DETERMINATION OF THE ADSORPTION OF IONS BY THE METHOD OF ADSORPTION POTENTIALS.

III. THE ADSORPTION OF K^+ AND Br^- ON PLATINUM

A. N. Frumkin, O. A. Petrii, and Yu. G. Kotlov

UDC 541.135.52.92-183 : 546-128

It is essential for an understanding of the structure of the electric double layer on the platinum metals to know the potential dependence of the adsorption of anions and cations. Separate determination of the adsorption of anions and cations on the Pt/Pt electrode was first achieved by Balashova and Kazarinov (see the review [1]) using radiotracers. It has been shown in [2] that this problem can also be solved by the method of isoelectric potential shifts, by combining measurements of the shifts with pH [3] and with concentration of the adsorbing ions other than H^+ [4-9]. For brevity we shall refer to the latter as adsorption potential shifts, following the terminology used in earlier papers. In fact, according to [2],

$$\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{Q,\mu^{\pm}_{CA}} = -\left(\frac{\partial\Gamma_{A-}}{\partial Q}\right)_{\mu_{H+},\mu^{\pm}_{CA}} + \left(\frac{\partial\Gamma_{C+}}{\partial Q}\right)_{\mu_{H+},\mu^{\pm}_{CA}}, \tag{1}$$

$$\left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{H+}} = -\left(\frac{\partial\Gamma_{C+}}{\partial Q}\right)_{\mu^{\pm}_{CA},\mu_{H+}} - \left(\frac{\partial\Gamma_{A-}}{\partial Q}\right)_{\mu_{H+},\mu^{\pm}_{CA}}, \tag{2}$$

where φ_r is the potential with respect to a reversible hydrogen electrode in the same solution, μ_{H^+} and $\mu_{CA^\pm}$ are the chemical potential of H^+ ions and the mean chemical potential of the ions of the neutral salt CA, Q is the total surface charge, and Γ_{H^+}, Γ_{A^-}, and Γ_{C^+} are the Gibbs surface excesses of hydrogen ions, anions, and cations, respectively. Adding and subtracting Eqs. (1) and (2) and performing simple transformations one can obtain Eqs. (3) and (4):

$$\left(\frac{\partial\Gamma_{A-}}{\partial\varphi_r}\right)_{\mu_{H+},\mu^{\pm}_{CA}} = -\frac{1}{2}\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H+},\mu^{\pm}_{CA}}\left[\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{Q,\mu^{\pm}_{CA}} + \left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{H+}}\right], \tag{3}$$

$$\left(\frac{\partial\Gamma_{C+}}{\partial\varphi_r}\right)_{\mu_{H+},\mu^{\pm}_{CA}} = \frac{1}{2}\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H+},\mu^{\pm}_{CA}}\left[\left(\frac{\partial\varphi_r}{\partial\mu_{H+}}\right)_{Q,\mu^{\pm}_{CA}} - \left(\frac{\partial\varphi_r}{\partial\mu^{\pm}_{CA}}\right)_{Q,\mu_{H+}}\right]. \tag{4}$$

These relations make it possible to calculate the potential dependence of the adsorption of anions and cations on the basis of data on the isoelectric shifts with pH, of adsorption potential shifts, and of charging curves.

In the present work these measurements were employed for determining the adsorption of K^+ and Br^- ions on a Pt/Pt electrode in the solutions: $2 \cdot 10^{-3}$ N HBr + $5 \cdot 10^{-2}$ N KBr (I) and 10^{-2} N HBr + $3 \cdot 10^{-1}$ N KBr (II). All experiments were carried out at 20 ± 1°C. The true surface area of the electrodes was 3.0-2.3 m² for system I and 15.0-12.0 m² for system II. Electrode preparation, surface area evaluation, the technique of measuring isoelectric potential shifts with changing pH and of measuring adsorption potential shifts, and the direct determination of the adsorption of H^+ and Br^- ions has been described previously [9, 10].

