Permeation and Separation of Aqueous Alcohol Solutions through Grafted Poly(vinyl Alcohol) Latex Membranes

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Synopsis

The poly(vinyl alcohol)–acrylonitrile–2-hydroxy ethyl methacrylate (PVA–AN–HEMA) grafted latex membrane was synthesized by grafting AN and HEMA mixture on PVA in aqueous solution. The ceric ammonium nitrate in nitric acid was used as a catalyst. This membrane has well-balanced composition of hydrophilic and hydrophobic components and was proved by transition electron microscopy to process microstructure between continuous and disperse phases. The permeability of alcohol–water solution and separativity of phenol–water solution through this PVA–AN–HEMA membrane were studied. It was found that the permeation rate for aqueous solution as alcohol–water was greater than that for pure water, and the separativity of phenol–water solution by pervaporation increased as the amount of PHEMA increased.

INTRODUCTION

Pervaporation is a fractionative process which uses a polymeric membrane as a separative barrier between the vapor and the liquid phases of a membrane. In the pervaporation process, the membrane is brought into contact with the liquid mixture at atmospheric pressure. The liquid permeates the membrane and vaporizes thereafter. The vaporization is achieved by maintaining a low vapor pressure through a vacuum pump or an inert gas flow. The concentration gradient in the membrane serves as the driving force for this transport. The permeate is then trapped at liquid nitrogen temperature. This process is potentially useful when distillation is difficult to apply, such as the fractionation of azeotropic mixture, close-boiling components, isomeric mixture, or alcohol solution.

Kuznetsov and Malyusov[1,2] reported that pretreatment of cellophane membrane by boiling it in water increased its permeability but decreased its selectivity for a series of water–alcohol solutions. In addition, when the membrane was pretreated in water for 1 h at 100°C, dried with air to a constant weight, it displayed a permeability which was about 20–40% higher than the original value. Heisler et al.[3] investigated the relative permeations of water–ethanol solutions through a cellophane membrane. They reported that separation factor increased dramatically when water–soluble but ethanol-insoluble additive was added to the permeating mixture. Brun et al.[4] studied

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the separation of butadiene–isobutadiene mixture by pervaporation through a butadiene–acrylonitrile membrane and found that the permeation rate decreased as the acrylonitrile component in the membrane increased. Huang and Jarris[5] reported a series of poly(vinyl alcohol) membranes modified with radiation-induced graft copolymerization with acrylic and methacrylic acid monomers. The permeability of the grafted membrane was found to increase with the degree of grafting. However, there was no appreciable improvement in the selectivity toward alcohol–water mixture.

As a result of the above discussion, early works on the pervaporation of liquid mixture could be categorized using (1) pretreatment membrane, (2) extraction membrane, (3) copolymer membrane, and (4) radiation-grafted membrane. Till now, separation of a liquid mixture by grafted latex membrane had not been reported. This paper succeeds our previous study on grafted latex membrane[6] and deals specially with the separation of phenol–water mixture by pervaporation through a PVA–AN–HEMA-grafted latex membrane.

EXPERIMENT

Reagents

Poly(vinyl alcohol) (PVA, by Chang Chun Petrochemical Co., Ltd.) the average degree of saponification, 98.5–99.2%, acrylonitrile (AN), and 2-hydroxylethyl methacrylate (HEMA) were purified by reduced-pressure distillation. Ceric ammonium nitrate (Merck) was used after vacuum drying. Distilled water was used. All other chemicals were reagent grade and used without further purification.

Synthesis

Five grams of PVA was dissolved in 95 mL of distilled water in a four-necked flask. AN and HEMA were added to the solution. Stirring was continued for 1 h at room temperature under N_2 atmosphere. An adequate portion of $0.01N$ nitric acid containing a certain amount of ceric salt was added to the vessel. The reaction was quenched with aqueous ferrous salt solution.[7] The amount of each ingredient used and the composition of each membrane are listed in Table I. The graft copolymer latexes were adjusted to pH 1.5[8] with $1N$ hydrochloric acid and then spread on the poly(ethylene terephthalate) film stuck tightly on a glass plate using a Gardner knife. It was dried in air at room temperature in a dust-free laminar flow hood. The membrane was extracted with water at 80°C for 2 days to remove any water-soluble component. It was again treated with DMF at 55°C for 2 days to remove PAN homopolymer.[9] The membrane was stored in distilled water before use. The composition of the membrane was calculated by

$$a = 0.65935H + 9.42 \times 10^{-2}N - 9.15 \times 10^{-2}C$$
$$b = 3.79 \times 10^{-2}N$$
$$c = 10.81 \times 10^{-2}C - 13.92 \times 10^{-2}N - 0.6493H$$

where C, H, and N values were obtained by an elemental analyzer (Perkin-Elmer 240 C).

