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Stability and Related Thermodynamics of Chelation of Fe(II), Co(II), Ni(II) and Cu(II) Metal Ions with Diacetyl-bis-(4-methoxybenzoylhydrazone)

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Chelate formation of Fe(II), Ni(II), Co(II) and Cu(II) with diacetyl bis-(4-methoxybenzoylhydrazone) in water-dioxane (1 : 1) at constant ionic strength (0.1 M KNO_3) and at three different temperatures 20 ± 0.1°C, 30 ± 0.1°C and 40 ± 0.1°C have been studied potentiometrically. The proton-ligand and metal-ligand stability constants were determined by Irving-Rossotti pH-metric titration technique. Thermodynamic functions ΔG, ΔH, ΔS and ΔCp were evaluated by making the investigations at three different temperatures. The order of stability constant with respect to metal ions followed the natural order.

INTRODUCTION

In recent years there is growing interest on the chemistry of hydrazides and hydrazones owing to their biological activity[1-3] and analytical applicability[4]. Besides these, hydrazides and hydrazones have interesting ligational properties due to presence of several potential coordination sites.[5, 6] Although metal chelates of benzoylhydrazones have been studied in recent years but no reference is available on the potentiometric study of metal-ligand equilibria with diacetyl-bis-(4-methoxybenzoylhydrazone) (MBH). These facts prompted us to investigate the chelation of Cu(II), Ni(II), Co(II) and Fe(II) with MBH. The present paper describes the determination of practical proton-ligand stability constants and formation constants of metal chelates. The method involves pH-metric titration technique of Irving and Rossotti[7] in water dioxane (1 : 1) at three different temperatures and at constant ionic strength (0.1 M KNO_3).

EXPERIMENTAL

All the reagents used were of AR quality. Their solutions were made in double distilled CO_2-free water and purified dioxane. The metal contents were estimated by standard methods.[8]

A systronic (model 331) expanded scale pH meter with accuracy of ± 0.05 was employed. The pH-meter was calibrated with potassium hydrogen phthalate solution.

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A solution of diacetyl (0.86 g) in ethyl alcohol (30 mL) was added to a solution of 4-methoxy benzoylhydrazine (3.30 g) in hot ethyl alcohol (40 mL) at room temperature and refluxed for 4 h. The solution was cooled and the solid compound obtained was filtered off and washed with alcohol and dried in vacuum (m.p. 250°C; reported 250°C).

The following sets of mixtures were prepared for titration:

(i) 8 mL HNO_3 (0.1 M) + 4 mL water + 24 mL dioxane + 4 mL KNO_3 (1.0 M).

(ii) 8 mL HNO_3 (0.1 M) + 4 mL water + 22 mL dioxane + 2 mL ligand in dioxane (0.1 M) + 4 mL KNO_3 (1.0 M).

(iii) 8 mL HNO_3 (0.1 M) + 3.6 mL water + 22 mL dioxane + 2 mL ligand in dioxane (0.1 M)+ 4 mL KNO_3 (1.0 M) + 0.4 mL metal ion solution (0.1M).

pH-Metric titrations of 40 mL portion in (1 : 1) water-dioxane of the above mixtures against (0.1 M) NaOH solution were carried out at temperatures 20 ± 0.1°C, 30 ± 0.1°C and 40 ± 0.1°C. Ionic strength of the medium was kept constant throughout by adding requisite amount of KNO_3. Duplicate titration was made in each case under identical conditions. The use of very dilute solution of metal ion made the possibility of polymeric species minimum. The titration curves (pH *vs* volume of alkali added) were obtained (Fig. 1).

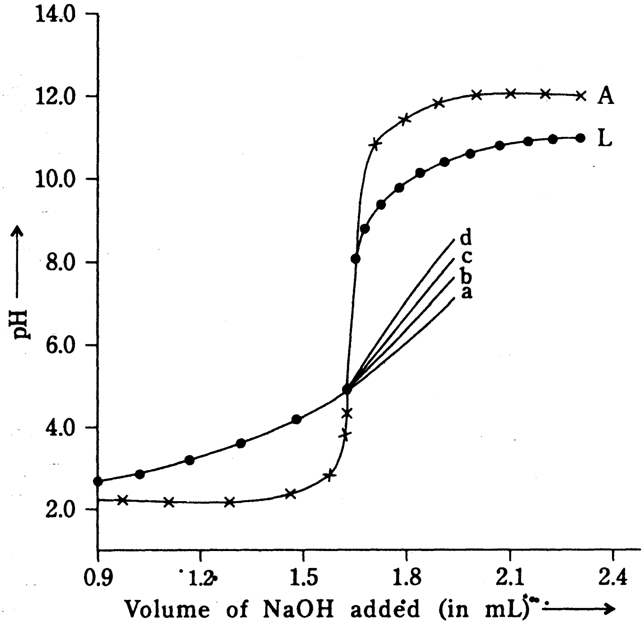


Fig. 1 Potentiometric titration of ligand MBH in presence of Cu(II), Ni(II), Co(II) and Fe(II) metal ions

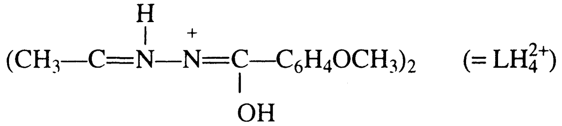
A = Acid mixture, L = mixture A + ligand MBH

a = Mixture L + Cu(II), b = Mixture L + Ni(II),

c = Mixture L + Co(II), d = Mixture L + Fe(II)

