

Polarographic Study of Complexation of Bi³⁺ with Schiff Bases in Acetate Buffer

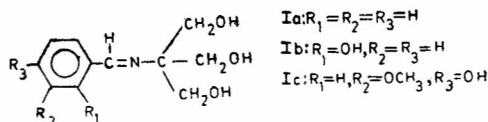
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Received 2 December 1976; accepted 24 June 1977

The complexation reaction of Bi³⁺ with three Schiff bases derived from benzaldehyde, salicylaldehyde and vanillin and tris buffer has been investigated polarographically in acetate buffer at three different temperatures. The quasi-reversible reduction wave in each case has been given three different treatments due to (i) Matsuda and Ayabe, (ii) Gellings and (iii) Koryta to calculate overall electrode reaction rate constant. The stability constants of the complexes and thermodynamic functions have also been determined.

POLAROGRAPHIC investigations on the complexation of Bi(III) with Schiff bases have not been carried out so far, though a few reports on the complexes of Bi(III) and Sb(III) are available¹⁻³. A detailed polarographic study of Bi(III) complexes with three Schiff bases such as benzaldehyde tris buffer (Ia), salicylaldehyde tris buffer⁴ (Ib) and vanillin tris buffer⁵ (Ic) has been carried out. In view of the quasi-irreversible nature of the reduction wave, the overall electrode reaction rate constants have been calculated employing (i) Matsuda and Ayabe, (ii) Gellings and (iii) Koryta treatments.



Materials and Methods

Salicylaldehyde and vanillin tris buffers were prepared by the literature method⁴, m.p.s. 134° and 158° respectively. Benzaldehyde tris buffer was prepared employing standard method⁵ for Schiff bases, m.p. 92°.

A stock solution of Bi(III) was prepared by dissolving bismuth trichloride (AR) in gl. acetic acid and then titrated against standard triplex III (C₁₀H₁₄N₂Na₂O₈·2H₂O) solution. The final solution contained 0.422 mM Bi(III) in 1.0M acetate buffer of pH 4.76, with 0.002% gelatin as the maximum suppressor. The ligands were also dissolved in 1.0M acetate buffer except BT which was first dissolved in gl. acetic acid and then diluted with acetate buffer. Its complexation was studied in 4.0M acetate buffer of pH 4.2.

Polarograms of the deaerated solution were recorded manually at the desired temperature (± 0.1°) using a Toshniwal polarograph type CLO2A and Beltronix microammeter. The capillary used had the characteristic: $m^{2/3} t^{1/6} = 2.2 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ in 1.0M acetate buffer of pH 4.76 at zero applied volt-

age. The average current was measured in each case against SCE.

Results and Discussion

A single well-defined reduction wave was obtained in each case. The plots of i_d vs $h_{\text{corr}}^{1/2}$ were linear. The temperature coefficients of the limiting current were in the range 1.1 to 1.6%/°C. These observations suggest the diffusion-controlled nature of the current.

Negative shifts of $E'_{1/2}$ on increasing [ligand] indicate complexation. The plots of $\log \bar{i}/i_d - \bar{i}$ vs E are curved near abscissa. The values of $k_e^* \sqrt{t}$ (between 10⁻² and 30) and of standard electrode reaction rate constant (between 2 × 10⁻² and 5 × 10⁻⁵ cm sec⁻¹) show the quasi-reversible nature of the reduction^{6,7}.

In order to calculate the overall standard reaction rate constants (k_e^0)_B for reaction (1)



Three different methods were used. The values of (k_e^0)_B thus obtained are listed in Table 1.

*Matsuda and Ayabe treatment*⁶ — The overall standard reaction rate constant (k_e^0)_B was determined using Eq. (2)

$$\log (k_e^0)_B = \log k_e^* + \frac{1}{2} \log (D')^z + \frac{1}{2} \log (D_{MX})^{\beta} + \log C_X^{\beta(n-p)} \quad \dots(2)$$

All the terms in the equation were determined as per the description given in the literature⁶. D' and D_{MX} are diffusion coefficients of the metal ion and complex species respectively determined from Ilkovic equation.

