Alcohol Recovery with Pervaporation: Effect of High 2-Butanol Concentration

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ABSTRACT: Poly dimethyl siloxane (PDMS) membrane was used to separate a synthetic mixture consisting of isopropanol, ethanol, 2-butanol, and *n*-butanol using the pervaporation separation technique. These alcohols are found to occur in naphtha reformate as a result of vapor-phase reaction of the alkenes in the presence of water and a catalyst. In this work the pervaporation separation efficiency of PDMS membrane toward different alcohols was evaluated by estimation of fluxes and separation factors at different temperatures and pressures. The coupling effect resulting from the presence of identical functional groups was investigated. The activation energies for the transport of each of these alcohols through the membrane were also evaluated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3164–3171, 2001

Key words: alcohols; PDMS membrane; separation factor; pervaporation; separation index; naphtha reformate

INTRODUCTION

Pervaporation is an attractive separation technique that has been the object of numerous experimental and theoretical investigations.[1–8] In most cases the main concern was the application of the process to the separation of aqueous solutions containing organic compounds; both hydrophilic and hydrophobic membranes were used to obtain either the dehydration of the stream or the permeation of the organic components. A widely used application is the dehydration of alcoholic mixtures, for example, for the production of absolute ethyl alcohol.[9–12] Hydrophobic membranes were used for the treatment of effluents[13–15] for the recovery of valuable organic substances from sidestreams of industrial processes[16,17] and for removing permeation products.[18,19] More recently the interest rose for the application of pervaporation for the separation of organic mixtures in industrial processes.[20,21] Poly dimethyl siloxane (PDMS) and poly[(1-trimethyl silyl)-1-propyne] (PTMSP) membranes are generally known to be highly alcohol permselective membranes.[22–26] The alcohol permselectivities of these membranes are attributed to their strong affinity for alcohol and the relatively high diffusivity of the alcohol through these membranes.

Naphtha reformate from Kuwait National Petroleum Company (KNPC) was analyzed for alcohols using a Chrompack gasohol chromatograph designed to detect alcohols in any mixture. The different alcohols detected by the gasohol analyzer in a typical sample of naphtha reformate obtained from KNPC is indicated in Table I. These alcohols could be formed by the vapor-

Table I   Alcohols Detected by Gasohol Analyzer[a]

Type of Alcohol	Estimated Total Concentration in Naphtha Reformate (%)
Methanol	—
t-Butanol	—
Isopropanol	1.8
Ethanol	1.7
2-Butanol	4.6
n-Butanol	1.3

[a] From typical sample of naphtha reformate obtained from Kuwait National Petroleum Company.

phase reaction of the alkenes in the presence of water and a catalyst at temperatures of 300°C. Normally these alcohols are removed in the vapor-phase process by scrubbing.

In this work the pervaporation separation efficiency of PDMS membrane toward separation of a synthetic alcohol mixture consisting of isopropanol, ethanol, 2-butanol, and n-butanol scaled on the basis of concentrations occurring in naphtha reformate is considered. The mixture of alcohols with an identical functional group environment could lead to particular synergistic or coupling effects when passing through a hydrophilic membrane. The effect of coupling of these alcohols through PDMS membrane was studied. In addi-

tion to reporting new pervaporation data relevant to the separation of alcohol mixtures this investigation also brings further understanding to the pervaporation of isomers in alcohol mixtures.

EXPERIMENTAL

Pervaporation experiments were conducted using a mini-PV lab unit (Fig. 1). Selective pervaporation of organic–organic solution requires elastomeric membranes.[6] Separation was effected using a flat hydrophilic PDMS membrane supplied by Mitsui Shipping and Building Company, Japan.

The effective membrane area was 0.5 m^2 with a thickness of 2 μm. The feed solution was circulated at a flow rate of 10 L/h from the feed tank. Experiments were conducted at four different temperatures: 45, 50, 55, and 60°C. The feed pressure was maintained at 1.0 kg fcm^{-2}. The initial synthetic feed mixture consisted of isopropanol (I) (15.5 cm^3), ethanol (e) (13.6 cm^3), 2-butanol (2b) (60.3 cm^3), and n-butanol (b) (10.62 cm^3). The mixture was kept constant to 2.5 L for all the runs. The feed composition was scaled on the basis of known volumes of pure alcohols, and volume changes on mixing were neglected.

