Use of the Synergic Solvent Extraction System for the Determination of the Stability Constants of Metal Complexes

By Tatsuya SEKINE, Mitsuo SAKAIRI, Fumitake SHIMADA
and Yuko HASEGAWA

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The liquid-liquid partition method has been used for the determination of the stability constants of metal complexes.

When a metal ion, M^{m+}, is extracted with an organophilic chelating acid, HA, the net distribution ratio, $D=[M]_{\text{total, org}}/[M]_{\text{total, aq}}$, and the extraction constant, K_0, can be described as:

$$M^{m+}+m\text{HA}(\text{org})\rightleftarrows \text{MA}_m(\text{org})+m\text{H}^+ \quad (1)$$

$$D=[\text{MA}_m]_{\text{org}}/[M^{m+}] \quad (2)$$

$$K_0=\text{D}[\text{H}^+]^m[\text{HA}]_{\text{org}}^{-m} \quad (3)$$

where the suffix "org" denotes the chemical species in the organic phase and "0" denotes no complex formation in the aqueous phase.

Metal complex formation in the aqueous phase with a ligand, L^{l-}, decreases the concentration of the free metal ion and:

$$[M]_{\text{total,aq}}=[M^{m+}](1+\sum_1^n\beta_n[L^{l-}]^n) \quad (4)$$

$$K=[\text{MA}_m]_{\text{org}}[\text{H}^+]^m[\text{HA}]_{\text{org}}^{-m}/[M^{m+}](1+\sum_1^n\beta_n[L^{l-}]^n) \quad (5)$$

Here, β_n is the over-all stability constant of the nth complex:

$$\beta_n=[\text{ML}_n^{m-nl}]/[M^{m+}][L^{l-}]^n \quad (6)$$

Therefore, the stability constants can be calculated by the following equation:

$$K_0/K=1+\sum_1^n\beta_n[L^{l-}]^n \quad (7)$$

However, the metal ion in the aqueous phase sometimes forms complexes not only with the ligand to be studied, L^{l-}, but also with the extracting chelating acid, HA, which has been distributed from the organic phase into the aqueous phase; the latter complexes, MA^{m-1}, $\text{MA}_2{}^{m-2}$, $\cdots$, also decrease the concentration of the free metal ion, just as has been shown in Eq. 4:

$$[\mathrm{M}]_{\mathrm{total,\ aq}}=[\mathrm{M}^{m+}](1+\sum_{1}^{n}\beta_n'[\mathrm{A}^-]^n) \qquad (8)$$

Here, $\beta_n'=[\mathrm{MA}_n^{m-n}]/[\mathrm{M}^{m+}][\mathrm{A}^-]^n$ and the distribution ratio in such systems can be written from Eq. 8, using $K_a=[\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}]$, $K_D=[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{HA}]$, as:

$$D=[\mathrm{MA}_m]_{\mathrm{org}}/[\mathrm{M}^{m+}]\{1+\sum_{1}^{n}\beta_n'(K_a[\mathrm{HA}]_{\mathrm{org}}/K_D[\mathrm{H}^+])^n\} \qquad (9)$$

and the distribution constant becomes:

$$K_0'=K_0/\{1+\sum_{1}^{n}\beta_n'(K_a[\mathrm{HA}]_{\mathrm{org}}/K_D[\mathrm{H}^+])^n\} \qquad (10)$$

Equation 10 indicates that the extraction constant, K_0, calculated by Eq. 3 is decreased by the increase in $[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{H}^+]$ and that thus the aqueous chelate complexes may cause a systematic error in the stability constants calculated by Eq. 7.

This deviation of K_0 from the constant value by the aqueous chelate complexes would be decreased by the use of the "synergic" solvent extraction system.*

When a neutral organophilic ligand, N, is added to a chelate extraction system, adduct complexes are sometimes formed:

$$\mathrm{MA}_m(\mathrm{org})+n\mathrm{N}(\mathrm{org})\rightleftarrows\mathrm{MA}_m\mathrm{N}_n(\mathrm{org}) \qquad (11)$$

$$[\mathrm{M}]_{\mathrm{total,\ org}}=[\mathrm{MA}_m]_{\mathrm{org}}(1+\sum_{1}^{n}\beta_n''[\mathrm{N}]_{\mathrm{org}}^n) \qquad (12)$$

where β_n'' is the stability constant of the nth adduct complex; that is,

$$\beta_n''=[\mathrm{MA}_m\mathrm{N}_n]_{\mathrm{org}}/[\mathrm{MA}_m]_{\mathrm{org}}[\mathrm{N}]_{\mathrm{org}}^n \qquad (13)$$

Therefore, the net distribution ratio is:

$$D=[\mathrm{MA}_m]_{\mathrm{org}}(1+\sum_{1}^{n}\beta_n''[\mathrm{N}]_{\mathrm{org}}^n)/[\mathrm{M}^{m+}] \qquad (14)$$

Thus the adduct formation of the chelate complexes in the organic phase makes the metal extraction $(1+\sum_{1}^{n}\beta_n''[\mathrm{N}]_{\mathrm{org}}^n)$ times higher, and so one can obtain a certain distribution ratio of the metal at a lower $[\mathrm{HA}]_{\mathrm{org}}/[\mathrm{H}^+]$ value.

