A STUDY OF DESALINATION USING A DOUBLE-LIQUID MEMBRANE

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Introduction

Desalination is almost always necessary in the downstream processing of biochemical products. For example, in fermentation processes, concentration of the salt in the broth is relatively high, compared with that of the product. Electrodialysis using ion-exchange membranes or resins has usually been adopted for this purpose, but the capital and the operating costs are not low.

Recently, liquid membranes have been found to be an effective separation technique in the fields of hydrometallurgy and bioengineering. We have attempted to apply this technique to desalination of solutions containing organic substances.

In the present work, we studied the construction of a desalination system using a double-liquid membrane system and the applicability of this system to aqueous solutions of carnitine.

1. Process Principles

1.1 Double liquid membrane system

Figure 1 shows the mechanism of desalting using double-liquid membranes. Sodium chloride is considered as a model salt here. Liquid membrane 1 and stripping phase 1 are for removing sodium ion from feed solution. Liquid membrane 2 and stripping phase 2 are for chloride ion. HR and ROH represent carriers (extractants) for sodium and chloride ions, respectively.

The cation and the anion in the feed solution permeate through the membranes and are concentrated into the respective stripping solutions, while the solute without net charge remains. The hydrogen and hydroxide ions are transported to the feed solution through the respective membrane and neutralized. Driving forces of the cation and anion transport are the concentration differences of hydrogen and hydroxide ions between the feed and the respective stripping solutions.

pH of the feed solution reaches a stationary value that depends on the initial conditions of the system.

1.2 Carriers

For industrial applications, the carriers must suffice the following requirements: 1. non-selective transport ability of cation or anion, 2. low price, and 3. chemical stability and non-toxicity. Di-2-ethylhexylphosphoric acid (D2EHPA) and tri-*n*-octylmethylammonium chloride (TOMAC) were selected as the cation and anion carriers, respectively.

1.3 Carnitine

Carnitine (β -hydroxy- γ -butyrobetaine) is a kind of vitamin (vitamin B₁₂) and is obtained as the hydrochloride salt (DL-(3-carboxy-2-hydroxypropyl)-trimethylammonium chloride). The value of pK_a is 3.98 and the pH of aqueous carnitine solution is about 2.3. Carnitine has no net charge at this pH, and it is not expected to be removed from feed solution during desalination.

2. Experimental

2.1 Reagents

D2EHPA supplied by Daihachi Chemical Industry Co., Ltd. as DP-8R (purity 97.6 %) was diluted with *n*-octane without further purification. TOMAC purchased from Dojindo Lab. as Capriquat was used as received and diluted with a mixed solvent of *n*-octane and *n*-decyl alcohol (30 vol%). The mixed solvent was used to improve the solubility of TOMAC and to avoid phase separation. In most experiments, tri-*n*-octylmethylammonium hydroxide (TOMAHO) was used as Cl⁻ carrier. The solution containing TOMAHO was prepared by washing that of TOMAC with 2 mol/dm³ NaOH solution several times.

The aqueous feed solution was prepared by dissolving sodium chloride and carnitine in distilled water. The stripping solutions were sulfuric acid and sodium hydroxide aqueous solutions for cation and anion, respectively.

The concentration of Na⁺ was determined by atomic absorption spectrometry and that of Cl⁻ was analyzed by absorptiometric analysis with iron(III) perchlorate and mercury (II) thiocyanate⁵⁾. Carnitine was analyzed by a HPLC with an ODS type column and an ultraviolet detector.

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Fig. 1 Principle of desalination using the double-liquid membrane

Fig. 2 Experimental apparatus of double-bulk liquid membrane for desalination.
1: Liquid membrane phase (oil phase) containing TOMAC as a carrier 2: Liquid membrane phase (oil phase) containing D2EHPA as a carrier 3: Alkaline soln. for Cl^- stripping 4: Feed soln. 5: Acidic soln. for Na^+ stripping 6: Teflon magnetic bar

All experiments were carried out at 298 K.

2.2 Apparatus

Figure 2 shows a stirred cell that works as the double-bulk liquid membrane system. The cell is made of acrylic resin and has five liquid phases: two liquid membranes, two stripping solutions and a feed solution. The volume of the feed solution is 0.30 dm^3 and those of all other solutions are 0.25 dm^3 . The liquid membrane phase and the corresponding stripping solution were agitated by a glass dual four-flat-blades turbine. A Teflon-coated magnetic bar was used for agitation of the feed solution. The agitation speed was selected as 120 rpm for all the phases to keep the interfaces between aqueous and liquid membrane phases flat. The interfacial area between the feed solution and the liquid membrane phase was 21.0 cm^2 and that of the stripping solution side was 36.0 cm^2 . pH of the feed solution was monitored by a pH electrode.

Fig. 3 Desalination of NaCl in D2EHPA-TOMAC system.
(a) Time-courses of Na^+ and Cl^- concentrations in the feed soln.
(b) Time-courses of Na^+ and Cl^- concentrations in each stripping soln.
Keys $\circ$ and $\square$ represent Na^+ and Cl^- , respectively.
Experimental conditions: Feed soln.: NaCl soln. ($C_{\text{NaCl},0} = 0.1 \text{ mol/dm}^3$), $\text{pH}_0 = 4.14$
Stripping solns.: $2 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ soln. for Na^+ , $2 \text{ mol/dm}^3 \text{ NaOH}$ soln. for Cl^- Oil phases: $1.0 \text{ mol/dm}^3 \text{ D2EHPA}$ - n -octane soln. for Na^+ , $0.2 \text{ mol/dm}^3 \text{ TOMAC}$ - n -decyl alcohol (30 vol%)- n -octane soln. for Cl^-

3. Results and Discussion

3.1 Desalination using the double-liquid membrane

For the first time, desalination from a feed solution containing only 0.1 mol/dm^3 of NaCl was carried out using D2EHPA and TOMAC as the carriers. The results are shown in Figs. 3 (a) and (b). Figure 3 (a) shows the time courses of the salt concentration and pH in the feed solution and (b) shows those in the stripping solutions. The concentration change in the feed solution seems to be divided into two regions. In the first region, the concentrations of the salt do not change and only pH increases. In the second region, the concentration of salt decreases and pH remains almost constant.

