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Comments on: STRUCTURE OF THE DOUBLE ELECTRIC LAYER AT THE METAL-SOLUTION BOUNDARY

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A review article concerning the structure of the double electric layer at the metal-solution and metal-melt boundaries appeared in Chemical Review last year. It was written by the Indian electrochemists Devanathan and Tilak [1]. This article is without doubt a valuable contribution to the electrochemical literature. It is a systematic and rather complete presentation of investigations concerning the adsorption of ions and organic molecules at the electrode-solution boundary and is of particular interest to electrochemists working on the theory of the double electric layer and electrochemical kinetics. At the same time, a certain number of critical remarks seem to be in order.

In the section concerning the thermodynamics of the electrode-solution boundary the authors differentiate between the thermodynamic properties of ideally polarizable and unpolarizable electrodes. We cannot agree with this approach. In fact, as early as 1923 Frumkin [2] gave a thermodynamic derivation of the principal equation of electrocapillarity valid for the ideally polarizable as well as for unpolarizable electrodes. Contrary to the conclusions in this investigation [2], which Devanathan and Tilak do not mention, the subsequent derivations of the principal equation of electrocapillarity are usually limited to ideally polarizable electrodes. Yet, in fact, this equation was widely applied to systems in which the condition of ideal polarizability is not satisfied (thallium amalgam, for example).

In describing the experimental results concerning negative adsorption of cations from strongly concentrated solutions at the negatively charged surface of mercury the authors note that these data remain unexplained (p. 640). In reality, this is not the case. Since the negative adsorption of cations at the negatively charged surface of mercury is usually difficult, let us examine this problem in some detail.

The thermodynamic method of calculating the adsorption of cations from concentrated solutions is related, on the basis of electrocapillary measurements, to the use of the equation:

$$-\left(\frac{\partial\sigma}{\partial\mu}\right)_{\varphi^-}=\Gamma_+-\Gamma_{H_2O}\cdot\frac{N_+}{N_{H_2O}}, \tag{1}$$

where σ is the surface tension; μ is the chemical potential of the electrolyte; φ^- is the potential measured with respect to an electrode which is reversible with respect to the anion in the same solution; Γ_+ and Γ_{H_2O} are the surface densities of cations and water as compared to that in the bulk of the solution; N_+ and N_{H_2O} are their respective molar fractions in the bulk of the solution. The left side of Eq. (1) can easily be determined experimentally. This is an equation with two unknowns: Γ_+ and Γ_{H_2O}. Therefore, to determine the numerical values of the adsorption of one of the components it is necessary to select the position of the separation boundary in the heterogeneous region between the two phases to which the values of adsorption determined experimentally will refer. Usually, this boundary is selected so that the adsorption of the solvent at this boundary is equal to zero: $\Gamma_{H_2O} = 0$ (Gibbs plane). In this case

$$\Gamma_+^0=-\left(\frac{\partial\sigma}{\partial\mu}\right)_{\varphi^-}, \tag{2}$$

where the upper zero index at Γ_+ means that the adsorption of cations refers to the plane where $\Gamma_{H_2O} = 0$.

In the case of dilute solutions, where the ratio N_+/N_{H_2O} is small and one can neglect the second term in (1), $\Gamma_+^0 \approx \Gamma_+$. In other words, in this case the surface excess is practically independent of the position of the discharge plane in the interphase region. With increasing concentration of the solution, the term $\Gamma_{H_2O} \cdot N_+/N_{H_2O}$ begins to

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increase. In this case $\Gamma_+^0 \neq \Gamma_+$ if Γ_+ represents the excess number of cations in the coating of the double layer oriented toward the solution. When $\Gamma_{H_2O} > 0$, i.e., under the condition that there remains a layer of water molecules between the surface of the metal and the adsorbed cations, the value of Γ_+^0 may become negative in spite of the fact that the concentration of cations in the double layer is higher than within the bulk of the solution, (i.e., $\Gamma_+ > 0$). It was recently shown in [3] that the occurrence of negative adsorption requires the existence of a dielectric layer with a dielectric constant considerably smaller than the volume dielectric constant of the solvent between the metal and the ions of the solution.

Let us examine the model methods of determining the adsorption of ions on the surface of mercury. Devanathan and Tilak did not take into account the fact that in solutions of electrolytes with concentrations of 1 N and higher the Gouy-Chapman diffusion theory ceases to be correct. Thus, the model method of Graham and Devanathan cannot be used to calculate the adsorption of ions from concentrated solutions.

On p. 647 Devanathan and Tilak note correctly that in the presence of specific adsorption of ions the position of the minimum on the curve of the differential capacitance in dilute solutions does not coincide with the point of zero charge. It is assumed, apparently, that in the absence of specific adsorption these potentials always coincide. However, this is not true. The second condition for the coincidence of the potential of the minimum with the point of zero charge is that the electrolyte be symmetrically valent—NaF, for example. If one uses a surface-inactive electrolyte of the asymmetric valence type (H_2SO_4, for example), then, as was shown in [4], the position of the minimum on the curve of differential capacitance in dilute solutions is very different from the position of the zero charge point.

