

SELECTIVE SEPARATION OF WATER-ETHANOL MIXTURES THROUGH COPOLYMERIC MEMBRANES: I. ACRYLIC ACID AND ACRYLONITRILE COPOLYMER AND ITS IONIZED MEMBRANES

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ABSTRACT

The copolymer of acrylic acid and acrylonitrile has been synthesized and pervaporation properties of the copolymeric membranes have been investigated. In order to elucidate the influence of membrane-permeate interaction on the pervaporation of water-ethanol mixtures and to prepare much improved membranes, the membranes have been treated with alkali metal, alkali earth metal and transition metal salt aqueous solutions. The treated membranes (ionized membranes) exhibited higher separation factors than the untreated membranes. The separation factors of various alkali metal cation membranes decreased in the following order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, and the permeation rates showed an opposite tendency. The dependence of pervaporation behavior on the copolymer composition, feed concentration and operating temperature have been studied with both ionized and non-ionized membranes. The apparent activation energies of water and ethanol permeation were calculated.

INTRODUCTION

In recent years, membrane process for water-ethanol separation has been attracted much attention and greater efforts have been made to develop effective membranes. It is well known that for the water perm-selective membranes, more hydrophilicity of the membrane is favourable to permselective separation of water, therefore the incorporation of ionic moieties in membrane structure is effective to increase the permselectivity of water^[1-3].

From this point of view, copolymers of acrylic acid and acrylonitrile were synthesized and their pervaporation separation characteristics were investigated. In order to improve the permselective behavior of these membranes, the ionized membranes by treating with alkali metal, alkali earth metal and transition metal salt aqueous ethanol solutions have been prepared and tested. The dependence of pervaporation separation on the copolymer composition, feed concentration and operating temperature have been examined.

EXPERIMENTAL

Materials

Commercially available acrylic acid (AA) and acrylonitrile (AN) were distilled

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before use. Ammonium peroxydisulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, sodium hydrogen sulphite (NaHSO_3), N,N-dimethylformamide (DMF) and other reagents were used without purification.

Preparation of copolymers of acrylic acid and acrylonitrile

AA and AN copolymers were prepared by radical copolymerization using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NaHSO_3 as initiator at 40°C for 2h. Water was used as precipitating agent. The resulting copolymer was washed with deionized water and ethanol twice, respectively, then dried in vacuum at 60°C for 24h.

The chemical composition of copolymer was determined by elemental analysis.

Membrane formation

All membranes were obtained by casting from DMF solutions. The solutions were casted on glass plates, and the solvent was allowed to evaporate at 80°C for 1h.. These membranes were $5 - 21\mu\text{m}$ thick.

The ionized membranes were prepared by soaking at $5 \times 10^{-3}M$ metal salt in 1:1 water/ethanol solution at room temperature for 2 days and washed with deionized water twice.

Pervaporations

The permeation cell was made of stainless steel with rubber connection. Pervaporation separation of water-ethanol mixtures was carried out with a membrane area of 22.1cm^2 and downstream pressure of 667Pa (5.0 torr). The water-ethanol mixture was recirculated at about 200ml/min and its temperature was kept constant.

The permeated vapor was collected in a cold trap (-35°C). The permeation rate (J) was obtained by weighing the trapped permeate and given in $\text{g/m}^2 \cdot \text{h}$. The separation factor ($\alpha_{w/E}$) was calculated from the following equation:

$$\alpha_{w/E} = (Y_w/Y_E)/(X_w/X_E)$$

where Y_w and Y_E are the concentrations of water and ethanol in the permeate and X_w and X_E are those in the feed.

The permeation rates of water (J_w) and ethanol (J_E) were defined as:

$$J_w = J \times Y_w; \quad J_E = J \times Y_E$$

The compositions of permeate were determined by refractometer with a composition standard curve which was calibrated by gas chromatography with a deviation of 5%.

RESULTS AND DISCUSSION

Effect of AA content in the copolymer and membrane thickness

A series of AA and AN copolymers containing different AA contents were synthesized and the results are listed in Table 1.

