INFLUENCE OF pH OF SOLUTION ON THE STATE OF SURFACE OF A PLATINIZED PLATINUM ELECTRODE

Academician A. N. Frumkin, O. A. Petrii, and T. Ya. Kolotyrkina-Safonova

UDC 541.138

The dependence of the state of the surface on the pH of solutions is related to a number of fundamental characteristic features of metals which adsorb hydrogen and oxygen. This dependence was first observed in the case of a platinized platinum (Pt/Pt) electrode in [1, 2]. Because of the experimental difficulties during the measurements in the region of medium pH, further studies were carried out mainly in acidic and alkaline solutions [3-6]. We developed the method of potentiometric titration at a constant full-surface charge [7] so that it is possible to study in detail the influence of pH on the structure of the surface layer, including that in the region of medium pH, which was previously inaccessible to experimental investigation.

In the present work, the results given were obtained by this method for the Pt/Pt electrode in 0.1 N KCl. The method of measurements and preparation of electrodes are described in [7]. The titration was carried out with solutions containing 10^{-3} N H_3PO_4, which makes it possible to attain a good reversibility of the titration results [7]. The measurements showed that the charging curves in solutions of 0.1 N KCl + 10^{-2} N HCl and 0.1 N KCl + 10^{-2} N HCl + 10^{-3} N H_3PO_4 completely coincide. Thus, it can be assumed that the addition of 10^{-3} N H_3PO_4 has no influence on the results, since the adsorbability of the Cl^- ions is higher than that of phosphate anions [3]. The potentials with reference to a reversible hydrogen electrode in this solution are designated by φ_r. The actual surface of the electrode was determined from the hydrogen region of the charging curve in 1 N H_2SO_4. The experiments were carried out at 20±0.1°C.

Figure 1 shows the dependences of the potential of the Pt/Pt electrode on pH of the solution under isoelectric conditions with gradual increase (black circles on Fig. 1), and subsequent gradual decrease (light circles) in pH. Over the whole pH range a good reversibility of φ_r vs pH curves could be attained. It should be noted that the time necessary for the establishment of the equilibrium values of the potential during change in pH increases with increase in φ_r, and depends on the value of pH. Thus, in the hydrogen region, when the pH is changed by 0.5-1 unit, the equilibrium values of φ_r are established after almost 10 to 15 min, while in the case of the double layer and the oxygen regions, in the pH range of 6-10 not less than 1 to 2 h are required. According to [5, 9], the change in φ_r is ~58 mV during a change in pH of one unit, which characterizes the real double-layer region of the Pt/Pt electrode. According to the data of Fig. 1, the differential isoelectric shifts in the potential $(\partial\varphi_r/\partial\mu_{H^+})_Q$, where μ_{H^+} is the chemical potential of hydrogen ions and Q is the full surface charge [8], were calculated. For solutions at pH 2.3 and 12, these shifts were found to be close to those obtained previously by the method of isoelectric shifts of the potential [5, 9].

From the charging curve in an acidified 0.1 N KCl solution at pH 2.3, and from the data in Fig. 1, charging curves were plotted corresponding to other pH values of the solution. The charging curve at pH 12, plotted from the charging curve at pH 2.3 and the φ_r vs pH curve, practically coincided with the experimental curve, which is an additional confirmation of the correctness of the measurements and calculations made.

From the slope of the charging curves and the corresponding isoelectric shifts in the potential, the dependences of the Gibbs adsorption of hydrogen ions Γ_{H^+} on φ_r in solutions at different pH were calculated from the equation [5, 9]:

M. V. Lomonosov Moscow State University. Translated from Doklady Akademii Nauk SSSR, Vol. 222, No. 5, pp. 1159-1162, June, 1975. Original article submitted March 18, 1975.

