Asian Journal of Chemistry Vol. 14. No. 1 (2002), 81–89

Evaluation of Thermodynamic Functions for Complexation Reactions in 1 : 1 : 1 Ternary Lanthanide(III)-EGTA-SA/SSA/DNSA Systems

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Formation of 1 : 1 : 1 ternary complex species (MAL) has been inferred and the relevant equilibrium has been established from pH measurements on the interaction of M^{3+} ions {M = Tb(III), Dy(III), Ho(III) and Er(III)} with ligand A [A = ethylene glycol bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA)] in the presence of the ligand L (L = SA/SSA/DNSA) in aqueous medium at varying ionic strengths of 0.05, 0.10 and 0.15 and at varying temperatures 25, 35 and 45°C. A treatment has been worked out for obtaining information on the extent of metal ion distribution among the various species over the entire pH-range of study. Thermodynamic stability constants together with thermodynamic parameters and relative stabilization has been evaluated and correlated on the basis of basicity, denticity and statistical aspects.

Key words: Ternary lanthanide(III) complexes, ethylene glycol bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid, salicylic acid, sulfosalicylic acid, 3,5-dinitrosalicylic acid.

INTRODUCTION

The stability constants of biligand complexes are of great interest for understanding the role of metal ion and the nature of the two ligands in determining the stability of the mixed ligand complexes[1]. Salicylic acid and its substituted derivatives are of great pharmaceutical importance[1–3]. Many metabolic and toxicological functions of these ligands are dependent on stability of their complexes[4]. Binary complexes of salicylic acid and its substituted derivatives with lanthanide(III) ions have been investigated[5–10]. Ethylene glycol bis(2-aminoethyl ether)-N,N,N′,N′-tetraacetic acid (EGTA) is an important member of aminopolycarboxylic acid class of compounds and finds many applications in medical and biological fields. The formation of binary and ternary complexes by ethyleneglycol bis(2-aminoethyl ether)-N,N,N′,N′ tetraacetic acid (EGTA) with lanthanides has been studied pH-metrically and spectrophotometrically[11–23]. Due to the favourable geometry of its donor groups EGTA forms stable binary complexes with many metal ions.

Ternary complexes of lighter lanthanide(III) metal ions with aminopolycarboxylic acids in presence of salicylic acid and its derivatives have been reported[24–27]. However, no information is available on the ternary complexes of EGTA with heavier lanthanides with salicylic acid (SA), sulfosalicylic acid (SSA) and 3,5-dinitrosalicylic acid (DNSA). The present work deals with the determination of formation constants of ternary complexes of Tb(III), Dy(III), Ho(III) and Er(III) metal ions with EGTA and SA/SSA/DNSA.

EXPERIMENTAL

All the chemicals used were of analytical grade and their solutions were prepared in double distilled CO_2-free water. Standard solutions of rare earth nitrates were prepared by dissolving the accurately weighed amounts of their nitrates in 0.10 M nitric acid solution and standardised by usual methods[28]. Solution of disodium salt of EGTA (Na_2H_2EGTA) and salicylic acid, monosodium salt of sulfosalicylic acid and 3,5-dinitrosalicylic acid were prepared by dissolving their accurately weighed amounts. An Elico pH-meter fitted with a combined glass SCE electrode assembly was employed. It was calibrated with standard buffer solutions of pH = 4.00 and 9.20.

Following series of solutions were prepared in aqueous medium. Initial volume of each solution was 50 mL. These solutions were titrated potentiometrically against standard alkali solution of 0.10 M.

1. HNO_3 (2.0×10^{-3} M)
2. HNO_3 (2.0×10^{-3} M) + ligand Na_2H_2EGTA (1.0×10^{-3} M)
3. HNO_3 (2.0×10^{-3} M) + ligand SA/SSA/DNSA (1.0×10^{-3} M)
4. HNO_3 (2.0×10^{-3} M) + ligand Na_2H_2EGTA (1.0×10^{-3} M) + metal ion (1.0×10^{-3} M)
5. HNO_3 (2.0×10^{-3} M) + ligand SA/SSA/DNSA (1.0×10^{-3} M) + metal ion (1.0×10^{-3} M)
6. HNO_3 (2.0×10^{-3} M) + ligand Na_2H_2EGTA (1.0×10^{-3} M) + ligand SA/SSA/DNSA (1.0×10^{-3} M) + metal ion (1.0×10^{-3} M)

