A METHOD OF INVESTIGATING SURFACE TENSION, CHARGE, AND PRESSURE ON A SOLID ELECTRODE UNDER NONSTATIONARY CONDITIONS

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A sensitive and rapid method of investigating the surface properties of solids is proposed which can be employed to analyze the structure and test the purity of metal and semiconductor surfaces, and to observe during absorption and other processes associated with a change in the properties of an interphase boundary.

A new method of nonstationary measurements on the surface tension of solid electrodes which we have developed makes it possible to investigate the electrode processes and surface tension of a solid. These measurements are performed with the aid of devices [1] in which the electrode immersed in the electrolyte consists of a film which is plated on a dielectric plate or is in the form of a stretched thread which is mechanically coupled to a piezoelectric element. In addition to a specified carrier potential φ_m, which can vary rapidly over a wide range, the electrode has superimposed on it a periodically varying potential (or current) of low amplitude at a frequency that is rather high with respect to the rate of change of φ_m. The variable forces generated at the electrode under these conditions are sensed by the piezoelectric element. Since the deformations of the piezoelectric element are negligibly small, the variation of the force being measured under the test conditions is not accompanied by a variation in the shape and dimensions of the electrode and by stirring of the electrolyte. Thus, when there is a change in the surface forces acting along the stretched thread, which is fastened at each end, the length of the thread remains constant (except for a shift at the anchoring points, one of which is the piezoelectric element). In the other device for investigating the forces acting on an electrode during a change in the surface tension, inertial forces are transmitted to the piezoelectric element which are produced as a result of very small longitudinal or transverse vibrations in the plate that is fastened to the electrode. The greatest sensitivity (10^{-6} $G/\mu V$) is attained by a device in which the frequency of the superimposed potential is equal to the resonant frequency of the electrode-piezoelectric element mechanical system. Several resonant frequencies are usually found in the system within the audio range (20 to 20,000 Hz).

Let us consider the basic relationships between the voltage θ on the plates of the piezoelectric element, which is proportional to the variable component of the surface tension σ, and the potential φ on the electrode. Let the interphase boundary be a double layer with a charge $\varepsilon(\varphi)$ on the metal plate and a differential capacity $c(\varphi)$. The specified potential is $\varphi = \varphi_m - \Delta\varphi \cos \omega t$ (t is time, $\omega = 2\pi\nu$, ν is frequency, and Δ is the amplitude of the corresponding variable). Let us assume that $\varepsilon_m = \varepsilon(\varphi_m)$, $c_m = c(\varphi_m)$, etc. By utilizing the Gibbs absorption equation we will obtain σ in the form of a sum of the harmonics:

$$\sigma = \sigma_0 + \sum_{k=0}^{\infty} (-1)^{k+1} \{\Delta\sigma_k \cos k\omega t - \gamma_k \varepsilon_m \Delta\varphi \cos (k\omega t + 1/4\pi)\}, \tag{1}$$

$$\Delta\sigma_{2p-1} = \sum_{s=p}^{\infty} \frac{2^{2-2s}}{(s-p)!\,(s+p-1)!} \left(\frac{\partial^{2s-2}\varepsilon}{\partial\varphi^{2s-2}}\right)_m (\Delta\varphi)^{2s-1},$$

$$\Delta\sigma_{2p} = \sum_{s=p}^{\infty} \frac{2^{1-2s}}{(s-p)!\,(s+p)!} \left(\frac{\partial^{2s-1}\varepsilon}{\partial\varphi^{2s-1}}\right)_m (\Delta\varphi)^{2s}. \tag{2}$$