We cannot agree with the detailed description of the model representation of the double electric layer presented in the review.

In the case of solutions not containing surface-active organic substances Devanathan starts with the equation:

$$\frac{1}{C}=\frac{1}{K_{m\text{-}1}}+\left(\frac{1}{K_{1\text{-}2}}+\frac{1}{C_d}\right)\left(1-\frac{dq_1}{dq}\right), \tag{3}$$

where C is the total differential capacitance; $K_{m\text{-}1}$ is the capacitance of the space between the metal surface and the inner Helmholtz plane; $K_{1\text{-}2}$ is the capacitance of the space between the inner and outer Helmholtz planes; C_d is the differential capacitance of the diffusion layer; q_1 is the charge of the specifically adsorbed ions; and q is the charge of the electrode. If $K_{m\text{-}1}$ and $K_{1\text{-}2}$ represent differential capacitances then Eq. (3) is correct. But according to Devanathan's theory, $K_{m\text{-}1}$ and $K_{1\text{-}2}$ are integral capacitances whose values are independent of the charge of the surface. Since the variation of the orientation of adsorbed water molecules and also the effects of the deformation of adsorbed ions as the result of the variation of the intensity of the field in the double electric layer lead of necessity to the dependence of $K_{m\text{-}1}$ and $K_{1\text{-}2}$ on q, the assumption by Devanathan that these capacitances are constant cannot be correct. On the other hand, when $K_{m\text{-}1}$ = const and $K_{1\text{-}2}$ = const then the experimental result $q_1 = 0$ at $q \approx -13\ \mu C/cm^2$ using Eq. (3) and the experimental curves of differential capacitance lead automatically to the conclusion that all the ions without exception (including Na^+ and F^-) have a considerable specific adsorption on a mercury electrode when q is not equal to $-13\ \mu C/cm^2$. Also, under these conditions the specific adsorption of anions at $q > 0$ must increase with increasing differential capacitance. When the value of anodic q is large the capacitance in $NaNO_3$ or $NaClO_4$ solutions is lower than in the NaF solution and therefore the specific adsorption of the F^- anion must be greater than the adsorption of the NO_3^- or ClO_4^- anions. All these conclusions contradict the experimental data obtained by the thermodynamic method, which also shows the incorrectness of Devanathan's assumption concerning the constancy of capacitances $K_{m\text{-}1}$ and $K_{1\text{-}2}$. Let us note that Devanathan's concepts concerning the double electric layer in the absence of additional organic elements were recently criticized in [5].

Devanathan's concepts concerning the double electric layer in the presence of organic compounds were examined in [6] and also in [5]. The critical remarks in these publications were not noted in the article by Devanathan and Tilak. One should give particular attention to the value of the coefficient in the expression of the dependence of the potential difference χ_{dip} occurring at the metal-solution boundary on the effective dipole moment μ_d and the number of dipoles adsorbed per unit surface N_d. Instead of the accepted expression (the notations are those of Devanathan and Tilak):

$$\chi_{dip}=4\pi N_d\mu_d/\varepsilon, \tag{4}$$

where ε is the dielectric constant, Devanathan and Tilak (p. 659) assume that:

$$\chi_{\text{dip}} = 2\pi N_d \mu_d / \varepsilon. \tag{5}$$

The fact that the arguments presented in the earlier work by Devanathan [7] are erroneous was shown in [6]. In their present article Devanathan and Tilak do not use their previous argument completely, but rather assume that when the discreteness of the dipole is considerably the value of the coefficient, equal to 2, is justified even in the case of adsorption at the metal-vacuum boundary. However, this assumption contradicts the laws of electrostatics, according to which the potential difference between two points on both sides of the dipole layer at a distance of the order of magnitude greater than the size of the dipole and the distance between them, independently of the structure of the dipole layer, is determined by Eq. (4). Also, the value of μ_d cannot be identified with the value of the dipole moment of the molecules in vacuum because of the interaction between the dipoles and the solvent and also with the neighboring dipoles as the result of incomplete orientation, etc. At the same time, the ionic conductivity of the solution, contrary to the opinion of Devanathan and Tilak, has no significant influence on the value of the effective dipole moment, as follows from the independence of the shift of the point of zero charge on the concentration of inactive electrolyte when organic substances are added to the electrolyte. Let us note that on p. 46 the coefficient 2 in the equation for χ_{dip} is explained, although with some reservation, by the fact that the molecule of organic substance is not located entirely within the dense layer, while on p. 663 [Eq. (95)] the same coefficient of 2 is used in the case of water dipoles situated entirely in the dense layer.

The interpretation of desorption of organic molecules is questionable. It is not understandable and it lacks experimental verification according to which the desorption of compounds containing polar groups would be slower than the desorption of hydrocarbons.

