POLAROGRAPHIC BEHAVIOUR OF Cu (II) IN PRESENCE OF CROTONATE IONS.

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The reduction of Cu (II) in presence of crotonate ion at dme has been found to be diffusion controlled. Although the plots of log $i/(i_d-i)$ vs $E_{d.e.}$ are linear, the slopes are very much higher than required for two-electron reversible reduction. The slopes increased with ligand concentration, thus indicating the increasing irreversibility of the electrode process. The kinetic parameters of the irreversible (K°_f and α) electrode process have been calculated.

The polarographic behaviour of copper complexes with dimethyl malonate and phenyl malonate[1] picolinate[2] and salicylate ions[3] and the electrode kinetics of Cu (II) in sulphate media[4] have been studied in our laboratories. The present paper deals with the polarographic investigation of Cu (II) in presence of crotonate ions.

Experimental

Stock solutions of Cu (II) and crotonate ions were prepared by dissolving weighed amounts of copper nitrate and sodium crotonate respectively. The ionic strength was kept constant at $\mu = 1.0$ by adding required amounts of $NaClO_4$. The pH was kept constant 6.5 ± 0.1. A manual polarograph was used to obtain the polarograms, The dropping mercury electrode had the characteristics : m 2.9 mg sec, and t 3.5 sec. (open circuit). All the measurements were carried out at $30 \pm 0.1°C$. The electrolysis was carried out in an H-type cell saturated with NaCl agar-agar plug.

Solutions containing 1.0mM Cu (II) with increasing concentrations of crotonate ion were prepared at $\mu = 1.0$ and polarographed after deaeration with purified nitrogen.

Results and Discussion

In each case a single well defined reduction wave was obtained. The plots of i_d vs $\sqrt{h}$ (h = effective height of mercury column) were linear and passed through the origin. The $E_{\frac{1}{2}}$ shifted to more negative values and the i_d decreased with ligand concentration, indicating complex formation. The plots of log $i/(i_d - i)$ vs $E_{d.e.}$ were linear but the slope was much higher than required for 2-electron reversible reduction. Moreover, the value of slope increased regularly with ligand concentration. These results show that although the electrode process is diffusion-controlled, the irreversibility of the electrode process increases with ligand concentration.

Kinetics of the electrode process have been studied by Koutecky's[5] method and its modifications[6—7].

The mathematical solution of the problem of diffusion to an expanding spherical surface is given in the form :

$$i_l/i_l = F(x) - \xi . H_c(x) = F'(x) \qquad ...(1)$$

For a Cathodic process

$$X = \left(\frac{12t}{7}\right)^{\frac{1}{2}} \frac{K_f}{\sqrt{D^2}} \qquad ... (2)$$

and $$\xi = 50.4\, D^{\frac{1}{2}} . t^{1/6} m^{-\frac{1}{3}} \qquad ...(3)$$

where i_l is the maximum limiting current along the polarogram, i_d is the maximum diffusion current, t is the drop time and D is the diffusion coefficient of the depolariser.

The rate constant K_f, for the forward reaction of a cathodic process varies with the electrode potential, E, according to the equation,

$$K_f = K^\circ_f \exp(-\alpha n FE/RT) \qquad ...(4)$$

where α is the transfer coefficient, n is the number of electrons involved in the rate-determining step and K°_f is the rate constant of the electron transfer reaction at zero volts. These equations have beed used in the analysis of Cu (II)-crotonate ion system at different ligand concentrations.

A plot of log K_f vs E is a straight line, with a slope α nF/2.303 RT. Extrapolation of the plot to zero volts gives the value of K°_f.

Meites and Israel[6] extended Koutecky's method for irreversible waves and gave a mathematical form in place of graphical representation and very recently, Gaur and Bhargava[7] have extended the Koutecky's treatment for irreversible waves.

The plot of $E_{\frac{1}{2}}$ vs-log C_X was found to be a straight line, which may be due to the formation of only one complex. The value of 'p' i.e. coordination number was determined by the equation

$$\frac{\Delta E_{1/2}}{\Delta \log C_X} = -p.\frac{0.06}{n} \text{ (at 30°C), which comes to 3.}$$

Due to the irreversibility of the electrode process the reversible half wave potentials are not known and thus the stability constants cannot be obtained by the usual methods.

The plots of -log K_f vs applied voltage are linear and are presented in Fig. 1. The values of $K°_f$ are obtained by extrapolation of this plot to zero volts.

The results are summarised in Table 1. It has been observed that as the concentration of the crotonate ion increases, the value of α decreases and that of $K°_f$ increases. Thus the electrode process becomes more and more irreversible with increasing ligand concentration. The values of $K°_f$ calculated by Gaur and Bhargavas method are more reliable in comparison to Koutecky's method, as it involves no graphical extrapolation. Furthermore these workers have considered diffusion to the electrode surface is spherical one as compared to Meites and Israel who assumed the diffusion to be a linear process.

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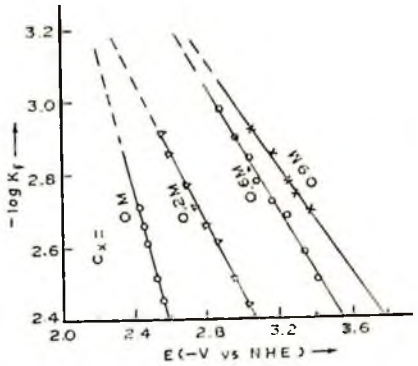


FIG 1 Plots of $-\log K_f$ vs E(-V vs N.H.E.) for Cu(II) - Crotonate system.

Table 1 Polarographic characteristics and Kinetic parameters of Cu (II)-crotonate system at 30°C

Cu (II) = 1.0 mM μ = 1.0

C_X, M	i_d, μA	$-E_{\frac{1}{2}}$	Slope	$D^{\frac{1}{2}} \times 10^3$	ξ	Koutecky's Method			Meites	Gaur
						$K°_f \times 16^6$	α		Israel $K°_f \times 10^5$	Bhargava $K°_f \times 10^5$ α
				(cm^2/sec)		(cm/sec).			(cm/sec)	
0.0	8.85	-0 000	49.5	3.0	0.126	0.01	0.56	0.002	0.003	0.57
0.1	8.66	0.012	76.0	2.9	0.122	1.32	0.36	0 13	0.21	0.37
0.2	8.02	0.034	84.0	2.7	0.114	3.02	0 31	0.41	0.68	0.33
0.3	7.72	0.046	89.5	2.6	0.109	1.44	0 33	0.78	1.28	0.34
0.4	7.72	0.055	93 5	2.6	0.109	3.45	0.27	1.20	1.99	0 30
0.5	7.65	0.0 2	103.5	2.6	0.109	5.25	0.25	2.18	3.61	0.27
0.6	7.05	0.068	107.5	2.3	0 097	4.17	0.25	2.54	4.17	0.26
0.7	6.75	0.073	114.0	2.2	0.092	2.63	0.26	3.32	5.42	0.25
0.8	6.75	0.077	116.0	2.2	0.092	6.61	0.22	3 77	6.16	0.24
0.9	6.67	0 081	116 5	2 2	0.092	7.08	0.22	4 18	6.83	0.24

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