ON HIGHER HARMONICS OF THE SURFACE TENSION IN SOLID ELECTRODES

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The relationship between the surface tension harmonics excited by fluctuations of charge and electrode potential are discussed theoretically and experimentally.

The dependence of the surface tension of solid electrodes [1] on the potential is accessible to direct measurement. In the method proposed for this purpose [1], the surface tension fluctuations of the solid electrode are produced by superimposing a small periodic component to the average electrode potential and are measured by means of a piezo element attached to the electrode above the meniscus which touches the solution with its lower end. Since the dependence of the surface tension (γ) on the potential (φ) and the charge (ε) of the electrode is nonlinear, a spectrum of surface tensions corresponds to a single frequency of potential current, i.e., in addition to the fundamental harmonic, higher harmonics, which are multiples of the fundamental, are present in the surface tension fluctuations. The higher surface tension harmonics can be isolated and used for obtaining additional information on the surface phenomena.

One can choose φ or ε as the independent variable in the relations between γ, φ and ε. If the alternating current is given, i.e., the first harmonic of the charge ε with the amplitude $\Delta\varepsilon = \text{const}$ at any φ_m (Δ and m are the symbols for the amplitude and average) the spectra of the harmonics γ and φ are excited. We shall then speak of the n-th harmonic of γ (or φ) to the first harmonic of ε, and write it as $\Delta_{n1}{}^{\varepsilon}\gamma$ (or $\Delta_{n1}{}^{\varepsilon}\varphi$). Since a certain spectrum of the harmonics γ also corresponds to one n-th potential harmonic we shall write the k-th harmonic of this spectrum as $\Delta_{kn}{}^{\varphi}\gamma$, terming it the k-th harmonic of γ to the n-th harmonic of φ. Where necessary we shall also indicate the frequency ν of this harmonic of γ, $\Delta_{kn}{}^{\varphi}\gamma_{\nu}$. The expansion into a series in powers of $(\Delta_{n1}{}^{\varepsilon}\varphi)^2$:

$$\Delta_{kn}^{\varphi}\gamma_{k\alpha} = \frac{2^{1-k}}{k!}(\Delta_{n1}{}^{\varepsilon}\varphi_{\alpha})^{k}\left\{\left(\frac{\partial^{k}\gamma}{\partial\varphi^{k}}\right)_{k\alpha} + \frac{1}{4(k+1)}\left(\frac{\partial^{k+2}\gamma}{\partial\varphi^{k+2}}\right)_{k\alpha}(\Delta_{n1}{}^{2}\varphi_{\alpha})^{2} + \ldots\right\}_{m} \qquad (1)$$

is applicable when γ practically depends at the given frequency $k\alpha$ only on the potential and is independent of time. For this it is sufficient that the relative variation of concentration of the solution around the electrode be small (an estimate of this factor is given in [1]), and also that in the frequency range to be used the change of state of the interphase layer with the potential be a fairly rapid reversible process. The calculations show that $\Delta\varphi < 0.1$ V can be used as a criterion of the smallness of $\Delta\varphi$ for the first two harmonics. Then,

$$\Delta_{kn}{}^{\varphi}\gamma_{k\alpha} = (2^{1-k}/k!)(\partial^{k}\gamma/\partial\varphi^{k})_{k\alpha}(\Delta_{n1}{}^{\varepsilon}\varphi_{\alpha})^{k}. \qquad (2)$$

At n = 1 follows from this a simple method of experimental verification of whether the smallness criterion $\Delta\varphi$ is satisfied. Instead of calculating the sum of the series (1) and comparing it with the first term, it is sufficient to check whether the measured surface tension amplitude is proportional to the corresponding power of the potential or current amplitude, $\Delta_{k1}{}^{\varphi}\gamma \sim (\Delta\varphi)^{k}$; $\Delta_{k1}{}^{\varphi}\gamma \sim (\Delta j)^{k}$; the same holds for $\Delta_{k1}{}^{\varepsilon}\gamma$.

