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

II. THE ADSORPTION OF Br^- ON RHODIUM AND IRIDIUM

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It has been shown in [1] that it is possible to employ the method of adsorption potentials [2-5] for the quantitative investigation of reversible specific adsorption of Br^- ions on platinum. In the present work the method of adsorption potentials is extended to rhodium and iridium electrodes where the adsorption of Br^- ions is determined from 0.01 N HBr + 1 N H_2SO_4 solutions.

The potential dependence of Br^- ion adsorption (Γ_{Br^-}) was found from the equation [1, 6]:

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

where μ_{Br^-} is the chemical potential of Br^- ions in electrical units, Q is the total surface charge [6, 7], and φ_r is the potential with respect to a reversible hydrogen electrode in the same solution.

The experimental technique has been described in detail in [1]. The preparation, preworking, and calculation of the surface area of the rhodium and iridium electrodes were carried out as in [8, 9]. The experiments were run at 20 ± 1°C.

The adsorption potential shifts were determined by substituting an 0.1 N HBr + 0.91 N H_2SO_4 solution for a 0.001 N HBr + 1.009 N H_2SO_4 solution. The time required for establishing φ_r of the test electrode depended strongly on φ_r, both in the initial and final solution. Thus at $\varphi_r < 0.3$ V, i.e., at φ_r in the hydrogen region, the potentials at both electrodes became stable on open circuit in the initial solution after 2-4 h of polarization of the electrode using a potentiostat, just as noted previously for Pt [1]. When the solution was changed to one that was more concentrated in Br^-, φ_r was established within 5-15 min. At more anodic φ_r, stabilization of the potential required no less than 7-15 h, while the time required for establishing φ_r in the final solution rose to 1 h and more. Even after such long periods the potential always continued to drift slowly toward the cathodic side. The time required for stabilizing the potential became longer the larger φ_r. These phenomena indicate that adsorption equilibrium on Rh and Ir is established slowly in the presence of Br^- ions when φ_r is sufficiently anodic, and that the rate of equilibration depends on φ_r. From our experiments we could not, however, establish any essential differences in the rates of attainment of adsorption equilibrium on the various metals.

Figure 1 gives adsorption potential shifts on the electrodes studied. At small φ_r the shifts are similar for all the metals and tend to zero as φ_r goes toward zero. At more anodic φ_r, the magnitudes of the shifts depend on the metal. Thus, a Pt electrode at $\varphi_r \sim 0.5$-0.7 V behaves approximately as a reversible bromide electrode, while on Rh and Ir the smallest value of $(\partial\varphi_r/\partial\mu_{Br^-})_Q$ is only −0.75 to -0.7, i.e., in this case the potential shift is even less than would correspond to the absence of the Esin-Markov effect [10]. One can point to a few reasons for this phenomenon. It is possible that this is due to lack of equilibrium for the φ_r regions considered in the present systems, and it is shown below that this is indeed the case. On the other hand, the effect observed as well as the rise in $(\partial\varphi_r/\partial\mu_{Br^-})_Q$ at more anodic φ_r, which on Ir begins earlier than on Rh, may be linked to earlier oxygen deposition on these metals, because of which hydrogen and oxygen adsorption regions overlap.

In fact, Eq. (1) can be presented in the form [1]:

$$\left(\frac{\partial\varphi_r}{\partial\mu_{Br^-}}\right)_Q = \frac{(\partial\Gamma_{Br^-}/\partial\varphi_r)_{\mu_{Br^-}}}{(\partial A_H/\partial\varphi_r)_{\mu_{Br^-}} - (\partial\varepsilon/\partial\varphi_r)_{\mu_{Br^-}}} \simeq \frac{1}{(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} - 1}, \quad (2)$$

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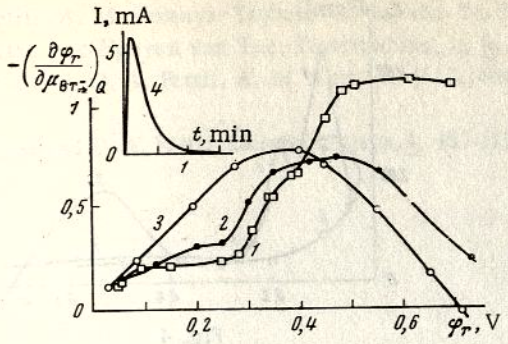

