ON THE POLAROGRAPHY OF ZINC IN ETHYLENEDIAMINE MEDIUM

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Abstract

Polarography of zinc in ethylenediamine medium has been carried out. The equilibrium potentials have been determined by amalgam polarography. The standard rate constant for the electrode reaction and the stability constants of the complexes have been calculated.

Introduction

Nyman *et al.* (1955) obtained a slope of 32 mv. for the log-plots in their polarographic studies of zinc in ethylenediamine medium. The stability constants, calculated on the basis of a reversible electrode reaction, were higher than those obtained by other methods (Carlson, McReynolds and Verhock, 1945; Bjerrum and Anderson, 1945). The higher values were attributed to the presence of gelatin causing the irreversibility of the electrode reaction, though the log-plots indicated reversibility. A detailed study of this system is reported here.

Experimental

Current-potential curves were taken on a manual set-up using an H-cell. The two arms of the cell were filled with the test solution thereby avoiding the use of agar. A saturated calomel electrode (S.C.E.) served as a reference electrode. All measurements were carried out with deaerated solutions at $30 \pm 0 \cdot 5^{\circ}$ C. in a supporting electrolyte of $0 \cdot 5$ M potassium chloride. The capillary characteristics were: $m = 1 \cdot 43$ mg. sec.$^{-1}$ and $t = 4 \cdot 36$ sec. (open circuit). The currents reported here were corrected for the residual current. A Cambridge Bench Type pH meter was used for pH measurements.

The dropping amalgam electrode was prepared by electrolysing a solution of zinc sulphate for about 12 hours (usually overnight) at 10–15 V using 30 ml. of mercury pool as cathode. After electrolysis, the amalgam was transferred to another reservoir and forced down the polarographic capillary with nitrogen under pressure.

The stock solution of zinc sulphate (B.D.H. AnalaR) was standardised by the oxinate method. Ethylenediamine (B.D.H. AnalaR) was standardised by titration with standard hydrochloric acid using a mixture of bromocresol green and methyl red as indicator. $0 \cdot 008\%$ gelatin was used to suppress the pronounced maximum.

Results and Discussion

Zinc gave a well-defined wave in $0 \cdot 5$ M potassium chloride with the half-wave potential at $-1 \cdot 01$ V *vs.* S.C.E. Polarograms of solutions containing $0 \cdot 3$ mM zinc were taken at different concentrations of ethylenediamine. The slopes of the log-plots were nearly the same as that of the simple ion and the stability constants calculated from the half-wave potentials were different from the reported values, as observed by the earlier workers.

In order to investigate the discrepancy between the values of the stability constants obtained by the polarographic and pH methods, the reversibility of the electrode reaction was further checked by calculating α, the transfer coefficient and K_s, the standard rate constant. Composite polarograms of zinc were taken at different concentrations of ethylenediamine using a dropping amalgam electrode. The current in the region of zero was plotted on an enlarged scale and the potential corresponding to zero current gave E_r, the apparent reversible potential (Sathyanarayana, 1964). The equilibrium potential, E_e, was then calculated from the Nernst equation substituting the cathodic and anodic diffusion currents for the concentrations of oxidant and reductant respectively. A plot of E_e *vs.* log (*en*) is given in Fig. 1. These equilibrium potentials were used for the calculation of η, the overpotential, in the calculation of α and K_s from the cathodic waves (Milner, 1958). The final equation is of the form (*loc. cit.*)

$$\log \frac{h}{1 + \exp. \beta\eta} = \log \left(\frac{3}{7D}\right)^{\frac{1}{2}} K_s - \frac{\alpha\beta\eta}{2 \cdot 303} \qquad (1)$$

and the values of α and K_s were obtained from a plot of $\log (h/1 + \exp. \beta\eta)$ *vs.* η. A few typical plots are given in Fig. 2 and the values of α and K_s at different concentrations of ethylenediamine are given in Table I.

The standard rate constants were of the order of 10^{-4} and 10^{-5} cm. sec.$^{-1}$ in the higher and lower ranges of concentration of amine respectively. This is in accordance with the results obtained by Morinaga (1956), in potassium nitrate medium. The quasi-reversible nature of the electrode reaction would result in a shift of the cathodic waves to more negative potentials and, con-

