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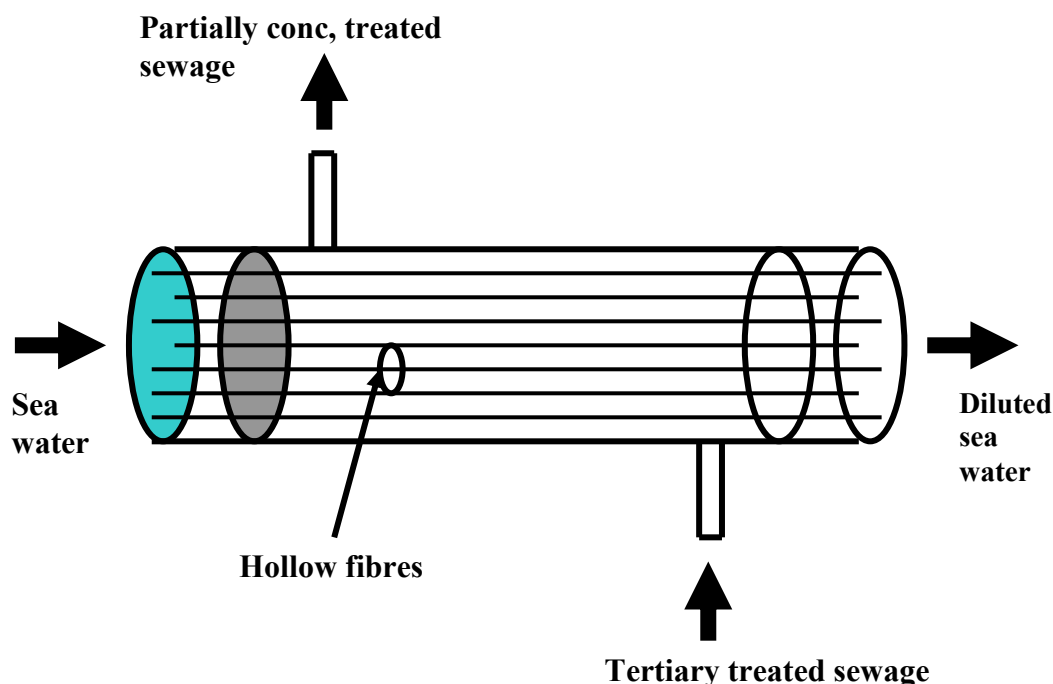
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A study of Osmotic Distillation.

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Graphical Abstract:



Abstract:

Tertiary treated sewage water has a much lower osmotic pressure than seawater and so an osmotic distillation process could be used to simultaneously concentrate sewage waste water and dilute seawater, without direct fluid contact. Although this process has many potential advantages, it also has some practical difficulties which were examined in this study. In osmotic distillation, liquid is transferred through the vapour phase, from a solution with a low concentration of non-volatile solutes, to a solution with a higher concentration, in the process concentrating the dilute solution, and diluting the concentrated solution. This process may have commercial advantages because the cost of desalinating water is directly linked to its salt concentration. Also, concentrating treated sewage can reduce its disposal costs. The use of a hydrophobic membrane, such as porous Teflon or polypropylene, allows only vapour transfer between the two solutions which might improve the public acceptance of 'toilet to tap' recycled drinking water, since there is no direct physical contact between the treated sewage and the product drinking water. A model system was designed, using NaCl solution, pure water, and a commercially available hydrophobic hollow-fibre membrane. The membrane flux that could be expected from a process such as this was measured, and compared with predictions based on theoretical calculations, and experimental data. Although a low flux was observed with the laboratory scale system used in this study, improvements in design and scaling effects may significantly improve these results. A new method is also proposed for the precise measurement of osmotic pressure.

Keywords: Membrane, distillation, water vapour, osmotic pressure.

1. Introduction

1.1. Theoretical Principle of Osmotic Distillation

The curvature of a water/air meniscus within a membrane pore depends on the degree of wetting of the pore walls. Water wets clean glass and so makes a zero contact angle (θ) with the walls. If the walls are coated with grease or made hydrophobic in some way, the water forms a higher angle. A naturally hydrophobic surface such as Teflon or polypropylene forms water droplet contact angles significantly greater than 90° and so water will not readily enter these pores and therefore a substantial pressure has to be applied to force water into the pores. The minimum pressure required to force liquid water into the pores is called the ‘‘Laplace Pressure’’. This is the basis of the water-proofing action of Goretex clothes, which repel water but pass vapours, allowing clothes to ‘breathe’. Water actually has a high contact angle of about 110° on Teflon (and about 105° on polypropylene) and so will not easily enter Teflon pores¹. This situation is illustrated in Fig. 1.

