Effect of Organic Molecules on the Adsorption of Hydrogen on the Electrode Surface*

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(Received June 22, 1953)

Introduction

The effect of solvents on the hydrogen overpotential has been discussed recently by J. O'M. Bockris1)~3) and A. Wetterholm.4) They have obtained many interesting results relating to the mechanism of the hydrogen electrode reaction, and the theoretical presumption on these phenomena has been given. According to these authors,

(a) The solvent effect depends on both the cathode material and the nature of organic solute and therefore does not seem to depend principally upon solvation of the hydrogen ion, which should have some effects according to the slow discharge theories.

(b) The solute layer, held on the surface of the electrode by coulombic or van der Waals adsorption force, affects the velocity of the recombination of hydrogen atoms, which may be the rate-determining step of the electrolytic evolution of hydrogen molecules.

(c) The solvent effect on the adsorption energy of hydrogen molecules on the surface of the working electrode5) may change the hydrogen overpotential.

The measurement of the number of metal atoms on the electrode surface covered by organic molecules during the evolution of hydrogen being very difficult, the above theoretical presumption has only poor and indirect experimental evidence.

J.A.V. Butler 6)7) has proposed the method of measuring the electrode potential in the initial stage of cathodic polarization with a cathode ray or an electromagnetic oscillograph and calculated the number of hydrogen atoms adsorbed on the electrode surface. By this method, we studied about the relation between the hydrogen overpotential and the effect of the adsorption of organic molecules especially in case of a smooth platinum electrode which has been assumed to obey the catalytic mechanism in the cathodic current density between 10^{-3} and 1 A./cm^2.

Under the assumption that the cathode area available for the hydrogen evolution decreases by the steric hindrance of organic molecules adsorbed on the cathode surface, we8) estimated the number of surface points covered by organic molecules, by analysing these polarization curves.

Experimental Procedures

The measuring cell was divided into three rooms separated from each other by diaphragms of glass filter. A platinum electrode, having an available area of approximately 3.6 cm^2, was placed between two auxiliary platinum electrodes in the middle room.

The change of the potential difference was recorded with an electromagnetic oscillograph (Yokogawa N-3, D-Type) through a suitably set 1-valve amplifier. At the same time the potential scale was given by a potentiometer through the amplifier.

During experiments air and free oxygen were removed from the apparatus by bubbling hydrogen, purified by passing through heated palladium asbestos in a silica tube. The electrode was first anodically polarized to remove adsorbed hydrogen and to give a constant electrode potential, and then a cathodic current was passed. By this procedure, we obtained curves of good reproducibility. As shown in Fig. 1 three main stages in the initial build up of cathodic polarization have been distinguished, corresponding to the ionisation of adsorbed oxygen (stage α), the charging of a double layer (stage β), and the adsorption of hydrogen at the electrode (stage γ) respectively.

The number of sites of the electrode surface covered by discharged hydrogen atoms can be calculated from the quantity of electricity consumed during the stage γ9). The difference in above numbers before and after the addition of organic molecules to the solution shows the

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* This paper was read at the annurl meeting of this society on April, 8. 1953.

1) J. J. O'M. Bockris: *Discuss. Farad. Soc.* No. 1. 95 (1947).

2) J. O'M, Bockris and S, Ignatowicz: *Trans, Farad,* **44**, 519 (1948).

3) J. O'M, Bockris and R, Parsons: ibid. **44**, 860 (1948).

4) Allan Wetterholm: ibid. **45**, 861 (1949).

5) R. Parsons and J.O'M. Bockris: ibid. **47**, 914 (1951).

6) R. Pearson and J. A. V. Butler: *Trans. Farad. Soc.* **34**, 1163 (1938).

7) F.P. Bowden: *Proc. Roy. Soc.* **125A**, 446 (1929).

8) M. Oikawa and T. Mukaibo: *J. Electrochem. Soc., Japan.* **20**, 568 (1952).

9) J. A. V. Butler: "Electrocapillarity." p. 178, (1940).

