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COMPLEX FORMATION OF EUROPIUM WITH THENOYLTRIFLUOROACETONE AND TRI-n-OCTYLPHOSPHINE OXIDE IN MICELLAR SOLUTION OF NONIONIC SURFACTANT

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The distribution behavior of europium between micellar and bulk phases was investigated in aqueous solutions of europium-TTA and europium-TTA-TOPO complexes with nona-oxyethylene dodecyl ether by spectrophotofluorimetric method. Apparent equilibrium constants of these complexes were estimated.

Recently, the present author reported the spectrophotofluorimetric method for the determination of europium and samarium with thenoyltrifluoroacetone (TTA) and tri-n-octylphosphine oxide (TOPO) in aqueous solutions containing nonionic surfactant.[1] Though studies for liquid-liquid extraction of rare earth complexes have been widely reported, those for equilibrium of the complexes between nonionic surfactant micelle and bulk phase have been scarcely done. This communication will describe the complex formation of europium with TTA and TOPO in micellar solutions of nona-oxyethylene dodecyl ether (BL-9EX). In a previous paper,[2] it was recognized by a spectrophotometric method that most of TTA exists outside the micelle, i.e. in the bulk phase. On the other hand, europium-TTA and europium-TTA-TOPO complexes were found to exist in the micelle because these complexes could not be dissolved in an aqueous solution if the concentration of the surfactant was less than about 0.01% (w/v).[1] Also, the recent study using the continuous variation method showed that the composition of these complexes were $Eu(TTA)_3$ and $Eu(TTA)_3(TOPO)_2$, respectively.[3] From these results, the complex $Eu(TTA)_3$ is presumed to be formed by the following equilibrium.

$$Eu^{3+}_{(b)} + 3HTTA_{(b)} \rightleftharpoons Eu(TTA)_{3(m)} + 3H^{+}_{(b)}$$

the subscripts (b) and (m) referring to mutually equilibrated bulk and micellar phases, respectively; the equilibrium constnat is defined by

$$k_1 = [Eu(TTA)_3]_{(m)}[H^+]^3_{(b)}/[Eu^{3+}]_{(b)}[HTTA]^3_{(b)}. \quad (1)$$

Equation (1) can be expressed as follow :

$$\log D_1 + 3\log [H^+]_{(b)} - 3\log [HTTA]_{(b)} - \log k_1 = 0 \quad (2)$$

where

$$D_1 = [Eu(TTA)_3]_{(m)}/[Eu^{3+}]_{(b)}. \quad (3)$$

When Equation (2) is differentiated with respect to $\log [H^+]_{(b)}$ at constant HTTA concentration, Equation (4)

$$d\log D_1/ d\log [H^+]_{(b)} = -3 \quad (4)$$

is obtained; here, the concentration of HTTA can be assumed to be constant in the presence of a large excess of the reagent against the metal ion. (The ionic strength is held constant at about 0.1.)

Similarly, the following equilibrium is expected for the complex $Eu(TTA)_3(TOPO)_2$.

$$Eu^{3+}_{(b)} + 3HTTA_{(b)} + 2TOPO_{(m)} \rightleftharpoons Eu(TTA)_3(TOPO)_{2(m)} + 3H^{+}_{(b)}$$

for which

$$k_2 = [Eu(TTA)_3(TOPO)_2]_{(m)}[H^+]^3_{(b)}/[Eu^{3+}]_{(b)}[HTTA]^3_{(b)}[TOPO]^2_{(m)} \qquad (5)$$

$$d \log D_2/d \log [H^+]_{(b)} = -3 \qquad (6)$$

where

$$D_2 = [Eu(TTA)_3(TOPO)_2]_{(m)}/[Eu^{3+}]_{(b)}. \qquad (7)$$

From Equations (1) and (5), the following reaction is derived by Equation (8).

$$Eu(TTA)_{3(m)} + 2TOPO_{(m)} \rightleftharpoons Eu(TTA)_3(TOPO)_{2(m)}$$

$$K_3 = [Eu(TTA)_3(TOPO)_2]_{(m)}/[Eu(TTA)_3]_{(m)}[TOPO]^2_{(m)} = k_2/k_1 \qquad (8)$$

