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FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF SOME TERNARY CHELATES

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ABSTRACT

The formation constants of ternary chelates of Cu(II), Ni(II), Cd(II), Zn(II), Co(II) with Cis 1,2,3,4 Cyclopentanetetracarboxylic acid (CPTA) and 8-Hydroxyquinoline (Hq) in the 1 : 1 :1 ratio have been determined at 30^o, 40^o, 50^o $(\pm 1^0 C)$ and at ionic strength $\mu = 0.2M$ ($Nac10_4$). The free energy (ΔF^o) enthalpy (ΔH^o) and entropy (ΔS^o) have also been calculated. The order of the stability constants of the complexes is found to be Cu(II) > Zn(II) > Cd(II) > Ni(II) > Co(II).

The studies have been carried out by potentiometric titration technique using the modified method of Irving and Rossotti[1,2].

CPTA (Aldrich), $NaCl0_4$ (Reidel), $HC10_4$(E.Merck), HQ (BDH) grade were used. The stock solutions of metal perchlorates were prepared by dissolving the metal carbonates in $HC10_4$ till an excess amount of salt was left unreacted so that no free $HC10_4$ remains. Solutions were filtered through G_4 sintered crucible and then metal ions were estimated by conventional gravimetric methods[3].

The solutions of CPTA was prepared in conductivity water. Hydroxyquinoline was dissolved in calculated quantity of HCl (AR).

The pH titrations were carried out with a philips digital pH meter PP 9045 with an accuracy pHrange 0.02 unit at 30,40 and 50 ($\pm 1^0 C$) maintaining the temperature constant with the help of a thermostat. The volume of each solution to be titrated was kept 50 ml and its ionic strength was maintained $\mu =$ 0.2M $NaC10_4$. The following solutions in duplicate were titrated against 0.2M NaOH at different temperature as mentioned earlier.

a) $2 \times 10^{-2} M\ \ HC10_4$
b) $2 \times 10^{-2} M\ \ HC10_4 + 2\ X\ 10^{-3} M\ HQ$
c) $2 \times 10^{-2} M\ \ HC10_4 + 2\ X\ 10^{-3} M$ metal perchlorate + $2X10^{-3}$M CPTA
d) $2 \times 10^{-2} M\ \ HC10_4 + 2\ X\ 10^{-3} M$ metal perchlorate + $2X10^{-3}$M CPTA + $2X10^{-3} M$ tannic acid.