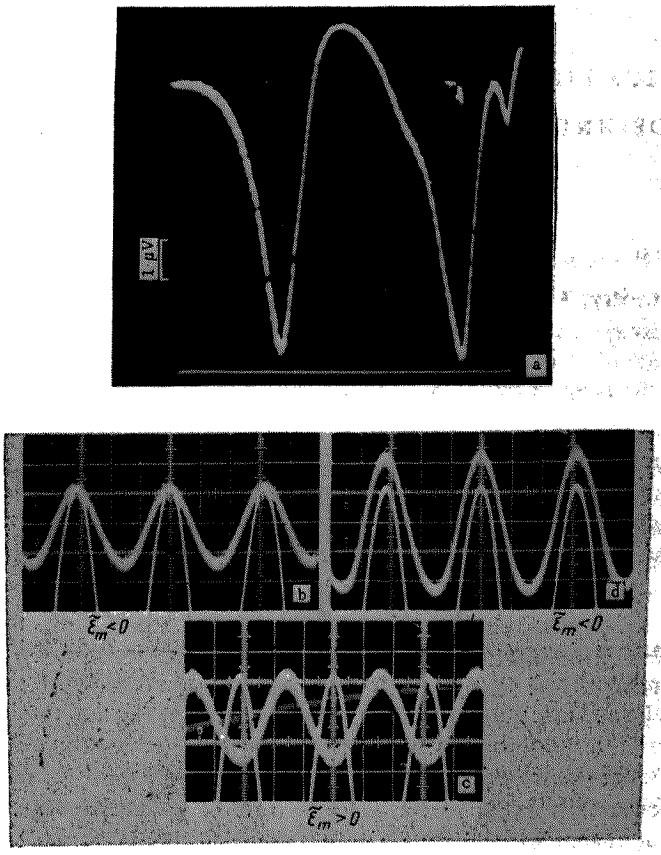


Fig. 1. Oscillograms of the electrode-piezoelectric element system for small oscillations of the current (j) and the potential (φ) on the electrode at a resonance frequency of 3200 Hz and 20°C: a) Voltage amplitude on the plates of the piezoelectric element as a function of φ_m; the zero line is the noise level (1 μV); b), c), and d) the prescribed current j (shown by the positive peaks of a sinusoid) and the voltage $\theta \sim \sigma$, taken simultaneously on a double beam oscilloscope for φ equal, respectively, to +0.64, +0.23 and −0.1 V.

The terms with γ_k in Eq. (λ) take into account the change in the electrolyte concentration near the electrode. For moderate concentrations they are small and can be discarded with, for example, the following result: When $|\varepsilon_m|$ is sufficiently large, to infinitesimal higher orders of accuracy $\gamma_1 = (1-x)RTc_m(\omega/D)^{1/2}/(nF)^2u_m$, where x and n are the number of the migration and the charge on the ions that form the ionic coating of the double layer; D and u_m are the diffusion coefficient and the concentration of the electrolyte, F is the Faraday constant, R is the gas constant, and T is temperature. For $D = 10^{-5}$ cm^2/sec, T = 298°K, n = 1, $c_m = 30$ μF/cm^2, $u_m = 10^{-4}$ mole/cm^3, γ_k is < 0.01; γ_k is a still smaller quantity for higher values of u_m. From Eqs. (1) and (2) for the first harmonic

$$\sigma_1 = \Delta\sigma_1 \cos\omega t = \left\{\varepsilon_m\Delta\varphi + \frac{1}{8}\left(\frac{\partial c}{\partial\varphi}\right)_m \times (\Delta\varphi)^3 + \ldots\right\}\cos\omega t. \qquad (3)$$

Equations (1) to (3) are valid when $\Delta\varphi$ values are not arbitrarily small. With small $\Delta\varphi$ in Eq. (3) the terms beginning with the second can be neglected; we find that when $\varepsilon_m = 2\cdot10^{-5}$ C/cm^2, $(\partial c/\partial\varphi)_m = 100$ μF/cm$^2\cdot$V, the second term in Eq. (3) is 160 times smaller than the first. Smaller amplitudes of φ are easily realized in practice.

By utilizing mechanical resonance and selective amplification in the proposed devices the individual harmonics of σ can be isolated. The variables φ, σ, and j (the charging current) then characterize the first harmonic for small

