DETERMINING THE ADSORPTION OF IONS ON PLATINUM BY THE METHOD OF ADSORPTION POTENTIALS

I. ADSORPTION OF Br^- FROM ACID SOLUTIONS

O. A. Petrii and Yu. G. Kotlov

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Obrucheva [1, 2] suggested the "Method of adsorption potentials" for studying the adsorption of ions on platinum. The essence of this method is to determine the potential shift of an insulated electrode when specifically adsorbed ions are added to the solution. The quantitative theory of adsorption potential shifts was developed in [3, 4, 6].

In this paper we give our results on the adsorption of Br^- ions from a solution of 0.01 N HBr + 1 N H_2SO_4 on to a Pt/Pt electrode; we measured this by the method of adsorption potential shifts.

As shown in [3], in this case the adsorption potential shift is related to the adsorption of surface-active ions by the equation

$$\left(\frac{\partial\varphi_r}{\partial\mu_i}\right)_{\Gamma_H} = \left(\frac{\partial\Gamma_i}{\partial\varphi_r}\right)_{\mu_i} : \left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_i}, \tag{1}$$

where φ_r is the electrode potential, measured relative to a reversible hydrogen electrode in the same solution, and μ_i, Γ_i, and Γ_H are the chemical potential and the surface densities of the surface-active ions and of atomic hydrogen in the Gibbs sense. The values of Γ and μ are expressed in electrical units.

From the experimental values of $(\partial\Gamma_H/\partial\varphi_r)_{\mu_{Br^-}}$ and $(\partial\varphi_r/\partial\mu_{Br^-})_{\Gamma_H}$, Eq. (1) enables us to calculate how Γ_{Br^-} depends on φ_r. The latter, in turn, can be found by an independent experimental method. On comparing the experimental graph of Γ_{Br^-} versus φ_r with that predicted by (1), we can verify the applicability of the thermodynamic theory of adsorption potential shifts to the system under investigation.

The experimental method was described in [1, 2, 5]. The experiments were performed with platinized-platinum electrodes at room temperature (20±1°C). Before an experiment, the working electrodes were cathodically polarized in alkali. The HBr solutions were subjected to prolonged cathodic purification on a Pt/Pt electrode. The apparent surface areas of the working electrodes were 20 and 60 cm^2; the true areas were found from the length of the hydrogen section of the charging curve [7]. The values found were: 2.1 m^2 for the first electrode and 4.2-5 m^2 for the second. The second electrode was used only for direct adsorption measurements. As in [5], a correction was made for the change in the electrode surface area during the work.

The experimental values of Γ_{Br^-} were determined from the changes in the Br^- concentration during the formation of the electrical double layer by a method similar to that used in [8] to determine the adsorption of hydrogen ions. As the initial potential for these measurements we used the reversible hydrogen potential in the same solution; the electrode (60 cm^2) was then brought to the chosen potential. Since there were then changes in the solution composition (due to transport phenomena and changes in the surface charge), after stabilization of the potential the solution in the working part of the cell was repeatedly changed on open circuit for 0.01 N HBr + 1 N H_2SO_4. The electrode was then saturated with hydrogen and the change in Br^- concentration, due to the difference between the surface charges for the initial value of φ_r and for $\varphi_r = 0$, found. To determine Γ_{Br^-} at $\varphi_r = 0$, the Pt/Pt electrode, carefully washed with double-distilled water, dried in air, and saturated with hydrogen, was brought into contact with a solution of 0.01 N HBr + 1 N H_2SO_4 saturated with hydrogen at atmospheric pressure, and the change in solution composition, due to the formation of an electrical double layer at reversible hydrogen potential, was recorded.

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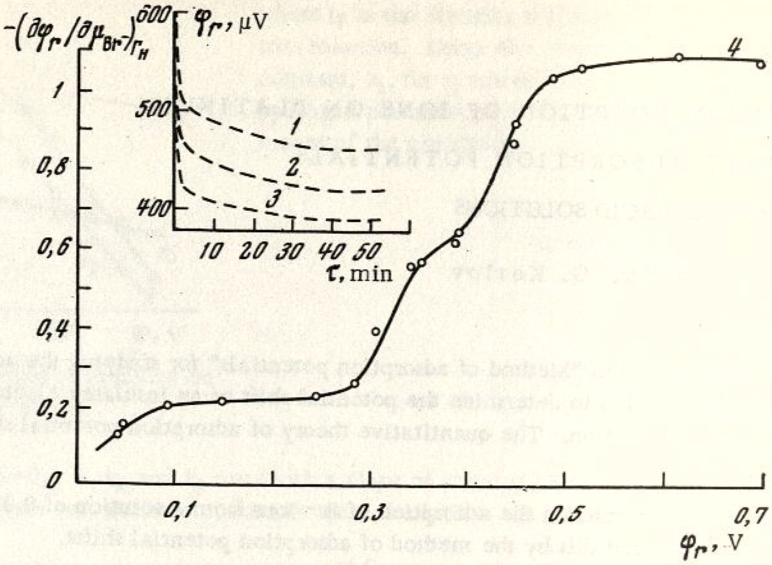

Fig. 1. Time dependence of potential when Br^- concentration was changed (from 0.001 N HBr + 1.009 N H_2SO_4 to 0.1 N HBr + 0.91 N H_2SO_4), for various initial potentials [1-3]. Graph of isoelectric potential shifts versus φ_r (4).

