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Pervaporation of aqueous ethanol solution through poly(amidesulfonamide)s (PASAs) membranes

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Symmetric non-porous membranes derived from five poly(amidesulfonamide)s were prepared for the separation of ethanol–water mixtures by the use of the pervaporation technique. It was found that water preferentially permeated through all PASA membranes in all ranges of feed compositions. The relationship between the polymer structure and its pervaporation performance will be discussed. The dependence of permeation rate on the feed composition was explained by the 'carrier-mediated' mechanism. The effect of temperature on the pervaporation characteristics of the materials was investigated in details. Experimental results revealed that the polymer based on the diamino monomer containing the piperazine moiety and isophthaloyl chloride emerged as the best system in terms of separation factor and permeation rate in the dehydration of ethanol. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(amidesulfonamide)s; pervaporation; dehydration of ethanol)

INTRODUCTION

Membrane technology represents one of the most effective and energy-saving applications to a wide range of separation processes, including ultrafiltration (UF), reverse osmosis (RO), gas separation and pervaporation (PV)[1]. In particular, pervaporation is an emerging membrane separation process which has been extensively studied for the selective separation of organic–aqueous and organic liquid systems from both an academic interest and possible industrial applications[2]. Because of practical demands, most applications of pervaporation to date have been concerned with the separation of binary mixtures of water and organic solvents, especially ethanol. Most publications of membrane separation of aqueous ethanol solution by pervaporation deal with separation by selective permeation of water by glassy polymeric membranes[3–10]. Although many functional polymeric membranes can achieve a separation factor of well above 500, the total flux of many materials is below $0.03\ \mathrm{g\ m^{-2}\ h^{-1}}$. These kinds of separation characteristics do not meet the stringent requirements amenable to industrial applications. However, a few publications report separation by selective permeation of ethanol[11–16], but the separation factors for these elastomeric membranes are usually less than 20. The necessity of finding new polymeric materials with improved pervaporation properties has been evident and continues to be the focus of intensive investigations.

In response to this research challenge, we have designed and synthesized a series of new poly(amidesulfonamide)s (PASAs)[17]. Subsequently, their suitability as new membrane materials for reverse osmosis applications have been explored and demonstrated[18]. Experimental findings revealed that this class of new membrane materials possesses several desirable membrane characteristics including high intrinsic viscosity able to fabricate tough membranes, high chemical stability resistant to many corrosive chemicals and hydrophilic properties favouring the permeation of water[19]. Furthermore, their general pervaporation characteristics toward aqueous alcoholic mixtures appears to be promising[20].

To upgrade the ethanol content of fermentation products and dehydrate azeotropic ethanol solutions, the pervaporation technique has been proved to be an economical and energy-saving alternative process. In this report, we describe our effort in using selected PASA materials for the preparation of pervaporation membranes intended for water–ethanol separation. The scope and limitation of using each of the PASA membranes in the prevaporation process for dehydration of ethanol solutions will be discussed.

EXPERIMENTAL

Materials

PASAs of a variety of structures were prepared by low temperature solution polycondensation of the respective diamino monomers (I_A–I_E) (*Figure 1*) with phthaloyl chlorides as reported elsewhere[17]. *N,N*-Dimethylacetamide (DMAc) was purchased from Fluka and dried over 4A prior to use. Absolute ethanol was obtained from Merck.

Membrane preparation

Depending on the intrinsic viscosity of each of the polymers, the respective casting solutions of various PASAs were prepared by dissolving an appropriate amount of the polymers in dried DMAc (*Table 1*). The solutions were cast onto a glass plate with an applicator (casting thickness 0.315 mm) and the solvent was allowed to evaporate at 70°C for 30 min to give non-porous symmetric membranes with a thickness of about 20 μm. The membranes could be stored in a dry atmmosphere when not in use.

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Pervaporation experiments

Permeation of water–ethanol mixtures through PASA membranes was carried out as described previously[20]. The membrane area in contact with liquid was 3.32×10^{-3} m^2. The down stream pressure was maintained at 0.5 torr Hg by a vacuum pump (Edwards). The permeate sample collected in the first hour was discarded while that collected in the subsequent 4 h was kept in a cold-trap cooled with liquid nitrogen. Pervaporation experiments on different membranes were performed at different feed compositions and/or temperature ranging from 20 to 60°C.

