The Hydrogen Evolution Reaction at Mercury and Amalgam Electrodes in the Presence of Diphenylamine

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The hydrogen evolution reaction of mercury and indium amalgam electrodes follows volmer Heyrovsky mechanism. This reaction is accelerated in presence of sulphur containing compounds and diphenyl amine. The accelerating effect of diphenyl amine is larger near PZC and this is due to the adsorption of protonated diphenyl amine. In case of indium amalgam electrodes, the acceleration of the h.e.r. reaction is similar to that at mercury electrodes because it occurs nearer the PZC.

The hydrogen evolution reaction (h.e.r.) follows the Volmer Heyrovsky mechanism at mercury and indium electrodes. The h.e.r. at indium amalgam electrodes of composition varying from 0-62 mole percent was studied in detail by Butler and coworkers (1) and recently by Dayalan (2). The h.e.r. at mercury electrodes is accelerated by the presence of sulfur containing compounds and diphenylamine (DPA) (3). Acceleration by DPA was attributed to the reduction of an adsorbed DPA which is protonated ($DPAH^+$) (4). The influence of thiourea and its N-substituted derivatives on the h.e.r. at mercury and indium amalgam electrodes was studied in great detail by Dayalan and the acceleration was attributed to the reduction of protonated thiourea which provides a faster alternate route (5,6). The present paper describes and discusses the results observed in the presence of diphenylamine (DPA) on the h.e.r. at mercury, 20% and 63% indium amalgam electrodes.

EXPERIMENTAL

The cathodes were in the form of dropping mercury or amalgam electrodes. Indium forms a one phase amalgam upto 63% mole percent of indium. The amalgams were made by mixing weighed quantities of the two metals and preserved under a layer of dilute acid. The rates of flow of the mercury and amalgam were obtained in the usual way. A potentiostat was used to apply the desired polarising potential and the current growth was recorded on a x-t recorder. The current magnitudes after a time of 1 sec of flow of the electrode material was converted to current density and the E-log I plots were made. The counter electrode was a large platinum gauze and a hydrogen electrode in the test solution was generally the reference electrode.

The solutions were deaerated using purified nitrogen.

The electro capillary curves were obtained by recording the time required for five drops to be formed at various potentials and calculating the average life time per drop. The droptimes with the amalgam were not highly reproducible. The temperature was maintained at 30 ± 1°C.

RESULTS AND DISCUSSION

Figs 1 and 2 are the polarisation curves obtained for the h.e.r. at the mercury electrode. It is seen that the h.e.r. is accelerated by the addition of DPA. The saturation solubility of DPA was approximtely 1 mM in 1M HCl. The acceleration effect is restricted to a range of potentials and the polarisation curves tend to merge with the original curve at high negative potentials. This variation is the same as reported by earlier workers (3,4). The accelerating effects by any concentration of DPA increases with the concentration of the acid (Fig 2).

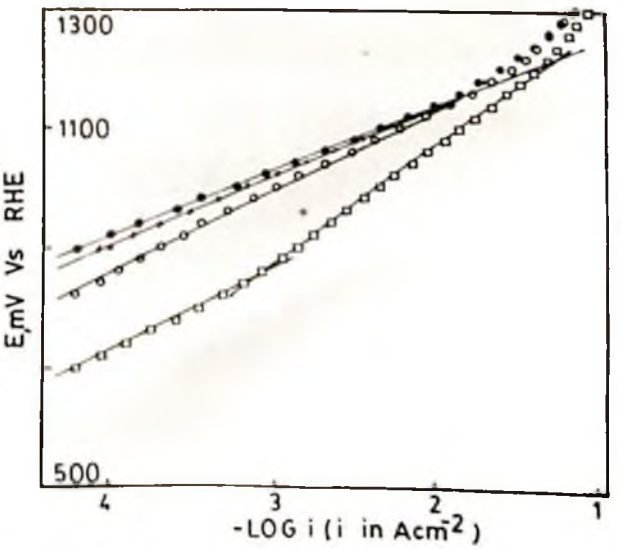


Fig. 1 Polarisation Curves In 0.1 M HCl in the Presence of DPA-Mercury Electrode.

The electrocapillary curves show (fig 3a,b) that DPA is strongly adsorbed at the interface over a wide range of potentials and tends to be desorbed at negative polarisation.

