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Application of supported ionic liquid membranes using a flat sheet and hollow fibers to lactic acid recovery

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ABSTRACT

Application of supported ionic liquid membranes using a flat sheet and hollow fibers has been studied for the separation and recovery of lactic acid, which is the raw material of biodegradable polylactic acid. We optimized the supported ionic liquid membrane system for recovering undissociated lactic acid. Ionic liquids having a hydrophobic cation and a chloride anion, such as quaternary ammonium salt (Aliquat 336) and phosphonium salt (Cyphos IL-101), were shown to be able as membrane solvent from the viewpoints of membrane stability and the permeability of lactic acid. Lactic acid in the feed phase actively permeated through the supported ionic liquid membrane to the stripping phase containing hydrochloric acid. The permeation of lactic acid was improved by keeping the pH of the feed phase constant. For separation of a realistically high concentration of lactic acid, Aliquat 336 was superior to Cyphos IL-101 due to its higher capacity for extracting lactic acid under the condition of a constant pH. Aliquat 336 was successfully impregnated in polypropylene hollow fibers with a thinner membrane thickness and larger specific area than a flat sheet. Lactic acid permeated through the hollow fiber membrane impregnated with Aliquat 336, and the permeation flux was higher than the estimated value from the flat sheet membrane. The results indicate that the supported ionic liquid membrane system is promising for lactic acid recovery from fermentation broth.

Keywords: Lactic acid; Supported liquid membrane; Ionic liquid; Hollow fiber; Separation

1. Introduction

Lactic acid, CH₃CHOHCOOH, is the most frequently occurring hydroxycarboxylic acid and it is widely used in the food, pharmaceutical, cosmetics, and chemical industries. In particular, lactic acid production by fermentation has gained much interest because optically pure lactic acid is the raw material of biodegradable polymer [1]. The economics of the process, however, depend on the development of an effective recovery method for lactic acid from the broth because the separation and purification steps account for up to 50% of the production costs [2]. Therefore, current research is focused on effective, efficient and economical downstream processes for recovering lactic acid from fermentation broth [3]. A number of processes for lactic acid recovery, such as solvent extraction, adsorption, direct distillation and electrodialysis, have been studied. Currently, electrodialysis is considered the most

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promising technique. The process is effective and efficient but not necessarily economical. Although solvent extraction has been proposed as a promising recovery technique, it suffers from the environmental problems caused by using a volatile organic solvent [4]. Recently, the suitability of ionic liquids as "green" solvents for chemical processes has been extensively recognized due to their having effectively no vapor pressure. This characteristic makes ionic liquids good replacements for volatile conventional organic solvents [5].

However, using a large amount of ionic liquids as solvents in liquid-liquid extraction systems is expensive due to the extremely high cost of ionic liquids compared with conventional organic solvents. Thus, a supported liquid membrane, which is a porous solid structure impregnated with liquid, has been studied using ionic liquids as an impregnating liquid [6]. A supported liquid membrane process, which combines the extraction and stripping processes, has several advantages over liquid-liquid extraction systems, such as low energy consumption, high selectivity, and a reduction in the amount of solvent used [7,8]. Nevertheless, the application of supported liquid membranes on an industrial scale is still limited due to membrane instability. The main causes of this instability are the solubilization of membrane liquid in the adjacent aqueous phases and its displacement from the pores by the trans-membrane pressure resulting from hydraulic and/or osmotic pressure differences across the membranes [7]. Several techniques have been reported to overcome these drawbacks. Recently, Livingston et al. proposed a composite-supported liquid membrane that consists of a thin non-porous layer and a microporous support with its pores filled with a polymeric liquid like polypropylene glycol [9]. They reported that the operational stability of this membrane exceeded two months. On the other hand, a supported liquid membrane based on ionic liquids gave steady fluxes over one month without any modification [10].

