Stability Constants of Ternary Complexes of Rare Earth Metal Ions with Phthalic Acid & O⁻, O⁻; O⁻, N & N,N Donor Ligands & Thermodynamic Parameters of Their Formation

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The interaction of La(III), Gd(III), Tb(III) and Dy(III) with the ligands capable of coordinating through O⁻, O⁻ (phthalic, maleic, fumaric, succinic and salicylic acids and pyrocatechol), O⁻, N (o-aminophenol and 8-quinolinol) and N,N-(2,2'-bipyridyl and ethylenediamine) donor atoms have been investigated pH-metrically in aqueous medium at 25°, 30°, 35° and 40°C and $\mu = 0.1\,M\,(KNO_3)$. The stability constants of the ternary complexes have been evaluated and discussed in terms of donor atoms, size of the chelate rings, neutralization of charge on the metal ion and metal-ligand orbital interactions. The thermodynamic parameters like $\Delta G\ddagger$, $\Delta H\ddagger$ and $\Delta S\ddagger$ and other parameters such as $\Delta\Delta H$ and $\Delta\Delta S$ have also been calculated.

In continuation of our earlier work[1-3], on the stability constants of metal ion complexes of biological importance, we report in this note the stability constants and thermodynamic parameters of the complexes of La(III), Gd(III), Tb(III) and Dy(III) with phthalic acid (phA), (O,O-donor ligand) and varying the other ligand such as maleic acid (MA), fumaric acid (FA), succinic acid (ScA), salicylic acid (SA) or pyrocatechol (PC) (O,O-donor ligands); o-aminophenol (o-AP) or 8-quinolinol (8-HQ) (O,N-donor ligands); and 2,2'-bipyridyl (bipy) and ethylenediamine (en) (N,N-donor ligands) in aqueous medium at different temperatures and $\mu = 0.1\,M$ (KNO₃) employing pH titration technique.

The lanthanide nitrates (AR) (Indian Rare Earths Limited, Udyogamandal, Kerala) were dissolved in doubly distilled water and standardised by the method of Flaschka[4]. All other reagents used were of AR grade. The ligands were recrystallized/distilled before use and their purity was checked. All the solutions were prepared in doubly distilled water except the solution of 8-HQ, which was prepared in 50% (v/v) ethanol.

The experimental details and the method of measurement of pH have been given in our earlier publications[1-3].

The formation of the mixed ligand complex in solution was established initially by recording the pH of precipitation for MA, ML and MAL (A = phthalic acid and L = O⁻, O⁻, O⁻, N and N,N donor ligands) and by comparing the mixed ligand titration curve with the composite curve. The titration data reveal that the interaction of the two ligands with the metal ion is different for different systems. The ligands PC, o-AP, bipy, en and PhA interact with the metal ions in stepwise manner to form ternary complexes, whereas the ligands MA, FA, ScA and PhA form the ternary complexes by disproportionation of the binary species MA and ML as per the equilibrium: MA + ML⇌MAL + M. In the case of the ligands SA, 8-HQ and PhA the deviation of the curve at low pH suggests the simultaneous interaction of the ligands with the metal ions.

The ionization constants of ligands and stability constants of binary complexes of La(III), Gd(III), Tb(III) and Dy(III) with the above ligands have been calculated by Irving and Rossotti's method[5,6] at 25°, 30°, 35° and 40°C and $\mu = 0.1\,M$ (KNO₃). The stability constants of ternary complexes were determined by different methods[7,8] depending on the nature of interaction between the metal ions and the ligands. The accuracy in the ionization constants of ligands and stability constants of the binary and ternary complexes is of the order of ±0.05 log units. The data thus obtained are given in Tables 1 and 2.

The thermodynamic parameters like $\Delta G\ddagger$, $\Delta H\ddagger$ and $\Delta S\ddagger$ were evaluated using standard equations.

There are two methods to characterize the stabilities of mixed ligand complexes in solution: (i) By comparing the difference in stabilities $\Delta\log K (= \log K_{MAL}^{MA} - \log K_{ML}^{M})$; and (ii) the disproportionation constant X, $(X = [MAL]^2/[MA_2][ML_2])$.

All these parameters have been calculated (Table 2) and discussed in terms of the donor atoms of the ligands.

The order of stabilities of the ternary complexes of PhA and of O⁻, O⁻ donor ligands in terms of $\Delta\log K$ is MA > ScA > FA. The log X values also confirm this stability order.

The ternary complexes involving SA are more stable than those involving PC complexes. The electronegativity of the phenolate oxygen is higher than that of carboxylate oxygen. Further in the case of SA, one of the donor atoms is carboxylate oxygen and the other is a phenolate oxygen, while in PC both the donor atoms are phenolate oxygens thus resulting in less stable ternary complex.