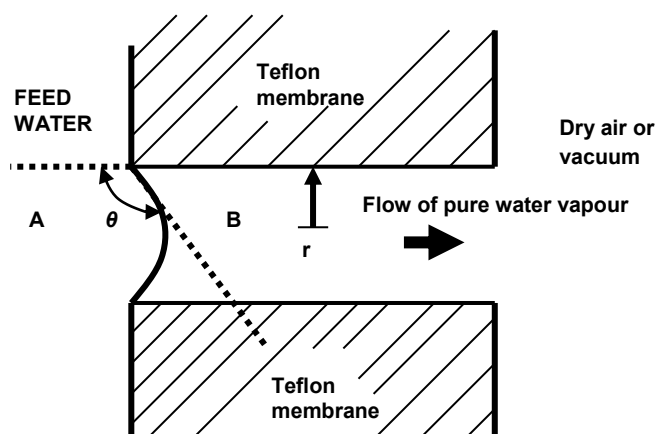


Figure 1. Schematic representation of water penetration into a hydrophobic pore, within a hydrophobic membrane. The liquid water (phase A) will not readily enter a vapour-filled pore or channel (phase B) in a hydrophobic material, such as Teflon or polypropylene, due to the high water contact angle, θ , on the hydrophobic surface. Although liquid water will not enter the fine hydrophobic porous network, water vapour will easily pass through the pores, into dry air or a vacuum.

The Laplace equation (1) gives the pressure difference (ΔP)

across any curved fluid interface:

$$\Delta P = \frac{2\gamma}{r} \quad (1)$$

where γ is the surface tension of the liquid and r is the radius of curvature of the water-air interface, which is usually assumed to be spherical. If r_c is the radius of a capillary tube or pore, it follows from simple geometry (again assuming that the meniscus is spherical and that $\theta > 90^\circ$) that the radius of the meniscus, r , is given by:

$$r = \frac{-r_c}{\cos\theta} \quad (2)$$

and hence the Laplace pressure (positive by definition) is given by the equation (for $\theta > 90^\circ$):

$$\Delta P = -\frac{2\gamma\cos\theta}{r_c} \quad (3)$$

This is the minimum pressure required to force liquid water into the pores, where the pore walls have a water contact angle of θ .

One industrial application of the Laplace pressure generated in a pore is the use of porous Goretex (*i.e.* Teflon) or polypropylene membranes to remove dissolved gases from water down to the ppb range^{2,3}. This process depends on the Laplace pressure preventing water flow into the hydrophobic pores. On one side of the membrane is water and on the other a vacuum. As can be seen from the Laplace equation, as long as the water contact angle remains high, say at around 110° , the pressure required to push water into the pores is greater than 1 atm (see Fig. 2). The Laplace pressures generated in a hydrophobic membrane depend on the water contact angle on the membrane surface, as illustrated in Figure 2.

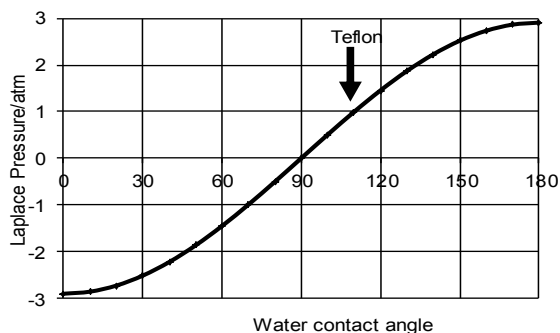


Figure 2. This graph gives the magnitude of the Laplace pressure, in atm, required to force liquid water through a 1 micron pore, for porous materials with a range of different water contact angles. A hydrophilic pore material, with a contact angle below 90° , will draw water through the pore, while a hydrophobic material, with a contact angle greater than 90° , will require the application of a substantial pressure. Teflon, with a contact angle of about 110° , will require a pressure of about 1atm for 1 micron pores.

Thus, the Laplace pressure generated across a curved meniscus (as shown in Fig. 1, between points A and B) in a Teflon pore of $1\mu\text{m}$ diameter is about 1atm^4 . Pores of this size (or less) will therefore allow the pressure in the water to be at 1atm, with a vacuum, or water vapour (at a pressure of about 20mm of Hg at 20°C) on the other side, without allowing liquid water to flow through the pores. This method works because water has a high surface tension (73mJm^{-2}) and Teflon has a very low tension (of about 18mJm^{-2}). The water-Teflon interfacial tension is also high at about 45mJm^{-2} and hence the water contact angle on Teflon is very high, at about 110° .

