

# PERVAPORATION-AIDED ESTERIFICATION OF OLEIC ACID

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Esterification of oleic acid with ethanol in the presence of *p*-toluenesulfonic acid was carried out at temperatures up to 383 K and initial molar ratios of ethanol to oleic acid,  $m_0$ , up to 6. A kinetic equation having both a term of rate reduction due to water and a  $m_0$ -dependent rate constant are presented. The esterification, aided with pervaporation through asymmetric polyimide membranes, was carried out at 348 K and 371 K under atmospheric and elevated pressures respectively. Almost complete conversion was attained for  $m_0$  of 2 in a short time with a low concentration of the catalyst at 371 K. Only water and ethanol permeated through the membranes. The permeation flux was expressed by the product of the permeability constant,  $P$ , and the permeant concentration of the liquid.  $P$  depended on the concentration of oleic acid and ethyl oleate at 371 K, but not at 348 K. A model in which the kinetic equation is combined with the permeation flux equation taking both volume change and sampling loss of the reaction mixture into consideration represented the experimental time course of the reaction sufficiently well. The influence of operating parameters on the reaction time required for a conversion of 98% and on the productivity was investigated by simulation from the model.

## Introduction

The use of membranes in chemical reaction processes is attracting much attention. A number of investigations have concentrated on the application of hydrogen separation membranes to reversible gas-phase reactions<sup>10</sup>. Other recent investigations have been made on the application of water-permeable membranes to liquid-phase reactions<sup>1-5,7</sup>. In previous papers we reported on pervaporation (PV)-aided esterification of carboxylic acids with alcohols<sup>4,5</sup>. These studies showed that membrane separation of water produced from the reaction mixtures favorably shifts the chemical equilibrium, resulting in a much higher conversion in a shorter reaction time as compared with esterification without PV. We also proposed a simple kinetic model of the process of PV-aided esterification<sup>5</sup>. More detailed models were later proposed by Neel *et al.*<sup>1,2</sup>) and by us<sup>8,9</sup>).

For preparation of non- or less-volatile ester-chemicals such as perfumes and ester-waxes, two-step esterification of the corresponding raw acids with large excess of lower alcohols is commonly used to accomplish an esterification degree of more than 95%. PV-aided esterification is, therefore, interesting as an efficient process for preparation of the esters. In the present study, the PV-aided esterification of oleic acid with ethanol was investigated experimentally and theoretically.

## 1. Experimental

Asymmetric membranes of two kinds of polyimide, poly-etherimide (PEI) and poly(4,4'-oxydiphenylene pyromellitimide) (POPMI), were prepared by the phase inversion method, as described elsewhere<sup>4-6</sup>).

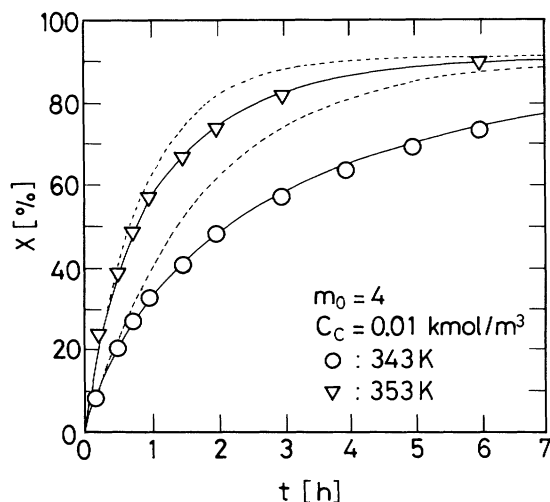
The PV and the PV-aided reaction were carried out at temperatures below 353 K under atmospheric pressure using an ordinary apparatus described previously<sup>5</sup>, and also at temperatures above 353 K under elevated pressures using a hermetically sealed PV cell equipped with a stirrer.

All reagents were purified by ordinary methods. As catalyst, *p*-toluenesulfonic acid was used. Oleic acid was fed to the PV cell heated to a given temperature. Ethanol containing a small amount of *p*-toluenesulfonic acid was heated in a flask to a given temperature and then added to the PV cell to start the reaction. Product samples (ca. 0.4 g every sampling) were withdrawn periodically and were analyzed by titration for oleic acid and by gas chromatography for water and ethanol, as described elsewhere<sup>3</sup>). Blank reaction without PV was carried out, using the PV cell installed with a stainless steel plate instead of a membrane. The experimental conditions are listed in **Table 1**.

