

Study on Complex Formation Equilibria of Tervalent Lanthanons with Fluorinated β -Ketoesters in Aqueous Dioxane Medium

J. P. Shukla^{1,*} and R. S. Sharma²

¹ Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India

² Reactor Chemistry Section/RSMD/RG, CIRUS, BARC, Bombay-400085, India

Summary. The thermodynamic stepwise formation constants ($\log^T K_n$) of nine trivalent lanthanons (La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} and Lu^{3+}) with three fluorinated β -ketoesters (methyltrifluoroacetoacetate, ethyltrifluoroacetoacetate, and ethylpentafluoropropionylacetate) have been evaluated potentiometrically in a 50% dioxane–water mixture at 25 and 35 ± 0.01 °C. The values of $\log^T K_n$ do not follow a linearity when plotted against Z/r and invariably obey the sequence: $\text{La}^{3+} < \text{Nd}^{3+} < \text{Pr}^{3+} < \text{Sm}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+} < \text{Dy}^{3+} \leq \text{Er}^{3+} \leq \text{Lu}^{3+}$ in all instances. The standard thermodynamic parameters (ΔG_1^0 , ΔH_1^0 , ΔS_1^0) associated with $\log^T K_n$ have also been calculated. The validity of the chosen equilibrium model was examined by an error analysis using S_{\min} values (sum of the squared residuals), scatter plots, and slopes and intercepts of Abrahams–Kave type normal probability plots.

Keywords. Complexation; Formation constant; Lanthanons; β -Ketoesters; Activity coefficients; Speciation.

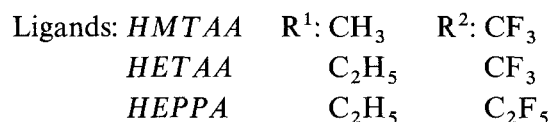
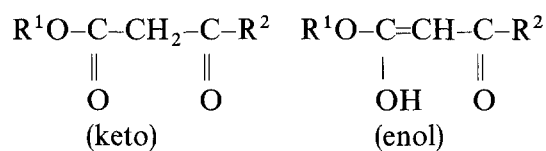
Komplexbildungsgleichgewichte von dreiwertigen Lanthanoiden mit fluorierten β -Ketoestern in wäßrigem Dioxanmedium

Zusammenfassung. Es wurden die thermodynamischen stufenweisen Komplexbildungskonstanten ($\log^T K_n$) von 9 dreiwertigen Lanthanoiden (La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} und Lu^{3+}) mit drei fluorierten β -Ketoestern (Methyltrifluoracetoacetat, Ethyltrifluoracetoacetat und Ethylpentafluoropropionylacetat) in 50% Dioxan-Wasser bei 25 und 35 ± 0.01 °C potentiometrisch bestimmt. Die Werte für $\log^T K_n$ ergeben keine lineare Abhängigkeit gegenüber Z/r , sie gehorchen stets der Reihenfolge: $\text{La}^{3+} < \text{Nd}^{3+} < \text{Pr}^{3+} < \text{Sm}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+} < \text{Dy}^{3+} \leq \text{Er}^{3+} \leq \text{Lu}^{3+}$. Die thermodynamischen Standardparameter ΔG_1^0 , ΔH_1^0 und ΔS_1^0 wurden ebenfalls berechnet. Die Gültigkeit des gewählten Gleichgewichtsmodells wurde unter Verwendung der Summe der Quadratreste (S_{\min}), von Streukurven und Steigung/Ordinatenabschnitt der Normalwahrscheinlichkeitsdarstellung nach Abrahams–Kave untersucht.

Introduction

β -Ketoesters represent a special class of β -dicarbonyl compounds containing carbonyl groups in β position i.e. separated by one methylene group. Similarity in donor sites of these compounds to that of β -diketones provides some interesting

comparisons. It is surprising that the β -ketoesters, which may have similar applications, stand largely neglected. Therefore, while studying a host of dicarbonyl compounds for their interaction with lanthanons we now report the thermodynamic formation constants, $\log^T k_n$, of three fluorinated β -ketoesters namely methyltrifluoroacetoacetate (*HMTAA*), ethyltrifluoroacetoacetate (*HETAA*) and ethylpentafluoropropionylacetate (*HEPPA*) with La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} and Lu^{3+} . The $\log^T k_n$ values were determined by potentiometry in a 50 vol. % dioxane–water mixture at 25° and 35 °C. Most interestingly, these compounds have found immense applications particularly in the synthesis of various pharmacological and herbicidal agents [1–3]. For a rational application of such ketoesters in analytical chemistry, a quantitative knowledge of the stabilities of their chelates with various metal ions seems to be rather inevitable.