It follows from (2) that in the coordinates $\Delta_{kn}{}^{\varphi}\gamma - \varphi$ (harmonic to potential vs. potential) and $\Delta_{kn}{}^{\varepsilon}\gamma - \varepsilon$ (harmonic to charge vs. charge) the amplitude of the (k+1)-th harmonic is proportional to the derivative of the amplitude of the k-th harmonic. However, from the experimental point of view, the oscillograms obtained in the mixed coordinates $\Delta_{kn}{}^{\varepsilon}\gamma - \varphi$ (harmonic to charge vs. potential) are more accurate, which corresponds to the given periodic current component with the amplitude $\Delta j = \text{const}$ against the background of the given average electrode potential φ_m.

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Here, the amplitude of the (k+1)-th harmonic is no longer proportional to the derivative of the amplitude of the k-th harmonic with respect to the potential

$$\Delta^{\varepsilon}_{k+1,1}\gamma = [\Delta\varepsilon/2(k+1)(\partial\varepsilon/\partial\varphi)]\,\partial(\Delta_{k1}{}^{\varepsilon}\gamma)/\partial\varphi, \tag{3}$$

since $\partial\varepsilon/\partial\varphi$, the electrode capacitance, which depends on the potential, enters into the coefficient. Nonetheless, even in these coordinates, zero amplitudes of the (k+1)-th harmonic correspond to the extrema of the amplitude of the k-th harmonic, and to the simple zeros of the amplitude of the k-th harmonic correspond nonzero amplitudes of the (k+1)-th harmonic. Indeed, according to (3) the values of $\Delta_{k+1,1}{}^{\varepsilon}\gamma = 0$, correspond to the extrema of $\Delta_{k1}{}^{\varepsilon}\gamma$. This correspondence is mutually unambiguous because $0 < |\partial\varepsilon/\partial\varphi| < \infty$. This constitutes the simple method which makes it possible independently of the phase measurement, to distinguish in the $\Delta_{k1}{}^{\varepsilon}\gamma - \varphi$ oscillograms a simple zero of the k-th harmonic from its extremum.

The first harmonics of γ with respect to charge and potential are identical, $\Delta_{11}{}^{\varepsilon}\gamma_{\nu} = \Delta_{11}{}^{\varphi}\gamma_{\nu}$. The second harmonics, generally speaking, are not, $\Delta_{21}{}^{\varepsilon}\gamma \neq \Delta_{21}{}^{\varphi}\gamma$. Using (2) for the harmonics of γ to ε (substitution of ε for φ and φ for γ) and also the relation $\partial^2\gamma/\partial\varepsilon^2 = (\partial^2\gamma/\partial\varphi^2)(\partial\varphi/\partial\varepsilon)^2 + (\partial\gamma/\partial\varphi)(\partial^2\varphi/\partial\varepsilon^2)$, we obtain:

$$\Delta_{21}{}^{\varepsilon}\gamma_{\nu} = \Delta^{\varphi}{}_{21}\gamma_{\nu} + \Delta_{12}{}^{\varphi}\gamma_{\nu}, \tag{4}$$

i.e., on the second surface tension harmonic, excited by the first potential harmonic, is superposed the first surface tension harmonic, excited by the second potential harmonic. We find the relative difference between $\Delta_{21}{}^{\varepsilon}\gamma_{\nu}$ and $\Delta_{21}{}^{\varphi}\gamma_{\nu}$, $s = |\Delta_{12}{}^{\varphi}\gamma_{\nu}/\Delta_{21}{}^{\varepsilon}\gamma_{\nu}|$. From (2)

$$\Delta_{12}{}^{\varphi}\gamma_{\nu} = (\partial\gamma/\partial\varphi)_{\nu}\Delta_{21\varepsilon}\varphi_{\nu}, \qquad \Delta_{11}{}^{\varepsilon}\gamma_{\nu} = \Delta_{11}{}^{\varphi}\gamma_{\nu} = (\partial\gamma/\partial\varphi)_{\nu}\Delta_{11}{}^{\varepsilon}\varphi_{\nu}.$$

Hence

$$s = |\Delta_{11}{}^{\varepsilon}\gamma_{\nu}\Delta_{21}{}^{\varepsilon}\varphi_{\nu}/\Delta_{11}{}^{\varepsilon}\varphi_{\nu}\Delta_{21}{}^{\varepsilon}\gamma_{\nu}|, \tag{5}$$

or $s = L(\gamma)/L(\varphi)$, where $L(\beta) = |\Delta_{11}{}^{\varepsilon}\beta_{\nu}/\Delta_{21}{}^{\varepsilon}\beta_{\nu}|$.