TABLE I
Components of PVA–AN–HEMA-Grafted Latex Membrane after Extraction
with Hot Water and DMF[a]

No.	PVA (g)	H₂O (g)	AN (g)	HEMA (g)	Composition of membrane and in weight fraction		
					PVA	AN	HEMA
1	5	95	15	—	0.33	0.67	—
2	5	95	15	1.0	0.356	0.605	0.039
3	5	95	15	2.5	0.337	0.525	0.138
4	5	95	15	5.0	0.294	0.478	0.228
5	5	95	17.5	5.0	0.344	0.554	0.102
6	5	95	12.5	5.0	0.341	0.470	0.189

[a] Reaction condition: $[C_e^-]$ = 0.01N; 10.5 mL; temperature 30°C; reaction time 2 h; membrane thickness 0.11 ± 0.02 mm.

Water Permeability

The test apparatus is the same as our previous report.[6] The membrane was placed under desired conditions at constant temperature and pressure drop. The water permeability coefficient K (cm²) was calculated by[10]

$$k = VL\eta/tA \, \Delta P$$

where V is the volume (cm³) of water permeated, L is the membrane thickness (cm), η is the viscosity of water (cP), t is the transportation time (s), A is the membrane area (cm²), and ΔP is the pressure drop (dyn/cm²).

Selectivity Coefficient[11]

The selectivity coefficient $\alpha_{B/A}$ is defined as

$$\alpha_{B/A} = \frac{y_B/y_A}{x_B/x_B}$$

where x_A and x_B denote the weight fractions of A and B in the permeant and y_A and y_B denote the weight fractions of A and B in the permeant. In this study, A and B denote phenol and water, respectively. A is the specie which is evaporated first.

Investigation of the Microstructure

Membranes were cut into ultra thin sections of about 700 Å in thickness. They were stained by a 2 wt % O_sO_4 solution and photographed with a transmission electron microscope (JEOL TEM-100B). The surface structures of the membranes were fractured in liquid nitrogen, shadowed with gold, and examined under a scanning electron microscope (JEOL SEM-U3).

RESULT AND DISCUSSION

The Structure of PVA–AN–HEMA-Grafted Latex Membrane

PVA in a water-soluble polymer. On addition of AN, which is hydrophobic in nature, AN could be graft-copolymerized with PVA in aqueous solution with an aid of ceric ammonium nitrate. The purpose of incorporating PAN is to enhance the strength of the membrane. The PVA–AN graft latex thus possessed both hydrophilic and hydrophobic components. The hydrophobic moieties serve as effective crosslinks between neighboring chains. These crosslinks may assume the form of crystallites with the hydrophobic moiety embedded in an amorphous hydrophilic matrix. In addition, owing to the strong polarity of the CN group on the hydrophobic component (PAN), it associates with neighboring chains to form like a hydrogen bond.[12] Therefore, only a few solvents can dissolve the membrane (e.g., DMF and DMSO). Most solvents cannot even swell it easily. The alcohol–water and phenol–water solutions cannot enter the PAN phase in the PVA–AN graft latex membrane with ease.

In order to facilitate material transport, the PHEMA graft was introduced. The PAN and PHEMA components graft on PVA chains randomly. The rigid PAN phase was thus lossed up. The PAN–PHEMA component made the membrane swell easily but not dissolved by solvents.

