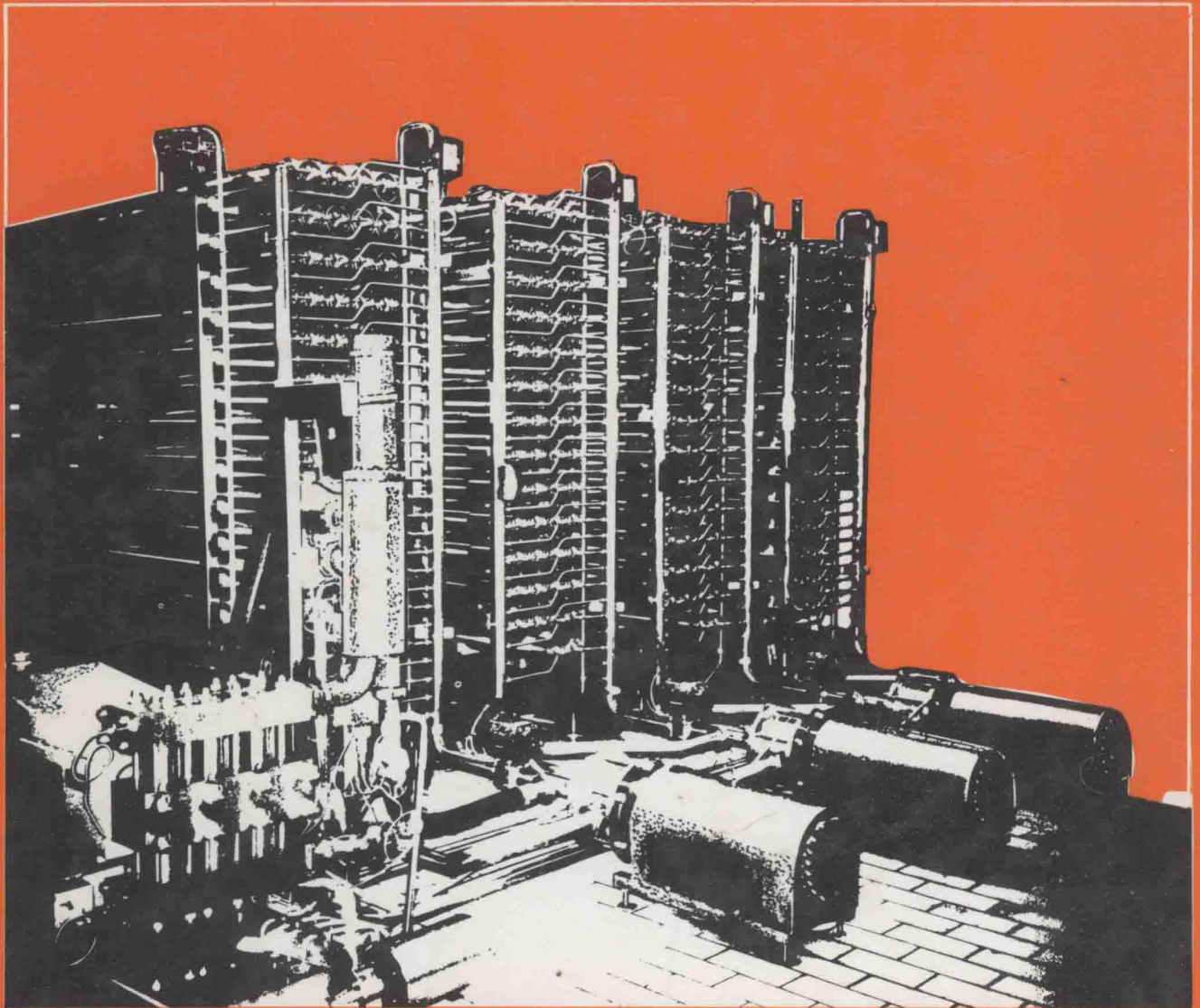

MEMBRANE SEPARATION PROCESSES

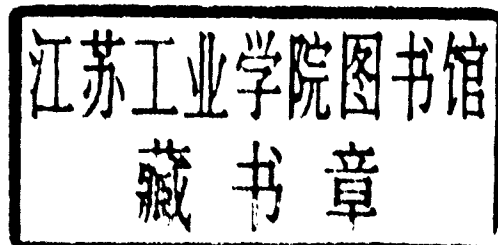


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MEMBRANE SEPARATION PROCESSES

