Solvent Extraction of Lanthanoid(III) with 18-Crown-6 and Trichloroacetate Ion

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Liquid-liquid extraction of metal ions with macrocyclic crown ethers has received much attention because of their unique complexing properties. They form more stable complexes with the metal ions which better fit into the cavities of those macrocyclic agents. Recently, some studies on the extraction of lanthanoid(Ln(III)) have been made using various macrocyclic crown ethers[1-5], but selectivity shown for adjacent Ln(III) not so good.

In the present report, the extraction of Ln(III) is studied using 18-crown-6(18C6) and trichloroacetate(TCA$^-$) ion as a counter anion. Trichloroacetate has not been used so far in the extraction with crown ethers.

18-Crown-6 was recrystalized from hexane. Lithium trichloroacetate solutions were prepared by mixing a standard solution of trichloroacetic acid and lithium hydroxide. Radioisotopes, ^{140}La, ^{141}Ce, ^{142}Pr, ^{147}Nd, ^{153}Sm, ^{160}Tb, ^{170}Tm, and ^{177}Lu, were produced by neutron irradiation of each high purity oxide or nitrate in a nuclear reactor of the Japan Atomic Energy Research Institute. ^{152,154}Eu was obtained from the Radiochemical Centre (England). An aqueous solution (5 ml) of lithium trichloroacetate (0.05-2.5 M) containing 10^{-6}-10^{-3} M Ln(III) labeld with its radioisotope was shaken with a 1,2-dichloroethane solution (5 ml) containing 18-crown-6 (0.003-0.2 M) for 1-60 min. After centrifugation, an aliquot was pipetted from each phase. The γ-activity was measured with a well type NaI(Tl) scintillation counter and the distribution ratio(D) of Ln(III) was calculated. The equilibrium pH value was measured immediately after shaking. All procedures were done in a thermostated room at 25±0.5 °C.

The extraction of Ln(III) with $1.0×10^{-2}$ M 18-crown-6 from 1.0 M lithium trichloroacetate solution was examined at varying pH values. The results are shown in Fig. 1, where the extraction equilibrium was readily attained by shaking within 5 min. The distribution ratio of Ln(III) is constant at pH 3 to 4.5. In this pH range, the protonation of 18-crown-6 and trichloroacetate is negligible, so that the distribution ratio is not dependent on pH. The distribution ratio of La(III), Pr(III), and Tb(III) was not dependent on the metal concentration at the range of $1×10^{-6}$ — $1×10^{-3}$ M. This means that no polymerization of the extractable species occurs. Hence the extraction equilibrium can be expressed as follows,

$$Ln^{+3} + n\ 18C6_{org} + 3\ TCA^- \rightleftharpoons Ln(18C6)_n(TCA)_{3,org}\ , \tag{1}$$
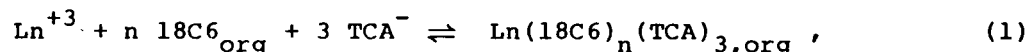
where the subscript org refers to the organic phase. When the complexation of Ln(III) with 18-crown-6 or trichloroacetate in the aqueous phase is negligible, the distribution ratio of Ln(III) can be written; $D = [Ln(18C6)_n(TCA)_3]_{org}/[Ln^{3+}]$. Therefore,

$$\log D = 3 \log[TCA^-] + n \log[18C6]_{org,init} + \log(K_{ex}\, P_L^{\ n}(1+P_L)^{-n}), \qquad (2)$$

where K_{ex} and P_L denote the extraction constant for Eq. 1 and the partition coefficient of 18-crown-6 respectively. The plot of log D against log[TCA$^-$] for La(III), Ce(III), and Pr(III) at a constant ionic strength of 1.0 M(using lithium chloride) gave the straight line with the slope of 2.8, 2.8, and 2.9 respectively and indicated the formation of the 1:3 complex. Figure 2 shows the plots of log D against logarithmic value of the initial concentration 18-crown-6 in the organic phase. The plot for La(III), Ce(III), Pr(III), Nd(III), and Eu(III) is the straight line and the slope is almost unity. On the other hand, the plot of Tb(III), Tm(III), and Lu(III) appears to be also linear but the slope is about 1.5. This result shows that the light Ln(III) forms only the 1:1 complex with 18-crown-6 and extracted into the organic phase with three molecules of the trichloroacetate ion, while heavy Ln(III) seems to form the 1:1 and 1:2 complex with 18-crown-6.

