IMPEDANCE OF A SMOOTH PLATINUM ELECTRODE DEPENDING ON THE KIND OF ANIONS IN THE ELECTROLYTE

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The effect of anions on the impedance of a platinum electrode in acidic electrolytes was studied in [1-5]. The measurements there have produced data for a qualitative evaluation of the effect which the adsorption of SO_4^{2-}, Cl^-, Br^-, and I^- anions has on the kinetics of the discharge-ionization reaction involving hydrogen adsorbed at a platinum surface

$$H_3O^+ \bar{e} = H_{ads} + H_2O$$

on the capacitance of the electric double layer, and on the trend of the amount of adsorbed hydrogen as a function of the potential. The exchange current (i_0) of reaction (1) has been found to increase with increasing adsorptivity of the anions within a certain range of the degree of surface coverage with adsorbed hydrogen H_{ads}, which agrees with the theory of retarded discharge applied to hydroxonic ions in [6]. One must note the inconsistency of the test data in [1-5], however, which calls for a further study concerning the effect of anions on the impedance of a platinum electrode and for applying in this study modern methods of electrode preparation, electrolyte purification, and data evaluation.

Such a study was made in 10^{-2} N H_2SO_4 + 1.0 N NaX electrolytes ($X = SO_4^{2-}$, Cl^-, Br^-, or I^-). The salts had been twice recrystallized from twice-distilled water and then annealed (NaI in a hydrogen atmosphere). The sulfuric acid was twice distilled under vacuum. Thrice-distilled water was used for the preparation of electrolytes. The latter were additionally purified, immediately before a measurement, with large Pt/Pt grids at potentials of hydrogen release.

A platinum wire 50 μ in diameter and with an active surface area of approximately 0.005 cm^2 served as the working electrode. The surface area had been determined on the basis of hydrogen adsorption at the potential $\varphi_r = 0$ V.* Measurements were made with an ac bridge connected to a potentiostat [7]. The electrode was activated by means of anodic–cathodic pulses at potentials $\varphi_r = 1.2$ and 0.05 V in sulfate electrolytes, at $\varphi_r = 1.0$ and 0.05 V in chloride electrolytes, at $\varphi_r = 0.9$ and 0.05 V in bromide electrolytes. Each pulse was held for 1 sec. Following a cathodic pulse, 10 sec later, an operating potential was applied to the electrode at which then the impedance components were measured. The balancing of the bridge was made to coincide with the end of the activating pulse. No activation of the working electrode was needed in an iodide electrolyte, because of the early oxidation of iodide ions at a platinum surface.

The C_s vs φ_r curves and the R_s vs φ_r curves for 11 different frequencies of the alternating current ν_i from 40 to 50,000 Hz (C_s and R_s denoting the capacitance and the resistance, both measured in a series circuit) have been recalculated on a model BÉSM-6 computer according to the method shown in [8], to refer to components of the Dolin–Érshler circuit [1]. As the minimizing function was used $F = \sum_{i=1}^{11} \frac{|z_t^i - z_e^i|^2}{|z_e^i|^2}$ with z_t^i and z_e^i denoting, respectively, the theoretical and the experimental values of impedance at the i-th ac test frequency. As independent variables were used the following Dolin–Érshler circuit parameters: capacitance of the electric double layer C_1, capacitance of the adsorption layer C_2, reaction resistance r,

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*φ_r referred to a reversible hydrogen electrode in the same electrolyte.

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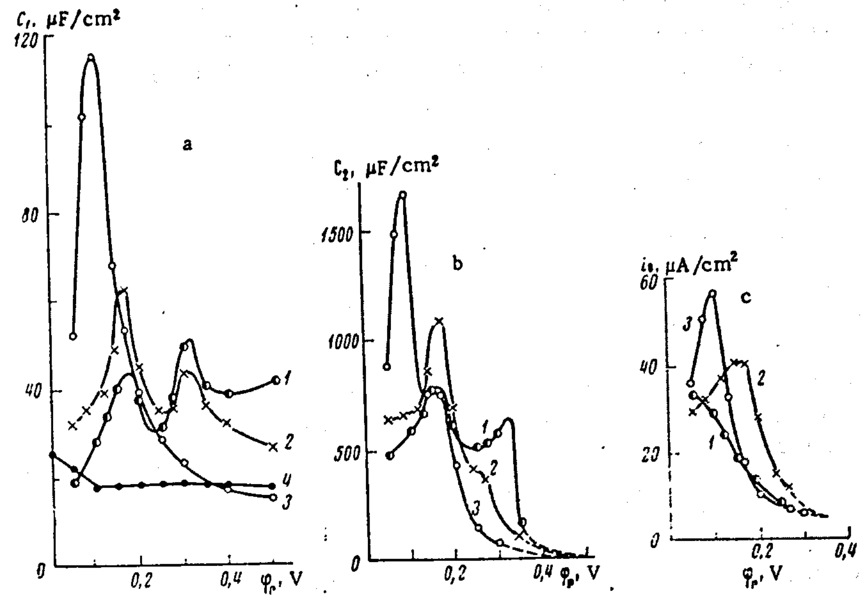