where Na_2H_2EGTA = disodium salt of ethyleneglycol bis(2-amino-ethylether)-N,N,N′,N′-tetraacetic acid, SA = salicylic acid, SSA = monosodium salt of sulfosalicylic acid, DNSA = 3,5-dinitrosalicylic acid and metal ion = Tb(III), Dy(III), Ho(III) and Er(III). These titrations were repeated at three ionic strengths (0.05, 0.10 and 0.15 M ($NaNO_3$) at 25°C and only one ionic strength of 0.10 M ($NaNO_3$) at 35 and 45°C.

RESULTS AND DISCUSSION

From the titration curves the moles of alkali used per mole of ligand/metal ion for various systems were evaluated. As a representative case the plots of 'a' *vs.* pH corresponding to proton-ligand, binary metal-ligand (ML and MA) and ternary metal-ligand (A-ligand L) are presented for Tb(III)-EGTA-Sa system (Fig. 1). The plot of 'a' *vs.* pH for theoretical composite curve for ternary system has also been shown in Fig. 1. The values of proton dissociation constants of the ligands, metal-ligand stability constants of 1 : 1 binary complexes were calculated by algebraic method[29].

In Fig. 1 it is observed from curve 3 that the formation of binary M(III)-EGTA

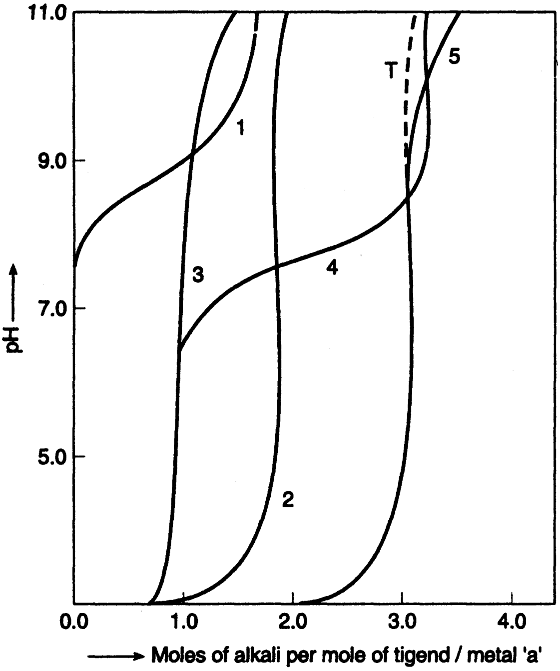

Fig.1 Plot of 'a' Vs pH for 1 : 1 : 1 Tb(III)-EGTA-SA EGTA . . . (1), Tb(III)-EGTA . . . (2), SA . . . (3), Tb(III)-SA . . . (4), Tb(III)-EGTA-SA . . . (5) Composite curve . . . (T)

complex takes place at lower pH value as indicated by the occurrence of a sharp inflection at a = 2, pH ≈ 4.5. The steep inflection continues to remain at a = 2 up to pH ≈ 10.5. This indicates that the formation of 1 : 1 $[M(III)\text{-}EGTA]^-$ complex takes place at lower pH values and it remains stable up to higher pH. The ternary 1 : 1 : 1 [M(III)-EGTA-SA] curve runs superimposed on the theoretical composite curve T up to pH ≈ 8.5, indicating that the ligand SA/SSA/DNSA does not combine with the metal. The divergence of the mixed ligand titration curve at pH ≈ 8.5 from the theoretical composite curve T indicates the combination of SA/SSA/DNSA resulting in the formation of ternary complex. Non-appearance of any opacity/turbidity/precipitate during the titration of mixed ligand also supports the ternary complex formation. The above observations suggest that the formation of mixed ligand complexes takes place by the stepwise coordination of the two ligands. In the region of $0 < a < 3$, where the mixed ligand titration curve runs superimposed on the theoretical composite curve, the equilibrium can be shown as:

$$Ln^{3+} + H_2EGTA^{2-} + H_2L \xrightleftharpoons{0<a<3} [Ln(III)\text{-}EGTA]^- + HL^- + 3H^+$$

(where H_2L = SA/SSA/DNSA).

