BULK LIQUID MEMBRANE WITH POROUS PARTITION MEMBRANE

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Studies have been made of mass transfer characteristics of a novel operation mode of the liquid membrane. In this operation, feed and recovery sides were partitioned by a hydrophobic porous membrane, and a membrane solution was forced to flow with a feed or recovery solution within each flow channel. The membrane solution moves through the pores of the porous membrane freely, and the solute extracted within the feed-side channel was transferred across the porous partition membrane by the bulk motion of the membrane solution as well as by diffusion, i.e., the organic phase acts as a bulk liquid membrane. By decreasing the depth of flow channels, a large specific interfacial area can be obtained, which becomes an advantage in practical use. It was shown that this operation mode has possibilities of fast separation and concentration in comparison with operation in a supported liquid membrane. To evaluate the contribution of bulk motion of the membrane solution across the porous membrane, a transfer coefficient of membrane based on a model for the present mode is introduced and correlated with organic phase velocity. Experimental results for circulating membrane solution between the feed-side and the recovery-side channels suggest that efficient concentration of solute can be achieved in this operation mode.

Introduction

Supported liquid membranes (SLM) have been studied extensively for the application of gas separation, concentration of metal ions from an aqueous solution and separation of organic acids from fermentation products. The SLM has the advantages of small amount of membrane solution and carrier, easy preparation and operation, and absence of surfactant, which is an emulsion-type liquid membrane having problems of a loss of membrane solution as fine droplets, contamination of products with the surfactant, etc. However, there are some problems associated with the use of the SLM: the loss of membrane solution from the supporting porous membrane by evaporation or dissolution of membrane solution into the feed and recovery solutions, which results in breakage of the liquid membrane and accumulation of substances that interfere with mass transfer across the liquid membrane. To overcome these problems, studies have been made on continuous regeneration and prolongation of the lifetime of the SLMs. Takahashi and Takeuchi used a flat-sheet SLM in a horizontal configuration, wherein a small amount of membrane solution was forced to flow with the recovery solution to stabilize the SLM. Fujinawa and Hozawa used a vertical laminated film module with a reservoir of the membrane solution at the top of the module, where one end of the film was soaked into the reservoir. Nakano et al. used a vertical hollow-fiber SLM module wherein the membrane solution was supplied by buoyant force to the pore-continua within supporting solids. These studies aimed at refilling the pores of the solid with the membrane solution by supplying the solution continuously.

In the present study, we propose a novel operation mode of a liquid membrane as shown in Fig. 1; i.e., a large amount of membrane solution is supplied on the feed and recovery sides, wherein the two aqueous phases are partitioned by a hydrophobic porous membrane, and the membrane solution flows along the membrane surface. Owing to the local pressure difference across the membrane, the organic solution can move through the pores of the membrane. The solute dissolves into the membrane solution, and then is transferred across the porous membrane with the bulk motion of the membrane solution; i.e., the organic phase acts as a bulk liquid membrane. The movement of a membrane solution across the porous membrane can enhance the mass-transfer rate, which enables rapid separation of the solute.

In the operation, a large interfacial area between aqueous and organic phases can be realized by decreasing the channel depth and inserting a hydrophobic mesh spacer. Although a relatively large amount of membrane solution is needed for the operation in comparison with the SLM, this method might be effective in concentrating and separating unstable substances such as antibiotics from dilute solution rapidly.
Fig. 1 Conceptual figure of bulk liquid membrane operation.

This view will be demonstrated by comparison of the fractions of solute removal from feed solution between bulk liquid membrane operation (BLM) and SLM operation. In addition, mass-transfer coefficients for aqueous and organic phases and the porous membrane were measured at various aqueous and organic flow velocities.

