

$$\Phi(R, a, x) \simeq \frac{2L_i(a)L_i(x)}{\epsilon R L_H^2} e^{-R/L_D} \quad (4.4)$$

for the potential. The first of them holds when (4.5) or (4.6) is fulfilled, while the second holds when (4.7) or (4.8) is fulfilled:

$$L_D \gg \epsilon L_H; \quad R \gg \epsilon L_H \quad (4.5)$$

$$\epsilon L_H \gg L_D \gg x_0; \quad R \gg \epsilon^2 L_H^2 / L_D \quad (4.6)$$

$$L_D \gg \epsilon L_H \gg R \gg x_0 \quad (4.7)$$

$$\epsilon L_H \gg L_D \gg x_0; \quad \epsilon^2 L_H^2 / L_D \gg R \gg x_0. \quad (4.8)$$

These relations only contain experimentally measurable quantities. For example, for the Hg/H₂O interface we have $\epsilon L_H \simeq 24 \text{ \AA}$; $L_i(x)$; $L_i(a) \leq L_H = 0.3 \text{ \AA}$, i.e., $L_i(a)$ and $L_i(x)$ are between 0.1 and 0.3 Å for different ions. On this basis one can readily estimate the magnitude of interaction between the adsorbed ions.

We note in conclusion that all relations of Section 4 other than (4.2) remain valid in the rather more general model when there is a nonlocal link between induction $\vec{D}(\vec{r})$ and electric field $\vec{E}(\vec{r})$, and a sharp metal/solution boundary cannot be introduced.

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RELAXATION PROPERTIES OF THE COMPACT PART OF THE ELECTRIC DOUBLE LAYER

S. Kh. Ait'yan, I. A. Bagotskaya,
V. S. Markin, and Yu. A. Chizmadzhev

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Equilibrium and relaxation properties of the electric double layer — the capacity, characteristic reorientation frequency, and admittance — are calculated in terms of a model of reorientation of solvent molecules adsorbed on the electrode. Comparison is made with experiment. Nonlinear effects in the double layer are included.

1. INTRODUCTION

Polar solvent molecules adsorbed on the electrode can substantially influence the electric characteristics of the double layer. Since the solvent molecules have a nonzero natural dipole moment, they evidently can undergo reorientation when the electrode potential changes. The first quantitative calculation of a model with two possible orientations of the adsorbed solvent molecules was performed in the work of Watts-Tobin [1] and Mott and Watts-Tobin [2]. However, the model with two states of the adsorbed solvent molecules produces a potential dependence of double-layer capacity having just one maximum, and in a number of cases is at variance with the experimental data [3-5].

Damaskin and Frumkin [6] suggested that the solvent molecules on the electrode surface can associate into groups, thus forming a third possible state. Similar models are analyzed in a number of papers of Bockris

and Habib [7, 8] and of Damaskin [9]. Parsons [10] generalized the model of Damaskin and Frumkin by suggesting that the aggregates can exist in two possible states.

It must be noted that it is quite a complicated task to correctly allow for the presence of aggregates, particularly when (as in [9]) the number of molecules contained in them is arbitrary. Thus, already in the case of dimers, for instance, considerable difficulties arise. It was assumed in [7, 8] that the aggregates consist of two solvent molecules with opposite dipole orientations. However, the third state (the aggregates) did not play an important part in these papers, since it was assumed that the aggregates (or dimers), because of their zero dipole moment, are not involved in the redistribution of statistical weights of the different states with changing external potential. This assumption in general is not true, as pointed out in [11]. In fact, the energy level of an aggregate does not depend on the external potential, while the energy levels of the other states change with potential, which leads to a mutual redistribution of the statistical weights of all states. Therefore, on account of the limited number of sites on the electrode, the number of aggregates in the double layer depends on potential.

An attempt was made in [9] to include aggregates without limiting the number of solvent molecules contained in them. However, relation (1) in [9] for the statistical-weight distribution of the different states is limited in its applicability, since it was formulated for identical particles, while the individual adsorbed solvent molecules and the aggregates in essence are different particles.

The entropy of the adsorbed solvent molecules and its connection with double-layer capacity has been examined in [7, 12].

