The Synergistic Extraction of Lanthanides with Trifluoroacetylcycloalkanones and Trioctylphosphine Oxide

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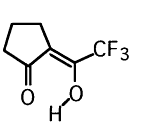
(Received May 9, 1997; CL-970348)

The separation of lanthanides in the solvent extraction into chloroform with trifluoroacetylcycloalkanones having a narrowed oxygen-oxygen distance has been found to improve by an addition of trioctylphosphine oxide as a synergist.

The utilization of a Lewis base in the solvent extraction of metal ions has been well-known as so-called synergism. Although the extractability is enhanced adding a Lewis base as an auxiliary neutral ligand, it is known that the separability becomes poorer in many cases. Only some cases in which the separation is improved have been reported in the synergistic extraction of lanthanides utilizing 1,10-phenanthroline or 2,2'-bipyridine as a bidentate synergist.[1]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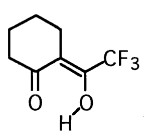
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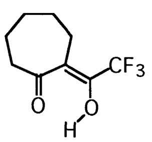
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In the previous paper,[2] 2-trifluoroacetyl-cyclopentanone(**1**), -cyclohexanone (**2**) and -cycloheptanone (**3**) in which the distance between the two donating oxygens is controlled by the cyclic-structure have been prepared. It was revealed that the strength of the intramolecular hydrogen bond increases in the order, **1**<**2**≈**3**, depending on the distance between the two donating oxygens in the enol form and the pK_a values increase as the intramolecular hydrogen bond strengthens (**1**<**2**≈**3**). Owing to the stronger acidity of **1** than **2** and **3**, lanthanide ions (La^{3+}, Pr^{3+}, Eu^{3+}, Ho^{3+}, and Yb^{3+}) were readily extracted by **1**. On the contrary, better separation for lanthanides was achieved with **2** and **3**.

In the extraction of lanthanides (Ln^{3+}) with an acidic extractant (HA),[3] the extraction equilibrium and the extraction constant, K_{ex}, can be expressed in eqns. (1) and (2), where the subscript o stands for the species in the organic phase and D the distribution ratio of metal ions defined as $[Ln^{3+}]_o/[Ln^{3+}]$.

$$Ln^{3+} + 3HA_o \rightleftharpoons LnA_{3,o} + 3H^+ \qquad (1)$$

$$K_{ex} = [LnA_3]_o[H^+]^3/[Ln^{3+}][HA]_o^3 = D[H^+]^3/[HA]_o^3 \qquad (2)$$

When TOPO is added into the organic phase, the adduct formation reaction takes place. The distribution ratio of Ln in the presence of TOPO, D*, is written in eqn (3).

$$D^* = \{[LnA_3]_o + [LnA_3(TOPO)]_o + \cdots + [LnA_3(TOPO)_s]_o\}/[Ln^{3+}] \qquad (3)$$

The synergistic extraction of lanthanides with **1** and TOPO is illustrated in Figure 1. Dividing D* by D, the distribution ratio in the absence of TOPO, gives eqn. (4), where β_s is an adduct formation constant defined in eqn. (5).

$$D^*/D = 1 + \sum \beta_s[TOPO]_o^s \qquad (4)$$

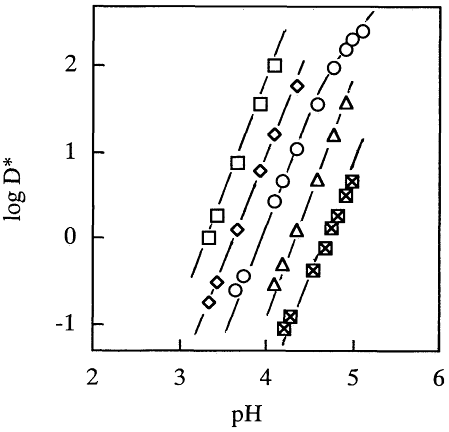

Figure 1. The synergistic extraction of lanthanides with **1** and TOPO. (□) Yb, (◇) Ho, (○) Eu, (△) Pr, (☒) La. $[\mathbf{1}]_o$ = 0.05 mol dm^{-3}, $[TOPO]_o$ = 0.01 mol dm^{-3} in chloroform.

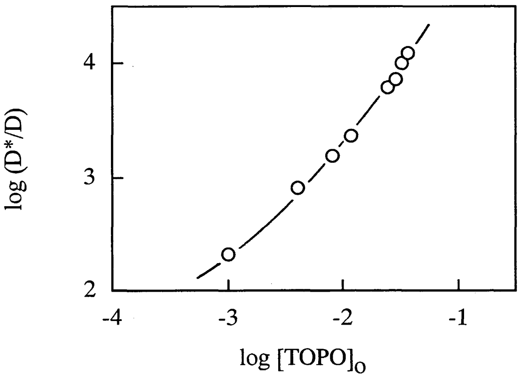

Figure 2. Plots for log (D*/D) vs. log $[TOPO]_o$. $[\mathbf{2}]_o$ = 0.05 mol dm^{-3} in chloroform.