1. Experimental

The hydrophobic porous membrane used in this study is Duragard 2500 of 25 μm in thickness, 0.45 porosity, and 0.4 x 0.04 μm pore size, and is made of polypropylene. On both sides of the membrane, flow channels of rectangular cross section (1 x 10 mm) are set on PTFE spacers of 1mm thickness. Within the flow channel, a mesh of hydrophobic surface is inserted. The experimental setup of the BLM operation is schematically shown in Fig. 2a. The membrane module shown in Fig. 2b was installed vertically. In the figure of module A, the broken line indicates the flow channel on the opposite side of the membrane, and hatched parts the existence of flow channels on both sides of the membrane. Effective membrane length is 98 cm.

Feed solution was an aqueous solution of I₂-KI, the membrane solution was n-heptane and the recovery solution was an aqueous solution of Na₂S₂O₃. Iodine in the feed solution was extracted by the membrane solution, then was transferred from feed side to recovery side across the porous membrane and was stripped from the membrane solution by the recovery solution. The aqueous feed solution was mixed with the organic membrane solution just before the inlet of the module, and then the two-phase mixture was supplied to the feed-side channel at the bottom of the module. Another two-phase mixture of the recovery solution and the membrane solution was fed to the recovery-side channel and flowed upward in parallel with the feed-side flow. The two-phase mixture leaving the module from each channel was sent to a phase separator in which the interface level was adjusted by two levelers for aqueous and organic phases. The membrane solution from the recovery side was pumped to the feed side and that from the feed side to the recovery side; i.e., the membrane solution was circulated between the channels of feed and recovery sides. The recovery solution from the leveler was returned to the reservoir. The iodine concentrations in aqueous solution from the feed side were determined by titration with an aqueous solution of Na₂S₂O₃. To clarify the concentration of membrane solution when the solute transfers from aqueous feed to recovery solution through the membrane phase, experiments without circulation of the membrane solution were also carried out in which iodine-free n-heptane was supplied to both channels. The iodine concentrations in the membrane solutions coming out of the module were measured by a spectrophotometer.

For comparison between the BLM and the SLM, experiments without supply of membrane solution were carried out as an operation of the SLM. Flow rates of aqueous solutions and organic solutions at the outlet of channels were measured by taking the solution from the leveler with a measuring tube for a given time, and those of organic solutions at the inlet of channels with flow meters.

Overall capacity coefficients based on aqueous concentration within the flow channel were obtained by the extraction of iodine from I₂-KI aqueous solution into n-heptane with a single flow channel. In module A, the organic phase was almost in equilibrium with the aqueous phase at the outlet of the module at every flow rate. Thus, it is difficult to evaluate mass-transfer characteristics with module A, which has a long flow path. Then, module B shown in Fig. 2b, which had a short flow path, was used to measure mass-transfer characteristics. Distribution coefficients of iodine between
organic and aqueous phases were measured with solutions in individual runs. Capacity coefficients of organic phase were also measured from stripping experiments of iodine from n-heptane to Na₂S₂O₃ aqueous solution in a single flow channel. The iodine reacts with Na₂S₂O₃ at the interface, and there is no mass-transfer resistance in the aqueous phase. For the measurement of mass-transfer coefficient in organic phase across the porous membrane, a two-phase mixture of deionized water and iodine n-heptane solution was supplied to the feed-side channel, and another two-phase mixture of deionized water and iodine-free n-heptane to the recovery-side channel. Concentrations in organic phases from both channels were measured as well as flow rates.