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**Table 1.** Experimental conditions

| Parameters                   | Blank reaction | PV-aided reaction   |
|------------------------------|----------------|---------------------|
| $m_0$                        | 2 - 6          | 2 and 3             |
| $T$ [K]                      | 343 - 383      | 348 and 371         |
| $C_C$ [kmol/m <sup>3</sup> ] | 0.005 - 0.03   | 0.01 - 0.02         |
| $V_0$ [cm <sup>3</sup> ]     | 20 - 100       | 55 - 100            |
| $S$ [cm <sup>2</sup> ]       | —              | 19.2, 22.1 and 39.2 |

**Fig. 1** Conversion-time curves of the blank reaction. Solid and broken lines were calculated from Eqs. (1) and (2) with and without parameter  $a$ , respectively

## 2. Results and Discussion

### 2.1 Kinetics of esterification reaction

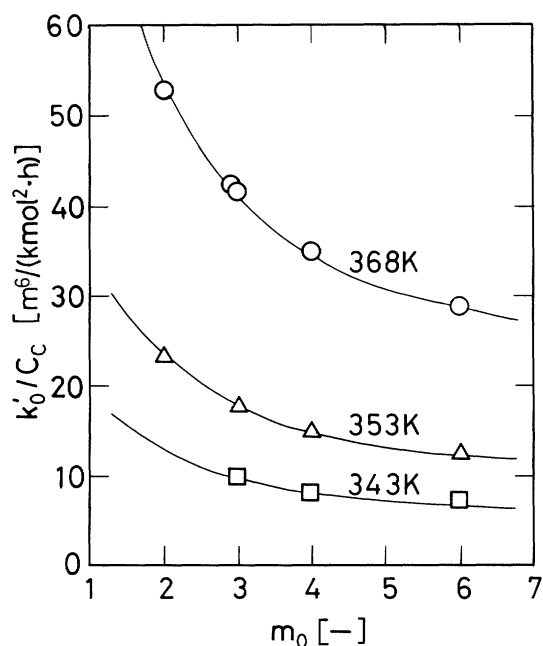
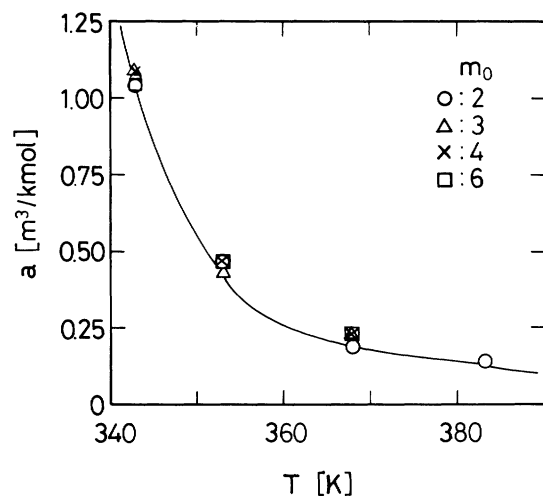
According to the general expression for second-order reversible reaction, the rate of esterification is written as:

$$-dC_A/dt = kC_A C_B - (k/K_e) C_E C_W \quad (1)$$

However, the esterification reaction of oleic acid with ethanol in the presence of *p*-toluenesulfonic acid did not obey simple second-order kinetics, as mentioned below.

**Figure 1** shows typical conversion-time curves without PV. 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, neglecting the backward reaction. The broken lines shown in Fig. 1 were calculated from Eq. (1) using the values of  $k$  and  $K_e$ . The experimental data points deviate downward from the calculated lines as the reaction proceeds, suggesting that the water produced reduced the reaction rate. This was confirmed by the fact that the initial reaction rate decreased with the increase in initial concentration of

\* The reduction effect could also be expressed by the term of  $\exp(-aC_W)$  as reported in Ref. 8. There is little reason to choose between these two expressions.

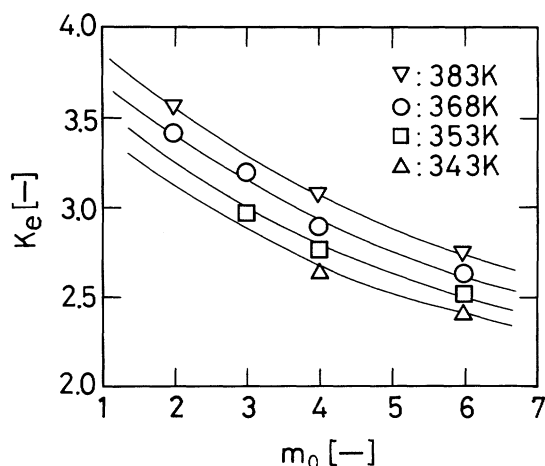
**Fig. 2** Dependence of initial molar ratio on forward rate constant**Fig. 3** Dependence of temperature on reduction parameter  $a$ 

water. In the present study, the effect of water produced on the reaction rate was taken into account in the term  $(1 + aC_W)^{-1}$ ;

$$k = k'_0 / (1 + aC_W) \quad (2)$$

Each experimental conversion-time curve was compared with the predicted curves for arbitrary values of the forward rate constant,  $k'_0$ , and the reduction parameter,  $a$ . A set of the values of  $k'_0$  and  $a$ , which gave the best fit between the experimental and predicted curves, was determined. The solid lines in Fig. 1 were calculated from Eqs. (1) and (2) using the thus-determined values of  $k'_0$  and  $a$ . They are in good agreement with the experimental data.

