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Selective Sorption of Latex Membranes with Ethanol–Water Mixtures

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ABSTRACT

Latex membranes have recently found use in pervaporation separation. The sorption of water–ethanol mixtures to latex membranes was carried out on three types of latex membranes, poly(acrylonitrile-*co*-butyl acrylate) [P(AN-BuA)], poly(methyl methacrylate-*co*-butyl acrylate) [P(MMA-BuA)], and poly(styrene-*co*-butyl acrylate) [P(ST-BuA)], which were prepared in our laboratory by direct casting of polymer latexes synthesized by emulsion polymerization. These latex membranes all exhibit preferential sorption and permeation toward water. Both water and ethanol sorption to the latex membranes exhibited nonideal sorption, with water sorption being enhanced greatly by the presence of ethanol. It was shown that the solubility parameter theory did not give correct predictions for the preferential sorption of latex membranes. Better results were obtained by using the Flory–Huggins interaction parameter.

Key Words. Latex membrane; Sorption; Pervaporation; Ethanol–water mixtures

INTRODUCTION

A number of polymers have been employed as pervaporation membranes, most of which are obtained from casting of polymer solutions. Pervaporation with ethanol–water mixtures using latex membranes,

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which were prepared from direct casting of polymer emulsions, has been investigated recently (1). These latex membranes shows preferential permeation toward water during pervaporation. According to the current solution-diffusion mechanism, such a preferential permeation is a result of the joint contribution of selective sorption and selective diffusion (2). High pervaporation selectivity is achieved if both the upstream sorption and the inside diffusion favor the transport of the same component. Otherwise the competition between the two aspects results in rather poor selectivity.

The sorption to a polymer membrane is determined by the interactions between the components and the polymer. In a multicomponent mixture, since the interactions between the polymer and the individual components are different, selective sorption occurs. For a given liquid mixture, the selective sorption of its components to a polymer membrane prepared from solvent casting can be predicted satisfactorily by the estimation of the solubility parameters based on the solubility parameter theory (3). However, as shown in the following, this approach does not give the correct prediction for the selective sorption to the latex membranes. By using the Flory–Huggins interaction parameters which are calculated from the experimental results of the equilibrium sorption of a single component–membrane pair, better prediction is obtained.

THEORETICAL

The sorption properties are characterized by the sorption amount Q and the sorption selectivity α^s:

$$Q = \frac{\text{total liquid amount sorbed (g)}}{\text{dry membrane weight (g)}} \tag{1}$$

$$\alpha^{s}_{(ij)} = \frac{c_{m,i}/c_{m,j}}{X_i/X_j} \tag{2}$$

where α^s is the sorption selectivity (when $\alpha^s > 1$, the polymer preferentially absorbs component i) and X and c_m are the weight fractions in the feed solution and in the membrane. i, j represent water and ethanol, respectively.

If the sorption process is ideal, the sorption amount of one component is proportional to its concentration in feed and is independent of the other components. To characterize the nonideal sorption, sorption ratios can be defined similarly to permeation ratios (4):

$$\begin{aligned} \phi_i &= Q_i/X_iQ_i^0 \\ \phi_j &= Q_j/X_jQ_j^0 \end{aligned} \tag{3}$$

where ϕ_i is the sorption ratio, X_i is the weight fraction of component i in the feed, and Q_i and Q_i^0 are the actual and ideal sorption amount of component i, respectively. When $\phi_i = 1$, component i shows ideal sorption (i.e., independent sorption). If $\phi_i > 1$, the sorption of i positively deviates from the ideal case, in other words it is enhanced by the existence of the other component; while $\phi_i < 1$ indicates negative deviation from ideality, or the hindrance of its sorption by the other one.

