Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Dagaonkar, M. V. , Sawant, S. B. , Joshi, J. B. and Pangarkar, V. G.(1998) 'Sorption and Permeation of Aqueous Alkyl Piperazines through Hydrophilic and Organophilic Membranes: A Transport Analysis', Separation Science and Technology, 33: 3, 311 — 331

To link to this Article: DOI: 10.1080/01496399808544771

URL: http://dx.doi.org/10.1080/01496399808544771

SEPARATION SCIENCE AND TECHNOLOGY, 33(3), pp. 311–331, 1998

Sorption and Permeation of Aqueous Alkyl Piperazines through Hydrophilic and Organophilic Membranes: A Transport Analysis

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ABSTRACT

A detailed analysis of separation of *N*-methyl piperazine (NMP), *N*-ethyl piperazine (NEP), and water was undertaken by the pervaporation technique. A systematic study of sorption and permeation of the aqueous alkyl piperazines through poly(dimethylsiloxane) (PDMS), styrene-butadiene rubber (SBR), PDMS filled with zeolites NaX and silicalite (SA-5), polyimide (PI), and poly(acrylonitrile-*co*-acrylic acid) (PAN-*co*-AA) was carried out at different concentrations and temperatures. Organophilic membranes showed higher selectivity toward alkyl piperazines during sorption, but permeation was in favor of water. Hydrophilic membranes, however, showed higher affinity toward water during both sorption and permeation. PI membrane showed higher selectivity for water than PAN-*co*-AA. A model was used to estimate the diffusion coefficients of the various permeants. It was found that the transport selectivity for water in organophilic membranes was due to high diffusion selectivity (for water) although sorption selectivity favored the piperazines.

Key Words. Sorption; Permeation; Poly(dimethylsiloxane); Styrene-butadiene rubber; NaX; Silicalite; Polyimide; Poly(acrylonitrile-*co*-acrylic acid); Pervaporation

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INTRODUCTION

Membrane pervaporation is becoming an effective process tool for the separation of liquid mixtures. Due to its favorable economics and simplicity, it can be easily integrated into distillation and rectification processes and can even replace them (1).

Many organic corrosive liquids such as acids and bases are hydrated due to their manufacturing processes or become hydrated during their use. Pervaporation (PV) can be used to separate these mixtures provided that efficient membranes with good resistance to these liquid media are available (2). Membrane material is selected in such a way that it exhibits very high sorption for the component that has to be removed.

In this study the separation characteristics of NMP–water and NEP–water mixtures by means of various hydrophilic and organophilic membranes are discussed. At temperature above 15°C the piperazines tend to cake and darken. Exposure to atmosphere causes caking and discoloration. The piperazine containers should remain properly closed until they are needed. Hence the piperazines are termed heat sensitive, and they pose difficulty in separation by distillation which is carried out at higher temperatures (3). Alkyl piperazines are basic and are soluble in water in all proportions. They are used as intermediates in the pharmaceutical industries. Thus, PV is an alternative to separate such mixtures. There are two ways to separate them: 1) by using hydrophilic membranes to remove water and 2) by using organophilic membranes for removal of the alkyl piperazines. The type of membrane to be employed will depend upon the type of component to be removed. In order to look into these aspects, both types of membranes were used in the present study. The various organophilic membranes used were poly(dimethylsiloxane) (PDMS), styrene-butadiene rubber (SBR), and PDMS filled with zeolites NaX and silicalite SA-5. The hydrophilic membranes used were polyimide (PI) and poly(acrylonitrile-*co*-acrylic acid) (PAN-*co*-AA). Apart from the flux and selectivity studies, this work was extended to examine the diffusion coefficients of the various penetrants for both systems.

THEORY

Transport through dense (nonporous) homogenous membranes is usually described by a solution-diffusion model (4). According to this model, each component of the mixture dissolves into the membrane and diffuses through the membrane because of a driving force. This driving force is the gradient of the chemical potential across the membrane. The assumptions in the model are as follows:

In multicomponent permeation it is very difficult to predict the transport properties because of the coupling phenomena during separation, both in solution and in the diffusion process. The interaction parameters have to be incorporated in the equation. A number of empirical equations have been proposed to explain the permeation of binary mixtures (5–8). Among these, the model proposed by Rautenbach et al. (8), which considers the effect of both components in a binary mixture on each other, is more realistic and hence is used here. According to this model the diffusivities are given by

$$D_i = D_{i0} \exp(w_{i_M} + A_{ij} w_{j_M}) \tag{8}$$

$$D_j = D_{j0} \exp(w_{j_M} + A_{ji} w_{i_M}) \tag{9}$$

Substituting Eq. (8) into Eq. (7) and integrating over the entire membrane thickness:

$$\int_0^L J_i dx = -\rho_M D_{i0} \int_{w_{i_M}}^{w_{ip}} \exp(w_{i_M} + A_{ij} w_{j_M})\, dw_{i_M} \tag{10}$$

The downstream solvent volume fraction w_{ip} can be assumed to be close to zero for a very low downstream pressure, and thus Eq. (10) reduces to

$$J_i = \frac{\rho_M D_{i0}}{L} [\exp(w_{i_M} + A_{ij} w_{j_M}) - 1] \tag{11}$$

Similarly, for Component j,

$$J_j = \frac{\rho_M D_{j0}}{L} [\exp(w_{j_M} + A_{ji} w_{i_M}) - 1] \tag{12}$$

For hydrophilic membranes the plasticization process, which is responsible for the coupling effect, can be restricted to the water component (i) only due to the strong interaction between polymer and water. Thus the constant A_{ij} of Eq. (11) is neglected. Hence

$$J_i = \frac{\rho_M D_{i0}}{L} [\exp(w_{i_M}) - 1] \tag{13}$$

EXPERIMENTAL

Materials

Silicone rubber (RTV 2/VP 7660) was kindly supplied by Wacker Chemie, Germany. Zeolite NaX was supplied by M/s ACC, Mumbai, India. Silicalite SA-5 was a gift of UOP. Polyimide sheet was supplied by