2. Results and Discussion

2.1 Comparison between SLM and BLM

Figure 3 shows the iodine concentration ratios of outlet-to-inlet aqueous solution of feed-side channel for the BLM with and without the circulation of the membrane solution, and those for the SLM. The ratio increases with increase in aqueous flow velocity, because the residence time decreases with \( U_{aqF} \). The fraction of iodine removed from the feed solution in the BLM operation is much higher than that in the SLM. At \( U_{aqF} = 0.005 \text{ m/s} \), the BLM (with circulation) can achieve an outlet concentration as small as about 1/3 for the SLM in spite of small residence time of the BLM. Under the same \( U_{aqF} \), the residence time of the BLM is smaller than that of the SLM, because the membrane solution is supplied with the feed solution in the case of the BLM. In the present experiments, \( U_{orF} = U_{orR} = 0.02 \text{ m/s} \), and the residence time of the BLM is about 1/5 that of the SLM at \( U_{aqF} = 0.005 \text{ m/s} \). The BLM can realize a large recovery fraction with small residence time. Flow velocities to get \( C_{aqF}/C_{aqF1} = 0.4 \) are 0.02 and 0.005 m/s for the BLM and the SLM, respectively, i.e., the throughput of the BLM is four times as large as that of the SLM for the same separation. Thus it is expected that highly efficient separation and concentration are achieved in this novel operation mode. For experiments without circulation of membrane solution, iodine-free heptane was supplied to both channels, and the values of \( C_{aqF}/C_{aqF1} \) were smaller than those in the case of circulation of membrane solution as shown in Fig. 3.

2.2 Mass-transfer characteristics

To analyze the separation process of the BLM, it is necessary to know the mass-transfer characteristics: the mass-transfer coefficient between aqueous and organic phases in the flow channel and the mass-transfer coefficient in organic phase across the porous membrane. For two-phase flow in a single-flow channel where iodine is extracted from aqueous phase into organic phase, the mass balance differential equation is expressed as

\[
K_{aq} \frac{d}{dl} \left( C_{aq} - C_{or} / m \right) dl = -U_{aq} \frac{d}{dl} C_{aq}
\]

where \( K_{aq} \) is an overall capacity coefficient based on aqueous concentration, \( m \) the iodine distribution ratio between aqueous and organic phases and \( U_{aq} \) the aqueous-phase flow velocity. The distribution ratio of iodine between n-heptane and 1₂-KI aqueous solution and changes of distribution ratio with [KI] were given in the previous paper \(^{5,6} \). In experiments of measuring mass-transfer characteristics, the value of \( m \) was in the range from 6 to 8. When iodine-free n-heptane is supplied, iodine concentration in the organic phase is given by

\[
C_{or} = \left( C_{aq} - C_{aq} \right) U_{aq} / U_{or}
\]

By substituting Eq. (2) into Eq. (1), the following equation is derived.
Fig. 4 Effects of both $U_{or}$ and $U_{aq}$ on $K_{aq\alpha}$

$$K_{aq\alpha} \, dl = - \frac{U_{aq} \, d \, C_{aq}}{[U_{or} \, m + U_{aq}] \, C_{aq} - U_{aq} \, C_{aq\alpha}}$$ (3)

$K_{aq\alpha}$ is obtained by integrating Eq. (3) from the inlet to the outlet of the channel as follows.

$$K_{aq\alpha} \frac{U_{aq} \, u_{or} \, m}{L \, (U_{or} \, m + U_{aq})} \ln \left( \frac{U_{or} \, m \, C_{aq\alpha}}{U_{or} \, m + U_{aq} \, C_{aq\alpha}} \right)$$ (4)

where $C_{aq\alpha}$ and $C_{aq}$ are iodine concentrations in aqueous phase at the inlet and the outlet of the channel, respectively. Figure 4 shows the effects of $U_{or}$ and $U_{aq}$ on the overall capacity coefficient, $K_{aq\alpha}$, which increases with both $U_{or}$ and $U_{aq}$.

