VOLTAMMETRIC, CYCLIC VOLTAMMETRIC, CHRONOPOTENTIOMETRIC AND CHRONO-AMPEROMETRIC REDUCTION OF ZINC AT GOLD AMALGAM WIRE ELECTRODE

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The electrode kinetics of Zn(II) reduction was studied in sodiumperchlorate, potassium nitrate, tetra ethyl ammonium chloride, tetra ethyl ammonium bromide and tetra ethyl ammonium iodide media at gold amalgam wire indicator, platinum wire auxiliary and saturated calomel reference electrode on Electroscan- 30.

The K°_{fh} (heterogenous forward rate constant) value are increasing in the order of $I^- > Br^- > NO_3^- > Cl^- > ClO_4^-$ and appears to correlate only with decreasing charges at the electrode surface due to increased specific adsorption of the anions.

Randles <1> and Sevcik <2> were among the first to consider the single scan method to correlate the current and concentration for a reversible reaction taking place at a plane electrode. The theory was extended to totally irreversible charge transfer reaction by other workers <3,4>.

The electrode kinetics study can be performed using any of the electroanalytical techniques, but particularly so by using cyclic voltammetry, chronopotentiometry and chronoamperometry. It is desirable to test the extent of agreement for the values obtained by these techniques, thus arriving at their respective reliabilities. This is one of the aims of the present study.

Though recently, the work with wire electrodes has gained momentum, the comprehensive data is not yet available. The use of mercury coated metal wire electrodes helps in extending the favourable characteristics of residual curent curves at solid wire electrodes. The amalgam wire electrode may behave either as a mercury electrode or a metal electrode, thus combining the advantages of both <5,6>. Since Zn(II) reduction is very close to that of Hydrogen in all media, it was thought that the better separation could be effected with amalgam wire electrode.

Silver amalgam electrode has been used in potentiometric<7,8> and polarographic work but the characteristics of this amalgam electrode changes with time<9,10>. Detailed study using silver and amalgam wire electrode in polarography, carried out earlier in our laboratory, reveals that reproducible curves are obtained only for silver and mercury reductions and no other cations <11,12>. Electrodeposition of mercury on a platinum electrode usually does not give satisfactory adherent coating <10,13>. The present work undertakes to study the performance of gold amalgam wire electrode in voltammetric study in different supporting electrolytes.

EXPERIMENTAL

A Beckman Electroscan- 30 recording instrument was used in the present work.

Gold Amalgam Electrode:

The mercury plated gold electrode was prepared by fusing about 2.0 cm length of gold wire, (radius 1 mm) in a soft glass tubing (radius, 0.5 cm, length 4.0 cm) in such a way that 1.0 cm of the gold jutted out of the glass tubing. Mercury was deposited onto this portion by electrolysis from a 0.01 M mercuric nitrate solution in 0.1 M HNO_3 at -0.5 V vs SCE for two minutes. The electrode thus prepared is stable for a month.

Auxiliary and reference electrodes employed were platinum wire and saturated calomel respectively.

Cell

The cell consists of three compartments; one containing a fritted junction for an

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isolated auxiliary platinum eletrode, the second also containing a fritted junction and filled with agar-agar and saturated potassium chloride solution for contact with calomel electrode, the middle arm or compartment contains the working amalgam electrode fitted in a rubber bung and dipping in sample solution. To the middle compartment, two purge tubes are provided- one for bubbling the nitrogen and the other for maintaining the nitrogen atmosphere during electrolysis. Temperature of the cell was maintained at 23°C ± 0.1°C.

Solutions

AnalaR grade chemicals were used. Solution of zinc perchloride was prepared by dissolving pure zinc granules of 20 mesh (manufactured by General Chemical Division, USA, ACS specification) in perchloric acid, evaporating the excess acid and finally making up to the desired volume with distilled water.

RESULTS

Polarographic Work

The Zn(II) reduction was tried in five different supporting electrolytes - 0.1M each of tetra ethyl ammonium iodide, tetra ethyl ammonium bromide, tetra ethyl ammonium chloride, sodium perchlorate, and potassium nitrate. The peak potentials obtained for 0.6 mM Zn(II) were -1.08, -1.08, -1.03, -1.07 and -1.04 vs SCE respectively and the peak currents were 41.0, 36.0, 44.0, 50.0 and 56.5 μA repectively. Each value is the mean of three experiments. The values are constant and reproducible, unlike that of the silver amalgam electrode. With different zinc concentrations, the peak potential remains constant e.g. in 0.1M ethyl ammonium iodide, for 0.2, 0.4, 0.6 & 0.8 mM Zn(II) concentration, the peak potentials are -1.07, -1.08, -1.08 and -1.08 V vs SCE. Clearly, the gold amalgam electrode is much superior to the silver amalgam electrode in polarographic work. The current concentration proportionality was satisfactorily observed for Zn(II) in each of these supporting electrolytes.