The flux of each run was determined by weighing the permeate sample collected during the four hour period. The permeation flux J was obtained from

$$J = \frac{Q}{A \times h} \tag{1}$$

where Q is the total amount (g) of permeate sample collected over a time of h hour, and A (m^2) is the effective surface area of the membrane.

The separation factor α was calculated by determining the composition of the feed liquid mixtures and the permeates. The composition analysis was carried out on a Shimadzu GC-8A gas chromatograph equipped with a 1 m-long column packed with Hayesep DB, using a thermal conducting detector. The separation factor is defined by

$$\alpha = \frac{Y_{\mathrm{water}}/Y_{\mathrm{ethanol}}}{X_{\mathrm{water}}/X_{\mathrm{ethanol}}} \tag{2}$$

where Y_i is the weight fraction of the component i in the permeate and X_i is that in the feed.

Estimation of solubility parameter

The solubility parameters (δ_{sp}) which are made up of dispersion forces (δ_d), dipole forces (δ_p), and hydrogen bonding (δ_h), were calculated for each membrane[21]. The space distance between ethanol and membrane (DEM) and that between water and membrane (DWM) are defined by equation (3) and equation (4) with the following values: $\delta_{d,E} = 15.82$, $\delta_{p,E} = 8.80$, and $\delta_{h,E} = 19.44$ J$^{1/2}$ cm$^{-3/2}$ for ethanol[22]; and $\delta_{d,W} = 19.52$, $\delta_{p,W} = 17.84$, $\delta_{h,W} = 17.64$ J$^{1/2}$ cm$^{-3/2}$ for water[23].

$$\mathrm{DEM} = [(\delta_d - \delta_{d,E})^2 + (\delta_p - \delta_{p,E})^2 + (\delta_h - \delta_{h,E})^2]^{1/2} \tag{3}$$

$$\mathrm{DWM} = [(\delta_d - \delta_{d,W})^2 + (\delta_p - \delta_{p,W})^2 + (\delta_h - \delta_{h,W})^2]^{1/2} \tag{4}$$

$$\delta = \mathrm{DWM}/\mathrm{DEM} \tag{5}$$

RESULTS AND DISCUSSION

Solubility parameters of PASA materials

It has been recognized that the membrane permeation is governed by both the chemical nature of the materials and the physical structure of the membrane. To develop new materials for membrane application, molecular architecture in relation to the optimization of membrane performance should be considered at the onset of the investigation. Furthermore, if pervaporation application of membrane is pursued, by using the prevalent solution-diffusion model, the flux and the separation factor of a component in a binary system through a membrane are functions of the solubility and diffusivity of the component. Bearing these factors in mind, new membrane materials selection can be achieved by exploring their differences in either solubility or diffusivity. For quantitative characterization of the new materials in terms of solubility, solubility parameter can be employed. In this connection, based on the known values of water and ethanol, the space distance between water and a particular PASA (DWM) and that between ethanol and the membrane (DEM) may also be evaluated. Results of such calculations for five different PASAs are compiled in

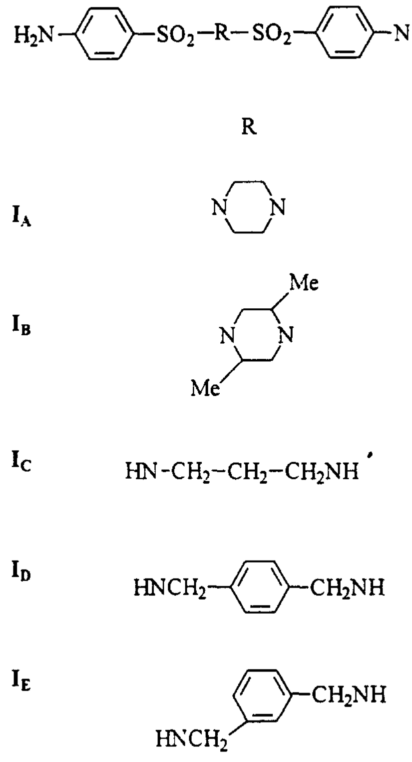

Figure 1 Structure of the diamino monomer I_A–I_E

Table 1 Formulation of various PASA casting solutions and results of carbonyl absorption measurements of PASA membranes by FT-IR

Polymer	Diaminomonomer	Diacidchloride used	$[\eta]_{\mathrm{intrinsic}}$(dl g^{-1})[a]	Concentration of casting solutions (wt%)	$\nu_{c=0}$/cm^{-1}
II_{AM}	I_A	isophthaloyl	0.85	12.0	1681.1
II_{BM}	I_B	isophthaloyl	0.69 or 0.85	12.0	1681.6
II_{CM}	I_C	isophthaloyl	1.36	11.5	1666.8
II_{DM}	I_D	isophthaloyl	0.85	14.0	1667.1
II_{EM}	I_E	isophthaloyl	0.75	17.0	1669.9

[a] Viscosity in DMAc solution at 25.00 ± 0.05°C.

