FREE SURFACE ENERGY OF A PLATINUM ELECTRODE AS FUNCTION OF POTENTIAL AND SOLUTION COMPOSITION

Academician A. N. Frumkin and O. A. Petrii

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According to concepts developed in [1], two Lippmann equations can be obtained for the reversible platinum–hydrogen electrode:

$$(\partial\sigma / \partial\varphi_A)_{\mu_{HA},\, \mu_{CA}} = \Gamma_H = -Q', \tag{1}$$

$$(\partial\sigma / \partial\varphi_A)_{\mu_H,\, \mu_{CA}} = -\Gamma_{H^+} = -Q'', \tag{2}$$

where σ is the free surface energy; φ_A is the potential relative to a reference electrode which is reversible with respect to the anion A^-; μ_H, μ_{HA}, and μ_{CA} are the chemical potentials of hydrogen atoms, the acid HA, and the salt CA, respectively; Q' and Q" are the total surface charge densities; and Γ_H and Γ_{H^+} are the Gibbs surface excesses of atomic hydrogen of hydrogen ions (the quantities Γ and μ are expressed in electrical units). Under the condition [HA] << [CA] and with μ_{CA} = const, the potential of an electrode which is reversible with respect to the anion A^- can be taken as constant, the suffix at φ_A can be dropped, and the quantity μ_{HA} in Eq. (1) replaced by μ_{H^+}. Under this condition, too, the quantity Γ_{H^+} approximately expresses the free surface charge density. Relations analogous to the equations (1) and (2), which were deduced for an acidified solution of the composition CA + HA, can be derived for an alkalized solution of the composition CA + COH. Equations (1) and (2) have been obtained under the assumption that $\Gamma_{H_2O} = 0$, where Γ_{H_2O} is the Gibbs surface excess of water; therefore, the adsorption of oxygen Γ_0 is equivalent to the negative adsorption of hydrogen [2, 3]: $\Gamma_0 = Q'$. In the following we shall drop the index at the quantity Q'.

Relation (1) can be considered as the Lippmann equation for a platinum electrode under the provision that μ_{H^+} is constant. Relation (2) is the Lippmann equation under conditions where potential change arises from a change in μ_{H^+} at constant μ_H. Thus, for a platinum electrode two curves representing plots of free surface energy against potential can be constructed, in accordance with Eqs. (1) and (2). Along one of these curves, the change in electrical potential is determined by the change in the chemical potential of the reductant (a $\Delta\sigma - \varphi$ curve of the first kind), along the other it is determined by that of the oxidant (a $\Delta\sigma - \varphi$ curve of the second kind).

In the present work, $\Delta\sigma - \varphi$ curves of the first and second kind are calculated for a platinized platinum (Pt/Pt) electrode in solutions of different compositions.

It follows from Eq. (1) that the $\Delta\sigma - \varphi$ curve of the first kind can be obtained by integrating the equilibrium charging curve of a platinum electrode measured at μ_{H^+} = const. Such curves have been obtained previously [4-6] for the solutions 10^{-2} N H_2SO_4 + 1 N Na_2SO_4, 10^{-2} N HCl + 1 N KCl, 10^{-2} N HBr + 1 N KBr, 10^{-2} N NaOH + 1 N Na_2SO_4, and 10^{-2} N KOH + 1 N KX, where X = Cl^-, Br^-, or I^-. A method for determining the potential $\varphi_{Q=0}$ corresponding to maximum free surface energy at μ_{H^+} = const has been discussed in [7], where values were also given for $\varphi_{Q=0}$ of a platinum electrode.

Figure 1 shows Q as functions of φ_r for a Pt/Pt electrode in solutions of different composition; the curves were positioned with the aid of $\varphi_{Q=0}$ values. The potentials φ_r are referred to the reversible hydrogen electrode in the same solution. The initial portions of the $Q - \varphi_r$ curves were extrapolated to $\varphi_r = 0$ as shown in dashed lines, when calculating the $\Delta\sigma - \varphi$ curves of the first kind.