The  $k'_0$  value was proportional to the concentration of the catalyst,  $C_C$ , and was dependent on the initial



**Fig. 4** Dependence of initial molar ratio on equilibrium constant

molar ratio of ethanol to oleic acid,  $m_0$ , as shown in **Fig. 2**. The parameter  $a$  depended only on temperature, as shown in **Fig. 3**, irrespective of  $C_C$  and  $m_0$ . The value of  $a$  decreased with increase in temperature. Zhou *et al.* reported on the kinetics of esterification of oleic acid with methanol at temperatures ranging from 383 K to 413 K<sup>11)</sup>. They found no effect of water on the reaction rate at these temperatures. This is reasonable, judging from the temperature dependence of parameter  $a$ .  $K_e$  depended on  $m_0$ , as shown in **Fig. 4**. Finally,  $k'_0$ ,  $a$ , and  $K_e$  were expressed by the following experimental equations.

$$\begin{aligned} k'_0 &= k_0 C_C f(m_0) \exp(-E/RT) \\ k_0 &= 4.1313 \times 10^8 \text{ m}^6 (\text{kmol}^2 \cdot \text{h}) \\ E &= 60.66 \text{ kJ/mol} \\ f(m_0) &= 230.10 - 190.82m_0 + 71.69m_0^2 - 11.61m_0^3 \\ &\quad + 0.65m_0^4 \end{aligned} \quad (3)$$

$$\begin{aligned} a &= 9924.85 - 103.959T + 0.40814T^2 \\ &\quad - 7.1175 \times 10^{-4}T^3 + 4.65171 \times 10^{-7}T^4 \end{aligned} \quad (4)$$

$$\begin{aligned} K_e &= K_{e,0} g(m_0) \exp(-\Delta H_r / RT) \\ K_{e,0} &= 2.871 \\ \Delta H_r &= 3.36 \text{ kJ/mol} \\ g(m_0) &= 4.207 - 0.361m_0 + 0.019m_0^2 \end{aligned} \quad (5)$$

## 2.2 PV separation of quaternary system

In PV separation of ethanol-water solution through asymmetric PEI and POPMI membranes, the permeation flux of each component,  $q_i$ , was proportional to the concentration of the corresponding component,  $C_i$ , at a low content of water (less than ca. 15 wt%).

$$q_i = P_i C_i \quad i = B \text{ or } W \quad (6)$$

Membrane performances in the ethanol-water system of

**Table 2.** Typical membrane performances for ethanol-water system

| Membranes           | $T$<br>[K] | $q_w^{a)}$<br>[mol/(m <sup>2</sup> ·h)] | $\alpha_{w/B}^{a)}$<br>[—] | $P_w$<br>[10 <sup>-4</sup> m/h] | $P_B$<br>[10 <sup>-4</sup> m/h] |
|---------------------|------------|---|----------------------------|---------------------------------|---------------------------------|
| PEI                 | 348        | 82.2                                    | 60                         | 315                             | 5.11                            |
| POPME <sup>b)</sup> | 348        | 66.6                                    | 110                        | 181                             | 1.76                            |
| POPME <sup>c)</sup> | 371        | 45.6                                    | 106                        | 111                             | 1.05                            |

a) at 10 wt% water

b) imidized at 473 K for 10h

c) imidized at 473 K for 10h and then heat-treated at 553 K for 5h

**Table 3.** Plasticization parameters for asymmetric POPMI membranes<sup>a)</sup>

| Parameters                    | $\delta_{w,A}$ | $\delta_{w,E}$ | $\delta_{B,A}$ | $\delta_{B,E}$ |
|-------------------------------|----------------|----------------|----------------|----------------|
| values [m <sup>3</sup> /kmol] | 0.26           | 0.85           | 0.09           | 0.68           |

a) at 371 K for the membranes finally treated at 553 K for 5 h.

the membranes used for PV-aided esterification are listed in **Table 2**.

In PV separation of the quaternary system, neither oleic acid nor ethyl oleate permeated through these membranes. At 348 K, the permeation flux of water and ethanol components obeyed Eq. (6) with practically the same values of  $P_B$  and  $P_W$  as for the ethanol-water system. On the other hand, at 371 K the permeation flux was significantly larger than that estimated from Eq. (6) using the  $P_B$  and  $P_W$  values obtained for the ethanol-water system, and depended on both  $C_A$  and  $C_E$ , indicating that both oleic acid and ethyl oleate plasticize the membranes. The situation was similar to that for the asymmetric POPMI membranes treated at 553 K for 5 h. It is noted that an increase in temperature of 23 K resulted in plasticization of the membranes.