Table 2 Solubility parameter of PASA membranes, water, ethanol and value of DWMs and DEMs

Membranematerials/permeate	δ_{sp}/J $^{1/2}$cm $^{-3/2}$	DWMJ $^{1/2}$cm $^{-3/2}$	DEMJ $^{1/2}$cm $^{-3/2}$	Δ
II_{AM}	31.588	25.168	12.018	2.094
II_{BM}	30.181	25.628	10.954	2.340
II_{CM}	31.165	25.299	11.470	2.206
II_{DM},II_{EM}	30.745	26.242	11.736	2.236
Water	46.594	–	–	–
Ethanol	26.522	–	–	–

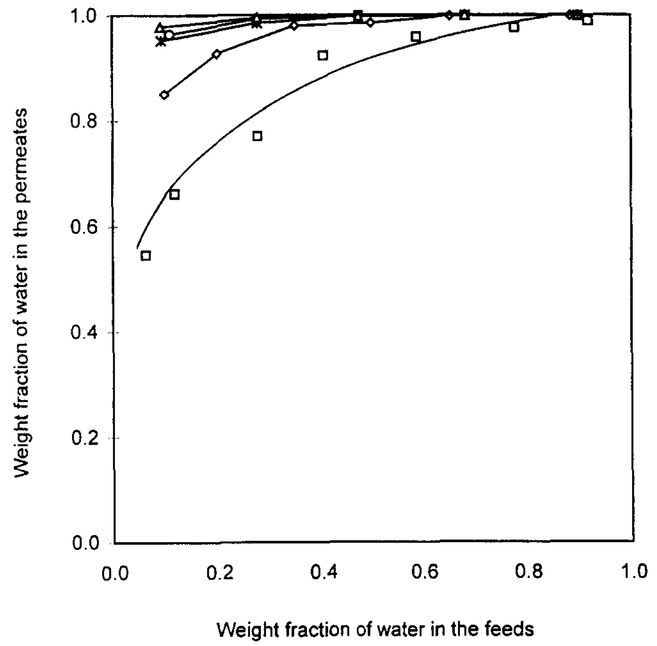

Figure 2 Effect of feed composition on the separation of water–ethanol pervaporation through membranes: II_{AM}, ◇; II_{BM}, □; II_{CM}, *; II_{DM}, °; and II_{EM}, Δ, at 20°C

Table 2. Qualitatively speaking, the solubility of water and ethanol in a membrane increases as its respective DWM or DEM value decreases. In this regard, all five PASA materials listed are hydrophobic in nature because they possess a smaller DEM value in comparison with the corresponding DWM value. Incidentally, the results of solubility parameter calculation for this series of materials are in accord with the swelling experiments [20]. For indexing purpose, the Δ value of each PASA was calculated (the last row of *Table 2*). This ratio indicated that in a relative sense, among five polymers, polymer II_{AM} is the most hydrophilic whereas II_{BM} is the most hydrophobic. This observation helps us to interpret the pervaporation performance of the polymers (see below).

Separation of water–ethanol mixtures by pervaporation through PASA membranes

Using our specially designed pervaporation device, various PASA membranes were fabricated and employed for the separation of water–ethanol mixtures of different compositions. *Figure 2* shows that all five PASA materials under the studied conditions are preferentially water-permeable membranes; the water content in the permeates was very much enhanced as compared with the feeds, irrespective of their composition. In particular, polymers II_{CM}, II_{DM} and II_{EM} exhibited a tremendous water preference in the separation process. Despite the fact that all PASAs are 'hydrophobic' based on the solubility parameter calculation and the swelling experiments, they are in fact water-permselective membrane materials in pervaporation applications. In accord with observations associated with pervaporation performance of many other glassy polymers[24], the pervaporation process of this type of materials is diffusion-controlled. Furthermore, polymers II_{CM}, II_{DM} and II_{EM} were found to possess a fairly high degree of crystallinity as revealed by the XRD studies. In comparison with the water molecule, the diffusivity of larger molecules like ethanol is hampered through the microcrystallinity domain of the polymer matrix, resulting in a much smaller ethanol flux rate and a high separation factor in favour of water permeation. In contrast, II_{AM} and II_{BM}, to a less extent, possess a larger free volume allowing ethanol molecule to diffuse more freely through the polymers. Apparently, with regards to pervaporation performances, II_{AM} and II_{BM} should be classified as one group while the other three fall in another group. Most of our subsequent discussion will be based on this grouping.

