ROLE OF ELECTROSTATIC EFFECT AND THE SOLUTION STABILITIES OF BILIGAND LANTHANIDE COMPLEXES WITH ARS

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Bjerrum had defined 'total effect' [1] in order to explain the variation in stability between two successive binary complexes, ML and ML_2 . In the case of biligand complexes of the type $M + A \rightleftharpoons MA$, $MA + L \rightleftharpoons MAL$ (charges-omitted), the first step is accompanied by a coulombic attraction with anionic ligands, and the second step by an attraction, or repulsion depending on the charges on the metal and ligands involved [2]. Besides, other direct or indirect cooperative effects may also be operative [3].

The present work describes the role of electrostatic effect in influencing the solution stabilities of biligand complexes of the type [Ln.A.L], where Ln=La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} or Dy^{3+} A=NTA, HEDTA, or EDTA and L=alizarine red-sulphonate (ARS). These systems have been designed so as to vary the charge on the primary complex, [Ln.A] resulting in the possibility of no or some coulombic repulsion in the formation of [Ln.A.L].

EXPERIMENTAL

The lanthanide nitrates (99.9% purity) were supplied by Indian Rare Earths Ltd. Other chemicals were of Sigma/Merck (G.R.) grade. The solutions were prepared in double distilled water. The Ln-solutions were standardised by complexometric titrations with EDTA [1]. The formation constants were determined by employing the Irving-Rossotti approach [2] at 25° C and ionic strength, I = 0.2 mol dm^{-3}, $NaClO_4$. An Elico digital pH-meter (model LI-120) and a microburette with 0.01 ml accuracy were used for pH titrations. Only reproducible titration data were used for calculations. The formation constant values were refined algebraically by the method of linear plot [9] and also statistically by the 'Q -test'.

RESULTS AND DISCUSSION

The calculated values of the formation constants log K^{M}_{ML} log K^{MA}_{MAL}, and Δ log K

TABLE 1

FORMATION CONSTANTS, log K^{M}_{ML} AND log K^{MA}_{MAL} AND Δ log K (= log K^{MA}_{MAL} - log K^{M}_{ML}) VALUES FOR THE Ln (III) COMPLEXES.

(In all the cases ligand added is ARS)

	La^{3+} ($4f^0$)	Ce^{3+} ($4f^1$)	Pr^{3+} ($4f^2$)	Nd^{3+} ($4f^3$)	Sm^{3+} ($4f^5$)	Eu^{3+} ($4f^6$)	Gd^{3+} ($4f^7$)	Tb^{3+} ($4f^8$)	Dy^{3+} ($4f^9$)
log K^{M}_{ML} (ARS)	9.85 (±0.02)	10.06 (±0.02)	10.07 (±0.01)	10.20 (±0.01)	10.24 (±0.02)	10.32 (±0.03)	10.18 (±0.02)	10.34 (±0.03)	10.37 (±0.02)
log K^{MA}_{MAL} (NTA)	6.41 (±0.02)	6.53 (±0.02)	7.00 (±0.01)	7.96 (±0.03)	8.64 (±0.02)	8.56 (±0.03)	8.11 (±0.03)	9.56 (±0.03)	9.62 (±0.02)
- Δ log K	3.44	3.53	3.07	2.24	1.60	1.76	2.07	0.78	0.75
log K^{MA}_{MAL} (HEDTA)	5.32 (±0.02)	5.38 (±0.02)	5.58 (±0.01)	5.63 (±0.01)	5.96 (±0.01)	6.08 (±0.02)	6.04 (±0.02)	6.76 (±0.01)	6.86 (±0.02)
- Δ log K	4.53	4.68	4.49	4.57	4.28	4.24	4.14	3.58	3.51
log K^{MA}_{MAL} (EDTA)	4.75 (±0.03)	5.06 (±0.03)	5.22 (±0.02)	5.40 (±0.02)	5.45 (±0.02)	5.56 (±0.02)	5.48 (±0.03)	5.90 (±0.02)	6.14 (±0.02)
- Δ log K	5.10	5.00	4.85	4.80	4.79	4.76	4.70	4.44	4.23

Note: Values in parentheses below the formation constants indicate standard deviations.

0013 466 x SN 26 (36) 285-286

($=\log K^{MA}_{MAL} - \log K^{M}_{ML}$) are reported in Table 1. It may be noticed that the formation constants of the biligand [Ln.A.L] complexes lie in the sequence NTA > HEDTA > EDTA, which is totally opposite of the (Known) sequence [3], EDTA > HEDTA > NTA for the binary [Ln.A] complexes. The reversal in the order of the stability can be explained on the basis of electrostatic effect involved in the formation of [Ln.A.L] complexes in two steps as shown below :

$$Ln^{3+} + NTA^{3+} \rightleftharpoons [Ln.NTA]^{\circ}$$
$$[Ln.NTA]^{\circ} + ARS^{2-} \rightleftharpoons [Ln.NTA.ARS]^{2-} \quad ...(1)$$

$$Ln^{3+} \quad HEDTA^{3-} \rightleftharpoons [Ln.HEDTA]^{\circ}$$
$$[Ln.HEDTA]^{\circ} + ARS^{2-} \rightleftharpoons [Ln.HEDTA.ARS]^{2-} \quad ...(2)$$

$$Ln^{3+} + EDTA^{4-} \rightleftharpoons [Ln.EDTA]^{-}$$
$$[Ln.EDTA]^{-} + ARS^{2-} \rightleftharpoons [Ln.EDTA.ARS]^{3-} \quad ...(3)$$

The formation of [Ln.A] complex in all the three cases involves combination of two oppositely charged species accompanied by a large electrostatic attraction. This should result in a considerably large and favourable entropy change [4]. In the second step ARS^{2-} combines with the neutral(eqs 1,2) or negative (eq 3) [Ln.A] species to form the biligand complex $[Ln.A.L]^{n-}$. With HEDTA, a greater steric constraint is involved in comparison to NTA [5], but with EDTA evidently coulombic repusion is involved which lowers the stability of the biligand complex. Thus, it is the second step of complexation in which the normal stability sequence gets reversed.

The present Δ log K values are negative because of the electrostatic effect and lie numerically in the order NTA < HEDTA < EDTA. We may generalise this by stating that greater negative charge on A leads to larger negative value of Δ log K. A stability sequence similar to that observed in the present work has been reported [6] for the Ni(II) complexes as

$$K^{Ni\text{-}Hist}_{Ni\text{-}Hist\text{-}L} > K^{Ni\text{-}IMDA}_{Ni\text{-}IMDA\text{-}L} > K^{Ni\text{-}NTA}_{Ni\text{-}NTA\text{-}L} > K^{Ni\text{-}EDTA}_{Ni\text{-}EDTA\text{-}L}$$

for a variety of secondary ligands.

Another interesting feature of the present Δ log K values is their dependence on the size of the Ln(III) ions. In general the numerical values gradually decrease with decrease in ionic radius of the Ln(III) ions resultsing in the stability sequence $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Eu^{3+} > Gd^{3+} < Tb^{3+} < Dy^{3+}$. A lowering at Gd(III) in this series shows the occurrence of tetrad-effects [12,13], the details of which have been communicated elsewhere [8].

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