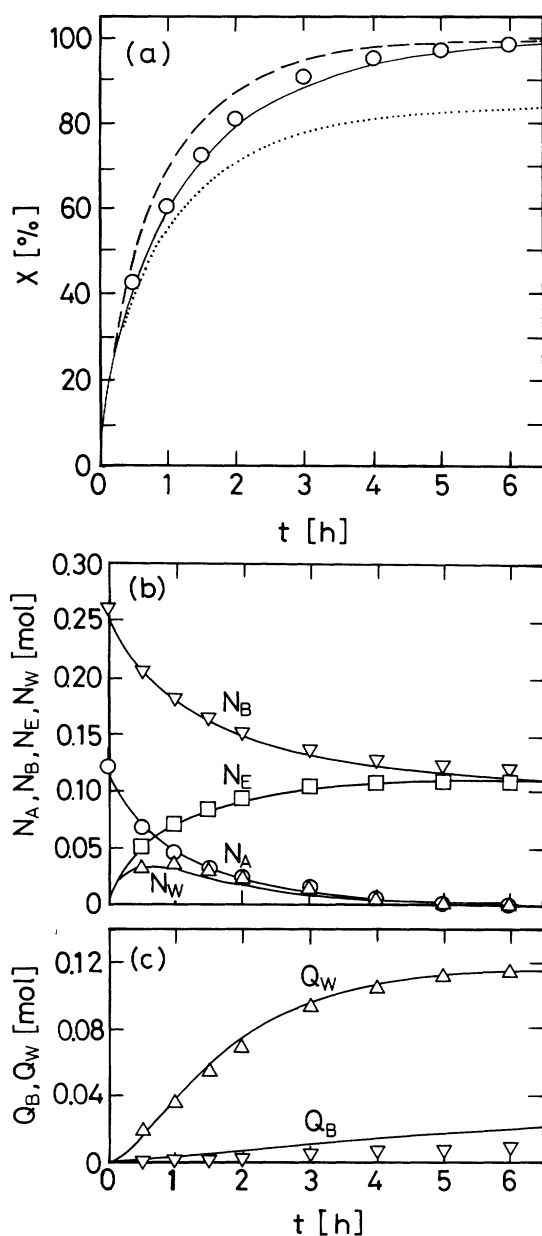
At 371 K, the plasticization effect of oleic acid and ethyl oleate was taken into account in the term  $\exp(\delta_{i,A}C_A + \delta_{i,E}C_E)$ ;

$$q_i = P_i \exp(\delta_{i,A}C_A + \delta_{i,E}C_E) C_i \quad (7)$$

where  $\delta_{i,A}$  and  $\delta_{i,E}$  are the plasticization parameters of oleic acid and ethyl oleate, respectively, on the permeation of component  $i$  ( $i = W$  or  $B$ ). These parameters were experimentally determined from the PV separation of the four-component system, varying the composition, and are listed in **Table 3**.

## 2.3 PV-aided esterification

For the PV-aided esterification at 348 K, variations in the conversion,  $X$ , the amount of component  $i$  in the reaction mixture,  $N_i$ , and the cumulative permeation amount of component  $i$ ,  $Q_i$ , with time are shown in **Figs. 5** (referred to as Ex. No.1) and **6** (Ex. No.2) for asymmetric PEI and POPMI membranes respectively. The

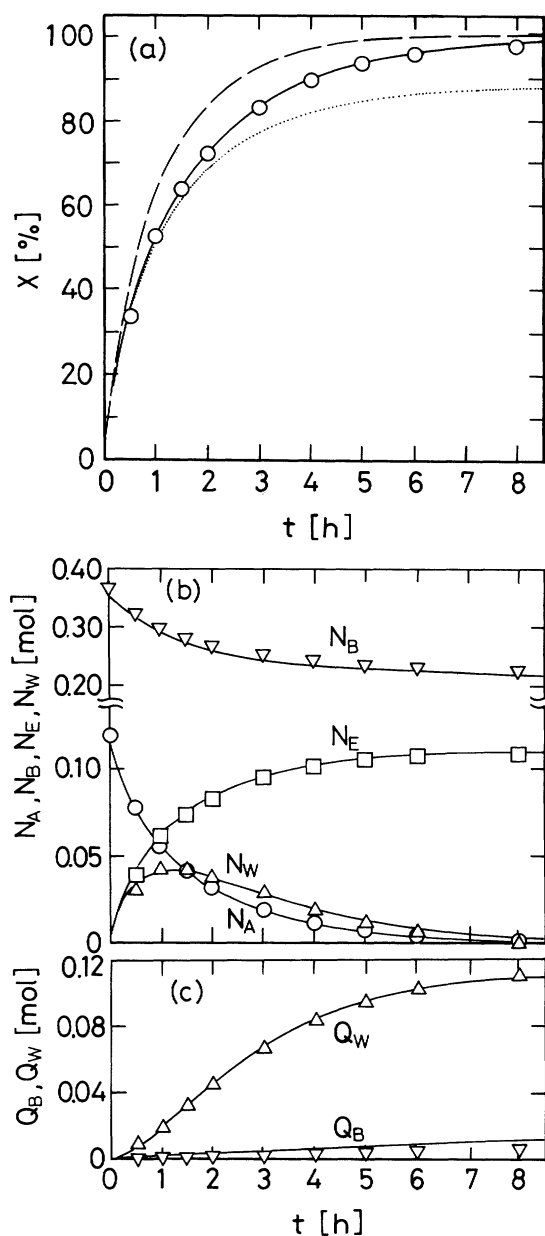


**Fig. 5** Time-course of esterification with PV separation through an asymmetric PEI membrane.  $S = 22.1 \text{ cm}^2$ ,  $V_0 = 56.3 \text{ cm}^3$ ,  $C_C = 0.0190 \text{ kmol/m}^3$ ,  $m_0 = 2.10$ , and  $T = 348 \text{ K}$ . Dotted and broken lines were calculated respectively for the blank reaction and the reaction with ideal PV separation. Solid lines are simulation lines calculated from the model.

conversion at the  $j$ -th sampling,  $X_j$ , was calculated from Eq. (8), taking the sampling loss of oleic acid,  $S_{A,j-1}$ , into account.

