Complex Formation of Indium(III) with Oxalate Ion in 1 M Sodium Perchlorate Media

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Much work has been devoted to the complex formation of indium(III) in aqueous solutions with various ligands.[1] It has been shown that indium(III) is a good acceptor of various ligands, forming stable complexes in aqueous solutions.

The complex formation of some trivalent metal ions with oxalate ion has also been studied, and it has been reported[2] that lanthanum(III), europium(III), luthetium(III) and americium(III) form oxalate complexes, $MC_2O_4^+$, $M(C_2O_4)_2^-$ and $M(C_2O_4)_3^{3-}$, in 1 M sodium perchlorate media.

For the complex formation of indium(III), Lacroix reported[3] that a tripositive indium ion combines with two oxalate ions. Moreover, White, Tang and Li[4] reported that indium(III) forms a complex species, $InHC_2O_4^{2+}$. However, no quantitative data on the successive formation of indium(III) complexes seem to have been published.

For the present paper, the authors studied the complex formation of indium(III) with oxalate ions in 1 M $Na(ClO_4)$ at 25°C. A liquid-liquid distribution method was employed in conjunction with an indium-114 m tracer in order to keep the metal ion concentration very low and to avoid the formation of indium oxalate precipitates. The complex formation was determined from the decrease in the metal extraction with thenoyltrifluoroacetone. The stability constants were determined graphically by a curve-fitting method.

Experimental

Most of the reagents and procedures were the same as those described previously[5,6] except the following.

Tracer and Reagents.—Indium-114 (half-life; 50.0 days) was prepared by the irradiation of five-nine indium metal with thermal neutrons in the JRR-2 reactor of the Japan Atomic Energy Institute. The irradiated sample was dissolved in aqua regia and evaporated to dryness. The residue was dissolved in perchloric acid and used as the stock tracer solution. The chloroform was washed three times with water.

Procedures.—In the present study, sulfanilic acid-sulfanilate was used to buffer the aqueous phase between pH 3.0 to 3.4, and a chloroform solution of 0.01 M

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[1] L. G. Sillen and A. E. Martell, "Stability Constants," Spec. Pub. **17**, the Chemical Society, London (1964).

[2] T. Sekine, *Acta Chem. Scand.*, **19**, 1476 (1965).

[3] S. Lacroix, *Ann. Chim.*, **4**, 5 (1949).

[4] J. M. White P. Tang and N. C. Li, *J. Inorg. Nucl.*, **14**, 255 (1960).

[5] T. Sekine and Y. Hasegawa, This Bulletin, **39**, 240 (1966).

[6] T. Sekine, M. Sakairi and Y. Hasegawa, This ibid., **39**, 2141 (1966).

thenoyltrifluoroacetone (TTA) was used as the organic phase. The initial concentration of indium(III) in the aqueous phase was always less than 3×10^{-7} M.

Results and Discussion

The dissociated oxalate ion concentration in the solutions at different hydrogen ion concentrations was calculated from the total oxalate concentration, using the acid dissociation constant. The details of the statistical treatment have been given in previous papers[2,5,6]; only the final equations will be given in Table I.

TABLE I. ABRRIBATIONS AND EQUATIONS

D: Net distribution ratio

$$D=\frac{\gamma\text{-radioactivity per ml. org. phase}}{\gamma\text{-radioactivity per ml. aq. phase}} \qquad (1)$$

D_0: Distribution ratio in the absence of ligands

$$D_0=[\mathrm{InA_3}]_{org}/[\mathrm{In}^{3+}]_{aq} \qquad (2)$$

K_{ex_0}: Extraction constants

$$K_{\mathrm{ex}_0}=D_0[\mathrm{H}^+]^3[\mathrm{HA}]_{org}{}^{-3} \qquad (3)$$

$$=10^{-3.83}\text{ (determined from the data in Fig. 1)}$$

β_n: The stability constant for the "nth" complex

$$\beta_n=[\mathrm{InL}_n{}^{3-2n}]/[\mathrm{In}^{3+}][\mathrm{L}^{2-}]^n \qquad (4)$$

$$\log(1+\sum\beta_n[\mathrm{L}^{2-}]^n)^{-1}=\log D[\mathrm{H}^+]^3[\mathrm{HA}]_{org}{}^{-3}/K_{\mathrm{ex}_0} \qquad (5)$$

Figure 1 gives the $\log D$ vs. $-\log[\mathrm{H}^+]$ plot when the aqueous phase contains no oxalate. The plot in the figure falls on the straight line of slope 3 (cf. Eq. 3).

