

## NOTES

**Formation Constants of Complexes of Disalicylamide with Co(II), Ni(II), Cu(II) and Zn(II)**

MISS A. GUPTA and B.S. PANNU

*Department of Chemistry  
Punjab Agricultural University  
Ludhiana-141 004, India*

The present paper describes the proton-ligand stability constants of disalicylamide and stability constants of its complexes with Co(II), Ni(II), Cu(II) and Zn(II).

Salicylamide and disalicylamide possess molluscicidal activity<sup>1</sup>. The kinetics and mechanism of formation and hydrolysis of boric acid esters of disalicylamide have been studied with special reference to the factors influencing their stabilities<sup>2,3</sup>. The present communication describes the proton-ligand stability constants of disalicylamide and stability constants of its complexes with Co(II), Ni(II), Cu(II) and Zn(II) determined by pH titration technique. The effects of ionic strength and composition of the solvent medium have been studied.

Disalicylamide was prepared by the reaction of salicylic acid with thionyl chloride followed by treatment with liquor ammonia in chilled condition. Disalicylamide solution (0.02 M) was prepared in methanol. Metal(II) nitrates or chlorides of Sarabhai M. Chemicals Limited, G.R. grade were dissolved in double glass distilled water and standardized to 0.01 M solution. Sodium nitrate (1 M) solution was used to adjust ionic strength. Nitric acid of BDH AnalaR grade was used to prepare 0.05 M HNO<sub>3</sub>. Carbonate-free KOH was used to prepare 0.10 M KOH solution.

A Systronics Type 33 pH meter with glass and calomel electrode assembly was used to measure pH. It was calibrated with standard buffers before use. SICO (Calcutta) thermostat type TBS was used to regulate the temperature of titration mixture at 25 ± .10°C. The Bjerrum-Calvin pH titration technique<sup>4,5</sup> as adopted by Irving and Rossotti<sup>6</sup> was used for the studies. The following three solutions were titrated against 0.10 M KOH.

- (A) 20.00 ml 0.05 M HNO<sub>3</sub>
- (B) A + 5.00 ml 0.02 M ligand
- (C) B + 2.00 ml 0.01 M metal ion

The ratio of metal to ligand was kept 1 : 5 in order to fulfil the condition of maximum coordination number. The total initial volume was 20.0 ml in methanol-water system.

The average protonation number,  $\bar{n}_A$ , the formation function,  $\bar{n}$ , and free ligand

concentration,  $pL$ , were calculated from the titration curves by the Irving and Rossotti method<sup>7</sup>. The proton ligand stability constants were obtained by the following relationships:

$$\log K_1^H = B + \log \frac{\bar{n}_\Lambda}{1 - \bar{n}_\Lambda} \text{ for } \bar{n}_\Lambda < 1$$

$$\log K_2^H = B + \log \frac{\bar{n}_\Lambda - 1}{2 - \bar{n}_\Lambda} \text{ for } 1 < \bar{n}_\Lambda < 2$$

$$\log K_3^H = B + \log \frac{\bar{n}_\Lambda - 2}{3 - \bar{n}_\Lambda} \text{ for } 2 < \bar{n}_\Lambda < 3$$

where B is pH-meter reading.

The plots of  $\log \frac{\bar{n}_\Lambda}{1 - \bar{n}_\Lambda}$  versus B,  $\log \frac{\bar{n}_\Lambda - 1}{2 - \bar{n}_\Lambda}$  versus B and  $\log \frac{\bar{n}_\Lambda - 2}{3 - \bar{n}_\Lambda}$  versus B give  $\log K_1^H$ ,  $\log K_2^H$  and  $\log K_3^H$  as intercepts along X-axis respectively. These are given in Table 1. The protonation occurs at  $-NH-$  group which is responsible for the release of three protons.

TABLE 1  
PROTON-LIGAND STABILITY CONSTANTS OF DISALICYLAMIDE IN METHANOL-WATER SYSTEM AT VARIOUS IONIC STRENGTHS AT  $25 \pm 10^\circ\text{C}$

Methanol : water composition	Ionic strength M	$\log K_1^H$	$\log K_2^H$	$\log K_3^H$
25 : 75	0.10	11.25	9.20	6.50
25 : 75	0.25	11.20	9.10	6.20
25 : 75	0.50	10.84	8.90	5.80
35 : 65	0.10	11.50	9.50	6.80

In the case of metal complexes value of formation function  $\bar{n}$  does not go beyond 1. This suggests the formation of 1 : 1 metal complexes. The values of  $\log K_1$  obtained are given in Table 2.

The thermodynamic stability constants were obtained from the plots of  $\log K_1$  versus  $\sqrt{\mu}$  and extrapolating to zero ionic strength. The proton-ligand stability constants and  $\log K_1$  values for metal complexes decrease with increase of ionic strength and increase with the increase of methanol in solvent medium. The stability order for the metal complexes is  $\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$ . This agrees with Irving-Williams natural order and some other orders<sup>9,10</sup>. The stability of Zn(II) complex is higher than those of Co(II) and Ni(II) complexes. This may be due to donation of electrons from the oxygen donor sites. It has been found in the case of some other oxygen donors that the stability of Zn(II) complexes is higher than those of Co(II) and Ni(II) complexes<sup>11</sup>. The high values of stability constants suggest that these complexes are chelates in nature.

TABLE 2  
STABILITY CONSTANTS OF METAL DISALICYLAMIDE COMPLEXES IN  
METHANOL WATER SYSTEM AT VARIOUS IONIC STRENGTHS AT  $25 \pm .10^\circ\text{C}$

Metal ion	Methanol : water composition	Ionic strength	log $K_1$
$\text{Co}^{2+}$	25 : 75	0.00	7.45
	25 : 75	0.10	7.00
	25 : 75	0.25	6.60
	25 : 75	0.50	6.40
	35 : 65	0.10	7.60
$\text{Ni}^{2+}$	25 : 75	0.00	9.20
	25 : 75	0.10	8.20
	25 : 75	0.25	7.60
	25 : 75	0.50	7.00
	35 : 65	0.10	9.50
$\text{Cu}^{2+}$	25 : 75	0.00	15.40
	25 : 75	0.10	13.00
	25 : 75	0.25	10.80
	25 : 75	0.50	9.20
	35 : 65	0.10	14.70
$\text{Zn}^{2+}$	25 : 75	0.00	12.45
	25 : 75	0.10	10.50
	25 : 75	0.25	9.50
	25 : 75	0.50	8.20
	35 : 65	0.10	11.70

## REFERENCES

1. E. Schraufstaetter, W. Mieser and R. Goennert, *Z. Naturforsch*, **16b**, 95 (1961).
2. D.W. Tanner, Dissertation 1968, *Chem. Abstr.*, **69**, 35093 J (1969).
3. D.W. Tanner and T.C. Bruice, *J. Am. Chem. Soc.*, **89**, 6954 (1969).
4. J. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Haase & Sons, Copenhagen, 1941.
5. M. Calvin and K.W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
6. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904, (1954).
7. \_\_\_\_\_, *J. Chem. Soc.*, 3397 (1953).
8. H.M. Irvin and R.J. P. Williams, *J. Chem. Soc.*, 3192 (1953).
9. D.P. Mellor and L.E. Maley, *Nature*, **159**, 370 (1947).
10. G.A. Carlson, J.P. McReynolds and F.H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1334 (1945).
11. J.K. Nepal and S.N. Dubey, *J. Indian Chem. Soc.*, **66**, 469 (1989).