Table 1 Copolymers of AA and AN^{a)}

Copolymer	Monomer (g)		AA mol fraction in		Yield (%)	[η] ^{b)} (l/g)
	AA	AN	monomer	copolymer		
1	3.15	21.76	0.0963	0.0971	91.3	0.527
2	4.73	20.55	0.145	0.153	87.7	0.587
3	6.31	19.34	0.194	0.208	83.2	0.593
4	7.88	18.14	0.242	0.258	80.8	0.602
5	9.46	16.93	0.292	0.302	80.1	0.538

a) $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{NaHSO}_3=9:1$ (mol ratio); 40°C ; 2h.

b) Viscosity was measured at $c=1.0\text{g/l}$ in DMF at $30\pm0.01^\circ\text{C}$.

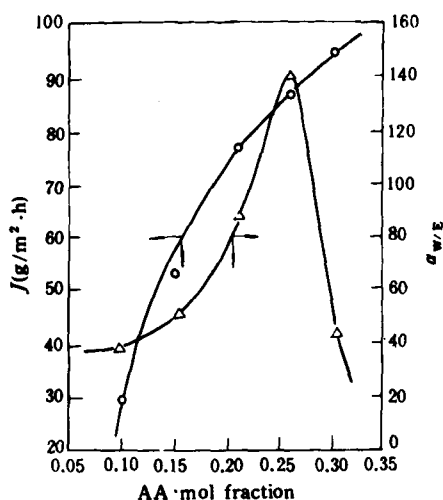


Fig.1 Dependence of water-ethanol permeation on the AA mol fraction

Operating temperature: 28°C .

Membrane thickness: $17\mu\text{m}$.

Ethanol concentration in the feed: 90 wt%.

Figure 1 shows the results of pervaporation through the above copolymeric membranes, where the separation factors ($\alpha_{W/E}$) and total permeation rates plotted versus AA mol fraction. As seen in Fig.1, the total permeation rates and the values of $\alpha_{W/E}$ increase with increasing the AA mol fraction and the value of $\alpha_{W/E}$ reaches a maximum value at AA mol fraction of 0.258. This might be related to the increment of the hydrophilicity of membrane with higher AA content which strengthens the hydrogen-bonding interaction between the membrane and water molecule in the feed. The separation factors drop at AA mol fraction more than 0.258 due to overswelling of the membrane with excessive hydrophilic group of AA.

The dependence of separation characteristics on membrane thickness is summarized in Table 2.

Table 2 Separation behavior of membrane with different thickness

Membrane thickness (μm)	Weight fraction of water in permeate	Permeation rate ($\text{g/m}^2 \cdot \text{h}$)	Separation factor
12	0.889	115.3	72.4
14	0.930	109.2	120
17	0.940	88.4	141
21	0.960	47.2	216

AA mol fraction: 0.258; operating temperature: 28°C .

Ethanol concentration in the feed: 90 wt%.

It can be seen that the separation factors rise while the total permeation rates drop with increasing thickness of the membrane.

Effect of treatment with metal ions (Ionized Membrane)

Recently, Cabasso et al.^[1, 4], Reineke et al.^[5] and Mochizuki et al.^[6] reported the separation behavior of water-ethanol mixtures through polyelectrolyte membranes and the effect of counter cation (H^+ , Li^+ , Na^+ , K^+ and Cs^+) on the permselectivity of membranes.

We have investigated the separation characteristics of membrane treated with different metal salt aqueous ethanol solutions as shown in Table 3.

Table 3 Effect of counter cations on separation characteristics

Counter cation	H^+	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}	Fe^{3+}	Co^{2+}	Cu^{2+}
Permeation rate ($g/m^2 \cdot h$)	115.3	82.1	105.8	203.3	102.9	167.0	150.3	52.9	244.5	64.6
Separation factor	72.4	351	111	92.4	290	89.0	891	591	89.0	251

AA mol fraction : 0.258 ; Operating temperature : 28 °C

Membrane thickness : 12 μm ; Ethanol concentration in the feed : 90 wt% .

It can be seen from Table 3, the separation factors of all membranes with metal cations (ionized membranes) are higher than those of the untreated membranes. This is attributed to the strengthening of the hydrogen-bonding interaction between membrane and water molecule in the feed and hydration of metal cation with water molecules which might come from the enrichment of charge density of carboxyl groups in membrane surface. Data in Table 3 also indicate that permeation rates of various alkali metal ionized membranes increase in the following order: $Li^+ < Na^+ < K^+$, which is well consistent with the sequence of hydration energies of the cation^[5]. This result is in agreement with Reineke's and Mochizuki's reports. It appeared that higher water mobility within the K^+ version membrane would result from the more facile displacement of water from the K^+ ion hydration shell. The effect of alkali metal cations on the separation factor is different from Reineke's and Mochizuki's reports. The separation factors decrease in the order: $Li^+ > Na^+ > K^+ > H^+$. This order may be caused by their difference in hydration and hydrogen-bonding interaction.