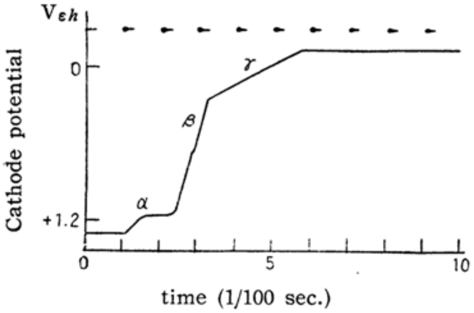

Fig. 1.
Polarization curve of platinum cathode in N. H_2SO_4

number of sites covered by organic molecules.[8] Cathodic current densities were limited between 10^{-3} & 5×10^{-1} A./cm². In this range we can assume that the mechanism of hydrogen electrode reaction belongs to that of the catalytic.[10][11] During the experiments the cell was saturated with pure hydrogen gas, the pressure of which was maintained about one atmosphere.

Results and Discussions

A. Preliminary Experiments. Table I shows the length of stage γ on the smooth platinum electrode in pure N. H_2SO_4 solution. It was found that the length of the stage was almost independent of the current density over the range of $3.0\times10^{-3}\sim1\times10^{-1}$ A./cm².

TABLE I

Cathodic Current Density D.A./cm² $\times10^{-3}$	Stage γ Coul. $\times10^{-3}$	Log D (D,A/cm²)	Electrode Potential V, ε_h
3.2	3.3	−2.49	0.000
5.0	3.3	−2.29	0.015
10.0	3.5	−2.00	0.035
32.0	3.6	−1.49	0.070
100.	3.6	−1.00	0.11

Moreover it was confirmed that the oxygen adsorbed during the anodic polarization was perfectly consumed in the stage α.[8] Though the length of stage α had a wide range of values by the time of duration of the anodic polarization or by the anodic current density, the length of stage γ was almost independent of such conditions, as shown in Table II.

TABLE II

Anodic Polarization (mA.×sec.) /3.6cm²	Cathodic Polarization (A./3.6cm²)	Stage γ (coul.) $\times10^{-3}$
5×30	36.4	3.5
5×60	36.5	3.6
2×30	36.9	3.7
10×20	36.3	3.7
2×20	11.5	3.5
3×30	18.0	3.5

Taking the diameter of a platinum atom as 2.5Å, we calculated the quantity of electricity required to deposit one hydrogen atom on each platinum atom of the electrode surface to be 2.7×10^{-4} coulombs/cm². The same quantity found experimentally by the above mentioned procedure was about 9.7×10^{-4} coulombs per sq. cm. of the apparent surface. This value agrees with the calculated one if we assume the real area of the electrode to be about 3.6 times the apparent area of it. Though there is some uncertainty as to this ratio at the smooth platinum surface, the value 3.6 obtained by us may be reasonable when compared with those estimated by many other authors which lie between 2 and 4[12]. From the values in column 3 and 4 of Table I we get Tafel's constant b of about 0.08.

Then, by adding organic compounds at various concentrations to N. H_2SO_4, we obtained the results shown in Fig. 2 and Fig. 3.

The quantity of electricity consumed in the stage γ is sharply affected by the addition of acetaldehyde; and the larger the concentration of it the smaller becomes the length of the stage.

Fig. 2 shows the relation between the concentration of acetaldehyde in the bulk of the solution and the number of adsorption points covered by molecules of acetaldehyde.

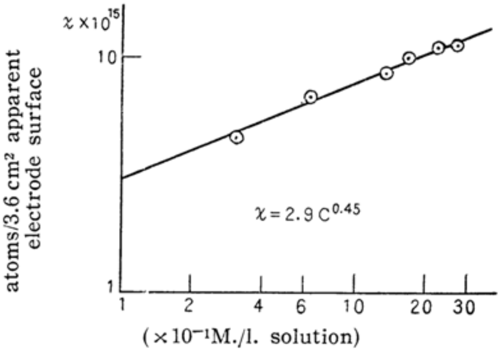

Fig. 2.
Freundlich's adsorption isotherm of the electrode surface (measured at the current density 10mA./cm², 3°C)
x: number of adsorption point covered by acetaldehyde
c: concentration of acetaldehyde (M./l. solution) x and c in log. scale

This figure shows also that the relation fits Freundlich's isotherm very well. The parameters of the equation were determined and are shown also. From Fig. 3 we can see that there exists a parallelism between the adsorption of organic molecules and the electrode potential. This fact suggests to us that the relation between these factors is very important.