Basically, PVA–AN–HEMA copolymer was in a latex state, and its structure is suggested as previous[6]: PVA constitutes the continuous phase while PAN and PHEMA constitutes the dispersion phase. According to the transmission electron microscope result (Fig. 1), this latex has apparent hydrophobic and hydrophilic structures in which the block domain is PAN–PHEMA and the white matrix is PVA. The more the PHEMA component exists in the membrane, the less is the microstructure. Interfaces of hydrophilic and hydrophobic areas are not clear which agrees with the scanning electron microscope studies by Ohtsuka and Hirabayashi.[13]

The Permeability of Alcohol–Water Solution

Membrane no. 4 was used, to test the permeability of an alcohol–water solution. It was found that when a small amount of alcohol was added to H_2O, the permeation rate reached a maximum. This result is similar to the permeability study of alcohol–water solution through cellophane and PVA membrane.[14] It is also similar to the permeability studies of various aqueous alcohol solutions through cellophane membrane,[15] too.

Figure 2 indicates several facts:

(i) The permeation rates of aqueous solutions containing alcohol above $0.07M$ are greater than that of pure water.

(ii) Among the various aqueous alcohol solutions, $0.03M$ alcohol solution has the maximum permeation rate.

(iii) Among the aqueous alcohol solutions testes, propanol has the highest permeation rate.
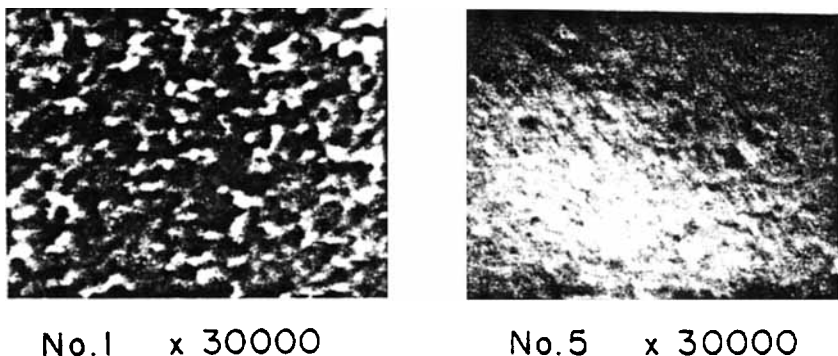
No.1   x 30000   No.5   x 30000

Fig. 1.   TEM micrographs of PVA–AN–HEMA grafted latex membranes; (a) No. 1 (PVA 33%, AN 67%); (b) No. 5 (PVA 26.9%, AN 37.9%, HEMA 35.2%).
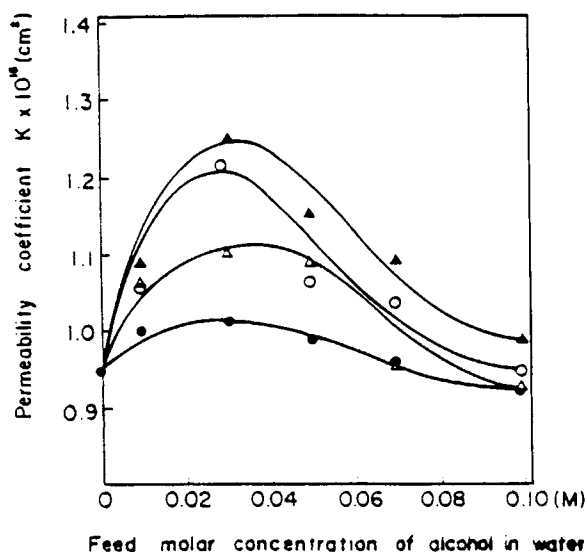

Fig. 2.   Effect of alcohol concentration on the permeability of several alcohols through PVA–AN–HEMA membrane with 0.12 mm thickness: (●) methanol; (○) ethanol; (▲) propanol; (△) butanol.

It was found that H_2O molecules formed a three-dimensional network, or a cluster through strong hydrogen bonding.[16] A large cluster of H_2O affects the diffusivity of molecules in the membrane. It has been shown[17] that when solutes having hydrophilic groups, e.g., hydroxyl or amine, are added to water, hydrogen bonds within the water clusters will be destroyed, and there will be fewer water clusters than in pure water. These factors, therefore, contribute to the increase of the permeation rate for alcohol–water solution. Thus, the permeation rate for aqueous alcohol solutions are greater than that for pure water.

