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# Application of zeolite membranes to esterification reactions

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## Abstract

Pervaporation-aided esterification of acetic acid with ethanol was investigated at 343 K using zeolite T membranes. Almost complete conversion was reached within 8 h when initial molar ratios of alcohol to acetic acid were 1.5 and 2. The reaction time courses were well described by a simple model based on the assumptions that the reaction obeyed second-order kinetics and the permeation flux of each component was proportional to its concentration. The influence of operating parameters on variation in conversion with reaction time was investigated by means of the simulation using the model. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Esterification; Zeolite T; Permeation flux; Membrane reactor; Ester

## 1. Introduction

The hybrid process of reaction with membrane separation has been increasingly attracting much attention. There have been a number of investigations done for hydrogen-permeable membrane reactors applied to reversible gas-phase reactions [1,2]. Some investigations have focused on water-permeable membrane reactors applied to liquid-phase reactions [3–8]. The esterification of oleic acid with ethanol could be improved by vapor permeation (VP) separations with asymmetric polyimide hollow fiber membrane [6]. Further improvement of the esterification was achieved by VP separation with zeolite NaA membrane because of its extremely high permeation flux [7]. However, the zeolite NaA membranes are unstable to acids and are not applied to the system where they directly contact with acids. Recently, we reported zeolite T membranes showed high pervaporation (PV) performance for water–organic liquid mixtures as well as good stability to acid solutions [9].

In this study, PV separation with zeolite T membranes is applied to the esterification of acetic acid with ethanol.

## 2. Experimental

Zeolite T membrane was grown hydrothermally on the surface of a porous cylindrical alumina support (Nikkato, 12 mm outer diameter, 1.5 mm thickness, 1.3 μm average pore size). The aluminosilicate gel used in the synthesis was prepared by mixing precipitated silica, alkaline aluminate, sodium hydroxide, potassium hydroxide and water. The molar composition of the resulting gel was $SiO_2:Al_2O_3:(Na_2O + K_2O):H_2O = 1:0.055:0.37:11.6$. The porous support was coated by a water slurry of seed zeolite T crystals

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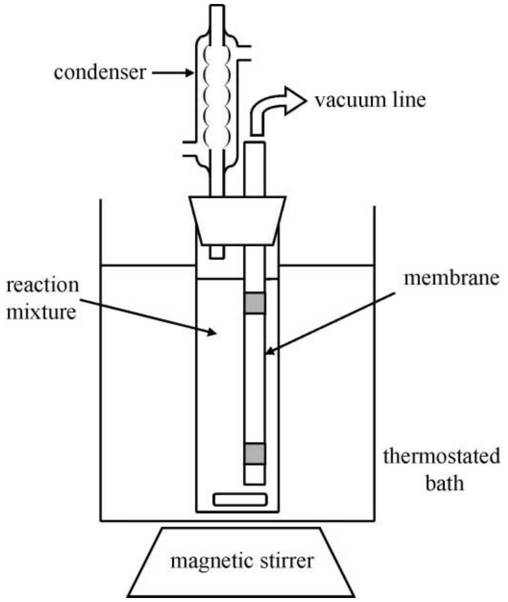

Fig. 1. Schematic diagram of the experimental apparatus.

(Bayer) and then dried at 343 K for 3 h. The seeded support tube was placed in the gel. After hydrothermal synthesis at 373 K for 28 h, the tube was taken out, washed with water for 1 h and air-dried at ambient temperature. The formation of zeolite T crystal was confirmed by X-ray diffraction (XRD). The XRD pattern of the zeolite T membrane consists of strong zeolite T peaks and weak alumina peaks.

The PV-aided esterification of acetic acid with ethanol was carried out using the apparatus shown in Fig. 1. A reaction cell consisted of a cylindrical glass vessel and a condenser. The cylindrical reactor was placed in a thermostated water bath. The membrane was set in a reaction mixture and the permeate side was connected to a vacuum line. The effective membrane area was 38 $\mathrm{cm}^2$. The inside of the membrane tube was evacuated and the permeate was condensed in a trap cooled by liquid nitrogen. The PV performance of the membrane was evaluated by a permeation flux ($Q$ in $\mathrm{kg\,m^{-2}\,h^{-1}}$) and a separation factor ($\alpha$). The permeation flux was calculated by weighing trapped permeate. The separation factor was defined by $\alpha = (Y_W/Y_O)/(X_W/X_O)$, where $Y_W/Y_O$ is the weight ratio of water to organic compounds in the permeate and $X_W/X_O$ is that in the feed.