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[10] J. O'M. Bockris and A. M. Azzam: *Trans. Farad. Soc.* **48**, 145 (1952).

[11] J. O'M. Bockris: *Chem. Rev.*, 43, 525 (1948).

[12] J. A. V. Butler: "Electrocapillarity" p. 73 (1940).

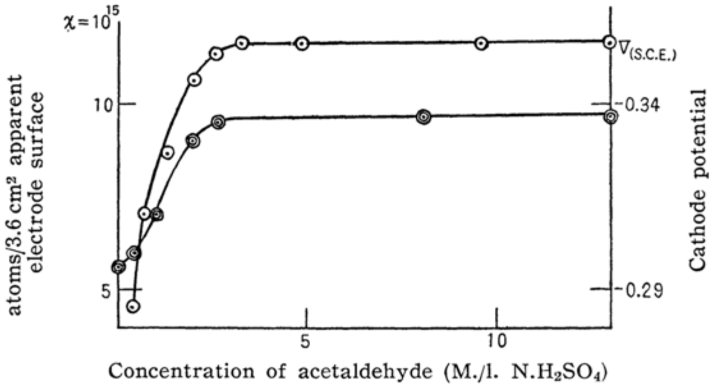

Fig. 3.

The relation between the adsorption of acetaldehyde (⊙) and the cathode potential (◎) (at 3°C)

V: potential in volts referred to the saturated calomel electrode (S.C.E.) the amount of adsorption of acetaldehyde and the electrode potential were all measured at the cathode density 10 mA./cm².

B. Case 1. According to J. O'M. Bockris, an increase of the concentration of an organic compound occurs at the metal-solution interface and this positive adsorption is influenced by several factors, such as the dipole moment of the solute and the properties of the cathode surface. So in the first place we added acetaldehyde to the electrolyte as the organic compound soluble in water and having the dipole moment larger than that of the solvent. Though we feared that acetaldehyde might be reduced at the cathode, it was confirmed by the preliminary experiments that acetaldehyde was not reducible at the platinum cathode in the N. H_2SO_4 solution.[13,14,15]

We measured the hydrogen overpotential on the platinum electrode dipped in the electrolyte containing a different amount of acetaldehyde, under several cathodic current densities.

The results are shown in Table III and Fig. 4.

TABLE III

Composition of Electrolyte	Log D* (D.A./cm²)	Available Area** cm²	Log D'*** (D',A./cm²)	Electrode**** Potential V, ε_h
0.96M. Acetaldehyde/L of N. H_2SO_4	−2.49	1.67	−2.16	0.02
	−2.29	1.94	−2.03	0.03
	−2.00	2.00	−1.70	0.05
	−1.48	2.54	−1.33	0.08
0.48M. Acetaldehyde/L of N. H_2SO_4	−2.49	1.95	−2.23	0.01
	−2.29	2.00	−2.04	0.02
	−2.00	2.25	−1.80	0.04
	−1.67	2.75	−1.56	0.06
	−1.48	3.00	−1.41	0.07

* D: Cathodic current density A./cm² apparent area.

** Cathode area for hydrogen evolution reaction corrected by taking the steric hindrance of organic molecules.

*** D': $(D\times 3.6)$/(available area), 3.6cm²: apparent area of the cathode.

**** Considering the exactness of our data, we took the numerical value of the electrode potential to the order of 10 mV when the electrolyte contained organic molecules.

In column 4, D' is the current density corrected by taking the steric hindrance of acetaldehyde into consideration, that is, it was assumed that the surface points covered by organic molecules did not take part in the discharge of hydrogen ions.