From the concentration changes with time of the stripping solutions (Fig. 3 (b)), it is found that only Cl^- concentration increases, and Na^+ does not permeate through the liquid membrane in the first region. This behavior can be explained as follows. Under the initial condition, pH in the feed solution is too low for D2EHPA to extract Na^+ and TOMAC cannot extract Cl^- from the feed solution since TOMAC is a chloride salt. Therefore, in the first region the extraction reaction occurs only at the interface between the liquid membrane phase containing TOMAC and the stripping solu-

Fig. 4 Desalination of NaCl from the feed soln. in D2EHPA-TOMAHO system.
(a) Time-courses of Na⁺ and Cl⁻ concentrations in the feed soln.
(b) Time-courses of Na⁺ and Cl⁻ concentrations in each stripping soln.
Experimental conditions; Oil Phases: 0.2 mol/dm³ TOMAHO/*n*-decylalcohol (30 vol%)/*n*-octanesoln. for Cl⁻. Other experimental conditions and keys are the same as in Fig. 3.

tion, and yields TOMAHO (tri-*n*-octylmethylammonium hydroxide) by exchanging Cl⁻ for OH⁻ in the stripping solution. Then the TOMAHO that reaches the interface of the feed side extracts Cl⁻ from the feed solution and pH becomes high enough for D2EHPA to extract Na⁺ from the feed solution. Therefore, it is not efficient to begin the experiments with TOMAC as the Cl⁻ carrier.

Figure 4 shows the result using TOMAHO instead of TOMAC. Time courses of Na⁺ and Cl⁻ concentrations and pH of the feed solution are shown in Fig. 4 (a) and those of the stripping solutions are shown in Fig. 4 (b). The time courses of the salt concentrations and pH in the feed solution are different from the case (Fig. 3) using TOMAC. In the beginning pH increases rapidly and maintains a constant value. The constant value of pH indicates that mass fluxes of Na⁺ and Cl⁻ through the corresponding liquid membranes are almost the same. It takes 15 hours to remove ninety percent of Na⁺ and Cl⁻ from the feed solution.

3.2 The desalination of carnitine solution

Figure 5 shows the time course of the concentration of the feed solution in the carnitine system. Apparently, 80 % of NaCl in the feed solution is removed into

Fig. 5 Time-course of carnitine concentration in feed soln. in D2EHPA-TOMAHO system.
Keys ○, □ and △ represent Na⁺, Cl⁻ and carnitine, respectively.
Experimental conditions; Feed soln.: NaCl soln. ($C_{\text{NaCl},0} = 0.1$ mol/dm³) containing carnitine ($C_{\text{Car},0} = 0.01$ mol/dm³), $\text{pH}_0 = 2.92$.
Other experimental conditions are the same as in Fig. 3.

the strip solution in 30 hours, while the carnitine concentration of the feed solution does not change. The results of desalination experiments for a dense solution of carnitine and the salt are shown in Fig. 6. Figure 6 (a) shows the behavior of carnitine and NaCl concentrations of the feed solution and Fig. 6 (b) shows that in the respective stripping solutions. The concentration difference between Na⁺ and Cl⁻ of the feed solution is due to the fact that carnitine was added as the chloride salt. Carnitine acts as a buffer reagent; therefore, pH is low. The condition of low pH is suitable for extraction of Cl⁻ by TOMAHO, but the extraction rate of Cl⁻ is smaller than that in the carnitine-free system. It is suggested that carnitine also acts as a kind of masking reagent to prevent the extraction of Cl⁻. As a result, a long time is required to remove the salt from the feed solution. The concentration of carnitine, however, is constant through the lengthy operation.

The time required for the desalination is expected to be reduced by using liquid surfactant membranes. It is also important to find good carriers, especially for cations.

Conclusions

The double-liquid membrane system for desalination was proposed and studied with sodium chloride solution as a model salt. It was found that the process is basically possible using D2EHPA as a cation carrier and TOMAC as an anion carrier.

This technique was used to remove the salt from a carnitine solution. In the case of carnitine solution, it was found that desalination can be successfully performed although it takes a long time to remove the salt.

Fig. 6 Long-time test of desalination from high concentration of NaCl soln. containing carnitine in D2EHPA-TOMAHO system.
(a) Feed soln. (b) Stripping solns.
Experimental conditions; Feed soln.: NaCl soln. ($C_{\text{NaCl},0} = 1.0 \text{ mol/dm}^3$) containing carnitine ($C_{\text{Car},0} = 0.5 \text{ mol/dm}^3$), $\text{pH}_0 = 2.92$. Other experimental conditions and keys are the same as in Fig. 5.

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Nomenclature

C_i = concentration of species i [mol/dm³]
 t = time [h]

<Subscripts>

Car = carnitine
f = feed solution

s = stripping solution
0 = initial value

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