

Mixed chelates by solvent extraction—Mixed chelates of indium with β -diketones in carbon tetrachloride and xylene media

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Abstract. Mixed complex formation of indium with a number of β -diketones has been studied from carbon tetrachloride and xylene media. The extraction of indium by BFA and FFA was studied and the nature of the complexes established. The formation of the mixed complexes with BFA and BA/DBM, FFA and BA as well as BFA and FFA have been studied and their equilibrium constants calculated. The statistical and stabilisation constants have been calculated and interpreted on the basis of the participating ligands.

Keywords. β -Diketones; solvent extraction; indium chelates.

1. Introduction

Mixed complexes generally exist in a solution containing a metal and two ligands. Systematic studies were however initiated only recently to explain the formation and stabilisation of mixed complexes. Solvent extraction affords a convenient method for the study of mixed complexes. Marcus *et al* (1965) have studied the mixed halides of mercury while Sekine and Dyrssen (1967) have studied the mixed chelates of copper, zinc, europium and indium with TTA and IPT. Mixed β -diketones of uranium have been studied by Newman and Klotz (1967), Marcus and Eliezer (1969), Fridman (1970). Alimarin and Shlenskaya (1970) have reviewed the work on the study of mixed complexes and have also considered the theoretical aspects. A systematic study of indium chelates (Sudersanan and Sundaram 1975) by mixed β -diketones has been taken up in these laboratories and the results in carbon tetrachloride and xylene media are presented here.

2. Experimental

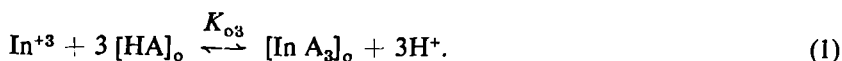
Indium was obtained in the form of In^{114m} from Isotope Division, BARC and was assayed by β -counting using a liquid G. M. Detector (M/s. Electronics Corporation of India, Hyderabad).

Benzoylacetone (Fluka), benzoyltrifluoroacetone (K & K Laboratories) and dibenzoylmethane (Koch Light) were used without further purification. Benzene (BDH, AnalaR) was used as the diluent. The ionic strength was maintained at 0.1 with sodium perchlorate.

Extraction experiments were carried out by equilibrating an aqueous solution containing the metal, sodium perchlorate and perchloric acid with an equal volume of the organic phase containing the β -diketone or their mixture for about 8 hr in a thermostated mechanical shaker at $30 \pm 1^\circ\text{C}$. After equilibration, the phases were separated and indium in the organic phase was assayed by β -counting after stripping with an aqueous solution containing about 0.3 M acid. Indium in the aqueous phase was assayed directly. The pH of the aqueous phase was measured using a Beckman Expandomatic SS-2 pH meter. Spectrophotometric measurements were made with a Beckman DU spectrophotometer in the UV region with 1 cm quartz cells.

3. Theory

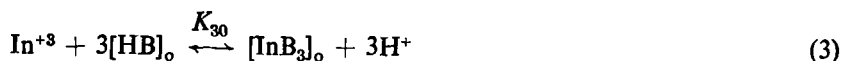
The extraction of indium by a β -diketone, HA, can be written as



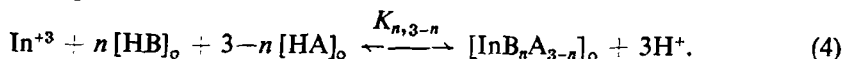
It is assumed that (i) indium exists in the aqueous phase as uncomplexed metal ion (ii) the complexes of perchlorate and β -diketones are not present to any appreciable extent in the aqueous phase, and (iii) hydrolysis effects can also be neglected in the case of indium in view of its extraction at low pH. The equilibrium constant, K_{o3} , is given by

$$K_{o3} = [\text{InA}_3]_o [\text{H}]^3 [\text{In}]^{-1} [\text{HA}]_o^{-3} \quad (2)$$

In the presence of another β -diketone, HB, the reaction



takes place. In the presence of both the ligands, mixed complex formation occurs, the reaction being



The formation of substitution type of complexes is favoured in the case of coordinately saturated complexes. Sekine and Dyrssen (1967b) also observed no adduct formation in the extraction of $\text{In}(\text{TTA})_3$ with TBP or MIBK. The distribution ratio, D , in the presence of the two ligands is given by

$$D = \{[\text{InA}_3]_o + [\text{InBA}_2]_o + [\text{InB}_2\text{A}]_o + [\text{InB}_3]_o\} [\text{In}]^{-1} \quad (5)$$

Substituting in terms of the equilibrium constants one gets

$$F_o = D[\text{H}]^3 [\text{HA}]_o^{-3} = K_{o3} + K_{12} [L] + K_{21} [L]^2 + K_{30} [L]^3 \quad (6)$$

where $[L]$ represents $[\text{HB}]_o [\text{HA}]_o^{-1}$. This can be solved for the equilibrium constants.

