SOLVENT EXTRACTION STUDIES OF INDIUM

II. Lactate Complexes

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INTRODUCTION

SOLVENT extraction has been used[1] extensively to study complex formation between a metal and a ligand. The technique has also been extended to study competitive reactions[2, 3] in systems containing a metal and two ligands, A and X, in which only the complexes of the auxiliary ligand, A, are extracted in the organic solvent. This is generally done by measuring the variation in the distribution ratio of the metal at a constant concentration of the auxiliary ligand at various concentrations of the complex-former. The study of indium-lactate complexes, using TTA as an auxiliary ligand, is presented here.

EXPERIMENTAL

In-114 m, used in the present work, was obtained from Isotope Division B.A.R.C. Thenoyl trifluoroacetone was purified by vacuum distillation and carbon tetrachloride (B.D.H., A.R.) was used as the solvent. All experiments were carried out at a constant ionic strength of 1·0 by the addition of sodium perchlorate obtained by neutralising standard sodium hydroxide and perchloric acid (E. Merck, G.R.). The pH of the aqueous phase was measured with a Cambridge Bench Type pH meter. The optical density of TTA solutions was measured with a Beckman DU Spectrophotometer in the UV range.

Equal volumes of the aqueous phase containing indium, lactic acid when necessary, sodium perchlorate and perchloric acid and the carbon tetrachloride phase containing TTA (0·01 to 0·1 M) were equilibrated in a mechanical shaker for 8–12 hours. The phases were then separated and indium in the organic phase was stripped with an aqueous phase of nearly the same composition as that used for extraction but of higher acidity. This procedure eliminated the need for correction for the absorption losses.

Radioactive measurements were made using a liquid G.M. Counter (M/s. Electronics Corporation of India, Hyderabad). A quenching unit was also incorporated which enabled statistical corrections to be made when the counting rate was more than 2,000 c.p.m.

RESULTS AND DISCUSSION

The reaction between indium and thenoyl trifluoroacetone (HTTA) can be described by the general equation

$$In^{+3} + nTTA^{-} \rightleftharpoons In(TTA)_n^{3-n}. \quad (1)$$

Hydrolysis and polymerisation of indium can be neglected in view of the low concentration of indium and the pH range of investigation. Since only the neutral complex, $In(TTA)_3$, is extracted in the organic phase, the distribution ratio of indium can be written as

$$D_0 = \frac{[In(TTA)_3]_{org}}{[In]_{aq}}. \quad (2)$$

Indium is present in the aqueous phase as $In(TTA)_n$. The partition coefficient, P_3, of $In(TTA)_3$ is given by

$$P_3 = \frac{[In(TTA)_3]_{org}}{[In(TTA)_3]_{aq}}. \quad (3)$$

Hence, eq. (2) can be written as

$$D_0 = \frac{P_3\beta_3[A]^3}{1 + \beta_1[A] + \beta_2[A]^2 + \beta_3[A]^3} \quad (4)$$

where [A] represents the concentration of $(TTA)^-$ and β's represent the overall stability constants.

Eq. (4) can be rearranged to obtain

$$D_0^{-1}[A]^3 = \frac{1}{P_3\beta_3}\{1 + \beta_1[A] + \beta_2[A]^2 + \beta_3[A]^3\}. \quad (5)$$

The distribution ratio (Fig. 1) was measured at different concentrations of HTTA and pH. The concentration of the anion was calculated from the pK value of 6·20 [2] from

$$K = \frac{[H][TTA]}{(HTTA)_{to}} \cdot (D_{HA} + 1) \quad (6)$$

where D_{HA} represents the distribution ratio of HTTA. This was determined in a separate series of experiments by equilibrating HTTA in carbon tetrachloride with sodium perchlorate and analysing the aqueous phase by spectrophotometry. The value of $[P_3\beta_3]^{-1}$ was obtained from the intercept of a plot of $D_0^{-1}[A]^3$ *vs.* [A]. The stability constants were calculated by the extrapolation method by Rydberg[4] and by the two-parameter method of Dyrssen and Sillen[5] and are listed in Table I.

