Pervaporation of Water-Carboxylic Acids Solutions with Ion Exchange Membranes*

Hirofumi MIYOSHI**, Karl W. BÖDDEKER, Karl HATTENBACH and Axel WENZLAF

Department of Chemistry, GKSS Research Center, Max-Planck-Strasse, 2054 Geesthacht, West Germany
** Present address : Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka 593
(Received Aug. 3, 1987)

The pervaporation of water-carboxylic acids mixtures was studied using various kinds of ion exchange membranes. It was found that the flux of water was much greater than that of carboxylic acids. The relation between the concentration of water in the feed solution (\(X_w\)) and that in the pervaporated solution (\(Y_w\)) can be approximately represented by an equation, \(Y_w = 1 - E/X_w'\) where \(E\) is a constant, in the range 20 < \(X_w\) < 80 wt%. Neosepta CM-1 was the best of all ion exchange membranes used for the pervaporation to separate water or acetic acid from their mixtures. The activation energies were 28.7 kJ mol\(^{-1}\) for Neosepta CM-1 membrane, and 26.8 kJ mol\(^{-1}\) for Nafion 324 membrane. In addition, the flux decreased with an increase in molecular weight of the carboxylic acid employed.

Key words : Pervaporation, Ion exchange membrane, Carboxylic acid, Selectivity, Sorption

Introduction

Pervaporation is a membrane separation process involving liquid-gas systems applicable to a variety of liquid mixtures, and is especially useful for such separation of azeotropic mixtures or mixtures of liquids with small differences in vapor pressure that has never been easy by a conventional distillation method\(^1\)\(^-\)\(^5\). Yoshikawa \(et\ al.\)\(^6\) has studied the separation of water-acetic acid mixture by pervaporation through polymer membranes. Pervaporation of water-alcohol solutions with ion exchange membranes has already been studied by Wenzlaff \(et\ al.\)\(^7\), Cabasso \(et\ al.\)\(^8\), and Böddecke \(et\ al.\)\(^9\).

In this manner, pervaporation is known to be useful for the separation of liquid mixtures, but has only recently been employed in practice. On the other hand, it is desired to establish a new method for separating carboxylic acids from their aqueous solutions because recent development in biotechnology facilitates mass production of carboxylic acids. Therefore, the pervaporation of water-carboxylic acid solutions is investigated by using various kinds of ion exchange membranes in this study.

Experimental Equipment and Procedure

Figure 1 shows a diagram of the equipment used for the pervaporation experiment.

The tank (1) in Fig.1 was filled with the respective concentrations of acetic acid solutions. The concentration of the feed solution (\(X_w\)) in the tank (1) was changed from 1 to 100. \(viz.,\) 1.
Table 1 Characteristics of the ion exchange membranes for the pervaporation experiment.

<table>
<thead>
<tr>
<th></th>
<th>Neosepta</th>
<th></th>
<th></th>
<th></th>
<th>Nafion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CM-1</td>
<td>CM-2</td>
<td>CL-25T (I)</td>
<td>CL-25T (II)</td>
<td>AV-4T</td>
</tr>
<tr>
<td>Exchange capacity</td>
<td>2.0-2.5</td>
<td>1.6-2.2</td>
<td>1.5-1.8</td>
<td>1.5-1.8</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>[meg g⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>324</td>
</tr>
<tr>
<td>Thickness [mm]</td>
<td>0.146</td>
<td>0.147</td>
<td>0.175</td>
<td>0.175</td>
<td>0.150</td>
</tr>
<tr>
<td>Type</td>
<td>cation</td>
<td>cation</td>
<td>cation</td>
<td>cation</td>
<td>anion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cation</td>
</tr>
<tr>
<td>E (= C/A)ᵇ²</td>
<td>0.0600</td>
<td>0.0539</td>
<td>0.0611</td>
<td>0.0750</td>
<td>0.1050</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1130</td>
</tr>
</tbody>
</table>

a): Data from the catalogue of Tokuyama Soda Co. Ltd.
b): see text

Fig. 1 Schematic diagram of the equipment for pervaporation.