Sorption is a physical process during which the solvent molecules absorb onto the polymer surface and then penetrate into the membrane. Sorption is induced by the interactions between the component molecules and the polymer, and causes the swelling of the polymer, which ends up with the solution of the polymer if the polymer has no physical or chemical crosslinks. To analyze the interactions, the three-dimensional solubility parameters δ_d, δ_p, and δ_h are commonly used to represent the three interactions due to dispersion forces, polar forces, and hydrogen bonds, respectively. The overall solubility parameter is given by

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

If the solubility parameters of the polymer and the liquid molecules are close, strong interactions occur between them. Another parameter, Δ, which is the distance between the end points of the vectors representing polymer and solvent, was also used as a measurement of the interactions (5). Δ is calculated by

$$\Delta = [(\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2]^{1/2} \tag{5}$$

where the subscripts p and s refer to the polymer and the liquid component, respectively. A smaller value for Δ indicates a greater interaction between the polymer and the component, thus a greater solubility of this component in the membrane. In a binary liquid mixture, the preferential sorption can be marked by the Δ ratio (6):

$$\Delta_{ip/jp} = \Delta_{ip}/\Delta_{jp} \tag{6}$$

where subscript i and j refer to components. Apparently $\Delta_{ip/jp} < 1$ indicates a preferential sorption to solvent i.

The Flory–Huggins interaction parameter is related to the excess free energy of mixing. For a binary system (solvent–polymer):

$$\Delta G_m/RT = n_1 \ln \phi_1 + n_p \ln \phi_p + \chi_{1p} n_1 \phi_p \tag{7}$$

where n is the mole fraction, ϕ is the volume fraction in equilibrium sorption, and χ_{1p} is the Flory–Huggins interaction parameter characterizing the interaction between solvent 1 and the membrane p. A larger value of χ_{1p} indicates a weaker interaction between the solvent and the polymer membrane. It has been shown that (7)

$$\chi_{1p} = -\frac{\ln(1 - \phi_p) + \phi_p}{\phi_p} \tag{8}$$

EXPERIMENTAL

Membrane Preparation

Latexes of poly(acrylonitrile-*co*-butyl acrylate) [P(AN-BuA)], poly(methyl methacrylate-*co*-butyl acrylate) [P(MMA-BuA)], and poly(styrene-*co*-butyl acrylate) [P(ST-BuA)] were synthesized with emulsion polymerization, as described in Ref. 1. After being filtered with a nylon screen, the latexes are cast directly onto the glass plates. The thickness of the films ranges from 80 to 120 μm.

After drying at ambient temperature in a filtration hood for 7 days, the membrane was carefully removed from the plate. The film was then applied to vacuum drying at ambient temperature for 12 hours to remove any volatile residuals.

Sorption Measurement

To obtain the sorption data for the latex membranes, the equilibrium liquid uptakes were measured. The preweighed dry and square-shaped membranes were immersed in the bulk liquid of known ethanol concentrations at 25°C for 2 weeks to allow the membranes to reach sorption equilibrium. After careful blotting off the surface liquid with tissue paper, the membranes were weighed as quickly as possible and then put into a dry flask which was connected to a cold trap and a vacuum pump. The desorbed liquid was collected, weighed, and analyzed for the composition with a Perkin-Elmer 8310 Gas Chromatograph to give the sorption amount and selectivity.

RESULTS AND DISCUSSION

Sorption

The sorption of the three types of latex membranes prepared are shown in Fig. 1. It can be seen from this figure that the latex membranes showed different sorption behaviors. For the P(AN-BuA) copolymer membrane (Fig. 1b) and the P(MMA-BuA) copolymer membrane (Fig. 1c), the total sorption amount changes slightly into a bell shape with increasing ethanol content in bulk liquid and has a maximum sorption value at about 0.5 weight faction ethanol in the feed. For both of these membranes, the pure water uptake is only slightly higher than the pure ethanol uptake, which suggests similar interactions between ethanol molecules and the membrane. By looking at the structures of the latex membranes, it was found that the films consist of both hydrophilic and organophilic units so that the membranes are swollen by both water and ethanol. The total sorption of the P(ST-BuA) copolymer membrane (Fig. 1a) exhibited a much greater increase when the ethanol content was increased. Moreover, this membrane has the highest pure ethanol uptake and the P(MMA-BuA) membrane has the highest pure water uptake. It is interesting to note here that even though there exists the strong polar group (—CN) in the P(AN-BuA) membrane, it shows a lower water uptake than the other two.

