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Homogeneous Liquid-Liquid Extraction of Metal Ion Utilizing Upper Critical Solution Temperature of Propylene Carbonate

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ABSTRACT

This study was undertaken to investigate the extraction of In^{3+} and Ga^{3+} by 7-(4-ethyl-1-methyloctyl)-8-hydroxy-quinoline (Kelex100), which has been found to be a slow extraction process. Homogeneous liquid-liquid extraction utilizing upper critical solution temperature of 4-methyl-1,3-dioxolan-2-one (propylene carbonate, abbreviated as PC) was used to eliminate the interface and speed up the extraction, since distribution between two phases was thought to be the rate-determining step. The effect of contact time on the percentage of metal extraction was examined at 80°C using Kelex100 dissolved in toluene and PC solutions and the difference between two solvents was evaluated. The results clearly show that the use of homogeneous liquid-liquid extraction using PC with Kelex100 is faster than traditional two phase extraction.

KEYWORDS

Liquid-liquid extraction;
propylene carbonate; upper
critical solution temperature;
Kelex100

Introduction

In the liquid-liquid extraction of metal ions, broadly speaking, the solvent is composed of at least two components, an extractant to interact with metal ions and a solvent. Although the extractant has significant influence on performance, it is also well known that some solvents also strongly affect metal extraction; these solvents are called functional solvents. Functional solvents are classified into two categories. The first is a solvent possessing metal extractability inherently and the second has an ability of a reversible phase transition from a homogeneous (water miscible) phase to heterogeneous (water immiscible) two-phase system. Typical examples of former solvent are diethyl ether or 4-methyl-2-pentanone used for the extraction of iron(III) chloride^[1] and 3-isopropoxy-N-isopropyl-propanamide, which extracted gold(III) ions directly without using any extractants.^[2] The second category contains solvents, where a phase transition from a two-phase system to a single system occurs. This extraction method is called as Homogeneous Liquid-Liquid Extraction (HLL)^[3], a range of phase separation methods such as salting out^[4,5], pH dependence^[6], solubility change with the temperature^[7,8] etc. have been reported to strip the desired solute.

This study focused on the application of the use of the upper critical solution temperature (UCST) of 4-methyl-1,3-dioxolan-2-one (abbreviated as PC, see Figure 1) to extract the metal from an aqueous phase. Thus below UCST the aqueous phase containing metal ions is immiscible with the organic phase containing PC and extractant. When the temperature is increased beyond the UCST, the mixture forms a single phase providing enhancement in the extraction rate between the metal ions and the extractant. PC is less volatile, non-toxic, and a highly polar solvent and is used in cosmetics such as a nail polish

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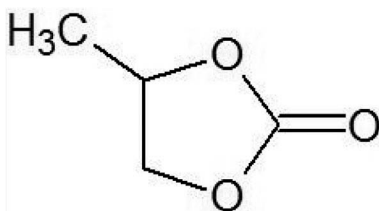


Figure 1. Structure of propylene carbonate (PC).

remover and as an LSI washer in semiconductor manufacture. Although some studies on the application of PC in metal extraction have been reported^[9–11], PC has not become popular as an extracting solvent yet. Other than the favorable properties as an extraction solvent mentioned above, PC has an UCST of 72°C. However, the application of the UCST of PC to metal extraction has only been reported in the study on the extraction of iron(III) thenoyltrifluoroacetate (TTA) reported by Murata *et al.*^[12] They reported qualitatively that the extraction rate of iron(III) (Fe^{3+}) was promoted by elevating temperature and forming homogeneous phase in TTA-PC extraction system.

It was expected that the mass transfer of very hydrophobic extractants at an interface could be improved dramatically by making a homogeneous solution. For example, 7-(4-ethyl-1-methyloctyl)-8-hydroxy-quinoline (Kelex100) is well-known as a hydrophobic extractant. Kelex100 solubility in the aqueous phase is very small, complex formation proceeds mainly at the interface and therefore, the extraction rate is slow and dependent on the interfacial area compared to 8-quinolinol which is a basic structure of Kelex100. For example, it was reported that the extraction of gallium(III) (Ga^{3+}) with Kelex100 from weakly acidic solution required 5 days to attain equilibrium.^[13] Therefore, the present study was undertaken to examine whether the use of PC in place of toluene in the extraction of trivalent metal ion such as aluminum(III) (Al^{3+}), Fe^{3+} , Ga^{3+} and indium(III) (In^{3+}) with Kelex100 could significantly enhance the extraction rate.

