Asian Journal of Chemistry Vol. 4, No. 1 (1992), 15-21

Polarographic Study of Cd(II) and Zn(II) Complexation with Solochrome Mordant Dyes

P. N. GUPTA* AND ANJU RAINA

Department of Chemistry, University of Kashmir
Srinagar-190 006, India

Present communication reports complexation behaviour of solochrome yellow 2GS, solochrome black WDFA, solochrome fast navy 2RS and solochrome dark blue B150 with Cd(II) and Zn(II) studied polarographically at temperatures 25°, 35° and 45°. Thermodynamic functions have been calculated to intepret results. Aggregation is overruled by the presence of tetramethyl ammonium perchlorate; monomeric form of dye established, subsequently the equilibrium between metal-ligand is made reliable and reproducible.

INTRODUCTION

Solochrome mordant dyes (mostly azo type) form an important class of compounds due to their various analytical applications[1] and formation of highly stable complexes[2]. Sillen and Martell[3] in a review on metal complexes emphasized the need for determination of stability constants of commercial dyes for better practicability. This communication reports polarographically determined successive stability constants of Cd(II) and Zn(II) with four commercially important dyes[4] *viz.*, solochrome yellow 2GS (SY 2GS), solochrome black WDFA (SB WDFA), solochrome fast navy 2RS (SFN 2RS) and solochrome dark blue B150 (SDB B150). Thermodynamic parameters evaluated by variation in temperature, favour complex formation. Percentage distribution of complex species present in the solution as a function of ligand concentration have been presented.

EXPERIMENTAL

The dye samples, supplied by ICI, India, were purified by repeated recrystallization from 50% ethanol. The resulting products were desiccated over silica gel and tested for purity by chromatography and elemental analysis. All other chemicals used were BDH AnalaR product while tetramethyl ammonium perchlorate (TMAP) a sigma product was used as such. AC/DC universal polarograph OH-105 (Radelkis) was used for recording C-V curves. DME had capillary characteristics $m^{2/3}t^{1/6} = 2.109$ mg$^{2/3}$ s$^{-1/2}$ in 0.1M $NaClO_4$ in open circuit at h = 42 cm. All potentials refer to SCE. Measurements were made at constant temperatures 25° ± 0.1, 35° ± 0.1 and 45° ± 0.1 by making use of ultrathermostat (NBE). pH-meter PR 9405 was connected in series with polarising circuit in order to note pH.

Solutions containing 1×10^{-5} M of metal ions with varying concentration of ligand(s) were placed in cell and subjected to polarographic study. Ionic strength ($\mu = 1.5$M) was maintained by adding $NaClO_4$ and Triton X-100 (0.005%) served as maximum suppressor. pH of solution was adjusted at 6.0 ± 0.1 by adding $HClO_4$ or NaOH when required. Cell solutions were deoxygenated by bubbling pre-purified nitrogen prior to recording polarograms.

RESULTS AND DISCUSSION

Role of tetramethyl ammonium chloride and bromide[5] has been established to reverse the process of aggregation[6] with certain azo dyes. Contribution of 0.7M tetramethyl ammonium perchlorate (TMAP), instead of suggested ones, was to maintain monomeric form of dye which was tested from diffusion coefficient data; for instance, SY 2GS ($10^{-5} - 10^{-6}$M) in Britton-Robinson buffer resulted in $\overline{D} = 11.78 \times 10^{-6}$ cm² s⁻¹ while a value close to dimer (calculated from decrease in current) at a dye concentration of 5×10^{-4} M was noticed. Addition of TMAP enhanced $\bar{D}$ which agreed well with monomeric value.

Single well defined waves were observed for both metal ions. Diffusion controlled reduction behaviour was established from direct proportionality of i_l vs. C, i_l vs. $\sqrt{h}$ and low temperature coefficient. The log plots predicted polarographic reversibility in all cases. In order to maintain accuracy, graphically obtained i_d and $E_{1/2}$ values were subjected to simultaneous refinement by applying least-squares based computer programme described in earlier papers[7,8]. Invariable negative shift in $E_{1/2}$ and decrease in i_d with addition of ligand provided ample evidence in favour of complex formation, plots of $E_{1/2}$ vs. log C_x being curves, suggested presence of more than one complex in solution. DeFord and Hume method[9] of successive equilibria was employed to evaluate overall stability constants of successively formed complexes. F(X) functions for various metal-ligand systems were evaluated and plots of F(X) vs. ligand concentration resulted in β values. Fig. 1 depicts one such plot as a representative case. Analysis of $F_n(X)$ vs. C_x showed formation of three complexes in case of Zn(II) whereas Cd(II) revealed variation in this regard.

