

Study of mixed chelates of thulium by solvent extraction

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Abstract. Mixed chelates of thulium with some β -diketones like thenoyltrifluoroacetone, benzoyltrifluoroacetone, naphthoyltrifluoroacetone, trifluoroacetylacetone, furolyltrifluoroacetone and dibenzoylmethane have been studied. The nature of the extracted species has been investigated by the method of slope analysis. The statistical stabilisation constants have been evaluated. A linear correlation has been observed between the stability of chelates and properties of the chelating agents.

Keywords. Solvent extraction; thulium; mixed chelates.

1. Introduction

Mixed chelates of thulium with some β -diketones have been studied by the method of solvent extraction. Such studies help in understanding the influence of terminal groups of β -diketones on extraction as well as on the application of statistical theories on the stability of mixed chelates.

2. Experimental

Thulium as Tm-170 was obtained from the Isotope Group, BARC, and was assayed by gamma-ray spectrometry. Benzoyltrifluoroacetone, HBFA, naphthoyltrifluoroacetone, HNTA, thenoyltrifluoroacetone, HTTA, trifluoroacetylacetone, HTFA, furoyltrifluoroacetone, HFTA, and dibenzoylmethane, HDBM, were used as solutions in toluene. The ionic strength was maintained at 1.0 with sodium perchlorate. The pH was adjusted with acetic acid–sodium hydroxide (total concentration ≈ 0.02 M). All experiments were carried out at $30 \pm 2^\circ\text{C}$.

3. Results and discussion

Extraction of thulium by a mixture of β -diketones was studied with a view to investigate the formation of mixed chelates. β -diketones having varying solubilities

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were chosen so that the influence of partition coefficients on the stability of mixed chelates could be studied.

The distribution ratio, D , was measured as a function of the concentration of one β -diketone, keeping that of the other constant at 0.01 M. The pH was maintained constant at about 4.4.

The distribution ratio, D , in presence of a mixture of two β -diketones, HA and HB can be related to the equilibrium constants for the formation of mixed chelates (Malhotra and Sudersanan 1986; Pushparaja and Sudersanan 1981). The equation was solved by a graphical extrapolation method to obtain the various constants. The concentration of the β -diketones in the organic phase was calculated taking into account their partition coefficients (Sekine *et al* 1973). The values of their dissociation constants, pK , and partition coefficients, P_{HA} , are given in table 1.

The results indicated the formation of mixed chelates in all the cases. The values of equilibrium constants for the parent chelates, K_{03} and K_{30} , as well as those for the mixed chelates, K_{12} and K_{21} , were evaluated from the plots of various F_j functions. The plots are not presented for the sake of brevity. The values of various constants are summarized in table 1.

The use of two ligands leads to an enhancement in extraction due to the formation of

Table 1. Values of equilibrium constants.

K_{BA}	$-\log K_{BA}$	$\log P_{HA}$	pK	$\log P_{HA}\beta_{HA}$	X^*	$-\log K_{stat}$	$\log K_S$	$\log K_M$
<i>HBFA (HA)–HNTA (HB)</i>								
K_{03}	8.00	2.66	6.01	18.01	8.67	—	—	—
K_{12}	7.40	3.04	6.10	20.02	9.14	7.39	–0.01	0.47
K_{21}	7.36	3.41	6.19	21.44	9.60	7.25	–0.11	0.37
K_{30}	7.60	3.78	6.28	22.58	10.06	—	—	—
<i>HBFA (HA)–HTTA (HB)</i>								
K_{03}	7.52	2.66	6.01	18.49	8.67	—	—	—
K_{12}	6.39	2.36	6.10	18.99	8.46	6.67	0.28	0.76
K_{21}	6.35	2.05	6.19	18.37	8.24	6.29	–0.06	0.42
K_{30}	6.39	1.73	6.28	17.64	8.01	—	—	—
<i>HBFA (HA)–HFTA (HB)</i>								
K_{03}	7.30	2.66	6.01	18.71	8.67	—	—	—
K_{12}	6.40	2.11	6.07	18.14	8.18	6.51	0.11	0.59
K_{21}	6.55	1.55	6.12	16.46	7.67	6.21	–0.34	0.14
K_{30}	6.39	0.98	6.18	15.09	7.16	—	—	—
<i>HBFA (HA)–HTFA (HB)</i>								
K_{03}	8.19	2.66	6.01	17.82	8.67	—	—	—
K_{12}	7.96	1.83	6.04	15.65	7.87	—	—	—
K_{21}	8.05	0.99	6.06	13.10	7.05	—	—	—
K_{30}	—	0.19	6.09	—	6.24	—	—	—
<i>HDBM (HA)–HBFA (HB)</i>								
K_{03}	—	5.35	9.20	—	14.55	—	—	—
K_{12}	8.30	4.45	8.14	29.47	12.59	—	—	—
K_{21}	7.52	3.55	7.07	24.34	10.62	—	—	—
K_{30}	7.41	2.66	6.01	18.60	8.67	—	—	—

* $X = pK + \log P_{HA}$.

mixed chelates. However, the enhancement is less than that observed in synergistic extraction using a mixture of a β -diketone and a neutral donor. This can be attributed to the formation of adducts in the case of mixtures of β -diketones and donors which have higher stability constants as compared to mixed chelates.

The stabilisation of mixed chelates has been characterised on the basis of certain parameters like statistical stability constant, K_{stat} , stabilisation constant, K_S , and mixing constant, K_M (Marcus and Eliezer 1969; Sudersanan and Sundaram 1975; Pushparaja and Sudersanan 1981). These constants give a measure of the compatibility of the ligands in the inner coordination sphere of the metal ion.

The values of various constants are given in table 1. The values of K_M are greater than unity indicating the compatibility of ligands. The value of $\log K_M$ is in the range of 0.4 ± 0.2 and is close to the value of 0.48 expected on statistical considerations.

Correlations have been observed between the stability constants and pK values of ligands as well as between the partition coefficients of the chelates and chelating agents. A correlation between the two-phase stability constant $P_N\beta_N$ and $[pK + \log P_{HA}]$ have been observed for some systems (Pushparaja and Sudersanan 1981; Malhotra and Sudersanan 1986). The validity of this relation has been extended to the mixed chelates of thulium. The mixed chelate was thought to be derived from a hypothetical ligand whose partition coefficient and dissociation constant were considered to be the geometric mean of those of parent chelating agents. The values of $P_N\beta_N$ were calculated from the equilibrium constants and are summarised in table 1. A good correlation was observed for both binary and mixed chelates and all the data fitted into a single straight line. This indicates that the stability of a chelate is determined by those of the participating ligands. A value of 2.4 was obtained for the slope which can be interpreted as the ratio of the molar volumes of the chelates and the chelating agents. In the studies reported here, the pK values of the ligands are nearly the same, while there is a large variation in the partition coefficients. Consequently, the effects on $P_N\beta_N$ reflects the change in the values of P_N rather than on the stability constants. The interpretation of the results on the basis of molar volumes is therefore more appropriate.

References

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