

PERVAPORATION OF ORGANIC LIQUID-WATER MIXTURES THROUGH SUBSTITUTED POLYACETYLENE MEMBRANES

TOSHIO MASUDA, MUNEHIRO TAKATSUKA, BEN-ZHONG TANG and TOSHINOBU HIGASHIMURA

Department of Polymer Chemistry, Kyoto University, Kyoto 606 (Japan)

(Received March 14, 1989; accepted in revised form August 18, 1989)

Summary

A poly[1-(trimethylsilyl)-1-propyne] [poly(TMSP)] membrane proved highly permselective for ethanol in EtOH-H₂O pervaporation, where the separation factor, $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$, reached 17 at 10 wt.% of ethanol in the feed. This value is similar to that for poly(dimethylsiloxane), a well-known ethanol-permselective membrane. Because of membrane swelling, the $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ value decreased and the total specific permeation rate increased with increasing ethanol content in the feed. In the pervaporation of combinations of water and various organic liquids through poly(TMSP), the $\alpha_{\text{H}_2\text{O}}^{\text{org.liq}}$ values for acetonitrile and acetone exceeded 70 at $\approx 10\%$ of organic liquid in the feed. In the EtOH-H₂O pervaporation through various substituted polyacetylene membranes, aliphatic polymers {e.g., poly[1-(n-hexyldimethylsilyl)-1-propyne] and poly(1-chloro-1-octyne)} showed more or less ethanol permselectivity, while aromatic polymers [e.g., poly(1-chloro-2-phenylacetylene) and poly(1-phenyl-1-propyne)] were rather water-permselective.

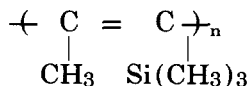
Introduction

Pervaporation is a process involving permeation of liquid(s) through a membrane and subsequent evaporation of liquid(s). This process has been attracting increasing attention as a method for separating liquid mixtures, especially those with close boiling points [1-3].

From a practical viewpoint, pervaporation would be useful for concentration of ethanol from dilute aqueous solutions (<10%) obtained by the fermentation of biomass. The membranes for this purpose may be either ethanol-permselective or water-permselective. Many polymer membranes permeate water preferentially, whereas only a few membranes are ethanol-permselective; examples of the latter include poly(dimethylsiloxane) [poly(DMS)] [4-6], FT30 (composition unpublished) [7], poly(DMS) graft copolymers [8], poly(DMS) block copolymers [9], and poly(styrene-co-methacrylate)s [10].

We have recently succeeded in the synthesis of new high molecular weight polymers from substituted acetylenes using group V and VI transition metal catalysts [11,12]. In our preliminary experiments on the EtOH-H₂O perva-

poration through substituted polyacetylenes, it was found that the permselectivity of membranes greatly depended on the kind of substituents [13,14]. In particular, poly[1-(trimethyl-silyl)-1-propyne] [poly(TMSP)] showed a high ethanol permselectivity similar to that of poly(DMS), which had been known as a representative ethanol-permselective membrane. The ethanol permselectivity of poly(TMSP) was also found independently by two other research groups [15,16].



poly(TMSP)

The present paper is concerned with a detailed study on the behavior of poly(TMSP) membrane in the pervaporation of aqueous ethanol solution, as well as of other organic liquid-H₂O mixtures. The separation behavior of various substituted polyacetylenes in the EtOH-H₂O pervaporation is also discussed.

Experimental

Polymer synthesis

Substituted polyacetylenes were synthesized according to the literature methods [11, 17-20]. Table 1 lists the kind of polymers, polymerization conditions and molecular weight data. Polymer yields were determined by gravimetry. The weight-average molecular weights (\bar{M}_w) and polydispersity ratios (\bar{M}_w/\bar{M}_n) of the polymers were determined by gel permeation chromatography (GPC) using a Jasco Trirotar chromatograph (Shodex A804, A806 and A807 polystyrene gel columns; eluent CHCl₃; \bar{M}_w and \bar{M}_n calculated on the basis of a polystyrene calibration).

TABLE 1

Synthesis of substituted polyacetylenes

-(CR=CR')_n		Catalyst	Polymeri- zation conditions ^a	Yield (%)	$\bar{M}_w^b \times 10^{-3}$	\bar{M}_w/\bar{M}_n^b	Ref.
R	R'						
Me	SiMe ₃	TaCl ₅	A	100	1100	2.8	16
Me	SiMe ₂ -n-C ₆ H ₁₃	TaCl ₅ -Ph ₃ Bi	A	75	1200	1.8	17
Me	SiMe ₂ CH ₂ SiMe ₃	TaCl ₅	A	100	1200	3.3	18
Cl	n-C ₆ H ₁₃	MoCl ₅ -n-Bu ₄ Sn	B	90	800	2.2	19
Cl	Ph	MoCl ₅ -n-Bu ₄ Sn	B	90	750	2.7	10
Me	Ph	TaCl ₅ -n-Bu ₄ Sn	A	70	1400	2.5	10

^aPolymerized in toluene for 24 hr, $[M]_0 = 1.0 M$, $[\text{Cat}] = [\text{Cocat}] = 20 \text{ mM}$; A, at 80°C; B, at 30°C.

