

Microporous membranes in membrane distillation

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Abstract - When a microporous hydrophobic membrane separates two aqueous solutions at different temperatures, selective mass transfer across the membrane is obtained. The process can be carried out at the atmospheric pressure and at temperatures which might be much lower than the boiling point of the solution. At the optimal membrane microporosity, polymer hydrophobicity and thermal conductivity, only water vapor is transported in the membrane phase and condenses as liquid on the low temperature side of the membrane. The driving force is the vapor pressure difference between the liquids at the two solution-membrane interfaces. Various hydrophobic polymeric membranes are available, prepared from polypropylene, PVDF and Teflon, in the flat sheet or capillary configuration. The membranes prepared by thermal phase-separation technique are particularly interesting.

INTRODUCTION

Membrane Distillation is a new, rapidly increasing membrane technology, characterized by the possibility of overcoming some limits of other membrane processes, such as reverse osmosis (ref. 1,2). When compared to traditional evaporation, membrane distillation offers also the basic advantages of membrane separations: easy scaling up, simplicity of operations, possibility of high membrane surface/volume ratio, etc. Moreover, there exists the possibility of treating solutions with thermosensitive compounds and high level of suspended solids, at a temperature much lower than the boiling point and at the atmospheric pressure. Theoretical 100% rejections might be predicted for all electrolyte and non-electrolyte solutes. The possibility to reach a high solute concentration in the feed is of particular interest, considering the limits of RO due to the osmotic pressure increase with concentration.

PROCESS MECHANISM

When a microporous hydrophobic membrane separates two aqueous solutions at a different temperature, a net pure water flux from the warm side to the cold one is observed. The process can be described by the following steps: water evaporation at the solution-membrane warm interface, transport of the vapor phase through the microporous system, and condensation at the cold membrane-solution interface (see Fig. 1). The driving force for the vapor transport in this process is given by the vapor pressure difference between the two solution-membrane interfaces due to the existing temperature gradient.

The hydrophobic properties of the polymeric material prevent the bulk liquid transport of the liquid phase across the membrane. The morphology of the polymeric membrane is, however, a critical parameter of the process. A maximum critical pore size exists at which the liquid penetrates the microporous hydrophobic phase. This value is given by the Kelvin law:

$$P = 2\gamma \cos \phi / r$$

where γ is the surface tension of the liquid; θ is the contact angle between the liquid and the membrane; r is the radius of the pore; P is the applied pressure.

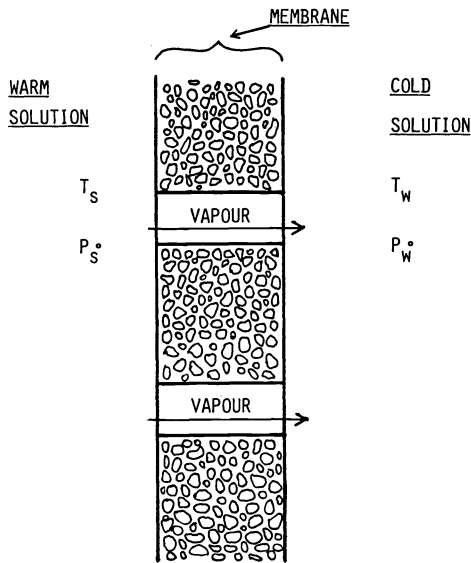


Fig. 1. Membrane distillation mechanism.

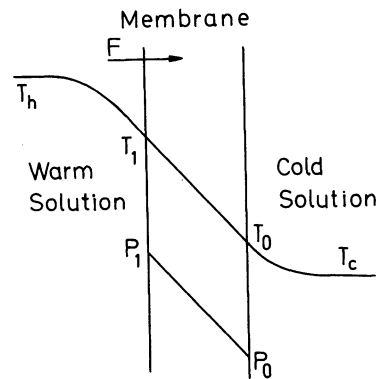


Fig. 2. Temperature and pressure profiles in membrane distillation.

For a given pore size a critical penetration pressure P_c exists. For applied hydrostatic pressure higher than the P_c value, the liquid phase is transported across the membranes.

Membranes with a very narrow pore size distribution and high level of porosity should be preferred for this application.