TABLE I

Indium-TTA complexes

Log P_3 $\beta_3 = 20 \cdot 3$

Log β	Graphical method	Two-parameter method	Literature value	
β_1	6·51	6·22	6·0[6]	..
β_2	11·97	11·9	12·0	11·6[7]
β_3	17·17	17·0	18·0	..

In the presence of lactate, the distribution ratio can be written as:

$$D = \frac{[In(A)_3]_{org}}{[In] + [InA] + [InA_2) + \ldots + [InX] + [InX_2] + \ldots} \quad (7)$$

where [X] denotes the lactate ion. Representing the stability constants of indium-lactate complexes by β_n', we obtain

$$D = \frac{P_3\beta_3 [A]^3}{\sum_0^N \beta_n [A]^n + \sum_1^N \beta_n' [X]^n}. \quad (8)$$

Eqs. (4) and (8) can be combined to obtain

$$P_3\beta_3 [A]^3 (D^{-1} - D_0^{-1}) = \sum_1^N \beta_n' [X]^n = F_0. \quad (9)$$

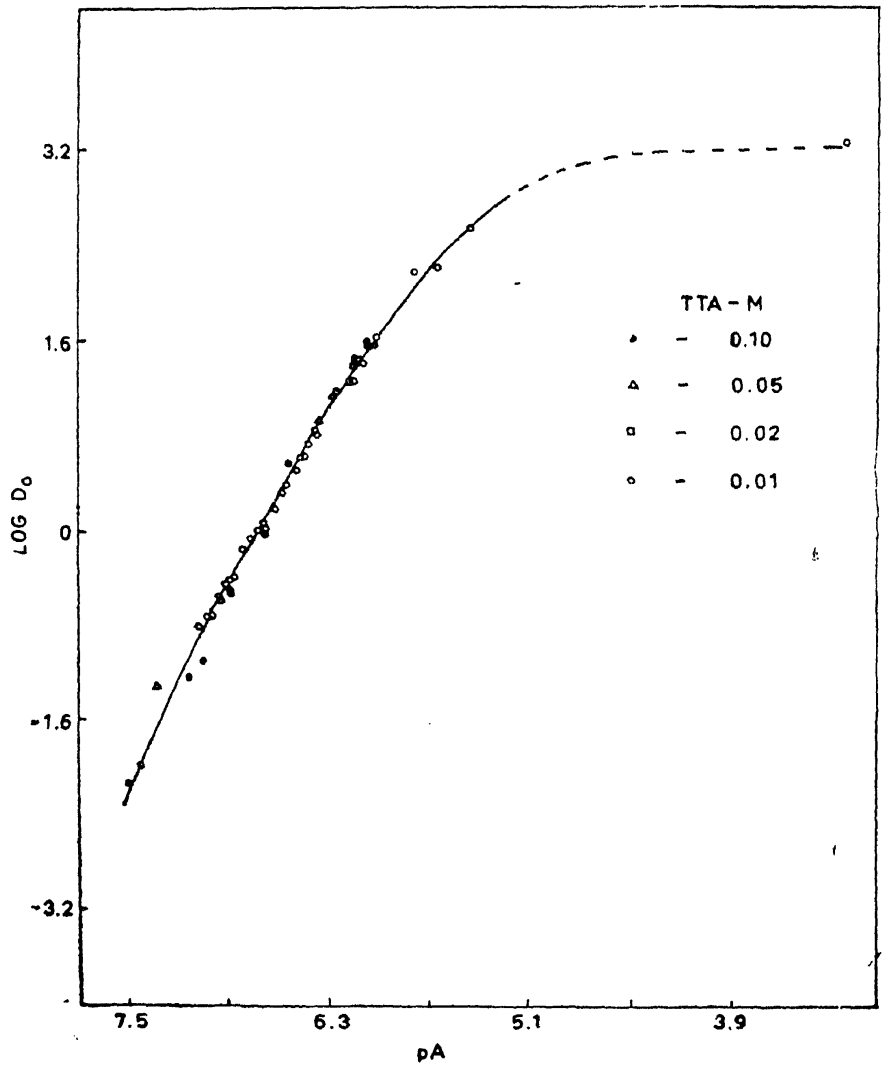
Eqs. (4) and (8) can also be combined to obtain

