &amp; properties</th>
<th>Temperature °C</th>
<th>Feed</th>
<th>Brine</th>
<th>Flux obtained kg.m⁻².h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbe et al, 1998</td>
<td>Flat sheet PP, PVDF, PTFE; dₚ=0.012-0.45μm, δ=25-150μm, A=155cm²</td>
<td>25</td>
<td>Grape and orange juice</td>
<td>CaCl₂ 45%</td>
<td>2.02-6.70</td>
</tr>
<tr>
<td>Gostoli, 1999</td>
<td>Tube-shell PP, dₚ=0.2μm with dₚ=1.0mm, 25-50</td>
<td>Water</td>
<td>NaCl</td>
<td>0.8-2.4</td>
<td></td>
</tr>
<tr>
<td>Study</td>
<td>Membrane Material</td>
<td>Pore Diameter, (d_p)</td>
<td>Membrane Thickness, (\delta)</td>
<td>Outer Diameter, (d_o)</td>
<td>Concentrate</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------</td>
<td>-------------------------</td>
<td>-------------------------------</td>
<td>-------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Bailey et al, 2000</td>
<td>(\delta=200\mu m), (A=0.04m^2); and (\delta=400\mu m), (A=0.104m^2)</td>
<td>PP hollow fibre Liqui-Cell module, (A=1.0m^2), others - not specified.</td>
<td>(d_o=2.6mm)</td>
<td>Grape juice</td>
<td>CaCl₂</td>
</tr>
<tr>
<td>Courel et al, 2000(^b)</td>
<td>Flat sheet PTFE, (d_p=0.2\mu m), (\delta=178\mu m), (A=40cm^2)</td>
<td>20-35</td>
<td>Sucrose solution 30-60°Brix</td>
<td>CaCl₂</td>
<td>30-45%</td>
</tr>
<tr>
<td>Shaw et al, 2001</td>
<td>PP hollow fibres, (d_p=0.2\mu m), (A=10.3m^2), others - not specified.</td>
<td>30</td>
<td>Orange and passionfruit juices to 43.5°Brix</td>
<td>CaCl₂</td>
<td>4.6M</td>
</tr>
<tr>
<td>Vaillant et al, 2001</td>
<td>PP hollow fibres, (d_p=0.2\mu m), (d_o=2.6mm), (\delta=400\mu m), (A=10.2m^2)</td>
<td>30</td>
<td>Passionfruit juice up to 60% Water</td>
<td>CaCl₂</td>
<td>5.3M</td>
</tr>
</tbody>
</table>

-Membrane material: \(PP\) – Polypropylene, \(PTFE\) – Polytetrafluoroethylene, \(PVDF\) – Polyvinylidene difluoride
-Parameters: \(d_p\) – pore diameter, \(d_o\) – outer diameter of fibres or tube, \(\delta\) - membrane thickness, \(A\) – membrane area.
2.3. OSMOTIC DISTILLATION MEMBRANES

In the OD process, a hydrophobic membrane is employed. Therefore, hydrophobicity is the dominant factor of OD membrane selection. Durham (1992) and Hogan et al (1998) listed four main hydrophobic membranes used in OD. They include Polypropylene -CH$_2$-CH(CH$_3$)- (PP), Polyethylene -CH$_2$-CH$_2$- (PE), Polytetrafluoroethylene -CF$_2$-CF$_2$- (PTFE) and Polyvinylidene difluoride -CH$_2$-CF$_2$- (PVDF). They can be configured in plate and frame, spiral wound, or hollow fibre modules. The hollow fibre modules appear to be the best used for OD for its high area/volume ratio, and no supports required (Hogan et al, 1998).

The criteria of choosing the OD membrane are proposed by Johnson, Valks and Lefebvre (1989). These criteria are to ensure the stability of the membrane during the OD process with maximal flux rate. They include:

- The membrane must be as highly hydrophobic as possible so that to prevent liquid penetration into the membrane pores under hard conditions.

- The membrane should be highly porous since the flux $J$ is proportional to porosity $\varepsilon$. However, too high porosity of the membrane will lead to insufficiency of the solid polymer material necessary for effective heat transfer to reduce the negative effect of temperature polarisation, hence a compromise between the membrane thermal conductivity and porosity is necessary, and must be worked out.

- The pores should be as large as possible as the flux is proportional to $r$ (Knudsen model) or $r^2$ (Poiseuille model). In addition, as Barbe et al (1998) indicated the larger the pore, the higher the retention of volatile components of the final products. However, the maximum tolerable pore radius to prevent liquid penetration is 250 nanometres as stated by Hogan et al (1998).

In contrast, under certain conditions when ordinary diffusion of gaseous water molecules is predominant, the pore size may have no effect on the OD flux as indicated in equations (2-7) and (2-9), and smaller pores
provide stronger hydrophobicity and higher bubble point to the membrane which is critically crucial in osmotic distillation.

Therefore, the membrane pore size is a subject of optimisation in osmotic distillation.

- The membrane should be as thin as possible, and should be well thermally conductive, as the flux is inversely proportional to the pore length or membrane thickness $\delta$, and thin membrane with high thermal conductivity will lessen the effect of temperature polarisation. However, the membrane must be thick enough to provide sufficient strength to be stable during the OD process.

Since osmotic distillation and membrane distillation employ hydrophobic membranes, and are driven by the same driving force, membranes used in these two processes are similar, though under different requirement of thermal conductivity. The most widely used membranes in osmotic distillation experiments are listed in table 2-2 (Barbe et al, 1998; Lawson & Lloyd, 1997).

### 2.4. OSMOTIC PRESSURE AGENTS

Osmotic pressure agent refers to the salt used to prepare the brine or the stripping solution in osmotic distillation. The selection of the osmotic pressure agent (OPA) is very important since the OPA not only creates the driving force for the OD process, but also affects the performance of the OD system in general.

First of all, it is desirable for an OPA to provide a solution with as low water vapour pressure as possible, however, it must qualify for other qualities to ensure the integrity of the OD process, the safety and the quality of the final products, and the economy as well.
Table 2-2. Properties of hydrophobic membranes suitable for use in osmotic distillation

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Trade name</th>
<th>Polymer</th>
<th>ε (%)</th>
<th>δ μm</th>
<th>d_p μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoechst-Celanese</td>
<td>Celgard 2400</td>
<td>PP</td>
<td>13-38</td>
<td>25</td>
<td>0.012-0.04</td>
</tr>
<tr>
<td></td>
<td>Celgard 2500</td>
<td>PP</td>
<td>27-35</td>
<td>25</td>
<td>0.075-0.25</td>
</tr>
<tr>
<td>Membrana</td>
<td>Accurel 1E-PP</td>
<td>PP</td>
<td>29</td>
<td>90</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Accurel 2E-PP</td>
<td>PP</td>
<td>32</td>
<td>150</td>
<td>0.2</td>
</tr>
<tr>
<td>Millipore</td>
<td>Durapel VVSP</td>
<td>PVDF</td>
<td>29</td>
<td>120</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Durapel GVSP</td>
<td>PVDF</td>
<td>30</td>
<td>120</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Durapore</td>
<td>PVDF</td>
<td>75</td>
<td>140</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Durapore</td>
<td>PVDF</td>
<td>75</td>
<td>110</td>
<td>0.45</td>
</tr>
<tr>
<td>Gore</td>
<td>Gortex L31189&lt;sup&gt;a&lt;/sup&gt;</td>
<td>PTFE</td>
<td>54</td>
<td>50</td>
<td>0.2</td>
</tr>
<tr>
<td>Enka (Akzo)</td>
<td>PP</td>
<td></td>
<td>70</td>
<td>150</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td></td>
<td>75</td>
<td>140</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>PP</td>
<td></td>
<td>75</td>
<td>100</td>
<td>0.2</td>
</tr>
<tr>
<td>Gelman Inst. Co.</td>
<td>TF200</td>
<td>PTFE</td>
<td>60</td>
<td>60</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>TF450</td>
<td>PTFE</td>
<td>60</td>
<td>60</td>
<td>0.45</td>
</tr>
</tbody>
</table>

<sup>a</sup>-membranes with wide range of parameters

(ε is the membrane porosity; d_p is the nominal pore diameter; and δ is the membrane thickness)

Therefore, the qualities of an OPA include:

- Non-toxicity to humans and animals since the OPA is separated from food products by only a thin membrane barrier that may be wetted and OPA may diffuse into the food product during OD operation.
- Chemical stability at temperatures up to the normal boiling point of the saturated solution of salts. It is that because the brine concentration has to be recovered during the OD process, and that recovery usually involves heating up the brine to boiling point.
- Substantial incapability of forming precipitates when exposed to volatile components of feed solutions.

- Odourlessness and tastelessness in aqueous solution so that not to affect the flavour and taste of the concentrated food products by this technique.

- Non-corrosiveness to process equipment to avoid or minimise the destruction of the OD system parts that are in contact with the brine.

- Large positive temperature coefficients of solubility in aqueous solution.

- High surface tension of OPA aqueous solution. It is of a paramount importance to ensure no penetration of brine into the membrane pores to preserve the OD process integrity.

In general, the most commonly used OPA in the early day of the OD study was NaCl because of its low cost and non-toxicity (Sheng, Johnson & Lefebvre, 1991; Durham, 1992, Mengual et al, 1993). However, NaCl has low solubility and the lowest water activity of the saturated NaCl solution is about 0.75 which is much higher than the one of calcium chloride of about 0.25. It means that NaCl is not capable of producing low water vapour pressure (which is desirable in the OD process) if compared to calcium chloride or possibly other salts. The other disadvantage of NaCl is that it poses a risk of causing corrosion to the process equipment.

The brine prepared from LiCl.H₂O, KC₂H₃O₂, and MgCl₂ is much more efficient than NaCl. Saturated solutions of LiCl.H₂O, KC₂H₃O₂, and MgCl₂ can produce as higher osmotic pressures as up to 292, 215 and 152atm respectively in comparison to 39atm of NaCl. However, application of these salts should be considered in term of safety and economy. In the recent years, CaCl₂ has emerged to be of a wide use in osmotic distillation (Bailey et al, 2000; Courel et al, 2000b; Shaw et al, 2001; Vaillant et al, 2001). It is that because of its availability on the market, low cost, non-toxicity, and high osmotic pressure up to about 200atm.
Reconcentration of the dilute brine solution is also an important step in the OD process to recover the concentration of the brine. It can be by different means including conventional evaporation, solar ponding, pervaporation or a combination of them. Johnson, Valks and Lefebvre (1989); and Petrotos and Lazarides (2001) suggested the use of reverse osmosis and electrodialysis (respectively) to reconcentrate the brine solution. However, it may be doubtful because these two processes are principally effective for low concentration solutions with low osmotic pressures only.

Syrinx Equipment Pty Ltd has developed a simple pervaporation method to reconcentrate the dilute brine (Johnson, Valks & Lefebvre, 1989). The dilute brine is heated to 50°C and passed through a hollow-fibre membrane, while air at 50°C counter-currently flows outside the fibres. A reverse cycle air-conditioner is then used to condense the extracted water and reheat the air for recirculation.

Solar desalination approach may be used for reconcentration of the diluted brine. Kunze (2001) reported a new improvement in using solar energy to displace water from brine solution. Solar collectors were used to supply energy for water evaporation. The cool brine was circulated through the condenser’s coil while only a small part of the brine (3:20) from the outlet of the condenser was diverted to the surface of the evaporator (just next to the solar collectors) where it receive the solar energy. All the solar collectors, evaporator and condenser were assembled in one compact unit. The unit described was able to remove up to 1.20-1.57 litres of pure water per square metre of solar energy collectors per hour. This unit had the advantage of compact and energy efficient, while concentrating the brine it kept the brine still at low temperature.

Another method for reconcentration that should be considered is evaporation in a counter current flow of air. The diluted brine is sprayed downward while the air is forced to flow counter-currently and strips away water from the brine. This method should be more effective in the regions where the weather is usually dry (Nguyen, H.M., 2001, pers. Comm., 15 March).
Though the above brine re-concentration methods have been discussed, detailed evaluation of these methods are not given. Therefore, some effort on this issue should be done.

2.5. CLEANING OF OD MEMBRANES

In membrane processes, cleaning is a very important for flux restoration, and also affects the service life of the membrane because it is usually conducted at the conditions that are very close to the physical limits of the membrane material (Lawrence et al, 1998). Therefore, cleaning the OD membrane must pay attention to the preservation of the membrane hydrophobicity and its restoration afterwards. In addition, cleaning of the membrane can also affect the quality and safety of the concentrated food products (Durham, 1992).

As disassembly of membrane modules is impractical, access to the surface of hollow-fibre, tubular and spiral wound membrane is impossible, and direct cleaning of the membrane surface may cause abrasive damage, cleaning of the membrane modules must be conducted on the basis of Clean-In-Place (CIP) procedures (Beaton, 1979).

Factors that should be considered when cleaning a membrane include cleaning agents, cleaning agent concentration, cleaning time, temperature, and agitation. Cleaning agents include acids, alkalis, detergents, enzymes and complex agents. The selection of cleaning agents depends on the nature of the membrane composition and the foulant (Durham, 1992).

In osmotic distillation, cleaning is not only to remove the foulants, but also to maintain the membrane’s hydrophobicity, which is essential for the OD process integrity.

A study by Durham and Nguyen (1994) on cleaning of OD membrane Goretex10387 (PTFE) and Gelman11104/2TPR (cross-linked acrylic fluorourethane copolymer) using different agents such as alkaline (0.5-1%NaOH), acid (1%HNO₃), alkaline and acid combination (1%NaCl and 1%HNO₃), Enzymatic (0.25% lipolase, alkalase, palatase) and the commercial ones 1%P3 Ultrasil series as cleaning agents showed that 1%P3 Ultrasil56 was suitable for Gelman11104/2TPR, but destructive to the hydrophobicity of
Goretex10387, while 1%NaOH was acceptably suitable for both types of membrane. Unfortunately, the study was confined to only two kinds of membrane and two types of cleaning agents. Thus, the information provided was very limited, but it gave a concept of choosing a suitable agent when cleaning an OD membrane. Therefore, a detailed study of the effect of cleaning procedures on OD membrane hydrophobicity and its restoration is still needed.

Another method for cleaning an OD membrane is being developed by the US-Filter Company. Pressure-driven water flushing is used to remove foulants, and hot pressurised air is followed to restore the hydrophobicity of the OD membrane. Moreover, NaOH solution of concentrations up to 5% w/w can be used safely to clean PP, and 1%NaOH or 1000ppm chlorine solution for PVDF membrane while the hydrophobicity is intact (Muller, J. 2001, pers. comm., 10 May). However, the information about the effectiveness of the method has not yet been published.

So far, studies on, and the published information about cleaning of OD membrane are still very limited. Therefore, further research on this area is required.

### 2.6. OD APPLICATION IN FRUIT JUICE CONCENTRATION

#### 2.6.1. Concentration ability of OD

As OD is conducted at relatively low temperature, it is able avoid the problem of heat degradation that conventional evaporation incurs (Nguyen, 1991). Reports of Wilson (1991) and Thompson (1991) indicated that OD could be used for the concentration of a number of fruit juices, resulting in high quality concentrate with regards to flavour, colour and aroma retention. Vaillant et al (2001) and Shaw (2001) also indicated that passionfruit and orange juices prepared by OD showed no significant difference when compared with a fresh one. Wilson (1994) and Hogan et al (1998) also pointed out that OD could be used to selectively separate alcohol from wines to produce reduced alcohol wines, and OD appears to be superior to reverse osmosis and dialysis for this purpose.
OD has been reported to be able to concentrate fruit juice to very high concentration, up to 75-80% TS (Johnson, Valks & Lefebvre, 1989) without suffering from the fouling problems associated with RO (Sheng, Johnson & Lefebvre, 1991). Many studies and experiments have observed a little change of the flux during OD process, which ranges from 1.5 to 3.5 l/m²h. Johnson Valks and Lefebvre (1989) even reported a flux of 5 to 10l/m²h when concentrating fruit juice. Almost the same flux rate have Courel et al (2000⁵) reported for concentration of sucrose up to 65%TS.

In addition, OD can be used for pre-concentration of biological and pharmaceutical products to reduce the cost of freeze-drying. OD can also be used for concentration of vaccine and biological solutions (Hogan et al, 1998).

In conclusion, even though as a new and not fully studied technique, OD has been proving its ability to provide high quality concentrates with very high concentration and the flux rates are applicable. Thus, OD appears to be a very competitive alternative for the concentration of fruit juice.

2.6.2. OD applications in industry

Since the concept of OD was established, there have been many trials on pilot plant scale in Australia (Sheng, Johnson & Lefebvre, 1991; Wilson, 1991; Thompson, 1991; Johnson, Valks & Lefebvre, 1989; Hogan et al, 1998), and in France (Vaillant et al, 2001; Shaw et al, 2001).

In most OD installations, the two solutions are pumped in a counter-current flow. The membranes used can be flat, spiral-wound or hollow fibres with the feed flowing inside the fibres.

Johnson, Valks and Lefebvre (1989) stated that OD was successfully applied for concentration of apple juice, orange juice, grape juice, sugarcane juice, coffee, tea and skim milk in pilot scale studies, reaching up to 75% TS of the concentrate with vapour flux rating at 5 to 10l/m²h.

Wilson (1991) and Thompson (1991) reported an application of OD in Australia for concentrating grape juice for winemaking. The authors stated that it was very hard to distinguish between wines made from reconstituted juice
and those made from single strength juice. According to Thompson (1991), the pilot plant installation at Sunnyciff Wines, established in January 1990, with a feed rate of approximately 80 to 100 litres per hour was successful to produce approximately 20 to 25 litres per hour of 68°Brix concentrate of grape juice for winemaking purposes. The success of the trial lead to the construction of an industrial OD installation at Sunnyciff Wines’ Iraak – Victoria in 1991 to process 10,000 to 23,000 litres daily.

Unfortunately, both Wilson and Thompson did not indicate any information about the flux rates and the operating conditions of the OD modules at those plants.

2.6.3. Development of a hybrid system for fruit juice concentration

Many membrane techniques have been successfully used in the food industry. For instance, microfiltration is used for pulpy food clarification, ultrafiltration for separation of large molecules such as carbohydrates and proteins, nanofiltration for concentration of sweet whey with acid and salt reduction, and reverse osmosis for concentration of liquid foods and effluent treatment (Nguyen, 1999). These processes principally are effective and consume least energy in comparison to conventional thermal processes. However, using reverse osmosis (RO) to concentrate fruit juices up to more than 30% TS is neither practical nor economic due to high osmotic pressure and fouling problem (Hogan et al, 1998; Nguyen, 1991).

As the OD process involves water evaporation, vapour transfer though the membrane and vapour condensation, it is much slower than in other methods. This fact provides a background for Hogan et al (1998) to claim that using OD alone to concentrate fruit juice is not economic. OD may be efficient if used in conjunction with other techniques such as ultrafiltration (UF), reverse osmosis (RO), and/or freeze concentration (FC) in a hybrid system (Hogan et al, 1998; Nguyen, 2000). It is worth noting that using UF prior to OD can significantly increase the flux in OD process by approximately 1l/m²h (Bailey et al, 2000), and preserve the membrane hydrophobicity as well due to protein removing by UF. However, one might be sceptical that such combination would result in
high investment if UF, RO and FC have not yet been established in the factory. Therefore, a comparison between the sole use of OD with larger membrane area, and OD in combination with UF, RO and/or FC should be conducted.

A hybrid system using OD in conjunction with UF and RO is illustrated in figure 2-6.

![Diagram of a hybrid system using OD]

**Fig.2-6:** Schematic diagram of a hybrid system using OD

2.7. CONCLUSIONS

Osmotic distillation is a novel concentration technique with attractive advantages over conventional techniques. Some industrial OD applications have already been in operation, but the success is still not known. Further fields of applications are being investigated and realised in laboratories and pilot plants.
However, the characteristics of the OD process have not yet been fully understood, and the operation conditions are not yet optimised. There have been research and investigations on the OD process. However, the published materials do not satisfactorily describe the OD process in terms of providing the fundamentals of the process as well as the practical issues. The results of the experiments given in the literature are not in full agreement with each other.

It is essential to comprehend the concentration and temperature polarisation phenomenon near the membrane surface, and its role in the OD process. Quantification of the concentration and temperature profiles at the membrane surfaces would be useful to study the contribution of the polarisation phenomena to the reduction of OD flux.

Further, modelling is necessary to simulate and optimise the OD process to reduce the cost of operation and make the OD process more attractive and competitive for liquid food concentration.

Moreover, hydrophobicity of the membrane, a critical point in osmotic distillation, may be damaged during the operation alone or during cleaning procedures. Therefore, more investigation on cleaning and on aspects to enhance and preserve the hydrophobicity of the OD membrane is required as a step forward in realisation the OD process in the industry.
CHAPTER 1: INTRODUCTION

1.1. BACKGROUND AND JUSTIFICATION

The preference of consuming fruit juices with high quality rather than the whole fruits has been long recognised. However, transport and storage of single strength juices up to the point of consumption is uneconomic and unsuitable as it is bulky and subject to rapid spoillage (Addison, 1986).

Concentration of liquid foods in general, and fruit juices in particular to high concentration up to 70-80%, on the other hand, will remove a significant amount of water, hence a significant reduction in transport, packaging, and storage cost with much greater stability of the concentrates (Ramteke, 1993; van Niestelrooij, 1998). This lays the motivation to perfect the concentration techniques so that low cost, but high quality concentrates can be produced.

Recently, many modern techniques have been used for concentration purposes in the food industry. They include evaporative concentration, reverse osmosis, and freeze concentration. However, these techniques suffer disadvantages and in one way or another do not fully satisfy the manufacturers and the customers.

Evaporative concentration has long been established in the food industry; hence the most developed and widely applied technique. The development of energy recovery system reduced energy consumption to the level comparable to other concentration techniques, but significantly increased the investment cost up to 300% (Addison, 1986). Moreover, the conventional evaporation occurs at relatively high temperature at minimum of 50°C, hence results in undesirable heat effect or off-flavour of the final product. This problem can be reduced by vacuum evaporation, but significant loss of aroma of juices due to evaporation is unavoidable (Yu & Chiang, 1986), resulting in poor aroma and flavour of the final product.

Freeze concentration is another technique that is claimed to be able to provide superior quality of the concentrates since it operates at low temperature (Ramteke, 1993; van Niestelrooij, 1998). However, its application is still limited
in the industry due to its too high investment and the limit of final concentration of the concentrate, just up to 45 to 50% (Nguyen, 2000).

Reverse osmosis (RO) is a membrane technique that is considered efficient for concentration of liquid foods up to 25%TS. It requires lowest cost for investment and operation in comparison to evaporation and freeze concentration (Ramteke, 1993). However, using RO to concentrate fruit juice above 30% TS is not practical and economical due to high osmotic pressure and fouling problem (Hogan et al, 1998; Nguyen, 1991).

Osmotic Distillation Process and Justification

Recently, another membrane technique, called Osmotic Distillation (OD), has become of increasing interest to many researchers and food manufacturers as a competitive alternative to other concentration techniques.

Studies indicated that OD could be used to concentrate fruit juices to high concentrations, up to 75% with high quality concentrate (Thompson, 1991; Johnson, Valks & Lefebvre, 1989). Moreover, OD could operate well without suffering the problems associated with RO (Sheng, Johnson & Lefebvre, 1991).

Therefore, OD appears to be a competitive alternative for concentration of fruit juices in terms of achieving high concentration with high quality, but requiring much lower investment.

Many factors, such as liquid temperature, fluid flow rate, liquid concentration, and the membrane properties affect the rate of water removal in OD process. There have been reports on the effect of those factors on the performance of the OD process. However, the discrepancy between those reports revealed the uncertainty and curiosity of the information provided (Kunz, Benhabiles & Ben-Afm, 1996). Further, little information has been published on the optimal operating condition for, and successful applications of, OD process in the food industry.
Introduction

Therefore, a research project of the OD process should be carried out both on laboratory and pilot plant scale to provide the fundamentals of its understanding and practical aspects, a step forward, to its realisation in the food industry.

1.2. AIM AND OBJECTIVES OF THE PROJECT

The aim of this project is to clarify the effect of operating conditions on the performance of osmotic distillation process as a confirmation of its applicability and a step forward of its commercialisation in the food industry.

The project is to be carried out on both laboratory and pilot scale with the following specific objectives:

1. To quantify the effect of operating conditions on OD flux rate.

2. To quantify the concentration and temperature polarisations, and their contribution to flux reduction in osmotic distillation.

3. To develop a model for OD flux prediction.

4. To test and confirm the applicability of OD for fruit juice concentration.

1.3. LIMITATIONS OF THE STUDY

The study is limited to hollow fibres due to their high ratio of membrane area to unit volume of membrane module, ease of controlling the operating conditions and ease of cleaning; hence high potential of application in the industry.

The solution to be concentrated on laboratory scale will be glucose solution 30 to 60% w/w since glucose is similar to fructose, the main sugar in fruit juices, but is more industrially important relating to other food processing areas. And using glucose instead of fresh juices on laboratory scale will allow avoiding the confounding matter of membrane fouling.

On pilot scale, clarified apple and also grape juice will be used since their aromas are very sensitive to processing changes.
CHAPTER 3: LABORATORY EXPERIMENTATION OF OSMOTIC DISTILLATION IN HOLLOW FIBRE MODULES

3.1. INTRODUCTION

Osmotic distillation (OD) and membrane distillation (MD) are processes of removing water from an aqueous solution through a hydrophobic membrane. They are similar in term of the process driving forces. That is the water vapour pressure gradient across the membrane. However, in MD, the driving force is primarily created by the temperature difference across the membrane, while in OD, it is created by the differences of the compositions of the solutions that are isothermal and in direct contact to the membrane surfaces. Therefore, OD can be operated at or below ambient temperatures, and under about the atmospheric pressure, thus avoiding the quality degradations associated with conventional evaporative processes like “cooked” flavour, loss of aromas and colour changes due to heat exposure.

OD is a complex heat and mass transfer process that is hypothesised to be under the effect of many factors including the hydrodynamic conditions of the system such as fluid velocities, liquid temperatures, liquid concentrations; and the membrane properties.

This chapter reports on the set up of the laboratory OD system on laboratory scale using hollow fibres as presented on figure 3.1; and the effect of the operating conditions on the flux rate of the OD process.

3.2. SETTING UP THE LABORATORY SCALE OD SYSTEM

3.2.1. Preliminary design

The purpose of this section is to outline the design of the most crucial element of the laboratory scale experimental OD system, the hollow fibre module. Other ancillary elements are a matter of selection.
Hollow fibres are tube-like membrane with diameter of tenths of millimetres to some millimetres. They were supplied in “fresh form”. Therefore, using them for osmotic distillation experiment required “potting” them in a module with configuration similar to a “tube and shell” heat exchanger.

![Diagram of laboratory scale OD system configuration.](image)

**Fig. 3-1:** Laboratory scale OD system configuration.
1, 5, 5'- Hollow fibre module; 2, 2'- Pressure gauges; 3- Feed pump; 4- 10ml-pipette; 5, 5'- Thermometers; 6-Feed tank; 7, 7'- Water baths; 8, 8'- Filters; 9-Brine tanks; 10- Brine pump; 11- Tubing; 12-flowmeter.

**Length of the modules**

The module potted for the experimental purposes in this work was to maintain not only certain operating conditions namely the liquid velocity inside the fibre, but also the integrity of the OD process.