All reagents were purified by ordinary methods. The catalyst used was a cation exchange resin (Amberlyst 15, Organo). The catalyst of 100 g/l and a certain amount of ethanol were set in the reactor and the reactor was kept at a given temperature (343 K). Acetic acid was then poured into the reactor to start the esterification. The initial amount of the reaction mixture was 50 g. The esterification experiments with and without PV were carried out for the initial molar ratios of ethanol to acetic acid $m_0$ of 1.5 and 2.0. A sample (0.2 g) was withdrawn periodically and analyzed by gas chromatography for acetic acid, ethanol, ethyl acetate and water. The conversion was calculated from the composition of acetic acid.

## 3. Results and discussion

Table 1 lists typical PV performance of zeolite membranes for a water/ethanol (10/90 in wt.%) mixture at 348 K. Fig. 2(a) and (b) shows variation in the conversion with reaction time for the esterification with and without PV for $m_0$ of 1.5 and 2, respectively. The conversion for every PV-aided reaction exceeded the thermodynamic equilibrium. Almost complete conversion of 100% was reached for the reactions of $m_0 = 1.5$ and 2 within 8 h.

Fig. 3(a) and (b) shows variation in the composition of the reaction mixture for $m_0 = 1.5$ and 2, respectively. Water content in the reaction mixture increased in the early stage of less than 1 h and then decreased gradually. The water content was less than 7 wt.% during the reaction. The $\alpha$ was higher than 200. The total permeated amount of ethanol, which was major organic component in the permeate was 0.4 wt.% of the initial amount of ethanol. It is evident

Table 1
PV performance of zeolite membranes for water/ethanol mixture (10/90 wt.%) at 348 K

| Zeolite membrane | Si/Al ratio | Flux $Q$ ($\mathrm{kg\,m^{-2}\,h^{-1}}$) | Separation factor $\alpha$ |
|---|---|---|---|
| A | 1 | 2.15 | 10000 |
| X | 1.3 | 0.89 | 360 |
| Y | 1.9 | 1.59 | 130 |
| T | 3.6 | 0.81 | 830 |
| T | 3.6 | 0.60 | 4400 |

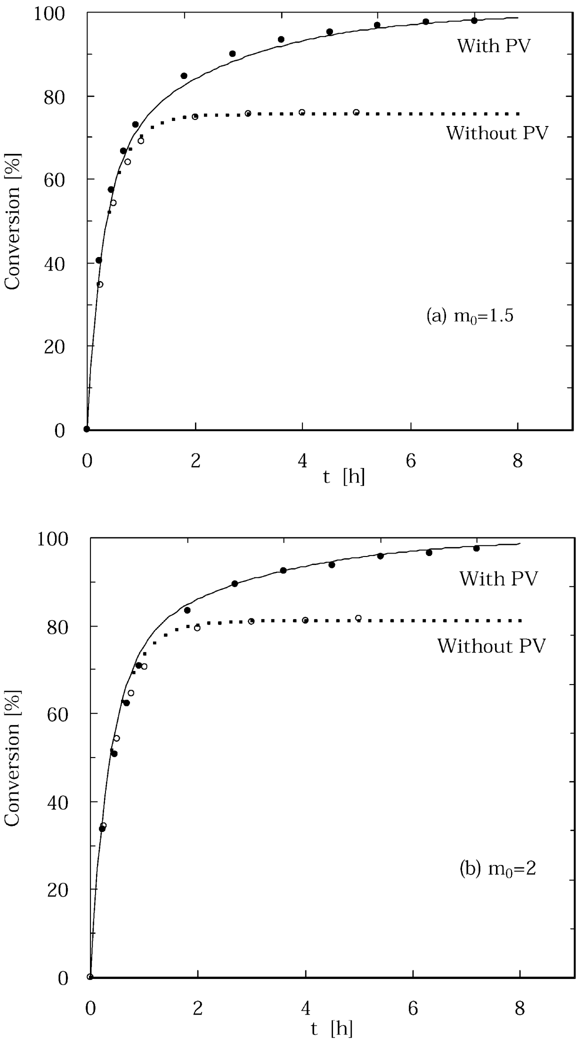

Fig. 2. Variation in the conversion with reaction time for the esterification with and without PV for $m_0$ of (a) 1.5 and (b) 2 at 343 K. The dotted lines were calculated from Eq. (1) with $k$ of 0.0026 l/(mol min)$^{-1}$ and $K_e$ of 3.2. The solid lines were calculated from Eqs. (1)–(4) using $q_{W10}$ of: (a) 1.1; (b) 0.5 kg m$^{-2}$ h$^{-1}$, respectively.

that the selective removal of water by PV separation shifted the equilibrium in favor of ester formation.