When concentration of the feed alcohol is greater than $0.03M$, the so-called critical micelle concentration is reached. This implies that the number of

water clusters remains the same as before. Therefore, in the experiment the decrease in permeation rate at $> 0.03M$ alcohol is due mainly to the permeation resistance caused by the feed viscosity increase.[15]

Permeation experiment with homologous series of linear alcohols, e.g., methanol, ethanol, and n-propanol, had been conducted with cellophane and poly(vinyl alcohol) membranes by Huang et al.[14] They concluded that either the permeation rate or the selectivity was related to the linearity of the permeating molecules, and the size of the molecules was a predominate factor for compounds with only small chemical differences. However, in our experiment, we found that propanol, instead of methanol, had the greatest permeation rate. The polarity of methanol which is the smallest in size is the highest, whereas that of butanol, which is the largest in size, is the lowest. In summary, the permeation rate decreases as the molecular size increases, since the diffusivity difference is determined largely by the size and hydrophobicity increases. The permeation rate decreases as the polarity of the molecule increases, since mutual association of water and alcohol molecules occurs. Therefore, hydrophilicity (polarity factor) and hydrophobicity (size factor) of various aqueous alcohol solutions must be balanced.

Separation of Phenol–Water Solution

The pervaporation apparatus was the same as used by Huang.[11] The membrane was situated in the stainless steel pervaporation cell. Phenol–water feed solution was then placed in the upper compartment of the cell. The membrane was immersed for 24 h at 25°C. Phenol solution was withdrawn rapidly from the lower compartment, with a vacuum pump at 10 mm Hg. Collection of the pervaporate was started after equilibrium (about 1 h) was reached. The trapes were cooled in liquid nitrogen ($-196°C$). In order to keep the composition constant, fraction of the pervaporate collected (about 2–4 g) during a run were small compared with the feed (about 250 g). The composition of the mixture was determined with a refractometer (Abbe-3L).

The pervaporation of a liquid mixture through a polymeric membrane involves two steps[18]: (1) dissolution of the liquid within the film surface in contact with the liquid charge; (2) migration through the body of the film. Desorption then occurs which is assumed to be relatively fast and nonselective since a vacuum is maintained at the downstream side of the membrane. The solubility differences among permeating species depend primarily on the differences in their chemical natures. The shape of these molecules and also by the degree of aggregation among the diffusing species within the polymer.

The permeabilities and selectivities of phenol–water solutions through PVA–AN–HEMA membrane are shown in Figures 3–6. It is clear that (i) when the phenol concentration in the phenol–water solutions increases, the permeation rate decreases, whereas the selectivity increases (Figs. 3 and 4) and (ii) when the number of hydrophilic groups in the membrane increases, the permeation rate decreases, but the selectivity increases (Figs. 5 and 6).