$$\beta_s = [LnA_3(TOPO)_s]_o/[LnA_3]_o[TOPO]_o^s \qquad (5)$$

Figure 2 illustrates the plots of log (D*/D) vs. log $[TOPO]_o$ for the extraction of holmium with **2** and TOPO as a typical example. The slope of the plots increases as $[TOPO]_o$ increases and is almost two at the higher $[TOPO]_o$ region, indicating that the number of TOPO molecules in the adduct is one and two. The adduct formation constants, β_1 and β_2, were obtained by the non-linear least-squares method on the basis of eqn. (4) and are seen in Table 1. When $[TOPO]_o$ is high enough, the overall equilibrium and the synergistic extraction constant, $K_{ex,s}$, are expressed as follows:

$$Ln^{3+} + 3HA_o + sTOPO_o \rightleftharpoons LnA_3(TOPO)_{s,o} + 3H^+ \qquad (6)$$

$$K_{ex,s} = [LnA_3(TOPO)_s]_o[H^+]^3/[Ln^{3+}][HA]_o^3[TOPO]_o^s \qquad (7)$$

Table 1. Parameters for the synergistic extraction of lanthanides[a]

	1				**2**				**3**			
	$\log K_{ex}$	$\log K_{ex,s}$	$\log \beta_1$	$\log \beta_2$	$\log K_{ex}$	$\log K_{ex,s}$	$\log \beta_1$	$\log \beta_2$	$\log K_{ex}$	$\log K_{ex,s}$	$\log \beta_1$	$\log \beta_2$
La^{3+}	-13.26	-6.19	4.69	7.07	—	—	—	—	—	—	—	—
Pr^{3+}	-11.80	-5.52	4.19	6.28	-17.27	-11.51	4.59	5.76	-17.55	-11.13	4.10	6.42
Eu^{3+}	-10.81	-5.25	4.53	5.56	-16.52	-10.68	4.72	5.84	-16.23	-9.87	4.57	6.36
Ho^{3+}	-10.34	-4.41	4.76	5.93	-15.74	-9.22	5.26	6.52	-15.60	-9.22	4.91	6.38
Yb^{3+}	-9.62	-4.48	5.02	5.14	-14.61	-8.25	5.01	6.36	-14.56	-7.90	4.89	6.66

[a]The $\log K_{ex}$ values are taken from ref. 2.

Table 2. Separation factors for lanthanides

	1		**2**		**3**	
	SF	SF*	SF	SF*	SF	SF*
La^{3+}						
	1.46	0.67	—	—	—	—
Pr^{3+}						
	0.99	0.27	0.75	0.83	1.32	1.26
Eu^{3+}						
	0.47	0.84	0.78	1.46	0.63	0.65
Ho^{3+}						
	0.72	0.07	1.13	0.97	1.04	1.32
Yb^{3+}						
SF(Yb/Pr)	2.18	1.04	2.66	3.26	2.99	3.23

The values of $\log K_{ex,s}$ are summarized in Table 1. Separation factor, SF or SF*, are defined as the difference of the $\log K_{ex}$ or $\log K_{ex,s}$ values for certain metal ions and listed in Table 2. Comparing the separation factor between praseodymium and ytterbium, SF(Yb-Pr), the separations for **2** and **3** in the absence of TOPO are better than that for **1**. When TOPO was added as a synergist, SF for **1** decreased drastically to 1.04, whereas SF for **2** and **3** increased to 3.26 and 3.23, respectively. SFs for **2** and **3**, which are better than that for **1** even in the absence of TOPO, improved utilizing synergism with TOPO. As seen in Table 1, while the β_2 values for **1** decrease rapidly as the atomic number increases, those for **2** and **3** increase. Such trend for **1** is usually seen in the synergistic extraction of lanthanides, resulting in poor separability.[4]

The present work could present a unique case that synergism with a monodentate Lewis base improves the separation of lanthanides. Since the separation became poorer with **1** which has a wider O-O distance, the O-O distance should be the leading factor that governs the selectivity. No satisfying explanation has been given to the mechanism of synergism that improves or reduces the selectivity. The present results may suggest the significant role of the geometry of **2** and **3** characterized by the narrowed O-O distance. In the lanthanide complexes with **2** or **3**, the shorter O-O distance could provide a larger space for the synergist to attach to the central metal ion, which might make the adduct formation with a heavier lanthanides more stable.

Another characteristic of the present adduct formation reaction is that the ß values do not so much depend on the acidity of the extractants. In many cases, the strong acidity of the extractants stabilizes the adduct formation reaction. This could be interpreted by the fact that the acidity of the present extractants is affected not only by the substituent effect but also by the strength of the intramolecular hydrogen bond; the former affects the electron density on the donating oxygens through the electron donating or withdrawing nature.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References and Notes

1 a) Y. Sasaki and H. Freiser, *Inorg. Chem.*, **22**, 2289(1983); b) S. Nakamura and N. Suzuki, *Polyhedron*, **5**, 1805(1986); c) S. Nakamura and N. Suzuki, *Polyhedron*, **7**, 155(1988).

2 a) S. Umetani, Y. Kawase, H. Takahara, Q. T. H. Le, and M.Matsui, *J. Chem. Soc., Chem. Commun.*, **1993**, 78; b) S. Umetani, Y. Kawase, Q. T. H. Le, T. Sasaki, and M. Matsui, *Inorg. Chim. Acta*, in press.

3 Extractions were made at 25 °C. Sodium acetate (0.01 mol dm^{-3}) was employed as a buffering component. Sodium perchlorate (0.1 mol dm^{-3}) was added to the aqueous phase to keep the ionic strength at 0.1. The concentrations of metal ions were measured by ICP atomic emission spectrometry. The shaking time of 1 h was found to be long enough to reach to the equilibrium.

4 S. Umetani and H. Freiser, *Inorg. Chem.*, **26**, 3179 (1987).