Polymer Bulletin 28, 683–687 (1992)

Polymer Bulletin

Permselectivities of poly(vinyl chloride) membrane for binary alcohol mixtures in pervaporation

Hiroshi Okuno[1], Koji Morimoto[1], and Tadashi Uragami[2,]*

[1]Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan
[2]Chemical Branch, Faculty of Engineering, Kansai University, Suita, Osaka 564, Japan

Summary

Permeation and separation characteristics of binary alcohol mixtures for relatively hydrophobic polymer, poly(vinyl chloride) (PVC), membrane were investigated on pervaporation. In single component measurements, it was found that small-sized alcohol had high solubility and high normalized permeation rate for the PVC membrane. In binary mixture measurements, small-sized alcohol was preferentially incorporated into the PVC membrane in all alcohol mixtures and was predominantly permeated through the membrane. It was found that the solubility and diffusivity of small-sized alcohol was higher than those of other alcohols in all systems.

Introduction

Recently, membrane technology has been developed in so many fields. Membrane separation techniques are also studied by many workers. In the field of membrane separation, pervaporation is useful for the separation and concentration of azeotropic mixtures, close-boiling point mixtures, heat-sensitive mixtures and so on (1). For an aqueous alcohol solution, hydrophilic polymers are generally used as membrane material in pervaporation in order to obtain water-permselective membranes. There are few reports relating to hydrophobic polymer membranes in pervaporation for an aqueous alcohol solution.

We previously reported that hydrophobic polymer membranes such as polystyrene (2), poly(vinyl chloride) (3) and poly(vinyl *p-tert*-butyl benzoate) (4) preferentially incorporated alcohol and predominantly permeated water from aqueous alcohol solutions in pervaporation. These results were attributed to a strong interaction between the alcohols and the hydrophobic polymers, and to the fact that water molecules are easily diffused through the hydrophobic polymer membranes because of its small molecular size.

In this report, the solubilities and permeabilities of linear C_1 to C_4-alcohols and permselectivities of various binary alcohol mixtures for poly(vinyl chloride) (PVC) membrane were studied in detail in order to clarify the permeation and separation mechanism through relatively hydrophobic polymer membranes in pervaporation.

Experimental

Preparation of membrane

The PVC (supplied from Kanegafuchi Chemical Co. Ltd., $\overline{DP}$=480) membrane was

*Corresponding author

prepared from a casting solution of 4 wt% in tetrahydrofuran at 25 °C.

Permeation measurements

Pervaporation apparatus was reported elsewhere (4). The permeation measurements were conducted under the following conditions: 40 °C of permeation temperature, 0.01 Torr of reduced pressure, 13.8 cm² of effective membrane area. The compositions in the feed and permeate were determined by gas chromatography (Shimadzu GC-9A). The permeation rate and separation factor were obtained by general method (4).

Degree of swelling

The degree of swelling of the membrane (DS) was measured by the procedure in an earlier paper (4) and calculated by following equation:

$$DS\ (\%) = \frac{W_S - W_D}{W_D} \times 100$$

where W_S and W_D are the weight of the swollen membrane and dry membrane, respectively.

Composition of alcohol in membrane

The PVC membrane was immersed in 50 wt% of a binary alcohol mixture at 40 °C. The membrane was wiped with filter paper and put on a boat of pyrolyzer (Shimadzu PYR-2A). The alcohol mixture in the PVC membrane was completely vaporized in a furnace at 250 °C. The composition of alcohol was determined by gas chromatography (Shimadzu GC-14A), connected with the pyrolyzer.

Results and discussion

Single components

The normalized permeation rates, estimated by a product of permeation rate and membrane thickness, of linear C_1 to C_4-alcohols through the PVC membrane in pervaporation are plotted against the carbon number of linear alcohols in Figure 1. The normalized permeation rate decreased with increasing the carbon number of alcohol.