The change in Br^- concentration was determined by titrating the test solution with $AgNO_3$ solution with eosin as indicator by the method of Fajans [9]. The solution for titration was prepared from anhydrous $AgNO_3$; the titer of the $AgNO_3$ solution was periodically measured against KBr. During the experiments we did not detect any change in this titer.

We found $(\partial\varphi_r/\partial\mu_{Br^-})\Gamma_H$ as a function of φ_r by changing the 0.001 N HBr + 1.009 N H_2SO_4 solution for a solution of 0.1 N HBr + 0.91 N H_2SO_4.

During stabilization at φ_r < 300-400 mV, the potential relatively rapidly became steady, both in the initial solution and when the HBr concentration was altered. When φ_r was 300-600 mV, a longer time was required to establish the potentials; the higher φ_r, the longer the time (when φ_r = 0.6 V, 10-12 h were required). Figure 1 curves 1-3, plots the potential shifts for changes in the bromine-ion concentration in this region. We see from this figure that after the solution was replaced by one of greater Br^- concentration, the potential became steady after 45-50 min. This phenomenon shows that in the presence of Br^- ions, adsorption equilibrium on Pt/Pt is reached slowly.

Curve 4 in Fig. 1 plots $(\partial\varphi_r/\partial\mu_{Br^-})\Gamma_H$ versus φ_r. At small values of φ_r, $(\partial\varphi_r/\partial\mu_{Br^-})\Gamma_H$ is nearly zero. According to Eq. (1), this means that in this case $(\partial\Gamma_{Br^-}/\partial\varphi_r)_{\mu_{Br^-}}$ tends to zero. This is apparently due to a decrease in Br^- adsorption at $\varphi_r \to 0$. At 500-700 mV, $(\partial\varphi_r/\partial\mu_{Br^-}) \simeq -1$; in other words, the electrode potential changes by 58 mV when the bromine-ion potential changes by an order of magnitude, i.e., the Pt/Pt electrode behaves like a reversible bromine electrode. Similar shifts are also observed when the Br^- ion concentration is changed in a narrower range (0.005 N HBr + 1 N H_2SO_4 was replaced by 0.02 N HBr + 1 N H_2SO_4). These results indicate that there is no Esin-Markov effect on platinum in solutions of Br^- ions. In fact, according to Frumkin et al.[3], Eq. (1) can be rewritten as follows:

$$\left(\frac{\partial\varphi_r}{\partial\mu_{Br^-}}\right)_{\Gamma_H} = \left[\left(\frac{\partial A_H}{\partial\Gamma_{Br^-}}\right)_{\mu_{Br^-}} - 1 + \left(\frac{\partial\Gamma_{C^+}}{\partial\Gamma_{Br^-}}\right)_{\mu_{Br^-}}\right]^{-1}, \tag{2}$$

where A_H is the quantity of hydrogen adsorbed by 1 cm^2 of surface, expressed in electrical units, and Γ_{C^+} is the Gibbs adsorption of cations.

When φ_r = 500-700 mV, in the presence of Br^-, $A_H = 0$; then $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} = 0$ and $\Gamma_H = -\varepsilon$, where ε is the double-layer charge. In this case the equation $(\partial\varphi_r/\partial\mu_{Br^-})\Gamma_H = -1$ means that $(\partial\Gamma_{C^+}/\partial\Gamma_{Br^-}) = 0$, i.e., the Esin-Markov effect is absent.