A Green (Editor)



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PAPER A1

TITLE: APPLICATION OF MEMBRANE PERVAPORATION TO THE DEHYDRATION OF
ALCOHOLS IN CHEMICALS AND PHARMACEUTICALS PROCESSING

AUTHORS AND D A COLMAN AND T D NAYLOR (BP INTERNATIONAL)
AFFILIATION: G K PEARCE AND R D WHITBY (KALSEP)

The dehydration of aqueous alcohols by membrane pervaporation offers significant potential for both capital and operational cost savings particularly when a complex feedstock is difficult to dehydrate by conventional processes. Consequently, the considerable economic advantages to be gained make the technology an exciting prospect for future use in the pharmaceuticals and chemicals industries.

BP has developed a novel proprietary membrane for alcohol dehydration that exhibits considerably higher levels of performance than that of currently available membranes. Typically, a permeate (water) flux of 1 kg/(m²hr) at feed concentration of 5% and permeate quality >99% water is achievable with this new membrane. The membrane has also been shown to be compatible with feedstocks containing components other than alcohol and water. While the membrane's high flux and selectivity properties are of great importance, equal emphasis has been put on the design of the overall membrane system to ensure optimum use of the membrane surface. In particular, careful selection of feed flow conditions is essential to minimise the adverse effects of concentration polarisation. Similarly, the feed physical properties (notably viscosity) and permeate pressure conditions are major influences on membrane performance.

This paper describes experimental results that highlight the enhancement of membrane performance by optimum plant design. It also outlines applications for pervaporation systems to be marketed by Kalsep (a BP Ventures subsidiary) in the pharmaceuticals and chemicals industries.

NOMENCLATURE

A	absolute flux constant	kg/(m ² .d) per % water
A'	flux constant	"
B	concentration offset	% water
C _b	bulk concentration of feed	w/w % water
C _w	feed concentration at membrane surface	"
D	mass diffusivity in feed	m ² /s
D _m	membrane diffusivity	m ² /d
P	polarisation index = $\frac{A'}{A}$	
Re	Reynolds Number = $\frac{4 \text{ flowrate}}{\pi d \delta}$	
Sc	Schmidt Number = $\frac{v}{D}$	
Sh	Sherwood Number = $\frac{kd}{D}$	
a } b } c }	constants in empirical equation for Sh	
d	tube diameter	m or mm
k	mass transfer coefficient	m/s
j	membrane flux	kg/(m ² .d) or kg/(m ² .s)
m _c	membrane : feed concentration equilibrium constant	
m _p	membrane : permeate equilibrium constant	
p	permeate pressure	% water/mbara mbara
S _m	membrane thickness	m or mm
ρ	feed density	kg/m ³
v	kinematic viscosity	m ² /s

1. INTRODUCTION

1.1 Principles of Pervaporation

Pervaporation is a membrane separation process for miscible liquids. Separation is effected by preferential absorption of one of the components of the liquid by the membrane, diffusion of this component across the membrane and evaporation, as permeate vapour, into the partial vacuum applied to the underside of the membrane, Figure 1. The driving force for the process is therefore the concentration gradient set up within the membrane by evaporation of the permeating liquid from the underside of the membrane into the low pressure permeate stream.

The active membrane itself is usually supported on an asymmetric ultrafiltration membrane as a substrate which offers little resistance to the flux of permeate vapour. By careful choice of the membrane polymer the liquid-vapour equilibrium between feed and permeate may be very significantly perturbed leading to highly selective membranes, Figure 2.

A typical dehydration pervaporation process is shown in Figure 3. Wet liquid feed (eg alcohol and water) enters the membrane module. Water permeating across the membrane evaporates into the low pressure (typically 10 mbara) on the permeate side of the membrane, leaving a dehydrated product. The permeate may then be condensed as shown or (if practical) passed through a suitable vacuum source to atmosphere.

1.2 History of Pervaporation

The term "pervaporation" was first applied in 1917 to the evaporation of water through the walls of a collodion membrane (1). Although the first reported separation of a liquid mixture by this process was in 1906 (2), the first study of alcohol dehydration by pervaporation was a thesis published in France in 1949 (3), but it was the work by Binning and coworkers between 1958 and 1962 which established the principles and highlighted the potential of pervaporation (4,5).

