Study of indium complexes by solvent extraction and ion exchange

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ABSTRACT

Complexes of indium with hydroxy carboxylic acids like glycollic, mandelic and thioglycollic acids have been investigated by the method of competitive reactions using HTTA as the auxiliary ligand. An ion exchange study has been made in some cases to confirm the results. An ion exchange study of indium fluoride complexes has also been made. The data have been analysed for the stability constants of the indium complexes.

1. INTRODUCTION

SOLVENT extraction has been used for the study of non-extractable complexes by the method of competitive reactions. This method has been adopted by Stary,[1] Sekine[2] and others for the study of complexes of lanthanum, europium and other metals with chloride, thiocyanate, oxalate, etc. The complexes of indium[3,4] with thiocyanate, malonate and lactate have been reported earlier from these laboratories. In continuation of this work, complexes of indium with hydroxy carboxylic acids have been presented in this paper. The technqiue of ion exchange has also been used for such studies and the relative advantages of the methods have been pointed out.

2. EXPERIMENTAL

Indium in the form of In^{114m} was obtained from Isotope Division, B.A.R.C. and was assayed by liquid G. M. Detectors (M/s. Electronics Corporation of India Ltd., Hyderabad). Thenoyltrifluoroacetone (Koch-Light Labortories) was used as a solution in benzene (B.D.H., AnalaR). Dowex 50W–X8 (Baker Analysed Reagent) in sodium form was used as the ion exchanger. Stock solutions of glycollic (Riedel De Haen Ag Seelze, Hannover) and mandelic (B.D.H., recrystallised from hot water) acids were standardised by titration with sodium hydroxide. The ionic strength was maintained at 1·0 with sodium perchlorate.

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase containing the metal, complexing agent, perchloric acid to vary the pH and requisite amounts of sodium perchlorate with an equal volume of the extractant for about eight hours at $30 \pm 1°$ C in a thermostated mechanical shaker. After separation of the two phases, the metal in the organic phase was stripped with an aqueous solution of nearly the same composition but of higher acidity and was assayed. The pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter.

3. THEORY

The extraction of indium by thenoyltrifluoroacetone (HTTA) can be written as

$$In + 3 [HTTA]_0 \rightleftharpoons [In (TTA)_3]_0 + 3H^+ \tag{1}$$
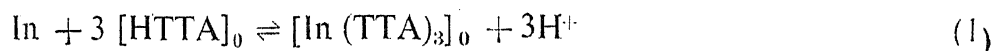
and the distribution ratio, D_0, is given by

$$D_0 = [In]_0/[In]. \tag{2}$$

The concentration terms can be replaced in terms of the stability constants of indium chelates and the concentration of the free ligand A, as

$$D_0 = P_3\beta_3 [A]^3/(1 + \beta_1 [A] + \beta_2 [A]^2 + \ldots) \tag{3}$$

where P_3 represents the partition coefficient of the neutral species. In the presence of another ligand, X, complexes of the type InX_n are formed and the overall distribution ratio, D, can be written in terms of the stability constants as

$$D = P_3\beta_3 [A]^3/(1 + \beta_1 [A] + \beta_2 [A]^2 + \ldots + \beta'_1 [X] + \beta'_2 [X]^2 + \ldots) \tag{4}$$

where β'_n represents the stability constant of the compex MX_n. Eqs 3 and 4 can be combined to obtain

$$P_3\beta_3 [A]^3 (D^{-1} - D_0^{-1}) = F_0 = \beta'_1 [X] + \beta'_2 [X]^2 + \ldots \tag{5}$$

which was used in the present work for the calculation of the stability constants.

4. RESULTS AND DISCUSSION

The complexes of indium with glycollate, thioglycollate, mandelate and fluoride were studied by this method. HTTA was chosen as the auxiliary ligand in view of its low pK value and because of its ability to extract indium at low pH so that the formation of hydroxy complexes could be neglected.

INDIUM-TTA CHELATES

The extraction of indium by HTTA in benzene was investigated to obtain the values of $P_3\beta_3$ and the distribution ratios under identical conditions adopted in the present studies. The distribution ratio was measured as a function of pH and the concentration of HTTA. The concentration of the anion of HTTA was calculated from the pK value of $6\cdot20$ and the pH of the solution using the relation[5]

$$-\log [A] = pA = pK - \log (HTTA)_{tot} - pH + \log (p_{HA} + 1). \quad (6)$$

A value of 42 for the partition coefficient of HTTA, p_{HA}, reported by Wakahayashi et al[6] was used for the present calculations. The plot of log D vs. pA is shown in figure 1.

