

Thermodynamic parameters and stability constants of some trivalent lanthanide complexes of 1-(3-aryl-5-hydroxy 4-isoxazolylazo) 4-sulphonic acids

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Abstract. The stability constants of some trivalent lanthanide chelates of 1-(3-aryl-5-hydroxy 4-isoxazolylazo) 4-sulphonic acid (PHI-4S) and its substituents have been carried out by potentiometric and spectrophotometric methods. The results indicated the formation of 1:1 and 1:2 complexes with an order: Yb(III) > Y(III) > Gd(III) > Dy(III) > Tb(III) > Sm(III) > Nd(III) > Pr(III) > La(III). The stabilities increase with a decrease in the ionic or crystal radii [except a small break at Gd(III)], indicates the absence of extensive covalent bonding due to the non-availability of 4f-orbitals for bond formation. Structure-reactivity relationships of complex formation have been discussed by Hammett's and Irving-Rossotti theories. Thermodynamic parameters have been discussed in terms of iso-equilibrium relationship.

Keywords. Trivalent lanthanide complexes; 1-(3-aryl 5-hydroxy 4-isoxazolylazo) 4-sulphonic acids; substituent effect; isoequilibrium temperature.

1. Introduction

We have earlier reported the synthesis, characterisation and dissociation constants of 1-(3-phenyl 5-hydroxy 4-isoxazolylazo) 4-sulphonic acid (PHI-4S) and its substituents (Nagarjun Rao 1985; Nagarjun Rao *et al* 1988). During the past few decades, the formation of trivalent lanthanide complexes with a variety of nitrogen and oxygen heterocyclics have been explored by several workers (Garg *et al* 1982; Omprakash *et al* 1982, 1985). However, such studies are scarce with PHI-4S compounds. In continuation of our studies on the formation of metal chelates (Nagarjun Rao 1985) of PHI-4S ligands with a variety of metal ions we present the stability constants and thermodynamic parameters of some trivalent lanthanide complexes of PHI-4S in this paper.

2. Experimental

The chemicals employed are of either BDH or E-Merck make. Sodium salts of PHI-4S compounds have been prepared and characterized according to the procedure reported by us earlier. The structure of ligand is assigned as in figure 1 (Nagarjun Rao 1985; Nagarjun Rao *et al* 1988). Methanol has been further purified

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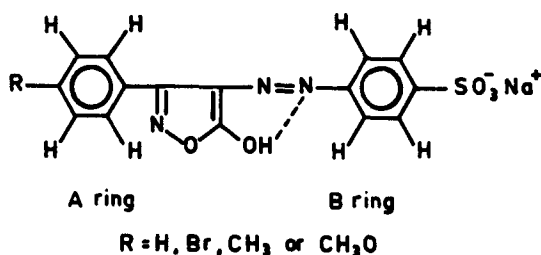


Table 1. Formation constants of [Ln-RPHI-4S] chelates. Solvent = 40% aqueous methanol; temperature = 303 K; $\mu = 0.05 \text{ mol dm}^{-3}$; Values in parenthesis are pK_a values.

Parameter	Yb(III)	Y(III)	Dy(III)	Tb(III)	Gd(III)	Sm(III)	Nd(III)	Pr(III)	La(III)
<i>(A) MeOPHI-4S system (8.18)</i>									
Log K_1	4.37	4.24	4.13	4.08	4.18	3.85	3.75	3.68	3.46
log K_2	3.47	3.33	3.25	3.21	3.26	2.99	2.89	2.80	2.56
log β_2	7.84	7.57	7.38	7.29	7.44	6.84	6.64	6.48	6.02
<i>(B) MePHI-4S system (7.86)</i>									
log K_1	4.27	4.14	4.08	4.03	4.10	3.78	3.66	3.62	3.40
log K_2	3.27	3.12	3.00	2.97	3.05	2.76	2.68	2.64	2.50
log β_2	7.54	7.26	7.08	7.00	7.15	6.54	6.34	6.26	5.90
<i>(C) PHI-4S system (7.58)</i>									
log K_1	4.16	4.05	3.98	3.94	4.00	3.70	3.58	3.53	3.35
log K_2	3.01	2.83	2.72	2.69	2.78	2.45	2.39	2.37	2.30
log β_2	7.17	6.88	6.70	6.63	6.78	6.15	5.97	5.90	5.65
<i>(D) BrPHI-4S system (7.16)</i>									
log K_1	4.05	3.95	3.87	3.82	3.92	3.65	3.50	3.45	3.25
log K_2	2.55	2.38	2.28	2.24	2.31	2.20	2.15	2.10	2.00
log β_2	6.60	6.33	6.15	6.66	6.23	5.85	5.65	5.55	5.25