5, 20, 40, 60, 80, 95 and 100 (pure water) weight percent water. The solution in the tank (1) was circulated by a pump (4), and the flow rate was checked by a pressure gauge (7).

Each ion exchange membrane shown in Table 1 was set in a pervaporation cell (9 in Fig. 1) made of titanium; the net area of the membrane was 100 cm². Table 1 shows the characteristics of the ion exchange membranes used for this pervaporation experiment.

The vapor on the side of the permeation was withdrawn by a vacuum pump (13). The pressure measured by a manometer (10) was 5 mmHg.

The pervaporated solution was collected in a liquid nitrogen cold trap (11). After preliminary pervaporation for 30 or 60 minutes to obtain a constant flux, the trap was set up. The flux of the pervaporated solution was obtained by measuring the weight of the solution collected in the cold trap (11) per unit time.

The temperature of the circulating solution was kept constant at 313 K in experiments other than the one in which the temperature effect was studied between 298 and 333 K.

The concentrations of water in both the feed solution (Xw) and the pervaporated solution (Yw) were calculated from the carboxylic acids contents determined by a titration method with KOH solution.

Results and Discussion
1 Pervaporation of water and acetic acid
The results of the pervaporation experiment on water-acetic acid solutions are shown in Fig. 2 for each kind of ion exchange membrane used.

It is found from this figure that water per-
vaporates more easily than acetic acid through a membrane because the values of $Y_w$ are seen larger than those of $X_w$ in all the ranges of $X_w$ adopted. This might be due to the following three reasons.

The first is that the ion exchange membrane is scarcely swollen by acetic acid and can only slightly sorb acetic acid while it can sorb much water\textsuperscript{10}.

The second is that the moving resistance of acetic acid is larger than that of water through the pore of the membrane because the molecular diameter of acetic acid is larger than that of water.

The third is that H\textsuperscript{+} ions of acetic acid can easily go into the pore of the cation exchange membrane and can move freely combining successively with the fixed-ions in the membrane. On the other hand, many of the CH\textsubscript{3}COO\textsuperscript{-} ions remain outside the membrane. Thus, since the potential difference arises between inside and outside the membrane, that is, owing to the Donnan exclusion, H\textsuperscript{+} ions of acetic acid only slightly permeate through the membrane. The same may be true for CH\textsubscript{3}COO\textsuperscript{-} ions in the anion exchange membrane.

Therefore, water pervaporates preferentially through the ion exchange membrane, and acetic acid is concentrated in the feed solution during the pervaporation process by using the ion exchange membrane.

2 Pervaporation and sorption

The values of the sorption data\textsuperscript{10} ($X_w$) are also shown in Fig. 2 for comparison. In this figure, the amounts of water concentrated during the permeation through the respective membranes ($Y_w - X_w$) are smaller than those concentrated during the sorption from the feed solution into the membranes ($X_w - X_w$). Therefore, it is evident that the pervaporation process is significantly influenced by the sorption during the passage of water-acetic acid solution through ion exchange membranes.
3 Influence of $X_w$ on $J$

The dependences of the total flux ($J_t$), the flux of water ($J_w$) and the flux of acetic acid ($J_a$) on $X_w$ are shown in Fig. 3. Similar to Fig. 2, Fig. 3 also shows that water pervaporates more easily than acetic acid through the membranes, because $J_w$ is observed much larger than $J_a$.

Figure 3 proves that the flux of the Neosepta AV-4T anion exchange membrane is small in comparison with the cation exchange membranes. This is considered to be due to the following reason. The free volume in the pore of the anion exchange membrane is smaller than that of the cation one, because fixed-ions of the anion exchange membrane combine with their counter-ions ($\text{CH}_3\text{COO}^-$), but the cation analogues combine with $\text{H}^+$ ions of the smaller diameter. Thus, the flux in the anion exchange membrane is smaller than that in the cation ones.