Kinetic Parameters for Zn(II) Reduction

(a) Cyclic Voltammetry

Calculations of kinetic parameters depend mainly on whether the electrode reaction is reversible or irreversible. For wire electrodes, this information can be obtained by cyclic voltammetry.

The cyclic voltammograms of 0.4 mM Zn(II) in nitrate medium shows that the reduction is totally irreversible because ΔE_p is 580 mV instead of 30 mV and $(i_p)_c - (i_p)_a$ is 36 μA instead of being zero (Fig. 1). Similar results were obtained in other media also.

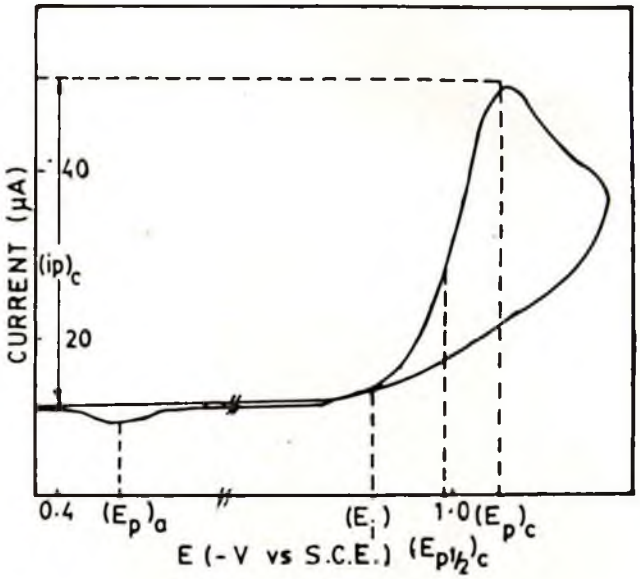


Fig. 1 Cyclic Voltammogram for 0.4mM Zn in 0.1M KNO_3 Scan Rate ν = 0.020V/Sec.

(b) Electrode Area and Diffusion Coefficients

The effective area A of the gold amalgam wire electrode was found to be 0.46 cm^2 by the Cottrell method, using 0.1 M KNO_3 as the supporting electrolyte. For the calculation of the area, the diffusion coefficient value of 7.0×10^{-6} cm^2/sec for Zn^{2+} in 0.1 M KNO_3 is taken from the literature (15). Having thus obtained the effective area of the electrode, the diffusion coefficients in the other media were obtained by employing the same Cottrell equation (Table 1). The values were checked by using the chronopotentiometric technique and the values tallied with each other very well.

(c) Voltammetry

The peak potential for an irreversible system is given by (16)

$$E_p = E^1 - \frac{0.05915}{\alpha n_a}\left[0.4565 + \log \frac{(\alpha n_a D_o \nu)^{1/2}}{k^1_{f,h}}\right] \quad \ldots(1)$$

TABLE 1

KINETIC PARAMETERS FOR Zn^{2+} IN 0.1M SUPPORTING ELECTROLYTE
A (ELECTROCHEMICAL AREA OF THE ELECTRODE) = 0.46 Cm^2

Supporting Electrolyte	Voltammetry		Chronopotentiometry			Chronocamperometry	
	$-\log k^{\circ}_{s,h}$	$\propto n_a$	$-\log k^{\circ}_{f,h}$	$-\log k^{\circ}_{f,h}$	$\propto n_a$	$-\log k^{\circ}_{f,h}$	$D^{1/2}$
$NaClO_4$	5.57	0.90	16.23	15.45	0.94	15.3	2.29
KNO_3	5.50	0.95	15.66	14.48	0.88	14.50	2.65
Et_4NCL	5.56	0.95	15.76	15.08	0.92	14.87	2.30
Et_4NBr	5.50	0.81	14.45	14.14	0.81	14.00	2.21
Et_4NI	5.45	0.79	14.24	14.14	0.82	13.82	2.30

All rate constants are in cm_2/sec units;

D is ---> * Calculated by Cottrell's equation and is in cm^2/sec.

While the half peak potential is described by

$$Ep/2 = E_p + \frac{0.04771}{\propto n_a} \quad ..2$$

where $K^{1}_{f,h}$ is the heterogeneous rate constant at the potential E^{1}, at which the electrolysis starts, $\propto$ is the transfer coefficient, λ is the voltage scan rate and the other symbols have the usual significance.