As due to the flow friction, there is a pressure drop through the fibres and the tubing system when a liquid is pumped through. Thus, the liquid at the beginning of the
hollow fibre module must be maintained at least at pressure equal to the pressure drop. This pressure indicates the absolute pressure expressed on the membrane body, though reducing over the length of the fibres if the pressure outside the fibres (the shell side) is assumed to be neglected. However, this pressure must be maintained below the bubble point of the membrane itself to ensure no liquid penetration into the membrane pores, which is critical to preserve the OD process integrity. Therefore, the design requires the calculation of the appropriate length of the fibres exposed to the pressure of the liquid that is flowing at certain velocity.

The fibres used in the experiments were supplied by Memcor Australia (South Windsor, New South Wales, Australia). The properties of the fibres are listed in table 3-1.

**Table 3-1**

*Properties of hollow fibres used in the experiments*

<table>
<thead>
<tr>
<th>Code</th>
<th>PV375</th>
<th>PV660</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>PVDF</td>
<td>PVDF</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>d_i</td>
<td>mm</td>
</tr>
<tr>
<td>External diameter</td>
<td>d_o</td>
<td>mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>δ</td>
<td>μm</td>
</tr>
<tr>
<td>Nominal pore diameter</td>
<td>d_p</td>
<td>μm</td>
</tr>
<tr>
<td>Bubble point</td>
<td>P_{bp}</td>
<td>kPa</td>
</tr>
<tr>
<td>Porosity</td>
<td>ε</td>
<td>%</td>
</tr>
</tbody>
</table>

*(Data obtained from the fibre supplier)*

As planned before, glucose solutions at concentrations up to 60% w/w would be used as the feed flowing inside the fibres, and the experiments would be running at temperature from 25 to 45°C. Therefore, to cope with the hardest conditions in term of pressure drop, the calculations were based on the highest concentration and lowest temperature for each type of fibres.

- For PV375:
  - Concentration C_{r}=40%, which corresponds to viscosity μ=5cP at 25°C
-Velocity \( v_f = 0.9 \text{ms}^{-1} \) as recommended by Geankoplis (1993)

And due to the fact that the fibre diameter is very small in comparison to the one of the tubing system, the pressure drop due to friction through the fibres is predominant throughout the system. Therefore, pressure drop due to contraction and expansion at two ends of the fibres can be neglected. From the fundamental equation for laminar flow in pipes (Reynolds number \( \text{Re}=37-226 \)), the pressure drop is given in (3-1).

\[
\Delta P = \frac{32\mu \cdot v_f \cdot L}{d_i^2}
\]  

(3-1)

As to preserve the OD process integrity, the maximal pressure drop was chosen up to 60% of the bubble point of the fibres, which was about 200kPa. Then the maximal length of the fibres was determined as:

\[
L = \frac{\Delta P \cdot d_i^2}{32\mu \cdot v_f} = \frac{200 \times 10^3 \times (0.375 \times 10^{-3})^2}{32 \times 5 \times 10^{-3} \times 0.9} = 0.195 \text{m}.
\]

- For PV660 (Re=5-104):
  
  - Concentration \( C = 60\% \), which corresponds to viscosity \( \mu \approx 29 \text{cP} \) at \( 25^\circ \text{C} \)

  - Velocity \( v_f = 0.6 \text{ms}^{-1} \) as recommended by Geankoplis (1993)

  - \( \Delta P_{\text{max}} = 250 \text{kPa} \)

Then the maximal length of the fibres was:

\[
L = \frac{\Delta P \cdot d_i^2}{32\mu \cdot v_f} = \frac{250 \times 10^3 \times (0.660 \times 10^{-3})^2}{32 \times 29 \times 10^{-3} \times 0.6} = 0.189 \text{m}.
\]

So for a compromised value of the length of the fibres, it was chosen to be \( L = 190 \text{mm} \).

The potted parts at two ends of the modules were about 30mm long, thus, the total length of the modules was 250mm.

**Potting material**

Epoxy resin was chosen to be the potting material as according to Massingill, Bauer and Bauer (2000) it is highly resistant to chemicals and solvents, excellently adhesive to a broad range of material, flexible, and has low order of shrinkage on cure.
Resin of Permatex (Australia) was obtained from the local market and used for potting hollow fibre modules. The resin came in two twin syringes containing 15ml each of epoxy resin and hardener. Equal amounts from these syringes were thoroughly mixed, and applied for potting the modules. There were two types of Permatex resin: one to harden after 20 minutes, and one to harden after just 5 minutes. However, only the 5-minute-to-harden resin was used for potting purposes.

The shell

The shell was set up by gluing a glass tube of diameter $D_1/D_2=10/7.5\text{mm}$ to two PVC T-bars 13mm (external diameter – see fig.3-2), ensuring the total length of 250mm. Details of setting up the shell will be discussed in the next section.

Number of fibres in one module

The number of fibres potted in one module was managed to be as many as possible to maximise the total area of the membrane used in the experiment. It was that with the purpose to gain maximal amount of water removed from the feed during the experiment, so that to maximise the accuracy of the reading. The fibres were 50 for PV375, and 28 for PV660.

Tubing

The minimal diameter of the tubing was set to ensure the velocity of the liquids in the tubes not exceeding the recommended values by Geankoplis (1993), which were $2.5\text{ms}^{-1}$ for system using PV375 and $0.6\text{ms}^{-1}$ for system using PV660 (due to different viscosity range), but at the same time to ensure the flow rate passing through the fibres at velocities discussed before. The bigger tube was chosen as a norm for the whole system. Similar is the procedure for determining the tube diameter on the shell side. All the tubes in the system were set to the minimal values to minimise the dead volume of the system.
Continuity equation for a flow in a channel was used in the calculation. The tube diameter for the feed side was then set at 3mm, and the for the brine side – 6mm.

The circulating pumps
The circulating pumps were chosen on the basis of pump head which is equal to the pressure drop mentioned above and the flow rate, which is necessary for liquids to travel at maximal pre-designed velocity.

Other auxiliaries
They were chosen so as to be compatible for the system. For example, the tanks were to be able to hold the necessary volumes of the solutions; the pressure gauges were to cover the pressure ranges; and the same was for thermometers.

3.2.2. Potting a hollow fibre module
Potting a hollow fibre module for lab scale OD experiment was a challenging task due to the fact that the resin was highly viscous, and the fibres were so thin and vulnerable to physical damages. Unless an appropriate technique was used, the high viscosity of the resin would prevent itself from penetrating to the tiny spaces between the fibres, as well as the spaces between the fibre bundle and the shell, which may result in incomplete filling of the resin and the failure of potting a hollow fibre module. Followings were the steps used in this work for potting a hollow fibre module. The technique resulted in about 90% success with consistency of the modules. The modules were named after the codes of the fibres used.

Step 1: Setting up the shell (see fig.3-2)
The shell was set up by gluing two PVC T-bars 13mm to a glass tube with the dimensions as shown on fig.3-2.
The glass tube was cut from a 1 metre long tube. Then the edges were blunted or rounded by carefully exposing them to a Bunsen burner flame for about three to five minutes. Then it was left to cool down by air.

![Diagram showing the setup of the shell for potting a hollow fibre module](image)

**Fig.3-2:** Setting up the shell for potting a hollow fibre module

The T-bars were selected carefully so that not to have any sharp edges as they may cause physical damage to the fibres.

The glue was 5-minute-to-harden Permatex epoxy resin.

Gluing started at one end at a time. Then the glued end was left to the hardened status for about five minutes before starting gluing at the other end. It must be stressed here that only a thin layer of the resin was applied to the surfaces for gluing. Otherwise, excessive amount of resin may drop out and harden inside the glass tube or the T-bar that later may cause failure of potting the module.

The shell was then left for air-drying for overnight to achieve complete hardening of the resin.

**Step 2: Making a fibre bundle and placing it into the shell** (see fig.3-3)

The fibres were about 350 to 370mm long, or about 50 to 60mm longer than the shell at each end to ease moving the bundle during the next steps of potting.

The fibres were carefully selected by visual inspection for any deformation.
Fig.3-3: Placing the fibre bundle into the shell

Once being selected, the fibre was stuck onto a sticky tape at its ends. The next fibre was placed parallel to the previous one at a distance of about 1mm. After the last fibre had been stuck onto the tape, the two strips of the sticky tape were rolled at the same time and at the same pace to ensure the parallel-ness of the fibres being in the bundle. Then the ends of the bundle were tightened up by a string to make the fibres relatively unmoved to each other. The bundle was then pulled gently through the shell.

Step 3: Primary potting at the first end (see fig.3-4)
The primary tube was 30mm long, and 10mm in diameter. The clearance between the T-bar and the primary tube must be large enough so that the primary tube can move freely in the T-bar.
The fibre bundle was pulled aside.
Then about 10g of 5-minute-to-harden Permatex epoxy resin and hardener were mixed thoroughly. The mixed resin was then applied to the fibres at the place as shown on figure 3-4 by a soft plastic rod. Applying the resin to the fibres must be gentle so that not to deform or torture the fibres, and make sure that resin is applied to every single fibre.
Next, on the inside surface of the primary tube was applied a layer of resin. Then it was put through the tightened end of the bundle to cover up the potted part. Care was taken to make sure that no single tiny drop of resin was stuck neither to the outer surface of the primary tube, nor to the inside surface of the T-bar, as it will harm the
mobility of the primary tube in the T-bar. Any excessive amount of the resin can be wipe out at this stage.

Fig.3-4: Primary potting at one end of the module

All the actions of this step should be completed for about 2 to 3 minutes before the resin became hardened.
The potted part was then left for air-drying for at least two hours before moving to the next step.

Step 4: Primary potting at the other end (see fig.3-5)
Before starting potting the other end of the cartridge, the fibre bundle was marked for the distance of 250mm between two ends as shown on figure 3-5.

Fig.3-5: Primary potting at the other end of the module

The bundle with one plotted end was moved toward the other end until the primary tube touched the glass tube.
Then the same procedure was applied for the other end of the module that started at the marked point.
After 2 hours of air-drying the other end, the module was then ready for final potting.

**Step 5: Final potting** (see fig.3-6)
After finishing step 4, the mobility of the primary tubes together with the fibre bundle in the shell, but limited by the glass tube, was checked again, then returned to the position as on figure 3-5.

![Diagram](image.png)

*Fig.3-6: Final potting of the hollow fibre module*

A small amount of well-mixed resin was prepared.
Then a layer of the resin was applied to the external surface of the primary tube on the right hand side, and on the internal surface of the T-bar of the shell on the left hand side (see fig.3-5) in a quick manner. Then the whole bundle together with the potted ends were forced moving toward the left hand side by slightly pressing on the right hand side end and pulling the extended part of the bundle on the left, while keeping the shell unmoved. Moving the bundle ended until it was positioned as on figure 3-6. It must be stressed here that moving the bundle should not cause any stress to the fibres. To achieve that, they must be moved monotonously at the same pace.
Finally, additional resin was applied to the two ends to reinforce the potting as shown on fig.3-6.
The potted module was then left to dry for 48 hours.
Step 6: Edge trimming and module testing

After 48 hours of hardening and drying, the two potted ends of the cartridge were subject to cutting to obtain the final one like on figure 3-7. To achieve that, a very sharp knife was used to cut the edges of the module.

![Fig.3-7: The final potted hollow fibre module](image)

Then the module was allowed 24 hours for further air-drying to achieve a complete stability before being tested for its integrity.

For testing, distilled water was pumped through the fibres at pressure of 100kPa for about 10 minutes. If no leakage of liquid water into the shell side was detected, and the flow was relatively the same through every single fibre (by visual observation), then the module was considered consistent for the experiment. Otherwise, the module was discarded.

It must be noticed that without using the primary tube, but potting directly the resin into the spaces between the fibre bundle and the shell would not result in a satisfactory success. Because if potting in that way, there would be pores filled with air trapped within the bundle, and even between the bundle and the shell. This would lead to leakage through the potted parts, and the module – not usable.

There were several trials of potting hollow fibre modules, but only two types of them were used for the experiment. The modules were named PV375 and PV660 after the codes of the membranes. The specifications of those two modules are listed in table 3-2, and the modules are shown on figure 3-8.
Table 3-2

Specifications of the hollow fibre modules used in the experiment

<table>
<thead>
<tr>
<th>Module</th>
<th>PV375</th>
<th>PV660</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>PV375</td>
<td>PV660</td>
</tr>
<tr>
<td>Number of fibres</td>
<td>n</td>
<td>50</td>
</tr>
<tr>
<td>Total length of module</td>
<td>L_T</td>
<td>mm</td>
</tr>
<tr>
<td>Total effective length</td>
<td>L_E</td>
<td>mm</td>
</tr>
<tr>
<td>Effective area(^a)</td>
<td>A</td>
<td>cm(^2)</td>
</tr>
<tr>
<td>Cross-section flow area of the feed side (inside the fibres)</td>
<td>A_F</td>
<td>mm(^2)</td>
</tr>
<tr>
<td>Cross-section flow area of the brine side (outside the fibres)</td>
<td>A_B</td>
<td>mm(^2)</td>
</tr>
</tbody>
</table>

\(^a\)-the area of the internal surface of the fibres.

Fig.3-8: Hollow fibre modules for lab scale OD system

3.2.3. Setting up the OD system

The OD system elements
The OD system configuration was arranged as illustrated on figure 3-1. The specifications of the elements of the system are as follows:

- 1- Hollow fibre module PV375 or PV660
- 2- Pressure gauge 0-400kPa
- 2'- (skipped)
- 3, 10- Feed and brine pumps Easy-Load Materflex peristaltic pumps with variable speed control, Model 7518-00, tube 0640-2
- 4- 10ml-pipette for flux reading
- 5, 5'- Thermometers 0-100°C mercury thermometer
- 6- Feed tank 1-litre glass bottle
- 7, 7'- Water baths 15-litre water baths with temperature regulator 20-100°C
- 8, 8'- Filters Coarse stainless-steel mesh filter 0.5mm
- 9- Brine tank 5-litre plastic tank
- 11-Tubing 3mm PVC clear tube for the feed side
  6mm PVC clear tube for the brine side
- 12-Flowmeter (on the feed side) Oval gear flowmeter, model GM2RSP-2RD (GPI-USA) coupled with digital Courier Totaliser/Ratemeter, model 53300-405
- Ancillary connectors and fittings.

The feed and brine pumps were peristaltic pumps with variable speed control that allowed controlling the flow rate of the two streams. However, the pressure drop on the feed side was very sensitive to the flow rate and the liquid viscosity, leading to a great fluctuation of flow rate at a specified speed of the pump during the course of running the experiment. Hence, a flowmeter (12) was installed into the feed stream to monitor the flow rate, so that adjustment of the pump speed could be taken on time to ensure the specified flow rate. The GM2RSP-2RD (GPI-USA) series meter has a flow range of up to 500 Litres/Hour for liquid viscosities above 5 centipoises which was in the range of the experiment (7-25 litres/hour). The standard oval rotors of the meter were able to handle a maximum viscosity of 1000 centipoises. The accuracy of the meter was ±1ml/min. However, due to the pulsation by the peristaltic pump, the fluctuation of the monitored flow rate of the feed was ±10ml/min.
On the other side, the brine stream, the pressure drop was negligible, and the flow rate appeared to be constant at a specified speed of the pump. Therefore, it was unnecessary to install the pressure gauge and the flowmeter on the brine stream.

Pump speed and water bath temperature controller calibration

The flow rates of the streams were calculated as a function of the fluid velocity (v) and the cross-sectional area of the stream channel. Calibration of the flow rate were carried out before running the experiment by measuring the volume of liquid by a graduated cylinder over an interval of time, say 30 seconds. Then the speed of the pump was marked on the pump control. The uncertainty of the calibration in this way was ±10ml/min. However, for the feed stream, it was just a relative measure as the high pressure drop affected the elasticity of the pump tube and therefore the flow rate. Hence, a person must be at all time during the experiment to monitor the feed stream flow rate and make adjustment on time.

The water baths with temperature control were used to keep the feed and the brine isothermal to avoid any effect of the so-called membrane distillation created by the liquids' temperature difference. In addition, the water baths also provided the heat to compensate the heat loss through the wall of tubing due to temperature difference between the liquid streams (feed and brine) and the environment. In order to achieve this objective, water in the water bath must be set to a certain temperature level to ensure a certain temperature difference between the feed or brine and the water in the water bath. This level of temperature depends on the experiment temperature, and the streams (feed or brine) as due to different heat exchange areas. To set those levels for the two water baths, some preliminary experiments were carried out, and the temperature levels were marked on the thermostat control of the water baths.
After marking the speed control of the pumps, and the temperature control of the water baths, the OD system was ready for the experiment.

3.2.4. Material

Fig.3-9: Lab scale OD system using hollow fibre module
The materials used in the experiment were as follows:

- For the feed: Glucose powder with purity 100% (Glucodin Energy Powder, Australia).
- For the brine: Analytical grade CaCl$_2$.2H$_2$O crystals 99+% (Aldrich Chemical Company Inc., USA).
- The solvent: Distilled water.

3.3. EXPERIMENTAL DESIGN AND METHODOLOGY

3.3.1. Experimental design

Different factors that affect the flux rate of osmotic distillation process include the feed cross-section flow velocity ($v_f$), the brine cross-section flow velocity ($v_b$), the OD process temperature ($T$), the concentrations ($C$) and compositions of the feed and brine, and the membrane itself. However, including all the factors in a full factorial experiment will dramatically increases the number of treatments. Therefore, some of the factors were eliminated to reduce the number of the treatments to achieve the
objectives of the project within a time limit. The eliminated factors included the concentration and the composition of the brine solution. As it is desirable in OD that the brine solution to have as low as possible the water vapour pressure (or water activity $a_w$) to maximise the flux rate, hence nearly saturated $\text{CaCl}_2$ solution ($45\% \text{ w/w}$) was used as brine in the experiment.

The levels of the factors were chosen on the basis of previous studies, the nature of the OD process, and the capability of the elements of the laboratory OD system as described in part 3.2. Thus, the levels of factors and the conditions of the experiment were defined as given in table 3-3. The experiments were under a full factorial experimental design.

### Table 3-3
Levels of factors and conditions in OD laboratory experiment

<table>
<thead>
<tr>
<th>Module</th>
<th>PV375</th>
<th>PV660</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross flow velocity on the feed side $v_f$ m.$s^{-1}$</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Cross flow velocity on the brine side $v_s$ m.$s^{-1}$</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Temperature $T$ °C</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Feed concentrations (glucose) $C_f$ %</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>(pumped through inside the fibres)</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>Brine solution: CaCl$_2$ 45% w/w $C_s$ %</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Flow direction Co-current, upward</td>
<td>Co-current, upward</td>
<td></td>
</tr>
<tr>
<td>Number of treatments</td>
<td>81</td>
<td>108</td>
</tr>
</tbody>
</table>
The flow direction was chosen as co-current and upward due to the fact that the hollow fibre modules used in the experiment were short, and upward steam could ease air escaping from the module on both sides of the fibres.

The full factorial experiment has the advantages of providing the researcher with more powerful approach to, and more systematic method of, investigating the interaction between the factors and their effects on the response (Snedecor & Cochran, 1989). It is because each observation in a full factorial experiment supplies information of all the factors and the response to one factor is in relation to different levels of other factors (Kuehl, 2000).

In the experiments, glucose was used as the feed due to the fact that glucose and fructose, the main sugar in most fruit juices, have similar viscosity and water activity behaviours (Chirife & Buera, 1997; Chirife, Favetto & Fontan, 1982), however, glucose is more industrially important. In addition, using glucose instead of fruit juices would avoid the fouling problem that is usually associated with fruit juices due to the presence of protein, fat and wax.

Based on the conditions defined in table 3-3, and the configuration of the modules shown in table 3-2, the flow rates for the experiments were estimated as in table 3-4.

**Table 3-4**

*The flow rates applied during the experiments*

<table>
<thead>
<tr>
<th>PV375</th>
<th>Feed</th>
<th>Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Velocity m.s⁻¹</td>
<td>Flow rate ml.min⁻¹</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>264</td>
</tr>
<tr>
<td>PV660</td>
<td>Feed</td>
<td>Brine</td>
</tr>
<tr>
<td></td>
<td>Velocity m.s⁻¹</td>
<td>Flow rate ml.min⁻¹</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>288</td>
</tr>
</tbody>
</table>
3.3.2. Methodology

3.3.2.1. Method of OD flux identification
The OD flux ($J$) is defined as the amount of water ($W$) transferred across a unit membrane area in a unit of time. It is usually expressed in [kg.m$^{-2}$.h$^{-1}$], [l.m$^{-2}$.h$^{-1}$], [kg.m$^{-2}$.s$^{-1}$], or [l.m$^{-2}$.s$^{-1}$]. The OD flux can be identified by measuring either the changes of the feed weight or volume, or the changes of the brine weight or volume over a period of time.

Direct reading of the changes of the feed weight (or alternatively brine weight) requires emptying the feed stream, disconnecting the feed tank from the system after a period of time of running the OD process and weighing. These actions are time-consuming, and the incomplete emptying may lead to inaccuracy of the reading.

Other method of direct reading the feed weight changes is to stop the pump, disconnect the feed tank from the system, and weigh the tank on a scale, while the so-called dead volume remains in the tubing and the membrane module. However, this method for a system using peristaltic pump may result in inaccuracy, because when the pump is stopped, the tubing of the system will hold a certain amount of the dead volume of the feed solution, which certainly depends on the position of the roles of the pump.

In the experiment of this work, a more accurate method was employed. The schematic of the method is illustrated on figure 3-10.

The thermometer, the outlet, the inlet and the 10ml-pipette were potted to the cap of the bottle with epoxy resin. No extension from the bottoms of the pipette into the bottle was allowed, as it would trap bubble inside the feed bottle, and lead to inaccuracy of the reading.

Over a period of time, which was set to be 15 minutes, the amount of water removed from the feed was indicated by the lowering of the liquid level in the pipette; hence the OD flux was estimated. It should be stressed that reading was taken place while the pumps were still in operation. And due to the pulsation by the peristaltic feed pump, the level of the feed in the pipette vibrated up and down; therefore reading of the volume of water removed from the feed could be by the changes of either the lowest
points or the highest points of the level in the pipette. Then that volume was converted into mass of water at the corresponding temperature. Eventually, the mass OD flux was estimated based on the internal area of the fibres in the module.

![Diagram of a 1-litre bottle with a thermometer and 10ml-pipette](image)

**Fig.3-10:** Construction of the feed bottle

In case that the amount of water removed exceeded 10ml in within 15 minutes, an extra amount of water was added to the pipette when the level went down to 9ml. Then the total amount of water removed from the feed was as the addition of 9ml to the new reading.
3.3.2.2. Method of factor level control

The cross flow velocities of the feed and the brine solutions were controlled by the pumps’ speed control as described in the previous section. The cross flow velocity of the feed solutions (through the inside of the fibres) were double-controlled by the flow meter installed in the stream as illustrated on figure 3-1. During the course of the experiment, adjustment to the feed pump speed was taken at the time when the there was a deviation from the set flow rate. The deviations for both streams were in within the limit of ±10ml per minute, which corresponds to ±10/flow rate (table 3-4) or less than 9% of the pre-designed velocity for the lowest flow rate.

The temperatures of the feed and brine solutions were monitored by mercury thermometers. Controlling those temperatures via the water baths’ temperature was preset by a series of preliminary experiments as discussed before. The fluctuations from the pre-designed temperatures were about ±0.5°C.

The concentrations of the two solutions were kept relatively constant during the experiment by using large amount of those solutions relative to the amount of water removed (from the feed) or deposited (to the brine) over the duration of one experimental treatment, which was set at 15 minutes. Thus, the volumes were 1 litre and 4 litres for the feed and the brine solutions respectively.

For the feed solution, distilled water was added back to the bottle via the pipette after every treatment. Therefore, the feed solution concentration was kept almost constant with uncertainty of ±0.5%.

For the brine solution, an amount of CaCl₂, just enough to be diluted by the water deposited over the treatment time to produce 45% solution, was added to the brine tank. Therefore, the brine concentration deviation was just about ±0.2%.
3.3.2.3. Process operation

Solution preparation

Glucose powder with purity 100% (Glucodin Energy Powder, Australia) and analytical grade CaCl₂·2H₂O crystals 99% (Aldrich Chemical Company Inc., USA) were used in the experiment, and the solvent being distilled water.

Moisture content of the glucose powder was checked by conventional moisture content test in an oven at 105°C for 24 hours prior to use. In the mean time, the glucose powder was held in a sealed container. The moisture content of the powder was recorded at 10±0.01%. Distilled water and the glucose powder were weighed by a scale with precision of ±0.01g to prepare solutions of concentrations 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0% w/w. Pearson Square principle was employed in the calculations of the weights the reagents. The preparation by this way may lead to an error of ±0.03%.

Unlike glucose powder, calcium chloride crystals are very hygroscopic that absorbs moisture rapidly. So dilution should take place immediately after opening the sealed CaCl₂·2H₂O container. In order to obtain the intended CaCl₂-equivalent concentration of 45.0% w/w, that concentration was converted into the corresponding molarity m in which molecular weight of 110.98 for CaCl₂ was used instead of 147.02 for CaCl₂·2H₂O. Then the molarity m was multiplied by 147.02 to obtain the necessary weight of CaCl₂·2H₂O for solution preparation. The amount of distilled water was then equal to 1000g deducted by m×(2×18.015) g, which accounts for the presence of 2 molecules of water in the dihydrate calcium chloride molecule. Weighing the calcium chloride encountered an error of ±0.05g, which lead to solution concentration uncertainty of ±0.15%.

Adequate amount of the reagents and distilled water for glucose solution of about 1300g and CaCl₂ solution of about 4500g were used. The sealed containers of those solutions were then shaken well and held in hot water (60°C) for an hour to ensure complete dissociation of all the crystals. The containers were then cooled down by tap water until the desired temperature reached. It should be noted that calcium chloride solution of 45% at 20°C is at critical saturation point; hence any decrease of
temperature below 20°C or presence of any foreign CaCl₂ crystals in 45% solution at 20°C will rapidly cause crystallisation. If re-crystallisation occurred, heating up in hot water must be carried out again. The concentrations were then double-checked by comparing the refractive index with the one obtained from the CRC handbook of physics and chemistry (Lide, 2001).

**Process operation**

The prepared glucose and calcium chloride solutions were transferred into the feed and brine tanks, and connected to the system as shown on figure 3-1. The feed bottle must be tightly sealed. After the feed and the brine tanks were placed into the water baths, it was until temperatures of the two solutions reached the desired ones, the OD process could start. Following was the procedure of the operation:

1. Start the feed pump at low speed to fill up the dead volume of the system.
2. Fill up the feed bottle with the extra feed solution of the same concentration via the pipette.
3. Slowly increase the feed pump speed until the desired flow rate reached. Then continue topping up the feed solution into the pipette until it levels to the top (at zero).
4. Start the brine pump and adjust the speed control to the preset position to obtain the desired flow rate of the brine stream.
5. Allow the system to run for 5 minutes to establish the stability of the operating and hydrodynamic conditions of the system.
6. Top up the pipette with distilled water to replace the amount of water removed from the feed over those 5 minutes.
7. Start the stopwatch (preset at 15 minutes), and take the reading as described before while the pumps were operating.

After one flux had been read, followings were the next step:

8. Set the speed of the two pumps to another pair in a random way.
9. Top up the level of liquid in the pipette with distilled water (with exactly the amount of water removed).

10. Start the stopwatch, and take the reading for the new treatment.

11. Repeat step (8) until one run finish.

One run was conducted at one temperature and one feed concentration with nine variable speed combinations of the feed and brine pumps. There were totally 9 treatments in one run.