An ionic liquid is a liquid that consists of only ions. Ionic liquids at room temperature have a bulky and asymmetric organic cation, such as 1-alkyl-3methylimidazolium, 1-alkylpyridinium, N-methyl-Nalkylpyrrolidinium, ammonium and phosphonium ions. They have extremely low vapor pressure and the miscibility of ionic liquids with water and organic solvent can be controlled by changing the structure of cation and anion moieties. Currently, a number of practical applications are being considered, and Plechkova and Seddon described how ionic liquids are starting to leave academic labs and find their way into a wide variety of industrial applications [11]. Studies on ionic liquids as separation media are just now in the initial stage. Previously, three classes of compounds have been transported by supported ionic liquid membranes: 1) gases such as CO₂, 2) hydrophobic organic compounds such as aromatic hydrocarbon, and 3) hydrophilic biomolecules such as organic acids and amino acids. Although the properties that ionic liquid membranes require depend on the compounds transported, in the separation of hydrophilic biomolecules, most works deal with ionic liquids having an imidazolium cation [12]. Recently, Schlosser et al. reported the permeation of lactic acid through supported liquid membranes containing phosphonium ionic liquids diluted in n-dodecane [13]. However, there have been few studies on lactic acid permeation where ionic liquids serve as a membrane solution without a diluent.

Consequently, we investigated the practical application of supported ionic liquid membranes to the recovery of lactic acid. The main challenges in realizing such practical application are 1) to optimize the membrane solution and 2) to reduce the load on the subsequent steps as much as possible. For the first task, we examined various hydrophobic ionic liquids as membrane solution from the viewpoints of the permeation capacity of lactic acid and the stability of the membranes. Furthermore, lactic acid was recovered as sodium lactate in the stripping solution by using a sodium hydroxide solution. In this method, lactate must be acidified to produce lactic acid for the subsequent step. For the second task, we developed a single-step process for the separation of lactate from the fermentation broth and their acidification to produce undissociated lactic acid. This was accomplished by a novel supported ionic liquid membrane technique using an acidic aqueous media as the stripping solution.

2. Materials and methods

2.1. Chemicals

L(+)-lactic acid was diluted with distilled water to approximately 1 mol/dm³ and heated under total reflux for at least 12 h to hydrolyze any lactic acid polymers. The structures of the ionic liquids used are shown in Table 1. Hydrophobic ionic liquids were selected. All other chemicals were used without further purification.

2.2. Permeation of lactic acid through flat sheet membrane

A porous polyvinylidene fluoride membrane (Millipore, 125 μ m, pore size 0.45 μ m) was used as a liquid membrane support. The supported ionic liquid membrane was prepared at room temperature by

Table 1

Structure $C_{6}H_{13}$ $P^{+}C_{14}H_{29}$ Cl ⁻ $C_{6}H_{13}$ C ₆ H ₁₃
$C_{6}H_{13}$ P^{*}_{1} $C_{14}H_{29}$ Cl^{-}_{1} $C_{6}H_{13}$ $C_{6}H_{13}$
$C_{6}H_{13}$ $P^{+}C_{14}H_{29}$ $C_{6}H_{13}$ $C_{6}H_{13}$ $C_{6}H_{13}$
$\begin{array}{ccc} C_{6}H_{13} & O_{12} \\ & & & O_{13} \\ & & & & O_{14}H_{29} \\ C_{6}H_{13} & C_{6}H_{13} & O_{14}H_{17} \\ \end{array}$
$C_{6}H_{13}$, SO_{2} CF $C_{6}H_{13}$, $C_{6}H_{13}$, SO_{2} CF SO_{2} CF SO_{2} CF
$C_{8}H_{17}$ CH_{3} CH_{3} CH_{17} CH
$\begin{array}{c} \overbrace{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}}}}}}}}}}$
$[(CF_3SO_2)_2N]^-$
$[(CF_3SO_2)_2N]^-$

impregnating ionic liquids in a vacuum desiccator overnight. It was sandwiched between two cells of the flat sheet membrane apparatus shown in Fig. 1(a). A membrane with an effective area, A, of 12 cm² was fixed in the apparatus. The feed solution was an

aqueous lactic acid solution whose pH was adjusted to 5 with a concentrated sodium hydroxide solution. Stripping solutions include aqueous acidic solutions such as those with hydrochloric, nitric and sulfuric acids. In some cases, the pHs of the feed and stripping



Fig. 1. Experimental apparatus: (1) supported ionic liquid membrane; (2) feed solution; (3) stripping solution; (4) stirring bar.

solutions were maintained at desired values by adding concentrated HCl and NaOH solutions during the experiments. The transport experiment was initiated by adding 100 ml of each solution at room temperature to their respective compartments. The stirring speed of the magnetic bar in each cell was controlled at 300 rpm. Samples from both solutions were withdrawn at regular time intervals, and the concentration of lactic acid and the pH in both cells were measured with HPLC and a pH meter, respectively.