By comparing the sorption data in Fig. 1, it is found that the P(ST-BuA) copolymer membrane shows the largest total sorption over the entire concentration range while that of the P(AN-BuA) copolymer membrane is the smallest.

It can be seen from Fig. 1 that for all the latex membranes, ethanol sorption in the latex films increases with increasing ethanol concentration in the bulk liquid. The water sorption for the P(AN-BuA) and P(ST-BuA) membranes, however, shows maximum values around the 0.3 weight fraction of ethanol in the feed. The water sorption in the P(MMA-BuA) membrane decreases almost monotonously with increasing ethanol concentration. It is also observed, as expected, that both water and ethanol sorption are nonideal sorption, and their sorption ratios are presented in Fig. 2. From this figure it is apparent that water sorptions all positively deviate from ideal sorption, indicating that the sorption of water to the latex membranes is enhanced by the presence of ethanol, especially for the P(ST-BuA) membrane. Ethanol sorption for the P(ST-BuA) copolymer membrane displays little negative deviation from ideal sorption, especially at higher ethanol feed concentrations. In contrast, ethanol sorption for the other two membranes is also enhanced by the presence of water in the membrane.

Despite the existence of hydrophilic groups, interactions between the polymer segments and alcohol molecules may still be significant. The membrane can have a high degree of swelling or even be partially dissolved at high alcohol concentration, as in the case of the P(MMA-BuA) membrane, particularly when the degree of crosslinking is not high enough. This situation must be avoided when the membrane is used for the dehydration of alcohols.

Preferential Sorption

Figure 3 gives the sorption selectivities of the latex membranes as a function of the feed concentration. For all three types of latex membranes

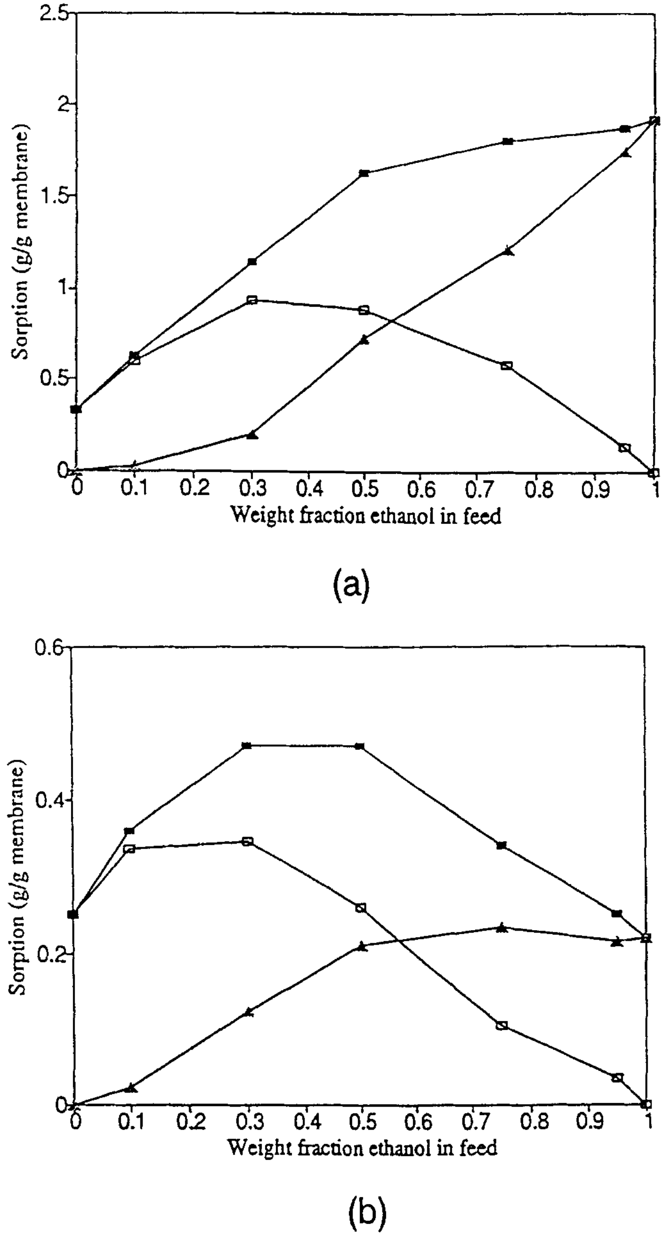
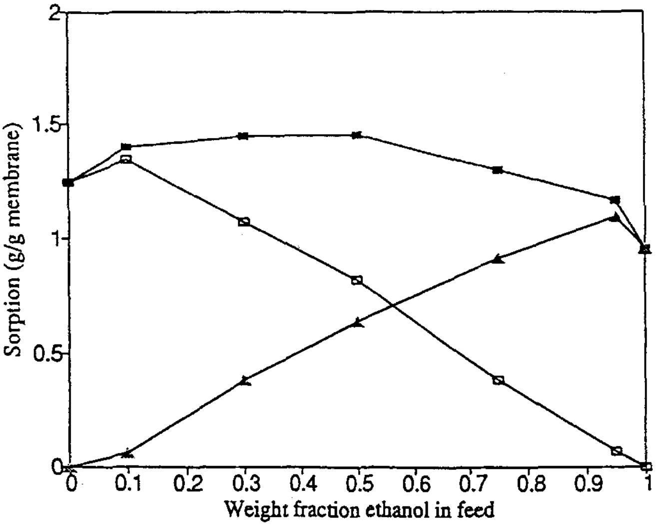