Effect of feed concentration and operating temperature

The effects of ethanol concentration (X_E wt%) of the feed on the permselectivity of the H^+ version membrane (non-ionized membrane) and Na^+ version membrane (ionized membrane) is shown in Fig. 2 and 3, respectively. The curves on the two figures are very similar in tendency and it indicates that the permeation rates decrease with increasing ethanol concentration from 10 to 90 wt% and separation factors have an opposite tendency. The decrease of permeation rates is probably caused by the decreasing of swelling degree of the membranes.

Operating temperature is one of the important factors affecting the separation characteristics. The effect of operating temperature in the range of 10—60 °C on the permselectivity of both H^+ version and Na^+ version membranes is illustrated in Fig. 4 and 6. The total permeation rate at each temperature is separated into that of respective water and ethanol components illustrated in Fig. 5 and 7.

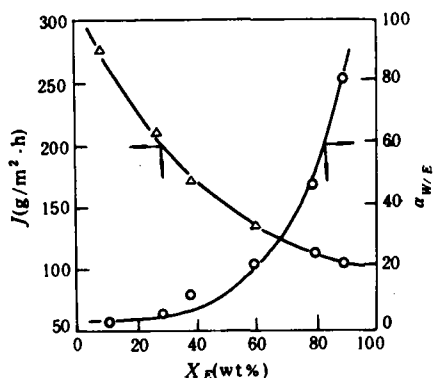


Fig. 2 Effect of ethanol concentration on permselectivity of H^+ version membrane
AA mol fraction: 0.258.
Operating temperature: 25 °C.
Membrane thickness: 12 μ m.

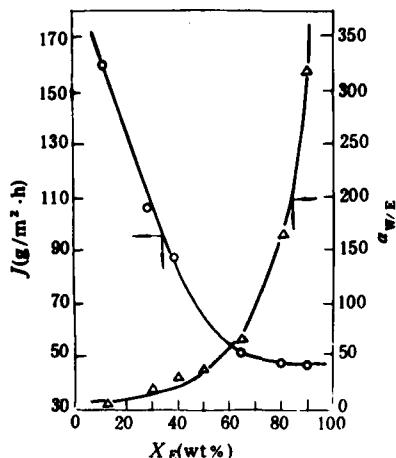


Fig. 3 Effect of ethanol concentration on permselectivity of Na^+ version membrane
AA mol fraction: 0.258.
Operating temperature: 25 °C.
Membrane thickness: 21 μ m.

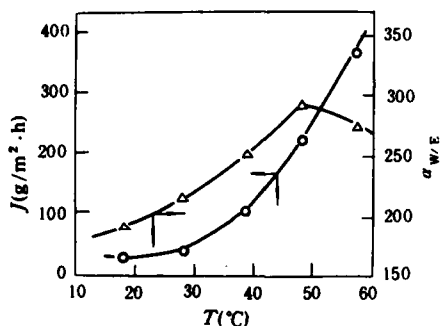


Fig. 4 Effect of operating temperature on permselectivity of H^+ version membrane
AA mol fraction: 0.258.
Membrane thickness: 21 μ m.
Ethanol concentration in the feed: 90 wt%.

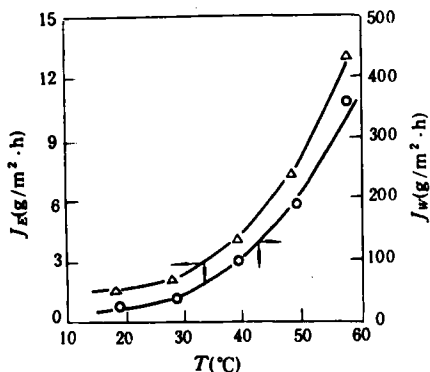


Fig. 5 Dependence of permeation rates of water and ethanol on operating temperature (H^+ version membrane)
Conditions are the same as Fig. 4.