2.3. Permeation of lactic acid through hollow fiber membrane

A porous polypropylene hollow fiber membrane was purchased from Kitz Micro Filter Corp. (Japan). The properties of the hollow fibers are listed in Table 2. The membranes were prepared by immersing the hollow fibers in the ionic liquid for 24 h in a desiccator. The experimental apparatus using hollow fibers is shown in Fig. 1b. The experiments were carried out in a batch mode. Before the permeation experiment, distilled water was fed into the interior of the hollow fibers at 0.5 ml/min with a microtube pump to remove excess ionic liquid. The feed solution was an aqueous lactic acid solution whose pH was adjusted to 5 with an aqueous sodium hydroxide solution, and a hydrochloric acid solution was used as the stripping solution. Hollow fibers impregnated with ionic liquid were

Table 2 Properties of hollow fibers

Polypropylene 450 μm
550 µm
50 µm
0.01 µm
30 cm
5

immersed in the feed solution. The stripping aqueous solution was fed into the interior of the hollow fibers and circulated at a flow rate of 0.5 ml/min with a microtube pump. The total volume of each solution was 100 ml. The stirring speed of both the feed and the receiving solution was 300 rpm. The concentrations of lactic acid and the pH in both cells were measured with HPLC and a pH meter, respectively.

2.4. HPLC analysis

Lactic acid concentrations were determined by HPLC (Shimadzu LC-10ADvp) with an RI detector (Shimadzu RID-10A). Analysis was performed using a Shodex SUGAR SH-1011 (Showa Denko) column and 5 mM H_2SO_4 solution as the mobile phase.

3. Results and discussion

2.1. Use of acidic media as stripping agent

In most solvent extraction processes of organic acid, with or without specific chemical interaction, organic acids are recovered as salts in the stripping solution. Our aim is to obtain undissociated lactic acid in a single ionic liquid membrane process. So we examined the use of acidic media as a stripping agent to recover undissociated lactic acid. Yabannabar and Wang proposed hydrochloric acid as a stripping agent in the extraction of lactic acid with a tertiary amine, Alamine 336. In their paper, a relatively high recovery ratio of 83% was obtained, but stable emulsion was formed at the interface of the organic solvent and the stripping solution, and thus clear phase separation could not be attained [14]. On the other hand, in the supported liquid membrane system, the interface of the immiscible aqueous and organic phases is immobilized at the pore mouths of the microporous membrane. Therefore, in this section, we examine the use of acidic media, having a



Fig. 2. Time courses of lactic acid concentration in feed (\bullet) and stripping (O), and pH of feed ($\mathbf{\nabla}$) and stripping (∇) phases with Aliquat 336 and 0.01 mol/dm³ hydrochloric acid as membrane and stripping solutions, respectively.

pH much smaller than the pKa of lactic acid, as the stripping agent.

Fig. 2 shows typical results of the time courses of lactic acid concentration and pH in the feed and stripping solutions using Aliquat 336 and 0.01 mol/dm³ HCl solutions. Consequently, lactic acid successfully permeated to the stripping phase, and weight of the membrane after the permeation experiment was virtually unchanged. We also observed that pH decreased in the feed solution but increased in the stripping solution. This suggests the permeation of hydrochloric acid by forming the HCl adduct of Aliquat 336. In the following, the effects of various factors on permeation and membrane stability are examined.

2.1.1. Effect of ionic liquids

The ionic liquids selected must be immiscible in water, so we examined hydrophobic ionic liquids having different cation structures. The anion structures of the ionic liquids investigated were not the same because the chloride salts of imidazolium, pyrrolidium and pyperidinium were water-soluble and available ammonium salts were limited. Fig. 3 shows the extent of lactic acid permeated after 24 h based on the change in concentration of lactic acid in the stripping phase. Although lactic acid seemed to permeate through all ionic liquid membranes, we found that imidazolium, pyrrolidium and pyperidinium salts, which have hydrophobic anions, nearly always leaked from the membrane. On the other hand, in the cases of Aliquat 336 and Cyphos IL 101, no leakage of impregnated ionic liquids was observed. It may be necessary for an ionic liquid to have a hydrophobic cation to form



Fig. 3. Effect of ionic liquids on permeation of lactic acid after 24 h.

a stable ionic liquid membrane. Therefore, we later examined the ionic liquids of phosphonium and ammonium types.