FIG. 1 Total and individual sorption amount in latex membranes as a function of ethanol concentration in feed at 25°C. (■) Total sorption, (▲) ethanol sorption, (□) water sorption; (a) P(ST-BuA), (b) P(AN-BuA), (c) P(MMA-BuA).



(c)

FIG. 1 Continued

prepared, sorption selectivity is greater than 1, indicating that water is preferentially absorbed.

It is widely accepted that the sorption, and thus the solubility, is mainly determined by interactions between the components and the membrane. A convenient method to predict solubility behaviors is to use the solubility parameter theory (3) in which the three-dimensional solubility parameters are employed to represent these interactions. Based on the repeating units of the copolymers synthesized (1), and using the data provided by van Krevelen (8), the solubility parameters of the copolymers are calculated and listed in Table 1. According to the values in Table 1, ethanol should have a greater affinity than water for the copolymer membranes, i.e., these latex membranes should show preferential sorption for ethanol compared to water.

The discrepancy between the prediction from solubility theory and from experimental results indicates that the solubility parameter approach does not correctly predict the preferential sorption of latex membranes.

In the latex membranes there exist sources of hydrophilic groups other than the functional groups in the polymers. For example, the emulsifier used in conventional emulsion polymerization, although homogeneously mixed with the polymers in a bound form, is a kind of hydrophilic additive