To fully assess the pervaporation properties of the materials, the total flux rate and separation factor of each of the PASA membranes were evaluated by using different feed solutions. *Figure 3a* and *b* show the effect of feed composition on the flux and separation factor of five PASA materials. As revealed by these figures, the difference in the total flux rate between this two classes of PASAs is fairly obvious. For a wide variety of feed solutions, the total flux of polymers II_{CM}, II_{DM} and II_{EM} is smaller than that of II_{AM} and II_{BM} by almost an order of magnitude, whereas the separation characteristics of the former materials appear to be generally superior to that of the latter. By comparing the structure difference of polymers II_{AM} and II_{BM}, the additional two methyl groups in the piperazine ring of II_{BM} renders it more flexible and diminishes its discriminating power towards water and ethanol molecules. As indicated in *Figure 3a*, the values of α through membrane II_{AM} tend to remain initially constant at around 70 with the weight fraction of water in the feed below 0.5, then to increase abruptly to a value of 1300 when the weight fraction of water was 0.9. In comparison, the dependence of values through membrane II_{BM} on the feed composition was less dramatic, with α values averaging at around 15. It is noteworthy to point out that the relatively poor separation factor demonstrated by membrane II_{BM} in contrast to II_{AM} may be partly attributed to its low viscosity in the polymer preparation. Nevertheless, if practical use for dehydration of ethanol is intended, polymers II_{AM} and II_{BM} definitely lend their potential for further investigation because they both demonstrated a good balance of reasonable flux rate and separation characteristics. The extremely low permeability of II_{CM}, II_{DM} and II_{EM}, with less than 10 g m^{-2} h^{-1}, precludes them from any practical application in pervaporation processes (*Figure 3b*).

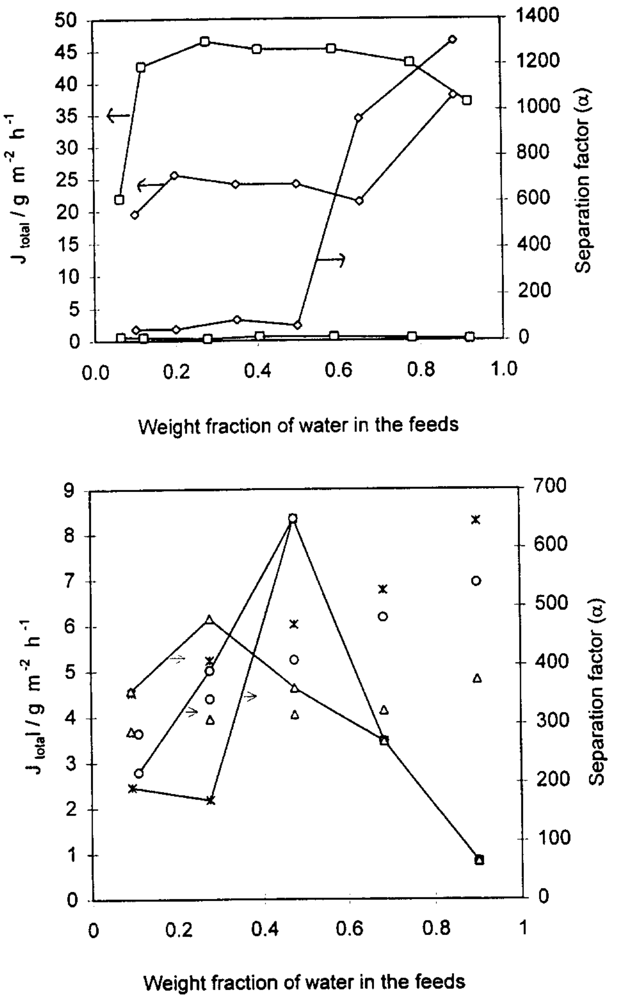

Figure 3 Effect of feed compositon on total flux (J_{total}) and separation factor (α) of the permeates in the pervaporation separation of water–ethanol through membranes: a: II_{AM}, ◇; II_{BM}, □; b: II_{CM}, ; II_{DM}, ○; and II_{EM}, △

