

Equilibrium Studies of Cobalt (II) and Copper (II) with Diethylene Triamine Penta Acetic Acid (DTPA)

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Abstract: *Biologically important complexes involving DTPA have been investigated potentiometrically in aqueous medium under the well-defined condition of temperature and ionic strength. SCOGS computer program is used to obtain the speciation of various protonated, nonprotonated binary and ternary species formed in a particular equilibrium. The percentage formation of complexes is appreciably high which is evident from speciation curves. The stability constants and thermodynamic parameters ΔG° , ΔH° , and ΔS° support the favourable formation of mixed metal species. Negative values of $\Delta \log K$ indicates higher stability of ternary species.*

Keyword: Equilibrium Studies, DTPA, SCOGS, Cobalt, Copper

1. Introduction

Recently there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method [1-3]. The metal complexes play an important role in various fields of biological, analytical, industrial and medicinal chemistry. Biological system contains various essential and nonessential or potentially toxic metal ions [4, 5].

Some publications on multiple equilibria and chemical distribution of biometals with some biologically potential ligands is worth mentioning [6, 7]. Heterobinuclear complexes of transition metals have been investigated by Nair and his group [8]. Few interesting investigations on heterobimetallic complexes having Mixed-ligand, mixed-metal complexes involving more than one metal ions of the same or different types may prove as better models for multimetal multiligand equilibria occurring in the biological systems may be reported in 2014 [9-10]. Chemical literature reveals that although mixed ligand systems have been explored extensively, but equilibrium studies on mixed metal complexes have gained attention in recent past [8, 11-12]

In the present work some metal complex equilibria involving DTPA are investigated. The metal chosen for the present studies are Co (II) and Cu (II).

2. Experimental

All the chemicals used were of highest purity Merck/Aldrich product. Solution of disodium salt of DTPA was prepared by dissolving accurately weighed amount of acid (A.R) in two equivalents of standard sodium hydroxide (0.10M) to get a solution of 0.01M. All other solutions were prepared by standard method in deionised water having pH ~6.8.

The protonation and coordination equilibria were investigated by pH-metric titration in aqueous medium. An Elico digital pH-meter model LI-127 with ATC probe and combined electrode type (CL-51B-Glass Body; range 0-14 pH unit; 0-100°C Automatic/manual) with accuracy \pm

0.01 was employed for pH measurement throughout the present work.

Following sets of titration mixture were prepared, keeping total volume 50 mL and titrated against 0.10M NaOH solution at two different temperatures (i.e. $20 \pm 1^\circ\text{C}$ and $30 \pm 1^\circ\text{C}$) and three different ionic strengths ($\mu = 0.05\text{M}$, 0.10M , 0.15M) maintained by NaNO_3 :

1. Acid titration: HNO_3 ($2.0 \times 10^{-3}\text{M}$).
2. ((Ligand 'A' titration: HNO_3 ($2.0 \times 10^{-3}\text{M}$) + Ligand 'A' ($1.0 \times 10^{-3}\text{M}$).
3. Metal (M)-Ligand 'A' (1:1) titration: HNO_3 ($2.0 \times 10^{-3}\text{M}$) + Ligand 'A' ($1.0 \times 10^{-3}\text{M}$) + Metal nitrate ($1.0 \times 10^{-3}\text{M}$).
4. Metal (M')-Ligand(1:1) titration: HNO_3 ($2.0 \times 10^{-3}\text{M}$) + Ligand 'A' ($1.0 \times 10^{-3}\text{M}$) + Metal' nitrate ($1.0 \times 10^{-3}\text{M}$).
5. Metal (M) - Metal (M') -Ligand(1:1:1) titration: HNO_3 ($2.0 \times 10^{-3}\text{M}$) + Ligand 'A' ($1.0 \times 10^{-3}\text{M}$) + Metal nitrate ($1.0 \times 10^{-3}\text{M}$) + Metal' nitrate ($1.0 \times 10^{-3}\text{M}$).