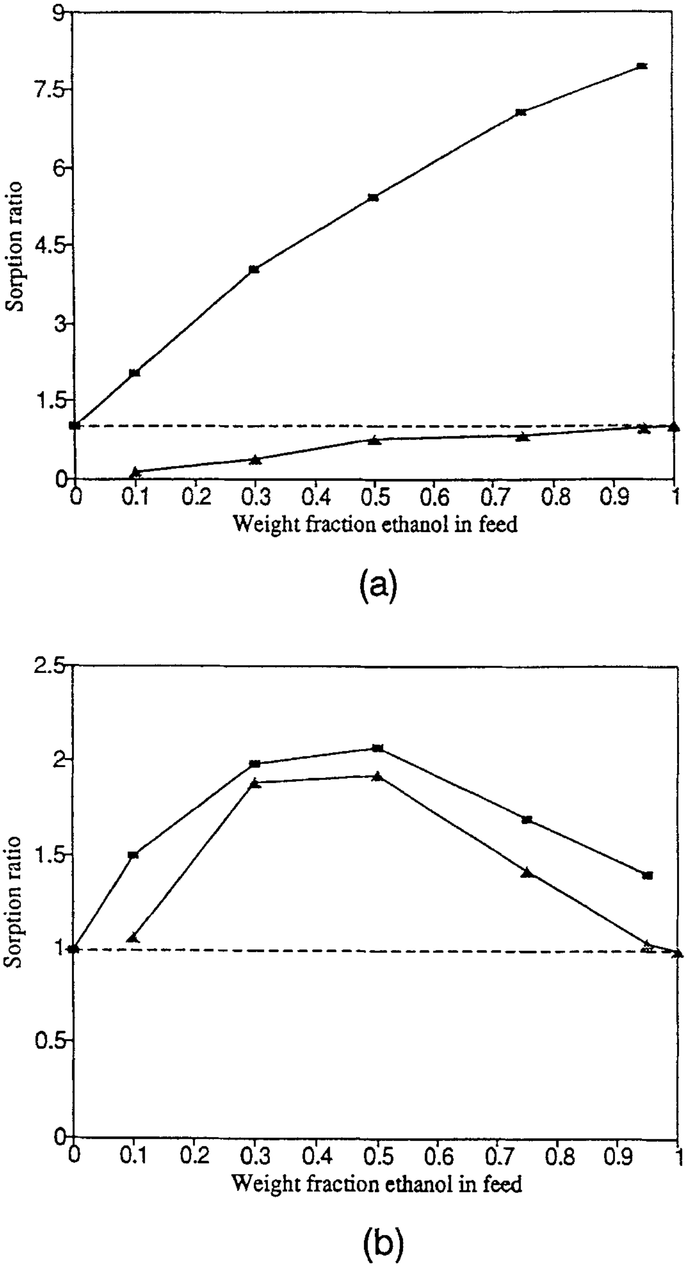


FIG. 2 Sorption ratios vs ethanol concentration in feed at 25°C. (■) Water sorption ratio, (▲) ethanol sorption ratio; (a) P(ST-BuA), (b) P(AN-BuA), (c) P(MMA-BuA).

