THE NATURE OF THE POTENTIAL ON A PLATINUM ELECTRODE IN ETHANOL SOLUTIONS

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Translated from Doklady Akademii Nauk SSSR, Vol. 150, No. 2,
pp. 349-352, May, 1963
Original article submitted February 23, 1963

When introduced into a solution in contact with a platinized platinum electrode that has been polarized to potentials of the double layer region, many organic substances produce a displacement of the potential toward more negative values. Ideas on the mechanism whereby potentials arise under these conditions are contradictory [1-5]. Thus, in some work the development of these potentials was related to the orientation of the adsorbed dipoles [1] or to the displacement of the electron shells of the adsorbed molecules toward the metal [2], in other work the displacement of the potential toward negative values was considered an indication of the direct transfer of electrons from the molecule of the organic substance to the electrode [3, 4]. The purpose of our work was the elucidation of the nature of these potentials with ethanol as an example.

The investigation method was as follows. The substance investigated was introduced into an electrolyte solution in contact with a platinized platinum electrode that had been polarized to a given potential and the change in potential with time was measured. After determination of the potential, the solution with the substance investigated was removed and the electrode washed with successive portions of oxygen-free electrolyte solution. The number of washes was such that the form of the charging curve plotted in the last portion of wash solution did not change with an increase in the number of washes; eight washes were usually sufficient to achieve this in practice. The values of the potential relative to a reversible hydrogen electrode in the same solution are denoted φ_r and relative to a normal hydrogen electrode by φ. The C_2H_5OH concentration was 0.5 M in all the experiments given. The true electrode surface was calculated from the length of the hydrogen lag on the charging curve for 0.1 N H_2SO_4 with the assumption that when $\varphi_r = -0.01$ V, there is one adsorbed hydrogen atom per platinum atom on the surface [6], and this was found to be 0.2-0.4 m^2 (with an apparent surface of 2 cm^2).

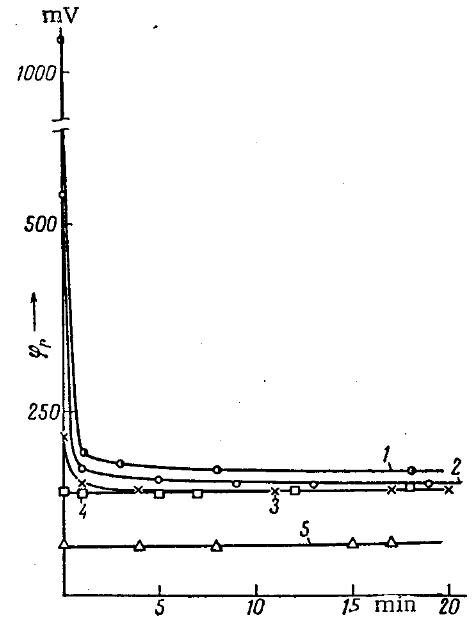

Fig. 1. Relation of the curves of the electrode potential on introduction of ethanol (0.1 N H_2SO_4 + 0.5 M C_2H_5OH) to the original potential: 1) 1045 mv; 2) 540 mv; 3) 215 mv; 4) 140 mv; 5) 65 mv.

As Fig. 1 shows, the shifts in potential on introduction of ethanol into 0.1 N H_2SO_4 are qualitatively similar to the shifts in potential produced by the specific adsorption of Cl^-, Br^-, and I^- anions, which were studied by Obrucheva [7, 8]. However, the mechanisms whereby the potentials we studied arise and those of the adsorption potentials are different. In actual fact:

a) The value of φ_r established after the introduction of C_2H_5OH (Fig. 1) is almost independent of the starting potential when the latter exceeds a certain limit (130 ±5 mV) while the potential established after the introduction of specifically adsorbed ions is shifted toward the positive side with an increase in the potential at which the substance investigated was introduced [8].

b) The value of φ_r established with the introduction of C_2H_5OH is practically independent of the solution pH

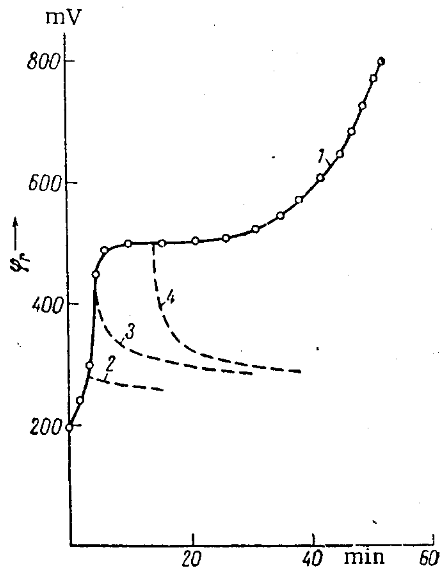

Fig. 2. Charging curve for 0.1 N H_2SO_4 with ethanol adsorbed on the platinum surface (1) and shift in potential on disconnection of anode polarization at different points on this curve (2, 3, 4). Current density $1 \cdot 10^{-4}$ A/cm^2 of apparent surface.