On pp. 662-663 the authors describe the theory of the influence of the electric field on the adsorption of organic molecules, using the model of the double electric layer given in [8] However, this model is based on the assumption of the penetration of two water molecules into the space between the surface of the metal and the outer Helmholtz plane. Earlier (p. 665) the authors note that this distance is 3.72 A (see also [9, 10]), i.e., this contradicts the theory in [8].

To explain the expulsion of the molecules of the organic substance by water molecules the authors introduce the concept of "superpolarizability" of water molecules because of the inadequate treatment of this phenomenon in [8]. In fact, this concept, although quite qualitative, corresponds to the assumptions made in [6], which is not indicated in the article.

In selecting the independent variable, potential, or charge (a problem for much discussion) the authors select the charge without refuting the arguments presented in favor of another selection in [11] and [12].

To obtain reproducible results concerning the capacitance of the double layer on the platinum electrode the authors propose to treat the electrode in KI before the experiment. After this treatment the capacitance of the double layer turns out to be close to 17 μF/cm^2. According to the results in [13] cited by the authors, this treatment of the platinum electrode does not lead to the formation of a chemisorbed layer of iodine atoms on the surface, i.e., to the poisoning of the electrode (see also [14]). The capacitance of such a complex boundary of separation can hardly be identified with the "capacitance of the solvent," as is done by these authors.. Their point of view concerning the adsorption of halide ions on platinum is not understandable. On one hand, they assume that platinum cannot easily form covalent compounds with halide ions and on the other they assume that the halides are adsorbed in the form of atoms (p. 671).

On p. 677 these authors propose a new interpretation of the ascension of the curves of differential capacitance in molten electrolytes, namely as the result of pseudo-capacitance preceding the discharge of cations or dissolution of the metal. However, this interpretation is unacceptable, since first of all the measurements were made under conditions where there was no dispersion of capacitance; secondly, there was a quantitative agreement between the experimental electrocapillary curves and the curves calculated on the basis of the data on capacitance using the equation of Lippman (Ukshe, et al.). The authors also give a new explanation of the increase of capacitance at the point of zero charge $C_{\min}$ with increasing temperature t. But according to these authors the electron cloud of the metal shifts with increasing temperature with respect to the ion carcass toward the melt. This leads to the decrease of the effective distance (and therefore to the increase of capacitance) between the centers of the ions of the melt forming the inner envelope of the double layer and the imaginary plane which one can arbitrarily call the surface of the metal. However, it is difficult to agree with this interpretation. In fact, the distance of closest approach between the ions of the melt and metal surface d is determined by short range forces which are sufficiently strong that the increase in the temperature of the experiment cannot affect the properties of the potential curve and induce the decrease of d. It is well known that even during melting of solids the distance between the closest neighbors remains practically constant and that the change of volume occurs as the result of the injection of "holes."

The critical remark by Devanathan and Tilak concerning the explanation of the increase of capacitance with temperature given earlier in [8] is due to a misunderstanding, since the value of λ in [15] characterizing the size of the region of close order or the radius of correlation is interpreted erroneously by the author as the "wavelength," i.e., as the magnitude characterizing the distance between the maxima of the radial distribution function, which is practically independent of temperature.

In conclusion, let us note a few contradictions and also a few incorrect conclusions which are probably due to misunderstandings.

For example, according to the data in Fig. 10, when the charge of the mercury surface is $-15\ \mu C/cm^2$ the adsorption of cations K^+ is greater than the adsorption of the cations $[(CH_3)_4N]^+$ (data from [8]). But according to the results in Fig. 21 under the same conditions the adsorption of the cathions K^+ is one-tenth that of the cations of tetramethylammonia (data from [8]).

On p. 656 the authors disagree with the possibility of extrapolating the linear dependence of 1/C on 1/C to 1/c = 0 (C is the capacitance and c is the concentration). This extrapolation is used in the Frumkin-Damaskin theory. The disagreement is based on the fact that the dependence of C on c is not linear. But if the dependence of 1/C on 1/c is linear, i.e.,

$$1/C = a + b/c, \tag{6}$$

where a and b are constants, then it is obvious that one cannot expect a linear dependence of C on c.

Another argument against the Frumkin-Damaskin theory [6] advanced by these authors is based on the assumption that the linear dependence of the attraction constant on the potential of the electrode cannot be theoretically justified (p. 657). However, this justification was presented in [17].

On p. 665 the authors ascertain that the observed charge of the surface in the presence of I^- ions does not exceed 40 $\mu C/cm^2$. In fact, however, on the anodic end of the electrocapillary curve in the 1 N KNO_3 + 0.01 N KI solution the charge on the surface of mercury is equal to 90 $\mu C/cm^2$ [2].

The presence of some unjustified assertions somewhat decreases the value of the work presented by Devanathan and Tilak.

In conclusion, we would like to express our gratitude to Devanathan and Tilak for sending a photocopy of their article, which gave us the opportunity of acquainting ourselves with it before publication.

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