Table 1—Formation Constants of Binary Complexes

$[\mu = 0.1\, M\ KNO_3;\ temp = 25^\circ C]$

Metal/Ligand	La(III)		Gd(III)		Tb(III)		Dy(III)	
	$\log K_{ML}^{M}$	$\log K_{ML_2}^{ML}$	$\log K_{ML}^{M}$	$\log K_{ML_2}^{ML}$	$\log K_{ML}^{M}$	$\log K_{ML_2}^{ML}$	$\log K_{ML}^{M}$	$\log K_{ML_2}^{ML}$
Phthalic acid	2.95	—	3.82	3.03	4.17	3.25	4.31	3.21
Maleic acid	4.76	3.32	4.81	3.27	5.48	3.29	5.78	3.43
Fumaric acid	3.01	—	3.05	—	3.10	—	3.18	—
Succinic acid	3.56	3.00	3.58	3.00	3.76	3.08	3.77	3.13
Salicylic acid	9.64	—	9.98	—	10.11	—	10.26	—
Pyrocatechol	7.24	5.12	8.72	5.70	8.82	6.03	9.12	6.82
o-Aminephenol	6.24	3.83	6.26	4.57	6.28	4.70	6.30	4.94
8-Quinolinol	6.57	5.49	7.13	6.10	7.48	6.44	7.60	6.67
2,2'-Bipyridyl	3.43	2.92	3.85	2.95	4.29	2.97	4.33	2.99
Ethylenediamine	4.88	4.19	5.34	4.85	5.52	5.08	5.63	5.15

Table 2—Formation Constants ($\log \beta_{MAL}^{M}$) $\Delta \log K$ and $\log X$ of Ternary Complexes

[Phthalic acid (A)-M(III)-Ligand(L)]

$[\mu = 0.1\, M\ (KNO_3);\ temp. = 25^\circ C]$

Ligand(L)	La(III)			Gd(III)			Tb(III)			Dy(III)		
	$\log \beta_{MAL}^{M}$	$\Delta \log K$	$\log X$	$\log \beta_{MAL}^{M}$	$\Delta \log K$	$\log X$	$\log \beta_{MAL}^{M}$	$\Delta \log K$	$\log X$	$\log \beta_{MAL}^{M}$	$\Delta \log K$	$\log X$
Maleic acid	7.92	0.21	1.65	8.34	−0.29	2.74	9.16	−0.48	2.26	9.34	−0.65	1.91
Fumaric acid	5.70	−0.26	−0.26	6.22	−0.65	0.14	6.24	−0.92	0.11	6.41	−1.08	0.02
Succinic acid	6.38	−0.13	0.43	7.08	−0.32	0.73	7.31	−0.61	0.49	7.38	−0.70	0.34
Salicylic acid	14.99	2.40	2.40	15.56	1.76	2.55	15.69	1.42	2.30	15.80	1.23	2.68
Pyrocatechol	10.26	0.07	2.19	11.85	−0.89	2.43	11.81	−1.17	1.48	12.14	−1.29	0.82
o-Aminophenol	12.42	3.23	5.64	13.39	3.31	9.10	13.44	3.00	8.61	13.72	3.11	8.68
8-Quinolinol	14.66	5.14	6.22	15.58	4.63	11.08	15.96	4.32	10.71	16.16	4.25	10.53
2,2'-Bipyridyl	11.17	4.79	5.30	11.33	3.66	9.01	11.44	2.99	8.33	11.57	2.93	8.30
Ethylenediamine	8.28	0.45	1.14	9.04	−0.12	1.04	9.06	−0.62	0.23	9.33	−0.61	0.36

The $\Delta \log K$ and $\log X$ values of ternary complexes involving o-AP and 8-HQ are exceptionally high (Table 2). This favoured formation of ternary complexes may be due to the neutralization of charge on the tripositive metal ions.

The greater stabilities of the ternary complexes involving 8-HQ as compared to those involving o-AP may be attributed to the greater metal-ligand interaction in ternary systems involving 8-HQ. To account for this the electronic spectra of binary and ternary complexes of Dy(III) with the ligands under investigation have been recorded. o-AP exhibits bands at 43,290, 35,211 and 22,969 cm^{-1}. The low energy band corresponds to $\pi \to \pi^*$ transition. The o-AP binary complex exhibits bands at 35088 and 22024 cm^{-1}, while its ternary complex absorbs at 35842 and 22883 cm^{-1}. The absorption bands of 8-HQ and its binary and ternary complexes appear at 41494, 39370 and 31847 cm^{-1} (8-HQ); 41494 and 32051 cm^{-1} [Dy(III)-8-HQ]; and 41152, 39841 and 32057 cm^{-1} [Dy(III)-8-HQ-PhA]. From these data it may be concluded that in the formation of ternary complexes

π-interactions are more in 8-HQ complexes resulting in the greater stability of its complexes. Similar observations have been recorded by Patel et al.[9], and Gershon et al.[10], in the case of mixed ligand complexes of copper(II)-8-HQ.

