WETTING OF SOLID ELECTRODES

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A systematic investigation of the influence of the potential on the wetting of liquid electrodes has been carried out in the work of A. N. Frumkin and collaborators [1-3]. Under certain conditions on the electrode−gas boundary a film of electrolyte was detected [2], the stability of which follows from theory [4]. Recently, papers have been published dealing specially with the wetting of solid electrodes [5-9]. A series of studies by Morkos must be noted in which the relation between the angle of wetting of a flat solid electrode and the potential is determined [6-9]. We shall present below an approach to the problem of wetting based on the connection between the direct and reverse effects.

Consider a solid electrode of arbitrary shape partly immersed in a liquid electrolyte solution (Fig. 1). Let z be the vertical coordinate (the depth of immersion counted from the horizontal liquid level), $\mathscr{P}$ is the weight of the partly immersed electrode with fixed z (the force experienced by the object on which the electrode is suspended), Q is the total charge on the electrode, φ is the electrode potential relative to a reference electrode in the same electrolyte. If the remaining parameters of the system are kept constant and the processes taking place in it are reversible the total differential of its free energy F amounts to

$$dF = -\mathscr{P}dz + \varphi dQ. \tag{1}$$

Then we obtain the fundamental equations

$$\frac{\partial \mathscr{P}}{\partial Q} = -\frac{\partial \varphi}{\partial z}, \tag{2}$$

$$\frac{\partial \mathscr{P}}{\partial \varphi} = \frac{\partial Q}{\partial z} \tag{3}$$

The change in weight of the partly immersed electrode with change in potential corresponds to the change in the electrode charge on immersion.

We shall carry out a further analysis with respect to a vertical electrode of arbitrary cross section: The surface of the electrode is cylindrical with a vertical generating line and with a directrix of arbitrary shape (e.g., a vertical rectangular plate). The electrode waterline is the periphery of the cross section of the electrode horizontal to the plane at the level of the solution away from the meniscus. The limit of wetting does not coincide with the waterline and in the general case is not a plane curve. For instance, at the edges of the plate the meniscus is lower than in its central portion (Fig. 1).

Let us introduce the notations: s is the waterline length and, what is the same, the perimeter of the electrode cross section; q_i and q_n are respectively the charge densities on the immersed and nonimmersed parts of the electrode; if the electrode is not smooth then q_i and q_n must be substituted in subsequent equations by αq_i and αq_n, where α is the roughness factor. The total charge on the electrode is

$$Q = s[zq_i + (H - z)q_n], \tag{4}$$

where H is the electrode height. The densities q_i and q_n are independent of z. Therefore,

$$\frac{1}{s}\frac{\partial Q}{\partial z} = q_i - q_n. \tag{5}$$

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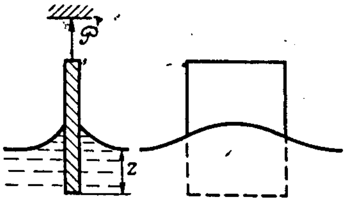

Fig. 1. Semiimmersed electrode in the shape of a rectangular plate.

Dividing (3) by s and substituting in (5) we arrive at the equation for the wetting of solid electrodes:

$$\frac{1}{s}\frac{\partial \mathcal{P}}{\partial \varphi}=q_i-q_n. \tag{6}$$

This equation is fundamental for the applications. It enables q_i-q_n to be determined directly from the relation between the electrode weight and the potential. Here no limitations are imposed on the shape of the electrode cross section and the shape of the meniscus. Admissible are: the irregularity of the wetting line, for example, the fall in the meniscus at the plate edges; the existence of a film of liquid in the form of a transition region between the wetted and unwetted parts of the surface. In fact, the shape of the wetting line and the width of the transition region do not vary with the immersion and therefore make no contribution to the derivative dQ/dz.

Similarly the equation

$$\frac{1}{s}\frac{\partial \mathcal{P}}{\partial \mu}=G_i-G_n \tag{7}$$

can be obtained, in which μ is the chemical potential of the adsorbed substance, G_i and G_n are the percentage superficial excesses of this substance respectively on immersed and nonimmersed parts of the electrode. The relativity is associated with the simultaneous adsorption of solvent molecules from the liquid and the vapor.

Under conditions in which q_n is independent of φ, differentiation of Eq. (6) gives

$$\frac{1}{s}\frac{\partial^2 \mathcal{P}}{\partial \varphi^2}=C, \tag{8}$$

where $C=\partial q_i/\partial\varphi$ is the differential capacity of the electrode. The extremum of the weight $\mathcal{P}$ is reached when $q_i=q_n$. It is a minimum because C is always >0. In the particular case when $q_n=0$ the minimum of weight $\mathcal{P}$ coincides with the zero-charge point.