The first and second harmonic enter into (5) with equal frequencies ν. Hence, in the following, when the experimental data for (5) are obtained, the first harmonics of γ and φ are excited by a current with frequency ν, and the second harmonics by a current with frequency $\nu/2$. It is evident from (5) that $s = 0$ at the potentials at which the first surface tension harmonic $\Delta_{11}{}^{\varepsilon}\gamma_{\nu}$ or the second potential harmonic $(\Delta_{21}{}^{\varepsilon}\varphi_{\nu})$ have zeros. Thus, at these potentials the second harmonics of γ to ε and φ have equal amplitudes. In contrast to (4) the expressions for $\Delta_{k1}{}^{\varepsilon}\gamma$ at $k \geq 3$ contain terms corresponding to combination fluctuations:

$$\Delta_{31}{}^{\varepsilon}\gamma = \Delta_{31}{}^{\varphi}\gamma + 2(\Delta_{12}{}^{\varphi}\gamma\Delta_{21}{}^{\varphi}\gamma/\Delta_{11}{}^{\varphi}\gamma) + \Delta_{13}{}^{\varphi}\gamma, \tag{6}$$

where the second component is the contribution of the combination frequency $\alpha + 2\alpha = 3\alpha$.

Figure 1a shows the oscillograms of the amplitudes of the first and second harmonics of the surface tension of platinum in a solution of 1 N KI during variation of the mean electrode potential φ_m. In this potential range (from -0.26 to -0.72 V; here and below 25°, the potentials are given in the normal hydrogen equivalent scale) the first harmonic passes through zero once, $\varphi_0 = -0.68$ V; the phase measurements show that at this point the phase of the first harmonic changes by π. From this and also from the shape of the curve near the zero line it is evident that this is a simple zero of the function $\Delta\gamma(\varphi)$ (in a wider sense, the zero can be defined as the center of the neighborhood on the potential axis in which the phase reversal takes place). The second harmonic (Fig. 1a) has five zeros: Of the four minima which practically descend to the noise level (1 μV) the first, third and fourth (from left to right) correspond to simple zeros; at each of them the phase of the second harmonic changes by π. The second minimum from the left is the result of a fusion of two zeros (multiple zero); this is confirmed by the absence of a phase difference on either side of this point, which is equivalent to a change in phase by 2π. The five zeros of the second harmonic correspond to the five extrema of the first harmonic which are clearly visible in Fig. 1a. The correspondence is manifested in the number of these singularities on the oscillograms of the first and second harmonics as well as in the closeness of their potentials (there is no complete coincidence of the potentials in this experiment, however). On the other hand, to the zero of the first harmonic (-0.68 V) in Fig. 1a corresponds not the zero of the second harmonic but, conversely, its rapid increase, which is in agreement with theory. The fact that with variation of φ_m, the second surface tension harmonic (to ε and φ) changes sign, makes the absence of a parallelism between it and the electrode capacitance obvious.