^bDetermined by GPC on the basis of a polystyrene calibration.

Membrane preparation

Membranes were prepared by casting the polymers from toluene solution (2–5%). Polymer solutions were poured onto a glass plate and spread out with a scalpel. The solvent was evaporated slowly at room temperature over a few days, and the occluded solvent was then removed as perfectly as possible by keeping the membranes in a vacuum drying oven at room temperature for a further few days. This procedure gave homogeneous membranes with uniform thickness. The membrane thickness was measured by a micrometer and, unless otherwise specified, was around 30 μm . To prepare thicker membranes (thickness > 100 μm), polymer solutions were poured into a flat-bottomed petri dish, and the solvent was removed as described above.

Pervaporation procedures

Figure 1 illustrates a schematic diagram of an apparatus for pervaporation experiments. The system is composed of a feed solution in a temperature-controlled bath, a membrane permeation apparatus (Model GTR-11L, Yanagimoto Co., Japan), a gas chromatograph (GC; Model GC4B, Shimadzu, Co., Japan), a Pirani gauge, and a vacuum pump. The direct connection of the permeation apparatus and the GC permitted the use of a very small sample size (≈ 1 mg) and the exclusion of moisture.

Mixtures of deionized water and anhydrous ethanol (special grade, Wako Ltd., Japan) were used as feeds. Membranes were immersed in the feed at room temperature for one day before use. The membrane was then mounted onto the cell (stainless steel; effective permeation area 9.62 cm^2); a piece of filter paper was placed between the membrane and the porous stainless steel plate of the cell in order to prevent breakage of the membrane. The feed solution

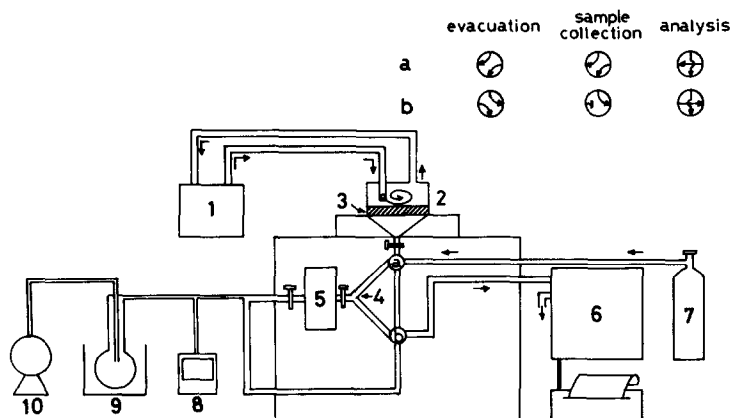


Fig. 1. Schematic diagram of pervaporation apparatus. 1: temperature-controlled feed, 2: pervaporation cell, 3: membrane, 4: permeate collector, 5: supplementary tank, 6: gas chromatograph, 7: carrier gas cylinder, 8: Pirani gauge, 9: cold trap, 10: vacuum pump.

was circulated between the thermostatted bath (1 L, usually at 30°C) and the upstream side of the membrane in the cell. The path of the permeate vapor was maintained at 120°C to avoid condensation. After a short period of thermal equilibration, the downstream compartments were evacuated to 0.1 mmHg, and a steady state was reached after ca. 6 hr. By turning valves a and b, aliquots of the permeate were taken in the permeate collector (volume 3.57 mL) for given periods, typically 30, 60 and 90 sec. In the case of a large permeate flux, the supplementary tank (volume 500 mL) was also used. The collected samples were routed directly to the GC [column: Porapak Q (50–80 mesh), Waters Associates, Inc., USA, 3 m; column temp. 85°C; thermal conductivity detector]. The amount and composition of the permeate were determined from the GC peaks by use of calibration curves.

The performance of membranes in EtOH–H₂O pervaporation was evaluated by the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) and the total specific permeation rate (R_{total}). Specific permeation rates for the components (R_{EtOH} and $R_{\text{H}_2\text{O}}$) were calculated when necessary. $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ is defined by eqn. (1), where X_{EtOH} and Y_{EtOH} are the weight fractions of ethanol in the feed and in the permeate, respectively. The specific permeation rates are expressed by eqns. (2)–(4), where F_{total} , F_{EtOH} and $F_{\text{H}_2\text{O}}$ denote the collected amounts of the whole permeate, ethanol and water in grams, and θ , a and t are membrane thickness (m), membrane area (m²) and time (hr), respectively.

$$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}} \equiv \frac{Y_{\text{EtOH}}/(1 - Y_{\text{EtOH}})}{X_{\text{EtOH}}/(1 - X_{\text{EtOH}})} \quad (1)$$

$$R_{\text{total}} \equiv \frac{F_{\text{total}} \theta}{at} \quad (2)$$

$$R_{\text{EtOH}} \equiv \frac{F_{\text{EtOH}} \theta}{at} \quad (3)$$

$$R_{\text{H}_2\text{O}} \equiv \frac{F_{\text{H}_2\text{O}} \theta}{at} \quad (4)$$