Despite the fact that the first industrial trials of pervaporation date from 1949 (3), it is only more recently (~ 1982) that the process has been successfully commercialised (6). The main reason is that it is only recently that the ability to tailor a polymer membrane to give a viable separation has been achieved. Additionally, in pervaporation, unlike other membrane processes, one or part of one component of the liquid feed is evaporated. This requires input of the necessary latent heat of evaporation and the removal of the permeate as vapour.

With these advances pervaporation offers the potential for significant capital and energy savings in applications to mixtures that are difficult to separate by more conventional techniques, such as azeotropic mixtures or mixtures of close boiling components. Other applications may include the separation of heat sensitive products or the enrichment of organic pollutants.

1.3 Pervaporation Development Within BP

In recent years work at BP Research Centre, Sunbury has resulted in the development of a new generation of high performance polymeric pervaporation membranes that combine an exceptionally strong selectivity for water with a high permeate flux. In the vapour phase diagram of Figure 2 the mole fraction of water in the permeate is essentially 1. The membranes have been developed primarily for the dehydration of alcohols and their high selectivity ensures that the permeate has a very low solvent content while the high flux allows a substantial separation from a compact plant.

The membranes show good chemical resistance and thus offer potential for dehydrating complex feedstocks that are not easily handled by conventional processes. Consequently, the considerable economic advantages to be gained make the technology an exciting prospect for future use in the pharmaceuticals and chemicals industries.

This paper describes experimental results from this work which highlight the importance of plant design and operation for this membrane.

2. EXPERIMENTAL

2.1 The Membranes and Test Rig

The pervaporation membranes were prepared by casting the active polymeric on the inside of tubular proprietary polyethersulphone ultrafiltration membranes which formed the substrate. The membrane tubes were 1.2 m long and 12.5 mm internal diameter. These were supported in a standard single tube UF module by a perforated metal support tube.

Single tubes were tested in the test rig shown in Figure 4. This was designed with a recycle loop to allow membrane testing at flowrates up to 20 l/min cross flow. Wet feed was delivered by a metering pump into the recycle loop at ~50 ml/min. Flow around the recycle loop and through the membrane was by way of a seal-less centrifugal pump. A pressure control valve on the product line maintained pressure within the loop at ~2-4 bar in order to prevent flashing of the hot feed 70°C (the pervaporation process is independent of feed side pressure). The product could be returned to the feed reservoir (as shown) or to a separate reservoir. Product sample analysis gave the moisture content at the downstream end of the membrane which at most flowrates (> 1 l/min) was effectively the overall concentration within the recycle loop.

The permeate vacuum which was applied to the shell side of the module was provided by a two stage liquid ring pump with air ejector, and permeate samples could be collected in a 'Cardice' acetone cold trap.

2.2 Feedstocks

The majority of tests reported in this paper used isopropanol (IPA) with 1-10% by weight water. In some tests up to 40% polypropylene glycol was added to the feed in order to increase its viscosity. One test is also reported showing the performance of the membrane with a particular customer feedstock comprising wet IPA with an organic salt. All tests were carried out at 70°C and the relevant physical properties, density and viscosity, of the feedstocks are shown in Table 1.

2.3 Sample Analysis

Product samples were analysed for water content (<10%) by the Karl Fischer titration method. Samples of condensed permeate vapour which were predominantly water were analysed by gas chromatography in order to determine any leak of solvent into the permeate stream.

3. MEMBRANE PERFORMANCE RESULTS

3.1 Effect of Feed Water Content on Permeate Flux

A tubular membrane was tested over a range of flowrates (0.1 - 5 l/min) with an IPA feed at 70°C and water contents in the range 1-10%. For each flowrate, the mean permeate flux of water is plotted against the water content of the feed entering the membrane in Figure 5. Over this concentration range the flux is linear with feed concentration with an offset at ~0.5% water which is a function of permeate pressure (section 4.1).

It should be noted that, because of the high selectivity of the BP membranes the solvent content of the permeate is less than 0.1% in a defect free membrane.

3.2 Effect of Feed Flowrate on Permeate Flux

The increase in flux with flowrate (Figure 5) as the flow goes from laminar at the lower flows (0.1 and 1 l/min) to turbulent at the higher flows (2 and 5 l/min) clearly demonstrates the existence of concentration polarisation and its dependence upon the mass transfer coefficient; this is discussed more fully in section 4.2.

