POLAROGRAPHIC STUDY OF *Cd*-SCHIFF BASE COMPLEX

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Polarographic behaviour of Cd^{2+} with a schiff base salicylaldehyde trisbuffer has been studied in DMF water media of three different compositions (*viz.*, 0 %, 30% and 50% v/v of DMF). Stability constant, free energy change $\triangle G$, enthalpy change $\triangle H$ and entropy change $\triangle S$ of the systems are calculated for all the three media at three different temperatures (*viz.*, 30°, 40° and 50°C.). A relation of halfwave potential of the system with the dielectric constant of the medium has also been verified.

Schiff base complexes have recently been studied[1–4]. New schiff bases have also been prepared by several workers[5]; however, literature on polarographic study of schiff base complexes is limited[6]. Present study deals with the polarographic behaviour of the *Cd* salicylaldehyde trisbuffer complex in DMF water media. Three different compositions of the solvents are used viz. 0%, 30% and 50% (v/v) of DMF.

EXPERIMENTAL

All the chemicals used were of A.R. grade. Final concentration of Cd^{2+} was 0·2*m*M in 0·1 M KNO_3 containing 0·01% gelatin. Preparation and characteristics of the ligand salicylaldehyde trisbuffer (ST) are reported elsewhere[3]. Ligand concentration used in the study was varied from 0·005M to 0·125M. The complexation study at all the concentrations was made at the original *p*H of the metal ligand system i.e. *p*H 8·5±0·1 as nature of the ligand is affected by the *p*H[7]. Polarograms of the metalions were recorded at *p*H 7·5 as the ions precipitate above this *p*H.

Complexation behaviour was marked from polarograms obtained on a recording polarograph type CL 25. Final polarograms were recorded manually[8] on a Toshniwal polarograph type CLO 2A with Beltronix microammeter. Oxygen free nitrogen gas was bubbled through the system to remove oxygen in each case. The definite temperature of the system was attained in a Toshniwal temperature bath type GL 15 within an accuracy of ±0·1°C. The half wave potentials in volts *vs.* SCE (Table 1) are corrected for the IR drop for each medium used, and the current measured was also corrected for the residual current. The resistance of the system (50% DMF) was 0·850 K Ω

In all three solvent compositions, Capillary characteristics $m^{2/3}\,t^{1/6} = 2.3$ $mg^{2/3}$ $sec^{-\frac{1}{2}}$ at 0 volt in 0·1M KNO_3

RESULTS AND DISCUSSION

A single, well defined reduction wave was obtained in each case. Temperature coefficient of the limiting current lies between 1·1% to 1·3%/°C. Plot of i_d vs $\sqrt{h_{corr}}$ is a straight line. These facts indicate that the limiting current is diffusion controlled. The value of n was approximated at 30°C as two, using relation $I/1\cdot6=n$*. The plot of E vs. log $\bar{i}/(i_d-\bar{i})$ is a linear with a slope of 35± 2 mv. This value of the slope suggests 2 electron reversible reduction.

With increasing ligand concentration, there is negative shift in the half wave potential (Table 1), which clearly indicates complexation behaviour. Further, limiting current also decreases with the complexation.

The plot of $E_{\frac{1}{2}}$ vs. log C_x is linear showing thereby only one complex species present in the system. From the slope of the linear plot, ligand number p was found out using (1).

$$-\frac{d\,(E_{\frac{1}{2}})_c}{d\,\log C_x} = p\cdot\frac{2.3\,RT}{nF} \qquad (1)$$

p comes out to be 1 in all the three compositions of solvents i.e. aqueous, 30% DMF—water and 50% DMF—water media. It clearly suggests that only 1:1 complex prevails in the bulk of the solution. This observation is quite plausible because the ligand ST is pentadentate[5] and the main co-ordination number of the metal is four.

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*Where I is the diffusion current constant.

The method of Lingane[9] was used to calculate the stability constants of the complex present in all the three systems studied. The expression used was

$$\frac{0.4343\ nF}{RT}\ \triangle E_{\frac{1}{2}} = -\log K - p \log C_s \tag{2}$$

where

$\triangle E_{\frac{1}{2}}$ is the difference of half wave potential between free metal ion and the complex.

TABLE 1

POLAROGRAHPIC BEHAVIOUR OF THE *Cd– ST* COMPLEXIN DMF WATER MIXTURES OF DIFFERENT COMPOSITIONS

Ligand conc. (M)	Temperature (°C)	$-E_{\frac{1}{2}}$ of the system in volts *vs* SCE			Diffusion current constant *I*		
		water	30% DMF	50%DMF	water	30%DMF	50%DMF
0·000	30	0·571	0·571	0·574	3·64	2·75	2·50
	40	0·568	0·568	0·571	4·16	3·05	2·94
	50	0·564	0·565	0·568	4·48	3·34	3·20
0·005	30	0·571	0·575	0·580	3·61	2·65	2·30
	40	0·568	0·568	0·576	4·00	2·89	2·81
	50	0·565	0·565	0·568	4·35	3·45	3·07
0·010	30	0·577	0·586	0·594	3·61	2·56	2·30
	40	0·571	0·579	0·584	3·96	2·81	2·82
	50	0·565	0·572	0·577	4·41	3·04	3·09
0·020	30	0·586	0·594	0·602	3·52	2·44	2·43
	40	0·580	0·589	0·594	3·90	2·70	2·69
	50	0·573	0·582	0·586	4·38	3·10	2·94
0·040	30	0·596	0·606	0·614	3·36	2·38	2·57
	40	0·592	0·602	0·608	3·74	2·62	2·56
	50	0·584	0·596	0·602	4·25	3·04	2·94
0·080	30	0·606	0·618	0·625	3·16	2·37	2·30
	40	0·603	0·615	0·617	3·64	2·56	2·56
	50	0·592	0·608	0·611	4·12	3·00	3·07