ABR Organics Limited, Hyderabad, India. SBR sample was supplied by Gujarath Apar Polymers Limited, Ankleshwar, India. AR grade acrylonitrile (AN), acrylic acid (AA), sodium hydroxide, calcium chloride, ammonium persulfate, sodium bisulfide, sodium lauryl sulfate (SLS), sodium bicarbonate, toluene, ethyl acetate, and dimethylformamide (DMF) were used in the synthesis of PAN-*co*-AA. NMP and NEP were kindly supplied by Catapharma Chemicals Pvt. Limited, Nashik, India.

Membrane Preparation

Silicone rubber and crosslinker were mixed in a 9:1 proportion using isooctane as the solvent and then spread over a Perspex sheet with a doctors knife. The resulting membrane was kept overnight at room temperature and then cured at 80°C for 24 hours. The SBR membrane was also prepared by the solution casting technique. A 2% solution of SBR was prepared using hexane as the solvent. Tetratex (porous polytetrafluroethylene film), kindly supplied by Tetratec Corporation, USA, was used as a supporting material. The Tetratex film was dipped in methanol for 2 hours and subsequently dipped in water for 2 hours. This water-soaked film was then spread on a glass plate, and the SBR solution was uniformly spread over it with a doctors knife. The polymer film was allowed to dry overnight and then annealed at 50°C for 2 hours. Filled PDMS membranes were prepared by adding the respective fillers (NaX and Silicalite SA-5) to the polymer solution and then spreading it on a Perspex sheet with a doctors knife. The curing period and temperature were the same as those employed for the unfilled PDMS membrane.

The PI, supplied in the form of a sheet, was cut to the required size and used as such. Acrylonitrile (AN) was washed with sodium hydroxide and then with distilled water to remove the alkali traces. It was then kept over fused $CaCl_2$ overnight and distilled under vacuum before use. AA was also distilled under vacuum. Copolymerization of AN with AA in a 5:1 ratio was carried out in a four-necked reactor at 70°C for 6 hours (9). The reactor was fitted with a stirrer, thermometer, condenser, and N_2 inlet tube. Water was used as a dispersing agent and SLS as an emulsifier. The pH was adjusted by the addition of sodium bicarbonate. Ammonium persulfate and sodium bisulfide (0.5 and 0.25% of the total monomer weight) were used as a pair of redox initiator. The emulsion was precipitated after polymerization and washed with water, toluene, and ethyl acetate to remove unreacted monomer and emulsifier. The purified copolymer was then dried at 45°C for 6 hours in a vacuum drier. The PAN-*co*-AA thus prepared was then dissolved in DMF solution in a definite proportion, and the homogeneous solution was then cast on a glass plate.

This was dried at 60°C for 5 hours and then immersed in a water bath for 2 hours to separate the membrane from the glass plate.

Sorption Studies

Membranes of known weight and thickness were immersed in aqueous solutions of alkyl piperazine of different known concentrations. These films were allowed to equilibrate for 72 hours at constant temperature. The films were then removed and weighed after the superfluous liquid was wiped off with tissue papers. Any increase in membrane weight is due to sorption of both alkyl piperazine and water. In order to determine the amount of water sorbed, a Karl Fischer titration was performed. The amount of alkyl piperazine sorbed was deduced from the material balance. Sorption studies were performed at 30, 40, and 50°C.

Permeation Studies

The equipment and procedures used to conduct the PV experiments were identical to those used by Netke et al. (10). The effective membrane area in contact with the liquid was 38 cm^2. The vacuum employed during the experiments was 1 mmHg. All experiments were of 1 hour duration. The permeate samples were analyzed on a Bausch and Lomb Refractometer. The permeation studies for both systems were performed with all the aforementioned membranes over the entire concentration range at 30, 40, and 50°C.

RESULTS AND DISCUSSION

Hydrophilic Membranes

Sorption Studies

Figure 1 shows the sorption plot of water, NMP, and NEP for both the membranes at 30°C. It is evident that the membranes exhibit preferential sorption of water over the whole composition range. The sorbed NMP and NEP concentrations are practically independent of the feed concentration for both the membranes and are much lower than the sorbed water concentration, implying that the membranes employed yield high sorption selectivity with respect to water.

Water sorption in the present case belongs to the Type II category as described by Rogers (11), which is a combination of the Type II category at lower concentrations and the Type III category at higher concentrations. At low water concentration there is a preference for the formation of a polymer–penetrant pair. Thus, sorption initially occurs on some specific