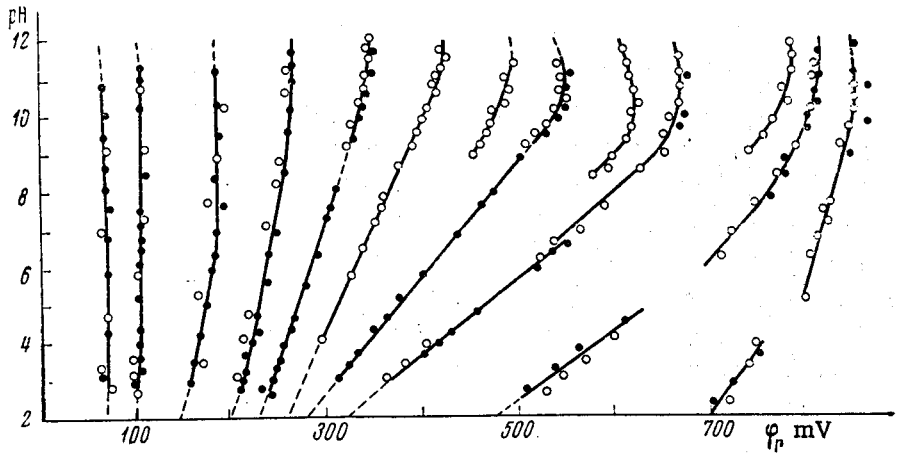

Fig. 1. Dependence of Pt/Pt electrode potentials on pH at a constant full-surface charge in 0.1 N KCl.

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

Relationship (1) holds for systems with excess of the salt. In the absence of charge transfer during the adsorption of solution ions, the value of Γ_{H^+} can be compared to the free surface charge ε [8]. In the compilation of the Γ_{H^+} vs φ_r dependence in the integral form, the Γ_{H^+} values at $\varphi_r = 0$ were used as the integration constants. They were obtained by the method of potentiometric titration with a large indicating electrode [10].

Figure 2 shows the Γ_{H^+} vs φ_r dependences for solutions at different pH. The curves for solutions at pH 2.3 and 12 are similar to those obtained previously in [5, 9] for 1 N KCl. To explain the transfer to the surface, negatively charged over the total φ_r range, observed with increase in pH, the simultaneous action of two factors must be taken into account. Firstly, with increase in pH, the potential range over which the measurements are made is shifted with respect to the constant reference electrode to the negative side which, in principle, should lead to an increase in the negative charge at constant φ_r, and hence, to an increase in the adsorption of cations. Secondly, with increase in pH, the removal of the adsorbed hydrogen is hindered, and deposition of oxygen is facilitated. It can be assumed that the hydrated oxide groups which thus appear on the surface have a weakly acidic character and split a hydrogen ion in alkaline solutions [3, 5]. As a result, an adsorption of cations in the form of $PtOK^-$ becomes possible, which leads to desorption of anions from the platinum surface. Thus, in alkaline solutions a transition is observed from the adsorption of cations, caused by the ionization of the adsorbed hydrogen atoms, and decreasing with increase in φ_r, to the adsorption of cations by the oxide groups on the surface, which increases in a certain range of φ_r. As a result, for example, at pH 10, over a relatively large φ_r range, conditions arise when the Pt surface practically carries no free charge. The presence of a plateau on the Γ_{H^+} vs φ_r curve in acidic solutions, and a Γ_{H^+} minimum in alkaline solutions in the hydrogen region of φ_r, is probably due to a decrease in the capacitance of the electric double layer with the filling of the surface with H_{ads}, and also by the participation in the formation of a potential jump of hydrogen dipoles, aligned with their positive ends toward the solution [3, 5].

From the data given in Fig. 2, charging curves of the second kind [7] were plotted, i.e., dependences of the free charge on the potential at φ_r = const (Fig. 3). These curves have a simpler form than the usual charging curves corresponding to the condition μ_{H^+} = const, since at φ_r = const, the changes in the amounts of hydrogen and oxygen adsorbed are relatively small. Dependence of the slope of the second kind of curves on the φ_r is due to the transition with increase in φ_r from the cation adsorption region to the anion adsorption region. By integrating the usual charging curves, electrocapillary curves of the first kind were obtained, while by integrating the charging curves of the second kind electrocapillary curves of the second kind [11] were obtained. It was thus possible to construct the surface of the reversible surface work of the Pt electrode. The last is a paraboloid in form and is cut by μ_{H^+} = const planes to form cross sections corresponding to the electrocapillary curves of the first kind, while cross sections formed by the φ_r = const planes correspond to the electrocapillary curves of the second kind.