Where, ligand 'A' = DTPA (Diethylene triamine penta acetic acid) and $\text{M}' = \text{Co (II)}$ and Cu (II)

Volume of alkali used in each set of titration is converted into moles of alkali per mole of ligand / metal and is denoted as 'a'. Representative titration curves are given in the form of **Figure 1**.

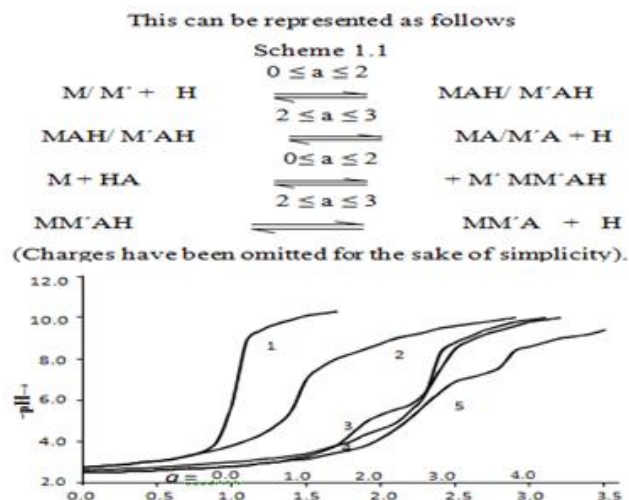


Figure 1: pH vs. Vol. of NaOH Curves for Cu(II)-Co(II)-DTPA (1:1:1) System at 30°C [$\mu=0.10M$ NaNO₃]

Curve 1 represents Acid titration curve.

Curve 2 represents Ligand 'A' (DTPA) titration curve.

Curve 3 represent Metal (M)-Ligand 'A' (1:1) titration curve.

Curve 4 represents Metal' (M')-Ligand 'A' (1:1) titration curve.

Curve 5 represents Mixed Metal (1:1:1) titration curve.

The protonation constants of ligand and formation constants of binary and ternary systems were calculated by method of Chaberek and Martell [13-14] as modified by Nayan and Dey [15] and values were refined by SCOGS computer program [16-17]. Thermodynamic formation constants were obtained by extrapolating the $\log \beta$ vs $\sqrt{\mu}$ plot to zero ionic strength. The values are given in **Tables 1, 2 & 3**.

Table-1: Dissociation constants of ligand ($\log \beta_{\mu \rightarrow 0}$).

Parameter	DTPA	
	20°C	30°C
$\log \beta_{HA}$	9.81	9.66
$\log \beta_{H_2A}$	17.68	17.50
$\log \beta_{H_3A}$	21.35	20.97

Table 2: Thermodynamic formation constants of metal- ligand complexes of M(II)/M'(II)-DTPA in equimolar systems

Parameters	Co(II)		Cu(II)	
	20°C	30°C	20°C	30°C
$\log \beta_{MAH}$	20.25	19.22	18.95	18.24
$\log \beta_{MA}$	15.37	14.62	13.96	13.05
$\log K_{MAH}^M$	9.89	9.38	9.27	8.91
pK_{MAH}^H	5.56	4.78	5.98	5.30

Thermodynamic formation constants were obtained by extrapolating the $\log \beta$ vs $\sqrt{\mu}$ plot to zero ionic strength.

Table 3: Thermodynamic parameters of M(II) –M'(II) – ligand 'A' (DTPA) ternary complexes in equimolar systems along with $\Delta \log K$ values

System	20°C			30°C			- ΔH° kJmol ⁻¹	ΔS° JK ⁻¹ mol ⁻¹
	logK (μ→0)	- ΔG° (kJ mol ⁻¹)	ΔlogK	logK(μ→0)	- ΔG° (kJmol ⁻¹)	ΔlogK		
Cu(II)–Co(II)-DTPA								
log β _{MM'AH}	24.16	-	-	23.89	-	-13.57	-	-
			15.04					
log β _{MM'A}	21.42	120.1	-7.91	21.14	122.6	-6.53	47.60	247.6
log K _{MM'AH} ^{MM'}	14.19	79.60	-	13.87	80.46	-	54.39	86.04