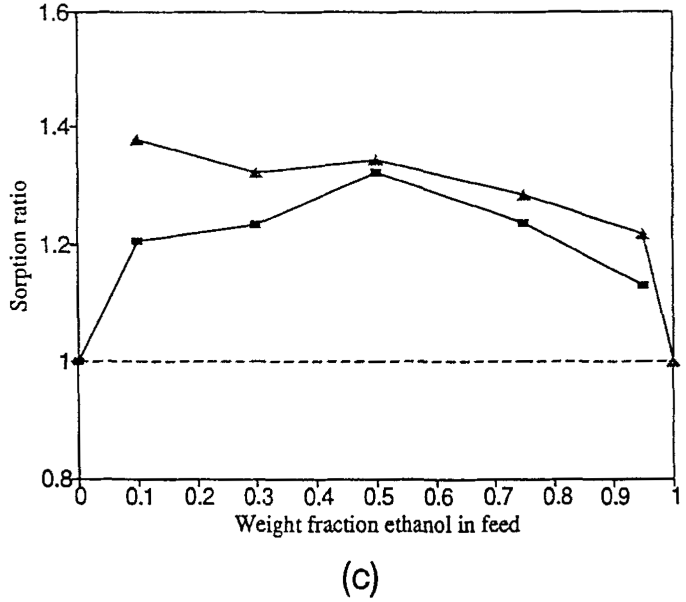


FIG. 2 Continued

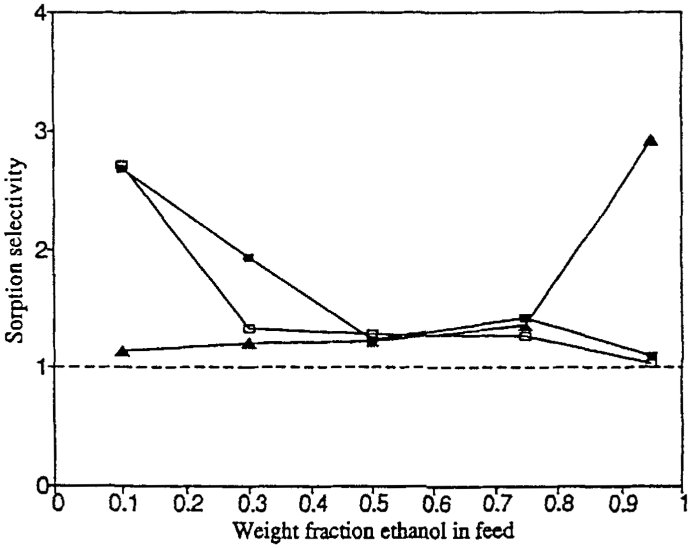


FIG. 3 Sorption selectivity of latex membranes vs ethanol weight fraction in feed at 25°C. (■) P(ST-BuA), (▲) P(AN-BuA), (□) P(MMA-BuA).

TABLE 1
Solubility Parameters of Copolymers and Solvents

Material	δ_d[a]	δ_p	δ_h	δ	Δ_{WM}[b]	Δ_{EM}[c]
P(ST-BuA)	17.82	2.39	5.77	18.88	40.96	15.25
P(AN-BuA)	17.86	7.82	7.86	21.02	35.76	11.82
P(MMA-BuA)	16.41	4.73	8.22	18.96	37.42	11.97
Water[d]	12.29	31.34	34.21	47.90	—	—
Ethanol	15.84	8.80	19.46	26.47	—	—

[a] The unit of solubility parameter is $J^{1/2}/cm^{3.2}$.

[b] Δ_{WM} represents the Δ value between water and the polymer.

[c] Δ_{EM} represents the Δ value between ethanol and the polymer.

[d] Solubility parameters taken from Ref. 12.

present in the membrane. This effect may be eliminated by preparing latexes by soap-free emulsion polymerization. The hydrophilic end groups in the polymer chains, which originate from the initiation reactions, also make the membrane more hydrophilic. Furthermore, latex membranes are formed by the coalescence of latex particles, which is different from conventional solvent-cast membranes. Since such latex membranes cannot become perfectly homogeneous (9–11), sorption in the particle–particle boundary region contributes to the overall sorption. Since solubility parameter theory only takes into account polymer composition, great deviations in predicting sorption result when other effects related to membrane composition and structure are significant.

An option for predicting the preferential sorption of a solvent mixture to latex membranes is to use the Flory–Huggins interaction parameter χ_{ip}. Table 2 lists the parameters calculated according to Eq. (8). The values in this table show a stronger interaction between water and the latex membranes, and this agrees with experimental observations. Since the actual sorption data were used in the calculation, it is not surprising that the interaction parameter gives a better prediction. This approach requires

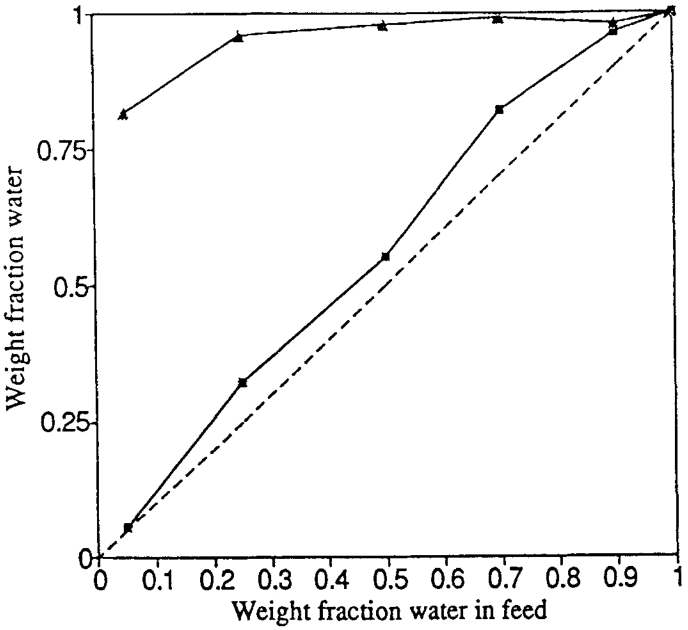
TABLE 2
Flory–Huggins Interaction Parameters