The formation of mixed complexes has been considered on statistical grounds (Marcus and Eliezer (1962)). It can be shown that

$$K_{12\text{stat}} = 3(K_{30}K_{03}^2)^{1/3} \quad (7)$$

and $K_{21\text{stat}} = 3(K_{30}^2K_{03})^{1/3} \quad (8)$

and the stabilisation factor, K_S , defined by

$$K_S = (K_{BA})_{\text{obs}} / (K_{BA})_{\text{stat}} \quad (9)$$

is a measure of the stabilisation of the complex over the statistical value. Marcus and Eliezer (1969) define a function, K_M , called the mixing constant as

$$(K_M)_{12} = \frac{K_{12}}{K_{30}^{1/3} K_{03}^{2/3}} \quad (10)$$

so that in the case of indium

$$3 K_S = K_M \quad (11)$$

K_M or K_S has been used as a measure of stabilisation of the mixed complex over the simple complex.

4. Results and discussion

4.1. Partition coefficients of β -diketones

The partition coefficients of benzoyltrifluoroacetone (BFA) and furoyltrifluoroacetone (FFA) between 0.1M sodium perchlorate and carbon tetrachloride or xylene was determined spectrophotometrically. The β -diketone was equilibrated with 0.1M sodium perchlorate and the optical density in the aqueous phase was measured in the ultra-violet region. The partition coefficients as well as the dissociation constants are summarised in the respective tables.

4.2. Extraction of indium by benzoylacetone (BA)

The extraction of indium by BA from carbon tetrachloride media has been studied by Rudenko and Stary (1958) as well as Zolotov (1970). This system has been re-investigated for obtaining the distribution ratios of indium in 0.1M sodium perchlorate at low pH where hydrolysis of indium need not be considered, the values being required for calculating the equilibrium constants of the mixed chelates.

The distribution ratio of indium by BA from the two media was studied as a function of pH and the concentration of the ligand. The initial slope of three of a plot of $\log D$ vs. pH (figure 1) indicated that indium was present as free metal ion in the aqueous phase. The equilibrium constant was calculated from eq. (2) as $10^{-6.2}$ and $10^{-6.4}$ in carbon tetrachloride and xylene media respectively.

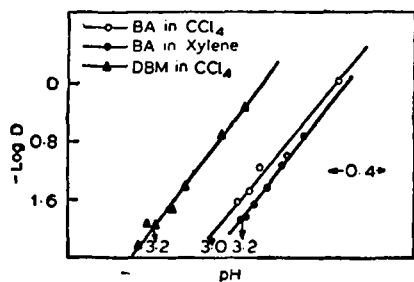


Figure 1. Extraction of indium by BFA and FFA

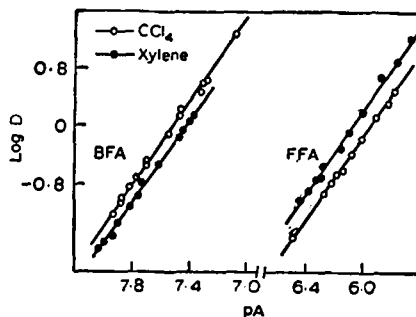


Figure 2. Extraction of indium by β -diketones

4.3. Extraction of indium by dibenzoylmethane (DBM)

The results on the extraction of indium by DBM from carbon tetrachloride media are given in figure 1. The equilibrium constant was calculated as $10^{-6.5}$.

4.4. Extraction of indium by benzoyltrifluoroacetone (BFA) and furoyltrifluoroacetone (FFA)

In the case of a fluorinated β -diketone, the extraction takes place at a lower pH facilitating the formation of InA_3 in the organic phase and preventing hydrolysis of indium in the aqueous phase. The extraction of indium by BFA as well as FFA was studied in a similar fashion and the results obtained in both the media are presented in figure 2. The plot of $\log D$ vs. pA is a straight line with a slope of three in both the cases.

