SURFACE TENSION OF PLATINUM ELECTRODE

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The surface tension of a solid differs from the surface formation energy [1]. The method described in [2] made it possible to measure the change in surface tension of solid electrodes γ with change in either the electrode charge density ε or the potential φ. We will call this quantity, $\partial\gamma/\partial\varepsilon$ or $\partial\gamma/\partial\varphi$, the estance (a term of the same type as impedance, admittance, etc.) and also ε-estance ($\partial\gamma/\partial\varepsilon \equiv \gamma_\varepsilon$) and φ-estance ($\partial\gamma/\partial\varphi \equiv \gamma_\varphi$). As shown in [3],

$$\frac{\partial\gamma}{\partial\varphi} = -\varepsilon - \frac{\partial\varepsilon}{\partial\vartheta}, \tag{1}$$

where ϑ is the ratio of the solid surface area after deformation to the area before deformation. This applies, for example, to an anisotropic rectangular plate of metal, the width of which is fixed by constraints sliding along the side edges while forces which equalize the variation in γ ($\partial\gamma/\partial\varphi$ at ϑ = const) or which cause deformation ($-\varepsilon - \partial\varepsilon/\partial\vartheta$ at φ = const) are applied to the transverse edges. Constancy in width is not essential, and its variation can be taken into account by calculation [3]. During electrostatic adsorption, for example, under conditions where all the adsorbed ions are in the diffuse part of the double layer, the $\partial\varepsilon/\partial\vartheta$ term becomes zero (with an accuracy up to the negligibly small effect of the change in the work function during deformation of the metal in a solvent or in vacuum), since the degree of diffuseness (and ε) does not depend on the deformation of the metal (ϑ). Unlike metals of the cadmium type, the role of electrostatic adsorption in the formation of an interphase layer on platinum in aqueous solutions is relatively small owing to electrochemisorption of hydrogen and oxygen, which consumes a considerable part of ε. Since the points where these particles fall are localized and during deformation follow the surface, in the case of platinum the $\partial\varepsilon/\partial\vartheta$ term is clearly not equal to zero. Therefore, for platinum the dependences of the surface tension and free surface energy on φ differ substantially. From Eq. (1) and the data given below it follows, for example, that the surface density of hydrogen adsorbed on platinum in 1 N sulfuric acid solution increases during elastic extension around 0 and +0.16 V with reference to the normal hydrogen electrode.

The complex (modulus, phase) $\partial\gamma/\partial\varepsilon - \varphi$ relationships for platinum were measured in alkaline and acidic media (up to 36 N sulfuric acid) at frequencies between 20 Hz and 256 kHZ. Increase in the frequency and in the pH value affects the various elements of the $\gamma_\varepsilon - \varphi$ curve in a similar manner, particularly in the O region of φ. Below 1 kHz in 1 N sulfuric acid solution ε falls little behind φ, and $\partial\gamma/\partial\varepsilon$ can be considered to be substantial. Then, as φ is displaced, the estance $\partial\gamma/\partial\varepsilon$ changes sign four times: oxygen zero (between +0.6 and +1.2 V); zero at +0.2 V; two zeros near +0.1 V, referred to the normal hydrogen electrode [2]. In the O region of φ (surface oxide) the estance does not depend on the frequency ν between 1 and 200 kHz. This is the result of deformation of the PtO monolayer in the electric field. At +1.45 V, $\partial\gamma/\partial\varepsilon$ = 3 V (converted [3] to true surface). In the H region (between +0.4 and -0.05 V) the two sections corresponding to strong dependence of estance on frequency (more positive than +0.2 V and near +0.1 V) alternate with the two sections where this dependence is slight; the latter are separated by a peak at +0.1 V. The peak itself increases rapidly with frequency, rising from the bottom of the hollow (Figs. 1 and 2). There, where the estance depends little on frequency, it increases with coverage of the surface by hydrogen Γ_H. At these values the bond energy of the adsorbed hydrogen decreases with increase in Γ_H, the same $\Delta\Gamma_H$ value is "pushed" more strongly away from the surface, and $|\Delta\gamma|$ becomes greater. It is possible to give a quantitative explanation for this fact; by substituting in Eq. (1) the linear dependence of ε ($\approx -\Gamma_H$) on φ, $\varepsilon = p + q\varphi$,

