Reverse Osmosis Separation of Binary Organic Mixtures Using Cellulose Acetate Butyrate and Aromatic Polyamide Membranes

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SYNOPSIS

A systematic investigation has been conducted to demonstrate applicability of reverse osmosis (RO) fractionation of organic liquid mixtures by laboratory-prepared cellulose acetate butyrate (CAB) and aromatic polyamide (PA) membranes. The determination of preferential sorption was also conducted by using liquid chromatography technique. It was found that reverse osmosis was applicable to the fractionation of organic liquid mixtures. It was also found that the component of the binary mixture that is enriched in the membrane permeate can be predicted by considering the preferential sorption and Stokes' radius for each constituent of the feed mixture.

INTRODUCTION

Reverse osmosis (RO) is recognized nowadays as a versatile separation process for the treatment of aqueous and nonaqueous solutions.[1] Its application covers a wide range of industrial separation processes such as sea water desalination, waste water treatment, food processing etc. Most of applications are for the treatment of aqueous solutions, though there are industrial practices in a limited scale for the recovery of organic solvents and hydrocarbons.[2,3] Though attempts were made to separate organic solvent mixtures soon after the development of reverse osmosis membranes for sea water desalination,[4,5] further progress in this area has been hampered mainly due to insufficient tolerance of polymeric membranes to organic solvents. Emergence of inorganic membranes with pore sizes small enough to separate or fractionate the components of organic mixtures is yet to come.

Regarding fundamental research for membrane transport and the prediction of membrane performance data under various operating conditions, we have derived a set of transport equations on the basis of the surface force–pore flow model, which is a quantitative expression of the preferential sorption–capillary flow model proposed by Sourirajan, and we have performed a computer simulation using the transport equations so developed.[6] We have also confirmed that the results of the calculation could reproduce the experimental data for the separation of ethanol/n-heptane mixtures by cellulose membranes reasonably well. In particular, the relative sizes of the permeant molecules, the pore size on the membrane surface, and the interaction forces working between the permeant molecules and the membrane material were identified as important factors that govern the membrane performance data including the separation factor and the permeation rate. Briefly, the conclusions obtained from the computer simulation can be summarized as follows:

1. The transport equations enable the quantitative prediction of the membrane performance data.
2. An increase in difference of the radii of the component molecules increases the membrane selectivity.
3. A decrease in the membrane pore size increases the membrane selectivity.

4. A stronger preferential sorption increases the membrane selectivity.

5. For a given pore size, an increase in the membrane selectivity is accompanied by a decrease in the permeation rate.

6. The operating pressure has little effect on the membrane selectivity.

This work is one of a series of papers on the separation of organic mixtures by reverse osmosis. The objective of this work is to determine if the conclusions obtained in our previous work can be satisfied at least qualitatively by experimental results obtained under various conditions. In particular, the effects of the following variables on the membrane performance were tested:

1. The effect of the relative sizes of the permeant molecules.
2. The effect of the membrane pore size.
3. The effect of the preferential sorption.
4. The effect of the pressure.

It has been found that the experimental data were generally consistent with the conclusions of the previous paper, though some modifications were necessary.

EXPERIMENTAL

Materials. Unless otherwise stated, chemicals were of reagent grade, supplied by the BDH Chemicals.

Membrane Preparation. Cellulose acetate butyrate (CAB-171-40) was supplied by the Eastman Kodak Co. The polymer powder was dried at 60°C for 24 h before use. The casting solution of the composition, cellulose acetate butyrate (CAB-171-40), 14.0 wt %, acetone, 74.0 wt %, water, 9.0 wt %, and magnesium perchlorate, 3.0 wt %, was cast on a glass plate to the nominal thickness of 0.025 cm. After 1 min of acetone evaporation at ambient temperature, the cast film was immersed into ice cold water, together with the glass plate, for gelation. The membrane was kept in the gelation medium overnight. The post-treatment of the membrane so prepared consisted of shrinkage at 70°C for 10 min and pressurization at 3448 kPag (500 psig) under distilled water for 2 h.

The laboratory synthesized aromatic polyamide material was poly(m-phenylene-iso(70)-cotere(30)-phthalamide (abbreviated as PA)) of molecular weight 31,300.[7] The intrinsic viscosity in 96% sulfuric acid at 20°C was 1.80 dL/g. The PA polymer

was dried under vacuum for 48 h before use. The casting solution of the composition, aromatic polyamide, 16.91 wt %, lithium nitrate, 6.93 wt %, and dimethyl acetamide (DMA), 76.16 wt %, was cast on a glass plate to the nominal thickness of 0.025 cm. The solvent was then evaporated at 95°C for 10 min before the cast film was immersed in ice cold water for gelation together with the glass plate. The membrane stayed in the gelation medium overnight. The posttreatment of the membrane consisted of pressurization at 3448 kPag (500 psig) for 2 h.

Reverse Osmosis Experiments. The static cell used in the reverse osmosis experiment and the experimental procedure have been described elsewhere in detail.[8] The reverse osmosis experiments were carried out at 1724 kPag (250 psig) and at ambient temperature unless otherwise stated. In each experiment pure water permeation rate (PWP) and product rate (PR) were collected. All (PWP) and (PR) data reported are those corrected to 25°C using relative density and viscosity of water. The effective membrane area was 9.6 cm². The quantities (PWP) and (PR) are defined as the permeation rate per effective membrane area in the absence and presence of the solute in the feed, respectively, and have the dimension of kg/(s effective film area). They are, however, reported in this paper as g/h so that consistency can be maintained with our earlier work. The solute separation defined as

$$f = [\text{ feed solute (ppm)} - \text{product solute (ppm)}]/$$

$$[\text{feed solute (ppm)}] \quad (1)$$

was also determined for each reverse osmosis experiment. Some of reverse osmosis experiments were conducted for separation of sodium chloride solute from the feed aqueous solution of 3500 ppm. In such experiments sodium chloride concentration in water was determined by conductivity measurement.