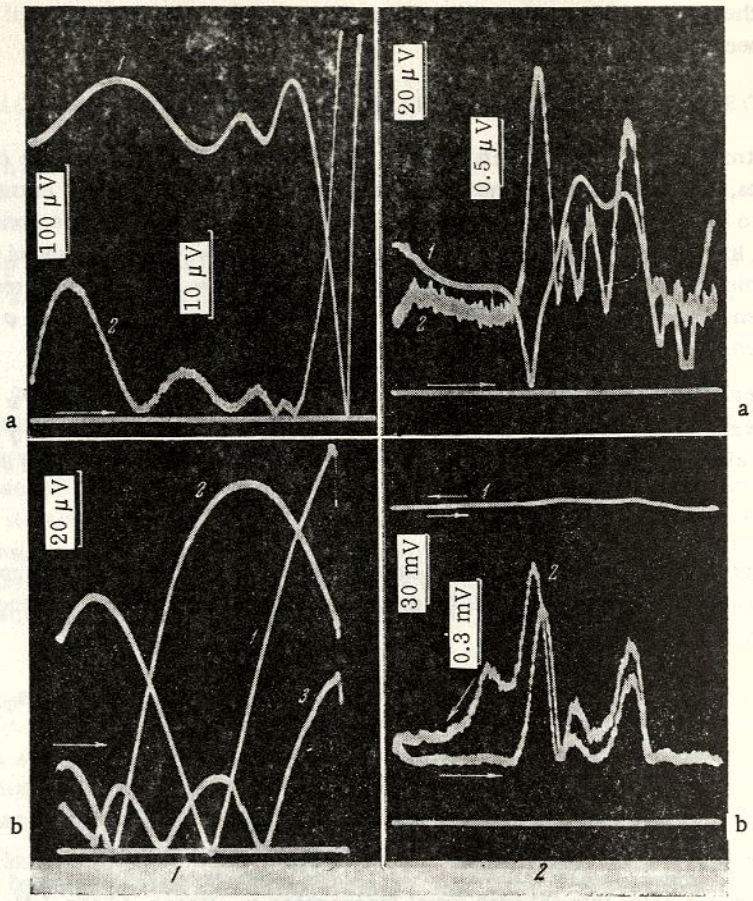

Fig. 1 Fig. 2

Fig. 1. Correspondence between the harmonics of the surface tension (the numbers above the $\Delta^{\varepsilon}\gamma$ vs. φ_m curves represent the order of the harmonics): a) Pt in 1 N KI, pH = 4.5; φ_m varies from left to right from −0.26 to −0.72 V (normal hydrogen equivalent) at a rate of 0.01 V/sec; the delay τ_0 = 30 sec at the initial φ_m; the dimensions of the working surface of the electrode are 8 × 4 × 0.35 mm; 1) Δj = 0.02 A/cm^2, the frequencies of the current and surface tension are $\nu_j = \nu_\gamma$ = 2250 cps; 2) Δj = 0.05 A/cm^2, ν_j = 2650 cps, ν_γ = 5300 cps. b) liquid amalgam Hg/Au (Au backing 8 × 4 × 0.5 mm) in 0.2 N H_2SO_4, φ_m from +0.22 to −0.35 V; 0.01 V sec; τ_0 = 10 sec. 1) ν_j = 4970 cps, 2) ν_j = 2485 cps; 3) ν_j = 1657 cps; 1, 2, 3) Δj = 0.05 A/cm^2, ν_γ = 4970 cps.

Fig. 2. Amplitudes of the first (1) and second (2) harmonic of the surface tension (a) and the potential (b) to the charge for Pt in 1 N H_2SO_4; φ_m from +1.27 (left) to −0.03 V (along the zero line); 0.03 V/sec in the direction of the arrows; τ_0 = 2 min; 8 × 4 × 0.35 mm; Δj = 0.05 A/cm^2; 1) ν_j = 5140 cps; ν_γ = 5140 cps; 2) ν_j = 2570 cps; ν_γ = 5140 cps.

The diagram 1b illustrates the application of the proposed method to liquid electrodes. The lower side (8 × 4 mm) of the gold electrode is coated with a layer of saturated gold amalgam (volume of the layer 6 mm^3). The first, second and third harmonics are recorded at the same frequency of 4970 cps. The frequencies of the electrode potential are 4970 (first harmonic), 2485 cps (second) and 1657 cps (third). In the first harmonic there is one zero at −0.08 V. As in the case of the solid electrode, the extremum of the first harmonic corresponds to the zero of the second. However, such a correspondence is not found between the second and third harmonics.

An analysis of the data presented here and of other data obtained in investigations on liquid electrodes, leads to the following conclusions: 1) At any realizable thickness of the layer of liquid metal, the first harmonic of the recorded fluctuations is proportional to the first harmonic of the surface tension of the liquid electrode and can be