Lanthanons are known to possess an extra affinity for the ligands containing oxygen donor atoms and more so with dicarbonyl compounds. On this basis, lanthanons have been classified as “*hard acids*” or acceptors [4]. No attempt appears to have been made to study the interaction of these oxodonor ligands with lanthanons. Therefore, as a prelude to our studies on the solvent extraction properties of these compounds with lanthanons, it was imperative to assess $^T K_n$ of their chelate species. The aquo-organic solvent medium was chosen for this work owing to insufficient solubility of β -ketoesters and their resulting metal chelates in pure aqueous medium.

Experimental Part

A Beckmann Research *pH*-meter, in conjunction with a glass combination electrode (0–14 *pH* range) was used for all *pH* measurements. This *pH*-meter could be read up to 0.002 units of *pH*. The *pH*-meter was standardized with phthalate and phosphate buffers before performing any titration.

Perchlorate solutions of lanthanons were prepared from A.R. grade metal oxides (Alfa Germany). Working solutions were made from stock solutions by dilution (usually 2 mM). The concentration of lanthanon was determined by titration with *EDTA* using xylenol orange as the indicator and hexamethyltetramine as buffer. Free perchloric acid in the metal perchlorate solutions was estimated following Gran's method [5]. β -Ketoesters were procured from K & K lab USA and used as such. The solutions of known tetraethylammonium hydroxide (*TEAH*) concentrations were prepared in appropriate dioxane–water mixtures. All other chemicals used were of A.R. or G.R. grade. *p*-Dioxane was purified as recommended [6].

Titration Procedure

The general procedure involved the titration of following solution against 0.1M *TEAH* in a thermostated double walled titration vessel maintained within ± 0.01 °C by circulating water of

constant temperature through the annular space of reaction vessel:

- i) β -ketoester, 0.01 M;
- ii) metal ion solution, 0.002 M;
- iii) perchloric acid, as per requirement.

All titrations were repeated at least twice and the agreement between the pH -readings of the different titrations was usually within ± 0.02 pH -units. The solutions were stirred continuously with a magnetic stirrer.

Titrations were made at different metal to ligand ratios to show that no polynuclear species were formed at pH -regions where the titrations were made. No complications arose from hydrolysis of the central ion. It is easily seen from the magnitude of the formation constants and the pH of the solution that hydrolysis is completely negligible for all the systems investigated here.

Thermodynamic proton ionization constants were determined under identical conditions in the absence of metal ion and perchloric acid [7].

Calculations

The pH -meter readings (B) were converted to pH using the Van Uitert and Hass equation (1) [8]

$$pH = B + \log U_{\text{H}}^0 + \log(1/\gamma_{\pm}) \quad (1)$$

The values of correction factor $\log U_{\text{H}}^0$, were taken from literature [9] and those of the mean activity coefficient $\log(1/\gamma_{\pm})$ were computed by equation (2) [10]

$$\log(1/\gamma_{\pm}) = \left[\frac{|Z_1 Z_2| 1.29 \cdot 10^{-6} \sqrt{2\mu}}{(\epsilon T)^{3/2}} \right] \left/ \left[1 + \frac{(35.56 \text{ \AA} \sqrt{2\mu})}{(\epsilon T)^{1/2}} \right] \right. \quad (2)$$

where μ is the ionic strength, T is the absolute temperature, Z_1 , Z_2 are charges on the positive and negative ions, and \AA is the mean ionic diameter in \AA (taken as 10\AA [11]). The value of dielectric constant, ϵ , of 50 vol% dioxane–water was calculated from the procedure of Harned et al. [12].

A computer program TITRE was written in Fortran-77 for evaluating $\log^T K_n$ of mono nuclear complexes from the potentiometric data. TITRE incorporates a slightly modified weighted linear least-squares method of Schaefer [13]. Since the titrations were not carried out at fixed ionic strength, formation constants were corrected due to changes in the ionic strength. Therefore, the ionic strength of the titre was calculated at each point and activity coefficients were calculated using Eq. (2). Activity coefficient corrections were directly applied to the linear equations following the algorithm suggested by Nancollas [14]. The realistic estimates of standard deviation (esd) of $\log^T K_n$ were obtained by multiplying the standard deviation values of least-squares refinements with the factors proposed by Avdeef et al. [15]. These factors arise from the uncertainties in activity coefficients, junction potentials, buffer pH values and other unavoidable systematic errors.

Abrahams–Keve type normal probability curves [16] were drawn by plotting the computed probability (using a NAGLIB Fortran library) versus that obtained experimentally. Any systematic experimental error would be shown by the slopes and intercepts of these curves. For an ideal experiment, slope and intercept ought to approach unity and zero, respectively. The ligand number (\bar{n}) values were calculated from the final refined ${}^T\beta_n$ values as follows:

$$\bar{n} = \frac{\sum n^T \beta_n l^n}{\sum {}^T \beta_n l^n} \quad (3)$$

where l denotes the activity of ligand anion i.e. $L^- \cdot \gamma_L$. The experimental \bar{n} values were computed from the analytical concentrations using the relation:

$$\bar{n} = \frac{T_L - HL - l}{T_M} \quad (4)$$

here T_L , T_M and HL denote the total ligand concentration, total metal concentration and undissociated β -ketoester, respectively.