In order to conduct reverse osmosis experiments for the binary mixture of organic solvents as feed, the water in the membrane was replaced by ethanol, and then ethanol was replaced by one of the constituents of the binary mixture. The replacement by ethanol was done by successive permeation of ethanol/water solutions, which were progressively more concentrated in ethanol, under pressure. The ethanol in the membrane was then replaced by pure organic liquid (A) which constitutes one of the components of the binary mixture (A and B). After measuring the permeation rate of the pure organic liquid (A), the permeation rates of binary mixtures with progressively higher concentrations of the other constituent (B) were determined. Sometimes, the

direction of the change in the composition of the binary mixture was reversed, i.e., the feed composition was changed progressively from pure solvent (B) to pure solvent (A). Each permeate sample of the binary mixtures was subjected to analysis by refractometry using a Waters differential refractometer Model R401.

Liquid Chromatography Experiments. Cellulose acetate butyrate powder supplied from Eastman Kodak Co. was dried at 60°C overnight. The particle size of the powder was adjusted to the range 38–53 μm by sieving before being packed into stainless steel tubing of 0.6096 m (2 ft) length and 0.001575 m (0.062 in.) diameter. The amount of the powder required to fill the column was 0.512 g. Aromatic polyamide polymer powder was also packed into the column in a similar manner except that the polymer was crushed in a ball mill before the particle size was adjusted by sieving. The amount of the polymer required to fill the same length of the column was 0.796 g. A Waters Associate liquid chromatograph (Model 501) fitted with a R401 refractometer was used for the liquid chromatography experiments. Either pure solvent A, or pure solvent B, or the mixture of solvent A and solvent B of various compositions was pumped into the column as chromatography solvent. Then, 10 μL of either pure A or pure B was injected into the solvent stream at the column inlet and the retention time recorded. The retention volume [V'_R] was calculated as the product of retention time and solvent flow rate, which was maintained at 0.3 mL/min. The pressure drop across the entire column length was kept below 300 psi. The experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The following equation was used to calculate the surface excess of the component A at the interface between the mixture of A and B, the composition of which is given by mole fractions $X_{A,b}$ and $X_{B,b}$, and the polymer surface[9]

$$\Gamma_A A_P \bar{V}_A = \frac{X_{A,b} X_{B,b} \bar{V}_A \bar{V}_B}{(X_{A,b} \bar{V}_A + X_{B,b} \bar{V}_B)^2}$$
$$\times ([V'_R]_A - [V'_R]_B) \quad (2)$$

where Γ, A_P, $\bar{V}$, and X_b indicate the surface excess (mol/m^2), surface area of the polymer in the column (m^2), molar volume (m^3/mol), and mole fraction in the bulk liquid mixture, which means the mole

fraction in the solvent stream in the chromatography column, respectively. Subscripts A and B indicate components A and B. The details of the derivation of the above equation have been given elsewhere.[10]

Results of liquid chromatography experiments are illustrated in Figures 1 and 2 for CAB and PA materials, respectively. In the above figures, the component that shows positive surface excess values is considered to be preferentially sorbed. One of the components was preferentially sorbed in the entire range of the composition with respect to the binary mixtures of ethanol/p-xylene, p-xylene/n-heptane, and ethanol/n-heptane for both CAB and PA materials. For the system CAB/ethanol/1-hexanol, ethanol was preferentially sorbed except in a narrow range of ethanol mole fraction, X_A, from 0.52 to 0.58 where 1-hexanol was preferentially sorbed. As for the PA/ethanol/1-hexanol system, 1-hexanol was preferentially sorbed in the range of ethanol mole fraction, X_A, from zero to 0.63, whereas the opposite was the case in the range of ethanol mole fraction from 0.63 to unity. From the above results, the order in the strength of the interaction force between the component molecule and the polymer can be given for both CAB and PA polymers as

$$p - \text{xylene} < \text{ethanol} < n\text{-heptane} \quad (3)$$

Reverse Osmosis Results. The results of reverse osmosis experiments at two pressure levels, 3448 kPag (500 psig) and 5172 kPag (750 psig), are summarized in Figures 3 and 4. These results show that the separation of organic mixtures do take place in all cases studied. In particular, ethanol is preferentially transported through both CAB and PA membranes for feed binary mixtures of ethanol/n-heptane, ethanol/p-xylene, and ethanol/1-hexanol, whereas n-heptane is preferentially transported through the above membranes for the binary mixture of n-heptane/p-xylene.