After one run finished, the following steps were employed to clean and dry the system:

12. Drain the system and collect the liquids in their respective tanks by disconnecting the suction pipes.

13. Disconnect the tanks from the system, and replace them with two 2-litre tanks (glass cylinders).

14. Fast flushing the two streams of the system by pumping about 2 litres distilled water through each side without recycling. The discharged streams are collected into a bucket.

15. Fill up the tanks with distilled water and recycle the system for 5 minutes, then disconnect the discharge into a bucket until the system is drained.

16. Repeat step (15) for another 3 times.

17. Disconnect the oval gear flow meter from the system as it is recommended not to run with air. Then blow filtered compressed air through the system to dry all the tubing for 15 minutes. The flow meter is dried separately.

18. Disconnect the hollow fibre module from the system, and further dry it with filtered compressed air for another 30 minutes at pressure of about 50kPa to ensure complete drying of the module.

For the next run, a new glucose solution was prepared, while the brine solution was reused. The concentration of the brine was double-checked by its refractive index.
3.4. RESULTS AND DISCUSSION

Laboratory scale experiments were carried out for two hollow fibre modules PV375 and PV660 under the conditions as described in the experimental design. The full sets of the obtained data depicting the effect of the operating factors on the OD flux rate are in Appendix1.

The full set of data was subject to statistical analysis using least significant difference (LSD), analysis of variance (ANOVA) to work out the significance level of the effect of the factors on the response \( J \), the significant interaction between them. Analysis was carried out with the help of Microsoft Excel 5.0 and Statgraphics Plus softwares.

The obtained data were also used for further fundamental studies of the OD process in hollow fibre module that will be discussed in chapter 5.

Followings are some representatives of the date sets to describe the effect of the operating conditions on the flux rate.

1. Effect of feed velocity: Effect of the feed velocity on OD flux for both modules is displayed on figures 3-11 to 3-14.

![Fig.3-11: Effect of feed velocity on flux at 25°C and different feed concentrations for module PV375 (v_f=0.4m/s)](image1)

![Fig.3-12: Effect of feed velocity on flux at 45°C and different feed concentrations for module PV375 (v_f=0.4m/s)](image2)
Fig. 3-13: Effect of feed velocity on flux at 25°C and different feed concentrations for module PV660 ($v_f = 0.4 \text{m/s}$)

Fig. 3-14: Effect of feed velocity on flux at 45°C and different feed concentrations for module PV660 ($v_f = 0.4 \text{m/s}$)

It appears that at 45°C (see fig. 3-12 & 3-14), the feed velocity improves the OD flux rate significantly and consistently, while it is not for the case at 25°C (see fig. 3-11 & 3-13). This fact was expected as at low temperature, the flux rate is low, hence less polarisations at the membrane surfaces, and consequently the flux is less dependent on the feed velocity.

Though operated at different ranges of feed velocities, a rough comparison of the figures on graphs 3-12 and 3-14 shows that the OD flux increases about 0.06 kg/m².h over a feed velocity increase of 0.4 m/s for the feed concentration range 30-40%, while it is about 0.09 kg/m².h over a feed velocity increase of 0.3 m/s for the feed concentration range 45-60%, or averagely an increase of 0.12% of flux rate for PV375 compared to 0.31% for PV660. In other words, the magnitude of feed velocity effect on the OD flux increases at higher concentration range.

2. Effect of brine velocity: Effect of the brine velocity on OD flux for both modules is displayed on figures 3-15 to 3-18.

In general, the graphs show that brine velocity consistently improves the flux rate, and the magnitude of flux dependence on brine velocity increases with the increase of temperature. The explanation for this is based as on the same concept as with the previous case.
temperature. The explanation for this is based as on the same concept as with the previous case.

**Fig.3-15:** Effect of brine velocity on flux at 25°C and different feed concentrations for module PV375 ($v_f=0.4 m/s$)

**Fig.3-16:** Effect of brine velocity on flux at 45°C and different feed concentrations for module PV375 ($v_f=0.4 m/s$)

**Fig.3-17:** Effect of brine velocity on flux at 25°C and different feed concentrations for module PV660 ($v_f=0.4 m/s$)

**Fig.3-18:** Effect of brine velocity on flux at 45°C and different feed concentrations for module PV660 ($v_f=0.4 m/s$)

However, in contrast to the feed velocity, the brine velocity has larger effect on the flux rate at lower feed concentration range. This phenomenon was also expected, as at lower feed concentration range, the flux rate is higher; hence more intensified polarisation at the membrane surface on the brine side, and consequently the flux rate is more dependent on the brine velocity at lower feed concentration range.
3. **Effect of feed concentration**: Effect of the feed concentration on OD flux for both modules is displayed on figures 3-19 to 3-20.

![Graphs showing flux dependence on feed concentration](image)

**Fig.3-19**: Average flux dependence on feed concentration at different liquid velocities and temperatures for module PV375; the error bars show the confidence limits at $\alpha=0.05$.

**Fig.3-20**: Average flux dependence on feed concentration at different liquid velocities and temperatures for module PV660; the error bars show the confidence limits at $\alpha=0.05$.

The plots are based on the mean values of flux at variable liquid velocities, and the error bars are the confidence intervals of the flux at confident level $\alpha=0.05$. They are determined as given in (A2-1) to (A2-4) (see Appendix 2).

The effect of feed concentration (while the brine concentration is remained constant) on OD flux lies on the basis of water vapour pressure difference across the membrane, the OD process driving force. As the feed concentration increases, its water activity (and water vapour pressure) decreases which results in reduction of the driving force; and consequently the OD flux decreases.

From graphs 3-19 and 3-20, it can be seen that the OD flux decay at any temperature over an increment of 5% of the feed concentration from 30 to 40% and from 45 to 55% remains almost constant, and only intensified when the feed concentration increases from 55 to 60%. This behaviour is probably due to the fact that changes of water activity and viscosity of glucose solution over an increment of 5% in the range from 55 to 60% are much larger than that in the range from 30 to 50% as referred to models discussed in chapter 4.
The decay mentioned above also increases as the temperature increases. On average, the flux decay over an increment of 5% feed concentration at 45°C is as much as three times more than that at 25°C. This dependence is due to the changes of the driving force in accordance to water activity dependence of the two solutions on temperature. More clearly, water activity of calcium chloride solution of 45% (which was used in the experiment) increases much more rapidly in comparison to that of glucose solution when the temperature increases (referred to experimental data of water activity in chapter 4); hence larger decrease of the driving force; and consequently larger decay of the OD flux.

4. **Effect of temperature**: Effect of the temperature on OD flux for both modules is displayed on figures 3-21 to 3-22. The plots are of the mean values of the flux over variable feed concentration and liquid velocity ranges, and the error bars indicate the confidence limits at $\alpha=0.05$. Their estimation is based on the equations given in (A2-1) to (A2-4) (see Appendix 2).

![Fig.3-21](image1): Average flux dependence on temperature at different operating conditions for module PV375; the error bars show the confidence limits at $\alpha=0.05$.

![Fig.3-22](image2): Average flux dependence on temperature at different operating conditions for module PV660; the error bars show the confidence limits at $\alpha=0.05$. 
The solid lines on graphs 3-21 and 3-22 are the exponential trend lines. Coefficients of the displayed equations and the R-square can be determined by equations based on (A2-5) to (A2-7), but converted for curvilinear regression (see Appendix2). Good fitness of the trend lines with high values of R-square of more than 0.99 for both modules is a clear indication that the OD flux is exponentially dependent on the temperature. This form of dependence was expected because of the exponential dependence of water vapour pressure of pure water on temperature, hence the driving force of the OD process. Mathematically, it can be described as follows:

For any pair of concentrations of the solutions (in the bulk) on both sides of the membrane with water activity are \( a_{w,t} \) and \( a_{w,s} \) for the feed and brine solutions respectively, their vapour pressures are defined as given in (2-10) (chapter 2); hence the bulk driving force:

\[
\Delta P_b = (a_{w,f} - a_{w,r}) \times P_0 = \Delta a_w \times P_0 = \Delta a_w \times \exp \left( -\frac{B}{T - C} \right) \approx \Delta a_w \times \exp(T)
\]

where \( A \), \( B \) and \( C \) are constant in Antoine equation, and \( T \) is the solution temperature which is equal for both solutions (in the bulk).

The expression clearly shows the exponential relationship between temperature and the driving force of OD process, which pave the foundation for explanation of the exponential effect of temperature on the OD flux.

The above demonstrations of OD flux dependence on operating conditions show a complex relation between them. The significance level of the effect of factors was derived by multi-ANOVA for whole set of data for each modules using Statgraphics Plus software, and are shown on figures 3-23 and 3-24.

The values shown on graphs 3-23 and 3-24 (the standardised effect) are the effects of factors divided by the standard error SE. The effect hereby is defined as the change in the average of the responses (the flux \( J \)) between two factor-level combinations or two experimental settings. For a factor, the effect is the mean response at the high level of the factor minus the mean response at the low level of the factor.
A factor is considered to have significant effect if the standardised effect of that factor exceeds the limit of 2. The plus symbol indicate positive effect, the minus – negative effect.

**Standardized Pareto Chart for Flux J - Module PV375**

A: Temperature
D: Brine velocity
B: Feed Concentration
C: Feed velocity

**Standardized Pareto Chart for Flux J - Module PV660**

A: Temperature
B: Feed Concentration
D: Brine velocity
C: Feed velocity

![Standardized Pareto Chart for Flux J - Module PV375](image)

![Standardized Pareto Chart for Flux J - Module PV660](image)

**Fig.3-24:** The standardised effect of operating conditions on flux for module PV660

The graphs show that temperature has strongest effect on the flux, while the feed velocity has the weakest one and its effect is not significant according to the statistics.
It is interesting to notice that at low feed concentration range as in the case with module PV375, the effect of brine velocity is larger than that of the feed concentration (see figure 3-23), while it is in the opposite for the case with module PV660 where higher feed concentration is concerned (see figure 3-24). It is that because in the case with module PV375, the flux rate is much higher than in the case with module PV660, leading to more intensified polarisations at the membrane surfaces (including the one on the brine side); hence brine velocity is more important than the feed concentration. In the case with module PV660, the feed concentration is in the range that sensitively affects the driving force and viscosity (as discussed before), and the flux is much lower; hence the feed concentration is more important than the brine velocity.

3.5. CONCLUSIONS

The rate of water removal by osmotic distillation in hollow fibre modules under the operating conditions of this study statistically ranged from 1.67±0.02 to 4.73±0.08kg.m⁻².h⁻¹ for module PV375, concentrating glucose solutions from 30 to 40°Brix; and 1.00±0.02 to 2.87±0.05kg.m⁻².h⁻¹ for module PV660, concentrating glucose solutions from 45 to 60°Brix. If considering the experimental conditions such as temperature, feed and brine solutions composition, and the membrane thickness of previous studies, the flux rates obtained in this study were comparably similar to the ones obtained by Sheng, Johnson & Lefebvre (1991), Durham (1992), Vahdati & Priestman (1994), Gostoli (1999), and Bailey et al (2000).

Temperature appears to pose the strongest effect on the OD flux. This effect seems to obey the exponential law. The temperature effect is mainly due to the improvement of the driving force and reduction of solution viscosity.

Feed concentration and brine velocity have significant effect on OD flux, too. However, the order of importance of those two factors depends on the feed concentration range.
At lower feed concentration range, the brine velocity is more important, while it is the opposite at higher feed concentration range. The effect of the feed velocity on flux is not significant, especially at low feed concentration range. However, it tends to be significant at high feed concentration range.
CHAPTER 4: PREDICTION OF WATER ACTIVITY AND VISCOSITY OF GLUCOSE AND CALCIUM CHLORIDE SOLUTIONS

4.1. INTRODUCTION

In osmotic distillation, heat and mass transfer are spontaneous processes with complex interactions (Gostoli, 1999; Courel et al, 2000; Mengual et al, 1993). Therefore, to describe the osmotic distillation process, quantitative characterisation of the liquid flows, the heat and mass transfer, and the driving force in relation to the solution composition and thermodynamic conditions is required. In other words, knowledge of the physical properties of solutions such as water activity, viscosity, thermal conductivity, specific heat, etc. is required.

As aqueous glucose and calcium chloride solutions were involved in the experiment, their physical properties are important for characterising the flows, and the heat and mass transfer processes in osmotic distillation. Mathematical expression of those properties in relation to the independent variables of the solutions such as concentration and temperature has a crucial role in the modelling of osmotic distillation process.

This section is an attempt to derive models for determination the water activity, and viscosity of aqueous glucose and calcium chloride solutions. Models derived in this section are based on experimental data or on the analysis of data from the literature. Other properties such as diffusivity, thermal conductivity, etc. are gathered from the literature, and listed in appendix 3.

4.2. WATER ACTIVITY OF GLUCOSE AND CALCIUM CHLORIDE SOLUTIONS

Water activity $a_w$ of a solution is a quantity through which water vapour pressure can be determined, hence, the water vapour pressure difference across the membrane or the driving force in osmotic distillation.

Data of water activity at 25°C of glucose in relation to its solute content have been well documented in literature (Chirife, Favetto & Fontan, 1982). This is
also true in the case of CaCl₂ (Robison & Stokes, 1959). However, the effect of temperature on water activity of these two solutions has not yet been fully studied. Therefore, a study of the \( a_w \) of glucose and CaCl₂ solution in relation to temperature and solute content would be useful and beneficial for controlling and modelling the osmotic distillation process as well as other osmotic processes.

### 4.2.1. Theory

As pointed out by Prausnitz, Lichtenthaler and Azevedo (1986), water activity \( a_w \) can be defined as:

\[
a_w(T, P, x) = \gamma_w(T, P, x)x_w = \frac{f_w(T, P, x)}{f_w^0(T^0, P^0, x^0)} \tag{4-1}
\]

Where \( x_w \) is the mole fraction of water; \( \gamma_w \) – activity coefficient of water; \( f_w \) - fugacity of water in the system at the current condition; \( T, P, x \) - temperature, pressure and mole fraction of solute of the system; and the superscript \( (0) \) refers to the reference condition.

Assuming the ideality of the behaviour of gaseous water at ambient temperature and atmospheric pressure, one can take the ratio of the fugacities as equal to the ratio of partial pressures of water. Hence, the \( a_w \) of a system can be defined as:

\[
a_w = \frac{P_w}{P_w^0} = \frac{RH}{100} \tag{4-2}
\]

Where \( P_w; P_w^0 \) are the vapour pressures of water in the system and of pure water at the same temperature; RH is the equilibrium relative humidity of the air layer just above the system.

Several theoretical and empirical models have been developed to predict \( a_w \) of electrolyte and non-electrolyte solutions as reviewed by Sereno et al (2001). Details of the models are described by individual authors, but some of them are summarised by Bell & Labuza (2000). Most of the late models are complicated and requiring other data inputs. Among them, the Norrish model,
while simple, is the most suitable for the determination of water activity of solutions in the intermediate moisture range (Chirife, Favetto & Fontan, 1982; Leiras, Alzamora & Chirife, 1990; Bell & Labuza, 2000).

In our study, the Norrish equation has been employed to describe the effect of solute content on \( a_w \) of a solution. For a multi-component solution, the water activity can be determined by:

\[
\ln(a_w) = \ln(X_w) + \left( K_i^{0.5} X_i + K_{i+1}^{0.5} X_{i+1} + \ldots \right)^2
\]  \hspace{1cm} (4-3)

where \( K_i \) are constants \((i=2 \text{ to } n)\); \( X_w \) is the mole fraction of water; and \( X_i \) is the mole fraction of solute \((i)\) in the solution.

For a single solute solution as in the case of our study, equation (4-3) can be written as follows:

\[
\ln(a_w) = \ln(X_w) + K_2 X_2^2
\]  \hspace{1cm} (4-4)

or

\[
\ln \left( \frac{a_w}{X_w} \right) = K_2 X_2^2
\]  \hspace{1cm} (4-5)

Hence, a plot of \( \ln(a_w/X_w) \) versus the square of \( X_2 \) will be a straight line with the slope \( K_2 \). It is true for non-electrolyte solutions over the whole range of concentrations (Chirife, Favetto & Fontan, 1982). However, it is worth noting that \( K_2 \) values for electrolyte solutions are constant over a specific range of concentrations, but it may vary when the solution concentration switches from one range to another (Bell & Labuza, 2000). An intercept, therefore, should be included in the equation when the solute content range starts from a point other than zero. Hence equation (5) can be modified as follows:

\[
\ln \left( \frac{a_w}{X_w} \right) = K_2 X_2^2 + A
\]  \hspace{1cm} (4-6)

Where \( A \) is the intercept.

Beside the solute content, temperature also affects the \( a_w \) of a solution. From the well-known Gibbs-Helmholtz equation described by Prausnitz, Lichtenthaler and Azevedo (1986), and Raal and Mühlbauer (1998):
Water Activity and Viscosity Prediction

\[ \left[ \frac{\partial (G^E / RT)}{\partial T} \right]_{p,x} = - \frac{H^E}{RT^2} \quad (4-7) \]

(Where \( G^E \), \( H^E \) are excess Gibbs free energy and excess enthalpy of a solution, J, respectively; \( R \) is the ideal gas constant J/mol.K)

The dependence of the activity coefficient (and water activity) on temperature can be derived by writing (4-7) on the partial property basis in noting that:

\[ \ln(y_i) = \frac{g_i^e}{RT} \quad (4-8) \]

Replacing (4-8) into (4-7), we obtain:

\[ \left[ \partial \ln(y_w) \right]_{p,x} = - \frac{h^e}{R} \frac{\partial T}{T^2} \quad (4-9) \]

where \( g_i^e \); \( h^e \) are the molar Gibbs free energy and molar excess enthalpy or partial molar heat of mixing respectively (J/mol).

Integrating the above equation with respect to constant pressure and solute content along the path of temperature \( T_1 \) to \( T_2 \), and with regard to equation (4-1), one can derive the dependence of water activity of a solution on temperature as follows:

\[ \ln \left( \frac{a_{w1}}{a_{w2}} \right) = \frac{h^e}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4-10) \]

where \( a_{wi} \) is the water activity at temperature \( T_i \) (i=1,2).

Equation (4-10) is the well-known Clausius-Clapeyron equation.

From equation (4-10) it can be seen that a plot of \( \ln(a_w) \) versus \( 1/T \) will be a straight line and the slope is the value of \( (h^E/R) \). Therefore, if the water activity of a solution of a specified concentration is measured at two different temperatures, at least, then it can be determined at any given temperature by interpolation or extrapolation in a range of \( \pm 10 \text{K} \).

In our study, four temperatures were employed to determine the best-fit slope \( (h^E/R) \) for different concentrations of glucose and calcium chloride solutions.
4.2.2. Experimental water activity measurement

Solution preparation

Glucose and calcium chloride solutions were prepared by the procedure already described in chapter 3 (see pages 48, 53, 54 for sources and preparation).

About 200g of each of 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0% w/w glucose solutions, and 27.0, 31.5, 36.0, 40.5, 45.0% w/w of CaCl₂ were kept tightly closed in a plastic screw-capped container. The container was then shaken well and held in hot water (60°C) for an hour to ensure dissociation of all the crystals. It should be noted that calcium chloride solution of 45% at 20°C is at critical saturation point; hence any decrease of temperature or presence of any foreign CaCl₂ crystals would rapidly cause crystallisation. The concentrations were then double-checked by comparing the refractive index with the one obtained from the CRC handbook (Lide, 2001).

All the containers were then kept in a water bath at the temperatures of 20, 25, 30, 35°C for 3 hours prior to any aw measurement.

Water activity measurement

The instrument used in the study was an "AQUA LAB" water activity meter, model series 3TE by "Decagon Devices, Inc. Pullman", Washington 99163, USA. This is a temperature-controlled water activity meter with a built-in infrared temperature sensor and a cooled-mirror dewpoint sensor. Water activity of the sample is determined on the basis of the dewpoint temperature of the air at equilibrium state in the sealed chamber and the sample surface temperature. These temperatures are measured by the sensors. The equipment operates within the temperature range of 5-43°C, and measures the aw values from 0.030 to 1.000 with a precision of ±0.001.

After 30 minutes of warming up the water activity meter, standard salt solutions were used to confirm the proper functioning of the instrument.

To minimise temperature drop of a sample when being placed in the holder, the spare holder was held in front of an air heater while the other one was in use.
Samples were randomly taken and filled up to half of the holder for measurement. The measurements were in triplicate and here means were taken for analysis.

The interval between measurements of the samples must be at least 15 minutes to allow the deposited moisture to escape from the instrument thus ensuring the accuracy of the readings.

4.2.3. Results and Discussion

The experimental measurements of the $a_w$ of the two solutions of different concentrations and temperatures are tabulated in table 4-1. The obtained data indicate that temperature and solute content of a solution have significant effect on water activity, but the effect of the solute content is predominant.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>$a_w$ of glucose solution</th>
<th>Temperature (°C)</th>
<th>$a_w$ of CaCl₂ solution</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>30.0</td>
<td></td>
<td>0.954</td>
<td>0.955</td>
<td>0.956</td>
</tr>
<tr>
<td>35.0</td>
<td></td>
<td>0.942</td>
<td>0.943</td>
<td>0.944</td>
</tr>
<tr>
<td>40.0</td>
<td></td>
<td>0.927</td>
<td>0.929</td>
<td>0.930</td>
</tr>
<tr>
<td>45.0</td>
<td></td>
<td>0.910</td>
<td>0.912</td>
<td>0.913</td>
</tr>
<tr>
<td>50.0</td>
<td></td>
<td>0.891</td>
<td>0.891</td>
<td>0.893</td>
</tr>
<tr>
<td>55.0</td>
<td></td>
<td>0.865</td>
<td>0.867</td>
<td>0.869</td>
</tr>
<tr>
<td>60.0</td>
<td></td>
<td>0.835</td>
<td>0.837</td>
<td>0.839</td>
</tr>
</tbody>
</table>

For comparison purpose and for prediction of water activity of the two solutions at 25°C as a reference, the $K_2$ value in equation (4-5) for glucose solution was taken as equal to -2.11±0.11 obtained from Chirife, Favetto & Fontan (1982) as recommended by Sereno et al (2001), while $K_2$ for CaCl₂ was obtained from the best fit analysis of the data of Robison & Stokes (1959) as shown on figure 4-1. Determination of $K_2$ and $r^2$ were by the equations as given in (A2-5) to (A2-7) (see Appendix 2).
For $m=0.75$, $K_2 = -86.68^E$; $r^2 = 0.9984$
For $m=7.5-10$, $K_2 = -44.33^{E1.2}$; $A = 2.9$, $r^2 = 0.9977$

Fig. 4.1: Linear regression between ln($a_w/X_w$) and square of solute content $X_2^2$ of CaCl$_2$ at 25°C.

(m: solute molarity; $K_2$, $A$: constants in equation (6); $r^2$: coefficient of determination)

By using the $K_2$ values shown on figure 4-1 for CaCl$_2$ (where $m$ is the molarity of solute, $r^2$ is the square of the correlation coefficient), and $K_2=-2.11$ for glucose (Chirife, Favetto & Fontan; 1982), the measured $a_w$ at 25°C and the predicted ones are in very good agreement as shown on table 4-2.

Table 4-2
Comparison between measured and predicted values by equation (4-6) of $a_w$ at 25°C.

<table>
<thead>
<tr>
<th>Glucose solution</th>
<th>CaCl$_2$ solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.955</td>
</tr>
<tr>
<td>35</td>
<td>0.943</td>
</tr>
<tr>
<td>40</td>
<td>0.929</td>
</tr>
<tr>
<td>45</td>
<td>0.912</td>
</tr>
<tr>
<td>50</td>
<td>0.892</td>
</tr>
<tr>
<td>55</td>
<td>0.867</td>
</tr>
<tr>
<td>60</td>
<td>0.837</td>
</tr>
</tbody>
</table>

($^a$ Chirife, Favetto & Fontan; 1982; $^b$ This work)
The effect of temperature on water activity of the two solutions is shown in figures 4-2 and 4-3, and the slopes \( k^E/R \) derived from the best-fit regression are listed in table 4-3. It should be mentioned that temperature readings on the water activity meter differed from the preset one by ±0.2°C even though the temperatures of the solutions had been carefully monitored during the experiment.

![Graph showing effect of temperature on water activity](image)

**Fig. 4-2 – Effect of temperature on \( a_w \) of glucose solution**

### Table 4-3

**The best-fit constant \( k^E/R \) along the path 20°C to 35°C**

<table>
<thead>
<tr>
<th>Glucose solution</th>
<th>C%</th>
<th>( k^E/R ) (K)</th>
<th>( r^2 )</th>
<th>CaCl₂ solution</th>
<th>C%</th>
<th>( k^E/R ) (K)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
<td>-16.95</td>
<td>0.846</td>
<td></td>
<td>27.0</td>
<td>-102.16</td>
<td>0.891</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-19.15</td>
<td>0.999</td>
<td></td>
<td>31.5</td>
<td>-138.32</td>
<td>0.961</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-19.58</td>
<td>0.844</td>
<td></td>
<td>36.0</td>
<td>-219.91</td>
<td>0.966</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-25.82</td>
<td>0.970</td>
<td></td>
<td>40.5</td>
<td>-356.24</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-28.19</td>
<td>0.882</td>
<td></td>
<td>45.0</td>
<td>-476.48</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>-35.47</td>
<td>0.983</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-43.12</td>
<td>0.999</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- the slopes \( k^E/R \) and \( r^2 \) were estimated by (A2-5) to (A2-7), Appendix 2
- \( r^2 \) is the coefficient of determination
Fig. 4-3: Effect of temperature on $a_w$ of CaCl$_2$ solution

The data illustrate a trend that absolute values of ($h^E/R$) depend on the nature of the solute and increase as the concentration of the solution increases. Analysis of the data indicates a very good correlation between ($h^E/R$) and concentration as shown on figures 4-4 and 4-5. Knowing that when solute concentration approaches 0% the value of ($h^E/R$) approaches 0, too. In other words, the intercepts of the derived equations must be 0.

Fig. 4-4: Effect of glucose concentration C on ($h^E/R$)

Fig. 4-5: Effect of CaCl$_2$ concentration C on ($h^E/R$)
The derived equations to describe the relationship between the \((h^E/R)\) values and the concentration \(C\) of the two solutions are as follows:

For glucose:  
\[
\frac{h^E}{R} = -446.52C^3 + 349.34C^2 - 120.92C \tag{4-11}
\]

For \(\text{CaCl}_2\):  
\[
\frac{h^E}{R} = -9561.7C^3 + 2853.8C^2 - 422.4C \tag{4-12}
\]

Where \(C\) is the solute content of the solutions in decimal figures.

Application of equations (4-11) and (4-12) show consistency of the values of \((h^E/R)\) when extrapolating to low concentration of the two solutions. In addition, the \(r^2\) values are more than 0.99 (see fig.4-4 and 4-5), the derived equations can be successfully used to predict the temperature effect on water activity of both solutions.

