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The Effect of Solvent on the Liquid – Liquid Extraction of Lanthanides Using DODGAA as an Extractant

Kaoru FUJINAGA^{1*}, Yuka KOBAYASHI¹, Naoto SHIMIZU², Shin-ichi KAWANO³,
Syunichi OSHIMA¹, Muneaki SAKAMOTO¹ and Yu KOMATSU⁴

¹ College of Bioscience and Chemistry, Kanazawa Institute of Technology,
3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan

² Agilent Technologies Co. Ltd., 9-1 Takakura-cho, Hachioji, Tokyo 192-8510, Japan

³ Nomura Micro Science Co. Ltd., 2-9-8 Okada, Atsugi, Kanagawa 243-0021, Japan

⁴ Office for Industry-University Collaboration, Kanazawa Institute of Technology,
7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

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Abstract

4-Methyl-1,3-dioxolan-2-one and 4-ethyl-1,3-dioxolan-2-one are well-known solvent in the name of propylene carbonate (PC) and butylene carbonate (BC), respectively, and PC is classified to level 1 in terms of combustibility and health hazard by National Fire –Protection Association. Therefore, PC is less toxic and environment-friendly solvent compared to the usual solvents, such as hexane and toluene. PC and BC are not only safe but also are having strong polarity, however, their application to solvent extraction of metal chelates as an extraction solvent were not carried out so much. Then, in this study, PC and BC were applied to N,N-diocetyl diglycolamic acid (DODGAA) extraction of lanthanides as the diluent and their extractabilities were compared with that of hexane. Lanthanum and scandium were found to be affected with solvent comparatively strongly to the other lanthanides. It was observed in the slope analysis of in the relationship between $\log D$ vs. pH plots that the some slopes of straight lines in DODGAA-PC and DODGAA-BC system deviated from theoretical value of 3. The possibilities of the change of metal ion concentration based on the volume change due to the mutual dissolution and the formation of different kind of complex other than LnR_3 were considered as the causes for the deviations in a slope analysis and were examined experimentally.

Keywords: Propylene carbonate, Butylene carbonate, Solvent extraction of lanthanides, DODGAA

1. Introduction

In the liquid-liquid extraction, solvent plays an important role of not only dissolving the extracted species but also modifying the extractability of analyte. 4-Methyl-1,3-dioxolan-2-one (propylene carbonate, PC) and 4-ethyl-1,3-dioxolan-2-one (butylene carbonate, BC) are an advisable solvent which has good characteristics such as high flush point, heavier than water, polar with dielectric constant of 65.1 (for PC). Moreover, PC and BC are assigned in level 1 and 0 as for health,

respectively, and both are classified in level 1 as for flammability and level 0 as for instability by National Fire Protection Association¹⁾. PC is widely used for cosmetics such as nail polish remover and used in industries as a solvent to extract aromatics from naphtha²⁾.

Generally, since the extracting solvent affects to extractability in the ion association extraction systems more strongly than that in chelate extraction system, PC was mainly examined in the former systems. For example, B. G. Stephens

* Corresponding author

E-mail: fujinaga@neptune.kanazawa-it.ac.jp

et al. has reported the extraction of ferroin complexes using PC as a solvent with different derivatives of 1,10-phenanthroline³⁻⁵⁾, and PC was also used for the extracting solvent in the polarographic determination of halo-complex ions of some metals^{6,7)}. On the other hand, only few attempts to applying PC to chelate extraction system were reported^{8,9)}, and the paper on the solvent extraction of metal ions using BC could not be found at all by reviewing the literature.

PC and BC were applied to N,N-dioctyldiglycolamic acid (DODGAA) extraction of lanthanides as the diluent in this study, because it was studied in detail under the several extraction conditions¹⁰⁻¹³⁾ and seemed to be a suitable to evaluate the extractability of solvent.

2. Experimental

2.1 Reagents

DODGAA and BC were purchased from Tokyo Chemical Industry Co., Ltd. and was used without further purification. PC was obtained from Kanto Chemical Co., Inc. and was used as it was. All other reagents were of analytical grade.