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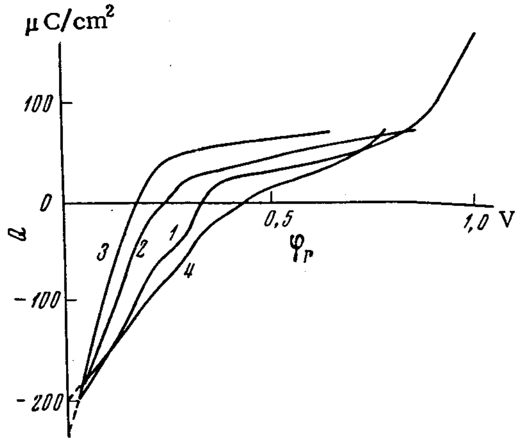

Fig. 1

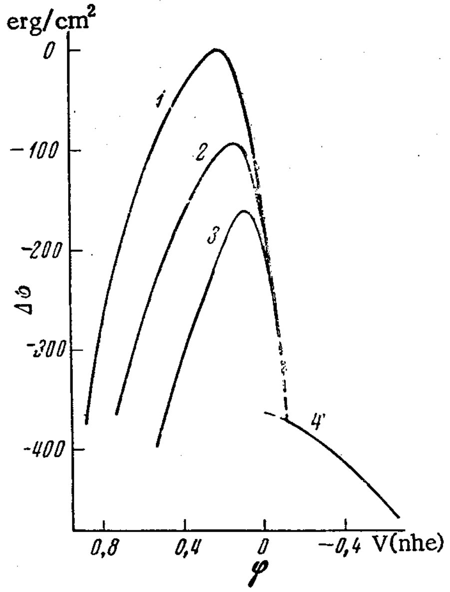

Fig. 2

Fig. 1. Charging curves for a Pt/Pt electrode in the solutions: 1) 10^{-2} N H_2SO_4 + 1 N Na_2SO_4; 2) 10^{-2} N HCl + 1 N KCl; 3) 10^{-2} N HBr + 1 N KBr; 4) 10^{-2} N NaOH + 1 Na_2SO_4.

Fig. 2. Curves representing the potential dependences of free surface energy of the first (curves 1-3) and second (curve 4) kind in the solutions: 1) 10^{-2} N H_2SO_4 + 1 N Na_2SO_4; 2) 10^{-2} N HCl + 1 N KCl; 3) 10^{-2} N HBr + 1 N KBr; 4) 1 N Na_2SO_4, KCl, or KBr.

For a calculation of $\Delta\sigma-\varphi$ curves of the second kind according to Eq. (2) one must locate Γ_{H^+} as a function of pH at φ_r = const. We are presently working on an accurate method of determining this relation; this method is based on the potentiometric titration of the test solution with two platinum electrodes [8]. In the present work we have used an approximate method of constructing $\Delta\sigma-\varphi$ curves of the second kind. To this end we have picked values of Γ_{H^+} at φ_r = const for pH 1.5-4 and 12 from the data of [4]. Values of Γ_{H^+} for other pH were found by interpolation. The $\Delta\sigma-\varphi$ curves of the second kind were then calculated by integrating the $\Gamma_{H^+}-\varphi$ curves.

The $\Delta\sigma-\varphi$ curves calculated for a platinum electrode are shown in Figs. 2-4. Portions obtained by extrapolation are shown as dashed lines in these plots. Since the integration constants are not known, $\Delta\varphi$ was conditionally set equal to zero in the maximum of one of the curves presented in the corresponding figures. The direction of the abscissa was taken opposite to that in Fig. 1, i.e., in the same direction as that used when constructing the electrocapillary curves of a mercury electrode.

The relative position of the curves of first and second kind can be unambiguously defined for solutions of the same salt, despite the fact that absolute values of the free surface energy cannot be found with the calculations performed. In fact, different points on a curve of the second kind correspond to solutions of different pH. In particular, one of the points refers to a solution having the same pH as the solution for which a curve of the first kind was constructed. Since the free surface energy is a unique function of φ and of solution composition, this point must be common for curves of the first and second kind. Using this concept one can also, after constructing a curve of the second kind, define the mutual disposition of $\Delta\sigma-\varphi$ curves of the first kind in acid and alkaline solutions of the same salt.

When comparing $\Delta\sigma-\varphi$ curves of the first kind in solutions of different composition but the same pH (Figs. 2 and 4) we displaced these curves in the vertical direction so that their descending branches would merge at negative potentials. There the anions of the solution are not adsorbed at platinum, and the electrode surface is practically fully occupied by adsorbed hydrogen. Small differences in the adsorbability of Na^+ and K^+ ions can to a first approximation be neglected. The free surface energy must, therefore, be the same as these potentials for solutions of different composition. This assumption also provided the basis for extrapolating the $Q-\sigma_r$ curves in acidified solutions to $\varphi_r = 0$ in Fig. 1. With this method of comparing the $\Delta\sigma-\varphi$ curves of the first kind, the $\Delta\sigma-\varphi$ curves of the second kind $\varphi_r = 0$, also practically coincided in 1 N Na_2SO_4, KCl, and KBr solutions, which proves that the assumption made is correct.