Sorption experiment

A dry, weighed membrane (≈ 200 mg) was soaked in an EtOH–H₂O mixture at 30°C for one day, and the swollen membrane was wiped with a piece of tissue paper to remove the adherent solvent, then weighed again. The degree of swelling (DS) was determined by eqn. (5):

$$\text{DS} \equiv \left(\frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}} - 1 \right) \times 100 (\%) \quad (5)$$

The EtOH–H₂O composition in a swollen membrane was determined as follows. A small piece (dry weight ≈ 30 mg) of swollen membrane was cut out

and placed in the closed cell of the membrane permeation apparatus, and the permeate collector was evacuated. The ethanol and water in the membrane were evaporated by opening the valves between the cell and the permeate collector, and then the vapor was directly sent to the GC for determination of the EtOH-H₂O ratio.

Vapor permeation experiment

Nitrogen was bubbled into the EtOH-H₂O feed kept at 30°C, and the vapor evolved was introduced into the membrane permeation apparatus along with nitrogen as a carrier gas. The composition of the permeate was determined in the same way as in the pervaporation experiment.

Results and discussion

EtOH-H₂O pervaporation through poly(TMSP)

Effect of feed composition

The effect of feed composition on the EtOH-H₂O pervaporation through poly(TMSP) was studied under the following operating conditions: membrane thickness 30 μm, feed temperature 30°C, downstream pressure 0.1 mmHg.

As seen in Fig. 2(a), the permeate composition curve stays above the diagonal, indicating the ethanol permselectivity of poly(TMSP) in the whole range of feed composition. It deserves special attention that, even for the 10 wt% feed solution, the ethanol content in the permeate reaches ca. 65 wt%.

The separation factor $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ sharply increased with decreasing ethanol content in the feed [Fig. 2(a)] to give $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}} = 17$ at 10 wt% ethanol (the value was reproducible at 17 ± 2 in several replicated runs). The value in our previous

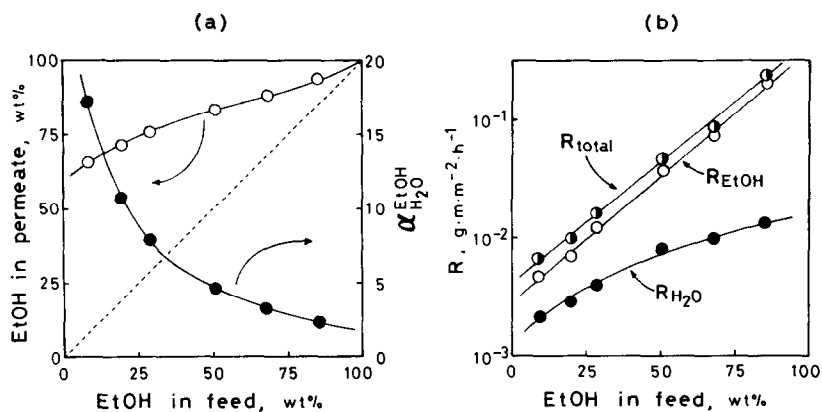


Fig. 2. Permeate composition curve, and $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R values as functions of feed composition in EtOH-H₂O pervaporation through poly(TMSP) (30°C, 0.1 mmHg).

communication [13] was 12, which was obtained by the method of collecting the permeate in a cold trap and determining the permeate amount by gravimetry. We believe that the present $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ value is more accurate because moisture condensation can be avoided. The present value of 17 is similar to or somewhat larger than that for poly(DMS) [4-6]. The high $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ values at low ethanol contents show that the poly(TMSP) membrane is suitable for concentrating ethanol from dilute aqueous solutions.

The total specific permeation rate (R_{total}) was $(7.1 \pm 2.0) \times 10^{-3} \text{ g}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ at 10% ethanol in the feed, and it increased with increasing ethanol content [Fig. 2(b)]. This is attributable to swelling of the poly(TMSP) membrane by ethanol (see below). Furthermore, not only the specific permeation rate for ethanol (R_{EtOH}) but also that for water ($R_{\text{H}_2\text{O}}$) increased monotonically with ethanol content in the feed. Clearly, this increase in $R_{\text{H}_2\text{O}}$ results in the decrease in $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ at higher ethanol feeds.

Effect of operating conditions

Effects of operating conditions were examined at an ethanol content of 10 wt% in the feed with use of membranes that had been immersed in the feed at room temperature for one day in advance. Figure 3 shows variations of $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} with operating time. For the initial few hours, $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ increased slightly, and R_{total} decreased a little; this suggests that a steady state has not been completely attained. After 5 hr and subsequently, however, both $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} appear to be constant within experimental error. This means that the swelling of the membrane reaches an equilibrium in ca. 5 hr if the membrane is pre-treated with the EtOH-H₂O feed for one day. The data in the present study were therefore obtained for operating times longer than 6 hr.