Membrane	χ_{ep}[a]	χ_{wp}	χ_{wp}/χ_{ep}
P(ST-BuA)	0.620	0.519	0.84
P(AN-BuA)	1.191	1.046	0.88
P(MMA-BuA)	0.724	0.720	0.99

[a] The subscripts e, w, and p refer to ethanol, water, and polymer, respectively.

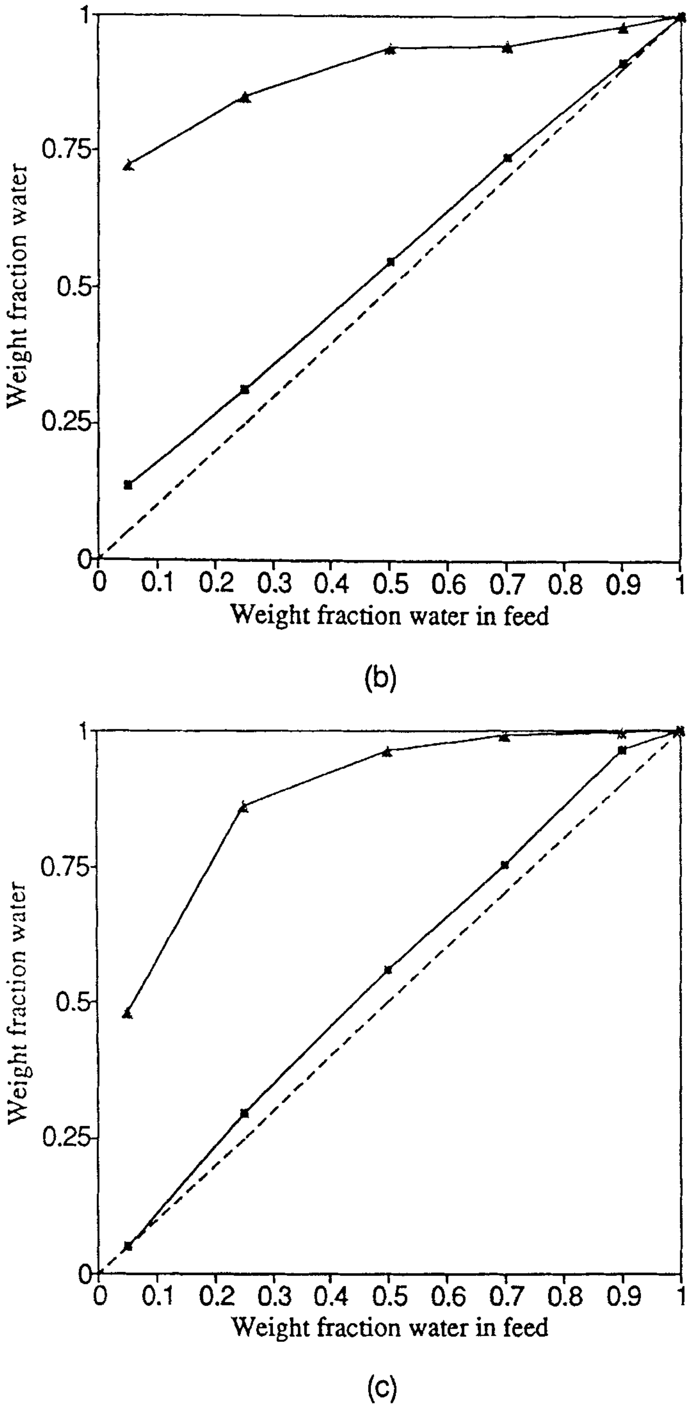
only the sorption data of the binary system (solvent–membrane) which can be obtained by doing a simple equilibrium sorption experiment. Therefore, it can be conveniently employed in performing a rough estimation of the preferential sorption or when making a rough membrane material selection, particularly for latex membranes. It is noted that the sorption in a ternary system (binary mixture–membrane) is more difficult to predict accurately due to a significant coupling effect.

