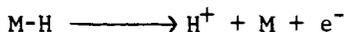


THE USE OF THE POTENTIAL OF THE HYDROGEN ELECTRODE TO DETERMINE
THE MECHANISM OF REDUCTION OF COMPOUNDS

T. C. Franklin, D. H. McClelland, P. E. Hudson, J. Barrett

Chemistry Department, Baylor University, Waco, Texas 76703

If the electron transfer reaction at the hydrogen electrode is



where M is the bare adsorption site and M-H is the adsorbed hydrogen atom exchanging electrons with the metal surface, then the equilibrium potential of the electrode should be given by the expression

$$E = E^0 + \frac{RT}{F} \ln \frac{A_H}{(A_{H^+})A_M}$$

If the activity of the adsorbed hydrogen is represented by θ , then the activity of the bare metal can be represented by $1-\theta$, and at constant hydrogen ion concentration and at 25°C

$$E = E^0 + 0.059 \log \frac{\theta}{1-\theta}$$

The presence of organic or inorganic additives can alter the potential of the hydrogen electrode by changing the hydrogen adsorbed on the electrode. The additive can remove hydrogen by either displacing the hydrogen or reacting with the hydrogen. A study was made of the effect of different additives on the amount of adsorbed hydrogen and the potential of the electrode.

Experimental

The amount of hydrogen adsorbed on the electrode at equilibrium or under steady state conditions was measured by the coulometric method described previously. (1,2) In the case of the platinized platinum electrodes hydrogen was bubbled over the electrodes until a steady potential was attained. The flow of hydrogen was stopped and sufficient time was allowed for equilibrium to be established between the hydrogen dissolved in the solution and that adsorbed on the electrode. The potential of the electrode was then measured potentiometrically against a reference electrode and the adsorbed hydrogen was removed by polarographic oxidation. The area under the polarographic curve was the number of coulombs needed to oxidize the hydrogen adsorbed on the electrode. This procedure was repeated after the addition of various amounts of the additive.

The experiments on nickel and iron were quite similar except that the hydrogen was electrolytically generated on the surface of the nickel since these metals would not adsorb hydrogen from solution.

The platinum electrodes were platinum wires sealed in glass and plated for three minutes in 3% solution of chloroplatinic acid containing a trace of lead acetate. The electrodes were washed with distilled water and aged for several hours in the solvent to be used in the experiment. Just prior to use these electrodes were polarized anodically for several minutes.

The nickel electrodes were prepared by sealing nickel wire in teflon spaghetti. The iron electrodes were made from iron wires previously etched with nitric acid, washed with doubly distilled water and placed directly in the cell for study. The electrodes were oxidized and reduced several times before the experiments were started.

The temperature was maintained at $25^{\circ} \pm 0.1^{\circ}\text{C}$. The p-benzoquinone was purified by sublimation and the acetonitrile was purified by distillation. Other reagents were the purest grade available commercially.

The additives studied were acetonitrile and p-benzoquinone on platinum, 2,7 disodium naphthalenedisulfonate and sodium hypophosphite on nickel, and acetonitrile on iron.

Data and Results

Figure 1 shows a typical current voltage curve obtained for the oxidation of hydrogen on platinized platinum in two normal sulfuric acid. The shaded area was taken as being proportional to the amount of adsorbed hydrogen. Figure 2 shows a similar plot for iron. The nickel curve was similar to this.

It has been previously reported (1) that a linear relationship exists between the logarithm of the amount of adsorbed hydrogen and the potential when acetonitrile was used as an additive and platinized platinum was the electrode. However, the scatter in the data was very large and an accurate slope was not easily obtained. By not bubbling hydrogen over the electrode during the measurement of potential, it is possible to obtain much more precise data. Figure 3 shows the results obtained in two normal sulfuric acid. It can be readily seen that there is a linear relationship between the potential and the logarithm of the fraction of the surface covered with adsorbed hydrogen. (Logarithm of the amount of hydrogen adsorbed with additive minus the logarithm of the amount of adsorbed hydrogen without additive.) The slope of this line is 0.059 volts. Similarly slopes of approximately 0.059 have been obtained with plots of ΔE versus $\log \theta$ when sodium hypophosphite was used as an additive on nickel (Figure 4) and at low hydrogen coverages when acetonitrile was used as an additive on iron (Figure 5).