Since phenol is a poor solvent for a hydrophilic membrane, phenol molecules in the membranes thus cause the membrane to shrink. The membrane structure becomes dense, which is resistant to the transport of the feed solution. Therefore, the permeation rate decreases as the phenol concentration
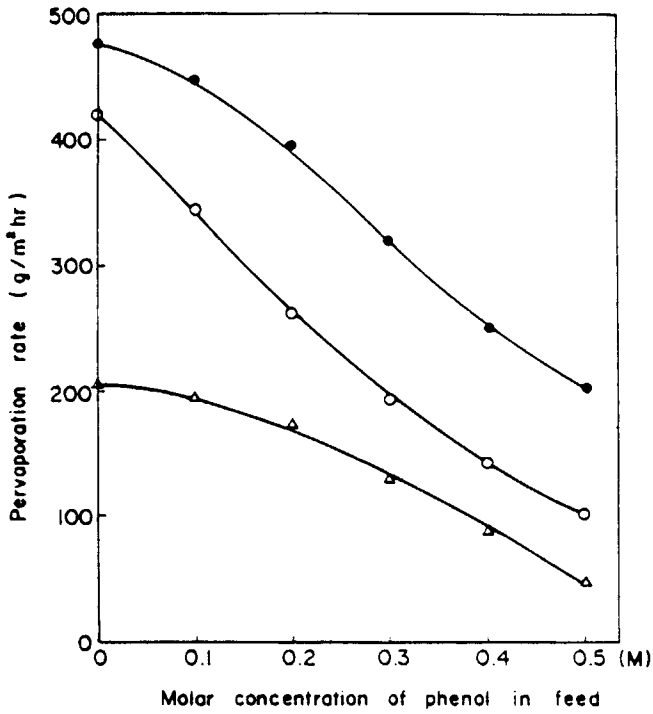
Fig. 3. Effect of phenol concentration the pervaporation rate, membranes thickness: 0.11 ± 0.02 mm; (●) membrane no. 1; (○) no. 2; (△) no. 4.
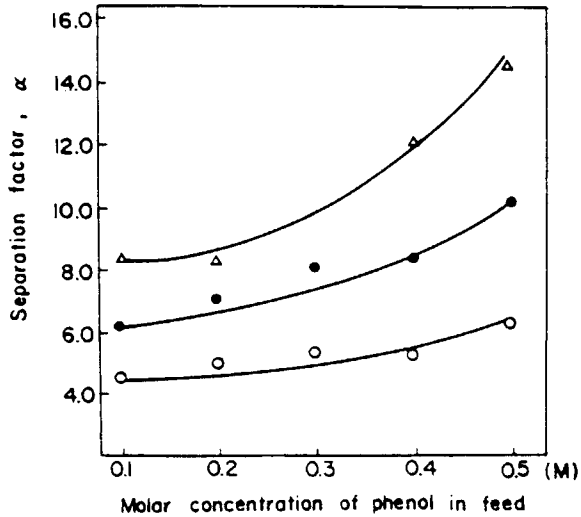

Fig. 4. Effect of phenol concentration the separation factor, membranes thickness: 0.11 ± 0.02 mm; (●) membrane no. 1; (○) no. 2; (△) no. 4.
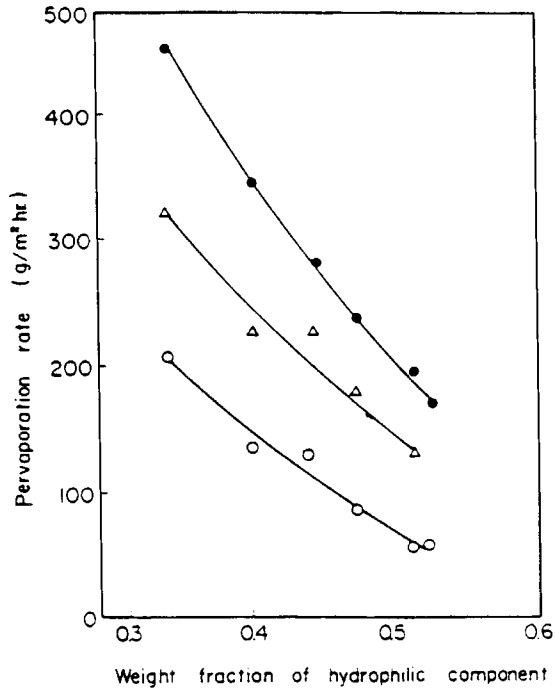
Fig. 5. The influence of hydrophilic component on the pervaporation rate, membrane thickness: 0.11 ± 0.02 mm; phenol concentration: (●) $0.1M$; (△) $0.3M$; (○) $0.5M$.
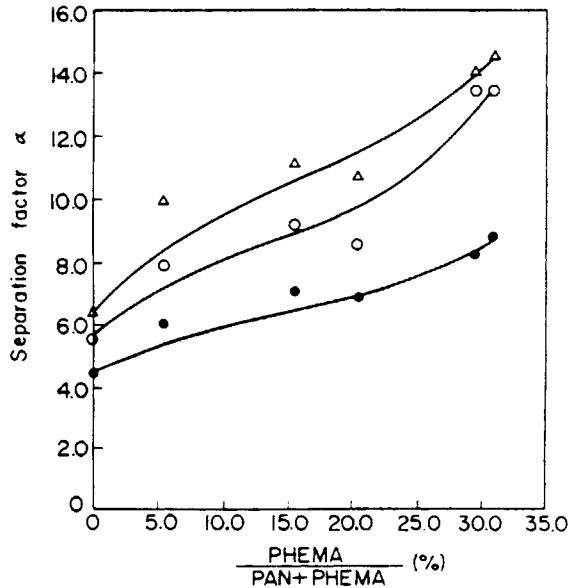

Fig. 6. The influence of hydrophilic component on the separation factor, membrane thickness: 0.11 ± 0.02 mm; phenol concentration: (●) $0.1M$; (△) $0.3M$; (○) $0.5M$.

