HYDROGEN ION ADSORPTION ON PLATINUM AT THE REVERSIBLE HYDROGEN POTENTIAL AS A FUNCTION OF SOLUTION pH

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Frumkin and Shlygin [1] have proposed potentiometric titration involving an indicator electrode with large true surface area for studying the structure of the electric double layer on platinum. Hydrogen ion adsorption, Γ_{H^+}, was studied by this method as a function of potential φ in 1 N NaCl and NaBr at atmospheric hydrogen pressure [1, 2]. However, this method has not been applied further on in investigating the surface properties of platinum metals. Yet it is of appreciable interest because it allows the $\Gamma_{H^+} - \varphi$ curve in a system at constant hydrogen pressure to be found relatively simply; this curve is required for finding the φ dependence of the second kind of the reversible work of formation of unit surface area (the excess surface free energy), σ [3].

In the present investigation the method of potentiometric titration was used for determining the φ dependence of Γ_{H^+} at atmospheric hydrogen pressure in 0.1 N Li_2SO_4, Na_2SO_4, NaCl, NaBr, NaI, K_2SO_4, Cs_2SO_4, CsCl, $Ba(ClO_4)_2$, and $BaCl_2$.

The working electrode was a platinized platinum net with an apparent surface area of 80 cm². The polarization was carried out as in [4, 5], extending over 20–30 h in order to deposit 0.03–0.05 g of platinum per cm² of apparent surface area. The true surface area of the working electrode as determined from hydrogen adsorption by the standard method [6] was 10–20 m². Any deviations of the charging curves for the electrodes used here from the usual charging curves were not observed, despite the fact that the deposits were rather thick. Charging curves were measured periodically after a few experiments in order to assess the changes in true surface area of the electrodes which occurred upon recrystallization.

An experiment was carried out as follows. The working electrode, which had been subjected to prior anodic and cathodic polarization in 0.1 N H_2SO_4, was carefully washed with twice distilled water, shaken to remove water drops, and introduced into the dry cell. The system was saturated with hydrogen, and the cell filled with a portion of acidified solution (15 ml) of the corresponding salt, which was also hydrogen-saturated. Solutions were usually used where the acid concentration was 10^{-3} N, e.g., 0.1 N NaCl+0.001 N HCl. With higher acid concentration the effects became smaller, and the accuracy decreased when, with the electrodes employed, the same volume of the solution being titrated was used.

The thermostated cell was fitted with a buret through which hydrogen could be passed. The buret was filled with an alkalized solution of the corresponding salt, e.g., 0.1 N NaCl + 0.01 N NaOH, which was hydrogen-saturated. Portions of this solution were introduced into the working part of the cell within defined time intervals after a constant potential value had been established. The intervals were especially long during the first stage of titration in iodide solutions, where they were 2–3 h for the addition of 0.5 ml of alkaline solution. This is due to the slow establishment of adsorption equilibrium in the adsorption of I^- on the platinum electrode [6]. To check that equilibrium was indeed attained during the measurements, the alkalized iodide solution was titrated with an acidified iodide solution. The results of these two titrations coincided. In other systems the portions of alkaline solution were added within 10–20 min. It appears that such intervals were necessary, essentially, in order to establish constant solution composition in the working part of the cell and the corresponding temperature regime.

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After the experiment with a large Pt/Pt electrode, titration was carried out in the same manner with a small, weakly platinized platinum indicator electrode (apparent surface was 2 cm^2).

The experiments were done at 20±0.02°C. A saturated calomel electrode linked to the cell via a salt bridge containing saturated KCl solution served as reference electrode. In the paper the potentials φ are reported relative to the n.h.e.

Typical potentiometric titration curves with the small and large electrode are shown in Fig. 1. Hydrogen ion adsorption in $\mu C/cm^2$ was calculated from two curves according to Eq. (1), which was deduced from the condition that the solution composition in different experiments is the same at identical φ:

$$\Gamma_{H^+} = -\frac{(c_1 + c_2)(b - a)\,96500 \cdot 10^6}{(1 + a/V)\,1000S}, \tag{1}$$

where c_1 is the concentration of acid in the solution being titrated, c_2 is the concentration of alkali, a and b are the amounts of alkali added in order to attain a given φ with the small and large electrode, respectively, V is the initial solution volume in the working part of the cell, and S is the true surface area of the large electrode.*

The $\Gamma_{H^+} - \varphi$ curves in solutions of different composition, which demonstrate the effect of the salt cation on the adsorption of hydrogen ions at the Pt/Pt electrodes, are presented in Fig. 2a. Similar curves in Fig. 2b for sodium salt solutions reflect the effect of the anion on the adsorption of hydrogen ions.