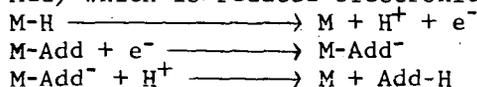
However, if p-benzoquinone is used as an additive in 2N sulfuric acid and platinized platinum is used as the electrode, Figure 6 shows that a plot of ΔE versus $\log \theta$ gives a straight line, but in this case the slope is equal to 0.14. Again if the disodium salt of 2,7 naphthalenedisulfonate is used as an additive in 2N sodium hydroxide solutions with nickel as the electrodes (Figure 7), a plot of the shift in potential against $\log \theta$ gives a straight line with a slope of 0.12.

Discussion of Results

The additives can change the amount of adsorbed hydrogen by blocking the surface sites. This merely changes the value of θ ; equilibrium is reached at a new point; and the potential will shift in accord with $\Delta E = 0.059 \log \frac{\theta}{1-\theta}$ or if θ is small $\Delta E = 0.059 \log \theta$. (1)

The additive can also change the amount of adsorbed hydrogen by reacting with the adsorbed hydrogen. If the reaction occurs directly with the hydrogen atoms, the potential of the hydrogen electrode will

still be calculatable from Equation (I) if the rate of exchange of electrons between adsorbed hydrogen atoms and the electrode is rapid. However, there is a second mechanism of reduction which involves the transfer of an electron from the hydrogen through the metal to the adsorbed additive (M-Add) which is reduced electronically.



In this case the additive behaves like an anodic current and at constant hydrogen ion concentration the shift in potential is given by the equation

$$\Delta E = \frac{RT}{\alpha F} \ln \theta - \frac{RT}{(1-\alpha)F} \ln (1-\theta). \quad (3)$$

At 25°C if α is assumed to be $\frac{1}{2}$ this becomes

$$\Delta E = 0.12 \log \frac{\theta}{1-\theta}.$$

If θ is small compared to one, this equation reduces to

$$\Delta E = 0.12 \log \theta. \quad (II)$$

The decomposition of the hypophosphite ion on the surface of nickel increases the amount of hydrogen on the surface. This increase undoubtedly is influenced by the presence of adsorbed reactants and products. It can be seen (Figure 3) that, in agreement with theory, the change in potential in this situation follows Equation (I).

The effect of acetonitrile on the potential of the platinized platinum hydrogen electrode has been previously attributed to the blocking action of the nitrile. However, it has been shown that, under the conditions of the experiment, acetonitrile is reduced both on platinized platinum (4) and iron (5). Since the shift in potential (Figure 4 and 5) follows Equation (I), it is evident that this reduction occurs by direct addition of adsorbed hydrogen atoms.

The graphs showing the effect of p-benzoquinone on the potential of the platinum-hydrogen electrode and the disodium salt of 2,7 naphthalenedisulfonate on the nickel-hydrogen electrode indicates that this data follows Equation (II). This shows that these compounds are reduced by the electronic mechanism in agreement with the accepted mechanism (6). The reduction of the sulfonate at nickel electrodes has been discussed by several workers (7,8) and it is probable that it is an electronic mechanism.

In summary it has been shown that the shift in potential of a metal-hydrogen electrode upon the addition of an additive can be used to indicate the mechanism of interaction of the additive with the hydrogen. From the observed data it was concluded that acetonitrile is reduced by direct addition of atomic hydrogen on iron and platinized platinum electrodes. It was also concluded that the reduction of p-benzoquinone on platinized platinum and the 2,7 naphthalenedisulfonate ion on nickel proceeds by an electronic mechanism.

