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# Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

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# On the Nature of the Potentials of a Platinum Electrode Arising in Ethanol Solutions

Many organic substances, when introduced into a solution in contact with a platinized platinum electrode polarized to potentials of the double-layer region, cause a shift of the potential toward more negative values. Ideas concerning the mechanism by which the potentials arising under these conditions are established are contradictory ([1]-[5]). Thus, in some works the appearance of these potentials was associated with the orientation of adsorbed dipoles ([1]) or with a displacement of the electron shells of adsorbed molecules toward the metal ([2]); in others it was assumed that the shift of the potential in the negative direction serves as evidence of direct transfer of electrons from molecules of the organic substance to the electrode ([3], [4]). The aim of our work was to clarify the nature of these potentials using ethanol as an example.

The method of investigation used was as follows. The substance under study was introduced into the electrolyte solution washing the platinized platinum electrode, polarized to a specified potential, and the change in potential with time was measured. After the potential had been established, the solution containing the substance under study was drained off and the electrode was washed with a series of successive portions of electrolyte solution free of oxygen. The number of washings was determined by the condition that the form of the charging curve recorded in the last washing portion no longer changed when the number of washings was increased; in practice, eight washings were usually sufficient for this. Potential values measured relative to the reversible hydrogen electrode in the same solution are denoted by $\varphi_r$, and relative to the normal hydrogen electrode by $\varphi$. The concentration of $C_2H_5OH$ in all the experiments cited was $0.5\,M$. The magnitude of the true surface of the electrode, calculated from the length of the hydrogen hold-up region of the charging curve in $0.1\,N$ $H_2SO_4$ on the assumption that at $\varphi_r = -0.01$ V there is one atom of adsorbed hydrogen per platinum atom located on the surface ([6]), was 0.2-0.4 $m^2$ (with a visible surface of 2 $cm^2$).

Fig. 1. Dependence of the electrode-potential shift curves upon introduction of

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ethanol ($0.1\,N$ $H_2SO_4 + 0.5\,M$ $C_2H_5OH$) on the initial potential: 1 −1045 mV; 2 −540 mV; 3 −215 mV; 4 −140 mV; 5 −65 mV.

As can be seen from Fig. 1, the potential shifts upon introduction of ethanol into $0.1\,N$ $H_2SO_4$ are qualitatively similar to the potential shifts caused by the specific adsorption of the anions $Cl^-$, $Br^-$, and $J^-$, which were studied by Obruche–

···water ([7],[8]). However, the mechanism by which the potentials we have studied are established differs from that of adsorption potentials. Indeed:

a) the value of $\varphi_r$ established after the introduction of $C_2H_5OH$ (Fig. 1) is almost independent of the initial potential, so long as the latter exceeds a certain limit ($130 \pm 5$ mV), whereas the potential established upon introduction of specifically adsorbing ions shifts in the positive direction as the potential at which the substance under study was introduced is increased ([8]);

**Table 1**

| Background electrolyte | pH | Potential of introduction of $C_2H_5OH$ ($\varphi_r$), mV | Final value $\varphi_r$, 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 |
| $0.3N$ ($KH_2PO_4$+ KOH) | 8.0 | 499 | 162 |
| $0.1N$ KOH | 11.0 | 507 | 158 |
| $0.1N$ KOH | 13.0 | 500 | 145 |

b) the value of $\varphi_r$ established upon introduction of $C_2H_5OH$ is practically independent of the pH of the solution (Table 1), which cannot be explained by assuming an adsorption character of the potential being established;

c) the polarization curves indicate oxidation of the alcohol in the potential region in which a decay is observed ([4]);

d) on the charging curve in $0.1N$ $H_2SO_4$, measured after washing the electrode (Fig. 2, 1), there is a characteristic plateau corresponding to the oxidation of a layer of ethanol strongly adsorbed on the platinum surface. Switching off the polarization before or after reaching the plateau of the charging curve of $Pt(C_2H_5OH)_{ads}$ is accompanied by a shift of $\varphi_r$ to 260–290 mV (Fig. 2, 2, 3, and 4). In other words, the potential returns to values close to those observed after washing the electrode before the onset of anodic polarization (190–210 mV).