Next we examine the effect of the anion of an ionic liquid on permeation as shown in Fig. 4. In this figure, because the carbonated form of Aliquat 336 was reported to be more efficient than the original chloride one [13], the counter-anion of Aliquat 336 was exchanged with the desired anion by contacting Aliquat 336 with its sodium salt in a stoichiometrically excessive amount. In phosphonium salt, the order of permeability was $Cl^- \ge Br^- > (CF_3SO_2)_2N^- > (C_8H_{17}O)_2P^-$. In quantemary ammonium salt, this order was $Cl^- \ge Br^- \ge CO_3^{2-}$, but the differences in permeability are smaller than those of phosphonium.



Fig. 4. Contribution of anion moiety in ionic liquids to permeation of lactic acid after 24 h.



Fig. 5. Effect of acids in stripping phase on permeation of lactic acid after 24 h.

These facts suggest that ionic liquids having a hydrophilic anion and a hydrophobic cation are suitable for the permeation of lactic acid to acidic media. Actually, ionic liquids such as Aliquat 336 are well known as ionexchange extractants in the field of solvent extraction. Kyuchoukov et al. proposed the following two extraction reactions of lactic acid with Aliquat 336 in the diluent, and at pH > 5 a high degree of extracted lactic acid was reported [15].

$$E^{+}Cl^{-} + L^{-} \rightleftharpoons EC^{+}L^{-} + Cl^{-}$$
⁽¹⁾

$$E^{+}Cl^{-} + L^{-} + HL \rightleftharpoons E^{+}L^{-}HL + Cl^{-}$$
⁽²⁾

where E^+Cl^- is the chloride form of the quaternary ammonium salt, and L^- and HL represent lactate and lactic acid, respectively.

3.1.2. Effect of acid

In the previous section, we used hydrochloric acid as a stripping agent, so we examine the effect of acid on the permeation of lactic acid using Aliquat 336 shown in Fig. 5. Hydrochloric acid is the best among the investigated acids. Sulfuric acid caused a steeper decrease in pH in the feed phase than did hydrochloric acid (data not shown), suggesting that sulfuric acid permeated faster through the membrane than hydrochloric acid; this may cause suppression of lactic acid permeation due to a decrease in the effective carrier for lactic acid permeation and the decrease in the dissociated form of lactic acid. On the other hand, nitric acid did not result in a decreased pH in the feed phase but gave the worst results for the permeation of lactic acid. This may be due to the high stability of quaternary



Fig. 6. Effect of anion of ionic liquids and stripping phases on permeation of lactic acid.

nitrate. Furthermore, we examined whether a common anion used for both the ionic liquid and the stripping phase has an influence on the permeation of lactic acid. The results obtained when the same anions were used for ionic liquids and stripping phases are shown in Fig. 6. As is evident from Figs. 4–6, using a chloride anion as the stripping agent was essential.

3.1.3. Effect of pH control

In the next experiment, Cyphos IL-101 and Aliquat 336 are used as the membrane solution and hydrochloric acid is used as the stripping agent. Figs. 7 and 8 show the time courses of permeation of lactic acid with membranes impregnated with Aliquat 336 and Cyphos IL-101 with a stripping solution of 0.1 mol/dm³ HCl.



Fig. 7. Time courses of lactic acid concentration in feed (\bigcirc) and stripping (\bigcirc), and pH of feed (\bigtriangledown) and stripping (\bigtriangledown) phases with Aliquat 336 and 0.1 mol/dm³ hydrochloric acid as membrane and stripping solutions, respectively.



Fig. 8. Time courses of lactic acid concentration in feed (\bigcirc) and stripping (\bigcirc), and pH of feed (\bigtriangledown) and stripping (\bigtriangledown) phases with Cyphos IL 101 and 0.1 mol/dm³ hydrochloric acid as membrane and stripping solutions, respectively.