Teflon and polypropylene porous membranes are also used commercially to concentrate wine and fruit juice for export^{5,6}. These processes are referred to as membrane distillation and osmotic distillation (OD)⁷. In each of these processes, the solution to be concentrated is flowed around the exteriors of porous hollow fibres of these materials, while a vapour pressure gradient is used to draw vapour from the solution into the interiors of the fibres. In the case of membrane distillation, this is achieved either by applying a vacuum to the fibre interiors, or by circulating through them a solvent at a lower temperature than that of the feed solution. In the case of osmotic distillation, concentrated brine is used as the low vapour pressure fluid. In these processes it is important that the high contact angle be maintained and so the membranes are regularly washed to prevent adsorption of surface active agents.

The concentrative effect of osmotic distillation occurs due to the effect of solutes on the chemical potential of the water. For ideal mixtures, the chemical potential of the water depends upon the mole fraction of water in the solution, according to the relation:

$$\mu_w(l) = \mu_w^*(l) + RT\ln(x_w) \quad (4)$$

where $\mu_w(l)$ and $\mu_w^*(l)$ are the chemical potentials of water in the solution and in the pure state, respectively, and x_w is the mole fraction of water in the solution. At equilibrium, the vapour phase chemical potential $\mu_w(v)$, must be equal to $\mu_w(l)$ and for an ideal system Raoult's law relates the reduced vapour pressure to the mole fraction of water in the solution:

$$x_w = \frac{p_w}{p_w^*} \quad (5)$$

where p_w and p_w^* are the vapour pressures of water in the solution and for pure water, respectively. The vapour pressure of the solvent (e.g. water) decreases, in direct proportion to a decrease in mole fraction of the solvent, in the solution.

A pressure gradient can therefore be created between two solutions with the same solvent, but with different, non-volatile, solute concentrations. If two such solutions are kept separate, but their vapours are allowed to mix, the chemical potential difference will drive net vapour transfer to dilute the more concentrated solution. This process will continue until equilibrium is reached, which may occur when the chemical potential of the solvents is equalized by, say, a temperature differential, convergence of solution concentrations, or a combination of both. This process may be accelerated by the use of thin, porous hydrophobic membranes to separate the liquids, but allowing the passage of vapour. The use of a membrane can lead to the process occurring over a very large surface area, increasing the rate at which the vapour is transferred.

The process of osmosis is also driven by differences in water chemical potentials across a membrane. The osmotic pressure of a solution, is equal to the pressure which must be applied to prevent net flow from a pure water reservoir into the solution via a semi-permeable membrane. The change in chemical potential of water caused by applying a pressure is given by the relation:

$$\mu_w(P + \Pi) = \mu_w^*(P) + \int_P^{P+\Pi} V_m^w dp \quad (6)$$

where V_m^w is the molar volume of water, P is the standard pressure and Π is the additional, applied (osmotic) pressure. Using equation (4) and equating the change in chemical potential caused by the applied pressure with the change produced by adding solute, gives the relationship:

$$RT\ln(x_w) = - \int_P^{P+\Pi} V_m^w dp = -V_m^w \Pi \quad (7)$$

assuming that the solvent is incompressible. For dilute solutions $\ln(x_w)$ can be approximated as $-x_s$, the mole

fraction of solute, which, in turn, allows us to replace $\frac{\ln(x_w)}{V_m^*}$ with $\frac{n_s}{V}$, where n_s is the number of moles of solute, and V is the volume of solvent. Applying these approximations leads to the well known van't Hoff equation:

$$\Pi = \frac{n_s}{V} RT \text{ or } \approx c_s RT \quad (8)$$

where Π is the osmotic pressure, V is the water (solvent) volume and n_s is the number of moles of solute. Applying Raoult's law to equation (7), we obtain the result:

$$RT \ln \left(\frac{p_w}{p_w^*} \right) = -\Pi V_m^w \quad (9)$$

This relationship demonstrates that the osmotic pressure can be calculated directly from vapour pressure measurements.

In an alternative approach, it can be shown that this correlation arises due to the Kelvin effect, where the curvature of the interface affects the vapour pressure of the liquid, according to the Kelvin equation:

$$\ln \left(\frac{p_w}{p_w^*} \right) = \frac{-2\gamma V_m^w}{rRT} \quad (10)$$

In the case of a salt solution, where the vapour pressure has been depressed according to Raoult's law, it may be increased back to its normal value by creating an interface with a positive radius of curvature,

$$r = \frac{-2\gamma V_m^w}{RT \ln(x_w)} \quad (11)$$

The curvature of the interface creates a Laplace pressure, and hence according to equation (1):

$$\Pi = \frac{-RT \ln(x_w)}{V_m^w} \quad (12)$$

which leads us back to the van't Hoff equation, (9), demonstrating that the hydraulic pressure applied to the concentrated phase required to equalise the vapour pressures of the two phases is identical to the osmotic pressure.