The feed mixture was introduced into a feed tank, the components were vaporized through the PDMS membrane mounted on a porous metallic support of the plate and frame type, and the per-
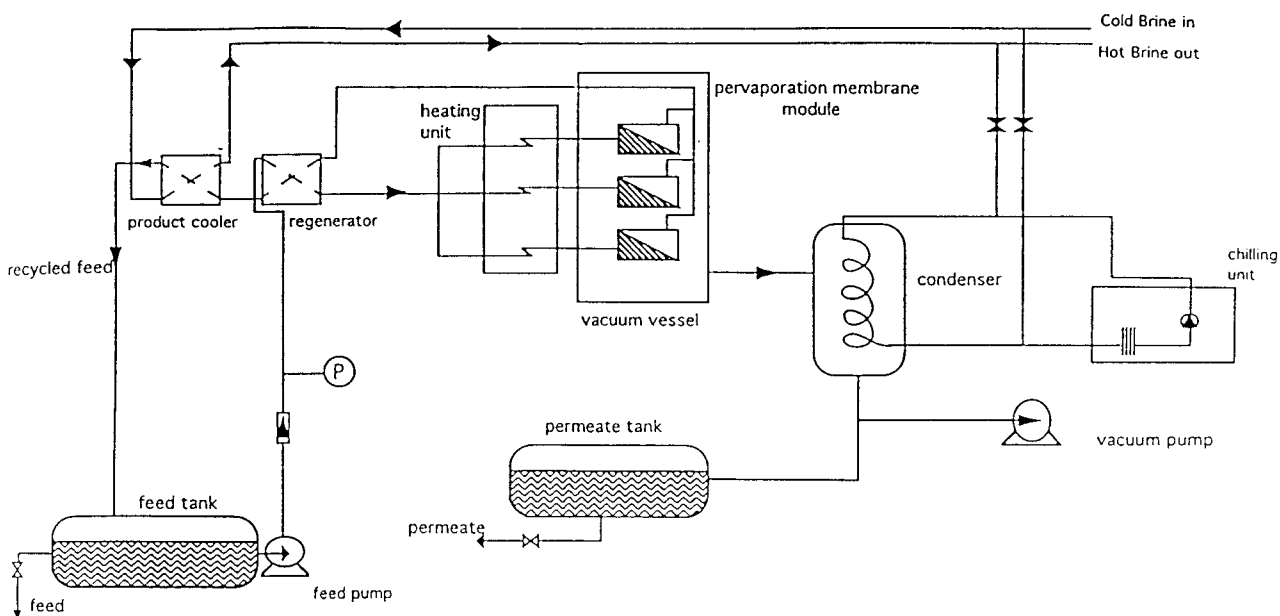

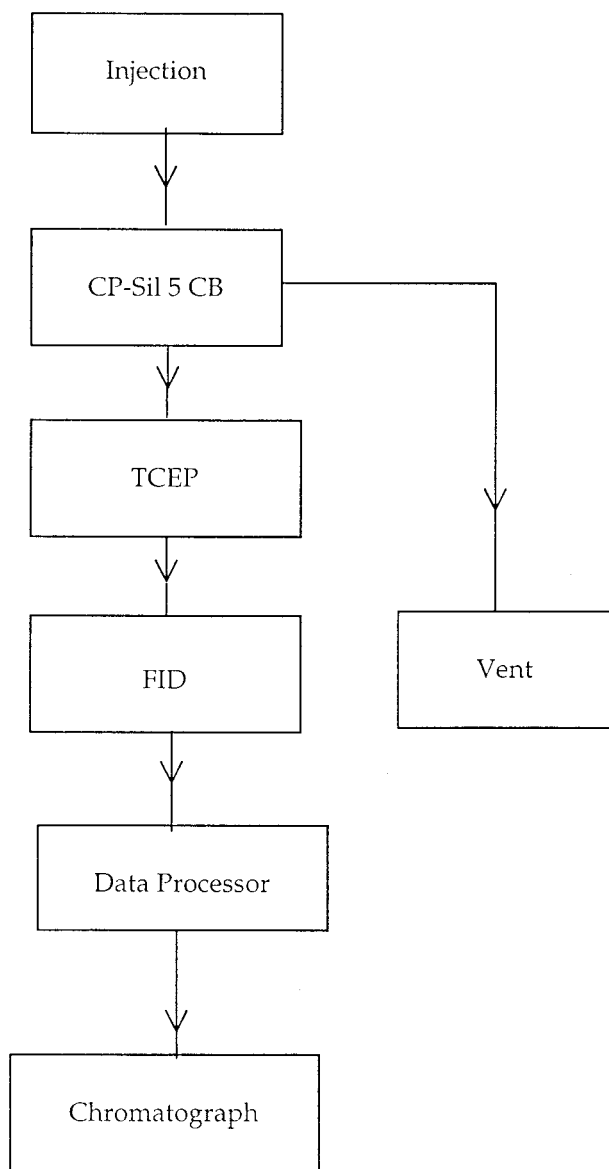**Figure 1.**   Process flow diagram of PV unit.