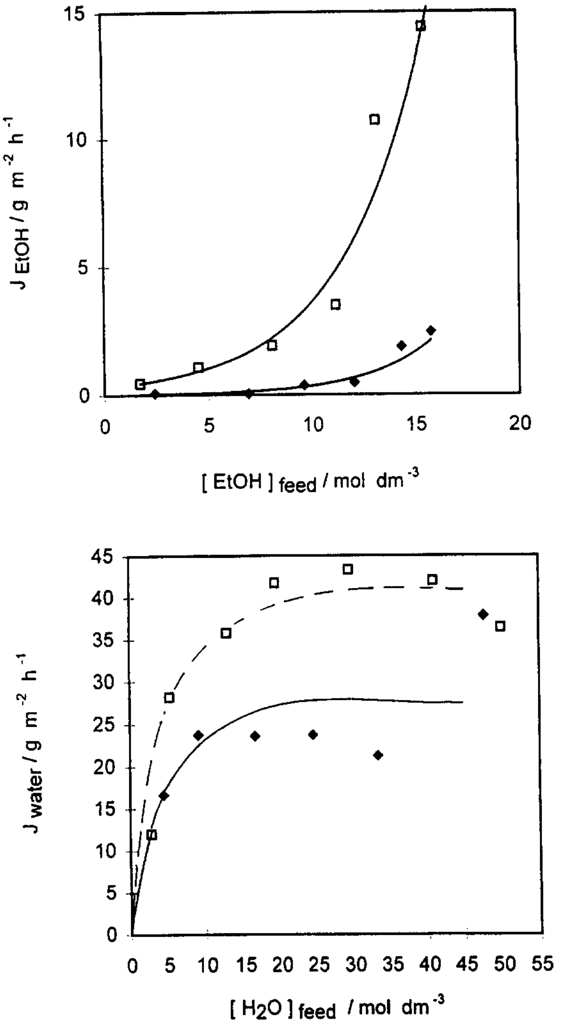

Figure 4 Effect of (a) ethanol and (b) water concentrations on their respective flux in ethanol–water pervaporation through membranes: II_{AM}, ◆; and II_{BM}, □

Permeation mechanism through PASA membranes in the pervaporation process

To examine the permeation mechanism of the present polymeric materials, we separated the observed fluxes into their respective ethanol and water components, so that the flux of each component could be plotted against its feed concentration (*Figure 4* and *Figure 5*). These results clearly show that II_{AM} and II_{BM} follow one type of permeation mechanism, whereas II_{CM}, II_{DM} and II_{EM} follow another. In this context, for II_{AM} and II_{BM}, the relationship between ethanol flux and ethanol concentration in the feed shown in *Figure 4a* reveals an exponential profile. Both show an abrupt increase in ethanol flux at around 12 mol dm^{-3} of ethanol concentration. In agreement with the solubility parameter calculation, II_{BM} having the greatest solubility in ethanol possesses the highest ethanol flux among all PASAs. The exponential relationship demonstrated between the flux and concentration of a permeate is typically for cases of substantially swollen materials[25]. For these two materials, the dependence of water flux on the water concentration in the feed exhibits a typical Michaelis–Menten-type profile (*Figure 4b*). As the water concentration in the feed increases, the water flux through membranes II_{AM} and II_{BM} approaches an asymptotic limit at 25 and 40 g m^{-2} h^{-1}, respectively. These findings support a carrier-mediated mechanism for water permeation through these membranes.