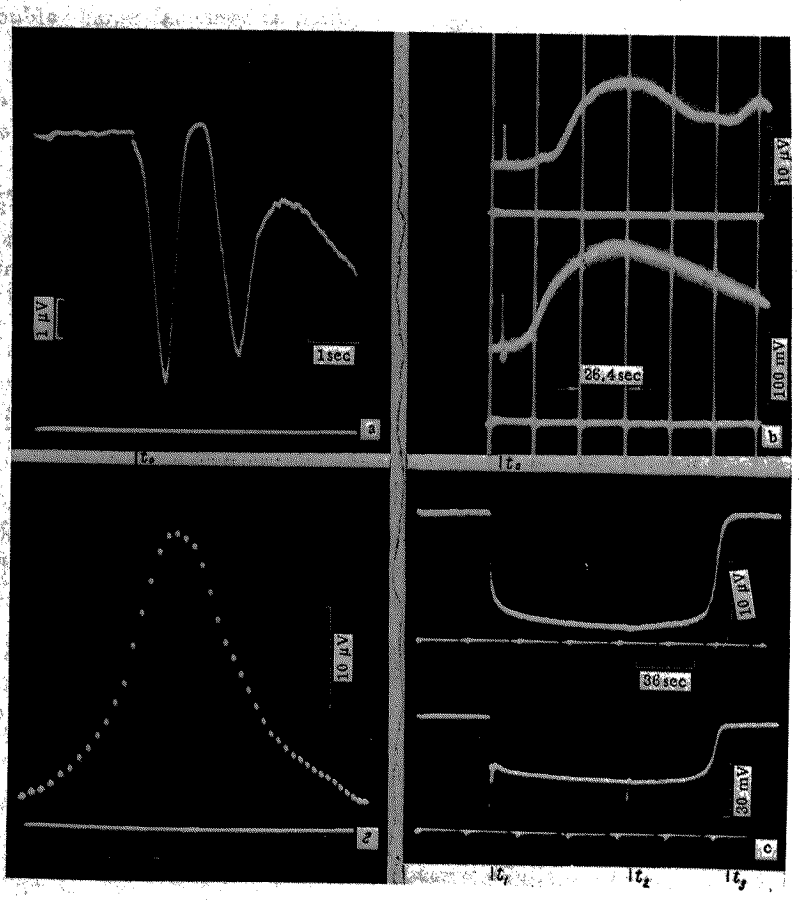


Fig. 2. Change of the surface tension with a change in the potential and with time for various systems: a) Change of $\Delta\theta \sim |d\sigma/d\varepsilon|$ with time after an abrupt change of the potential at time t_0; b) $\Delta\theta \sim |d\sigma/d\varepsilon|$ and $\Delta\varphi \sim |d\varphi/d\varepsilon|$ as a function of φ_m for a prescribed $\Delta j = 0.038$ A/cm^2; 1-M KI + 0.005-M KI_3; c) change of $\Delta\theta(t)$ and $\Delta\varphi(t)$ + const for a prescribed $\Delta j = 0.012$ A/cm^2; 1-M $AgNO_3$; $\varphi_m(t) = +0.40$ V (Ag) when $t < t_1$ and $t > t_2$, $\varphi_m(t) = -0.40$ V (ag) when $t_1 < t < t_2$; d) change of $\Delta\theta$ with frequency ν of the current from 2750 to 3825 Hz every 25 Hz (points); 1-M KI + 0.005-M KI_3; $\varphi_m = -0.42$ V (Pt); $\Delta j = 0.060$ A/cm^2.

values of $\Delta\varphi$. Thus, $\varphi = -\Delta\varphi \cos\omega t$, $\sigma = \varepsilon_m \Delta\varphi \cos\omega t$, $j = c_m d\varphi/dt = c_m \Delta\varphi\omega \sin\omega t = \Delta j \sin\omega t$, or $\sigma = (\varepsilon_m/c_m)(\Delta j/\omega)\cos\omega t$. When $\varepsilon_m > 0$, the surface tension leads the current by a phase angle of $\pi/2$, $\sigma(\omega t) \sim j(\omega t + {}^1/_2\pi)$; when $\varepsilon_m < 0$, it is still $\pi/2$ while the current, which is passing a positive charge to the electrode, is positive.

Let us consider a device in which small vibrations of the electrode-piezoelectric element system are produced by the inertial force developed during the deformation of the plate attached to the electrode. The calculations presented below are valid for any form of vibrations. The deformation x of the plate (average displacement) is proportional to σ. The force acting on the plate is proportional to $\ddot{x}$, and $\ddot{x}(\omega t) \sim \ddot{\sigma}(\omega t) \sim \sigma(\omega t - \pi)$. Under the test conditions the voltage θ on the plates of the piezoelectric element is proportional to the displacement y of the system as a whole. The agreement of the signs for θ and y is checked by providing a calibrating ac current for the magnetic field in the device, and then is obtained, for example, by switching the polarity of the piezoelectric element. As is well known, at resonance the vibration lags bv $\pi/2$ behind the driving force, i.e., $y(\omega t) \sim \ddot{x}(\omega t - {}^1/_2\pi)$. From the relationships derived we find for $\varepsilon_m > 0$ that $\theta(\omega t) \sim y(\omega t) \sim \ddot{x}(\omega t - {}^1/_2\pi) \sim \sigma(\omega t - {}^1/_2\pi - \pi) \sim j(\omega t - {}^1/_2\pi - \pi + {}^1/_2\pi) = j(\omega t - \pi)$.