If the mole fraction of water \(X_w\) and the mole fraction of solute \(X_i\) of the two solutions in equation (4-6) are calculated by the solutions’ concentration \(C\) (in decimal figures), then combining equations 4-6, 4-10 and equations 4-11, 4-12 with \(T_1=25^\circ\text{C}\) as the reference temperature will yield the final equations for water activity prediction for the two studied solutions at any given concentration and temperature as follows:

For glucose solution: (equation 4-13)

\[
a_w = \frac{1-C}{1-0.9C} \cdot \exp\left[-2.11 \left(\frac{C}{10-9C}\right)^2\right] \cdot \exp\left[\left(-446.52C^3 + 349.34C^2 - 120.92C\right)\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]
\]

For \(\text{CaCl}_2\) solution:

- if \(m=0-7.5\) (equation 4-14)

\[
a_w = \frac{1-C}{1-0.83766C} \cdot \exp\left[-86.68 \left(\frac{C}{6.16-5.16C}\right)^2\right] \cdot \exp\left[\left(-9561.7C^3 + 2853.8C^2 - 422.4C\right)\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]
\]

- if \(m=7.5-10\) (equation 4-15)

\[
a_w = \frac{1-C}{1-0.83766C} \cdot \exp\left[-44.33 \left(\frac{C}{6.16-5.16C}\right)^2 - 0.522\right] \cdot \exp\left[\left(-9561.7C^3 + 2853.8C^2 - 422.4C\right)\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]
\]

The developed equations successfully predict water activity of glucose and calcium chloride solutions with good agreement to the measured ones. For glucose solution, the average error is in a just a small margin of \pm 0.001. For
calcium chloride solution this figure is ±0.006. Though a bit higher, this accuracy is considered acceptable.

4.2.4. Conclusion

The results reported in this section confirm that water activity of electrolyte and non-electrolyte solutions in the intermediate concentration range can be measured and predicted by applying the Norrish equation.

The value of $(\ln R/2)$ correlates very well with the solute content of the solutions, hence the derived polynomial equations can be used to describe the temperature effect on water activity.

Application of the models shows that temperature has a significant effect on water activity of a solution when its $a_w$ value is below 0.975, or at a concentration higher than 20% and 7% for glucose and calcium chloride solutions respectively.

Equations 4-13, 4-14 and 4-15 can be applied to successfully determine the water activity of glucose and calcium chloride solutions over the studied concentration and temperature ranges. The equations can also be used to predict water activity of these two solutions up to temperature of 45°C. Outside of these ranges, the application of the models could not be confirmed due to lack of data in the literature and the incapability of the instrument for water activity measurement available for this study.

Finally, it is important to note that instrument calibration, proper solution preparation, temperature control, and time between observations are essential features to ensure the accuracy of $a_w$ reading.

4.3. VISCOSITY OF GLUCOSE AND CALCIUM CHLORIDE SOLUTIONS

Viscosity is an important property of a fluid to characterise its flow in a channel, as well as heat and mass transfer in many food-processing processes.
Data of viscosity at different concentrations and temperatures for glucose and calcium chloride solutions, the fluids involved in our experiment, have been currently well documented in the literature. However, they are not expressed or unsatisfactorily expressed mathematically in relation to solute content and temperature, but in the form of raw data. Therefore, this section is dealing with development of models for viscosity prediction for those two particular solutions to suit the purpose of modelling the osmotic distillation process.

4.3.1. Definition

When a stress or force per unit area is applied to a fluid in a channel, it will flow at a velocity that increases with increasing stress. The fluid then exhibits a resistance to the flow. And the resistance is then characterised by a fluid property called viscosity.

In laminar flow, the fluid can be considered as a body of adjacent layers that slide past one another at a velocity of $\Delta v_z$ without eddies or swirls like playing cards with area A (fig.4-6). If the force required for the movement of the layers is $F$, then the fluid viscosity $\mu$ is defined as:

$$\frac{F}{A} = \mu \frac{\Delta v_z}{\Delta y} \quad (4-17)$$

Let $\Delta y$ approaches zero, then (4-17) can be written as:

$$\tau_{yz} = \mu \frac{dv_z}{dy} \quad (4-18)$$

where $\tau_{yz} = F/A$ is the shear stress or force per unit area in [N.m-2]. The fluid viscosity has the dimension of [Pa.s] in the SI system.

Fig.4-6: Illustration of the sliding layers in a fluid flow
Based on the behaviour of the flow, a fluid can be classified as *Newtonian fluid* if the viscosity is constant and independent of the shear rate, the ratio of the shear stress $\tau_{\nu}$ to the velocity gradient $\frac{dv}{dy}$; and *non-Newtonian fluid* when the viscosity is not constant and dependent on the shear rate.

*Relative viscosity* $\mu_r$ of a solution is the ratio between its viscosity $\mu$ and the viscosity of pure solvent (water) at the same temperature $\mu_0$.

$$\mu_r = \frac{\mu}{\mu_0} \quad (4-19)$$

### 4.3.2. Models for viscosity of glucose and calcium chloride solutions

The viscosity of aqueous calcium chloride, a strong electrolyte, in the low concentration region from 0.002 to 0.1M can be described by Jones-Dole equation (Stokes & Mills, 1965; Waghorne, 2001; Goldsack & Franchetto, 1977):

$$\mu_r = \frac{\mu}{\mu_0} = 1 + A\sqrt{m} + Bm \quad (4-20)$$

where $\mu$ is the viscosity of the solution; $\mu_0$ is the viscosity of pure water at the same temperature; $\mu_r$ is the relative viscosity of CaCl$_2$ solution; $m$ is the mole fraction of the solute in solution; $A$ and $B$ are constants.

The $A$ constant describes the inter-ionic attraction in the solution. It can be determined theoretically or experimentally. The constant $B$ is an empirical constant.

The $A$ and $B$ constants can be determined experimentally by plotting

$$\left(\frac{\mu}{\mu_0} - 1\right)\sqrt{m} \text{ versus } \sqrt{m}.$$ The intercept is $A$, and the slope – being $B$, or they can be determined by direct multi-regression analysis for the relation of $\mu_r$, and $\sqrt{m}$ and $m$ with the help of JMP In 4.0 software (see Appendix 2).

However, our interest is the viscosity of aqueous calcium chloride solution in the range from 1M to saturation that is usually applied in osmotic distillation. In such concentration region, the dependence of viscosity to temperature can be
represented by Andrade’s semi-empirical equation (Stokes & Mills, 1965; Goldsack & Franchetto, 1977; Korotkov, Kuznetsova & Ovchinnikova, 1999):

\[ \mu = \mu_0 \cdot \exp \left( \frac{A}{T} \right) \]  

(4-21)

where \( \mu_0 \) and \( A \) are constant at a specific concentration.

The viscosity of electrolyte solution also relates to the concentration by exponential law, which is attributed to Suryanarayana and Venkatensen (Stokes & Mills, 1965):

\[ \mu = \mu_0 \cdot \exp \left( B \cdot m \right) \]  

(4-22\(^a\))

where \( \mu_0 \) and \( B \) are constants at a specific temperature; \( m = m/m_s \) – the ratio of the mole fraction to saturation mole fraction of solute at the same temperature.

Application of (4-22\(^a\)) is inconvenient due to the fact that it requires data input of solubility of the solute at different temperatures. In a similar sense, it must be noticed the complication of use of the model developed by Goncalves and Kestin (1979) as given in (4-22\(^b\)) as it requires too many computations.

\[ \mu_{\text{CaCl}_2} = \sum_{k=0}^{4} \sum_{j=0}^{3} a_{kj} m^k T^j \]  

(4-22\(^b\))

where \( a_{kj} \) are constant \((k=0, 1, 2, 3, 4; j=0, 1, 2, 3; or 5 \times 4 = 20 \text{ of them})\).

Aimed at simpler, but effective model, consideration was directed to model of equation (4-21). In this equation, \( \mu_0 \) and \( A \) are constant at a specific concentration, but they may change and correlate to the solute content. Thus, equation (4-21) can be considered as a model to correlate the viscosity of CaCl\(_2\) solution to its temperature and concentration.

Based on (4-21), similar equations were proposed to correlates the viscosity data of calcium chloride solution to both concentration and temperature as given in (4-23, 4-24).

Power law:

\[ \mu = \mu_0 \times m^a \times \exp \left( \frac{B}{T} \right) \]  

(4-23)
Exponential law:

\[
\mu = \mu_0 \times \exp(A \cdot m) \times \exp\left(\frac{B}{T}\right)
\]  \hspace{1cm} (4-24)

where \(m\) is the solute molarity of the solution, \(\mu_0\), \(A\) and \(B\) are constants.

For a number of fruit juices, researches of Ibarz group showed that the relation of viscosity to temperature and concentration was as the same as illustrated in equations (4-21), (4-23) and (4-24) though the concentration was expressed in a different way such as °Brix (Ibarz, Gonzales, & Esplugas, 1994; Ibarz et al, 1992; Ibarz & Pagán, 1987). Therefore, such relation can be applied for glucose solution.

Chirife and Buera (1997) found the relation of the relative viscosity of glucose solution and its solute content at 20°C as given in (4-25). Unfortunately, this relation was not extended to other temperatures.

\[
\mu_r = 0.954 \cdot \exp\left(\frac{27.93m}{55.51 + m}\right)
\]  \hspace{1cm} (4-25)

Therefore, fitting data obtained from the literature for the viscosity of calcium chloride and glucose solutions was based on the proposed equations (4-21), (4-23) and (4-24).

### 4.3.3. Results of data fitting

The raw data for viscosity of calcium chloride were obtained from Wahab and Mahruddin (2001), while the ones for glucose solution - from the handbook of sugars (Pancoast & Junk, 1980, pp.271).

Data of viscosity were fitted into equation (4-21) by plotting \(\ln(\mu)\) and \(1/T\) at the specified concentrations. The plot was a set of straight lines with intercepts \(\ln(\mu_0)\) and slopes \(A\) (figures 4-7 and 4-8) (see Appendix 2 for determination the derived regression equations).
The slopes and the intercept of the straight lines on fig.4-7 and fig.4-8 were then converted into $\mu_0$ and $A$, and plotted against the concentrations of the two solutions. It was found that $\mu_0$ and $A$ of both calcium chloride and glucose solutions were very well correlated to the concentration $m$ expressed in molarity, though different trends and patterns. The plots and the derived correlations are presented on figures 4-9 to 4-12.
The model based on equation (4-21) was assigned as model1 for both solutions.

**Model1**

For aqueous CaCl$_2$ solution (equation 4-26):

$$\mu = 10^{-3}\cdot\left(-0.3098m^2 + 2.3155m + 0.1257\right)\cdot\exp\left(\frac{35.576m^2 - 156.91m + 2032}{T}\right)$$

For aqueous glucose solution (equation 2-27):

$$\mu = 10^{-3}\cdot2.0041\exp(-0.4324m)\cdot\exp\left(\frac{242.58m + 1889.3}{T}\right)$$

Fitting data of the viscosity of CaCl$_2$ and glucose solution into the power law (4-23) shows poor correlation to concentration and temperature with $R^2=0.64$ and 0.94 respectively. Therefore, the power law is considered unsuitable and discarded.

Data were also fitted into equation (4-24) by a multi-way regression between $\ln(\mu)$ and m & $1/T$ with the help of JMP-In software. The correlation was much better than the previous model with $R^2=0.99$ and 0.98 for CaCl$_2$ and glucose solution respectively.

The model based on equation (4-24) was assigned as model2 for both solutions.
**Model2**

*For aqueous CaCl2 solution (equation 4-28):*

\[ \mu = 10^{-3} \times 0.7934 \times \exp(0.3719m) \times \exp(2068.075/T) \]

*For aqueous glucose solution (equation 4-29):*

\[ \mu = 10^{-5} \times 4.3565 \times \exp(0.3244m) \times \exp(3116.436/T) \]

All models express viscosity in centipoise cP.

**4.3.4. Model evaluation**

In order to evaluate the accuracy and precision of the two models, the predicted viscosity by them were compared to the ones obtained from the literature by plotting them one against another.

For CaCl2, the models were compared to the experimental viscosity of Wahab and Mahiuddin (2001). The comparison is presented on figures 4-13.

For glucose, the models were compared to the data from Pancoast and Junk (1980), and the derived model of Chirife and Buera (1997) (see equation 4-25). The comparisons are shown on figures 4-14 and 4-15.

It was observed that outside of the range specified here on fig.4-13, individual pairs might differ from each other up to 12%. However, the models satisfactorily predicted the viscosity of aqueous CaCl2 solution within the specified range with an uncertainty up to 0.55±0.62% for model1 and 0.14±0.87% for model2 in comparison to the original data according to the statistics with 95% confidence level. In absolute value, about 90% of the pair differences were below 0.25cP for both models. However, it must be pointed out here that model1 for CaCl2 solution is valid only for molarity m<6.63. If m>6.63, model2 is appropriate and applicable. Therefore, model2 was accepted for viscosity prediction of CaCl2 solution.

For glucose solution, model1 over-predicted with an uncertainty of 5.93±2.22%, while model2 under-predicted with 4.58±4.70% in comparison to the original data according to the statistics with 95% confidence level. In
absolute value, 83% of the pair differences were below 0.50cP for model1, while about 75% of the pair differences were below 0.70cP for model2. This indicated that the model1 was considered more acceptable than model2.

**Fig.4-13:** Comparison of viscosities predicted by the derived models and the experimental ones of Wahab and Mahiuddin (2001) for aqueous CaCl₂ solution of m=0.5-6.63; T=20-45°C

**Fig.4-14:** Comparison of viscosities predicted by the derived models and the ones obtained from Pancoast and Junk (1980) for aqueous glucose solution of m=1.5-10.5; T=25-75°C
When compared to the model of Chirife and Buera (1997) at temperature of 20°C, model1 appeared to be a consistent model for glucose solution viscosity (see fig. 4-15). The discrepancy between model1 and Chirife and Buera (1997) model was only 2.0±2.1% according to the statistics. Therefore, model1 was chosen as the final glucose solution viscosity predictor.

![Graph showing comparison of viscosity predictions for different models](image)

**Fig.4-15:** Comparison of the derived models and the model of Chirife and Buera (1997) for glucose solution viscosity at 20°C.

In conclusions, the models developed here for prediction of the viscosity of glucose and calcium chloride solution can be adopted with satisfaction. Model1 was accepted for CaCl₂, while model2 was accepted for glucose solution. The poorer accuracy of the models for glucose solution perhaps reflects the need of a more comprehensive set of data.

### 4.4. CONCLUSIONS

Models for prediction of water activity and viscosity of aqueous glucose and calcium chloride solutions in relation to their concentration and temperature were developed.
Models for water activity for both solutions showed very good prediction with the largest difference being only ±0.006.

Very good agreement was also found between the experimental viscosity of Wahab and Mahiuddin (2001) and the predicted ones by the models in this section. Model 2 was found to be appropriate over range of concentration and temperature.

Models for viscosity of glucose solution, however, yielded a poorer accuracy in comparison to the one for calcium chloride solution, but still acceptable and useful. The poor accuracy was due to the very few data obtained from the literature. Comparison over wide range of concentration and temperature, and the comparison to the derived model of Chirife and Buera (1997) at 20°C found that model 1 was more acceptable than model 2 for glucose solution.
CHAPTER 5: MODELLING THE OSMOTIC DISTILLATION PROCESS IN HOLLOW FIBRE MODULES

5.1. INTRODUCTION

In osmotic distillation, water is removed from the feed in the form of water vapour through the membrane pores. Several models for water vapour transport such as Ordinary Diffusion, Knudsen, Poiseuille, or a combination of them such as the model of Scholfield, and Dusty-Gas model have been proposed. However, there is a need of validation of the models for a particular membrane at particular conditions.

In the OD process, the flux, the rate of water removal from the feed, is significantly dependent on the operating conditions such as the composition and concentration of the feed and brine, their cross-flow velocities, the temperature, and the membrane structure as shown in the previous section. There are also hidden factors that affect the performance of the OD process. Such factors are the physical properties of the fluids involved in the OD process as they directly affect the profiles of fluid temperature and concentration at the membrane surface. Thus, the flux relation to those factors is further complicated.

The presence of temperature and concentration polarisations inhibits the flux rate in osmotic distillation. The extent to which they affect the flux rate varies with the operating conditions. Therefore, their contribution to the flux reduction has to be evaluated quantitatively.

The objectives of this section are as follows:

- To validate the mass transfer and the water vapour transport models.
- To quantify the effect of temperature and concentration polarisations in OD.
- And to develop models for OD flux prediction.

5.2. LITERATURE REVIEW
The osmotic distillation flux \( J \) is proportional to the driving force, the water vapour pressure difference across the membrane surfaces, \( \Delta P_m \); and the membrane permeability or the so-called mass transfer coefficient of the membrane \( K_m \). Hence, the basic equation used to describe the flux in osmotic distillation is given by (5-1).

\[
J = K_m \times \Delta P_m = K_m \times (P_{f,m} - P_{s,m}) \quad (5-1)
\]

- \( P_{f,m} \) - Water vapour pressure at membrane surface on the feed side
- \( P_{s,m} \) - Water vapour pressure at membrane surface on the brine side

However, the water vapour pressures at the membrane surfaces are not readily measurable. They depend on the concentrations and compositions of the liquids as well as the temperatures at both sides of the membrane surfaces. Therefore, a more practical equation for OD flux determination is given by (5-2) (Mengual et al, 1993; Courel et al, 2000a).

\[
J = K \times \Delta P_b = K \times (P_{f,b} - P_{s,b}) \quad (5-2)
\]

- \( K \) - the global mass transfer coefficient of the system.
- \( P_{f,b} \) - Water vapour pressure in the bulk on the feed side
- \( P_{s,b} \) - Water vapour pressure in the bulk on the brine side

The global mass transfer coefficient \( K \) is dependent on the physical properties of the solutions, and the hydrodynamic conditions of the system.

Determination of coefficient \( K \) will be discussed at the end of this section.

5.2.1. Mass transfer at the membrane surfaces in osmotic distillation

As reviewed in chapter 2, in osmotic distillation, the process of removing water from the feed involves the evaporation of water at the membrane surface on the feed side, the transport of water vapour through the membrane pores, and the condensation of water vapour at the other membrane surface on the brine side (Johnson, Valks & Lefebvre, 1989; Hogan et al, 1998; Courel et al, 2000a,b), thus, creating the concentration and temperature boundary layers with thickness of \( \delta_i \) at the membrane surfaces. The concentration profiles at both membrane surfaces can be presented by
the flux ($J$) and the mass transfer coefficients in the liquids at the feed side ($k_f$) and at the brine side ($k_s$) with the relations as given in (5-3), (5-4) (Mengual et al, 1993) (refer to fig.2-4, pp.16).

$$C_{f,m} = C_{f,b} \times \exp \left( \frac{J}{\rho_w \times k_f} \right)$$  \hspace{1cm} (5-3)

$$C_{s,m} = C_{s,b} \times \exp \left( -\frac{J}{\rho_w \times k_s} \right)$$  \hspace{1cm} (5-4)

with $k_i = \frac{D_{i,\text{w}}}{\delta_i}$ ($i$=f for feed or s for brine),

$D_{i,\text{w}}$ is the diffusion coefficient of solute ($i$) in water.

Obviously, the mass transfer coefficients $k_i$ is inversely proportional to the layers' thickness $\delta_i$, which in turn depends on the physical properties of the liquids such as viscosity and density, and the hydrodynamic conditions of the system such as the fluid velocity and the system configuration.

The coefficients $k_i$ can be obtained either by gas permeation experiment or be calculated from the empirical equations of the dimensionless number such as Sherwood (Sh), Reynolds (Re) and Schmidt (Sc), which have the common form as in (5-5).

$$Sh = A \cdot Re^\alpha \cdot Sc^\beta$$  \hspace{1cm} (5-5)

where $A$, $\alpha$, and $\beta$ are constants. The dimensionless numbers are estimated as follows:

$$Sh_i = \frac{k_i \cdot d_{hi}}{D_{i,\text{w}}}$$  \hspace{1cm} Re$_i = \frac{\nu_i \cdot d_{hi} \cdot \rho_i}{\mu_i}$  \hspace{1cm} Sc$_i = \frac{\mu_i}{\rho_i \cdot D_{i,\text{w}}}$

The subscript ($i$) can be either $f$ or $s$, which stand for feed or brine solution. In the definition above, $d_h$ is the characteristic diameter of the channel (m), $\rho$ is the density (kg.m$^{-3}$), $\nu$ is the cross-flow velocity (m.s$^{-1}$), and $\mu$ is the viscosity of the liquids (Pa.s). For a flow inside a pipe, the characteristic diameter $d_h$ equals to the diameter of the pipe. However, for a flow in a non-circular channel, the characteristic diameter can be determined as $d_h = 4A/C$ where $A$ is the cross-sectional area and $C$ is the wetted
circumference of the flow channel. For the shell side of a hollow fibre module \( d_h \) can be determined as given in (5-6)

\[
d_h = \frac{D_i^2 - n \cdot d_0^2}{D_i + n \cdot d_0}
\]

(5-6)

where \( n \) is the number of fibres, \( d_0 \) is the outside diameter of the fibres, and \( D_i \) is the inside diameter of the shell.

Courel et al (2000) investigated the mass transfer in osmotic distillation for flat sheet membrane. The group proposed a step-by-step procedure to calculate and correlate the (Sh), (Re) and (Sc) numbers when the feed is pure water. The mass transfer equation at the brine side was \( Sh = 6.9 \times 10^{-9} Re^{0.91} Sc^{1.60} \). However, the temperature effect on the feed side, and the concentration effect on the brine side in the boundary layers’ regions were neglected in the calculation, leading to unsatisfactory and poor precision of mass transfer prediction of the brine side. Further, the relation between the activity coefficient and the solution concentration and temperature was not clearly stated.

**Another model for osmotic distillation flux prediction on flat sheet membrane** was proposed by Mengual et al (1993). In the model, the global mass transfer \( K \) in equation (5-2) was estimated as given in (5-7). The study was carried out with pure water as the feed; therefore, the mass transfer at the feed side was neglected and the global mass transfer \( K \) was dependent only on the membrane permeability \( K_m \) and the convective mass transfer coefficient at the boundary layer on the brine side \( k_s \).

\[
K = \frac{K_m \cdot k_s}{k_s + \left[ \frac{d\Delta P}{dc} \right]_{\text{bulk}} \cdot K_m \cdot C_{s,b}}
\]

(5-7)

\( k_s \) was proposed to be estimated by the stirring rate \( \omega \) as given in (5-8)

\[
k_s = a + b \cdot \omega^\varphi
\]

(5-8)

where \( a \), \( b \), and \( \varphi \) are to be determined experimentally.

Equations (5-2), (5-7) and (5-8) lead to:

\[
\frac{1}{J_\omega - J_0} = X + \frac{Y}{\omega^\varphi}
\]

(5-9)
where \( J_\infty, J_0 \) are the flux at stirring rate \( \omega \) and without stirring respectively; \( X, Y \) are the complicated functions of a, b, temperature and concentration of the solution.

Equation (5-9) provides the background for fitting the experimental data. At infinite stirring rate, parameter \( X \) can be obtained from the corresponding \( J_\infty \). Consequently, the membrane permeability \( K_m \) can be estimated as

\[
K_m = (J_0 + 1/X)\Delta P_0
\]

(5-10)

It should be pointed out that the model neglected the temperature polarisation effect, which is "substantial" as indicated in the study of Gostoli (1999). However, the model successfully predicted the OD flux in the case of their experiment. The success probably was due to very low OD flux in the case (refer to table 2-1, pp.21), which leads to minor temperature polarisation effect.

So far the models reviewed in this section were developed for flat sheet membranes, using pure water as the feed. However, as there are certain differences in the geometry, the models are not suitable for hollow fibre modules.

Hollow fibre module is a bundle of tiny porous fibres packed randomly into a shell. The configuration is similar to a shell and tube heat exchanger. Here the two sides of a hollow fibre module are distinguished as tube side, inside the fibres, and the shell side, outside the fibres.

**5.2.1.1. Mass transfer at the tube side**

When a solution is flowing inside the fibre (tube side), regardless of the distribution of the fibres in the module, the mass transfer can be derived by heat and mass transfer analogy of laminar flow inside a pipe. In other words, the Sieder-Tate equation (Geankoplis, 1983 & 1993; Heldman & Singh, 1981) and its analogous mass transfer given in (5-11) and (5-12) respectively can be used to describe heat and mass transfer inside the fibres. The equations were successfully applied in membrane distillation (Prasad & Sirkar, 1988; Izquierdo-Gil, García-Payo & Fernández-Pineda, 1999\textsuperscript{a,b}; Martínez-Diez, Florido-Díaz & Vázquez-González, 2000; and Banat et al, 1999).

\[
Nu = 1.86 \left( \text{Re} \cdot \text{Pr} \cdot \frac{d_h}{L} \right)^{1/3} \left( \frac{\mu_b}{\mu_m} \right)^{0.14} \quad \text{if } G_z = \text{Re} \cdot \text{Pr} \cdot \frac{d_h}{L} \geq 100
\]

(5-11\textsuperscript{a})
\[ Sh = 1.86 \left( \frac{Re \cdot Sc \cdot d_h}{L} \right)^{1/3} \] (5-12a)

or

\[ Nu = 3.66 + \frac{0.085Gz}{1 + 0.047Gz^{2/3}} \left( \frac{\mu_h}{\mu_m} \right)^{0.14} \text{ if } Gz = \frac{Re \cdot Pr \cdot d_h}{L} < 100 \] (5-11b)

\[ Sh = 3.66 + \frac{0.085Gzm}{1 + 0.047Gzm^{2/3}} \text{ where } Gzm = \frac{Re \cdot Sc \cdot d_h}{L} \] (5-12b)

(L is the total effective length of heat and mass transfer)

In the equations, Nu and Pr are the dimensionless Nusselt and Prandtl numbers respectively. They are defined as:

\[ Nu = \frac{h \cdot d_h}{k} \quad \text{;} \quad Pr = \frac{c_p \cdot \mu}{k} \]

where \( h \), \( k \), and \( c_p \) are the heat transfer coefficient, thermal conductivity and specific heat of the solution.

5.2.1.2. Mass transfer at the shell side

Unlike at the tube side, mass transfer at the shell side in hollow fibre modules behaves in different ways due to the packing randomness of the fibres in this region, hence different turbulence at different locations of the shell side (Costello et al., 1993; Wu & Chen, 2000; Gawronski & Wrzesinska (2000), Lipnizki & Field, 2001; Prasad & Sirkar, 1988; Lemanski & Lipscom, 1995; and Chen & Hlavacek, 1994).

Studies on mass transfer at the shell side in hollow fibre modules in microfiltration and ultrafiltration showed that packing density (\( \phi \)) of the fibres in hollow fibre modules affects the mass transfer in this region. However, the trend and the magnitude of the effect of the packing density differ one from another. While Costello et al (1993), Prasad and Sirkar (1988), and Gawronski and Wrzesinska (2000) observed the significantly negative effect of the packing density on mass transfer, Wu and Chen (2000) observed negative effect when the packing density was below 50%, but positive effect beyond that point. Other studies of Yang and Cussler (1986), and
Lipnizki and Field (2001) showed a little or non-effect of the packing density on mass transfer at the shell side. Those models can be effectively used to depict the concentration profiles at the membrane surfaces at the shell side of hollow fibre modules in osmotic distillation.

However, due to the discrepancy of the outcomes of the mentioned studies, and the different conditions of their experiment, those models listed in table 5-1 in osmotic distillation must be validated through the experimental data as discussed later in part (5.4) of this section.

The packing density is defined as the ratio of the cross sectional area occupied by the fibres to the total cross sectional area of the shell.

\[
\phi = \frac{\text{Total cross-sectional area of fibres}}{\text{Total cross-sectional area of the shell}} = n_{\text{fibres}} \times \left(\frac{d_s}{D_t}\right)^2
\]  (5-13)

In order to evaluate the development of the velocity and concentration profiles, the lengths of those profiles can be estimated as given in (5-14) to (5-17).