Experimental

Reagents

Kelex100 was supplied with purity of 96.3% by HighChem Company Limited and was used as it was. PC, toluene, and all other reagents were purchased from Kanto Chemical Co., Inc., as analytical-grade reagents.

Extraction procedure

Aqueous phases were prepared by mixing 0.1 mmol/L Al^{3+} , Fe^{3+} , Ga^{3+} , In^{3+} nitrates with 0.01 mol/L NH_4NO_3 , and 0.1 mol/L triammonium citrate and pH of the mixed solution was adjusted using 3 mol/L ammonia water and 3 mol/L HNO_3 . An organic phase was prepared by dissolving Kelex100 in PC or toluene to a concentration of 0.01 mol/L. Two phases were heated by immersing in a water bath at 80°C for 30 min. Equal volumes of the organic and aqueous solutions were transferred into 50 mL extraction vial and shaken at 80°C for 24 hours. After cooling to room temperature and phase separation by centrifugation, the metal ions in the organic phase were back-extracted into equal volume of 1 mol/L HCl. The concentration of metal ions in the aqueous phase and the receiving phase were measured using inductively coupled plasma optical emission spectrometry (Vista-Pro, Varian). The equilibrium pH values of the aqueous phases were also measured. The extraction at 25°C was conducted in the same manner as described above except for maintaining the temperature of solution at 25°C throughout the course of extraction. The extraction percentage (%E) was calculated by Equation (1).

$$\%E = \frac{[M]_{org}}{[M]_{aq,init}} \quad (1)$$

where $[M]_{aq,init}$ and $[M]_{org}$ are the initial concentration of the metal ion in the aqueous phase and the final concentration of the metal ion in the organic phase, respectively.

Results and discussion

UCST of propylene carbonate

PC is fairly insoluble in water at room temperature, however, its solubility increases with increasing temperature. If both phases were heated to 60°C, PC gradually dissolved in water and the water layer becomes opaque (Figure 2a). When the temperature was raised to more than 72°C, PC and water dissolve in each other and become homogeneous (Figure 2b). PC and water separate into two phases again by lowering the temperature to less than 72°C (Figure 2a).

Extraction at 25°C

Figure 3a,b show extraction curves obtained with toluene and the PC extraction system at 25°C, respectively. The two extraction systems have shown some similarities in their extraction of these metals. For example, Al^{3+} is not extracted over the whole range of pH irrespective of solvent. As for Fe^{3+} and Ga^{3+} , the maxima of extraction, %E, in PC system was 77% at pH 3.33 for Fe^{3+} and 89% at pH 2.86 for Ga^{3+} . This was slightly higher than in the toluene system, that is, 57% at pH 1.78 for Fe^{3+} and 53% at pH 2.12 for Ga^{3+} . The percentage extraction of In^{3+} increased with increasing pH and reached a maximum in both systems, in the pH range of 6.55–8.89 for toluene and in the pH range of 6.23–7.24 for PC. The clear advantage of PC as an extraction solvent over toluene was not recognized in the extraction at low temperature. Yamada *et al.* reported that $5 \times 10^{-4} \text{ mol dm}^{-3} Al^{3+}$, In^{3+} , and Ga^{3+} were completely extracted within 3 h with $2 \times 10^{-2} \text{ mol dm}^{-3}$ 8-quinolinol 1-octanol/octane mixed solution from neutral pH region in perchlorate solution.^[14] The lower extractability in the present extraction system compared with that in 8-quinolinol 1-octanol/octane extraction system can be ascribed to the use of a more hydrophobic extractant, Kelex100 and the addition of citrate salt as a masking reagent as to prevent hydrolysis of metal ions.

Extraction at 80°C

Figure 4a shows extraction curves obtained with toluene extraction system at 80°C. In the toluene extraction system, the extent of metal extraction was not affected by the increase in temperature. The extraction behaviors of metal ions is similar to those obtained at 25°C (Figure 3a). That is, only In^{3+} was