The effect of membrane thickness was also examined (Fig. 4). As the membrane was thickened, $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ gradually increased, whereas R_{total} remained virtually unchanged. The constancy of R_{total} implies that the flux of permeate is inversely proportional to the membrane thickness. Therefore, if one requires

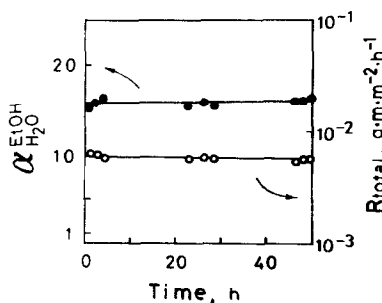


Fig. 3. Time dependence of EtOH-H₂O pervaporation through poly(TMSP) (EtOH 10wt%, 30°C, 0.1 mmHg).

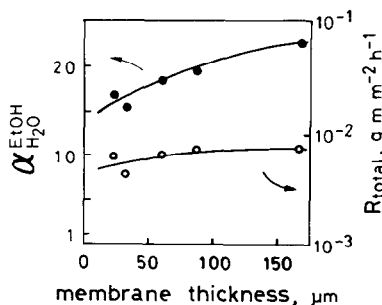


Fig. 4. Effect of membrane thickness on EtOH-H₂O pervaporation through poly(TMSP) (EtOH 10 wt%, 30°C, 0.1 mmHg).

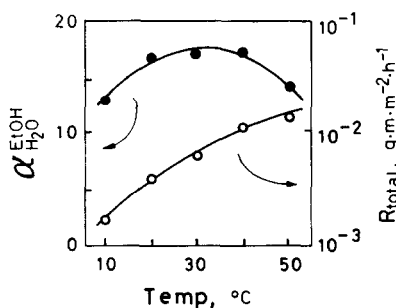


Fig. 5. Effect of feed temperature on EtOH-H₂O pervaporation through poly(TMSP) (EtOH 10 wt%, 0.1 mmHg).

a large flux, the membrane should be made thinner. Unlike the case of poly(DMS), the preparation of a thin membrane of poly(TMSP) is quite easy because the polymer is glassy at room temperature [11].

Concerning the effect of feed temperature, the $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ value showed a maximum of 17 around 30°C (Fig. 5). In contrast, R_{total} increased monotonically with increasing temperature, under which conditions the membrane swells more and, in turn, the diffusivity of both ethanol and water increases. This swelling should be responsible for the monotonic increase of R_{total} with temperature, and might be associated with the convexity of the curve of $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ to temperature axis.

Even when the downstream pressure was varied over a wide range from 0.01 to 100 mmHg, $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ had a practically constant value (Fig. 6); R_{total} was also approximately independent of downstream pressure if the pressure was lower than 10 mmHg. However, R_{total} decreased sharply above 10 mmHg. Since the downstream pressures above 10 mmHg are comparable with the partial pressures of ethanol and water at 30°C (EtOH 79 mmHg; H₂O 32 mmHg), evaporation of these liquids from the membrane surface should be suppressed under such high pressures.

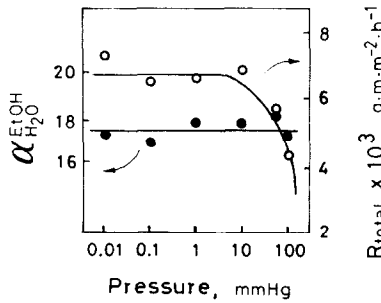


Fig. 6. Effect of downstream pressure on EtOH-H₂O pervaporation through poly(TMSP) (EtOH 10 wt.%, 30°C).

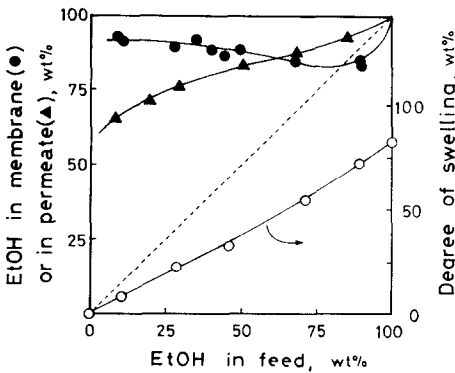


Fig. 7. Sorption behavior of poly(TMSP) for EtOH-H₂O mixtures (30°C); pervaporation data (▲) from Fig. 2(a).

Sorption behavior

Figure 7 illustrates effects of feed composition on the composition of sorbed EtOH-H₂O mixtures and on the degree of swelling of the poly(TMSP) membrane. Irrespective of feed composition, the ethanol content in the membrane was 80 wt% and above (filled circles), indicating a high selectivity for ethanol sorption. The degree of swelling was negligible in water alone, and increased roughly in proportion to the ethanol content in the feed (open circles). These findings mean that the poly(TMSP) membrane has a fairly strong affinity for ethanol but not for water. The rather anomalous composition curve for sorption suggests that much water is sorbed when the membrane swells enough in the presence of a large amount of ethanol.