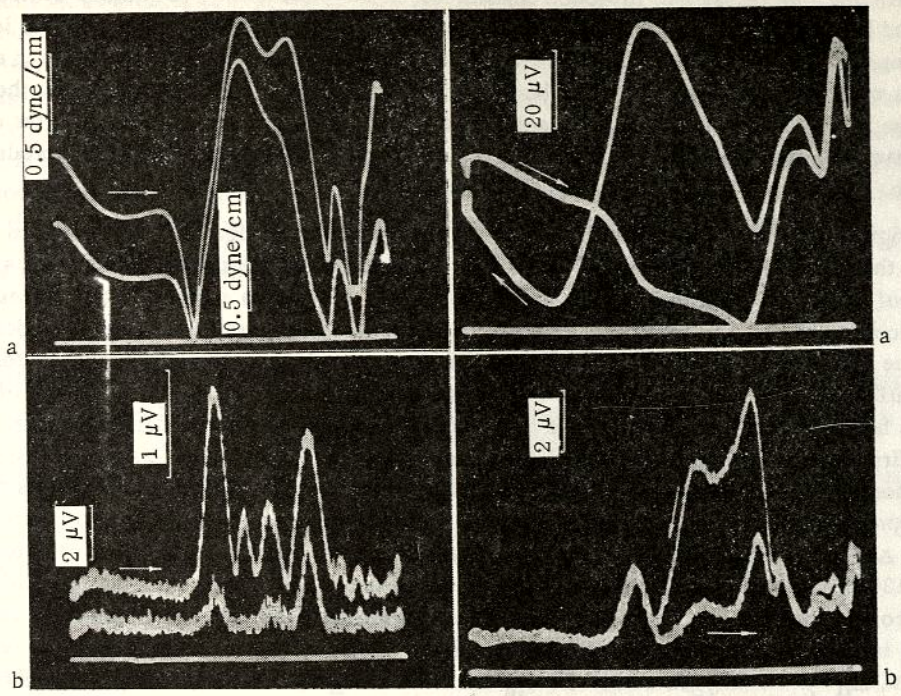

Fig. 3 Fig. 4

Fig. 3. Amplitude oscillograms of the first (a) and second (b) harmonic of the surface tension of Pt in 1 N H_2SO_4, each of which was recorded at two frequencies simultaneously: a) top: $\nu_\gamma = \nu_j = 5140$ cps; $\Delta_j = 0.01$ A/cm^2; bottom: $\nu_\gamma = \nu_j = 910$ cps; $\Delta_j = 0.002$ A/cm^2, $\tau_0 = 30$ sec; b) top: $\nu_\gamma = 5140$ cps; $\nu_j = 2570$ cps, $\Delta_j = 0.05$ A/cm^2; bottom: $\nu_\gamma = 900$ cps, $\nu_j = 455$ cps, $\Delta_j = 0.01$ A/cm^2, $\tau_0 = 2$ min. Rest as Fig. 2.

Fig. 4. Amplitudes of the first (a) and second (b) harmonics of the surface tension of Ir in 1 N H_2SO_4 with direct (from left to right, from +1.23 V to −0.05 V relative to normal hydrogen equivalent) and inverse variation of φ_m; 0.07 V/sec; $\tau_0 = 20$ sec; 7 × 2 × 0.1 mm; $\Delta_j = 0.05$ A/cm^2; a) $\nu_\gamma = \nu_j = 6270$ cps; b) $\nu_\gamma = 6270$ cps; $\nu_j = 3135$ cps.

obtained in the same broad frequency range as in the case of a solid electrode. 2) If the layer of liquid metal has a considerable thickness (Fig. 1b) the second, and even more so the third harmonic are distorted by metal convection in the layer and thus cannot be used for the measurements. Their amplitudes are commensurable with the amplitude of the first harmonic, whereas in the case of a solid electrode under the same conditions the amplitude of the second harmonic is one to two orders of magnitude smaller than that of the first harmonic. 3) Absolute measurements of the surface tension amplitude, analogous to the measurements on the solid electrode [1] are possible only on the condition that convection is completely eliminated, which can be attained by the following methods: a) by decreasing the thickness of the liquid metal layer; b) by increasing the potential frequency; c) by equalizing the distribution of the alternating component of the potential over the surface of the liquid electrode. Thus, the convection of the liquid metal, although it can give rise to anomalous fluctuations of the piezo element, is here not an auxiliary means of investigation but an interference which can be eliminated in principle.