2.2 Extraction procedure

Organic phases were prepared by dissolving DODGAA in PC or in BC or in hexane containing 5 vol.% 1-octanol as an solubilizing adjuvant. Aqueous phases contained 0.1 mmol dm⁻³ of metal ions and 0.1 mol dm⁻³ NH₄NO₃. The pH values of the aqueous phases were adjusted using HCl and NaOH. Five milliliters of the aqueous and organic phases were shaken for 60 min at 100 rpm and then the phases were separated by centrifuge for 20 min at 2000 rpm. The metal ions in the organic phase were back-extracted into 3 mol dm⁻³ HCl. The concentration of metal ions in the aqueous phase and in 3 mol dm⁻³ HCl was measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Vista-Pro, Varian).

3. Results and Discussion

3.1 Selection of solvent

Properties of PC and BC were summarized in **Table 1** as well as those of usual solvents. PC and BC have higher flash point, higher E_T value and higher dielectric constant than other solvents and their density are higher than water. National Fire

Table 1 Properties of solvents¹⁴⁾

	Propylene carbonate ¹⁾	1,2-Butylene carbonate ¹⁵⁾	Hexane	Toluene	Nitrobenzene	1-Octanol	Water
Density (g/cm ³)	1.19 (25°C)	1.15	0.66	0.87	1.20	0.82	1.00
Boiling point (°C)	240	75 (0.2 kPa)	68	110	210	194	100
Melting point (°C)	-55	–	-95	-95	6	-16	0
Ignition point (°C)	455	421	225	480	480	253	–
Flash point (°C)	116	135	-22	5	88	83	–
Solubility in water ¹⁶⁾ (25°C, g/L)	175	–	0.0095	0.52	1.90	6	–
Solubility of water in solvent (mol/L) ¹⁷⁾	–	–	2.58×10^{-3}	2.66×10^{-2}	–	2.09	–
Dipole moment (Debye, 20°C)	5.00	–	0.085	0.31	4.00	1.76	1.82
E_T value (kcal/mol)	46.1	45.8	–	33.9	41.9	48.3	–
Dielectric constant (20°C)	65.1	–	1.8	2.3(25°C)	34.8	10.3	80.2
Hazard	Irritative	–	Flammability Noxious Irritative Staining	Flammability Noxious	Toxicity Staining	Irritative	–

Fig. 1 Effect of shaking time on the extraction of Y^{3+} , Eu^{3+} and Yb^{3+} . $[Ln^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[HR] = 0.01 \text{ mol dm}^{-3}$. ●: Y (24h), ■: Eu (24h), ▲: Yb (24h), ○: Y (1h), □: Eu (1h), △: Yb (1h).

Protection Association (NFPA) classifies PC in level 1 for human health and for flammability and in level 0 as for reactivity. PC has been widely used as a solvent for cosmetics like a nail remover and can be considered nontoxic solvent. Although the information of BC on safety could not be obtained, BC is considered to be also less toxic compared to the usual solvent judging from the similarity of molecular structure between PC and BC.

3.2 Effect of shaking time

In a preliminary test, it was ascertained that Y^{3+} , Eu^{3+} and Yb^{3+} attained to the equilibrium by shaking for 10 min in both hexane and PC extraction system, and therefore the shaking time was set to 1 h in this study. In addition, the effect of shaking time on the extraction of Ln^{3+} was examined with BC extraction system and the results were shown in Figs. 1 and 2. As shown in Fig. 1, significant variation in neither slope of the line in $\log D$ vs. pH nor $pH_{1/2}$ value were observed in the extraction of Y^{3+} , Eu^{3+} and Yb^{3+} by prolonging the shaking time from 1 h to 24 h. Therefore, it can be said that Y^{3+} , Eu^{3+} and Yb^{3+} quickly attained to the equilibrium in BC extraction system as well as hexane and PC extraction systems. However, in the case of Sc^{3+} and La^{3+} , Fig. 2 shows that slope of the line in $\log D$ vs. pH and $pH_{1/2}$ value were both fairly changed by extending the shaking time. Especially, $pH_{1/2}$ value of Sc^{3+} shifted from 3.73 to 1.17, and the slope of line increased from 1.4 to 2.1 with prolonging the shaking time from 1 h to 24 h, respectively. Based on these results, hereafter, the extractability of PC and BC was mainly examined with Y^{3+} , Eu^{3+} and Yb^{3+} under the experimental condition of 1 h shaking.