Regarding the relationship between pervaporation and sorption, the following considerations are possible. (i) A high ethanol permselectivity was observed at low ethanol contents in the feed. It is reasonable to assume that the permselectivity becomes higher with decreasing membrane swelling. (ii) R_{total}

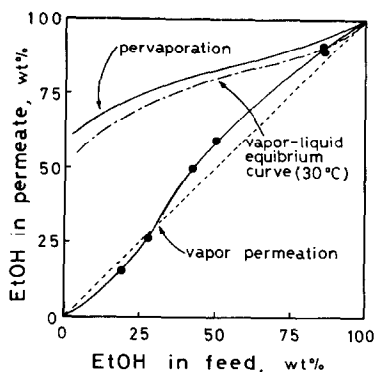


Fig. 8. Permeate composition curve in EtOH-H₂O vapor permeation through poly(TMSP) (30°C).

increased with increasing ethanol content in the feed. This result is explainable on the ground that the swelling of membrane is caused mainly by ethanol.

Vapor permeation

Pervaporation comprises solution, diffusion and vaporization of liquid(s), involving a phase change from liquid to gas on the membrane surface. On the other hand, vapor permeation, where a vapor mixture permeates a membrane, consists of sorption, diffusion and desorption, involving no liquid phase, and accordingly the effect of membrane swelling is smaller than in pervaporation.

With poly(TMSP) membranes, as seen in Fig. 8, the ethanol content in the permeate was close to that in the feed vapor, irrespective of feed composition. In vapor permeation ethanol is more easily sorbed in the membrane than water, but diffuses less easily; this seems to result in the low permselectivity in vapor permeation. Besides these factors, the high volatility of ethanol compared with water should favor ethanol permselectivity in pervaporation. If the vapor-liquid equilibrium is taken into account in vapor permeation (the dotted-dashed line, Fig. 8), the permeate composition closely resembles that in pervaporation.

Pervaporation of various organic liquid-H₂O mixtures through poly(TMSP)

Figure 9 depicts permeate composition curves for the pervaporation of several combinations of organic liquids with water through poly(TMSP). All the composition curves lie above the diagonal, indicating that the poly(TMSP) membrane allows these organic liquids to permeate in preference to water.

Particular data for low organic liquid contents in the feed for acetonitrile and acetone are as follows: CH₃CN (7%)-H₂O (93%) in the feed, $\alpha_{\text{H}_2\text{O}}^{\text{CH}_3\text{CN}} = 101$, $R_{\text{total}} = 6.6 \times 10^{-2} \text{ g-m-m}^{-2}\text{-hr}^{-1}$, CH₃CN 88% in the permeate; (CH₃)₂CO (10%)-H₂O (90%) in the feed, $\alpha_{\text{H}_2\text{O}}^{(\text{CH}_3)_2\text{CO}} = 76$, $R_{\text{total}} = 6.5 \times 10^{-2} \text{ g-m-m}^{-2}\text{-hr}^{-1}$, (CH₃)₂CO 89% in the permeate. Thus, it is quite interesting to note that the contents of acetonitrile and acetone in the permeate are over 85

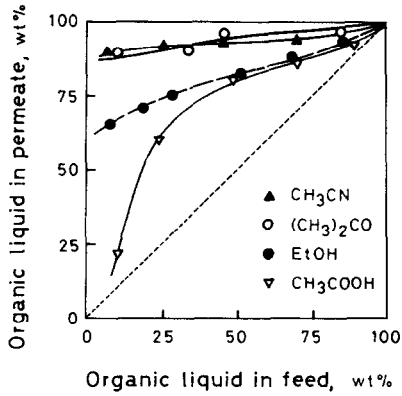


Fig. 9. Permeate composition curves in organic liquid-H₂O pervaporation through poly(TMSP) (30°C, 0.1 mmHg).

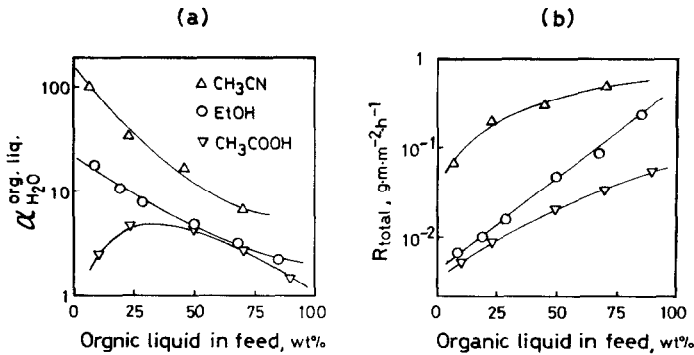


Fig. 10. $\alpha_{\text{H}_2\text{O}}^{\text{org.liq.}}$ and R_{total} as functions of feed composition in organic liquid-H₂O pervaporation through poly(TMSP) (30°C, 0.1 mmHg).

wt% even if their contents in the feed are as low as ca. 10 wt%. Further, it should be noted that the R_{total} values in these systems are almost 10 times as large as those in the EtOH-H₂O system.

The permselectivity for acetic acid as organic liquid is similar to the case of ethanol with high acetic acid contents in the feed, but is lower at lower contents in the feed (Fig. 9). This unusual shape of the composition curve may be associated with a change in the proportion of dimeric and monomeric forms of acetic acid with feed composition.