Figure 2. Schematic flow diagram of the gasohol analyzer.

meate was collected in a vacuum vessel maintained at low pressure by a vacuum pump. Permeate samples were collected at known time intervals and were weighed for further calculations.

The analyses were performed using a free induction delay (FID) chrompack, gasohol, gas chromatograph (CP-9000). The chromatograph had two different capillary columns of 10 and 50 m length. The short column (CP-Sil 5 CB) consisted of fused silica. The 50-m column, labeled TCEP, consisted of used silica but of finer pore size. The gasohol analyzer (Fig. 2) is mainly used for oxy-

genated additive analysis. The main features of the analyzer include analysis of C1–C4 alcohols, methyl t-butyl ether (MTBE), t-amyl methyl ether (TAME), methyl ethyl ketone (MEK), and benzene. A 0.5-μL sample was used for the analysis. During the analysis the injected sample passes through a short-fused silica CP-Sil 5 CB capillary column. The short column separates all C1–C4 alcohols and other oxygenates from nonoxygenated compounds. The CP-Sil 5 CB column is then automatically switched, to backflush all unwanted hydrocarbons. The C1–C4 alcohols pass on to the TCEP fused silica column and are separated for quantification.

RESULTS AND DISCUSSION

Pervaporation data were collected for a mixture of isopropanol, ethanol, 2-butanol, and n-butanol. The concentration of isopropanol, ethanol, 2-butanol, and n-butanol in the naphtha reformate is indicated in Table I. The present work was carried out in the concentration range that is present in the naphtha reformate so that the data could be of industrial interest. The data were collected at operating temperatures of 45, 50, 55, and 60°C. The PV system was operated at different constant pressures of 8, 8.5, 9, and 9.5 Torr.

The feed pressure was kept constant at 1.0 Torr. The flow rate was kept constant at 10 L/h. The following includes discussion of collected data and collected system variables, which were defined in the previous section. The discussion is based on the variations in system parameters, that is, temperature and pressure at a constant flow rate and concentration.

The permeate flux (J) is defined as

$$J = \frac{W}{At} \qquad (1)$$

where W, a, and t represent the weight of the permeant (g), effective membrane area (m^2), and operating time (h), respectively. Figure 3 is a typical plot indicating the variation of permeate flux as a function of weight fraction of ethanol in the feed at 50°C and 8 Torr pressure. Flux values of 370, 110, 85, and 80 g m^{-2} h^{-1} were obtained for 2-butanol, n-butanol, isopropanol, and ethanol, at low ethanol concentration in the feed. The dimensions of the solvents used in this work are indi-
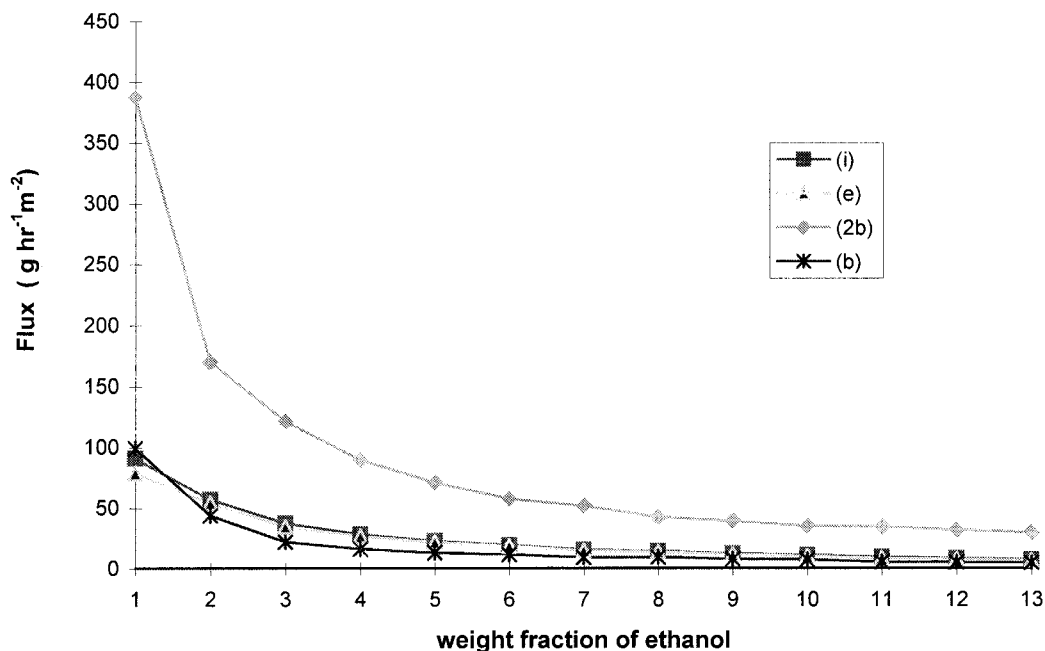
Figure 3.   Plot of variation of flux as a function of weight fraction of ethanol at 8 Torr and 50°C.

