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Solvent extraction studies of indium-mixed chelates with β-diketones in benzene media

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ABSTRACT

Mixed chelate formation of indium with several β-diketones has been studied from benzene media. The extraction of indium by BFA and FFA has been carried out as a function of pH and concentration of the ligand to ascertain the nature of the complexes. The extraction of indium by a mixture of β-diketones, *viz.*, BFA–BA, BFA–DBM, FFA–BA, FFA–DBM, FFA–BFA and DBM–BA has also been studied as a function of the solution parameters. The nature of the mixed complexes formed as well as their equilibrium constants, statistical and stabilisation constants have been evaluated.

1. INTRODUCTION

THE study of mixed complexes by different techniques like polarography, potentiometry, spectrophotometry, etc. has acquired great impetus in recent years. Such studies by the method of solvent extraction has however been confined to the adduct formation of metals with β-diketones or organophosphorus acids with neutral organophosphorus esters. This phenomenon, called synergism, has evinced considerable interest. Another type involves the formation of mixed chelates, *e.g.*, β-diketones, which on account of their similarity in structure are compatible and are likely to form mixed chelates. Sekine and Dyrssen[1] have studied the mixed chelates of copper, zinc, europium and indium with HTTA and IPT. Mixed β-diketones have also been studied by Newman and Klotz[2] as well as Shigematsu and Honjyo[3]. Marcus and Eliezer[4] and Fridman[5] have listed the mixed complexes studied by various methods and have discussed in general their formation. An extensive study of the formation of mixed chelates of indium with several β-diketones has been taken up in these laboratories and this paper reports the results obtained in benzene media.

2. EXPERIMENTAL

Indium in the form of In^{114m} was obtained from Isotope Division of BARC and was assayed using a liquid G.M. detector (Electronics Corporation of India Limited, Hyderabad). Benzoylacetone (Fluka AG, Buchs, SG), dibenzoylmethane, acetylacetone (Koch-Light Laboratories), benzoyltrifluoroacetone and furoyltrifluoroacetone (K and K Laboratories) were used without further purification. Benzene (B.D.H., AnalaR) was used as the diluent.

Extraction experiments were carried out by equilibrating 10 ml of the aqueous phase containing indium, perchloric acid and sodium perchlorate to keep the ionic strength at 0·1 with 10 ml of the organic phase containing the β-diketone in a thermostated mechanical shaker at 30° C for about eight hours. After separation of the two phases, indium in the organic phase was stripped with an aqueous phase containing about 0·3 M perchloric acid and 0·2 M sodium perchlorate and was estimated using a liquid G.M. detector. The pH of the aqueous phase was measured using a Beckman Expandomatic SS–2 pH meter.

The distribution coefficients of benzoyltrifluoroacetone (BFA) and furoyltrifluoroacetone (FFA) between 0·1 M sodium perchlorate and benzene were determined in a separate series of experiments using a Beckman DU spectrophotometer in the ultraviolet region. The final concentration of FFA in the test solutions was calculated taking into account the distribution coefficient of 10·0. In the case of BFA, benzoylacetone (BA) and dibenzoylmethane (DBM) the coefficients were high and hence the correction for their presence in the aqueous phase was negligible.

3. RESULTS AND DISCUSSION

The reaction between indium and a β-diketone (HA) can be written as

$$In^{+3} + 3\,[HA]_0 \rightleftharpoons [InA_3]_0 + 3H^+ \tag{1}$$

and the equilibrium constant is given by

$$K_{03} = \frac{[InA_3]_0\ [H]^3}{[In]\,[HA]_0^3} \tag{2}$$

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

$$In^{+3} + 3\,[HB]_0 \rightleftharpoons [InB_3]_0 + 3H^+ \tag{3}$$

as well as the formation of the mixed chelate

$$In^{+3} + n\,[HA]_0 + 3\text{-}n\,(HB)_0 \rightleftharpoons [InA_n\,B_{3-n}]_0 + 3H^+ \tag{4}$$

takes place. The equilibrium constant for the formation of the mixed species can be written as

$$K_{3-n,\,n} = \frac{[InA_nB_{3-n}]_0\,[H]^3}{[In]\,[HA]_0^n\,[HB]_0^{3-n}} \tag{5}$$

The distribution ratio of indium, D, in the presence of the two ligands is given by

$$D = \frac{[InA_3]_0 + [InBA_2]_0 + [InB_2A]_0 + [InB_3]_0}{[In]} \tag{6}$$

Substituting in terms of the equilibrium constants and on rearranging we get

$$F_0 = \frac{D\,[H]^3}{[HA]_0^3} = K_{03} + K_{12}\,[L] + K_{21}\,[L]^2 + K_{30}\,[L]^3 \tag{7}$$

where $[L]$ represents $[HB]_0/[HA]_0$ and can be solved by graphical or numerical methods.