A linear relationship between the water vapor trans-membrane flux and the vapor pressure gradient across the membrane (see eq.(1)) adequately describes, in the range of the temperature gradients explored, the mass transfer in membrane distillation (ref. 2):

$$J = K_m \Delta P \quad (2)$$

The expression for the membrane constant K_m is related to the mass transfer mechanism in the membrane phase. It might occur by convective and diffusive transport of water vapor molecules. Knudsen diffusion and molecular diffusion models have been indicated as the most appropriate by R.W. Schofield et al. (ref. 3). The heat transfer across the membrane, given by the latent heat transfer accompanying the vapor flux and by the heat transfer by conduction across the membrane, can be expressed by eq.(3)

$$Q = K_h / \delta \Delta T \quad (3)$$

where the effective thermal conductivity $K_h = \epsilon K_g + (1 - \epsilon) K_s$, K_s and K_g being the solid and gas conductivities, respectively (ref. 4).

Concentration polarization phenomena have a lower control in membrane distillation. On the contrary, thermal polarization phenomena related to the building up of temperature gradients in solutions, as shown in Fig. 2, might significantly affect the overall mass transfer across the membranes, being directly related to the process driving force. The thermal conductivities of the polymer used in the membrane formation is therefore a controlling parameter of the process.

A strong and stable hydrophobic character, good thermal and chemical resistance, low thermal conductivity, high mechanical properties are some of the basic requirements for the polymer systems of potential interest for membrane distillation.

Microporous membranes in flat and capillary configurations are available. PTFE, polypropylene, PVDF are the polymers which have been indicated as the most promising for this application.

Microporosity can be induced by mechanical stretching, or by the so-called thermal phase separation technique (ref. 5).

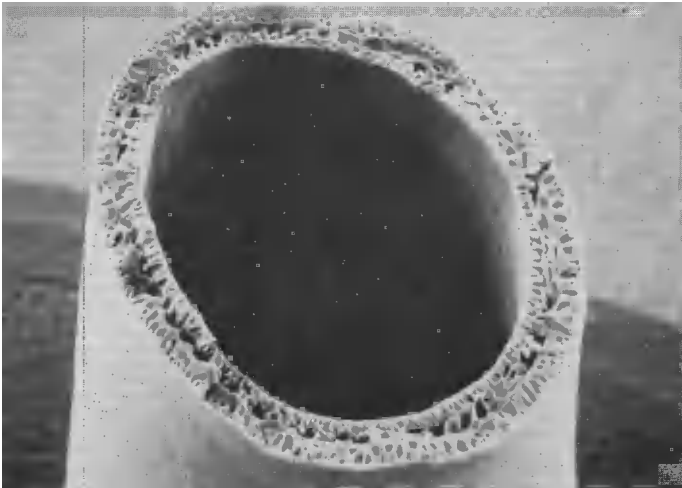


Fig. 3. SEM picture of hydrophobic PVDF capillaries (ref. 6)

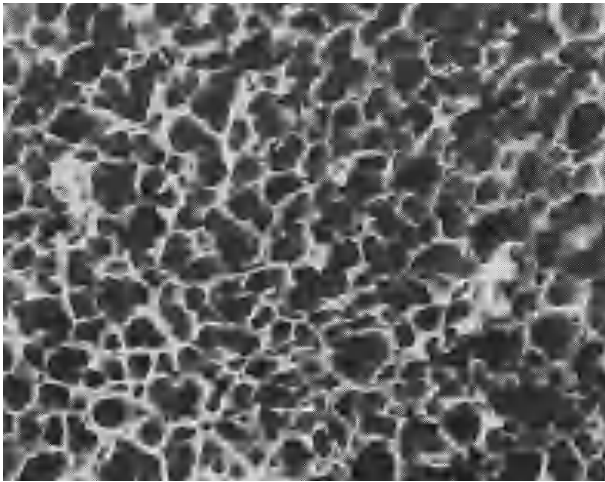


Fig. 4a. Polypropylene microporosity by thermal phase inversion.

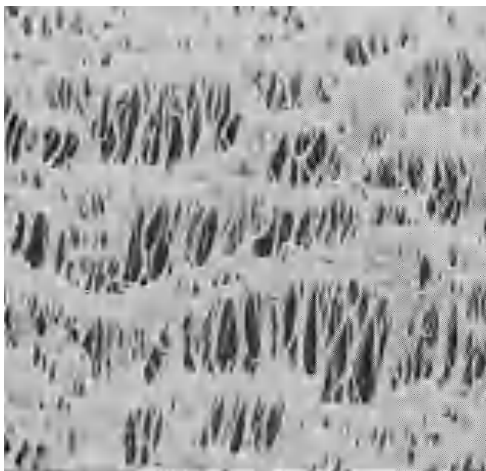


Fig. 4b. Mechanical stretching.

