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Potentiometric Study of the Biligand 1 : 1 : 1 Ln(III)-CDTA-Valine/Leucine/Serine Complexes and Evaluation of Thermodynamic Parameters

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Ternary 1 : 1 : 1 Ln(III)-L-L′ complexes have been investigated by potentiometric titration method [Ln(III) = Tb(III), Dy(III), Ho(III) and Er(III), L = cyclohexane diamine N,N,N′,N′-tetraacetic acid and L′ = valine, leucine and serine]. The stability constants of these ligands together with thermodynamic parameters. *viz.*, free energy of formation ΔG, enthalpy change ΔH and entropy change ΔS at different ionic strengths (μ = 0.05, 0.10 and 0.15 M KNO_3) and varying temperatures, *i.e.*, 25, 35 and 45°C, have been investigated. Relative order of stabilities observed as Tb(III) < Dy(III) < Ho(III) < Er(III).

Key Words: Ternary lanthanide(III) complexes, Cyclohexane diamine N,N,N′,N′-tetraacetic acid, Valine, Leucine, Serine.

INTRODUCTION

The formation constants of mixed ligands complexes using cyclohexane diamine N,N,N′,N′-tetraacetic acid (CDTA) as primary ligands have been investigated by using Irving-Rosotti pH titration technique[1]. CDTA is an important member of amino polycarboxylic acid class of compounds and forms stable binary and ternary complexes. Some important amino polycarboxylic acids like, NTA, IMDA, HEDTA, EDTA, CDTA, PDTA, DTPA have attracted the attention of researchers in order to investigate the complex equilibria of these multidentate ligands with Ln(III) ions. Binary complexes of these ligands with Ln(III) ions as well as ternary complexes with many metal ions have been investigated[2–4]. Chelates of amino polycarboxylates like HEDTA, EDTA, EGTA, DTPA and CDTA are much important in analytical chemistry[5, 6]. Mixed ligand complexes (in solution) of transition metal and lanthanide ion with CDTA and thioglycollic acid thiomaleic acid and norleucine have been reported[7, 8]. Amino acids are very important ligands and play major role in biological and chemical systems[9, 10]. Involvement of some amino acids has been reported in Cu(II) transport in blood[11]. Stability constants of amino acid complexes in aqueous and non-aqueous media

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and mixed solvents have also been reported[12–19]. The present work is intended to investigate the formation of ternary complexes 1 : 1 : 1 Ln(III)-CDTA-amino acids taking the CDTA as primary ligand and amino acids (valine, leucine and serine) as secondary ligands.

EXPERIMENTAL

A pH-meter (digital Li-120) having glass electrode and saturated calomel electrode (ER-70) with reproducibility ± 0.02 pH unit was used for titration. The instrument was standardized with potassium hydrogen sulphate and phosphate buffers. All the solutions were prepared in doubly distilled CO_2 free water. The chemicals used were of analytical grade. Solutions of the ligands, valine, leucine and serine were prepared in ethanol. Metal nitrate solutions were standardized by usual methods[20].

Following sets of titrations were performed under nitrogen atmosphere against 0.10 M NaOH at three different ionic strengths (μ = 0.05 M, 0.10 M and 0.15 M KNO_3) and temperatures 25, 35 and 45°C.

1. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 35 mL distilled water.
2. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 5 mL CDTA (0.01 M) + 30 mL distilled water.
3. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 5 mL metal nitrate (0.01 M) + 5 mL CDTA (0.01 M) + 25 mL distilled water.
4. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 5 mL ligand L′ + 30 mL distilled water.
5. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 5 mL metal nitrate (0.01 M) + 5 mL ligand L′ (0.01 M) + 25 mL distilled water.
6. 10 mL nitric acid (0.01 M) + 5 mL potassium nitrate (1.0 M) + 5 mL metal nitrate (0.01 M) + 5 mL CDTA (0.01 M) + 5 mL ligand L′ + 20 mL distilled water.

The ratios of the concentration of metal : ligand in mixtures 3 and 5 and metal : CDTA : ligand L′ in mixture 6 were kept 1 : 1 and 1 : 1 : 1 respectively in each case of the system.

RESULTS AND DISCUSSION

Identical titration curves were obtained for corresponding systems of lanthanide metal ions. Hence, only the curve for 1 : 1 : 1 Ln(III)-CDTA-Valine has been discussed to show the evidence of mixed ligand complex formation in general.

For illustration, the plot of moles of alkali per mole of ligand/metal against pH is shown in Fig. 1 for binary and ternary systems involving Tb(III), CDTA and valine.