The derivative $(\partial\varphi_r/\partial\mu_{CA^+})_{Q,\mu H^+}$ was determined as function of φ_r by replacing a $2 \cdot 10^{-3}$ N HBr + 10^{-2} N KBr solution with a $2 \cdot 10^{-3}$ N HBr + $2.5 \cdot 10^{-1}$ N KBr solution for system I and by replacing a 10^{-2} N HBr + $6 \cdot 10^{-2}$

M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 5, No. 10, pp. 1214-1218, October, 1969. Original article submitted February 28, 1969.

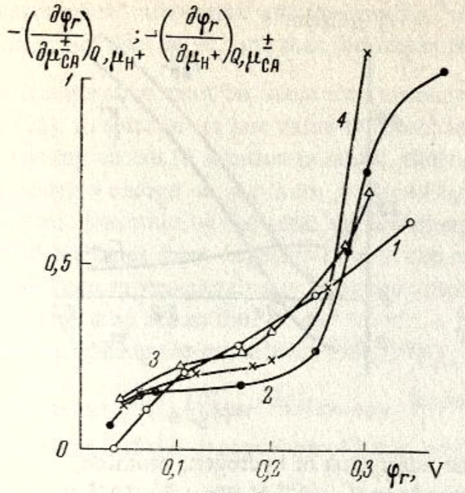

Fig. 1

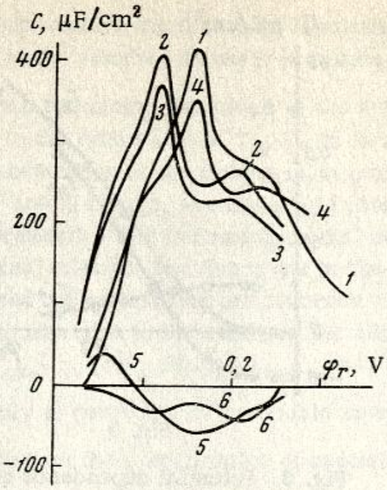

Fig. 2

Fig. 1. Potential dependence of the isoelectric potential shifts during pH change of the solution (curves 1 and 3) and of the adsorption potential shifts (curves 2 and 4) for a platinized platinum electrode in $2 \cdot 10^{-3}$ N HBr + $5 \cdot 10^{-2}$ N KBr (1 and 3) and 10^{-2} N HBr + $3 \cdot 10^{-1}$ N KBr (2 and 4).

Fig. 2. Potential dependence of the equilibrium differential capacity of the double layer (1 and 2) and of the capacities contributed by anions (3 and 4) and cations (5 and 6) in the electric double layer, for a platinized platinum electrode in $2 \cdot 10^{-3}$ N HBr + $5 \cdot 10^{-2}$ N KBr (1, 4, 5) and 10^{-2} N HBr + $3 \cdot 10^{-1}$ N KBr (2, 3, 6).

N KBr solution with a 10^{-2} N HBr + 1.5 N KBr solution for system II. The derivative $(\partial\varphi_r/\partial\mu_{H^+})_{Q,\mu_{CA}\pm}$ was determined by replacing a $5 \cdot 10^{-4}$ N HBr + $5 \cdot 10^{-2}$ N KBr solution with an $8 \cdot 10^{-3}$ N HBr + $4.2 \cdot 10^{-2}$ N KBr solution for system I and a $2 \cdot 10^{-3}$ N HBr + $3 \cdot 10^{-1}$ N KBr solution with a $5 \cdot 10^{-2}$ N HBr + $3 \cdot 10^{-1}$ N KBr solution for system II.

The choice of solutions in determining isoelectric potential shifts was governed by the conditions imposed on the derivation of Eqs. (3) and (4) [2]: firstly, in varying the HBr or KBr concentration in the system one must always observe the inequality [HBr] << [KBr]. This condition imposes a limitation both on the magnitude of the ratio [HBr]/[KBr] and, of course, on the spans of concentrations where measurements are possible. Secondly, Eq. (2) strictly applies only to dilute solutions. Relations suitable for the entire concentration range of neutral salt are considered in [11]. The slowness of equilibration in solutions containing Br^- ions and the limitation of the reversible adsorption range of this ion on Pt toward anodic φ_r [9] have been taken into account in the measurements.