Thermodynamic functions have been calculated from the following relations :

$$\Delta G = -2.303RT \log \beta_n \tag{1}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{2}$$

$$\Delta H = (4.576\, T_1 T_2 \Delta \log \beta_n)/(T_2 - T_1) \tag{3}$$

ΔH was determined from the slope of plot between log β_n and 1/T. SY 2GS-metal system presented in Table 1 at temperatures 25°, 35° and 45° reveals increase in $-\Delta G$ with increasing number of ligands. ΔH remains constant while ΔS is constant for specific β *e.g.*, β_1 or β_2 but increases with coordination of more ligand molecules. Usually such trend[10] is employed for establishing complex formation with temperature. Table 1 infers that ΔS varies on an average between -1.85 and $+1.23$ for SY 2GS with Zn(II),

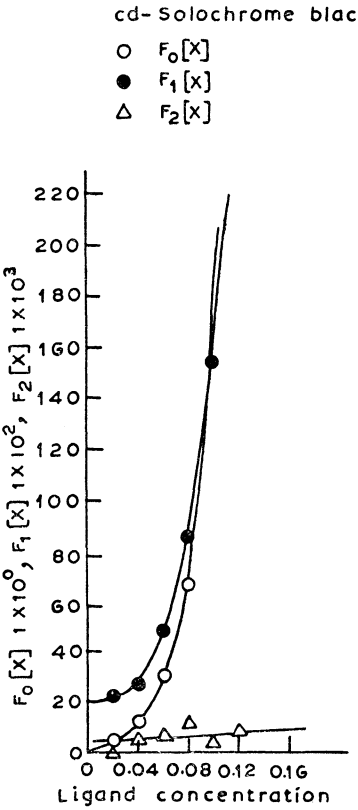

Fig. 1 The functions, $F_0[X]$, $F_1[X]$ and $F_2[X]$ plotted as functions of free ligand concentration for the Cd—SB WDFA system

while the range is from -1.71 to -0.75 for Cd(II). SFN 2RS gave two complexes with Cd(II); ΔS value ranging from $\log \beta_1$, -3.24 to $\log \beta_2$, -1.19 while Zn(II) yielded ΔS between -1.11 to $+2.23$ Cal K^{-1} mol^{-1}. SB WDFA gave reasonable ΔS variation, -1.39 to $+1.11$ and -2.08 to $+1.56$ for Cd(II) and Zn(II) respectively. A similar behaviour was observed for complexes of SDB B150.

Percentage composition of different metal ions present in various forms as a function of logarithm of ligand concentration in different systems were calculated by utilizing familiar equations.

$$M/C_M = 1/F_o(X) \tag{4}$$

$$MX_n/C_M = \beta_n(X)^n/F_o(X) \tag{5}$$

TABLE 1

THERMODYNAMIC FUNCTIONS OF METAL-SOLOCHROME MORDANT DYE SYSTEMS

T (°C)	n	$-\log \beta_n$	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$	ΔS (cal K^{-1} mol^{-1})	$-\log \beta_n$	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$	ΔS (cal K^{-1} mol^{-1})
		Cd(II)—SY 2GS				Zn(II)—SY 2GS			
25	1	2.09	2.850	3.36	−1.71	2.0	2.723	3.28	−1.87
35	1	2.01	2.833	3.36	−1.71	1.93	2.720	3.28	−1.82
45	1	1.94	2.823	3.36	−1.69	1.85	2.692	3.28	−1.85
25	2	2.32	3.163	3.60	−1.47	2.90	3.954	4.40	−1.50
35	2	2.24	3.157	3.60	−1.44	2.79	3.932	4.40	−1.51
45	2	2.16	3.143	3.60	−1.44	2.70	3.928	4.40	−1.48
25	3	3.08	4.200	4.55	−1.17	4.30	5.864	5.50	+1.22
35	3	2.99	4.214	4.55	−1.10	4.17	5.877	5.50	+1.23
45	3	2.88	4.191	4.55	−1.13	4.05	5.893	5.50	+1.24
25	4	3.26	4.445	4.67	−0.76				
35	4	3.15	4.439	4.67	−0.75				
45	4	3.05	4.438	4.67	−0.73				
		Cd(II)—SB WDFA				Zn(II)—SB WDFA			
25	1	2.34	3.191	3.61	−1·41	1.85	2.523	3.15	−2.10
35	1	2.26	3.185	3.61	−1.38	1.78	2.509	3.15	−2.08
45	1	2.18	3.172	3.61	−1.38	1.71	2.488	3.15	−2.08
25	2	3.60	4.909	4.58	+1.10	3.15	4.295	3.96	+1.12
35	2	3.50	4.924	4.58	+1.12	3.06	4.312	3.96	+1.14
45	2	3.39	4.933	4.58	+1.11	2.97	4.322	3.96	+1.14
25	3					3.30	4.500	4.04	+1.54
35	3					3.21	4.524	4.04	+1.57
45	3					3.11	4.540	4.04	+1.57