The combination of the ligand H_2L in all these mixed ligands is found to take place at such pH where the —COOH group of SA/SSA/DNSA is completely deprotonated and the ligands exist as HL^-. Therefore, in the region $3 < a < 4$, where the mixed ligand titration curve shows divergence from the theoretical composite curve, the formation of ternary complex takes place and the following equilibrium is established.

$$[Ln(III)\text{-}EGTA]^- + HL^- \xrightleftharpoons{3 < a < 4} [Ln(III)\text{-}EGTA\text{-}L]^{-2} + H^+$$

Percentage Distribution of Metal(III) ion among the various Complex Species and Evaluation of Ternary Formation Constants

In solution the following equilibria are expected to exist:

$$H_2A^{2-} \xrightleftharpoons{K_1^A} HA^{3-} + H^+ \qquad \text{(i)}$$

$$HA^{3-} \xrightleftharpoons{K_2^A} A^{4-} + H^+ \qquad \text{(ii)}$$

$$H_2L \xrightleftharpoons{K_1^L} HL^- + H^+ \qquad \text{(iii)}$$

$$HL^- \xrightleftharpoons{K_2^L} L^{2-} + H^+ \qquad \text{(iv)}$$

$$M^{3-} + A^{4-} \xrightleftharpoons{K_{MA}} MA^- \qquad \text{(v)}$$

$$M^{3+} + L^{2-} \xrightleftharpoons{K_{ML}} ML^+ \qquad \text{(vi)}$$

$$MA^- + L^{2-} \xrightleftharpoons{K_{MAL}^{MA}} MAL^{3-} \qquad \text{(vii)}$$

The total concentrations of H_2A, H_2L and M(III) ions represented as C_A, C_L and C_M respectively at any pH on the mixed ligand titration curve from $0 < a < 4$ may be given by the following mass and charge balance relations:

$$C_A = [H_2A] + [HA] + [A] + [MA] + [MAL] \qquad (1)$$

$$C_L = [H_2L] + [HL] + [L] + [ML] + [MAL] \qquad (2)$$

$$C_M = [M] + [MA] + [ML] + [MAL] \qquad (3)$$

$$aC_M = [HA] + 2[A] + 2[MA] + [HL] + 2[L] + 2[L] + 2[ML] + 4[MAL] \qquad (4)$$

a = moles of alkali per mole of ligand or metal ion in 1 : 1 : 1 ternary system (charges are omitted for simplicity).

As $C_A = C_L = C_M$ the following quadratic equation for the concentration of [A] is obtained from the equations (1), (2), (3) and (4).

$$[A]^2(a_2K_{MA} - b_2d^2K_{ML}) + [A](a_2 + db_2 + 2e_1db_2K_{ML}) - (b_2e_1 + b_2e_1^2K_{NL}) = 0 \qquad (5)$$

where $e_1 = (4 - a)C_M/b$ and $d = a_1/b_1$.

From the knowledge of proton dissociation constants of the ligands and the stability constants of their binary complexes the value of [A] is evaluated by solving the quadratic equation, whereby [L], [M], [MA] and [ML] were evaluated. Hence, the concentration of the mixed ligand complex $[MAL]^{3-}$ over the entire pH range was calculated. The percentage of each of the species out of the total M(III) ion concentration at the corresponding pH can be calculated. The results obtained are depicted in the distribution curve (Fig. 2) for the Tb(III)-EGTA-SA system. From this figure it is evident that no mixed ligand complex is formed up to pH ≈ 8.5. The pH from which the formation of MAL complex starts about 99% of the total metal ion exists as [MA] complex. Hence, the equilibrium for the mixed ligand complex formation reaction may be given as:

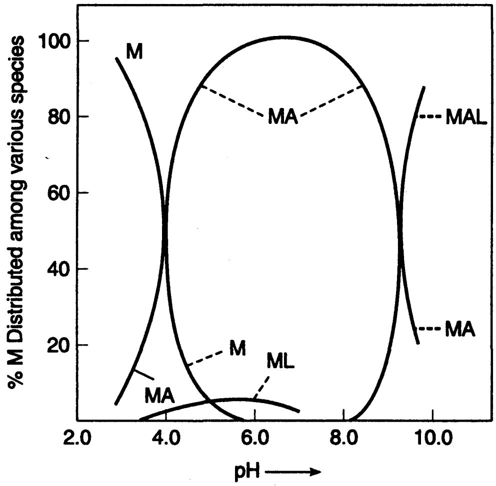

Fig. 2. % Distribution of M in various metal Complex species in 1 : 1 : 1 MAL system M = Tb(III), A = EGTA, L = SA

$$MA + L \xrightleftharpoons{K_{MAL}^{MA}} MAL$$

and the corresponding equilibrium constant is:

$$K_{MAL}^{MA} = [MAL]/[MA]L \qquad (6)$$

The value of K_{MAL} was calculated by substituting the values of [ML], [L] and [MAL] in equation 6. The values of proton-dissociation constants of the ligands and the formation constants of binary complexes are recorded in Tables 1 and 2. The values of formation constants of ternary complexes obtained at different ionic strengths, *e.g.*, 0.05, 0.10 and 0.15 M are recorded in Table-3. A comparative account of thermodynamic formation constants of binary and ternary complexes are recorded in Tables 3 and 4 together with Δ log K, [$\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}$], percentage relative stabilization (%) R.S. [(%)

R.S. = Δ log K × 100/ log K_{ML}], free energy changes, enthalpy changes and entropy changes.

TABLE-1

THERMODYNAMIC STABILITY CONSTANTS OF PROTON-LIGAND SYSTEMS

Proton-ligand systems	Temperature (°C)											
	25								35		45	
	μ = 0.15 M		μ = 0.10 M		μ = 0.05 M		μ → 0.00 M		μ = 0.10 M		μ = 0.10 M	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
EGTA	8.725	10.375	8.866	10.514	9.028	10.614	9.182	10.742	8.625	10.289	8.473	10.131
SA	2.961	12.391	3.105	12.628	3.176	12.825	3.286	12.931	2.931	12.441	2.773	12.278
SSA	2.935	10.662	3.039	10.775	3.118	10.906	3.208	11.015	2.848	10.590	2.695	10.431
DNSA	1.517	7.375	1.673	7.532	1.862	7.783	1.995	7.926	1.545	7.368	1.387	7.212

TABLE-2

THERMODYNAMIC STABILITY CONSTANTS OF BINARY METAL-LIGAND SYSTEMS AT DIFFFERENT TEMPERATURES

Metal-ligand systems	Temperature (°C)					
	25				35	45
	log K_{MA} (μ = 0.15 M)	log K_{MA} (μ = 0.10 M)	log K_{MA} (μ = 0.05 M)	log K_{MA} (μ → 0.00 M)	log K_{MA} (μ = 0.10 M)	log K_{MA} (μ = 0.10 M)
Tb(III)-EGTA	16.862	16.972	17.086	17.185	16.848	16.723
Dy(III)-EGTA	16.918	17.025	17.124	17.218	16.891	16.761
Ho(III)-EGTA	16.962	17.065	17.165	17.254	16.945	16.795
Er(III)-EGTA	16.991	17.093	17.191	17.291	16.972	16.830
	log K_{ML}	log K_{ML}	log K_{ML}	log K_{ML}	log K_{ML}	log K_{ML}
Tb(III)-SA	8.585	8.721	8.842	8.965	8.561	8.471
Dy(III)-SA	8.651	8.793	8.928	9.054	8.605	8.513
Ho(III)-SA	8.728	8.882	9.015	9.165	8.639	8.549
Er(III)-SA	8.791	8.961	9.081	9.224	8.735	8.587
Tb(III)-SSA	6.807	6.924	7.057	7.180	6.797	6.669
Dy(III)-SSA	6.885	7.018	7.141	7.275	6.841	6.705
Ho(III)-SSA	6.957	7.093	7.205	7.381	6.870	6.739
Er(III)-SSA	7.021	7.162	7.309	7.443	6.902	6.775
Tb(III)-DNSA	5.782	5.918	6.065	6.205	5.780	5.653
Dy(III)-DNSA	5.861	5.982	6.146	6.281	5.826	5.695
Ho(III)-DNSA	5.965	6.085	6.214	6.470	5.862	5.732
Er(III)-DNSA	6.023	6.139	6.271	6.622	5.905	5.769