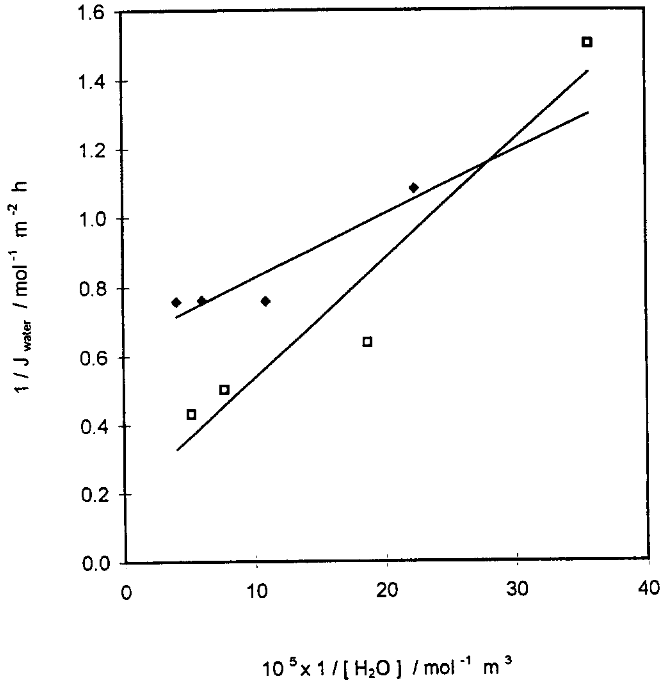

Figure 5 Relationship between reciprocal of water flux and reciprocal of water concentration through membranes: II_{AM}, ◆; II_{BM}, □

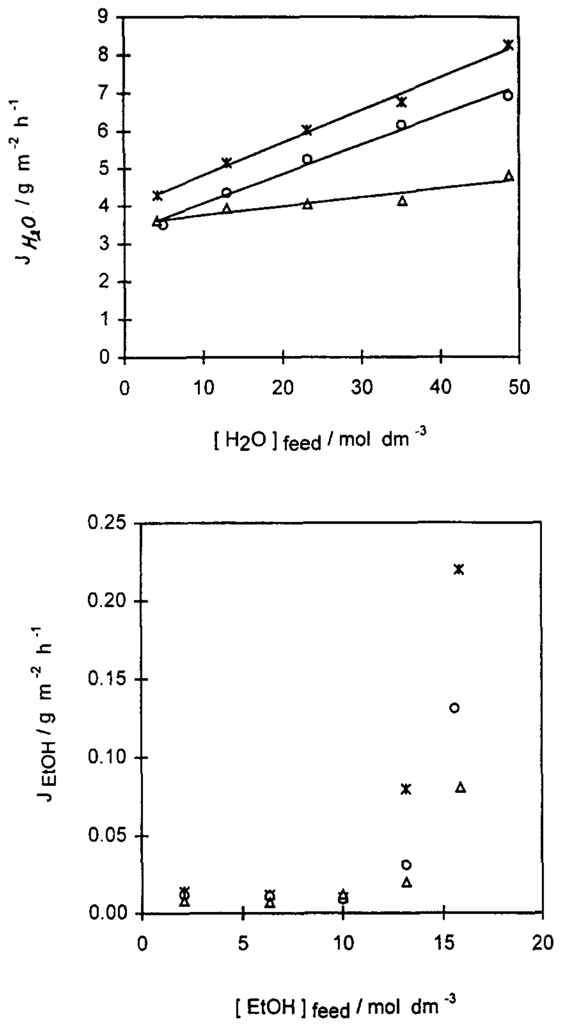

Figure 6 Effect of (a) water and (b) ethanol concentrations on their respective flux in water–ethanol pervaporation through membranes: II_{CM}, *; II_{DM}, °; II_{EM}, △

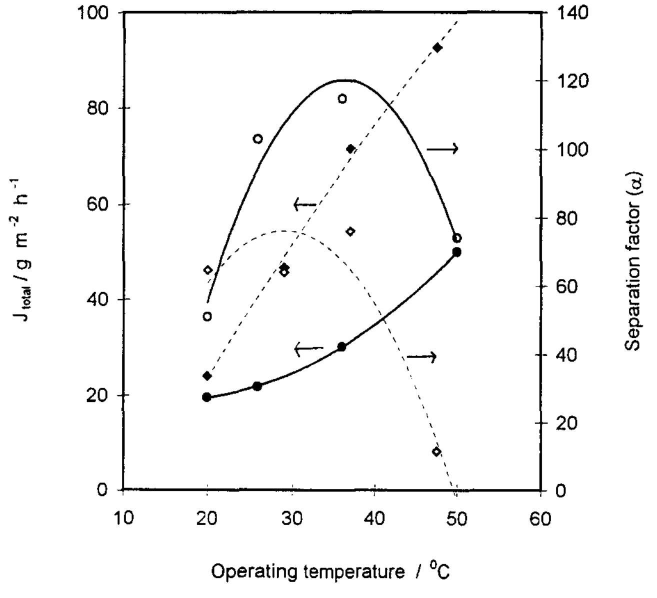

Figure 7 Effect of operation temperature on water–ethanol permeation through membrane II_{AM} (– – –, weight fraction of water in feed is 0.50; and ———, weight fraction of water in feed is 0.90)