Equation 3 can be rearranged as

$$D_0^{-1} [A]^3 = 1/P_3\beta_3(1 + \beta_1 [A] + \beta_2 [A]^2 + \ldots). \quad (7)$$

The value of $P_3\beta_3$ was obtained as $10^{21\cdot65}$ by extrapolating a plot of $D_0^{-1} [A]^3$ vs. [A] to [A] $\rightarrow$ 0. A fairly constant value indicated that the predominant species was $In(TTA)_3$ and that indium was present in the aqueous phase mainly as uncomplexed ion. This is a distinct advantages as the contribution due to the auxiliary ligand chelates in the aqueous phase is negligible.

INDIUM-GLYCOLLATE COMPLEXES

Complexes of indium with glycollic acid were studied by the method of competitive reactions. Extraction experiments were carried out at varying concentrations of glycollic acid and pH in the presence of the auxiliary ligand.
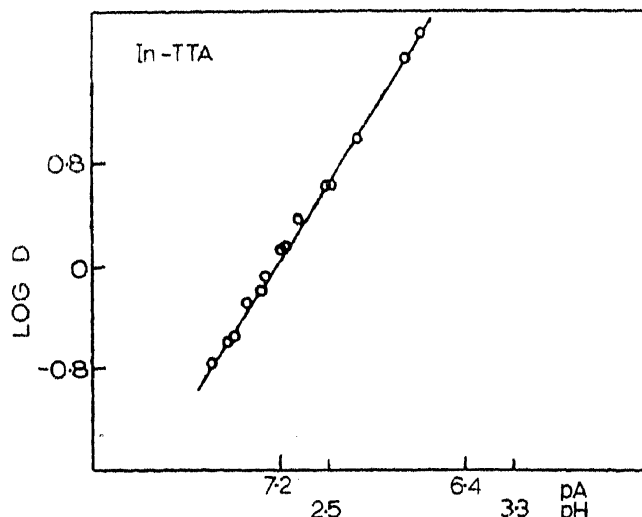

Figure 1. Plot of log D vs. pA/pH.

The concentration of the glycollate ion was calculated from the pH of the solution and the pK value of 3.30 ± 0.02 which was determined from a separate series of experiments under the same experimental conditions by the pH-titration technqiue[7,8] (figure 2). The concentration of the glycollate ion, X, was calculated from

$$[X] = \frac{KC}{[H]\left\{1 + \frac{K}{[H]}\right\}}$$ (8)

where C is the initial concentration of glycollic acid.

The function F_0 given by eq. 5 was calculated from the distribution ratios measured at different concentrations of glycollate ion (figure 3).
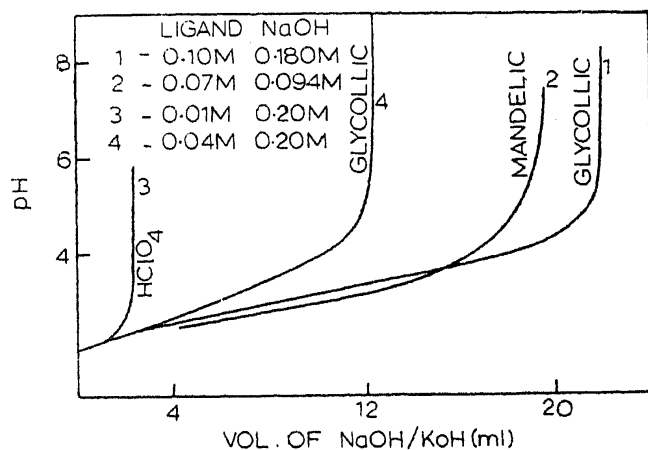
Figure 2. pH titrations.

Figure 3. Plot of log F_0 vs. log [X].

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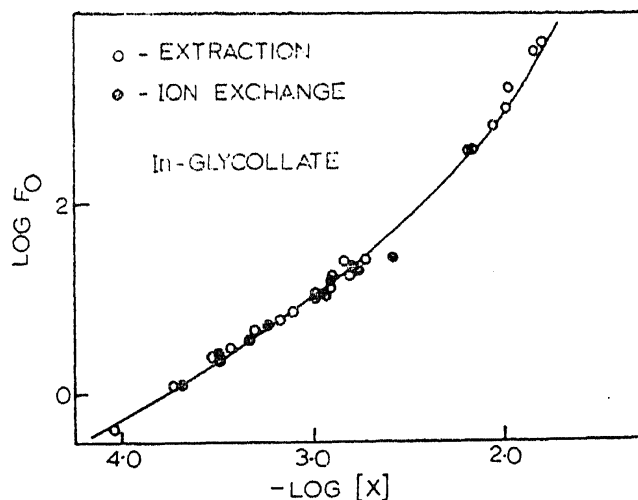
Table 1. Indium-fluoride complexes: Values of F_J functions

Dowex $= 0.25$ gm; $\mu = 1.0$; $D_0 = 120.4$ ml. gm^{-1}.