The displacement of Tb(III)-CDTA curve 2 from the CDTA ligand titration curve 1 in the initial stages of the titration followed by well defined inflection at 'a' = 2 ('a' = moles of alkali per mole of ligand or metal) and pH ≈ 4.45 indicates

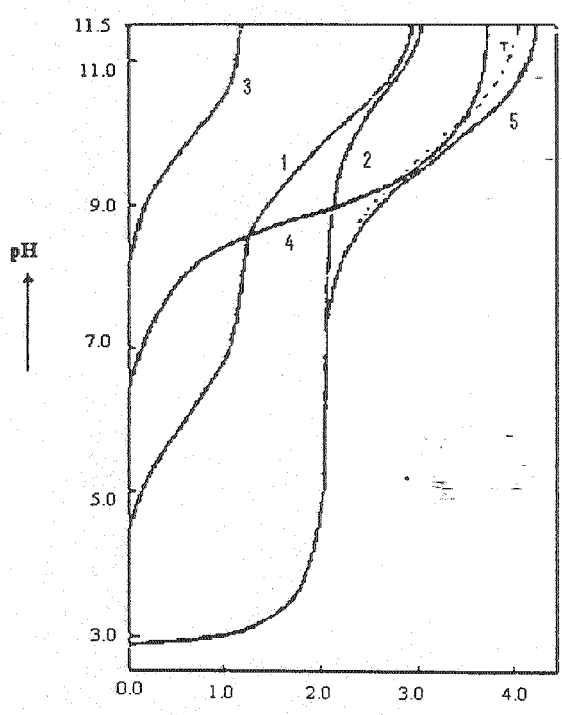

Fig. 1. Plot of 'a' *vs.* pH for 1 : 1 : 1 Tb(III)-CDTA-valine system: 1. CDTA, 2. Tb(III)-CDTA, 3. Valine, 4. Tb(III)-valine, 5. Tb(III)-CDTA-valine, and 6. Theoretical composite curve

that Tb(III) ion forms 1 : 1 chelate with CDTA in lower pH range. The inflection obtained at 'a' = 2.0 up to pH ≈ 10.0 which shows that this complex remains stable up to high pH. Curve 5 (Tb(III)-CDTA-valine) runs superimposed on the Tb(III)-CDTA titration curve 3 upto 'a' = 3 indicating that secondary ligand does not participate in the formation of mixed ligand complex up to this stage. Its comparison with theoretical composite curve (T) up to pH ≈ 7.6 and 'a' = 2 moles of alkali per mole of metal ions, in ternary 1 : 1 : 1 MLL′ system, suggests that the ligand L′ does not participate in complex formation up to this stage. However, at 'a' = 2, pH ≈ 7.6, the mixed ligand titration curve 5 deviates from the theoretical composite curve T to the right indicating the liberation of extra protons due to the formation of mixed ligand complex. The occurrence of precipitation during the titration of 1 : 1 Tb(III)-CDTA around pH ≈ 7.0 but non-appearance of any precipitation during mixed ligand titration further supports the formation of mixed ligand complex in solution. Hence it is evident that the ternary complex formation occurs through stepwise equilibria in which CDTA acts as primary ligand and valine, leucine and serine act as secondary ligands.

Following successive steps are involved in the equilibria of mixed ligand systems:

$$\text{I. } Ln^{3+} + H_2CDTA^{2-} \overset{0 \le a \le 2}{\rightleftharpoons} [Ln\text{-}CDTA]^{-} + 2H^{+}$$

$$\text{II. } [Ln\text{-}CDTA]^{-} + HL' \overset{2 \le a \le 3}{\rightleftharpoons} [[Ln\text{-}CDTA\text{-}L']^{2-} + H^{+}$$

The formation constant values of mixed ligand complexes were calculated by Thompson and Loraas method[21]. The values so obtained at different ionic strengths, *e.g.*, 0.05, 0.10 and 0.15 M (KNO_3) are recorded in Table-3.

TABLE-1
THERMODYNAMIC STABILITY CONSTANTS OF PROTON-LIGAND SYSTEMS AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

Proton-ligand systems	Temperatures (°C)											
	25								35		45	
	μ = 0.15 M		μ = 0.10 M		μ = 0.05 M		μ → 0.00 M		μ = 0.105 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
CDTA	6.17	11.00	6.21	11.08	6.35	11.20	6.44	11.32	6.15	10.91	6.00	10.60
Valine	9.55	—	9.68	—	9.77	—	9.81	—	9.64	—	9.40	—
Leucine	9.62	—	9.75	—	9.84	—	9.92	—	9.76	—	9.54	—
Serine	9.15	—	9.22	—	9.29	—	9.36	—	9.10	—	9.02	—

TABLE-2
THERMODYNAMIC STABILITY CONSTANTS OF BINARY METAL-LIGAND SYSTEMS AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

Metal-ligand systems	Temperatures (°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
Tb(III)-CDTA	15.48	15.62	15.80	15.96	15.44	15.36
Dy(III)-CDTA	15.54	15.66	15.84	16.02	15.51	15.40
Ho(III)-CDTA	15.61	15.73	15.90	16.05	15.58	15.45
Er(III)-CDTA	15.67	15.78	15.95	16.11	15.65	15.53
Tb(III)-Valine	6.22	6.45	6.48	6.57	6.20	6.04
Dy(III)-Valine	6.46	6.54	6.68	6.80	6.30	6.15
Ho(III)-Valine	6.75	6.81	7.00	7.08	6.65	6.53
Er(III)-Valine	6.84	7.90	7.07	7.25	6.76	6.66
Tb(III)-Leucine	6.06	6.14	6.28	6.36	6.02	5.95
Dy(III)-Leucine	6.14	6.24	6.33	6.40	6.08	6.00
Ho(III)-Leucine	6.21	6.32	6.38	6.46	6.14	6.08
Er(III)-Leucine	6.28	6.39	6.43	6.51	6.22	6.15
Tb(III)-Serine	5.15	5.24	5.36	5.42	5.10	5.03
Dy(III)-Serine	5.20	5.33	5.43	5.50	5.15	5.09
Ho(III)-Serine	5.31	5.44	5.55	5.61	5.27	5.17
Er(III)-Serine	5.40	5.51	5.63	5.70	5.33	5.25