From these equations $K^{1}_{f,h}$ and $\propto n_a$ are calculated. $K^{\circ}_{f,h}$ and the forward reaction rate constant at E = 0 vs N.H.E. is obtained by the equation (17). The mean value of $K^{1}_{f,h}$ is approximately equal to $k_{s,h}$, the heterogeneous standard ratio constant (15). The values of $\propto n_a$ and $k_{f,h}$ for all media are given in Table 1.

(d) Chronopotentiometric Studies

The potential time equation (17) for a totally irreversible reaction is

$$E = \frac{RT}{\propto n_a F} \ln \frac{nFC^{\circ} K^{\circ}_{f,h}}{i_o} + \frac{RT}{\propto n_a F} \ln [1-(t/T)^{1/2}] \quad ...(3)$$

A plot of logaritham of $[1 - (t/T)^{1/2}]$ vs potential is a straight line whose slope is 2.303 RT/ $\propto n_a F$ from which $\propto n_a$ can be readily calculated. The rate constant, $K^{\circ}_{f,h}$ is calculated from the potential at time zero by application of equation (3). The chronopotentiogram and the log plot in 0.1M KNO_3 medium is shown in Fig. 2 and 3. The order of $K^{\circ}_{f,h}$, values is the same as in voltammetry. The backward rate

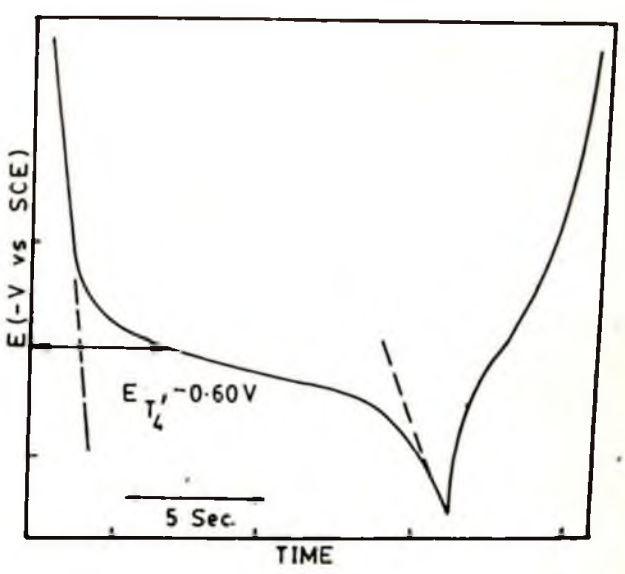


Fig. 2 Chronopotentiogram for 0.4mM Zn^{2+} in 0.1M KNO_3 i = 10 μA.

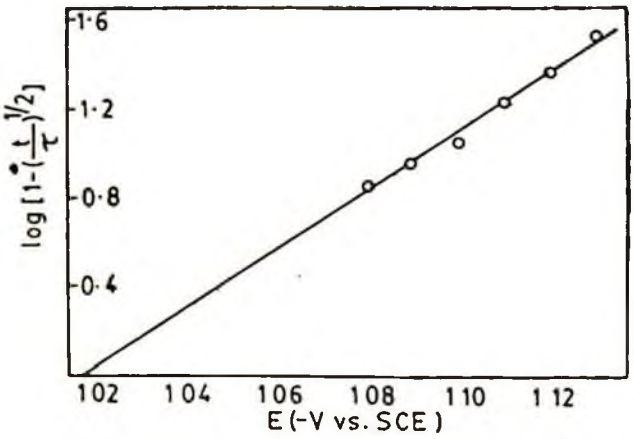


Fig. 3 Plot of log $1-(t/T)^{1/2}$ vs E (-V vs SCE) for 0.4 mM Zn^{2+} in 0.1 M KNO_3

constant $K^{\circ}_{f,h}$ could not be calculated due to the ill defined nature of the current reversal chronopotentiogram (Fig. 2).

(e) Chronoamperometric Studies

The reduction current at any particular time for totally irreversible system is given by <17>

$$i = i_d \left[\pi^{1/2} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)\right] \quad .....4$$

where

$$\lambda = k_{f,h} \, t^{1/2} / D_o^{1/2} \quad .....5$$

The values of λ corresponding to different ratio of i/i_d were obtained from literature <17>. Thus the variation of $k_{f,h}$ with potential can be studied by repeating the measurment of i/i_d at various potentials (Fig. 4). The values of $-\log k_{f,h}$ vs E (V vs NHE) are plotted and extrapolated to zero potential (Fig. 5) which gives the value of $-\log K^{\circ}_{f,h}$. The data is included in Table 1.

