CHARGING CURVES OF SECOND KIND AND POTENTIOMETRIC TITRATION UNDER ISOELECTRIC CONDITIONS

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According to the generalized concept of electrode charge [1],two types of charging curve should exist for platinum metals. The usual charging curves, which characterize the relation between the full charge $Q' = -\Gamma_H$ (where Γ_H is the Gibbs adsorption of hydrogen on the electrode) and the potential φ with the chemical potential of the hydrogen ions constant ($\mu_{H^+} = \text{const}$), can be called charging curves of the first kind. By integration of these curves it is possible to obtain the electrocapillary curves of the first kind (with an accuracy up to the integration constant) [2]. Methods for the production of charging curves of the first kind are well known [3]. Accordingly, the derivative $(\partial Q'/\partial\varphi)_{\mu_{H^+}} = -(\partial\Gamma_H/\partial\varphi)_{\mu_{H^+}}$ can called the differential capacitance of the first kind. In the literature this quantity is usually called the polarization or total capacitance of the electrode. Charging curves of the second kind represent the relationship between the total charge $Q'' = \Gamma_{H^+}$ (where Γ_{H^+} is the Gibbs adsorption of hydrogen ions on the electrode) and the potential with the chemical potential of the hydrogen in the system constant ($\mu_H = \text{const}$). Integration of these curves leads to electrocapillary curves of the second kind. The quantity $(\partial Q''/\partial\varphi)_{\mu_H} = (\partial\Gamma_{H^+}/\partial\varphi)_{\mu_H}$ can be called the differential capacitance of the second kind. (It can be equated with the double layer capacitance in a solution with an excess of an extraneous inactive electrolyte.)

To obtain charging curves of the second kind it is possible to use the method of potentiometric titration with a large platinum indicator electrode [4-6]. However, this method has so far only been used at a hydrogen pressure equal to atmospheric pressure ($p_{H_2} = 1$), i.e., at $\varphi_r = 0$, where φ_r is the potential referred to a reversible hydrogen electrode in the same solution. Charging curves of the second kind for $\varphi_r > 0$ have been calculated [2] from the Γ_{H^+}, φ_r curves relating to acidic (pH 1.5-3) and alkaline (pH 11-12) solutions. The Γ_{H^+} values for pH 3-11 were obtained by interpolation. In order to investigate the structure of the double layer on platinum metals in greater detail and its dependence on the pH of the solution it seemed of interest to develop a method of obtaining charging curves of the second kind for the whole range of pH in the region of anodic φ_r values.

The simplest method of measuring such curves involves the use of mixtures of hydrogen with inert gases. By reducing the partial pressure of hydrogen in the mixture it is possible to carry out potentiometric titration with a large indicator electrode at $\varphi_r > 0$. In this case the results are subsequently treated as described previously [4-6]. A disadvantage of the method is the fact that it is in practice only applicable to $p_{H_2} \sim 10^{-4}$ atm, i.e., $\varphi_r < 0.12$ V.

Let us imagine that a Pt/Pt electrode is in contact with a solution containing an acid HA and an excess of a salt CA. This electrode is separated from the reference electrode, for which we will use a Pt/Pt electrode at $P_{H_2} = 1$ atm, by a membrane permeable for H_3O^+ ions but impermeable for H_2 molecules. By means of a potentiostat we will apply a certain potential $\varphi_r = \text{const}$ to the working electrode. If a portion of an alkaline solution of CA + COH is added to the investigated solution a current which should decrease to zero with time appears in the circuit of the potentiostat. The amount of electricity passed is $\Delta Q'' = \Delta\Gamma_{H^+}$. If the potential of the working electrode is measured with reference to some constant reference electrode, we clearly obtain the relation between Q'' and φ, i.e., a charging curve of the second kind. Similar measurements could be made at various φ_r values. For the direct realization of these measurements it is necessary to have a membrane permeable for H_3O^+ and impermeable for H_2, which is quite