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Figure 2

Figure 2: Figure 2

The independence of the established potential from the initial value and its return after interruption of anodic polarization to values close to the initial one show that this potential is maintained by some oxidation-reduction system consisting of the adsorbed substance and solution components. The principal significance for determining the potential must evidently belong to adsorbed hydrogen*, the presence of which is also revealed by the initial portion of the charging curve of $Pt(C_2H_5OH)_{ads}$ (Fig. 2). Because of the large exchange current of the reaction (9):

$$H_{ads} \rightleftarrows H^+ + e \tag{1}$$

or

$$H_{ads} + OH^- \rightleftarrows H_2O + e^- \tag{1a}$$

as compared with the rate of oxidation of $C_2H_5OH$, which at the establishing stationary potential is very small, the latter must be is close to the equilibrium potential of reaction (1) (in acidic solutions) or (1a) (in alkaline solutions).

**Fig. 2.** Charging curve in $0.1N$ $H_2SO_4$ in the presence of adsorbed ethanol on the platinum surface (1) and the displacement of the potential when anodic polarization is switched off at different points of this curve (2, 3, 4). Current density—$1 \cdot 10^{-4}$ A/cm$^2$ of visible surface.

The appearance of H atoms on the platinum surface can be explained in different ways, depending on assumptions concerning the mechanism of oxidation of the adsorbed alcohol. It may be assumed that transfer of electrons from $C_2H_5OH$ molecules to the metal shifts the potential in the negative direction until it enters the hydrogen region and H atoms appear on the surface as a result of reactions (1) or (1a). It is possible, however, that the adsorption process itself leads to the splitting off of H atoms with formation of a dehydrogenation product.

In order to elucidate the mechanism by which the stationary potential is established, a study was made of the dependence of the oxidation rate of the adsorbed alcohol on the pH of the solution. Fig. 3 presents the dependence of the potential $\varphi_r$ of the plateau on the charging curve of $Pt(C_2H_5OH)_{ads}$ on the logarithm of the current density in $1N$ $H_2SO_4$ (pH 0.37) and in acidified $1N$ $K_2SO_4$ (pH 2.6)*. The discrepancy between the values of $\varphi_r$ for oxidation of the adsorbed

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* A similar view of the potential established in the presence of methanol had previously been expressed by other authors (5).

Fig. 3. Dependence of the oxidation potential of adsorbed ethanol on current density: 1 –1 N H2SO4 (pH 0.37); 2 –acidified 1 N K2SO4 (pH 2.6)

Figure 3: Fig. 3. Dependence of the oxidation potential of adsorbed ethanol on current density: 1 –1 N H2SO4 (pH 0.37); 2 –acidified 1 N K2SO4 (pH 2.6)

alcohol at the same current density in the measured range of densities does not exceed 15 mV, whereas the difference in the values of $\varphi$ is respectively 128(±15) mV. Since the shift of the potential upon addition of $C_2H_5OH$ is associated with its oxidation, the curve of the change in potential should reflect the kinetics of alcohol oxidation. The curves of the shift of $\varphi_r$ upon addition of $C_2H_5OH$ in $1N$ $H_2SO_4$ and in acidified $1N$ $K_2SO_4$ coincide to within 3 mV over the entire measured time interval (the experimental technique did not permit measurement of the potential displacement in the first 30-40 sec after introduction of the alcohol). In view of the small magnitude of the delays corresponding to oxidation of adsorbed ethanol, charging curves of $Pt(C_2H_5OH)_{ads}$ in solutions of phosphoric-acid salts and in KOH were not recorded. However, as the investigation showed, oxidation of adsorbed $C_2H_5OH$ in solutions with different pH at one current density ($10^{-4}$ A/cm$^2$ of visible surface) begins at comparatively close values of $\varphi_r$: $0.1N$ $H_2SO_4$ (pH 1.26) 505 mV; phosphate buffers $0.3N$ $(KH_2PO_4 + KOH)$ (pH 5.3; pH 8.0) 545; 547 mV (respectively); $0.1N$ KOH (pH 13.0) 0.510 mV. Apparently, the anions of phosphoric acid somewhat inhibit the oxidation process of $C_2H_5OH_{ads}$.