Assuming a statistical distribution of ligands, it can be shown[6] that

$$K_{21\ \mathrm{stat}} = 3\,(K_{03}\,K_{30}^2)^{1/3} \tag{8}$$

and

$$K_{12\ \mathrm{stat}} = 3\,(K_{03}^2\,K_{30})^{1/3}. \tag{9}$$

The stabilisation factor, K_S, defined by

$$K_S = (K_{AB})_{\mathrm{obs}}/(K_{AB})_{\mathrm{stat}} \tag{10}$$

is a measure of the stabilisation of the mixed species over the statistical value. Marcus *et al.*[4] define a function, K_M, called the mixing constant, as

$$(K_M)_{21} = K_{21}/K_{03}^{1/3}\,K_{30}^{2/3} \tag{11}$$

K_M is a dimensionless quantity and is a measure of the stabilisation of the mixed chelate. K_S and K_M are related in the case of indium by

$$3K_S = K_M \tag{12}$$

The ligands are said to be compatible if the value of K_M is greater than one.

4. EXTRACTION BY β-DIKETONES

The extraction of indium by the individual β-diketones was first studied. The extraction of indium by *AA*, *DBM*[7] and *BA*[7,8] had to be reinvestigated in view of the differences in the experimental conditions, like, temperature, ionic strength and the diluent used in this work. The extraction of indium

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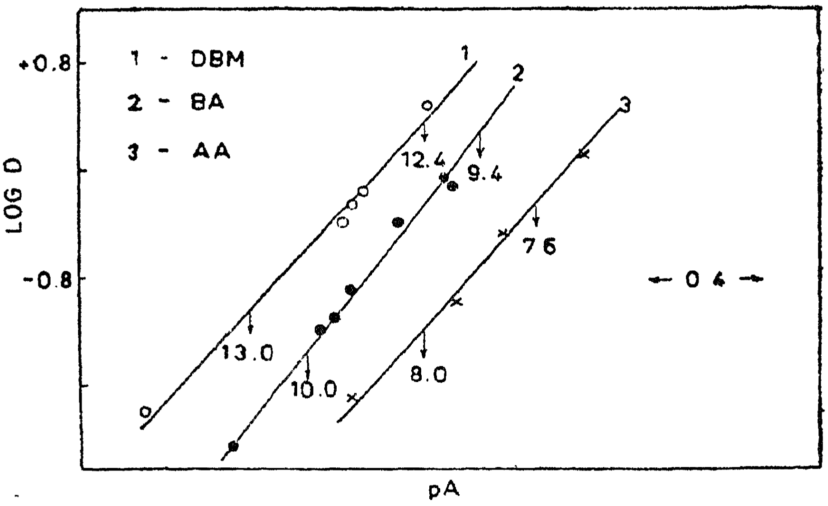

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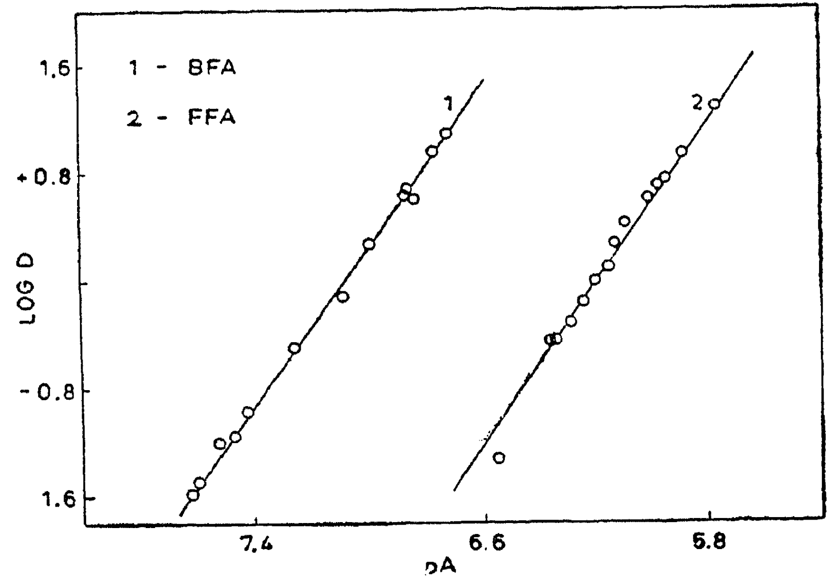


