Transportation and Separation of Copper (II) and Cobalt (II) Ions Through a Liquid Membrane with Ligands of β-Diketone

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Transportation and separation of copper (II) (Cu^{2+}) and cobalt (II) (Co^{2+}) ions through a liquid membrane with ligands of β-diketone types were studied using two types of transportation reaction cells, which were a double tube type and a supported liquid membrane type containing ionic liquid. Almost quantitative transportations of Cu^{2+} and complete separation of Cu^{2+} and Co^{2+} were observed using both of the liquid membrane transportation reaction cells. The control of transportation of Co^{2+} by pH was also achieved in the supported liquid membrane transportation. The electric potential gradient applied between the receiving phase and the suppling phase caused both to short the reaction time and to improve transportation efficiency in the transportation of Cu^{2+}. The transportation mechanisms were discussed.

1. Introduction

The separation and concentration of specific metal ions from an aqueous solution are necessary for analysis of trace metals or recovery of valuable metals. The simple, rapid and high efficient method has been requested. A liquid-liquid extraction is conventionally used for the separation and concentration of metal ions, which is consist of two phases of aqueous and organic phases. This method takes advantage of a phase transfer phenomenon of materials. On the other hand, a liquid membrane transportation method is consist of three aqueous/membrane/aqueous phases, which also utilizes phase transfer as such as the liquid-liquid extraction. The transportation of metal ions are achieved by complexation and dissociation of metal ions with ligands in the organic or membrane phase in both the liquid-liquid extraction and the liquid membrane transportation. By the sequence of complexation and dissociation at the interfaces, the transportation of metal ions is achieved from an aqueous phase to another aqueous phase via a membrane in liquid membrane transportation. The liquid membrane transportation has some advantages such as no phase separation operation, reducing hazardous organic solvent and so on, compared with the liquid-liquid extraction. However, it has several disadvantages such as slow kinetics, lack of innovation due to the basically same mechanism as the liquid-liquid extraction and so on.

Recently, the combination of liquid membrane and electrodialysis was proposed in order to enhance the efficiency of the transportation and separation of metal ions [1]. The addition of electric potential inclination between two aqueous phases connected by a membrane phase to a liquid membrane transportation system is expected to change the transportation mechanism and kinetics and to improve the efficiency of the transportation and separation of metal ions. The fundamental investigation was carried out in this work in order to evaluate the performance and usability of the liquid membrane transportation system and the effect of electric potential gradient applied between two aqueous phases on the transportation efficiency of metal ions.

Using two types of the liquid membrane cells of a double tube type and a supported membrane type containing ionic liquid, the liquid membrane transportation and separation of the first series transition metal ions of copper (II) (Cu^{2+}) and cobalt (II) ions (Co^{2+}) were investigated. Ion-exchange through metal complex formation by multidentate ligands at interface between two adjacent phases and ionic transportation in each phase are considered to play important role in transportation and separation in phase transfer system. The experimental conditions such as kinds of membranes and ionic liquids and pH levels of aqueous phases were optimized to enhance the performance of liquid membrane transportation and separation of Cu^{2+} and Co^{2+} ions. Furthermore, electric potential gradient was applied between two aqueous phases that are connected by membrane of electrically conductive ionic liquid to promote the phase transportation of metal ions. The effect of electric potential on the phase transportation of metal ions was also investigated.