In order to understand the above experimental results for the separation of the binary mixture, the preferential sorption–capillary flow model[8] described schematically in Figure 5 can be used. In Figure 5, t and x refer to the thicknesses of interfacial and bulk layers, respectively. According to the theory, the total flow of the fluid mixture consists of two parts, one the flow of the bulk fluid mixture in the central region of the pore and the other the flow of the interfacial fluid near the pore wall. Although the flow of the bulk fluid does not contribute to the separation of the fluid components at all, the separation is caused by the flow of the interfacial fluid. In order for separation to take place by the latter
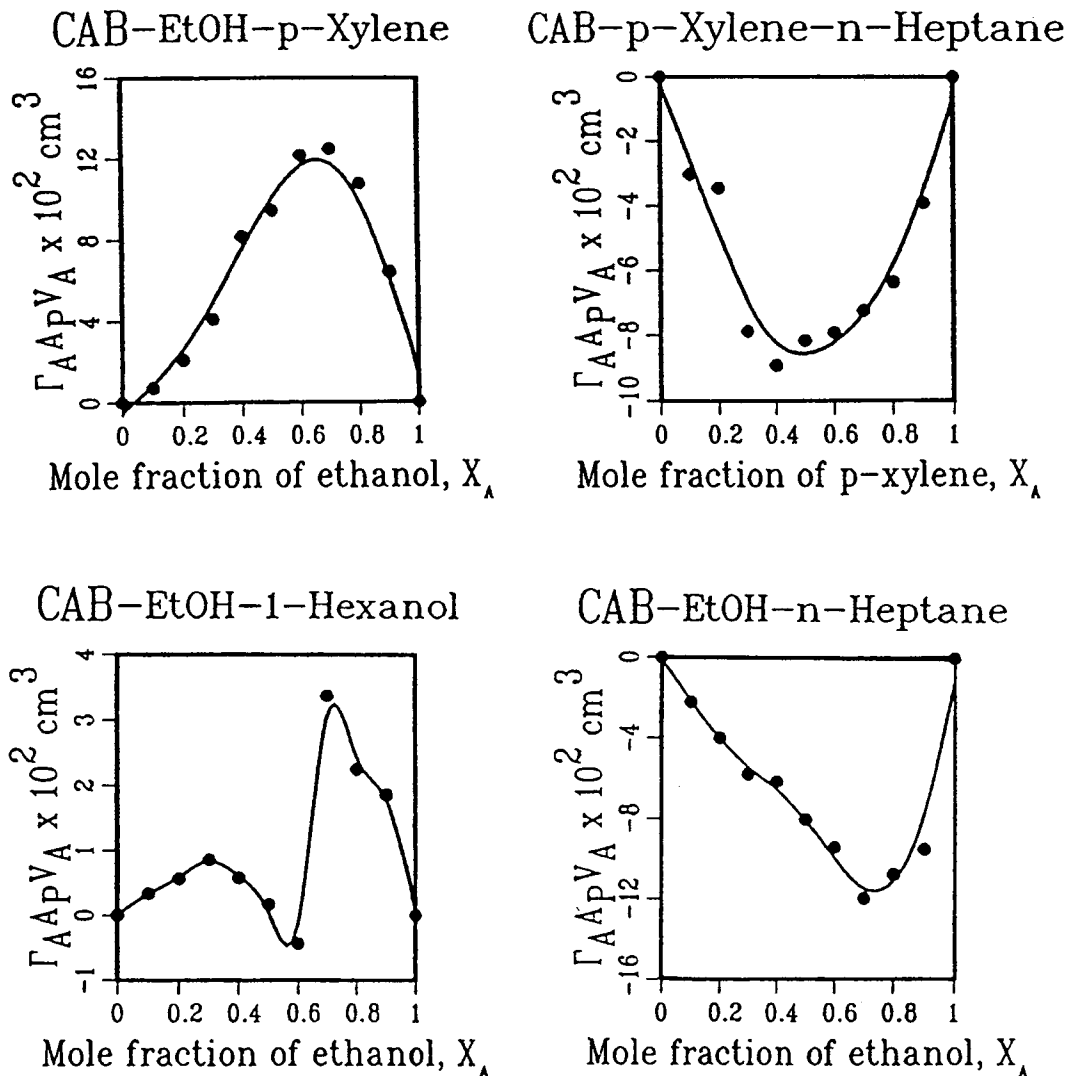
Figure 1 Surface excess data for cellulose acetate butyrate material.

flow, one of the components has to move faster than the other in the interfacial region. This may occur (1) when the former component is more concentrated in the interfacial region by preferential sorption to the membrane material (thermodynamic effect), (2) when the former component is more mobile than the latter component (kinetic effect), or (3) a combination of both. Which component is enriched in the permeate is governed primarily by the above factors. Liquid chromatography data provide sufficient information on the preferential sorption. As for the mobility of the component molecule, it is known that the permeant molecule is more mobile in the membrane pore when its (Stokes' radius/pore radius) ratio is smaller.[1] For a given pore radius,

