TECHNICAL REPORT

KINETICS OF ELECTRODE PROCESS AND FORMATION CONSTANTS OF ZINC COMPLEXES

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The reduction of Zn (II) at d. m. e. in aqueous medium in the presence of N-β aminoethyl-ethanolamine (AEEA) at constant ionic strength at 30°C is found to be diffusion-controlled but the electrode process is quasi-reversible. Three complex species are found to be present. The Kinetic parameters have been determined by Gelling's method.

The first treatment of current-voltage curves by Heyrovsky and Ilkovic[1] assumed that the potential of the d. m. e. is given by the Nernst equation. The treatment was successful in analysing the various types of reversible waves, but could not be applied to the irreversible polarographic wave which involves the determination of the formal kinetic parameters of an electrochemical reaction, taking into account of the slow rates of mass transfer and charge transfer. Many workers[2–9] studied Zn(11) complexes from electrode kinetics point of view. This investigation deals with the determination of kinetic parameters, composition and stability constants of the complexes of Zn (ii) with A E E A.

EXPERIMENTAL

Reagent grade chemicals were used. The solution of Zn (ii) was prepared by weighing as zinc nitrate and standardised as usual; AEEA was used as complexing agent. The ionic strength was kept constant by adding requisite amount of potassium nitrate. Gelatin was used as maxima suppressor. A manual polarograph was used to record polarograms. The dropping mercury electrode had the following characteristics: m = 1.274 mg/sec; t = 4.12 sec. (open circuit). A 'H'-type cell saturated with potassium chloride agar-agar bridge was used. The temperature was kept at 30 ± 0.01°C. Purified nitrogen was used for deaeration.

RESULTS AND DISCUSSION

In each case a single, well-defined reduction wave appeared. The plots of i_d vs. $\sqrt{h}$ (h is effective height of mercury column) and i_d vs. C (C = zinc conc) were linear and passed through origin, thereby indicating that the reduction was diffusion-controlled. The plots of $\frac{i}{(i_d - i)}$ vs. E_{de} were also linear with values of slopes found to be of the order of mV which were higher than that needed for 2 electron reduction. As the reduction was not reversible, the observed half wave potential could not be used for calculation of stability constants. For this purpose, the reversible half wave potential, $E^r_{\frac{1}{2}}$ values were determined by Gelling's[10] method which involved plotting of $\left[\left(E + \frac{(RT)}{nF}\right) \log \frac{(i)}{i_d - i} \right]$ vs. i and extrapolation of the curves to zero current value gives $E^r_{\frac{1}{2}}$. The $E^r_{\frac{1}{2}}$ shifted towards more negative values and the diffusion current decreased with concentration of A E E A, indicating the formation of complexes between Zn (ii) and A E E A.

The plot of $E^r_{\frac{1}{2}}$ vs. $-\log C_x$ gave a smooth curve indicating the formation of two or more complex species which are in equilibrium. The Deford and Hume's method[11] for stepwise complex formation has been used for calculation of composition and stability constants of the complexes formed. The values of $F_j(X)$ functions together with polarograghic characteristics for Zn (ii)-(AEEA) system at 30°C are given in table-1. The results show the existence of three complex species viz. $[(Zn(AEEA))]^{2+}$, $[(Zn(AEEA)_2)]^{2+}$ and $[(Zn(AEEA)_3)]^{2+}$ having log $B_1 = 8.00$, log $B_2 = 11.30$ and log $B_3 = 14.61$ respectively at 30°C.

The relative distribution of Zn(ii) in various species at different ligand concentration has also been calculated.

The Kinetic parametars have been calculated as the reduction of Zn(ii) at d. m. e. is quasireversible by using Gellings method. The plot of log (Z-1) vs. $(E - E^r_{\frac{1}{2}})$ were linear where Z is defined as.

$$\log (Z-1) = \log \frac{1-13}{\sqrt{td}} - \frac{(1-\alpha)nF}{2.303\,RT} (E-E^{r}_{\frac{1}{2}})$$

$$Z = \text{antilog} \left[\left(\frac{nF}{2.303RT} \right) (E^{r}_{\frac{1}{2}} - E) - \log \frac{(i}{i_d - i} \right]$$

where R, T, n and F have their usual significance. From the slopes and intercept of these plots, the values of α were obtained. The standard rate constant K_s is given by the relation $K_s = \alpha x D^{\frac{1}{2}}$ where D is the diffusion coefficient which is determined form diffusion current data by Ilkovic equation. The values of K_s was found to be of order of 10^{-3} cm/sec. which shows that the reduction process is quasireversible.

TABLE No. I Analysis of F_j (X), Functions and Kinetic Parameters

Ligand Conc. Moles.	$E^{r}_{\frac{1}{2}}$	i_d (Div.)	Fo (X) X10³	Fl (X) X10⁷	F2 (X) X10⁹	F_3 (X) X10¹²	$D^{\frac{1}{2}}$ Cm.²/Sec	α	K_s X 10³ Cm./Sec.⁻¹
0.000	1.0040	92	—	—	—	—	5.2890	0.4382	4.4100
0.002	1.2030	91	5062	253	765	282	4.8497	0.8740	4.2387
0.003	1.2190	91	14820	493	1310	370	4.8403	0.9381	4.5407
0.004	1.2295	89	33930	848	1870	417	4.7432	0.9808	4.6521
0.005	1.2375	89	62700	1253	2306	421	4.7929	0.6632	3.1781
0.006	1.2440	89	103300	1721	2701	416	4-7432	0.6554	3.0869
0 007	1.2500	87	167600	2394	3277	439	4.6366	0.9808	4.5475
0.008	1.2540	87	227800	2897	3433	404	4.5823	0.9808	4.6322
0.010	1.2625	86	442100	4420	4320	412	4.5296	0.9269	4.1985

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