Capacity coefficients for the organic phase, $k_{or\alpha}$, were obtained with back-extraction from n-heptanesolution of iodine to aqueous solution of Na$_2$S$_2$O$_3$. Since the concentration of Na$_2$S$_2$O$_3$ in aqueous phase was high enough to reduce iodine even at the outlet of the module, the iodine concentration in aqueous phase (i.e., at the interface) is considered to be zero. The mass balance equation for the organic phase of differential length $dl$ and unit width of the channel is written as

$$- U_{or} \, d \, C_{or} = k_{or\alpha} \, C_{or\alpha} \, dl$$ (5)

By integrating Eq. (5) from inlet to outlet of the channel, $k_{or\alpha}$ is given by

$$k_{or\alpha} = \frac{(U_{or} / L) \, \ln(C_{or\alpha} / C_{or})}{U_{or\alpha}}$$ (6)

where $C_{or\alpha}$ and $C_{or}$ are the iodine concentrations in the organic phase at the inlet and the outlet of the channel, respectively. The effects of $U_{or}$ and $U_{aq}$ on $k_{or\alpha}$ are shown in Fig. 5, and the following correlation was derived.

$$k_{or\alpha} = 5.2 \, U_{aq}^{0.51} \, U_{or}^{0.45}$$ (7)

The dependency of $k_{or\alpha}$ on $U_{aq}$ was somewhat larger than that on $U_{or}$. This might come from the fact that organic phase flowed along hydrophobic surfaces of the membrane and the mesh spacer in the channel as shown in Fig. 1. Thus the mass transfer through the interface was affected by the motion of an aqueous phase rather than the organic phase.

For the conditions of experiments in Fig. 4, $k_{or\alpha}$ were calculated from Eq. (7), and capacity coefficients, $k_{aq\alpha}$, in aqueous phase were determined with values of $K_{aq\alpha}$ and $k_{or\alpha}$ by use of the additive rule of mass-transfer resistances. Values of $K_{aq\alpha}$ were also correlated with aqueous and organic phase flow velocities as

$$k_{aq\alpha} = 2.6 \, U_{aq}^{0.68} \, U_{or}^{0.33}$$ (8)

For the transfer of solute in the membrane solution across the porous membrane, there are two different modes: one is the diffusional transfer attributed by the concentration gradient, the other is a bulk transfer due to the motion of membrane solution through the pore of membrane. As the transfer coefficient implying the contribution of these transfers, we introduce a mass-transfer coefficient, $k_g$, for membrane solution across the porous membrane. On the assumption that the amount of iodine dissolved in deionized water is negligible, mass balance for the differential section $dl$ shown in Fig. 6 is given as

$$- h \, d \, [U_{or\alpha} \, C_{or\alpha}] \, dl = k_g \, (C_{or\alpha} - C_{or}) + \nu \, C_{or\alpha}$$ (9)

where $h$ is the depth of the channel and $\nu$ the apparent velocity of membrane solution across the porous membrane. $k_g(C_{or\alpha} - C_{or})$ contains the bulk transfer expressed by $\nu \, C_{or\alpha}$ as well as the diffusional transfer. Since $dU_F$ is equal to $- \nu \, dl/h$, Eq. (9) is reduced to

$$- h \, U_{or} \, d \, C_{or} \, dl = k_g \, (C_{or\alpha} - C_{or})$$ (10)

By assuming that there is no accumulation in the porous membrane, the following equations are given

$$C_{or\alpha} = [U_{or\alpha} \, C_{or\alpha} - U_{or} \, C_{or}] / U_{or\alpha}$$ (11)

$$U_{or} = U_{or\alpha} - \nu \, l / h$$ (12)

$$U_{or\alpha} = U_{or\alpha} + \nu \, l / h$$ (13)
\[ U_{orF} + U_{orR} = U_{orFi} + U_{orRi} \]  \hspace{1cm} (14)

Eqs. (11) to (14) are substituted in Eq. (10), and rearranged as follows:

\[ k_B \left[ \frac{d}{U_{orF} - vF + \frac{d}{U_{orR} + vR}} \right] \]

\[ = - \frac{[U_{orF} + U_{orR}]h \cdot C_{orF}}{\left[ \frac{U_{orFi} + U_{orRi}}{C_{orF} - U_{orFi} \cdot C_{orFi}} \right]} \]  \hspace{1cm} (15)