TABLE 1 (Contd.)

		Cd(II)—SFN 2RS				**Zn(II)—SFN 2RS**			
25	1	1.08	1.473	2.44	−3.24	3.18	4.336	4.67	−1.12
35	1	1.02	1.438	2.44	−3.25	3.07	4.327	4.67	−1.11
45	1	0.97	1.411	2.44	−3.23	2.97	4.322	4.67	−1.09
25	2	2.60	3.545	3.90	−1.19	3.48	4.745	4.21	+1.80
35	2	2.50	3.523	3.90	−1.20	3.38	4.764	4.21	+1.80
45	2	2.42	3.522	3.90	−1.18	3.29	4.787	4.21	+1.81
25	3					5.0	6.818	6.16	+2.21
35	3					4.86	6.849	6.16	+2.24
45	3					4.72	6.868	6.16	+2.23
		Cd(II)—SDB B150				**Zn(II)—SDB B150**			
25	1	2.40	3.272	3.70	−1·44	3.30	4.50	4.58	−0.26
35	1	2.32	3.270	3.70	−1.40	3.19	4.496	4.58	−2.27
45	1	2.23	3.245	3.70	−1.43	3.09	4.496	4.58	−0.26
25	2	4.40	6.00	5.45	+1.85	4.17	5.686	5.20	+1.63
35	2	4.27	6.018	5.45	+1.84	4.05	5.708	5.20	+1.64
45	2	4.15	6.038	5.45	+1.85	3.93	5.718	5.20	+1.63
25	3					5.60	7.636	6.75	+2.97
35	3					5.44	7.667	6.75	+2.97
45	3					5.29	7.697	6.75	+2.98

The applicability of the above equations has been demonstrated for Zn(II) with four ligand systems vide Fig. 2. The results obtained indicate that for these systems, calculated n value using a set of stability constant related satisfactorily according to equation (5) with n calculated from β_n for the given metal-ligand system.

