POLAROGRAPHY OF ZINC IN ALANINE MEDIA

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Received March 18, 1967

Introduction

The polarography of zinc in the presence of amino-acids was taken up as a general programme of work in view of the results obtained in our studies on the polarography of zinc in ethylenediamine and glycine media (Sundaresan *et al.*, 1967). This paper reports the polarography of zinc in the presence of α- and β-alanine.

Experimental

The apparatus was the same as that used earlier. The capillary characteristics were: $m = 1{\cdot}27$ mg. sec.$^{-1}$ and $t = 5{\cdot}0$ sec. (open circuit).

α- and β-alanine were used without further purification. pH adjustments were made with a sodium hydroxide solution. Experiments were carried out at $30 \pm 0{\cdot}5°$ C. at 0·5 ionic strength in potassium chloride medium. No maximum suppressor was found necessary.

Results and Discussion

Polarograms of solutions containing zinc and alanine were taken at different pH. The half-wave potentials were determined from the log-plots and the concentration of alaninate ion was calculated from the pH of the solution and the pK values of 9·87 (Maley and Mellor, 1950) and 10·26 (Irving *et al.*, 1954) for α- and β-alanine respectively. The polarograms were also taken at a constant pH, varying the concentration of α-alanine. A plot of the half-wave potential *vs.* pA (Fig. 1) in the case of α-alanine indicated one straight line whereas the plot for β-alanine (Fig. 2) indicated three straight lines. The values obtained both at constant pH and at constant alanine concentration agreed well indicating the effect of hydroxyl ions to be negligible.

The reversibility of the electrode reaction was checked in a manner similar to that described earlier. Composite waves of solutions containing 0·3 mM zinc and alanine were taken at different pH and the equilibrium

potentials, Ee, were calculated (Figs. 1 and 2). Tables I and II give a summary of the values of α, the transfer coefficient and K_S the standard rate constant for the reduction of zinc in α- and β- alanine media.