$$X_j = (N_{A,0} - N_{A,j} - S_{A,j-1}) / (N_{A,0} - S_{A,j-1}) \quad (8)$$

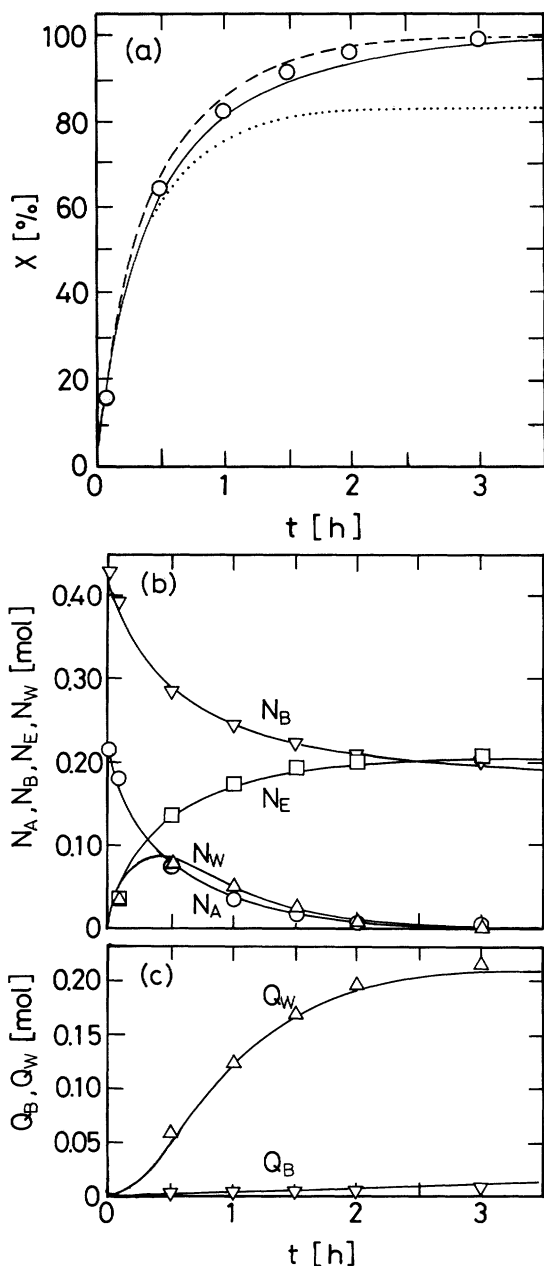
The dotted and broken lines in Figs. 5 and 6 were calculated for esterification without PV separation (blank reaction) and for that with ideal PV separation ( $P_W = \infty$  and  $P_B = 0$ ) respectively. In Ex. No.1, water disappeared completely from the reaction mixture at 6 h and the conversion became 98.3%, whereas  $C_W$  and  $X$  were 0.114



**Fig. 6** Time-course of esterification with PV separation through an asymmetric POPMI membrane.  $S = 19.2 \text{ cm}^2$ ,  $V_0 = 61.9 \text{ cm}^3$ ,  $C_C = 0.0142 \text{ kmol/m}^3$ ,  $m_0 = 3.07$ , and  $T = 348 \text{ K}$ . Dotted, broken, and solid lines are the same as in Fig. 5.

$\text{kmol/m}^3$  and only 95.9%, respectively, at 6 h in Ex. No.2. The losses of ethanol due to the permeation were 3.5% and 4.8% per  $N_{A,0}$  in Ex. No.1 and 2 respectively. The conversion-time curve is closer to the broken line in Ex. No.1 than in Ex. No.2. This is mainly because the capacity of eliminating water from the reaction system, which is expressed by  $P_W S / V_0$ , was larger in Ex. No.1 than in Ex. No.2 by a factor of 2.2.

The PV-aided reaction enables us to achieve the almost complete conversion even at  $m_0$  of 2, as the result of elimination of produced water from the reaction system. However, a long reaction time is still required for a high conversion at 348 K because of the low reaction rate. Therefore, the reaction temperature should be



**Fig. 7** Time-course of esterification with PV separation through an asymmetric POPMI membrane.  $S = 39.2 \text{ cm}^2$ ,  $V_0 = 99.1 \text{ cm}^3$ ,  $C_C = 0.0101 \text{ kmol/m}^3$ ,  $m_0 = 1.99$ , and  $T = 371 \text{ K}$ . Dotted, broken, and solid lines are the same as in Fig. 5.

raised.

**Figure 7** shows the results for esterification with PV separation through an asymmetric POPMI membrane at 371 K under elevated pressure (Ex. No.3). A conversion of 99.2% was attained at 3 h with  $C_C = 0.01 \text{ kmol/m}^3$ . The loss of ethanol due to the permeation was 3.5% per  $N_{A,0}$ . It is noted that both the reaction time and the catalyst concentration required were reduced by half by raising the reaction temperature by 23 K. The conversion-time curve is very close to that for the reaction with ideal PV separation (broken line). The capacity for eliminating water is estimated to be ca. 1.6 times larger in Ex.

No.3 than in Ex. No.1 because of the plasticization effect.