These equations contain several approximations and assumptions which causes the theoretical predictions of both the vapour and osmotic pressures of solutions to deviate significantly from real values, at high solute concentrations. Liquids are slightly compressible, and also the molar volume of the pure solvent is not the same as that of the solvent in a solution. Further, the replacement of $\frac{\ln(x_w)}{V_m^*}$ with $\frac{n_s}{V}$ is an approximation, and the vapour phases, at higher pressures, may not behave ideally. However, for simple, dilute solutions, these approximations do not produce significant errors. Another limitation is introduced by Raoult's law which predicts the reduction of water vapour pressure, up to

solution concentrations of about 2M NaCl. Beyond this concentration, the difference between the Raoult's law prediction and the experimental measurements⁸ becomes considerable, reaching about 25% at the limit of solubility (see Fig. 3).

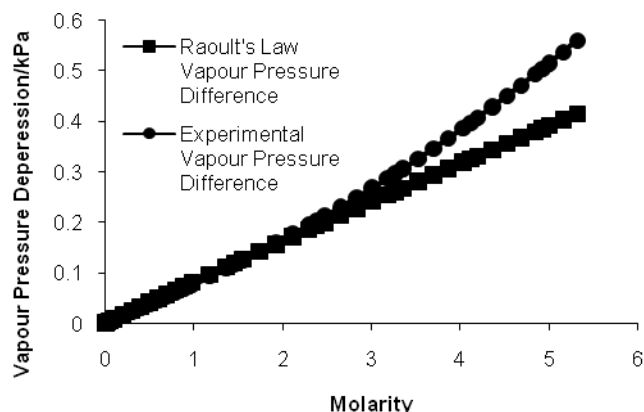


Figure 3. This graph shows the measured⁸ and ideal⁹ vapour pressure differences between pure water and varying NaCl solution concentrations, at 20°C. The depression in vapour pressure predicted using Raoult's law is linear, whereas the experimental data shows non-linear behaviour.

At higher concentrations, the water mole fraction must be replaced with the activity of the water, a_w , thus:

$$\mu_w(l) = \mu_w^*(l) + RT \ln(a_w) \quad (13)$$

Activities can be obtained directly from the measurement of vapour pressures, using the relation

$$a_w = \frac{p_w}{p_w^*} \quad (14)$$

Most of the data in the literature on osmotic pressure is given in terms of the 'Practical Osmotic Coefficient' ϕ ,¹⁰ which is defined as:

$$\phi = -\frac{n_1}{n_2} \ln_e a_1 \quad (15)$$

Where n_1 is the number of moles of solvent and n_2 the number of moles of solute and a_1 is the effective mole fraction (activity) of the solvent. For aqueous solutions this becomes:

$$\phi = -\frac{n_w}{n_s} \ln_e a_w \quad (16)$$

(Note that $a_w = x_w$ for ideal mixtures). Now, since the osmotic pressure is given by:

$$\Pi = -\frac{RT}{V_m^w} \ln_e a_w \quad (17)$$

where V_m^w is the partial molar volume of water in the solution, it follows that:

$$\Pi = \frac{RT}{V_m^w} \cdot \frac{n_s}{n_w} \cdot \phi \quad (18)$$

However, even this result is subject to approximations. The introduction of the activity of the water corrects for the non-ideal behaviour of the solution. It is still assumed, though, that the vapour phase behaves ideally. This is true to a very close approximation, under normal circumstances, where the vapour pressure is low. Under circumstances where the vapour pressure increases significantly, for example, at higher temperatures, or for very volatile solvents, it may become necessary to replace the pressure of the gas phase with the fugacity. However, this correction was not necessary under the circumstances of these experiments, since the vapour pressure of water at room temperature is low.

1.2. Limits of Conventional Methods of Determining Solution Osmotic Pressures

Equation (9) can be used to calculate the osmotic pressure of a solution from the measured vapour pressures¹⁰. However, this equation requires values for the molar volume of the water, or the partial molar volumes, for solutions. The partial molar volumes of water in concentrated salt solutions are not easily measured, and so for the purposes of such measurements it is usually assumed to be equivalent to the pure water molar volume. This approximation is often used in published osmotic pressure data^{9,10,11}. While the vapour pressure of the solution can be accurately measured, published osmotic pressure values, or their analogues (e.g. practical osmotic coefficients), include this error. However, by independently and directly measuring the vapour pressures of solutions, and their corresponding osmotic pressures, it would be possible to calculate the partial molar volume of water in concentrated salt solutions.