Higher HCl concentration was used to increase the permeation rate. Both the permeation rate of lactic acid through the Aliquat 336 impregnated membrane and the pH of the feed phase, however, decreased in comparison with the results shown in Fig. 2 with 0.01 mol/dm³ HCl solution. This suggests that hydrochloric acid preferentially permeated because of its higher concentration in the stripping phase than lactic acid in the feed phase, resulting in decreased pH in the feed phase. Furthermore, the pH drop in the feed phase causes the decrease in the dissociated form of lactic acid in the feed phase. If lactate permeated based on reactions (1) and (2) above, the enhanced hydrochloric acid permeation would cause not only a decrease in the effective carrier for lactic acid permeation but also a decrease in the permeated species, i.e., lactate. These assumptions were supported by the results using the membrane impregnated with Cyphos IL-101 shown in Fig. 8. In the Cyphos IL-101 impregnated membranes, a higher permeation rate of lactic acid and a smaller decrease in pH were observed than with Aliquat 336 impregnated membranes. To avoid an additional effect of hydrochloric acid in the permeation of lactic acid, that is, a decrease in pH in the feed phase, during the experiment we kept the pH of the feed phase constant (=5) with a pH-stat (Metrohm; 718 STAT Titrino). The results in Fig. 9 show a higher permeation rate of lactic acid, as expected. From these results, we expected a permeation mechanism based on the ion exchange between the lactate and chloride anions of ionic liquids as shown in Fig. 10. In this mechanism, it is noted that the pH values of the feed and stripping solutions are set at larger and smaller values than pKa of lactic acid, respectively.



Fig. 9. Time courses of lactic acid concentration in feed (\bigcirc) and stripping (O), and pH of feed (\bigtriangledown) and stripping (\bigtriangledown) phases with Aliquat 336 and 0.1 mol/dm³ hydrochloric acid as membrane and stripping solutions, respectively. Feed pH was kept approximately constant.

Consequently, we concluded that the hydrochloric acid concentration in the stripping phase should be at the same or lower level as the lactic acid concentration in the feed phase. Furthermore we found that pH control of the feed phase is effective for enhancing the permeation rate of lactic acid. Moreover, Cyphos IL-101 impregnated membranes seemed to be better than Aliquat 336 impregnated membranes due to the smaller decrease in pH in the feed phase.

3.1.4. Effect of initial concentration of lactic acid in feed phase

We next examine whether the proposed technique can actually be used in a practical high concentration range. Figs. 11 and 12 show time courses of permeation of lactic acid and pH using Aliquat 336 and Cyphos IL-101 impregnated membranes, respectively, under the conditions of pH control of the feed phase, lactic acid concentration of 0.5 mol/dm³ in the feed phase, and hydrochloric acid concentration of 0.1 mol/dm³ based on the findings obtained in the previous section. The permeabilities through membranes impregnated with Aliquat 336 and Cyphos IL-101 were 35.0 and 24.8% after 72 h, respectively, contrary to our expectation from the results obtained with the 0.01 mol/dm³ initial concentration of lactic acid as shown in Figs. 7 and 8. Fig. 13 shows the effects of ionic liquids and pH control on the initial permeation flux, J, defined by the following equation.

$$J = -\frac{V}{A}\frac{dC_f}{dt}$$
(3)



Fig. 10. Permeation mechanism of lactic acids with supported ionic liquid membrane.

where *A* is effective contact area, *V* is volume of feed phase, and $C_{\rm f}$ is concentration of lactic acid in the feed phase. From this figure, we can determine that Aliquat 336 has higher permeation rates of both lactic and hydrochloric acid than Cyphos IL-101. Under the experimental condition of low concentration of lactic acid, hydrochloric acid preferentially permeated through Aliquat 336 impregnated membranes and resulted in a rapid decrease in pH in the feed phase and a significant decrease in the dissociated form of lactic acid. However, under the pH-controlled condition and in the presence of a higher lactic acid concentration compared with hydrochloric acid, as the lactic acid permeated through both membranes, the difference in the extraction capacity is considered to directly reflect the results of the permeation fluxes. To confirm this, we measured the distribution ratio of lactic acid between ionic liquids and water. However, because a certain equilibration could not be attained using pure ionic liquids due to their extremely high viscosity, we examined the distribution ratio (i.e., lactic acid concentration in organic phase/ that in aqueous phase) of lactic acid using ionic liquids diluted by 1-decanol. The pH effect on the distribution ratio of lactic acid is shown in Fig. 14. As expected, Aliquat 336 has a larger extraction capacity of lactic acid than does Cyphos IL101, and this result supports the higher permeability with an Aliquat 336 impregnated membrane under the pHcontrolled condition.

3.2. Application to hollow fiber membrane

In the above sections, we optimized the supported ionic liquid membrane system for lactic acid recovery by using Aliquat 336 as an ionic liquid and hydrochloric acid, whose concentration was kept as low as possible, as a stripping agent. Now we apply such a system to hollow fiber membranes, which are considered a practical configuration due to their high specific area.