therefore, Stokes' radius offers a measure of the mobility of the component molecule. Table I summarizes Stokes' radii obtained for the component molecules involved in this study. Table II further summarizes the preferential sorption and the mobility for four binary mixtures studied in this work. The fourth column of the table indicates the component to be enriched in the permeate when considering both preferential sorption and mobility. The last column indicates the component that has been actually enriched in the permeate by RO experiment. Agreement between the theoretical prediction and the experimental data is very good. The above results indicate that the component to be enriched can be predicted by considering the preferential sorption
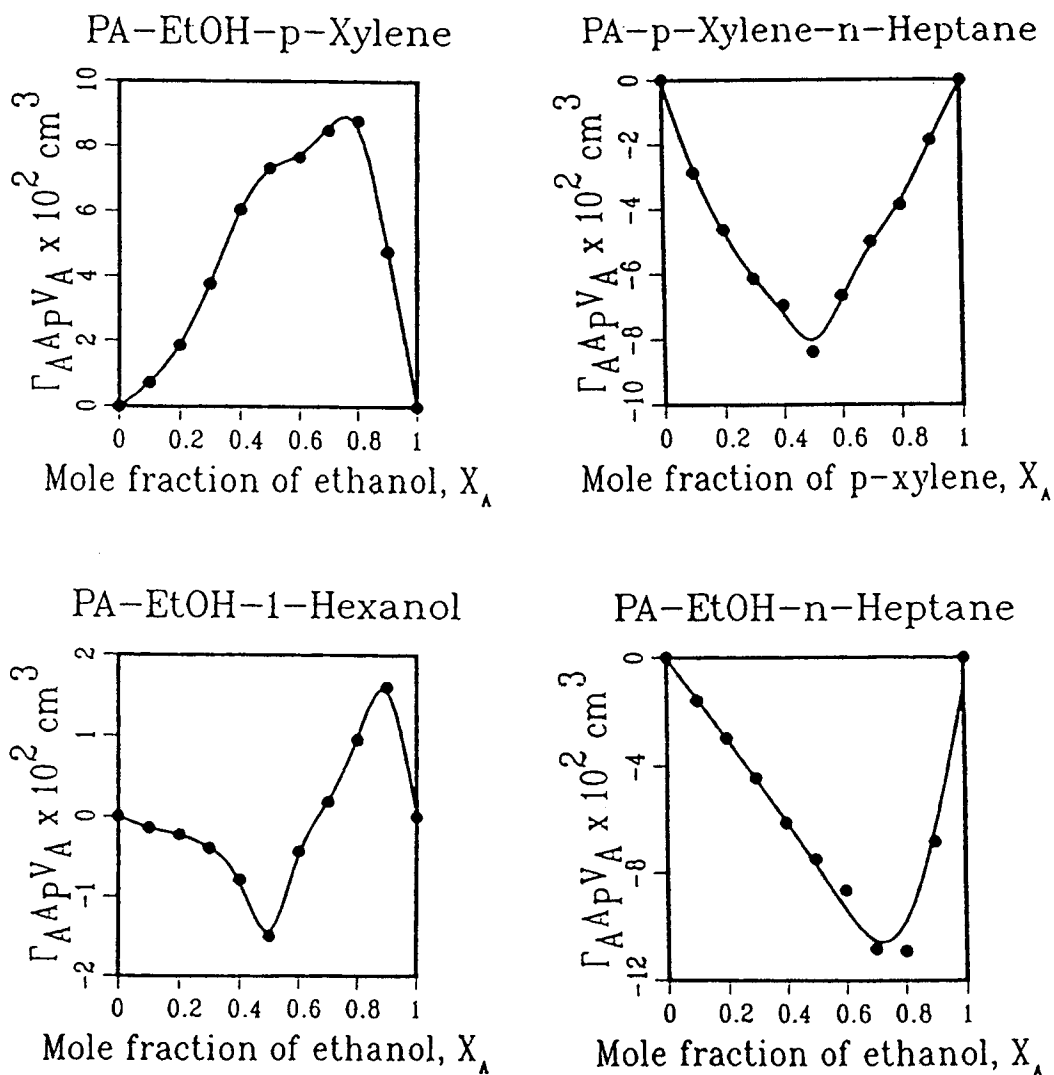
PA−EtOH−p−Xylene

PA−p−Xylene−n−Heptane

Mole fraction of ethanol, X_A

Mole fraction of p−xylene, X_A

PA−EtOH−1−Hexanol

PA−EtOH−n−Heptane

Mole fraction of ethanol, X_A

Mole fraction of ethanol, X_A

Figure 2 Surface excess data for aromatic polyamide material.

and Stokes' radius without doing any reverse osmosis experiment.

Based on the foregoing discussion an operational line can be drawn as illustrated in Figure 6. The physical meaning of Figure 6 is as follows. The curve for the composition of the adsorption phase is an arbitrary one which indicates that the component A is preferentially sorbed on the polymer material. The symbols r_{AB} and r_{BA} refer to Stokes' law radii of solute A in solvent B and solute B in solvent A. When $r_{AB} < r_{BA}$, which means that molecule A is more mobile than molecule B in the membrane pore, the enrichment of the component A in the permeate is both thermodynamically and kinetically favorable. This enhances the concentration of A in the permeate. A shift in the operational line in Figure 6

reflects such an increase. Ethanol/1-hexanol and ethanol/p-xylene binary mixtures are two typical examples of the case. When $r_{AB} \simeq r_{BA}$, which means molecules A and B are almost equally mobile in the membrane pore, the operational line and the adsorption line are almost equal. The binary mixture of n-heptane/p-xylene is a typical example of the case. When $r_{AB} \gg r_{BA}$, which means that the preferentially sorbed component is far less mobile than the other component in the membrane pore, the operational line is shifted downwards. Ethanol/heptane binary mixture is one such example, where less preferentially sorbed ethanol is enriched in the permeate because of its much higher mobility.