Figure 4 shows the dependence of the potentials of the zero full $\varphi_{Q=0}$ and the zero free $\varphi_{\varepsilon=0}$ charges on the pH of the solution. Curve 1 was obtained directly by carrying out the titration with a Pt/Pt electrode, whose

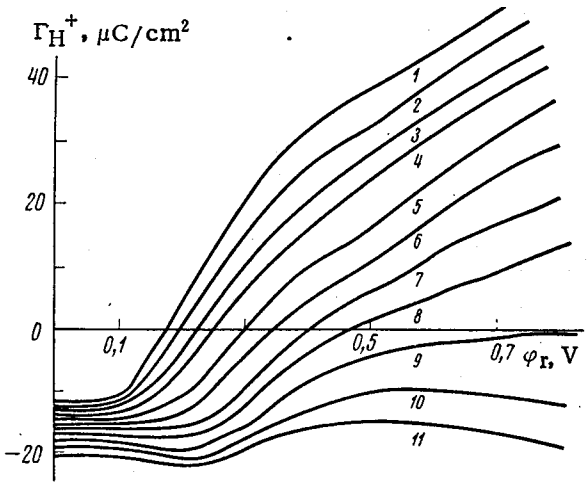

Fig. 2. Dependence of the free surface charge of the Pt/Pt electrode on the potential in 0.1 N KCl at different pH: 1) 2.3; 2) 3; 3) 4; 4) 5; 5) 6; 6) 7; 7) 8; 8) 9; 9) 10; 10) 11; 11) 12.

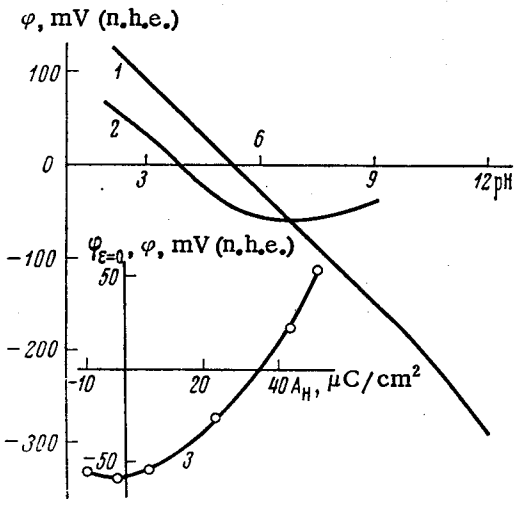

Fig. 4. Dependences of the potentials of zero full (1) and zero free (2) charges on the pH of the solution, and also the dependence of the potential of the zero free charge on the amount of adsorbed hydrogen (3) on a Pt/Pt electrode in 0.1 N KCl.

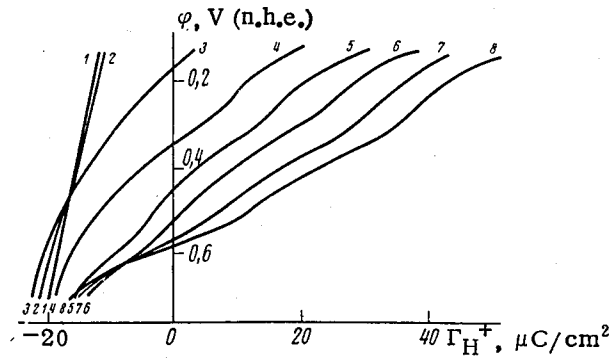

Fig. 3. Charging curves of the second kind on a Pt/Pt electrode in 0.1 N KCl at different φ_r: 1) 0; 2) 100; 3) 200; 4) 300; 5) 400; 6) 500; 7) 600; 8) 700 mV.

potential was stabilized at $\varphi_{Q=0}$. Curve 2 was plotted from the results of calculation, shown in Fig. 2. The dependence of $\varphi_{Q=0}$ on pH is linear with a slope of ~40-45 mV in the pH range 2.3-10, and with a slope of ~55 mV in the pH range of 10-12. According to the thermodynamic theory [5]

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

where A_H is the amount of H_{ads} per cm² of the surface. The $\varphi_{Q=0}$ vs pH dependence found shows that at pH < 10, $(\partial\varepsilon/\partial A_H)_{\mu H^+} < 0$, i.e., the free charge increases when φ_r is shifted to the positive side. At pH > 10, $(\partial\varepsilon/\partial A_H)_{\mu H^+} \simeq 0$, which corresponds to a relatively slight dependence of ε on φ_r in alkaline solutions (see Fig. 2).