Whilst vapour pressures can be measured accurately, measuring osmotic pressures directly is more difficult. Osmotic membranes, such as those used in reverse osmosis, do not totally exclude solutes. When used for seawater desalination, typically up to 5% of the salt passes through the membrane, instead of being excluded. Even new, high-quality membranes allow up to 1% of dissolved salt to cross the membrane^{12,13}. As a result, a system that uses RO membranes to measure osmotic pressures will not produce accurate results. An alternative method would be to use vapour phase transfer across a hydrophobic membrane. Transfer through the vapour phase should effectively eliminate unwanted solute transfer, allowing a direct pressure measurement that can then be compared with vapour pressure

measurements, to calculate the partial molar volume of the solvent, at that concentration. It is expected that the partial molar volume will have a small impact on osmotic pressure calculations, of the order of about 2%, even for the most concentrated salt solutions¹⁴. However, the lack of availability of partial molar volume data leaves some uncertainty. Apparent molar volumes of salts are usually estimated assuming that water has a constant partial molar volume¹⁵.

2. Methods and Materials

A solution of AR grade sodium chloride (Merck) in laboratory deionised water was recirculated through the interiors (lumenside) of the hollow fibres in a Liquicel 2.5x8 Extraflow hollow fibre cartridge (Membrana, Charlotte NC, USA), with X40 fibres (polypropylene fibres with 25% porosity). A 100mL measuring cylinder was used as a reservoir to contain the excess solution, and to monitor the change in volume of the solution. Purified water was likewise circulated around the exteriors (shellside) of the hollow fibres. The flow rate of both liquids was equal, and was controlled and maintained at 50mL per minute, using a small peristaltic pump. The hollow fibre cartridge was positioned below the reservoirs, in order to exclude air, as far as possible, by keeping the liquids under a positive hydrostatic pressure. This arrangement was designed to force any entrapped air out through the hollow fibre walls. This configuration is illustrated in Fig. 4.

The volume of the liquids in the reservoirs was recorded every 15 minutes, for 1 hour and 15 minutes per run, before both liquids were drained from the apparatus and replaced. The conductivity of the liquids was recorded, at the beginning and the end of each run, with a Radiometer CDM210 4-pole conductivity probe. This was to ensure that there was no mixing of the liquids due to damage to the membrane, or faulty tubing, etc. Sodium chloride solutions were used, at concentrations of 0.1, 0.5, 1, 2, 3, 4 and 4.5 M. The experiment was repeated until at least four stable, consistent and reproducible results were recorded, for each concentration. The hollow fibres were also tested for leakage, using a Liquicel MiniModule, 1.7x5.5 hollow fibre cartridge, with X50 fibres (polypropylene fibres with 40% porosity). The cartridge was fed, as above, with 1M NaCl, and purified water. The purified water was dyed with methylene blue dye (Aldrich). No trace of dye was visible in the salt solution, even after several hours of fluid flow.

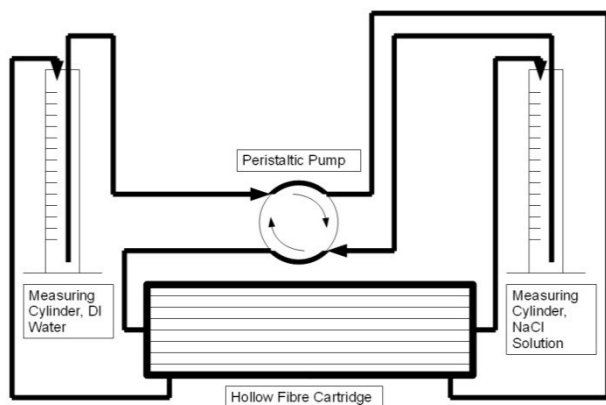


Figure 4. Schematic diagram of the experimental apparatus used in this study. The apparatus consisted of a peristaltic pump, which drew solutions from two measuring cylinders, at equal flow rates, circulated them through the hollow-fibre cartridge, and returned them to their respective cylinders. One cylinder contained de-ionised water, which was passed over the hollow-fibre exteriors (shellside), while the other contained aqueous NaCl solutions, of various concentrations, which was passed through the fibre interiors (lumenside). The transfer of water through the membrane was measured by observing the solution levels in the measuring cylinders.

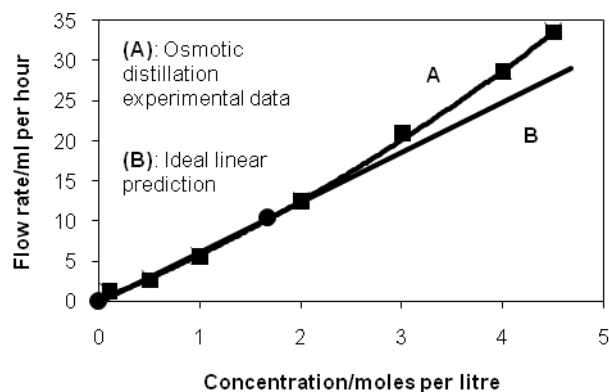


Figure 5. Experimentally measured flow rates across the hollow fibre membranes, from pure water into salt solutions, as a function of the salt concentration. The experimental results are compared with the ideal, linear prediction from Raoult's law. The experimentally measured rate of transfer of water vapour, by osmotic distillation, was found to vary with solution concentration in a non-linear manner. The measured flux follows a greater than proportional relationship with the concentration difference between the dilute and concentrated feed solutions. The shape of this curve is very similar to that of the published experimental vapour pressure data, as shown in Fig. 3.