The first harmonic of the surface tension of platinum in 1 N H_2SO_4 (Fig. 2a) has four zeros at each of which the phase jumps by π. The first zero on the left (+0.72 V) corresponds to the removal of the adsorbed oxygen. It is irreversible—its position on the φ axis depends on the sense in which φ varies. The other zeros (+0.20 V; + 0.10 V; +0.08 V relative to the normal hydrogen equivalent at the frequency 5140 cps) are reversible:—the section of the $\Delta_{11}{}^{\varepsilon}\gamma$ vs. φ curve on which they are located is independent of the direction of variation of φ. To all zeros of the first harmonic correspond the amplitudes of the second harmonic which differ greatly from zero (Fig. 2, the noise level in the scale of the second harmonic, 0.6 μV, coincides with the beginning of this curve on the left). To all extrema of the first harmonic (there are six) correspond zeros of the second harmonic. The potentials of the two extrema between the three reversible zeros (+0.20; 0.10 V; +0.08 V) coincide exactly with the potentials of the zeros

of the second harmonic. In this range, hydrogen is adsorbed on the platinum. The marked decrease in the amplitude of the second harmonic γ in this region is due to the fact that the electrode capacitance C is here an order of magnitude greater than in the double-layer region ($\varphi > 0.25$ V) and, consequently, at a given $\Delta\varepsilon$ the amplitude of $\Delta\varphi$ is an order of magnitude smaller. It can be shown that in the case of the first harmonic the effects of increase in ε and decrease in $\Delta\varphi$ on the surface tension amplitude compensate each other whereas in the case of the second harmonic with inversely proportional variation of C and $\Delta\varphi$ the square term $(\Delta\varphi)^2$ exerts a predominating influence on the amplitude.

The oscillograms of the four amplitudes of formula (5) are shown in Fig. 2a, b for platinum in 1 N H_2SO_4. In accordance with the requirements of formula (5) they are all recorded at the same frequency ν = 5140 cps. Owing to the smallness of the second harmonics, the noise level must be taken into account in the processing of the experimental data. It coincides with the minimum distance between the oscillograms of the amplitudes of the second harmonics and the zero line. In the case of the surface tension (Fig. 2a) this is mainly random noise, 0.6 μV. In the case of the potential (Fig. 2b) this is the residue of the first harmonic 0.21 mV (in the recording of the surface tension the selectivity is better because of the use of the resonance frequencies of the mechanical system electrode-piezo element). The first harmonic of potential at the frequency 5140 cps (Fig. 2b, top) is strongly distorted by the vectorially superimposed ohmic drop whose amplitude is independent of φ_m. As measurements at a lower frequency of 910 cps show (approximately the same can be calculated from Fig. 2b), at +0.60 V the maximum potential amplitude is attained, $\Delta_{11}{}^{\varepsilon}\varphi$ = 42 mV. However, this maximum is only weakly apparent against the background of the ohmic losses of 135 mV: $\sqrt{(135)+(42)^2}$ mV = 141 mV, which is only 4% higher than the level of the ohmic losses. Since under the conditions of a given Δ_j the ohmic losses contain only the first harmonic, their contribution to the second harmonic is zero and the corresponding distortions are absent during the recording of the second harmonic. At φ_m = + 0.72 V, $\Delta_{11}{}^{\varepsilon}\gamma = 0$ (oxygen zero). At φ_m = + 0.60 V, $\Delta_{21}{}^{\varepsilon}\varphi = 0$. According to formula (5), s = 0 at these points. Using (5), we find s at φ_m = + 0.68 V, which corresponds to the maximum of $\Delta_{11}{}^{\varepsilon}\gamma_5$ (the subscript 5 is the frequency in kcps). From Fig. 2a, b: $|\Delta_{11}{}^{\varepsilon}\gamma_5| \sim 21.2$ μV; $|\Delta_{21}{}^{\varepsilon}\gamma_5| \sim 2.5$ μV (noise taken into account: $\sqrt{(2.6)^2-(0.6)^2}$ μV); $|\Delta_{11}{}^{\varepsilon}\varphi_5|$ = 33 mV (the measurement at 5140 cps is in agreement with the more accurate measurement of 910 cps, $\Delta_{11}{}^{\varepsilon}\varphi_5 \approx \Delta_{11}{}^{\varepsilon}\varphi_1$), $|\Delta_{21}{}^{\varepsilon}\varphi_5|$ = 0.57 mV (background accounted for: [0.72-0.21 sin (π/4)mV]), s = (21.2 μV/2.5 μV) · (0.57 mV/33 mV) = 0.15.