In the case that the concentration of the surfactant was in the range of 0.2 - 1.0% with large excess of TTA and TOPO, the fluorescence intensities were almost constant. From this result, the following assumptions can be introduced : (i) the concentration of europium in the micellar phase is linearly proportional to the fluorescence intensity (λ_{ex} 350 nm, λ_{em} 610 nm) and (ii) all the europium species exist in the micellar phase in a certain pH range in which the fluorescence gives a constnat and maximum intensity (pH 5.3 - 5.7 for Eu-TTA complex and pH 3.2 - 3.8 for Eu-TTA-TOPO complex). From the spectrophotofluorimetric experiment, the approximate values of D_1 and D_2 were calculated. The slopes of the observed curves log D_1 vs. log $[H^+]_{(b)}$ and log D_2 vs. log $[H^+]_{(b)}$ are almost linear (about -3) as shown in Fig. 1. The values of log k_1, log k_2, and log k_3 obtained from the curves were -4.3, 9.8, and 14.1, respectively. The results for other β-diketone systems will be reported in near furture.

References

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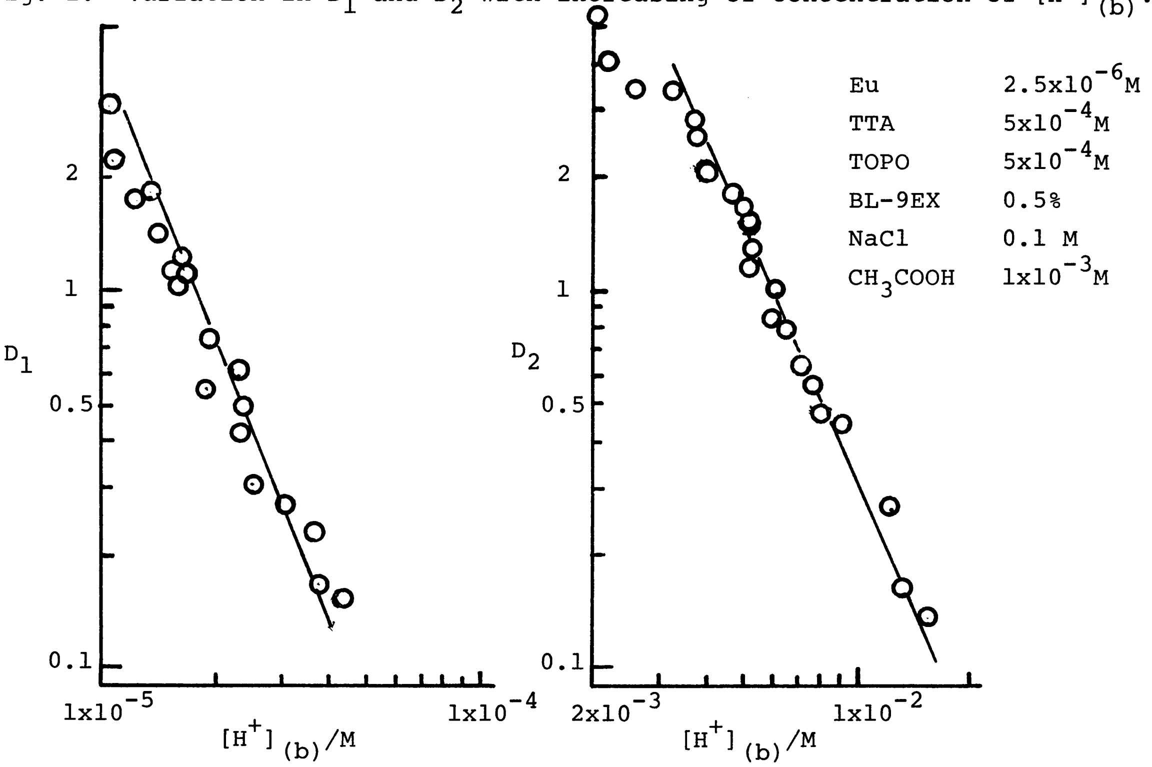
2) T.Taketatsu and A.Sato, Bull. Chem. Soc. Jpn., 53, 3713 (1980).
3) T.Taketatsu and A.Sato, 29th Annual Meeting of the Japan Society for Analtical Chemistry, October, 1980, Abstr. No. 1A23.

Fig. 1. Variation in D_1 and D_2 with increasing of concentration of $[H^+]_{(b)}$.



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