POTENTIAL VARIATION OF AN ELASTICALLY DEFORMED ELECTRODE

A. Ya. Gokhshtein

UDC 541.13

For a direct determination of the charge on a solid electrode, experiments have been devised where the electrode is subjected to a small periodical elongation, and the oscillations of the potential φ are recorded at constant total charge Q (i.e., constant during a period), or the fluctuations of Q (i.e., of the charging current) are recorded at constant φ. It is one of the special features of the method described that even in presence of a considerable absolute increase in surface area S of the interface, the relative deformation can be made however small it be desired, so that the properties of the electrode material and along with these the amount of chemisorbed species would not change. On the other hand, in the case of electrostatic adsorption, for example, the amount of adsorbed species is determined by the surface area S, and the ratio $\Delta Q/\Delta S$ (where Δ denotes amplitude) gives the charge density q corresponding to these species. For Q = const, the time constant of the cell for the application of a mean potential φ_m becomes much greater than the period of the vibrations of the electrode. Then one has $\Delta\varphi = [q(u) + (1+u)q'(u)](1-\sigma)\Delta p / EC$, where, referring to the electrode, C is the differential capacitance, u is the relative variation in S, E is the elastic modulus, σ is Poisson's ratio, and p is the tensile stress; C and q contain a roughness factor which at small u is constant. Measurements for various u have shown that $u = 10^{-5}$ is sufficiently small and that q'(0) is much less than q(0). Hence $\Delta\varphi \approx q/C$.

An oscilloscopic trace of $\Delta\varphi$ against φ_m taken in this fashion over the φ_m range from +1.25 to 0 V (nhe) for smooth platinum in 1 N H_2SO_4 has accurately reproduced the known, detail-filled oscilloscopic trance of $\Delta\gamma$ against φ_m at ΔQ = const (where γ is the surface tension): it had the same null-points at +0.6 V, +0.2 V, and the double null-point at +0.1 V. Experiments were performed on all 11.5 × 1 cm ribbon made of 10-μ foil, at Δp = 10 kg (force)/cm^2, with a stretching frequency of 38 Hz, and an initial stretching with forces of 0.1, 0.2, and 0.3 kg; under these conditions, the largest signal measured was $\Delta\varphi = 2\ \mu V$ at $\varphi_m = +0.5$ V. The coincidence of the curves that were measured by independent methods and, what is most interesting, also for different physical parameters-$\Delta\varphi$ and $\Delta\gamma$-confirms the premises of the method described: Q = Q(S, u); one measures dQ/dS; $dQ/dS \approx \partial Q/\partial S$ with systems where $\partial Q/\partial u$ is small; under certain conditions, for example in equilibrium: $(\partial\gamma / \partial\varphi)_S = -(\partial Q / \partial S)_\varphi$, $(\partial\gamma / \partial Q)_S = (\partial\varphi / \partial S)_Q$. The surface tension method gives the left-hand side of the two last equations, the elastic charging method gives the right-hand side, while γ and S may refer both to a surface with macroroughness and to its averaged surface plane. In the general case the results of these methods must only be combined with one another on the basis of defined model of the interphase—even when the curves coincide, which, as can be shown, is not at all necessary for an arbitrary system.

LITERATURE CITED

1. A. Ya. Gokhshtein, Elektrokhimiya, 2, 1318 (1966); 4, 619 665 (1968); Dokl. Akad. Nauk SSSR, 181, 385 (1968); 183, 859 (1968); Priroda, No. 12, 8 (1968).

Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 5, No. 5, pp. 637-638, May, 1969. Original article submitted January 13, 1969.