Figure 10(a) presents data on the dependence of $\alpha_{\text{H}_2\text{O}}^{\text{org.liq.}}$ on feed composition in the CH₃CN-H₂O and CH₃COOH-H₂O systems. In the case of acetonitrile, the $\alpha_{\text{H}_2\text{O}}^{\text{CH}_3\text{CN}}$ value at ca. 10 wt% CH₃CN in the feed is nearly 100, showing a very high permselectivity. The $\alpha_{\text{H}_2\text{O}}^{\text{CH}_3\text{CN}}$ value sharply decreases, however, with

increasing acetonitrile content in the feed, which is a tendency analogous to that for ethanol. In contrast, the $\alpha_{\text{H}_2\text{O}}^{\text{CH}_3\text{COOH}}$ value shows a unique dependence on feed composition, which possesses a maximum.

As apparent in Fig. 10(b), the R_{total} of the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ system is much larger than that of the $\text{EtOH}-\text{H}_2\text{O}$ system. This can be attributed to the stronger affinity of acetonitrile to the membrane and, in turn, to its capability of swelling the membrane. The increase of R_{total} with increasing content of organic liquid in the feed proves to be a general tendency for all the combinations of organic liquid and water employed in this study.

In general, the $\alpha_{\text{H}_2\text{O}}^{\text{org.liq.}}$ and R_{total} values depend on the following three factors concerning the nature of the organic liquid: (i) affinity to the membrane, (ii) bulkiness of the molecule, and (iii) vapor pressure. These factors correlate with the solution, diffusion and vaporization, respectively, in pervaporation. The large $\alpha_{\text{H}_2\text{O}}^{\text{org.liq.}}$ and R_{total} values observed with acetonitrile and acetone can be attributed mainly to factor (i). In the case of acetone, which has a low boiling point, upstream vapor pressure may also have some effect.

Ethanol-H₂O pervaporation through various substituted polyacetylenes

Figure 11 is a plot of $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ versus R_{total} for various substituted polyacetylenes and several conventional polymers at an ethanol content of 50 wt% in the feed. The $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ values smaller than unity means that the membrane allows water to permeate preferentially.

Most of the conventional polymer membranes with high permselectivity are

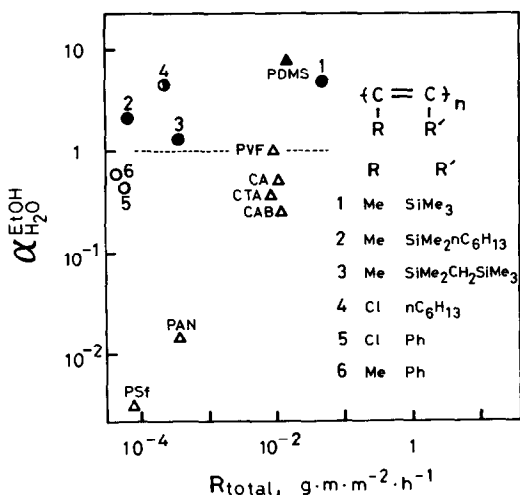


Fig. 11. Plot of $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}-R_{\text{total}}$ in $\text{EtOH}-\text{H}_2\text{O}$ pervaporation through substituted polyacetylenes and some conventional polymers (EtOH 50 wt%, 30°C). PDMS: poly (DMS), PVF: poly (vinylidene fluoride), CA: cellulose acetate, CTA: cellulose triacetate, CAB: cellulose acetate butyrate, PAN: poly (acrylonitrile), PSf: poly (sulfone). Data for conventional polymers from Refs. [1] and [2].

water-permselective. As mentioned in the Introduction, the number of ethanol-permselective polymers so far known is restricted, and of them poly(DMS) is a typical example.

One can see from Fig. 11 that poly(TMSP) exhibits the largest values for both $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} values among the substituted polyacetylenes examined. Other heteroatom-containing aliphatic polyacetylenes (samples 2-4) also tend to permeate ethanol preferentially. In contrast, aromatic polyacetylenes (samples 5 and 6) exhibit some water permselectivity, and their R_{total} values are quite small.

It is noteworthy that the points for poly(TMSP) and poly(DMS) in Fig. 11 are very close to each other. This is quite interesting if it is taken into account that these polymers are appreciably different in physical properties [e.g., poly(TMSP) is glassy at room temperature, while poly(DMS) is rubbery].

Silicon-containing polyacetylenes

It seems of interest to examine the pervaporation behavior of other Si-containing polyacetylenes for the purpose of helping clarify the high ethanol permselectivity of poly(TMSP). As seen in Fig. 12, two analogues of poly(TMSP) with a longer and/or bulkier substituent $\{-\text{CMe}=\text{C}(\text{SiMe}_2\text{R})-\}_n$; $\text{R}=\text{n-C}_6\text{H}_{13}$, CH_2SiMe_3 were essentially ethanol-permselective, but their selectivities were lower than that of poly(TMSP).

The $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ values of the two analogues were no more than one-fifth that of poly(TMSP), irrespective of feed composition [Fig. 13(a)]. The $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ values of these polymers also decrease with increasing ethanol content in the feed. Further, the R_{total} values of the two poly(TMSP) analogues are much smaller than that of poly(TMSP) [Fig. 13(b)]. The tendency for R_{total} to increase with increasing EtOH content in the feed is, however, just the same as in poly(TMSP).