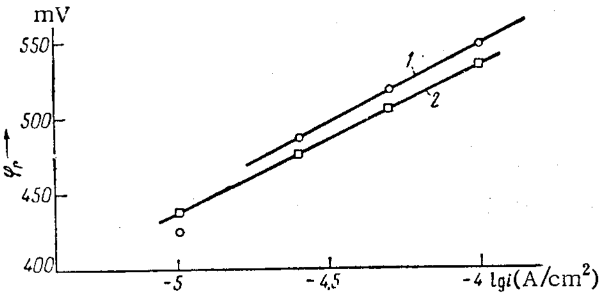

Fig. 3. Relation of the oxidation potential of adsorbed ethanol to current density: 1) 1 N H_2SO_4 (pH 0.37); 2) acidified 1 N K_2SO_4 (pH 2.6).

(Table 1) and this cannot be explained on the assumption that the potential established has an adsorption nature.

c) The polarization curves indicated oxidation of the alcohol in the potential region where a fall is observed [4].

d) The charging curve for 0.1 N H_2SO_4 measured after washing of the electrode (Fig. 2, 1) has a characteristic plateau which corresponds to oxidation of the ethanol layer firmly adsorbed on the platinum surface. Switching off the polarization before or after the formation of the plateau on the charging curve of $Pt(C_2H_5OH)_{ads}$ is accompanied by a shift in φ_r to 260-290 mV (Fig. 2, 2, 3, and 4). In other words, the potential returns to values close to those which are observed after washing of the electrode before the start of anode polarization (190-210 mV).

The lack of dependence of the potential established on the starting value and its return to values close to the initial ones after the interruption of anode polarization indicate that this potential is maintained by some oxidation–reduction system of the adsorbed substance and solution components. Adsorbed hydrogen, whose presence was also detected by means of the initial section of the charging curve of $Pt(C_2H_5OH)_{ads}$ (Fig. 2), evidently must be of fundamental importance in the determination of the potential.* As a result of the high exchange current of the reaction [9]:

$$H_{ads} \rightleftarrows H^+ + e \qquad (1)$$

or

$$H_{ads} + OH^- \rightleftarrows H_2O + e^- \qquad (1a)$$

in comparison with the rate of oxidation of C_2H_5OH, which is very low at the steady potential established, the latter must be close to the equilibrium potential of reaction (1) (in acid solutions) and (1a) (in alkaline solutions).

The appearance of H atoms on the platinum surface may be explained differently, depending on the oxidation mechanism assumed for the adsorbed alcohol. It may be assumed that the transfer of electrons from C_2H_5OH molecules to the metal displaces the potential toward negative values until it passes into the hydrogen region and H atoms appear on the surface as a result of reaction (1) or (1a). However, it is possible that the adsorption process itself leads to the elimination of H atoms with the formation of a dehydrogenation product.

The relation of the rate of oxidation of the adsorbed alcohol to the solution pH was investigated in order to elucidate the mechanism by which the steady potential is established. Figure 3 gives the relation of φ_r of the plateau on the charging curve of $Pt(C_2H_5OH)_{ads}$ to the logarithm of the current density in 1 N H_2SO_4 (pH 0.37) and in acidified 1 N K_2SO_4 (pH 2.6).† The discrepancy between values of φ_r for the oxidation of adsorbed alcohol at the same current density, within the range of densities measured, did not exceed 15 mV, while the corresponding difference in the value of φ was 128 (± 15) mV. As the shift in potential on introduction of C_2H_5OH is related to the oxidation of the latter,

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*A similar opinion on the potential established in the presence of methanol was put forward previously by other authors [5].

†Only 4-5 points were plotted over a narrow range of current densities (10^{-4}-10^{-5} a/cm^2 of apparent surface) so that not more than 10-15% of the adsorbed ethanol would be oxidized during plotting of the polarization curve.

TABLE 1

Base electrolyte	pH	Potential at which C_2H_5OH was introduced (φ_r), mV	Final value of φ_r, mV
1N H_2SO_4	0,37	508	158
0,1N H_2SO_4	1,26	503	156
0,3N (KH_2PO_4 + KOH)	5,3	504	157
	8,0	499	162
	11,0	507	158
0,1 N KOH	13,0	500	145

the curve of the potential change must reflect the kinetics of the alcohol oxidation. The curves of the shift in φ_r on introduction of C_2H_5OH into 1 N H_2SO_4 and into acidified 1 N K_2SO_4 agree with an accuracy up to 3 mV over the whole time interval measured (the experimental technique did not allow measurement of the potential shift within the first 30-40 sec. after introduction of the alcohol). Polarization curves were not plotted for solutions of phosphates and KOH as the lags corresponding to oxidation of the adsorbed ethanol were small on the charging curves of $Pt(C_2H_5OH)_{ads}$ in these solutions. However, as investigation showed, the oxidation of adsorbed C_2H_5OH in solutions with different pH values and the same current density (10^{-4} A/cm^2 of apparent surface) started at relatively similar values of φ_r: 0.1 N H_2SO_4 (pH 1.26) 505 mV; phosphate buffers 0.3 N (KH_2PO_4 + KOH) (pH 5.3; pH 8.0) 545, 547 mV (respectively); 0.1 N KOH (pH 13.0) 0.510 mV. The phosphate anions evidently inhibited the oxidation of $C_2H_5OH_{ads}$ somewhat.