The equilibrium constants for the extraction of indium by BA, DBM, BFA and FFA from benzene (Sudersanan and Sundaram 1975), carbon tetrachloride and xylene media are listed in table 1. The equilibrium constants for the individual

Table 1. Equilibrium constants for indium chelates

Ligand	Diluent	pKa	$\log P_{HA}$	$-\log K_{03}$
Benzoylacetone	Benzene* ^a			6.4
	CCl_4	8.9 ^b	2.82 ^c , 2.81 ^d	6.2
	xylene		—	6.4
	Benzene			6.4
Dibenzoylmethane	CCl_4	9.35 ^e	4.51 ^e	6.5
Benzoyltrifluoroacetone	Benzene			3.66
	CCl_4	6.30 ^f	2.40 ^a	3.53
	xylene		2.40 ^a	3.76
Furoyltrifluoroacetone	Benzene			2.0
	CCl_4	5.87 ^f	0.76 ^a , 0.71 ^d	2.0
	xylene		0.93 ^a	2.16

* K_{03} values for benzene are given for comparison (Sudersanan and Sundaram 1975)

(a) Present work; (b) Rydberg (1950); (c) Stary (1964); (d) Sekine *et al* (1973); (e) Moucka and Stary (1961), (f) Schreck (1967).

ligands are nearly the same in the three media indicating the absence of any interaction by the solvents in the extraction equilibria due to the formation of coordinately saturated chelates in the case of indium. The extraction increases in the order: xylene < benzene < carbon tetrachloride.

5. Study of mixed chelates

The mixed chelates of indium with the various β -diketones were also studied in the two solvents. The ligands were selected such that a more or less statistical behaviour can be expected in view of the minimum structural changes. Complications due to stereochemistry can also be avoided in such systems. Hence, systems were chosen such that (i) the two β -diketones differ in stability, e.g., BFA and BA or DBM; FFA and BA and (ii) the stability of the ligands is nearly the same, e.g., FFA and BFA.

5.1. Chelates of different stability

5.1.1. *Indium-benzoyltrifluoroacetone (HB)—benzoylacetone (HA)*: The formation of mixed chelates of indium with BFA and BA was studied in carbon tetrachloride and xylene media. Experiments were carried out at varying concentrations of BFA or BA, keeping the concentration of the other ligand constant. The results are presented in table 2. The data obtained at different pH fitted in a single curve indicating the formation of chelates of the type $\text{InB}_n\text{A}_{3-n}$ and the absence of adducts of type $\text{InB}_n\text{A}_{3-n}(\text{HA})_n$.

The extraction of a mixed chelate could be described by eq. (4) from which the equilibrium constants for the formation of the mixed chelate could be calculated. The function $\log D [\text{H}]^3 [\text{HA}]_0^{-3}$ (or $\log F_0$ in eq. (6)) was plotted as a function of $\log [(\text{HB})_0/(\text{HA})_0]$ (or $\log [L]$ in eq. (6)) in figure 3. The function F_0 was solved from eq. (6) for the individual equilibrium constants by the graphical extrapolation method. Since the value of the K_{03} was quite small compared to F_0 , it was taken from the data on simple chelates. Hence eq. (6) can be rewritten as

$$F_1 = \frac{F_0 - K_{03}}{[L]} = K_{12} + K_{21}[L] + K_{30}[L]^2. \quad (12)$$