cated in Table II. Ethanol is the smallest species in the system. The low flux values of *n*-butanol, isopropanol, and ethanol relative to that of 2-butanol could be attributed to their low initial concentration in the feed mixture. As a result, the total amount of these species permeating through the membrane over the same operation period is lower than that for 2-butanol. 2-Butanol has the maximum concentration in the feed mixture, thus resulting in maximum permeation. Another possible explanation could be that the permeability of hydrophobic membranes toward aliphatic alcohols involves transfer of polar molecules (the alcohols) into a nonpolar environment (the mem-

Table II   Dimensions of the Organic Substances

No.	Organic Substance	r_d[a]	D[b]	Boiling Point (°C)
1	Ethanol	1.98	2.03	78–80
2	Isopropanol	2.16	2.45	81–83
3	*n*-Butanol	2.41	2.10	117
4	2-Butanol	3.23	2.45	97–100

[a] Stokes radius.
[b] The distance parameter estimated by Matsuura et al.[27]

brane). Increasing the chain length of the alcohols would imply decreasing the polarity, favoring membrane permeability. The effect of temperature on the partial flux of 2-butanol, the maximum permeating species, is shown in Figure 4. An increase in temperature to 60°C was found to have no effect on the permeation rate of 2-butanol. The data do not indicate higher permeation flux with rising temperature.

Figure 5 shows the plot indicating the effect of varying pressures on the rate of permeation of 2-butanol at a typical temperature (50°C). The rate of permeation of 2-butanol is found to have no pronounced effect on increasing the temperature or pressure. Figure 6 is a typical Arrhenius plot indicating the variation of flux as a function of temperature at 8 Torr. The plausible explanation for the behavior noted in Figures 4 and 5 is that the high concentration of 2-butanol in the feed mixture causes the amorphous regions of the membrane to swell, thus causing the polymer chains to become flexible and to increase the space available for diffusion of relatively more nonpolar molecules.

In Figure 6 the experimental observation shows that the plots of the logarithm of individual pervaporation fluxes versus the reciprocal of ab-
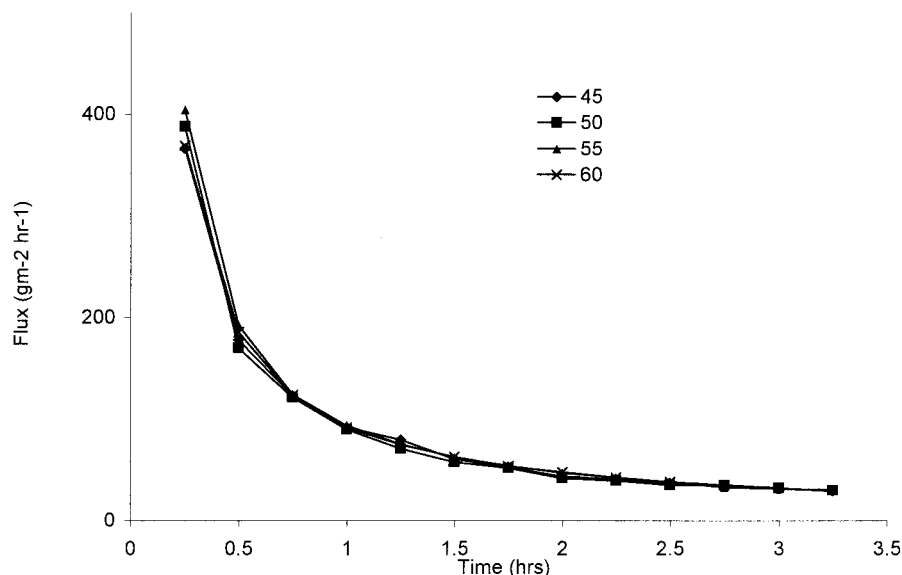
Figure 4. Plot of the variation of flux for 2-butanol as a function of time and temperature at 8 Torr.

