

pH-Metric Studies on Mixed Ligand Chelates of some 3d Bivalent Transition Metals, involving some Organic Acids as Primary Ligands and Glutathione as Secondary Ligand alongwith their Correlations with some Properties of Central Metal Ions

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In view of the importance of mixed ligand complexes in various biological processes¹, the present communication reports the stability constants of mixed ligand chelates involving anthranilic, ascorbic, nicotinic and sulphanilic acids as primary ligands and glutathione (GSH) as secondary ligand alongwith their correlations with some properties of central metal ions.

Results and Discussion

From the pH titration curve (Fig. 1), it is observed that secondary ligand titration curve (B) and mixed ligand complexation curve (D) are well separated from

the acid titration curve (A), indicating that liberation of protons occurs during complexation. Also, the primary ligand complexation curve (C) is separated from the mixed ligand complexation curve (D) at pH 3.0, which indicates that addition of primary ligand occurs in this pH range. The mixed ligand complexation curve (D) is separated from the secondary ligand complexation curve (B) at pH 5.0 due to self-dissociation of the secondary ligand. After pH 5.5, mixed ligand complexation curve shows the indication of attachment of secondary ligand with Zn^{II} .

Mixed ligand stability constants : Mixed ligand stability constants of chelates were obtained by using Irving and Rossotti equations². Formation curve for mixed ligand stability constant was obtained by plotting n values against pL , and $\log K_1$ was evaluated using half-integral method at $n = 0.5$, corresponding to pL values. \bar{n} values extend from 0 to 0.79 indicating that 1 : 1 : 1 complex is formed. The order of stability of mixed ligand complexes with respect to metal ions follows the Irving-Williams natural order³: $Mn^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$.

The values for mixed ligand stability constants ($\log K$) for different metal ions are presented in Table I. $\log K$ decreases with increase in temperature from Mn^{II} to Zn^{II} mixed ligand complexes in each system, suggesting an exothermic nature of the metal-ligand interaction, i.e. $\log K$ is inversely proportional to temperature.

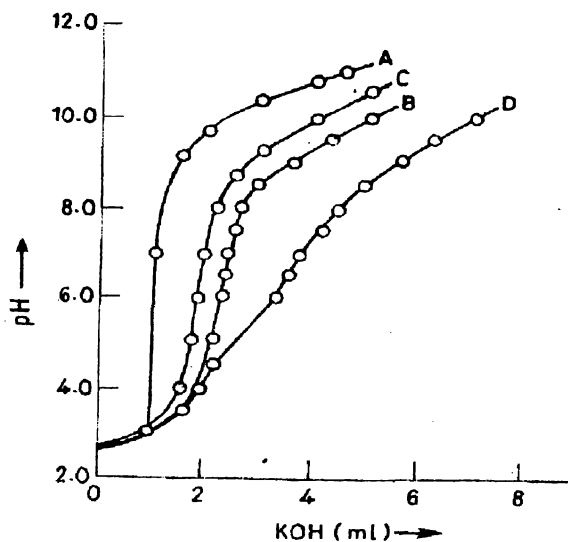
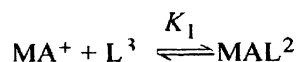
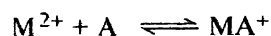


Fig. 1. pH-titration curves [Zn-AA-GSH] system: temp. = 30°, $I = 0.1 M$ (KNO_3).

TABLE I - STABILITY CONSTANTS OF THE MIXED LIGAND COMPLEXES AT A CONSTANT IONIC STRENGTH ($I = 0.1 \text{ M KNO}_3$) AT DIFFERENT TEMPERATURES (± 0.1)

System	log K at temperature		
	30	40	50
Mn AA GSH	5.60	5.05	4.70
Mn ASA GSH	5.75	5.38	5.15
Mn NA GSH	5.40	4.89	4.60
Mn SA GSH	6.79	6.59	6.40
Co AA GSH	6.05	5.83	5.56
Co ASA GSH	6.48	5.78	5.68
Co NA GSH	5.98	5.83	5.33
Co SA GSH	7.60	7.19	7.00
Ni AA GSH	6.25	5.87	5.67
Ni ASA GSH	6.83	6.64	6.44
Ni NA GSH	6.25	6.05	5.67
Ni SA GSH	7.95	7.73	7.53
Cu AA GSH	7.72	7.50	7.20
Cu ASA GSH	8.70	8.40	8.20
Cu NA GSH	8.92	8.70	8.60
Cu SA GSH	9.90	9.80	9.50
Zn AA GSH	5.89	5.50	5.20
Zn ASA GSH	6.89	6.52	6.30
Zn NA GSH	6.00	5.70	5.40
Zn SA GSH	7.50	6.90	6.80