Results and Discussion

HMTAA, *HETAA*, and *HEPPA* behave as weak monoprotic acids and their $^T pK_a$ increase in the order: *HEPPA* < *HMTAA* < *HETAA* which is as expected from the terminal group substituents [7]. Tables 1–3 summarize the $\log^T K_n$ data calculated for these β -ketoesters with the trivalent lanthanons. The quantities given along with $\log^T K_n$ values in Tables 1–3 are the *esds* of these values. The very small systematic error in the selected equilibrium models can be seen from Abrahams–Keve type normal probability plots (Fig. 1) (for brevity the normal probability plot is shown for the La^{3+} -*HMTAA* system only). However, these systematic effects appear to be negligible since slopes and intercepts of such plots are not very far from the expected values, i.e. 1 and 0, and also the goodness-of-fit can easily be judged from considerably smaller values of S_{\min} (least-squares). The $\log^T K_1$ values of these ligands follow the sequence of their basicities. Generally, values of $\log^T K_1 > \log^T K_2 > \log^T K_3$ have been observed for all lanthanon-diketoesters studied. An interesting observation for the Ln^{3+} -*HEPPA* system is the magnitude of $\log^T K_2$,

Table 1. Stepwise formation constants of trivalent lanthanon complexes of *HMTAA* in a 50 vol% dioxane–water mixture

Ln^{3+}	Temp. (°C)	Weighted least-squares			NPP ^a		S_{\min}
		$\log^T K_1$	$\log^T K_2$	$\log^T K_3$	Slope	Intercept	
H^+	25	8.48 ± 0.02					
	35	8.27 ± 0.01					
La (4f ⁰)	25	5.34 ± 0.01	4.64 ± 0.01	3.98 ± 0.02	0.98	+0.001	6.31E-6
	35	5.10 ± 0.01	4.44 ± 0.02	3.01 ± 0.03	0.97	+0.002	3.37E-6
Pr (4f ²)	25	5.50 ± 0.03	4.81 ± 0.03	4.24 ± 0.04	0.93	+0.004	6.31E-6
	35	5.48 ± 0.01	4.78 ± 0.01	4.04 ± 0.02	1.00	−0.006	4.16E-6
Nd (4f ³)	25	5.28 ± 0.03	4.79 ± 0.04	4.42 ± 0.04	1.01	−0.002	1.10E-5
	35	5.26 ± 0.02	4.65 ± 0.03	4.14 ± 0.04	0.97	+0.079	1.44E-5
Sm (4f ⁵)	25	5.68 ± 0.01	5.03 ± 0.02	4.25 ± 0.04	0.99	+0.001	2.18E-5
	35	5.49 ± 0.01	4.93 ± 0.02	4.09 ± 0.03	1.01	+0.000	2.70E-5
Eu (4f ⁶)	25	6.00 ± 0.01	5.17 ± 0.01	4.37 ± 0.02	0.96	+0.000	6.87E-6
	35	5.76 ± 0.01	5.08 ± 0.02	4.11 ± 0.02	1.00	+0.000	9.95E-6
Gd (4f ⁷)	25	5.99 ± 0.01	5.10 ± 0.02	4.46 ± 0.02	0.94	+0.001	1.35E-5
	35	5.70 ± 0.01	4.97 ± 0.01	4.07 ± 0.01	0.92	+0.000	9.33E-6
Dy (4f ⁹)	25	6.03 ± 0.01	5.14 ± 0.01	3.87 ± 0.02	0.90	+0.025	1.25E-5
	35	5.95 ± 0.01	5.03 ± 0.03	3.70 ± 0.03	1.00	+0.007	3.17E-6
Er (4f ¹¹)	25	6.03 ± 0.02	5.10 ± 0.03	3.86 ± 0.03	0.93	+0.095	1.78E-5
	35	5.93 ± 0.02	5.09 ± 0.02	3.77 ± 0.04	0.92	+0.075	6.64E-6
Lu (4f ¹⁴)	25	6.07 ± 0.02	5.14 ± 0.02	3.91 ± 0.03	0.98	+0.000	9.59E-6
	35	5.96 ± 0.02	5.13 ± 0.02	3.77 ± 0.01	0.97	+0.004	5.72E-6

^a NPP Normal probability plots

Table 2. Stepwise formation constants of trivalent lanthanon complexes of *HETAA* in a 50 vol% dioxane–water mixture

