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**EXTRACTION BEHAVIOR OF LANTHANUM (III) WITH MONOTHIO-
THENOYLTRIFLUOROACETONE AND CROWN ETHERS**

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The extractability of lanthanum (III) with monothiothenoyltrifluoroacetone (STTA) increased in the order of cyclohexane < monochlorobenzene, *o*-dichlorobenzene < benzene < nitrobenzene. The phases were equilibrated for 10 min or more. In the presence of crown ethers, a large synergistic effect was observed in the order of 12C4 < 15C5 < 18C6. The time needed for the attainment of the synergistic extraction equilibrium was within two min. The composition of the extracted species was $\text{La}(\text{STTA})_3 \cdot 18\text{C}6$ in benzene, and the stability constant ($\log \beta$) was 5.72. The extraction of La(III) using STTA along with 18C6 in benzene is useful for complete La(III) extraction by avoiding its hydrolysis in an aqueous solution.

1. Introduction

There is some information on the investigation of the extraction behavior of lanthanum (III), (La(III)), with monothiothenoyltrifluoroacetone (STTA) ($\text{pH}_{1/2} = 6.52$, pH at half extraction, and the extraction constant, $\log K_{ex} = -13.54$, with 10^{-2} M STTA in benzene)¹⁾ and crown ethers²⁾.

In the present work, some factors affecting the extraction of La(III) using STTA in various organic diluents with or without crown ethers have been studied.

2. Experimental

2.1 Apparatus

A Shimadzu model ICPS-1000III sequential type plasma emission spectrometer (ICP-AES) was used for the determination of La(III). The phases were mixed by shaking using a Taiyo model SR-II reciprocating shaker. A Tomy Seiko model CD-50R centrifugal separator was used for phase separation. pH measurements were performed with a Horiba model F-12 pH meter.

2.2 Materials

A standard stock solution of La(III) was obtained from Kanto Chemical Co. Ltd. Deionized distilled water (DDW) was prepared with a Barnstead Nano-pure apparatus and was used in all experiments. Buffer solutions used were prepared by dissolving a weighed quantity of sodium acetate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$, Ishizu Pharmaceutical Co. Ltd.), 2-morpholinoethanesulfonic acid (MES, Dojindo Co. Ltd.) and 3-morpholinopropanesulfonic acid (MOPS, Dojindo Co. Ltd.), and by diluting to an appropriate volume. Hydrochloric acid (Kanto Chemical) and/or a solution of sodium hydroxide ($\text{NaOH}\cdot\text{H}_2\text{O}$, Merck) were used for pH adjustment. STTA, that is, the monothio-derivative of TTA (thenoyltrifluoroacetone), was purchased from Dojindo Co. Ltd. Standard solutions of STTA in the organic diluents were stored in a refrigerator at 5°C . 12-crown-4 (12C4), 15-crown-5 (15C5) and 18-crown-6 (18C6) of guaranteed grade were purchased from MERCK.

2.3 Procedures

An aqueous solution (15 ml) containing $10^{-6} \sim 10^{-5}$ M (1.389-13.89 ppm) La(III) and 10^{-2} M CH_3COONa , MES and MOPS, as buffer solutions, was placed in a ground-glass stoppered centrifuge tube. The ionic strength was adjusted to 0.1 with sodium chloride. The aqueous solution was shaken mechanically with the same volume of the organic solvent containing $10^{-3} \sim 10^{-2}$ M STTA with or without $10^{-3} \sim 10^{-2}$ M crown ether for 0.5 ~ 30 min at room temperature ($25 \pm 2^\circ\text{C}$). Both phases were centrifugally separated, and the pH of the aqueous phase was measured again by means of a pH meter. Then 10 ml of the organic phase after extraction was shaken with 10 ml of 1 M hydrochloric acid for 10 min and then centrifuged. The concentration of La(III) back-extracted into an aqueous solution was then measured by using ICP-AES.

3. Results and Discussion

3.1 Effect of organic solvent

The extraction of La(III) was carried out with STTA in five organic diluents i.e. cyclohexane, benzene, monochlorobenzene, *o*-dichlorobenzene and nitrobenzene.