TABLE-3

CONDITIONAL AND THERMODYNAMIC STABILITY CONSTANTS OF TERNARY COMPLEXES TOGETHER WITH Δ log K, (%) R.S. AND ΔG° AT DIFFERENT TEMPERATURES

Ternary complexes	Temperature (°C)								
	25							35	45
	log K_{MAL}^{MA} (μ = 0.15 M)	log K_{MAL}^{MA} (μ = 0.10 M)	log K_{MAL}^{MA} (μ = 0.05 M)	log K_{MAL}^{MA} ($\mu \rightarrow$ 0.00 M)	Δ log K	(%) R.S.	ΔG° kcal mol^{-1}	log K_{MAL}^{MA} (μ = 0.10 M)	log K_{MAL}^{MA} (μ = 0.10 M)
Tb(III)-EGTA-SA	5.760	5.876	5.960	6.060	–2.905	–47.937	–8.234	5.757	5.583
Dy(III)-EGTA-SA	5.788	5.898	5.984	6.095	–2.959	–48.547	–8.282	5.778	5.656
Ho(III)-EGTA-SA	5.817	5.927	6.019	6.126	–3.040	–49.632	–8.323	5.806	5.695
Er(III)-EGTA-SA	5.845	5.948	6.050	6.155	–3.099	–50.598	–8.363	5.825	5.720
Tb(III)-EGTA-SSA	5.352	5.460	5.556	5.695	–1.485	–26.075	–7.738	5.340	5.235
Dy(III)-EGTA-SSA	5.381	5.486	5.576	5.718	–1.560	–27.296	–7.765	5.363	5.268
Ho(III)-EGTA-SSA	5.407	5.513	5.599	5.730	–1.651	–28.813	–7.786	5.389	5.304
Er(III)-EGTA-SSA	5.421	5.544	5.629	5.755	–1.688	–29.331	–7.820	5.420	5.335
Tb(III)-EGTA-DNSA	5.037	5.142	5.235	5.336	–0.869	–16.285	–7.250	5.028	4.917
Dy(III)-EGTA-DNSA	5.064	5.177	5.261	5.365	–0.916	–17.073	–7.290	5.061	4.940
Ho(III)-EGTA-DNSA	5.085	5.202	5.278	5.382	–1.088	–20.215	–7.313	5.084	4.995
Er(III)-EGTA-DNSA	5.106	5.239	5.307	5.406	–1.216	–22.493	–7.346	5.123	5.029

Negative values of (%) R.S. indicate that the ligand [L] binds better to aquo metal ion than the binary [Ln(III)-EGTA]$^-$ complex. This may be probably due to the extra strain caused by the coulombic repulsion between the binary complex [Ln(III)-EGTA]$^-$ and incoming ligand [L] in the mixed ligand complexes and the availability of lesser number of coordination sites for the coordination of ligand [L] on binary [Ln(III)-EGTA]$^-$ complex compared to free Ln(III) aqueous ion[29]. The order of stability with respect to Ln(III) ion is found to be:

$$\text{Tb(III)} < \text{Dy(III)} < \text{Ho(III)} < \text{Er(III)}$$

which is the order of increasing ionic potential of the lanthanide ions. The stability sequence with respect to ligand H_2L is found to be:

$$\text{DNSA} < \text{SSA} < \text{SA}$$

which follows the basicity order of the ligands.

It has been observed that with increase in temperature, stability constants show a decreasing trend. The thermodynamic parameters (ΔG, ΔH and ΔS) have also been calculated from the stability constants using Gibb's Helmholtz equation and are given in Table-4. The negative free energy change (ΔG) becomes more negative with decrease in temperature suggesting an increase in the extent of complex formation at lower temperatures. The exothermic nature of the reaction is supported by the negative values of ΔH. The ΔS values are positive for all the chelates showing that entropy is favourable for complex formation.