A comparative account of logarithmic values of binary complexes log K_{ML} and log K_{ML}' are given in Table-2 and formation constants of ternary complexes log K_{MLL}' together with Δ log K [Δ log K = log K_{MLL}' – log K_{ML}'], percentage relative stabilization [% RS = (Δ log K′ × 100)/log K_{ML}] are given in Table-3.

TABLE-3
THERMODYNAMIC STABILITY CONSTANTS OF TERNARY 1 : 1 : 1 METAL-LIGAND SYSTEMS AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

Ternary systems	Temperatures (°C)							
	25						35	45
	μ = 0.15 M	μ = 0.10 M	μ = 0.05 M	μ → 0.00 M	Δ log K	% R.S.	μ = 0.10 M	μ = 0.10 M
Tb(III)-CDTA-Valine	3.41	3.52	3.60	3.69	−2.93	−18.758	3.35	3.27
Dy(III)-CDTA-Valine	3.48	3.59	3.70	379	−2.95	−18.838	3.42	3.35
Ho(III)-CDTA-Valine	3.57	3.68	3.79	3.90	−3.13	−19.898	3.50	3.41
Er(III)-CDTA-Valine	3.68	3.75	3.87	3.98	−3.15	−19.962	3.56	3.47
Tb(III)-CDTA-Leucine	3.34	3.41	3.49	3.55	−2.73	−17.478	3.26	3.21
Dy(III)-CDTA-Leucine	3.40	3.49	3.57	3.64	−2.75	−17.561	3.34	3.28
Ho(III)-CDTA-Leucine	3.46	3.56	3.64	3.73	−2.76	−17.546	3.40	3.35
Er(III)-CDTA-Leucine	3.55	3.61	3.71	3.79	−2.78	−17.617	3.44	3.41
Tb(III)-CDTA-Serine	3.25	3.34	3.40	3.47	−1.90	−12.146	3.21	3.13
Dy(III)-CDTA-Serine	3.31	3.42	3.46	3.54	−1.91	−12.197	3.28	3.18
Ho(III)-CDTA-Serine	3.40	3.48	3.55	3.61	−1.96	−12.460	3.34	3.27
Er(III)-CDTA-Serine	3.46	3.53	3.60	3.66	−1.98	−12.548	3.38	3.35

Negative values of (%) R.S. indicate that the ligand [L′] binds better to aquo metal ions than the binary [Ln(III)-CDTA]$^-$ complex. This may be attributed to the extra strain caused by coulombic repulsion between the binary complex [Ln(III)-CDTA]$^-$ and incoming ligand [L′] in the mixed ligand complexes and availability of lesser number of coordination sites for the coordination of [L′] on binary complex [Ln(III)-CDTA]$^-$ compared to free Ln(III) aqueous ion[22]. The order of stability w.r.t. Ln(III) ions is found to be: Tb(III) < Dy(III) < Ho(III) < Er(III) which is the order of increasing ionic potential of the lanthanide ions. The stability sequence w.r.t. secondary ligands HL′ is found to be:

Valine > Leucine > Serine

which follows the order of increasing pK value of the secondary ligands.

The values of stability constants at different temperatures indicates that the stability constants show a decreasing trend with increase in temperature. The thermodynamic parameters (ΔG, ΔH and ΔS) have also been calculated and recorded in Table-4.

TABLE-4
THERMODYNAMIC PARAMETERS OF TERNARY COMPLEXES AT 35°C AND μ = 0.10 M (KNO_3)

Ternary systems	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} $degree^{-1}$)
Tb(III)-CDTA-Valine	–20.759	–29.877	–29.603
Dy(III)-CDTA-Valine	–21.172	–29.877	–28.262
Ho(III)-CDTA-Valine	–21.703	–31.634	–32.245
Er(III)-CDTA-Valine	–22.116	–33.392	–36.611
Tb(III)-CDTA-Leucine	–20.111	–26.362	–20.297
Dy(III)-CDTA-Leucine	–19.914	–26.368	–20.935
Ho(III)-CDTA-Leucine	–20.314	–28.119	–25.344
Er(III)-CDTA-Leucine	–20.599	–29.877	–30.124
Tb(III)-CDTA-Serine	–19.638	–22.847	–10.225
Dy(III)-CDTA-Serine	–20.170	–24.605	–14.399
Ho(III)-CDTA-Serine	–20.523	–24.605	–13.250
Er(III)–CDTA-Serine	–20.818	–26.362	–17.999

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