The dependence of the surface tension amplitude on the potential differs with frequency since the rates of the surface processes are limited. Figure 3a, b, shows the oscillograms of the amplitudes of the first and second harmonic for platinum in 1 N H_2SO_4, recorded simultaneously at two frequencies. For this purpose a periodic potential in the form of the sum of two sine curves is superimposed on the average potential (at given Δ j) in such a way that the electrode participates simultaneously in the mechanical vibrations at two resonance frequencies, in this case 910 and 5140 cps. The complex signal taken from the piezo element is again superimposed on the frequencies by means of selective amplifiers. The two oscillograms of Fig. 3a were traced on the screen simultaneously during a single variation of φ_m from +1.27 to −0.03 V. They do not distort each other within an error of 0.1% of the higher of the two amplitudes with fixed φ_m. Figure 3b was recorded in an analogous manner.

Figure 4a, b, shows the first and second surface tension harmonics with direct and inverse variation of φ_m for iridium in 1 N H_2SO_4. The marked zero on the oscillogram curve at +0.31 V (normal hydrogen equivalent) corresponds to a phase reversal of γ by π. Information on the charge zero of iridium is not found in the literature. The sense of the variation of φ_m does not affect the shape of the curve near the zero as long as φ_m is greater than +0.2 V. In the opposite case (reverse curve Fig. 4a) the section near the zero is slightly deformed; nonetheless, the phase reversal again takes place near +0.3 V. The outer zero on the reverse curve at +0.3 V is similar to the extremum of the first harmonic; however, the amplitude of the second harmonic at these potentials is considerable, which, in addition to the phase reversal, indicates the zero of the first harmonic. The case in which at the zero of the harmonic its minimum amplitude is not zero, is connected with the simultaneous occurrence of several surface processes and the combination of several variable components of surface tension, differing in phase, for example, under nonequilibrium conditions.

The literature contains a reference [2] to the difference between the potentials of platinum at which the charge of the ion lining at the phase boundary vanishes after deduction of the adsorbed hydrogen ions and of the total charge of all the adsorbed particles. Under equilibrium conditions the method of [1] should give zero at the potential at which the total charge is zero; according to [2] this potential is practically in the double layer region. With iridium (Fig. 4a), the zero of +0.31 V is actually located in the double layer region. With platinum there is no zero in this region if during the continuous recording of the oscillogram the initial potential φ_{mo} exceeds +1 V (Fig. 3a, φ_m = + 1.27 V). However, if φ_{mo} = + 0.8 V and the platinum has not previously been subjected to anodic polarization,

then even platinum shows a clear zero at +0.33 V (1 and 5 kcps). When φ_{mo} increases to +1 V this zero is gradually, within a few minutes, shifted to another stationary but now nonequilibrium value of +0.22 V (1 kcps) where it remains during further increase in φ_{mo} (Fig. 3a). Thus, for smooth platinum the strong shift of the potential to the oxygen region also leads to a subsequent upsetting of the equilibrium in the hydrogen region. The method of [1] also gives clear $\Delta\gamma$ vs. φ_m curves for platinized platinum. They are similar to the curves for smooth platinum but the equilibrium here is more stable and can be upset only by more intense anodic polarization. Special investigations, which made it possible to determine by means of the method of [1] the thermal effects of the electrode processes, have shown that these effects do not cause any significant distortions in the experiments of Figs. 1-4.

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LITERATURE CITED

1. A. Ya. Gokhshtein, Zavod. Lab., 32, 815 (1966); Author's Certificate Nos. 178161, No. 179043; Élektrokhimiya, 2, 1061 (1966); Élektrokhimiya, 2, 1318 (1966); Dokl. Akad. Nauk SSSR, 174, 394 (1967); Fiz. i Tekh. Poluprov., 1, 1486 (1967). Fiz. i Tekh. Poluprov., 1, 1787 (1967).
2. A. N. Frumkin, N. A. Balashova, and V. E. Kazarinov, J. Electrochem. Soc., 113, 1011 (1966).