DISCUSSION

The error resulting from the capacity current is overcome by choosing the appropriate concentration for each technique <17>, the maximum error due to capacity was calculated and found to be less than two percent.

The values of the forward rate constant $k^{\circ}_{f,h}$ by all the techniques are in the order of

$$I^- > Br^- > NO_3^- > Cl^- > ClO_4^-$$

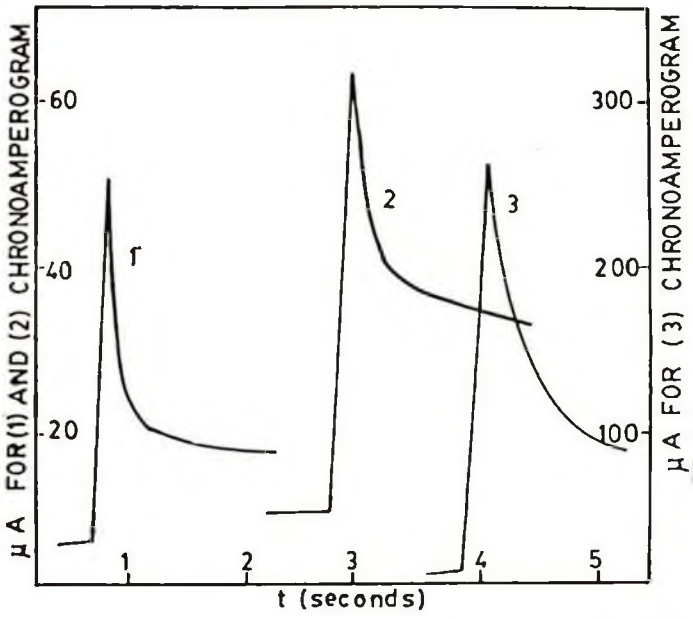


Fig. 4 Chronoamperograms of 0.8 mM Zn^{2+} in 0.1 M $NaClO_4$ at different potentials (1) At -0.95 V (vs SCE) (2) At -.075 V (vs SCE) (3) At -1.20 V(vs SCE)

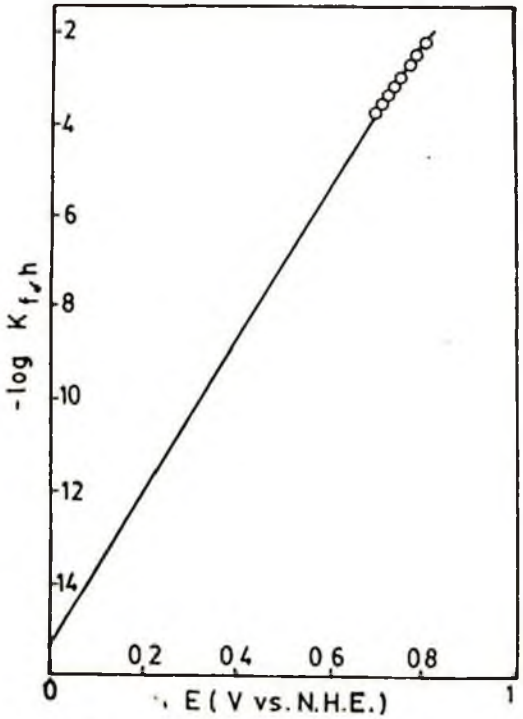


Fig. 5 Plot of $-\log k_{f,h}$ vs. E (- V vs. N.H.E) for 0.8 mM Zn^{2+} in 0.1 M $NaClO_4$

The order of the forward reaction rate constant is thus indicative of the adsorbability of the anion on the electrode surface. The only surprising thing is that nitrate ion is adsorbed to a greater extent than the chloride ion. However, this order is exactly the same as that reported by Kinard and Philip, for Eu^{3+} reduction on DME<18>. They have correlated the order only with decreasing charge at the electrode surface due to increasing specific adsorption of the anions.

It will be noticed from Table 1, that the $-\log K^{\circ}_{f,h}$ values for chronopotentiometry and chronoamperometry are close together, while they are slightly higher in voltammetry in all the media. In voltammetric calculations, the choice of the initial potential which is related to $k_{f,h}$ value is rather arbitrary. Secondly, an extra experimental parameter of the square root of scan rate ($\vartheta^{1/2}$) is involved. These two factors, alone or in combination may be responsible for the slight higher values by the voltammetric method. Chronopotentiometry and chronoamperometry seem to be better suited to calculate the kinetic parameters for irreversible reactions

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