3. Results

The vapour pressure of solutions is dependent upon the temperature, and therefore the vapour transfer rate may be expected to vary significantly with substantial temperature variations in the feed solution. The proportional differences between the vapour pressures of the concentrated and dilute solutions will remain constant at different temperatures, and therefore the rate of transfer may be expected to increase at higher temperatures, where the liquid vapour pressures are higher, and the absolute vapour pressure difference is greater. Likewise, a lower temperature may be expected to retard the process. All of the experimental osmotic distillation measurements reported here were carried out in a climate-controlled room, at 21-23°C.

In all of the osmotic distillation experiments, the volume of the salt solution was observed to increase steadily, whilst the volume of water reduced by a corresponding amount. The conductivity of the liquids indicated that there was no detectable liquid leakage across the membrane. The relationship between the average hourly flow rate and the concentration of the salt solution was found to be non-linear and increased with concentration difference. The averaged results, from many osmotic distillation experiments, carried out at room temperature, are summarized in Fig. 5. All of the data obtained at high concentrations fell within 20% of the overall average flux rates given in Fig. 5. In these transfer flux experiments, careful flushing was required when salt solutions were changed to different concentrations, to obtain consistent membrane transfer rates. Care was also required in the exclusion of air from the system, especially following solution changes.

The conductivity of the pure water never exceeded $16\mu\text{Scm}^{-1}$, and never changed significantly over the course of an experiment. This indicates that at no point were significant amounts of salt present in the pure phase, and that any salts that were present in the pure phase were not transferred by leakage, over the course of an experiment, but rather by trace contamination during the setup of each new experiment. The use of a dyed solution in a similar cartridge also indicated that there was no direct liquid transfer through the membrane.

These results can be used to predict the size of installation needed to treat water at a given rate, based only on the concentration difference between the two aqueous solutions. The total area of the hollow fibres inside the cartridge, based on the manufacturer's specifications, was 1.4m^2 , with a porosity of 25%. Assuming that concentrated reject brine from a reverse osmosis process is used as a feed, and low salt waste as the dilute solution, a concentration difference of about 1M is expected. At this concentration difference, the observed flow rate was found to be about 4mL of water transferred, per m^2 of membrane, per hour. If an installation was required to dilute the concentrated reject stream to half of its original level, this would yield a 2x higher product flow rate.

4. Analysis and Discussion

4.1. Comparison of Observed Transfer Rate with Industrial Membrane Processes

For a concentration difference of 2M NaCl, corresponding to an osmotic pressure of about 100atm, an observed OD flow

rate of about 9mL per m² per hour was observed. By comparison, a forward osmosis system, using the same concentration of NaCl and distilled water as feeds, produces flow rates of about 20 litres per m² per hour¹⁶. Much of this difference can be accounted for by the different densities of the fluid being transferred across the membranes. For example, 1cm³ of liquid water corresponds to about 1g of water, while 1cm³ of water vapour, at a vapour pressure of about 23 mbar (*i.e.* water vapour pressure at 20°C), represents about 17µg of water vapour. Hence, the transfer of water as a vapour is intrinsically slow. The hydrophobic membranes are also 80 microns thick, as opposed to an active layer of 0.2 microns, or less, for commercial reverse osmosis membranes, further reducing the thermodynamic drive of the vapour transfer process.

The rate of flux of the OD process can be increased by increasing the cross flow rate, adjusting the liquid temperatures, and by increasing the concentration difference between the feed solutions. Increasing the cross flow rate, either by increasing the liquid feed rate, or by stirring, will reduce the formation of concentration gradients and boundary layers. Increasing the concentration difference will increase the vapour pressure difference. Increasing the temperatures of both solutions will increase the water vapour pressures and will therefore increase transfer flux rates. Increasing the temperature of the dilute solution more than the concentrated solution will increase the vapour pressure difference driving the process. This process is then referred to as membrane distillation, or membrane osmotic distillation, rather than osmotic distillation, in acknowledgement of the fact that the difference in vapour pressures is created by thermal means, rather than by osmotic pressure differences.