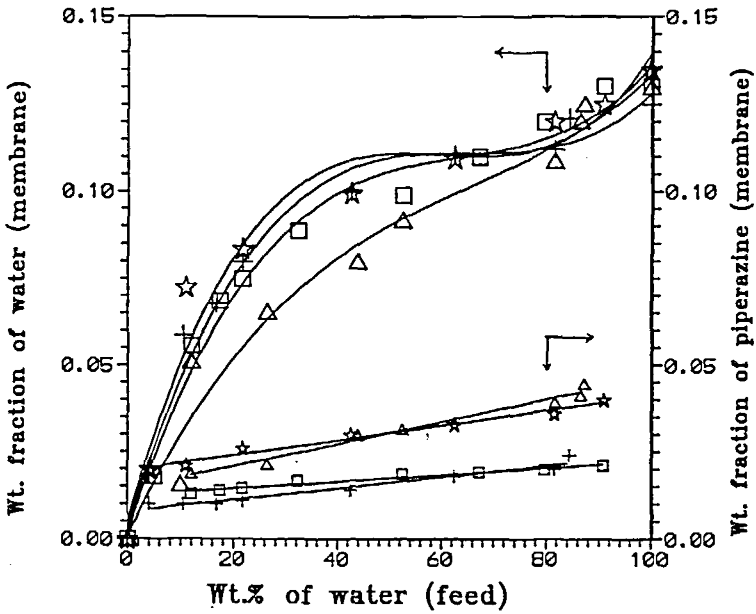

FIG. 1 Sorption plot at 30°C. (□) PI:aq. NEP, (△) PAN-*co*-AA:aq. NMP, (☆) PI:aq. NMP, (+) PAN-*co*-AA:aq. NEP.

(hydrophilic) sites of the polymer. After exhaustion of such sites (at higher water concentration) a small amount of solute dissolves in the polymer in a randomly distributed manner. At high concentrations, due to the preference for solute–solute pairs, the sorbed water concentration increases steadily.

At higher temperatures the amount of water sorbed decreases, implying a negative enthalpy of sorption.

Permeation

Figures 2 and 3 show the pervaporation characteristics of alkyl piperazine at 30°C. VLE data for both systems are also plotted to compare PV and distillation. The separation factor for both the membranes is greater than 1, indicating their selectivity for water over the entire concentration range. The permeate concentration was almost independent of the feed temperature for both systems.

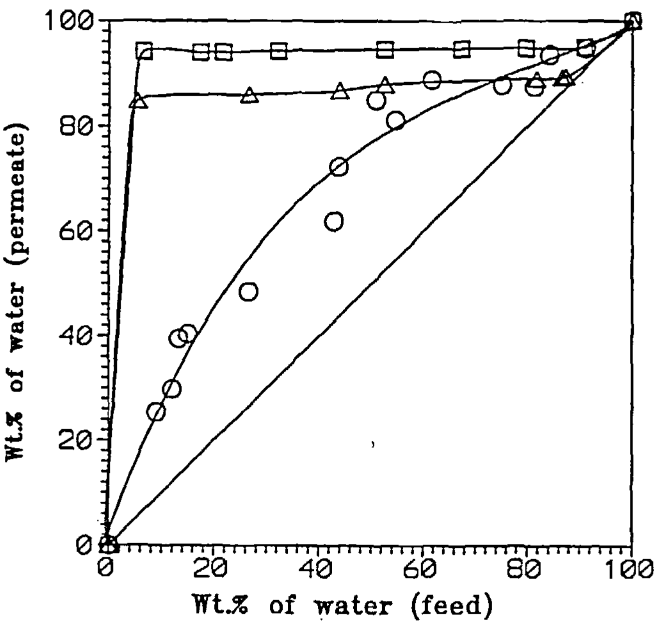

FIG. 2 Permeation characteristics of NMP–water system at 30°C: (□) PI, (△) PAN-*co*-AA, (○) VLE.

Figure 4 shows that initially up to 40 wt% there is a steep increase in the water flux with feed water concentration and then the flux levels off. At low water concentration the small fluxes measured are due to poor swelling of the membrane. For the higher concentrations, however, due to the increasing plasticization of the polymer, there is an increase in the water flux. Figure 5 shows the effect of feed temperature on water flux for PI/NMP–water. Feed temperature has a significant effect on water flux. The higher the operating temperature, the more significant is the permeation enhancement. The increase in water flux with the temperature is due to the increase in the diffusivity of water, which in turn is due to the increase in the segmental mobility of the polymer chains with temperature. Similar results were obtained for the other membrane and for the NEP–water system.

It was observed that the selectivity with respect to water initially falls rapidly with an increase in the feed concentration and then gradually levels off at higher concentration. Selectivity as high as 402 (PI, 6.6 wt% water)

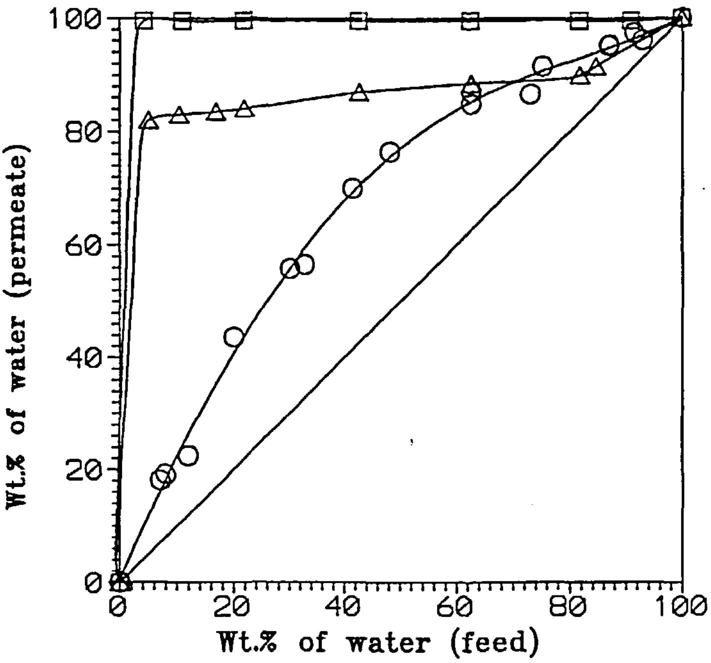

FIG. 3 Permeation characteristics of NEP–water system at 30°C: (□) PI, (△) PAN-*co*-AA, (○) VLE.