(NaF) $\times 10^4$ M	pH	pX	$\dfrac{D}{ml, gm^{-1}}$	$\log\left(\dfrac{D_0}{D} - 1\right)$	$\log F_1$
1.0	2.85	4.30	104.2	-0.81	..
2.0	2.89	3.98	80.2	-0.30	3.68
3.0	2.90	3.80	69.2	-0.13	3.67
4.0	2.90	3.68	59.7	0.01	3.69
5.0	2.90	3.58	49.8	0.15	3.73
5.0	2.96	3.55	38.7	0.32	3.87
20.0	3.18	2.87	13.0	0.92	3.77
30.0	3.48	2.61	10.2	1.03	3.64
40.0	3.54	2.48	5.2	1.35	3.83
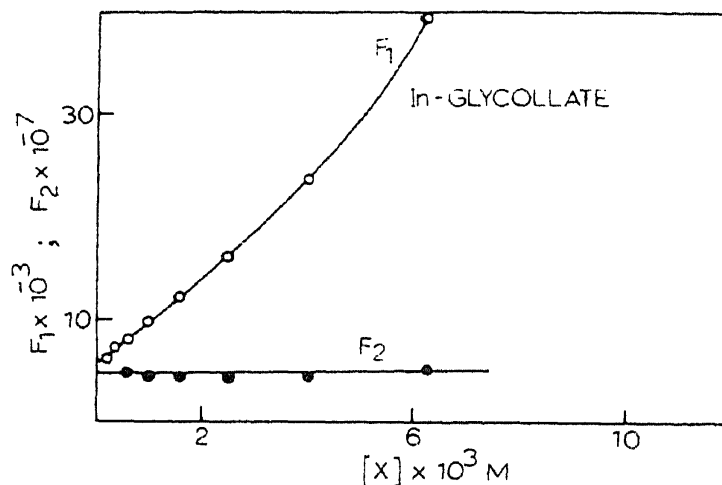
Figure 4. Plot of F_J functions.

The stability constants were obtained by a graphical extrapolation method by rearranging eq. (5) as

$$F_1 = F_0/[X] = \beta'_1 + \beta'_2 [X] + \ldots \ldots \tag{9}$$

A plot of F_1 vs. [X] yields β'_1, as the intercept. Other functions can be written in a similar fashion and solved for the other constants. Figure 4 gives the various plots. Only two complexes, In $(X)^{+2}$ and $[In\ X_2]^+$ could be identified under the experimental conditions with the stability constants as $10^{3.72}$ and $10^{6.68}$.

Equation 5 was also solved by the method of least squares using a Honeywell-400 computer. A program was written for this purpose such

that the negative values, if any were eliminated and the constants were re-evaluated for the stability constants as well as their standard deviations. The values obtained both by graphical and computer methods are listed in table 2.

ION EXCHANGE STUDIES

The indium-glycollate system was also studied by the ion exchange method using Dowex 50W-X8 in sodium form as the cation exchanger. A known weight of the resin was equilibrated with a solution containing indium, sodium perchlorate to maintain the ionic strength at $1 \cdot 0$ and requisite amounts of glycollic acid for about eight hours at $30 \pm 1^\circ$ C. The resin was separated from the aqueous phase after equilibration and the activity of indium remaining in solution was assayed. The amount of the

Table 2. Stability constants of indium complexes.