Inner Surface

1 μm

Dissolving a polymer in a solvent at an elevated temperature, and casting this solution on a flat surface at controlled temperature, provided that the system polymer/solvent shows a miscibility gap, are the basic steps of the method. Extraction of the solvent is done with low molecular weight alcohols. Pore dimensions and structures can be varied widely, changing the polymer concentration, the solution temperature, and particularly the solution cooling rate. In particular, a rapid cooling rate produces a small pore size and a slower cooling rate results, in general, in a larger pore size.

Polyvinylidene fluoride appears of particular interest in membrane distillation processes because of its high melting point and good temperature resistance; its resistance to oxidation and gamma radiation, to solvents and to abrasion are also of interest. For these reasons, studies on microporous PVDF membranes, particularly in hollow fiber configurations, are in progress.

Porosity of an order of 70 + 80% can be obtained. Membranes with a nominal pore size of an order of 0.2 μm , 0.45 μm , and 0.8 μm have been prepared by Enka AG from polypropylene (Accurel (R) process). PVDF capillary membranes have also been prepared in our laboratory (ref. 6), by dissolving the polymer in DMF. Additives were added to the casting solution. The molecular weight of these compounds and their concentration strongly affect the final membrane morphology. The additive is extracted from the membrane structure during the coagulation step. Fig. 3 shows SEM pictures of typical hydrophobic PVDF capillaries prepared by this technique.

A significantly different morphology can be observed in microporous polypropylene or PTFE membranes prepared by mechanical stretching, as shown in Fig. 4. The degree of porosity usually reached in this case is generally lower and of an order of 45%.

EXPERIMENTAL RESULTS

In this study experiments have been carried out on capillary microporous polypropylene and PVDF membranes characterized by different morphologies, using the apparatus shown in Fig. 5; generally, NaCl and glucose aqueous solutions, at various average feed temperature T_s and applied ΔT across the membranes, have been studied.

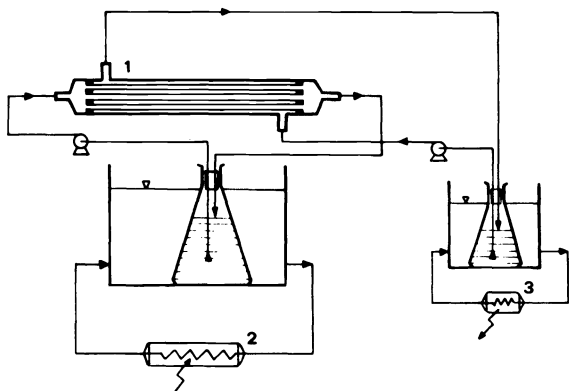


Fig. 5. Experimental apparatus.

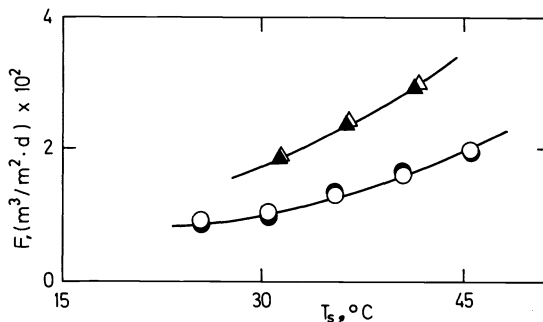


Fig. 6. Distillate flux vs. T_s . Glucose solution. T constant.
 $\circ \bullet \Delta T = 4.5^\circ\text{C}$ $\Delta \blacktriangle \Delta T = 8.5^\circ\text{C}$
 $\circ \Delta C_0 = 10$ g/l $\bullet \blacktriangle C_0 = 30$ g/l

In Figs 6, 7 and 8 typical experimental results are reported in terms of the transmembrane flux, F , as a function of T_s , ΔT and ΔP .

As predicted by the transport mechanism previously discussed, the flux increases non-linearly with increasing T_s and ΔT . A linear relationship between the fluxes and the vapor pressure difference across the membrane is observed, on the contrary, as expected from eq. (2). The increase in the solute concentrations decreases the transmembrane fluxes due to the decrease in the vapor pressure differences. This phenomenon has been observed particularly at high solute concentrations, as shown in Fig. 9. The fluxes decay observed are, however, significantly higher than that predicted by the vapor pressure decrease. The increase in the viscosity of the solution, and other phenomena, such as the thermal polarizations in the solutions facing the membranes, have a still more controlling effect on the observed fluxes decay (ref. 7).

