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Study of the Ternary 1:1:1 Ln(III)-CDTA-Phenyl Alanine/Tyrosine/Tryptophane Complexes

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1:1:1 Ln(III)-CDTA-L mixed ligand complexes have been investigated by potentiometric titration method [Ln(III) = Tb(III), Dy(III), Ho(III) and Er(III), CDTA = cyclohexane diamine N,N,N`,N`-tetraacetic acid and L = phenyl alanine/tyrosine/tryptophane]. The stability constants of these ligands together with free energy of formation and entropy change at different ionic strengths ($\mu = 0.05$, 0.10 and 0.15 M KNO_3) and varying temperatures *i.e.* 25, 35 and 45 ºC have been investigated in aqueous medium. Thermodynamic parameters *e.g.*, ΔG, ΔH and ΔS have been calculated. Relative order of stabilities of the complexes observed as Tb(III) < Dy(III) < Ho(III) < Er(III) and with respect to ligand it was phenyl alanine < tyrosine < tryptophane.

Key Words: Ternary lanthanide(III) complexes, Cyclohexane diamine N,N,N`,N`-tetra acetic acid, Phenyl alanine, Tyrosine, Tryptophane, Thermodynamic parameters.

INTRODUCTION

The stability constants of mixed ligands complexes using 1,2-diaminocyclohexane N,N,N`,N`-tetra acetic acid (CDTA) as primary ligand have been investigated by using Irrving-Rossotti pH titration technique[1]. CDTA is an important member of amino poly carboxylic acid class of compounds and forms stable binary and ternary complexes. Some important amino poly carboxylic acids like EDTA, EGTA, CDTA, PDTA, DTPA, HEDTA, NTA, IMDA have attracted the attention of researchers in order to investigate the complex equilibria of these multidentate ligands with Ln(III) ions. Binary and ternary complexes of these ligands with Ln(III) ions as well as ternary complexes with many metal ions have been investigated[2-4].

Complexes of amino polycarboxylates like EDTA, EGTA, DTPA, HEDTA and CDTA are much important in analytical chemistry[5,6]. Mixed ligand complexes (in solution) of transition metal and lanthanides ion with CDTA and thioglycollic acid thiomaleic acid, norleucinate, valine, leucine and serine have already been reported[7,8].

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Amino acids are very important ligand 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 and mixed solvents have been reported[12-19].

The present work deals with the investigation of formation of ternary complexes 1:1:1 Ln(III)-CDTA-amino acids taking CDTA as primary ligand and aromatic amino acids *e.g.*, phenyl alanine, tyrosine and tryptophane as secondary ligands.

EXPERIMENTAL

All chemicals used were of analytical grade. All the solutions were prepared in doubly distilled CO_2 free water. The solution of the disodium salt of CDTA (H_2A^{2-}) was prepared in distilled water, while solutions of the ligands phenyl alanine/tyrosine/tryptophane were prepared in ethanol. Metal nitrate solutions were prepared by dissolving accurately weighed amount of corresponding metal nitrates and standardized by usual methods[20].

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.

Following sets of titrations were performed under nitrogen atmosphere against 0.10 M NaOH at three different ionic strengths (μ = 0.05, 0.10 and 0.15 M KNO_3) and temperatures 25, 35 and 45 ºC: (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) + 5mL potassium nitrate (1.0 M) + 5 mL metal nitrate (0.01 M) + 5 mL ligand L` (0.01 M) + 25 mL distilled water and (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.

Metal = Tb(III), Dy(III), Ho(III) and Er(III), CDTA = disodium salt of cyclohexane diamine N,N,N`,N`-tetra acetic acid and L` = phenyl alanine, tyrosine and tryptophane. The ratio of the concentration of metal:ligand in mixture 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 obtained for corresponding systems of lanthanide metal ions. Hence only the curves for 1:1:1 Ln(III)-CDTA-phenyl Alanine has been discussed to show the evidence of mixed ligand complex formation in general.

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

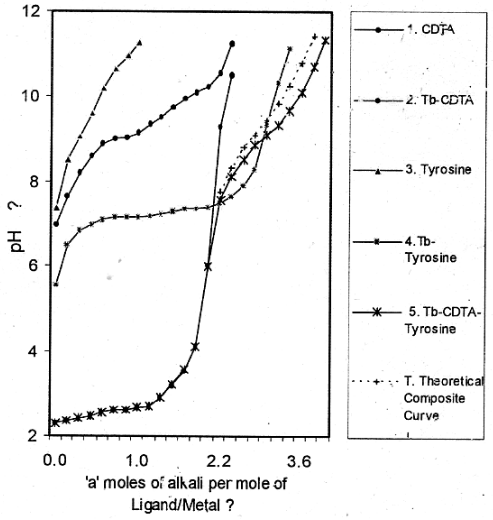

Fig. 1. Plot of 1:1:1 Tb(III)-CDTA-tyrosine system

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 moles of ligand or metal) and pH ≈ 4.8 indicates 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 upto high pH. Curve 5 (Tb(III)-CDTA-phenyl alanine) runs superimposed on the Tb(III)-CDTA titration curve 3 upto 'a' = 3 and pH ≈ 7.5 indicating that secondary ligand does not participate in the formation of mixed ligand complex upto this stage. Its comparison with theoretical composite curve (T) up to pH ≈ 7.5 and 'a' = 2 moles of alkali per moles of metal ions, in ternary 1:1:1 MAL system suggests that the ligand HL 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 that 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 act as primary ligand and phenyl alanine/tyrosine/tryptophane act as secondary ligands.