and 97 (PAN-*co*-AA, 5.4 wt% water) was obtained at 30°C for the NMP–water system. For the NEP–water system the highest selectivity obtained was 4539 (PI, 4.2 wt% water) and 36 (PAN-*co*-AA, 10.4 wt% water). The selectivity for water was found to be almost constant in the temperature range studied for both membranes and for both systems. It was observed that the selectivity of PI for water was higher and the corresponding flux was lower than that of PAN-*co*-AA for both systems. This is due to the dense structure of the membrane and the absence of any hydrophilic and carboxyl group, which would yield lower water flux and higher selectivity.

Diffusion

The activation energy for permeation (ΔE_p) at various feed concentrations can be obtained from the corresponding ln(flux) versus ($1/T$) plots. Similarly, the heat of solution (ΔH_s) at various concentrations is obtained

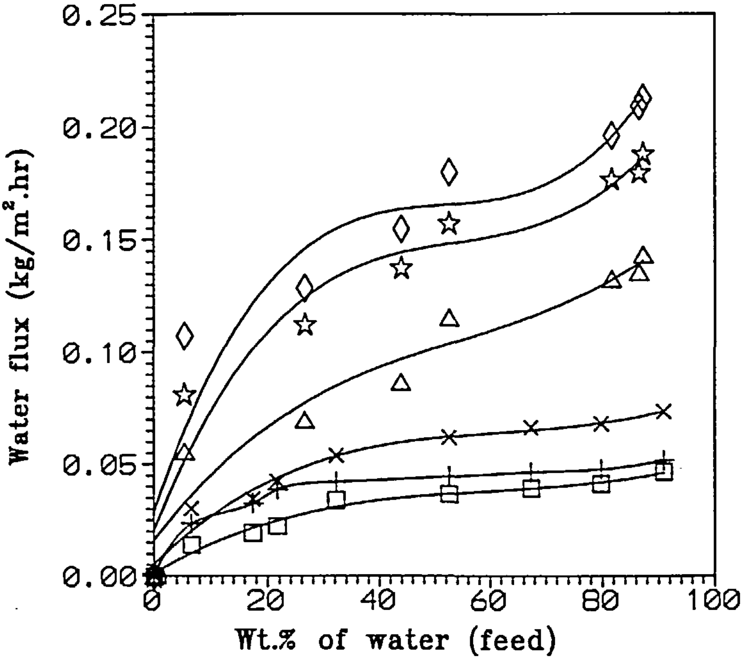

FIG. 4 Variation of water flux with concentration and temperature (system: –NMP–water). (Δ) PAN-*co*-AA, 30°C; (☆) PAN-*co*-AA, 40°C; (◇) PAN-*co*-AA, 50°C; (□) PI, 30°C; (+) PI, 40°C; (×) PI, 50°C.

from ln(S) versus ($1/T$) plots, where S is the equilibrium weight fraction of water in the membrane. The activation energy for diffusion (ΔE_d) is calculated from Eq. (6). Tables 1 and 2 give the values of ΔE_p, ΔH_s, and ΔE_d for a particular feed concentration for NMP–water and NEP–water systems. It was found that ΔE_p and ΔE_d decrease with an increase in the feed concentration due to the increasing plasticization of the polymer. This plasticization yields increased flexibility of the polymer chains, thereby facilitating diffusion of the solute molecules.

Model Comparison

The diffusion coefficient through a membrane at infinite dilution for a particular temperature was obtained by plotting water flux versus water concentration in the membrane phase as shown in Fig. 5. Diffusion coeffi-

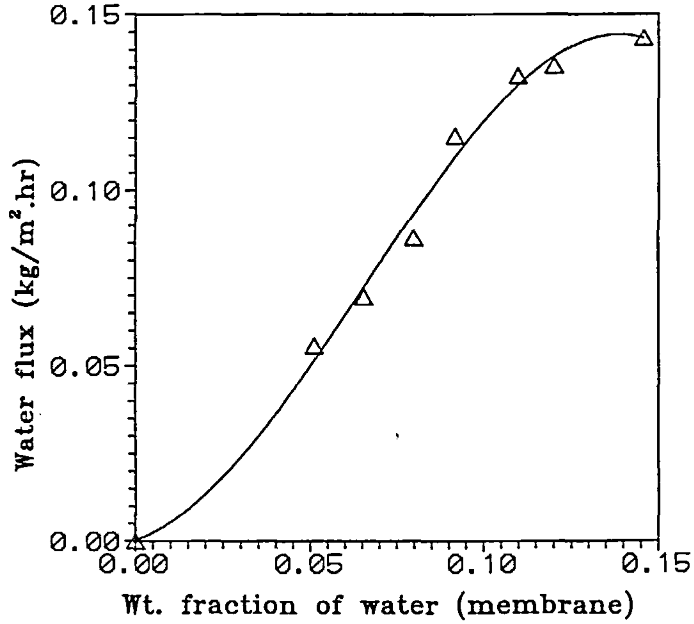

FIG. 5 Variation of water flux at 30°C with weight fraction of water in membrane phase. (Δ) PAN-*co*-AA.

cients at different feed concentrations and temperatures were calculated from Eqs. (8) and (9). The same procedure was repeated to determine the diffusion coefficients of NMP and NEP in both membranes. The values of model parameters and diffusion coefficient at infinite dilution for water, NMP, and NEP for different conditions are listed in Tables 3 and 4. The

