

PERVAPORATION SEPARATION OF WATER-ACETIC ACID MIXTURES THROUGH AN-co-AA MEMBRANES TREATED WITH RARE EARTH METAL IONS*

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ABSTRACT

Pervaporation separation of water-acetic acid mixtures through Poly (AN-co-AA) membranes and rare earth metal ions treated Poly(AN-co-AA) membranes was investigated for the first time. The results showed that the treatment with rare earth metal ions could greatly improve the characteristics of the separation of water-acetic acid mixtures.

INTRODUCTION

Acetic acid is an important basic chemical in the chemical industry, ranking among the top 20 organic intermediates. The process of separating acetic acid from its aqueous solution by azeotropic distillation is an energy-consuming one, thus a new energy saving separation process is desirable. The pervaporation technique is a potential candidate for this purpose and a few studies on the separation of water-acetic acid system by pervaporation have been reported recently^[1,2].

The authors have previously prepared a series of acrylonitrile copolymeric membranes which were used to separate water-ethanol mixtures by pervaporation with satisfactory results, especially, by acrylonitrile and

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acrylic acid copolymeric membrane (poly (AN-co-AA) membrane)^[3-5].

In this study, pervaporation separation of water-acetic acid mixtures through the poly (AN-co-AA) membranes and rare earth metal ions (RE ions) treated poly (AN-co-AA) membranes was investigated for the first time. The results showed that the treatment with RE ions could greatly improve the characteristics of the separation of water-acetic acid mixtures.

EXPERIMENTAL

Preparation of Poly (AN-co-AA), membrane formation and measurement of membrane characteristics were the same as in our earlier works^[3].

The molar fraction of AA in the copolymer was 0.258 determined by elemental analysis.

The permeation rate (J) was obtained by weighing the trapped permeate and given in $\text{g}/\text{m}^2\text{h}$. The permselectivity of water to acetic acid ($\alpha_{W/A}$) was defined as follows:

$$\alpha_{W/A} = (Y_W/Y_A) / (X_W/X_A)$$

where Y_W and Y_A represent the weight fraction of water and acetic acid in the permeate and X_W and X_A those in the feed, respectively.

Swelling of membrane was measured by weighing dry and wet membrane and calculated from the following equation:

$$\text{Swelling}(\%) = \frac{G_W - G_D}{G_D} \times 100\%$$

where G_D and G_W are the weights of dry and wet membrane which was soaked in 90 wt% acetic acid aqueous solution at 25°C for 3 days.

RESULTS AND DISCUSSION

The properties of treated and untreated AN-co-AA copolymer membranes are summarized in Table 1.

Table 1 The dependence of membrane properties on counter ions

Counter ion	Swelling (%)	Strength (Kg/cm^2)	J ($\text{g}/\text{m}^2\text{h}$)	$\alpha_{W/A}$
H^+	19.7	312.4	113.4	58.9
La^{3+}	22.4	347.3	154.3	100.0
Nd^{3+}	24.9	379.1	194.7	195.5
Y^{3+}	29.1	404.5	229.1	299.1

T : 50°C; X_A : 90wt%; membrane thickness: 12 μm

It can be seen from Table 1, the permeation rate, separation factor, membrane strength and swelling degree of all membranes are higher than those of the untreated one. The higher swelling of membranes treated with RE ions might be due to the higher coordinative ability of RE ions with acetic acid. The increment of permeation rate and separation factor is probably attributed to the strengthening of the hydrogen-bonding interaction between membrane and water molecule in the feed which might come from the enrichment of charge density of carboxyl groups on the membrane surface after treated with RE ions.

The influence of feed concentration on the separation properties is similar to other pervaporation processes, i. e. the permeation rates rise with increment of water content in the feed and the separation factors show an opposite tendency.

Operating temperature is an important factor affecting the separation characteristics. The higher the operating temperature, the larger the permeation rates of all membranes (see Fig. 1a). On the other hand, the separation factors have different trends for the treated and untreated membranes as shown in Fig. 1b.

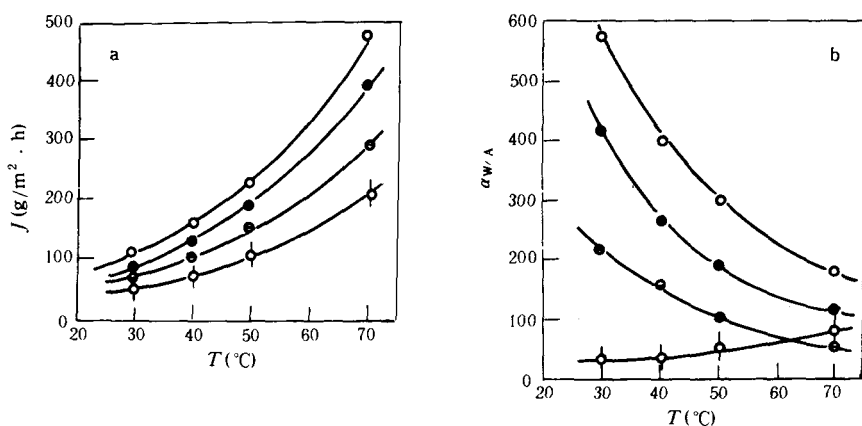


Fig. 1 Effect of operating temperature on separation properties X_A : 90wt%; membrane thickness: 12 μ m

○ H⁺; ⊙ La³⁺; ● Nd³⁺; ○ Y³⁺

It can be seen from Fig. 1b that the separation factors of the treated membranes are higher than the untreated one and drop at higher temperature, which is in accordance with the result of water-ethanol separation with AN-co-AA membrane^[3]. The reason is supposed that after

treating with RE ions the hydrogen-bonding interaction between membrane and water molecule in the feed is promoted because of the carboxyl group ($-\text{COOH}$) of the membrane transformed into carboxylic ion ($-\text{COO}-$). Meanwhile, the lower separation factor at lower temperature for the untreated membrane is due to the hydrogen-bonding interaction between carboxyl group itself hindering the hydrogen-bonding interaction between membrane and water molecule in the feed.

According to the Arrhenius equation, the activation energies of water and acetic acid through the treated and untreated AN-co-AA membranes are calculated and listed in Table 2.

Table 2 Activation energy data

Counter Ion	Activation energy (KJ/mol)		
	Total	Water	Acetic acid
H^+	28.8	30.8	15.9
La^{3+}	29.9	29.0	56.4
Nd^{3+}	31.6	31.0	59.2
Y^{3+}	33.2	32.8	57.4

It can be found that the activation energy of acetic acid rises greatly after treated with RE ions. Higher activation energy of acetic acid shows that the permeation of acetic acid through the membrane is more difficult, therefore, the separation factor of water to acetic acid increased after treated with RE ions.

Keywords:

Pervaporation separation; Water-acetic mixture; Poly (AN-co-AA) membranes; Rare earth ions

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