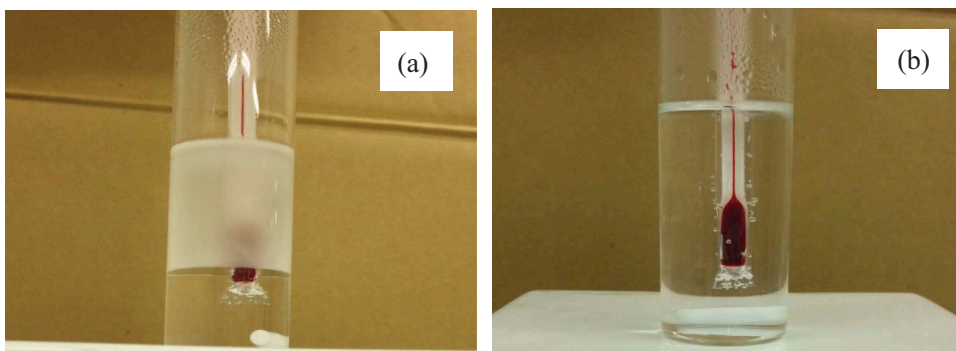


Figure 2. Dissolution behavior of PC in water. (a): At lower than 65°C, (b): at higher than 72°C.

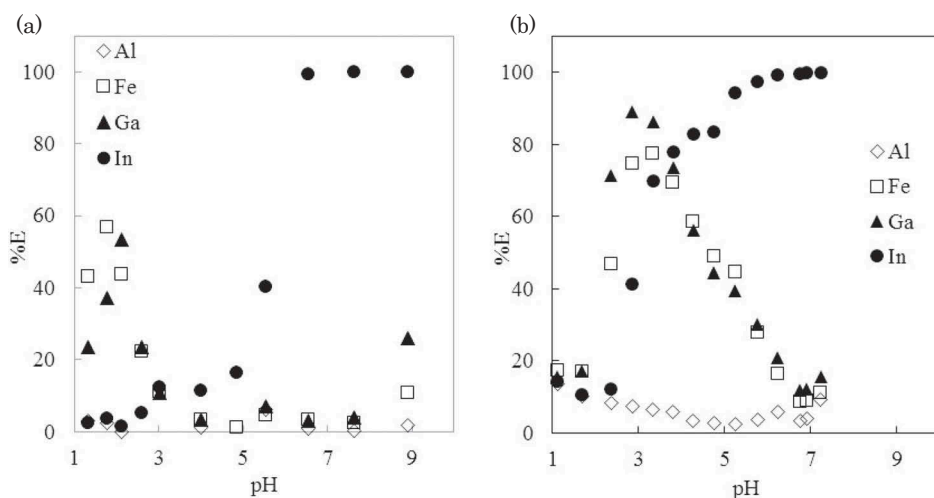


Figure 3. Effect of equilibrium pH on the extraction percentage at 25°C. (a): Toluene, (b): PC.

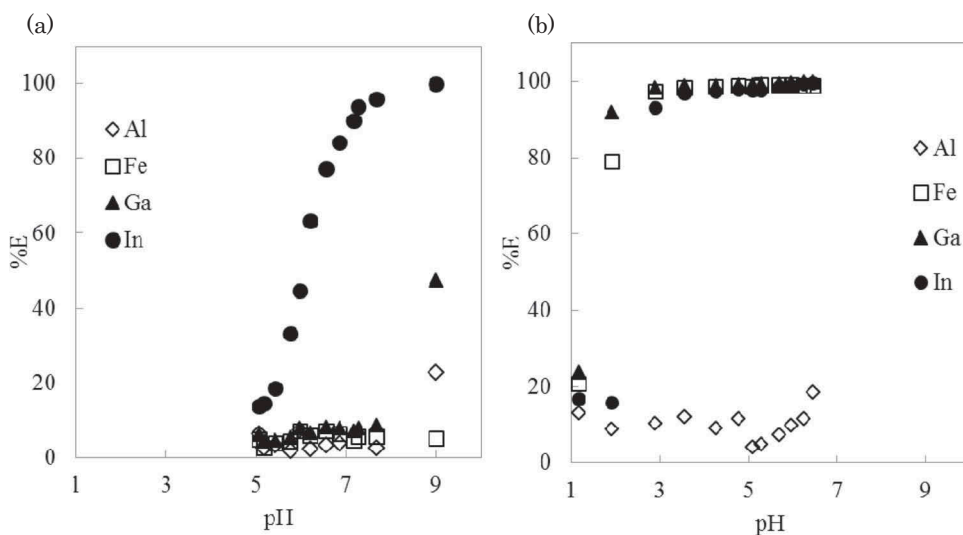


Figure 4. Effect of equilibrium pH on the extraction percentage at 80°C.