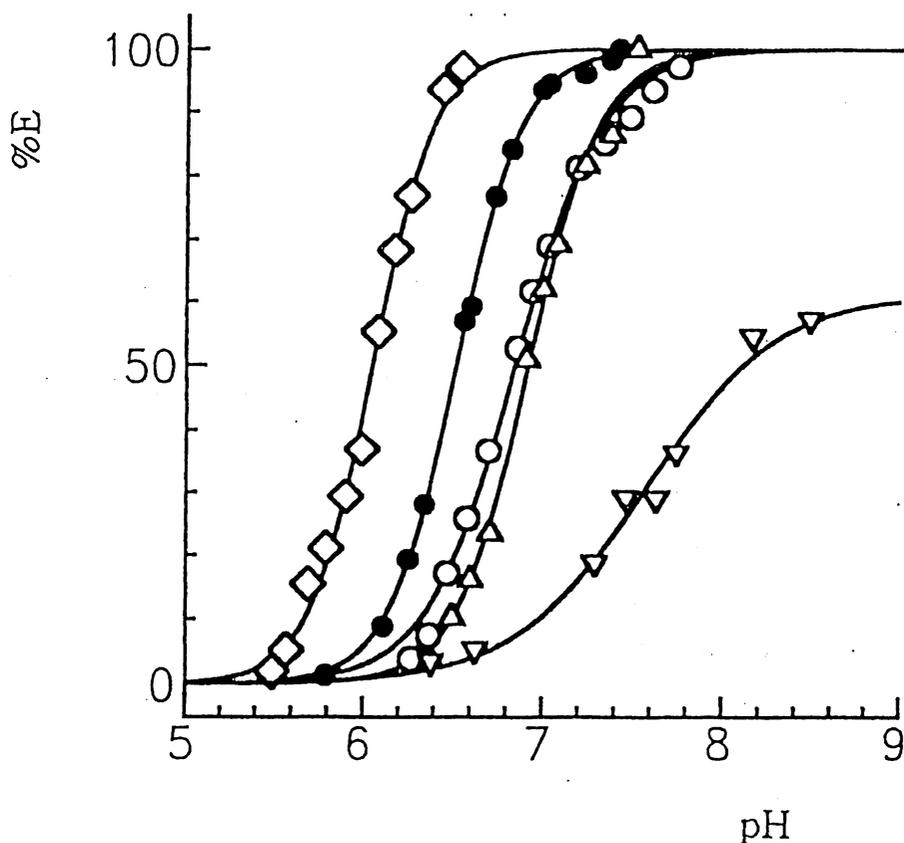


Fig.1. Extraction of La(III) with 0.01M STTA in various diluents.

◇: nitrobenzene, ●: benzene, △: monochlorobenzene, ○: *o*-dichlorobenzene,
▽: cyclohexane

The extractability of La(III) increased in the order of cyclohexane < monochlorobenzene, *o*-dichlorobenzene < benzene < nitrobenzene, as shown in Fig.1. Although nitrobenzene gave the most effective extractability of La(III) with STTA, benzene was selected for the study of the synergistic extraction of La(III) with STTA in the presence of crown ethers.

3.2 Effect of shaking time

In order to ascertain the shaking time required to reach equilibrium in the extraction of La(III), the extractability of La(III) with STTA in benzene was determined for various shaking times (0.5 ~ 30 min) at fixed pH (6.25 ~ 6.82). It

was found that the extraction reached equilibrium after 10 min or more. The time needed for the attainment of the extraction equilibrium was within two min, when 0.01 M STTA-0.01 M 18C6-benzene extraction system was employed at pH 5.82.

3.3 Extraction and back extraction

The extraction of La(III) was carried out at a fixed concentration of STTA (0.01 M) at various pH values. The log D vs. pH plots on applying the least-squares method, gave straight lines with a slope of 2.36 for La(III), as seen in Fig.2. This deviation from a slope of 3 seems to be caused by hydrolysis of La(III) to form some hydroxo complexes such as $\text{La}(\text{OH})^{2+}$. This result suggests that three hydrogen ions were released during the extraction of La(III) with STTA. The extraction of La(III) with various concentrations of STTA ($10^{-3} \sim 10^{-2}$ M) in benzene at a fixed pH (6.95) was also investigated. The log D vs. log [STTA] plot gave a straight line with a slope of 3. Judging from the results described above, it was confirmed that the ratio of La(III) : STTA in the extracted complexes was 1 : 3, that is, the formation of the $\text{La}(\text{STTA})_3$ chelate in benzene¹⁾.