After the reaction at 371 K, the membranes used were washed with ethanol, dried and subjected to measurement of membrane performance in the ethanol-water system. The permeation flux decreased by 10- 15%, but the selectivity remained almost constant. It was possible to use the membranes for the PV-aided esterification at 371 K several times.

## 2.4 Simulation of PV-aided esterification

**1) Theoretical model** It is important to obtain a model to simulate the time course of the PV-aided reaction and to predict the influence of various operating parameters. In the present model, the reaction kinetics (Eqs. (1) - (5)) are combined with the permeation rate equation (Eq. (7)), taking both volume change of the reaction mixture with the proceeding reaction and sampling loss of the reaction mixture into consideration.

Taking permeation of water and ethanol components through a membrane into account, variations in  $C_B$  and  $C_W$  with time are represented by Eqs. (9) and (10).

$$dC_B/dt = dC_A/dt - P_B \exp(\delta_{B,A}C_A + \delta_{B,E}C_E)(S/V)C_B \quad (9)$$

$$dC_W/dt = -dC_A/dt - P_W \exp(\delta_{W,A}C_A + \delta_{W,E}C_E)(S/V)C_W \quad (10)$$

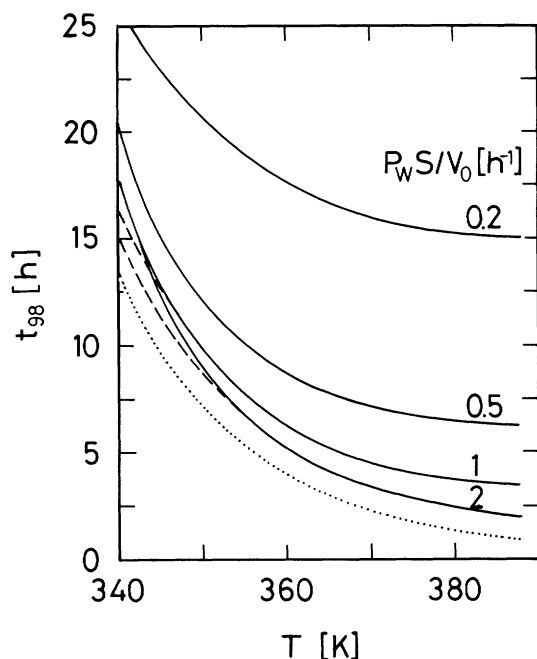
The volume of the reaction mixture,  $V$ , is given by Eq. (11) according to the additivity of volume.

$$V = N_A M_A / \rho_A + N_B M_B / \rho_B + N_E M_E / \rho_E + N_W M_W / \rho_W \quad (11)$$

The following values of density at 358 K were used for the calculation:  $\rho_A = 852$ ,  $\rho_E = 827$ ,  $\rho_B = 741$ , and  $\rho_W = 970 \text{ kg/m}^3$ .

Eqs. (1) - (5) and (9) - (11) can be numerically solved by the Runge-Kutta-Gill method, taking sampling loss of the reaction mixture into consideration. The solid lines in Figs. 5 and 6 were thus calculated using the  $P_B$  and  $P_W$  values in Table 2. The calculated lines are in good agreement with the experimental data except for  $Q_B$ . The calculated values of  $Q_B$  were twice the experimental values. However, this discrepancy hardly affected the other calculated values because of  $N_B \gg Q_B$ . Similarly good agreement between experimental and calculated curves was obtained for the PV-aided esterification at 348 K under different conditions, provided that both  $P_B$  and  $P_W$  in the ethanol-water system were previously determined for the membranes used in the reaction.

In the PV-aided esterification at 371 K, the plasticization effect was significant even for the asymmetric POPMI membranes treated at 573 K. The solid lines in Fig. 7 were calculated using the  $P_B$  and  $P_W$  values in Table 2 together with the plasticization parameters in Table 3. The calculated lines are in good agreement with the experimental data, indicating that the permeation flux in the PV-aided esterification is well expressed by

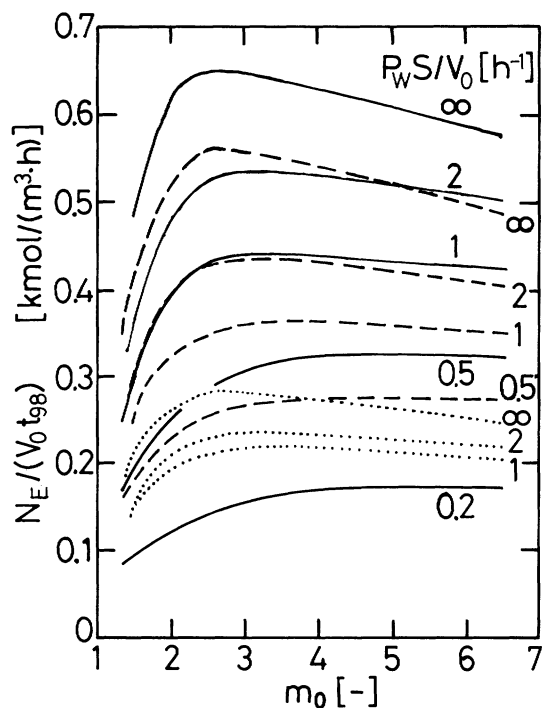


**Fig. 8** Influence of temperature and capacity of water elimination on time required for conversion of 98%.  $m_0 = 2$  and  $C_C = 0.01$  kmol/m<sup>3</sup>. Solid and broken lines are for  $P_W/P_B$  of 100 and 500 respectively. Dotted line is for ideal PV separation.