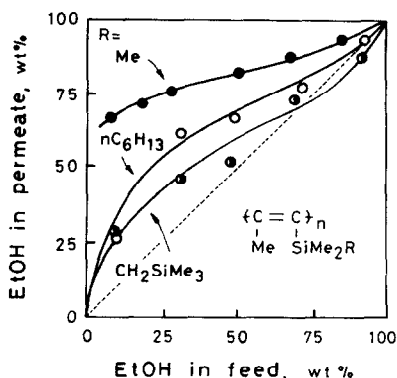


Fig. 12. Permeate composition curves in EtOH-H₂O pervaporation through Si-containing polyacetylenes (30°C, 0.1 mmHg).

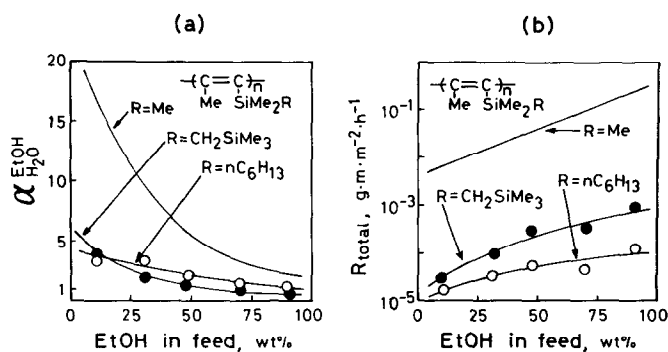


Fig. 13. $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} as functions of feed composition in EtOH-H₂O pervaporation through Si-containing polyacetylenes (30°C, 0.1 mmHg).

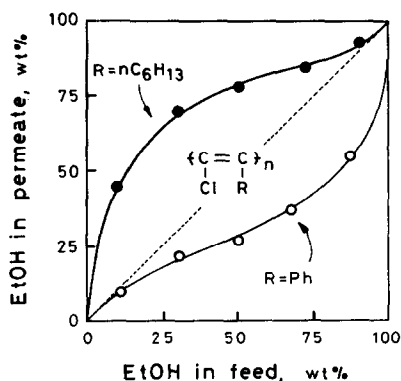


Fig. 14. Permeate composition curves in EtOH-H₂O pervaporation through Cl-containing polyacetylenes (30°C, 0.1 mmHg).

The above results lead one to the following conclusions: (i) there is no direct correlation between the Si content in the polymer and the values of $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} ; (ii) since the affinities of ethanol to these three polymers are not very different from one another, the large differences in their $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} values are thought to stem from the membrane structure; (iii) the large $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} of poly(TMSP) might be attributed to high diffusivity of ethanol and water, especially of the former, owing to the sparse supramolecular structure of poly(TMSP); (iv) the gas permeability of these polymers [21] corresponds to their pervaporation behavior, and is also explainable in terms of their supramolecular structures.

Chlorine-containing polyacetylenes

Figure 14 illustrates permeate composition curves for two Cl-containing polyacetylenes, viz., poly(1-chloro-1-octyne) and poly(1-chloro-2-phenylacety-

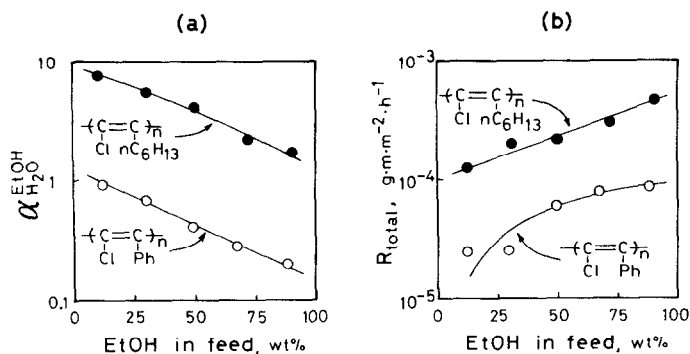


Fig. 15. $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ and R_{total} as functions of feed composition in EtOH-H₂O pervaporation through Cl-containing polyacetylenes (30 °C, 0.1 mmHg).

lene). It is clear that poly(1-chloro-1-octyne) is ethanol-permselective, whereas poly(1-chloro-2-phenylacetylene) is water-permselective. Not only poly(1-chloro-2-phenylacetylene), but also other aromatic polyacetylenes like poly(1-phenyl-1-propyne), allow water to permeate preferentially. These results might be attributed to the less hydrophobic nature and/or the more stacked (denser) structure of the aromatic polyacetylenes.

The $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ of poly(1-chloro-1-octyne) is fairly large, 7.5 at 10 wt% ethanol in the feed [Fig. 15 (a)]. The value decreases with increasing EtOH content in the feed. The $\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$ of poly(1-chloro-2-phenylacetylene) was close to unity at low EtOH contents in the feed, but fell to ca. 0.2 at 90% EtOH. As seen in Fig. 15(b), the R_{total} values increased with increasing EtOH content in the feed, which is a tendency similar to those for other polyacetylenes. It is noted that the permeation rates for these Cl-containing polyacetylenes are much smaller than that for poly(TMSP).