We wish to thank the Robert A. Welch Foundation of Houston for their support of this study.

References

1. T. C. Franklin and R. D. Sothern, *J. Phys. Chem.* 58, 951 (1954).
2. T. C. Franklin and S. L. Cooke, Jr., *J. Electrochem Soc.* 107, 556 (1960).
3. S. Glasstone, "An Introduction to Electrochemistry", D. Van Nostrand Company, Inc., New York (1942) 448.
4. B. Foresti and S. Musumeci, *Boll. sedute accad. Givernia sci. nat. Catania* 5, 330 (1949).
5. T. C. Franklin and N. F. Franklin, *Plating* 51, 890 (1964).
6. K. J. Vetter, *Z. Elektrochem* 56, 797 (1952).
7. S. E. Beacom and B. J. Riley, *J. Electrochem Soc.* 108, 758 (1961).
8. H. Gotthard and D. Trivich, *Electrochimica Acta* 1, 369 (1962).

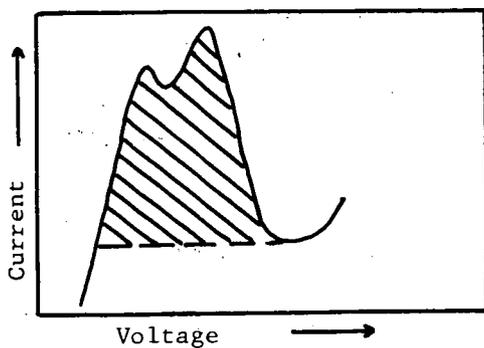