Fig. 2 Effect of shaking time on the extraction of Sc^{3+} and La^{3+} . $[Ln^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[HR] = 0.01 \text{ mol dm}^{-3}$. ●: Sc (24h), ◆: La (24h), ○: Sc (1h), ◇: La (1h).

3.3 Effect of pH

Effect of pH on the $\log D$ was shown in Fig. 3 and slope of the straight lines for $\log D$ vs. pH plots and $pH_{1/2}$ values, which are the pH values at $\log D = 0$ were summarized in Table 2. Here, D is distribution ratio and was calculated indirectly by using Eq.(1).

$$D = \frac{[M]_{\text{init}} - [M]_{\text{aq}}}{[M]_{\text{aq}}} \quad (1)$$

$[M]_{\text{init}}$ and $[M]_{\text{aq}}$ refer to the metal ion concentration in the original solution and in the equilibrated aqueous solution, respectively. In Table 2, the values in the parenthesis in the upper row are the slope of line and those in the lower row are $pH_{1/2}$ value. The some values of $pH_{1/2}$ for Y^{3+} and Eu^{3+} using typical ionic liquids were quoted from the literature¹³⁾ to evaluate the separation ability of PC and BC. The extraction performance of PC and BC for Y^{3+} and Eu^{3+} were worse than that of $[C_4\text{min}]$ and better than that of $[C_{12}\text{min}]$. While, the extraction performance of PC for Y^{3+} , Eu^{3+} and Yb^{3+} were almost similar to hexane, but that of BC were inferior to hexane. By using the difference of $pH_{1/2}$ value between Y^{3+} and Eu^{3+} , $\Delta pH_{1/2(Y-Eu)}$, separation performance of PC and BC were similar to those of ionic liquids.

In the chelate extraction system, when trivalent metal ion is extracted in the form of neutral chelate complex, overall extraction process is written as

where Ln^{3+} is lanthanide ion and HR is DODGAA, and subscript (o) represents species in the organic phase, respectively. The relationship between $\log D$ vs. pH and

$\log [\text{HR}]_{(\text{o})}$ in Eq. (2) is expressed as

$$\log D = \log K_{\text{ex}} + n \log [\text{HR}]_{(\text{o})} + npH \quad (3)$$

where K_{ex} is the extraction constant. Since Shimojo *et al.*

Fig. 3 Relationships between $\log D$ and pH . $[\text{Ln}^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[\text{HR}] = 0.01 \text{ mol dm}^{-3}$. $\bullet$: Sc, $\circ$: Y, $\blacklozenge$: La, $\diamond$: Eu, $\blacktriangle$: Yb.

reported that lanthanides were extracted in the form of LnR_3 with DODGAA hexane solution¹²⁾, the slope of straight lines for $\log D$ vs. pH and $\log D$ vs. $\log [\text{HR}]_{(\text{o})}$ should be 3 theoretically. Unfortunately, most of slopes of lines for $\log D$ vs. pH were deviated from the theoretical value, except for those for Y^{3+} and Yb^{3+} in the DODGAA-hexane extraction system and La^{3+} in DODGAA-BC one. Possible causes for these deviations in the slopes of lines for $\log D$ vs. pH from 3 can be considered as follows: (1) PC is fairly soluble in water and then the volume change due to the mutual dissolution might affect on the metal ion concentration, and (2) different kind of complex other than LnR_3 was formed and extracted into the organic phase.

3.4 Effect of mutual dissolution

In order to avoid the volume changes of phases by shaking, both phases were saturated with the counter phase prior to use. That is, the organic phase was shaken vigorously with same volume of $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$ aqueous solution for 2 h using reparatory funnel and set aside for 12 h to separate phases. The aqueous phase containing $0.1 \text{ mmol dm}^{-3} \text{ La}^{3+}$ and Eu^{3+} and $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$ was also treated with PC in a similar manner to the organic phase. After that, both phases were subjected to extraction.