Ln^{3+}	Temp. (°C)	Weighted least-squares			NPP ^a		S_{\min}
		$\log^T K_1$	$\log^T K_2$	$\log^T K_3$	Slope	Intercept	
H^+	25	8.79 ± 0.01					
	35	8.49 ± 0.01					
La (4f ⁰)	25	5.39 ± 0.02	4.88 ± 0.02	4.23 ± 0.03	0.99	+0.001	4.25E-6
	35	5.31 ± 0.03	4.80 ± 0.04	4.09 ± 0.04	1.00	+0.104	9.93E-6
Pr (4f ²)	25	5.56 ± 0.02	5.15 ± 0.03	4.31 ± 0.03	1.01	-0.054	7.35E-6
	35	5.37 ± 0.02	5.02 ± 0.02	4.22 ± 0.02	1.00	+0.114	6.00E-6
Nd (4f ³)	25	5.49 ± 0.02	5.03 ± 0.03	4.84 ± 0.04	1.00	-0.014	7.20E-6
	35	5.36 ± 0.03	4.95 ± 0.04	4.53 ± 0.04	1.01	+0.069	1.34E-5
Sm (4f ⁵)	25	5.98 ± 0.03	5.24 ± 0.04	4.48 ± 0.05	0.96	-0.002	1.92E-5
	35	5.60 ± 0.03	5.19 ± 0.04	4.31 ± 0.04	1.00	+0.028	2.71E-5
Eu (4f ⁶)	25	6.03 ± 0.02	5.35 ± 0.02	4.50 ± 0.02	1.01	+0.007	6.01E-6
	35	5.65 ± 0.02	5.29 ± 0.03	4.27 ± 0.03	1.02	+0.002	6.96E-6
Gd (4f ⁷)	25	6.01 ± 0.03	5.31 ± 0.04	4.69 ± 0.05	0.98	-0.029	1.13E-5
	35	5.64 ± 0.02	5.24 ± 0.03	4.34 ± 0.03	1.00	+0.092	1.02E-5
Dy (4f ⁹)	25	6.20 ± 0.02	5.37 ± 0.02	4.20 ± 0.03	1.00	+0.036	9.14E-6
	35	6.02 ± 0.02	5.30 ± 0.02	3.83 ± 0.02	0.99	-0.067	6.95E-6
Er (4f ¹¹)	25	6.14 ± 0.02	5.29 ± 0.02	4.14 ± 0.02	0.97	+0.006	7.37E-6
	35	6.00 ± 0.02	5.22 ± 0.02	3.88 ± 0.02	0.99	+0.275	6.14E-6
Lu (4f ¹⁴)	25	6.15 ± 0.02	5.33 ± 0.02	4.06 ± 0.03	0.97	+0.076	7.56E-6
	35	6.01 ± 0.02	5.28 ± 0.03	3.84 ± 0.03	0.97	+0.221	8.29E-6

^a NPP Normal probability plots

which is almost equal to that of $\log^T K_1$ in all the cases, whereas $\log^T K_2$ values are smaller than $\log^T K_1$ by 0.8 or 0.6 units of log for the other two ligand systems. Probably, the weaker binding between lanthanons and the $EPPA^-$ anion results in a higher dipole on $Ln(EPPA)^{2+}$ as compared with $Ln(MTAA)^{2+}$ and $Ln(ETAA)^{2+}$. The stability of the second complex of the lanthanons and *HEPPA*, therefore, increases and gives rise to the observed result, namely $\log^T K_1 \approx \log^T K_2$ whereas the $\log^T K_1$ and $\log^T K_2$ of the complexes of *HMTAA* and *HETAA* differ by almost one log unit. The fact that the average values for $\log^T K_1/T K_2$ are about 0.75, 0.59, and 0.15 for *HMTAA*, *HETAA*, and *HEPPA* complexes respectively, and those of $\log^T K_2/T K_3$ are 0.94, 0.91, and 0.74, reflects some destabilization of 1:3 (metal to ligand) species as a consequence of steric crowding of the ligand anions about the Ln^{3+} ions.

Dutt et al. [17] failed to detect 1:2 and higher complex species for Ln^{3+} -ethylacetoacetate (*HEAA*, a typical β -ketoester) in a 75 vol% acetone–water mixture and the value of \bar{n} hardly crossed beyond 0.6 as opposed to 2.2 as the highest \bar{n} value obtained for Ln^{3+} -*HETAA* complexes in the present work. These authors ascribed lower \bar{n} values to the steric factors and concluded the existence of 1:1 complex as the highest species formed by isolating $Ln(OH) \cdot (H_2O) \cdot (EAA)$ type of solid complexes [18]. The absence of 1:2 and 1:3 species for *HEAA* could be accounted

Table 3. Stepwise formation constants of trivalent lanthanon complexes of HEPPA in a 50 vol% dioxane–water mixture

