CONTRIBUTION OF ADSORBED HYDROGEN ATOMS AND OF DOUBLE-LAYER IONS TO THE POTENTIAL DROP AT PLATINUM AND RHODIUM ELECTRODES

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In the development of a potential drop at the interface between an electrode and a solution, both the ions of the electric double layer and the atoms H_{ads} and O_{ads} participate when one deals with a metal adsorbing hydrogen and oxygen [1-4]. The contributions of the atoms and ions to the potential drop are quantitatively determined, respectively, by the functions [2] $X = (\partial\varphi/\partial A_H)_{\Gamma_{H^+}}$ and $Y = (\partial\varphi/\partial\Gamma_{H^+})_{A_H}$, where φ is the electrode potential with respect to a constant reference, A_H is the quantity of atomic hydrogen adsorbed per 1 cm^2 of surface, and Γ_{H^+} is the Gibbs surface excess of hydrogen ions; A_H and Γ_{H^+} are expressed in electrical units.

X and Y can be linked to experimentally accessible quantities [2, 4, 5] with the aid of the thermodynamic relations

$$X = -[(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r} - (\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}] : Z, \quad (1)$$

$$X + Y = [(\partial Q/\partial\varphi_r)_{\mu_{H^+}} - (\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}] : Z, \quad (2)$$

$$Z = (\partial Q/\partial\varphi_r)_{\mu_{H^+}} (\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r} - (\partial\Gamma_{H^+}/\partial\varphi_r)^2_{\mu_{H^+}}, \quad (3)$$

where Q is the charge imparted on the electrode, φ_r is the potential relative to a reversible hydrogen electrode in the same solution, μ_{H^+} is the chemical potential of hydrogen ions. The values of $(\partial Q/\partial\varphi_r)_{\mu_{H^+}}$ in these relations can be found from the charging curve, those of $(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}$ from measurements of the isoelectric potential shifts [6]. The greatest difficulties exist in the experimental determination of $(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r}$ for a narrow pH region. Up to the present time, therefore, only the trends of X and Y were evaluated [4].

In the present work we attempt to calculate X and Y on the basis of adsorption curves determined previously [7] for platinum and rhodium electrodes at different pH. When the Γ_{H^+} values from [7], which cover a narrow pH range ($\Delta pH \simeq 2$), were directly used for calculations according to Eqs. (1)-(3), a rather considerable scatter in the points resulted, which made it impossible to establish with certainty the course of the $X-\varphi_r$ and $Y-\varphi_r$ curves over the entire pH range. Therefore, a way of "correcting" the experimental data was adopted which consisted in the following. Points of the adsorption curves corresponding to the lowest and highest pH values were so transposed within the error limits ($\pm$ 1 to 2 μC/cm^2) that in the end we obtained practically complete agreement between calculated and experimental $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}} - \Gamma_{H^+}$ curves (see [7]). The "corrected" data were then used for the calculation.

In addition, X and Y were calculated from the $Q-\varphi_r$, $A_H-\varphi_r$, and $\Gamma_{H^+}-\varphi_r$ curves for a wide pH range ($\Delta pH \simeq 10$) with the same method that was used in [4], i.e., taking into account the isoelectric shifts when going from one solution to another. From Eqs. (1) and (2) and the equations of [7, 8] one can, finally, obtain the relation

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

which allows the ratio X/(X + Y) to be calculated from the experimental values of $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}}$ and $(\partial\varphi_r/\partial\mu_{H^+})_Q$. A comparison of the results of calculations by different methods served as confirmation of the correct determination of the $X-\varphi_r$ and $Y-\varphi_r$ curves. Results of the calculation of $X-\varphi_r$ and $Y-\varphi_r$ curves are shown in Figs. 1-3.

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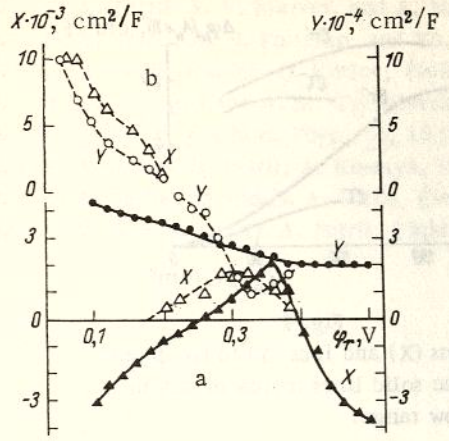

Fig. 1. Potential dependence of the contributions of atoms (X) and ions (Y) to the potential drop developed at Pt (a) and Rh (b) in sulfate solutions. The solid lines represent calculations for a wide pH range, dashed lines are for a narrow range.