Effect of the Operating Pressure. Referring further to Figures 3 and 4, the effect of the operating
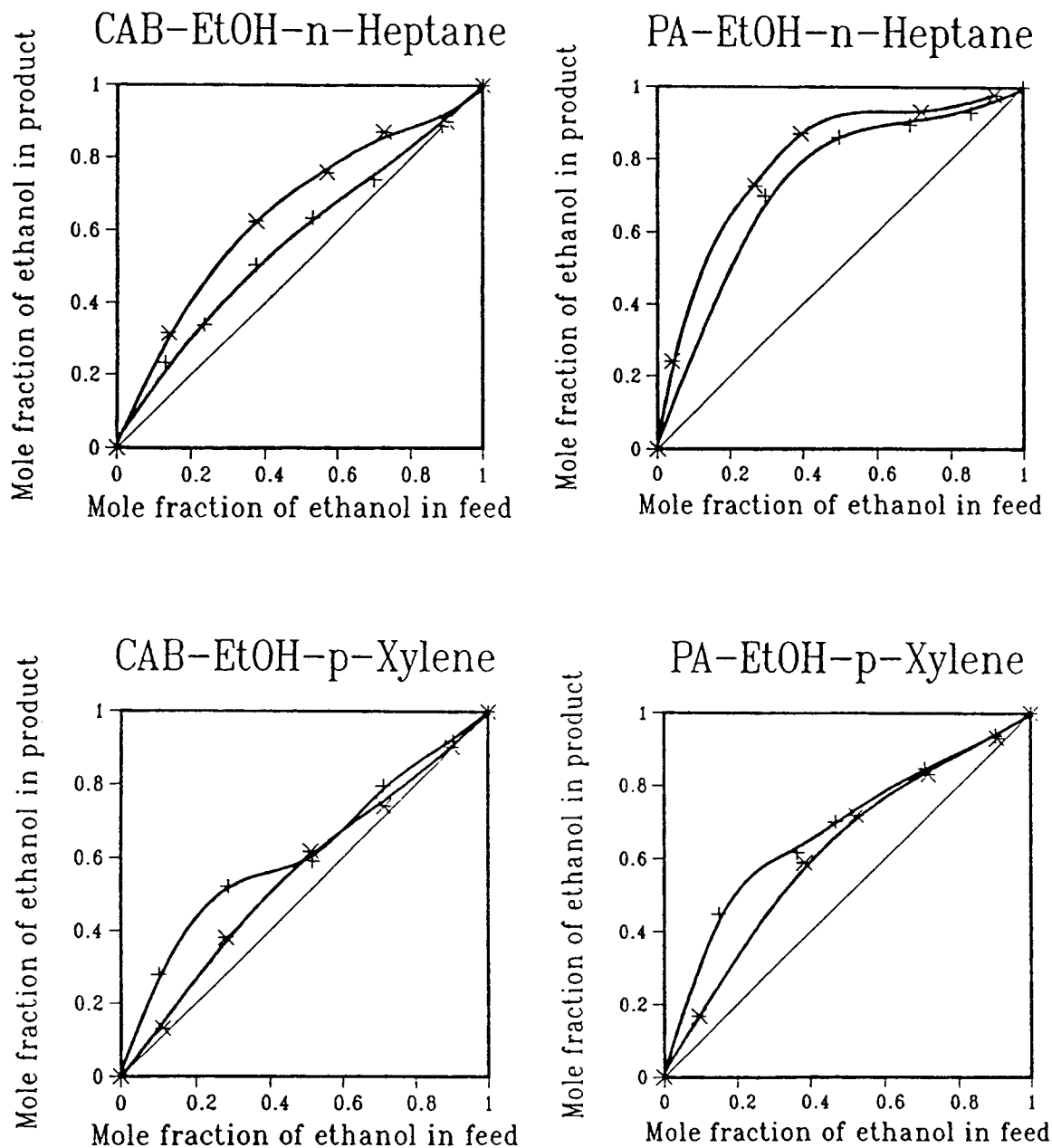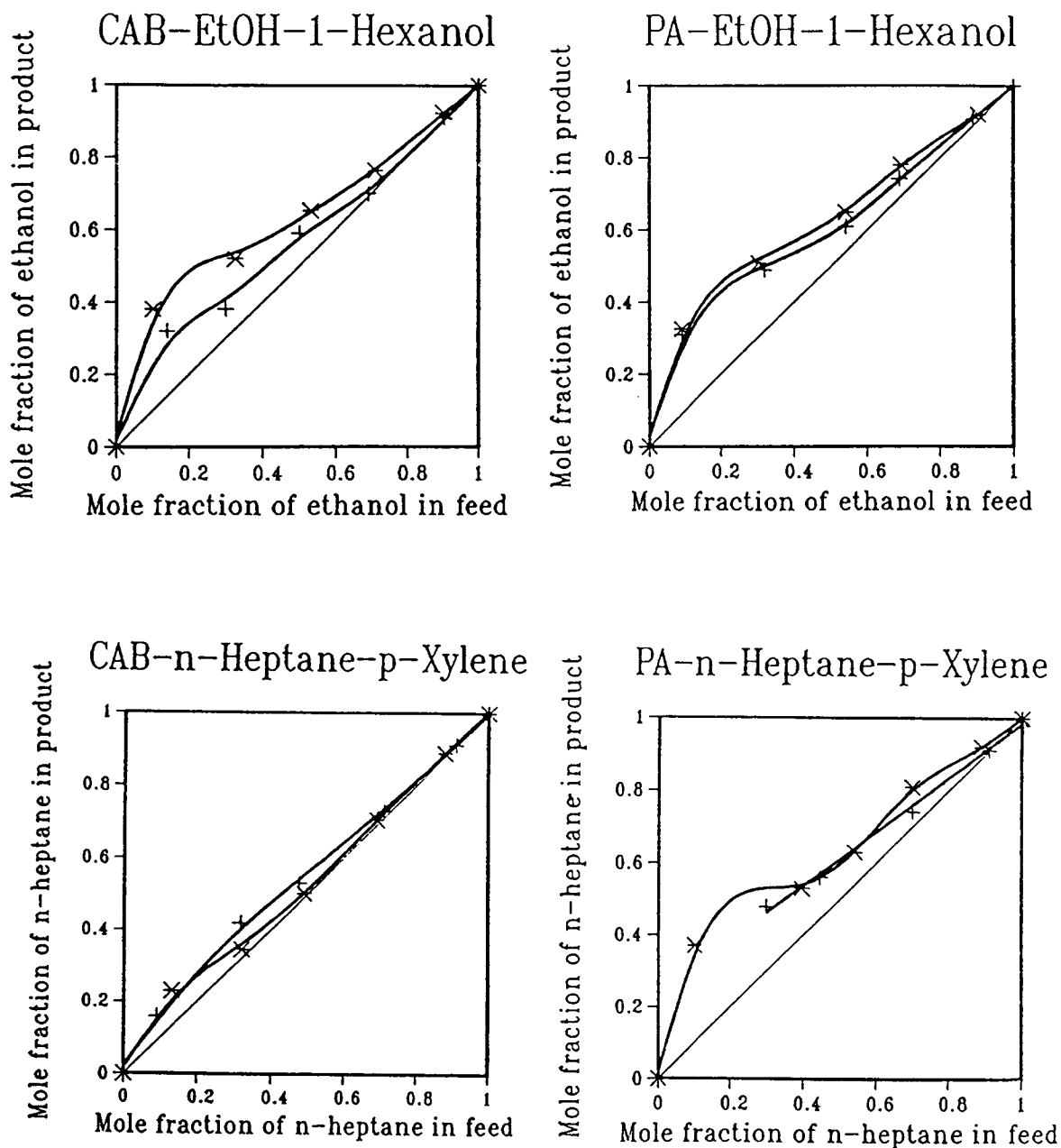
Figure 3 Reverse osmosis data for the separation of binary organic mixtures by cellulose acetate butyrate and aromatic polyamide membranes. Operating pressure: (+) 1724 kPa g (250 psig); (*) 3448 kPa g (500 psig); operating temperature, ambient; system, ethanol/ n-heptane and ethanol/p-xylene.

pressure on the separation of the binary mixtures falls into either one of the following categories:

1. The separation increases with an increase in the operating pressure. Examples are the separation of ethanol/n-heptane and ethanol/1-hexanol mixtures by both CAB and PA membranes.

