

## Potentiometric Studies on Some Bivalent Metal Complexes of 2-Hydroxy-1-naphthaldehyde Monosemicarbazone (HNAS)

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The proton-ligand stability constants of 2-hydroxy-1-naphthaldehyde monosemicarbazone and metal-ligand stability constants of its complexes with  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $UO_2^{2+}$  have been determined potentiometrically at different ionic strengths in 75% (v/v) aqueous dioxan medium. The method of Bjerrum and Calvin as modified by Irving and Rossotti has been used to find out the values of  $\bar{n}$  and  $pL$ . The stability constants have been calculated on IBM 360 FORTRAN IV computer using the weighted least squares method. The values of  $S_{min} = \chi^2$  have also been calculated. The order of stability constants is found to be:  $UO_2^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Mn^{2+} > Mg^{2+}$ . The other thermodynamic parameters and ligand field stabilization energies have been calculated from the stability constants.

The semicarbazones and thiosemicarbazones of certain aldehydes and ketones have significant antimicrobial activities<sup>1-5</sup>. Domagk *et al.*<sup>6</sup> reported for the first time the antitubercular activities of metal thiosemicarbazones and semicarbazones. The activity of semicarbazones is thought to be due to their strong chelation with trace metal ions present in biological systems.

As a part of a study undertaken in our laboratories on the stabilities of metal complexes of biologically active ligands, we report here the stabilities of the complexes of some bivalent metal ions with 2-hydroxy-1-naphthaldehyde monosemicarbazone (HNAS) at various ionic strengths in 75% (v/v) aqueous dioxan medium.

A digital pH meter (ECIL, model pH 5651) in conjunction with a glass electrode (0-14 pH range) was used for pH measurements. All the measurements were made at a constant temperature using an MLW (FRG) (NBE type) thermostat. An IBM 360 FORTRAN IV computer was used for most of the calculations.

### Preparation of ligand

2-Hydroxy-1-naphthaldehyde (1.038 g) was dissolved in the minimum amount of ethanol and an aqueous solution containing equal amounts of semicarbazide hydrochloride (0.672 g) and anhydrous sodium acetate was added to it. The mix-

ture was refluxed for 2 hr, filtered (if necessary) and cooled in ice. The semicarbazone was precipitated by adding dilute hydrochloric acid and recrystallized from ethanol. 2-Hydroxy-1-naphthaldehyde monosemicarbazone (HNAS) solution was prepared in 75% (v/v) aqueous dioxan medium. The decomposition point of the ligand (HNAS) is 214°C. The purity of the ligand was checked by TLC, elemental analyses, IR and NMR spectra. The solutions of bivalent metal ions were standardised by conventional methods.  $Me_4NOH$  (TMAH) (E Merck, AG Darmstadt) in 75% aqueous dioxan was used as the titrant. The solution was standardised with oxalic acid.  $HClO_4$  was standardised with prestandardised  $Na_2CO_3$  and diluted to the required strength ( $0.05 \text{ mol l}^{-1}$ ) with doubly distilled water. Sodium perchlorate (E Merck, AG Darmstadt) was used to maintain the ionic strength constant for different sets. Dioxan (Merck) was purified before use.

Investigations were carried out at different ionic strengths (0.1, 0.05, 0.025 and  $0.01 \text{ mol l}^{-1}$ ). pH correction factor and volume correction factor were applied for getting accurate values of stability constants. For each set of experiments, the final volume was made up to  $20 \text{ cm}^3$ , maintaining 75% aqueous dioxan medium. Each set was titrated against 0.05 M TMAH in 75% aqueous dioxan. Requisite amount of  $NaClO_4$  was added to maintain the ionic strength at 0.1, 0.05, 0.025 and 0.01 M. These titrations were carried out in a closed double walled container in an atmosphere of nitrogen, which was presaturated with 75% aqueous dioxan.

Values of  $\bar{n}_H$  were calculated at various pH values from the above titration curves. The values of  $\log \bar{n}_H / 1 - \bar{n}_H$  versus pH gave linear plots having intercept equal to  $pK_a$  (ligand dissociation constant) and slopes equal to unity. From the titration curves of solutions,  $\bar{n}$  values of the metal complexes were determined at various pH values. From  $pK_a$  and  $\bar{n}$  values at different pH values, the corresponding values of  $pL$  were calculated. The  $\bar{n}$  and  $pL$  data were subjected to the weighted least squares method developed by Sullivan *et al.*<sup>10</sup> on an IBM 360 FORTRAN IV computer to get  $\beta_n$  values. The weighted least square treatment determined the set of  $\beta_n$  values which make the function U

$$U = \sum_{n=0}^N (y - x - nz) \beta_n x^n$$

Table 1 – Stability Constants of Bivalent Metal Complexes of 2-Hydroxy-1-naphthaldehyde Monosemicarbazone

