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Thermodynamic Equilibrium Constants of Mixed Ligand Complexes of Cu(II) with Ethyleneglycol bis (2-amino ethyl ether)–N,N,N',N' Tetraacetic acid as Primary and Alanine and Phenylalanine as Secondary Ligands

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Equilibrium studies were carried out potentiometrically for 1 : 1 : 1 MAB (A = primary and B = secondary ligand) systems. Ternary complexation reaction occurs through stepwise equilibria. Thermodynamic equilibrium constants and parameters ΔG°, ΔH° and ΔS° have been calculated.

INTRODUCTION

The uptake of a second ligand by metal aminopolycarboxylic acid is a fairly frequent phenomenon[1–5]. Variety of mixed ligand systems involving different aminopolycarboxylic acids as one of the ligands, have been reported in literature. Ethyleneglycol bis (2-amino ethyl ether)-N,N, N′,N′-tetraacetic acid (EGTA) an important chelating agent in biology and medicine, is well known to form stable binary complexes with many metal ions at low pH values[6–8]. However, no considerable attention is devoted to investigate the mixed ligand equilibria involving EGTA and only a few publications appear on record as regards the formation of mixed ligand complexes in solution[9,10]. The present communication describes the results of equilibrium studies on 1 : 1 : 1 Cu(II)-EGTA alanine and Cu(II)-EGTA-phenylalanine, mixed ligand systems.

EXPERIMENTAL

All the chemicals used were of analytical grade and the solutions were prepared in doubly distilled CO_2 free water. Stock solutions of the secondary ligands (HB) were prepared by dissolving their accurately weighed amounts. Solution of disodium salt Na_2H_2EGTA, (H_2A^{2-}) was prepared by dissolving its acid (H_4EGTA) in two equivalents of standard NaOH solution. Cupric nitrate solution was prepared and standardised by usual method[11]. The pH-titrations were made with an Elico pH-meter LI–120 (accuracy ± 0.01 pH unit) in conjunction with glass (EN-66) and Calomel (ER–70) electrodes.

Following sets of titrations were performed under nitrogen atmosphere against 0.10M NaOH at three different ionic strengths (μ = 0.01M, 0.05M and 0.1M) maintained by $NaNO_3$ and at temperatures 25°C, 35°C and 45°C. Total volume in each set was kept 50 ml.

(1) HNO_3 (2.0×10^{-3}M)

(2) HNO_3 (2.0×10^{-3}M) + ligand A (1.0×10^{-3}M)

(3) HNO_3 (2.0×10^{-3}M) + ligand A (1.0×10^{-3}M)
+ metal ion (1.0×10^{-3}M)

(4) HNO_3 (2.0×10^{-3}M) + ligand B (1.0×10^{-3}M)

(5) HNO_3 (2.0×10^{-3}M) + ligand B (1.0×10^{-3}M)
+ metal ion (1.0×10^{-3}M)

(6) HNO_3 (2.0×10^{-3}M) + ligand A (1.0×10^{-3}M)
+ ligand B (1.0×10^{-3}M) + metal ion (1.0×10^{-3}M)

RESULTS AND DISCUSSION

Algebraic method of Martell and Chaberek[12] as modified by Dey *et al*[13] has been used to obtain the values of the dissociation constants of the various ligands and the stability constants of 1 : 1 binary and 1 : 1 : 1 ternary complexes.

Formation of mixed ligand complex is evidenced by the comparison of 1 : 1 : 1 mixed ligand titration curve with the theoretical composite curve[14]. It is observed that the former runs superimposed on the latter upto a = 2, pH ≈ 7.8 (where 'a' is the moles of alkali per mole of metal ion in 1 : 1 : 1 MAB) system, which suggests the non-interaction of secondary ligand upto this stage. However, at $a > 2$ the experimental curve is displaced from the composite curve, providing evidence for the increased interaction in presence of two ligands, thereby suggesting the formation of ternary complex, through stepwise equilibria. The occurrence of precipitate in 1 : 1 Cu(II)-alanine and Cu(II)-phenylalanine systems at pH ≈ 7.8, but the non-appearance of any solid phase in ternary systems further supports the formation of mixed ligand complex in solution.

In the solution following equilibria would be expected to exist.

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

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

$$HB \overset{K_1^B}{\rightleftharpoons} B^- + H^+ \qquad (iii)$$

$$M^{2+} + A^{4-} \overset{K_{MA}}{\rightleftharpoons} MA^{2-} \qquad (iv)$$

$$M^{2+} + B^- \overset{K_{MB}}{\rightleftharpoons} MB^+ \qquad \text{(v)}$$

$$MA^{2-} + B^- \overset{K_{MAB}}{\rightleftharpoons} MAB^{3-} \qquad \text{(vi)}$$

Hence at any pH in mixed ligand system

$$C_M = [M^{2+}] + [MA^{2-}] + [MB^+] + [MAB^{3-}] \qquad (1)$$

$$C_A = [H_2A^{2-}] + [HA^{3-}] + [A^{4-}] + [MA^{2-}] + [MAB^{3-}] \qquad (2)$$

$$C_B = [HB] + [B^-] + [MB^+] + [MAB^{3-}] \qquad (3)$$

where $C_A = C_B = C_M$

From mass balance

$$aC_M = [HA^{3-}] + 2[A^{4-}] + 2[MA^{2-}] + [B^-] + [MB^+] + 3[MAB^{3-}] \qquad (4)$$

where 'a' is the moles of alkali per mole of metal ion in 1 : 1 : 1 MAB system.