3.4 Synergistic extraction with crown ether

The extraction of La(III) with 10^{-2} M STTA was carried out in the absence and presence of the crown ethers 12C4, 15C5 and 18C6. In the STTA-crown ether-benzene extraction system, the presence of the buffer solutions of CH_3COONa , MES, and MOPS, and the ionic strength adjustment reagent NaCl did not influence the extraction behavior of La(III). As shown in Fig.2, every crown ether studied caused a remarkable enhancement in the extractability of La(III) for each extraction system, namely a "synergistic effect". The large synergistic effect was observed in the order of $12\text{C}4 < 15\text{C}5 < 18\text{C}6$. Here, the logD vs. pH plots gave straight lines of slope 3. Crown ethers are relatively bulky neutral ligands and have ion size-fitting ability in their cavities. The cavity radius is 0.06 ~ 0.075 nm for 12C4³⁾, 0.086 ~ 0.092 nm for 15C5⁴⁾, and 0.134 ~ 0.143 nm for 18C6⁵⁾ respectively, and the ionic radius of La(III) is 0.116 nm⁶⁾. Therefore, it was considered that 18C6 is suitable for size recognition of the La(III) and thus formation of a stable adduct which causes the synergistic effect, as observed in Ba-TTA-crown extraction system⁷⁾.

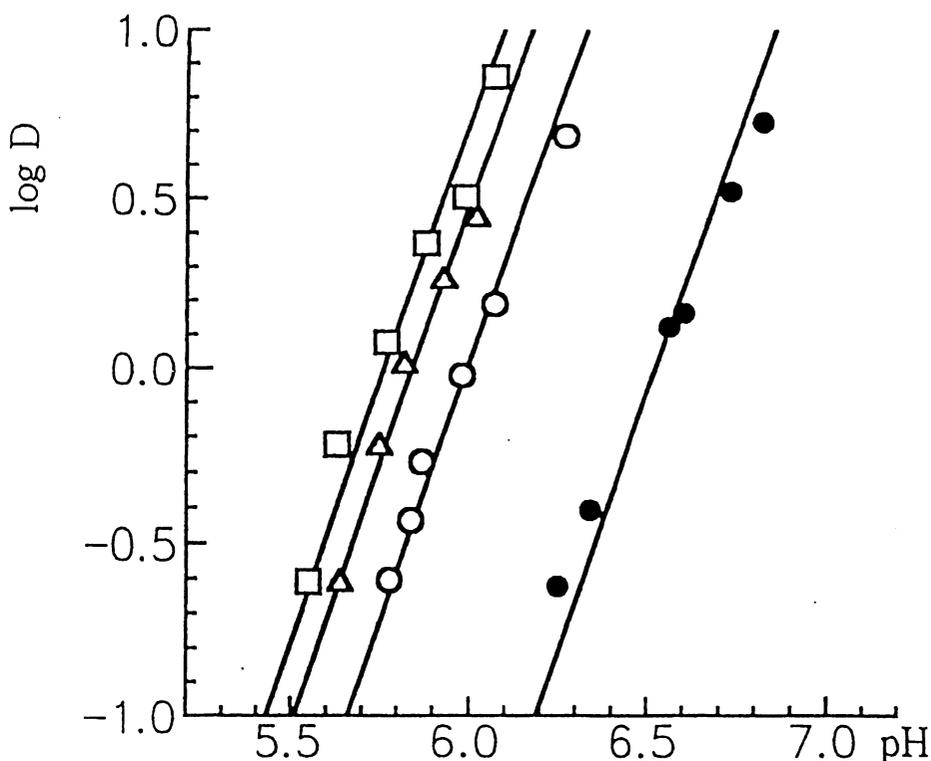


Fig.2. Extraction of La(III) with 0.01M STTA in benzene in the presence and in the absence of 0.01M crown ethers.

