Relative Stabilisation and Relative Astatisticality of Stability Parameters of Some Lanthanide Mixed Ligand Complexes

Rajesh Nagar*

Department of Chemistry, Institute of Basic Sciences, Agra University, Khandari, AGRA - 282 002.

** Address: 32, Keshav Kunj II, Pratap Nagar, AGRA - 282 010.*

Formation constants of binary, ternary and quaternary complexes of lanthanide metal ions viz. La^{3+}, Pr^{3+} and Nd^{3+} with ethylenediamine N,N,N',N'-tetraacetic acid (EDTA), oxydiacetic acid (ODA), iminodiacetic acid (IDA) and glycine (GLY) as ligands have been determined by potentiometric method at 25 ± 0.5° C and ionic strength of 0.1 mol dm^{-3} KNO_3. The results show that the order are as: La(III) <Pr(III) <Nd(III) in formation constants of metal ions, binary <ternary <quaternary in terms of complex species and IDA <GLY in the case of amino acids. The Δlog K values are negative for all the ternary and quaternary systems. However, Δ Δlog K values are significantly postive indicating intramolecular hydrophobic ligand-ligand interactions. The formation constants, determined by potentiometry, have been used to study the electrostatic and astatistical factors involved in the formation of these mixed complexes.

Studies on ternary complexes involving transition metals [1-4] and rare earths [5-6] have been reported, but the work on metal complexes having three different ligands is rather enexplored [7]. Since, lanthanide ions appear to attain an unusually high coordination number - greater then six, the study of quaternary complexes of these metals with multidentate ligands would be more interesting. Statistical aspects of mixed ligand complexes have been discussed at length [8-10]. The term 'total effect' has been proposed [11] for various factors — stastistical, electrostatic and other factors — operative during the formation of complexes. In the present paper potentiometric studies of complexes in solution of three of lanthanides - La(III), Pr(III) and Nd(III) with EDTA, oxidiacetic acid (ODA), iminodiacetic acid (IDA) or glycine (GLY) are reported.

MATERIALS AND METHODS

All the chemicals were of AR. BDH or GR. E Merck grade. The solutions were prepared in double distilled water. Standard solutions of nitrates of La, Pr, and Nd were prepared and standardized by oxalate method [12]. Glycine was used in its diprotonated form. IDA was used in its mono protonated form. The solutions of ODA and glycine were prepared by direct weighing method and

© ECSI, Bangalore

the concentration of solutions was further checked potentiometrically. The ionic strength (0.1 mol dm^{-3} KNO_3), total volume (50 dm^{-3}) and temperture (25 ± 0.5° C) were kept constant at the beginning of each titration. pH measurements were carried out with Toshniwal digital pH meter (accuracy ± 0.01). Each titration (against 0.01 M potassium hydroxide solution) was repeated twice.

The dissociation constants of K_2EDTA (pK_1 = 5.50 and pK_2 = 9.78), ODA (pK_1 = 3.10 and pK_2 = 4.18), KIDA (pK_1 = 9.05) and GLY (pK_1 = 9.77) were evaluated by Chaberek and Martell method [13]. Metal ligand stability constants (log K^{M}_{MA}, log K^{M}_{MAB}, log K^{MA}_{MAL}', log K^{MA}_{MAL}", log K^{MB}_{MBL}', log K^{MB}_{MBL}", log K^{MAB}_{MABL} and log K^{MAB}_{MABL}', were computed by the modified method [14] of Ramamoorthy and Santappa [15] for the simultaneous chelation of the ligands. In case of stepwise chelation, Thomson and Loraas method was applied [16].