According to the general kinetic expression for second-order reversible reaction, the reaction rate of esterification is written as

$$-\frac{dC_A}{dt} = kC_AC_B - \left(\frac{k}{K_e}\right)C_EC_W \qquad (1)$$

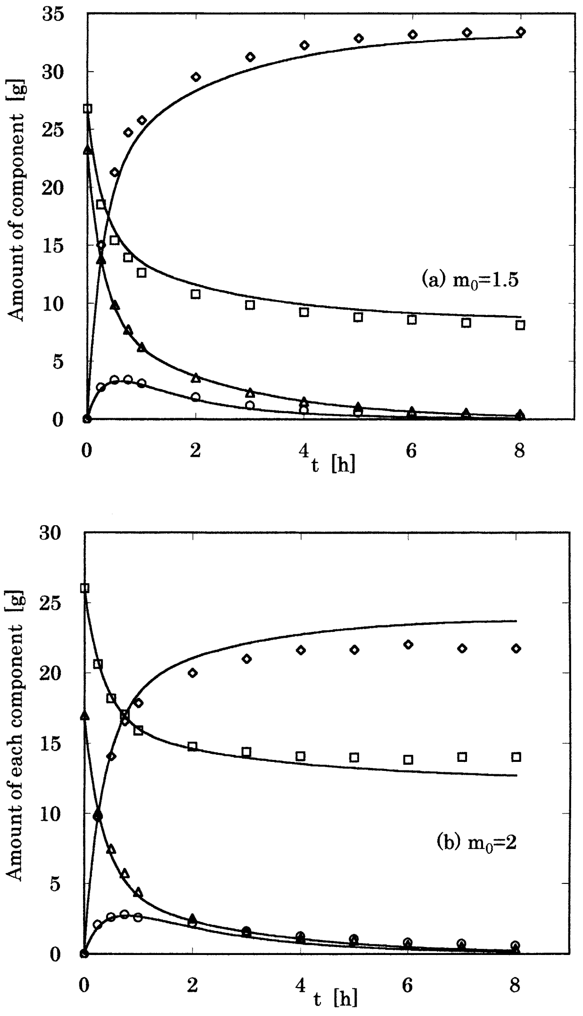

Fig. 3. Variation in the amount of each component in the reaction mixture with reaction time for $m_0$ of (a)1.5 and (b) 2 at 343 K. The solid lines were calculated from Eqs. (1)–(4). (△) Acetic acid; (□) ethanol; (○) water; (◇) ethyl acetate.

where $C_A$, $C_B$, $C_E$ and $C_W$ are the concentration of acetic acid, ethanol, ethyl acetate and water, respectively. The equilibrium constant $K_e$ was determined from the composition of the reaction mixture at equilibrium. The forward rate constant $k$ was determined from the initial stage of the reaction. The broken lines shown in Fig. 2(a) and (b) were calculated from Eq. (1) using the values of $k$ and $K_e$ determined thus. The calculated lines were in good agreement with the experimental values, indicating that the esterification of acetic acid with ethanol obeys the simple second-order kinetics.

Permeation flux of each component is generally considered to be proportional to its composition. When $\alpha$ is higher than 200, the permeated amounts of organic components may be neglected. On these assumption, the time course of PV-aided esterification was calculated by solving the following equations together with Eq. (1):

$$-\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t} = kC_\mathrm{A}C_\mathrm{B} - \left(\frac{k}{K_\mathrm{e}}\right)C_\mathrm{E}C_\mathrm{W} \tag{2}$$

$$\frac{\mathrm{d}C_\mathrm{E}}{\mathrm{d}t} = kC_\mathrm{A}C_\mathrm{B} - \left(\frac{k}{K_\mathrm{e}}\right)C_\mathrm{E}C_\mathrm{W} \tag{3}$$

$$\frac{\mathrm{d}C_\mathrm{W}}{\mathrm{d}t} = kC_\mathrm{A}C_\mathrm{B} - \left(\frac{k}{K_\mathrm{e}}\right)C_\mathrm{E}C_\mathrm{W} - \frac{q_\mathrm{W10}S}{V}\frac{C_\mathrm{W}}{0.1} \tag{4}$$

where $q_\mathrm{W10}$ was the water flux in kg m$^{-2}$ h$^{-1}$ at 10 wt.% water composition, $S$ the effective membrane area in m$^2$. The amount of reaction mixture $V$ (kg) was calculated by subtracting the permeate and sampling amount from the initial amount of the reaction mixture $V_0$. The solid lines in Figs. 2 and 3 were calculated from these equations using the water flux measured for the water–ethanol mixture (10 wt.% water) as $q_\mathrm{W10}$. The solid lines were also in good agreement with the experimental results for PV-aided esterification.