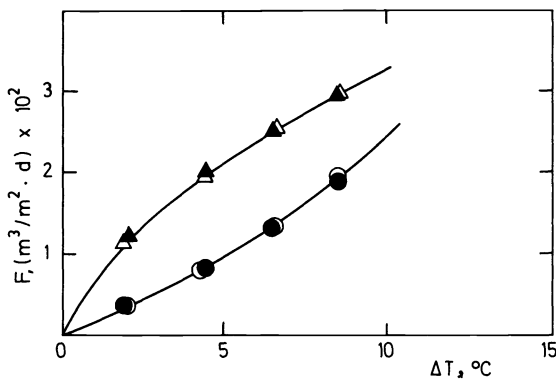


Fig. 7. Distillate flux vs. ΔT . Glucose solution.

○ ● $T_{\text{water}} = 20^\circ\text{C}$ $\Delta \blacktriangle T_{\text{sol}} = 50^\circ\text{C}$
 ○ $\Delta C_0 = 10 \text{ g/l}$ $\bullet \blacktriangle C_0 = 30 \text{ g/l}$

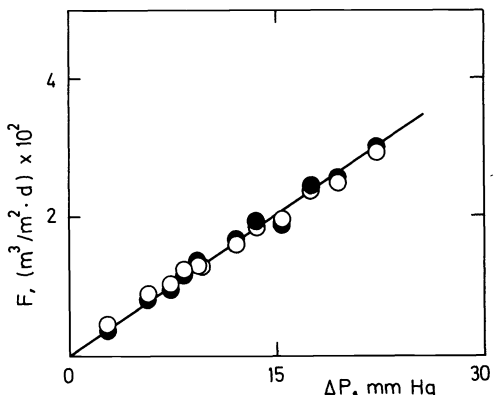


Fig. 8. Flux behaviour vs. P . Glucose solution.

○ $C_0 = 10 \text{ g/l}$ ● $C_0 = 30 \text{ g/l}$

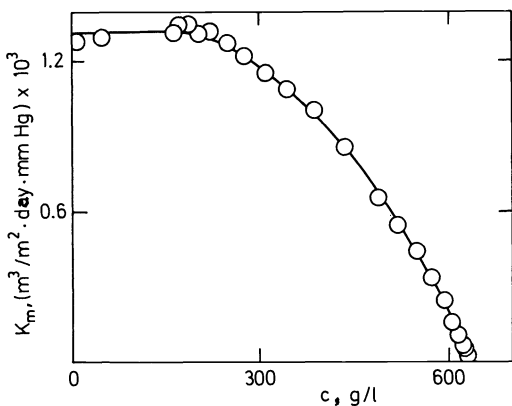


Fig. 9. K_m vs. feed concentration. Glucose solution.

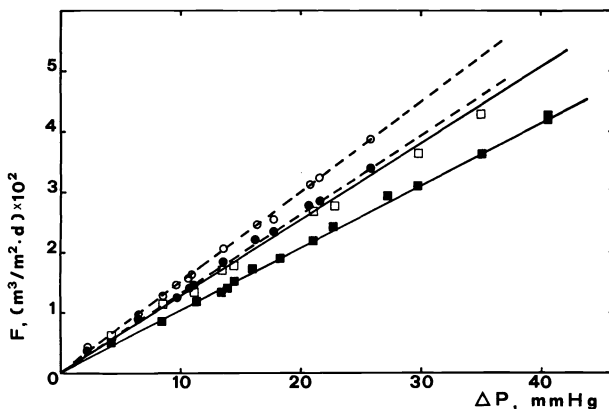


Fig. 10. Flux vs. vapor pressure difference across the membrane, P . NaCl solution.

□ I $C = 0.05 \text{ M}$ ○ II $C = 0.05 \text{ M}$
 ■ I $C = 0.05 \text{ M}$ ● II $C = 0.05 \text{ M}$

Interesting results have been obtained in an experiment with PVDF capillary membranes. Rejection for the glucose has been practically of 100%, with fluxes of an order of $5 \text{ l/m}^2\text{h}$ ($T_S = 30^\circ\text{C}$ and $\Delta T = 10 - 15$).