In this particular case, the presence of amide groups in the polymer backbones interacting with water molecules through hydrogen bonds serve as fix-carriers. The water flux noted in *Figure 4b* may be represented by the following equation

$$J = \frac{DK[C]_0[H_2O]_{feed}}{L \times \{1 + K[H_2O]_{feed}\}} \qquad (6)$$

In the above equation, K is the complex formation constant between the amide group (the fix carrier) and water (the permeate); D is the diffusion coefficient in the membrane for water; L is the membrane thickness; $[C]_0$ denotes the carrier concentration in the membrane, and $[H_2O]_{feed}$ is the water concentration in the feed. Taking the reciprocal of equation (6) gives

$$\frac{1}{J} = \frac{L}{DK[C]_0}\,\frac{1}{[H_2O]_{feed}} + \frac{L}{D[C]_0} \qquad (7)$$

Values of the constants in equation (7) may be estimated by plotting $1/J$ versus $1/[H_2O]_{feed}$ (*Figure 5* Lineweaver–Burk plot), using the data shown in *Figure 4b*. Thus, two straight lines with linearity (r) 0.9239 and 0.8743 were obtained for membranes II_{AM} and II_{BM}, respectively. The K values for membranes II_{AM} and II_{BM} were found to be 3.48×10^{-4} and 5.52×10^{-5} mol^{-1} m^{3}, respectively, calculated from the slope and intercept of the two straight lines. Since the solubility parameter calculations revealed that II_{AM} is more hydrophilic than II_{BM}, the estimated complex formation constants between the membrane and water confirms that a stronger complex can be formed between water and II_{AM} than that with II_{BM}.

Using similar plots, the dependence of water and ethanol flux through membranes II_{CM}, II_{DM} and II_{EM} on the concentration of the corresponding component in the feed can be demonstrated (*Figure 6*). Regarding the permeation of water, the correlation is a straight line (*Figure 6a*), which implies that water permeated without any specific interaction with any of the membranes. Presumably, the relatively compact nature of the polymeric chains of these materials in contrast to II_{AM} and II_{BM} favours intermolecular hydrogen bond formation via the amide carbonyl group and an adjacent –NH– group which, in turn, excludes its accessibility to interact with penetrated water molecules. The IR spectroscopic studies support this hypothesis (last column, *Table 1*). The IR stretching bands of the amide carbonyl of II_{CM}, II_{DM} and II_{EM} are of lower energy than that of II_{AM} and II_{BM}, indicating that the presence of hydrogen bonds in the first three materials substantially weakens the strength of the carbonyl group. Thus, a red shift of almost 10 cm^{-1} was observed between these two class of polymers. Furthermore, due to the lack of specific interaction between water and the membranes II_{CM}, II_{DM} and II_{EM}, the permeation of water can in no way be facilitated. With these closely packed polymeric matrices, the permeation of a larger ethanol molecule through these membranes was almost completely retarded (*Figure 6*b).

Effect of evaluation temperature

It is well established that the selectivity and the flux are affected by the operating temperature. Accordingly, the effect of the operating temperature on the permeation through the membrane II_{AM} was investigated under the conditions that the weight fraction of ethanol was fixed at around 0.9 or 0.5. The effect of temperature was assessed

Table 3 Activation energy of permeation by pervaporation obtained from the Arrhenius plots

Membrane materials	Weight fraction of ethanol in the feeds	Activation energy ΔE_{water}/kJ mol^{-1}	Activation energy $\Delta E_{\text{ethanol}}$/kJ mol^{-1}
II_{AM}	0.9	+ 28.9	+ 28.9
	0.5	+ 38.5	+ 78.2
II_{BM}	0.9	+ 18.4	+ 19.7
II_{CM}	0.5	+ 28.9	+ 28.5
II_{DM}	0.5	+ 36.8	+ 49.0
II_{EM}	0.5	+ 31.8	+ 34.3

Table 4 Comparison of water–ethanol separation of PASA II_{AM} with other hydrophilic membranes in pervaporation