solute temperature generally fall on straight lines when covering the temperature range from 45 to 65°C. For the system under investigation, it is seen that the activation energy values are scattered, ranging from 0.2 to 30 kJ/mol (Table III). This scatter in the values of E_p is reasonable, considering reported activation energies of different alcohol systems that are found to range from 5 to 583 kJ/mol.[6] The activation energy values of the present system are low (considering the data in Ref. 6), indicating that temperature cannot

greatly affect and/or accelerate separation in the system studied in this investigation. This finding goes well with the observation noted in Figure 4 over the temperature range studied in this investigation.

Figure 7 indicates that 2-butanol (the species with the highest flux) has separation factor values lower than that of n-butanol and higher than that of isopropanol. The values are found to range approximately between 1 and 2.5. Theoretically a trade-off exists between the permeation flux (J)
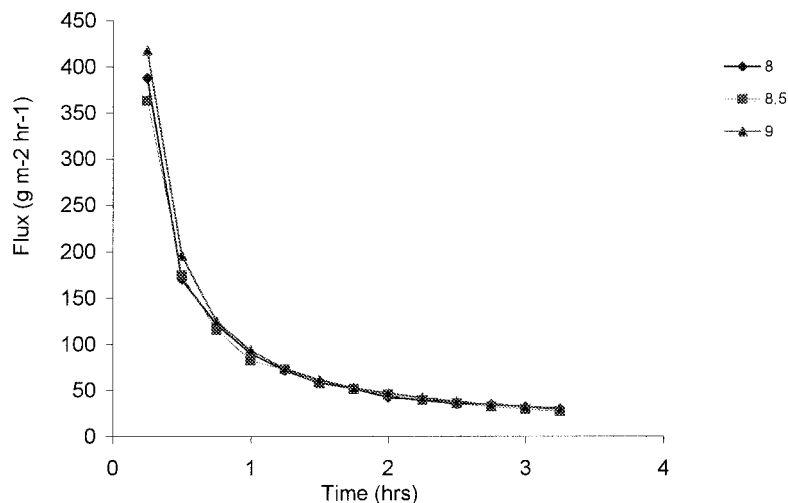

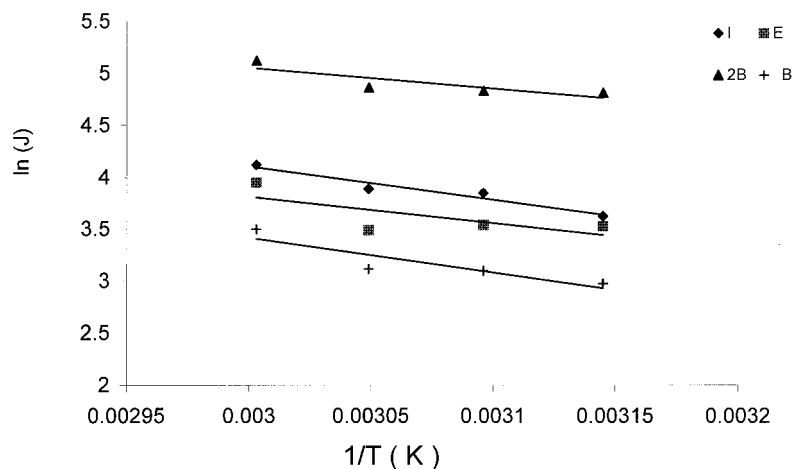**Figure 5.** Plot of variation of flux as a function of pressure for 2-butanol at 50°C.