Fig.1. Current Voltage Curve for Oxidation of Hydrogen on Platinum in 2N H₂SO₄

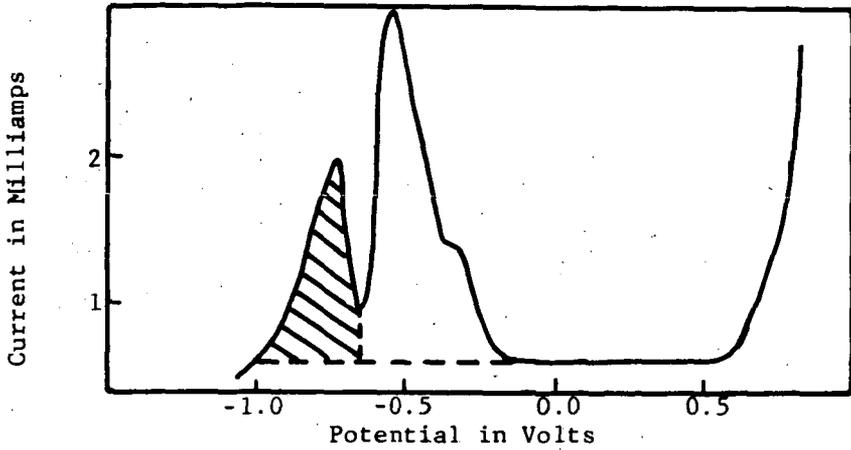


Fig.2. Current Voltage Curve for Oxidation of Hydrogen on Iron in 2N NaOH

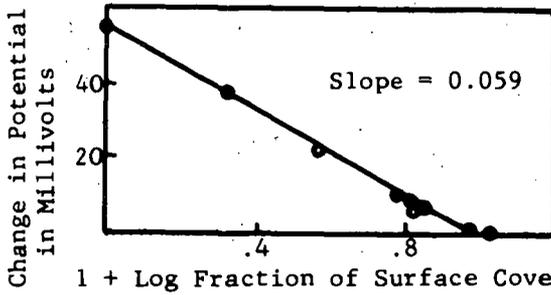


Fig.3. Effect of Acetonitrile on Platinum-Hydrogen Electrode in 2N H_2SO_4

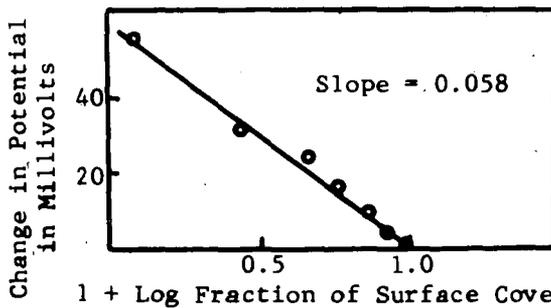


Fig.4. Effect of Sodium Hypophosphite on Nickel-Hydrogen Electrode in 2N NaOH

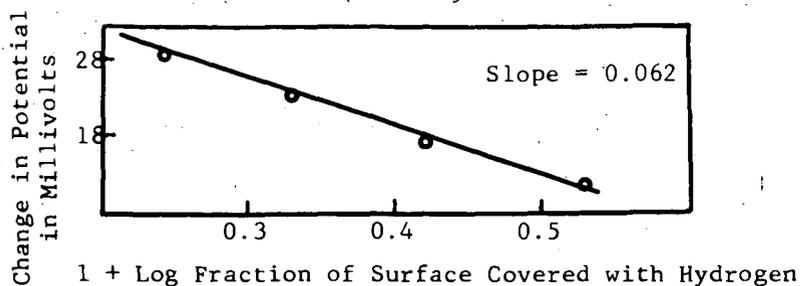


Fig.5. Effect of Acetonitrile on the Iron-Hydrogen Electrode in 2N NaOH

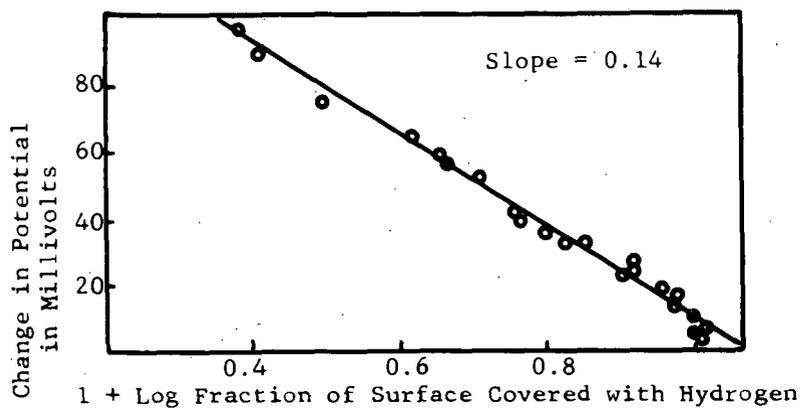


Fig.6. Effect of P-Benzoquinone on the Platinum-Hydrogen Electrode in 2N H_2SO_4

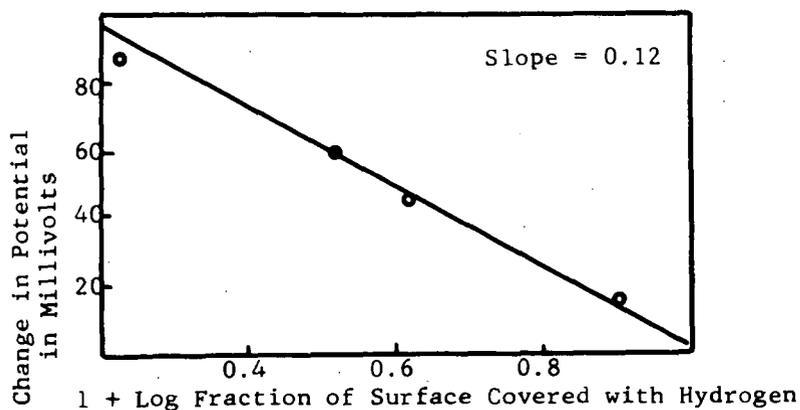


Fig.7. Effect of 2,7 Naphthalenedisulfonate on Nickel-Hydrogen Electrode in 2N NaOH