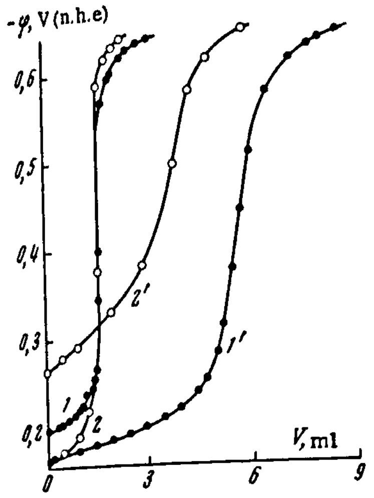

Fig. 1. Potentiometric titration curves of the solutions: 0.1 N Na_2SO_4 + 0.001 N H_2SO_4 (1, 1') and 0.1 N NaI + 0.002 N HCl (2, 2') by the solutions: 0.1 N Na_2SO_4 + 0.01 N NaOH and 0.1 N NaI + 0.02 N NaOH, correspondingly, using a small (1, 2) and a large (1', 2') Pt/Pt electrode at 20°C. The true surface area of the large electrode was 39 m^2 (1') and 26 m^2 (2').

It follows from Fig. 2b that in the presence of SO_4^{2-}, Cl^-, and Br^- ions, the Γ_{H^+} values do not differ significantly. Neither were any differences found between the $\Gamma_{H^+} - \varphi$ curves in the solutions: 0.1 N Cs_2SO_4 and CsCl, $Ba(ClO_4)_2$ and $BaCl_2$. This indicates, in harmony with literature data [7, 8], that there is no adsorption of these anions at the reversible hydrogen potential over the entire range of solution pH in the systems studied. An effect is only observed in the presence of I^-. At strongly negative potentials, which correspond to alkaline solutions, the I^- ions become desorbed from the surface [9], and Γ_{H^+} assumes the same values as in the presence of other anions. It can be seen from Fig. 2b that in solutions of salts not containing strongly adsorbing anions, one can equate with sufficient approximation the quantity $-\Gamma_{H^+}$ to the adsorption of the cation at the electrode surface Γ_{C^+}. The data of Fig. 2a, therefore, give indications as to the relative adsorbability of the various cations on platinum. The result following from Fig. 2a, viz., that the adsorbability of the cations rises when going from Li^+ to Cs^+, and the values of the Γ_{C^+} themselves are in harmony with literature data [5, 7, 10]. The values for Ba^{2+} ion adsorption at low pH are between those for K^+ and Cs^+. At pH > 8 the adsorption of Ba^{2+} begins to rise more rapidly with pH than that of other cations. The increase of Ba^{2+} adsorption in alkaline solutions relative to that in acidic solutions has been noted previously [7, 11].

Within the framework of the electric double-layer model usually used for platinum [12], Γ_{H^+} can be considered as the charge on the metal side of the double layer, ε. It can be seen from Figs. 2a and b that in sulfate, chloride, and bromide solutions, the $\varepsilon - \varphi$ curves are not straight lines, and that their slope increases in the region of more negative potentials. Since the slope of the $\varepsilon - \varphi$ curves gives the capacity of the double layer, this result then points to the dependence of the latter on electrode potential. The shape of the $\varepsilon - \varphi$ curves in the present cases turns out to be appreciably simpler than that of similar curves at constant hydrogen ion concentration in solution [1], despite the deviations of the present curves from linearity. This is due to the fact that the surface coverage by adsorbed hydrogen at a constant hydrogen pressure of

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*A similar equation is reported in [2], but there the condition of equal hydrogen ion concentrations at identical φ is incorrectly written down.