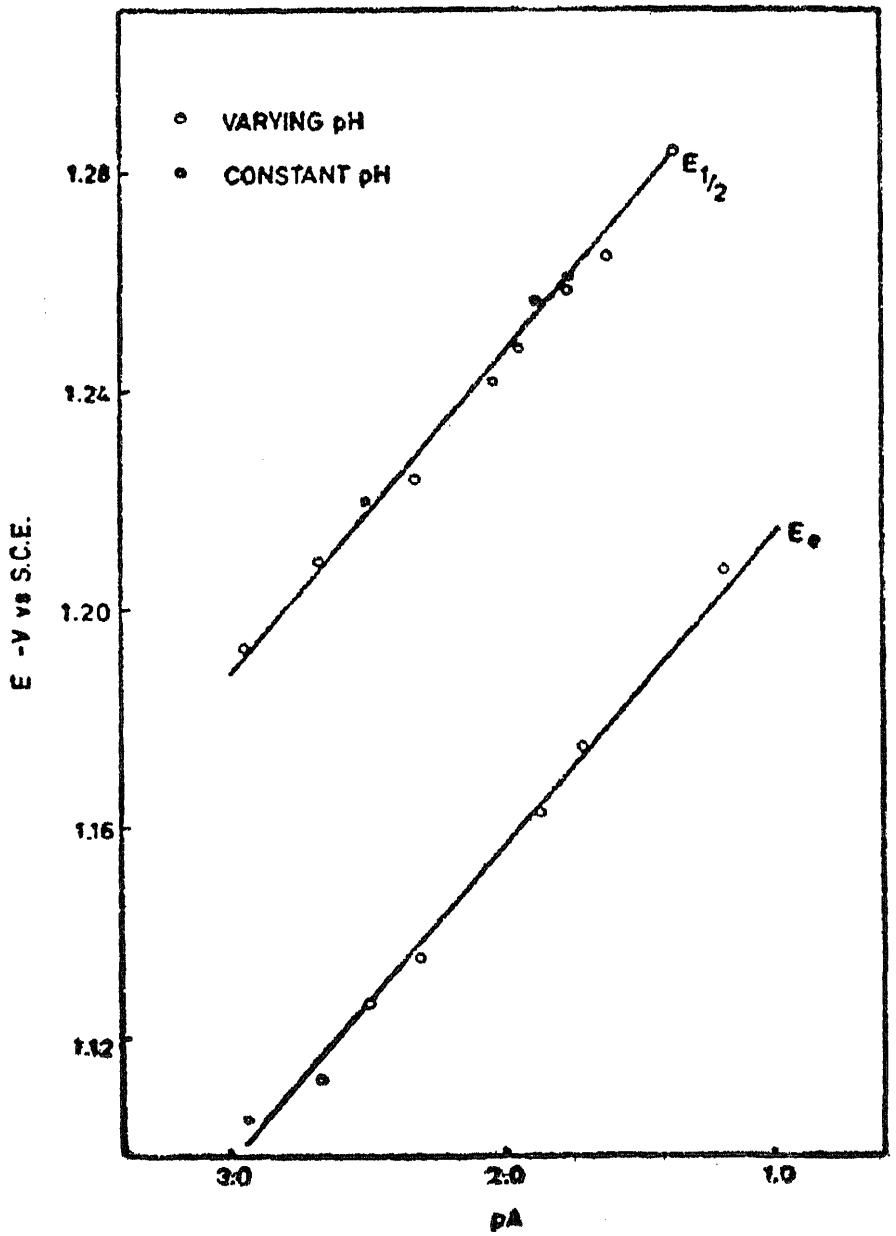

FIG. 1. Zinc α-alanine: Plot of $E_{\frac{1}{2}}$ and E_e *vs.* pA

The standard rate constant for the reduction of zinc in α-alanine media is $\sim 2 \times 10^{-5}$ cm. sec.$^{-1}$ indicating an irreversible electrode reaction. The co-ordination number was calculated from the plot of E_e *vs.* pA as two. The stability constant of $10^{8 \cdot 85}$ calculated for the second species at an ionic strength of 0·5 agreed with the reported value of $10^{9 \cdot 50}$ at an ionic strength of 0·01 (*loc. cit.*).

Three straight lines were obtained in the case of β-alanine for the plot of half-wave potential *vs.* pA but the plot of equilibrium potentials indicated only two straight lines. This is understandable from the rate constants calculated for this system. Above pA 2, the reduction of zinc in β-alanine