From equations (1), (2), (3), (4) and by introducing the dissociation constants of the ligands we have

$$C_M(3-a) = a_1[A^{4-}] + b_1[B^-] \qquad (5)$$

where $a_1 = \frac{2[H^+]^2}{K_1^A K_2^A} + \frac{[H^+]}{K_2^A}$ and $b_1 = \frac{[H^+]}{K_1^B}$

Further,

$$C_M - C_A = [M^{2+}] + [MB^+] - [H_2A^{2-}] - [HA^{3-}] - [A^{4-}] = 0 \qquad (6)$$

and

$$C_M - C_B = [M^{2+}] + [MA^{2-}] - [HB] - [B^-] = 0 \qquad (7)$$

Introducing the dissociation constants of the ligands and the formation constants of the binary complexes, equations (6) and (7) can be respectively written as :

$$[M^{2+}]\{1 + K_{MB}[B^-]\} = a_2[A^{4-}] \qquad (8)$$

and

$$[M^{2+}]\{1\ K + {}_{MA}[A^{4-}]\} = b_2[B^-] \qquad (9)$$

where $a_2 = \left(\frac{[H^+]^2}{K_1^A K_2^A} + \frac{[H^+]}{K_2^A} + 1\right)$ and $b_2 = \frac{[H^+]}{K_1^B}$

Equating (8) and (9) and then putting the value of $[B^-]$ from equation (5) we obtain

$$[A^{4-}]^2 (a_2K_{MA} - b_2d^2K_{MB}) + [A^{4-}](a_2 + db_2 + 2e_1db_2K_{MB}) - (b_2e_1 + b_2e_1^2K_{MB}) = 0 \qquad (10)$$

where $e_1 = \frac{(3-a)C_M}{b_1}$ and $d = \frac{a_1}{b_1}$

Solving the quadratic equation (10), the value of $[A^{4-}]$ was obtained. Only the positive roots of the equation (10) were considered. The value of $[B^-]$ was then calculated from equation (5). The concentration of the free metal ion at different pH was calculated using equation (8) or (9). The concentration of MA^{2-} and MB^+ species were obtained with the help of following expressions using their formation constants of binary species.

$$[MA^{2-}] = K_{MA}[M^{2+}][A^{4-}]$$

and

$$[MB^+] = K_{MB}[M^{2+}][B^-]$$

Finally the concentration of the mixed ligand species MAB^{3-}, over the entire pH range, was calculated from equation (1) by substituting the values of C_M, $[M^{2+}]$, $[MA^{2-}]$ and $[MB^+]$

Analysis of mixed ligand titration data between $a = 0$ and 3, from pH ≈ 3.5 to pH ≈ 10.0, on the above grounds gave the concentration of various complex species and free metal ion at different pH. A plot of percentage distribution of metal ion among various complex species as a function of pH is drawn, from which it is observed that upto pH ≈ 7.8, no mixed ligand species is formed. It is clearly evident that the pH from which formation of MAB^{3-} complex starts, about 99% of total metal ion exists as in MA^{2-} complex. Thus the relevant equilibrium for mixed lig-complex formation reaction is:

$$MA^{2-} + B^- \overset{K_{MAB}}{\rightleftharpoons} MAB^{3-}$$

The trends observed for the values of the dissociation constants of the ligands and the formation constants of the metal complexes at different ionic strengths are in agreement with earlier observations[15,16]. With increasing temperature stability constants show a decreasing trend. The parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ are calculated and presented in Table 1.

$(Cu.EGTA)^{2-}$ Binary complex is found to have lower value of stability constant as compared to $(Cu.EDTA)^{2-}$ complex, as reported in literature[17]. EGTA has two extra coordinating sites (the two ether oxygen atom) as compared to EDTA. If these two oxygens were involved in bonding the stability of $(Cu.EGTA)^{2-}$ complex would have been higher than $(Cu.EDTA)^{2-}$ species. Thus it can be assumed that in $(Cu.EGTA)^{2-}$ chelate the ligand is coordinated through its two iminodiacetate groups only

TABLE 1

THERMODYNAMIC EQUILIBRIUM CONSTANTS$^{(Z)}$ OF PROTON DISSOCIATION, METAL-LIGAND AND MIXED LIGAND FORMING SYSTEMS, WITH ΔG°, ΔH° and ΔS° FOR MIXED LIGAND COMPLEXES

Temp °C	$-\log K_1^A$	$-\log K_2^A$	$-\log K_1^B$	$\log K_{MA}$	$\log K_{MB}$	$\log K_{MAB}$	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (Jk^{-1} mol^{-1})
	(i) Cu(II)-EGTA-Alanine								
25	8.87	10.47	9.81	14.53	7.82	3.67	20.83	—	—
35	8.62	10.29	9.73	14.42	7.65	3.60	20.45	12.21	106.03
45	8.52	10.10	9.60	14.30	7.54	3.48	19.74	20.99	128.08
	(ii) Cu(II)-EGTA-Phenylalanine								
25	8.87	10.47	9.40	14.53	7.61	2.86	16.10	—	—
35	8.62	10.29	9.29	14.42	7.53	2.75	15.90	19.24	109.55
45	8.52	10.10	9.09	143.0	7.44	2.63	14.93	20.99	112.98

(Z) Thermodynamic equilibrium constants were obtained by extrapolating the data at three different ionic strengths to zero ionic strength.

which is consistent with earlier suggestion[18]. Cu(II) ion which is generally considered to have CN = 6 in solution, thus gets all its coordination sites saturated in forming primary complex with EGTA. The formation of the ternary complex thus can be explained to occur by the displacement of some metal-primary ligand bonds.

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