TABLE II
Component of PVA-AN-HEMA Membranes

No.	PVA	PAN + PHEMA	PHEMA (%) PAN + PHEMA
1	1	2.0	0
2	1	1.8	6
3	1	2.0	21
4	1	2.3	32
5	1	1.9	16
6	1	1.9	29

in the phenol–water solution increases. In addition, since the diameter of the phenol molecule is larger than that of water, the transport of phenol molecules is slower and the selectivity increases as the phenol concentration in the phenol–water solutions increases.

It has been postulated by several workers[19] that the permeation of water through a polymeric membrane is hindered by water clusters. Due to the interaction of polar groups in the membrane with phenol or water molecules, a tendency is observed that when the number of hydrophilic groups in the membrane increases, the permeation rate decreases, but the selectivity increases (Figs. 5 and 6).

The composition of the PVA–AN–HEMA graft latex membrane is listed in Table II. Various amounts of AN and HEMA were graft copolymerized on 5 g of PVA. Table II shows that the value of AN–HEMA is really constant. Figure 7 shows that as the PHEMA component in the graft chain increases,
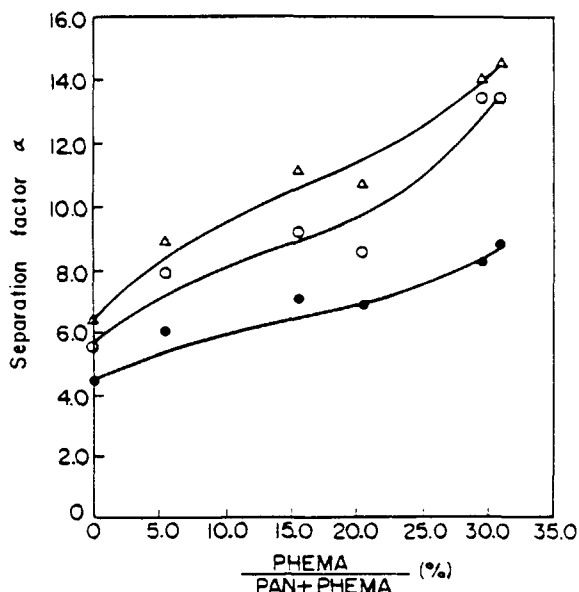

Fig. 7. The influence of PHEMA on the separation factor of phenol aqueous solutions, membrane thickness: 0.11 ± 0.02 mm; phenol concentration: (●) 0.1M; (○) 0.3M; (△) 0.5M.

the selectivity of the phenol–water solution increases too. Since increase of PHEMA in the membrane loosens up the rigid PAN phase, the degree of microphase-separated structure in the membrane is reduced. Thus, the interface between the continuous and the dispersion phases in the membrane does not have a clear contour, i.e., the membrane structure becomes more dense. So the permeation of water which has smaller size dominates over phenol molecular and results in the increment of selectivity as the PHEMA component increases.

CONCLUSION

There are three characteristics for the PVA–AN–HEMA graft latex membrane when used in the permeability and selectivity studies:

(i) When PHEMA component in the membrane increases, the interface between the continuous and the dispersion phases is not obvious. PHEMA component loosens up the rigid PAN phase. Therefore, PHEMA contributes a lot to good selectivity.

(ii) Alcohol–water solutions with above $0.07M$ alcohol concentration have greater permeation rates than that for pure water. The permeation rate reaches a maximum at $0.03M$ alcohol. Among the linear alcohols tested, the permeation rate for propanol is the highest.

(iii) When phenol concentration in the phenol–water solutions increases, the permeation rate decreases, but the selectivity increases. When the number of hydrophilic groups (PVA + PHEMA) in the membrane increases, the permeation rate decreases. Increase of PHEMA component in the membrane causes the selectivity of phenol–water solution to increase.

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