Membrane materials	Wt.fraction of ethanol in the feed	Temp./°C	α	J/g m^{-2}h^{-1}	PSI/g m^{-2}h^{-1}	Refs.
Poly(acrylic acid-co-acrylonitrile)	0.815	10	900	10	900	3
N,*N*-Dimethylamino-ethyl methacrylate-grafted-pp	0.90	40	6.8	1000	6800	5
Polyion complex	0.95	50	3320	1230	4×10^6	6
Modified polysulphone	0.90	25	63.8	8.37	534	7
Derivatized PPO	0.90	25	3.3	110	363	8
4-Vinylpyrindine-homo-grafted-poly-carbonate	0.90	25	6300	153	9.6×10^5	9
PASA II_{AM}	0.90	20	51	19.6	1000	This work
	0.90	36	115	30.1	3462	
	0.50	20	65	24	1560	
	0.50	37	76	72	5472	

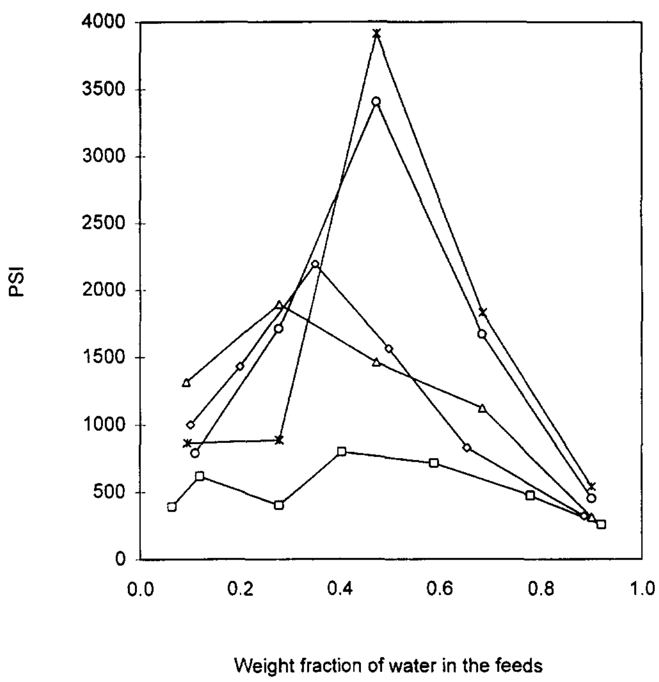

Figure 8 Effect of feed composition on PSI in the separation of water-ethanol mixtures at 20°C through membranes: II_{AM}, ◇; II_{BM}, □; II_{CM}, *; II_{DM}, ○ and II_{EM}, △

by separation experiments carried out at around 20, 30, 40 and 50°C. *Figure 7* summarizes the dependence of membrane selectivity and total flux on the operating temperature at two different feed solutions. About a 4-fold and 2-fold increase in the total flux was observed for 50% and 90% aqueous ethanol solution, respectively, as the temperature changed from 20 to 50°C. However the values of the separation factors in these two feed solutions reached a maxima at around 40°C. In other words, both selectivities toward water and the total flux of II_{AM} appeared to decrease on lowering the operating temperature. Such results are consistent with the fact that a fairly strong interaction of membrane II_{AM} hindered the migration of water among carriers from upstream to downstream. It was found that the temperature dependence of the flux rate of each component of aqueous ethanol feed solutions can be expressed by Arrhenius-type relationships. These relationships were confirmed by Arrhenius plots. The activation energies of permeation for water and ethanol in the binary mixtures were calculated (*Table 3*) and ranged from 18.4 to 78.2 kJ mol^{-1}. In most of the systems studies, the flux rates of the permeate increased by a factor of about 1.5 for every 10 degree increment in temperature.

Overall evaluation of PASAs as membrane materials for pervaporation process

Since the separation ability of a membrane can be expressed in terms of the flux rate and separation factor which usually operate in opposite senses, the pervaporation separation index (PSI) defined as the product of a separation factor and a flux rate was widely used as a measure of the separation ability of a membrane. With the exception of II_{BM}, all other membrane materials studied exhibited PSI values well above 1000 over feed solutions with different composition (*Figure 8*). Furthermore, a maximum value of PSI emerged from each material when the weight fraction of water was around 0.3 to 0.5. In order to make a sensible assessment of the potential of using PASAs as membrane materials for pervaporation applications in the dehydration of ethanol, the performance of II_{AM}, a representative of this class of materials, together with that of selected materials in the recent literature, are shown in *Table 4*. Considering the ready availability and the highly chemically resistant properties of PASA membranes, the pervaporation characteristics demonstrated by PASAs in this study have certainly proved their potential for further investigation. Efforts to further enhance the permeability of the materials by improving the membrane technology are underway.

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