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# Stability Constants of Hydrazine Carboxylic Acid Complexes with Some Bivalent Metal Ions

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The proton-ligand stability constants of hydrazine carboxylic acid (HCA) and stability constants of its chelates with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been determined, using Calvin-Bjerrum pH-metric method as modified by Irving and Rossotti in aqueous media at a constant ionic strength of 0.1M KCl and at a constant temperature (20 ± 0.2°C). The stability constants of the complexes follow the order Cu(II) > Zn(II) > Ni(II) > Co(II) > Cd(II) which is in accordance with Irving-Williams natural order.

## INTRODUCTION

The literature survey reveals that hydrazine carboxylic acid (HCA) frequently called carbazic acid and some of its metal-complexes have received considerable attention in last few years[1–6]. No attempt, however, appears to have been made so far to determine the stability constants of these complexes. In the present investigation, stability, constants of complexes of HCA with Co (II), Ni (II), Cu (II) Zn (II) and Cd (II) have been determined in aqueous media at a constant ionic strength and at a constant temperature by potentiometric method.

## EXPERIMENTAL

The ligand, HCA (m.pt. 90°, decomp.) was prepared as a white powder by the reported method[7]. The titration was performed in aqueous medium. Double distilled water was used throughout the investigation. Standard aqueous solutions of HCl, HCA, metal (II) chlorides, neutral KCl and KOH were used as mineral acid, complexing reagent, metal ion, background inert electrolyte alkali respectively. The metal ion solutions were standardised complexometrically by EDTA titrations[8]. Carbonate free KOH solution was prepared by washing KOH pellets with boiling water and finally dissolving it in $CO_2$—free double distilled water. It was standardised against oxalic acid potentiometrically. This standard solution of KOH was then used to standardise HCl solution potentiometrically. HCA solution was standardised with the help of potassium iodate titration[8].

The expanded pH meter-324 (systronics) with combined glass electrode and a calomel reference electrode was used for pH measurements after caliberating it with the help of buffer solutions of pH 4 and pH 9.2. After each experiment the calibration was checked and the temperature was maintained constant at 20 ± 0·2°C. The following mixtures were prepared and the total volume in each case was made equal to 50ml by adding appropriate volume of double distilled water.

Mixture (A) — 5 ml 0.04 M-HCl + 5 ml M KCl.

Mixture (B) — Mixure (A) + 5 ml 0.02M HCA.

Mixture (C) — Mixture (B) + 5 ml 3.004M metal ion.

These mixture were individually titrated potentiometrically against 0-2M KOH solution in the atmosphere of $N_2$ gas. A graph between

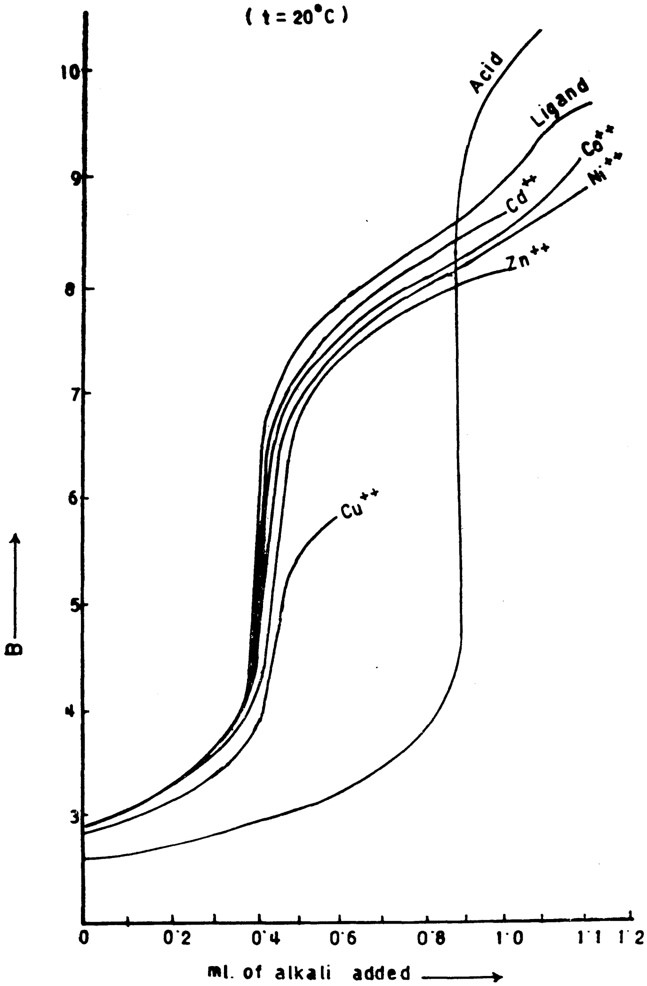

Fig. 1. Titration curves

B-values (pH meter readings) and the volume of alkali added was plotted in each case. The three titration curves so obtained were referred to as (i) acid, (ii) ligand and (iii) complex titration curves, respectively as shown in Fig. 1.

