TECHNICAL REPORT

POTENTIOMETRIC STUDY OF SOME SCHIFF BASE COMPLEXES

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Potentiometric study of the complexation reaction of Al, In, Ce, Mn, Ni, Co, Cd, Ag and Pb with a Schiff base derived from salicylaldehyde and tris buffer has been carried out in aqueous medium at 35°C. The stability constants are determined by employing the half integral method of Irving & Rossotti. Free energy change for the complexation reaction has also been derived.

The potentiometric investigation of the complexes of Cu(II), Zn(II) and Hg(II) with the schiff base derived from salicylaldehyde and tris buffer (ST) is reported in an earlier paper[1]. Complexes of Bi(III) and Sb(III) with ST are investigated polarographically[2,3]. The present work deals with the potentiometric study of Al (III), Ce(III), In(III), Mn(II), Ni(II), Co(II), Cd(II), Ag(I) and Pb(II) complexes with ST, as a part of the programme to study the nature of Schiff base complexes of transition and non-transition metals. In order to evaluate the stability constants of the complexes, Irving Rossotti half integral method was utilized as 1 : 1 complex is formed in each case.

Experimental

With AR grade chemicals, the solutions were prepared in doubly distilled water. The following three sets were prepared keeping ionic strength constant at $\mu = 0.1$ with $NaClO_4$.

(1) 0.01M $HClO_4$ + 0.1M $NaClO_4$

(2) 0.01M $HClO_4$ + 0.005 M ligand ST + 0.1M $NaClO_4$

(3) 0.01M $HClO_4$ + 0.1M $NaClO_4$ + 0.005M ligand ST + Metal (0.001M in case of Al, In, Cd, Pb, & Ag, and 0.0015M in case of Mn, Ni, Co & Ce).

The sets were titrated against carbon dioxide free 0.5M NaOH.

Results and Discussions

The stepwise ligand - proton stability constant was determined by plotting $\bar{n}_A$ against pH. The value of $\bar{n}_A$, the number of protons attached to protonated ligand, was found by:

$$\bar{n}_A = Y + \frac{(V' - V'')\ N + E)}{(V^\circ + V')\ T_l} \qquad (1)$$

where all the symbols are traditional[4].

From the structure of the ligand it seems that the number of the displaceable protons Y = 1, but in presence of the metal ion, the alcoholic -OH also dissociates[5]; hence in the present case, Y = 2. The values of the protonation constants were obtained from the graph $\bar{n}_A$, — pH taking values of $\bar{n}_A$ at $pH_{n-\frac{1}{2}}$ where n represents step of dissociation[4]. The values are: $\log \beta_1 = 8.95$ and $\log \beta_2 = 7.40$.

In order to evaluate stability constants of the complexes, Bjerrum's formation function $\bar{n}$, defined as the average number of ligand per metal ion, was calculated by:

$$\bar{n} = \frac{(V''' - V'')[N + E + T_l(Y - \bar{n}_A)]}{(V^\circ + V'')\bar{n}_A\ T_m} \qquad (2)$$

The free ligand concentration was calculated by:

$$pL = \log \left[\frac{\sum_{n=o}^{n=j} \left({}^n\beta_n^H\ (1/\text{anti log } B)^n \right)}{T_l - \bar{n}\ T_m} \right]$$

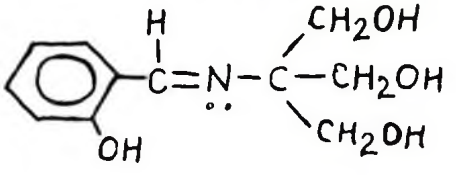


TABLE 1. Thermodynamic functions of complexes.

Metal	Al	In	Mn	Co	Ni	Ag	Cd	Pb	Ce
log β	7.13	7.53	3.07	2.68	3·48	4.48	3.88	3.83	—
$-\Delta G$ kcal	10.05	10.61	4.33	3.78	4.90	6.31	5.47	5.40	—

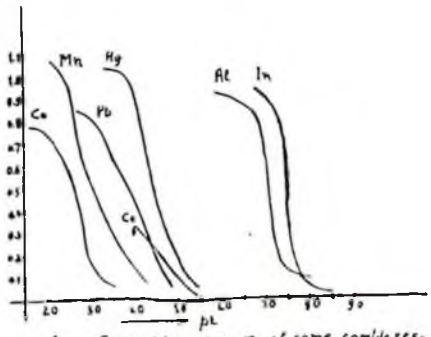


Fig 1 Formation curves of some complexes.

A graph of $\bar{n}$ vs pL was plotted and the formation curve thus obtained, extended from zero to one in each case (fig. 1), as only 1 : 1 complex is formed except Ce(III) where due to early precipitation, it extended only upto 0.34 and hence stability constant of Ce(III) is not reported.

The stability constants (table - 1) were obtained from the formation curves by the interpolation at half $\bar{n}$ values[6], and the decrease in free energy for the complexation reaction, ΔG, as reported in table-1 was calculated by :

$$\Delta G = -2.303\ R\Gamma \log \beta \qquad (4)$$

Experimental results show that the non-transition metals like Al(III) and In(III) form far more stable complexes than the transition metals. This might be due to the ionic character of the ligand[5]. As in the presence of the metal ion, two protons dissociate leaving two units of negative charge on the ligand, a metal - ligand ionic bond may be expected as verified by Rustagi and Rao[5]. Now, in the case of Al and In, after two valencies are satisfied by the ligand, one positive charge is still left which causes strong co-ordinate bonds with the remaining -OH and the tertiary amine.

The fact that $\log \beta_{In} > \log \beta_{Al}$ also suggests the ionic character of the ligand as the first ionization energy for In is less than that of Al. These metals show the same trend with other similar ligands[7].

The stability of the transition metal complexes are in the expected order. The d electrons of Ag(I) are involved in back-bonding with the π orbitals of $\begin{matrix} | \\ C = N - \\ | \end{matrix}$. This accounts for the higher stability of Ag-ST than other transition metals even though Ag is monovalent.

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REFERENCES

1. M. S. Patel, T. Trivedi & D. N. Vyas, J. Indian Chem. Soc. (In press).
2. M. S. Patel, T. Trivedi & D. N. Vyas, J. Electrochem. Soc. of India, 25-4 (1975) 159.
3. M. S. Patel, T. Trivedi & D. N. Vyas, Indian J. Chem. (In press).
4. H. Irving & H. S. Rossotti, J. Chem. Soc. 8 (1954) 2904.
5. S. C. Rustagi & G. N. Rao, Indian J. Chem., 13 (1975) 702.
6. H. Irving & H. S. Rossotti. J. Chem. Soc , 10 (1953) 3397.
7. M. S. Patel, T. Trivedi & D. N. Vyas (Private communication).