Figure 1. Extraction of indium by β-diketones.

Figure 2. Plot of log D *vs.* pA

by *BFA* and *FFA* has not been studied earlier and hence these systems were studied in detail as a function of pH and the concentration of the β-diketone. The results are shown in figures 1 and 2 where log *D* is plotted as a function of the concentration of the anion, [*A*], of the ligand which was calculated from

$$[A] = K_a \, [HA]_{\text{tot}}/(P_{HA} + 1 \cdot 0) \, [H] \tag{13}$$

where K_a represents the dissociation constant and P_{HA} is the distribution coefficient of the β-diketone.

The slope of the plot is close to three indicating the predominance of a single species, InA_3 and the absence of water soluble complexes. The results are summarised in table 1. It can be seen that the extraction constant increases in the order: $DBM \approx BA < BFA < FFA$ which is also in the order of decreasing pK_a values of the ligands.

Table 1. Equilibrium constants of indium chelates

Equilibrium constant	AA	BA	DBM	BFA	FFA
pK	$8\cdot90^{9,11}$	$8\cdot90^{9,10}$	$9\cdot35^{12}$	$6\cdot30^{13}$	$5\cdot87^{13}$
log P_{HA}	$0\cdot76^{14}$	$2\cdot79^{15}$	$5\cdot35^{13}$	$2\cdot00^{+}$	$1\cdot00^{+}$
$-\log K_{03}$	6·2	6·4	6·4	3·66	2·04

$^{+}$ Present work.

5. Extraction of Mixed Chelates

The extraction of indium in the presence of two β-diketones was also studied. The β-diketones were chosen such that the two ligands were of equal stability or differed considerably in stability, with a view to bring out the effect of the variation in the dissociation constants of the ligands.

COMPLEXES WITH DIFFERENT STABILITY:

5.1 *Indium-BFA (HB)-BA/DBM (HA) system*

As an example of this group, the extraction of indium by a mixture of BFA and BA/DBM was studied at a constant pH as a function of the ratio of the concentrations of BFA and BA or DBM in the organic phase. The function, $D\,[H]^3/[HA]_0^3$ (*i.e.*, F_0 in eqn. 7) was calculated as a function of $[HB]_0/[HA]_0$ (*i.e.*, $[L]$ in equation 7). Typical results obtained in the extraction of indium by BFA and BA are presented in table 2. The plot of log F_0 *vs.* log $[L]$ is presented in figure 3. The equilibrium constants were calculated by a solution of equation 7 by the graphical extrapolation method. The value of K_{03}, being much smaller compared to K_{12}, was taken from the data obtained earlier and hence equation 7 was modified as

$$F_1 = F_0 - K_{03} = K_{12}\,[L] + K_{21}\,[L]^2 + K_{30}\,[L]^3 \qquad (14)$$

and was solved for the other constants by the graphical method (figure 4). The equilibrium constants are listed in table 3. The constants were also calculated using a weighted least square program on Honeywell-400 computer. The variance and the standard deviation 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 indicating the