Eq. (7). The small difference between the experimental and calculated conversion-time curves seems mainly due to experimental error in controlling the reaction temperature.

2) **Influence of operating parameters** In the previous section it was confirmed that the present model for the PV-aided esterification could represent the time course of the reaction sufficiently well. In this section, the reaction time to attain a conversion of 98%,  $t_{98}$ , is calculated from the model, varying operating parameters such as  $m_0$ ,  $T$ ,  $C_C$ ,  $P_W S/V_0$  and  $P_W/P_B$ , to evaluate their influence. Although  $P_W$ ,  $S$  and  $V_0$  can be varied independently, it is better to treat  $P_W S/V_0$  as one parameter which expresses the capacity of eliminating water from the reaction system, in the calculation. Here, for simplicity, both  $P_W$  and  $P_B$  are assumed to be independent of composition and temperature.

**Figure 8** shows the influence of  $T$  and  $P_W S/V_0$  on  $t_{98}$  with a constant value of  $m_0 = 2$ . In the present experiments,  $P_W S/V_0$  was in the range of 0.5 to 2 h<sup>-1</sup>. At every temperature, increasing  $P_W S/V_0$  from 0.2 to 1 h<sup>-1</sup> reduces the reaction time significantly. For  $P_W S/V_0$  less than 0.5 h<sup>-1</sup>, it is less effective to raise the temperature over 365 K. At temperatures below 350 K, for  $C_C = 0.01$  kmol/m<sup>3</sup>, it is less effective to raise  $P_W S/V_0$  over 1 h<sup>-1</sup>, because the loss of ethanol due to the permeation does not become negligible either at long reaction time or with low selectivity of membrane. In this case, it is necessary to increase both  $P_W S/V_0$  and  $P_W/P_B$ , as shown by the broken lines in Fig. 8. For  $P_W S/V_0$  greater than 1 h<sup>-1</sup>, it is very effective even for membranes with low selectivity to

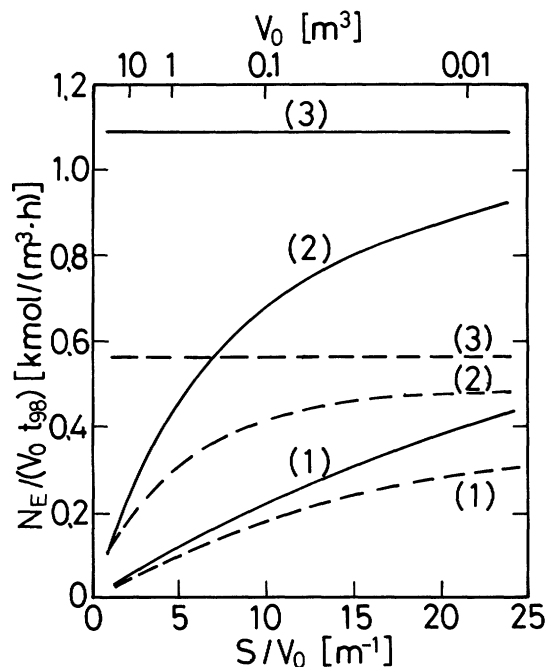


**Fig. 9** Influence of initial molar ratio and capacity of water elimination on productivity.  $P_W/P_B = 100$ . The lines for  $P_W S/V_0 = \infty$  refer to ideal PV separation. Solid line:  $T = 363$  K and  $C_C = 0.01$  kmol/m<sup>3</sup>. Broken line:  $T = 348$  K and  $C_C = 0.02$  kmol/m<sup>3</sup>. Dotted line:  $T = 348$  K and  $C_C = 0.01$  kmol/m<sup>3</sup>.

raise the temperature over 365 K.

The production per reaction time and volume,  $N_E/(V_0 t_{98})$ , can be used as a measure of productivity of the process. **Figure 9** shows the influence of  $m_0$ ,  $P_W S/V_0$  and  $C_C$  on  $N_E/(V_0 t_{98})$ . For the reaction with ideal PV separation,  $N_E/(V_0 t_{98})$  increases rapidly with increase in  $m_0$ , reaches a maximum at  $m_0 = 2.5$ , and then decreases gradually. It has a maximum at  $m_0 = 3$  for  $P_W S/V_0$  of 2 h<sup>-1</sup>, whereas for  $P_W S/V_0$  less than 0.5 h<sup>-1</sup>, it increases continuously with increase in  $m_0$  and does not reach a maximum even around  $m_0 = 6$ . In the actual batch reactor process, the optimum  $m_0$  may be 2 - 2.5, taking working time required before and after the reaction, the loss of ethanol due to permeation, and recovery of excess ethanol into consideration. The loss of ethanol due to permeation increases by about 50% with an increase in  $m_0$  from 2 to 3. An increase in  $C_C$  is effective in increasing  $N_E/(V_0 t_{98})$  at lower reaction temperatures; at 348 K, the productivity with ideal PV separation at  $C_C$  of 0.01 kmol/m<sup>3</sup> is attained with  $P_W S/V_0$  of 0.7 h<sup>-1</sup> at  $C_C$  of 0.02 kmol/m<sup>3</sup>.