Although $q_\mathrm{W10}$, $S$ and $V_0$ can be varied independently, $q_\mathrm{W10}S/V_0$ can be treated as one parameter which expresses the capacity of eliminating water from the reaction system. Fig. 4(a) and (b) shows the simulation curves calculated from the simple model described above for $m_0 = 1.5$ and 2, respectively. The $q_\mathrm{W10}S/V_0 = 0$ corresponds to the esterification without PV. The curve for $q_\mathrm{W10}S/V_0 = 0.64$ was the same as that for the ideal PV separation, that is, the esterification neglecting the back reaction. The simulation curve for $q_\mathrm{W10}S/V_0 = 0.16$, which was a quarter of the value for the ideal PV separation, did not differ from the one for the ideal separation so much. In this study, the $q_\mathrm{W10}S/V_0$ was in the range 0.05–0.08. It is possible to design the large-scale reactor having roughly twice larger $S/V_0$ ratio compared to the laboratory scale used in this study, where only one membrane was installed.

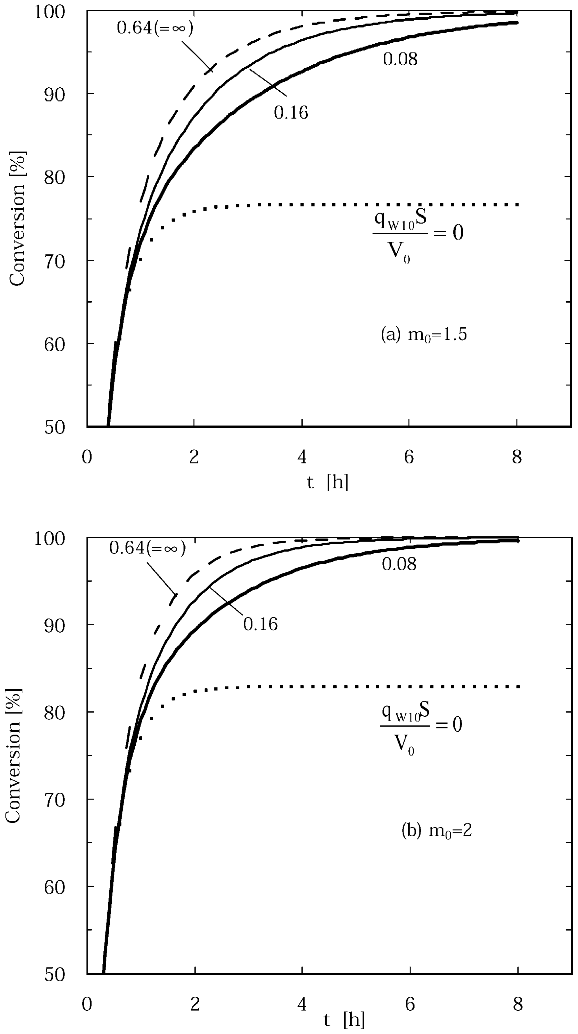

Fig. 4. Influence of the capacity of eliminating water from the reaction mixtures on variation in the conversion with the reaction time for $m_0$: (a) 1.5 and (b) 2 at 343 K.

The stability of zeolite T membrane to acid was tested by immersing the membrane in a water/acetic acid (50/50 wt.%) mixture. Table 2 lists variation in PV performance of the zeolite T membrane with immersion time. Although $Q$ did not change largely, the $\alpha$ decreased gradually. It should be noted that the $\alpha$ value partly recovered by immersing the membrane into aqueous alkaline solution. The zeolite T membrane was stable to acid to some extent, but further study is still necessary about the long-term stability and the recovery process with aqueous alkaline solution.

Table 2
Variations in $Q$ and $\alpha$ of zeolite T membrane with immersion in a water/acetic acid (50/50 wt.%) solution[a]

| Immersion time (day) | $Q$ ($\mathrm{kg\,m^{-2}\,h^{-1}}$) | $\alpha$ |
|---|---|---|
| (3 h) | 1.46 | 182 |
| 4 | 1.90 | 120 |
| 15 | 1.81 | 56 |
| 23 | 1.86 | 46 |
| 32 | 1.82 | 37 |
| 36[b] | 1.77 | 86 |
| 36[b] | 1.10[c] | 260[c] |

[a] PV for water/acetic acid (50/50 wt.%) at 348 K.

[b] Prior to the PV measurement, the membrane was immersed in an aqueous NaOH solution of pH = 10 at room temperature for 10 h and washed with water for 1 h.

[c] PV for water/ethanol (10/90 wt.%) at 348 K.

## 4. Conclusion

The PV separation with zeolite T membrane was applied to the esterification of acetic acid with ethanol. The conversion exceeded the equilibrium limit and reached to almost 100% within 8 h for $m_0 = 1.5$ and 2, respectively. The PV-aided esterification process was simulated using a simple model. The long-term stability of the zeolite T membrane should be examined to discuss the feasibility. This is now under investigation.

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