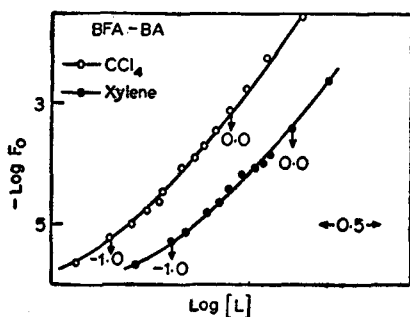


Figure 3. Plot of $\log F_0$ vs $\log [L]$

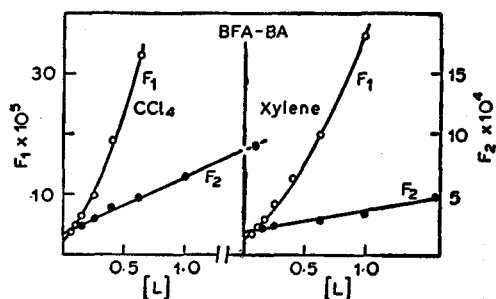


Figure 4. Plot of F_j functions

Table 2. Extraction of indium by BFA and BA

[BA] _o × 10 ³ M ^a	[BFA] _o × 10 ³ M	$\frac{[BFA]_o}{[BA]_o}$	Carbon tetrachloride			Xylene		
			pH	log <i>D</i>	$-\log \frac{D [H]_o^3}{[BA]_o^3}$	pH	log <i>D</i>	$-\log \frac{D [H]_o^3}{[BA]_o^3}$
2.0	0.1	0.05	3.32	-0.78	5.65	3.21	-1.12	5.65
2.0	0.2	0.10	3.29	-0.45	5.22	3.21	-0.73	5.31
2.0	0.3	0.15	3.29	-0.22	4.99	3.24	-0.49	5.12
2.0	0.4	0.20	3.29	0.00	4.78	3.20	-0.30	4.80
2.0	0.5	0.25	3.30	0.18	4.63	3.21	-0.10	4.62
2.0	0.6	0.30	—	—	—	3.19	0.05	4.41
2.0	0.8	0.40	3.12	0.20	4.05	3.19	0.31	4.17
2.0	1.0	0.50	3.13	0.40	3.90	3.21	0.47	4.05
2.0	1.2	0.60	3.13	0.59	3.69	3.23	0.63	3.97
2.0	1.5	0.75	3.13	0.84	3.45			
2.0	2.0	1.00	3.19	1.37	3.10			
1.5	2.0	1.33	3.18	1.29	2.78			
1.0	2.0	2.00	3.13	1.14	2.24			
0.5	2.0	4.00	3.15	0.97	1.57			
1.5	1.0	0.68				3.22	0.32	3.85
1.0	1.0	1.00				3.23	0.27	3.42
0.5	1.0	2.00				3.21	0.11	2.62
2.3	0.6	0.26	3.12	0.01	4.44			

The value of K_{12} can be obtained by extrapolation to $[L] \rightarrow 0$ of a plot of F_1 vs $[L]$. The other constants can be obtained in a similar fashion. The results are presented in figure 4. The mixing and stabilisation constants were also calculated (table 3).

The equilibrium constants for the formation of simple and mixed chelates were also calculated using a weighted least square program on Honeywell-400 computer. The variance and standard deviations of the constants were also estimated. The calculated and experimental spread of the data using these constants were also determined and the fit was found to be good. This can be seen in the various plots of $\log F_o$ where the curve represents the calculated values and the points refer to the experimental data.

5.1.2. *Indium-benzoyltrifluoroacetone (HB)—dibenzoylmethane (HA)*: DBM which is similar in extraction behaviour to BA was also studied. Experiments were carried out in carbon tetrachloride medium and the results are presented in figure 5. The data were analysed for the equilibrium constants (figure 6).

The mixing and stabilisation constants have also been calculated (table 3). It can be seen that the stabilisation constants for In-BFA-BA and In-BFA-DBM in carbon tetrachloride are small and are nearly constant compared to higher values in the case of In-BFA-BA in xylene medium. The stability of the chelates of BFA with BA or DBM in benzene media were similar. As the same trend was observed in the present case and the diluent did not affect the values, no work in xylene medium was carried out.

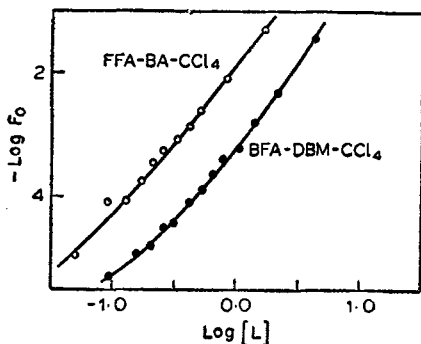
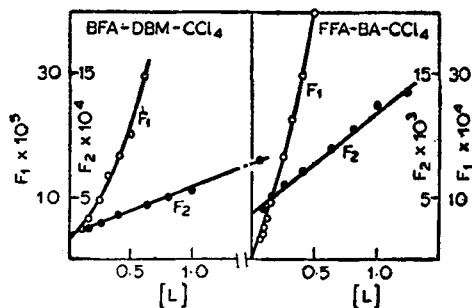
Figure 5. Plot of $\log F_0$ vs $\log [L]$ Figure 6. Plot of F_j functions