Fig. 1

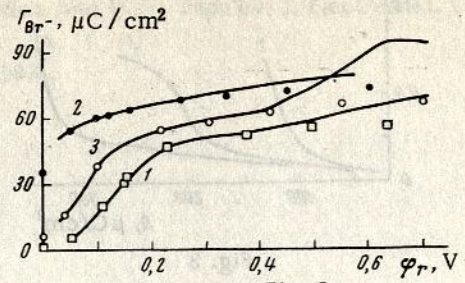

Fig. 2

Fig. 1. Dependence of the adsorption potential shift on potential for the Pt/Pt (1), rhodium (2), and iridium (3) electrode in 0.01 N HBr + 1 N H_2SO_4 solutions. 4) Time dependence of the current, starting from the time when the 0.001 N HBr + 1.009 N H_2SO_4 solution was replaced by 0.1 N HBr + 0.91 N H_2SO_4 under potentiostatic conditions at φ_r = 110 mV.

Fig. 2. Potential dependence of Br^- ion adsorption on platinum (1), rhodium (2), and iridium (3) in 0.01 N HBr + 1 N H_2SO_4 solution. Solid curves are calculated, the points are experimental.

where A_H is the amount of atomic hydrogen per cm^2 of surface area in electrical units, and ε is the free surface charge, because on platinum metals sufficiently far from the point of zero charge $(\partial\varepsilon/\partial\Gamma_{Br^-})_{\mu_{Br^-}} \simeq 1$.* Thus the minimum value of $(\partial\varphi_r/\partial\mu_{Br^-})_Q$, which is -1, is only reached in the case where $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} = 0$ and particularly when $A_H = 0$. When $A_H \neq 0$, then $0 > (\partial\varphi_r/\partial\mu_{Br^-})_Q > -1$ so long as $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} < 0$. The latter condition is satisfied at $(\partial\Gamma_{Br^-}/\partial\varphi_r)_{\mu_{Br^-}} > 0$ because $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} = (\partial A_H/\partial\varphi_r)_{\mu_{Br^-}}/(\partial\Gamma_{Br^-}/\partial\varphi_r)_{\mu_{Br^-}}$ and always $(\partial A_H/\partial\varphi_r)_{\mu_{Br^-}} < 0$. In the region of oxygen adsorption $(\partial\Gamma_{Br^-}/\partial\varphi_r)_{\mu_{Br^-}} < 0$ and consequently $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}}$ becomes a positive quantity. At $(\partial A_H/\partial\Gamma_{Br^-})_{\mu_{Br^-}} > 1$, the adsorption shifts become positive, i.e., the potential shifts to the positive side, rather than to the negative side, when the Br^- ion concentration increases. This is true for iridium at $\varphi_r \gtrsim 0.7$ V.

In Fig. 2, $\Gamma_{Br^-} - \varphi_r$ curves calculated from Eq. (1) are compared with experimental curves found as in [1]. Quantitative agreement between calculation and experiment is observed up to $\varphi_r \sim 400$ mV. The divergence at more anodic φ_r, which is particularly noticeable in the case of Ir, seems to indicate that at these φ_r equilibrium is not completely established during Br^- adsorption.

It must be noted that while agreement between calculation and experiment can be concluded regardless of the assumptions made in determining the true surface areas of the electrodes [8, 9], the relative position of the $\Gamma_{Br^-} - \varphi_r$ curves depends on correct surface area determination. However, at least for φ_r in the hydrogen region it can be concluded that Br^- adsorption rises in the series Pt < Ir < Rh.

Figure 3 shows anodic equilibrium charging curves [10, 11] on the metals studied in 0.01 N HBr + 1 N H_2SO_4. The increase in Br^- adsorption when going from Pt to Rh leads to a shrinking of the hydrogen portions on the curves in the same direction. The reduced slope of the charging curve for the Ir electrode at $\varphi_r > 0.45$ V indicates oxygen adsorption on the electrode. In all cases the equilibrium curves are somewhat longer than the usual curves in the same solution, which is due to slow equilibration during Br^- adsorption.