**At the shell side:** (Lipnizki & Field, 2001)

- Length of velocity profile \(L_{HR}\):

\[
\frac{L_{HR}}{d_h} = 0.002 \times \text{Re} \times \phi^{1/4}
\]  (5-14)

- Length of concentration profile \(L_{CR}\):

\[
\frac{L_{CR}}{d_h} = 0.002 \times \text{Re} \times Sc^{0.6} \times \phi^{1/4}
\]  (5-15)

**At the tube side:**

Length of velocity profile \(L_{HR}\): (Geankoplis, 1993)
### Table 5-1

**Empirical equations for mass transfer at the shell side of hollow fibre modules**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Re number</th>
<th>Packing density $\phi$ (%)</th>
<th>$d_o$ (mm)</th>
<th>$d_h/L \times 10^3$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sh = (0.53 - 0.58\phi)Re^{0.53}Sc^{0.33}$</td>
<td>(5-13)</td>
<td>31.9 to 75.8</td>
<td>0.670</td>
<td>30-93</td>
<td>Costello et al, 1993</td>
</tr>
<tr>
<td>$Sh = 5.85(1 - \phi)\left(\frac{d_h}{L}\right)Re^{0.6}Sc^{0.33}$</td>
<td>(5-14)a</td>
<td>Up to 500</td>
<td>4 to 40</td>
<td>0.140, 0.240</td>
<td>Prasad &amp; Sirkar, 1988</td>
</tr>
<tr>
<td>$Sh = (0.3045\phi^2 - 0.3425\phi + 0.0015)Re^{0.9}Sc^{0.33}$</td>
<td>(5-15)</td>
<td>100</td>
<td>8.4 to 70.22</td>
<td>1.000</td>
<td>2.3 to 36</td>
</tr>
<tr>
<td>$Sh = 0.09(1 - \phi)Re^{(0.48+0.16\phi)}Sc^{0.33}$</td>
<td>(5-16)b</td>
<td>10</td>
<td>35 to 79</td>
<td>0.630-1.320</td>
<td>Gawronski &amp; Wrzesinska, 2000</td>
</tr>
<tr>
<td>$Sh = 1.25\left(\frac{Re \cdot d_h}{L}\right)^{0.93}Sc^{0.33}$</td>
<td>(5-17)</td>
<td>0.1-1000</td>
<td>2.5 to 26</td>
<td>0.466</td>
<td>Yang &amp; Cussler, 1986</td>
</tr>
</tbody>
</table>

| $Sh_1 = 3.66 + 1.2\left(\sqrt{\phi}\right)^{0.8}$                      | Re<2300, Fully developed velocity and concentration profiles | Lipnizki & Field, 2001 |
| $Sh_2 = 1.615\left[1 + 0.14\left(\sqrt{\phi}\right)^{0.5}\right]\sqrt{Re \cdot Sc \cdot \frac{d_h}{L}}$ | Re<2300, Developing concentration profile and fully developed velocity profile |
| $Sh_3 = \left(\frac{2}{1 + 22Sc}\right)^{1/6} \left(Re \cdot Sc \cdot \frac{d_h}{L}\right)^{1/2}$ | Accounting for the influence of the entrance region |

| $Sh = (Sh_1^3 + Sh_3^3)^{1/3}$                                           | (5-18)    |                                                            | Re<2300, Fully developed velocity and concentration profiles, and the inclusion of the entrance effect |
| $Sh = (Sh_2^3 + Sh_3^3)^{1/3}$                                           | (5-19)    |                                                            | Re<2300, Fully developed velocity profile, developing concentration profile, and the inclusion of the entrance effect |

*a Correlation is valid for 0<Re<500 and 300<Sh<1000

b Correlation is valid for Gz<161
\[
\frac{L_{HR}}{d_h} = 0.0575 \times \text{Re} \quad (5-16)
\]

- Length of concentration profile \( L_{CR} \): it was adopted from (5-16) and the similarity as in the formulas of Lipnizki and Field (2001)

\[
\frac{L_{CR}}{d_h} = 0.0575 \times \text{Re} \times \text{Sc}^{0.6} \quad (5-17)
\]

5.2.2. Heat transfer at the membrane surfaces in osmotic distillation

Osmotic distillation is essentially an isothermal process, but the phase changes of water in the feed and in the brine, that is evaporation and condensation respectively, induce in the formation of the so-called temperature polarisation that makes the temperatures at the membrane surfaces differ from the bulk values as shown in figure 2-5 (pp.17). The induced lower temperature at the feed side and higher temperature at the brine side reduce the water vapour pressure difference across the membrane, and substantially inhibit the OD flux rate as reported in the study of Gostoli (1999).

Sheng, Johnson and Lefebvre (1991) applied a numeric method to analyse the experimental data of osmotic distillation in a plate and frame module. However, the study could not depict the temperature profiles at the membrane surfaces, and the effect of the temperature polarisation on the flux could not be defined quantitatively.

Gostoli (1999) investigated the thermal effect in osmotic distillation with flat sheet membrane in both theoretical and experimental ways. The study depicted the temperature difference between the feed and the brine at the outlet of the module, but not at the membrane surface. It showed that the temperature difference increased with reduced flow rate (or reduced cross flow velocity) of the feed stream. Also, the higher the inlet (bulk) temperature, the larger the temperature difference at the outlet of the module. It clearly showed that the higher the flux, the severer the temperature polarisation; and turbulence improved the heat transfer at the membrane surface by increasing the heat transfer coefficients in the boundary layer regions and reducing the severity of temperature polarisation in osmotic distillation. However, the study could
not quantify the contribution of temperature polarisation in the reduction of the OD flux. Further, the author assumed that the water activity coefficients in the boundary layers were constant while they are changing in this area. This may have lead to some uncertainty in evaluation the driving force of the process.

The temperature profiles at the membrane surfaces, however, can be depicted by applying various heat transfer equations in the energy balance of the so-assumed steady-state heat transfer across the membrane as given in (5-18).

\[
Q = H \cdot \Delta T_b = h_f(T_{f,b} - T_{f,m}) = h_t(T_{s,m} - T_{s,b}) = J \cdot \Delta H_w + h_m(T_{f,m} - T_{s,m}) \tag{5-18}
\]

where \( Q \), \( H \), and \( \Delta H_w \) are the total heat transferred across the membrane, global heat transfer coefficient and latent heat of evaporation of pure water; \( \Delta T_b \) is the temperature difference between bulk temperatures of the solutions; \( h_t \), \( h_f \), and \( h_m \) are the heat transfer coefficients at the feed side, at the brine side and of the membrane itself. Other parameters are defined as before.

The global heat transfer coefficient \( H \) can be determined as in (5-19) which is already established in membrane distillation (Lawson & Douglas, 1997).

\[
H = \left( \frac{1}{h_f + \frac{1}{h_m + \frac{1}{\frac{J \cdot \Delta H_w}{\Delta T_m} + \frac{1}{h_t}}}} \right)^{-1} \tag{5-19}
\]

The membrane is considered as a porous body consisting of air trapped stagnantly in the pores and the solid polymer. Thus, \( h_m \) for a cylindrical geometry based on the internal surface can be approximated as:

\[
h_m = \frac{k_m^T}{r_i \cdot \ln(r_0 / r_i)} = \frac{\varepsilon \cdot k_{air}^T + (1 - \varepsilon)k_p^T}{r_i \cdot \ln(r_0 / r_i)} \tag{5-20}
\]

where \( \varepsilon \) is the porosity or void fraction of the membrane; \( k_m^T \), \( k_{air}^T \), \( k_p^T \) are the thermal conductivity of membrane, air and the solid polymer; and \( r_0, r_i \) are the internal and external radius of the fibres. The thermal conductivity of air \( k_{air}^T \) can be obtained from Lide (2001, pp.6-188), and the thermal conductivity of polyvinylidene fluoride (PVDF)
polymer $k^T_p$, the material employed in our experiment, can be obtained from the polymer handbook (Brandrup, Immergut & Grulke, 1999, pp.V49-V51).

Further rearranging equation (5-18) with the assumption that $T_{f,b} = T_{s,b}$ (isothermal osmotic distillation) one can derive the equation as given in (5-21) to determine the temperature difference across the membrane $\Delta T_m$ (also available in Courel et al, 2000a).

$$\Delta T_m = T_{s,m} - T_{f,m} = \frac{J \cdot \Delta H_w}{h_m + \left(\frac{1}{h_f} + \frac{1}{h_s}\right)^{-1}}$$

Equation (5-21) indicates the effect of mass transfer on heat transfer in osmotic distillation, and clearly shows that the magnitude of the temperature polarisation or the temperature difference across the membrane is proportional to the flux rate. This statement has been confirmed by the study of Gostoli (1999). The created temperature difference across the membrane results in heat conduction $h_m (T_{s,m} - T_{f,m})$, which is equal to the heat transferred across the membrane due to the latent heat of evaporation $J \cdot \Delta H_w$, and equation (5-18) is agreed. Further, equation (5-21) indicates the role of the membrane properties in reducing the temperature polarisation effect, as higher coefficient of heat transfer of the membrane will result in smaller $\Delta T$ leading to the improvement of the osmotic distillation process. That is why thinner and better thermally conductive membranes are desirable in osmotic distillation (Johnson, Valks & Lefebvre, 1989; Hogan et al, 1998).

Equation (5-21) determines the temperature difference across the membrane, but it is not enough to determine the temperature at the membrane surfaces on both sides of the liquids. Therefore, further rearrangements were carried out to earn the following equations (5-22) and (5-23) to suit the target.

$$T_{f,m} = T_b - \Delta T_m \left(\frac{2h_m}{h_f} + \frac{h_s}{h_f + h_s}\right)$$

(5-22)
\[ T_{s,m} = T_b + \Delta T_m \left( \frac{2h_m}{h_s} + \frac{h_f}{h_f + h_s} \right) \]  \hspace{1cm} (5-23)

As in our case, \( h_m \ll h_f + h_s \), as the heat transfer of the membrane \( h_m \) is in the order of 0.5 while heat transfer of the feed side and the brine side \( h_f \) and \( h_s \) are of the order of 2000 W.m\(^{-2}\).K\(^{-1}\), the first part in the parentheses in the above equations can be ignored.

*Equations (5-22) and (5-23) first appeared in this work.*

Equations (5-18), (5-21), (5-22), (5-23) are the fundamental equations to describe the temperature profiles at the membrane surfaces in osmotic distillation. The convective heat transfer coefficients hereby are determined by the empirical equations of the dimensionless numbers Nusselt, Reynolds and Prandtl as described in part 5.2.1.

### 5.3. VALIDATION OF MASS TRANSFER AND WATER VAPOUR TRANSPORT MODELS

In the case of the experiments in this work, the gaseous water molecules transport through the membrane pores at temperature range from 25°C to 45°C and total pressure of about 1 atm. Under these conditions, the mean free path of gaseous water molecules \( \lambda \) ranges from 0.047\( \mu \)m to 0.053\( \mu \)m, which results in \( K_n \) ranging from 0.235 to 0.265. It indicates that the transport of gaseous water molecules may be under the ordinary molecular diffusion mechanism or under the mechanisms of the transition regime such as Scholfield model and Dusty-Gas model.

Application of those models requires the knowledge of the membrane properties such as thickness, pore size, porosity and tortuosity. While the thickness of a membrane can be measured by a normal microscope, the membrane pore size and porosity can be estimated through the electronic scanning microscopy (ESM) with some uncertainty. The tortuosity of a membrane, on the contrary, is not measured, but arguably accepted from 1.5 to 10 (Geankoplis, 1983), which leads to uncertain accuracy of applying the transport models up to 10/1.5 or about 667%. Through the
experimental data, however, the membrane factor K1 as defined in the models can be estimated.

In this section, the following models were under consideration for validation:

- Three models for water vapour transport through the membrane. They include Ordinary diffusion model, Scholdfield model and Dusty-Gas model.
- Six mass transfer models at the shell side of hollow fibre module as listed in table 5-1.

The criterion for validation of the gaseous water diffusion models is based on the fact that at known flux rate and the water vapour pressures at the membrane surfaces, the membrane parameter K1 must have a consistent and reasonable value so that the membrane tortuosity τ is in the range 1.5-10. This range is normal for commercial membrane being used in the industry (Geankoplis, 1983).

The criterion for validation of the mass transfer models at the shell side of hollow fibre module is based on the equation (5-1). If a mass transfer model is valid for the case, the calculated water vapour pressure difference across the membrane and the flux rate must agree with equation (5-1). In other words, they must be linearly related to each other with a slope of $K_m$.

The conditions under which the experiments were carried out are summarised in table 5-2. It can be seen that the conditions of the experiments in this work are mostly similar to that of Costello et al (1993) and Wu & Chen (2000).

**Table 5-2**

*The conditions of the experiments*

<table>
<thead>
<tr>
<th>Module</th>
<th>Re</th>
<th>Packing density $\phi$ %</th>
<th>Fibre diameter mm</th>
<th>$d_p/L \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV375</td>
<td>Tube side</td>
<td>37.3-225.9</td>
<td>0.375</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shell side</td>
<td>11.4-69.6</td>
<td>34.7</td>
<td>5.27</td>
</tr>
<tr>
<td>PV660</td>
<td>Tube side</td>
<td>5.8-103.2</td>
<td>0.660</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shell side</td>
<td>19.1-73.1</td>
<td>49.8</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**5.3.1. Method of validation**
• Reuse the experimental data in chapter 3.

• Obtain the physical properties of glucose and calcium chloride solutions as from the appendix 3 and the models developed in chapter 4.

• Apply the Sieder-Tate equation and its analogous mass transfer equation for the tube side.

• Apply the mass transfer equations listed in table 5-1, and their analogous heat transfer equations for the shell side.

• Apply the fundamental equations for concentration and temperature polarisation in osmotic distillation as discussed in part (5.2), to determine the concentrations and temperatures of the two solutions at the membrane surfaces.

• Apply the water activity models (equations 4-13, 4-14, chapter 4, pp.75) and the Antoine equation (equation 2-5, chapter 2, pp.8) to determine the water vapour pressures at the membrane surfaces in relation to solute concentration and solutions’ temperature.

• Plot the experimental fluxes \( (J) \) against the water vapour pressure differences across the membrane \( (\Delta P_m) \), and access the validity of the mass transfer models at the shell side.

• Fit the flux rate data \( (J) \) and the \( (\Delta P_m) \) produced by the valid mass transfer models for the shell side to the models of water vapour transport across the membrane to determine the membrane parameter \( K_1 = \frac{\delta}{\tau} \).

• Evaluate \( K_1 \) for its consistency and the membrane tortuosity values \( \tau \) to validate the water vapour transport models.

All the calculations, plotting graphs and data analysis in this section were carried out with the help of Microsoft Excel 5.0 software.
5.3.2. Validation of the mass transfer models at the shell side:

The choice of the empirical equations depends on the hydrodynamic parameter of the system under the experimental conditions such as the Reynolds number Re (listed in table 5-2), Graetz number Gz and the development of the velocity and concentration profiles in the channel, and it must comply the conditions as discussed in part (5.2.). Such parameters are listed in table 5-3.

As the Graetz numbers are less than 100, equations (5-11\(^b\)) and (5-12\(^b\)) were used for the tube side. Application of the models after Lipnizki and Field (2001), however, depends on the development of the concentration profiles at the shell side. As indicated in table 5-3, and complying the conditions in table 5-1, both equations (5-18) and (5-19) were used at certain experiments.

Table 5-3
The hydrodynamic parameters of the system under the experimental conditions

<table>
<thead>
<tr>
<th>Module</th>
<th>Parameter</th>
<th>Tube side</th>
<th>Shell side</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PD375</td>
<td>Re</td>
<td>37.3-225.9</td>
<td>11.4-69.6</td>
<td>Laminar flow</td>
</tr>
<tr>
<td></td>
<td>Gz</td>
<td>5.1-10.9</td>
<td>3.7-10.9</td>
<td>&lt;100</td>
</tr>
<tr>
<td></td>
<td>L(_{HR})</td>
<td>1.1-4.9</td>
<td>0.2-0.8</td>
<td>Fully developed velocity profile</td>
</tr>
<tr>
<td></td>
<td>L(_{CR})</td>
<td>132-341</td>
<td>76-340</td>
<td>Both developing and fully developed concentration profile</td>
</tr>
<tr>
<td>PV660</td>
<td>Re</td>
<td>5.8-103.2</td>
<td>19.1-73.1</td>
<td>Laminar flow</td>
</tr>
<tr>
<td></td>
<td>Gz</td>
<td>4.6-12.7</td>
<td>5.2-13.2</td>
<td>&lt;100</td>
</tr>
<tr>
<td></td>
<td>L(_{HR})</td>
<td>0.3-3.9</td>
<td>0.3-1.0</td>
<td>Fully developed velocity profile</td>
</tr>
<tr>
<td></td>
<td>L(_{CR})</td>
<td>132-384</td>
<td>118-327</td>
<td>Both developing and fully developed concentration profile</td>
</tr>
</tbody>
</table>

The plots of the experimental fluxes based on the internal surface of the fibres against the water vapour pressure differences across the membrane are shown on figures 5-1 to 5-4 for module PV375, and figures 5-5 to 5-8 for module PV660.
For module PV375:

**Fig. 5.1** - The linearity between $\Delta P_m$ and flux $J$ based on Wu & Chen (2000) on the shell side.

$\text{Flux } J \text{ (Kg m}^{-2}\text{h}^{-1})$

![Graph showing linearity between $\Delta P_m$ and flux $J$.]

$y = 1.0556x - 0.2381$

$R^2 = 0.9416$

**Fig. 5.2** - The linearity between $\Delta P_m$ and flux $J$ based on Costello et al (1993) on the shell side.

$\text{Flux } J \text{ (Kg m}^{-2}\text{h}^{-1})$

![Graph showing linearity between $\Delta P_m$ and flux $J$.]

$y = 0.984x - 0.3047$

$R^2 = 0.9989$

**Fig. 5.3** - The linearity between $\Delta P_m$ and flux $J$ based on Lipnizki & Field (2001) on the shell side.

$\text{Flux } J \text{ (Kg m}^{-2}\text{h}^{-1})$

![Graph showing linearity between $\Delta P_m$ and flux $J$.]

$y = 1.3113x - 0.8331$

$R^2 = 0.9764$

**Fig. 5.4** - The linearity between $\Delta P_m$ and flux $J$ based on Gawronski & Wrzesinska (2000) on the shell side.

$\text{Flux } J \text{ (Kg m}^{-2}\text{h}^{-1})$

![Graph showing linearity between $\Delta P_m$ and flux $J$.]

$y = 1.4684x + 0.6953$

$R^2 = 0.6938$

For module PV375, the models of Prasad and Sirkar (1988), and Yang and Cussler (1986) were immediately discarded as they resulted in unacceptable changes of concentrations and temperatures at the membrane surface of the shell side leading to even negative water vapour pressure differences across the membrane. The same is
the case with module PV660. It is probably due to the fact that these models had been developed for smaller fibres.

Gawronski and Wrzesinska (2000) model was also considered unsuitable for describing the heat and mass transfer at the shell side of this module as it resulted in poor linearity between the flux rate and the pressure difference across the membrane.

Lipnizki and Field (2001) model, on the other hand, produced an acceptable linearity of \( J \propto \Delta P_m \) for the whole range of the experiment, but not in the specific regions as shown on figure 5-3 and on table 5-4. It was found that within either 25°C, or 35°C, or 45°C region there was no correlation between \( J \) and \( \Delta P_m \). In contrast, Wu & Chen (2000) model resulted in good linearity within either 25°C, or 35°C, or 45°C region with increasing slopes when the temperature of the process increased. Therefore, application of those models should be under careful consideration.

Linear regression analysis showed that the most suitable model was the model of Costello et al (1993) with highest regression coefficient (\( R^2 \)) as shown on the figures and smallest standard error (0.0424). The linearity of \( J \propto \Delta P_m \) was established not only in within different temperature ranges, but in the whole range of the experiment.

**Table 5-4**

*Correlation coefficients between \( J \) and \( \Delta P_m \) as a result of applying Lipnizki & Field (2001) and Wu & Chen (2000) models at different temperatures*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Lipnizki &amp; Field model</th>
<th>Wu &amp; Chen model</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>0.487</td>
<td>0.872</td>
</tr>
<tr>
<td>35°C</td>
<td>0.143</td>
<td>0.924</td>
</tr>
<tr>
<td>45°C</td>
<td>-0.326</td>
<td>0.952</td>
</tr>
</tbody>
</table>

The negative intercepts in the linear equations as shown on the figures indicate that the water vapour pressure difference \( \Delta P_m \) must be at a certain value before the mass transfer occurs. Perhaps, this value of \( \Delta P_m \) is needed to trigger the initial evaporation
of water on the feed side or to overcome the capillary friction between the gaseous water molecules and the pore wall.

For module PV660:

**Fig.5-5**—The linearity between $\Delta P_m$ and flux J based on Wu & Chen (2000) on the shell side.

**Fig.5-6**—The linearity between $\Delta P_m$ and flux J based on Costello et al (1993) on the shell side.

**Fig.5-7**—The linearity between $\Delta P_m$ and flux J based on Lipnizki & Field (2001) on the shell side.

**Fig.5-8**—The linearity between $\Delta P_m$ and flux J based on Gawronski & Wrzesinska (2000) on the shell side.

The plot on figures 5-7 and 5-8 showed that application of Gawronski and Wrzesinski (2000), and Lipnizki and Field (2001) models further dispersed the pair points of $J \propto \Delta P_m$ from the linearity. Therefore, it was concluded that those models were not
suitable for describing the mass transfer at the shell side under the experimental conditions of this work.

Wu and Chen (2000) model, however, turned out to be suitable for module PV660, producing a very good linearity of the relation $J \propto \Delta P_m$ for the whole range of the experiment. Model of Costello et al (1993) was again the fittest model. It is interesting to notice that the good linearity of $J \propto \Delta P_m$ by those two models resulted in very similar membrane permeability $K_m$ or the slopes of the regression as shown on the figures 5-7 and 5-8.

If considering Costello et al (1993) model as the most suitable model for describing the mass transfer at the shell side of both modules, it was found that the hypothesised initial water pressure difference $\Delta P_{m_{initial}}$ to trigger mass transfer for both modules was of the same order of 300Pa (309Pa for PV375 and 305Pa for PV660). The difference of 4Pa is considered negligible within the error of the experimental data.

In summary, Costello et al (1993) model was found to be the best-fit model to describe mass transfer at the shell side for both modules. Wu and Chen (2000) model was also found to be suitable for module PV660, but acceptably applicable for module PV375 with some uncertainty. And finally, the hypothesised initial water pressure difference $\Delta P_{m_{initial}}$ to trigger mass transfer was found to be about 300Pa for both modules.

5.3.3. Validation the water vapour transport models:

As Costello et al (1993) model was found to be the most suitable to describe the mass transfer at the shell side of both two modules, the pressure difference yielded by it $\Delta P_m$ was used to fit into the models for water vapour diffusion. The derived membrane parameter $K_1$ for membrane of both modules is listed in table 5-5. The coefficients a and b in Scholfield models were obtained from the study of Fernández-Pineda et al (2002) for PVDF membrane and water vapour. It must be stressed that those coefficients a, and b, valued at $2.7 \times 10^{-6}$kg.m$^{-2}$.s$^{-1}$.Pa$^{-1}$, and 0.5 respectively, were derived at reference pressure of 150kPa. Therefore, they were modified to the reference pressure of 100kPa to suit the experimental condition as discussed in chapter 2 (equations 2-15 and 2-15).
The modified a and b were \(2.25 \times 10^{-6}\text{kg.m}^{-2}\text{s}^{-1}\text{Pa}^{-1}\), and 0.4 respectively.

**Table 5-5.**  
The derived membrane parameter \(K1\) for different water vapour transport models

<table>
<thead>
<tr>
<th>Model</th>
<th>Membrane parameters</th>
<th>PV375</th>
<th>PV660</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\varepsilon) %</td>
<td>74</td>
<td>64</td>
</tr>
<tr>
<td>Ordinary diffusion</td>
<td>Mean (K1 = \frac{\varepsilon}{\tau})</td>
<td>0.1166</td>
<td>0.1098</td>
</tr>
<tr>
<td></td>
<td>SD of (K1)</td>
<td>0.0011</td>
<td>0.0017</td>
</tr>
<tr>
<td></td>
<td>Membrane tortuosity</td>
<td>(6.3)</td>
<td>(5.8)</td>
</tr>
<tr>
<td>Scholfield model</td>
<td>Mean (K1 = \frac{\varepsilon}{\tau})</td>
<td>0.1416</td>
<td>0.1242</td>
</tr>
<tr>
<td></td>
<td>SD of (K1)</td>
<td>0.0020</td>
<td>0.0023</td>
</tr>
<tr>
<td></td>
<td>Membrane tortuosity</td>
<td>(5.2)</td>
<td>(5.2)</td>
</tr>
<tr>
<td>Dusty-Gas model</td>
<td>Mean (K1 = \frac{\varepsilon}{\tau})</td>
<td>0.0623</td>
<td>0.0579</td>
</tr>
<tr>
<td></td>
<td>SD of (K1)</td>
<td>0.0026</td>
<td>0.0519</td>
</tr>
<tr>
<td></td>
<td>Membrane tortuosity</td>
<td>(11.9)</td>
<td>(11.9)</td>
</tr>
</tbody>
</table>

\(a\) Data obtained from Memcor Australia, the membrane manufacturer.  
\(b\) Calculated from the derived parameter \(K1\).  
SD: standard deviation of the data.

Data obtained in table 5-5 indicate that in order to agree with equation (5-1), the membrane parameter \(K1\) in Dusty-Gas model must be almost two times smaller than the one in Ordinary Diffusion and Scholfield models. Further, the tortuosity of the membrane in Dusty-Gas model goes beyond the limit of 10. Therefore, Dusty-Gas model is considered unsuitable to govern the water vapour transport in osmotic distillation under the experimental conditions of this work.

Ordinary diffusion and Scholfield models ended in reasonable values of the membrane tortuosity. Although Ordinary diffusion model resulted in different tortuosity, while Scholfield model yielded the same tortuosity for the two membranes, it is difficult for one to conclude which of the two models is better since tortuosity of a membrane is a parameter ambiguously accepted by researchers, but essentially dependent on the
membrane structure. However, the Ordinary diffusion model has the advantage of being simpler, while Scholfield models requires more data input such as coefficients a and b.

Therefore, both models can be validated to govern the water vapour transport through the membrane in osmotic distillation under the conditions of our experiment. However, one should be aware of using the membrane parameter $K_1$ as derived in table 5-5 to gain accurate prediction of the osmotic distillation flux.

5.4. QUANTIFICATION THE CONCENTRATION AND TEMPERATURE POLARISATIONS AND THEIR EFFECT IN OSMOTIC DISTILLATION

5.4.1 Quantification the concentration and temperature profiles at the membrane surfaces

As Costello et al (1993) model was found to be the best fit for mass transfer at the shell side, it was employed to determine the mass and heat transfer coefficients of the brine solution at the shell side, while Sieder-Tate equation was used for the feed solution at the tube side. All calculations were based on the experimental fluxes. Equations (5-3), (5-4) were used to estimate the concentrations of the two solutions at the membrane surfaces, while equations (5-21), (5-22) and (5-23) were applied for the temperatures.

As expected, any of the operating factors that affect the flux rate contributed to the changes of concentrations and temperatures of the feed and brine solutions at the membrane surfaces. The effect of operating conditions on the temperature and concentration profiles at the membrane surfaces could be attributed directly to the mass and heat transfer coefficients or indirectly to the flux rate of the osmotic distillation process. For example, an increase of the brine velocity (while other factors remained unchanged) would directly reduce the temperature changes at the brine side, but at the same time, it would increase the temperature changes at the feed side due to the increased flux rate.