TABLE-4
THERMODYNAMIC PARAMETERS OF THE TERNARY COMPLEXES AT 35°C AND $\mu = 0.10$ M ($NaNO_3$)

Ternary complexes	ΔG° (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° (cal mol^{-1} degree^{-1})
Tb(III)-EGTA-SA	8.085	4.980	10.081
Dy(III)-EGTA-SA	8.115	5.022	10.042
Ho(III)-EGTA-SA	8.154	5.064	10.032
Er(III)-EGTA-SA	8.181	5.147	9.850
Tb(III)-EGTA-SSA	7.499	5.022	8.042
Dy(III)-EGTA-SSA	7.532	5.147	7.743
Ho(III)-EGTA-SSA	7.568	5.189	7.724
Er(III)-EGTA-SSA	7.612	5.189	7.866
Tb(III)-EGTA-DNSA	7.061	4.771	7.435
Dy(III)-EGTA-DNSA	7.108	4.854	7.318
Ho(III)-EGTA-DNSA	7.140	4.938	7.149
Er(III)-EGTA-DNSA	7.195	5.022	7.055

REFERENCES

1. N. Mirsky, A. Weiss and Z. Dori, *J. Inorg. Biochem.*, **8**, 419 (1979).
2. Y. Anjaneyulu, R.Y. Swamy and R.P. Rao, *J. Indian Chem. Soc.*, **63**, 346 (1985).
3. D.R.H. Gourley, in: E. Burle (Ed.), Medical Chemistry, Wiley-Interscience, New York (1960).
4. A. Albert, Selective Toxicity, Chapman and Hall, London (1979).
5. I.M. Batyaev and N.L. Pzankova, *Zh. Neorg. Khim.*, **18**, 981 (1973).
6. S.N. Dubey and B.C. Bhuvan, *Indian J. Chem.* **21A**, 442 (1982).
7. T.A. Boranova, S.B. Prikes, A.A. Bugaevskis, Yu. V. Kholin and N.A. Kostromina, *J. Chem. Thermodyn.*, **23**, 543 (1991).
8. S.B. Prikes and A.V. Lapitskova, *Zh. Neorg. Khim.*, **20**, 1415 (1975).
9. B.R. Choppin and N.C. Liuqing, *Lanthanide Actinide Res.*, **5–6**, 285 (1986).
10. Chan Ki-Won and Park Kwang-won, *Anal. Sci. Technol.*, **8**, 305 (1995).
11. A.K. Das and A. Chakraborty, *J. Indian Chem. Soc.*, **57**, 653 (1980).
12. M. Nurmond, Z. Bayat and S. Yourefi, *Polyhedron*, **11**, 827 (1982).
13. A.K. Pandey, M. Chandra, B.V. Agrawala and A.K. Dey, *J. Indian Chem. Soc.*, **57**, 32 (1980).
14. Tong-Ming Hseu and Kao-Ming Jyi, *J. Chem. Soc. (Taipai)*, **28**, 119 (1981).
15. J. Avarez, D. Maria, G.J. Colmas, S. Maria, P.G. Balanero and R. Andreu, *An. Quim. (Spain)*, **78B**, 136 (1982).
16. R. Kiraly and E. Brucher, *J. Less Common Metals*, **112**, 227 (1985).
17. R. Ahuja and K. Dwivedi, *J. Indian Chem. Soc.*, **68**, 643 (1991).
18. Vishnu Kolhe and K. Dwivedi, *J. Electrochem. Soc. (India)*, **44**, 211 (1995).
19. G.K. Chaturvedi, *J. Indian Chem. Soc.*, **56**, 854 (1979).
20. A.M. Pirkes and K.N. Munshi, *Indian J. Chem.*, **15A**, 636 (1977).
21. S.N. Limaye and M.C. Saxena, *J. Inst. Chem.* (India), **57**, 79 (1985).
22. A.K. Pandey, M. Chandra, B.V. Agrawala and A.K. Dey, *Indian J. Chem.*, **19A**, 924 (1980).
23. ———, *Rev. Chem. Mirror*, **17**, 214 (1980).
24. S. Verma and M.C. Saxena, *J. Electrochem. Soc. (India)*, **39**, 75 (1990).
25. R. Ahuja and K. Dwivedi, *J. Indian Chem. Soc.*, **68**, 643 (1991).
26. ———, *Asian J. Chem.*, **5**, 74 (1993).
27. Vishnu Kolhe and K. Dwivedi, *J. Indian Chem. Soc.*, **73**, 265 (1996).
28. H.A. Flaschka, EDTA Titration, Pergamon Press, 2nd Edn. (1964).
29. R. Nayan and A.K. Dey, *Indian J. Chem.*, **14A**, 892 (1976).

(*Received*: 25 June 2001; *Accepted*: 29 September 2001) AJC-2454