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DIRECT DETERMINATION OF HYDROGEN ADSORPTION ON PLATINUM IN HYDROCHLORIC ACID

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In [1, 2] a method for the direct determination of hydrogen adsorption on electrodes with developed surface area at any potential had been suggested. This method had first been applied to tungsten carbide, but only qualitative results had been obtained, owing to corrosion of the carbide during heating in electrolyte solutions. In order to validate the method so that it could be used in quantitative studies, it was extremely interesting to apply it to some classical system. The simplest electrochemical system is platinum in hydrochloric acid solution.

A certain amount of platinum black was exposed at specified potential to 1 N HCl until equilibrium was established, then the potentiostat was turned off and the cell was heated while slowly passing argon through it until hydrogen had completely desorbed from the platinum (details of the procedure are described in [1, 2]). One knows that hydrogen is completely desorbed from platinum when it is heated for a few minutes at 400-450°C [3, 4]. We conducted the desorption by raising the temperature over a period of 30 min to 600°C and then holding it there for 15 min. It was shown by special experiments that the amount of hydrogen desorbed will not change when the final temperature of desorption is varied between 500 and 600°C. The hydrogen carried along with the argon stream was collected in a buret, and its quantity determined chromatographically. The hydrogen chloride which interfered with the chromatographic determination of hydrogen was absorbed by passing the gas through a column with alkali.

The results obtained on platinum black in 1 N HCl at room temperature are presented in Fig. 1. The solid curve is the amount of hydrogen calculated from the charging curve, with approximate deduction of the electric double-layer charge (the double-layer capacity was assumed to be constant over the entire potential range, and to have the value of the capacity in the double-layer region). The points show the amount of hydrogen found at the different potentials after its thermodesorption from platinum. Even with an accuracy of the

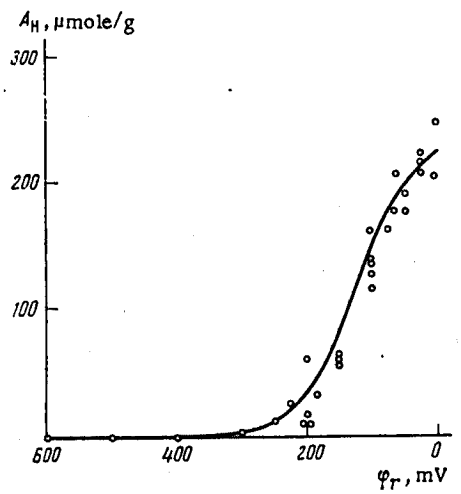


Fig. 1. Hydrogen adsorption on platinum in 1 N HCl (explanations in the text).

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direct analytical determination of hydrogen which so far is not very high, the large number of experimental points allows us to claim that to a first approximation the results obtained by these methods are in agreement.

It is very important that the thermodesorption method yields the absolute amount of hydrogen. One thus can verify the one fundamental assumption which is at the basis of calculations of the amount of adsorbed hydrogen from charging curves, and thus at the basis of the thermodynamic theory of the hydrogen electrode. In acidic solutions containing a large quantity of chloride or bromide ions, total and free charge as functions of potential run parallel over the potential range from 0.3 to 0.7 V [5]. This indicates that in this potential range, hydrogen adsorption is either constant or zero. Frumkin suggested long ago that in HCl and HBr there is no adsorbed hydrogen at potentials above 300 mV. The results reported in Fig. 1 fully support this suggestion.

It would have been interesting to apply the suggested method to other systems, but in the form described this has not been possible so far. Sulfuric acid upon heating is reduced by the adsorbed hydrogen, which causes loss of part of the hydrogen. Phosphoric acid, according to thermodynamic data, should not be reduced by hydrogen, since the equilibrium of the reaction

$$H_3PO_4+H_2 \rightleftharpoons H_3PO_3+H_2O$$

under the usual conditions is shifted strongly to the left. But during hydrogen thermodesorption from platinum in the presence of phosphoric acid one obtains low quantities of hydrogen. This seems to be due to the fact that during heating in the argon stream water is continuously carried away, and the equilibrium is shifted to the right, so that part of the hydrogen is oxidized.