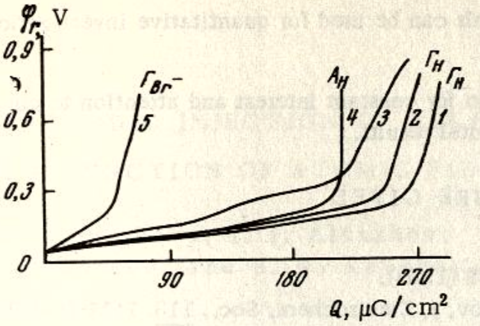

Fig. 2

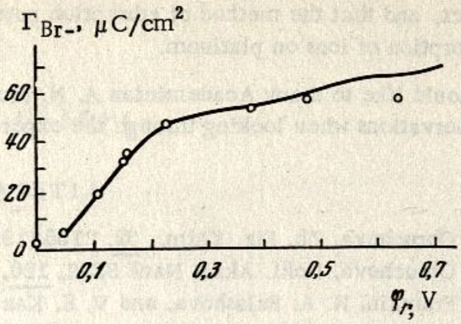

Fig. 3

Fig. 2. Charging curves on Pt/Pt electrode in 0.01 N HBr + 1 N H_2SO_4 (1 and 2) and in 1 N H_2SO_4 (3) (curve 1 recorded in equilibrium conditions), and curves of quantities of adsorbed hydrogen (4) and Br^- ions (5) versus φ_r.

Fig. 3. Curve of φ_r dependence of Br^- ion adsorption. The curve is calculated from (1); the points are experimental data.

Frumkin et al. [6] established the absence of the Esin-Markov effect on platinum in the presence of Cl^- ions with the aid of straight lines of measurements, and explained it by supposing that the charges of specifically adsorbed ions are transferred to the platinum surface. This assumption clearly also applies to the chemisorption of Br^- ions. It must be admitted that our values for the potential shifts accompanying changes in the Br^- ion concentration are different from the adsorption shifts observed by Obrucheva [1]. According to her, for φ_r in the double-layer region, $(\partial \varphi_r/\partial \mu_{i^-})_{\Gamma_H} \approx -2$. As noted by Frumkin et al. [3], this result is inconsistent with Eq. (2) and with data which shows that hyperequivalent adsorption of ions on platinum is negligible. In [3] the hypothesis was proposed that the high values of $(\partial\varphi_r/\partial\mu_{i^-})_{\Gamma_H}$ might be due to the fact that adsorption equilibrium is not reached in more dilute solutions. Our present work supports this hypothesis.

The charging curves on Pt/Pt in 0.01 N HBr + 1 N H_2SO_4, measured by the usual method, are quite reversible; however, to approach the conditions of an experiment in which a given potential is maintained for a long time, we measured the equilibrium charging curve by the method of [6]. As we see from Fig. 2, the equilibrium charging curve is somewhat longer than the usual charging curve; this is apparently due to the slow adsorption of bromine ions. This process is evidently unconnected with the presence of adsorbed oxygen on the electrode.

In Fig. 3 the Γ_{Br^-} and φ_r curves given by (1) are compared with experimental values found by titrating the solution. As constant of integration we used the value of Γ_{Br^-} for $\varphi_r = 0.12$ V. We see that theory and experiment agree up to $\varphi_r \cong 550$ mV. The shape of the (Γ_{Br}, φ_r) curve found by us coincides with that for 10^{-3}N HBr + 10^{-3}N H_2SO_4. described in [10]. When $\varphi_r > 550$ mV we note a certain discrepancy between the experimental and theoretical values of Γ_{Br^-}. Perhaps at these values the hypothesis of reversibility is no longer fully applicable.

In Fig. 2 we show the φ_r dependence of the quantity of hydrogen adsorbed by the electrode, A_H, calculated from the equation $Q = \Gamma_{Br^-} - A_H$. On the (A_H, φ_r) curve there is a vertical section corresponding to $A_H = 0$. At these potentials, electricity transferred to the electrode is expended only on changing the free surface charge.

The curve of equilibrium differential capacitance C_-, due to addition of anions to the electrical double layer, was found from (1) and is plotted in Fig. 4. At double-layer potentials in 10^{-2}N HBr + 1 N H_2SO_4, the capacitance is ~ 40 μF/cm². As φ_r decreases, the (C, φ_r) curve passes through a maximum with a height of 450 μF/cm². These high capacitance values are evidently due to displacement of anions by adsorbed hydrogen dipoles [6] with their negative ends towards the solution.

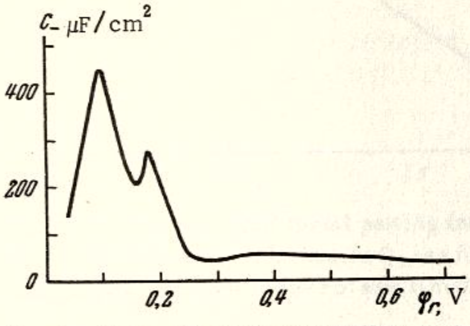

Fig. 4. Curve of equilibrium differential capacity due to contribution of anions to the double layer in a solution of 0.01 N HBR + 1 N H_2SO_4.

Thus the results plotted in Fig. 3 lead us to conclude that the thermodynamic theory of adsorption potential shifts, developed in

[3], is correct, and that the method of adsorption potentials can be used for quantitative investigation of reversible specific adsorption of ions on platinum.

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