The volume of the meniscus is reckoned from the liquid level. With wettability the meniscus weight is positive and with nonwettability negative. A force equal to the meniscus weight is applied to the electrode along the wetting line. We shall project a small length of this line on the waterline. We shall call the ratio of the corresponding fraction of the meniscus weight to the length of the projection the gravimetric tension δ. The gravimetric tension is the same at all points on the waterline whatever its shape. This is obvious for a waterline in the shape of a circle. For the general case this is shown at the end of the article. Thus, the meniscus weight is equal to $s\delta$ and

$$\frac{\partial \delta}{\partial \varphi}=\frac{1}{s}\frac{\partial \mathcal{P}}{\partial \varphi}. \tag{9}$$

Hence from Eqs. (6) and (7) there follow the equations

$$\frac{\partial \delta}{\partial \varphi}=q_i-q_n, \tag{10}$$

$$\frac{\partial \delta}{\partial \mu}=G_i-G_n. \tag{11}$$

From Eqs. (6) and (8) ensue formulas relating to particular electrode shapes. Suppose, for instance, that the electrode is a thin layer of metal coated onto the inner surface of a capillary of radius a, and a column of liquid with height h and density ρ is drawn into the capillary from the main mass of solution. Then $s=2\pi a$ and, with accuracy equal to that of the constants, $\mathcal{P}=\pi a^2 h\rho$ (the weight of the liquid column in the capillary). Equation (8) at once gives the result

$$\frac{\rho a}{2}\frac{\partial^2 h}{\partial \varphi^2}=C, \tag{12}$$

which agrees with the equation obtained previously by Bonnemay by differentiating the Young equation and examining the geometry of the meniscus in the capillary [5]. Measurement of the liquid rise by an optical method, the transmission of x-rays [5], is fraught with an error comparable with the capillary radius.

Nevertheless, as follows from the general equation [6] there is no need to consider the meniscus geometry, to employ Young's equation, and to carry out calculations individually for every electrode shape and determine the parameter inherent only to the given electrode. It is sufficient to determine the effect of the potential on the parameter which is common to all the electrodes – the weight. This considerably simplifies the experiment, and increases its accuracy and sensitiveness.

In fact, it becomes possible to use electrodes with a simple shape, for example, narrow plates with a twisted wetting line. Access to the electrode for the optical measurements is unnecessary. The electrode weight is unambiguous, whereas the optical measurements depend on the choice of the meniscus point monitored. The accuracy of the optical measurements diminishes with reduction in the wetting angle. The variation of electrode weight can be recorded with high sensitivity.

Consider now the connection between the gravimetric tension δ and the wetting angle θ. In certain parts of the specimen surface the wetting line is at a certain angle β to the horizontal. Let Δs be the length of a quite small section of the waterline. Then the length of the corresponding section of the wetting line is $\Delta s/\cos\beta$. From the determination of δ the weight of the meniscus at the selected section of waterline is $\delta\Delta s$. It is held by the surface tension of the liquid σ_0 which, at an angle θ to the horizontal, acts on the wetting line. Thus, the force $f = \sigma_0\Delta s/\cos\beta$ is applied to the section of wetting line referred to above. The projection of this force on the vertical axis $f\cos\theta\cos\beta$ is equal to the meniscus weight $\delta\Delta s$. Hence

$$\delta=\sigma_0\cos\theta, \tag{13}$$

i.e., the gravimetric tension is independent of the angle β and consequently the same at all points on the waterline independently of its shape. This property of gravimetric tension can also be obtained thermodynamically. Because the total meniscus weight $s\delta$ is known from experiment Eq. (13) makes the determination of θ possible. It follows from Eqs. (10) and (13) that

$$q_i-q_n=-\sigma_0\sin\theta\frac{\partial\theta}{\partial\varphi}. \tag{14}$$

The relation between the electrode weight and the potential may also be used in the case of the boundary between two nonmiscible liquids intersected by the electrode surface.

By reduction from Eqs. (6) and (10) it can be seen that they are applicable both to isotropic and to anisotropic surfaces. The charge densities on the right-hand side of Eq. (10) are independent of the orientation of the anisotropic surface during immersion. Therefore the left-hand side of Eq. (10) is also scalar. From this it follows that the quantity δ represents the work of wetting but has no relation to the surface tension of the solid, because the tension is a tensor and depends on the orientation of the anisotropic surface.

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