[Ionic strength = 0.1 M NaClO<sub>4</sub>; temp. = 20 ± 0.5°C]

Metal ion/ ligand	Weighted least squares method			
	log K <sub>1</sub>	log K <sub>2</sub>	log β <sub>2</sub>	S <sub>min</sub>
H <sup>+</sup>	10.45	—	—	—
Mg <sup>2+</sup>	3.22	3.03	6.25	0.0051
Mn <sup>2+</sup>	5.03	4.17	9.20	0.0341
Cd <sup>2+</sup>	5.65	4.23	9.88	0.0302
Pb <sup>2+</sup>	6.05	5.80	11.85	0.0548
Zn <sup>2+</sup>	7.82	6.43	14.25	0.0190
Co <sup>2+</sup>	8.60	7.58	16.18	0.0097
Ni <sup>2+</sup>	8.93	7.99	16.92	0.2232
Cu <sup>2+</sup>	9.10	8.24	17.34	0.2512
UO <sub>2</sub> <sup>2+</sup>	9.98	9.36	19.34	0.1163

nearest to zero, by minimizing S

$$S = \sum_{i=1}^I W_i U^2(x_i, y_i, z_i)$$

with respect to variation in β<sub>n</sub>. S<sub>min</sub> has the same statistical distribution as χ<sup>2</sup> with K degrees of freedom and the weight defined in accordance with Sullivan *et al.*<sup>11</sup>. S<sub>min</sub> can be equated to χ<sup>2</sup>.

The order of stability constants of the metal complexes with HNAS is: UO<sub>2</sub><sup>2+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Zn<sup>2+</sup> > Pb<sup>2+</sup> > Cd<sup>2+</sup> > Mn<sup>2+</sup> > Mg<sup>2+</sup>. The order is in good agreement with the order found by Mellor and Maley<sup>12</sup> and Irving and Williams<sup>13,14</sup>. In all the systems, the values of log K<sub>1</sub> are greater than log K<sub>2</sub> values. The log K<sub>1</sub>, log K<sub>2</sub>, log β<sub>2</sub> and S<sub>min</sub> values at different ionic strengths are given in Table 1. All the complexes appear to be high spin.

Finally, in view of the very low (5.0 × 10<sup>-4</sup> M) concentration of metal ions used in the titration, it has been assumed that the possibility of formation of polynuclear complex is negligible. In the present studies, it has been observed that the value of dissociation constant (pK<sub>a</sub>) of the ligand (HNAS) and stability constant decreases with increasing ionic strength of the medium, which is in agreement with Debye-Huckel equation<sup>15</sup>. The thermodynamic stability constants were obtained by extrapolating the linear plot of log K<sub>1</sub> versus √μ to zero ionic strength.

The ligand field stabilization energy, 'δH' and E<sub>r</sub> (Mn–Zn) values have been calculated according to the method of George and McClure and listed in Table 2. The orders of enthalpies, free energies and ligand field stabilization energies

 Table 2 – E<sub>r</sub>(Mn–Zn) and δH Values for Complexes of HNAS

Parameters	Metal ions				
	Mn <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
log K <sub>1</sub> <sup>o</sup>	5.95	9.28	9.33	10.45	8.02
ΔG	7.98	12.44	12.51	14.01	10.75
ΔG <sub>r</sub>	—	4.46	4.53	6.03	2.77
ΔH <sub>H</sub>	—	43.00	62.00	63.00	47.00
ΔH <sub>L</sub>	—	47.46	66.53	69.03	49.77
[(n-5)/5]E <sub>r</sub>	—	19.91	29.86	39.82	—
δH	—	27.55	36.67	29.21	—

ΔG = Free energy change = 2.303 RT log K<sub>1</sub><sup>o</sup>, where R, T and K<sub>1</sub><sup>o</sup> have usual significance and temp. = 293K.

ΔG<sub>r</sub> = Change in heat content for the formation of the complex in solution.

ΔH<sub>H</sub> = Heat of hydration of metal ion.

ΔH<sub>L</sub> = Heat of complexation referred to metal ion in gaseous and ligand in solution state.

n = Number of electrons in 3d orbital.

[(n-5)/5]E<sub>r</sub> = Lattice energy difference for Zn<sup>2+</sup> and Mn<sup>2+</sup> complexes.

δH = Thermodynamic stabilization energy.

log K<sub>1</sub><sup>o</sup> = Value employed for the above calculations, have been obtained by extrapolating the log K<sub>1</sub> versus √μ (linear) to zero ionic strength.

'δH' have been found to be: Mn < Co < Ni < Cu > Zn; Mn < Co < Ni < Cu > Zn and Co < Ni > Cu respectively.

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