The plot of $E'_{1/2}$ vs $\log C_X$ was linear in each case and the value of n was determined as 1 using relation (3)

$$n = \frac{ZF}{2.3RT} \cdot \left(\frac{\Delta(-E'_{1/2})}{\Delta \log C_X} \right) \quad \dots(3)$$

The above fact suggests that a 1:1 complex prevails in the bulk of the solution. The ligand

number p of the complex actually reduced at the electrode was found from relation (4).

$$p = (1-\alpha)n + \frac{\Delta \log k_e^*}{\Delta \log C_X} \quad \dots(4)$$

In the present case $p = 0$ which shows that metal ion itself is reduced after dissociating from the complex at the electrode.

The standard electrode reaction rate constant was calculated from Eq. (5) (ref. 6)

$$(k_e^*)_B = k_e^* \cdot \left(\prod_{\mu=p+1}^N K_\mu \right)^\beta \quad \dots(5)$$

where $\beta =$ backward transfer coefficient and $K_\mu =$ dissociation constant, with $\mu = N, N-1, \dots, p+1$. The complex actually reduced at the electrode is assumed as MX_p^{Z+} .

*Gellings treatment*⁸ — Though this treatment is valid to calculate k_e^* for a metal ion in non-complexing media, this was modified according to the arguments given by Meites⁹: The modification was achieved by simply introducing the ligand concentration term to the equation developed for the reduction of simple metal ion.

Eq. (6) given by Gellings

$$\log k_e^* = \log \Lambda + \frac{1}{2} \log D'^\alpha + \frac{1}{2} \log D_{MX}^\beta \quad \dots(6)$$

was modified to get Eq. (7)

$$\log (k_e^*)_B = \log \Lambda + \frac{1}{2} \log D'^\alpha + \frac{1}{2} \log D_{MX}^\beta + \log C_X^{\beta(n-p)} \quad \dots(7)$$

In the present case $p = 0$, and to evaluate Λ , the value of $E_{\frac{1}{2}}^*$ was obtained from the intercept on the ordinate of the plot

$$-\left[E + \frac{2.3RT}{nF} \cdot \log \frac{i}{i_d - i} \right] \text{ vs } i/i_d \text{ (ref. 10, 11)}$$

*Koryta treatment*¹² — This was also modified similar to the Gellings treatment. $(k_e^*)_B$ was evaluated using Eq. (8)

$$(k_e^*)_B = \frac{i'}{i_d - 2i'} \cdot \frac{\sqrt{D'^\alpha D_{MX}}}{0.886t^{\frac{1}{2}}} C_X^{\beta n} \quad \dots(8)$$

where i' is the current when $E = E_{\frac{1}{2}}^*$. The value of $E_{\frac{1}{2}}^*$ is obtained by drawing an asymptote of the log plot from the region $E \rightarrow +\infty$. The potential at which this asymptote cuts the abscissa is $E_{\frac{1}{2}}^*$.

Stability constants of complexes — The stability constant ($\log K$) of each complex was determined using the method given by Lingane¹³, taking series of ligand concentrations. The values are given in Table 2.

The structures of the ligands suggest that the stability of Bi-ST should be greater than the other two complexes as ST (Ib) has -OH group in the ring at *ortho* position which may form an additional coordinate bond with the central metal ion. Such possibility is not seen with other ligands. The experimental results obtained are quite in agreement with this fact. The stabilities are in the order: Bi-ST > Bi-VT \approx Bi-BT.

For all the three complexes, the reduction of the complex is slower than that of the metal ion. The

reduction rate increases with temperature (Table 1). Thermodynamic functions of electrode reaction (Table 3) support this fact. Higher the stability of the complex, lower is the reduction rate. As free energy change is positive it can be predicted that the reaction is not spontaneous and requires activation energy.