Table 3. Equilibrium constants of mixed chelates of indium

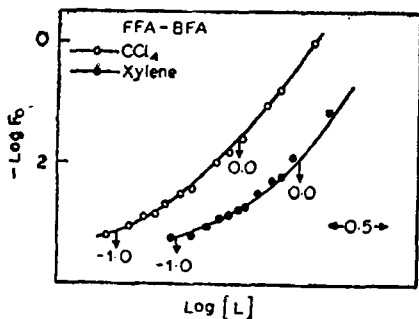
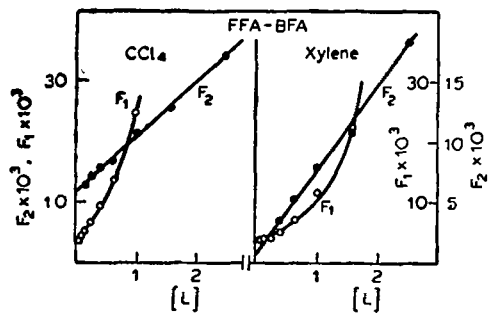
System		$-\log$ (Equilibrium constant) Graphical	Computer	$-\log K_{stat}$	$\log K_M^*$	$\log K_S^*$
BFA-BA- CCl ₄	K_{02}	6.20				
	K_{12}	4.62	4.64	4.78	0.64	0.16
	K_{21}	3.73	3.64	3.83	0.58	0.10
	K_{30}	3.35	3.41			
BFA-BA- Xylene	K_{03}	6.40				
	K_{12}	4.60	4.64	5.06	0.94	0.46
	K_{21}	3.70	3.64	4.21	0.99	0.51
	K_{30}	3.85	3.51			
BFA-DBM- CCl ₄	K_{03}	6.50				
	K_{12}	4.57	4.59	4.99	0.90	0.42
	K_{21}	3.75	3.77	3.95	0.68	0.20
	K_{30}	3.40	3.39			
FFA-BA- CCl ₄	K_{03}	6.20				
	K_{12}	3.96	—	4.34	0.86	0.38
	K_{21}	2.44	2.33	2.95	0.99	0.51
	K_{30}	2.05	2.15			
FFA-BFA CCl ₄	K_{03}	3.53				
	K_{12}	2.50	2.50	2.66	0.64	0.16
	K_{21}	1.94	1.94	2.06	0.60	0.12
	K_{30}	2.02	2.04			
FFA-BFA- Xylene	K_{03}	3.76				
	K_{12}	2.42	2.44	2.56	0.62	0.14
	K_{21}	3.30	2.91	2.22	-0.60	-1.08
	K_{30}	2.13	2.17			

*Calculated from graphical values.

5.1.3. *Indium-furoyltrifluoroacetone (HB)—benzoylacetone (HA)*: The extraction of indium by mixtures of FFA and BA was studied in carbon tetrachloride medium and the results are given in figure 5. The solution of the F_j functions by the extrapolation method is given in figure 6.

5.2. Chelates of equal stability

5.2.1. *Indium-furoyltrifluoroacetone (HB)—benzoyltrifluoroacetone (HA)*: The extraction of indium was also studied in the two media by mixtures of BFA and FFA

Figure 7. Plot of $\log F_0$ vs $\log [L]$ Figure 8. Plot of F_j functions

representing a case of two ligands having almost equal extraction abilities. The results are presented in figures 7 and 8. A compilation of the values obtained for the various systems is also presented in table 3.

The above studies illustrate the application of the method of solvent extraction for the study of mixed complexes. Mixed chelates are formed and stabilised in all the media. The stabilisation is positive in many of the cases and the chelates are more stabilised than expected statistically. The stabilisation in general, is found to be less in carbon tetrachloride than in xylene. The stabilisation increases with increase in difference in equilibrium constants of the individual ligands as has been observed by Marcus and Eliezer. Thus the extent of stabilisation increases in the order : FFA-BFA < BFA-BA < FFA-BA which is also the order of increasing difference of extractability of the individual ligands. The mixed complexes are stabilised probably because of the more flexible electron path provided in the mixed chelates than in the case of parent chelates. It is possible to correlate the data on simple and mixed chelates on the basis of the stability and the dissociation constants of the ligands which will form the subject for a subsequent publication.

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