It can be seen from Fig. 4 and 6 that the permeation rates for both H^+ version and Na^+ version membranes have the same variation trends, but Na^+ version membrane's variation is more drastic. Higher permeation rate obtained at higher temperature is probably due to the increased vapor pressure resulting in larger driving forces for permeation. The variation trends of separation factors for H^+ version and Na^+ version membranes are different. The separation factor for the Na^+ version membrane drops at higher temperature and the result is in accordance with other pervaporation membranes. However, the separation factor for the H^+ version membrane shows a maximum value in the range of 40 — 60 °C because the hydrogen-bonding interaction among carboxylic acids at

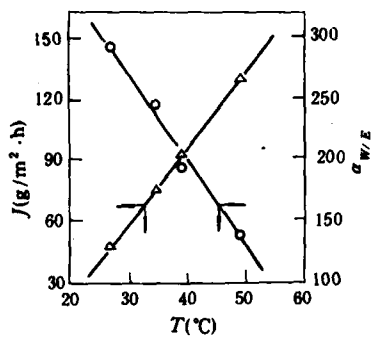


Fig.6 Effect of operating temperature on permselectivity of Na⁺ version membrane
Conditions are the same as Fig.4 .

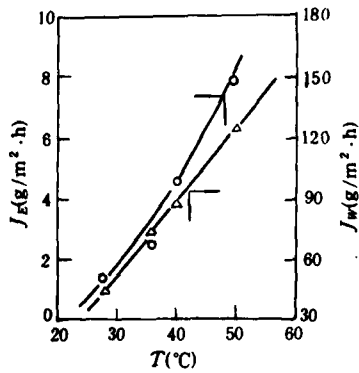


Fig.7 Dependence of permeation rates of water and ethanol on operating temperature (Na⁺ version membrane)
Conditions are the same as Fig.4 .

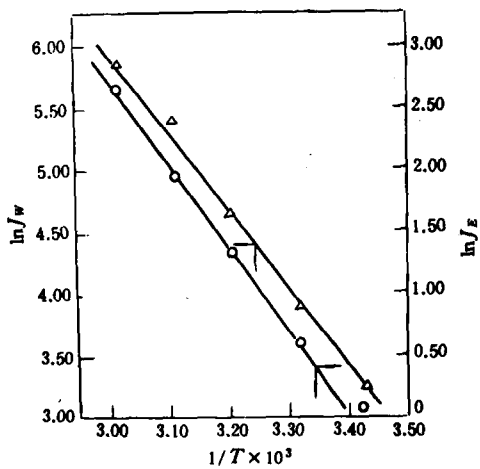


Fig.8 Relation of ln J_E, ln J_W and 1/T
H⁺ version membrane

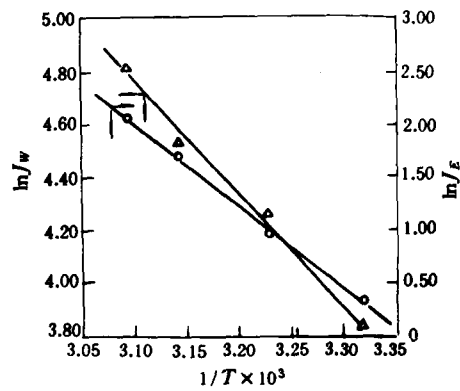


Fig.9 Relation of ln J_E, ln J_W and 1/T
Na⁺ version membrane

lower temperature hinders the formation of hydrogen-bonding interaction between membrane and water molecule in the feed . This result is consistent with the Yoshikawa's^[7] .

Figure 8 and 9 show the Arrhenius plots of permeation through H⁺ version and Na⁺ version membranes , respectively . From the slopes , the activation energy data of water and ethanol permeation are calculated and listed in Table 4.

Table 4 Apparent activation energies of water and ethanol for permeation

Counter ion	Activation energy (KJ/mol)	
	Water	Ethanol
H ⁺	46.08	57.01
Na ⁺	35.71	64.65

The values of activation energy obtained in this study may be the approximate ones because of limited data of permeation, but the trends that the activation energy of water reduces and the activation energy of ethanol increases in the ionized membrane are conceivable.

Keywords :

Pervaporation; Separation behavior; Water/ethanol mixture; Acrylonitrile-acrylic acid copolymer.

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