Table 2. Extraction of indium by BFA and BA in benzene

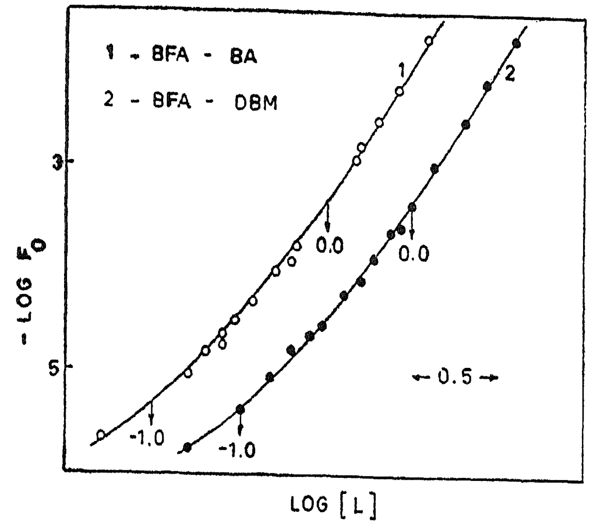
$[BA]_0$ $\times 10^2$ M	$[BFA]_0$ $\times 10^2$ M	$\frac{[BFA]_0}{[BA]_0}$	pH	log D	$-\log \frac{[DH]^3}{[BA]_0^3}$
2·00	0·10	0·05	3·42	−0·49	5·65
2·00	0·30	0·15	3·41	0·12	5·02
2·00	0·40	0·20	3·41	0·34	4·79
2·00	0·50	0·25	3·43	0·57	4·62
2·00	0·60	0·30	3·43	0·68	4·51
2·00	0·75	0·38	3·43	0·88	4·31
2·00	1·00	0·50	3·41	1·10	4·03
2·00	1·25	0·63	3·43	1·27	3·92
0·80	0·20	0·25	3·47	−0·64	4·76
0·60	0·40	0·67	3·42	−0·19	3·78
0·40	0·60	1·50	3·43	0·15	2·95
1·25	2·00	1·60	3·12	0·86	2·79
1·00	2·00	2·00	3·14	0·87	2·55
0·75	2·00	2·67	3·12	0·76	2·23
0·50	2·00	4·00	3·14	0·80	1·72

reliability of the constants obtained. The statistical stability constant, K_{stat}, mixing constant, K_M and the stabilisation constant, K_S are also listed in table 3.

5.2 *Indium-FFA (HB) and BA/DBM (HA)* in *system*

The mixed complexes of indium with FFA and BA or DBM has been studied as an example of the case in which one ligand forms a weaker complex and the other a stronger complex. The extraction was studied at varying concentrations of the two β-diketones and was found to be considerably higher in the presence of FFA and BA/DBM than due to the individual ligands alone. The plot of log F_0 vs log $[L]$ (figure 5) was a curve

(3)



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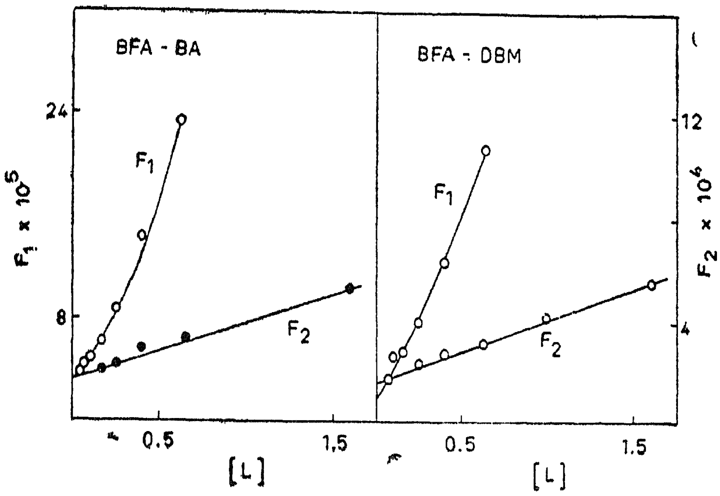


Figure 3. Plot of log F_0 vs log $[L]$.

Figure 4. Plot of F_j functions.

indicating the presence of mixed chelates. The data were analysed both by the graphical (figure 6) and numerical methods taking into account the value of K_{03} obtained from the data on simple complexes for reasons explained earlier. The values of K_M, K_S and the equilibrium constants are listed in table 3. The value of K_{30} obtained from the data on mixed chelates agreed well with that obtained from the data on individual chelates indicating the absence of any interaction and the reliability of the values reported here.