TABLE 1
Activation Energy of Permeation, Heat of Sorption, and Activation Energy of Diffusion of Water for NMP–Water System

Membrane	Feed water concentration (wt%)	ΔE_p (kJ/mol)	ΔH_s (kJ/mol)	ΔE_d (kJ/mol)
Polyimide	6.6	20.59	−6.691	27.28
Poly(acrylonitrile-*co*-acrylic acid)	5.4	13.09	−6.566	19.66

TABLE 2
Activation Energy of Permeation, Heat of Sorption, and Activation Energy of Diffusion of Water for NEP–Water System

Membrane	Feed water concentration (wt%)	ΔE_p (kJ/mol)	ΔH_s (kJ/mol)	ΔE_d (kJ/mol)
Polyimide	6.6	20.7	−6.691	27.39
Poly(acrylonitrile-*co*-acrylic acid)	10.4	11.26	−6.189	17.45

TABLE 3
Model Parameters for NMP–Water System

Membrane	Temperature (°C)	$\rho_M D_{i0}/L$ (kg/m²·s)	$\rho_M D_{j0}/L \times 10^5$ (kg/m²·s)	$D_{i0} \times 10^{11}$ (m²/s) (water)	$D_{j0} \times 10^{12}$ (m²/s) (NMP)	A_{ji}
Polyimide	30	0.00011	0.24	0.77	0.16	2
	40	0.00014	0.37	0.94	0.24	2
	50	0.00022	0.39	1.48	0.26	0.9
Poly(acrylonitrile-*co*-acrylic acid)	30	0.00025	1.3	2.1	1.1	1
	40	0.00034	1.35	2.8	1.25	0.9
	50	0.00037	1.5	3.1	1.27	1

TABLE 4
Model Parameters for NEP–Water System

Membrane	Temperature (°C)	$\rho_M D_{i0}/L$ (kg/m²·s)	$\rho_M D_{j0}/L \times 10^5$ (kg/m²·s)	$D_{i0} \times 10^{11}$ (m²/s) (water)	$D_{j0} \times 10^{12}$ (m²/s) (NEP)	A_{ji}
Polyimide	30	0.00026	0.098	1.68	0.066	1
	40	0.00029	0.14	1.95	0.098	1.6
	50	0.00031	0.26	2.08	0.175	1.4
Poly(acrylonitrile-*co*-acrylic acid)	30	0.00035	1.1	2.96	0.703	2.5
	40	0.00039	1.2	3.3	0.98	2
	50	0.00045	3	3.8	2	1

diffusion coefficient of NEP at infinite dilution is less than that of NMP, probably because of its bulkier structure. Also, the diffusion coefficient of water molecules in the NEP–water system was found to be higher than that in the NMP–water system, probably due to more retarding action of NMP than of NEP. It is clear that in this case the diffusivity of water is much higher than the diffusivity of alkyl piperazines. Further, as indicated earlier under sorption measurements, sorption selectivity also favors water. Therefore, a combination of high sorption and diffusion selectivities results in high overall permeation selectivity (12). The coupling parameter A_{ji} was estimated from the data and was found to be greater than zero for all cases, indicating that membrane plasticization was solely due to water. The water fluxes were calculated using Eq. (13). These were found to be in good agreement with the experimental fluxes obtained in the PV experiments. Regression analysis was carried out to analyze the data fit. The regression coefficients obtained were in the 0.96 to 0.98 range. A

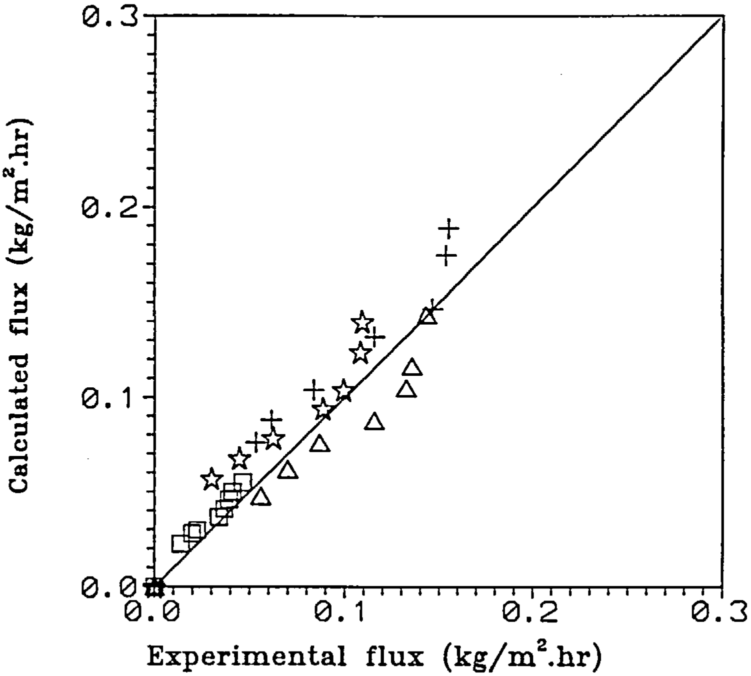

FIG. 6 Parity plot for water flux at 30°C (system: –NMP–water). (□) PI, aq. NMP; (△) PAN-*co*-AA, aq. NMP; (☆) PI, aq. NEP; (+) PAN-*co*-AA, aq. NEP.

parity plot showing the comparison of experimental water flux and calculated water flux for both membranes at 30°C for the systems is shown in Fig. 6.