RESULTS AND DISCUSSION

The pH metric titration curves of all the three lanthanide ions were found similar in nature. Here, the formation curves of 1:1:1:1 lanthanum (III)-EDTA-ODA-IDA/GLY quaternary complexes is shown (Fig 1). Curves from a to g have already been discussed earlier [17-19]. Curve h represents the potentiometric titration of 1:1:1 M(III)-EDTA-IDA/GLY ternary system. Two inflections at m=2 and m=3 show the formation of 1:1, M(III)-EDTA

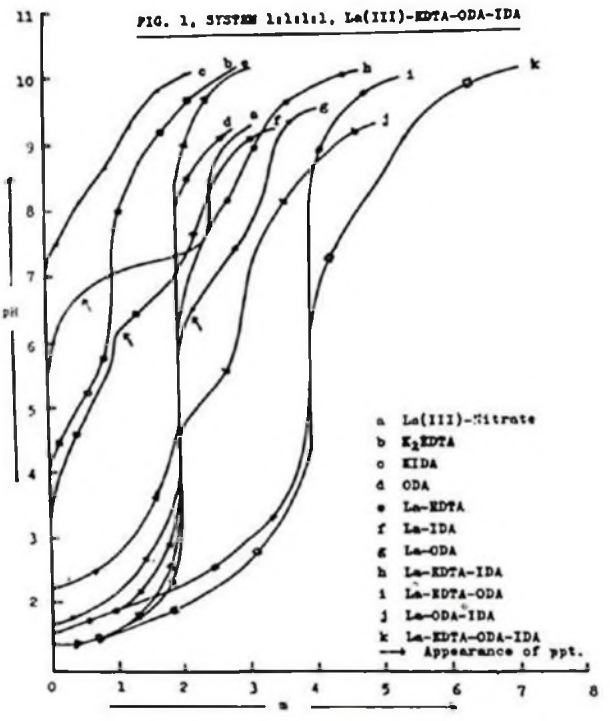


Fig 1 System 1:1:1:1 La(III) - EDTA -ODA - IDA

initially and the addition of IDA/GLY takes place later on. However, a well defined inflection at m=4 (in curve i) depicts the simultaneous chelation of EDTA and ODA to the metal ion forming 1:1:1 M(III)-EDTA-ODA species. An inflection at m=2 on curve j shows the formation of 1:1 M(III)-ODA species. Another inflection at m=3 depicts the addition of IDA/GLY to the initially formed 1:1 M(III)-ODA species. Curve k illustrates the titration of 1:1:1:1 M(III)-EDTA-ODA-IDA system. An inflection at m=4 may be due to the titration of only four protons of the two ligands, two each from K_2EDTA and ODA.

forming 1:1:1, M(III)-EDTA-ODA complex. This soluble complex appears to add IDA/GLY in the higher buffer region giving 1:1:1:1 M(III)-EDTA-ODA-IDA/GLY quaternary complex as shown by one more inflection at m=5.

All the binary, ternary and quaternary complexes formed, are found to be soluble in the region of their formation. The binary system are of type M + A <==>MA: M + B <==> MB: ternary system of the type MA + L <==>MAL: MB + L <==> MBL: M + A + B <==> MAB: and quaternary systems are of type MAB + L <==> MABL (A = EDTA, B=ODA, L = ODA/IDA). The stability constants (Table 1) have been found to lie in the sequence La(III) < Pr(III) < Nd(III), which is the order of increasing occupancy of the 4f orbitals and accompanied by a gradual decrease in their ionic radii. Free energy of formation (Table 1) has been evaluated and found to be negative in all the cases, indicating complex formation is almost spontaneous in nature.

The general order of stability for the complexes has been found to be $\log K^{M}_{MA} > \log K^{MA}_{MAL} > \log K^{MAB}_{MABL}$ and $\log K^{M}_{MA} > \log K^{MA}_{MAL}{}' > \log K^{MAB}_{MABL}{}'$. But the overall stability (Table 2) of quaternary complexes is greater than that of ternary complexes which is itself greater than that of binary complexes i.e. $\log K^{M}_{MA} < \log K^{M}_{MAB} < \log \beta_3 < \log \beta_4 < \log \beta_5 <$ log B6.