Permeability is generally determined by two factors such as the solubility and diffusivity (5). The solubility is related to the affinity between polymer and permeants. The diffusivity is influenced by the size and shape of permeants and by concentration of permeants in the membrane. Table 1 is summarized the degrees of swelling of the PVC membrane for various alcohols and the space distances (Δ) between the solubility parameter of PVC and alcohols (6). The degree of swelling of the PVC membrane was in the order of methanol > ethanol > *n*-propanol > *n*-butanol. This order agreed with the order of decreasing normalized permeation rate in Figure 1. The diffusivity of large-sized alcohol in the PVC membrane is predictable to be lower than that of small-sized alcohol. The decrease of the normalized permeation rate in Figure 1 is due to both the decrease of solubility and diffusivity with the increase of the molecular size of alcohol. The order of decreasing degree of swelling cannot be simply understood because the Δ value was in the order of methanol > ethanol > *n*-propanol > *n*-butanol. That is, the affinity between PVC and *n*-butanol should become stronger and the degree of swelling for *n*-butanol should become higher than methanol if the solubility parameter can be used as a measure of affinity. The degree of swelling of the PVC membrane in Table 1 cannot be explained by the solubility parameter. The solubilities of alcohols may be dependent on the fine structure of the PVC membrane and the molecular size of alcohol. At present the solubilities of alcohols is being investigated using various PVC membranes with a different density and crystallinity.

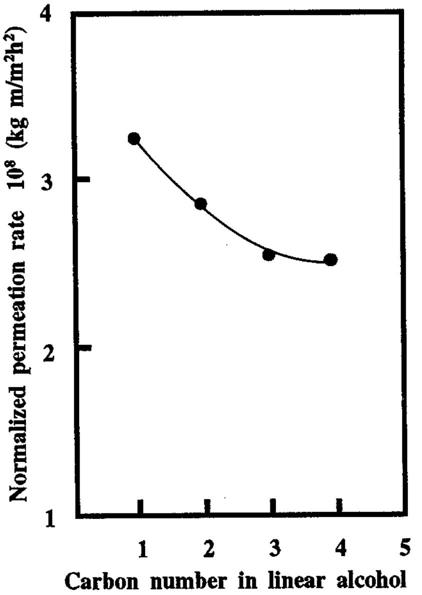

Figure 1 Relationship between the carbon number of linear alcohol and the normalized permeation rate for them through the PVC membrane in pervaporation

From the results of single components both in Figure 1 and Table 1, it was found that the normalized permeation rate for the PVC membrane decreased with the decrease of the degree of swelling of the PVC membrane. In general, the the permeation rate in pervaporation decreases with decreasing the degree of swelling of the membrane. In water/ethanol system, the permeation rate of the PVC membrane did not related to the degree of swelling which was very low in all compositions of aqueous ethanol solution (3). The degrees of swelling of the PVC membrane in Table 1 are very low for all alcohols, just as the case of PVC/aqueous ethanol solution. In the present case, it may not be considered that the effect of swelling of the PVC membrane significantly contributes to the permeation rate.

Table 1 Degree of swelling (DS) of the PVC membrane and the space distances (Δ) between the solubility parameter vectors of PVC and alcohols

	methanol	ethanol	*n*-propanol	*n*-butanol
DS (%)	5.4	4.2	3.0	2.3
Δ [a] (MPa)$^{0.5}$	19.7	16.6	14.9	13.7

a) $\Delta = [(\delta_{D,s} - \delta_{D,p})^2 + (\delta_{P,s} - \delta_{P,p})^2 + (\delta_{H,s} - \delta_{H,p})^2]^{0.5}$

Table 2 Preferential adsorption into the PVC membrane from the binary alcohol mixtures (50/50 in wt.)

	methanol	ethanol	*n*-propanol	*n*-butanol
methanol	——	methanol(64.6)	methanol(69.9)	methanol(72.0)
ethanol		——	ethanol(56.2)	ethanol(61.3)
n-propanol			——	*n*-propanol(57.7)
n-butanol				——

Values in parentheses are the alcohol content preferentially incorporated into the PVC membrane (wt%)

Binary mixtures

The compositions of alcohol incorporated preferentially into the PVC membrane are summarized in Table 2. In methanol/other alcohol systems, methanol was preferentially incorporated into the PVC membrane. Preferential adsorption of methanol in methanol/*n*-butanol system was the highest in all methanol/alcohol systems. This result is presumable from the degree of swelling of the PVC membrane for the single component measurement in Table 1.