In Fig. 10 we reported data obtained with NaCl solutions on capillary polypropylene membranes, characterized by a different porosity and a different morphology. One can see a lower transmembrane flux F for the membranes with a 45% porosity (module type 1), compared with the ones obtained on membranes with a 70% porosity (module type 2). These differences are less significant in experiments with glucose solutions, as shown in Fig. 11.

The influence of nominal pore size on the membrane rejection is evidenced by the data plotted in Fig. 12.

In our studies it has been shown that membranes having nominal pore diameter of an order of $0.2 \mu\text{m}$ show rejection for NaCl and glucose solution always higher than 99%, and generally approaching 100%.

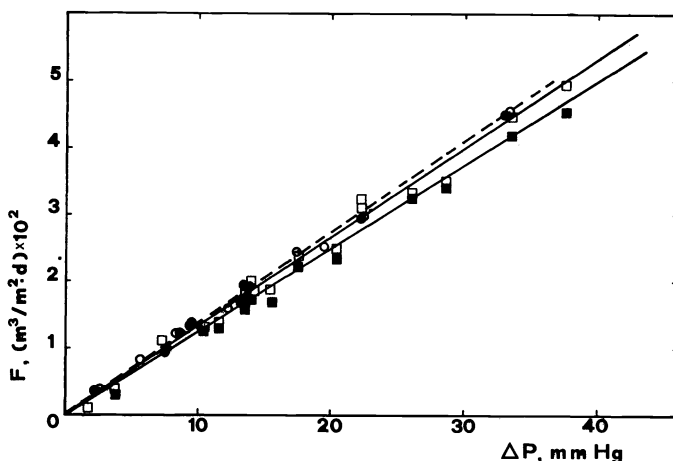


Fig. 11. Flux vs. vapor pressure difference across the membrane, P. Glucose solution.

□ I C = 0.05 M ○ II C = 0.05 M
 ■ I C = 0.05 M ● II C = 0.05 M

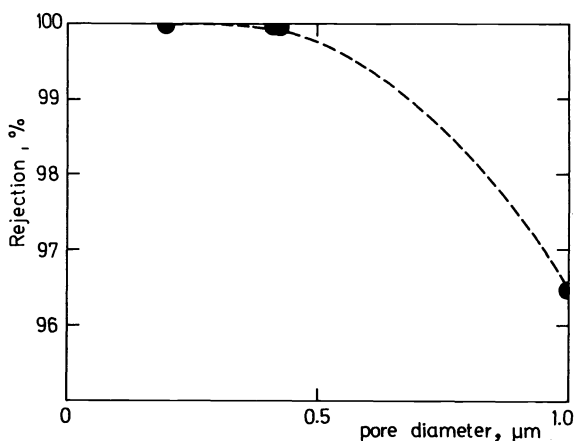


Fig. 12. NaCl rejection vs. membrane nominal pore diameters.

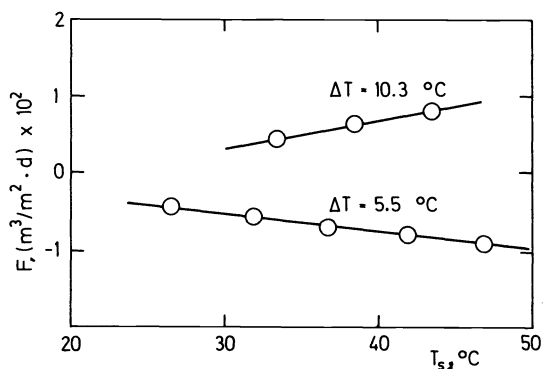


Fig. 13. Flux vs. T_s , for NaCl solutions 5.3 M.

When membrane distillation operates in solution at a particularly high concentration, the possibility of the appearance of significant fluxes from the cold side to the warm one has to be considered. A set of experiments has been carried out to analyze the phenomenon related to the difference of salt concentration across the membranes. In Fig. 13 typical data are plotted, obtained in an experiment with 5.3 M NaCl solutions, at a different average temperature of the feed, T_s . As shown, negative fluxes characterize the process when the ΔT 's are of an order of 5°C. For ΔT of an order of 10.3°C, the net fluxes are from the warm to the cold face of the membrane.

CONCLUSIONS

Membrane distillation offers a possibility for concentrating aqueous solutions to values approaching saturation, producing ultrapure water as the permeate. The process can be generated also at low temperatures, with interesting performances. Hydrophobic character, high porosity, defined pore structure with a narrow pore size distribution and high penetration pressure for water, high thermal and chemical resistance, are properties of the polymers of interest for this specific membrane process.

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