Table 1

Metal ligand Stability Constants and related parameters
Temp. 25 ± 0.5° C; Ionic Strength 0.1 mol dm^3 KNO_3

Property	La(III)	Pr(III)	Nd(III)
1:1 M-EDTA			
$\log K^{M}_{MA}$	5.45	5.67	5.91
-ΔG	7.43	7.73	8.06
1:1:1: M-CDA-IDA			
$\log K^{MB}_{MBL}$	2.12	2.30	2.39
- ΔG	2.89	3.14	3.26
- Δlog K	0.29	0.23	0.28
- (%) R.S.	62.67	61.92	62.36
$\log K_s$	4.04	4.28	4.51
(%) R.A.	47.52	46.26	47.00
1:1:1 M-ODA-GLY			
$\log K^{MB}_{MBL}{}'$	2.29	2.41	2.52
-ΔG	3.12	3.29	3.44
-Δlog K	0.12	0.12	0.15
- (%) R.S.	59.18	57.64	56.70
$\log K_s$	3.69	3.79	3.93
(%) R.A.	37.94	36.41	35.88
1:1:1 M-EDTA-IDA			
$\log K^{MA}_{MAL}$	4.23	4.79	5.14
-ΔG	5.77	6.53	7.02
-Δlog K	1.22	0.88	0.77
- (%) R.S.	25.53	20.69	19.05
$\log K_s$	5.53	5.79	6.86
(%) R.A.	23.51	17.27	25.07
1:1:1 M-EDTA-GLY			
$\log K^{MA}_{MAL}{}'$	4.59	4.99	5.38
-ΔG	6.26	6.80	7.34
-Δlog K	0.86	0.68	0.53
- (%) R.S.	18.18	12.30	15.27
$\log K_s$	5.49	5.67	5.89
(%) R.A.	17.30	11.99	8.66
1:1:1:1 M-EDTA-ODA-IDA			
$\log K^{MAB}_{MABL}$	3.25	3.58	4.06
-ΔG	4.43	4.88	5.53
-Δlog K	0.41	0.37	0.26
- (%) R.S.	42.78	40.73	36.06
$\log K_s$	8.25	8.72	9.26
(%) R.A.	60.60	58.94	56.15
1:1:1:1 M-EDTA-ODA-GLY			
$\log K^{MAB}_{MABL}{}'$	3.41	3.78	4.29
-ΔG	4.65	5.15	5.85
-Δlog K	0.25	0.17	0.03
- (%) R.S.	39.22	33.57	26.29
$\log K_s$	8.47	8.90	9.43
(%) R.A.	59.74	57.53	54.51

Table 2

Overall Stability of Ternary and Quaternary Complexes

System	Property	La(III)	Pr(III)	Nd(III)
1:1:1 M-EDTA-ODA	$\log K^{M}_{MAB}$	9.11	9.62	10.23
1:1:1 M-ODA-IDA	$\log \beta_1$	4.53	4.83	5.06
1:1:1 M-ODA-GLY	$\log \beta_2$	4.70	4.94	5.19
1:1:1 M-EDTA-IDA	$\log \beta_3$	9.68	10.46	11.05
1:1:1 M-EDTA-GLY	$\log \beta_4$	10.04	10.66	11.29
1:1:1:1 M-EDTA-ODA-IDA	$\log \beta_5$	12.36	13.20	14.29
1:1:1:1 M-EDTA-ODA-GLY	$\log \beta_6$	12.52	13.40	14.52

A comparison of the stability constants of the binary and ternary complexes gives a measure of the relative ease or difficulty experienced by the secondary ligand in combing with the binary complex to form the mixed complexes. This is measured by Δlog K. In the present paper 1:1 binary, 1:1:1 ternary and 1:1:1:1 quaternary complexes have been studied with sytems containing equal amounts of metal and ligands. Hence, Δlog K (Table 1) has been used to compare the stability of the ternary and quaternary complexes in relation to the binary complexes [20]. The Δlog K values are negative in all the cases which should be primarily due to the electronic repulsion induced by the secondary or tertiary ligands. The greater stabilization of the ternary and quaternary complexes may be explained on the basis of cooperative effect [21] between the primary, secondary and tertiary ligands in these cases. The existance of intramolecular hydrphobic interaction may be examined by $\Delta\Delta\log K = \log K_1 - \log K_2$. Significantly positive value of ΔΔlog K (Table 3) for ternary and quaternary system may be regarded as an evidence of hydrophobic interactions responsible for relatively greater stabilization of the mixed complexes.