Effect of Temperature

Half wave potentials of the systems are shifted to more positive values with increase in temperature. The stability constant of the complex decreases with temperature (Tables 2–4). These results suggest dissociation of the complex at higher temperatures.

Free energy change, enthalpy change and entropy change were calculated using equns., (3), (4) and (5) respectively.

$$\triangle G = -\ 2.3\ RT \log K \tag{3}$$

$$\triangle H = 2.303\ R \left(\frac{d \log K}{d\ \frac{1}{T}} \right) \tag{4}$$

$$\triangle S = \frac{\triangle H - \triangle G}{T} \tag{5}$$

$\triangle H$ was found out from the slope of the linear plot of log K *vs* $1/T$.

TABLE 2

THERMODYNAMIC PARAMETERS OF *Cd-ST* COMPLEX IN AQUEOUS MEDIUM

Temperature (°C)	log K	$\triangle G$ (kcal/mole)	$\triangle H$ (kcal/mole)	$\triangle S$ (cal/mole/°C)
30	2·18	—3·06	—4·6	—5·1
40	2·08	—2·99		
50	1·98	—2·94		

TABLE 3

THERMODYNAMIC PARAMETERS OF *Cd-ST* COMPLEX IN 30% DMF WATER MEDIUM

Temperature (°C)	log K	$\triangle G$ (kcal/mole)	$\triangle H$ (kcal/mole)	$\triangle S$ (cal/mole/°C)
30	2·44	– 3·43	– 6·01	– 8·45
40	2·34	– 3·35		
50	2·22	– 3·28		

TABLE 4

THERMODYNAMIC PARAMETERS OF *Cd-ST* COMPLEX IN 50% DMF WATER MEDIUM

Temperature (°C)	log K	$\triangle G$ (kcal/mole)	$\triangle H$ (kcal/mole)	$\triangle S$ (cal/mole/°C)
30	2·66	– 3·71	—7·07	—11·10
40	2·48	– 3·57		
50	2·35	– 3·49		

Enthalpy change $\triangle H$ is negative which shows the reaction is exothermic. Further, the free energy change $\triangle G$ increases with the increase in temperature. The results show that the reaction is difficult at higher temperature. $\triangle S$ values are negative which are indicative of fairly strong complexation (Tables 2–4). Further, more negative value of $\triangle S$ with the increase of DMF in the system again proves more stability of the complex with the increase in DMF percentage.

Effect of Solvent Composition on the Stability of the Complex

Stability of the complex increases with the increase in DMF. Almost linear relation is observed between stability constants and DMF percentage. The stability of any complex in particular solvent is strongly affected by the dielectric constant of the solvent and as found by Tur'yan *et. al*[10]., it is varying with the dielectric constant of the solvent. Since DMF has lower dielectric constant ($\epsilon = 36 \cdot 7$) than water, higher stability of the complex in mixed solvent is expected and the results agree with the expectation.

Interesting study was made by Nightingale and Holtzelaw[11] on effect of dielectric constants on half wave potential. Accordingly, the overall reaction of our system at *p*H 8·5 could be

$$(Cd\,X_2) + y\,Hg + 2H_2O \xrightarrow{+\,2e} Cd\,(Hg)\,y + 2HX + 2OH^-$$

if it is assumed that the chelate ions hydrolyse rapidly in aqueous solution. Further, the difference in free energy required for the reduction of a given complex in various compositions of solvents is supposed to arise from the free energy necessary to charge the ionic product, OH^-, in one solvent composition as compared to another.

The final equation for free energy is given as

$$\triangle G = \frac{N\,n^2\,e^2}{2\,r}\,\triangle\left(\frac{1}{\epsilon}\right) \text{ per mole} \tag{6}$$

where

$\triangle G$ is the Free energy change; n the charge of the ion; e the unit charge; ϵ the dielectric constant and r the radious of the ion.

Further, $\triangle E_{\frac{1}{2}} = \frac{\triangle G}{nF}$ is known.

Putting the values of the constants N and e and the values of n and r ($\approx 1{\cdot}76$ A°) of the OH^- ion, one gets

$$\triangle E_{\frac{1}{2}} = -4.09.\,\triangle\left(\frac{1}{\epsilon}\right) \text{ volt} \tag{7}$$

Plot of $E_{\frac{1}{2}}$ of the system at any of the ligand concentration studied *vs* inverse of dielectric constant $\left(\frac{1}{\epsilon}\right)$ was drawn for each temperature. It was a straight line with slope value nearly equal to 4·0, which is in very good agreement with (7). Here, calculations of the dielectric constants of the mixed solvent was made assuming additive nature of dielectric constant even in the solvent system studied.

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