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METAL CHELATES OF SOME TRANSITION METALS WITH OXYGEN AND NITROGEN DONOR LIGANDS

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Potentiometrictitrations are carried out for 1: 1: 1 ternary complex formation of Cu (II), Co (II), Zn (II), Cd(II) with L-Histidine as a primary ligand and 8-hydroxyquinoline (HQ) as a secondary ligand.

The formation constants of the resulting complexes indicate the order of stability as

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

Thermodynamic parameters for complexation were also calculated from pH titration data obtained at 30°, 40° and 50° (±1°c) and ionic strength $\mu = 0.2M$ ($NaC10_4$).

Potentiometric studies have been carried out by applying the modified Irving and Rossotti method[1,2].

L-histidine and HQ (BDH) $NaC10_4$ (Reidel) and$HC10_4$ (E.Merck) grade were used. 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 solution of L-histidine was prepared by dissolving it in conductivity water and that of HQ by dissolving it in calculated quantity of HCl acid.

The pH titrations were carried out with a Philips digital pH meter pp (9045) with an accuracy pH range ± 0.02 unit at 30, 40 and 50 (±1°c) maintaining the temperature constant with the help of a thermostat. The solutions were mixed in 1:1:1 ratio and the volume of each solution to be titrated was kept 50ml and its ionic strength (μ) was maintained at 0.2M with $NaC10_4$ Solution.

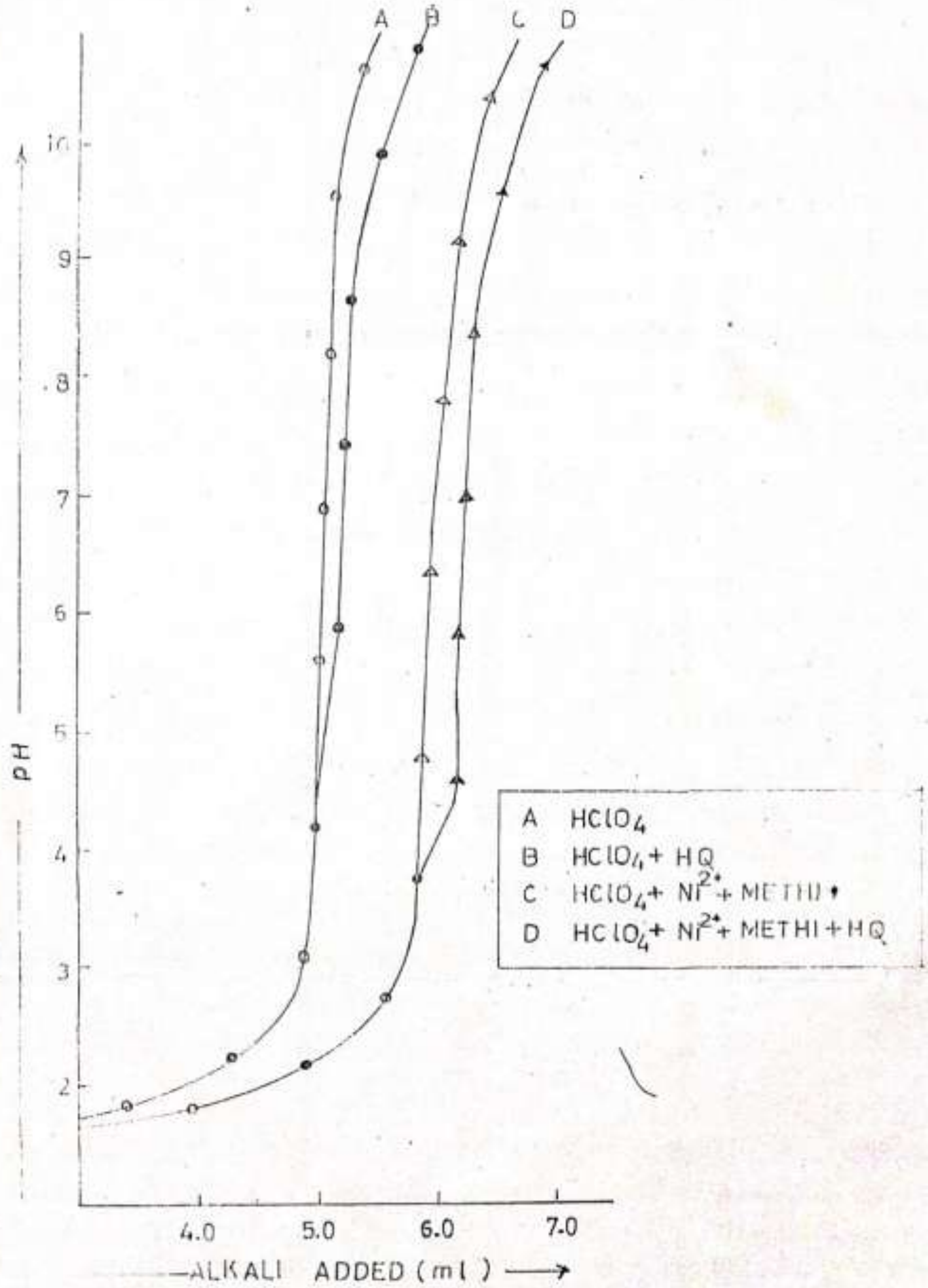
The following mixture of solutions were titrated against 0.2M NaOH solution and were repeated for the accuracy.