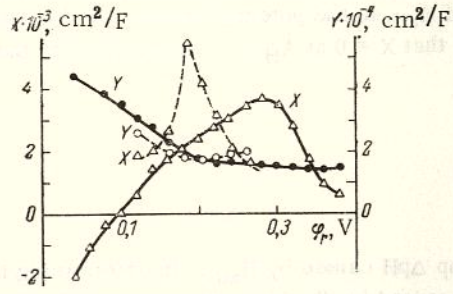

Fig. 2. Potential dependence of the contributions of atoms (X) and ions (Y) to the potential drop developed at platinum in chloride solutions. The solid lines represent calculations for a wide pH range, dashed lines are for a narrow range (the dashed lines are on a scale twice larger than indicated on the X and Y axes).

It must be noted, first of all, that the calculated data of the present work for chloride solutions (Fig. 2) are in satisfactory agreement with the calculated results of [4]. The calculations for the narrow and wide pH range are only in qualitative agreement with one another, which seems to be caused both by errors in the determination of the derivatives [primarily of $(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r}$] and because they refer to solutions of different pH (about 2 in the first case, about 7 in the second).

The value of X for the Rh electrode is positive at all φ_r. On Pt, X is positive only at small and intermediate coverages of the surface by adsorbed hydrogen and becomes negative at large coverages. A positive value of X indicates that the dipole of adsorbed hydrogen is turned with the negative end to the solution [2-4]. Hence, on Rh the dipole of H_{ads} has the same direction at all φ_r, confirming the conclusion in [4] that had been obtained by analyzing the pH dependence of hydrogen adsorption on Rh [9].

The change of sign of X on Pt can be explained by the appearance of dipoles of opposite orientation (with the positive end to the solution) [2-4]. This is in agreement with the results of electronic work function measurements on Pt [10], as noted previously in [3, 4].

In the cases considered, the contribution of H_{ads} to the development of a potential drop is considerably smaller than that of the double-layer ions, when the quantity of adsorbed species is the same. Thus, in sulfate solutions the difference amounts to almost two orders of magnitude at certain φ_r. The contribution of H atoms rises with increasing specific adsorbability of the anions of the base electrolyte. This result allows the dependence of pzc on solution pH to be explained [7]. In fact, the increase in the quantity $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0}$ when going from sulfate to bromide solutions can simply be explained with an increase in the relative contribution of H_{ads} to the potential drop. The shift of pzc with pH increases when going from Pt to Rh, and at the same time the ratio X/Y also rises above its value in sulfate solutions on Pt.

The quantity Y^{-1} represents the differential capacitance of the electrode at constant A_H. From the calculated results for the wide pH range, Y^{-1} is about 50 $\mu F/cm^2$ in presence of SO_4^{2-}, about 60 $\mu F/cm^2$ in presence of Cl^-, and about 100 $\mu F/cm^2$ in the presence of Br^- on Pt, i.e., it increases in the series $SO_4^{2-} < Cl^- < Br^-$. The value of Y^{-1} decreases by about 2-5 times on Pt and nearly by one order of magnitude on Rh when φ_r is reduced to zero, i.e., when the surface coverage of H_{ads} increases. This can be linked, in agreement with [4], both to the exchange of anions for cations in the double layer and to increasing surface coverage with H_{ads}. In contrast to the equilibrium differential-capacity curves [11] which have a complex form, Y^{-1} varies monotonically with potential. This confirms the conclusion in [11] that the complex dependence of the equilibrium capacity on φ_r is determined by a variation in the quantity of H_{ads} dipoles.

On the $X-\varphi_r$ curves shown above, a decrease in X with increasing φ_r is observed at sufficiently anodic values of φ_r, although it could have been expected [12] that with a nonhomogeneous surface, the first portions of adsorbed hydrogen should have the greatest aligned dipole moment. It is possible that the result obtained is caused by the character of distribution of hydrogen and anions between the various adsorption centers. However, a more detailed explanation is difficult at present.