As seen in Fig. 4 and 3, the hydrogen overpotential increases with the increase of the concentration of acetaldehyde in accordance with the results of Wetterholm ($10^{-5}\sim10^{-2}$A./cm²). Tafel's

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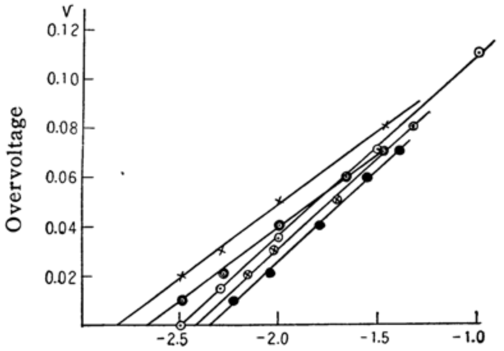
[13] C. J. Brockman: "Electro Organic Chemistry" p. 287 (1926).

[14] V. Stern and S. Polak: *Acta Phsicochim U. R. S. S.* **11**, 797 (1939).

[15] Böttger: "Physik. Methode d. Anal. Chem" Bd. II. p. 295, (1936).

constant *b* changes between 0.06~0.08, but after the correction of the effective cathode area which we supposed would diminish by the adsorption of acetaldehyde, *b* becomes about 0.08, the same value as when there is no addition. Though Tafel's another constant *a* also changes slightly, we may attribute the main effect of acetaldehyde to the steric hindrance of it on the electrode surface.

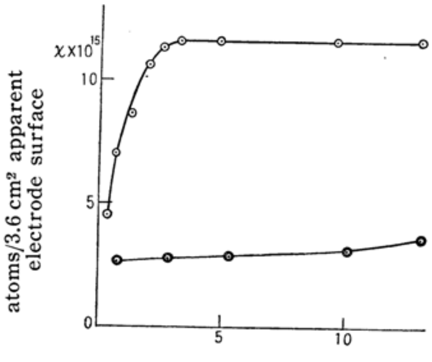


log *D*
Current density (A./cm²)

Fig. 4.
Effect of acetaldehyde on the relation between the cathodic current density and the overpotential (at 3°C)

(⊙) N.H_2SO_4, b=0.08
(×) 0.96M. acetaldehyde/L N.H_2SO_4, b=0.06
(◉) 0.48M. acetaldehyde/L N.H_2SO_4, b=0.06
(⊗) after the correction of the current density (0.96M. acetaldehyde/L N.H_2SO_4) b=0.08
(●) after the correction of the current density (0.48M. acetaldehyde/L N.H_2SO_4) b=0.08

Of course we must take account of the effect of the solute on δ, the thickness of the double layer, or the value of $\Delta H^{\ddagger}$ (the heat of activation of hydrogen evolution) as J. O'M. Bockris mentioned,[5,16] but according to our experiments the chief effect of the solute seemed to be the steric hindrance.



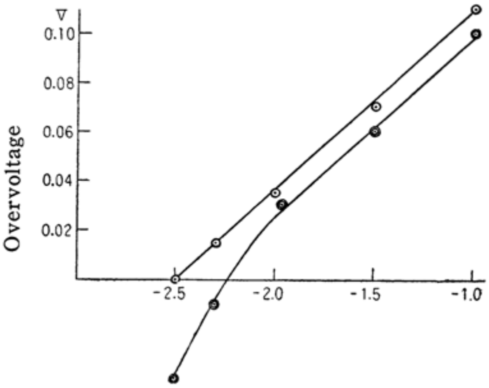
Concentration of acetaldehyde or ethyl alcohol M./l. N.H_2SO_4

Fig. 5.
Relation between the adsorbed amount of organic compounds and their concentration (at 3°C)

(⊙) acetaldehyde M./L N.H_2SO_4
(◉) ethyl alcohol M./L N.H_2SO_4 measured at the current density 10 mA./cm²

C. Case II. Next we examined the effect of the addition of ethyl alcohol as the solute having smaller dipole moment than that of water.