●: 0.01M STTA, ○: 0.01M STTA-0.01M 12C4, △: 0.01M STTA-0.01M 15C5, □: 0.01M STTA-0.01M 18C6

The effect of 18C6 on the $\log D/D_0$ vs. $\log [18C6]_0$ plot for La(III) at fixed pH (6.18 ~ 6.5) is shown in Fig.3. The composition of the extracted species and the stability constant of the adduct ($\log \beta$) was obtained by analyzing the data in Fig.3, by means of the curve-fitting method⁸⁾. The slope of the line gives the number of adduct molecule bound to the STTA-chelate, and the formation of the $La(STTA)_3 \cdot 18C6$ adduct corresponds to the slope of 1, at a 18C6 concentration region higher than 10^{-4} M. When the concentration of 18C6 is lower than 10^{-4} M, the slope deviates from 1, indicating the existence of a mixture of $La(STTA)_3$ and $La(STTA)_3 \cdot 18C6$ in benzene.

The logarithm of the distribution constant of 18C6 between benzene and water, $\log K_d$, is -1.197, and the decrease of the initial concentration of 18C6 in the organic phase was corrected for Na (0.1 M) complexation with 18C6 in the aqueous phase, but this was negligible for tracer concentrations of La(III) ($10^{-6} \sim 10^{-5}$ M). The stability constant ($\log \beta$) of the $La(STTA)_3 \cdot 18C6$ adduct in benzene was 5.72 (5.5 without

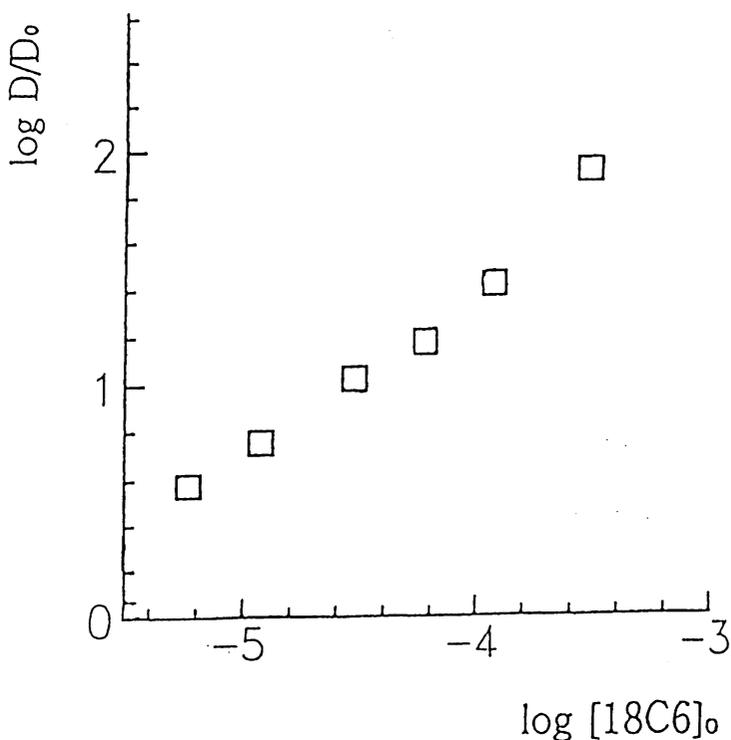


Fig.3. Variation of the distribution ratio of La(III) using 0.01M STTA with the concentration of 18C6.

□: La(III)-0.01M STTA-18C6-benzene

correction), which lies between the values of 4.38 for the $\text{La}(\text{BFA})_3 \cdot \text{TBP}$ adduct in benzene and 7.00 for the $\text{La}(\text{BFA})_3 \cdot \text{TOPO}$ adduct in benzene⁹⁾ where the β diketone and adduct molecules are BFA (benzoyltrifluoroacetone), TBP (tri-*n*-butylphosphate) and TOPO (tri-*n*-octylphosphineoxide), respectively. It is evident that STTA along with 18C6 in benzene is useful for extraction of La(III) completely and avoiding its hydrolysis in aqueous solution.

4. Conclusion

The extractability of La(III) with STTA in benzene was increased by the presence of 18C6 by avoiding its hydrolysis in aqueous solution, and equilibration was achieved within two minutes. The buffer solutions of CH_3COONa , MES, and MOPS, and the ionic strength reagent of NaCl had no effect on the synergistic extraction of La(III).

References

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