Figure 4 gives curves for the equilibrium differential capacity, C_-, caused by the contribution of Br^- ions to the electric double layer. A characteristic feature of these curves is the presence of maxima (on Pt and Ir) or of a sharp rise in capacity (on Rh) at φ_r in the hydrogen region. These phenomena are caused by expulsion of the Br^- ions by H_{ads} [10]. The maximum on the curve for the Ir electrode in the oxygen region seems to be due to a similar process of Br^- ion expulsion by adsorbed oxygen.

From the data obtained one can conclude that the method of adsorption potentials can be employed for the quantative investigation of Br^- ion adsorption on Rh and Ir. Here, as on Pt, one must take into account that the reversible adsorption range is limited toward anodic potentials.

*If $(\partial\varepsilon/\partial\Gamma_{Br^-})_{\mu_{Br^-}} > 1$, then in the double-layer region also $(\partial\varphi_r/\partial\mu_{Br^-})_Q > -1$.

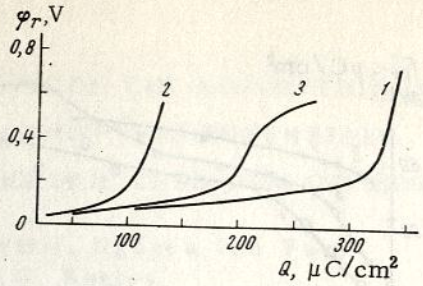

Fig. 3

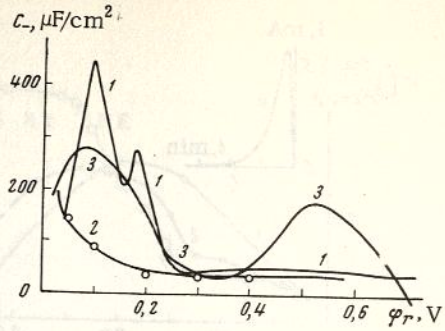

Fig. 4

Fig. 3. Equilibrium charging curves for platinum (1), rhodium (2), and iridium (3) in 0.01 N HBr + 1 N H_2SO_4 solution.

Fig. 4. Potential dependence of the equilibrium differential capacity caused by the contribution of anions to the electric double layer, on platinum (1), rhodium (2), and iridium (3). The points are results of determining the capacity by the potentiostatic method. The solution is 0.01 N HBr + 1 N H_2SO_4.

The adsorption of Br^- ions can also be determined by the potentiostatic method. In fact, the appearance of an anodic current I under potentiostatic conditions must correspond to a shift of φ_r in the negative direction when the Br^- ion concentration is increased under isoelectric conditions. The current must drop to zero when adsorption equilibrium is reached. By integrating the I-t curve observed under potentiostatic conditions one can find the charge, ΔQ, which is necessary for maintaining a constant potential while changing the solution composition, and one can obviously find the derivative $(\partial Q/\partial \mu_{Br^-})_{Q_r}$. It is shown below that the latter is the differential capacity caused by the contribution of anions to the double layer. In fact, the Gibbs equation for this case is of the form [6]:

$$d\sigma = -Qd\varphi_r - \Gamma_{Br^-}d\mu_{Br^-}, \tag{3}$$

where σ is the surface tension. From (3) follows

$$(\partial Q / \mu_{Br^-})_{\varphi_r} = (\partial \Gamma_{Br^-} / \partial \varphi_r)_{\mu_{Br^-}}. \tag{4}$$

Measurements with the potentiostatic method were carried out on a Rh electrode in 0.01 N HBr + 1 N H_2SO_4 solution. The potential was kept constant using a P-5611 potentiostat while replacing the 0.001 N HBr + 1.009 N H_2SO_4 solution by 0.1 N HBr + 0.9 N H_2SO_4. The time dependence of the current was recorded with a BP-5684 recorder.

As an example the I-t curve obtained at φ_r = 110 mV is shown in Fig. 1 (curve 4). C_- values found with the potentiostatic method are given as points in Fig. 4. The results of the potentiostatic measurements agree satisfactorily with the results of measurements by the method of adsorption potentials. The $\Gamma_{Br^-} - \varphi_r$ curves calculated from the $C_- - \varphi_r$ curves, both as obtained by the potentiostatic method and by the method of adsorption potentials, also practically coincide. Thus, the potentiostatic method described in the present work can be employed for the quantitative study of ion adsorption on platinum metals.

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