$$D_0 D^{-1} = \frac{\sum_0^N \beta_n [A]^n + \sum_1^N \beta_n' [X]^n}{\sum_0^N \beta_n [A]^n}. \quad (10)$$

If it is assumed[2], as has been done by several workers, that the complexes of the auxiliary ligand are negligible in the aqueous phase, *i.e.*, the term $\sum_{1}^{N} \beta_n [A]^n$ is zero, the above expression reduces to

$$(D_0 D^{-1}) - 1 = \sum_{1}^{N} \beta_n' (X)^n = F_0. \qquad (11)$$

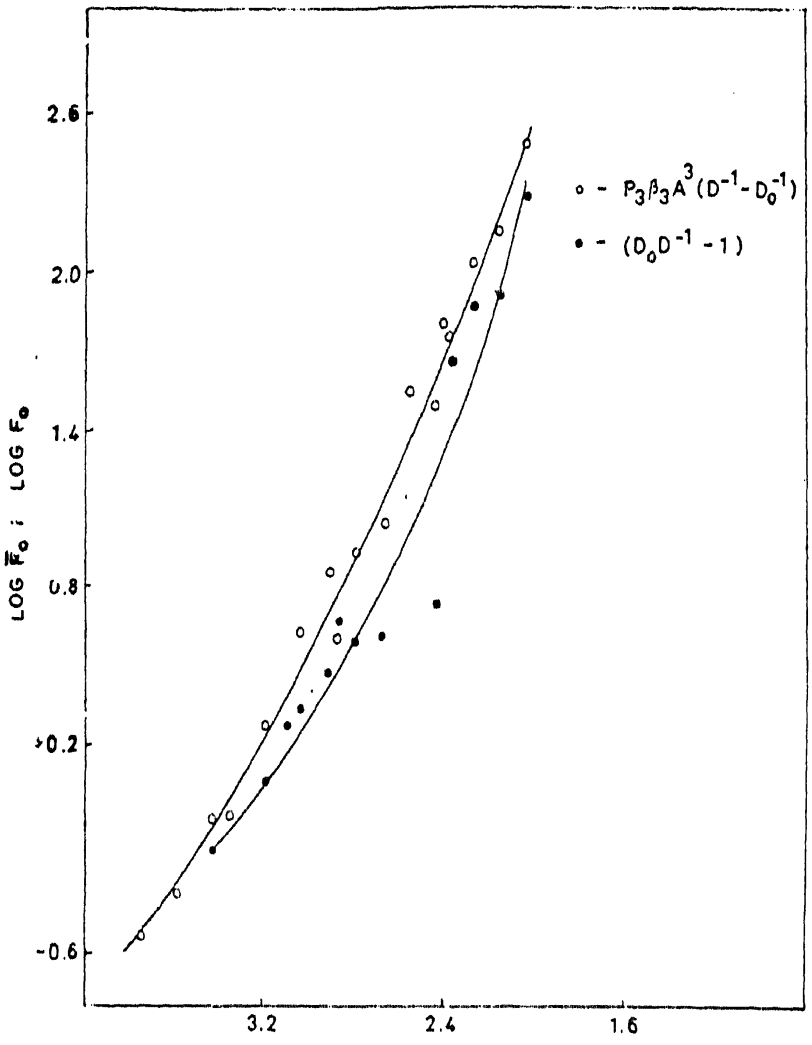
The relative accuracy of the two methods [eqs. (9) and (11)] has been tested earlier.[8] It has been shown that eq. (11) is applicable only at very low concentrations of the auxiliary ligand and a limitation is set in the measurement of low values of the distribution ratio.