The slope of the straight line in $\log D$ vs. pH for La^{3+} and Eu^{3+} were 1.6 and 2.0, and $\text{pH}_{1/2}$ value for La^{3+} and Eu^{3+} were 2.77 and 1.75, respectively. The slopes of lines obtained by using pretreatment of phases could not be improved satisfactorily from those obtained by using the untreated phases (Table 2), although the $\text{pH}_{1/2}$ value of La^{3+} was slightly changed. It can be elucidated as follows. In this study, $[\text{M}]_{\text{init}}$ in Eq.(1) was determined by using the pretreated aqueous phase containing $0.1 \text{ mmol dm}^{-3} \text{ Ln}^{3+}$ and $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$ by equilibrating with pure PC in accordance with usual extraction procedure. Therefore, the impact of the volume change on Ln^{3+} concentration due to mutual dissolution has already been discounted.

Table 2 Value of $\text{pH}_{1/2}$ and slope of $\log D$ vs. pH curve.

Solvent	Sc	La	Y	Eu	Yb
Hexane	(0.9) 3.14	(2.2) 2.82	(2.6) 1.63	(2.3) 1.89	(3.0) 1.47
PC	(1.4) 0.74	(1.5) 2.95	(2.3) 1.73	(2.1) 1.71	(2.2) 1.54
BC	(1.4)	(3.0) 3.95	(1.3) 2.16	(1.2) 2.28	(1.2) 2.12
$[\text{C}_4\text{min}]^{\text{a) } 13)}$			1.05	1.17	
$[\text{C}_{12}\text{min}]^{\text{b) } 13)}$			2.23	2.26	

a) 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

b) 1-Dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

Fig. 4 Effect of concentration of DODGAA on the distribution ratio of metal ion. $[M^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[HR] = 0.004\text{--}0.05 \text{ mol dm}^{-3}$. ●: Sc, ○: Y, ◆: La, ◇: Eu, ▲: Yb.

3.5 Effect of DODGAA concentration

Next, in order to certify the possibility of the formation of complex with the composition except LnR_3 , 3 kinds of experiments were undertaken. First, in order to determine the constitution of extracted complex, the relationship between DODGAA concentration and distribution ratio was determined. As can be seen in Fig. 4, most of the slope for the straight line for $\log D$ vs. $\log [HR]_{(o)}$ are closed to 3. The slope of the line in $\log D$ vs. pH plots was close to 2 for Eu^{3+} in hexane system and Y^{3+} , Eu^{3+} and Yb^{3+} in PC system, and that was closed to 1 for Y^{3+} , Eu^{3+} and Yb^{3+} in BC system (Table 2).

In order to logically explain the discrepancy between in slopes with $\log D$ vs. pH and $\log D$ vs. $\log [HR]_{(o)}$, the possibility of complexes having different composition from LnR_3 must be considered. In the former case, the extracted complex is thought to be contained 2 dissociated DODGAA molecules, 1 unknown anion, X^- , and 1 neutral DODGAA molecule.

In the latter case, the extracted complex possibly contained 1 dissociated DODGAA molecules, 2 X^- , and 2 neutral DODGAA molecule.

It is well known that polar solvent such as nitrobenzene extracts ion association complex consisting of complex ion and counter ion¹⁸⁾. PC and BC are highly polar, so that Ln^{3+} could be extracted in the form of species written in Eqs. (4) and (5).

3.6 Effect of nitrate concentration

Second, in order to clarify the presence of the complexes containing anion other than dissociated DODGAA, effect of

Fig. 5 Effect of concentration of NH_4NO_3 in aqueous phase on the distribution ratio. $[\text{Ln}^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[\text{HR}] = 0.1 \text{ mol dm}^{-3}$, pH 2.77 ± 0.01 in PC system. $[\text{Ln}^{3+}] = 0.1 \text{ mmol dm}^{-3}$, $[\text{HR}] = 0.01 \text{ mol dm}^{-3}$, pH 2.91 ± 0.03 in BC system. ○: Y, ◇: Eu, ▲: Yb.

nitrate concentration on the extractions of Y^{3+} , Eu^{3+} and Yb^{3+} in the PC and BC extraction systems were examined, since NH_4NO_3 was added into the aqueous phase in order to maintain ionic strength. **Fig. 5** shows the relationship between $\log D$ and the logarithm of nitrate concentration and demonstrates that the slopes of all line are close to 0. This means that nitrate ion was not involved in this extraction process.