Organophilic Membranes

Sorption

Figures 7 and 8 indicate the sorption plots of NMP, NEP, and water for all membranes at 30°C. All membranes exhibit preferential sorption of alkyl piperazines over the whole composition range. The sorbed water concentration is approximately constant and is much lower than the sorbed alkyl piperazines concentration, indicating that the membranes yield high sorption selectivity with respect to alkyl piperazines. Filled PDMS membranes showed higher sorption of the piperazines than the unfilled PDMS. This is due to the higher affinity of the fillers for the piperazines.

Sorption of alkyl piperazines in the present case belongs to the Type IV category (11), which is a combination of the Type II isotherm at lower

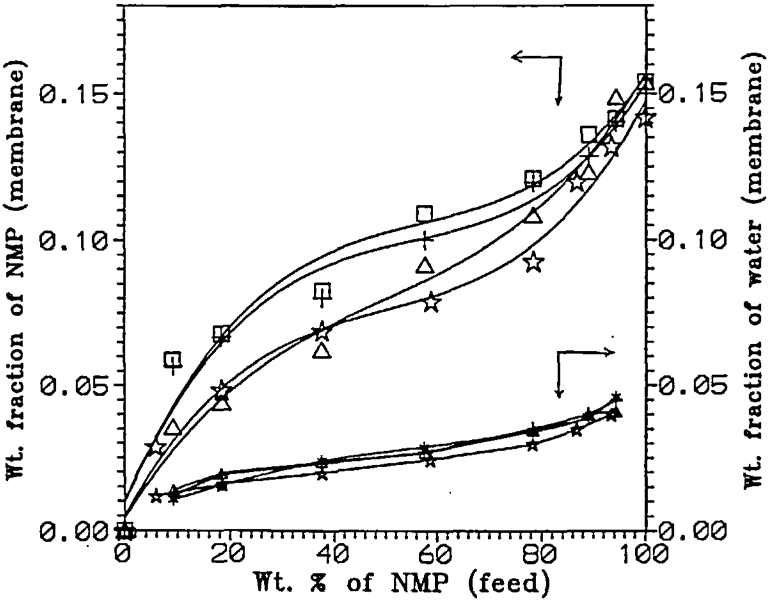

FIG. 7 Sorption plot at 30°C (system: –NMP–water). (△) PDMS, (☆) SBR, (+) PDMS + 40% NaX, (□) PDMS + 40% silicalite.

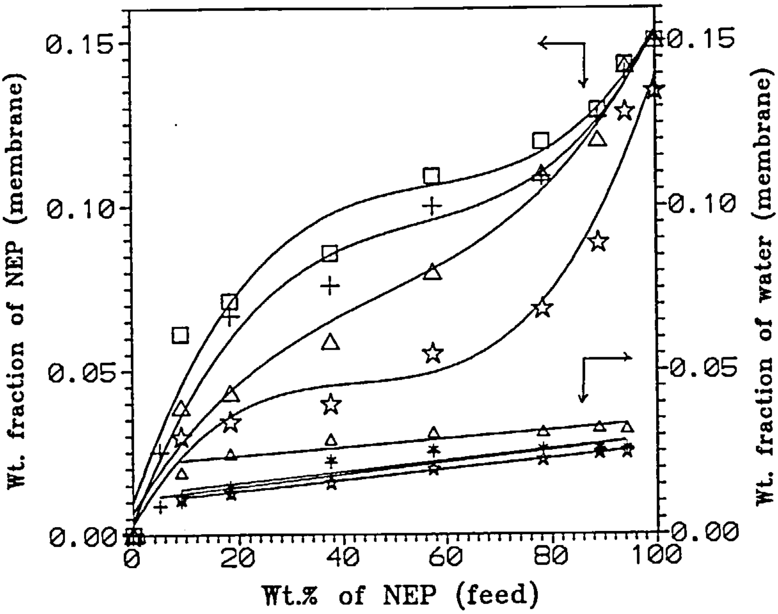

FIG. 8 Sorption plot at 30°C (system: –NEP–water). (Δ) PDMS, (☆) SBR, (+) PDMS + 40% NaX, (□) PDMS + 40% silicalite.

alkyl piperazine concentration and the Type III at higher concentration as mentioned earlier. At lower concentration there is a preference for the formation of the polymer–penetrant pair. Thus, sorption initially occurs on some specific (organophilic) sites of the polymer. After exhaustion of such sites, a small amount of solute dissolves in the polymer in a randomly distributed manner. At higher concentrations, due to the preference for solute–solute pairs, the sorbed concentration of the alkyl piperazine increases steadily.

The effect of temperature on liquid sorption was similar to that of water sorption in hydrophilic membranes.

Permeation

Figures 9 and 10 show the permeation characteristics of the aqueous alkyl piperazines at 30°C. PV selectivity is a combination of sorption selectivity and diffusion selectivity. When both the selectivities favor a particular component, a very high overall selectivity for that component is ob-