according to literature procedures (Vogel 1978). Aqueous solutions of lanthanide nitrates (Indian Rare Earths Ltd, Udyogmandal, Kerala) have been standardised complexometrically using EDTA as titrant (Schwarzenbach 1956). Potentiometric and spectrophotometric methods are similar to literature procedures (Irving and Rossotti 1953, 1954; Nagarjun Rao *et al* 1985) and pH values measured in aquo-methanol mixtures have been corrected suitably according to the method of van Uitert and Hass (1953). Formation constants which have been determined by using various computational methods, viz., Bjerrum's half integral, linear plots, least squares, correction term and Block and McIntyre's (1953) methods, are randomly confirmed by Leden's (1941) spectrophotometric method and found to be in concordance with each other within ± 0.05 log units (table 1). ΔH values have been calculated from Van't Hoff's isochore expression independently for K_1 , K_2 and β_2 . In order to check the accuracy of these values calorimetric measurements have been carried out at 30°C for a 1:1 system according to standard procedures (Mahadevan and Sathe 1979; Lahiri *et al* 1976; Freiser and Fleisher 1959). The other thermodynamic parameters have been evaluated according to standard procedures.

3. Results and discussion

3.1 Salient features of the study

- (i) The metal ion-ligand titration curves lie below the pure ligand titration curve. The absence of polynuclear species and metal ion hydrolysis in the observed pH range of complexation have been confirmed according to literature procedures (Rama Murthy and Santappa 1969).
- (ii) The \bar{n} values are in the range $0.1 < \bar{n} < 1.9$ indicating the formation of 1:1 as well as 1:2 complexes.
- (iii) Metal-ligand formation curves indicate that the difference between the two successive formation constants is less than one log-unit indicating simultaneous formation of both 1:1 and 1:2 complexes in solution.
- (iv) Overall formation constants β_1 and β_2 decrease upon increasing the ionic strength (μ) of the medium in the range 0.05 to 0.25 mol dm⁻³. Formation constants increase with an increase in the proportion of methanol in solvent mixture indicating the formation of a more stable complex in the solvent of low dielectric constant (D).
- (v) The stabilities of 1:1 and 1:2 chelates are in the order: Yb(III) > Y(III) > Gd(III) > Dy(III) > Tb(III) > Sm(III) > Nd(III) > Pr(III) > La(III) (table 1).
- (vi) The enthalpy values evaluated from calorimetric measurements for 1:1 systems (ΔH_1) are in good agreement with those derived by the temperature variation method within the limits of ± 1.50 kJ mol⁻¹.

3.2 Correlation of stabilities with various parameters

The data of formation constants (table 1) indicate that the stabilities increase with a decrease in ionic or crystal radii. However, a small break at Gd(III) which is popularly known as 'Gadolinium Break' (Schwarzenbach and Gut 1956; Mayadeo and Purohit 1981; Moeller *et al* 1965) has been observed in the present study. The anomaly observed in the case of Gd(III) can also be explained on the basis of electrostatic non-electrostatic and crystal field effects. If the bonding is purely electrostatic in these complexes, the stabilities should be completely controlled by ionic or crystal radii alone. However, the observed non-linearity of the plots of $\log K_1$ or $\log \beta_2$ as a function $1/r$ may point out the influence of non-electrostatic forces along with electrostatic forces on the bond formation. This point has also been indicated in solvent effect studies. Crystal fields are operative due to the presence of ligand and there may be a varying degree of interaction of the 4f-orbital with the ligand field (Steveley and Randall 1958; Choppin and Chopporian 1961; Rossotti 1958) and for trivalent gadolinium no such stabilization is expected. According to this theory, the stability constants of Y(III) and Gd(III) chelates must be equal, since both these ions do not have field stabilizations. But due to the smaller ionic size of Y(III), chelates of Y(III) are expected to have higher stabilities than Gd(III) chelates. The foregoing discussion thus supports the higher stabilities of Y(III) over Gd(III).