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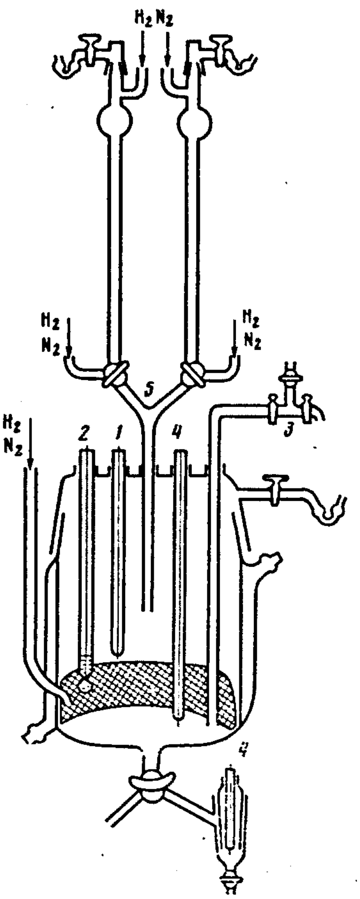

Fig. 1. Cell for potentiometric titration under isoelectric conditions: 1) Working electrode; 2) glass electrode; 3) connecting bridge to calomel electrode; 4) auxiliary electrodes; 5) system of burets.

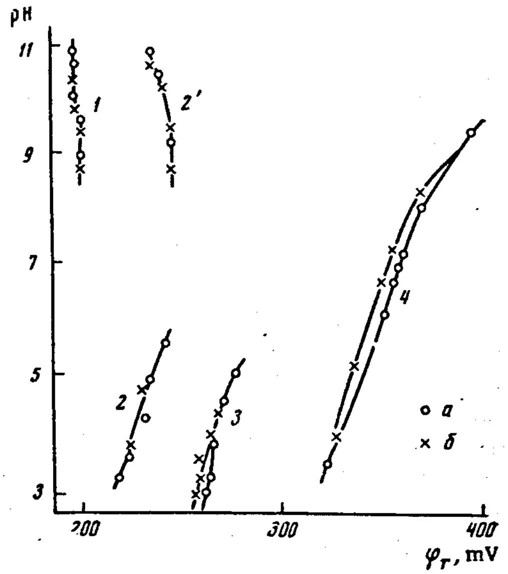

Fig. 2. Dependence of the potential of the Pt/Pt electrode on the pH of the solution in 0.1 N sodium sulfate under isoelectric conditions. Curve 4 was obtained in a solution with addition of 10^{-3} N phosphoric acid. a) Curves obtained during titration of an acidic solution with alkaline solutions; b) titration of an alkaline solution with acid solutions. Curves 2 and 2' correspond to the same total charge.

possible in principle but at the present time has not been developed as applied to the conditions of the present problem. The described method would be of interest as one method by means of which it would be possible to obtain charging curves of the second kind directly.

A method for the construction of charging curves of the second kind which can be realized in practice involves potentiometric titration under isoelectric conditions. A cell for titration under isoelectric conditions is shown in Fig. 1. A glass electrode is inserted into the central part of this cell, and this makes it possible to record the pH of the solution. By means of a system of burets it is possible to add alkaline or acidic solutions, which have been thoroughly blown with an inert gas, to the cell. The composition of the solution must be selected so that the concentration of the neutral salt considerably exceeds the concentration of HA or COH and is kept constant during the titration. A saturated calomel electrode serves for the determination of the potential φ of the working electrode.

A specific potential is first applied to the working electrode. For the realization of isoelectric conditions it is necessary that the potential in the initial solution should be greater than ~0.04 V on the φ_r scale [7]. After the addition of a specific amount of alkaline solution, the pH of the solution is recorded in the working part of the cell, and the potential φ of the working electrode is recorded. In this way, by potentiometric titration under isoelectric conditions it is possible to make direct detailed measurements of the isoelectric shifts of potential, which were previously obtained by replacement of a solution with a certain pH value by a solution with a different pH value, i.e., only near a certain pH value. The charge from the previously employed method to the method described here corresponds to a change from determination of the derivative $(\partial\varphi_r/\partial\mu_{H^+})_{Q'}$ for various previously specified values of μ_{H^+} to the direct determination of the φ_r. μ_{H^+} relation for the same condition Q' = const. In particular, by realization of the titration at an initial φ_r corresponding to Q' = 0 it is possible to obtain a relation between the potential of zero total charge and the pH of the solution.