## RESULTS AND DISCUSSION

The pH titration technique of Calvin and Bjerrum[9, 10] as modified by Irving and Rossotti[11] was used to obtain the values of $\bar{n}_A$, $\bar{n}$ and pL from pH titration curves. the proton-ligand stability constants, $pK_1^H$ and $pK_2^H$ were than obtained by half integral method as well as from the plot of $\log \frac{\bar{n}_A}{1-\bar{n}_A}$ vs B and $\log \frac{2-\bar{n}_A}{\bar{n}_A-1}$ vs B respectively. Both these values agree quite well.

The values of $\log K_1$ and $\log K_2$ were evaluated from the formation curves of metal complexion equilibria by half integral method. In the case of copper (II) complex the formation curve remains incomplete in its upper half portion and so the value of $\log K_2$ was computed using the equation, $\log K_1 K_2 = 2$ pL (at $\bar{n}=1$)[12]. In the case of Co(II), Ni(II) and Zn(II) complex systems, the difference between $\log K_1$ and $\log K_2$ values were found to be less than 1.78 log unit, so the same were calculated by least square method and are reported[12]. The values of $\log K_1$ and $\log K_2$ of copper (II) complex which differs considerably and the value of $\log K_1$ of cadmium (II) complex as calculated by half integral method, were further varified by linear plot method[12] and are reported.

TABLE 1

STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES
($t = 20°C$ AND $\mu = 0.1$ M KCl)

| Cations | $H^+$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ |
|---|---|---|---|---|---|---|
| $\log K_1$ | 9.62 | 4.65 | 5.21 | 10.09 | 5.70 | 4.60 |
| $\log K_2$ | 7.84 | 3.77 | 3.87 | 8.15 | 4.02 | — |

The value of $\log K_1^H$ for HCA as determined presently is of the same order of magnitude as those reported for a series of α-amino acids (9.8 for glycine, 9.87 for D-alanine, 9.72 for valine, 9,74 for leucine at 25°C)[13] and further since $\log K_2^H$ value of HCA has the same order of magnitude as reported for $\log K_1^H$ value of hydrazine (7.92 at 25°C)[14] so zwitter-ion structure may be suggested to HCA which is really iso-structural with α-amino acids. The stability of the metal complexes of HCA as investigated presently are almost of the same order of magnitude as those reported for glycine and D-alanine[13] which may be taken as another evidence in favour of zwitter ion hypothesis. Strong evidence in support of zwitter ion structure is provided by IR spectral studies of HCA. The IR spectrum of HCA taken in KBr-pellet in the range of 4000-400 $cm^{-1}$ does not display bands due to $\nu(C{=}O)$ and $\nu(O\text{-}H)$ which may be expected from a compound containing carboxyl group. The three strong absorptions 1610 $cm^{-1}$ (very broad with two shoulders at 1670 $cm^{-1}$ and 1640 $cm^{-1}$), 1460 $cm^{-1}$ and 1345 $cm^{-1}$ are observed, which may be assigned as asymmetric $CO\overset{-}{O}$ stretching vibration coupled with in-plane N-H bending vibration, out-of-plane N-H bending vibration of the amine salt i.e. $\underset{|}{\overset{|\;+}{—NH}}$ and symmetric $CO\overset{-}{O}$ stretching vibration respectively. α-Amino acids having zwitter ion structure are known to display these bands in the same or nearly the same regions[15].

Keeping in view the zwitter ion existence of HCA, the protonation and deprotonation processes of HCA and protonated HCA respectively can be considered to occur according to the following schemes.

Protonation in strongly acidic medium:

$$\overset{+}{H_3N}—NH—CO\overset{-}{O} + \overset{+}{H} \rightleftharpoons \overset{+}{H_3N}—NH—COOH$$

In the initial stages of the titration the ligand curve is shifted to the left of the acid curve which is attributed to the basic character of the ligand. The carboxylate anion group takes up a proton from the strongly acidic medium and this causes pH of the solution to increase.

Deprotonation in weekly acidic or alkaline medium.

$$\overset{+}{H_3N}—NH—COOH \overset{K_1}{\rightleftharpoons} \underset{\textstyle +\atop\textstyle H^+}{\overset{+}{H_3N}—NH—CO\overset{-}{O}} \overset{K_2}{\rightleftharpoons} \underset{\textstyle +\atop\textstyle H^+}{H_2N—NH\;CO\overset{-}{O}}$$

In the later stages of the titration, the ligand curve gets shifted to the right of the acid titration curve which is due to the deprotonation of the protonated species causing thereby pH of the solution to decrease. This is also suggestive of the fact that the number of dissociable proton per ligand molecule (Y) is one.

The stability constants follow the trend

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

This is in accordance with Irving-Williams natural order of stability[13]. The higher stability constant of copper (II) arises possibly due to Jahn-Teller distortion[16] while at the same time partial oxidation of HCA by copper (II) ion cann't at all be ruled out.

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