3.3 Structure-reactivity and thermodynamic relationships

The present study reveals that the formation constants (K_1 , K_{av} or β_2) for given metal ion follow the trend: $p - \text{OCH}_3 > p - \text{CH}_3 > \text{H} > p - \text{Br}$. Irving-Rossotti's

Table 2. Thermodynamic parameters for K_1 at 293° K ($\mu = 0.05 \text{ mol dm}^{-3}$)

Parameter	Yb(III)	Y(III)	Dy(III)	Tb(III)	Gd(III)	Sm(III)	Nd(III)	Pr(III)	La(III)
(A) MeOPHI-4S-Ln(III)									
log K_1	4.57	4.42	4.34	4.27	4.38	4.05	3.96	3.87	3.65
$-\Delta H_1$ } k J mol ⁻¹	34.0	30.6	35.7	32.3	34.0	34.0	35.7	32.3	32.3
$-\Delta G_1$ } k J mol ⁻¹	25.6	24.8	24.3	23.9	24.5	22.7	22.2	21.7	20.5
$-\Delta S_1$ J K ⁻¹ mol ⁻¹	28.7	19.8	38.9	28.7	32.4	38.6	46.1	36.2	40.3
(B) MePHI-4S-Ln (III)									
log K_1	4.45	4.31	4.24	4.19	4.28	3.96	3.85	3.80	3.60
$-\Delta H_1$ } k J mol ⁻¹	30.6	28.9	27.2	27.2	30.6	30.6	32.3	30.6	34.0
$-\Delta G_1$ } k J mol ⁻¹	24.9	24.2	23.8	23.5	24.0	22.2	21.6	21.3	20.2
$-\Delta S_1$ J K ⁻¹ mol ⁻¹	19.5	16.0	11.6	12.6	22.5	28.7	36.5	1.7	47.1
(C) PHI-4S-Ln(III)									
log K_1	4.31	4.21	4.13	4.09	4.15	3.85	3.73	3.68	3.50
$-\Delta H_1$ } k J mol ⁻¹	25.5	27.2	25.5	25.5	25.5	25.5	25.5	25.5	25.5
$-\Delta G_1$ } k J mol ⁻¹	24.2	23.6	23.2	22.9	23.2	21.6	20.9	20.6	19.6
$-\Delta S_1$ J K ⁻¹ mol ⁻¹	4.43	12.3	7.85	8.87	7.85	13.3	15.7	16.7	20.1
(D) BrPHI-4S-Ln (III)									
log K_1	4.21	4.10	4.02	3.97	4.07	3.80	3.65	3.60	3.40
$-\Delta H_1$ } k J mol ⁻¹	27.2	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5
$-\Delta G_1$ } k J mol ⁻¹	23.6	23.0	22.5	22.2	22.8	21.3	20.4	20.2	19.0
$-\Delta S_1$ J K ⁻¹ mol ⁻¹	12.3	8.53	10.2	11.3	9.21	14.3	17.4	18.1	22.2

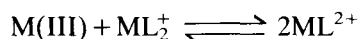
Table 3. $\log K$, ΔH_r , ΔG_r , and ΔS_r values for [RPHI-4S-Ln(III)] chelate formation. $\mu = 0.05 \text{ mol dm}^{-3}$; temp. = 293 K.