At the lowest flow (0.1 l/min, $Re = 190$) the estimated concentration difference along the membrane was 10% of inlet concentration; however at higher flows this difference was less than 1%. There was also a heat loss due to both vaporisation of the water in the permeate and normal convection. Again this was only significant at the lowest flowrate when a temperature difference of ~10°C was recorded; at higher flowrates the difference was 1°C or less.

3.3 Effect of Feed Properties on Permeate Flux

Because pervaporation is an absorption/diffusion process in the membrane, the relative affinity of the water for the membrane and the feed will control the absorption or membrane surface/feed equilibrium and hence in part the flux. For example with a particular customer feedstock comprising IPA and a salt with high affinity for water the permeate flux was reduced by a factor of ~6 in spite of polarisation being minimised by operating in turbulent flow (Figure 6).

In order to investigate more fully the effects of mass transfer upon membrane performance a series of tests was carried out in which the viscosity of the feed was increased by the addition of polypropylene glycol (PPG) (Table 1). This produced flux-against-concentration plots similar to

those of Figure 5 from which flux data discussed in section 4.2 were derived.

3.4 Effect of Vacuum on Permeate Flux

The driving force for pervaporation is provided by the vacuum which is applied to the underside of the membrane. The dependence of the permeate flux upon vacuum is shown in Figure 7 for IPA containing various water cuts. At all concentrations there is a relatively independent region at low permeate pressure but as pressure increases (above 15 mbara at 3.7% water and 25 mbara at 10% water) there is a steady decline in flux, with zero flux apparently being dependent upon feed concentration (see section 4.1).

Unexpectedly, however, flux rises steeply at the higher water contents when the permeate pressure falls below 10 mbara. This is believed to be a phenomenon characteristic of the BP membranes and may be due to changes in the diffusivity within the membrane. It is known that variability of membrane diffusivity is due to swelling on the upper surface where there is a higher water content.

Since the membrane is effectively 100% selective towards water, changes in the permeate pressure do not affect permeate quality as is the case with most other pervaporation membranes.

4. DISCUSSION

4.1 Permeate Flux

The flux j , of water through the BP pervaporation membrane is an absorption/diffusion/evaporation process and can thus be written down as

$$j = \frac{D_m}{\delta_m} (m_c C_w - m_p p) \quad (1)$$

where D_m is membrane diffusivity and δ_m is membrane thickness. These will be functions of concentration within the membrane. m_c and m_p are, to a first approximation at low flux, constants relating the equilibrium concentration of water in the membrane on the feed and permeate sides of the membrane to the feed water content at the surface, C_w , and partial pressure of water vapour in the permeate, p .

This expression is essentially the same as that derived by Rautenbach and Albrecht (9) for flux when there is only one permeating species and second order powers of permeate pressure are small.

Comparison with results shows this form of relation to fit reasonably well. The linearity of the flux against concentration plots at constant permeate pressure suggests, at $C < 10\%$, that $\frac{D_m}{\delta_m} m_c$ is constant.

As $C_w \rightarrow \frac{m_p}{m_c} \cdot p$ then $j \rightarrow 0$, which shows that if the permeate pressure

$p = 0$ then there will be an offset in the flux against concentration relation, as observed in Figure 5. Similarly, flux j decreases linearly with p increasing, as observed above 20 mbara in permeate pressure results (Figure 7). The constant m_c relates concentration in the feed to the concentration in the membrane at the surface and will be a function of membrane/feed interaction. In the case of the customer feed, containing salts with a high affinity for water, it appears that m_c was reduced by ~6 causing the observed reduction in membrane flux (Figure 6) and an increase in offset. Considering a difference in permeate pressure of 8 to 3 mbara between the two sets of data, the increase in offset from 0.5% to 0.75% is in reasonable agreement with equation 1.

The results reported in this paper were at 70°C. However membrane flux is a strong function of temperature, increasing by a factor of ~1.5 for every

10°C rise in temperature. 70°C has been found to be near optimum for the BP pervaporation membrane due mainly to temperature constraints imposed by the substrate.