It is difficult to prepare a commercial-size reactor having the same level of  $S/V_0$  as with the laboratory-size reactor. We now consider a cylindrical reactor equipped with membranes at the bottom and the side wall and with  $V_0 = \pi r^2 h$  and  $S = \pi r^2 + 2\pi r h$ . Assuming  $r = 2h$ ,  $N_E/(V_0 t_{98})$  is calculated from the model, varying  $r$  or  $V_0$ . The results are shown in **Fig. 10** for two levels of membrane



**Fig. 10** Influence of scale-up of cylindrical reactor on productivity for  $m_0 = 2.5$   
Solid line:  $T = 373$  K and  $C_C = 0.01$  kmol/m<sup>3</sup>.  
Broken line:  $T = 348$  K and  $C_C = 0.02$  kmol/m<sup>3</sup>.  
(1)  $P_W = 0.03$  m/h and  $P_W/P_B = 100$ .  
(2)  $P_W = 0.15$  m/h and  $P_W/P_B = 500$ .  
(3) ideal membrane ( $P_W = \infty$  and  $P_B = 0$ ).

performance. The membrane performance of  $P_W = 0.03$  m/h and  $P_W/P_B = 100$  is similar to the level of the membranes used in this study. The other level ( $P_W = 0.15$  m/h and  $P_W/P_B = 500$ ) is higher by a factor of 5. This figure clearly shows that the productivity decreases significantly with scaling up, especially at the present level of membrane performance. For practical use of PV-aided esterification it is necessary to design a large-scale reactor with much higher  $S/V_0$  and to develop membranes with much higher  $P_W$  together with excellent long-term durability for the reaction system.

## Conclusions

The PV-aided esterification of oleic acid can be performed more effectively at higher temperature, at least above 360 K, and the optimum  $m_0$  of 2 - 2.5 with  $P_W S/V_0$  greater than 1 h<sup>-1</sup>,  $P_W/P_B = 100$ , and  $C_C = 0.01$  kmol/m<sup>3</sup>. For practical use, it is necessary to develop both a large-scale reactor with high  $S/V_0$  and a membrane with high  $P_W$  together with excellent long-term durability.

## Nomenclature

|     |                            |                        |
|-----|----------------------------|------------------------|
| $a$ | = rate reduction parameter | [m <sup>3</sup> /kmol] |
| $C$ | = molar concentration      | [kmol/m <sup>3</sup> ] |

|              |   |                            |
|--------------|---|----------------------------|
| $E$          | = activation energy of reaction                                 | [kJ/mol]                   |
| $\Delta H_r$ | = average heat of reaction                                      | [kJ/mol]                   |
| $h$          | = height of cylindrical reactor                                 | [m]                        |
| $K_e$        | = equilibrium constant  | [-]                        |
| $K_{e,0}$    | = pre-exponential factor of equilibrium constant                | [-]                        |
| $k$          | = apparent forward rate constant                                | [m <sup>3</sup> /(kmol·h)] |
| $k'_0$       | = forward rate constant   | [m <sup>3</sup> /(kmol·h)] |
| $k_0$        | = frequency factor of forward rate constant                     | [m <sup>3</sup> /(kmol·h)] |
| $M$          | = molecular weight  | [kg/mol]                   |
| $m$          | = molar ratio of ethanol to oleic acid                          | [-]                        |
| $N_i$        | = amount of component $i$ in reaction mixture                   | [mol]                      |
| $P$          | = permeability constant   | [m/h]                      |
| $Q$          | = cumulative permeation amount                                  | [mol]                      |
| $q$          | = permeation flux   | [mol/(m <sup>2</sup> ·h)]  |
| $R$          | = gas constant  | [kJ/(mol·K)]               |
| $r$          | = inner radius of cylindrical reactor                           | [m]                        |
| $S$          | = effective membrane area                                       | [m <sup>2</sup> ]          |
| $S_{ij}$     | = cumulative sampling loss of component $i$ at $j$ -th sampling | [mol]                      |
| $T$          | = temperature   | [K]                        |
| $t$          | = time elapsed  | [h]                        |
| $t_{98}$     | = time required for 98% conversion                              | [h]                        |
| $V$          | = volume of reaction mixture                                    | [m <sup>3</sup> ]          |
| $X$          | = conversion  | [%]                        |

|            |  |                        |
|------------|--|------------------------|
| $\alpha$   | = water-to-ethanol separation factor                       | [-]                    |
| $\delta_i$ | = plasticization parameter for permeation of component $i$ | [m <sup>3</sup> /kmol] |
| $\rho$     | = density  | [kg/m <sup>3</sup> ]   |

## <Subscripts>

|   |                   |
|---|-------------------|
| A | = oleic acid      |
| B | = ethanol         |
| C | = catalyst        |
| E | = ethyl oleate    |
| i | = A, B, E or W    |
| j | = sampling number |
| W | = water           |
| 0 | = initial         |

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