Fig. 11. Time courses of lactic acid concentration in feed (\bullet) and stripping (O), and pH of feed ($\mathbf{\nabla}$) and stripping (∇) phases with Aliquat 336, 0.5 mol/dm³ lactic acid and 0.1 mol/dm³ hydrochloric acid as membrane, feed and stripping solutions, respectively.



Fig. 12. Time courses of lactic acid concentration in feed (\bigcirc) and stripping (O), and pH of feed (\bigtriangledown) and stripping (\bigtriangledown) phases with Cyphos IL-101, 0.5 mol/dm³ lactic acid and 0.1 mol/dm³ hydrochloric acid as membrane, feed and stripping solutions, respectively.

Here, the experiments use hollow fibers in the batch mode as shown in Fig. 1b; specifically, Aliquat 336 impregnated hollow fibers were immersed in the feed solution, and the stripping aqueous solution was fed into the interior of the hollow fibers and circulated.

Fig. 15 shows the time course of permeation from an experiment using hollow fiber membranes impregnated with Aliquat 336. Comparing these results with those in Fig. 2, a much faster permeation of lactic acid through hollow fiber membranes than through a flat sheet membrane was observed. The recovery ratio of lactic acid in the hollow fiber membrane system reached 87.1% after 10 h. The permeation fluxes in both cases are summarized in Table 3, along with the



Fig. 13. Effect of lactic acid concentration and pH control on permeation flux of lactic acid where "0.01 no control" indicates the experimental condition of 0.01 mol/dm³ of initial lactic acid in the feed phase and in the absence of pH control; the other labels indicate values in a similar manner.



Fig. 14. Distribution ratio of lactic acid with Aliquat 336 (●) and Cyphos IL-101 (O) diluted in 1-decanol.

membrane characteristics. Although the permeation flux for the hollow fibers is 4 times higher than that of a flat sheet membrane, if we consider the membrane thickness, it is only 1.6 times higher (last row in Table 3). This may reflect differences in the membrane microstructure such as porosity and tortuosity between PVDF and PP membranes. Therefore, application to a hollow fiber membrane was successful. Because hollow fibers can be easily scaled-up and modularized, a membrane process can be developed by estimating the required membrane area based on the permeation flux measured in this study.



Fig. 15. Time courses of lactic acid concentration in feed (\bullet) and stripping (O), and pH of feed ($\mathbf{\nabla}$) and stripping (∇) phases using Aliquat 336 impregnated hollow fiber membranes, 0.01 mol/dm³ lactic acid and 0.02 mol/dm³ hydrochloric acid as membrane, feed and stripping solutions, respectively.

Table 3 Flux of lactic acid through supported ionic liquid membrane in initial lactic acid concentration of 0.01 mol/dm³

	Flat sheet	Hollow fiber
Contact area [cm ²]	12.0	25.9
Membrane thickness [µm]	125	50
Permeation flux [mol $m^{-2} h^{-1}$]	3.71×10^{-6}	1.50×10^{-5}
Permeation flux [mol m ⁻² h ⁻¹ μ m]	4.64×10^{-4}	7.50×10^{-4}

4. Conclusion

The application of a supported liquid membrane, based on ionic liquids, to separating lactic acid was examined. A supported ionic liquid membrane system for recovering undissociated lactic acid was proposed to remove the acidification process of lactate. Ionic liquids having a hydrophobic cation and a chloride anion, such as Aliquat 336 and Cyphos IL-101, were found to be suitable as membrane solvent from the viewpoints of membrane stability and the permeability of lactic acid. Lactic acid in the feed phase successfully permeated through the supported ionic liquid membrane to the stripping phase containing hydrochloric acid against the concentration gradient of lactic acid. The permeation of lactic acid was improved by keeping the pH of the feed phase constant and keeping the lactic acid in the dissociated form. For separation with a realistically high concentration of lactic acid, Aliquat 336 was superior to Cyphos IL-101 due to its higher extraction capacity of lactic acid under the condition of constant pH. Aliquat 336 was successfully impregnated in polypropylene hollow fibers with thinner membrane thickness and larger specific area than a flat sheet. Lactic acid permeated through the hollow fiber membrane impregnated with Aliquat 336, and the permeation flux was higher than the estimated value from the flat sheet membrane. The supported ionic liquid membrane system was found to be promising for lactic acid recovery from fermentation broth on an industrial

scale. A task that remains for the future is the recovery of lactic acid from actual fermentation broth.

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