The $\Delta \log K$ values of M(III)-PhA-bipy systems are fairly high as compared to those of the M(III)-PhA-en systems (Table 2). This may be attributed to the π-interactions of bipy with the metal ion. The absorption bands of bipy and its binary and ternary complexes appear at 41553, 35336 and 32573 cm^{-1} (bipy); 42735 and 35461 cm^{-1} [Dy(III)-bipy] and 42735, 35211 and 32680 cm^{-1} [Dy(III)-bipy-PhA]. From these data it may be concluded that in the formation of ternary complexes the electron distribution is altered. No such π-interactions are expected in the case of en. The $\log X$ values are also in accord with the observed fact.

The overall stability constants, $\log \beta_{MAL}^{M}$ follow the order: La(III) < Gd(III) < Tb(III) < Dy(III) which is in agreement with the observations of Stagg and Powell[11]. This may be attributed to the decrease in size of the trivalent rare earth metal ions.

Table 3—Thermodynamic Parameters Associated with M(III)-Phthalic Acid-L-Systems

$(\mu=0.1\,M\,KNO_3;\,\Delta G$ and ΔH in kJ mol^{-1} and ΔS in JK^{-1}mol$^{-1})$

Ligand (L)	La(III)			Gd(III)			Tb(III)			Dy(III)		
	$-\Delta G^\ddagger$	$-\Delta H^\ddagger$	$\Delta S^\ddagger$	$-\Delta G^\ddagger$	$-\Delta H^\ddagger$	$\Delta S^\ddagger$	$-\Delta G^\ddagger$	$-\Delta H^\ddagger$	$\Delta S^\ddagger$	$-\Delta G^\ddagger$	$-\Delta H^\ddagger$	$\Delta S^\ddagger$
Maleic acid	41.59	41.51	0.34	47.57	38.28	31.13	52.26	45.10	23.97	53.30	59.58	−21.01
Fumaric acid	32.34	28.70	12.18	35.48	33.89	5.36	35.61	39.87	14.35	36.57	48.62	−40.38
Succinic acid	36.40	44.18	−26.11	40.42	31.92	28.54	41.72	42.80	−3.64	42.09	42.09	0
Salicylic acid	85.52	48.74	123.43	88.79	47.87	137.28	89.54	40.84	163.39	90.17	47.87	141.92
Pyrocatechol	58.53	44.85	45.90	67.61	56.98	35.73	67.40	46.28	70.88	69.29	46.40	76.86
o-Aminophenol	70.88	53.18	59.37	76.27	64.18	40.54	76.69	67.24	31.76	78.28	71.80	21.76
8-Quinolinol	83.64	45.94	126.44	88.91	54.69	114.77	91.09	60.38	103.05	92.22	68.24	80.42
2,2'-Bipyridyl	63.72	41.04	76.15	64.64	36.69	93.76	65.27	46.40	63.39	66.02	53.26	42.85
Ethylenediamine	47.24	35.77	38.49	51.59	46.65	16.49	51.71	43.51	27.49	53.22	49.79	11.55

The thermodynamic parameters, $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are presented in Table 3. The stability constants decrease with increase in temperature. The entropy values for the formation of ternary complexes of M(III)-phthalic acid with SA, o-AP, 8-HQ and bipy are more positive, suggesting that the complexes are stabilized by an entropy contribution. The positive $\Delta\log K$ values in these systems may be due to the difference in the solvation energies between the ternary and binary systems.

The $\Delta\Delta H$ and $\Delta\Delta S$ values (the differences between the enthalpy and entropy changes associated with ternary and binary complexes) of the ternary complexes of 8-HQ [2.24, 31.03 La(III); 3.45, 32.79; Gd(III); 1.27, 24.05, Tb(III); and 1.87, 25.72, Dy(III)] are more as compared to those of o-AP complexes [1.14, 10.96 La(III); −1.30, 10.70 Gd(III); 2.02, 6.96 Tb(III); and −2.29, 6.42 Dy(III)]. The data support increased metal-ligand π-interaction in the case of ternary complexes involving 8-HQ. The $\Delta\Delta H$ and $\Delta\Delta S$ values obtained for complexes containing N,N-donor atoms like bipy are more as compared to

those containing en. This is again due to the increase of π-interaction between metal-ligand orbitals in the case of bipyridyl.

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