Figure 1 shows the φ_r dependences of the isoelectric potential shifts for the systems studied. On the whole these curves are similar to those obtained previously for different systems [9, 11]; therefore, they do not require a more detailed description. The shift of the curves when going from system I to system II is produced by the increase in Br^- and H^+ ion concentration in the solution.

Figure 2 shows curves of the differential capacity caused by the contribution of anions and cations to the electric double layer as calculated from Eqs. (3) and (4), and curves of the equilibrium differential capacity of the double layer [11] calculated in the usual way [10] from the isoelectric shifts with changing solution pH. The nature of the maxima on the curves 1 to 4 has been discussed before [9, 11]. The cause of the maxima is expulsion of the anions by hydrogen dipoles which are directed with the negative end to the solution and which at the same time reduce the electric double layer capacity. The function $(\partial\Gamma_{K^+}/\partial\varphi_r)_{\mu_{H^+}\mu_{CA}\pm}$ changes sign when φ_r approaches 0, according to curve 5. This means that the adsorption of cations decreases as φ_r shifts to the negative side. The cause of this phenomenon, which was also noted in [2] (where reference is made to the data of Balashova, who had observed a similar phenomenon), seems to be expulsion of cations by adsorbing hydrogen. It is necessary here to take into account both the reduced capacity in the presence of H_{ads} and the possible appearance of hydrogen dipoles, at high surface coverages, which are directed with the positive end to the solution [8, 12].

In Fig. 3, calculated and experimental adsorption curves of H^+, K^+, and Br^- ions are compared for system I.

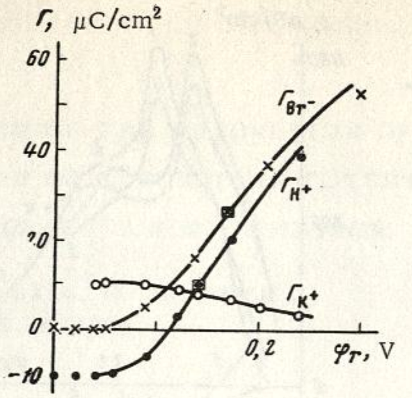

Fig. 3

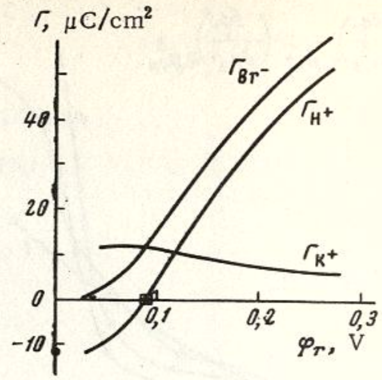

Fig. 4

Fig. 3. Potential dependence of the adsorption of hydrogen, bromide, and potassium ions for a Pt/Pt electrode in $2 \cdot 10^{-3}$ N HBr + $5 \cdot 10^{-2}$ N KBr solution. The solid lines are calculated, the points are from experiment.

Fig. 4. Potential dependence of the adsorption of hydrogen, bromide, and potassium ions for a Pt/Pt electrode in 10^{-2} N HBr + $3 \cdot 10^{-1}$ N KBr.

The calculation was carried out by integrating the curves of Fig. 2. Values of Γ_{H^+} and Γ_{A^-} found by experiment were used as integration constants. These values are marked by a special symbol in the figure. The experimental Γ_{K^+} values were found from the condition of electroneutrality: $\Gamma_{K^+} = \Gamma_{Br^-} - \Gamma_{H^+}$, by using the experimental Γ_{H^+} and Γ_{Br^-} values.

The good agreement between calculated and experimental K^+ and Br^- adsorption curves shows that it is possible to determine separately Γ_{A^-} and Γ_{C^+} by combining the methods of adsorption curves and isoelectric potential shifts. It must also be noted that when going from $\varphi_r = 40$ mV to $\varphi_r = 0$ in system I, it was possible to experimentally observe some alkalization of the solution, which corresponds to a decrease in Γ_{K^+} as $\varphi_r \to 0$, in agreement with the results of calculation.