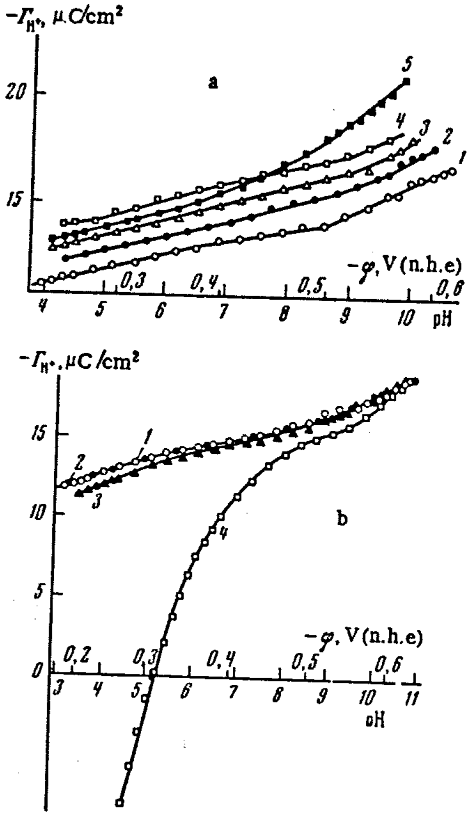

Fig. 2. Hydrogen ion adsorption at the Pt/Pt electrode at the reversible hydrogen potential as function of solution pH in 0.1 N Li_2SO_4 (1), Na_2SO_4 (2), K_2SO_4 (3), Cs_2SO_4 (4), and $Ba(ClO_4)_2$ (5) (Part *a*) and in 0.1 N Na_2SO_4 (1) NaCl (2), NaBr (3), and NaI (4) (Part b).

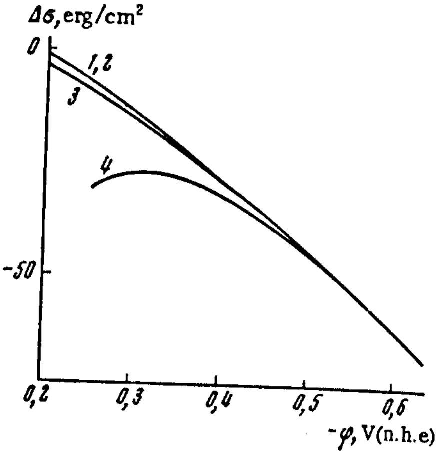

Fig. 3. Electrocapillary curves of the second kind for the Pt/Pt electrode in 0.1 N Na_2SO_4 (1), NaCl (2), NaBr (3), and NaI (4), at a hydrogen pressure of 1 atm in the system.

1 atm remains approximately constant at all potentials, and close to complete. The average value of double layer capacity as calculated from the slope of the $\Gamma_{H+}-\varphi$ curves in the potential range from −0.2 to −0.5 V in lithium and sodium sulfate solutions is 11-12 μF/cm². This is less than the capacity values at the same surface charge densities on the mercury electrode, and seems to be due to the coverage of the platinum surface by adsorbed hydrogen.

The electrode surface is charged negatively in sulfate, chloride, and bromide solutions over the pH range studied, and the potential of conditional zero free charge (p.z.c.) [12], which corresponds to a surface completely occupied by adsorbed hydrogen, can only be found by crude extrapolation of the $\Gamma_H-\varphi$ curve to its intersection with the abscissa in a potential range that cannot be attained experimentally by reducing the pH. Such an extrapolation indicates that in Li_2SO_4 solution, the p.z.c. is approximately 0.3 V. This is close to the value reported in [1]. It must be noted, however, that upon linear extrapolation of the initial sections of the $\Gamma_{H+}-\varphi$ curves, we arrive at the conclusion that there is an anomalously large difference in the p.z.c. in the presence of the various alkali metal cations. The question whether the extrapolation is reliable demands further investigation, therefore. In iodide solution the p.z.c. is −0.31 V.

From the data of Fig. 2b, $\sigma-\varphi$ curves of the second kind [3] were calculated, which may also be called electrocapillary curves of the second kind. The calculation was carried out according to the equation:

$$\Delta\sigma=\int_{\varphi_1}^{\varphi_2}\Gamma_{H+}\,d\varphi. \qquad (2)$$

The σ values are obtained accurately to the constants of integration. It was assumed when comparing the curves in different solutions that the σ values must be the same over the potential range where the $\Gamma_{H+}-\varphi$ curves coincide. The results of the calculation of the $\Delta\sigma-\varphi$ curves are shown in Fig. 3. In accordance with the superposition of the $\Gamma_{H+}-\varphi$ curves in sulfate, chloride, and bromide solutions, the corresponding $\Delta\sigma-\varphi$ curves also practically coincide. When I^- is present, the σ value is lower than in the presence of other anions in the potential region where I^- is adsorbed on platinum. The electrocapillary curves of the second kind that had been calculated before by an approximate method [3] agree with the curves obtained in the present work.

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