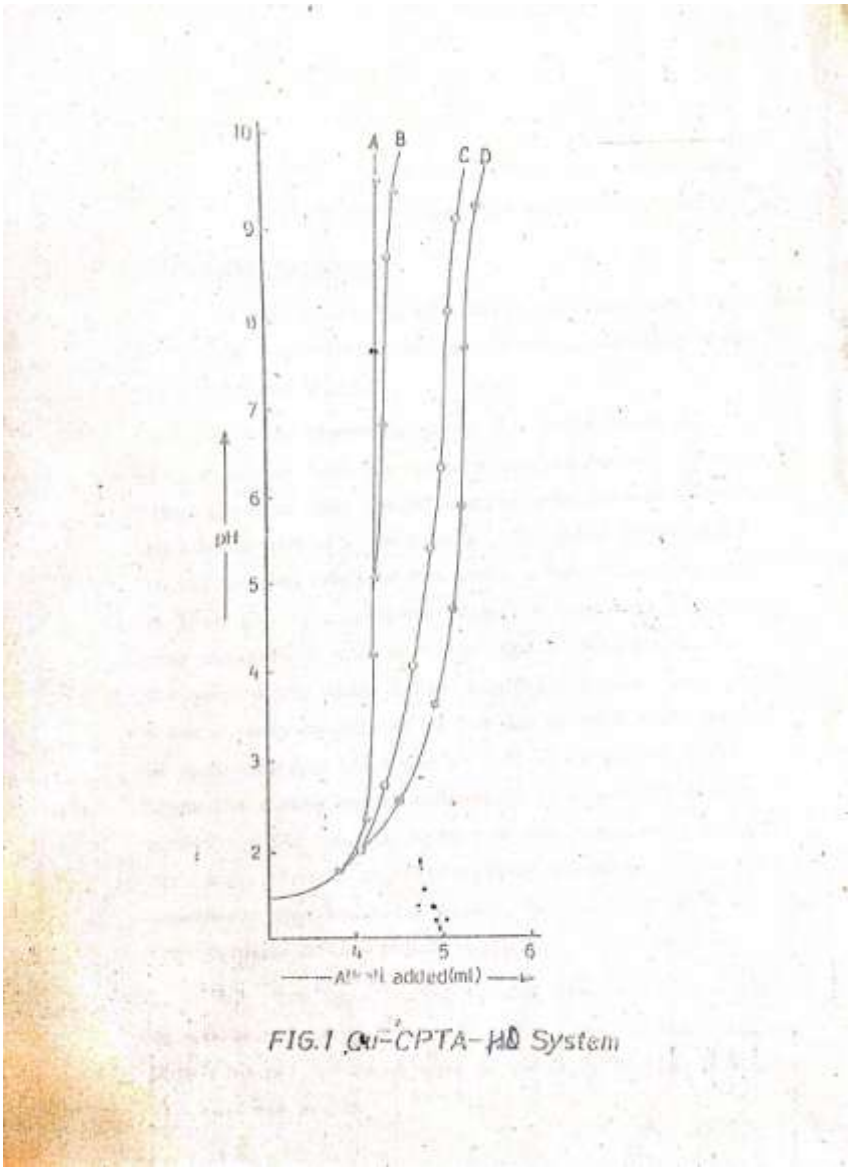

FIG.1 Ni-CPTA-HQ System

A graph was plotted between the alkali added Vs pH and $\bar{n}$value were calculated as described earlier[4].

Results and discussion

The pK value of hydroxyquinoline were calculated by Chabrek and Martell method[5] and are in agreement with the literature values.

The titration curves of [Cu(II)-CPTA-HQ] (Fig.1) reveal that the primary complex formation (curve C) takes place at very low pH and the calculations indicate that it is stable up to high pH. The curve D for mixed ligand complex overlaps the curve C for primary complex at lower pH. This indicates that the secondary ligand HQ does not combine with the metal ion in this pH range.

The curve D for mixed ligand complex separates from curve C for primary complex at pH 2.0 due to self dissociation of secondary ligand. After pH 2.75 mixed ligand curve shows the indication of attachment of secondary ligand with the metal ion. The colour of the solution changes from light blue to greenish yellow. Therefore, it can be considered that secondary ligand (HQ) combines with Cu(II)-CPTA forming [Cu(II)-CPTA-HQ] complex.

The log $K\,{}^{MA}_{MAB}$ values were calculated at $\bar{n}$ 0.5 by plotting a graph between $\bar{n}$ and pL for the mixed ligand complexes and are summerized in Table 1. The error limits are 0.04 log units.

Thermodynamic Parameters

The values of the changes in the free energy (ΔF^o), enthalpy (ΔH^o) and entropy (ΔS^o) have been calculated at three different temperatures and at constant ionic strength of 0.2M $NaC10_4$with the help of temperature coefficient and Gibbs-Helmholts equation and are summarized in Table 1.

Table – 1

Formation constant and thermodynamic parameters of some mixed ligand complexes.

$$u = 0.2\ M\ Nac10_4$$

S. No.	System	Tem ^oc	Log $K\,{}^{MA}_{MAB}$	$-\Delta F^o$ (K cal mol^{-1})	$-\Delta H^o$ (K cal mol^{-1})	ΔS^o (cal mol^{-1} deg^{-1})
1.	Cu^{II}-CPTA-HQ	30	10.03	13.90	3.58	34.00
		40	9.97	14.28		
		50	9.87	14.59		
2.	Zn^{II}-CPTA-HQ	30	8.80	12.20	3.81	27.73
		40	8.72	12.49		

		50	8.63	12.75		
3.	Cd^{II}-CPTA-HQ	30 40 50	8.68 8.57 8.38	12.04 12.27 12.39	6.94	17.02
4.	Ni^{II}-CPTA-HQ	30 40 50	8.60 8.48 8.25	11.92 12.14 12.19	7.83	13.76
5.	Co^{II}-CPTA-HQ	30 40 50	8.50 8.32 8.13	11.78 11.92 12.09	8.28	11.63

Discussion

The stability constants of different complexes investigated here follow the order:

$$Cu^{2+} > Zn^{2+} > Cd^{2+} > N1^{2+} > Co^{2+}$$

Which agrees well with the Irving- Williams order [6,7]. The above trend of stability constants is further confirmed by the value of ΔF^{o} obtained during the course of investigation. In all the cases the value of step wise formation constants decrease with the increase in temperature indicating that low temperature is favorable for complex formation. All the complexes are enthalpy stabilized and entropy factor is also found to be favourable.

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