The stabilisation constants for the systems In-FFA-BA/DBM are positive. The values obtained for In-FFA-BA system are comparable to those obtained for In-BFA-β-diketone systems except for In-FFA-DBM chelates. The stability of the mixed chelates are considerably higher than that of DBM or BA complexes and approach nearly the value required on the basis of a statistical distribution of the ligands over the available metal

Table 3. Equilibrium constants of mixed chelates in benzene

System	−log	[Equilibrium constant]		$-\log K_{satt}$	$\log K_M^*$	$\log K_S^*$
		Graphical	Computer			
In–BFA–BA	K_{03}	6·40				
	K_{12}	4·52	4·54	4·96	0·92	0·44
	K_{21}	3·77	3·73	4·09	0·80	0·32
	K_{30}	3·65	3·65			
	K_{03}	6·40				
In–BFA–DBM	K_{12}	4·70	4·65	4·99	0·77	0·29
	K_{21}	3·77	3·84	4·07	0·78	0·30
	K_{30}	3·62	3·60			
	K_{03}	6·40				
In–FFA–BA	K_{12}	3·90	3·86	4·46	1·04	0·56
	K_{21}	2·80	2·90	3·01	0·69	0·21
	K_{30}	2·05	2·02			
	K_{03}	6·40				
In–FFA–DBM	K_{12}	4·30	4·15	4·46	0·84	0·36
	K_{21}	2·98	3·13	3·01	0·51	0·03
	K_{30}	2·05	2·01			
	K_{03}	3·66				
In–FFA–BFA	K_{12}	2·53	2·53	2·64	0·59	0·11
	K_{21}	2·39	2·52	2·10	0·19	−0·29
	K_{30}	2·04	2·00			
	K_{03}	6·40				
In–DBM–BA	K_{12}	5·80	..	5·9	0·6	0·1
	K_{21}	5·80	..	5·9	0·6	0·1

* From graphical values.

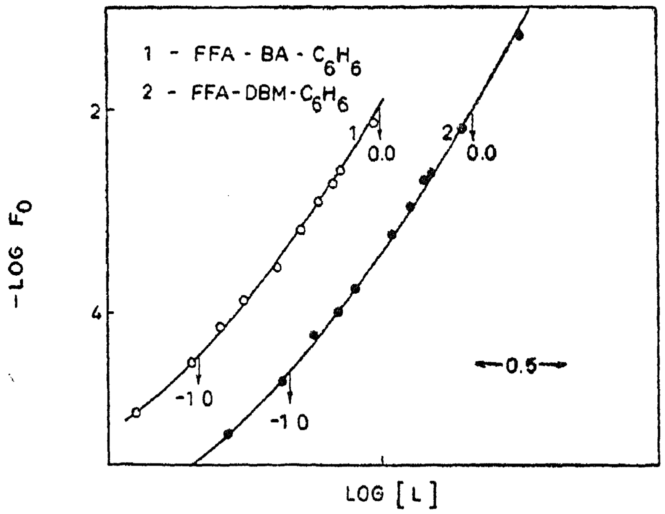
sites. This behaviour is general and is proof for the compatibility of the ligands although their individual extractabilities differ considerably.

COMPLEXES OF EQUAL STABILITY:

5.3 *Indium-FFA-BFA and DBM-BA systems*

The systems In-FFA-BFA and In-DBM-BA were selected as examples of this type where the ligands form chelates of almost equal stability. Experiments were carried out as described earlier. In the case of In-BA-DBM since the extraction in the presence of individual as well as a mixture of the ligands was quite low, the experiments were carried out at a low pH

(5)



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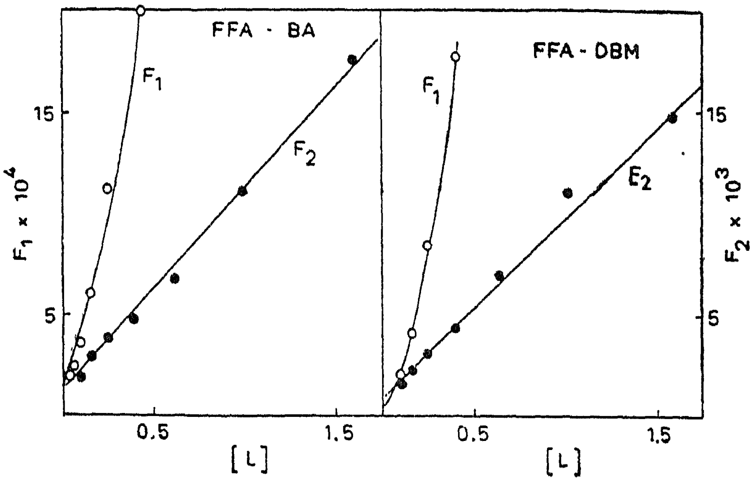


Figure 5. Plot of log F_0 *vs.* log $[L]$.