4 Relation between $X_w$ and $Y_w$

The value of $J_w$ increases almost linearly with the increase of that of $X_w$ in the range of $20 < X_w < 80$ wt% in Fig. 3. On the other hand, the value of $J_a$ is approximately constant in the above range although the concentration of acetic acid in the feed solution is changed widely. Therefore, $J_w$ and $J_a$ can be represented by Eqs. (1) and (2).

\[ J_w \approx AX_w + B \]  
\[ J_a \approx C \]

where $A$, $B$ and $C$ are constants.

The total flux ($J_t$) is given by the following equation.

\[ J_t = J_w + J_a \]
\[ = AX_w + (B + C) \]

The concentrations in the pervaporated solution ($Y_w$ and $Y_a$) are described by Eqs. (4) and (5).

\[ Y_w = J_w / J_t \]
\[ Y_a = J_a / J_t \]

When Eqs. (2) and (3) are put into Eq. (5), the relation between $X_w$ and $Y_w$ can be represented as follows.

\[ Y_w = 1 - Y_a \]
where $E = C/A$. Here it was assumed that the value of $(B + C)/A$ was negligibly small compared with that of $X_w$ in the range $20 < X_w < 80$ in Fig. 3. The values of $E$ are shown in Table 1 for the ion exchange membranes used.

Full lines in Fig. 2 represent Eq. (6). Fig. 2 shows that Eq. (6) fits the results well and that the relation between $X_w$ and $Y_w$ can be represented by Eq. (6) approximately.

**5 Dependence of $\beta$ and $J_t(\beta - 1)$ on $X_w$**

The influence of $X_w$ on the selectivity $\beta$ ($= Y_w/X_w$) is shown in Fig. 4 for various kinds of ion exchange membranes.

From the result shown in Fig. 4, it is apparent that the values of $\beta$ are the greatest near at $X_w = 10\text{wt}\%$. The values of $\beta$ for Neosepta CM-1 and AV-4T membranes are the largest among the membranes used.

The dependence of $J_t(\beta - 1)$ on $X_w$ proposed by Neel et al.\textsuperscript{11} is shown in Fig. 5 for another comparison of the capability of ion exchange membranes. The values of $J_t(\beta - 1)$ calculated from the data measured by Yoshikawa et al.\textsuperscript{6} for acetic acid by using poly(acrylic acid-co-acrylonitrile) membrane are shown in the same figure for comparison. However, their values were much smaller than ours.

Figure 5 shows that the value of $J_t(\beta - 1)$ for Neosepta CM-1 is the largest among the membranes used. Thus, it is found that the Neosepta CM-1 cation exchange membrane is the best for the pervaporation of the water-acetic acid solutions.

Moreover, it is evident that the Nafion 324 cation exchange membrane is the second best based on the value of $J_t(\beta - 1)$ in Fig. 5, although $\beta$ of the membrane is the smallest among the membranes in Fig. 4. On the other hand, the value of $J_t(\beta - 1)$ for the Neosepta AV-4T anion exchange membrane, which has a large value of $\beta$ in Fig. 4, is the smallest in Fig. 5, because the flux of the membrane is very small as
Effect of $T$ on $J$

The pervaporation flux is affected by the operation temperature. Fig. 6 shows the relation between $J_t$ and the temperature (298, 313 and 333 K) for the Neosepta CM-1 and Nafion 324 membranes. The dependences of each flux of $J_t$, $J_w$ and $J_a$ on $1/T$ for the Neosepta CM-1 membrane are shown in Fig. 7.

Plotting of log ($J_t$) vs. $1/T$ clearly gives straight lines. From these Arrhenius-type plots, the respective activation energies ($\mathcal{E}_A$) were calculated as an identical value of 28.7 kJ mol$^{-1}$ for the Neosepta CM-1 membrane, although $X_w$ were changed from 40 to 60 wt% in Fig. 6, and although the different kinds of flux (viz., $J_t$, $J_w$ and $J_a$) were employed in Fig. 7. Further, the value of $\mathcal{E}_A$ for the Nafion 324 membrane was the same value of 26.8 kJ mol$^{-1}$ for the different values of $X_w$ (40 and 60 wt%).