extracted effectively ($95 \pm 4.1\%$) in the pH range of 7.16–8.98, and other metals were not extracted sufficiently. While, in the PC extraction system, extraction behavior of metal ions at 80°C (Figure 4b) was quite different from those at 25°C (Figure 3b). Surprisingly, Fe^{3+} , In^{3+} and Ga^{3+} were all extracted with % E more than 98% over the pH range of 3.56–6.46; only Al^{3+} was not extracted. If chelate complex formation is exothermic, metal extraction is suppressed along with the increase of temperature and vice versa. Thus decreasing the distribution ratios along with increasing temperature has been reported for several extraction systems, such as extraction of silver(I) with dithizone chloroform(CHCl_3) solution, silver(I) and cadmium(II) with 8-quinolinol in CHCl_3 ^[15], and lanthanides with N,N-Diisobutyl-2-[octyl-(phenyl)- phosphoryl]-acetamide (CMPO).^[16] The values of enthalpy in Kelex100 extraction from NaOH solution, of which the extraction process was described by Equation (2), were determined to be -43 kJ mol^{-1} and -104 kJ mol^{-1} for Al^{3+} and Ga^{3+} , respectively, and the distribution ratio for both metal ion diminished with increase of temperature.^[17]



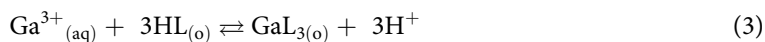
where HL is Kelex100.

Effect of contact time

The effect of heating on the extraction was examined by changing the contact time at 80°C. Figure 5 shows the relationship between %E and the contact time in toluene and Figure 6 shows the relationship between %E and the contact time in PC. As can be seen from Figure 3a,b, the rate of metal extraction was very slow at 25°C in both toluene and PC extraction systems. So the change of equilibrium during the course of cooling from 80°C to 25°C can be considered to be negligibly small. Therefore, the contact time was defined as the shaking time at 80°C and did not include the cooling time.

In the toluene extraction system, the extraction of In^{3+} took 1200 min to attain equilibrium, while other metals did not attain the extraction equilibrium even after 1440 min of contact. In the PC extraction system, %E of Fe^{3+} , In^{3+} , and Ga^{3+} exceeded 80%, 90%, and 97% in the first 5 min, respectively.

To compare the kinetics of extraction between toluene and PC more specifically, the extraction rate constant was calculated. The extraction mechanism of Al^{3+} in the sodium hydroxide solution using Kelex100 was reported as Equation (2) and the extraction rate was determined to be first order with respect to the Al^{3+} concentration in the aqueous phase.^[18] Inoue *et al.*, reported that Ga^{3+} was extracted with Kelex100 from weakly acidic solution according to Equation (3) and the extraction reaction was first order.^[13]



Since aluminum, gallium, and indium belong to group 13 in periodic table, it was assumed that metal ions were extracted with a first-order reaction in the present extraction system. The extraction rate of the first-order reaction is expressed in Equation (4).

$$\ln \frac{[M]_{\text{aq}}}{[M]_{\text{ini}}} = -k_{\text{ex}1} t \quad (4)$$

where $[M]_{\text{aq}}$ and $[M]_{\text{ini}}$ are metal ion concentration in the aqueous phase after shaking for a definite time and that before shaking with organic phase, respectively, and $k_{\text{ex}1}$ denotes the rate constant for metal ion extraction.

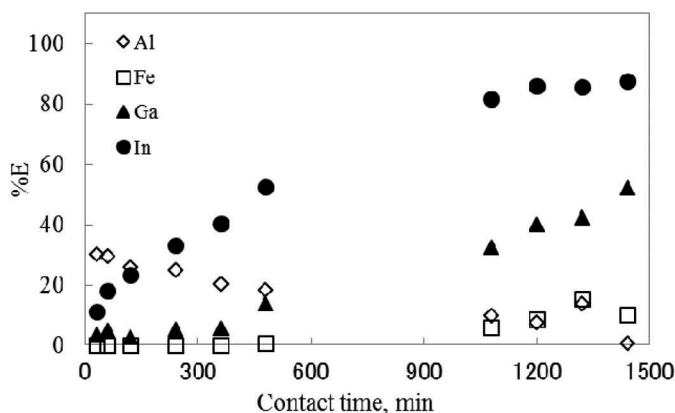


Figure 5. Effect of contact time on the extraction percentage of metal ions with toluene solution at 80°C. pH: 8.06 ± 0.03 .

