

NOTE

Effect of Temperature on the Formation of Cu(II) Ternary Chelates of Substituted Phenylhydrazonopropanoic acids

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Formation constants have been measured for the mixed ligand complexes Cu(II)-A-L or Cu(II)-L'-A, where A = 2-(phenylhydrazono)-propanoic acid, 2-(*p*-nitro-phenylhydrazono)-propanoic acid, 2-(*p*-tolylhydrazono)-propanoic acid; L = catechol, ethylenediamine, proline, hydroxyproline, β -alanine, glycine and L' = 1,10-phenanthroline, salicylic acid at 20°, 30°, 40° and 50°C in 40% (v/v) ethanol-water medium at 0.10 M (KNO₃) ionic strength. Thermodynamic parameters for the above systems have been evaluated and discussed in terms of the basicity of the ligands, electrostatic interaction, metal-ligand π -interaction, denticity and statistical aspects

In continuation of our earlier studies^{1,2} on the coordinating tendencies of phenylhydrazonocarboxylic acids, we report herein the results of potentiometric studies on the Cu(II)-A-L or Cu(II)-L'-A mixed ligand systems, where A = 2(phenylhydrazono)propanoic acid (PHP), 2-(*p*-nitro-phenylhydrazono)-propanoic acid (NPP), 2-(*p*-tolylhydrazono)propanoic acid (THP); L = catechol (Cat), ethylenediamine (en), proline (Pro), hydroxyproline (Hpr), β -alanine (Ala), glycine (Gly) and L' = 1,10-phenanthroline (Phe) and salicylic acid (SA).

All the reagents used were of AR grade. The purity of all the ligands was confirmed by IR data. Potentiometric measurements were carried out at 20°, 30°, 40° and 50°C with 0.10 M (KNO₃) as background electrolyte in 40% (v/v) ethanol-water medium using Santappa and Ramamoorthy titration technique³. The pH meter readings obtained for the aquo-organic mixture were corrected as suggested by the method of Van Uitert and Haas⁴.

The formation constants of ternary complexes, in general, depend upon the temperature of the reaction mixture. The various energy parameters in a ternary complexation reaction would be obtained from a study of the formation constants evaluated at various temperatures. The thermodynamic parameters would explain the bonding properties and structural aspects of complex species and also determine the conditions under which the complexes exist⁵. Thermodynamic parameters for the formation of a variety of metal complexes with nitrogen and carboxylate oxygen containing ligands in aqueous solution have been analysed

by Degischer and Nancollas in terms of temperature dependent and temperature independent parts⁶.

TABLE-1
THERMODYNAMIC PARAMETERS AND THEIR ELECTROSTATIC AND CRATIC COMPONENTS OF Cu(II) TERNARY CHELATES WITH PHP, NPP AND THP INVOLVING OTHER CHELATING AGENTS IN 40% (v/v) ETHANOL-WATER MEDIUM AT 0.10 M (KNO₃) IONIC STRENGTH

Ternary system	Thermodynamic parameters			Electrostatic components		Cratic Components	
	$-\Delta G^\circ$	$-\Delta H^\circ$	$+\Delta S^\circ$	$-\Delta G_c^\circ$	$+\Delta H_c^\circ$	$-\Delta G_c^\circ$	$-\Delta H_c^\circ$
PHP-Cat	70.70	17.73	174.80	45.39	17.70	35.43	35.43
NPP-Cat	71.80	19.15	173.80	45.17	17.61	36.76	36.76
THP-Cat	70.53	11.67	194.20	49.62	19.35	31.02	31.02
PHP-en	57.83	51.55	20.73	11.80	4.60	56.15	56.15
NPP-en	58.00	53.18	15.90	10.75	4.19	57.37	57.37
THP-en	57.59	34.36	76.67	23.99	9.35	43.72	43.72
PHP-Pro	47.27	23.93	77.02	24.07	9.38	33.32	33.32
NPP-Pro	48.02	31.15	55.69	19.42	7.57	38.72	38.72
THP-Pro	45.76	21.67	79.50	24.61	9.59	31.27	31.27
PHP-Hpr	43.50	25.63	58.97	20.14	7.85	33.48	33.48
NPP-Hpr	43.79	28.94	49.01	17.96	7.00	35.94	35.94
THP-Hpr	43.04	18.68	80.39	24.80	9.67	28.35	28.35
PHP-Ala	43.38	12.98	100.30	29.16	11.37	24.35	24.35
NPP-Ala	43.56	17.71	85.31	25.88	10.09	27.80	27.80
THP-Ala	43.56	9.57	112.20	31.73	12.37	21.94	21.94
PHP-Gly	42.34	14.36	92.35	27.41	10.69	25.05	25.05
NPP-Gly	42.57	19.15	77.32	24.13	9.41	28.56	28.56
THP-Gly	42.11	12.94	96.28	28.27	11.02	23.96	23.96
Phe-PHP	30.22	14.72	51.14	18.43	7.18	21.91	21.91
Phe-NPP	24.42	16.52	26.08	12.96	5.06	21.57	21.57
Phe-THP	34.51	15.29	63.44	21.11	8.23	23.52	23.52
SA-PHP	19.78	15.32	14.72	10.49	4.09	19.41	19.41
SA-NPP	16.01	11.49	14.92	10.53	4.11	15.59	15.59
SA-THP	22.27	12.18	33.30	14.54	5.67	17.85	17.85

$-\Delta G^\circ$, $-\Delta G_c^\circ$, $-\Delta G_c^\circ = \text{kJ mol}^{-1}$ at 303 K; $-\Delta H^\circ$, $+\Delta H_c^\circ$, $-\Delta H_c^\circ = \text{kJ mol}^{-1}$ between 293–323 K; $+\Delta S^\circ = \text{J deg}^{-1} \text{mol}^{-1}$ at 303 K.

In the present investigation, complexation equilibria of ternary complexes of Cu(II) with PHP, NPP and THP involving Cat, en, Pro, Hpr, Ala, Gly, Phe and SA at four different temperatures and 0.10 M (KNO₃) ionic strength have been studied. The values of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) along with their electrostatic and cratic components (ΔG_c° , ΔG_c° , ΔH_c° and ΔH_c°) were calculated and presented in Table-1. The decrease in log K_T values with increase in temperature shows that the reactions are exothermic and spontaneous in nature as is evidenced by the negative values of ΔH° and ΔG° . The magnitude of positive values of ΔS° for amino acid ternary systems is less than that of Cat ternary systems. This may be due to the fact that by increasing the charge on anion, the

tendency to lose water of hydration upon coordination increases. The enthalpy values of ternary complexes vary from those of corresponding binary complexes. Though both the enthalpy and entropy factors are favourable for the formation of ternary complexes, entropy factor appears to be the driving force, *i.e.*, $\log K_T > \log K_2$, when compared to the corresponding binary systems of secondary ligands¹. The $\log K_T$ values for these metal ions were found to be slightly less than the $\log K_1$ values. This could be due to the fact that the destabilization of ternary chelates caused by enthalpy changes is more prominent than the stabilization induced by the entropy changes. A comparison of the electrostatic and non-electrostatic or cratic components of the thermodynamic parameters for all the systems indicates that the values of ΔG_C^0 are significantly more negative than ΔG_e^0 suggesting that cratic forces are stronger than electrostatic forces. This indicates the more covalent character of bonds of Cu(II) ternary chelates.

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