Variation of $J_i$ with $M_i$

The relations between the molecular weight ($M_i$) of the carboxylic acids ($M_{\text{HCOOH}} = 46$, $M_{\text{CH}_3\text{COOH}} = 60$, and $M_{\text{CH}_2\text{CH}_2\text{COOH}} = 74$ g mol$^{-1}$) and the flux ($J_i$) of the respective carboxylic acids are shown in Fig. 8 for the Neosepta CM-1 and Nafion 324 membranes.

This figure indicates that the value of $J_i$ decreases linearly with increasing $M_i$, that is, the molecular diameter of carboxylic acids. The value of $J_i$ will become asymptotic to 0 at a large value of $M_i$.

Conclusions

The influence of $X_w$ on $Y_w$ was studied for pervaporation of water-acetic acid solutions with various kinds of ion exchange membranes. $X_w$
was found experimentally to be much greater than \( Y_w \). Therefore, it was evident that water pervaporated preferentially through the ion exchange membrane, and that acetic acid was concentrated in the feed solution during the pervaporation process.

Further, the pervaporation process was shown to be significantly influenced by the sorption based on the comparison between the amount of water pervaporated and that of water sorbed. The relation between \( X_w \), \( J_w \) and \( J_a \) was obtained for pervaporation of water-acetic acid solutions using various kinds of ion exchange membranes. It was evident that the flux of the anion exchange membrane was smaller than that of the cation one.

Moreover, \( J_w \) was found larger than \( J_a \). \( J_w \) increased linearly with increasing \( X_w \), while \( J_a \) was approximately constant over the whole range of \( X_w \) studied. From these relations between \( J_w \) and \( J_a \), the relation between \( X_w \) and \( Y_w \) was found to be represented approximately by Eq. (6) in the range \( 20 < X_w < 80 \).

Since the value of \( f(\beta - 1) \) of Neosepta CM-1 was the largest among the ion exchange membranes used, Neosepta CM-1 was concluded to be the best membrane for the pervaporation of the water-acetic acid solutions.

The activation energies for flux were measured as 28.7 \( \text{kJ mol}^{-1} \) for the Neosepta CM-1 membrane and 26.8 \( \text{kJ mol}^{-1} \) for the Nafion 324 membrane.

The relation between \( M_i \) and \( J_i \) measured experimentally showed that \( J_i \) decreased with increasing \( M_i \) of the carboxylic acid.

**Symbols**

\[
\begin{align*}
A, B, C, E : & \text{ constants } [-] \\
J_a : & \text{ flux of acetic acid } [\text{ kg m}^{-2} \text{ h}^{-1}] \\
J_i : & \text{ flux of carboxylic acid } [\text{ kg m}^{-2} \text{ h}^{-1}] \\
J_t : & \text{ total flux } [\text{ kg m}^{-2} \text{ h}^{-1}] \\
J_w : & \text{ flux of water } [\text{ kg m}^{-2} \text{ h}^{-1}] \\
M_i : & \text{ molecular weight } [\text{ g mol}^{-1}] \\
T : & \text{ temperature } [\text{ K}] \\
X_w : & \text{ concentration of water in the feed solution } [\text{ wt%}] \\
\bar{X}_w : & \text{ concentration of water in the membrane } [\text{ wt%}] \\
Y_w : & \text{ concentration of water in the pervaporated solution } [\text{ wt%}] \\
\beta : & \text{ selectivity } (=Y_w/X_w) [-] \\
\Delta E : & \text{ activation energy } [\text{ kJ mol}^{-1}] \\
\end{align*}
\]

**References**

4) S. Yamada: Membrane, 6, 168 (1981)