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Potentiometric Studies on Chelation of Cu(II), Ni(II), Co(II) and Fe(II) with *o*-Vanillinsemicarbazone

CHANDRA S. JHA
University Department of Chemistry
L.N. Mithila University, Darbhanga-846 008, India

Chelate formation of Cu(II), Ni(II), Co(II) and Fe(II) with *o*-vanillinsemicarbazone in H_2O-DMF medium (1:1) at constant ionic strength ($\mu = 0.1$ M KNO_3) and at constant temperature of 25 ± 0.1°C has been studied potentiometrically. The proton-ligand and metal-ligand stability constants were determined by Irving-Rossotti pH-metric titration technique. The results were discussed in details with reference to the results already reported in the literatures. The order of stability constant with respect to metal ions followed the natural order.

INTRODUCTION

Though a large number of metal chelates have been reported of semicarbazones in literature, but no reference is available regarding the potentiometric study of chelation of metal ions with *o*-vanillinsemicarbazone. Thus in the present paper potentiometric studies on metal-ligand equilibria at constant ionic stength (0.1 M KNO_3 and at constant temperature 25°C in H_2O-DMF medium have been performed and formation constant of metal chelates have been reported. The method of study involved pH-metric titration technigue as reported by Irving and Rossotti[1].

EXPERIMENTAL

All the solutions were prepared in double distilled CO_2-free water and the reagents used were of analytical grade. The metal contents were estimated by standard methods[2]. A systronic (model-331) expanded scale pH-meter with an accuracy of ± 0.05 was employed. The pH-meter was calibrated with potassium hydrogen phthalate solution. *o*-vanillinsemicarbazone was prepared by known method[3].

Petentionetric titrations

The following sets of mixtures were prepared for titrations:

(i) (0.1 M) 8 mL HNO_3 + 4.0 mL water + 24.0 mL DMF + (1.0 M) 4.0 mL KNO_3

(ii) (0.1 M) 8 mL HNO_3 + 4.0 mL water + 22.0 mL DMF + (0.1 M) 2.0 mL ligand solution in DMF + (1.0 M) 4.0 mL KNO_3.

(iii) (0.1 M) 8 mL HNO_3 + 3.6 mL water + 22.0 mL DMF + (0.1 M) 2.0 mL ligand solution in DMF + (1.0 M) 4.0 mL KNO_3 + (0.1 M) 0.4 mL metal ion solution in water.

pH-metric titrations of 40 mL portion in (1:1) H_2O-DMF of the above mixture against (0.1 M) NaOH solution was performed at 25 ± 0.1°C. Ionic strength of the medium was kept constant throughout the titration by adding requisite amount of .KNO_3. Duplicate titration was performed in each case under identical conditions. The use of very dilute solution of metal ions minimised the possibility of polymeric species. The rapid attainment of equilibria during the course of titration and by the absence of any significant drift in pH even after 2 h ascertained that the ligand did not undergo hydrolysis under the experimental conditions. This was confirmed by performing TLC from time to time.

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 the basic group, azomethine (—C═N—) present in the ligand. This basic group easily accepts protons from

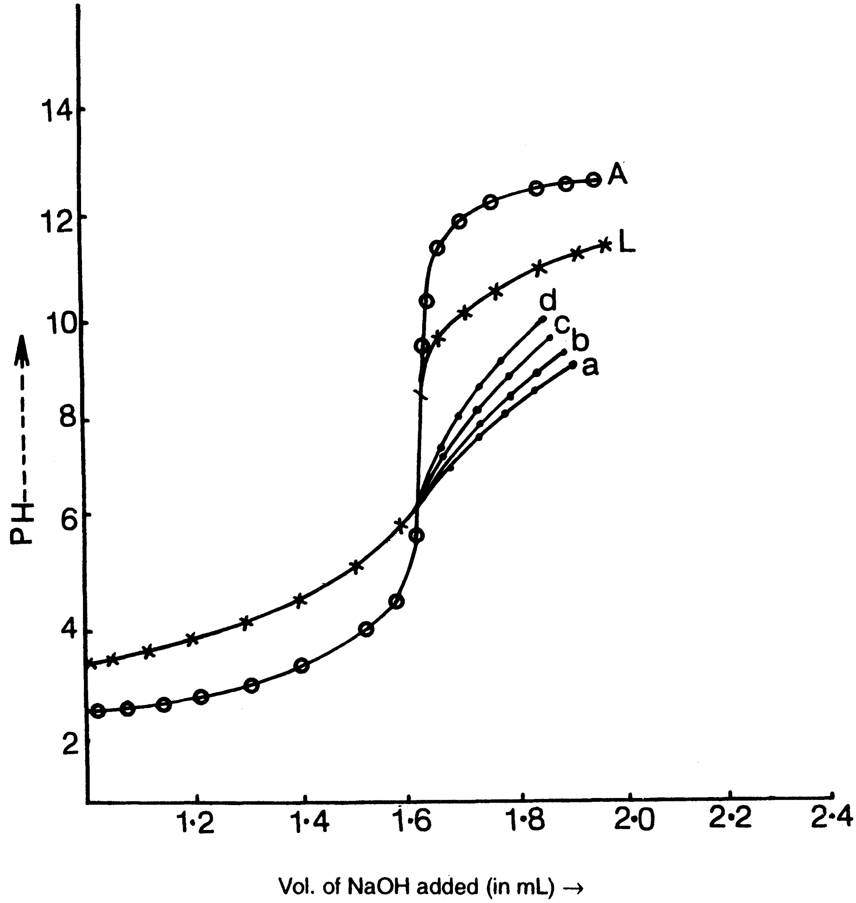
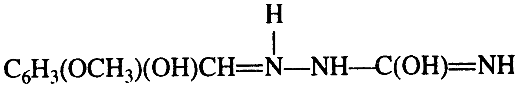