Sorption selectivity (α_{sorp}) (8) and separation factor (α_{sep}) (ordinary selectivity) in the methanol/other alcohol systems are listed in Table 3. The sorption selectivities were calculated using the data of Table 2. This parameter shows the selectivity at the surface of the membrane on the upstream side. Comparing the sorption selectivity with the separation factor indirectly provides an information of diffusivity selectivity through the membrane. It is clear that the separation factor is higher than the sorption selectivity. This implies that the diffusivity of methanol in the PVC membrane is higher than those of other alcohols. Namely, high solubility and diffusivity of methanol result in preferential permeation of methanol in the methanol/other alcohol systems.

In our previous work (3), it was found that the PVC membrane preferentially incorporated ethanol and predominantly permeated water from an aqueous ethanol solution. This result showed that the solubility of ethanol for the PVC was higher than that of water but the

Table 3 Sorption selectivities and separation factors of the PVC membrane for the methanol/other alcohol systems

	α_{sorp}	α_{sep}
methanol/ethanol	1.8	2.0
methanol/*n*-propanol	2.3	2.6
methanol/*n*-butanol	3.5	5.0

$\alpha_{sorp} = (M_A/M_B)/(F_A/F_B)$, $\alpha_{sep} = (P_A/P_B)/(F_A/F_B)$,
where F, M and P are the composition of one component in the feed, membrane and permeate, respectively.

diffusivity of water across the PVC membrane was much higher than that of ethanol. Consequently, the PVC membrane predominantly permeated water from an aqueous ethanol solution. The permeation and separation mechanism for the water/ethanol system through the PVC membrane is different from that for the methanol/other alcohol systems. However, it is a fact that high diffusivity of the small-sized permeant contributes to the permselectivity through the PVC membrane in both the water/ethanol and methanol/other alcohol systems.

The solubility selectivity and separation factor for the ethanol/*n*-propanol and ethanol/*n*-butanol systems are listed in Table 4. The separation factor for ethanol were somewhat higher than the sorption selectivity. This result shows that the diffusivity of ethanol is higher than those of *n*-propanol and *n*-butanol.

In binary alcohol mixtures, the permselectivities of small-sized alcohol through the PVC membrane are decided by two positive factors such as preferential solubility and predominant diffusivity of small-sized alcohol. The permeation and separation mechanisms of the PVC membrane in binary alcohol mixtures are different from those in aqueous alcohol mixtures. However, it was found that the permeability and selectivity of the PVC membrane was significantly affected by the molecular size of permeants.

Table 4 Sorption selectivities and separation factors of the PVC membrane for the ethanol/other alcohol systems

	α_{sorp}	α_{sep}
ethanol/*n*-propanol	1.3	1.4
ethanol/*n*-butanol	1.5	1.7

Acknowledgments

This work was supported by The Science Research Promotion Fund in Japan Private School Promotion Foundation.

References

1. Neel J, Aptel P, Clement R (1985) *Desalination* **53**: 297
2. Uragami T, Morikawa T (1989) *Makromol. Chem.* **190**: 399
3. Uragami T, Morikawa T, Okuno H (1989) *Polymer* **30**: 1117
4. Okuno H, Tsuchioka M, Uragami T (1990) *Sen-i Gakkaishi* **46**: 367
5. Crank J, Park GS (1968) Diffusion in Polymers Academic Press, New York, Chap. 1
6. Brandrup J, Immergut EH (1989) Polymer Handbook (3ed) Willey, New York, VII/519
7. Mulder MHV, Smolders CA (1991) *Sep. Sci. Technol.* **26**: 85

Accepted May 6, 1992 S