# THE EFFECT OF THE pH OF THE SOLUTION ON THE STATE OF THE SURFACE OF A RHODIUM ELECTRODE IN AQUEOUS KCl SOLUTIONS

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A method was proposed in [1, 2] for potentiometric titrations with a constant total surface charge which makes it possible to carry out detailed studies of the adsorption properties of the platinum metals at different pH values. In the present work this method has been applied to the rhodium electrode in 0.1 N KCl.

The method is based on the determination of (a) the dependence of the potential on the pH of the solution under isoelectric conditions, (b) the equilibrium charging curve [3] in a solution with any one pH value, and (c) the dependence of the value of the adsorption of hydrogen ions $\Gamma_{H^+}$ on the pH of the solution at a reversible hydrogen potential [4, 5]. Then the equation

$$(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}} = (\partial\varphi_r/\partial\mu_{H^+})_Q (\partial Q/\partial\varphi_r)_{\mu_{H^+}}, \quad (1)$$

where $\varphi_r$ is the potential according to the reversible hydrogen electrode in the same solution, $\mu_{H^+}$ is the chemical potential of the hydrogen ions, and Q is the total charge on the surface [6], is used to calculate the dependence of $(\partial\Gamma_{H^+}/\partial\varphi_r)\,\mu_{H^+}$ on $\varphi_r$. Equation (1) is applicable to solutions with an excess of salt, and we have $\Gamma_{H^+} = \varepsilon$ [6], where $\varepsilon$ is the charge (free charge) on the metallic portion of the double layer. Integration of the $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}$ versus $\varphi_r$ curves yields $\Delta\Gamma_{H^+}$ versus $\varphi_r$ dependences. The values of $\Gamma_{H^+}$ for $\varphi_r = 0$ found according to [4, 5] are used to make the transition from $\Delta\Gamma_{H^+}$ versus $\varphi_r$ to $\Gamma_{H^+}$ versus $\varphi_r$ curves.

The working electrode was prepared by rhodium plating of a platinum grid according to the method in [7] and had a true surface of $\sim 5$ m$^2$. The true surface was determined from the hydrogen region of the charging curve under the assumption that the adsorption of hydrogen per 1 cm$^2$ of rhodium surface equals 220 $\mu$C/cm$^2$ [8]. The experiments were carried out at 25 ± 0.1°C. The 0.1 N KCl solutions, which were acidified with HCl or alkalinized with KOH, contained $10^{-3}$ N $H_3PO_4$ in order to achieve the best reversibility of the titration results [1, 2].

Figure 1 shows the dependences of the electrode potential on the pH under isoelectric conditions. Practically complete reversibility of the $\varphi_r$ versus pH curve can be achieved over the entire pH range. The establishment of the equilibrium values of the potentials in the $\varphi_r$ = 0.3-0.5 region and at pH > 4 requires 4-5 h following a pH change of 0.5-1. In the other $\varphi_r$ and pH regions this time is less than 1h. From Fig. 1 it is seen that, in contrast to the data for 1 N KCl, on rhodium in 0.1 N KCl there is no true double-layer potential region. The minimum covering of the rhodium surface by hydrogen and oxygen at pH 3-7 is observed in the $\varphi_r$ = 0.3-0.5 V region.

Charging curves in solutions with pH values ranging from 2.1 to 11.7 were constructed from the equilibrium charging curves in a 0.1 N KCl solution acidified by HCl to pH 2.1 and the isoelectric potential shifts. Then Eq. (1) was used to calculate the $\Gamma_{H^+}$ versus $\varphi_r$ curves presented in Fig. 2. The $\Gamma_{H^+}$ values obtained in [5] at $\varphi_r = 0$ in 0.1 N NaCl, which were corrected for the value of the $\Gamma_{H^+}$ difference at $\varphi = 0$ in 0.1 N $K_2SO_4$ and 0.1 N $Na_2SO_4$, served as the $\Gamma_{H^+}$ values at $\varphi_r = 0$ for 0.1 N KCl. The correction amounted to $\sim 0.5$ $\mu$C/cm$^2$. The dependences of $\Gamma_{H^+}$ on $\varphi_r$ at the corresponding pH values are similar in shape to those previously found in [3, 7] for 1 N KCl with additions of 0.01 N HCl and 0.01 N KOH.

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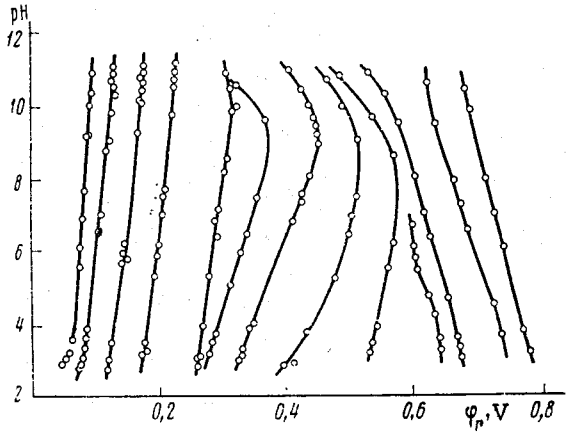


Fig. 1. Dependence of the potentials of the rhodium electrode on the pH at a constant total surface charge in 0.1 N KCl.