Eq. (15) is integrated between \( l = 0 \) and \( l = L \), and \( k_B \) is obtained as:

\[ k_B = \nu \frac{\ln \left[ \frac{U_{orR} \cdot C_{orR} / \left( [U_{orF} + U_{orR}] \cdot C_{orF} - U_{orFi} \cdot C_{orFi} \right) \right]}{\ln \left[ \frac{U_{orR} \cdot U_{orF} / \left( [U_{orR} \cdot U_{orR}] \right) \right]} \]  \hspace{1cm} (16)

**Figure 7** shows the effects of \( \tilde{U}_{or} \) and \( U_{aq} \) on \( k_B \) in the BLM operation. \( U_{or} \) is the average organic phase velocity on feed side and recovery side. In the experiments, aqueous phase velocities were equal on each side of the module. As can be seen in the figure, \( k_B \) does not depend on aqueous phase velocity but increases with 0.37 power of average organic phase velocity, i.e., the motion of membrane solution across the porous membrane increases with \( \tilde{U}_{or} \). The obtained correlation is as follows:

\[ k_B = 6.5 \tilde{U}_{or}^{0.37} \]  \hspace{1cm} (17)

Since the pore size and porosity of Duragard 2500 was relatively small, the values of \( k_B \) were not so high. It is expected that higher value of \( k_B \) can be achieved by use of the partition membrane of larger pore size and porosity.

**2.3 Simulation of BLM**

For simulating the solute concentration at the outlet of the module under various conditions, it is needed that a formulation of differential mass balance shown in Fig. 6 is established. The feed, the membrane and the recovery solutions flow in parallel with concentration change in the flow direction. Membrane solution moves across the porous membrane from feed side to recovery side with velocity \( v_F \) and in opposite direction with \( v_R \). A differential mass balance on the solute in feed solution is given by Eq. (1), and rearranged

\[ dC_{aqF} / dt = -K_{aqF} [C_{aqF} - C_{aqR} / m] / U_{aqF} \]  \hspace{1cm} (18)

in the recovery-side channel,

\[ dC_{aqR} / dt = K_{aqR} [C_{aqR} / m] / U_{aqR} \]  \hspace{1cm} (18')

In the present case of iodine transfer with the recovery solution of \( \text{Na}_3\text{S}_2\text{O}_3 \), the iodine concentrations in the aqueous phase and at the interface between aqueous and organic phases within the recovery channel were zero, and Eq. (18') was not used in the calculation.

For the organic phase in the feed-side channel

\[ h \cdot U_{orF} \cdot dC_{orF} = K_{aqF} [C_{orF} - C_{orR} / m] \cdot h \cdot dl \]

\[ - \left( k_B \left[ C_{orF} - C_{orR} \right] + v \cdot C_{orF} \right) dl \]  \hspace{1cm} (19)

\[ dC_{orR} / dt = K_{aqR} [C_{aqR} / m - C_{orR}] / U_{orR} \]

\[ - \left( k_B \left[ C_{orR} - C_{orF} \right] + v \cdot C_{orR} \right) / (h \cdot U_{orR}) \]  \hspace{1cm} (20)

and in the recovery-side channel

\[ h \cdot U_{orR} \cdot dC_{orR} = \left( k_B \left[ C_{orR} - C_{orF} \right] + v \cdot C_{orF} \right) h \cdot dl \]

\[ - K_{aq} \left[ C_{orR} / m - C_{orR} \right] h \cdot dl \]  \hspace{1cm} (21)

\[ dC_{orF} / dt = \left( k_B \left[ C_{orR} - C_{orF} \right] + v \cdot C_{orR} \right) / h \cdot U_{orF} \]

\[ - K_{aq} \left[ C_{orF} / m - C_{orF} \right] / U_{orF} \]  \hspace{1cm} (22)

In the present case, \(-k_{aqF} C_{orF} U_{orF}\) is used instead of the last term in Eq. (22). The change of organic phase velocity in flow direction is written as

\[ dU_{orF} / dl = - v / h \]  \hspace{1cm} (23)

The concentrations of \( C_{aqF}, C_{aqR}, C_{orF} \) and \( C_{orR} \) are obtained by solving the set of differential equations (18), (18'), (20), (22) and (23) according to the Runge Kutta method.