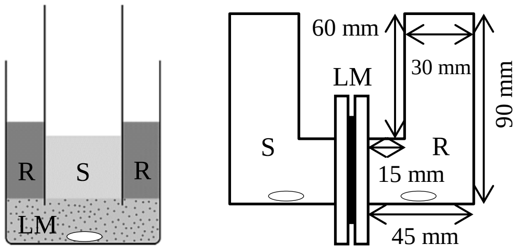
2. Experimental

2.1 Transportation of metal ions using a liquid membrane of chloroform

An bottomless inner glass tube with 30 mm diameter was set in the inside of an outer glass tube with 46 mm diameter (a 50 mL beaker) at the center, departed from the bottom of the outer tube at the distance of 5 mm (Figure 1a). The liquid membrane (LM) of 25 cm^3 chloroform with 0.1 mol dm^{-3} acetylacetone (acac) was set in the double tubes container [2]. The supplying phase (S) of 5 cm^3 volume of an aqueous solution ($[Cu(NO_3)_2]$, $[Co(NO_3)_2] = 2.0 \times 10^{-5}$ mol dm^{-3}, $[CH_3COONa] = 0.01$ mol dm^{-3}, $[HCl] = 2.0 \times 10^{-3}$ mol dm^{-3}, pH 5) was placed in the inner tube on the liquid membrane of the chloroform solution. The recieving phase (R) of 5 cm^3 volume of an aqueous solution ($[CH_3COONa] = 0.01$ mol dm^{-3}, $[HCl] = 0.1$ mol dm^{-3}, pH 1) was in the outer tube also on the liquid membrane of the chloroform solution. Three phases were stirred by a magnetic stirrer placed on the bottom of the outer tube at the rotation speed of 270 rpm to transport the metal ions of Cu^{2+} and Co^{2+} from the supplying phase to the receiving phase through the liquid membrane. After a certain period of reaction time the solution of each phase was removed using the 5 mL pipet from the double tubes container, the volume of which was mesured using a volumetric cilinder. The 5 cm^3 chloroform solution as the membrane phase was mechanically shaken with a 5 cm^3 portion of 0.1 mol dm^{-3} HCl in a 30 mL centrifugal tube with a screw cap to strip all of the metal ions from the chloroform solution to the hydrochloric acid. After the pH measurements of the aqueous supplying and receiving phases, the metals in each aqueous phase and the hydrochloric acid after stripping were analized by use of atomic absorption spectrophotometry. The amount of substance and the fraction of metal ions in each phase were calculated from the product of the metal concentration and the volume of each solution.

2.2 Transportation of metal ions using a supported membrane containing ionic liquid

The supported liquid membrane consist of the hydrophobic Durapore membrane filter made with polyvinylidene fluoride (PVDF) with 0.45 μm pores and 47 mm diameter containing ionic liquid of 1-butyl-3-dodecylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_4C_{12}im][Tf_2N]$) or 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6C_1im][Tf_2N]$) with 0.005 mol kg^{-1} 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) was set between polyethylene plates with a large hole together with two hollowed silicon rubber sheets at the center of the reaction cell (Figure 1 b) and fixed to the plates by bolts. Before use the membrane filter was soaked in a shallow bath of the ionic liquid containing dissolved PMBP for 24 hours to insorb the liquid. The 25 cm^3 of aqueous supplying phase with metal ions M^{2+} (Cu^{2+}, Co^{2+}) ($[M(NO_3)_2] = 2 \times 10^{-5}$ mol dm^{-3}, $[CH_3COONa] = 0.01$ mol dm^{-3}) and the 25 cm^3 of aqueous receiving phase without metal ions ($[CH_3COONa] = 0.01$ mol dm^{-3}) were pored into each part of the reaction cell separated by the membrane at the middle. The pH level of each aqueous phase was controlled by the amount of HCl added to keep the pH level of the supplying phase heigher than that of the recieving one. The magnetic stirrers were set at the bottoms of both containers for the aqueous solutions. Electric potential difference of 1.5 V and direct electric current were applied between two aqueous pahses through the membrane using carbon rods with 5 mm diameter as an electrode dipped at 15 mm deep in each aqueous phase for electrodialysis. After a certain period of reaction time the pH values, the volume and the metal concentration of the supplying and receiving aqueous phases were measured. The amounts of metal ions in membrane and on carbon electrodes were measured by putting these materials in 0.1 mol dm^{-3} HNO_3 and by applying reverse voltage to the carbon electrodes to strip reduced metal on them. The amount of substance and the fraction of metal ions in each phase were calculated from the product of the metal concentration and the volume of each solution.



a b

Figure 1. Reaction cells for liquid membrane transportation. A double tube type (a) and a supported liquid membrane type (b). A supplying phase (S), a liquid membrane phase (LM) and a receiving phase (R).

3. Results and Discussion

3.1 Transportation of metal ions using liquid membrane of chloroform

Figure 2 shows the dependence of the fraction of Cu^{2+} of each phase on reaction time at 20 ^oC using a chloroform solution with 0.1 mol dm^{-3} acac as a liquid membrane. The fractions in the figure mean the ratios of the amount of substance of Cu^{2+} in each phase after the transportation for that in the supplying phase before the transportation. The total sums of the amount of substance in each phase well agreed with total amounts before the transportation. The transportation of Cu^{2+} from the supplying phase to the receiving phase could be completely achieved for 4 hours. The fraction of Cu^{2+} of the receiving phase increases gradually although that of the supplying phase decreases rapidly, as shown in Figure 2. The reaction rate of the transportation from the membrane phase to the receiving one seems to be slower. In order to make the transportation faster, it is needed to fasten the dissociation of a metal complex at the interface between the membrane phase and the receiving one.