2. The separation decreases with an increase in the operating pressure. The separation of ethanol/p-xylene mixtures is an example for both CAB and PA membranes.

3. The operating pressure exerts hardly any effect on the separation. The separation of n-heptane/p-xylene mixtures is an example for both CAB and PA membranes.

CAB-EtOH-1-Hexanol

PA-EtOH-1-Hexanol

CAB-n-Heptane-p-Xylene

PA-n-Heptane-p-Xylene

Figure 4   Reverse osmosis data for the separation of binary organic mixtures by cellulose acetate butyrate and aromatic polyamide membranes. Operating pressure: (+) 1724 kPa g (250 psig); (*) 3448 kPa g (500 psig); operating temperature, ambient; system, ethanol/ 1-hexanol and n-heptane/p-xylene.

Going back to Figure 5, where the preferential sorption–capillary flow model is schematically illustrated, when the flow of the interfacial fluid is intensified more than that of the bulk liquid by an increase in the operating pressure, the separation increases by an increase in the operating pressure. This corresponds to the first category of the experimental results. The opposite will be the case when

the flow of the interfacial fluid is less intensified. This corresponds to the second category. When both flows are equally intensified there is no effect of the operating pressure. This, of course, corresponds to the third category.

Effect of the Contact Time. Figure 7 shows the performance data of a CAB membrane for the separation of ethanol/n-heptane binary mixtures. Two
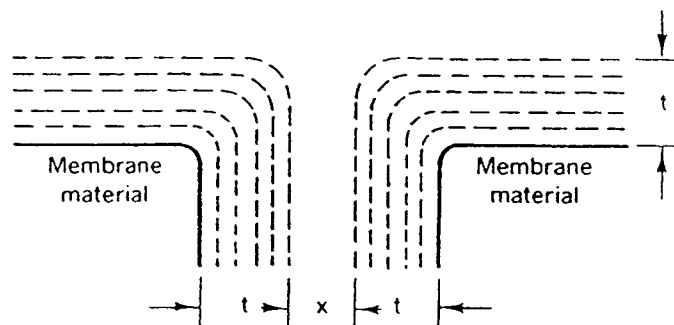
Figure 5   Schematic representation of preferential sorption capillary flow mechanism (from Sourirajan[8]).

experiments were carried out under the same operating conditions with a 30-day interval. The data shows that while the membrane permeation rate decreased, no significant change was observed for the separation data after 30 days of continuous contact of the membrane to the organic mixture. This suggests that the active skin layer of the membrane was almost unaffected whereas the structure of the porous sublayer collapsed during the contact period.

Effect of the Average Pore Size on the Membrane Surface. As mentioned earlier, the component whose (Stokes' radius/pore radius) ratio is smaller is more mobile in the membrane pore than the other component of the binary mixture. When the pore size is decreased, this tendency is intensified and the difference in mobilities of the smaller and the larger permeant molecule increases. As a consequence, the smaller molecule is more concentrated in the permeate. Figures 8 and 9 illustrate such an effect of the pore size on the membrane performance. In Figure 8 the separation data of ethanol/n-heptane by two PA membranes of different pore sizes are compared. Sodium chloride separation from the aqueous solution is given as a measure of the pore size of the membrane. The higher sodium chloride separation is considered to correspond to the smaller pore size. Of course, the membrane pore size may change when the feed solution is changed from aqueous system to nonaqueous system. However, it is assumed that the order in the pore size does not change even when the absolute pore size may change. Figure 8 indicates that the membrane of higher sodium chloride separation (smaller pore size) exhibits the higher concentration of ethanol in the permeate than the other membrane. Table I shows that the Stokes radius of ethanol is smaller than that of n-heptane; therefore, the expected result was obtained experimentally. Similarly, Figure 9 compares the

separation data for n-heptane/p-xylene binary mixtures by two CAB membranes of different pore sizes. In Figure 9 the concentration of n-heptane in the permeate decreased slightly with an increase in sodium chloride separation (decrease in the pore size). Looking into Table I, it is found that the Stokes radius of n-heptane is slightly larger than that of p-xylene. Therefore, this experimental result also confirms our theoretical prediction.

In Figure 10 the results for the separation of ethanol/n-heptane binary mixtures by CAB and PA membranes are compared. It is interesting to note that, although sodium chloride separation from water by CAB membrane is higher, the separation of the above binary mixture is higher for PA membrane. It is known that the rejective force exerted on sodium chloride solute in aqueous solution is stronger at the interface between water and cellulose acetate polymer than that at the interface between water and PA polymer. Therefore, the larger pore size on the surface of the cellulose acetate membrane may result in the higher sodium chloride separation. This is the reason why a cellulose acetate RO membrane can exhibit less separation of organic solutes in water than an aromatic polyamide RO membrane

Table I   Stokes' Law Radii for Various Binary Mixtures[a]

A–B	$r_{AB} \times 10^{10}$ (m)	$r_{BA} \times 10^{10}$ (m)
EtOH/1-hexanol	1.1	2.5
EtOH/p-xylene	1.1	2.3
n-Heptane/p-xylene	2.0	1.9
EtOH/n-heptane	1.1	2.5

[a] r_{AB} and r_{BA} = Stokes' radii of solute A in solvent B and solute B in solvent A, respectively.