In the case of Pt in sulfate solutions, X not only decreases with increasing φ_r but changes sign at $\varphi_r > 400$ mV. This is due, however, to oxygen deposition which already occurs, because in sulfate solutions, the adsorption ranges of hydrogen and oxygen on platinum overlap [13]. Since $\left(\frac{\partial\varphi}{\partial A_H}\right)_{\Gamma_{H^+}} = -\left(\frac{\partial\varphi}{\partial A_0}\right)_{\Gamma_{H^+}}$, where A_0 is the quantity of

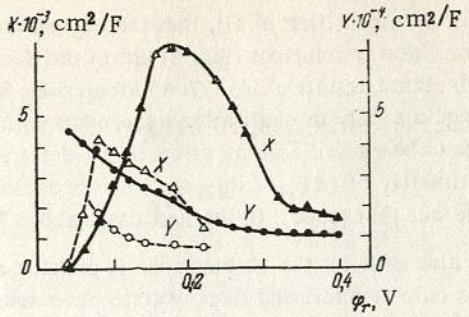

Fig. 3

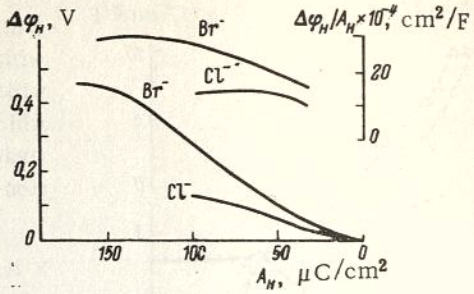

Fig. 4

Fig. 3. Potential dependence of the contributions of atoms (X) and ions (Y) to the potential drop developed at platinum in bromide solutions. The solid lines represent calculations for a wide pH range, the dashed lines are for a narrow range.

Fig. 4. Dependence of the potential drop caused by hydrogen dipoles on the quantity of adsorbed hydrogen on platinum for solutions of different composition. The calculation was made according to the $X-A_H$ curves for a narrow pH range.

oxygen adsorbed per square centimeter of surface, in electrical units, then $(\partial\varphi/\partial A_O)_{\Gamma_{H^+}} > 0$. This means that at small coverages, adsorbed oxygen forms dipoles turned with the negative end to the solution, just as does hydrogen.

The valuesof X and Y give the differential effects of introducing an atom and an ion into the surface layer. One can attempt to estimate approximately the absolute contribution of H_{ads} to the potential drops. To this end we represent X as a function of A_H, using the $A_H-\varphi_r$ curve. Assuming that X = 0 as A_H = 0, we extrapolate the $X-A_H$ curve to A_H = 0. The integral

$$\int_{A_H=0}^{A_H} (\partial\varphi/\partial A_H)\,\Gamma_{H^+}\,dA_H$$

gives approximately (cf. below) the A_H dependence of the potential drop ΔpH caused by H_{ads}. In determining the integration constant it can naturally be assumed that the potential drop caused by dipoles is zero at A_H = 0. Dividing $\Delta\varphi_H$ by the corresponding value of A_H one can find the potential drop caused by one H_{ads} atom. Figure 4 shows $\Delta\varphi_H-A_H$ and $(\Delta\varphi/A_H)-A_H$ curves. The decrease in the contribution of H_{ads} with decreasing surface coverage is retained on the integral curves. The adsorbed hydrogen dipoles cause a potential shift to the anodic side that reaches a few tenths of a volt, and which increases when going from Cl^- to Br^- solution. This can be explained by assuming that the Br^- ions are adsorbed preferentially on the same centers as are the H_{ads} dipoles which turn the positive end to the solution, and that they expel these, while the dipoles of opposite orientation are adsorbed on different centers.

It must be stressed that while X and Y have been determined rigorously, $\Delta\varphi_H$ is only found in a rough approximation. In fact,

$$\partial\varphi = (\partial\varphi/\partial A_H)_{\Gamma_{H^+}} dA_H + (\partial\varphi/\partial\Gamma_{H^+})_{A_H}\, d\Gamma_{H^+}. \qquad (5)$$

The integration could obviously give correct results only in the case where Γ_{H^+} remains constant when going from one point on the $X-A_H$ curve to another.

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