3.7 HPLC-MS

Thirdly, the attempt to determine the composition of extracted complex by the slope analysis was unsuccessful, then the structural analysis of the extracted complex into hexane and BC was carried out by using HPLC-MS. The analytical conditions of HPLC-MS were listed in **Table 3**. Four samples were prepared: (A,C) 1.0 mmol dm^{-3} DODGAA-hexane and -BC solution equilibrated with 0.1 mol dm^{-3} NH_4NO_3 aqueous solution and (B,D) 1.0 mmol dm^{-3} DODGAA-hexane and -BC solution equilibrated with aqueous solution containing 0.1 mol dm^{-3} NH_4NO_3 and 0.1 mol dm^{-3} Yb^{3+} , respectively. **Figure 6** shows the chromatogram of organic phases detected by the total ion current. The peak at around 0.9 min was observed in all organic phases and was identified to be DODGAA based on MH^+ of 358.2961. The peak of Yb^{3+} -DODGAA complex could not be detected with either of hexane and PC solution. Although the broad peak was observed in the DODGAA-hexane solution (**Fig.6-B**), but the fragmentation due to the isotope abundance ratio of Yb was not appeared. The nondetection of extracted Yb^{3+} -complex may be ascribed to the failure in ionization of complex under the operating condition.

Table 3 HPLC and MS analytical conditions.

HPLC				
Instrument	Agilent 1290 series			
Column	ZORBAX Eclipse Plus C8 (2.1 x 50 mm, 1.8 μm)			
Mobile phase	A; 10 mM HCOONH ₄ (0.1% HCOOH) B; CH ₃ CN C; 2-Propanol			
Gradient	min	A(%)	B(%)	C(%)
	0	10	80	10
	5.0	10	80	10
	10.0	0	10	90
	15.0	0	10	90
	15.1	10	80	10
	20.0	10	80	10
Flow rate	0.3 mL/min			
Oven temp.	25°C			
Injection vol.	2 μL			
MS				
Instrument	Agilent 6530			
Mass range	100~1500 (m/z)			
Polarity	Positive			
Ionization	ESI (Jet Stream)			
Nebulizer	N ₂ (50 psi)			
Drying gas	N ₂ (12 L/min)			
Drying gas temp.	280 °C

Fig. 6 Total ion chromatogram obtained with gradient mode for the equilibrated organic phase.

A: DODGAA-hexane solution equilibrated with NH_4NO_3 aqueous solution.

B: DODGAA-hexane solution equilibrated with aqueous solution containing NH_4NO_3 and Yb^{3+} .

C: DODGAA-BC solution equilibrated with NH_4NO_3 aqueous solution.

D: DODGAA-BC solution equilibrated with aqueous solution containing NH_4NO_3 and Yb^{3+} .

4. Conclusion

The extraction performance of PC and BC was examined with DODGAA extraction of Ln^{3+} . Since PC and BC are heavy solvent, the handling of aqueous phase, e.g., the measurement of pH and sampling of aqueous phase for the back extraction and for determination of Ln^{3+} concentration after equilibration, was much convenient compared to the usual light solvents such as hexane, toluene and so on. The extractability of PC and BC on the extraction most strongly appeared for Sc^{3+} and therefore, the separation of Sc^{3+} from other lanthanides also fairly varied from that in hexane extraction system. However, the quantitative results could not be obtained in the slope analysis, and several examinations including HPLC-MS analysis could not explain the reason why the slope of the straight line in the slope analysis differed from theoretical value of 3. Although some problems still remains unsolved in the slope analysis, this study explicitly shows that PC and BC are capable solvent of providing a different extraction mode from the usual solvents.

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