In - TTA : LOG D_0 vs. pA

FIG. 1

The distribution ratio, D, was measured in the presence of TTA at different concentrations of lactic acid. The concentration of lactate was



PLOT OF $\bar{F}_0$ AND F_0 vs. LOG [LACTATE]

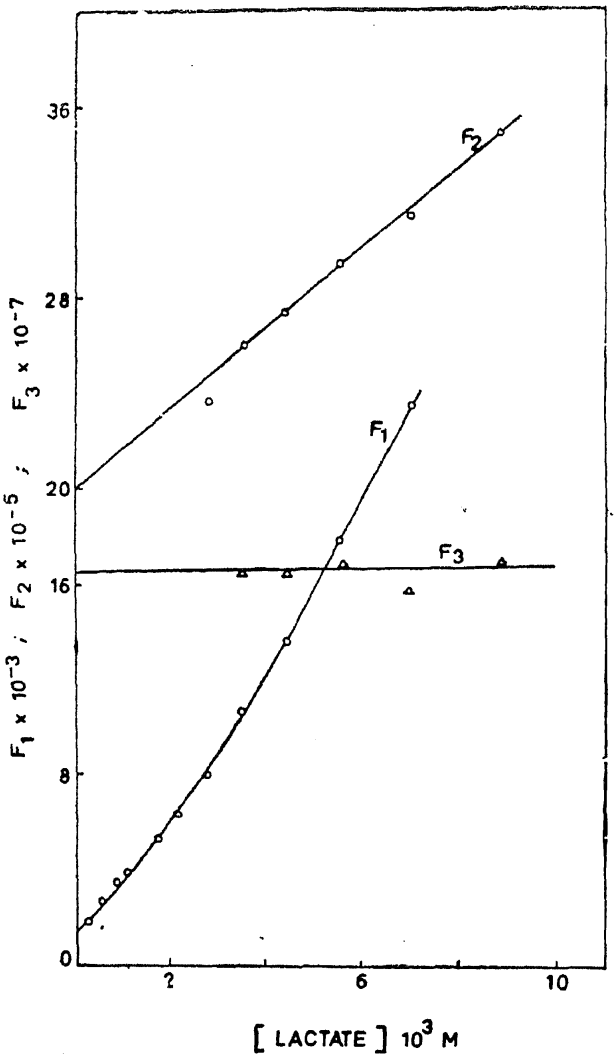
FIG. 2

TABLE II

Indium-lactate complexes

Log β'	Graphical method	Method of least squares	Literature value[10]
β_1'	3·11	3·17	3·0
β_2'	6·30	6·27	5·6
β_3'	8·21	8·25	..

calculated from the pH of the solution and pK value of 3·86[9]. The corresponding value of D_0 was read from the graph (Fig. 1). The function $\bar{F}_0$ was calculated from eq. (9) (Fig. 2). It can be seen from Fig. 2 that the values of F_0, calculated from eq. (11), are lower as the presence of the auxiliary ligand complexes has been neglected (*loc. cit.*). No attempt was, therefore, made to analyse this function for the stability constants.



SOLUTION OF $\bar{F}_0$ FUNCTION

FIG. 3

The stability constants were calculated from $\bar{F}_0$ by the graphical method (Fig. 3). The values were also calculated by a generalised least square method using a Fortran Program with computer CDC–3600 (Table II). Negatively charged higher complexes are possible but could not be

detected in the range of concentration of investigation. The stability constants of the three complexes are:

$$\log \beta'_1 = 3 \cdot 17; \quad \log \beta'_2 = 6 \cdot 27 \text{ and } \log \beta'_3 = 8 \cdot 25.$$

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