Thermodynamic formation constants were obtained by extrapolating the $\log \beta$ vs $\sqrt{\mu}$ plot to zero ionic strength

The value of thermodynamic stability constant, $K_{\mu \rightarrow 0}$, is used to calculate standard free energy change

(ΔG°) for the complexation reaction from van't Hoff isotherm:

$$\Delta G^\circ = -2.303RT \log K_{\mu \rightarrow 0} \dots\dots\dots (1)$$

$$\frac{d(\ln K_{\mu \rightarrow 0})}{dT} \dots\dots\dots (2)$$

Alternatively this can be represented as:

$$\log \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_1 - T_2}{T_1 T_2} \right) \dots\dots\dots (3)$$

The standard entropy change (ΔS°) is calculated by using following simple form of Gibb's Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots\dots\dots (4)$$

The values of thermodynamic parameters ΔG° (free energy change), ΔH° (enthalpy change) and ΔS° (entropy change) are given in **Table 3**.

The qualitative analysis on the basis of the trends of the titration curves are supported by the quantitative results obtained by subjecting the experimental data to computational analysis. Speciation curves show the variation of the concentration of different species formed in particular equilibria in the form of percentage distribution against pH. Speciation curves for Cu(II)-Co(II)-DTPA are given in Figure (2.1).

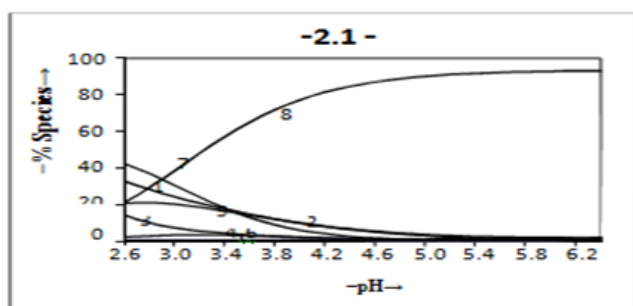


Figure 2.1: Cu(II) –Co(II)-DTPA

(1:1:1) Systems at 30°C ($\mu=0.10M(NaNO_3)$).

Where, Curve 1: [M] ; 2 [M'] ; 3 [MAH] ; 4 [MA] ; 5 [M'AH] ; 6 [M'A] ; 7 [MM'AH] ; 8 [MM'A]

It is noted that the formation of 1:1:1 heterobimetallic ternary complexes occur in pH range 2.5 to 6.5. The concentration of binary species is below 35% in all the cases. However, concentration of ternary species is found to be about 95%. This clearly indicates that in all cases percentage concentration of ternary species (MM'AH and MM'A) are much higher as compared to binary species. Protonated species is predominant in lower pH range and its concentration decreases continuously with the increase of pH, whereas concentration of MM'A heterobimetallic complex species increases gradually. Speciation curve also

Further, standard enthalpy change (ΔH°) is calculated by using van't Hoff isochore:

supports the simultaneous co-ordination of both metal ions with ligand.

3. Conclusion

From the above discussions it is concluded that the formation of heterobimetallic complexes occurs in a single step through simultaneous coordination of two metal ions and ligand. The metals used in present investigation are bivalent usually having coordination number six.

The ligand DTPA is octadentate in nature. So it can be assumed that in binary complexes, the metal ion get coordinated to the ligand by four/ six coordination sites, still leaving vacant coordination sites available for interaction with another metal, thus making the formation of mixed metal complex possible. As stated the percentage formation of ternary complexes is found to be higher in comparison to the binary species. The negative ΔG° in each case indicates that the complexation is spontaneous. The enthalpy changes are exothermic. The positive values for ΔS° indicate that complexation reactions are entropically favoured under the experimental conditions.

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