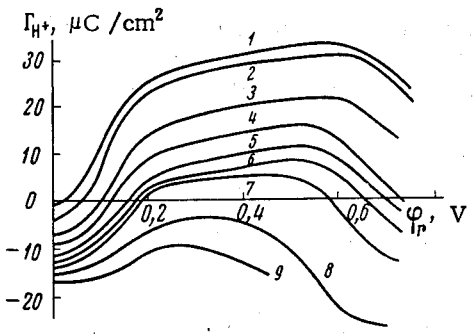


Fig. 2

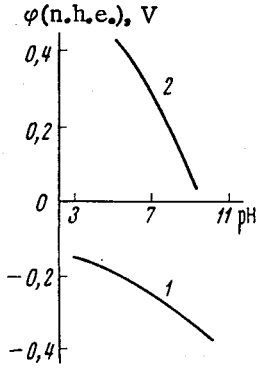


Fig. 3

Fig. 2. Plots of the free charge on the surface of the rhodium electrode as a function of the potential in 0.1 N KCl at various pH values: 1) 3; 2) 4; 3) 5; 4) 6; 5) 7; 6) 8; 7) 9; 8) 10; 9) 11.

Fig. 3. Plots of the potentials of zero free charge of the rhodium electrode as a function of the pH in 0.1 N KCl: 1) Usual potential of zero free charge; 2) inverted potential of zero free charge.

From Fig. 2 it is seen that the values of $\Gamma_{H^+}$ decrease with increasing pH over the entire range of $\varphi_r$ values. This law applies to all the platinum metals [2, 3, 9, 10]. The displacement of the range of potentials in which the measurements are carried out in the negative direction and the stronger overlapping of the regions for the adsorption of hydrogen and oxygen with increasing pH should be taken into account in interpreting this law. In addition it is necessary to assume that the hydrated surface oxide groups have a weakly acidic character and split off hydrogen ions in alkali media as they adsorb cations.

The presence of two potentials of zero free charge in a certain pH range is the most interesting feature of the system studied, and a shift in each of them with the pH can be observed. One of the potentials of zero free charge corresponds to the reduced rhodium, and the other corresponds to oxidized rhodium. The possibility of the appearance of two potentials of zero free charge on the platinum metals already followed from the data in [11, 12] and was confirmed in [13]. Two potentials of zero free charge were discovered in the case of iridium in 1 N KI + 0.01 N KOH [10]. Only the potential of zero free charge lying on the region for the adsorption of oxygen was found in the case of Ru [9], since the potential of zero free charge of reduced Ru corresponds to the potentials for the evolution of molecular hydrogen. When the potential is shifted in the anodic direction, the sign of the charge on the surface of the oxidized electrode changes from plus to minus $[(\partial \varepsilon / \partial \varphi_r)\mu_{H^+} < 0]$. Therefore, the potential of zero free charge of the oxidized electrode may be termed the inverted potential of zero free charge.

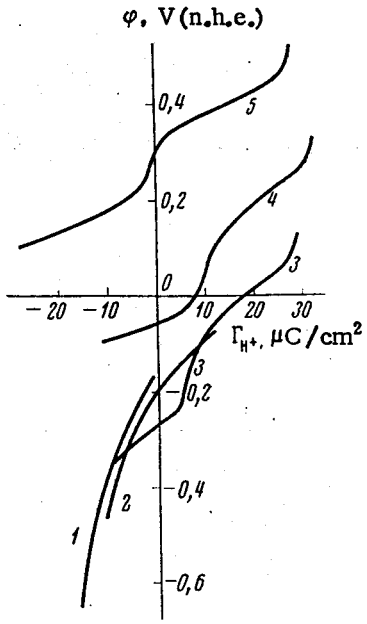


Fig. 4. Charging curves of the second kind on the rhodium electrode in 0.1 N KCl at various $\varphi_r$ values: 1) 0; 2) 0.1; 3) 0.3; 4) 0.5; 5) 0.7 V.

Figure 3 presents plots of the potential of zero free charge of the rhodium electrode as a function of the pH in 0.1 N KCl. As the pH is increased, both potentials of zero free charge are shifted in the negative direction. The shift in the potential of zero free charge of the reduced electrode resulting from a pH change of one unit is 13-30 mV in the pH 3-7 range and 43 mV in the pH > 7 range. The shift in the inverted potential of zero free charge of rhodium in the pH 6-9 range is 80-140 mV for every pH unit. In [10] a shift of ~120 mV for every pH unit was found for the inverted potential of zero free charge of iridium in potassium iodide solutions. In [14] it was also noted that the pH dependence of the constant charge potential is more strongly expressed on the descending portion of the $\Gamma_H$* versus $\varphi_r$ curve of platinum and rhodium than on the ascending portion.