Figure 6. Plot of F_j functions.

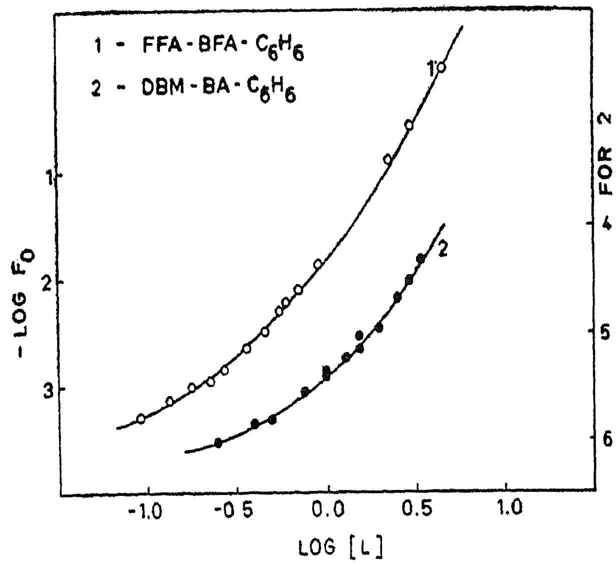
where about 20% of indium was extracted and hydrolysis effects were also negligible. The plot of log D $[H]^3/[HA]_0^3$ vs Log $[L]$ is shown in figure 7. The equilibrium constants were calculated by the graphical method (figure 8) as well as by the method of least squares. In the case of In-BA-DBM since the values of K_{03} and K_{30} were quite small, the function

$$F_0 - K_{03} - K_{30}\,[L]^3 = K_{12}\,[L] + K_{21}\,[L]^2 \qquad (15)$$

was calculated and was solved for the individual constants. The results are given in table 3.

Mixed β-diketones represent the case where the dentricities of the ligands do not change nor is the geometry of the complexes affected by the ligands. In a system where the ligands are comparable in structure but differ in stability as in the extraction of zirconium and hafnium by acetylacetone and trifluoroacetylacetone the stabilisation constants have been found to be small and positive[16]. Similar results have also been observed by Shigematsu

(7)



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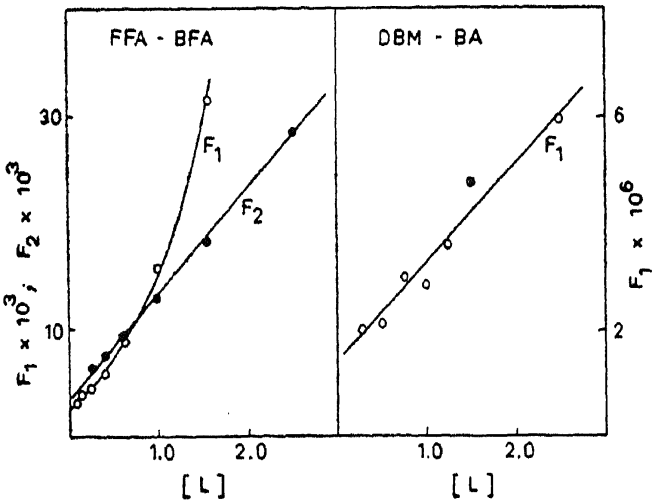

Figure 7. Plot of log F_0 vs. log $[L]$.

Figure 8. Plot of F_j functions.

and Honjyo[3] and the results reported here are in agreement with this general behaviour. The behaviour of mixed chelates with FFA approaches a near statistical behaviour which may be expected as the ligands are sufficiently 'different' and the mixed chelate is not stabilised considerably. On the other hand, the statistical behaviour is observed in the case of systems with more or less equal stability which is consistent with the smaller difference in the $\Delta \log K$ values of the parent complexes.

The extra stabilisation of the mixed chelates may be thought to arise from the π bonding ligands which allow a freer electron flow than in the case of the parent complex. If the two ligands also differ in polarity, the asymmetrical distribution of electron density stabilises the complex especially in a polar solvent. These two effects may be thought to operate in these systems.

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