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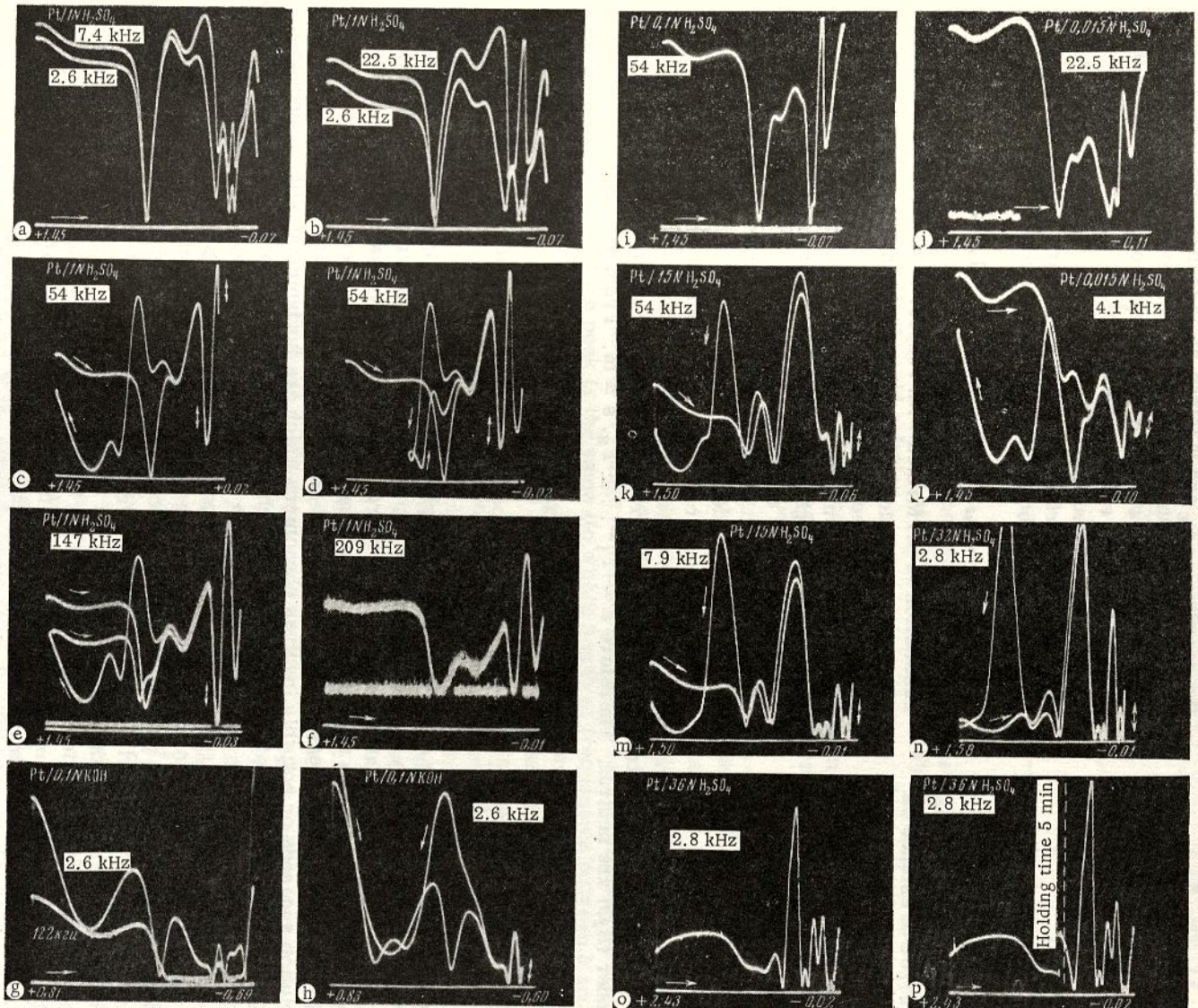