Table II   Preferential Sorption Characteristics and the Relative Mobility of Binary Mixtures and the Resulting Membrane Separation Performance

A–B	Preferential Sorption	Component of Higher Mobility	Component to be Enriched in Permeate	Actual Enrichment
EtOH/1-hexanol	EtOH[a]	EtOH	EtOH	EtOH
EtOH/p-xylene	EtOH	EtOH	EtOH	EtOH
n-Heptane/p-xylene	Heptane	Equally mobile	Heptane	Heptane
EtOH/n-heptane	Heptane	EtOH	EtOH/heptane	EtOH

[a] For CAB material ethanol is preferentially sorbed; for PA material ethanol is preferentially sorbed when the ethanol mole fraction ranges from 0.63 to 1.0.

whose sodium chloride separation is lower than that of the cellulose acetate membrane. The same argument can apply to the separation of the binary organic mixtures. Though the sodium chloride separation of the CAB membrane is higher, the pore size of the CAB membrane is larger. Therefore, the CAB membrane pore can not separate ethanol/n-heptane mixtures as effectively as the PA membrane.

CONCLUSIONS

From the foregoing experimental results the following conclusions can be drawn:
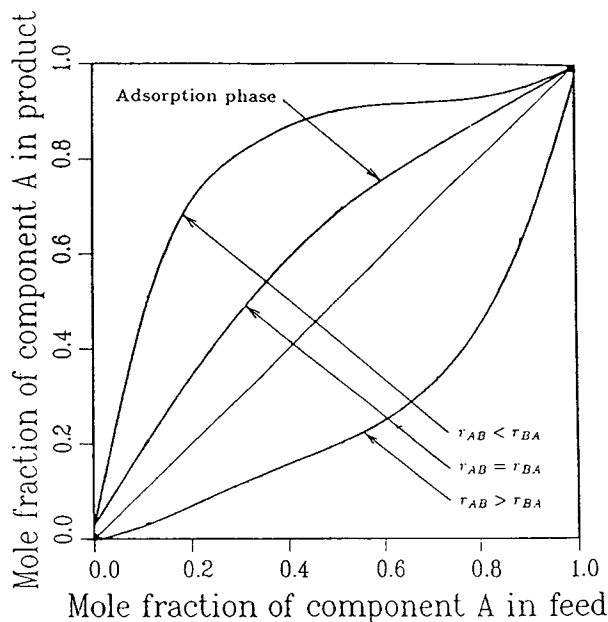

Figure 6   Composition in the adsorption phase and in the permeate.
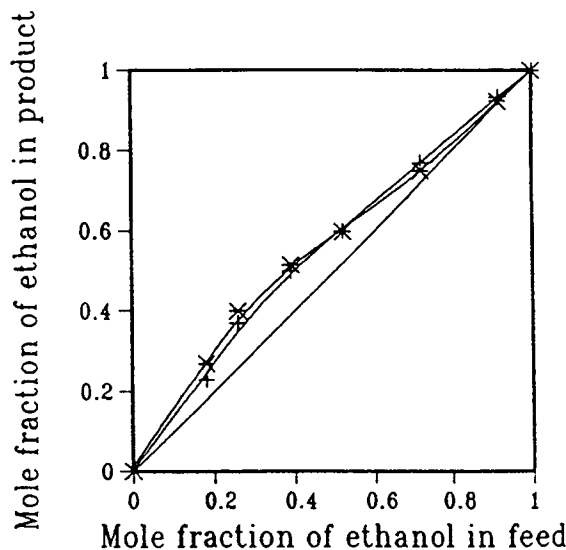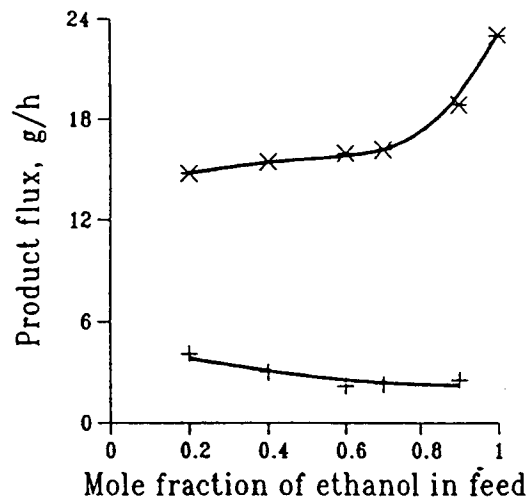