a) $2x10^{-2}$M $HC10_4$
b) $2x10^{-2}$M $HC10_4$ + $2x10^{-3}$M HQ. HCl
c) $2x10^{-2}$M $HC10_4$+ $2x10^{-3}$M metal perchlorate + $2x10^{-3}$M histidine
d) $2x10^{-3}$M $HC10_4$+ $2x10^{-3}$M metal perchlorate + $2x10^{-3}$M histidine + $2x10^{-3}$M HQ.HCl

After mixing the solutions, they were allowed to equilibrate by keeping them for one hour and each of the mixture was titrated against 0.2M NaOH solution at 30°, 40° and 50° (±1°c).

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

FIG. 1 TITRATION CURVES FOR Ni(II)-METHIONINE-HQ SYSTE



The formation constants were obtained by plotting n̄ against pL values.

RESULTS AND DISCUSSION

The pK values of hydroxyquinoline were calculated by Chabrek and Martell method[5].

A graph of pH vs alkali added for [Cu(II)-Hist.-HQ] system at 30°c is represented in Fig. 1. Similar curves are obtained for other systems also. Primary complex [Cu (II)-Hist.] curve (c) overlaps the secondary ligand curve (B) in the beginning upto pH 3.25 and then diverges.

Colour of the solution becomes bluish from colourless.

This indicates the attachment of histidine with Cu^{2+}. The curve further lowers and precipitation does not occur upto pH 11.00. This indicates the formation of [Cu (II)-Hist.] complex.

The mixed ligand complex curve (D) separates from the primary complex curve (C) at pH 2.25. It may be due to the self dissociation of secondary ligand hydroxy-quinoline. The colour of the solution changes from light yellow to greenish yellow and turbidity appears at pH 2.50. It may be due to metal hydroxide formation. Further lowering of the mixed ligand complex curve (D) indicates the suppression of [Cu(II)-Hist.-$(OH)_n$] and attachment of hydroxyquinoline with [Cu(II)-Hist.] complex. Calculation of average number of secondary ligand molecules associated with primary complex ($\bar{n}$) indicates the formation of 1 : 1 : 1 mixed ligand complex at 3.0 pH.

The log K^{MA}_{MAB} values were calculated at 0.5 by plotting a graph between $\bar{n}$ and pL for the mixed ligand. The thermodynamic parameters are tabulated in Table 1. The error limits are 0.05 log units.

Table 1- Stability constants and thermodynamic parameters of some mixed ligand complexes.

S. No.	System	Tem °c	Log K^{MA}_{MAB}	$-\Delta F^{o}$ ($\mathrm{K\,cal\,mol^{-1}}$)	$-\Delta H^{o}$ ($\mathrm{K\,cal\,mol^{-1}}$)	ΔS^{o} ($\mathrm{cal\,mol^{-1}\,deg^{-1}}$)
1.	Cu(II)-Hist.	30	9.79	13.57	7.16	21.37
		40	9.67	13.85		
		50	9.47	13.99		
2.	Co(II)-Hist.	30	8.79	12.18	9.40	9.16
		40	8.57	12.27		
		50	8.37	12.37		
3.	Zn(II)-Hist.	30	8.54	11.84	9.18	8.72
		40	8.32	11.91		
		50	8.13	12.01		
4.	Cd(II)-Hist.	30	8.04	11.14	6.49	15.04
		40	7.82	11.20		
		50	7.75	11.45		

The stability constants of the mixed ligand complexes with respect to metal ions investigated here follow the order:

$$\mathbf{Cu^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+}.}$$

Which is further confirmed by the values of free energies.

THERMODYNAMIC PARAMETERS

The value of the change in free energy (ΔF°), Enthalpy (ΔH°) and Entropy (ΔS°) have been calculated at three different temperatures and at constant ionic strength of 0.2M NaC10$_4$with the help of standard equations. The values are summarized in Table 1.

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