4.2 The Effect of Flow Regime upon Flux

For a given membrane, feed and permeate pressure, equation 1 can be written as

$$j = A (C_w - B) \quad (2)$$

where A is an absolute flux constant depending upon feed and membrane type and B is an offset constant given by the permeate pressure.

In a tubular membrane with cross-flow there will be a concentration boundary layer and the wall concentration $C_w < C_b$ the bulk concentration. Now the flux of water through this boundary layer and also through the membrane, will, by definition of the mass transfer coefficient k, be

$$j = k\rho (C_b - C_w) \quad (3)$$

(Note: unlike the case of membrane filtration, there is negligible bulk flow towards the membrane, the flux of water being determined by its diffusion through the bulk solvent).

Combining equations 2 and 3

$$j = A' (C_b - B) \quad (4)$$

$$\text{where } A' = \frac{A}{A/\rho k + 1} \quad (5)$$

is a flux constant measured in terms of the bulk concentration C_b and is a function of the mass transfer or hydrodynamics of the system. A' is the slope of the flux against concentration plots of Figure 5.

The increase in permeate flux with flow is illustrated by plotting the flux constant A' against flowrate, (Figure 8). Included in this Figure are flux constant data from tests with polypropylene glycol (PPG) added to the IPA/water feed. Addition of PPG increases the viscosity of the feed (Table 1) and at a given flowrate the resulting reduction in mass transfer and consequently A' due to the change in Reynolds number with viscosity is clearly shown.

The dominant effect of flow regime is more effectively shown in Figure 9 where the data of Figure 8 are re-plotted against Reynolds number. Data from another BP membrane with lower absolute flux, A, are also plotted in Figure 9 at Reynolds numbers > 10000 . As would be expected, there is a small increase in flux constant A' within the laminar regime $Re < 2000$ but, across the transition region to fully turbulent flow, there is a substantial and similar increase in A' for all viscosities. Within fully turbulent flow $Re > 3000$, A' continues to rise, showing that a concentration boundary layer still exists in spite of the turbulent flow, even above $Re = 10000$.

4.3 Mass Transfer Correlation and Polarisation Index

The existence of a concentration boundary layer in which $C_w < C_b$ and $A' < A$ means that a polarisation index can be defined

$$P = \frac{A'}{A} \quad (6)$$

$$= \frac{(C_w - B)}{(C_b - B)} \quad (7)$$

and from equation 5
$$P = \frac{1}{A/\rho k + 1} \quad (8)$$

which is a function of absolute membrane flux A and the mass transfer coefficient or system hydrodynamics. Most effective use of membrane area will occur when polarisation is minimised and $P \rightarrow 1$. From equation 8, if the absolute flux constant A is known for a given membrane, then the system hydrodynamics can be designed with suitable mass transfer k to reduce polarisation to an acceptable level.

The BP pervaporation membranes are effectively smooth and, unlike UF and MF membranes, there is effectively zero suction at the surface. Common mass transfer correlations for turbulent flow in a pipe can therefore be used based on the empirical form for Sherwood number

$$Sh = c Re^a \cdot Sc^b \quad (9)$$

where Sc is the Schmidt number and a, b, c are constants (7)

$$\text{and } Sh = \frac{kd}{D} \quad (10)$$

where d is tube diameter and D is mass diffusivity.

Substituting equations 9 and 10 into equation 5 gives an expression for the flux constant A' in turbulent pipe flow

$$A' = \frac{\frac{A Re^a}{c \rho \sqrt{D}^{1-b}} + \frac{D^{(1-b)}}{Re^a}}{D^{(1-b)}} \quad (11)$$

with the asymptote as $Re \rightarrow \infty$ of $A' \rightarrow A$.

Many values for the constants a, b and c have been put forward (7) but in the operating range of Re around 10^4 and high Sc (= 560), those suggested by Berger and Hau (8) provides a reasonable fit to the data $a=0.86$, $b=0.33$, $c=0.0165$. Data on the mass diffusivity is not readily available, however adopting these constants and a mass diffusivity $D = 1.6 \times 10^{-9} \text{ m}^2/\text{s}$ for the pure IPA/water feed, equation 11 was fitted to the data in Figure 9 and absolute fluxes for the two membranes of A=6 and 7.2 kg/(m².d) per percent water were derived. The fit as shown in Figure 9 is considered reasonable enough to assume the absolute flux values to be accurate to within 5%. In the case of the feeds with PPG the mass diffusivity is not known. However a possible fit, assuming similar ultimate flux A, uses $D = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$ and is shown in Figure 9.