Using a higher cross flow rate, and a greater concentration difference between the feed solutions, flux rates of about 140mL per m² per hour have been recorded experimentally¹⁷, in a system similar to that used here. Further gains may be made by using higher porosity membranes (40% porosity membranes are commercially available), more efficient membrane packaging and engineering to maximise the use of the available membrane surface area, and minimising entrapped air. The surface area of a membrane, for a given size of membrane cartridge, may be increased by use of alternative geometries, such as spiral winding, compared with the hollow fibres used here. Optimising OD membrane processes has produced fluxes as high as 1-6L per m² per hr¹⁸. A useful comparison of the productivity of the OD system is with the rate of productivity per unit of membrane area of a reverse osmosis system, which are specified commercially as producing up to 500L per m² per hr¹². This high flux is because reverse osmosis is driven by an applied pressure up to 35atm greater than the osmotic pressure, in the liquid phase, whereas the evaporative processes used in OD are driven by a pressure difference, in the vapour phase, of only a few percent of the vapour pressure, itself a small

fraction of one atmosphere. It should be noted that although OD has a lower flux rate, the process also has a significantly lower energy consumption, compared to SWRO.

Based on these results, an osmotic distillation system, used to pre-treat feedwater for a reverse osmosis process, would need several orders of magnitude more membrane area than the reverse osmosis process, and therefore several orders more floor space in an installation, to deliver treated water at a rate useful to the reverse osmosis system. However, the productivity of this system in a large scale installation may deviate substantially from predictions made on the basis of the laboratory scale data reported here. The continuous, high flow rate mode of operation of a large scale system could show a significantly higher rate of dilution than was observed here. An industrial process based on this principle could reduce the costs associated with SWRO, when there is ready access to comparable volumes of tertiary treated waste water. Use of this type of process might be more acceptable in the production of drinking water, effectively from recycled water. It would also remove the environmental issues associated with RO concentrate disposal.

4.2. Comparison of Observed Results with Theoretical Predictions

The experimental results obtained from this study showed a non-linear increase in the water transfer rate across hydrophobic hollow fibre membranes, as the concentration difference was increased, as shown in Fig. 5. When a direct comparison is made between the shapes of the curves of the transfer flux data and the vapour pressures¹⁰, in Fig. 3, an almost perfect match was observed. Interestingly, the osmotic pressure curve also deviates from the linear van't Hoff prediction in a similar manner, as shown in Fig. 6.

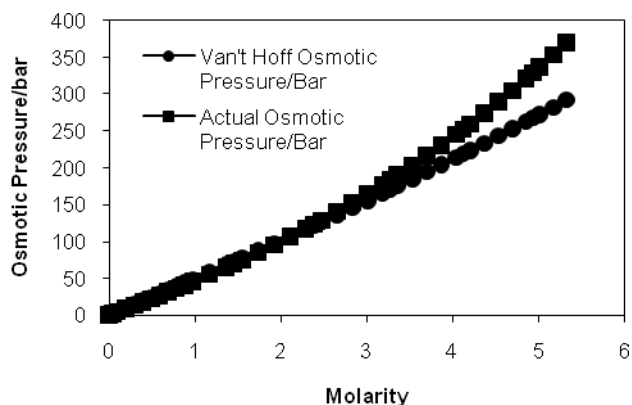


Figure 6. Ideal⁹ and measured⁸ osmotic pressures of various concentrations of NaCl solutions. The osmotic pressures of a variety of aqueous NaCl solutions can be theoretically predicted using the van't Hoff equation and are compared with values calculated from experimentally determined, published practical osmotic coefficient data⁸. Significant differences occur at concentrations above about 3M, for aqueous NaCl solutions.

A plot of the difference between the vapour pressures of the salt solution and pure water, against the process flux yields a straight line (Fig. 7), which is consistent with the above-mentioned correspondence between the shapes of the vapour pressure and flow rate curves. The slope of this curve can be used to predict the rate of vapour transfer across a membrane, for a known pressure difference. This dependence can, in theory, be applied to any situation where a partial pressure differential exists across a hydrophobic membrane. As an example, this can be used to calculate the loss of water vapour into a vacuum system or sweep gas, in the case of a hollow-fibre degassing arrangement, by combining the slope of the curve, or partial pressure of water in the sweep phase or vacuum, the membrane surface area, the membrane porosity, and approximate feed temperature. This may be of value in the design of commercial degassing systems, using vacuum pumps capable of tolerating the condensable vapours. The slope will depend on membrane type, feed composition and feed flow rate.