Experimental

All the reagents used were of analytical or reagent grade. Europium 152+154 in a tracer concentration was used for the determination of the net distribution ratio. Stoppered glass tubes were added with each 5 ml. of the organic and aqueous solutions and were then agitated mechanically in a thermostatted room at 25°C. Thenoyltrifluoroacetone (TTA) was used as the chelating ligand, and tributylphosphate (TBP) was used as the adduct-forming ligand, the organic solvent being hexane. The aqueous phase was a 0.1 M sodium perchlorate solution buffered with a small amount of sulfanilate or acetate. The hydrogen ion concentration was measured potentiometrically, and the γ count-rate was determined with a well-type scintillation counter.

Results and Discussion

Figure 1-a gives the plot of log D vs. log $[\mathrm{H}^+]^{-1}$, while Fig. 1-b gives the corresponding extraction constant calculated by Eq. 3. Figure 2 gives the increase in the extraction constant brought about by the addition of the adduct-forming ligand when the concentration of the chelating ligand is constant.

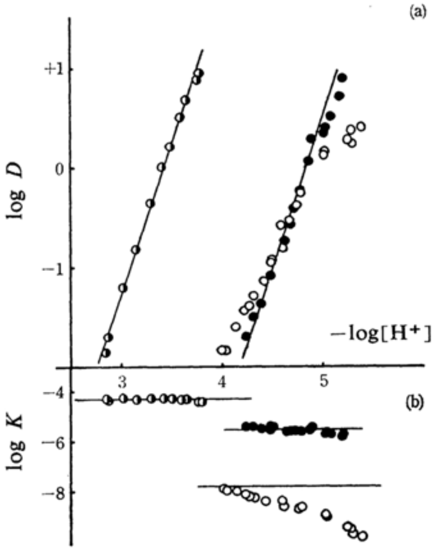

Fig. 1. (a) Distribution ratio of europium(III) as a function of a log $[\mathrm{H}^+]^{-1}$. (b) Extraction constant of europium(III) calculated from the data in Fig. 1-a. (cf., Eq. 3).
Aqueous phase: 0.1 M $\mathrm{NaClO_4}$
Organic phase: ○, 0.01 M TTA; ●, 0.001 M TTA + 3×10^{-5} M TBP; ◐, 0.01 M TTA + 1×10^{-4} M TBP; in hexane.

Equation 3 shows that D should be proportional to $[\mathrm{H}^+]^{-3}$ if Eu^{3+} is the only metal species in the aqueous phase at a constant $[\mathrm{HA}]_{\mathrm{org}}$ value. However, it may be seen in Fig. 1-a that the plot of log D vs. log $[\mathrm{H}^+]^{-1}$ of the extraction with 0.01 M TTA (open circles) deviates somewhat from slope 3, this

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* The synergic effect has been reported on the extraction of the actinides in various oxidation states, trivalent lanthanides, Ca^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, etc., with several chelating ligands and neutral ligands. A short review of the synergic solvent extraction systems was given in Ref. 1.

1) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).

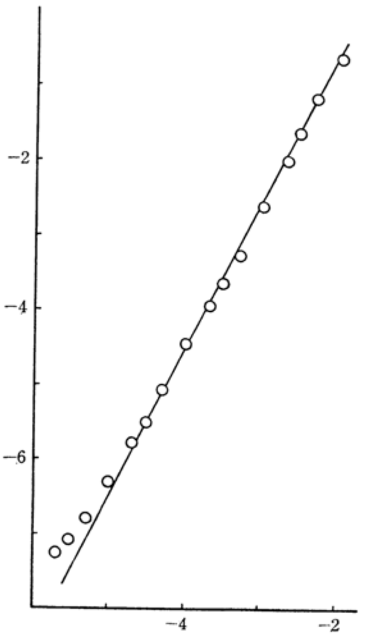

Fig. 2. Variation of the extraction constant (cf., Eq. 3) of europium(III) with 0.01 M TTA in hexane by the addition of TBP.

deviation may be due to the aqueous chelate complex formation. On the other hand, the D is proportional to $[H^+]^{-3}$ in the synergic extraction systems (closed and semiclosed circles); this may be expected from the facts that the $[HA]_{org}/[H^+]$ value for a certain D value is smaller in the synergic extraction systems and that, consequently, the concentration of the aqueous chelate complexes is smaller in these systems.

The extraction constants calculated from these data seem to show this more clearly. In Fig. 1-b, the extraction constant, K_0, in the single extraction system deviates very much from the constant value, but those in the synergic systems give nearly constant values (the log K_0 value is -5.52 for 0.001 M TTA+ 3×10^{-5} M TBP and -4.32 for 0.01 M TTA+ 1×10^{-4} M TBP). Thus, it may be concluded that the determination of β_n by Eq. 7 is possible only by the use of the synergic extraction system in the present case.

There is another advantage in the use of the synergic extraction system. As may be seen in Fig. 2, the extraction constant in the metal extraction system can be varied very widely only by changing the concentration of the adduct-forming ligand. For example, one can obtain the 50% extraction of europium(III) with 0.01 M TTA in hexane between log $[H^+]^{-1}$ at 5.0($[TBP]_{org}$ is zero) and at 2.0($[TBP]_{org}$ is about 0.03 M). Thus, the use of one mixed ligand extraction system is worth several single extraction systems with different abilities of metal extraction.

Examples of the determination of stability constants by the synergic extraction system can be seen in Ref. 2.

*Department of Chemistry
Tokyo College of Science
Kagurazaka, Shinjuku-ku
Tokyo*

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[2] T. Sekine, ibid., 26, 1463 (1964).