Figure 6. Arrhenius plot of variation of flux as a function of temperature at 8 Torr.

and separation factor (α), that is, when one factor increases, the other decreases. It can be seen from the results of this investigation (Fig. 7) that the latter statement does not fully comply for this system. This could be the result of a small variation between the values of separation factors for the different alcohols. Thus, great emphasis is not placed on this observation.

A third parameter, the pervaporation separation index (PSI), which is a product of flux and separation factor, has been widely used to evaluate the overall membrane pervaporation performance.[28] The results are shown in Figure 8. It was found that 2-butanol has a maximum value of 365 g m^{-2} h^{-1}, indicating that PDMS membrane was more productive for the feed with high 2-butanol content. This implies that in a feed mixture of alcohols comprising a high concentration of 2-butanol PDMS would be the ideal membrane to separate 2-butanol.

Table III   Activation Energy Values of Different Alcohol Systems

Pressure (Torr)	E_p (kJ/mol)			
	Isopropanol	Ethanol	2-Butanol	*n*-Butanol
8.0	8.6	30	8	9.8
8.5	27	21	16	28
9.0	12	13	10.1	14
9.5	17	24.8	14.2	21.2

CONCLUSIONS

The following conclusions were drawn from this study:

1. PDMS membrane was used to determine the flux of a synthetic alcohol system (simulated to the contents found in naphtha reformate) comprised of isopropanol (15.5 vol %), ethanol (13.6 vol %), 2-butanol (60.3 vol %), and *n*-butanol (10.62 vol %). The feed composition was kept constant for all measurements. The experiments were carried out at 45, 50, 55, and 60°C. The pressures used were 8, 8.5, 9, and 9.5 Torr. The maximum flux values 370, 110, 85, and 80 g m^{-2} h^{-1} were obtained for 2-butanol, *n*-butanol, isopropanol, and ethanol, respectively, at 8 Torr and 50°C.

2. Temperature and pressure did not exert a significant influence on the rate of flux of the alcohols under the conditions of this investigation.

3. 2-Butanol, which is at 60.3 vol % in the feed mixture, was found to have the maximum flux relative to that of other species under investigation.