The significance of predicting the sorption property in membrane material selection is shown by the fact that selective sorption often leads to selective permeation of the same species during pervaporation (3), especially when the component with a smaller molecular size is preferentially absorbed. This is also applicable to pervaporation with latex membranes. As can be seen from Fig. 4, which gives the water concentration in the membrane and permeate as a function of the feed content, water is preferentially absorbed and permeated over the entire concentration range.



(a)

FIG. 4 Water concentration in membrane and in permeate vs feed concentration. Feed temperature: 25°C. (■) Water concentration in membrane, (▲) water concentration in permeate; (a) P(ST-BuA), (b) P(AN-BuA), (c) P(MMA-BuA).



(b)

(c)

FIG. 4 Continued

CONCLUSIONS

Sorption results of latex membranes in ethanol–water mixtures indicate preferential water sorption in the entire concentration range. Both water and ethanol sorption shows deviation from ideal sorption, with water sorption enhanced by the presence of ethanol. The solubility parameter theory is inadequate for the correct prediction of preferential sorption in the latex membrane system. Better agreement with experimental results is found by using the Flory–Huggins interaction parameter. For latex membranes, the preferentially absorbed component is also preferentially permeated.

NOTATIONS

c_m	concentration in membrane
n	mole fraction
Q	total liquid sorption
T	membrane temperature in Kelvin scale
X	weight fraction in feed
α^s	sorption selectivity
δ_d	solubility parameter due to dispersion forces
δ_h	solubility parameter due to hydrogen bonds
δ_p	solubility parameter due to polar forces
Δ	the distance between the end points of the vectors representing polymer and solvent
Δ_{EM}	distance between end points of the vectors of ethanol and the membrane
Δ_{WM}	distance between end points of the vectors of water and the membrane
χ	Flory–Huggins interaction parameter
ϕ	sorption ratio

Subscript

e	ethanol
i, j	type of feed component
p	polymer
s	solvent

Superscript

s	sorption
0	ideal sorption

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REFERENCES

1. Y. Wei and R. Y. M. Huang, *J. Membr. Sci.*, *82*, 27 (1993).
2. M. H. V. Mulder, A. C. Franken, and C. A. Smolders, *Ibid.*, *23*, 41 (1985).
3. M. H. V. Mulder and C. A. Smolders, *Sep. Purif. Methods*, *15*(1), 1 (1986).
4. R. Y. M. Huang and C. K. Yeom, *J. Membr. Sci.*, *51*, 273 (1990).
5. M. H. V. Mulder, F. Kruitz, and C. A. Smolders, *Ibid.*, *11*, 349 (1982).
6. D. R. Lloyed and T. B. Meluch, *Material Science of Synthetic Membranes* (ACS Series 269), (D. R. Lloyed, Ed.), Washington, D.C., 1985, pp. 1–21.
7. C. K. Yeom and R. Y. M. Huang, *J. Membr. Sci.*, *67*, 39 (1992).
8. D. W. van Krevelen and P. J. Hoftyzer, *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, 2nd ed., Elsevier Scientific Publishing Company, Amsterdam, 1976.
9. E. B. Brandford and J. W. Vanderhoff, *J. Macromol. Chem.*, *1*, 335 (1966).
10. E. B. Brandford and J. W. Vanderhoff, *J. Macromol. Sci.—Phys.*, *B6*(14), 671 (1972).
11. J. W. Vanderhoff, E. B. Brandford, and W. K. Carrington, *J. Polym. Sci., Polym. Symp.*, *41*, 155 (1973).
12. J. Brandup and E. H. Immergut (Eds.), *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975.

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