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Functionality Materials – Design, Preparation and Control" from the Ministry of Education, Science and Culture, Japan (No. 63,604,560).

References

1. I. Frennsson, G. Trägårdh and B. Hahn-Hägerdal, Pervaporation and ethanol upgrading – a literature review, *Chem. Eng. Commun.*, 45 (1986) 277.
2. S.-T. Hwang and K. Kammermeyer, Pervaporation, in: *Membranes in Separations (Techniques of Chemistry, Vol. II)*, Wiley-Interscience, New York, NY, 1975, Chap. 7.

- 3 W.J. Koros, G.K. Fleming, S.M. Jordan, T.H. Kim and H.H. Hoehn, Polymeric membrane materials for solution-diffusion based permeation separations, *Prog. Polym. Sci.*, 13 (1988) 339.
- 4 H. Eustache and G. Histi, Separation of aqueous organic mixtures by pervaporation and analysis by mass spectrometry or a coupled gas chromatograph-mass spectrometer, *J. Membrane Sci.*, 8 (1981) 105.
- 5 K.C. Hoover and S.-T. Hwang, Pervaporation by a continuous membrane column, *J. Membrane Sci.*, 10 (1982) 253.
- 6 S. Kimura and T. Nomura, Pervaporation of alcohol-water mixtures with silicone rubber membrane, *Maku (Membrane)*, 7 (1982) 353.
- 7 P. Schissel and R.A. Orth, Separation of ethanol-water mixtures by pervaporation through thin, composite membranes, *J. Membrane Sci.*, 17 (1984) 109.
- 8 K. Ishihara, R. Kogure and K. Matsui, Separation of ethanol through styrene-dimethylsiloxane graft copolymer membranes by pervaporation, *Kobunshi Ronbunshu*, 43 (1986) 779.
- 9 K. Okamoto, A. Butsuen, S. Tsuru, S. Nishioka, K. Tanaka, H. Kita and S. Asakawa, Pervaporation of water-ethanol mixtures through polydimethylsiloxane block copolymer membranes, *Polym. J.*, 19 (1987) 747.
- 10 M. Yoshikawa, T. Ohsawa, M. Tanigaki and W. Eguchi, Application and development of synthetic polymer membranes. I. Separation of aqueous ethanol mixture by pervaporation through common polymer membranes containing methacrylic esters, *J. Polym. Sci., Part C, Polym. Lett.*, 26 (1988) 89.
- 11 T. Masuda and T. Higashimura, Polyacetylenes with substituents: their synthesis and properties, *Adv. Polym. Sci.*, 81 (1986) 121.
- 12 T. Masuda and T. Higashimura, Silicon-containing polyacetylenes: synthesis and properties, in: G. Fearon and J. Zeigler (Eds.), *Silicon-Based Polymer Science*, *Adv. Chem. Ser. No. 224*, American Chemical Society, Washington, DC, 1990, Chap. 35.
- 13 T. Masuda, B.-Z. Tang and T. Higashimura, Ethanol-water separation by pervaporation through substituted-polyacetylene membranes, *Polym. J.*, 18 (1986) 565.
- 14 For a review, see T. Masuda, Permeation of gases and liquids through membranes of substituted polyacetylenes (in Japanese), *Maku (Membrane)*, 13 (1988) 195.
- 15 K. Ishihara, Y. Nagase and K. Matsui, Pervaporation of alcohol/water mixtures through poly[1-(trimethylsilyl)-1-propyne] membrane, *Makromol. Chem., Rapid Commun.*, 7 (1986) 43.
- 16 Y. Fusaoka, E. Imazu and N. Kawabe, Ethanol-water separation by pervaporation through poly(substituted acetylene) membranes, *Abstracts 51st Autumnal Meet. Chem. Soc. Jpn.*, 1985, 3A2-15.
- 17 T. Masuda, E. Isobe and T. Higashimura, Polymerization of 1-(trimethylsilyl)-1-propyne by halides of niobium(V) and tantalum(V) and polymer properties, *Macromolecules*, 18 (1985) 841.
- 18 T. Masuda, E. Isobe, T. Hamano and T. Higashimura, Polymerization of silicon-containing acetylenes. 5. Polymerization of 1-silyl-1-propynes by TaCl₅-based catalysts, *J. Polym. Sci., Part A, Polym. Chem.*, 25 (1987) 1353.
- 19 E. Isobe, T. Masuda, T. Higashimura and A. Yamamoto, Polymerization of 1-(trimethylsilyl)-1-propyne homologs containing two silicon atoms by tantalum- and niobium-based catalysts, *J. Polym. Sci., Part A, Polym. Chem.*, 24 (1986) 1839.
- 20 T. Masuda, T. Yoshimura, K. Tamura and T. Higashimura, Synthesis and properties of poly(1-chloro-1-alkynes), *Macromolecules*, 20 (1987) 1734.
- 21 T. Masuda, Y. Iguchi, B.-Z. Tang and T. Higashimura, Diffusion and solution of gases in substituted polyacetylene membranes, *Polymer*, 29 (1988) 2041.