Figure 3 shows the time course of the transportation of each metal ion from the supplying phase that contains both Cu^{2+} and Co^{2+} ions. Only Cu^{2+} ions were transported to the receiving phase from the supplying phase because of the smaller complex formation constant of Co^{2+} than that of Cu^{2+} with acac [3]. The almost complete separation of Cu^{2+} and Co^{2+} ions was achieved by use of the liquid membrane transportation system. The transportation reaction rate of Cu^{2+} from the mixture was observed to be slower than that of Cu^{2+} separately transported, as shown Figure 3. This seems to be due to the competition with Co^{2+} ions in the complex formation in the supplying phase.

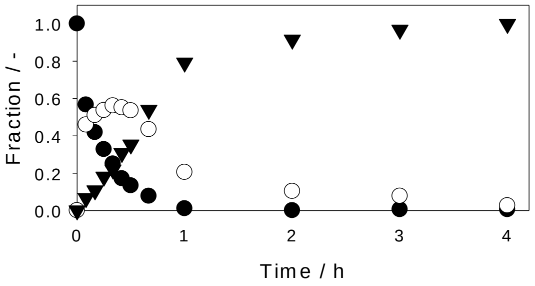


Figure 2. Molar fractions of Cu^{2+} in each phase by use of liquid membrane of chloroform with 0.1 mol dm^{-3} acac. The supplying phase (black circle), the liquid membrane phase (white circle) and the receiving phase (black triangle).

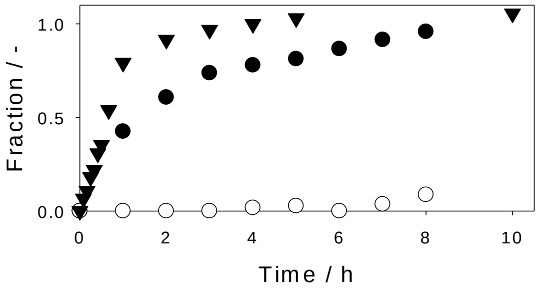


Figure 3. Respective molar fractions of Cu^{2+} and Co^{2+} in the receiving phase by use of liquid membrane of chloroform with 0.1 mol dm^{-3} acac. Cu^{2+} (black circle) and Co^{2+} (white circle) from the mixture and Cu^{2+} separately transported (black triangle).

3.2 Transportation of metal ions using supported membrane containing ionic liquid

Only about 15% of initial amount of Cu^{2+} was transported at maximum for 24 hours using acac with the concentration of 0.855 mol kg^{-1} in ionic liquid in the supported liquid membrane system. The remarkable decrease of the transportation efficiency of Cu^{2+} was observed in this system compared with the liquid membrane system of chloroform.

PMBP with the concentration of 0.005 mol kg^{-1} in $[C_4C_{12}im][Tf_2N]$ was employed as the ligand under the pH levels of the supplying and receiving phases set at 3 and 0, respectively. The results of the liquid membrane transformation of Cu^{2+} and Co^{2+} are summarized in Table 1 by showing the fractions of the metal ions in each aqueous phase for the initial amount of metal ions added in the supplying phase. The transportation efficiency of Cu^{2+} reached to 60% under this condition (No. 1). The transportation efficiency of Cu^{2+} was markedly enhanced using PMBP instead of acac, although the concentration of PMBP in ionic liquid is much lower than that of acac because PMBP is solid compared that acac is liquid at room temperature. Because of the large acid dissociation constant of PMBP (pK_a 3.92) [4-5] the activity of dissociated anion form species that forms a complex with a metal ion can be large even under an acidic condition.

In the transportation of Co^{2+} the transportation and no transportation of Co^{2+} could be controlled by the adjustment of pH levels of the supplying and receiving phases (Nos. 2 and 3). In the transportation of Cu^{2+} and Co^{2+} from the mixture only Cu^{2+} ions could reach to the receiving phase (No. 4). As the result, Cu^{2+} ions were completely separated form Co^{2+} ions in the receiving phase.

Table 1 Molar fractions of metal ions in aqueous phases and total recovery rates by use of the supported liquid membrane containing ionic liquid of $[C_4C_{12}im][Tf_2N]$ with 0.005 mol kg^{-1} PMBP for 24 hours.

