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NOTE

Stability Constants of Metal Complexes of Dithiocarbamates

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The stability constant of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with dithiocarbamates are studied in 60% ethanol-water mixture at 28°C using the pH titration technique. It is observed that the overall stability constants are in the order of

$$Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II).$$

There is growing interest in the use of sulphur containing compounds in analytical as well as structural studies of metal complexes. The present work deals with the determination of successive stability constants of complexes of pentamethylene dithiocarbamate (Pipdtc), diethyldithiocarbamate (Dedtc), ammonium pyrrolidine dithiocarbamate (Apdtc) and potassium ethyl xanthate (KEtx) with some transition metal ions by Calvin Bjerrum titration technique[1-3] as modified by Irving and Rossotti[4]. The ligands (Pipdtc) and (KEtx) were prepared by well established methods[5,6]. The ligands (Apdtc), (Dedtc) were obtained from S.D. Fine Chem. Pvt. Ltd., Bombay and Loba Chemie Indo Austranal Co., Bombay respectively. The solutions (0.01 M) were prepared in double distilled water. The solutions of metal ions (0.001 M) and sodium hydroxide (0.1 M) were prepared from BDH (AnalaR) sample of the salts in CO_2-free double distilled water and standardised by appropriate standard methods.

An Elico LI-120 digital pH meter was employed for measuring the pH of the solution. The pH meter was standardised at 28°C using appropriate buffer solutions of pH 4.02 and 9.20 equilibrated for 30 minutes before measurement.

The experimental procedure involved the titration of the following carbonate free solutions (total volume 50 ml.) against standard sodium hydroxide (0.1020 M). The ionic strength was maintained at 0.05 M (KNO_3). Since the chelates were insoluble in water the studies were carried out at 28°C in 60% ethanol-water medium.

(a) 5 ml of (0.1 M) nitric acid + 30 ml of ethanol + 15 ml of water.
(b) 1 ml of (0.01 M) ligand in water + 5 ml of (0.01 M) nitric acid + 30 ml of ethanol + 14 ml of water.

(c) 1 ml of (0.001 M) metal solution + 1 ml of (0.01 M) ligand + 5 ml of (0.01 M) of nitric acid + 30 ml of ethanol + 13 ml of water.

The dissociation constants (K_L) of the ligands were obtained from the formation curves of the proton ligand system by plotting $\bar{n}_A$ vs. pH. From these plots the log K_L were determined as 9.9, 9.0, 7.5 and 7.5 for the ligands Pipdtc, Dedtc, Apdtc, and KEtX respectively. The $\bar{n}_A$ values were calculated[4] at various pH values from the titration curves using solutions (a) and (b). From the titration curves of solutions (b) and (c) $\bar{n}$ and PL values were calculated[4]. Metal ligand formation constants of the complexes were calculated applying least square method[4] to the $\bar{n}$, PL data (Table 1). A plot of stability of complexes versus atomic number

TABLE 1

STABILITY CONSTANTS OF METAL COMPLEXES IN 60% ETHANOL-WATER

Ligand	Mn(II)			Fe(II)			Co(II)		
	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
Pipdtc	4.9	—	—	8.5	5.5	14.0	9.7	7.2	16.9
Dedtc	4.2	—	—	5.5	—	—	7.0	1.3	8.3
Apdtc	2.1	—	—	2.4	—	—	2.8	0.7	3.5
KEtx	1.2	—	—	1.9	—	—	2.1	—	—
	Ni(II)			Cu(II)			Zn(II)		
Pipdtc	10.0	7.8	17.8	10.5	8.9	19.4	9.8	6.5	16.3
Dedtc	8.8	4.4	13.2	8.8	4.9	18.7	7.2	3.6	10.8
Apdtc	5.0	1.8	6.8	5.4	3.3	7.7	4.0	1.5	5.5
KEtX	2.4	1.0	3.4	—	4.3	—	3.6	2.1	5.7

clearly displays the monotonic rise in stabilities upto copper followed by a lower value for zinc independent of the nature of ligand used[7].

It can be concluded from the results in Table 1 that the overall stability constants (log β_2) of the complexes were in the order of Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II), which follows the Irving Williams order[8].

REFERENCES

1. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).
2. M. Calvin and N. C. Melchior, *J. Am. Chem. Soc.*, **70**, 3270 (1948).

3. J. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Hause and Sons, Copenhagen, (1941).
4. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2904 (1954), 3397 (1953).
5. K. Glue and R. Schwab, *Angrew. Chem.*, **62**, 320 (1950).
6. I. Vogel, Text Book of Practical Organic Chemistry, 4th edition, Chapter III, p. 207 (1986).
7. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).
8. ———, *Nature*, **162**, 746 (1948).

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