With a knowledge of the isoelectric shifts of potential for various initial φ_r and the charging curve of the first kind for any one pH value it is possible then to plot the charging curves corresponding to other pH values. From the slope of the charging curves of the first kind and the corresponding isoelectric shifts of potential, the dependence of Γ_{H^+} on φ_r in solutions with various pH values is calculated by means of the previously employed [7-11] equation:

$$\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H^+}} = -\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{Q'}\left(\frac{\partial Q'}{\partial\varphi_r}\right)_{\mu_{H^+}}. \tag{1}$$

Sections of the family of Γ_{H^+}, φ_r curves corresponding to $\varphi_r = \text{const}$ represent the charging curves of the second kind. As integration constants in the calculation of the $\Gamma_{H^+}\varphi_r$ curves it is possible to use the Γ_{H^+} values obtained by potentiometric titration at $\varphi_r = 0$.

The amount of alkali added under isoelectric conditions, corrected when necessary by a "blank" test,* is numerically equal to the change in the Gibbs adsorption of the hydrogen ions $\Delta\Gamma_{H^+}$ with variation in the pH of the solution and with constant total surface charge Q'. Thus, by potentiometric titration under isoelectric conditions it is possible to obtain the derivatives $(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{Q'}$, or $(\partial\Gamma_{H^+}/\partial\varphi_r)_{Q'}$, which have not been determined before. According to the Gibbs equation,

$$(\partial\Gamma_{H^+}/\partial\varphi_r)_{Q'} = -(\partial Q/\partial\mu_{H^+})_{\Gamma_{H^+}}. \tag{2}$$

With a knowledge of the $\Delta\Gamma_{H^+}$ values, the charging curves of the first kind, and the Γ_{H^+}, φ_r curve for any one pH value it is then possible to calculate the charging curves of the second kind. The agreement of these curves with the curves calculated by the first method can serve as evidence for the accuracy of the calculations, although it is not a verification of any thermodynamic relationship.

In order to develop a method for potentiometric titration under isoelectric conditions, the Pt/Pt-electrode—0.1 N sodium sulfate system was investigated. The Pt/Pt electrode was prepared in the same way as for the determination of the isoelectric shifts of potential [7] and had a true surface area of 5-8 m^2.

During the measurements, hysteresis was discovered between the curves for forward and reverse titration if pH 7 was passed during the titration. Evidently, complete equalization of the H^+ and OH^- concentrations at various sections of the electrode is not achieved in neutral and close-to-neutral solutions. In fact, such equalization can occur as a result of diffusion processes in the solution and/or on account of the passage of current between the various sections of the electrode having different potentials. However, in neutral solutions the rates of the diffusion processes are low owing to the small H^+ and OH^- concentrations. Equalization of the H^+ and OH^- concentrations also does not occur in the second mechanism, since with the platinum electrode at the same potential its various sections sections can in principle be in contact with solutions having different pH values. Here the differences in μ_{H^+} are balanced by the differences in μ_H.

In order to realize the titration under conditions of complete equalization of pH, the working electrode was arranged in a ring around the periphery of the cell, and the alkaline and acidic solutions were delivered from the buret at the center of the cell. The titration was performed with agitation of the solution by a stream of inert gas. The pH was initially varied within narrow limits. If the electrode acquired the initial potential on return to the initial pH value, this demonstrated reversible variation in the state of the system during titration. In the following titration the amplitude of the pH variation was then increased towards pH 7. In this way it was possible to achieve reversible variation of potential in the ranges of pH 3-5.5 and 9-11 (Fig. 2). It was necessary to obtain the dependence of φ_r on pH for pH 5.5-9 by interpolation. Here, to determine the φ_r, pH curve in alkaline solutions corresponding to the φ_r, pH curve in the acidic medium (or vice versa), the shift of potential with an abrupt change from acidic to alklaine solution was measured.

The isoelectric shifts at the extreme pH values obtained by the developed method agree with those obtained earlier [12, 13].

Measurements at pH values close to 7 were found to be possible when 10^{-3} N phosphoric acid was added to the solution to give it buffering characteristics (Fig. 2). There is, however, some risk that specifically adsorbed ions of phosphoric acid [14] will have an effect on the measured shifts of potential. This method therefore makes it possible to obtain completely accurate results in the presence of the more strongly specifically adsorbed Cl^- and Br^- ions.

The measurements made in the present work show that potentiometric titration under isoelectric conditions can be used as the basis for detailed investigation of the effect of pH on the structure of the surface layer in platinum metals.

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*As follows from [5, 6], the corrections for the "blank" test are significant at pH < 3.5 and > 11.5.

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