A similar calculation can be carried out for $\varepsilon_m < 0$. Thus we have

$$\theta(\omega t) \sim j(\omega t - \pi);\ \theta(\omega t) \sim \varphi(\omega t - \pi/2)$$
$$\varepsilon_m > 0; \tag{4}$$
$$\theta(\omega t) \sim j(\omega t - 2\pi) = j(\omega t);$$
$$\theta(\omega t) \sim \varphi(\omega t + \pi/2)\ \varepsilon_m < 0.$$

From this we find that: 1) During a transition through the zero point ($\varepsilon_m = 0$) the phases of σ and θ change by the value π; 2) from the phase of the vibrations it is possible to determine the sign of the electrode charge; $\varepsilon_m < 0$ if the phases of θ and j agree; $\varepsilon_m > 0$ if they are opposite. The sign of the charge can be determined from the relationship of the phases of θ and φ; $\varepsilon_m > 0$ if θ lags behind φ by $\pi/2$. This is satisfactory when the charging current is masked by the current of the electrode reaction; 3) at the zero point the amplitude of the first harmonic σ becomes zero.

With a prescribed applied potential the amplitude $\Delta\varphi$ remains constant for various values of φ_m so that instead of $\Delta\theta \sim \Delta\sigma$ one can write $\Delta\theta \sim \Delta\sigma/\Delta\varphi \to d\sigma/d\varphi$ as $\Delta\varphi \to 0$. With a prescribed ac current the amplitude $\Delta\varepsilon$ of the electrode charge vibrations remains constant and we have $\Delta\theta \sim \Delta\sigma/\Delta\varepsilon \to d\sigma/d\varepsilon$ as $\nu \to \infty$ or as $\Delta j \to 0$. With the potential prescribed ($\Delta\varphi = \text{const}$) it is possible to investigate the electrode surface tension and the charge of the double layer under conditions where the reaction is proceeding intensively at the electrode, i.e., for any ratio of Faraday current and charging current. It is possible to determine $\sigma(\varphi)$ from experimental relationships for $d\sigma/d\varphi = f(\varphi)$ and $d\sigma/d\varepsilon = g(\varphi)$ by integrating. When $\Delta j = \text{const}$, $d\varphi/d\varepsilon = 1/c(\varphi)$ and $d\sigma/d\varphi = c(\varphi)$ $d\sigma/d\varepsilon = c(\varphi)g(\varphi)$.

The conclusions obtained for the double layer are essentially valid in the case of specific reversible and irreversible adsorption of particles at the electrode. With specific adsorption [2] the electrode-electrolyte boundary becomes "multilayered" and the gradients of the potential variation in adjoining layers can be opposite. The sign of $d\sigma$ during a change of the potential $d\varphi$ depends on how $d\varphi$ is distributed among the layers. For the same $d\varphi$ the energy changes of oppositely charged layers will be opposite in sign. In the case of irreversible adsorption, for instance, of oxygen by platinum during a rapid change in the potential, the changes in the adsorbed layer are small and it must be expected that the primary part of $d\varphi$ occurs here in the ionic portion of the interphase boundary. The first harmonics will in this case be the same as for the double layer where the signs of the charges are determined by the adsorbed oxygen.

The local value of $d\sigma/d\varphi$ ($d\sigma/d\varepsilon$) obtained by this method corresponds to the structure of the adsorbed layer at any given moment of time. When φ_m varies, this structure changes, not only with potential but also with time. The dependence of $d\sigma/d\varphi$ on time, and also measurements at various frequencies and higher harmonics, can be utilized for studying the rate of adsorption.

We note that the high frequency of the superimposed potential φ completely isolates the phenomena that would prevent measurements of σ under steady-state conditions: The penetration of foreign atoms from the solution into the lattice of the electrode by diffusion causes internal voltages to develop which are added to the slow variations of the surface tension. For a half-cycle in the order of 0.0001 sec or less the penetration effect does not distort the measurements for two reasons: 1) The concentration of the penetrating atoms changes very little during the half-cycle; 2) the change is aperiodic in character, i.e., it contains practically none of the harmonics at which the measurements are made.