RESULTS AND DISCUSSION

At the initial stage of titration the ligand titration curve (L) was above the acid titration curve (A) (Fig. 1). This is due to basic group azomethine (—C═N—) present in the ligand. This basic group easily accepts proton from the strongly acidic medium. The ligand is biprotic due to presence of two (—OH) groups in enol form of the ligand and the structure of protonated ligand is given:



$$(CH_3-C=\overset{H}{\overset{|}{N}}{}^{+}-N=\underset{OH}{\underset{|}{C}}-C_6H_4OCH_3)_2 \qquad (=LH_4^{2+})$$

The dissociation of protonated species of ligand (LH_4^{2+}) may be represented as

$$LH_4^{2+} = LH_3^{+} + H^{+}$$

$$LH_3^{+} = LH_2 + H^{+}$$

$$LH_2 = LH^{-} + H^{+}$$

$$LH^{-} = L^{2-} + H^{+}$$

where L^{2-} = deprotonated species of ligand MBH

From the titration curve (Fig. 1) the $\bar{n}_A$ values were calculated using the relation of Irving and Rossotti.[7] The proton -ligand formation curve relating $\bar{n}_A$ values to pH-meter reading was very symmetrical. The value of log K_1^H, log K_2^H, log K_3^H and log K_4^H were calculated by half integral and mid-point calculation method.[7] These values were further refined by linear plot method.[9] The average values were taken as the representative value and were recorded in Table-1. The $\bar{n}_A$ values corresponding to pH-values were recalculated using the experimentally determined values of log K_1^H, log K_2^H, log K_3^H and log K_4^H. The standard deviation (σ) was calculated using the expression[7]

$$\sigma = \pm\ [\Sigma(\Delta n)^2/\text{number of observations}]^{1/2}$$

where $\Delta n = \underset{(cal.)}{\bar{n}_A} - \underset{(expt.)}{\bar{n}_A}$

The limits of error of stability constant values were obtained from the maximum horizontal displacement of the calculated curve from the experimental one. Results were recorded in Table-1. The metal-ligand titration curves (a, b, c and d) separated from the ligand titration curve (L) at pH = 5.8 in all the cases of metal ion.The function $\bar{n}$ attained its maximum value not beyond 1.0, which was an indication of the formation of 1 : 1 metal chelates in all the cases. The chelate formation curves (relating $\bar{n}$ values to P^L values) were very symmetrical in shape. The values of log K_1 were calculated by half integral method. These values were further refined by linear plot of log $\bar{n}/1 - \bar{n}$ *vs* P^L.

The $\bar{n}$ values were recalculated from the equation using experimentally determined values of log K and P^L.

$$\underset{(cal)}{\bar{n}} = KL/1 + KL$$

The theoretical formation curves were drawn along with the experimental points. Standard deviation and error limit were also determined and results were presented in Table-1.

TABLE-1
VALUES OF PRACTICAL PROTON LIGAND AND METAL LIGAND STABILITY CONSTANTS

Metal ions	Constants	Temperature			σ	Precision
		20°C	30°C	40°C		
	log K_1^H	12.05	11.95	11.85		
	log K_2^H	10.30	10.11	10.02	± 0.012	± 0.05
	log K_3^H	4.10	4.00	3.91		
	log K_4^H	2.25	2.15	2.05		
Cu(II)	log K	12.60	12.41	12.20	± 0.021	± 0.05
Ni(II)	log K	11.51	11.36	11.22	± 0.024	± 0.04
Co(II)	log K	11.10	10.98	10.86	± 0.025	± 0.04
Fe(II)	log K	10.20	10.11	10.02	± 0.031	± 0.05

It was observed from these results that the stability of metal chelates followed the trend with respect to metal ions,

$$\text{Fe(II)} < \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)},$$

which is in conformity with Irving William's natural order.[10] The Irving William order runs roughly parallel to the 2nd ionization potential of the elements, which provides information about the affinity of the central atom to accept electrons from the ligand in the covalent bond formation. log K_1 of metal chelates was plotted against the respective 2nd IP and a straight line was obtained[11]. The point corresponding to Fe(II) however did not fall on the line and was below it, showing a low degree of stability of Fe(II) chelates with the ligand.

The thermodynamic functions ΔG, ΔH, ΔS and ΔC_P of chelation of metal ions with MBH were calculated using well known equations. Values of ΔG were calculated from the equation

$$-\Delta G = 2.303RT \log K.$$

The values of ΔH and ΔS were calculated from the slops and intercept (respectively) of the straight line obtained by the plot of log K_1 *vs* 1/T. The resulting straight line indicated that the assumption in the Gibbs-Helmholtz equation, that ΔH is constant at different temperatures, is true. The values of stability constant were found to decrease with the increase in temperature suggesting that the chelation of metal ions was exothermic in nature. The entropy change (ΔS) was calculated by the relation $\Delta S = \text{intercept} \times R$ (Table-2). The observed positive values of ΔS and negative value of ΔG indicated the spontaneous formation of the chelates.[12] The plot of log K *vs* 1/T were straight lines which indicated that value of ΔC_P was equal to zero.[13]

TABLE-2
VALUES OF THERMODYNAMIC FUNCTIONS OF CHELATION

Functions	Metal ions				Precision
	Cu(II)	Ni(II)	Co(II)	Fe(II)	
−ΔG (Kcal mol^{-1}) at 293 K	17.01	15.54	14.98	13.77	± 0.07
− ΔH (Kcal mol^{-1})	9.20	6.57	5.41	4.18	± 0.64
ΔS (Cal $degree^{-1}$ mol^{-1}) at 293 K	26.53	30.50	32.54	32.61	± 0.23

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