The distribution ratio of Ln(III) steeply decreases with the atomic number. This order agrees with that of decrease in the ionic radii of Ln(III) and is a reverse trend compared with that observed in the many previous extraction systems, e.g., di(2-ethylhexyl)phosphoric acid(HDEHP)[6] and some β-diketones.[7] This result suggests that the selectivity in the present extraction system is based on the fitness of the Ln(III) ions into the cavity of 18-crown-6. The cavity diameter of 18-crown-6 has been estimated to be 2.6 Å or 3.2 Å using different atomic models.[8] The ionic diameters of Ln(III) regularly vary from 2.432 Å for La(III) to 2.064 Å for Lu(III) if the coordination number of Ln(III) is assumed to be nine.[9] Accordingly, it seems that the ionic diameter of La(III) is better close to the cavity diameter of 18-crown-6. The separation factors for the adjacent Ln(III) and a pair of Ln(III) are summarized in Table 1. The separation factors especially for the light Ln(III) in the present 18-crown-6/trichloroacetate system are fairly larger than that reported previously in the HDEHP system.[6] In conclusion, a new extraction system having excellent selectivity for light Ln(III) has been developed using 18-crown-6 as a macrocyclic ligand and trichloroacetate ion as a counter ion.

References

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Table 1. Separation factors for lanthanoid (III) in the 0.010 M 18-crown-6/2.0 M LiTCA/ 1,2-dichloroethane system at 25°C.

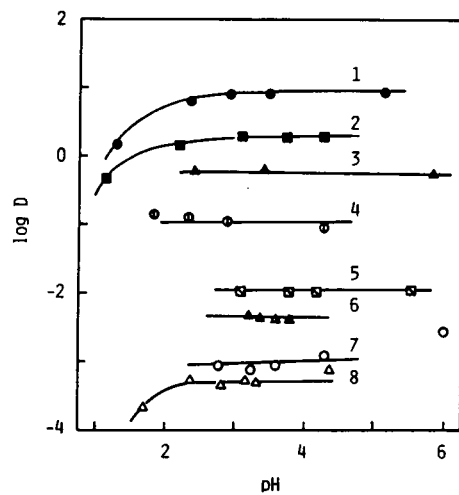| Ln1/Ln2	D_{Ln1}/D_{Ln2} Present work	D_{Ln2}/D_{Ln1} HDEHP*
La/Ce	5.38	6.1
Ce/Pr	2.75	1.35
Pr/Nd	4.90	1.42
Sm/Eu	2.60	4.18
La/Pr	1.48×10	1.02×10
La/Nd	7.24×10	1.51×10
La/Sm	5.91×10^2	1.40×10^2
La/Eu	1.54×10^3	3.20×10^2
La/Tb	7.76×10^3	2.80×10^3
La/Tm	9.99×10^3	1.84×10^5
La/Lu	1.20×10^4	1.24×10^6

*Ref. 6.

Fig. 1. Effect of pH on the distribution ratio of lanthanoid(III) between 1,2-dichloroethane and 1.0 M LiTCA solution. 0.010 M 18-crown-6, 1×10^{-5} M Ln(III). 1 La, 2 Ce, 3 Pr, 4 Nd, 5 Sm, 6 Eu, 7 Tb, 8 Lu.
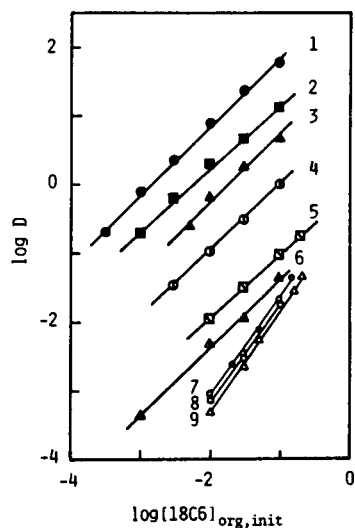

$\log [18C6]_{org,init}$

Fig. 2. Effect of 18-crown-6 concentration on the distribution ratio of lanthanoid(III). 1.0 M LiTCA, 1×10^{-5} M Ln(III). pH 3.0-4.8. 1 La, 2 Ce, 3 Pr, 4 Nd, 5 Sm, 6 Eu, 7 Tb, 8 Tm, 9 Lu.