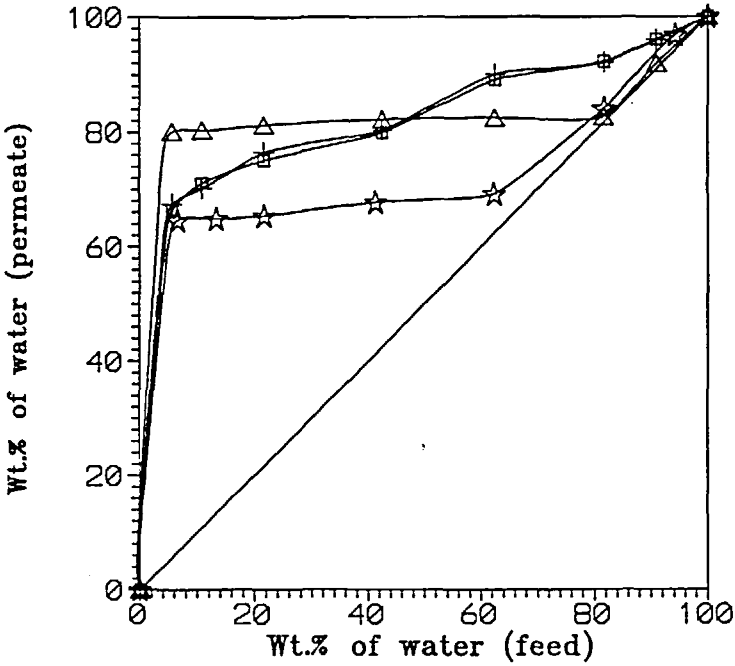

FIG. 9 Permeation characteristics of NMP–water system at 30°C. (△) PDMS, (☆) SBR, (+) PDMS + 40% NaX, (□) PDMS + 40% silicalite.

tained (12). The amount of NMP and NEP obtained in the permeate was consistently lower than that in the feed for the whole range of feed concentration, even though there was a rise in the permeate concentration with the feed. This indicates that PV selectivity favors water over alkyl piperazines. Thus, although our sorption study favored alkyl piperazines, the overall pervaporation selectivity did not. This may be due to a very high diffusion selectivity for water which overcame the sorption selectivity for the alkyl piperazines and thus yielded a higher overall PV selectivity for water. Filled PDMS membranes showed more separation of the alkyl piperazines than unfilled PDMS membranes. The permeate composition was found to be almost independent of the feed temperature.

The variation in the flux of alkyl piperazines with feed concentration was different for the plain (unfilled) and the filled membranes. The plain membranes showed a continuous rise in flux with increasing alkyl piperazine concentration. On the other hand, the flux in the filled membrane

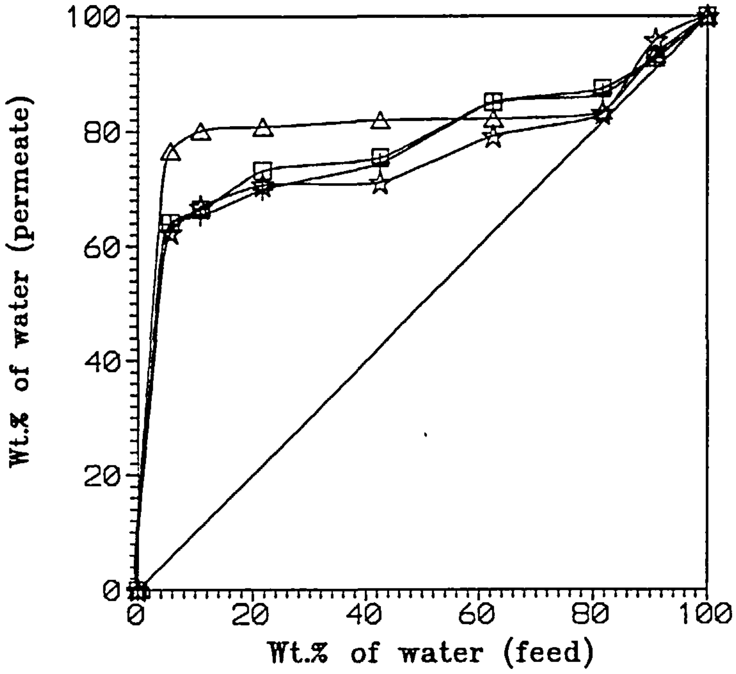

FIG. 10 Permeation characteristics of NEP–water system at 30°C. (△) PDMS, (☆) SBR, (+) PDMS + 40% NaX, (□) PDMS + 40% silicalite.

was relatively insensitive to the feed concentration up to 60 wt%, beyond which it showed a sharp increase. The fillers act as physical crosslinkers in a filled membrane. The plasticization process does not start as early as in the case of unfilled membranes.

The effect of a rise in feed temperature on NMP flux for all organophilic membranes was studied. It was observed that NMP flux increased with temperature. As the temperature rises, the frequency and amplitude of the polymer chain vibration increases (10), resulting in larger diffusion coefficients and hence in higher permeation rates. Similar results were obtained for the NEP–water system using all organophilic membranes.

Model Comparison

The diffusion coefficient of NMP and NEP through a membrane at infinite dilution for a particular temperature was obtained by plotting alkyl

TABLE 5
Model Parameters for NMP–Water System

Membrane	Temperature (°C)	$\rho_M D_{io}/L$ (kg/m²·s)	$\rho_M D_{jo}/L \times 10^5$ (kg/m²·s)	$D_{io} \times 10^{11}$ (m²/s) (water)	$D_{jo} \times 10^{12}$ (m²/s) (NMP)	A_{ij}	A_{ji}
PDMS	30	0.00021	2.6	1.8	2.2	0.1	0.007
	40	0.00024	2.9	2.1	2.5	0.1	0.007
	50	0.00025	3.1	2.2	2.7	0.07	0.007
SBR	30	0.00011	4.7	1.05	4.5	0.1	0.007
	40	0.00014	5	1.35	4.8	0.1	0.007
	50	0.00018	5.7	1.73	5.4	0.1	0.007

piperazine flux versus feed concentration in the membrane phase. The nature of curve was similar to that of Fig. 5. Diffusion coefficients of water and alkyl piperazines were estimated by Eqs. (8) and (9). The values of model parameters and diffusion coefficients of water, NMP, and NEP at infinite dilution are listed in Tables 5 and 6. It was found that the diffusion coefficient of water at infinite dilution was 5–10 times higher than that of the alkyl piperazines, supporting the fact that the diffusion selectivity for the organophilic membranes was in favor of water. The coupling parameters A_{ij} and A_{ji} (for alkyl piperazines and water) were also estimated from the data. It was found that for all cases $A_{ij} > A_{ji}$, indicating that the membrane plasticization was due to the alkyl piperazines. The fluxes were calculated from Eqs. (11) and (12). Regression analysis was