The equilibria involved in metal(II) mixed ligand complexes can be presented as



Correlation of log K with some properties of central metal ions This correlation gives information on the nature of chemical bonding in mixed ligand complexes viz (i) atomic number of the bivalent metals^{4,5} (ii) reciprocal of ionic radius of the bivalent metals⁵ (iii) electronegativity of the bivalent metals^{5,6} (iv) sum of first and second ionisation potentials of bivalent metal ions^{5,8} (v) reciprocal of temperature⁹ and (vi) enthalpy change (ΔH) vs atomic number¹⁰

The correlation between log K_1 values with the atomic numbers reveals that there is a monotonic rise

to a maximum of copper followed by a lower value of zinc. This is in conformity with the observations of Irving and Rossotti². The correlation between the stability constants with the reciprocal of ionic radius reveals that apart from Cu^{II} and Zn^{II} other metal ions show linear behaviour. A linear relationship is revealed between log K_1 values of mixed ligand complexes with the known electronegativity values for the same metals. It is observed that stability increases with increase in the electronegativity of the metals which suggest that the metal-ligand bond would be covalent⁸.

The plot of log K against the sum of first and second ionisation potentials shows that there is a rise to maximum of Cu^{II} followed by a lower value of Zn^{II} as observed by Calvin and Melchior⁷. The greatest deviation observed in case of Cu^{II} may be probably due to Jahn-Teller effect¹¹ resulting the distorted octahedral geometry. The comparatively smaller deviation in case of Zn^{II} as compared to Cu^{II} may be due to completely filled d^{10} system of Zn^{II} where no stabilisation occurs while in case of Cu^{II} d^9 stabilisation attains maximum value.

The plot of log K against reciprocal of temperature indicates that stability constant value (log K_1) decreases with increase of temperature suggesting that the interaction of metal ions with the ligand is exothermic in nature (i.e. spontaneous process). The plot of enthalpy change (ΔH) against atomic number shows that from Mn^{II} to Co^{II} enthalpy change decreases which remains constant from Co^{II} to Ni^{II} then maximum to Cu^{II} and finally lowers to Zn^{II} . This may be accounted for exothermic nature of the reaction i.e. complexation of the ligand with the metal ion is a spontaneous process.

Comparison of the plot of log K vs atomic number reciprocal of ionic radius etc. for other mixed ligand system viz M-ASA-GSH, M-NA-GSH and M-SA-GSH systems indicates no change in the curve. Thus it seems that similar type of mixed ligand complexes are formed in each case.

Experimental

The metal salts anthranilic, ascorbic, nicotinic and sulphanic acids, potassium hydroxide, potassium nitrate used were of A.R. grade. Glutathione (reduced) (Aldrich) was used. All solutions were prepared in con-

dictivity water. Metal salts were standardised complexometrically by EDTA¹².

A Systronics 331 pH meter and a Julabe F-40 HC thermostat were used.

Following four sets of mixtures were prepared, keeping the total volume 50 ml in each case : (A) 10 ml, 0.001 *M* HNO₃ + 5 ml, 0.1 *M* KNO₃ + 35 ml H₂O, (B) 10 ml, 0.001 *M* HNO₃ + 4.7 ml, 0.1 *M* KNO₃ + 10 ml, 0.001 *M* secondary ligand (GSH) + 25.3 ml H₂O, (C) 10 ml, 0.001 *M* HNO₃ + 4.8 ml, 0.1 *M* KNO₃ + 10 ml, 0.001 *M* primary ligand + 10 ml, 0.001 *M* metal(II) + 15.2 ml H₂O, and (D) 10 ml, 0.001 *M* HNO₃ + 4.6 ml, 0.1 *M* KNO₃ + 10 ml, 0.001 *M* primary ligand + 10 ml, 0.001 *M* secondary ligand (GSH) + 10 ml, 0.001 *M* metal(II) + 5.4 ml H₂O. These mixture were individually titrated against standard 0.01 *M* KOH solution under the atmosphere of nitrogen and the pH was recorded after addition of alkali.

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