Thus, the equation corresponding to the slow transfer of an electron from an alcohol molecule to the electrode [4]: $i = k[C_2H_5OH]_s \exp(\beta F\varphi/RT)$, where $[C_2H_5OH]_s$ is the surface alcohol concentration, does not hold in the case of adsorbed ethanol as with a change in pH, the current remained approximately constant at constant φ_r, and not at constant φ.* The hypothesis that $C_2H_5O^-_{ads}$ is the particle discharged slowly and $i = k[C_2H_5O^-]_s \exp(\beta F\varphi/RT)$ also does not explain the observed relation of $\underline{i}$ to pH when $\beta \neq 1$ (see below) and, furthermore, it is improbable in the case of acid and neutral solutions because of the low value of K_A of alcohol (pK_A 15.9) [10].

The experimental data obtained may be explained by assuming that the dehydrogenation of the adsorbed alcohol is the slow stage in its oxidation,† for example, according to the scheme:

$$\begin{gathered} C_2H_5OH_{ads} \xrightarrow{\text{slow}} CH_3\dot{C}HOH_{ads}{}^{‡} + H_{ads} \\ H_{ads} \xrightarrow{\text{fast}} H^+ + e^-. \end{gathered} \tag{2}$$

Taking into account the fact that the energy of the hydrogen bond changes with filling of the electrode surface [12], let us assume that some sections with the highest bond energy are also filled at values of φ_r at which alcohol oxidation occurs, and that the kinetics of dehydrogenation are determined by the maximum bond energy on the sections remaining unfilled. Then, as follows from the kinetics of a reaction on heterogeneous surfaces [12, 13] we may assume: $i = k_1 f([C_2H_5OH]_s) \exp(-\beta\mu_H/RT)$, where μ_H is the chemical potential of adsorbed atomic hydrogen, $f([C_2H_5OH]_s)$ some function of the surface concentration of adsorbed ethanol,** and k_1 and β are constants. As $\mu_H = -F\varphi_r$ + const, hence it follows:

$$i = kf([C_2H_5OH]_s)\exp(\beta F\varphi_r/RT). \tag{3}$$

Thus, the relation of the rate to the electrode potential (3), which is usually considered characteristic of a reaction with electron transfer, may be also obtained for a reaction with the abstraction of an atom (2) if the chemical potential of this atom in the final state is determined by the electrode potential. However, other variations of the mechanism of $C_2H_5OH_{ads}$ oxidation are possible over the range of potentials of 0.3-0.6 V. For example, one may assume that the oxidation proceeds through the adsorbed oxygen or OH radicals, which are present on the platinum surface in small amounts even at these potentials and whose bond energy falls with a rise in filling. In this case $\underline{i}$ is

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*Like subsequent conclusions this conclusion is more correct in the case of acid solutions; as with a change in pH in the latter the value $[C_2H_5OH]_s \simeq$ const and the specific effect of various anions is excluded and this is not the case in phosphate buffer solutions and KOH solution.

†The hypothesis that the primary act in the electrooxidation of alcohols is the elimination of H_{ads}, had been put forward previously, for example, by Justi [14], but with insufficient experimental proof.

‡ According to data on the radiolysis of ethanol [11], the formation of the radical $CH_3\dot{C}HOH$ is more probable than for the formation of the radical $CH_3CH_2\dot{O}$.

**The relation of $\underline{i}$ to the concentration of adsorbed ethanol will be examined in another paper.

proportional to exp $(\beta' \mu_{OH}/RT)$ and $\mu_{OH} = F\varphi_r +$ constant and we again arrive at Eq. (3).* As the steady potential lies within the hydrogen region scheme (2) appears to describe more accurately the process whereby it is established.

The value of the coefficient β, calculated from the slope of the curves of φ against log i (Fig. 3), varied from 0.5 to 0.65, depending on the electrode activity, the direction of the change in the current, and the composition of the electrolyte in acid solutions (1 N H_2SO_4, 0.1 N H_2SO_4, and acidified 1 N K_2SO_4).

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*This hypothesis is applicable only in cases with a low degree of filling of the surface with oxygen as a high degree of filling leads to inhibition of the oxidation of organic substances.