The complexation is less favoured at higher temperatures as the stability constants decrease with rise in temperature. Negative free energy change also decreases with the increase in temperature. The values of ΔS are nearly constant and negative, as must be the case with neutral ligands¹⁴.

Comparison of the three treatments — The values of $(k_e^*)_B$ obtained with the three different treatments are in good agreement, though the values obtained by Koryta treatment show slight variations. This

TABLE 1 — POLAROGRAPHIC BEHAVIOUR OF Bi(III) SCHIFF BASE COMPLEXES

[Ligand] M	Temp. (°C)	$-E_{\frac{1}{2}}^*$ (vs SCE)	$(k_e^*)_B \times 10^5$		
			Gellings	Koryta	Matsuda
Bi-BT					
0.00	34	0.193	39.0	58.0	56.0
	42	0.188	47.0	60.0	58.0
	50	0.186	54.0	62.0	60.0
0.025	34	0.209	3.3	3.6	3.4
	42	0.202	4.4	4.8	4.1
	50	0.200	6.2	6.6	6.3
0.035	34	0.213	4.5	5.7	4.5
	42	0.206	5.9	6.9	5.9
	50	0.204	7.5	8.3	7.3
0.050	34	0.218	5.5	5.9	5.6
	42	0.210	7.0	7.5	7.0
	50	0.208	8.6	8.9	8.7
Bi-ST					
0.00	34	0.158	59.0	59.0	62.0
	42	0.157	74.0	71.0	74.0
	50	0.156	99.0	97.0	93.0
0.029	34	0.211	2.2	1.9	2.3
	42	0.197	2.8	3.1	2.9
	50	0.184	5.0	5.6	5.3
0.040	34	0.216	0.8	0.7	0.9
	42	0.200	1.3	1.3	1.6
	50	0.190	2.6	2.4	2.9
0.045	34	0.218	0.3	0.3	0.4
	42	0.201	0.7	0.7	1.0
	50	0.191	1.8	1.7	1.9
Bi-VT					
0.024	34	0.178	1.1	0.9	1.3
	42	0.170	1.9	1.9	2.1
	50	0.166	3.1	2.5	3.1
0.045	34	0.184	1.1	0.7	0.6
	42	0.174	1.6	1.6	1.7
	50	0.170	2.7	2.0	3.0
0.060	34	0.192	1.1	1.1	1.5
	42	0.180	1.9	2.3	1.8
	50	0.174	2.7	2.7	3.7

TABLE 2 — STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS

Temp. (°C)	log K	ΔG kcal mole ⁻¹	ΔH kcal mole ⁻¹	ΔS e.u.
Bi-BT				
34	2.34	-3.32		
42	2.22	-3.23	-5.034	-5.62
50	2.15	-3.20		
Bi-ST				
34	4.2	-5.96		
42	3.5	-5.10	-37.5	-102.8
50	2.9	-4.33		
Bi-VT				
34	2.53	-3.51		
42	2.20	-3.17	-13.5	-32.6
50	2.05	-2.96		

TABLE 3 — THERMODYNAMIC FUNCTIONS OF ELECTRODE REACTION FOR Bi-VT

[Ligand] M	Temp. (°C)	ΔG kcal mole ⁻¹	ΔH kcal mole ⁻¹
0.00	34	+5.024	
	42	+5.016	+5.492
	50	+5.008	
0.045	34	+5.17	
	42	+5.13	+7.09
	50	+5.08	

may be due to the fact that the equation employed in Koryta treatment utilizes the value of $\bar{i}'/\bar{i}'_d - 2\bar{i}'$ which has less accuracy compared to the former methods.

In order to evaluate log Λ in Gellings treatment $E'_\frac{1}{2}$ was obtained by extrapolation method^{10,11}, while in Matsuda treatment $E'_\frac{1}{2}$ was obtained by calculation and hence it seems to be more accurate.

Acknowledgement

The authors thank Prof. K. A. Thaker for laboratory facilities, and the CSIR, New Delhi, for the award of junior research fellowships to two of them (M.S.P. and T.T.).

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