Fig. 1. Oscillograms for "estance $|\partial\gamma/\partial\varepsilon|$—potential φ" on smooth polycrystalline platinum in various media (from 0.1 N potassium hydroxide solution to 36 N sulfuric acid) at various frequencies; 20°C. The values are indicated for the ends of the zero line, referred to a Pt/H_2 electrode in the same solution [apart from g) and h), where φ is referred to the normal hydrogen electrode]. The holding time at the initial φ value after return from the final φ value was $\tau_0 = 2$ min, except for c) and d), where $\tau_0 = 1$ min, and g) and h). The length of the time base at one end is 56 sec (a, b, e), 32 sec (c, d), 160 sec (f, j, l), 18 sec (g, o, p) 64 sec (h, i, k, m), 41 sec (p); a), b), and g) were recorded simultaneously with two frequencies [2]: A small current was passed through the electrode in the form of the sum of two sinusoidal waves at 2.6 and 7.4 kHz (a) and 2.6 and 22.5 kHz (b). Scale of $|\gamma_\varepsilon|$: For 0.01 to 2 N sulfuric acid $|\gamma_\varepsilon (+1.45\ V)| = 3$ V (k, l, m: + should be on the right).

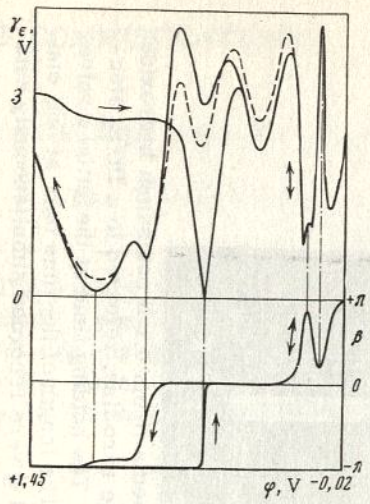

Fig. 2. Dependence of modulus $|\partial\gamma/\partial\varepsilon|$ and phase $\beta = \arg \partial\gamma/\partial\varepsilon$ of estance on potential φ for platinum in 2 N sulfuric acid solution at ν = 54 kHz, τ_0 = 2 min, and with time base 64 sec; the reverse curves were recorded from φ = +0.05 V (continuous line) and φ = 0 (dotted line) referred to Pt/H_2 electrode in the same solution.

we find that under certain conditions even $\partial\gamma/\partial\varphi$ depends linearly on φ: $\partial\gamma/\partial\varphi = -(p + \partial p/\partial\vartheta) - (q + \partial q/\partial\vartheta)\varphi$. A hollow of 0.13 V in extent at +0.1 V interrupts the increase in the estance.

According to the data from the tests (Figs. 1 and 2), $\Delta\gamma$ is composed of terms, some of which are proportional to $\Delta\varepsilon$, and others to $\Delta\varphi$. The former do not depend on frequency with the coordinates γ_ε and φ (since $\Delta\gamma$ is then recorded at $\Delta\varepsilon$ = const), and the latter do not depend on frequency with the coordinates $\gamma\varphi$ and φ. The preponderance of terms with $\Delta\varepsilon$ (at certain φ values) explains the sections with the slight dependence of γ_ε on frequency (Fig. 1a and b). In the general case, by introducing surface densities Γ_k of particles of sort k (k = 1, . . . , m), we obtain (for any frequency):

$$\Delta\gamma = \gamma_{\varphi 0}(\Gamma_1,\ldots,\Gamma_m)\,\Delta\varphi + \gamma_k(\Gamma_1\ldots,\Gamma_m)\,\Delta\Gamma_k; \qquad (2)$$

summation is performed with respect to k, and $\gamma_{\varphi 0}$ and γ_k are certain real functions of Γ_k; the individual Γ_k values can depend on φ; Δ is the sign of amplitude or increment. The term with $\Delta\Gamma_k$ represents the appearance of particles of sort k on the surface through conversion in the interphase layer or adsorption from the solution, $\gamma_k = \partial\gamma/\partial\Gamma_k$. The term with $\Delta\varphi$ represents formation of the interphase layer in the electric field. With considerable ν values the Γ_k and φ phases (arg $\Delta\Gamma_k$ and arg $\Delta\varphi$) can be distinguished through the fact that the adsorption of the particles falls behind the potential. The slowness of hydrogen adsorption by H^+ discharge on platinum [4] is substantial at ν > 1 kHz. Of m sorts only s are charged before adsorption (e.g., H^+), whereas the remainder (H_2O) are neutral. Therefore $\varepsilon = -\Gamma_1 - \ldots - \Gamma_s$, s ≤ m. From Eq. (2)