While these fits of equation 11 are approximate, they indicate the degree of polarisation in turbulent flow. In the higher flux membrane with IPA at $Re=10000$ (5.3 l/min) polarisation index P is 80%, while under similar conditions and the lower flux membrane P is 85%.

4.4 Implications for Module Design

From the above discussion it is apparent that with the BP pervaporation membranes the hydrodynamics and surface mass transfer assume a significant role in determining the overall membrane flux.

Thus in order to make most effective use of membrane area, a plant using the tubular pervaporation membranes would need to operate in turbulent flow mode and preferably at least $Re = 10000$. However, this creates further problems. Because of the high flow and relatively low flux, the net separation per unit length of membrane is low, thus requiring either a recycle system or many tubular membranes in series with associated pumping costs. For example dehydration of IPA from 10% to 1% at 5 l/min would require ~620 of the 1.2 m tubular membranes.

5. APPLICATIONS

Recovering used organic solvents by dewatering is a process which is of major importance to the pharmaceutical and chemicals processing industries. Azeotropic distillation, the traditional method of dehydrating wet solvents, is energy-intensive, expensive and uses entrainers which are frequently toxic. Pervaporation membranes offer an alternative method for removing water from wet solvents.

The performance of early pervaporation membranes was not good enough to enable cost effective processes to be developed. The new membranes developed within BP and described in the preceding sections are the basis of a new set of pervaporation processes being marketed by Kalsep (a BP Ventures subsidiary). Some benefits of pervaporation are:

- Energy requirements, and hence operating costs, are substantially lower than those of distillation, since only the aqueous component of the feedstock is vapourised. Typically, the energy costs for pervaporation are 35% lower than those of distillation when dehydrating alcohols.
- The energy advantages are greater in those cases where distillation would require a high reflux ratio or the use of entrainers. The absence of entrainers reduces health risks and environmental hazards.
- Operation at relatively low temperatures allows the use of low-grade or waste heat to provide the energy.
- Water can be readily removed from a mixture of organic materials. The mild operating conditions minimise the degradation of heat sensitive substances which might be present in the mixture.
- Pervaporation units have lower capital costs and are easier to install than distillation plant. They are particularly cost effective in small to medium scale applications as a consequence of their modular nature.
- Pervaporation and distillation may be combined in a hybrid process which minimises both capital and operating costs.

The performance of Kalsep's membrane pervaporation systems is optimised by operating them under a set of process conditions as defined by the foregoing results in terms of temperature, permeate pressure and hydrodynamics. Feedstocks containing up to 30% w/w water are normally accepted, and the pervaporation membrane is able to reduce the water content to 1% w/w. The permeate composition in such cases is usually higher than 99% water.

The membrane systems have been shown to dehydrate a range of alcohols (eg ethanol and isopropanol), amines (eg pyridine) and esters (eg ethyl acetate) and have the potential to dewater a wide range of the solvents found in pharmaceutical and speciality chemicals processing. In addition, the systems can be used to dewater multi-component aqueous-organic mixtures and to separate methanol from other organic liquids.

A pervaporation pilot plant has been supplied by Kalsep to a major UK pharmaceutical manufacturer for dehydration trials on a viscous isopropanol solution of an intermediate used in the manufacture of an important antibiotic. Previous attempts to dehydrate this feed by pervaporation had been unsuccessful, but these trials have demonstrated that the BP developed membrane can successfully dehydrate from an initial moisture content of 7% to the target of less than 2% (Figure 6).

6. CONCLUSIONS

- 6.1 The results of tests on tubular pervaporation membranes developed at BP's Research Centre, Sunbury have been reported and the implications of operating conditions for process design discussed.