The accelerating influence of DPA has been previously ascribed to the discharge of a proton attached to the adsorbed DPA (4). The equation 1 & 2 provide a faster, alternate discharge path to the usual step (equation 3) in the h.e.r.

$$DPA + H^+ \rightleftharpoons (DPAH^+)_{ad} \quad .... \quad 1$$

$$(DPAH^+)_{ad} + e \dashrightarrow DPA + H_{ad} \quad .... \quad 2$$

$$H_3O^+ + e \dashrightarrow H_{ad} + H_2O \quad .... \quad 3$$

$$H_{ad} + H_3O^+ + e \rightleftharpoons H_2 + H_2O \quad .... \quad 4$$

The earlier workers have also reported (4) that in acidic solutions (>6N HCl) the overpotential for hydrogen evolution was increased and not decreased by DPA. The adsorbed species $(DPAH^+)_{ad}$ has a two fold function in this context. These are:

(1) an alternate faster path for the discharge of hydrogen ions and (2) a shift of the ψ potential to positive values. This shift can inhibit the discharge of H_3O^+ ions in the normal sequence.

When acid concentrations are low, the discharge of $DPAH^+$ predominates but at high acid concentrations, the retardation by ψ potential shift over-rides the acceleration by $DPAH^+$ discharge.

Thiourea was reported to accelerate the h.e.r. both at mercury and amalgam electrodes (5,6). This acceleration was also ascribed to the discharge of a protonated thiourea species TUH^+ as being faster than the discharge of H_3O^+. Enough evidence was provided for this suggestion. However there are differences in the effects broought about by TU and by DPA.

a) The accelerating effects due to TU are not dependant on the acid concentration in the range of 0.001M to 1M.

b) The accelerating effects of TU are considerable even at negative potentials where the adsorption of thiourea is small. On the other hand the effects of DPA decrease with increasing negative polarisation.

c) The adsorption of DPA at potentials close to the p.z.c is much higher than that of

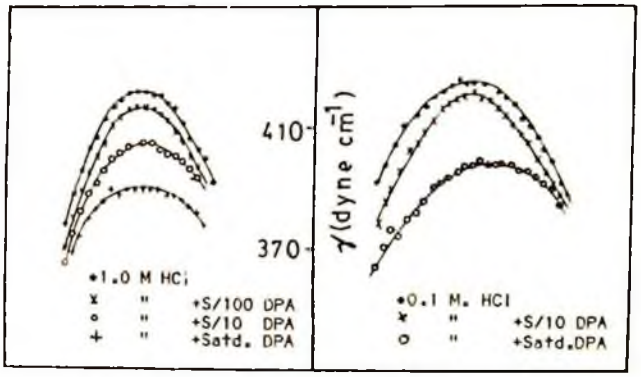


Fig. 3 Electrocapillary Curves of DPA in (a) 1M HCl and (b) 0.1 M HCl - Mercury Electrode.

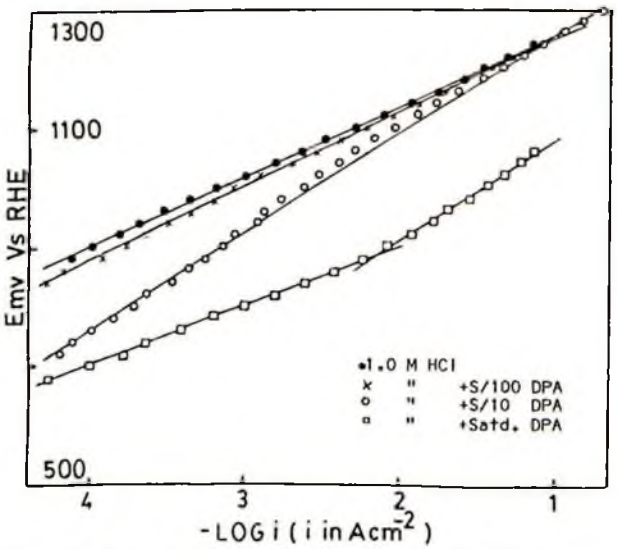


Fig. 2 Polarisation Curves in 1.0 M HCl in the Presence of DPA - Mercury Electrode.