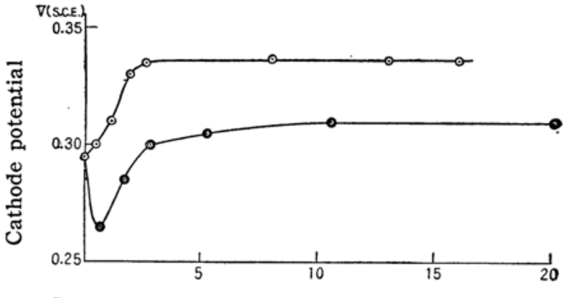
The results are shown in Fig. 5 to Fig. 7. In Fig. 5 we can see that the amount of adsorption of ethyl alcohol is very small as compared with the case of acetaldehyde even in the concentrated solution. In Fig. 6 we showed Tafel's lines in N.H_2SO_4 and in the solution of ethyl alcohol. The relation between the electrode potential and the concentration of ethyl alcohol is shown in Fig. 7.



log *D*
Current density (A./cm²)

Fig. 6.
Tafel's line on N.H_2SO_4 and on the solution of ethyl alcohol (at 3°C)

(⊙) N.H_2SO_4
(◉) ethyl alcohol (1.7M./l.N.H_2SO_4)



Concentration of acetaldehyde or ethyl alcohol M./l.N.H_2SO_4

Fig. 7.
The relation between the cathode potential and the concentration of organic compound (at 3°C)

(⊙) acetaldehyde (◉) ethyl alcohol measured at the cathode density 10 mA./cm²

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16) P. J. Hillson: *Trans. Farad. Soc.* **48**, 462 (1952).

The electrode potential decreases at first, but becomes high with the further increasing concentration of the alcohol. After reaching the value near that in pure N.H_2SO_4, it stays there over a wide range of concentration of ethyl alcohol (5∼35 M. EtoH/1), then decreases slowly at higher concentrations (ca. 35M./1).

In the concentrated solution of ethyl alcohol, we found that the bending point of the polarization curve in the oscillograph showing the saturation of the adsorption of the hydrogen atom disappears. From this fact, we may attribute the reason of the lowering of the potential in the concentrated solution to the existence of some reaction other than pure hydrogen evolution on the cathode surface. From these we may conclude as follows.

The organic molecules having dipole moments smaller than that of water such as ethyl alcohol are adsorbed very poorly on platinum cathode as shown in this experiment, so the change of electrode potential by its steric hindrance may be small.

Accordingly, the change of the electrode potential in this case may be largely due to another factor such as the change of adsorption energy of discharged hydrogen by the addition of ethyl alcohol, as J. O'M. Bockris proposed.[17,18]

Conclusion

The relation between the electrode potential and the adsorption of organic molecules was studied by measuring the adsorption by the oscillograph. We can divide in two types the effects of organic molecules adsorbed to the surface of the cathode, when the evolution of hydrogen is of catalytic mechanism.

Type I. The organic molecule having the dipole moment greater than that of water is strongly adsorbed on the surface of platinum cathode and by its steric hindrance, the cathode potential becomes less noble with the increase of its addition to the solution. On such a type, by correcting current densities as to the cathode area covered by organic molecules, Tafel's constant and also the potential become almost the same as when there is no addition.

Type II. The organic molecule having the dipole moment smaller than that of water is adsorbed only a little on the electrode and the effect of it on the electrode potential seems rather due to the solvent effect than to the steric hindrance, when the size of the molecule is small.

These conclusions may be reasonable in reference to the discussion of former authors, especially to that of J.O'M. Bockris.[1)~3)]

The expenses incured for this work were met by the Grant in Aid for Fundamental Scientific Research, to which our thanks are due.

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[17] J. O'M. Bockris & R. Parsons: *Trans. Farad. Soc.*, **44**, 860 (1948).

[18] R. Parsons & J. O'M. Bockris: ibid **47**, 914 (1951).