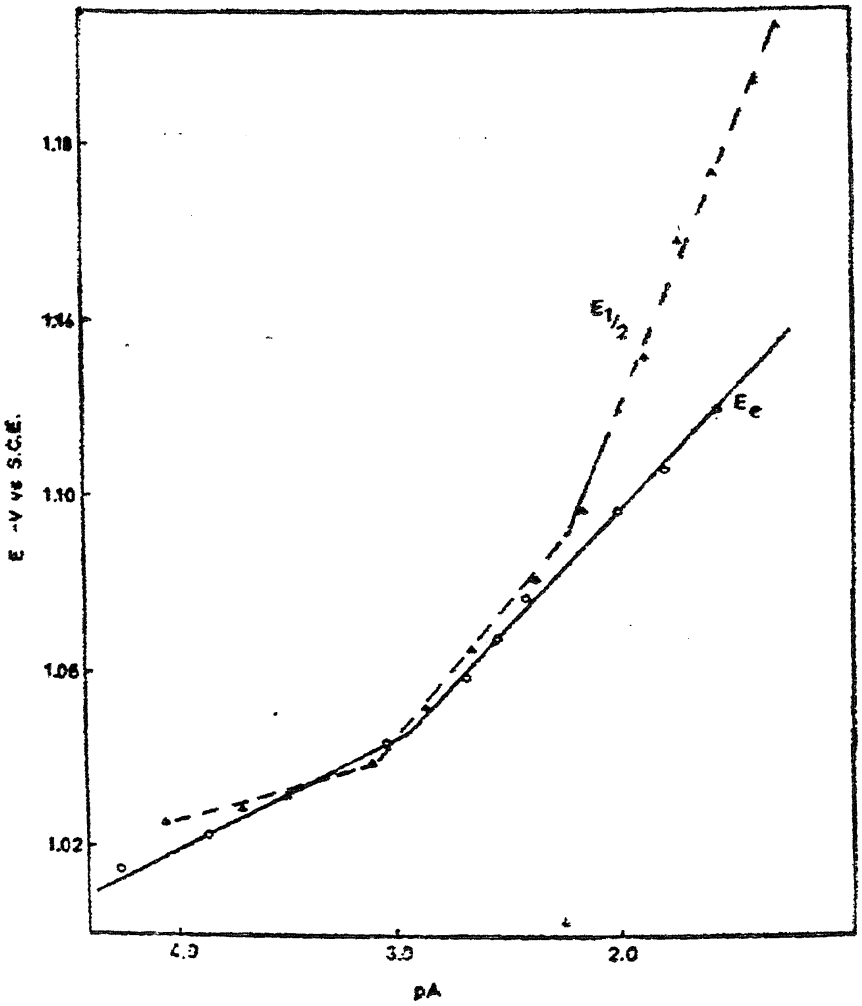

FIG. 2. Zinc β-alanine: Plot of $E_{\frac{1}{2}}$ and E_e *vs.* pA

media is nearly reversible but below this pA, where zinc exists mainly as the second species, the rate constant is $\sim 1 \times 10^{-4}$ cm. sec.$^{-1}$ with the electrode reaction tending to irreversibility as the concentration of β-alanine is further increased. This is also indicated by the larger deviations of the half-wave potentials from the equilibrium potentials. The third straight line in the plot of the half-wave potential is therefore due to the change in the irreversibility of the electrode reaction.

The co-ordination number of one calculated in the region of pA 3·2–4·0 indicated the presence of the first species, the stability constant being calculated as $10^{4\cdot2}$. The co-ordination number in the pA range of 2–3 was two and the stability constant was calculated as $10^{7\cdot0}$. The logarithm of the stability constant of the first species is reported as ~ 4 (*loc. cit.*) and that for the second species is reported here for the first time.

TABLE I

Zinc-α-alanine—Values of α and K_s

pH	pA	$E_{\frac{1}{2}}$ $-V$ *vs.* S.C.E.	E_c $-V$ *vs.* S.C.E.	α	$-\log K_s$
7·93	2·95	1·193	1·101	0·53	4·53
8·20	2·68	1·209	1·117	0·57	4·56
8·58	2·31	1·224	1·139	0·62	4·68
8·97	1·95	1·248	1·160	0·65	4·82
9·18	1·77	1·259	1·170	0·66	4·85
8·38	2·50	1·220	1·128	0·56	4·56
8·37	2·04	1·242	1·154	0·61	4·71
8·40	1·88	1·257	1·164	0·59	4·75
8·35	1·76	1·261	1·171	0·59	4·70

TABLE II

Zinc-β-alanine—Values of α and K_s

pH	pA	$E_{\frac{1}{2}}$ $-V$ *vs.* S.C.E.	E_c $-V$ *vs.* S.C.E.	α	$-\log K_s$
8·90	2·38	1·081	1·076	0·21	2·74
9·12	2·17	1·097	1·088	0·20	2·80
9·42	1·90	1·131	1·103	0·28	3·13
9·58	1·76	1·158	1·110	0·39	3·55
9·77	1·61	1·173	1·119	0·40	3·63
10·04	1·43	1·194	1·129	0·45	3·90
10·33	1·27	1·206	1·138	0·46	3·95

ACKNOWLEDGEMENTS

The authors wish to thank Dr. V. T. Athavale, Head, Analytical Division, for his kind interest.

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Sundaresan, R., Saraiya, S. C. and Sundaram, A. K. — Under publication.

411-67. Printed at The Bangalore Press, Bangalore City, by M. S. Narayanamurthy, Secretary and Published by B. S. Venkatachar, Editor, "Proceedings of the Indian Academy of Sciences," Bangalore