Some representatives of the operating condition factors’ effect on the temperature and concentration profiles at the membrane surfaces are presented on figures 5-9 to 5-23.
The effect of feed velocity:

**Fig.5-9:** Effect of feed velocity on temperature profile for module PV375, 
T=35°C, v<sub>f</sub>=0.2 m.s<sup>-1</sup>, C<sub>f</sub>=30%

**Fig.5-10:** Effect of feed velocity on temperature profile for module PV660, 
T=35°C, v<sub>f</sub>=0.2 m.s<sup>-1</sup>, C<sub>f</sub>=45%

As seen on fig.5-9 and 5-10, the feed velocity has a slight effect on reducing the temperature changes at the tube side, while the temperature at the brine side remains unchanged.

It should be noticed here that the temperature changes at the feed side are greater than the ones at the brine side for module PV660, but opposite is the case for module PV375. That is because the flux rate for module PV375 is higher than the one of PV660, which results in larger changes of the temperatures at the brine side. In addition, module PV375 was used for lower feed concentration, and the feed velocity was higher in comparison to the ones applied for module PV660, hence better turbulence in module PV375, and therefore, less temperature polarisation.

**Fig.5-11:** Effect of feed velocity on concentration profile for module PV375, 
T=35°C, v<sub>f</sub>=0.2 m.s<sup>-1</sup>, C<sub>f</sub>=30%

**Fig.5-12:** Effect of feed velocity on concentration profile for module PV660, 
T=35°C, v<sub>f</sub>=0.2 m.s<sup>-1</sup>, C<sub>f</sub>=45%
Figures 5-11 and 5-12 show the effect of feed velocity on the concentration profiles at the membrane surfaces. As the feed velocity increases, the concentration polarisation of the feed side is improved, but more severe polarisation is seen on the brine side due to the increased flux rate.

- The effect of brine velocity:

**Fig.5-13:** Effect of brine velocity on temperature profile for module PV375, $T=35^\circ C$, $v_f=0.4\text{ m.s}^{-1}$, $C_f=30\%$

**Fig.5-14:** Effect of brine velocity on temperature profile for module PV660, $T=35^\circ C$, $v_f=0.4\text{ m.s}^{-1}$, $C_f=45\%$

**Fig.5-15:** Effect of brine velocity on concentration profile for module PV375, $T=35^\circ C$, $v_f=0.4\text{ m.s}^{-1}$, $C_f=30\%$

**Fig.5-16:** Effect of brine velocity on concentration profile for module PV660, $T=35^\circ C$, $v_f=0.4\text{ m.s}^{-1}$, $C_f=45\%$
Similar to the feed velocity, the brine velocity has a profound effect on the concentration and temperature profiles at the brine side, but little effect on the feed side as just only due to the increased flux rate. Changes of concentration and temperature at the brine side due to the brine velocity are much larger than the ones at the feed side due to the feed velocity. This is because changes of heat and mass transfer coefficients at the brine side due to the Costello et al (1993) model are much larger ($k_b=13.81$ to $22.44 \times 10^{-6}$ m$^2$.s$^{-1}$; $h_b=3060$ to $4974$ W.m$^{-2}$.K$^{-1}$) than the ones at the feed side due to Sieder-Tate model ($k_f=21.68$ to $29.43 \times 10^{-6}$ m$^2$.s$^{-1}$; $h_f=2250$ to $2498$ W.m$^{-2}$.K$^{-1}$).

- The effect of feed concentration:

**Fig. 5.17:** Effect of feed concentration on temperature profile for module PV375, $T=35^\circ$C, $v_f=v_p=0.4$ m.s$^{-1}$.

**Fig. 5.18:** Effect of feed concentration on temperature profile for module PV660, $T=35^\circ$C, $v_f=v_p=0.4$ m.s$^{-1}$.

**Fig. 5.19:** Effect of feed concentration on concentration profile for module PV375, $T=35^\circ$C, $v_f=v_p=0.4$ m.s$^{-1}$.

**Fig. 5.20:** Effect of feed concentration on concentration profile for module PV660, $T=35^\circ$C, $v_f=v_p=0.4$ m.s$^{-1}$.
The feed concentration, as illustrated on figures 5-19 and 5-20, appears to worsen the polarisation in osmotic distillation on the feed side even though the flux rate decreases at higher feed concentration. It seems that the feed concentration has more significant effect on concentration polarisation at higher concentration range (45-60%). This worsening effect is due to the increased viscosity of the feed solution.

- The effect of bulk temperature:

**Fig.5-21:** Effect of bulk temperature on temperature profile for module PV375. The error bars show the confidence limits at $\alpha=0.05$.

**Fig.5-22:** Effect of bulk temperature on temperature profile for module PV660. The error bars show the confidence limits at $\alpha=0.05$.

**Fig.5-23:** Effect of bulk temperature on concentration profile for module PV375. The error bars show the confidence limits at $\alpha=0.05$.

**Fig.5-24:** Effect of bulk temperature on concentration profile for module PV660. The error bars show the confidence limits at $\alpha=0.05$. 

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(See Appendix 2 for determination of the confidence limits)

Figures 5-21 to 5-24 show the significant effect of bulk temperature on the temperature and concentration profiles under variable operating conditions. Although increased bulk temperature reduces solutions' viscosity, hence improves the flows, it is seen that the bulk temperature makes the polarisations in osmotic distillation more severe due to the exponentially increased flux rate as indicated in chapter 3.

In all cases, the polarisations are severer on the brine side due to smaller heat and mass transfer coefficients in comparison to the one at the feed side. In addition, the changes of concentration and temperature are larger in module PV375 than in module PV660. However, it should be stressed that it is mainly because of the higher flux yielded with module PV375. Descriptive analysis shows that temperature profile is less dependent on other operating conditions (with smaller standard deviation) than the concentration profile, as also illustrated on figures 5-21 to 5-24.

In summary, the velocity of liquids improves the osmotic distillation and reduces concentration and temperature polarisation. Feed concentration makes the polarisation worse due to the increased viscosity, while the bulk temperature causes large changes of temperature and concentration at the membrane surface due to increased flux rate. The quantification in this section also indicates the interaction between heat and mass transfer in osmotic distillation.

5.4.2. Quantification the effect of concentration and temperature polarisation (CP & TP) in osmotic distillation

Obviously, polarisations reduce the driving force in osmotic distillation, hence the flux rate. This section will give a quantitative evaluation for the contribution of TP & CP to the reduction of flux rate in osmotic distillation.

The reduction of flux rate hereby is defined as the difference of the flux evaluated at the bulk conditions and the actual flux accounting for the effect of concentration and temperature polarisations. As the OD flux is linearly proportional to the water vapour pressure difference across the membrane, the following definitions are used to quantitatively evaluate the contribution of CP and TP to OD flux reduction.
• **Concentration polarisation effect CP**: it is the flux reduction caused by the concentration polarisation without accounting for the effect of temperature polarisation. In other words, the temperature of the OD process is assumed unchanged.

\[
CP = \frac{\Delta P_b - \Delta P_{m,T}}{\Delta P_b} \times 100
\]  

(5-24)

where \(\Delta P_b\) is the water vapour pressure difference evaluated at bulk conditions, and \(\Delta P_{m,T}\) is the water vapour pressure difference across the membrane surfaces assessed at bulk temperature, but at concentrations at the membrane surfaces.

• **Temperature polarisation effect TP**: it is the flux reduction caused by the temperature polarisation without accounting for the effect of concentration polarisation. In this case, the concentrations of the liquids are assumed unchanged.

\[
TP = \frac{\Delta P_b - \Delta P_{m,C}}{\Delta P_b} \times 100
\]  

(5-25)

where \(\Delta P_{m,C}\) is the water vapour pressure difference across the membrane surfaces assessed at bulk concentration, but at temperatures at the membrane surfaces.

• **Polarisation effect on the feed side PE_f**: it is the flux reduction due to CP & TP on the feed side only.

\[
P_{E_f} = \frac{F_{f,b} - F_{f,m}}{\Delta P_b} \times 100
\]  

(5-26)

• **Polarisation effect on the brine side PE_b**: it is the flux reduction due to CP & TP on the brine side only.

\[
P_{E_b} = \frac{F_{b,m} - F_{b,b}}{\Delta P_b} \times 100
\]  

(5-27)

• **Total polarisation effect PE**: it is the flux reduction due to CP & TP that occur during the OD process.
\[ PE = PE_f + PE_s = \frac{\Delta P_b - \Delta P_m}{\Delta P_b} \times 100 \]  

(5-28)

Equations (5-24) to (5-28) are first defined in this work. Calculations were again based on Costello et al (1993) model for the shell side and Sieder-Tate model for the tube side with the help of Excel 5.0 software.

For module PV375:

**Fig.5-25:** The contribution of CP&TP to the OD flux reduction in module PV375. The error bars show the confidence limits at \( \alpha = 0.05 \)

**Fig.5-26:** The contribution of PE, & PE, to the OD flux reduction in module PV375. The error bars show the confidence limits at \( \alpha = 0.05 \)

For module PV660:

**Fig.5-27:** The contribution of CP&TP to the OD flux reduction in module PV660. The error bars show the confidence limits at \( \alpha = 0.05 \)

**Fig.5-28:** The contribution of PE, & PE, to the OD flux reduction in module PV660. The error bars show the confidence limits at \( \alpha = 0.05 \)
Figures 5-25 to 5-28 show that when at higher bulk temperatures (or at higher flux rate), CP&TP may contribute up to 18.0±1.23% for module PV375 and 16.8±0.58% to the reduction of the flux. Moreover, at lower feed concentration (30-40%) as in the case with module PV375 (fig.5-25, 5-26), CP seems to have significantly greater contribution to the flux rate reduction than TP, and polarisation on the feed side has predominant contribution to flux reduction.

At higher feed concentrations (45-60%) as in the case with module PV660 (fig. 5-25, 5-26), CT and TP appear to be at the same order, and polarisations on both sides of the membrane do not differ each other much in terms of reducing the flux rate, while at lower feed concentration (fig.5-24 & 5-25), CP is about 1.5 times greater than TP, and the flux reduction effect on the brine side is 2 times more than that on the feed side.

In conclusion, polarisation phenomena significantly contribute to the flux reduction in osmotic distillation. The flux reduction effect due to concentration polarisation significantly differs from the one due to temperature polarisation when the feed concentration is low. And lastly, the polarisations at the brine side have larger contribution to flux reduction in osmotic distillation.

5.5. DEVELOPMENT OF MODELS FOR OSMOTIC DISTILLATION FLUX PREDICTION

5.5.1. Model development

In the previous sections, it was found that Costello et al (1993) model was suitable to describe the mass and heat transfer at the shell side for both module PV375 and PV660, while Wu and Chen (2000) model was suitable just for module PV660. But whatever model used in the calculations, the outcome is the mass transfer coefficients $k_i (i=f,s)$ expressed in [m.s$^{-1}$]. Those coefficients are then used to determined the concentrations of the liquids at the membrane surfaces by the relations (5-3) and (5-4). However, the flux $J$ here is still unknown. In addition, the relation between water activity (and water vapour pressure) of a solution and its solute content and temperature is complicated as shown in chapter 3. Therefore, integrating equations (5-
3), (5-4) and the relationship \( P\propto(C,T) \) into equation (5-1) to predict the OD flux appears to be too complicated, and solution for the integrated equation is impossible. To overcome this problem, a more convenient and applicable model for OD flux prediction based on the bulk conditions is developed in this section.

The approach to solve this problem is to transform the driving force of the liquid film from molar concentration difference expressed in \([\text{m} \cdot \text{s}^{-1}]\) into water vapour pressure difference expressed in \([\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}]\). In this sense, if we symbolise the mass transfer coefficient of the liquid film at the feed side as \(K_f\) at the brine side as \(K_s\) and of the membrane as \(K_m\) as defined in equation (5-1), then the OD flux can be defined as given in (5-29).

\[
J = K_f (P_{f,m} - P_{f,br}) = K_m (P_{f,m} - P_{s,m}) = K_s (P_{s,m} - P_{s,br})
\]

(5-29)

where the water vapour pressures at the membrane surfaces are determined as described before.

Comparing equations (5-2) and (5-29), the global mass transfer \(K\) can be determined by equation (5-30).

\[
K = \left( \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s} \right)^{-1}
\]

(5-30)

Thus, if \(K_f\) and \(K_s\) can be estimated by models, then the OD flux can be predicted.

In this work, Costello et al (1993) model was used for both modules, while Wu and Chen (2000) model was used for module PV660 only to describe the mass and heat transfer at the shell side, while Sieder-Tate was applied for the tube side. Then based on the experimental flux \(J\), the transformed mass transfer coefficients \(K_f\) and \(K_s\) were determined by (5-29). \(K_m\) was virtually defined by Ordinary diffusion model using the respective tortuosity factors for the two modules as obtained in part (5.3).

The obtained \(K_f\) and \(K_s\) were then used to calculate the "transformed Sherwood number" by its standard definition:

\[
Sh_i^* = \frac{K_i \cdot d_{hi}}{D_{hi}} \quad \text{(where } i=f \text{ for feed, or } s \text{ for brine)}
\]

Then the modified Sherwood number, and Reynolds and Schmidt numbers of the experiment were fitted into the dimensionless equation (5-5).
Fitting data into model (5-5) could be either by plotting \( \log(\text{Sh}/\text{Sc}^\alpha) \times \log(\text{Re}) \) or \( \log(\text{Sh}/\text{Re}^\beta) \times \log(\text{Sc}) \) with the help of Excel 5.0 software. For this purpose, tables of \( \log(\text{Re}) \) and \( \log(\text{Sh}/\text{Sc}^\alpha) \), and \( \log(\text{Sc}) \) and \( \log(\text{Sh}/\text{Re}^\beta) \) were created with \( \alpha \) and \( \beta \) placed in a fixed cell. Then plots of \( \log(\text{Sh}/\text{Sc}^\beta) \times \log(\text{Re}) \) or \( \log(\text{Sh}/\text{Re}^\alpha) \times \log(\text{Sc}) \) were produced for the whole range of data with linear trendline and coefficient of determination \( R^2 \) added. Next, \( \alpha \) and \( \beta \) were varied until the best regression (with highest \( R^2 \)) was achieved. Once the best regression had been achieved, the slope was taken as the exponent \( \alpha \) for plot \( \log(\text{Sh}/\text{Sc}^\beta) \times \log(\text{Re}) \) or \( \beta \) for plot \( \log(\text{Sh}/\text{Re}^\alpha) \times \log(\text{Sc}) \); the intercepts of the plots were then converted to the constant \( A \) of equation (5-5) as \( A = 10^{\text{int} - \text{intercept}} \).

Results of data fitting are shown on figures 5-29 to 5-33. The exponents were taken directly as shown on the figures, while the constant \( A \) were calculated from the intercepts.

**Fig. 5-29:** Correlation of \( \log(\text{Sh}^{\alpha}/\text{Re}^{\beta}) \) vs \( \log(\text{Sc}) \), based on Sieder-Tate.

**Fig. 5-30:** Correlation of \( \log(\text{Sh}^{\alpha}/\text{Sc}^{2.43}) \) vs \( \log(\text{Re}) \), based on Costello.
Fig. 5.31: Correlation of $\log(\text{Sh}^{\prime}/\text{Re}^{0.9})$ vs $\log(\text{Sc})$, based on Sieder-Tate.

Fig. 5.32: Correlation of $\log(\text{Sh}^{\prime}/\text{Sc}^{2.43})$ vs $\log(\text{Re})$, based on Costello.

Fig. 5.33: Correlation of $\log(\text{Sh}^{\prime}/\text{Sc}^{2.43})$ vs $\log(\text{Re})$, based on Wu & Chen.

For module PV375, the mass transfer models are as follows:

- At the tube side:
  \[ \text{Sh}^{\prime} = 152.93 \times 10^{-9} \text{Re}^{0.9} \text{Sc}^{1.71} \]  \hspace{1cm} (5-31)

- At the shell side:
  \[ \text{Sh}^{\prime} = 35.97 \times 10^{-12} \text{Re}^{0.5401} \text{Sc}^{2.43} \]  \hspace{1cm} (5-32)

For module PV660, the mass transfer models are as follows:

- At the tube side:
  \[ \text{Sh}^{\prime} = 28.33 \times 10^{-9} \text{Re}^{1.3} \text{Sc}^{1.5407} \]  \hspace{1cm} (5-33)
At the shell side:

\[ Sh^* = 26.73 \times 10^{12} Re^{0.539} Sc^{2.43} \]  
(if based on Costello model) \hspace{1cm} (5-34)

\[ Sh^* = 5.94 \times 10^{12} Re^{0.9159} Sc^{2.43} \]  
(if based on Wu & Chen model) \hspace{1cm} (5-35)

It can be seen that the exponents of Reynolds number in equations (5-32) and (5-34) are almost the same and these equations differ from each other just with the constants \( A \) which is assumed to be caused by the packing density of the hollow fibre modules, as well as the fibre properties.

It should be stressed that the models were developed on the basis of the internal surface of the fibres. Therefore, the flux \( J \) predicted by those models will be on the basis of the internal surface area of the fibres. If the external surface is concerned, then a factor of \( (r_1/r_0) \) must be multiplied to \( K_r \) and \( K_s \).

5.5.2. Model validation

In order to validate the models for OD flux prediction, the predicted fluxes at the whole range of the experimental conditions were compared to the experimental data. The comparisons are shown on figures 5-34 to 5-36.

Figure 5-34 shows a very good agreement between the predicted and the experimental fluxes. The difference is being about 1.56±0.21%.

![Flux comparison for PV375 by applying models (5-31) & (5-32)](image1)

![Flux comparison for PV660 by applying models (5-33) & (5-34)](image2)
Fig. 5.36: Flux comparison for PV660 by applying models (5-33) & (5-35)

Figures 5.35 and 5.36 also show a very good agreement between the predicted and the experimental fluxes. The uncertainty of fluxes by equations (5-33) & (5-34) is being 0.84±0.43%, while the one by equations (5-33) & (5-35) is 1.08±0.50%.

Amongst the models, the pair (5-33) & (5-34) yields the most accurate flux prediction with 0.84% difference, while the pair (5-31) & (5-32) produces the most precise prediction with uncertainty of ±0.21%.

In conclusion, the models developed in this section are simple, but effective and convenient for use. The predicted fluxes and the experimental ones are in a very good agreement.

5.6. CONCLUSIONS

The process of transport of water vapour across the membrane in osmotic distillation under the condition of the experiment in this work can satisfactorily be considered under Ordinary diffusion mechanism or under the mechanism proposed by Scholfield with appropriate membrane tortuosity factors.

Costello et al (1993) model appeared to be the most suitable for describing mass and heat transfer at the shell side of hollow fibre modules in this work. Wu and Chen model
(2000) was suitable for module PV660 only. Other models were not suitable, probably due to the differences of the experimental conditions.

It was found that the feed concentration at higher range for 45 to 60% caused a significant increase to the concentration of the feed at the membrane surface even though the flux rate was then decreased. This effect was due to the increased viscosity in this region. Temperature, on the other hand, reduced the liquid viscosity, but elevated the polarisations in osmotic distillation due to the increased flux rate.

The concentration and temperature polarisations in OD were found to contribute up to 18% to the flux reduction. The flux reduction due to concentration polarisation was found to be larger than the one due to temperature polarisation. And the flux reduction due to polarisation on the feed side was smaller than on the brine side, especially when the feed concentration was low.

The models developed in this work were convenient to use and successfully predicted the flux rate based only on the variables measured in the bulk conditions.
CHAPTER 6: PILOT SCALE OSMOTIC DISTILLATION FOR CONCENTRATION OF FRUIT JUICES

6.1. INTRODUCTION

It is generally recognised that fruit juice concentrate at concentrations above 60°Brix or more are microbiologically stable under normal storage condition. Such concentrates are usually achieved by conventional vacuum evaporation, which is associated with heat damage to the product.

Osmotic distillation, on the other hand, is considered as a new alternative technique to achieve high concentration concentrates of more than 60°Brix without suffering from heat damage to the final products since it operates at low temperature. Moreover, the osmotic distillation process was successfully carried out in our laboratory for concentrating glucose solution up to 60°Brix with reasonably acceptable flux. Therefore, as a confirmation to the concept of OD in term of achieving high concentration concentrates with high quality, a pilot scale OD trial was set to be carried out to concentrate apple juice and grape juice. These juices were chosen to be the subject of the trial as their aroma and flavour are sensitive to processing.

The objectives of this section are: (i) to set up a pilot scale OD system; (ii) to develop a procedure of running an OD system; (iii) to evaluate the quality of the product; and (iv) to confirm the possibility of applying the mass transfer models for flux prediction of the laboratory modules to the pilot modules.

6.2. SETTING UP THE PILOT OSMOTIC DISTILLATION SYSTEM

As a part of the project, a pilot scale OD unit was set to be constructed. The setting up of the pilot OD system was based on the key part of the unit, the hydrophobic membrane modules supplied by Memcor Australia. The arrangement of the pilot OD unit is presented on figure 6-1.

Three types of hydrophobic hollow fibre modules were supplied with the features listed in table 6-1. The modules had been made in a way that they could easily be attached one to another when larger membrane area is needed.
The pilot OD unit was set up to use one to three modules at a time. And the pressure that the pump was required to maintain was just up to 60% of the bubble point (liquid penetrating pressure) of the fibres to ensure that no liquid penetration into the membrane pores occurred during operation.

Table 6-1

Properties of hydrophobic membrane modules used in pilot scale OD unit

<table>
<thead>
<tr>
<th>Module</th>
<th>PV375-1</th>
<th>PV660-042</th>
<th>PP375-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material of the fibres</td>
<td>PVDF</td>
<td>PVDF</td>
<td>PP</td>
</tr>
<tr>
<td>Inner diameter of fibres, mm</td>
<td>0.375</td>
<td>0.660</td>
<td>0.375</td>
</tr>
<tr>
<td>Outer diameter of fibres, mm</td>
<td>0.625</td>
<td>1.000</td>
<td>0.625</td>
</tr>
<tr>
<td>Total length of fibres, mm</td>
<td>470</td>
<td>470</td>
<td>470</td>
</tr>
<tr>
<td>Effective length of fibres, mm</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Effective area of fibres, m²</td>
<td>1.00</td>
<td>0.42</td>
<td>1.00</td>
</tr>
<tr>
<td>Number of fibres</td>
<td>2830a</td>
<td>677a</td>
<td>2830a</td>
</tr>
<tr>
<td>Pore size, μm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Bubble point, kPa</td>
<td>350</td>
<td>463</td>
<td>350</td>
</tr>
<tr>
<td>Porosity of fibres, %</td>
<td>75</td>
<td>64</td>
<td>75</td>
</tr>
<tr>
<td>Material of the housing</td>
<td>PP</td>
<td>PP</td>
<td>PP</td>
</tr>
<tr>
<td>Material of potting resin</td>
<td>PUR</td>
<td>PUR</td>
<td>PUR</td>
</tr>
<tr>
<td>Inner diameter of the shell, mm</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Feed side cross-section area, mm²</td>
<td>312a</td>
<td>232a</td>
<td>312a</td>
</tr>
<tr>
<td>Brine side cross-section area, mm²</td>
<td>1095a</td>
<td>1432a</td>
<td>1095a</td>
</tr>
</tbody>
</table>

(Data obtained from Memcor Australia; a-Data calculated)

PP – Polypropylene; PUR – Polyurethane

Therefore, based on the data of the membrane modules and considering the pressure drop due to fittings, valves, and flowmeters, the feed pump was chosen to be able to maintain a pressure of about 250kPa at the highest, and the brine pump – 200kPa.
It should be stressed here that the OD unit was originally designed to use the modules PV375-1 and PP375-1. Module PV660-042 was added to the system later for concentration up to 65°Brix of the juices. Therefore, calculations of the design were done on the basis of module PV375-1 (or PP375-1).

At a pressure drop of 200kPa between the two ends of the fibres ($L_T=0.47m$), the maximal cross flow velocity that the feed fluid can achieve in the fibres can be estimated as described in section (3.2.1) of chapter 3.

---

**Fig.6-1**: Pilot scale osmotic distillation unit

P1, P2 – pumps; T1, T2 – feed and brine tanks; V1 to V6 – PVC globe valves; F1, F2 – 100μm filters; FM1, FM2 – flow meters; TV1, TV2 – three-way valves; Th1, Th2 – thermometers, G1, G2 – pressure gauges; HM – Hollow fibre module; CM – conductivity meter; and $V_a$ – air vent.
As an approximation, the feed viscosity was taken as equal to $\mu=4\text{cP}$, then the cross flow velocity of the feed solution was:

$$v_f = \frac{\Delta P \cdot d^2_f}{32 \cdot \mu \cdot L_T} = \frac{200 \times 10^3 \times (0.375 \times 10^{-3})^2}{32 \times 4 \times 10^{-3} \times 0.47} = 0.47 \text{m/s}$$

Then the flow rates of the two streams when using two modules at a time were estimated as follows:

**Flow rate of the feed** = (velocity) x (cross-section area) x 2 modules

$$= (0.47\text{m/s}) \times (312 \times 10^{-6}\text{m}^2) \times 2 = 293.3 \times 10^{-6}\text{m}^3/\text{s}$$

$$= 17.6 \text{LPM (litres per minutes)}$$

**Flow rate of the brine** = (velocity) x (cross-section area) x 2 modules

$$= (0.47\text{m/s}) \times (1095 \times 10^{-6}\text{m}^2) \times 2 = 1029.3 \times 10^{-6}\text{m}^3/\text{s}$$

$$= 61.7 \text{LPM (litres per minutes)}$$

*The brine velocity was chosen as the same as the feed velocity*

Based on the flow rate and the pressure, the pumps and other ancillaries such as valves, flow meters were chosen to suit the system.

Details of all the main parts of the pilot OD units as well as their functions are as follow:

1. Feed pump P1 – Stainless steel POMPE VERGANI (Italy), model STM/70/75/S, max pressure 250kPa, capacity 0.55kW
2. Brine pump P2 - Stainless steel POMPE VERGANI (Italy), model STM/S70/50, max pressure 200kPa, capacity 0.37kW
3. Feed tank T1 – 30-litre PP food grade tank.
5. Valves V1, V2, V4, V6, and the three-way valves TV1, TV2 – PVC 1" valves; V3 and V6 are 1/4" valves, attached to the filters. V1 and V4 are the stop valves used to hold up the feed and the brine respectively during solution preparation. V2 and V5 are used for flow regulation. V3 and V6 are used for discharging the solutions. Besides, V6 functions as an inlet for water for cleaning the brine side (the shell side) when finishing the operation. The three-way valves TV1 and
TV2 are used to change the direction of the feed (upward or downward). The solid line shows the upward direction of the feed. During the operation or cleaning, TV1, and TV2 can divert the feed from the solid line into the dash line, and so the direction of the feed – downward.

6. Flowmeters FM1 and FM2 – 1" EZ-VIEW flow meters, Hedland, US with maximal flow rate 60LPM, deviation ±2.5LMP.

7. Thermometers Th1 and Th2 – mercury thermometer with deviation of ±0.5°C. The thermometer are used to monitor the changes of temperatures of the solutions during operation so that action can be taken on time to keep the solutions' temperatures in within the specified range.

8. Conductivity meter CM – OAKTON model FM1, Oakton, US, with deviation of ±0.1mS (mili Siemens), and measuring range 0-10mS. This conductivity meter monitors the conductivity of the feed solution. A dramatic increase of the feed solution conductivity indicates that salt of the brine is leaked into the feed solution, and the operation should be stopped immediately.

9. Pressure gauges G1 – up to 400kPa, G2 – up to 200kPa with deviation of ±5kPa. Special attention should be paid to G1 during the operation to ensure that the pressure is in the range limit. If it goes beyond the limit, the flow rate should be reduced by using V2.