It would appear that in alkali solution, just as in hydrochloric acid solution, there should in principle be no reactions between the platinum, hydrogen, and electrolyte. In fact, when ordinary, air-oxidized platinum black is heated in KOH solution in an argon stream, pure argon is collected from the cell at the exit. But after polarization of the platinum, changes occur in the system which have the effect that during heating, hydrogen appears in the gas phase even when the platinum had been prepolarized to potentials above 0.7 V. Numerous experiments at various potentials have shown that the amount of hydrogen which is desorbed is completely irreproducible, and often several times higher than would correspond to monolayer coverage of the platinum. The amount of hydrogen desorbed from the same samples of platinum in 1 N HCl always corresponds to the curve reported in Fig. 1.

In order to find out under what conditions excess hydrogen is obtained we conducted thermodesorption measurements at various HCl and KOH concentrations (over the entire pH range) and in pure water. Since in pure water it is impossible to set up any potential by passing current, the following technique was adopted. Dry, air-oxidized platinum black was reduced in the cell by passing hydrogen at room temperature. Then degassed electrolyte was introduced without opening the tightly closed vessel. Thermodesorption was carried out after purging the hydrogen from the gas phase.

In the alkali solutions and in pure water completely irreproducible results were obtained, and the amount of hydrogen often was several times that of a monolayer. In 10^{-2} to 10^{-3} N HCl the results were irreproducible, too, but there was already less hydrogen. Reproducible results were obtained beginning from 0.1 N HCl, and the amount of hydrogen corresponded to monolayer coverage of the platinum. But in neutral or alkaline KCl solution, the measurements are not reproducible, and give excess hydrogen even when the chloride ion concentration is high. It is important to note that during thermodesorption in the presence of pure water or of KOH solution one obtains more hydrogen the more profoundly prereduced the platinum.

All these experiments indicate that reduced platinum at sufficiently high temperatures is oxidized by water; the oxygen during heating is penetrating a few layers deep into the platinum, while the hydrogen is evolved into the gas phase. At high hydrochloric acid concentration the adsorption of chloride ions seems to prevent the interaction between platinum and water. The most accurate experiments have shown that for complete inhibition of this interaction one needs an HCl concentration above 1 M.

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CONDUCTIVITY OF SILVER BROMIDE/AMMONIUM BROMIDE SOLUTIONS IN DIMETHYLFORMAMIDE

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An examination of the properties of inorganic salt solutions in dipolar, aprotic solvents, especially those with moderate and high dielectric constants, is of theoretical and practical interest [1-3]. Among these solutions are silver bromide/ammonium bromide solutions in dimethylformamide (DMF), where silver can be cathodically deposited and anodically dissolved with 100% current yields over a wide range of temperatures, so that they can be used, for example, to build electrochemical integrating units with digital readout which will operate at temperatures above and below freezing. It is of interest under this aspect to examine the conductivity of these solutions as a function of component concentration and temperature. The literature does not contain work on the conductivity of such solutions.

The solubility (molality) of silver bromide in DMF is known to be $9.5 \cdot 10^{-4}$ [4]. However, silver bromide solutions containing up to 1.5 M AgBr are obtained when the silver bromide is dissolved together with ammonium bromide, because of the formation of highly soluble complex compounds of the type of $NH_4[AgBr_2]$, according to our previous findings [5]. From such solutions silver is electrolytically deposited and dissolved with appreciable rate and good quality of the silver coatings. These qualities are not found with dimethylformamide solutions of silver bromide with bromide salts not containing the ammonium group.

The methods of DMF and salt purification and the procedure of the conductivity measurements were described in the preceding paper [6].

In order to estimate the contribution of ammonium bromide to the conductivity of a solution of a compound of the type of $NH_4[AgBr_2]$ we measured the conductivity of ammonium bromide solutions, of solutions containing ammonium bromide and silver bromide at a ratio of 1.5, and also solutions having different concentrations of ammonium bromide but the same silver bromide concentration.

Figure 1 shows the measured values of specific conductance of ammonium bromide solutions (curve 2) and of silver bromide solutions containing ammonium bromide where the components were taken at a concentration

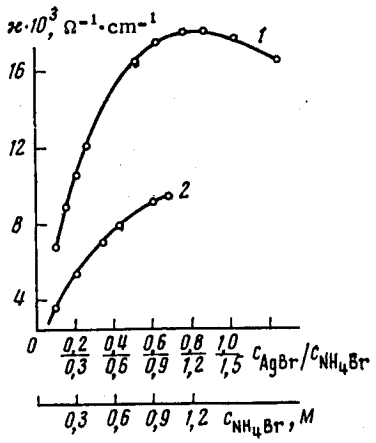


Fig. 1. Specific conductance of AgBr solutions with NH_4Br (1) and of NH_4Br solutions (2) in DMF at 25°C as function of salt concentration.

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