Figure 7   Experimental reverse osmosis results before and after the membrane contact with a ethanol/n-heptane mixture for 30 days. Membrane, cellulose acetate butyrate; operating pressure, 3448 kPa g (500 psig); operating temperature, ambient; (∗) before contact; (+) after contact.
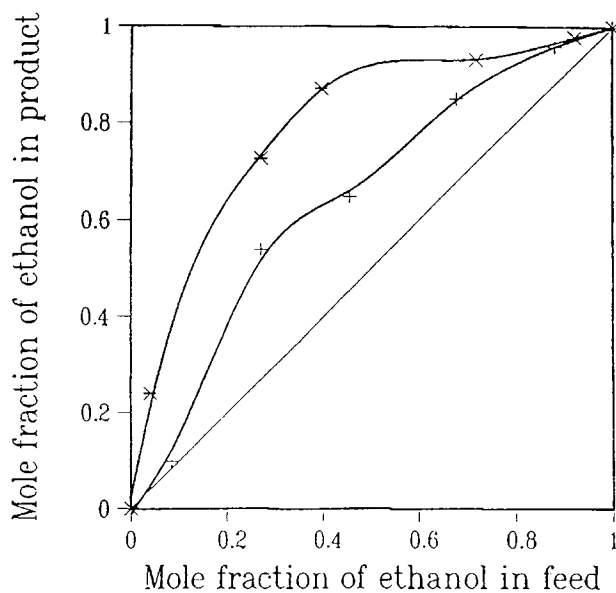
Figure 8   Experimental reverse osmosis results for the separation of ethanol/n-heptane mixtures by aromatic polyamide membranes of different pore sizes. Operating pressure, 3448 kPag (500 psig); operating temperature, ambient; (+) membrane with sodium chloride separation of 83.5%; (*) membrane with sodium chloride separation of 92.9%.
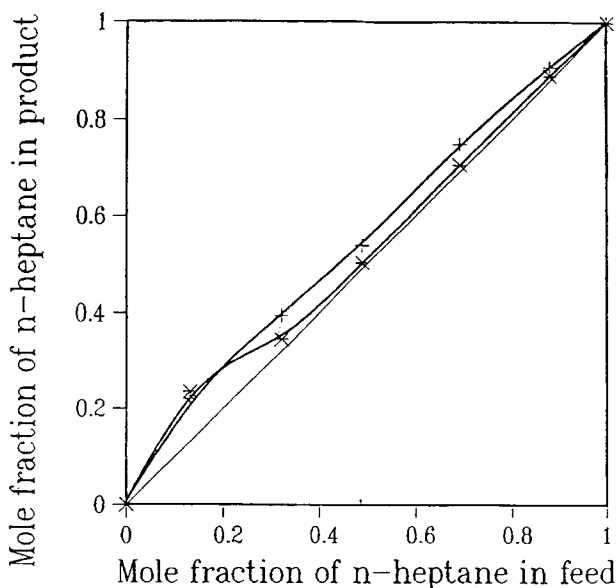

Figure 9   Experimental reverse osmosis results for the separation of n-heptane/p-xylene mixtures by cellulose acetate butyrate membranes of different pore sizes. Operating pressure, 3448 kPag (500 psig); operating temperature, ambient; (+) membrane with sodium chloride separation of 82.9%; (*) membrane with sodium chloride separation of 96.9%.
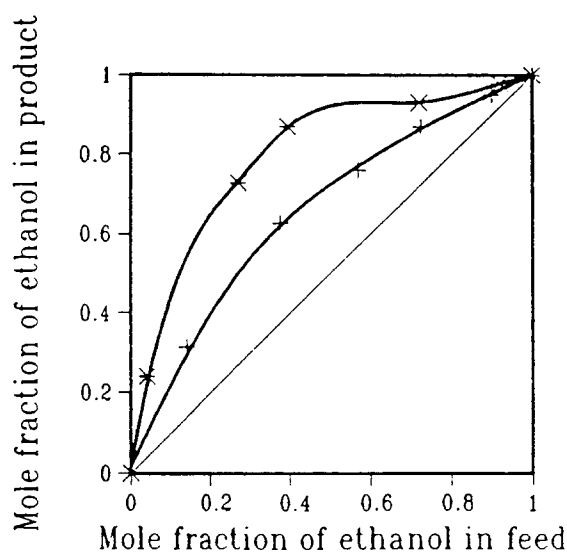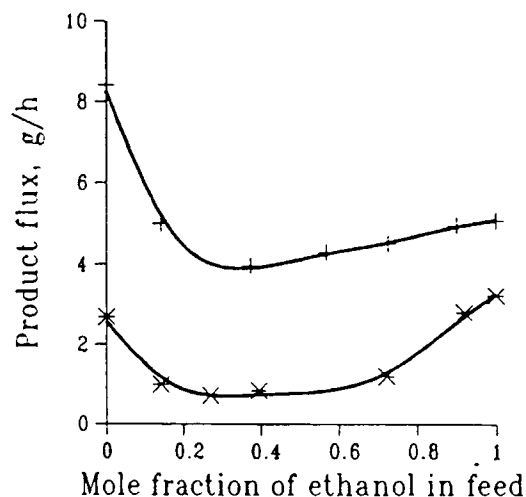

Figure 10   Experimental reverse osmosis results for the separation of ethanol/n-heptane mixtures by cellulose acetate butyrate and aromatic polyamide membranes. Operating pressure, 5172 kPag (750 psig); operating temperature, ambient; (+) cellulose acetate butyrate membrane with sodium chloride separation of 94.5%; (*) aromatic polyamide membrane with sodium chloride separation of 92.9%.

1. The separation of binary organic mixtures by reverse osmosis is possible by using polymeric membranes.
2. The preferential sorption between components involved in the binary organic mixture can be determined by the liquid chromatography technique.
3. The preferentially sorbed component tends to be enriched in the permeate.
4. The component of the smaller Stokes' radius tends to be enriched in the permeate.

5. The pressure effect on the membrane separation depends on whether the bulk flow or the interfacial flow is more intensified by an increase in the operating pressure.
6. The concentration of the permeant molecule with the smaller Stokes' radius increases in the permeate with a decrease in the pore size.

Most of the conclusions obtained by the computer simulation in the previous work have been, therefore, experimentally confirmed. However, some modifications are necessary. The third conclusion of the previous paper, that a decrease in the membrane pore size increases the membrane selectivity, is not always correct. This conclusion can be justified only when the mobility effect governs the membrane selectivity and the component of the smaller Stokes' radius is enriched in the permeate. When, on the other hand, the preferential sorption effect governs the membrane selectivity and the component of the larger Stokes' radius is enriched in the permeate due to strong preferential sorption, a decrease in the pore size decreases the membrane selectivity. Furthermore, the sixth conclusion in the previous paper stating that the operating pressure has little effect on the membrane selectivity is also not always correct. A modification in the computer program to include the pressure effect is called for.

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