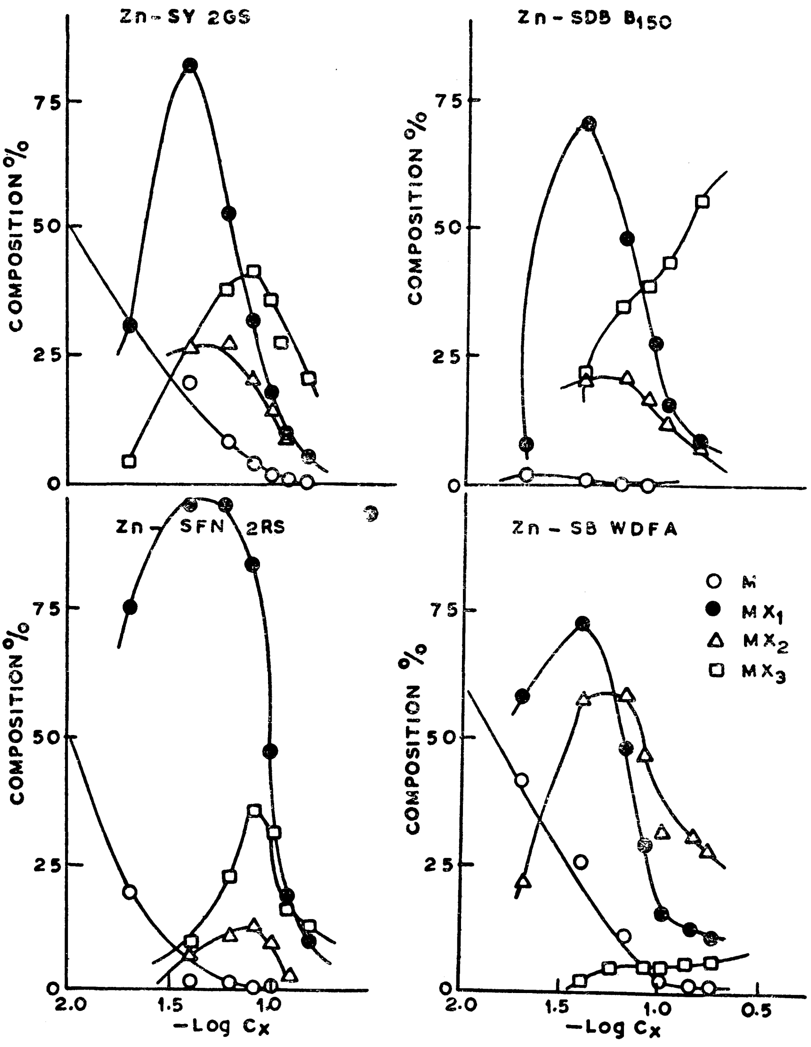

Fig. 2 Distribution of complex species in the Zn-Azo dye systems

Electron donating centre in these ligands being –N=N– group, the range of stability constant for electronically equivalent transition metal ions were anticipated to be the same. The diversity observed in stability constant values, however, is due to substituents present in dye molecules. The substituents alter electron density at $-N=N-$ position and hence bring about differences in coordinating ability. A similar behaviour was noticed in case of diazaphenanthrene[11], ephedrine and ψ-ephedrine[12] complexes. The ligands were retained in molecular form ($pK_1 = 6.23$–6.50 and $pK_2 = 11.13$–11.94)[13] by adjusting pH close to 6.

The equilibrium quotient expressions are described as follows:

$$M^{m+} + X \rightleftharpoons MX^{m+};\ \beta_1 = K = \frac{(MX^{m+})}{(M^{m+})(X)}$$

$$M^{m+} + 2X \rightleftharpoons MX_2^{m+};\ \beta_2 = K_1K_2 = \frac{(M(X)_2^{m+})}{(M^{m+})(X)^2}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$M^{m+} + nX \rightleftharpoons MX_n^{m+};\ \beta_n = K_1K_2 \cdots K_n = \frac{(M(X)_n^{m+})}{(M^{m+})(X)^n}$$

ACKNOWLEDGEMENTS

One of the authors (A.R.) is thankful to CSIR, New Delhi for Research Associateship.

REFERENCES

1. K. Venkataraman, The Analytical Chemstry of Synthetic Dyes, John Wiley, New York (1977).
2. S. Patai, The Chemistry of the Hydrazo, Azo and Azoxy Groups, Wiley Interscience, New York (1975).
3. L. G. Sillen and A. E. Martell, Stability Constants of Metal Ion complexes, Special Publication No. 17, Chemical Society, London (1970).
4. W. U. Malik and P. N. Gupta, *J. Electroanal. Chem. Interfac. Electrochem.*, **54,** 417 (1974).
5. G. Barone, L. Constantino and V. Vitagliano, *Ric. Sci.*, **A6,** 87 (1964); *Chem. Abstr.*, **62,** 14859f (1965).
6. W. U. Malik and P. N. Gupta, *J. Electroanal. Chem. Interfac. Electrochem.*, **62,** 441 (1975); *Indian J. Chem.*, **15A,** 273 (1977); *J. Electrochem. Soc. India*, **28,** 17 (1979).
7. P. N. Gupta and A. Raina, *J. Electrochem. Soc., India*, **33,** 365 (1984).
8. W. U. Malik, P. N. Gupta and A. Raina, *J. Indian Chem. Soc.*, **63,** 808 (1986).
9. D. D. De Ford and D. N. Hume, *J. Am. Chem. Soc.*, **73,** 4321 (1951).
10. M. H. Mihailov, V. Ts. Mihailova and V. A. Khalkin, *J. Inorg. Nucl. Chem.*, **36,** 145 (1974).
11. P. N. Gupta and A. Raina, *J. Electrochem. Soc., India*, **37,** 263 (1988).
12. ——, *Ann. Chim.*, **78,** 317 (1988).
13. P. N. Gupta and S. A. Bhat, *J. Electrochem. Soc. India*, **29,** 161 (1980).

[*Received* : 16 August 1989; *Accepted* : 25 August 1990) AJC—221