$$\gamma_\varphi = C\gamma_\varepsilon = \gamma_{\varphi 0} + C_k\gamma_k, \qquad (3)$$

where $C_k = \partial\Gamma_k/\partial\varphi$, $C = \partial\varepsilon/\partial\varphi = -C_1 - \ldots - C_s$ are complex capacitances; ReC is capacitance in the usual sense.

The estance peak at +0.1 V and the clear maximum (at high ν values) more positive than +0.2 V (Fig. 1) are similar in that φ for each of them corresponds to the capacity maximum measured at $\nu \to 0$ and in that they are retained at frequencies greater than 200 kHz, whereas the two capacity maxima are missing even at 5 kHz, and the capacity itself due to adsorption of hydrogen from the solution tend towards zero with increase in ν [4, 5]. Thus, the estance peak and maximum exist irrespective of whether adsorption of hydrogen from the solution succeeds or not; this involves phenomena which are fundamental with respect to adsorption of hydrogen from the volume of the solution and which stimulate this adsorption. They can be explained by the presence on the platinum of a chemisorbed, as a whole, electrically neutral compound which contains hydrogen and oxygen atoms. In the H region of φ this can be regarded as the product from chemisorption of water. With increase in $\varphi > 0$ this compound undergoes a series of reversible changes towards strengthening the bond with platinum (the peak at +0.1 V, the maximum between +0.2 and +0.3 V, the maximum near +0.8 V on the $|\gamma\varepsilon| - \varphi$ curve; with all three extrema $\gamma_\varepsilon < 0$). It then begins to be reduced electrochemically and irreversibly, at some of the sites on the surface to start with (zero γ_ε at +0.91 V and phase change by π) and then at the remaining sites (minimum at +1.13 V without change in phase). Between +0.9 and +1.1 V the stationary state of platinum varies reversibly with φ. In the H region of φ the free positive charge of the electrode is mainly concentrated inside the solid part of the interphase layer (platinum and locally adsorbed particles), and the negative charge is concentrated outside it. Change in the sign of the charge is accompanied by departure of the variable-field region from the solid electrode, and, as a result, a drop in the deformation component $\Delta\gamma$ (apart from the vicinity of +0.1 V). In fact, the potential of +0.17 V, below which the dependence of the estance on frequency (and on $\Delta\varphi$) becomes much weaker (the point where the curves join, 2.6 and 22.5 kHz in Fig. 1b), is close to the zero charge potential [6]. The $\gamma_\varepsilon - \varphi$ curves in perchloric acid solutions are similar in form.

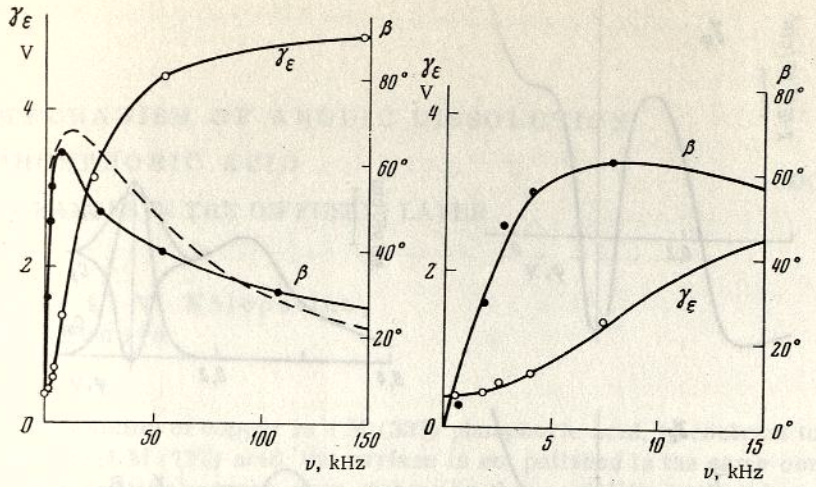

Fig. 3. Dependence of modulus $|\partial\gamma/\partial\varepsilon|$ and phase $\beta = \arg \partial\gamma/\partial\varepsilon$ of estance on frequency ν at peak potential (+0.1 V) for platinum in 1 N sulfuric acid solution.