11. Air vent V_a – 1/8" stainless steel valve. This vent is to allow air escaping from the feed stream at the beginning of the operation.

12. All the fittings are of 1" dimension, and made of food-grade PVC plastic.

All the parts were installed onto a corrosion-protected-by-paint frame made from L50 steel bar. The constructed OD unit was able to use one, two or three modules at a time in accordance to the need of membrane area. Illustration of the pilot OD unit is on figures 6-2 and 6-3.
6.3. OD CONCENTRATION OF APPLE JUICE AND GRAPE JUICE

6.3.1. Method of OD flux identification

On the pilot scale, the OD flux can be identified by monitoring changes of the feed volume over the time of operation. The dimension of the OD flux is then in \([\text{l.m}^{-2}\text{.h}^{-1}]\), or can be converted into \([\text{kg.m}^{-2}\text{.h}^{-1}]\) by multiplying to the density of water at the process temperature. With the process temperature ranging from 25 to 35°C, the density of water can be taken as equal to 1000\(\text{kg.m}^{-3}\).

To monitor the feed volume changes, a millimetre ruler was vertically stuck to the feed tank T1. Then calibration was made to identify the feed volume that corresponds to one millimetre on the ruler. For the case of our OD unit, 40mm on the ruler corresponds to 3 litres of the feed solution.

When starting the reading for flux, changes of the level of the feed solution is recorded over a period of time (15 minutes), and then the OD flux is identified. The flux
measured by this way can be of an accuracy of about ±0.15kg.m⁻².h⁻¹, and the flux should be understood as an average flux for that period of time.

6.3.2. Method of controlling the operating conditions
During the operation, due to heat and mass transfer, as well as due to the friction due to the pumps and other devices the following operating conditions may be changed and need to be under control:

- The temperatures of the two streams increase mainly due to the friction of the flow at the pump propellers. These temperatures can be relatively controlled by putting tightly closed ice bottles into the brine tank T2. As the brine temperature drops, the feed temperature drops too due to the heat transfer at the membrane.

- The pressure at the feed stream (G1) increases due to the increasing feed concentration during the OD process. When pressure reading from G1 exceeds the set value (normally at about 160kPa), valve V2 must be further partially closed to reduce to flow rate, and consequently the pressure.

- The brine concentration decreases as a result of absorbing water from the feed. To keep the brine solution at a certain concentration, as higher concentration is desirable to improve the OD process, a more concentrated brine solution can be added to the brine tank T2. The additional solution is usually an over-saturated solution, but not the pure and dry crystals or flakes of the salt, especially when CaCl₂ is used. It is that because if the dry crystals or flakes of the salt are added to the brine, their dissociation will generate a significant amount of heat that increases the brine temperature, and consequently worsen the performance of the OD process.

- Other factors such as brine flow rate and feed conductivity are just a matter of monitoring. When the feed conductivity by (CM) suddenly increases, which indicates the lead of brine into the feed, the process must be stopped immediately.

6.3.3. Operation procedure
6.3.3.1. Preparation step

a. Preparation of the OD unit:

Two hollow fibre modules obtained from Memcor Australia as listed in table 6-1 were used at a time in the pilot scale OD unit. Before the installation of the hollow fibre modules, the tanks, the pipeline, and other ancillaries had been washed and checked free of any dusts and potential contaminants.

After the installation of the hollow fibre modules, they were subjected to the integrity testing by pumping filtered water through the inside of the fibres at a pressure of 100kpa and temperature $30^\circ\text{C}$ for 30 minutes. Then the modules were uninstalled from the OD unit and were checked if there was any water accumulated at the shell side. If any leak occurs, the module must be discarded. After that all water in the inside of the fibre was blown out with filtered compressed air. Finally, they were reinstalled, and the OD machine was ready for the experiment.

During the integrity testing, a can of 4 litres and a stopwatch were also used to check the calibration of the flowmeter FM1. FM2 was assumed to have the same accuracy.

b. Preparation of the brine solution:

Commercial calcium chloride ($\text{CaCl}_2$) of 74% purity was used to prepare the brine solution. For the first trial for concentration of apple juice, 30 litres of filtered water were used to dilute 45kg of $\text{CaCl}_2$ to obtain a solution of 62.5$^\circ\text{Brix}$, which corresponds to about 42% w/w pure $\text{CaCl}_2$ solution. At the second trial for concentration grape juice, the brine of the previous batch, after reconcentration by steam-heated evaporation, was reused plus about 40kg of over-saturated brine (10 litres water/30kg $\text{CaCl}_2$) that was added later.

Then the salt solution was kept in the brine tank one day prior to use so that the brine solution could have enough time to cool down to ambient temperature. It had to be in that way to avoid the inverse effect of the so-called membrane distillation process due to the higher temperature of the brine compared to the one of the feed (fruit juice).
It should be understood that CaCl₂ solution of 42% w/w is nearly at saturation point at 20°C. When the ambient temperature is lower than 20°C, the prepared CaCl₂ solution should be more diluted, just below the saturation point at the lowest temperature of the day, so that to avoid any crystallisation in the brine pump and at any points of the system.

Another bucket of extra over-saturated CaCl₂ was also prepared for later addition to the brine tank to keep the brine solution at as high as possible concentration.

c. Preparation of the juices:

There were pilot trials for concentration of apple juice and grape juice.  

For apple juice: The fresh apple juice produced by Bilpin Company was obtained from the market. 11 three-litre bottles were used in the experiment. As the quality of the juice in different bottle may be different, all the juice was poured in the feed tank just before the experiment and mixed well. Then 3 litres was taken back for reference samples in the later quality evaluation testing. 

For grape juice: Fresh Chardonnay grape was obtained from the local vineyard, then pressed to obtain fresh grape juice of about 21°Brix. The juice was then depectinised by adding pectinase (Pectinex Ultra SP-L, Novo Nordisk Bioindustrial Pty. Ltd., Australia) at concentration of 100ppm at temperature 5°C for overnight. The depectinised juice was then ultrafiltered by a pilot ultrafiltration unit (Polysulfone UF, Romicon, Inc., US). The ultrafiltration was carried out at temperature ranging from 20°C to 45°C. Next, the ultrafiltered grape juice was cooled down to about 5°C in a cool room, and finally it was kept at ambient temperature (15°C) for overnight just before the OD process.

d. Preparation of other ancillaries:

One day before the OD experiment, about 25 two-litre plastic bottles of water were placed in a freezer (-20°C). They were later used as a temperature regulator of the solutions involved in the OD process.
Before running the trial, all monitoring devices such as conductivity meter and refractometer were calibrated by standard procedures. Sample containers were readily marked for sampling.

6.3.3.2. OD concentration of fruit juices

After finishing the preparation, the pilot osmotic distillation for concentration of fruit juices was carried out under the following procedure:

1. Close the valves V1, V3 and V4, V6. Then pour the juice and the brine into tanks T1 and T2 respectively. Initial level of the juice in T1 was marked for later reading of the dead volume of the system.

2. Fully open valve V4, and partially open valve V5. Allow about 5 seconds for the liquid to fill in the pump P2, and then start pumping of the brine solution through the shell side of the modules in the upward direction. Allow 5 minutes to stabilise the flow rate at about 45 to 50LPM, which corresponds to an average tangential velocity of about 0.34 to 0.38m/s in the shell side of the modules PV375-1 and PP375-1, and about 0.28 to 0.50m/s for modules PV660-042. The velocity was calculated as the flow rate divided by the cross-section area of the flow.

3. Fully open valve V1 and partially open valve V2. Allow about 5 seconds for the juice to fill in the pump P1, and then start pumping the juice through the fibres in the upward direction. Slightly open the air vent to allow air escaping from the feed stream, and collect the juice coming out through the vent for dead volume determination later. The dead volume of the system was then recorded by the change of the juice level in the feed tank from the initial level to the stabilised one minus the collected amount of juice from the venting. The dead volume of the system when using modules PV375-1 or PP375-1 was 4.5 litres, while the one with modules PV660-042 was 5.25 litres. The flow rate of the juice was maintained, by regulating valve V2, at 10LPM, which corresponds to an average tangential velocity of about 0.27m/s for modules PV375-1 and PP375-1, and about 0.36m/s for modules PV660-042. Determination of the velocity here is as the same as with the brine solution velocity.
4. Start the stopwatch set at 15 minutes interval for data recording. Data of the experiment were taken at the 15th ±1-minute of each interval. The data included:
   - Apple juice level in the feed tank by the ruler stuck vertically to the tank.
   - Apple juice and brine concentrations by a refractometer (Atago, Japan).
   - Apple juice and brine temperatures by thermometers Th1 and Th2 inserted in probes on the pipeline of the OD machine as illustrated on figure 6-1.
   - Flow rate of the two solutions by the in-line EZ-View flow meters FM1 and FM2.
   - Pressure of the solutions by the in-line pressure gauges G1 and G2.
   - Apple juice conductivity by OAKTON FM1 conductivity monitoring device CM.

5. During the concentration process, the temperature of the two streams increased. Therefore, ice bottles were used at a rate of about 6 litres per hour to relatively keep the temperature constant.

Near to the end of every run, due to the increased concentration of the feed, hence increased viscosity and pressure, there were some interventions to change the flow rate of the feed solution to maintain the pressure difference across the membrane below the level of 140kpa (or about 40% of the bubble point of the fibres). The concentration process was running until there was not enough juice for the pump to continue operation.

6. Stop all the pumps, then collect the juice concentrate from the OD unit through the discharge valve V3, and later distributed into 100ml jar for storage.

7. After finishing collection of the concentrate, cleaning of the OD system followed.

6.3.3.3. Cleaning and Finishing
As membrane fouling is a major problem in many membrane separation processes such as microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO), but not in the case of osmotic distillation (Sheng, Johnson & Lefebvre, 1991). It is that because in MF, UF and RO liquid and suspended particles are passing through the membrane
pores, forming a gel layer at the membrane surfaces and blocking the pores not only at the pore ends but also along the pore wall, then finally causing a very-difficult-to-clean fouling. While in osmotic distillation, no liquid or suspended particles are passing through the membrane pores but only water vapour, and due to the hydrophobic nature of the membrane employed in OD, there are few substances such as protein, fat, and wax that may stick to the membrane surface (Nguyen, H.M. 2001, pers. comm., 12 Jul).

Therefore, Cleaning of the OD system in this work was carried out mainly with filtered water, and NaOH 0.1-1% solution on the feed side as recommended by Durham and Nguyen (1994), and Memcor Australia – the membrane manufacturer. Following was the procedure of cleaning the OD unit:

1. First, valve V3 was closed and the feed tank was filled with water and pumping started as soon as possible to push out the stay-still juice remained inside the fibres and to prevent further concentration of the juice there, which may cause stickiness and crystallisation. The later is detrimental to the integrity of the hollow fibres, and in some cases, it may break the fibres.

2. Water in the feed tank was circulated for about 5 minutes, then drained from the feed tank via valve V3. This step was repeated for two more times to wash out any juice from the system.

3. The feed tank was filled with filtered water again and pumping was resumed.

4. In the meantime of running step (3), the brine solution was held in the brine tank by closing valve V4. The brine tank was then effectively isolated from the system by closing valve V4 and disconnecting the outlet pipe from the modules HM to the brine tank. The remaining brine in the pipeline and the hollow fibre modules was drained via the discharging valve V6.

5. A hose from the filtered water supply was connected to the opened valve V6. The water then flown through F2, V5, FM2, the shell side of the modules, and finally discharged into the drainage system. To get the pump P2 free of the brine, the bolt at the bottom of the pump was opened for some times so that water to run through there. As on this side only CaCl₂, a very strongly dissociated agent, was involved, rinsing only with water for 30 minutes was enough to get it clean.
6. After running step (3) for about 30 minutes, water was then again drained from the system via valve V3.

7. The feed tank was then filled with a solution of 0.1% NaOH and circulation was taken place for 30 minutes. Then it was drained and replaced with filtered water.

8. The feed side was then washed and rinsed with filtered water for another 3 times of about 5 minutes each.

9. After the cleaning finished, the modules were dismantled from the OD system. Then filtered compressed air at pressure of about 6- to 90kPa was used to dry the modules for about an hour. Finally, they were reinstalled into the OD machine, ready for the next use.

6.3.4. Results

6.3.4.1. Concentration of apple juice

Two modules of PP375-1 were used in the trial for concentration of apple juice. The pilot trial concentrated 30 litres of fresh apple juice with initial concentration of 9.5°Brix.

The experiment lasted for 8 hours to achieve a 5-fold concentration. The final concentrate was of 48°Brix.

During the experiment, the operating conditions were maintained as shown on figure 6-4.
Fig. 6-4: The operating conditions during pilot OD concentration of apple juice.
The feed and brine temperature $T_f$, $T_s$ are in °C; the feed and brine flow rate $V_f$, $V_s$ are in LPM; the hydrodynamic pressure of the two streams $P_f$, $P_s$ are in kPa.

As can be seen on figure 6-4, the temperature of the two solutions steadily increased from 23 to 31 for the juice and 25 to 33 for the brine, and the brine temperature was consistently higher than the one of the feed throughout the experiment. This temperature difference is not desirable in osmotic distillation as it reduces the driving force of the process.

While the flow rates of the two solutions were kept constant before and after the external intervention, the pressures of the two solutions were fluctuated during the time. It is that because the pressure drops depend on the flow rate and the viscosity of a solution, which in turn is a function of concentration and temperature.
The pressure of the brine dropped rapidly during the first hour of the trial, it then slowly decreased from 30 to 15kpa at the flow rate of 45LPM and from 24 to 18 at the flow rate of 15LPM.
rate of 60LPM. The pressure decreases were due to the decreased concentration and the increased temperature of the brine solution during the experiment.

In the opposite direction was the pressure of the juice. It was seen that the pressure rapidly increased in the juice concentration region of 23\(^0\)Brix up or after 5 hours of running. However, the maximum pressure difference was maintained below 140kpa, which was about 40% of the bubble point of the membrane and was considered as a safe pressure for the OD process.

The flux rate, juice conductivity and the concentration changes of the two solutions are illustrated in figure 6-5.

As mentioned above, due to the heat of mixing, the CaCl\(_2\) flakes could not be added to the brine solution during the process to maintain constantly high concentration of the brine solution for the purpose to lower the water vapour pressure of the brine to favour the flux rate. Even though then, the flux rate of the pilot OD trial appeared to be stable ranging from 2.25 at the beginning to 0.9kg.m\(^{-2}\).h\(^{-1}\) at the end. The average flux was 1.58kg.m\(^{-2}\).h\(^{-1}\).

The flux rate at the end of the trial remained unchanged even though the feed concentration increased rapidly. It is probably due to the increased temperature of the process. The flux obtained in the pilot OD trial was about 20% lower than the one obtained from the laboratory experiment, which had been conducted with glucose solution as the feed, and 45% CaCl\(_2\) (or 67\(^0\)Brix) as the brine, using PVDF fibres with the same properties. Exact comparison of the flux is difficult due to the differences in the operating conditions and the membrane materials used.
The conductivity of the juice increased consistently with the increase of the juice concentration and reached the highest value of 3.3mS at the juice concentration 28-32°Brix. At higher concentration, the conductivity was adversely influenced by the concentration.

The consistency of the changes of the conductivity of the juice indicated the integrity of the OD process. It means that there was no leak of Ca⁺ and Cl⁻ ions in the juice. It was further confirmed by titration with AgNO₃ reagent.

The product of the pilot trial was about 5 litres concentrate of 48°Brix of apple juice. The concentrate was clear, with a darker colour than the one of the fresh juice. However, when diluted to the initial 9.5°Brix, the diluted juice and the fresh one could not be distinguished by colour and taste. It was then distributed into 100ml jars for storage at 30, 5 and -20°C for later shelf life testing and sensory evaluation.
6.3.4.2. Concentration of grape juice

Having experienced from the previous trial that was to stop due to increased viscosity, hence pressure, and not-enough juice to run at the end, OD concentration of grape juice was planned on two stages. The first stage was to concentrate grape juice from 21°Brix to about 40-42°Brix by using modules PV375-1, and the second stage was to further concentrate the juice to above 60°Brix by using modules PV660-042. The idea was to use the so-called cascade effect in osmotic distillation. While most of the water would be removed from the juice during the first stage and the juice viscosity was still low, modules PV375-1 (with smaller fibres) with much higher flux were used; and only small amount of water would be removed during the second stage and the juice viscosity was high, modules PV660-042 were used to cope with the pressure problem associated with high concentration of the concentrate.

a. The first stage:

The first stage was to concentrate the juice from the initial concentration of 21°Brix to concentration when the feed stream pressure exceeded 140kPa due to the increased viscosity. Two modules PV375-1 were used in the trial. The operating conditions and the flux rate as well as the changes of solutions' concentrations are presented on figures 6-6 and 6-7.

The fluctuation of the feed pressure was due to the external intervention to reduce the feed flow rate (via valve V2) when the feed concentration, hence the viscosity, increased during the course of the trial. Even at the end of the trial, the flow rate was regulated to as low as 2LPM, which corresponds to cross flow velocity of 0.053m/s, the feed stream pressure was about 150kPa, and the trial was stopped there yielding a concentration of 42.5°Brix.

The temperature of the brine was again two degrees higher than that of the feed throughout the trial.
Fig.6-6: The operating conditions during pilot OD concentration of grape juice – The first stage. The feed and brine temperature $T_f$, $T_s$ are in $^\circ$C; the feed and brine flow rate $V_f$, $V_s$ are in LPM; the hydrodynamic pressure of the two streams $P_f$, $P_s$ are in kPa.

The flux of the trial was in a decreasing trend from 2.4 to 1.35kg.m$^{-2}$.h$^{-1}$ at the end. It was due to the decreasing driving force of the process as the brine got diluted, but the feed – concentrated (see figure 6-8). The average flux was about 1.88kg.m$^{-2}$.h$^{-1}$, which is 14% lower than the one achieved in the laboratory (see figure 3-21 for flux at 29$^\circ$C). However, the brine in this pilot trial was at lower concentration, and the brine temperature was two degrees higher than the one of the feed. Therefore, it can be concluded that the flux obtained in the pilot trial is comparable to the one obtained in the laboratory.

If the driving force, created by the composition and concentration of the feed and the brine in the case of concentrating apple juice where PP375 was used and concentrating grape juice where PVDF375 was used, is considered; the fluxes obtained in both cases are almost the same. The consistent changes of the feed conductivity indicated the process integrity. It reached the highest value of 3.0mS at
juice concentration of 28-32°Brix (which is the same concentration range of apple juice).

![Stage 1 - Pilot Concentration of Grape Juice](image)

**Fig. 6-7:** Changes of the flux, solutions’ concentrations and feed conductivity during the OD concentration of apple juice – the first stage. The flux J is in kg.m\(^{-2}\).h\(^{-1}\); the feed and brine concentrations C\(f\), C\(s\) are in °Brix; and the feed conductivity \(S_f\) is in mS.
(Note: The flux and conductivity were multiplied by 10)

After finishing the first stage, the semi-concentrate of 42.5°Brix was kept at ambient temperature for overnight before being further concentrated on the second stage.

**b. The second stage:**

The second stage was to concentrate the juice obtained from the first stage (42.5°Brix) to concentration when the feed stream pressure exceeded 140kPa due to the increased viscosity. Two modules PV660-042 were used in the trial. The operating conditions and the flux rate as well as the changes of solutions’ concentrations are presented on figures 6-8 and 6-9.
In the second stage, the brine from the first stage was reused after reconcentration by steam-heated evaporation. A further 10 litres of water and 30kg of CaCl₂ flakes were used to prepare an extra over-saturated brine solution that later was added to the brine tank T2 when the temperature was up to 30°C to avoid any problem of CaCl₂ crystallisation.

**Fig.6-8:** The operating conditions during pilot OD concentration of grape juice – The second stage.

The feed and brine temperature $T_f, T_s$ are in °C; the feed and brine flow rate $V_f, V_s$ are in LPM; the hydrodynamic pressure of the two streams $P_f, P_s$ are in kPa.

During the first 50 minutes, no ice bottle (cooling media) was used to allow the temperatures of the two streams raised up to about 30°C to ease the flows as well as the OD flux.

Due to the increase of temperature during the first 50 minutes, the feed pressure dropped, but the OD flux and the feed conductivity increased. From the 50th minutes of the trial, the OD flux appeared to be relatively stable until the last 100 minutes. It was that due to the fluctuation of the solutions' temperatures.

At the end of the trial, even though the feed flow rate was reduced to 3LPM, which corresponds to a cross flow velocity of 0.11m/s, the feed stream pressure was up to
160kPa before it came down to 155kPa when temperature was allowed to increase to 35°C.

**Stage 2 - Pilot Concentration of Grape Juice**

![Graph showing concentration changes](image)

**Fig.6-9:** Changes of the flux, solutions' concentrations and feed conductivity during the OD concentration of apple juice - The second stage.

The flux \( J \) is in kg.m\(^{-2}\).h\(^{-1}\); the feed and brine concentrations \( C_f \), \( C_s \) are in \(^o\)Brix; and the feed conductivity \( S_f \) is in mS.

(Note: The flux and conductivity were multiplied by 10)

The average flux obtained in the second trial was about 0.69 kg.m\(^{-2}\).h\(^{-1}\) at an average temperature of 31.7°C. This flux is about 2.7 times lower than that of the first stage. The low flux was mainly due to thicker membrane, and partially weaker driving force as the brine was more dilute while the feed was more concentrated.

If referred to figure 3-22 (chapter 2), it can be said that the pilot trial flux of PV660 fibres is much lower that that of the laboratory trial which is about 1.40 kg.m\(^{-2}\).h\(^{-1}\) at 31°C. However, the comparison should take into account the differences of the driving force in both cases since the fibres are the same. In both cases, the feed solutions were almost the same in term of concentration (40-66\(^o\)TS), hence almost the same water activity of about 0.850 (referred to Appendix 4) or so assumed. On the other hand, the brine solutions were at different concentrations as 67\(^o\)Brix (corresponding to
45% w/w, $a_w=0.275$, referred to Appendix 4) for the laboratory trial, and 52°Brix (corresponding to 34% w/w, $a_w=0.557$) for the pilot trial. As a result, it lead to the differences in the driving force of the OD process as follows:

- Lab trial: $\Delta P_{b,Lab} = \Delta a_w \times P_0 = (0.850 - 0.275) \times P_0 = 0.575 \times P_0$
- Pilot trial: $\Delta P_{b,Pilot} = \Delta a_w \times P_0 = (0.850 - 0.557) \times P_0 = 0.293 \times P_0$

$\Rightarrow \Delta P_{b,Lab} = 1.96 \times \Delta P_{b,Pilot}$

Since the OD flux is directly proportional to the driving force as described in chapter 5, it can be concluded that the pilot flux of 0.69kg.m$^{-2}$.h$^{-1}$ is comparable to the laboratory flux of 1.40kg.m$^{-2}$.h$^{-1}$ if the driving force and the solutions’ velocities are carefully considered. In other words, the fluxes would be identical if the same operating conditions were applied.

However, the modules PV660-042 should be used in a so-called cascade system as mentioned before just to remove a little amount of water from the feed, but to achieve high concentration of the final products.

6.4. SENSORY EVALUATION OF JUICES PREPARED BY OD

Apple juice concentrate of 48°Brix by OD was delivered into sterilised 100ml jars, and stored at -20°C and +5°C. Fresh samples (unprocessed) were kept in sterilised 100ml jars and stored at -20°C.

Samples of fresh apple juice are referred to as the reference; samples prepared from the concentrate stored at -20°C are referred to as sample 1; and samples prepared from the concentrate stored at +5°C are referred to as sample 2.

After one months of storage, a sensory evaluation of apple juice was carried out. One day before the sensory session, the concentrate samples were diluted with distilled water to 9.5°Brix as the same as of the fresh sample. Then all the samples were kept at +5°C for overnight.

Ranking test was used to discriminate if there was any significant difference between samples in term of colour, aroma, flavour and overall acceptability. The test procedure and data analysis followed the one described by Meilgaard, Civille and Carr (1999).
15 peer student panellists were employed in the sensory evaluation. The subjects were asked to rank the samples 1, 2 or 3 for colour, aroma and flavour. The rankings of each attribute of a sample were summed.

Friedman analysis was used to analyse the data. Following is the procedure of Friedman analysis:

1. Calculate the rank sum of sample j - $x_{rj}$

2. Calculate $T$

$$T = \left\{ \frac{12}{b.t.(l+1)} \sum_{j=1}^{t} x_{rj}^2 \right\} - 3.b(l+1)$$

$b$ – number of panellists

$t$ – number of samples

$x_{rj}$ – rank sum of sample j

3. Take the value of $\chi^2_{a,l-1}$-Distribution for $\alpha$-level of significance and $(t-1)$ degree of freedom from statistical table. For $\alpha=0.05$ and degree of freedom $(t-1)=2$ as in our case, $\chi^2_{a,l-1}=5.99$ (Meilgaard, Civille & Carr, 1999, pp.360).

4. If $T<\chi^2_{a,l-1}$, then the differences between samples are considered not-significant; if $T>\chi^2_{a,l-1}$, then calculate:

$$LSD_{rank} = t_{a/2,\infty} \sqrt{\frac{b.t.(l+1)}{6}}$$

$t_{a/2,\infty}$ - Student’s t-Distribution at $\alpha/2$-level and $\infty$ degree of freedom.

For $\alpha=0.05$, $t_{a/2,\infty}=1.960$ (Meilgaard, Civille & Carr, 1999, pp.355), and the calculated $LSD_{rank}=10.74$.

Two samples are considered significantly different if their rank sums differ from each other by more than the calculated $LSD_{rank}$. 
Results of the Friedman analysis are shown in table 6-2. Higher values of the attributes of a sample indicate better quality. For example, the colour of the sample was ranked 1 for the darkest, and 3 for the lightest; or 1 for the weakest aroma, and 3 for the strongest aroma; etc.

Comparing the scores of sample 1 and the reference one, it can be concluded that osmotic distillation does not, or very little, pose any damage to the quality of the juice according to the Friedman analysis. Flavour and overall acceptability scores of the samples clearly indicate the ability of osmotic distillation to produce fruit juice concentrate without “off-flavour” which is usually associated to the evaporative concentration technique.

The significant differences of the colour and aroma of sample 2 and the reference, however, indicate that fruit juice concentrate at 48°Brix is still not stable enough at the normal storage condition (+5°C).

**Table 6-2**

*Sensory evaluation of apple juice*

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>( x_{i,j} )</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>( T=13.33 &gt; \chi^2_{a,i-1} )</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Aroma</td>
<td>( x_{i,j} )</td>
<td>26</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>( T=17.73 &gt; \chi^2_{a,i-1} )</td>
<td>26</td>
<td>43</td>
</tr>
<tr>
<td>Flavour</td>
<td>( x_{i,j} )</td>
<td>29</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>( T=0.93 &lt; \chi^2_{a,i-1} )</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>Acceptability</td>
<td>( x_{i,j} )</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>( T=0.53 &lt; \chi^2_{a,i-1} )</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

(The values in the table are the rank sums of each attribute; for every attribute, values appear in the same row are not significantly different, while values appear in different rows are significantly different)
For the grape juice of 65°Brix, panellists agreed that there was a little change of the colour of the reconstituted juice, but the aroma and flavour were difficult to distinguish between the fresh and the reconstituted samples. And the likeliness was all the same.