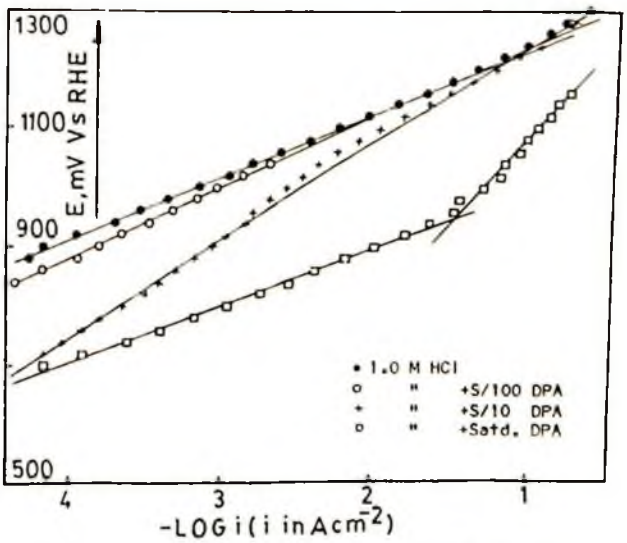


Fig. 4 Polarisation Curves in 0.1 M HCl in the Presence of DPA - 20% Indium Amalgam Electrode.

thiourea. The extent of lowering in interfacial tension caused by 1 mM DPA is equal to that brought about by 0.1M TU. 1 mM of thiourea causes negligible change in the interfacial tension but concentrations as low as 10^{-5} M TU can accelerate the h.e.r.

d) The ψ potential effects are smaller with TU.

e) The accelerating effect of thiourea were ascribed to a overall lowering of the free energy of activation by the simultaneous adsorption of both products of the discharge reaction. The sequence of reactions being

$$TUH^+ + e \longrightarrow TU_{ad} + H_{ad} \quad \ldots\ldots 5$$

$$H_{ad} + TUH^+ + e \longrightarrow TU_{ad} + H_2 \quad \ldots\ldots 6$$

TUH^+ is a species formed in small concentrations in solutions of low acid concentration but formed in appreciable concentration when the acid strength exceeds 2M. TUH^+ is not an adsorbed species.

It is also observed that the slopes of the polarisation curves increase from 120 mV in the absence of DPA to 165 mV in the presence of 10^{-4} M DPA. Similar observations were reported by Frumkin and Andreya (4). The change in slope is because the accelerating effect varies with the concentrations and polarising potentials. With increasing cathodic polarisation, the $DPAH^+$ is gradually desorbed. Hence the accelerating effect with any concentration DPA is largest at about -0.6 to .7V (close to the pzc) and least at about -1.2V when complete desorption occurs. This arguement should lead to a slope greater than 165 mV with the solution saturated with DPA (app. 10^{-3}M). However in the solution saturated with DPA (app. 10^{-3} M), the E-log i variations exhibit two linear regions. The region at lower current densities has a low slope and the second region has a high slope (> 200 mV). The change in slope becomes more pronounced as the concentration of indium in the amalgam is increased. Two linear regions are observed even with a lower concentration of DPA in the experiments with 63 mole percent indium in the amalgam (Fig.6)

The high slope region is the result of desorption of DPA at higher negative potentials or current densities. The low slope region indicates an extensive adsorption of DPA. This extensive adsorption accelerates considerably the hydrogen evolution reaction in a narrow range of potentials. The results indicate that the extent of adsorption depends primarily on the indium concentration in the amalgam and on the concentration of the acid in the solution.

The first linear region should have a slope of about 120 mV if the extent of adsorption did not change in this range of potential. It is observed that the slope varies between 80 and 100 mV in a solution saturated with DPA, depending on the indium concentration in this amalgam. The slope of the electrocapillary curves (Fig 3b for example) in the presence of DPA is much lower than that in its absence. The ψ potential tends to be less negative in the presence of DPA at the potentials where the h.e.r. occurs. Hence the accelerating effects of the ψ potential on the H_3O reduction in the normal Volmer mechanism is smaller, particularly at the more positive potentials nearer the pzc. Hence the slope of this Tafel region is smaller than 120 mV. Accurate interfacial data is necessary to correct for this changes in the ψ potential.

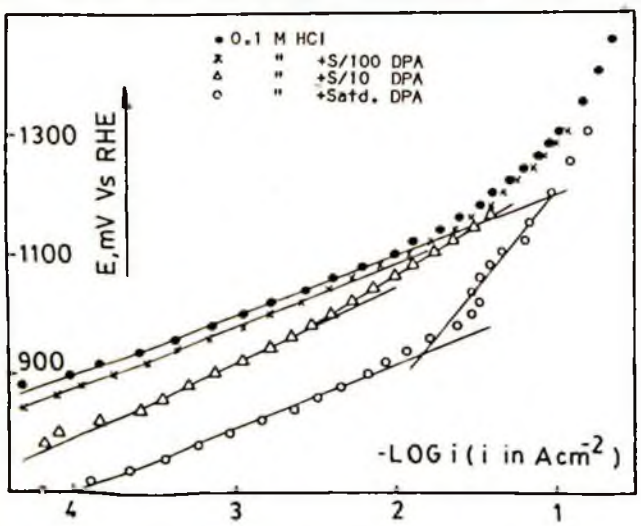


Fig. 5 Polarisation Curves in 0.1 M HCl in the Presence of DPA - 63% Indium Amalgam Electrode.