The stability constants of the oxalate complexes may be calculated by Eq. 5, and the stability constants may be determined by a "curve-fitting" method.[5,6]

The stability constants for the complex $\mathrm{InC_2O_4}^+$ and $\mathrm{In(C_2O_4)_2}^-$ species were determined by the curve-fitting method as $\log\beta_1=5.30$ and $\log\beta_2=10.52$. Figure 2 gives the $\log D[\mathrm{H}^+]^3[\mathrm{HA}]_{org}{}^{-3}/K_{\mathrm{ex}0}$ vs. $\log[\mathrm{C_2O_4}^{2-}]$ plot, together with the curve calculated from the stability constants obtained by the curve-fitting method.

Under the present experimental conditions, the hydrolysis of indium(III) may be neglected (for the calculation of the stability constants) because the hydrolysis constants have been given as $10^{-4.4}=[\mathrm{InOH}^{2+}][\mathrm{H}^+]/[\mathrm{In}^{3+}]$ and $10^{-3.9}=[\mathrm{In(OH)}^{2+}][\mathrm{H}^+]/[\mathrm{InOH}^+]$.[7]

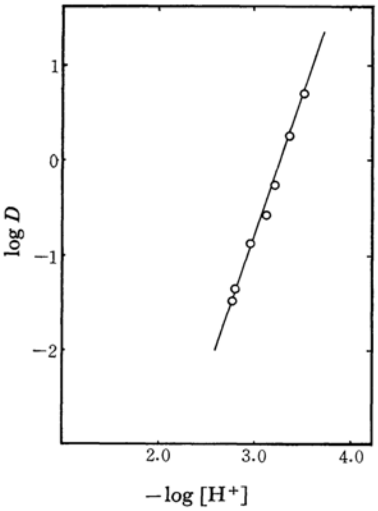

Fig. 1. Distribution ratio of indium(III) as a function of hydrogen ion concentration at 25°C when oxalate ion is absent in the aqueous phase.
Organic phase: 0.01 M TTA in chloroform
Aqueous phase: 1.0 M $\mathrm{NaClO_4}$

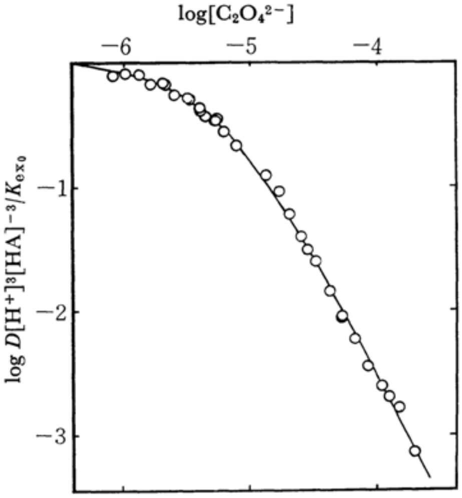

Fig. 2. Variation of $D[\mathrm{H}^+]^3[\mathrm{HA}]_{org}{}^{-3}$ of indium(III) as a function of the concentration of oxalate ion at 25°C.
Organic phase: 0.01 M TTA in chloroform
Aqueous phase: 1.0 M $\mathrm{Na(ClO_4)}$
The solid curve shows $\log D[\mathrm{H}^+]^3[\mathrm{HA}]_{org}{}^{-3}K_{\mathrm{ex}_0}{}^{-1}=-\log(1+2.0\times10^5[\mathrm{C_2O_4}^{2-}]+3.3\times10^{10}\times[\mathrm{C_2O_4}^{2-}]^2)$

It seems that the experimental data can be explained by assuming only the primary and the secondary complexes within the present oxalate concentration range. No stability constants of indium(III) oxalate complexes have been reported which can be directly compared with the present results, nor have such constants been reported for the oxalate complexes of aluminum(III), gallium(III) or thallium(III) under similar experimental conditions except for those by Dutt and Sur[8] in 1 M potassium nitrate at 32°C. It may be

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[7] G. Biederman, *Arkiv Kemi*, **9**, 277 (1956); *Rec. Trav. Chim.*, **75**, 716 (1956).

[8] N. K. Dutt and B. Sur, *Z. anorg. Chem.*, **293**, 195 (1957).

seen in their results that the K_2 of the aluminum(III) oxalate complex ($\log K_2 = 5.45$) is of the same order as that of the indium(III) complex in the present study ($\log K_2 = 5.22$).

The stability constants for the primary and the secondary oxalate complexes of lanthanum(III), europium(III), luthetium(III) and americium(III)[2] under the same experimental conditions are a little smaller than those of indium(III); the tertiary complex, such as was always found for these trivalent ions, was not found for indium(III).

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