Table 3

Possibility of Occurance of Intramolecular Hydrophobic Ligand-Ligand Interaction in Ternary and Quaternary Complexes

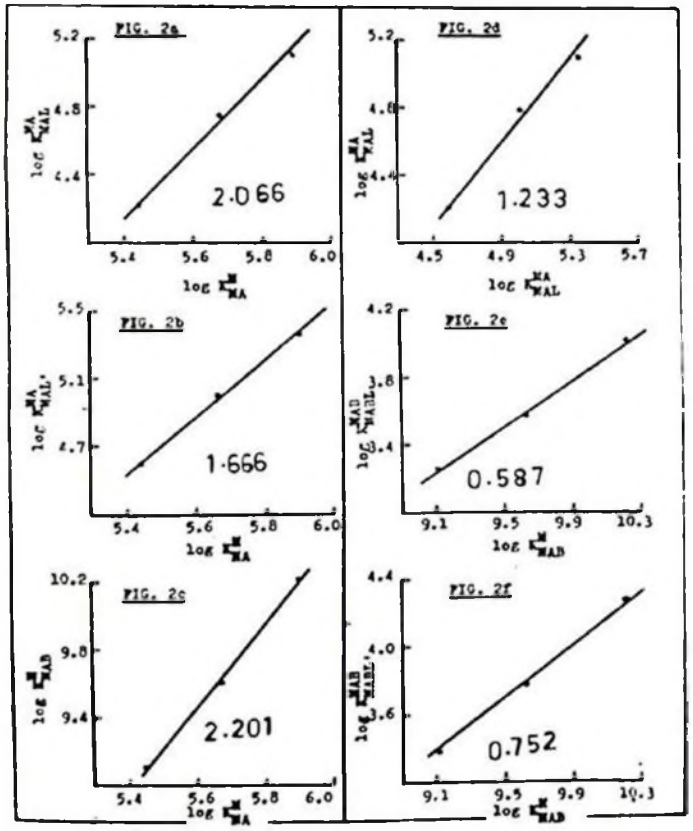
System	< — ΔΔlog K of — >		
	La(III)	Pr(III)	Nd(III)
1:1:1 M-ODA-IDA/GLY	0.17	0.11	0.13
1:1:1 M-EDTA-IDA/GLY	0.36	0.20	0.24
1:1:1:1 M-EDTA-ODA-IDA/GLY	0.16	0.20	0.23

A comparison of the relative stabilities of different mixed complexes can be more satisfactorily achieved on the basis of a new parameter - % Relative Stabilization. The % R.S. values are reported in Table 1. In the present work $\log K^{MA}_{MAL} < \log K^{M}_{ML}$ is due to the electrostatic repulsion involved beteen the primary and secondary ligands during the formation of ternary complex. Statistically the tendency of metal ion to combine with a ligand goes on decreasing with increase in the number of ligands bound to the metal ion. This idea would imply that the tendency of metal ion to bind itself to secondary ligand should decrease after it has already been bound to primary ligand. Thus statistically $\log K^{MA}_{MAL}$ should be less than $\log K^{M}_{ML}$. The statistical value

of Δlog K varies depending upon the geometry of the complex and denticity of the ligand [22].

Statistical stability constant (log K_s) of mixed complexes have been evaluated [23] and given in Table 1. It has been found that log K_s values are greater than log K^{MA}_{MAL} or log $K^{MAB}_{MABL'}$ which clearly indicates the involvement of astatistical factors such as electrostatic effect, steric effect, size of the chelate ring, asymmetry of the ligand field etc in the formation of mixed ligand complexes. A quantitative measure of astatistical factors involved in the formation of mixed ligand complexes may be expressed in terms of another parameter - % Relative Astatisticality. The values are positive and numerically high, indicating that the astatistical factors affect the stability of mixed complexes.

For log log type of stability correlation [24] the plots of (a) log K^{MA}_{MAL} vs log K^{M}_{MA} (b) log $K^{MA}_{MAL'}$ vs log K^{M}_{MA} (c) log K^{M}_{MAB} vs log K^{M}_{MA} (d) log K^{MA}_{MAL} vs log $K^{MA}_{MAL'}$ (e) log K^{MAB}_{MABL} vs log K^{M}_{MAB} and (f) log $K^{MAB}_{MABL'}$ vs log K^{M}_{MAB} have been given in Fig.2. All plots are linear, which shows that the affinity of the association of secondary and tertiary ligands in ternary and quaternary systems generally follows the same pattern as it does with aqueous metal ion, $M(H_2O)n$. The slope values obtained for various log log type correlation are shown in the figurs. The slope value depends on (a) ionization potential of the metal ion [25] (b) nuclear repulsions between the metal ion and donor atom [26] (c) the polarization of the ligands by metal ion [27].