Method		Stability constants		
		Graphical	Computer	Literature
Indium-glycollate; pK $= 3 \cdot 30$				
Solvent extraction	$\log \beta_1'$	$3 \cdot 72$	$3 \cdot 71$	$3 \cdot 75$* $\quad 3 \cdot 15^{16}$, $2 \cdot 93^{17}$
	$\log \beta_2'$	$6 \cdot 68$	$6 \cdot 72$	$6 \cdot 56$*
	$\log \beta_3'$			$8 \cdot 54$*
Ion exchange	$\log \beta_1'$	$3 \cdot 72$		
	$\log \beta_2'$	$6 \cdot 68$		
Polarography	$\log \beta_1'$	$3 \cdot 48$	$3 \cdot 46$	
	$\log \beta_2'$	$6 \cdot 30$	$6 \cdot 37$	
	$\log \beta_3'$	$8 \cdot 36$	$8 \cdot 36$	
Indium-mandelate; pK $= 3 \cdot 00$				
Solvent extraction	$\log \beta_1'$	$2 \cdot 87$	$2 \cdot 88$	
	$\log \beta_2'$	$5 \cdot 42$	$5 \cdot 42$	
Indium-lactate; pK $= 3 \cdot 86$				
Solvent extraction	$\log \beta_1'$	$3 \cdot 11$	$3 \cdot 17$	$3 \cdot 00^{13}$
	$\log \beta_2'$	$6 \cdot 30$	$6 \cdot 27$	$5 \cdot 60$
	$\log \beta_3'$	$8 \cdot 21$	$8 \cdot 25$	
Polarography	$\log \beta_1'$		$3 \cdot 30$	
	$\log \beta_2'$		$6 \cdot 31$	
	$\log \beta_3'$		$7 \cdot 68$	
Indium-fluoride; pK $= 2 \cdot 85$				
Ion exchange	$\log \beta_1'$		$3 \cdot 70$	$3 \cdot 70^{19}$, $3 \cdot 75^{20}$
				$3 \cdot 67^{21}$

* Assuming three constants.

metal in the resin phase was computed from the initial amount taken. The distribution ratio, D_0, can be defined as

$$D_0 = \frac{[In]_{\text{resin per gm of resin}}}{[In]_{\text{aq per ml of solution}}}. \tag{10}$$

In the presence of a complexing agent, X, the distribution ratio, D, can be written as

$$D = \frac{[In]_{\text{resin}}}{[In] + [InX_1] + [InX_2] + \ldots} \tag{11}$$

similar to the one derived in the case of solvent extraction. The above equation, derived by Schubert et al[9] has been applied to a number of systems[10] and assumes that the only species that partitions is In^{+3}. It has been found by several workers[11,12] that the adsorption of other complexes takes place to a considerably lesser extent because of reduced charges.

The distribution ratio was studied as a function of the concentration of glycollate ion and the results are given in figure 3, where the circles represent the data of solvent extraction and the filled points refer to those of ion exchange. No attempt was made to calculate the stability constants in view of the excellent agreement of the data by the two techniques.

INDIUM-MANDELATE COMPLEXES

Complexes of indium with lactic acid—an alkyl substituted glycollic acid—have been studied earlier in these laboratories by polarography[13] and solvent extraction.[3,4] As an example of an aryl substituted glycollic acid, mandelic acid complexes were investigated.

The distribution ratio of indium was measured as a function of pH and the concentration of mandelic acid. The pK value in $1\cdot0$ M sodium perchlorate was determined by the pH-titration technique (figure 2) as $3\cdot00 \pm 0\cdot02$. Figure 5 gives a plot of log F_0 vs mandelate ion concentration. The smooth curve as well as the slope of the plot indicated the predominance of In X^{+2} and InX_2^+ complexes. The data were analysed both by the graphical (figure 6) method and by the method of least squares and the values are reported in table 2.