Ln^{3+}	Temp. (°C)	Weighted least-squares			NPP ^a		S_{\min}
		$\log^T K_1$	$\log^T K_2$	$\log^T K_3$	Slope	Intercept	
H ⁺	25	7.39 ± 0.02					
	35	7.16 ± 0.01					
La (4f ⁰)	25	5.29 ± 0.03	5.06 ± 0.04	4.56 ± 0.05	0.99	+0.149	7.25E-6
	35	5.37 ± 0.02	5.07 ± 0.03	4.66 ± 0.03	0.98	+0.252	4.97E-6
Pr (4f ²)	25	5.35 ± 0.05	5.24 ± 0.06	4.85 ± 0.05	1.00	+0.115	1.72E-6
	35	5.41 ± 0.03	5.28 ± 0.04	4.89 ± 0.04	1.00	+0.100	1.45E-5
Nd (4f ³)	25	5.36 ± 0.03	5.24 ± 0.04	4.97 ± 0.01	1.00	+0.043	1.38E-5
	35	5.41 ± 0.03	5.25 ± 0.04	5.01 ± 0.05	0.99	+0.040	1.44E-5
Sm (4f ⁵)	25	5.77 ± 0.04	5.74 ± 0.04	5.21 ± 0.04	1.00	+0.181	1.55E-5
	35	5.82 ± 0.04	5.77 ± 0.05	5.23 ± 0.06	0.97	+0.167	1.87E-5
Eu (4f ⁶)	25	5.80 ± 0.03	5.79 ± 0.04	4.94 ± 0.03	0.93	+0.367	1.30E-5
	35	5.83 ± 0.03	5.82 ± 0.03	4.98 ± 0.04	0.94	+0.266	1.26E-5
Gd (4f ⁷)	25	5.73 ± 0.04	5.68 ± 0.04	4.45 ± 0.06	0.96	+0.311	2.04E-5
	35	5.71 ± 0.04	5.64 ± 0.04	4.46 ± 0.05	0.98	+0.250	1.87E-5
Dy (4f ⁹)	25	6.04 ± 0.03	5.98 ± 0.04	5.17 ± 0.03	0.98	+0.271	1.22E-5
	35	6.16 ± 0.02	5.74 ± 0.02	4.83 ± 0.04	0.95	+0.350	9.94E-6
Er (4f ¹¹)	25	5.90 ± 0.04	5.87 ± 0.05	4.59 ± 0.07	0.91	+0.391	2.02E-5
	35	6.05 ± 0.03	5.62 ± 0.04	4.54 ± 0.06	0.93	+0.415	1.16E-6
Lu (4f ¹⁴)	25	5.93 ± 0.05	5.91 ± 0.06	4.89 ± 0.05	1.00	0.141	2.38E-5
	35	6.15 ± 0.02	5.74 ± 0.02	4.81 ± 0.04	0.86	0.058	5.82E-6

^a NPP Normal probability plots

for by the very high basicity of this ligand ($TpK_a = 14$) and the nature of the solvent medium (acetone–water).

Figures 2–4 depict plots of $\log^T K_1$ values of Ln^{3+} -ketoester complexes as a function of Z/r , where Z, r are the ionic charge and cation radius, respectively. The patterns of these plots are not suggestive of any regularity but generally an increasing trend of the $\log^T K_1$ versus Z/r plot is indicative of a predominantly ionic nature of bonding between lanthanons and the β -ketoesters. Several complexing systems have been shown to have such mode of irregular variation in the relation between $\log K_1$ and the atomic number of lanthanide elements [19, 20]. Several attempts have been made to theorize the occurrences of such irregularities of $\log K_m$, which seek to propose its dependence on: (i) change in hydration number at a particular stage, (ii) total orbital angular momentum i.e. “*inclined W*” hypothesis [21], and (iii) change in coordination number [22]. None of these explanations seem to be yet fully acceptable [23]. Williams [24] has recently pointed out that the variation in ionic radii is basically a ligand effect, therefore the angular term of the ligand field is perhaps of smaller consequence than the radial terms. If it is so, the electron–electron repulsions should cause an uneven decrease in the ionic radii of lanthanons and this may lead to the occurrence of irregularities of such plots. This phenomenon ought to correlate closely with the changes in magnetic quantum

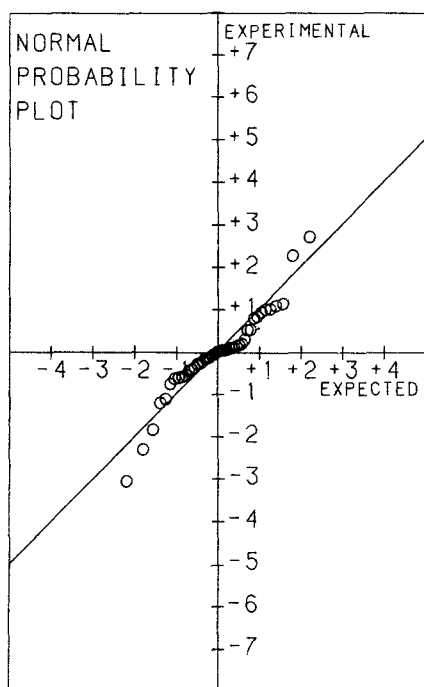


Fig. 1. Abrahams-Keve type normal probability plot for the La^{3+} -HMTAA complex in 50 vol% dioxane-water mixture at 25°C