4. Activation energy values ranging from 0.2 to 30 kJ/mol were estimated for the system under investigation. The activation energy values were found to be low and scattered, indicating that temperature does not have a pronounced effect on the separation of these alcohol mixtures.
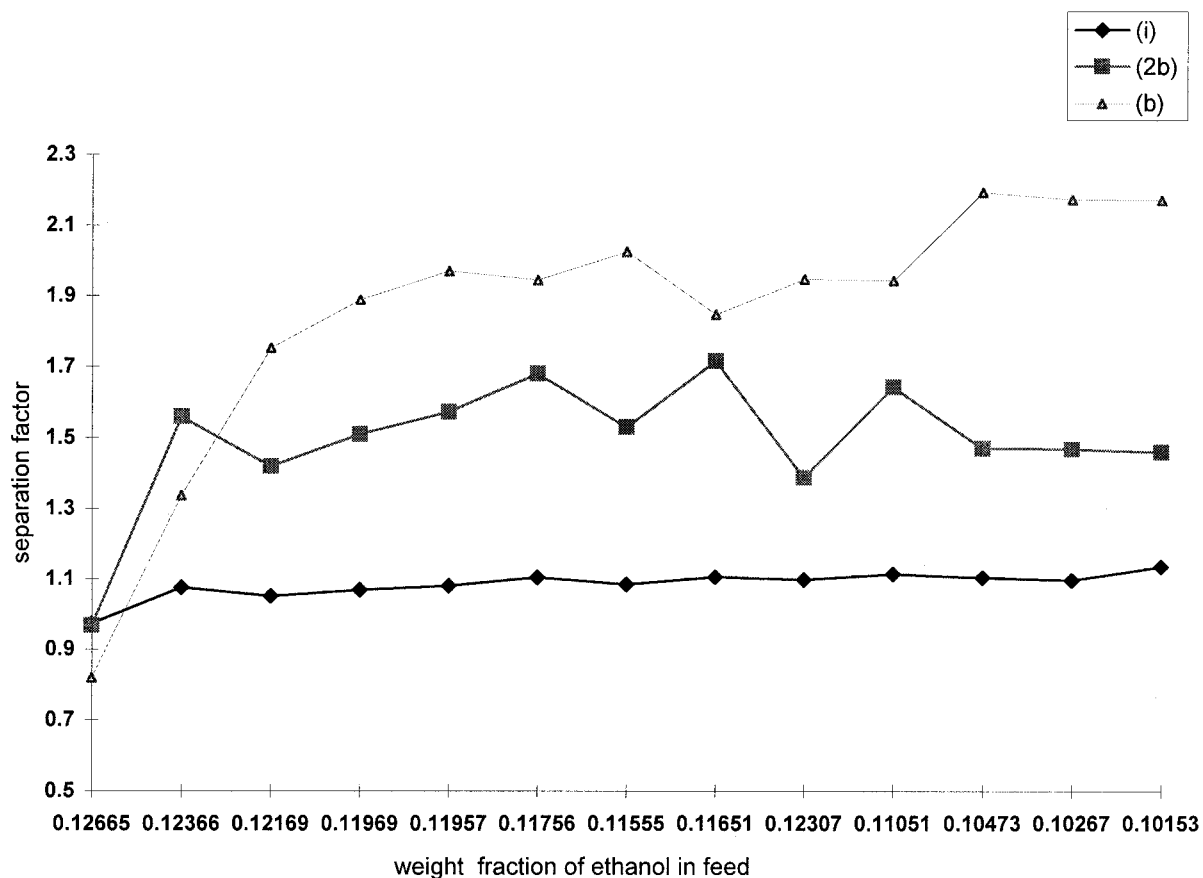
Figure 7. Plot of variation of separation factor as a function of weight fraction of ethanol in feed at 50°C and 8 Torr.
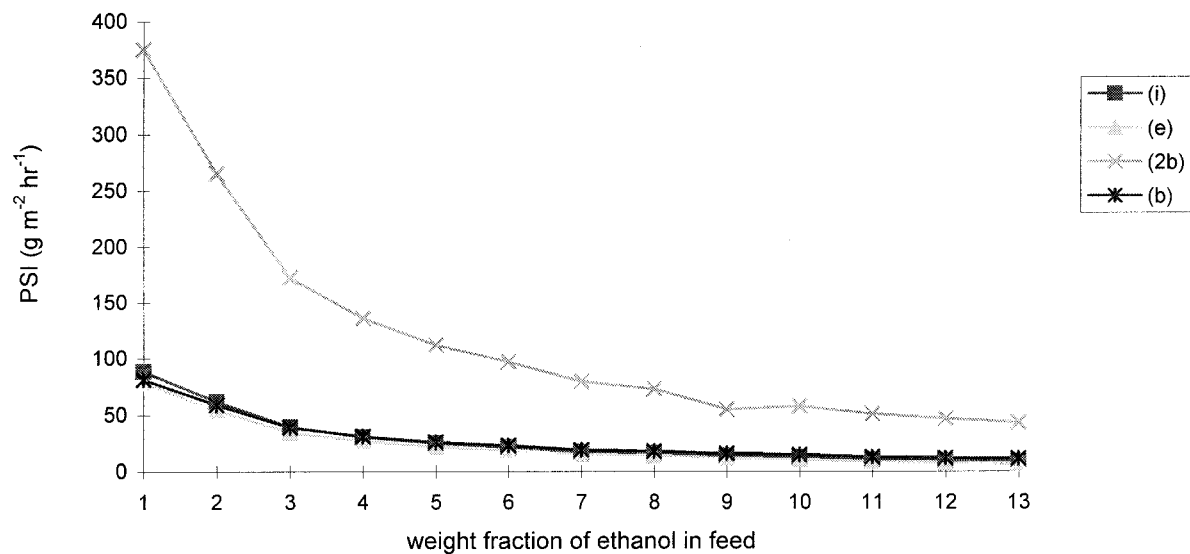

Figure 8. Plot of variation of pervaporation separation index (PSI) as a function of weight fraction of ethanol in feed at 8 Torr and 50°C.

5. PDMS membrane was found to be more productive to permeate 2-butanol, plausibly because of its high concentration in the feed mixture.

REFERENCES

1. Binning, R. C.; Lee, R. J.; Jenning, J. F.; Marin, E. C. Ind Eng Chem 1961, 53, 45.

2. Apetel, P.; Challard, N.; Cuny, J.; Neel, J. J Membr Sci 1976, 1, 271.

3. Rautenbach, R.; Albercht, R.; Herion, C. in Engineering Aspects of Pervaporation, Proceedings of the 1st International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R., Ed.; Bakish Materials Corp.: Englewood, NJ, 1986; p. 41.