Fig. 1. Capacitance of (a) the electric double layer C_1 (μF/cm²), (b) the adsorption layer C_2 (μF/cm²), and (c) exchange current i_0 (μA/cm²) in the hydrogen reaction, as functions of the potential φ_r (V), in 10^{-2} N $H_2SO_4 + 1.0$ N NaX electrolytes: 1) X = SO_4 2) X = Cl, 3) X = Br, 4) X = I.

and electrolyte resistance R_{p-pa}. The calculated resistance R_{p-pa} of each electrolyte did not depend much on the potential. The value of function F remained within approximately 0.40-0.45 for potentials $\varphi_r < 0.3$ V, indicating a satisfactory representation of test data by the Dolin–Érshler circuit within the 50-300-mV range of potential φ_r. The current in the exchange reaction (1) was determined from the r values according to the equation $i_0 = (RT/F)\ (1/r)$ [1]. For $\varphi_r > 0.3$ V in the sulfate and the chloride electrolytes and for $\varphi_r > 0.25$ V in the bromide electrolyte, on the other hand, this calculation of C_2 and r was found insufficiently accurate and, therefore, the respective segments of the C_2 vs φ_r curves and of the i_0 vs φ_r curves were drawn with dashed lines (Fig. 1). The C_1 vs φ_r curves fit almost perfectly the C_s vs φ_r test curve for $\nu = 50$ kHz.

The curves in Fig. 1a depict the capacitance C_1 of the electric double layer at the platinum surface, as a function of the potential in the various electrolytes. The C_1 vs φ_r curves for the chloride and the sulfate electrolyte have two peaks, the nature of these peaks having already been discussed in [9]. The C_1 vs φ_r curve for the bromide electrolyte has only one peak, namely at $\varphi_r = 0.1$ V, the capacitance at this peak being equal to approximately 115 μF/cm² and indicating, probably, an appreciable deformation of Br^- ions during adsorption. The curves in Fig. 1a characterize the true capacitance of the electric double layer [9]. The fact that this capacitance decreases in the order $C_1^{SO_4^{2-}} > C_1^{Cl^-} > C_1^{Br^-}$ at potentials $\varphi_r > 0.25$ V can, apparently, be explained by an increase, in the same order of the adsorption stability of the respective anions. At such potentials the bond of these anions with the electrode becomes covalent, and they transfer part of their charge to the platinum. At potentials $\varphi_r < 0.20$ V the capacitance C_1 changes in the opposite direction depending on the kind of anions (in sulfate, chloride, and bromide electrolyte, respectively). Such a trend of the capacitance of the electric double layer may be attributed to the anion–platinum bond whose covalence decreases as the potential shifts in the cathodic direction. Here, as in the case of a mercury electrode, the capacitance of the electric double layer also decreases in the order $C_1^{Br^-} > C_1^{Cl^-} > C_1^{SO_4^{2-}}$. The I^- ion is special. Its adsorption is so stable that the covalent interaction with the platinum surface begins to decrease only at potentials $\varphi_r < 0.1$ V, apparently, which then causes some increase in the capacitance C_1. A noteworthy feature of the C_1 vs φ_r curve for electrolytes containing I^- ions is the weak dependence of C_1 on φ_r over a wide range of φ_r. The capacitance of the electric double layer in electrolytes with I^- ions is close to the capacitance in 1.0 N $H_2SO_4 + 0.1$ N KI at 20-50 kHz and $\varphi_r = 0.4$ V, according to [5]. This indicates that, probably, the I^- adsorption depends only slightly on the pH factor in acidic electrolytes at potentials φ_r within the range of the electric double layer.

It ought to be noted here that such an effect of anion adsorption on the relation between the capacitance of the electric double layer and the electrode potential has been found not only in the case of platinum, but also in the case of several other metals, for instance, of metals of the iron group (e.g., nickel [10]) or copper [11].

The calculated C_2 vs φ_r curves (Fig. 1b) follow closely the C_s vs φ_r curves for 40 Hz and also the potentiodynamic I vs φ_r curves. The qualitative difference between the calculated C_2 vs φ_r curves and the curves of parallel capacitance versus potential φ_r obtained in [5] is probably attributable to the purer and more active platinum surface in our study, owing to the use here of continuously activated electrodes.

The current associated with the exchange of adsorbed hydrogen is shown in Fig. 1c as a function of the potential. This current i_0 is heavier in the chloride or the bromide electrolyte than in the sulfate electrolyte, as the adsorptivity of the anions increases over a certain range of potentials corresponding to a mediun degree of surface coverage with adsorbed hydrogen (H_{ads}) in the respective electrolytes. Owing to a lower bond energy of H_{ads} and a narrower range of hydrogen adsorption with a higher anion adsorptivity, at the same time, i_0 decreases more appreciably as the anode potential rises when the sulfate electrolyte is replaced by the chloride or the bromide electrolyte. The extremal character of the i_0 vs φ_r curves for the chloride and the bromide electrolytes is probably connected with the desorption of Cl^- and Br^- ions, respectively, as the potential $\varphi_r = 0$ V is approached. The current i_0 is lowest in the iodide electrolyte, but the calculation here has not been sufficiently accurate on account of the small spread of test values for C_s and R_s. The data pertaining to the dependence of current i_0 on the kind of anions may be interpreted qualitatively on the basis of the theory of retarded discharge, with the effect of anion adsorption on the ψ_1-potential and also on the $Pt-H_{ads}$ bond energy and on the surface coverage with H_{ads} taken into account according to [6].

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