6.5. APPLICATION OF MODELS FOR FLUX PREDICTION

Application of the models developed in chapter 5 for flux prediction of the pilot OD concentration of fruit juices is difficult due to variation of the operating conditions especially the temperature. The measured flux in the pilot trial was an average flux over a period of 15 minutes, while the temperature was recorded at the end of every 15th minute of the period. The predicted flux by models, on the other hand, is dependent on the exact operating conditions at that particular moment. Moreover, only modules PV375-1 and PV660-042 have the same membrane properties as the one used in the laboratory.

However, the predicted flux, based on the recorded operating conditions of the pilot trials, can be roughly compared to the measured one.

Assuming that physical properties of grape juice are as identical as the ones of aqueous glucose solution, and other operating conditions are as the same as the ones recorded during the pilot trials, the OD flux can be predicted by the developed models as described in equations (5-31) and (5-32) for PV375 fibres, and (5-33) and (5-34) for PV660 fibres.

The predicted and the measured fluxes are shown on figures 6-10 and 6-11 for PV375 and PV660 fibres respectively.

The graphs show some differences between the measured and the predicted flux. However, in general, they are comparably in good agreement. It is a further confirmation of the validity of the models developed in this work.
Fig. 6-10: Prediction of OD flux for the pilot OD concentration of grape juice by the developed model – The first stage.

Fig. 6-11: Prediction of OD flux for the pilot OD concentration of grape juice by the developed model – the second stage.
6.6. CONCLUSIONS

It can be concluded that the OD pilot concentration using Memcor Australia microporous hydrophobic PP and PVDF hollow fibre modules was successfully carried out at the pilot plant of the University of Western Sydney, Hawkesbury campus, Richmond, New South Wales, Australia.

The flux rates obtained from the pilot trials are similar to the results of experiments that have been carried out in the laboratory concentrating glucose solution under similar operating conditions for the case of PV375 and PV660 with regards to the driving force of the OD process. The average flux rate of 1.88kg.m\(^{-2}\).h\(^{-1}\) in the case of the first stage concentration of grape juice proves that the OD process can be applicable in the fruit juice industry, and cascade system should be applied for achieving high concentration of the concentrate.

PP and PVDF fibres appear to have almost the same OD flux if the same operating conditions are applied.

The flux obtained in the pilot trial of this work was comparable to that of Sheng, Johnson and Lefebvre (1991), Durham (1992), Hogan et al (1998), and Bailey et al (2000).

The final concentration achieved in the pilot trial was 65\(^{\circ}\)Brix. This concentration was considered high enough to ensure the stability of the concentrate to be stored at normal temperature.

The quality of the concentrate in term of clarity, colour, aroma and flavour achieved in this work indicates the advantage and superiority of the OD technology in achieving high concentration with high quality of fruit juice concentrate.

The pilot trials lasted for more than seven and a half hours, however the flux rate was relatively stable throughout the run even though when achieving 65\(^{\circ}\)Brix of the feed. This indicates that osmotic distillation is almost free from fouling. And this can be considered as another advantage over other membrane processes.
OVERALL SUMMARY

Three types of hollow fibres PV375, PV660 and PP375 were used in the study. The first two types were used in both laboratory and pilot scale experiments, while the last one was employed only in pilot scale experimentation.

A laboratory scale and a pilot scale osmotic distillation system were adequately designed and constructed, and successfully operated.

On laboratory scale, the osmotic distillation flux under the operating conditions of this study statistically ranged from 1.67±0.02 to 4.73±0.08kg.m⁻².h⁻¹ for module PV375, concentrating glucose solutions from 30 to 40°Brix; and 1.00±0.02 to 2.87±0.05kg.m⁻².h⁻¹ for module PV660, concentrating glucose solutions from 45 to 60°Brix over the temperature range from 25 to 45°C.

All operating factors such as temperature, feed concentration, and brine cross flow velocity, but not the feed cross flow velocity, were found to have significant effect of the osmotic distillation flux. Amongst them, temperature is the most significantly affecting factor with exponential effect.

The effect of the feed cross flow velocity on the osmotic distillation flux was not significant. However, it tends to be significant at higher feed concentrations.

Costello et al (1993), and Wu and Chen (2000) models for mass transfer in microfiltration hollow fibre modules were found to be the most appropriately applicable to describe the concentration and temperature profiles at the membrane surface on the shell side in the case of this study, while Seider-Tate equation was applicable for the tube side due to the symmetrical similarity of the geometry between the inside side of hollow fibres and a pipe. Thus, the concentration and temperature polarisations in osmotic distillation in hollow fibre modules were successful depicted, and their contribution to osmotic distillation flux decay was determined. Polarisation (including both concentration and temperature) was found to contribute up to 18.0±1.23% and 16.8±0.58% to flux reduction for module PV375 and PV660 respectively.
Scholfield and Ordinary Diffusion models were adequately validated for water vapour transport across a hydrophobic membrane in osmotic distillation under our experimental conditions.

The mass transfer models developed in this work successfully predicted the osmotic distillation flux based only on the bulk conditions for both laboratory and pilot scale trials.

Models for water activity and viscosity of aqueous glucose and calcium chloride solutions were successfully developed. The consistent prediction by model1 for glucose and model2 for calcium chloride solution is a proof of the success and the usefulness of the models in modelling the osmotic distillation process.

Pilot scale experimentation of osmotic distillation for concentration apple juice and grape juice resulted in relatively the same flux of that obtained in laboratory if the same operating conditions were applied. However, the average flux of about 1.88kg.m⁻².h⁻¹ under the pilot conditions with the consistency of the final products demonstrates the applicability and competitiveness of osmotic distillation in the fruit juice industry.

PP and PVDF fibres were found to have the same resistance to the osmotic distillation flux.

Cascade effect was successfully employed in the pilot trial by using bigger fibres to cope with high pressure associated with high concentration of the feed. The trial proved that OD was able to achieve 65°Brix or more of the concentrate without suffering any problem of fouling.

In summary, both laboratory and pilot osmotic distillation systems were adequately designed and successfully put into operation. The osmotic distillation process was found to be applicable for concentration of fruit juices with an acceptable flux rate, but achieving high solids concentration with most of the quality preserved. The validated mass transfer models are considered useful for flux prediction and designing purposes.
RECOMMENDATIONS

The feed cross flow velocity was found to be insignificant in affecting the flux rate of osmotic distillation, especially when the feed concentration is low. In addition, high feed velocity is associated with high pressure, which requires more energy and poses a threat of damaging the hydrophobicity of the membrane and the membrane itself. Therefore, moderate feed velocity should be applied in osmotic distillation.

The brine velocity, however, has significant effect on the flux and increasing the flow rate at the shell side (where the brine is) does not result in much increase of the pressure. Therefore, increased brine velocity should be beneficial to improve the OD process.

Temperature was found to be the most affecting factor on the performance of the OD process. It is recommended to use temperature as the key tool to control the OD process rather than the liquids' velocities. However, the effect of temperature on the quality of the final product should be studied.

A cascade system, which uses finer fibres to deal with low feed concentration and bigger fibres to cope with the pressure associated with high concentration of the feed, should be used to effectively achieve high solid content concentrates.

On industrial scale, a complete system for reconcentration of the brine should be available. This system must minimally have the same evaporation capacity of the osmotic distillation modules, and should be able to control the temperature of the brine solution.

In osmotic distillation, hydrophobicity of the membrane is a critical factor to ensure the process integrity. Therefore, it must be preserved not only during the operation, but also during cleaning and storage of the membrane.

Physically, the hydrophobicity of the membrane may be damaged by overpressure beyond the bubble point. Therefore, it is recommended to operate the OD process at pressure of about 40% of the bubble point to avoid the physical damage to the membrane.
Chemically, the hydrophobicity of the membrane may be damaged by the interaction between the liquid and the membrane, especially the cleaning reagent. The effect may be due to chemical reaction, concentration of the liquid, time of contact, and temperature as well. Unfortunately, due to the limit of time, this project could not be extended to this area of investigation. The outcome of a study in this area could also be a crucial step forward to successful application of osmotic distillation in the food industry,
Appendix 1: The Laboratory Experimental Data of OD Flux

1. For module PV375

Table A1-1
The laboratory experimental OD flux for module PV375

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T – Temperature of both solutions
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\nu_\text{f}, \nu_\text{s} – Cross flow velocity of glucose (feed), and brine solution.
W – The amount of water removed from the feed over 15 minutes with uncertainty ±0.05g.
J – The OD flux determined on the basis of the inner surface of the fibres (=106.0cm²).
The brine was always 45%w/w CaCl₂ aqueous solution.

2. For module PV660

Table A1-2
The laboratory experimental OD flux for module PV660

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<td>0.5</td>
<td>7.25</td>
<td>2.78</td>
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</tr>
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</table>

T – Temperature of both solutions

C_t – Glucose solution concentration in % w/w

V_f, V_s – Cross flow velocity of glucose (feed), and brine solution.

W – The amount of water removed from the feed over 15 minutes, with uncertainty ±0.05g.

J – The OD flux determined on the basis of the inner surface of the fibres (=104.5cm²).

The brine was always 45%w/w CaCl₂ aqueous solution.
Appendix 2: Equations Used in Statistics

Followings are the equations for calculating the statistical values used in this work. The equations are simply a citation from Weiss (1995).

- Mean of a sample $\overline{x}$:

The mean of a sample of size $n$ is given by (A2-1):

$$\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$  \hspace{1cm} (A2-1)

$n$ – number of pieces of data

$x_i$ – the $i^{th}$ value of the sample

- Standard Deviation $S$:

Standard deviation SD of a sample indicates the variation of data values in a data set from the mean. SD is given by (A2-2).

$$SD = S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1}}$$  \hspace{1cm} (A2-2)

- Standard Error of the Mean $S_{\overline{x}}$:

$$SEM = S_{\overline{x}} = \frac{SD}{\sqrt{n}}$$  \hspace{1cm} (A2-3)

- Confidence Interval (A1-4)

Confidence interval at a confidence level $\alpha$ indicates the limits within it will consist the mean of a sample with probability of $(1-\alpha)$. The confidence interval is determined by (A2-4).

$$\overline{x} - t_{\alpha}S_{\overline{x}} < \overline{x} < \overline{x} + t_{\alpha}S_{\overline{x}}$$  \hspace{1cm} (A2-4)

or

$$\overline{x} \pm t_{\alpha}S_{\overline{x}}$$

where $t_{\alpha}$ is the Student's t-Distribution at $\alpha$-level.

- The slope and intercept in linear regression:
When a population of \( n \) points \((x_i, y_i)\) is linearly related to a population of \( n \) points \((y_i)\) via the relation \( \hat{y} = b_0 + b_1 x \), then \( b_0 \) is called the intercept, and \( b_1 \) - the slope. They can be estimated as follows:

\[
b_1 = \frac{S_{xy}}{S_{xx}} \tag{A2-5}
\]

\[
b_0 = \frac{1}{n} \left( \sum_{i=1}^{n} y_i - b_1 \sum_{i=1}^{n} x_i \right) = \bar{y} - b_1 \bar{x} \tag{A2-6}
\]

where \( S_{xx} = \sum_{i=1}^{n} x_i^2 - \frac{\left( \sum_{i=1}^{n} x_i \right)^2}{n} \)

\[
S_{xy} = \sum_{i=1}^{n} x_i y_i - \frac{\left( \sum_{i=1}^{n} x_i \right) \left( \sum_{i=1}^{n} y_i \right)}{n}
\]

- R-square in linear regression (A1-7)

The R-square is also called the coefficient of determination. It can be determined as given in (A2-7).

\[
R^2 = 1 - \frac{SSE}{SST} \tag{A2-7}
\]

\[
SSE = \sum_{i=1}^{n} \left( y_i - \hat{y}_i \right)^2 : \text{Error sum of squares}
\]

\[
SST = \sum_{i=1}^{n} \left( y_i - \bar{y} \right)^2 : \text{Total sum of squares}
\]

\( \hat{y}_i \) is the predicted value that corresponds to \( x_i \).

In multiple regression with \( k \) variables \( x_1, x_2, ..., x_k \), the regression equation is:

\[
\hat{y} = b_0 + b_1 x_1 + b_2 x_2 + ... + b_k x_k
\]

Then determination of the regression coefficients can be carried out in the same way, employing \( x_k \) for \( b_k \). The intercept is then calculated as:

\[
b_0 = \bar{y} - b_1 \bar{x}_1 - b_2 \bar{x}_2 - ... - b_k \bar{x}_k
\]
The confidence interval of the slope:

\[ b_1 \pm t_{\alpha/2} \cdot \frac{s_e}{\sqrt{S_{xx}}} \]  \hspace{1cm} (A2-8)

where \( s_e = \sqrt{\frac{SSE}{n-2}} \) is the standard error of the estimate. Others are as defined above.

For other curvilinear regression, the data are simply converted in an appropriate form so that linear regression can be applied. For example, a relation of \( \hat{y} = b_0 + b_1 \cdot x + b_2 \cdot x^2 \) can be converted to a linear relation \( \hat{y} = b_0 + b_1 \cdot x + b_2 \cdot X \), where \( X = x^2 \). For a power or exponential relation between two sets of data \( x \) and \( y \), then they are simply converted into appropriate logarithms when needed as follows:

\[
\hat{y} = A \times e^{Bx} \quad \Rightarrow \quad \ln(\hat{y}) = \ln(A) + Bx
\]

\[
\hat{y} = A \times B \cdot x^x \quad \Rightarrow \quad \ln(\hat{y}) = \ln(A) + [\ln(B)]x
\]

\[
\hat{y} = A \times x^x \quad \Rightarrow \quad \ln(\hat{y}) = \ln(A) + B \times \ln(x)
\]

Then the standard linear regression can be used to determine the constants \( A \) and \( B \).
Appendix 3: The Physical Properties Of Aqueous Glucose and Calcium Chloride Solutions

A3.1. Density of aqueous glucose and calcium chloride solutions:

- The density of glucose over the concentration range from 0.5 to 60% w/w at 20°C can be obtained from CRC handbook of chemistry and physics (Lide, 2001). The glucose density at temperatures other than 20°C, however, can be obtained by using the volumetric conversion factor $f$ which is used in determination of the sucrose solution density over the concentration range of 0-70% w/w and temperature 0-100°C (Pancoast & Junk, 1980). The density of glucose solution at concentration $C$ and temperature $T$ is then calculated by (A3-1).

$$\rho_{c,T}^{\text{glucose}} = \rho_{c,20^\circ C} \left( \frac{1}{f_{c,T}} \right)$$ (A3-1)

- $\rho_{c,T}^{\text{glucose}}$ - Glucose solution density at concentration $C$ and temperature $T$.
- $\rho_{c,20^\circ C}$ - Glucose solution density at concentration $C$ and temperature 20°C.
- $f_{c,T}$ - Correction factor for sugar solution at concentration $C$ and temperature $T$ (Pancoast & Junk, 1980, pp.66)

- The density of calcium chloride solution over the concentration range $m=0.004-7.151\text{mol.kg}^{-1}$ and temperature $T=25-50^\circ C$ can be obtained from Wahab & Mahiuddin (2001). The authors proposed a linear correlation for the CaCl$_2$ solution density:

$$\rho_{\text{CaCl}_2} = a - b * T$$

where $a$ and $b$ are constants for a solution at a specified concentration and $T$ is in °C.

The derived constants $a$ and $b$ at different concentrations from 0.004 to 7.151 mol.kg$^{-1}$ by Wahab & Mahiuddin (2001) were successfully applied in the above
equation to predict the density of CaCl₂ solution at a specified concentration over the temperature range from 25 to 50°C.

It was observed that the constants a and b vary with concentrations. Therefore, they were further analysed, and were found to be linearly fitted to the concentration m by the following derivations:

\[ a = 64.153 \times m + 1030 \quad \text{[kg.m}^3\text{]} \]

\[ b = 0.0457 \times m + 0.3517 \quad \text{[kg.m}^3\cdot\text{°C]} \]

Hence, the density of CaCl₂ solutions over the concentration range of m=0.004-7.151 mol.kg⁻¹ and temperature T=25-50°C can be predicted as given by (A3-2).

\[ \rho_{m,T}^{\text{CaCl}_2} = 64.153 \times m + 1030 - (0.0457 \times m + 0.3517) \times T \quad (A3-2) \]

A3.2. Diffusion coefficients of glucose and calcium chloride in aqueous solutions:

The diffusivity of organic solute in liquids can be determined by the equation below (Geankoplis, 1983):

\[ D_{AB} = 1.173 \times 10^{-16} \times (\varphi M_s)^{0.5} \times \frac{T}{\mu_B V_A^{0.6}} \quad \text{for } V_A < 0.5 \quad (A3-3) \]

\[ D_{AB} = \frac{9.96 \times 10^{-16} \times T}{\mu \cdot V_A^{1/3}} \quad \text{for } V_A > 0.5 \quad (A3-4) \]

where:

- \( M_B \): molecular weight of solvent B (water)
- \( \mu_B \): viscosity of B in Pa.s (refer to equation (A3-15))
- \( \mu \): viscosity of solution in Pa.s (refer to chapter 4)
- \( V_A \): solute molar volume at the boiling point in m³.kgmol⁻¹
- \( \varphi \): association parameter of solvent. \( \varphi = 2.6 \) for water, 1.9 for methanol, 1.5 for ethanol, and 1 for benzene, ether and heptanes.
- \( D_{AB} \): in m².s⁻¹
The value of $V_A$ of an organic solute is a sum of the total atomic volumes of the forming elements. Such values are as for carbon $V_C=14.8\times10^{-3}$ m$^3$kgmol$^{-1}$, hydrogen $V_H=3.7\times10^{-3}$, for oxygen $V_O=7.4\times10^{-3}$, etc.

In our case, the diffusion coefficient of glucose (C$_6$H$_{12}$O$_6$) in aqueous solution can be determined as:

$$V_A = n_C^*V_C + n_H^*V_H + n_O^*V_O$$
$$= 6\times14.8 + 12\times3.7 + 6\times7.4 = 176.3\times10^{-3} \text{ [m}^3\text{kgmol}^{-1}]$$

As can be seen, $V_A<0.5$, therefore, the first equation should be used. Thus, the diffusion coefficient of glucose in aqueous solution is estimated as:

<table>
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<th>Temperature [$^\circ$C]</th>
<th>$D_{AB}$ [m$^2$.s$^{-1}$]</th>
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<td>$0.7582 \times 10^{-9}$</td>
</tr>
<tr>
<td>35</td>
<td>$0.9701 \times 10^{-9}$</td>
</tr>
<tr>
<td>45</td>
<td>$1.2082 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Unlike glucose, CaCl$_2$ is a strong electrolyte and its diffusion in aqueous solution is different from that of organic solution. Data of CaCl$_2$ diffusivity in aqueous solution can be obtained from the experimental data of Lyons & Riley (1954). The data covered the concentration range $m=0.02813$ to 6.004, and at temperature $T=25^\circ$C.

As in our case $m=7.3$, the diffusivity was accepted $D_{25^\circ C}=0.3\times10^{-9}$m$^2$.s$^{-1}$ as an extrapolation from the data set.

For diffusivity of CaCl$_2$ (with $m=7.3$) in aqueous solution at temperature other than $25^\circ$C, the following formula was applied:

$$\frac{D_T}{D_{25^\circ C}} = \left(\frac{T}{298.15}\right)^{1.75} \quad (A3-5)$$

where $D_T$ is the diffusivity of CaCl$_2$ 7.3M at temperature $T$
A3.3. Specific heat of aqueous glucose and calcium chloride solutions

The specific heat of a food system containing carbohydrate, protein, fat, ash and water can be assumed to be an accumulation of the specific heats of its constituents based on their mass fraction in the system. Therefore, it can be calculated by (A3-6) (Singh & Heldman 2001).

\[ C_{p,f} = 1.424X_c + 1.549X_p + 1.675X_f + 0.837X_a + 4.187X_w \]  
(A3-6)

where \( X \) is the mass fraction of the constituents. The subscripts \( c, p, f, a, \) and \( w \) stand for carbohydrate, protein, fat, ash, and water respectively. The specific heat determined by (A3-6) is in [kJ/kg.\(^\circ\)C]. The constants in (A3-6) are the average specific heats of the respective constituents of the system.

Glucose can be seen as a mixture of carbohydrate and water only. Therefore, the above equation can be used to determine the specific heat of glucose solution with \( X_p = X_f = X_a = 0 \). Hence, the specific heat of a glucose solution is determined by:

\[ C_{p,G} = 1.424X_c + 4.187X_w \]  
(A3-7)

It should be stressed that equation (A3-6) and (A3-7) do not include the effect of temperature on the specific heat. To include the temperature dependence, equation (A3-7) should be modified as given in (A3-8) (Singh & Heldman 2001).

\[
C_{p,G} = \left( 1.5488 + 1.9625 \times 10^{-3} T - 5.9399 \times 10^{-6} T^2 \right) X_G + \\
\left( 4.1762 - 9.0864 \times 10^{-5} T + 5.4734 \times 10^{-6} T^2 \right) X_w
\]  
(A3-8)

where \( T \) is the temperature in [\(^\circ\)C], and the subscript \( G \) stands for glucose.

For CaCl\(_2\) solution, the specific heat is determined in a similar way. As cited in Perry and Chilton (1973), the specific heat of pure CaCl\(_2\) is [in kJ/kg.\(^\circ\)C]:

\[ C_{p,\text{CaCl}_2}^* = 0.638 + 1.46 \times 10^{-4} T \]  
(A3-9)

Thus, the specific heat of calcium chloride solution in relation to concentration and temperature is defined by (A3-10).
\[ C_{p,\text{CaCl}_2} = (0.638 + 1.46 \times 10^{-4} T)X_{\text{CaCl}_2} + \\
(4.1762 - 9.0864 \times 10^{-5} T + 5.4734 \times 10^{-6} T^2)X_w \]  (A3-10)

### A3.4. Thermal conductivity of aqueous glucose and calcium chloride solutions

As glucose is very similar to fructose, the main sugar in many fruit juices, the thermal conductivity of glucose solution is assumed as the one of fruit juice. Kolarov and Gromov (in Rao, 1995) derived an equation for determination of the thermal conductivity of fruit juice:

\[ k_{fg}^T = 0.140 + 0.42W \]  (A3-11)

where \( W \) is the water content of the solution in decimal form, and the thermal conductivity is in [W/m.K].

Due to the lack of data in the literature, the thermal conductivity of calcium chloride it is obtained by extrapolation from only two points available in Perry and Chilton (1973), which are:

<table>
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<tr>
<th>CaCl₂ concentration</th>
<th>Thermal conductivity [W/m.K]</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>15%</td>
<td>0.588</td>
</tr>
</tbody>
</table>

Extrapolation from those two points earn the following relationship:

\[ k_{\text{CaCl}_2}^T = 0.3897 + 0.2333W \]  (A3-12)

where \( W \) has the same meaning as in (A3-11)

There is also an effect of temperature on the thermal conductivity of a solution. However, for the temperature range from 25 to 45°C of the experiments in this work, it is assumed to be approximately equal to the predicted by equations (A3-11) and (A3-12).
A3.5. Diffusivity of water vapour in air

The diffusion coefficient of water vapour is as listed in table A3-1.

<table>
<thead>
<tr>
<th>°C</th>
<th>K</th>
<th>(D_{wa} \text{ [m}^2\text{s}^{-1}\times10^4])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>273.15</td>
<td>0.220</td>
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<tr>
<td>25</td>
<td>298.15</td>
<td>0.260</td>
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<tr>
<td>42</td>
<td>315.15</td>
<td>0.288</td>
</tr>
</tbody>
</table>

(Source: Geankoplis, 1983, pp.386)

At pressures \(P\) other than 1 atm and temperatures \(T\) other than the ones in the table, the diffusion coefficient \(D_{wa}\) can be determined by (A3-13) (Geankoplis, 1983):

\[
\frac{D_{wa}}{D_{wa}^{ref}} = \frac{P^{ref} \times T_{ref}^{1.75}}{P \times T^{1.75}}
\]  \(A3-13\)

where the reference values can be taken from the table as:

\(P^{ref} = 1\text{ atm}; T_{ref} = 25^\circ\text{C}; D_{wa}^{ref} = 0.260\)

A3.6. Vapour pressure of pure water

The vapour pressure of pure water is determined by Antoine equation, which has the common form:

\[
\ln(P_0) = A - \frac{B}{T - C}
\]  \(A3-14\)

where \(P_0\) (Pa) is the vapour pressure of pure water at temperature \(T\) (K); \(A, B\) and \(C\) are constants.

There are a number of sources of this equation in the literature with different \(A, B\) and \(C\) constants as listed in table (A3-2).
Table A3-2

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>References</th>
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<td>23.193</td>
<td>3816</td>
<td>46.1</td>
<td>Middleman, 1998</td>
</tr>
<tr>
<td>23.1964</td>
<td>3816.44</td>
<td>46.13</td>
<td>Reid, Prausnitz &amp; Sherwood, 1977</td>
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<td>23.5377</td>
<td>4016.3632</td>
<td>38.6339</td>
<td>Fernández-Pineda et al, 2002</td>
</tr>
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<td>23.238</td>
<td>3841</td>
<td>45</td>
<td>Smith &amp; van Ness, 1975</td>
</tr>
<tr>
<td>23.237</td>
<td>3481.2</td>
<td>45</td>
<td>Banat &amp; Simandl, 1994</td>
</tr>
</tbody>
</table>

Clearly, there is a discrepancy of the constants A, B, and C. Therefore, a comparison between the calculated vapour pressure of pure water and the ones from Lide (2001) was carried out. The comparison showed that Antoine equation cited by Fernández-Pineda et al (2002) is the most accurate and precise one.

A3.7. Density of pure water

The density of pure water is available in CRC handbook of physics and chemistry (Lide, 2001). However, it can be accurately and precisely predicted by the proposed equation in the literature that was referred to by Goncalves & Kestin (1979):

\[
\rho_0 = \left[ \sum_{i=0}^{5} a_i * T^i \right] / (1 + b * T) \tag{A3-15}
\]

where \(a_i\) and \(b\) are constants; \(T\) is the temperature in °C; and the density is in [kg.m\(^{-3}\)]. The constants in equation (A3-15) are as follows:

\[
\begin{align*}
    a_0 &= 999.8396 \\
    a_1 &= 18.224944 \text{ (°C)}^{-1} \\
    a_2 &= -7.922210 \times 10^{-3} \text{ (°C)}^{-2} \\
    a_3 &= -5.44846 \times 10^{-5} \text{ (°C)}^{-3} \\
    a_4 &= 149.7562 \times 10^{-9} \text{ (°C)}^{-4} \\
    a_5 &= 393.2952 \times 10^{-12} \text{ (°C)}^{-5} \\
    b &= 18.159725 \times 10^{-3} \text{ (°C)}^{-1}
\end{align*}
\]
Appendix 4: Water Activity and Viscosity Prediction

1. Water activity prediction for aqueous glucose and CaCl₂ solution

Table A4-1

<table>
<thead>
<tr>
<th>C (%)</th>
<th>m</th>
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<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
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</thead>
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<td>15</td>
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C-solution concentration
m-molarity

Values are water activity predicted by equation 4-14
Table A4-2
Predicted water activity of aqueous glucose solution

<table>
<thead>
<tr>
<th>C (%)</th>
<th>m</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
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C-solution concentration
m-molarity
Values are water activity predicted by equation 4-13
2. Viscosity prediction for aqueous glucose and CaCl₂ solution

Table A4-3

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*C-solution concentration
m-molarity
Values are viscosity in centipoise cP predicted by equation 4-28 (model2)
## Table A4-4

**Predicted viscosity of aqueous glucose solution**

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*C-solution concentration
m-molarity

Values are viscosity in centipoise cP predicted by equation 4-27 (model1)
REFERENCES


References