Fig. 1. Potentiometric titration of legand *o*-vanillinsemicarbazone in oresence of Cu(II), Ni(II), Co(II) and Fe(II). a = Cu(II)-ligand system, b = Ni(II)-ligand system, c = Co(II)-ligand system, d = Fe(II)-ligand system.

the strougly acidic medium. The ligand is biprotic in nature and the structure of protonated ligand (LH_3^+) is represented as:



$$C_6H_3(OCH_3)(OH)CH{=}\overset{\displaystyle H}{\overset{|}{N}}{-}NH{-}C(OH){=}NH$$

o-Vanillinsemicarbazone.

(Protonated ligand LH_3^+)

The dissociation of protonated specises of the ligand may be represented as:

$$LH_3^+ = LH_2 + H^+$$

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

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

where L^{-2} = deprotonated *o*-vanillinsemicarbazone species.

From the titration curve (Fig. 1) $\bar{n}_A$ values were calulated using the relation given by Irving and Rossotti[1]. The proton-ligand formation curve relating $\bar{n}_A$ values to pH-meter reading, was very symmetrical. The values of $\log K_1^H$, $\log K_2^H$ and $\log K_3^H$ were calculated by half integral and mid-point calculation methods[4]. $\bar{n}_A$ values were recalculated using experimentally determined values of proton-ligand stability constant.

The standard deviation[1] (σ) was calculated using the expression

$$\sigma = \pm\,[\Sigma(\Delta n)^2/\text{no. of observations}]^{1/2}$$

where $\Delta n = \bar{n}$ (calcd.) – $\bar{n}$ (exptl.).

The error limits of the stability constant values were obtained from the maximum horizontal displacement of the calculated curve ($\bar{n}_A$ vs. pH) from the experimental one (Table-1).

TABLE-1
VALUES OF STABILITY CONSTANTS

Cation	$\log K_1$	$\log K_2$	$\log K_3$	σ
H^+	9.25 ± 0.03	5.75 ± 0.03	2.78 ± 0.03	±0.012
Cu(II)	8.34 ± 0.05	—	—	±0.021
Ni(II)	7.52 ± 0.04	—	—	±0.024
Co(II)	6.95 ± 0.04	—	—	±0.025
Fe(II)	6.78 ± 0.05	—	—	±0.031

The metal-ligand titration curves (a, b, c and d) separated from the ligand titration curve (L) at pH = 6.0 in all the cases of metal ions. The maximum value of n was upto 1.0, which was the indication of formation of (1:1) metal chelates. The chelate formation curves, relating n values to pL values, were very symmetrical in shape. Half integral and mid-point calculation methods were employed for the calculation of log K. It was further refined by linear plot of log $\frac{\bar{n}}{1-\bar{n}}$ vs. pL.

The $\bar{n}$ values were recalculated from the equation given below, using experimentally determined value of log K and pL.

$$\bar{n}\,(\text{calcd.}) = \frac{KL}{1 + KL}$$

The theoretical formation curves were drawn along with the experimental points. Standard deviation (σ) and error limits[5] were also determined. Results were recorded in Table-1

It was observed from these results that the stability of metal chelates followed the trend:

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

which is in conformity with Irving-William's natural order[6]

The natural order runs roughly parallel to the second I.P. of the elements, which provides information about the affinity of the central atom to accept electrons from the ligand in covalent bound formation. Values of log K were thus plotted against the respective second I.P. and a straight line was obtained. The point corresponding to Co(II), however does not fall on the line and was below it, showing that Co(II) chelates possessed a low degree of stability with *o*-vanillinsemicarbazone ligand.

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