The theory that has been expounded is supported by experiments, some of which are presented below. Figure 1, a shows an oscillogram of $|d\sigma/d\varepsilon|$ as a function of φ_m which was obtained by rectifying the first harmonic of σ with a frequency of 3200 Hz on the platinum electrode (in the form of a film 0.12 cm^2 in area deposited on the plate) in normal H_2SO_4 saturated with H_2 when φ_m varies from +0.7 V to −0.1 V (normal hydrogen equivalent). The potential changes from left to right at a rate of 0.003 V/sec. Prior to the test the platinum was in air. The value of $|d\sigma/d\varepsilon|$ is reduced almost to zero twice (when the potentials are, respectively, $\varphi_{01} = +0.56$ V and $\varphi_{02} = +0.15$ V). From what has been stated above concerning complex multiphase boundaries, which the platinum surface is in this experiment, it follows that the equation $d\sigma/d\varphi = 0$ can be satisfied and then, when the charges of each coexisting, oppositely charged layer are not equal to zero (if the electrical properties of the layers are not the same), the sum is not zero. Under these conditions the concept of a zero point requires a special definition. The premises of the theory are preserved if an effective charge $\tilde{\varepsilon}_m$ is introduced which is associated with an equivalent double layer. By definition $\tilde{\varepsilon}_m = d\sigma/d\varphi$. In accord with Eq. (4) the relation of the phases for θ and j (Figs. 1, b, c, and d) indicate a change

in the sign of $\tilde{\varepsilon}_m = 0$ ($d\sigma/d\varepsilon = 0$). During the reverse change in φ_m both zero points are shifted in a positive direction. The case of a double charge exchange on platinum (in considerably weaker solutions of H_2SO_4) is well known in the literature [3].

Following an abrupt change in potential from +1.5 V to −0.1 V (normal hydrogen equivalent) with the same electrolytic system the electrode passes through intermediate states in the course of time, among them both of the zero points (Fig. 2, a). Figure 2, b gives oscillograms of $|d\sigma/d\varepsilon|$ vs. φ and of $|d\varphi/d\varepsilon|$ vs. φ (the latter is correct except for the ohmic losses in the solution which do not depend on φ_m when Δj = const) which were made simultaneously on the platinum cathode; φ_m varies from 0 (t_0) to −1.0 V (relative to platinum in the same solution); when $\varphi_m = -1.0$ V (Pt), the beginning of a drop to the zero point is seen. Figure 2, c (Pt in 1-M $AgNO_3$) is evidence that the effect of $\Delta\theta$ is localized at the electrode and is not associated with the electrophoretic phenomena at the boundaries of the plate or with a displacement of the electrolyte's center of mass during the passage of current. For the condition Δj = const the deposition of Ag (beginning at time $t = t_1$) on the electrode is accompanied by a drop $\Delta\theta$. Figure 2, d shows $\Delta\theta$ as a function of ν in the vicinity of the resonance $\nu_0 = 3200$ Hz.

The results of a check on the pressure at the electrode indicated that when Ag is being electroplated (M = 107.9 g/M and n = 1), the change in kinetic pressure, as evaluated from the formula $\Delta p = \sqrt{RTM}\ \Delta j/nF$, amounts to Δp = 0.17 d/cm^2 at T = 293°K and Δj = 0.01 A/cm^2. It is possible to eliminate the effect of σ by reducing the frequency ν and increasing the stiffness of the plate attached to the electrode. It can be shown that $\Delta\theta = k\nu^2\Delta\sigma$, where k depends on the device parameters. This relationship has been verified experimentally. Tests were made at ν = 270 Hz, Δj = 0.01 A/cm^2, and an average current density of zero. Under these conditions the amount of Ag depositied was equivalent to 0.1 of a monomolecular layer which does not significantly distort the surface of the platinum electrode (0.6 × 0.9 cm in size). The value of $\Delta\theta$ observed in the tests, even if it is entirely due to the pressure, was 1.5 orders of magnitude lower than that calculated.

With this method it is possible to determine the zero points of solid electrodes, which constitute an important characteristic of a material's surface properties, whereas usually their determination is attended by great experimental difficulties. The method described is an independent one—the physical quantities measured with its help cannot be measured by other methods, for example, by the electrical capacity of the interphase boundary. Moreover, the range of conditions over which it can be used is substantially greater than the capacity method (recording the surface tension vibrations does not involve the isolation of the capacity current due to Faraday current flowing in the same circuit). The results obtained also indicate the possibility of using the method to control automatically processes in which the properties of the interphase boundary vary.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.