Parameter	Yb(III)	Y(III)	Dy(III)	Tb(III)	Gd(III)	Sm(III)	Nd(III)	Pr(III)	La(III)
(A) MeOPHI-4S-Ln(III) system									
$\Delta \log K$	0.97	0.97	1.04	0.94	0.98	0.95	0.94	0.94	0.96
$-\Delta H_r$, } k J mol ⁻¹	11.90	10.2	13.6	11.70	11.20	15.30	13.60	10.20	10.20
$-\Delta G_r$, }	5.40	5.50	5.40	5.20	5.50	5.30	5.30	5.30	5.40
$-\Delta S_r$, J K ⁻¹ mol ⁻¹	22.22	16.05	28.00	22.90	16.0	34.2	28.3	16.8	16.4
(B) MePHI-4S-Ln(III) system									
$\Delta \log K$	1.09	1.09	1.14	1.12	1.14	1.11	1.07	1.05	0.98
$-\Delta H_r$, } k J mol ⁻¹	15.3	11.9	10.20	10.20	15.3	15.3	15.3	11.9	15.3
$-\Delta G_r$, }	6.10	6.20	6.40	6.30	6.4	5.6	6.0	5.9	5.5
$-\Delta S_r$, J K ⁻¹ mol ⁻¹	31.4	19.41	12.97	13.28	30.35	31.09	31.72	20.4	33.5
(C) PHI-4S-Ln(III) system									
$\Delta \log K$	1.21	1.28	1.30	1.30	1.27	1.29	1.23	1.21	1.10
$-\Delta H_r$, } k J mol ⁻¹	10.2	10.2	6.8	8.5	8.5	6.8	3.4	8.5	8.5
$-\Delta G_r$, }	6.8	7.2	7.3	7.3	7.1	7.3	6.9	6.8	6.2
$-\Delta S_r$, J K ⁻¹ mol ⁻¹	11.6	10.25	-1.71	4.09	4.78	-1.7	-11.9	5.8	7.8
(D) BrPHI-4S-Ln(III) system									
$\Delta \log K$	1.56	1.63	1.64	1.62	1.56	1.50	1.40	1.40	1.30
$-\Delta H_r$, } k J mol ⁻¹	10.2	10.2	8.5	6.8	8.5	8.5	8.5	8.5	8.5
$-\Delta G_r$, }	8.7	9.2	9.2	9.0	9.3	8.4	7.8	7.9	7.2
$-\Delta S_r$, J K ⁻¹ mol ⁻¹	5.13	3.41	-2.4	-7.5	-2.69	0.3	2.4	2.1	4.40

plots ($\log K_1$, $\log K_{av}$ and $\log \beta_2$) as functions of pK_a have been found to be linear with positive unit slopes for all the metal chelates in different solvent media. The plots of $\log K_{ML}$ (where K may be K_1 , K_{av} or β_2) as a function of $\log K_{MA}$ have been found to be linear with all the metal ions and ligands studied according to the equation (Irving and Rossotti 1956),

$$\log K_{(ML)} = \log K_{(MA)} + \Delta pK_a.$$

When the formation constant data of metal chelates have been tested as a function of Hammett's ' σ ', the plots have shown a fairly good linear relationship with correlation coefficient values (r) in the range $1 > r > 0.980$. The magnitude of reaction constants (slope of the plots) indicate that the case of complex formation is more pronounced with electron releasing groups (Hammett 1940). Linearity of Leffler's (ΔH vs ΔS) and Exner's plots (Leffler 1955; Exner 1972) indicate that a similar type of complexation is operative in all the systems studied. Further Exner's analysis (log-log plot of β_2 at two different temperatures) indicated the value of the iso-equilibrium temperature (β) to be 220 K, which is far below the experimental temperature thus suggesting the importance of entropy factors in controlling the equilibria. $\log K_1$ values for all the trivalent lanthanides are found to be higher than those of $\log K_2$ values indicating the 1:1 complex to be more feasible energetically. ΔH_1 were found to be more negative than ΔH_2 in all the cases indicating that formation of ML_2 is more exothermic than the formation of ML (table 2 and 3). As pointed out by Ting Po and Nancollas (1972) if the formation of the 1:1 complex is more likely, then even the 1:2 complex reacts with free metal ion to form the 1:1 chelate.



The thermodynamic parameters ΔH_r , ΔG_r and ΔS_r for the above equilibrium have been calculated according to literature procedures (Ting Po and Nancollas 1972). The values of ΔG_r are negative, indicating the feasibility of 1:1 as well as 1:2 complex formation (table 3).

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