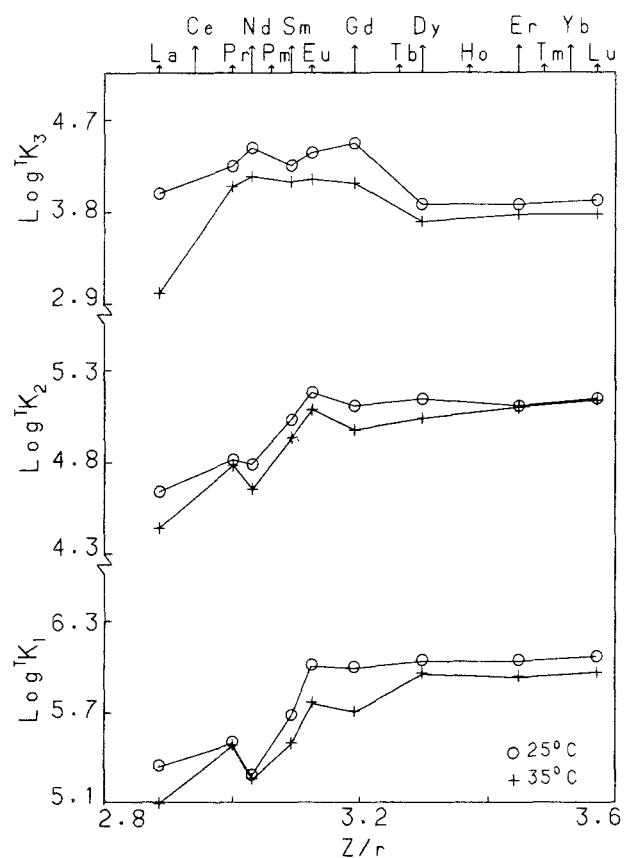


Fig. 2. Plots of $\log^T K_n$ against Z/r for Ln^{3+} -HMTAA complexes in 50 vol% dioxane-water mixture at 25° and 35°C

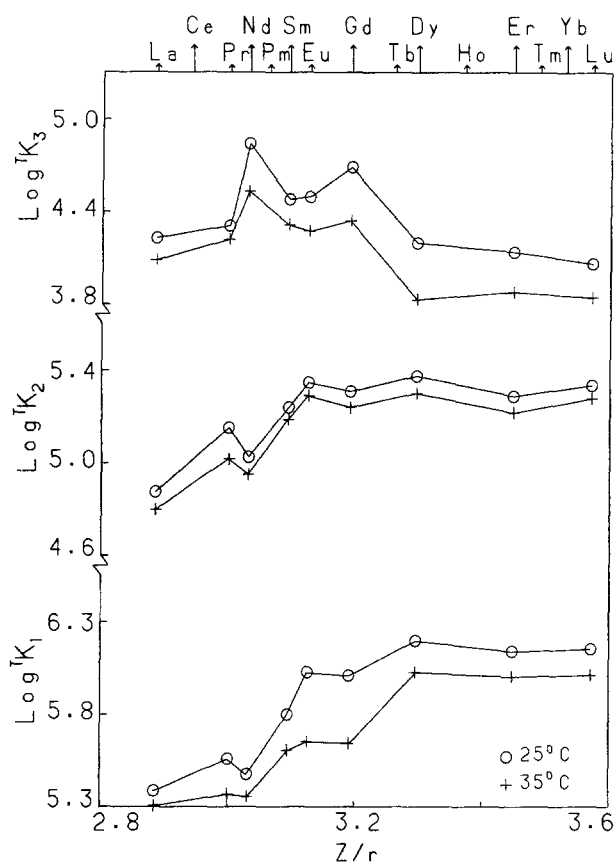


Fig. 3. Plots of $\log^T K_n$ against Z/r for Ln^{3+} -HETAA complexes in 50 vol% dioxane-water mixture at 25° and 35°C

number although the energetics of complexation are not related to magnetic energies.