With increase in pH, the potential $\varphi_{\varepsilon=0}$ is shifted in the pH-range of 2.3-5 to the cathode side by ~35 mV, when the pH is changed by one unit, which corresponds to the data in [5]. In the pH range of 5 to 9, the shift in $\varphi_{\varepsilon=0}$ is small. At pH > 7, $\varphi_{\varepsilon=0}$ begins to be shifted with increase in pH to the positive side. The complex course of the $\varphi_{\varepsilon=0}$ vs pH curve is due to the fact that $\varphi_{\varepsilon=0}$ is shifted from the hydrogen region to the double-layer region, and then to the region of deposition of the adsorbed oxygen. For the dependence $\varphi_{\varepsilon=0}$ vs pH, we obtain [5]

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

whence it is seen that the shift in $\varphi_{\varepsilon=0}$ with increase in pH to the positive side corresponds to $(\partial\varepsilon/\partial A_H)_{\varphi r} < 0$. At $A_H = 0$, $(\partial\varphi/\partial\mu_{H^+})_{\varepsilon=0} = 0$, and at $(\partial\varepsilon/\partial A_H)_{\varphi r} > 1$, the shift in $\varphi_{\varepsilon=0}$ to the positive side can take place.

At pH ≃ 7, $\varphi_{Q=0} = \varphi_{\varepsilon=0}$. In this case, $\varphi_{Q=0}$ and $\varphi_{\varepsilon=0}$ are in the double-layer region of the Pt electrode, i.e., in the region of its ideal polarizability, at which Q = ε.

From the data obtained, the dependence of $\varphi_{\varepsilon=0}$ of Pt vs A_H was plotted (Fig. 4, curve 3) and $\varphi_{\varepsilon=0}$ at A_H = 0 was found, i.e., for a Pt surface free from hydrogen and oxygen. The latter was found to be equal to −0.06 V (with reference to the n.h.e.) according to an approximate evaluation [12]. The negative values of A_H in Fig. 4 correspond to the adsorption of oxygen. Thus, $\varphi_{\varepsilon=0}$ of a hydrogen- and oxygen-free Pt is only 0.2-0.3 V more positive than $\varphi_{\varepsilon=0}$ of mercury. The value of the difference $\varphi_{\varepsilon=0,\,Pt}-\varphi_{\varepsilon=0,\,Hg}$ does not correlate with the well-known relationship between the work function and $\varphi_{\varepsilon=0}$ [13], since the difference between the work functions of

Pt and Hg is 0.9-1.0 V [14]. The problem of the possible reasons for this deviation requires further study. It is possible that this is due to the difference in the structure of the adsorbed water layer on Pt and Hg, and to the difference between the structure of the surface of the Pt crystallites, subjected to anodic-cathodic activation, and that of Pt treated at high temperatures in an ultravacuum before measurement of the work function.

LITERATURE CITED

1. A. Frumkin and A. Shlygin, Izv. Akad. Nauk SSSR, Otd. Matem. i Estestv. Nauk, Ser. Khim., 773 (1936); Acta Physicochim. URSS, 5, 819 (1936).
2. A. Shlygin (Slygin), A. Frumkin, and V. Medvedoskii (Medvedovsky), Acta Physicochim. URSS, 4, 911 (1936).
3. A. Frumkin, N. Balashova, and V. Kazarinov, J. Electrochem. Soc., 113, 1011 (1966).
4. N. A. Balashova, N. T. Gorokhova, and M. I. Kulezneva, Élektrokhimiya, 4, 871 (1968).
5. O. A. Petrii, A. N. Frumkin, and Yu. G. Kotlov, Élektrokhimiya, 4, 774 (1968); 5, 476, 735 (1969); 6, 725 (1970).
6. A. Frumkin and O. Petrii, Electrochim. Acta., 15, 391 (1970).
7. A. N. Frumkin, O. A. Petrii, and T. Ya. Kolotyrkina, Élektrokhimiya, 10, 1741 (1974).
8. A. N. Frumkin, O. A. Petrii, and B. B. Damaskin, Élektrokhimiya, 6, 614 (1970).
9. O. A. Petrii, R. V. Marvet, and A. N. Frumkin, Élektrokhimiya, 3, 116 (1967).
10. R. Notoya, O. A. Petrii, et al., Élektrokhimiya, 8, 904 (1972).
11. A. N. Frumkin and O. A. Petrii, Dokl. Akad. Nauk SSSR, 196, 1387 (1971).
12. A. Frumkin and O. Petrii, Élektrochim. Acta, 20 (1975).
13. A. Frumkin and A. Gorodetskaya (Gorodetzkaya), Z. Phys. Chem., 136, 215 (1928); A. Frumkin, Svensk. Kem. Tidsk., 77, 300 (1965); A. Frumkin, B. Damaskin, et al., Électrochim. Acta, 19, 75 (1974).
14. L. A. Larin, F. G. Voronina, and T. V. Kalish, Abstracts of Lectures at the Fifth All-Union Conference on Electrochemistry [in Russian], Vol. 1, Moscow (1975), p. 225.