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

I $$Ln^{3+} + H_2CDTA^{2-} \xrightleftharpoons{0 \leq a \leq 2} [Ln - CDTA]^{1-} + 2H^+$$

II $$[Ln - CDTA]^{1-} + HL` \xrightleftharpoons{2 \leq a \leq 3} [Ln\text{-}CDTA\text{-}L`]^{2-} + H^+$$

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

Proton-ligand system	Temperature (°C)											
	25								35		45	
	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
Phenyl alanine	9.18	–	9.31	–	9.55	–	9.75	–	9.16	–	9.00	–
Tyrosine	9.10	–	9.26	–	9.42	–	9.59	–	9.05	–	9.04	–
Tryptophane	9.21	–	9.42	–	9.66	–	9.75	–	9.36	–	9.28	–

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

Metal-ligand systems	Temperature (°C)					
	25				35	45
	$\mu = 0.15$ M	$\mu = 0.10$ M	$\mu = 0.05$ M	$\mu = 0.00$ M	$\mu = 0.10$ M	$\mu = 0.10$ 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)-Phenyl alanine	5.02	5.27	5.57	5.84	4.91	4.80
Dy(III)-Phenyl alanine	5.31	5.52	5.84	6.09	4.97	4.88
Ho(III)-Phenyl alanine	5.56	5.80	6.10	6.35	5.15	5.01
Er(III)-Phenyl alanine	5.85	6.12	6.40	6.62	5.24	5.11
Tb(III)-Tyrosine	5.26	5.42	5.60	5.80	5.15	5.06
Dy(III)-Tyrosine	5.49	5.68	5.86	6.01	5.27	5.18
Ho(III)-Tyrosine	5.71	5.94	6.10	6.28	5.41	5.35
Er(III)-Tyrosine	5.94	6.13	6.30	6.47	5.57	5.46
Tb(III)-Tryptophane	5.90	6.08	6.43	6.64	5.79	5.68
Dy(III)-Tryptophane	6.11	6.37	6.70	6.86	5.90	5.82
Ho(III)-Tryptophane	6.42	6.67	6.97	7.24	6.17	6.00
Er(III)-Tryptophane	6.67	6.97	7.24	7.50	6.35	6.24

The theoretical treatment of this type of equilibria for determining the various complex species at pH-values from 2.5 to 10.5 has already been given[6].

The formation constant values of mixed ligand complexes are calculated by Thompson and Loraas method. 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.

A comparative account of logarithmic values of binary complexes 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. Free energy changes ΔG, enthalpy changes ΔH and entropy changes ΔS have been calculated for above systems and recorded in Table-4.

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

Metal ligand systems	Temperature (ºC)						Δ log K	RS (%)
	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-Phenyl alanine	3.68	3.76	3.80	3.86	3.57	3.42	-1.52	-28.84
Dy(III)-CDTA-Phenyl alanine	3.79	3.84	3.90	3.97	3.64	3.50	-1.68	-30.43
Ho(III)-CDTA-Phenyl alanine	3.90	3.91	3.97	4.08	3.71	3.57	-1.89	-32.59
Er(III)-CDTA-Phenyl alanine	3.98	4.02	4.10	4.15	3.81	3.64	-2.10	-34.31
Tb(III)-CDTA-Tyrosine	3.81	3.86	3.95	4.00	3.73	3.68	-1.56	-28.78
Dy(III)-CDTA-Tyrosine	3.90	3.97	4.06	4.11	3.79	3.73	-1.71	-30.11
Ho(III)-CDTA-Tyrosine	4.02	4.10	4.18	4.25	3.86	3.80	-1.84	-30.98
Er(III)-CDTA-Tyrosine	4.16	4.19	4.26	4.33	3.95	3.87	-1.94	-31.65
Tb(III)-CDTA-Tryptophane	4.05	4.12	4.20	4.27	3.92	3.87	-1.96	-32.24
Dy(III)-CDTA-Tryptophane	4.16	4.24	4.28	4.35	4.01	3.91	-2.13	-33.44
Ho(III)-CDTA-Tryptophane	4.24	4.36	4.35	4.42	4.07	4.06	-2.32	-34.78
Er(III)-CDTA-Tryptophane	4.33	4.48	4.47	4.53	4.18	4.18	-2.49	-35.72

TABLE-4
THERMODYNAMIC PARAMETERS OF TERNARY COMPLEXES AT 35 ºC 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-Phenyl alanine	-21.43	-9.79	37.77
Dy(III)-CDTA-Phenyl alanine	-21.92	-10.88	35.83
Ho(III)-CDTA-Phenyl alanine	-22.31	-10.88	37.11
Er(III)-CDTA-Phenyl alanine	-22.94	-12.14	35.07
Tb(III)-CDTA-Tyrosine	-22.03	-9.21	41.62
Dy(III)-CDTA-Tyrosine	-22.65	-11.30	36.86
Ho(III)-CDTA-Tyrosine	-23.39	-13.39	32.47
Er(III)-CDTA-Tyrosine	-23.91	-12.97	35.50
Tb(III)-CDTA-Tryptophane	-23.51	-11.72	38.28
Dy(III)-CDTA-Tryptophane	-24.19	-11.30	41.86
Ho(III)-CDTA-Tryptophane	-24.82	-11.72	42.54
Er(III)- CDTA-Tryptophane	-25.56	-12.14	43.59

Negative values of (%) RS indicate that the ligand [L`] binds better to aqua 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]$^-$ complex compared to free Ln(III) aqueous ion[20]. The order of stability with respect to 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 with respect to secondary ligands HL` is found to be:

phenyl alanine < tyrosine < tryptophane

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

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