We will denote the surface density of chemisorbed compound in a certain initial condition by Γ_α and will write Eq. (2) in the simplest form: $\gamma_\varphi = a(\partial\Gamma_\alpha/\partial\varphi) + b\Gamma_\alpha$, where a and b are constants. With decrease in φ the drop in Γ_α (transformation, desorption) corresponds to drop in γ_φ preceded by a maximum – on account of $\partial\Gamma_\alpha/\partial\varphi$. The form of γ_ε is similar. This is consistent with experiment, where $\partial\Gamma_\alpha/\partial\varphi$ is maximum at the same φ value (+0.24 V) as the capacitance. The effect of the term $b\Gamma_\alpha$ on the φ value of the γ_ε maximum is here taken into account by replacing $b\Gamma_\alpha$ by the chord on which the maximum rests. The estance peak at +0.1 V differs from the maximum at +0.24 V in that: 1) It is narrow – its base is 0.13 V, and its half-width 0.06 V, which in the case of the Langmuir isotherm would correspond to a number of electrons n = 2; 2) The estance and its degree of change with frequency (Fig. 1a) are the same before and after the peak; 3) The potential of the peak is the same (to within 3 mV) at frequencies between 0 and 50 kHz; 4) The peak and (at low ν values) the hollow near +0.1 V are retained between 0.01 N and 36 N sulfuric acid – on the cathodic and anodic curves (Fig. 1n) up to 32 N and only on the cathodic curve, with a scan rate greater than 0.1 V/sec, at 36 N (Fig. 1o and p). Since the peak at +0.1 V is inseparable from the adsorption of H (in some state, H_m) – this is indicated by the independence of its φ value from ν – and, on the other hand, is not related to the departure of H^+ from the solution, the "proton donor" must exist here at the surface. It can be either 1) already adsorbed H_e ($H_e \rightleftarrows H_m$) or 2) a chemisorbed compound. Of these two mechanisms only the second gives a frequency dependence for the height and phase of the peak close to the observed (Fig. 3); in amplitude and phase $\partial\gamma/\partial\varepsilon$ at +0.1 V varies with ν like $\partial\varphi/\partial\varepsilon$ –(a value which is inversely proportional to C). By being discharged, the H^+ ions pass from the solution directly to the H_e state, and to the H_m state through the chemisorbed compound which blocks access to H_m. Hence the observed difference in the rate constant for the establishment of equilibrium ($2.6 \cdot 10^3$ sec^{-1} at $\varphi = 0.1$ V against $4 \cdot 10^3$ sec^{-1} at $\varphi > +0.16$ V and $\varphi < +0.03$ V). At $\nu > 50$ kHz the estance phase falls more slowly than would follow from the effect of the double layer along (Fig. 3a, dotted line). It is possible that the adsorption of hydrogen involves a high-frequency component, the relative contribution of which to low ν values is small.

We will denote the amounts of charge used on the adsorption of hydrogen in the H_e and H_m states per unit surface by ε_e and ε_m, where $\varepsilon_H = \varepsilon_e + \varepsilon_m$; $C_H = C_e + C_m$, where $C_e = \partial\varepsilon_e/\partial\varphi$ and $C_m = \partial\varepsilon_m/\partial\varphi$. Adsorption of H decreases γ ($\gamma_\varepsilon > 0$ far from +0.1 V, whence $\partial\gamma/\partial\Gamma_e < 0$), and H_m increases γ ($\gamma_\varepsilon < 0$ at +0.1 V, whence $\partial\gamma/\partial\Gamma_m > 0$). This and the frequency dependence of γ_ε indicate the origin of the hollow on the $|\gamma_\varepsilon| - \varphi$ curve near +0.1 V at low ν values; the closer to +0.1 V, the less the coverage with H_e increases with the same $\Delta\varphi$ value. At +0.1 V φ hardly affects the amount of H_e (the capacitance $\partial\varepsilon_e/\partial\varphi$ is close to 0), whereas on both sides of +0.1 V the effect is great (Fig. 4). This is possible if at +0.1 V the increment in φ is used mainly in changing the potential jump in the surface-adjacent layer with the metal (φ_m), whereas the jump in the solution (φ_e), which controls the adsorption of H_e, does not change, $\Delta\varphi = \Delta\varphi_m + \Delta\varphi_e$. The extent of the hollow along the φ axis is close to the maximum change in φ_m, $\delta\varphi_m \approx 0.13$ V. Such a change in φ_m may be due to the positioning of H_m within the metal, where $\delta\varphi_m$ corresponds to limiting coverage with H, the magnitude of which depends on the degree of homogeneity and purity in the surface. The