- 6.2 Pervaporation is an absorption/diffusion/evaporation process and a first approximation expression relating permeate flux to feed concentrations and permeate pressure has been suggested for the BP membrane which is highly selective towards water.
- 6.3 Results on the dehydration of IPA confirm the form of this relation by showing flux to be linear with feed concentration, having an offset, which is a function of permeate pressure. At feed concentration of 5% water, flux is 26 kg/(m².d) at operating temperature of 70°C and water content of the permeate is >99%.
- 6.4 Dehydration of a customer feedstock containing an organic salt with high affinity for water gave similar results, although flux was reduced by a factor of ~6 due to the presence of the salt.
- 6.5 Increases in permeate flux with flowrate in the tubular membranes have demonstrated the existence of a concentration boundary layer and a polarisation index has been derived in terms of the mass transfer coefficient and an absolute flux constant.
- 6.6 Using the polarisation index and empirical mass transfer data, the results with feeds of differing viscosities have been shown to correlate in the turbulent Reynolds number regime.
- 6.7 The use of superior membrane chemistry coupled with enhanced hydrodynamic flow design has allowed the manufacture of a cost effective membrane pervaporation system which has potential for use in a wide range of alcohol and solvent dewatering applications.

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Table 1: Physical Properties of the Test Fluids at 70°C

FLUID PPG CONTENT, % W/W	DENSITY (5% H ₂ O) kg/m ³	KINEMATIC VISCOSITY, m ² /s
0	757	0.9 x 10
20	801	3.5 x 10
30	823	6.4 x 10
40	845	11.3 x 10

Density at 70°C IPA 745 kg/m³
 Water 978 kg/m³
 PPG 966 kg/m³

Customer feed $\rho = 870 \text{ kg/m}^3$ $D = 5 \times 10^{-6} - 8 \times 10^{-6} \text{ m}^2/\text{s}$

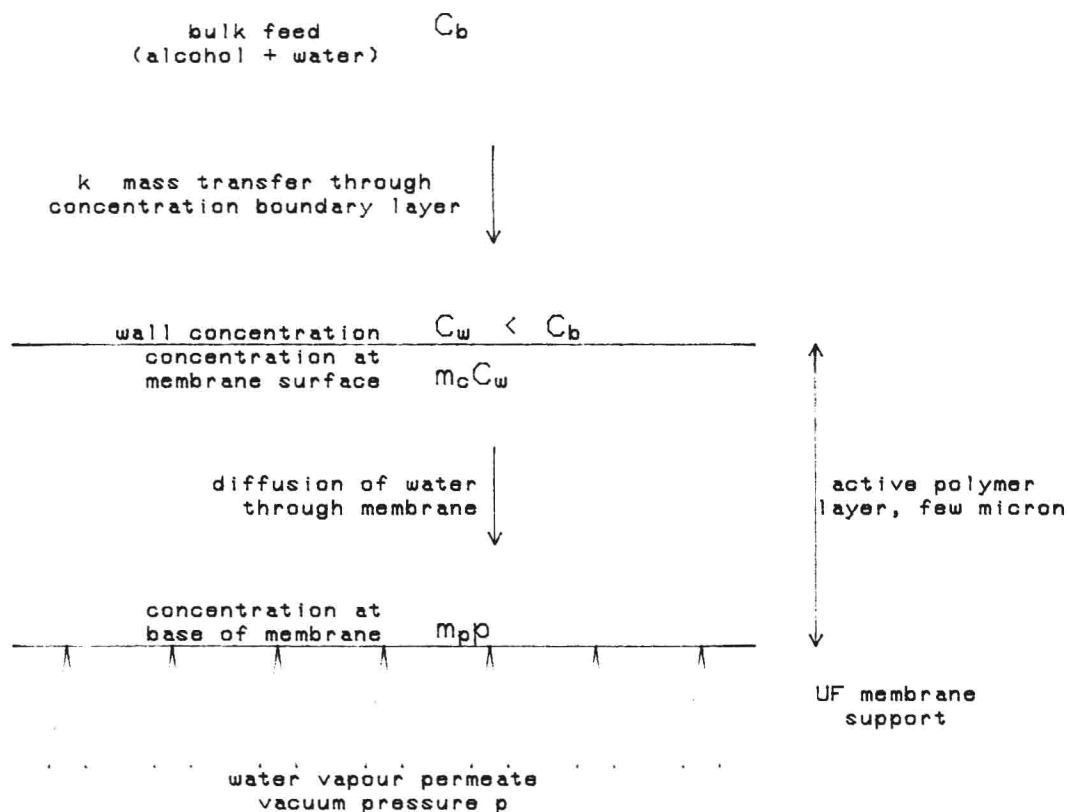


Fig 1 SCHEMATIC OF PERVAPORATION MEMBRANE