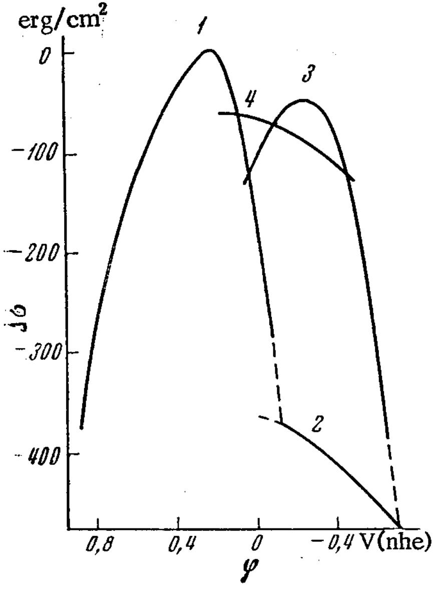

Fig. 3

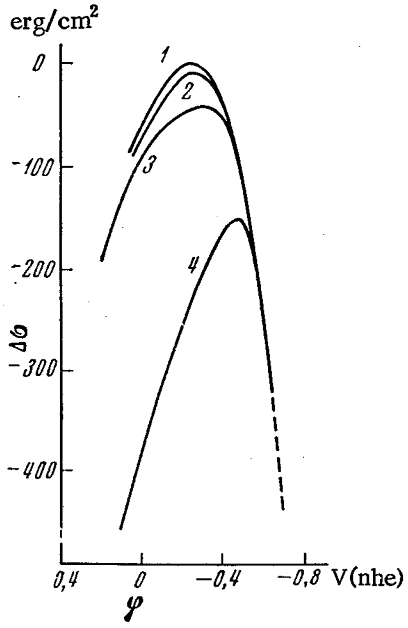

Fig. 4

Fig. 3. Curves representing the potential dependences of free surface energy of the first (curves 1 and 3) and second (curve 2: $\varphi_r = 0$ curve 4: $\varphi_r = 240$ mV) kind in the solutions: 1) 10^{-2} N H_2SO_4 + 1 N Na_2SO_4; 2 and 4) 1 N Na_2SO_4; 3) 10^{-2} N NaOH + 1 N Na_2SO_4.

Fig. 4. Curves representing the potential dependence of free surface energy of the first kind in the solutions: 1) 10^{-2} N NaOH + 1 N Na_2SO_4; 2) 10^{-2} N KOH + 1 N KCl; 3) 10^{-2} N KOH + 1 N KBr; 4) 10^{-2} N KOH + 1 N KI.

It follows from Figs. 2-4 that the $\Delta\sigma-\varphi$ curves of the first kind are reminiscent of the electrocapillary curves for a mercury electrode, both in their shape and in the way in which σ and $\varphi_{Q=0}$ depend on the anion of the salt. However, the free surface energy of a platinum electrode at μ_{H^+} = const varies rather more strongly with φ than does σ of a mercury electrode. This is primarily due to the adsorption of hydrogen and oxygen atoms on the platinum surface. Under conditions where μ_H = const ($\Delta\sigma - \varphi$ curves of the second kind), σ varies appreciably less strongly because here this variation is produced only by the changing charge of the electric double layer.

In acidified sulfate solutions, the values of σ in the maxima of the curves of the first kind are higher than are those in alkalized sulfate solutions (Fig. 3). This is so because at $\varphi_{Q=0}$, the surface coverage by ions and atoms is smaller in the acidic sulfate solution than it is in alkalized solution [6-8]. However, in acidified KCl and KBr solutions the σ values are lower than in the corresponding alkalized solutions, as can be seen when comparing the curves in Figs. 2, 3, and 4. This is due to the substantial adsorption of Cl^- and Br^- ions in acidic solutions [7, 9]. The curve of the second kind pertaining to $\varphi_r = 0$ lies far below the curve characterizing the surface state at φ_r = 0.24 V (Fig. 3), which is due to surface coverage by adsorbed hydrogen at $\varphi_r = 0$.

We note in conclusion that there seems to be missing in the literature a generally accepted name for the quantity σ, which in the case of a liquid interface is identical with the interfacial tension but which, in the general case, expresses the work required to generate unit surface area independent of the location of the interface [10]. The expression "excess free energy density" used in [11] is probably more correct than the abridged name used in the present paper as well as in the work of some other authors [12].

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