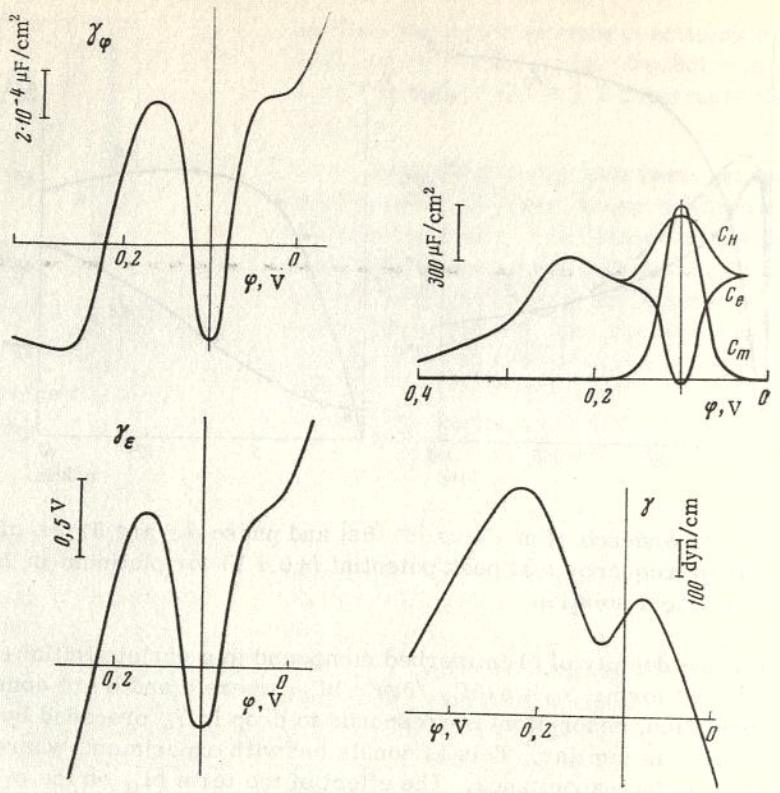

Fig. 4. Dependences of $\partial\gamma/\partial\varepsilon$, $C = C_e + C_m$, $\partial\gamma/\partial\varphi$, and γ on potential for platinum in 1 N sulfuric acid solution at $\nu \to 0$.

potential of the electrode is shifted towards the negative side upon coverage with H_m, and this is favorable for further increase in the coverage and is equivalent to a positive attraction constant in the Frumkin isotherm. These conclusions can be partly extended to the system of Pt in H_2.

At points more cathodic than the inflection at 0 V the slope of the $\gamma_\varepsilon - \varphi$ curve becomes steeper. Here the γ_ε (7.4 kHz) $- \gamma_\varepsilon$ (2.6 kHz) difference remains constant over a certain range of φ values (Fig. 1a). With increase in the frequency the φ region in which the current is not consumed on H_2 evolution expands; for 1 N sulfuric acid solution the beginning of the second jump in γ_ε moves from 0 V at $\nu = 0$ to -0.02 V at 4 kHz. Since $\Delta\varepsilon_H \approx \Delta\varepsilon = \text{const}$, this effect represents a delay in recombination. In combination with the impedance data this can be used for the analysis of $\partial\varepsilon_H/\partial\varphi$ at $\varphi < 0$.

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