Exp. No.	Metal ion	Supplying phase	Receiving phase	Recovery rate	Final pH Supp. / Rec.
1	Cu^{2+}	0.26	0.60	0.86	2.7 / 0.1
2	Co^{2+}	1.04	0.00	1.04	2.7 / 0.1
3		0.07	0.58	0.65	5.0 / 1.0
4	Cu^{2+}	0.16	0.56	0.72	2.7 / 0.1
	Co^{2+}	1.08	0.00	1.08	2.7 / 0.1

3.3 Effect of electrodialysis

Electrodialysis that cause a direct electric current through the phases was applied to the the supported liquid membrane system by applying voltage of 1.5 V between the aqueous phases. The same experimental conditions as the above except for using $[C_6C_1im][Tf_2N]$ as ionic liquid were employed. Figure 4 shows the dependence of the fraction of Cu^{2+} of each phase on reaction time. The transportation efficiency of 0.72 was obtained for 6 hours. Due to the effect of electric potential gradient, the best efficiency in this system was obtained even for much shorter reaction time.

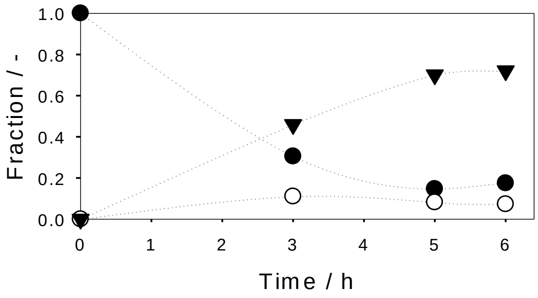


Figure 4. Molar fractions of Cu^{2+} in each phase by use of the supported liquid membrane containing ionic liquid of $[C_6C_1im][Tf_2N]$ with 0.005 mol kg^{-1} PMBP. The supplying phase (black circle), the liquid membrane phase (white circle) and the receiving phase (black triangle).

3.4 Mechanism of transportation

The most possible mechanism of transportation might be ion exchange reactions at the interfaces of the aqueous phases and liquid membrane one. A divalent metal ion and two protons are exchanged when the metal ion and the protons cross the interfaces reversely.

Ion exchange mechanism

$$Cu^{2+}{}_S + 2\,HL_{LM} \leftrightarrow CuL_{2,LM} + 2\,H^+{}_S \qquad \text{S/LM interface}$$

$$CuL_{2,LM} + 2\,H^+_R \rightarrow Cu^{2+}{}_R + 2\,HL_{LM} \qquad \text{LM/R interface}$$

Total reaction

$$Cu^{2+}{}_S + 2\,H^+{}_R \rightarrow 2\,H^+{}_S + Cu^{2+}{}_R$$

In the case of electrodialysis caused by electric potential gradient between the supplying and receiving phases using ionic liquid, electron transfer at electrodes and ion transfer due to electorneutrality are combined.

Electrode reaction

$$2\,H^{+}{}_{R} + 2\,e^{-} \rightarrow H_{2,R} \qquad \text{cathode in R}$$

$$2\,OH^{-}{}_{S} \rightarrow 1/2\,O_{2,S} + H_{2}O_{S} + 2\,e^{-} \qquad \text{anode in S}$$

Ion transfer

$$2\,C^{+}A^{-}{}_{LM} \rightarrow 2\,C^{+}{}_{R} + 2\,A^{-}{}_{S}$$

Overall reaction

$$Cu^{2+}{}_{S} + 2\,OH^{-}{}_{S} + 4\,H^{+}{}_{R} + 4\,Cl^{-}{}_{R} + 2\,C^{+}A^{-}{}_{LM}$$
$$\rightarrow 2\,H^{+}{}_{S} + 2\,A^{-}{}_{S} + 1/2\,O_{2,S} + H_{2}O_{S} + Cu^{2+}{}_{R} + 2\,C^{+}{}_{R} + 4\,Cl^{-}{}_{R} + H_{2,R}$$

The electron transfer at the electrodes could be oxidation and reduction of electrolysis of water or chloride ion. Bubbles on the electrodes generated by electrolysis were not observed because of the small electric current of about 70 μA. In order to keep electroneutrality in each phase, the transfer of cations and anions of ionic liquid into the aqueous phases occurs. The transportation of Cu^{2+} was accelerated under the influence of electric potential. This phenomenon might suggest that the formation and dissociation of a metal complex followed by the transportation of metal ions is promoted due to the effect of the electric field of electric double-layer formed at aqueous/membrane and membrane/aqueous interfaces.

4. Conclusion

The liquid membrane system studied almost completely achieved the transportation of Cu^{2+} and the separation of Cu^{2+} from the mixture with Co^{2+}. It was observed that the combination of ionic liquid and the electric potential gradient in this system accelerated the transportation reaction rate and improved transportation efficiency. The separation of metal ions by use of the liquid membrane system combined with electrodialysis is expected to be investigated further.

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