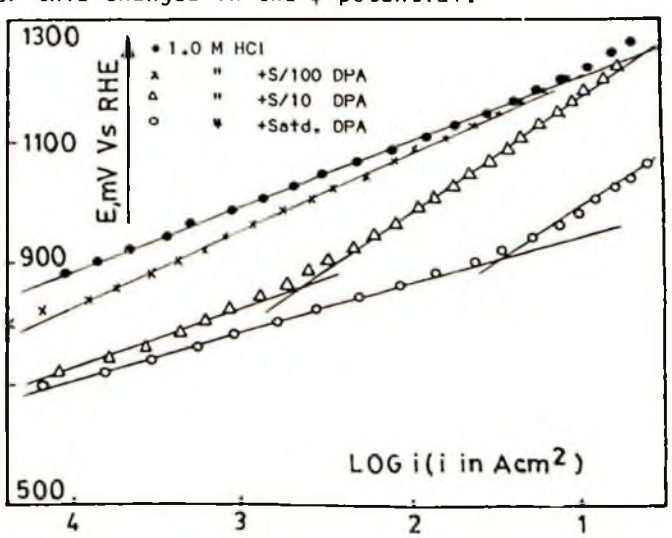


Fig. 6 Polarisation Curves in 0.1 M HCl in the Presence of DPA - 63% Indium Amalgam Electrode.

The polarization curves obtained with 20 and 63 mole percent indium amalgam in acid solutions containing DPA are similar to those obtained with mercury electrodes (Fig.4,5,6). DPA accelerates the h.e.r. at the amalgam electrodes. Table 1 shows the decrease in the hydrogen overvoltage at a current density of 10^{-4} A cm^{-2}. This current is chosen so that the polarising potential is sufficiently positive to make desorption effects minimum. The mechanism of reduction is unchanged with the composition of the amalgam. In acid solutions saturated with DPA, the reduction in overpotential is nearly the same for all compositions of amalgams. However as the DPA concentration is decreased, it is observed that overvoltage lowering is highest with 63 mole percent indium amalgam and lowest with mercury electrodes.

The drop-time potential curves in the presence of DPA indicates that the adsorption of DPA at the respective potentials of zero charge (where no charge effects but only chemical interactions are present) follows the order of 0 > 20 > 60% indium in amalgam. This is consistent with the variations in the metal nitrogen interaction (the hard and soft acid base concept) and metal-πelectron interactions. Hence the lowering in hydrogen overvoltage also must be maximum with mercury electrodes. However the h.e.r. occurs at potentials closer to the p.z.c. with the 63% amalgam electrode but at more negative potentials with the mercury electrodes. Hence the extent of adsorption and the consequent lowering in hydrogen overvoltage is larger with the amalgam electrodes.

The surface excess of DPA is perhaps the same with all electrode compositions due to the very extensive adsorption at potentials close to the p.z.c. when the solution is saturated with DPA and hence the overvoltage lowering is also the same for the current density of 10^{-4} A cm^{-2}. Any difference of the amalgam composition is reflected only through the slope of the Tafel region (Table 1). The slope is higher with mercury electrode since the polarisation potentials are more negative and decreasing adsorption with increasing negative potentials result in a faster decrease of the accelerating effects.

A 20% indium amalgam behaves virtually like a mercury electrode. A similar observation we observed with the effect of thiourea(6). This is due to the negative adsorption of indium at the interface resulting in a lower concentration of indium on the surface as comapred to that in the bulk of the amalgam.

TABLE 1

DECREASE OF THE HYDROGEN OVERVOLTAGE IN THE PRESENCE OF DPA AT MERCURY AND AT INDIUM AMALGAM ELECTRODE. TAFEL SLOPES GIVEN IN PARANTHESIS

Concentration of DPA	$\Delta\eta$ in mV at Hg	20% In-Hg	63% In-Hg
A - Solution 1.0 M HCl			
1 mM	200 (100)	200 (95)	190 (80)
0.1 mM	145 (165)	150 (165)	160 (95)
0.001 mM	25 (125)	30 (120)	55 (125)
B - Solution 0.1 M HCl			
Satd. solution	185 (135)	180 (115)	190 (105)
0.1 mM	55 (135)	55 (130)	90 (125)
0.01 mM	15 (115)	25 (115)	25 (105)

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