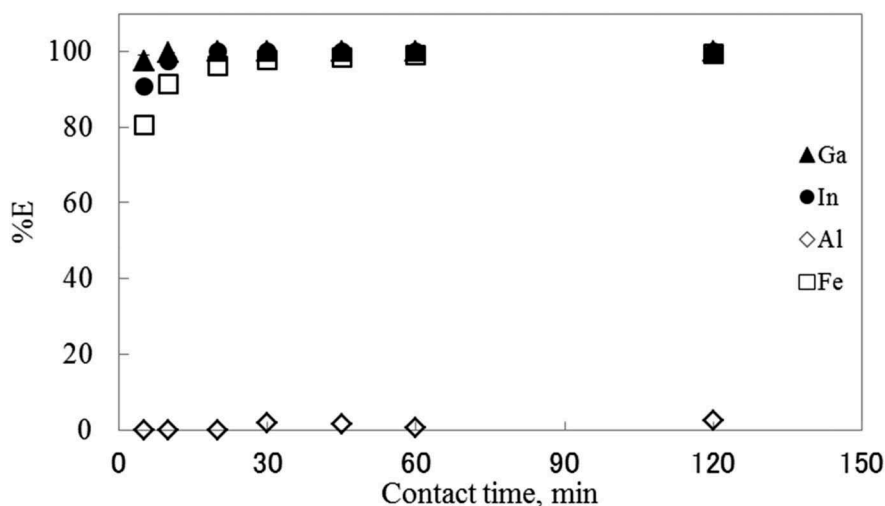


Figure 6. Effect of contact time on the extraction of metal ions with PC solution at 80°C. pH: 6.08 ± 0.15 .

The percent extraction of metal ion in Figures 5 and 6 were converted into $\ln([M]_{aq}/[M]_{ini})$ and plotted against contact time. The approximate curves were obtained with these plots, and then the linear function and correlation coefficient (r^2) were obtained. The slope in this linear function can be regarded as the apparent rate constant, k_{ex1} , of pseudo first order reaction and are summarized in Table 1. As can be seen Table 1, all the correlation coefficients for In^{3+} and Ga^{3+} were fairly good ($r^2 > 0.95$) in both solvents, and consequently, the assumption of a pseudo first order reaction seems to be appropriate. However, correlation coefficients for Fe^{3+} shows poor fit with the correlation coefficient of 0.666 in this PC extraction system and 0.822 in toluene. Thus, it was assumed that Fe^{3+} was extracted via a second order reaction. Since the integrated rate equation for the second order reaction can be expressed by Equation (5), the inverse of the metal ion concentration in the aqueous phase after contact for a definite time was plotted against contact time,

$$\frac{1}{[M^{3+}]_{ini}} - \frac{1}{[M^{3+}]_{aq}} = -k_{ex2}t \quad (5)$$

where k_{ex2} denotes the rate constant for metal ion extraction. The value of r^2 obtained in PC extraction system were greater than 0.95, the slopes of these linear functions were regarded as the apparent rate constant, k_{ex2} , these values were used to evaluate the extraction rate of Fe^{3+} . By simply comparing these rate constants, it can be concluded that the extraction rate of Fe^{3+} , Ga^{3+} , and In^{3+} in PC extraction system were around 15000, 740, and 380 times faster than those in toluene extraction

Table 1. Rate constant for metal extraction.

	Fe^{3+} k_{ex2} ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	Ga^{3+} k_{ex1} (s^{-1})	In^{3+} k_{ex1} (s^{-1})
PC	0.301 (0.974)	0.370 (0.974)	0.572 (0.961)
Toluene	0.00002 (0.890)	0.0005 (0.951)	0.0015 (0.993)

The values in the upper row are the rate constants and those in the parenthesis in the lower row are correlation coefficient.

system. Thus, the rate of metal extraction was accelerated dramatically by using PC at 80°C in the present Kelex100 extraction system. Taking into account the above-mentioned results, this improvement in the extraction rate can be ascribed to the disappearance of the interface between water and PC due to UCST with PC.

Conclusion

This study clearly demonstrates that the HLLC method by utilizing upper critical solution temperature of PC accelerated the extraction rate of In^{3+} and Ga^{3+} in Kelex100 extraction system 740 and 380 times compared with those in toluene extraction system, respectively. In the Kelex100 toluene extraction system, the extractability of the metal ion was not improved significantly by increasing temperature from 25°C to 80°C, and therefore, the acceleration of extraction rate in PC extraction system can be ascribed to the disappearance of the interface due to the formation of homogeneous solution. It was shown that the present HLLC method by utilizing upper critical solution temperature of PC has potential to improve the extraction rate in the slow extraction systems using extremely hydrophobic extractant such as Kelex100.

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