4. Rautenbach, R.; Albrecht, R. in Observations on the Performance of Pervaporation under Varied Conditions, Proceedings of the Europe–Japan Congress on Membranes and Membrane Processes; Drioti, E.; Nakagaki, M., Eds.; Plenum Press: New York, 1986; p. 595.

5. Bruschke, H. E. A. in Thermodynamics of Pervaporation, Proceedings of the 2nd International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R., Ed.; Bakish Materials Corp.: Englewood, NJ, 1987; p. 266.

6. Huang, R. Y. M., Ed. Pervaporation Membrane Separation Processes; Elsevier: Amsterdam, 1991.

7. Mulder, M. H. V.; Smolders, C. A. Sep Sci Technol 1991, 26, 85.

8. Okada, T.; Matsura, T. in Theoretical and Experimental Study of Pervaporation on the Basis of Pore Flow Mechanism, Proceedings of the 6th International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R., Ed.; Bakish Materials Corp.: Englewood, NJ, 1992; p. 137.

9. Huang, R. Y. M.; Jarvis, N. R. J Appl Polym Sci 1970, 14, 2341.

10. Neel, J.; Nguyen, Q. T.; Clement, R.; Francois, R. in Separation of Water/Organic Liquid Mixtures by Pervaporation, Proceedings of the 2nd International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R., Ed.; Bakish Materials Corp.: Englewood, NJ, 1987; p. 35.

11. Moktari–Nejad, E.; Schneider, W. in Industrial Separation of Azeotropic Mixtures by Pervaporation, Proceedings of the Europe–Japan Congress on Membranes and Membrane Processes; Drioloi, E.; Nakagaki, M., Eds.; Plenum Press: New York, 1986; p. 573.

12. Wenzlaft, A.; Boddekar, K. W.; Hattenbach, K. J Membr Sci 1985, 22, 333.

13. Nguyen, T. Q.; Nobe, K. J Membr Sci 1987, 30, 11.

14. Lipski, C.; Cote, P. Environ Prog 1990, 9, 254.

15. Blume, I.; Wijmans, J. G.; Baker, R. W. J Membr Sci 1990, 49, 253.

16. Morigani, Y.; Kondo, M.; Kidoguchi, A. in Zero Loss Solvent Recovery, Proceedings of the 2nd International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R. Ed.; Bakish Materials Corp.: Englewood, NJ, 1987; p. 200.

17. Mulder, M. H. V.; Oude Hendrikman, J.; Hegeman, H.; Smolders, C. A. J Membr Sci 1983, 16, 269.

18. Quereshi, N.; Maddox, I. S. Biochem Biotechnol 1992, 34, 441.

19. Bengtson, G.; Buddeker, K.W.; Brockmann, V.; Hanseen, H. P. in Pervaporation of a High Boiling Lactone from a Life Fermenter, Proceedings of the 6th International Conference on Pervaporation Processes in the Chemical Industry; Bakish, R. Ed.; Bakish Materials Corp.: Englewood, NJ, 1992; p. 340.

20. Schell, W. J.; Wensley, C. G.; Chen, M. S. K.; Venugopal, K. G.; Miller, B. D.; Stuart, J. A. Gas Sep Purif 1989, 3, 162.

21. Wesslsing, M.; Werner, U.; Huang, S. T. J Membr Sci 1991, 57, 257.

22. Hoover, K. C.; Hwang, S. T. J Membr Sci 1982, 10, 253.

23. Kimura, S.; Nomura, T. J Membr Sci 1983, 8, 177.

24. Mulder, M. H. V.; Hendrikmann, J. O.; Hegeman, H.; Smolders, S. C. J Membr Sci 1983, 16, 269.

25. Hennepe, H. J. C.; Bargeman, D.; Mulder, M. H. V.; Smolders, C. A. J Membr Sci 1987, 35, 39.

26. Ishihara, K.; Kogure, R.; Matsui, K. Kobunshi Ronbunshu 1986, 43, 779; 1988, 45, 653.

27. Matsuura, T.; Tweddle, T. A.; Sourirajan, S. Ind Eng Chem Process Des Dev 1984, 23, 673.

28. Huang, R. Y. M.; Feng, X. Sep Sci Technol 1993, 28, 2035.