ACKNOWLEDGEMENT

I am thankful to Prof. K.N. Mehrotra and Dr. R.C. Sharma of Agra University for their valuable suggestions during the investigation. I am also thankful to Dr. M.N. Jha, F.R.I. & College, Dehradun for many stimulating and useful discussions. Financial assistance fron Council of Scientific and Industial Research, New Delhi, under Scientist pool scheme is acknowledged.

REFERENCES

1. B.E.Fisher and H.J.Sigel, *J.Am.Chem.Soc.*, **102** (1980) 2998.
2. Y.Anjaneyulu, R.Y.Swamy & R.P.Rao, *J.Indian Chem. Soc.* **62** (1985) 346.
3. R.Nagar & R.C.Sharma, *J.Inst Chem.* **57** (1985) 223; *J.Indian Chem. Soc.* **65** (1988) 240.
4. R.Nagar, R.K.Parashar & R.C.Sharma, *Bull. Electrochem.*, **4** (1988) 405.
5. H.S.Rane & J.P.Tandon, *Indian J. Chem.* **14** (1976) 428.
6. E.Brucher, R.Kirly & I.Toth, *J. Inorg. Nucl. Chem.*, **12** (1976) 167.
7. S.P.Tripathi, R.C.Sharma & G.K.Chaturvedi, *Z. anorg. Allg. Chem.*, **462** (1980) 226.
8. Y.Marcus & I.Elzer, *J. Phy. Chem.*, **66** (1962) 1661.
9. S.Kida, *Bull. Chem. Soc. Japan.* **29** (1956) 805.
10. P.K.Bhattacharya, *J.Scientific & Ind. Res.*, **40** (1981) 382.
11. J.Bjerrum, *Metal Amine Complex Formation in Aqueous Solutions*, **P.Haas & Sons, Copenhagen** (1941).
12. M.A.Tishohohenko, I.I.Zheltvai & N.S.Polucktev, *Z. Neorg. Khim.*, **19** (1974) 179.
13. S.Chaberek & A.E.Martell, *J. Am. Chem. Soc.*, **74** (1952) 5052.
14. R.Kumar, G.K.Chaturevdi & R.C.Sharma, *J. Inorg. Nucl. Chem.* **43** (1981) 2503.
15. S.Ramamoorthy & M.Santappa, *Inorg. Nucl. Chem.*, **32** (1970) 1623, 33 (1971) 1775.
16. L.C.Thompson & J.A.Loreaas, *Inorg. Chem.*, **2** (1962) 89.
17. R.Kumar, R.C.Sharma & G.K.Chaturvedi, *Monatsh Chem.* **110** (1979) 967.
18. R.Nagar, I.K.Goud & R.C.Sharma, *J. Electrochem. Soc. India*, **37** (1988) 369.
19. P.C.Dwivedi, S.P.Tripathi & R.C.Sharma, *J. Indian Chem. Soc.* **61** (1984) 23.
20. R.Nagar & R.C.Sharma, *Indian J. Chem.*, (in press)
21. H.Sigel, IUPAC, Coordination Chemistry-**20**, (Ed) D Banergee, **Pargamon Press, Oxford** (1980).
22. H.Sigel, *Angew. Chem.* **87** (1975) 391.
23. R.Dewitt & J.Watters, *J. Am. Chem. Soc.* **76** (1954) 3810.
24. S.M.Limaye & M.C.Saxena, *J. Indian Chem. Soc.* **61** (1984) 842.
25. G.Schwarsanbach, H.Ackarmann & P.Ruckstuhl, *Helv. Chim. Acta.*, **32** (1949) 11.
26. L.G.Van Uitert & W.C.Fernolins, *J. Am. Chem. Soc.*, **76** (1954) 379.
27. J.G.Jones, J.B.Poole, J.C.Tomkinson & R.J.P.Williams, *J. Chem. Soc.*, **(1958)** 2001.