The difference between the shifts in the usual and inverted potentials of zero free charge calls for a special discussion. For this purpose, we shall take advantage of the same relationship as in [2], viz.,

$$(\partial\varphi/\partial\mu_{H^+})_{\varepsilon=0}=[1-(\partial\varepsilon/\partial A_H)_{\varphi_r}]^{-1}, \qquad (2)$$

where $\varphi$ is the potential according to a constant reference electrode and $A_H$ is the amount of hydrogen adsorbed per cm$^2$ of surface. In the region for the adsorption of oxygen $A_O$, which is the amount of adsorbed oxygen (in electrostatic units) per cm$^2$ of surface, should be substituted in place of $A_H$. We thus obtain

$$(\partial\varphi/\partial\mu_{H^+})_{\varepsilon=0}=[1+(\partial\varepsilon/\partial A_O)_{\varphi_r}]^{-1}. \qquad (3)$$

The shift of the inverted potential of zero free charge in the negative direction with increasing pH means that $(\partial\varepsilon/\partial A_O)\varphi_r > -1$. This condition is analogous to the shift of the usual potential of zero free charge in the negative direction with increasing pH, i.e., $(\partial\varepsilon/\partial A_H)\varphi_r < 1$. The shift of the inverted potential of zero free charge amounts to more than 59 mV for every unit of pH. This suggests that the inequality $-1 < (\partial\varepsilon/\partial A_O)\varphi_r < 0$ is fulfilled. The observed shifts of the potential of zero free charge in the negative direction imply that $(\partial\varepsilon/\partial A_H)\varphi_r < 0$.

The strong shift in the inverted potential of zero free charge with changes in the pH indicates that the changes in the structure of the electrical double layer due to the adsorption of oxygen are greater than those observed during the adsorption of hydrogen. This may be due to the comparatively high polarity of the bond between oxygen and the surface of platinum metals, as well as to the significant effect of adsorbed oxygen on the capacitance of the double layer. According to [14] we have

$$(\partial\varphi/\partial\mu_{H^+})_\varepsilon=-\frac{X}{X+Y}[1+(\partial\mu_{H^+}/\partial\varphi_r)_Q], \qquad (4)$$

where $X = (\partial\varphi/\partial A_H)_\varepsilon = -(\partial\varphi/\partial A_O)_\varepsilon$ is the contribution of an adsorbed hydrogen or oxygen atom, and $Y = (\partial\varphi/\partial\varepsilon)A_H = (\partial\varphi/\partial\varepsilon)A_O$ is the contribution of an ion in the double layer with the respective charge on the metal to the potential jump.* From Eq. (4) we find that in the region of the inverted potential of zero free charge the value of

*Since Eq. (4) expresses the dependence of $\varphi$ on $\mu_{H^+}$ in a differential form, to obtain a relation for $(\partial\varphi/\partial\mu_{H^+})_\varepsilon$ only with the quantities X and Y is impossible, and the derivatives of X and Y with respect to $\mu_{H^+}$ and $\varphi_r$ inevitably appear. Thus, for $(\partial\varphi_r/\partial\mu_{H^+})_Q$ we have

$$(\partial\varphi_r/\partial\mu_{H^+})_Q=\frac{(\partial X/\partial\mu_{H^+})_Q-(\partial X/\partial\mu_{H^+})_{\varphi_r}}{(\partial X/\partial\varphi_r)_{\mu_{H^+}}}=\frac{(\partial Y/\partial\mu_{H^+})_Q-(\partial Y/\partial\mu_{H^+})_{\varphi_r}}{(\partial Y/\partial\varphi_r)_{\mu_{H^+}}}.$$

Therefore, the shift in $\varphi_{\varepsilon=0}$ with the pH depends not only on X and Y, but also on their variation with the potential and the pH.

the ratio X/Y lies in the −0.45 to −0.19 range. At the same time, in the vicinity of the usual potential of zero free charge, the value of X/Y is approximately −0.1. This calculation confirms the conclusion that adsorbed oxygen has a stronger influence on the structure of the electrode–solution interface.

The potential of zero total charge of rhodium in 0.1 N KCl was not determined. It may be assumed that it is close to the potential of zero total charge of rhodium in 1 N KCl [7]. According to Fig. 1, in this case the dependence of the potential of zero total charge on the pH should be the same as for the platinum electrode in 0.1 N KCl [2] and the rhodium electrode in 0.1 N $Na_2SO_4$ [15].

Figure 4 presents charging curves of the second kind [1, 2].* As on the platinum electrode [2], these curves have a simpler shape than the usual charging curves, especially at low $\varphi_r$ values. In the region corresponding to the adsorption of oxygen the course of the curves becomes more complicated indicating the more substantial changes in the amount of adsorbed oxygen with changes in the pH under the condition $\varphi_r$ = const than those observed in the case of the adsorption of hydrogen.

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*An error was allowed in the production of Fig. 3 in [2]: The curves were not displaced along the y axis. The qualitative conclusions drawn in the text in [2] in the discussion of the charging curves of the second kind, however, remain in force.