**Figure 8** shows the plot of outlet concentrations of aqueous and organic phases in the feed side and organic phase in the recovery side for the experimental conditions of without circulation of membrane solution. Solid lines represent the calculated values obtained from the set of equations by using mass-transfer coefficients estimated from Eqs. (7), (8) and (17). The deviation
between the observed values and the solid lines might come from the different flow pattern of two phases in the module A and the module B shown in Fig. 2b. Within module A, it was observed that organic phase tends to flow in upper part and aqueous phase flows in lower part of the channel. In module B, the two phase flow was uniform. Thus there is a possibility of overestimate of capacity coefficients, $k_{or}a$ and $k_{aq}a$ for applying the BLM operation of horizontal flow channel.

To fit the calculated values to the observed values, effects of capacity coefficients on the calculated concentrations at the outlet of the module were examined. The decrease of $k_{or}a$ and $k_{aq}a$ led to the rise of $C_{aqF_0}$ and the fall of $C_{orF_0}$. In the figure, dashed lines represent the calculated values obtained by reducing capacity coefficients $k_{or}a$ and $k_{aq}a$ to 65% of the estimated values. The dashed lines are in a good agreement with the observed values. This suggests that the effective interfacial area in the horizontal flow might be about 65% of that in the vertical flow configuration. It was concluded that, the model presented in this study was applicable for predicting concentrations at the outlet of the module with a simple correction of capacity coefficients. For the observed results in Fig. 8, the ratio of $C_{orF_0}/C_{aqF_0} = 1.7$ which is much smaller than the equilibrium distribution ratio (in this experiment $m = 10$). This indicates that the mass transfer across the porous membrane acts effectively to reduce the concentration of $C_{orF}$.

Conclusions

Mass transfer characteristics in a novel operation mode of bulk liquid membrane with a porous partition membrane were studied systematically with iodine transfer experiments. It was found that the BLM operation is more effective for the rapid mass-transfer operation than the SLM operation. The basic equation was established, including the coefficient for bulk-transfer of membrane solution across the porous membrane; this coefficient was correlated with organic-phase velocity. The model developed in the present study predicted well the concentrations of aqueous and organic phases in the feed side and the recovery side at the outlet of the module with a simple correction of capacity coefficients estimated from the correlations obtained for the different flow pattern of two-phase flow.

Nomenclature

- $a$ = specific interfacial area [m$^2$/m$^3$]
- $C$ = concentration [mol/m$^3$]
- $h$ = depth of a flow channel [m]
- $k_{or}$ = mass-transfer coefficient in organic phase [m/s]
- $k_{aq}$ = mass-transfer coefficient for bulk transfer of the membrane liquid across porous membrane [m/s]
- $K_{aq}$ = overall mass-transfer coefficient based on aqueous-phase concentration [m/s]
- $l$ = distance in flow direction [m]
- $L$ = total flow length from inlet to outlet of the module [m]
- $m$ = distribution ratio of iodine between organic and aqueous phases [-]
- $\bar{U}_{or}$ = average velocity of organic phase in feed and recovery side [m/s]
- $v$ = net velocity of membrane solution across the porous partition membrane [m/s]
- $v_F$ = velocity of membrane solution from feed side to recovery side across porous membrane [m/s]
- $v_R$ = velocity of membrane solution from recovery side to feed side across porous membrane [m/s]

<Subscripts>

- $aq$ = aqueous phase
- $F$ = feed side
- $i$ = inlet
- $o$ = outlet
- $or$ = organic phase
- $R$ = recovery side

Literature Cited