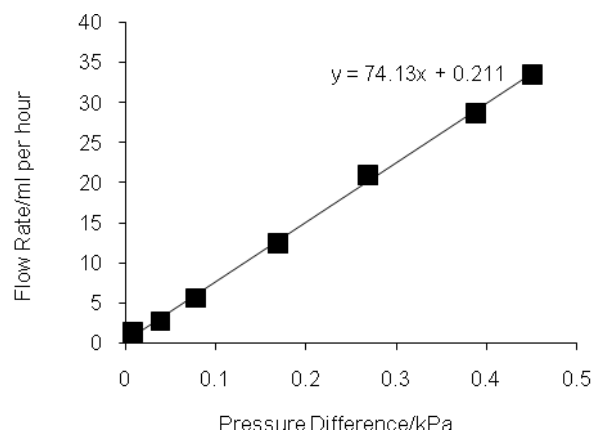


Figure 7. Experimental vapour transfer flux rates are compared with the calculated difference in vapour pressure between the two feed liquids. The rate of transfer of water through the hollow fibre membranes has a direct linear relationship with the vapour pressure difference between the two solutions⁸. The equation of the trendline could be used to predict the flow rate of the process for a known vapour pressure difference, generated by any means, e.g. by application of a vacuum, by temperature differential, or by osmotic pressure.

Careful comparison of Figs. 3, 5 and 6, shows that the data from the osmotic distillation experiments seem to match the curve of the vapour pressure data more precisely than the osmotic pressure curve. This indicates that the kinetics of the process is controlled by the vapour pressure differences across the membranes, rather than the osmotic pressure, although the differences are slight. This is consistent with the mechanism of the process, and the broad fit of the data with the pressure curves, indicates that the activity of the water is a reliable predictor of the rate of the vapour transfer process.

The data used in Fig. 6 was derived from the practical osmotic coefficients given by Colin et al⁸. For comparative purposes, the osmotic pressures were also calculated using the published vapour pressure data, from the same paper, by applying equation (9), and assuming that V_m^w is equal to the molar volume of pure water. The two sets of data that were calculated agreed to 3 significant figures, indicating that the practical osmotic coefficients were derived from vapour pressure values, and calculated using the same assumption.

The use of hydrophobic membranes could be extended to obtain direct measurements of osmotic pressures. As mentioned in the introduction, applying a pressure to a liquid, against a hydrophobic membrane, results in an increase in vapour pressure on the other side of the membrane, due to the Kelvin effect. If a hydrophobic membrane is used to separate a solution with a known osmotic pressure, from one with an unknown osmotic pressure, vapour will be transferred until the solvent activities, and therefore osmotic pressures, are balanced. Vertical tubes connected to the solutions on each side of the membrane and both open to the atmosphere, could simply be used to measure any small difference in pressure

between two closely matched solutions, to measure small differences in osmotic pressure accurately.

Osmotic pressures of solutions, or their osmotic coefficients, are usually determined by measuring the vapour pressure of the solution, and converting to the osmotic pressure using a relation, such as that shown in equation (9). This is because the osmotic pressure is difficult to measure accurately, due to problems with slow equilibration times, variability between osmotic membranes, and membrane ion leakage. Directly measuring the osmotic pressures of solutions using a hydrophobic membrane, would allow a good test of theory. The conversion from the vapour pressure to the osmotic pressure of a solution, or *vice versa*, requires accurate values for the partial molar volume of water in the solution. However, the partial molar volume is difficult to measure directly. Direct measurement of the osmotic pressure, and comparison with the directly measured vapour pressure would allow the partial molar volume of water to be calculated from equation (9). This method would also enable calculation of the partial molar volumes of the solutes.

5. Conclusions

The low transfer flow rates observed with the laboratory scale apparatus used in this study make the industrial applicability of this process to the treatment of a relatively low commercial value commodity, such as water, an unfavourable proposition. However, comparable data from related studies indicate that the process may be significantly improved, possibly to an extent where it might become industrially useful. The results presented here may help guide future studies into the development of these processes for the secure and safe re-use of waste water. The results obtained in this study are consistent with the trends predicted from vapour pressure data. Indeed, the results obtained here indicate that a suitable osmotic distillation process, or derivative of such a process, may be useful for measurements of thermodynamic quantities that are difficult to obtain by other means.

Appendix

Nomenclature

<i>a</i>	Activity
<i>c</i>	Concentration (moles/m ³)
<i>l</i>	Liquid
<i>n</i>	Number (moles)
<i>P</i>	Pressure (Pa)
<i>p</i>	Vapour pressure (Pa)
<i>R</i>	Gas constant (J/K mol)
<i>r</i>	Radius (m)
<i>T</i>	Temperature (K)
<i>v</i>	Vapour phase
<i>x</i>	Mole fraction
<i>V</i>	Volume (m ³)

Greek Symbols

γ	Surface tension (N/m)
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Δ	Difference
θ	Contact angle (°)
μ	Chemical potential
Π	Osmotic pressure (Pa)
Φ	Practical osmotic coefficient

Superscripts

*	Pure component
<i>w</i>	Water

Subscripts

<i>l,2</i>	Components 1, 2
<i>c</i>	Capillary
<i>m</i>	Molar
<i>s</i>	Solute
<i>w</i>	Water

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