TABLE 6
Model Parameters for NEP–Water System

Membrane	Temperature (°C)	$\rho_M D_{io}/L$ (kg/m²·s)	$\rho_M D_{jo}/L \times 10^5$ (kg/m²·s)	$D_{io} \times 10^{11}$ (m²/s) (water)	$D_{jo} \times 10^{12}$ (m²/s) (NEP)	A_{ij}	A_{ji}
PDMS	30	0.00021	2	1.8	1.75	0.1	0.007
	40	0.00022	2.5	1.81	2.2	0.1	0.007
	50	0.00033	2.8	2.8	2.4	0.07	0.007
SBR	30	0.00012	4.1	1.15	3.9	0.1	0.007
	40	0.00021	4.7	2	4.5	0.1	0.007
	50	0.00025	5.3	2.4	5	0.1	0.007

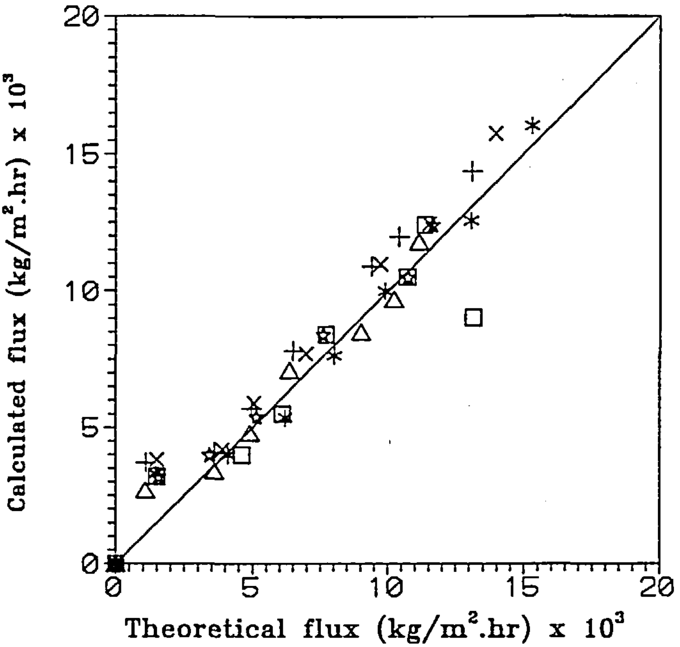

FIG. 11 Parity plot for PDMS membrane. (△) 30°C, aq. NMP; (□) 40°C, aq. NMP; (☆) 50°C, aq. NMP; (+) 30°C, aq. NEP; (×) 40°C, aq. NEP; (*) 50°C, aq. NEP.

carried out to analyze the data fit. The regression coefficients obtained were in the 0.95 to 0.97 range. A parity plot showing the comparison of experimental flux and calculated flux of NMP and NEP for PDMS and SBR membranes at 30°C is shown in Fig. 11.

CONCLUSIONS

A detailed analysis in terms of sorption and permeation of aqueous NMP and NEP solutions was carried out using various hydrophilic and organophilic membranes.

(a) Hydrophilic membranes. Sorption studies showed preferential sorption of water for the whole range of concentration and temperature for both systems. Permeation studies indicated very high values of selectivity of water for the polyimide membrane for both systems. The effect of temperature on selectivity for water was found to be marginal. The higher values of the coupling parameter indicated that plasticization of the membrane was due to water.

(b) Organophilic membranes. Sorption studies showed preferential sorption of NMP and NEP with all membranes for the whole range of concentration and temperature. However, permeation studies indicated the diffusion process was dominant over the sorption process, and hence reduced the overall permeation selectivity of the membranes with respect to the alkyl piperazines to the extent that water permeates selectively. The diffusion coefficient of water was found to be 5–10 times higher than that of the alkyl piperazines, supporting the above argument.

SYMBOLS

A_{ij}	coupling parameter for multicomponent transport in Eqs. (8), (10), and (11)
A_{ji}	coupling parameter for multicomponent transport in Eqs. (9) and (12)
D	diffusion coefficient (m^2/s)
E	activation energy (kJ/mol)
H	heat of sorption (kJ/mol)
J	solute flux ($kg/m^2 \cdot h$)
J_0	preexponential factor ($kg/m^2 \cdot h$) in Eq. (4)
L	membrane thickness (m)
T	operating temperature (°C)
w	weight fraction of the component
X	wt% of component in feed
Y	wt% of component in permeate

Greek Letters

α	permeation selectivity
Δ	difference operator
ρ_M	membrane density

Subscripts

A	component A
B	component B
D	diffusion
F	feed phase
i	component i
j	component j
M	membrane phase

P	permeate phase
p	permeation
s	sorption

ACKNOWLEDGMENT

The present work was supported by a research grant under the INDO-US Collaborative Material Sciences Program.

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Received by editor February 7, 1997
First revision received May 1997
Second revision received July 1997