**Fig. 3.** Dependence of the oxidation potential of adsorbed ethanol on current density: 1 –$1N$ $H_2SO_4$ (pH 0.37); 2 –acidified $1N$ $K_2SO_4$ (pH 2.6)

Thus, the equation corresponding to the slow donation of an electron by 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 concentration of alcohol, is not fulfilled for adsorbed ethanol, since with a change in pH there is approximate constancy of the current at constant $\varphi_r$, and not at constant $\varphi$**. The assumption according to which the slowly discharging particle is $C_2H_5O^-_{ads}$ and $i = k[C_2H_5O^-]_s \exp(\beta F \varphi / RT)$ also does not explain the observed dependence—dependence of $i$ on pH at $\beta \neq 1$ (see below); moreover, in the case of acidic and neutral solutions it is unlikely because of the low value of $K_A$ of the alcohol ($pK_A$ 15.9) (10).

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* Only 4-5 points were recorded in a narrow range of current densities ($10^{-4}$-$10^{-5}$ A/cm$^2$ of visible surface), so that during recording of the polarization curve no more than 10-15% of the adsorbed ethanol was oxidized.

** This conclusion, like the subsequent ones, is more rigorous with respect to acidic solutions, since in them, with a change in pH, the quantity $[C_2H_5OH]_s \simeq$ const and the effect of the specific action of different anions is excluded, which is not the case on going to phosphate buffer solutions and to KOH solution.

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

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

Taking into account that the bonding energy of hydrogen changes with the filling of the electrode surface $^{(12)}$, let us assume that some areas with the greatest bonding energy are filled at the values of $\varphi_r$ at which oxidation of the alcohol occurs, and that the kinetics of dehydrogenation is determined by the maximum bonding energy on the areas that remain unfilled. Then, as follows from the kinetics of reactions on heterogeneous surfaces $^{(12,13)}$, one may write: $i = k_1 f([|C_2H_5OH|_s) \exp(-\beta\mu_H/RT)$, where $\mu_H$ is the chemical potential of adsorbed atomic hydrogen, $f([|C_2H_5OH|_s)$ is a certain function of the surface concentration of adsorbed ethanol***, and $k_1$ and $\beta$ are constants. Since $\mu_H = -F\varphi_r + \text{const}$, it follows that:

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

Thus, the dependence of the rate on the electrode potential (3), which is usually considered characteristic of a reaction with electron transfer, can also be obtained for a reaction involving the detachment of an atom (2), if the chemical potential of this atom in the final state is determined by the electrode potential. However, other variants of the mechanism of oxidation of $C_2H_5OH_{\text{ads}}$ in the potential range 0.3-0.6 V are also possible. For example, one may assume that oxidation proceeds through adsorbed oxygen or OH radicals, which are already present on the platinum surface in small amounts at these potentials and whose bonding energy decreases with increasing coverage. In this case $i$ is proportional to $\exp(\beta'\mu_{\text{OH}}/RT)$, and $\mu_{\text{OH}} = F\varphi_r + \text{const}$, and we again arrive at equation (3)****. Since the stationary potential lies in the hydrogen region, scheme (2) is evidently more applicable to the process of its establishment.

The value of the coefficient $\beta$, calculated from the slope of the $\varphi - \lg i$ curves (Fig. 3), depending on the activity of the electrode, the direction of change of the current value, and the composition of the electrolyte in acidic solutions ($1N$ $H_2SO_4$, $0.1N$ $H_2SO_4$, acidified with $1N$ $K_2SO_4$), ranged from 0.5 to 0.65.

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[*] The notion that the primary act in the electrooxidation of alcohols is the detachment of $H_{ads}$ has also been expressed earlier, for example by Justi (14), but without sufficiently precise experimental evidence.

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

[***] The dependence of $i$ on the concentration of adsorbed ethanol will be considered in another paper.

[****] This assumption is applicable only in the case of small coverages of the surface by oxygen, since large coverages, as is known, lead to inhibition of the oxidation of organic substances.

*Note: Figure translations are in progress. See original paper for figures.*

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