Thermodynamic Parameters

Table 4 reports the data on the thermodynamic parameters ΔG_1^0 , ΔH_1^0 , and $T\Delta S_1^0$ calculated for $\log^T K_1$ only. The standard thermodynamic parameters for chelation were computed using following equations:

$$\Delta G_1^0 = -2.303 RT \log^T K_n \quad (5)$$

$$\Delta H_1^0 = 176.06 (\log^T K_1^{308} - \log^T K_1^{298}) \quad (6)$$

$$T\Delta S_1^0 = \Delta H_1^0 - \Delta G_1^0 \quad (7)$$

The negatively increasing magnitude of ΔG_1^0 across the lanthanons further testifies the electrostatic nature of the bond between Ln^{3+} -diketoesters studied here (Table 4). The exothermic mode of complexation is revealed by the invariably negative values of ΔH_1^0 for Ln^{3+} -HETAA and HMTAA systems which are in contrast to the generally positive (endothermic) values obtained for Ln^{3+} -HEPPA systems. In the former case, the energy required to break the bond between water molecules and Ln^{3+} is relatively less than the energy released upon complexation with the β -ketoester anion. The large positive enthalpy values are not characteristic

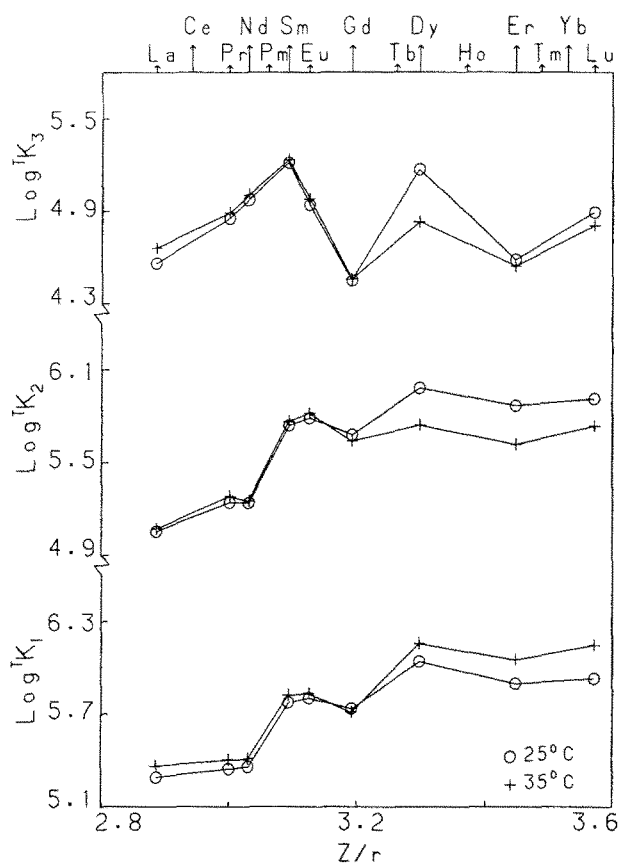


Fig. 4. Plots of $\log^T K_n$ against Z/r for Ln^{3+} -HEPPA complexes in 50 vol% dioxane-water mixture at 25° and 35°C

of chelate formation by a bidentate oxodonor (hard donor) with hard acceptors like lanthanons in aqueous medium [4]. Nevertheless, such observations have been made by many workers in aquo-organic solvent media [25–27] and the following possibilities have been suggested for these anomalies: (i) the presence of a non-polar organic component like dioxane decreases the dielectric constant of the medium, therefore the stability of the complex is increased due to increased electrostatic attraction between cations and ligand anions, and (ii) solvation of metal ions and ligand anions would be less in the mixture and hence less energy would be needed to rupture the small solvation sphere.

Positive ΔH_1^0 values obtained for HEPPA chelates are expected from its relatively weak bonding to lanthanons. The lower stability of Ln^{3+} -HEPPA complexes compared to that of the other two ligands can be attributed to its lowest $T_p K_a$ value. Therefore, the energy used for removing water molecules from the coordination sphere is much more than the energy released upon the weak bonding of the first HEPPA ligand anion.

Both positive and negative values of ΔS^0 obtained here and expected considering the following processes: (i) extent of solvation of reactants, (ii) solute solvent interactions (constructive or destructive), (iii) negative contribution to entropy arising from the loss of rotational entropy of the donor base molecule upon complexation, (iv) number of water molecules released from the solvation sphere, (v) negative entropy gain by binding of a ligand via water molecules, and (vi) binding

Table 4. Thermodynamic functions (ΔG_1^0 , ΔH_1^0 , $\Delta S_1^0/\text{kJ mol}^{-1}$) of lathanon- β -ketoester complexes in a 50 vol% dioxane-water mixture