The curves of Fig. 4, which were obtained by the above-described method for system II, are similar in shape to the curves of Fig. 3. An experimental value of Γ_{H^+} and an assumed value of $\Gamma_{Br^-} = 0$ at $\varphi_r = 0$ were used as integration constants in this case since, because of the high Br^- ion concentration in solution, it is not possible to determine Γ_{Br^-} directly in this case. The shape of the $\Gamma_{Br^-} - \varphi_r$ curve at small φ_r does, however, fully support the assumption that $\Gamma_{Br^-} = 0$ at $\varphi_r = 0$. Comparing the curves of Figs. 3 and 4 one can note an increase in Γ_{K^+} when going from system I to system II.

The method proposed for the separation determination of Γ_{A^-} and Γ_{C^+} requires knowledge of two integration constants for the calculation of absolute adsorption values, and their determination requires additional measurements. The principal merit of this method, however, must be seen in the possibility to determine the derivatives $(\partial\Gamma_{C^+}/\partial\varphi_r)_{\mu_{H^+}, \mu_{CA}^{\pm}}$, $(\partial\Gamma_{A^-}/\partial\varphi_r)_{\mu_{H^+}, \mu_{CA}^{\pm}}$, and $(\partial\Gamma_{C^+}/\partial\Gamma_{A^-})_{\mu_{H^+}, \mu_{CA}^{\pm}}$ with an accuracy that cannot be attained by other methods, and moreover for any solution concentration (including concentrated solutions, when the relations given in [11] are taken into account) that satisfies the above-mentioned condition for the ratio of acid and salt contents.

It follows from the data obtained, in agreement with [1], that to the right of the point of zero charge Γ_{K^+} decreases while Γ_{Br^-} quickly rises, and this rise begins while the surface charge is still negative. At sufficiently anodic φ_r, $(\partial\Gamma_{K^+}/\partial\Gamma_{Br^-})_{\mu_{H^+}, \mu_{CA}^{\pm}}$ seems to become approximately zero,* although Γ_{K^+} retains some finite value,

* A calculation with the data of Fig. 1 for $\varphi_r > 0.25$-0.3 V indicates that Γ_{K^+} increases a little with φ_r and then reaches a plateau. However, the calculation becomes unreliable at these φ_r because the system is not fully at equilibrium. Therefore, Γ values are given only to $\varphi_r \leqslant 0.25$-0.3 V in Figs. 3 and 4. According to the data of [1], Γ_{C^+} is potential independent at anodic φ_r.

as before. A high value of Br^- adsorption and the small K^+ adsorption indicate that there is relatively little superequivalent adsorption of Br^- ions on Pt, and that the larger part of the adsorbed anions is in a state close to atomic.

Superequivalent adsorption must be taken into account when examining the nature of the adsorption potentials as shown already in [13], in spite of its low value (as compared to the total value of Γ_{Br^-}). In fact, when the concentration of chemisorbing anions in solution is raised, their concentration in the surface layer could only increase at the cost of rising positive charge on platinum produced by H^+ ion discharge, and this would cause the potential to shift to the positive side. Maintaining the total surface charge constant while increasing the Br^- concentration one finds that the potential becomes more negative than in the original solution, and this is due to the fact that the potential drop arising between superequivalently adsorbed anions and the cations that are attracted to them is subtracted from the potential drop across the $^+Pt-Br^-$ layer. A final answer as to the nature of the adsorption potentials will be possible when comparing the quantities $(\partial\Gamma_{C^+}/\partial\mu^{\pm}_{CA})_{Q,\mu_{H^+}}$, $(\partial\Gamma_{A^-}/\partial\mu^{\pm}_{CA})_{Q\mu_{H^+}}$, and $(\partial\Gamma_{H^+}/\partial\mu^{\pm}_{CA})_{Q,\mu_{H^+}}$, as well as $(\partial\Gamma_{C^+}/\partial\varphi)_{\Gamma_{H^+}\mu_{H^+}}$ and $(\partial\Gamma_{H^+}/\partial\varphi)_{\Gamma_{C^+},\mu_{H^+}}$ (especially at potentials in the double layer region). This, however, requires knowledge of the dependence of ionic adsorption on the concentration of neutral salt at constant μ_{H^+}.

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