The order of stability of indium complexes with glycollic, mandelic and lactic acids is: mandelate < lactate < glycollate. The increased substitution of groups leads to a lowering of the stability due to the presence of hindering groups. The difference in the values for glycollate and lactate complexes is not considerable, being of the order of $0\cdot3$ log units. The stability of lactate and mandelate complexes, on the other hand, is considerably different in view of the presence of bulkier constituents.
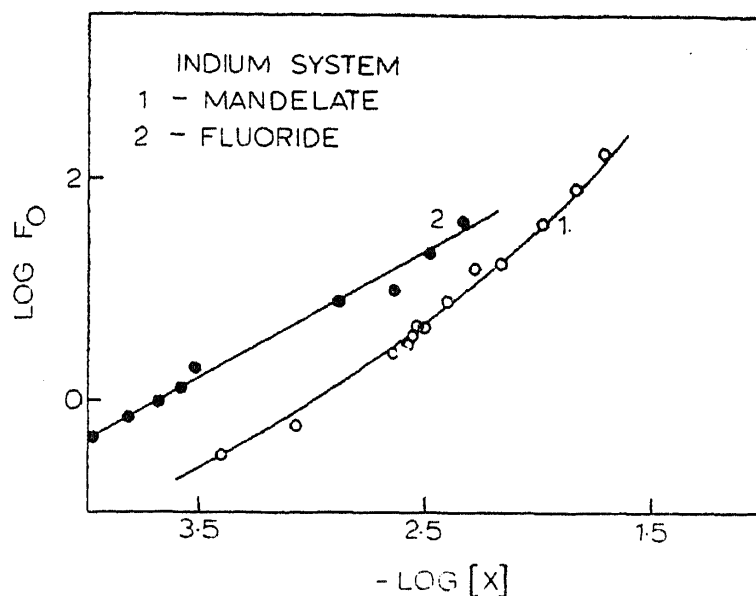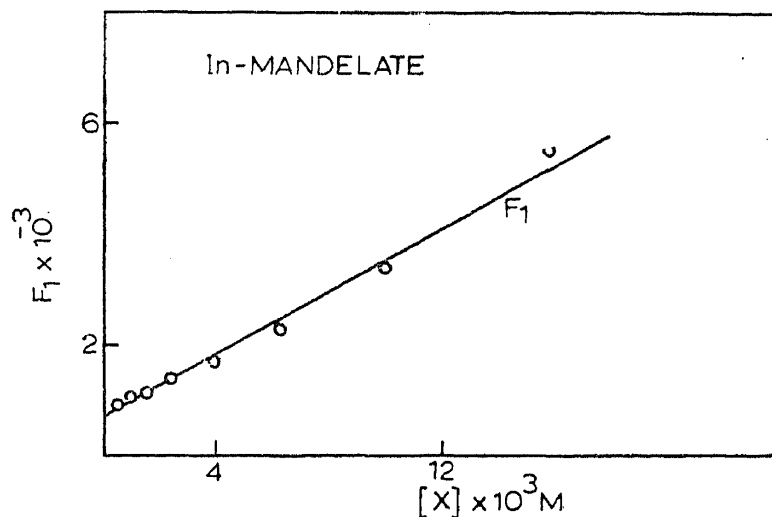
Figure 5. Plot of log F_0 vs. log [X].

Figure 6. Plot of F_1, vs. [X].

INDIUM-THIOGLYCOLLATE COMPLEXES

A study of the complexes of indium with thioglycollic acid was undertaken with a view to investigate the effect of the substitution of sulphur for oxygen in glycollic acid. Experiments were carried out in a similar manner. Extraction of indium was masked even at low concentrations of thioglycollic acid and was negligible even at high concentrations of HTTA so that no further work was possible. The increased masking may be due to the formation of stable thioglycollate complexes or mixed complexes with HTTA. This, however, could not be confirmed from the present studies.

Studies on the polarography of indium in thioglycollic acid by Yajnik[14] indicated the presence of three complexes. Tunaboylu and Schwarzenbach[15] reported a highly stable 1 :1 complex but the stability constant could not be evaluated by the pH-technique employed by them.

INDIUM-FLUORIDE COMPLEXES

Complexes of indium with fluoride were also studied by this method using the ion exchange technique. Distribution experiments were carried out at different concentrations of sodium fluoride using Dowex 50W–X8 in sodium form. Figure 5 gives a plot of log F_0 vs. (X). The concentration of free fluoride ion was calculated from the initial amount of fluoride present taking into account the dissociation constant of hydrofluoric acid as $10^{-2\cdot85}$. The stability constant of the first complex was calculated by a solution of the F_0 function (table 1). An approximate value of $10^{3\cdot7}$ was obtained, in agreement with the values reported in the literature. At higher concentrations of fluoride, the function F_0 decreased and an inversion was observed. This may be due to the exchange InF_n^{3-n} complexes whose exchange coefficients, however, are smaller than that of In^{+3} ion in view of reduced charges.

The above studies illustrate the applicability of solvent extraction and ion exchange methods for the study of complexes and the agreement in the values obtained by both the methods is good. The ion exchange method assmues that the exchange of ions other than In^{+3} is not considerable. This has been borne out in the case of indium complexes with glycollate. The increasing size of the ion with decreasing charges also leads to a lowering of the exchange coefficient so that only the exchange of free In^{+3} ion is important.[10] The exchange effect may, however, be considerable in the case of ions of smaller size. Hence the system indium fluoride was studied and an increase in the distribution ratio was observed at high fluoride concentrations. In the case of hydroxy carboxylic acids, however, such effects are not discernible.

ACKNOWLEDGEMENT

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