Ln^{3+}	ΔG_1^0		ΔH_1^0	$T\Delta S_1^0$	
	25°	35°		25°	35°
<i>HETAA</i>					
La	-30.93	-31.48	-14.33	16.60	17.15
Pr	-31.91	-31.85	-33.79	-1.88	-1.94
Nd	-31.43	-31.77	-21.41	10.03	10.36
Sm	-33.27	-33.24	-34.14	-0.87	-0.90
Eu	-34.59	-33.52	-66.34	-31.75	-32.81
Gd	-34.47	-33.46	-64.57	-30.10	-31.10
Dy	-35.56	-35.74	-30.25	5.31	5.49
Er	-35.23	-35.59	-24.24	10.99	11.36
Lu	-35.31	-35.65	-25.12	10.19	10.53
<i>HMTAA</i>					
La	-30.66	-30.25	-42.81	-12.15	-12.56
Pr	-31.55	-32.49	-3.54	28.01	28.95
Nd	-30.31	-31.17	-4.42	25.88	26.75
Sm	-32.57	-32.58	-32.37	0.20	0.21
Eu	-34.46	-34.16	-43.34	-8.88	-9.18
Gd	-34.38	-33.81	-51.13	-16.75	-17.31
Dy	-34.63	-35.29	-15.04	19.60	20.26
Er	-34.63	-35.16	-18.93	15.71	16.23
Lu	-34.82	-35.37	-18.57	16.25	16.79
<i>HEPPA</i>					
La	-30.37	-31.83	13.27	43.64	45.10
Pr	-30.68	-32.07	10.79	41.47	42.86
Nd	-30.76	-32.10	9.20	39.96	41.30
Sm	-33.14	-34.53	8.31	41.45	42.84
Eu	-33.30	-34.61	5.84	39.14	40.45
Gd	-32.90	-33.87	-3.89	29.01	29.98
Dy	-34.66	-36.52	20.70	55.36	57.22
Er	-33.84	-35.90	27.42	61.26	63.32
Lu	-34.03	-36.45	38.21	72.24	74.67

to Ln^{3+} ions at more than one place by the bidentate ligands like β -ketoesters would result in positive entropy by displacement of two water molecules.

Speciation

The equilibrium speciation curves were computed using the COMICS [28] program. The $T\beta_n$ values, obtained by least-squares method, were fed as input data. The concentrations of the metal containing species thus obtained were normalized with respect to total metal concentration and then converted to percentage formation. A typical depiction for La^{3+} -*HMTAA* speciation is given for brevity in Fig. 5. It

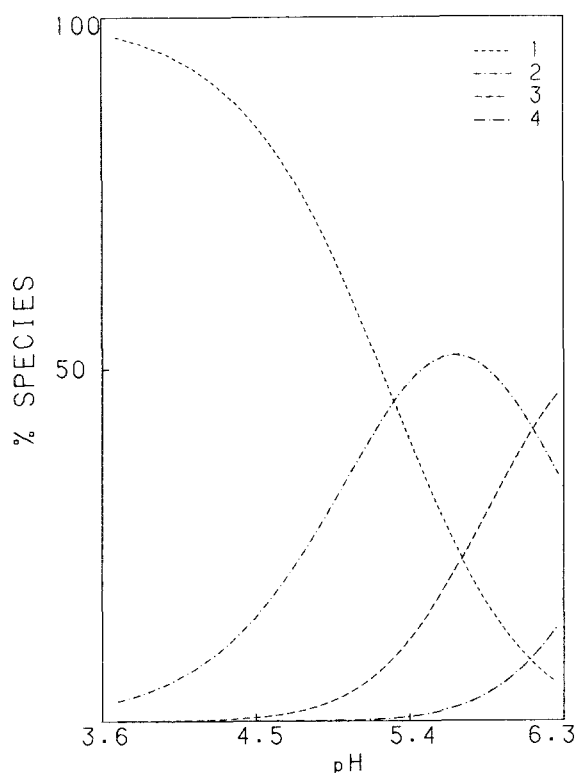


Fig. 5. Speciation diagrams for La^{3+} - HMTAA complexes in 50 vol% dioxane-water mixture at 25°C : (1) La^{3+} , (2) $\text{La}(\text{MTAA})_2^{2+}$, (3) $\text{La}(\text{MTAA})_2^+$, and (4) $\text{La}(\text{MTAA})_3$

may be noted from this figure that the formation of ML_1^{2+} species occurs through the entire pH range of titration and approaches its maximum value (52%) at 5.63 pH . The formation of the M^{3+} , ML_1^{2+} , ML_2^+ , and ML_3 species at 6.3 pH , at which the titration was curtailed, are 4.7%, 33.4%, 47.3%, and 14.6%, respectively. The most important observation is the relatively higher degree of neutral complex, LaL_3 , formation by HEPPA at a pH ca.4.56 (cut off pH for La^{3+} - HEPPA) among all the three ligands. The percentages of $\text{La}(\text{MTAA})_3$, $\text{La}(\text{ETAA})_3$ and $\text{La}(\text{EPPA})_3$ at 4.56 pH being 0.007, 0.01 and 16.6, respectively. Naturally, HEPPA has an edge over other two ligands for a chelate extraction process.

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