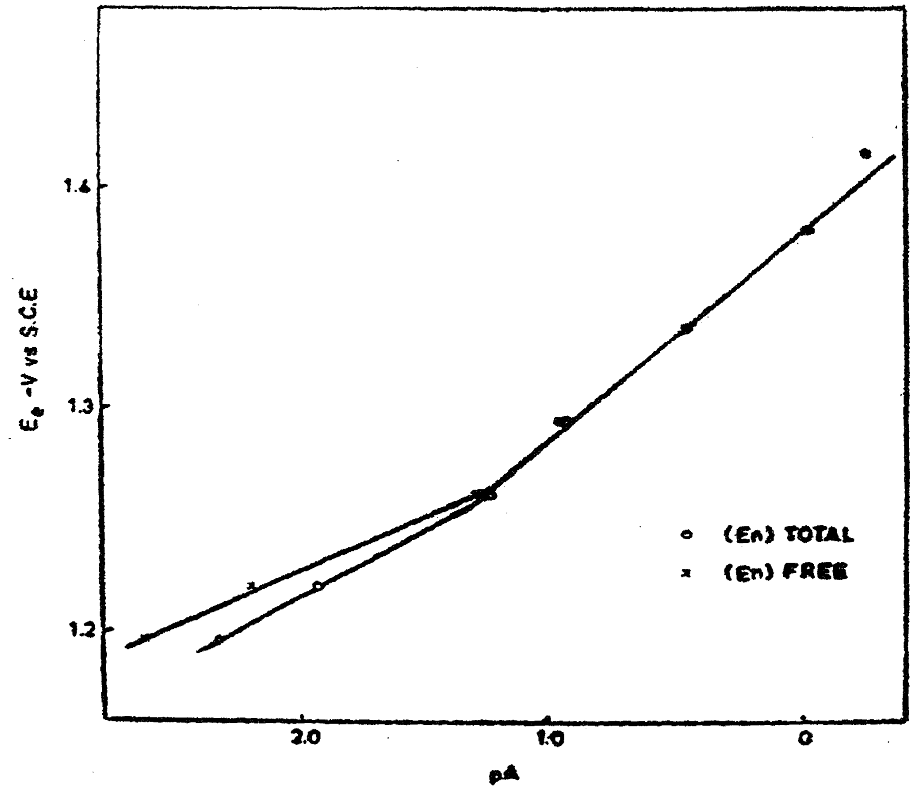

FIG. 1. Plot of E_e *vs* pA

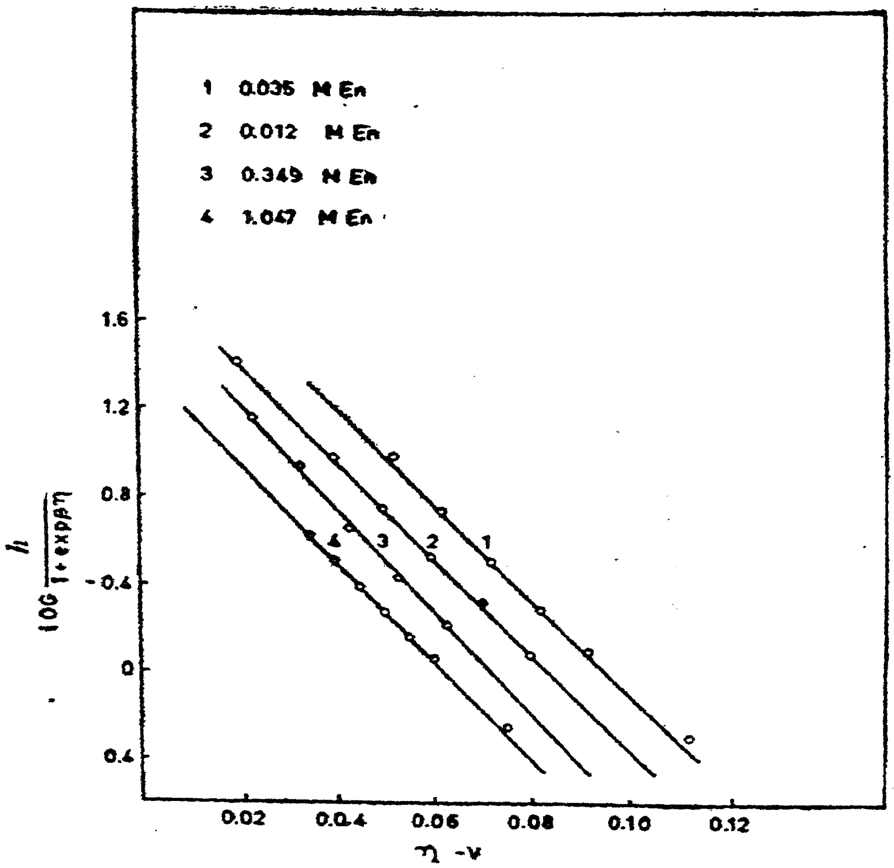

FIG. 2. Plot of η *vs* log $h/1+\exp\beta\eta$

sequently, the stability constants determined from the half-wave potentials would be higher than those calculated for a perfectly reversible wave.

A shift in the equilibrium potential as well as the half-wave potential was observed even at low concentrations of ethylenediamine. The concentration of free amine was calculated by taking into account the amount complexed with zinc and that existing as monohydrogen ethylenediamine ions, the pK of which was taken as 10·14. A plot of E_e *vs.* log (*en*) free given in Fig. 1 indicates two straight lines corresponding to the two species, *viz.*, $Zn(en)_2^{++}$ and $Zn(en)_3^{++}$. The stability constants calculated from the equilibrium potentials by the method of Lingane agree well (Table II) with the values obtained by other methods.

TABLE I

Values of α and Ks

En M	$E_{\frac{1}{2}}$ −V *vs.* S.C.E.	E_e −V *vs.* S.C.E.	α	$-\log K_s$
0·012	1·280	1·220	0·67	4·24
0·035	1·319	1·248	0·65	4·46
0·058	1·335	1·262	0·75	4·77
0·349	1·387	1·337	0·71	4·09
0·582	1·409	1·359	0·69	4·05
1·047	1·426	1·385	0·68	3·80
1·280	1·437	1·393	0·65	3·92
1·570	1·447	1·401	0·67	3·92
1·745	1·448	1·405	0·75	3·96

TABLE II

Values of stability constants

	Polarographic method		Potentiometric		pH
	From $E_{\frac{1}{2}}$	From E_e			
$\log \beta_1$	..	..	5·7	6·0	5·92
$\log \beta_2$	13·65	11·2	10·4	10·81	11·07
$\log \beta_3$	14·48	12·3	12·1	12·98	12·93

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