In all the investigations mentioned above, the authors restricted discussion to equilibrium properties of the compact part of the electric double layer. This was quite justified, since no indications existed that with the use of traditional electrochemical methods, capacity relaxation could be observed in any system. The situation changed radically when a frequency dependence of capacity of the compact double-layer part could be detected [13] for the Ga electrode in dimethylsulfoxide. With the temperature-jump technique developed in [14, 15], capacity relaxation could be observed in aqueous solutions of sodium fluoride and other electrolytes down to times on the order of 10^{-8} sec. It became relevant with the advent of these data to construct a theory of the nonequilibrium double layer; this is the concern of the present work. While sticking to the dipole model of the compact layer we shall link its equilibrium and relaxation characteristics to the ability of the solvent molecules to undergo reorientation in the electric field.

2. THE IMPEDANCE OF THE COMPACT PART OF THE ELECTRIC DOUBLE LAYER

2.1. The Equilibrium Case. Let an ideally polarizable electrode be immersed in a highly concentrated electrolyte solution. We shall assume that within the compact double-layer part, the solvent molecules can assume several fixed positions; in so doing they interact with the electrode and with neighboring molecules. A molecule's energy w_i in each state is made up of a nonelectric part u_i and an electric part $\mu_i \varphi_d / \delta$. Here φ_d is the potential drop across the compact layer,

$$\varphi_d = \frac{\varphi}{1 + \varepsilon_d / \varepsilon_s \delta \kappa_s}, \quad (2.1)$$

where φ is the potential of the electrode relative to the solution, ε_d and ε_s are the dielectric permittivities of the compact layer and the solution, respectively, δ is the thickness of the compact double-layer part, κ_s^{-1} is the Debye length in the solution, and μ_i is the projection of the dipole moment of molecule i onto the axis pointing in the direction of the electrode. In concentrated solutions $\varphi_d \approx \varphi$, and we shall assume in the following, therefore, that the potential drop is entirely across the compact layer.

We shall write the energy of a molecule in state i as,

$$w_i = u_i + \mu_i \varphi / \delta. \quad (2.2)$$

We shall use the dimensionless energies W_i and U_i stated in units of kT :

$$W_i = w_i / kT; \quad U_i = u_i / kT, \quad (2.3)$$

as well as the dimensionless value ρ_i of the projection of the dipole moment normalized to the absolute value of the molecule's dipole moment:

$$\rho_i = \mu_i / \mu, \quad (2.4)$$

where μ is some characteristic dipole moment.

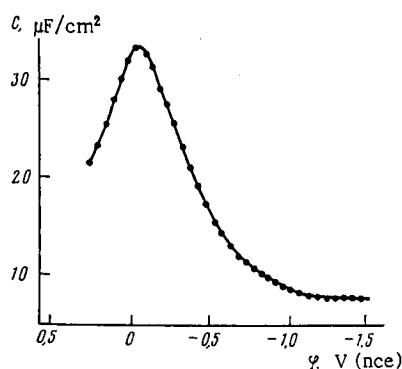


Fig. 1. Double-layer capacity as a function of potential. The points: experimental results from [16] (1 M KPF₆ in DMSO at 25°C); the solid line: theory.

The total number n of molecules on the electrode surface is constant. The molecules are distributed over the different states in accordance with the Boltzmann law:

$$n_i = n \frac{e^{-W_i}}{\sum_k e^{-W_k}}. \quad (2.5)$$

The potential difference between electrode and solution is determined by electrode charge q and by the distribution of molecules in the compact layer:

$$\varphi = \frac{q}{C_0} + \frac{4\pi \sum_i n_i \mu_i}{\varepsilon} = \frac{q}{C_0} + \frac{4\pi \mu}{\varepsilon} \sum_i n_i \rho_i, \quad (2.6)$$

where ε is the dielectric permittivity of the compact double-layer part, and C_0 is the specific capacity of the electrode; both of these quantities are defined with the solvent molecules "frozen":

$$C_0 = \varepsilon / 4\pi \delta. \quad (2.7)$$

When we now introduce the dimensionless potential

$$\Phi = \mu \varphi / \delta kT, \quad (2.8)$$

then

$$W_i = U_i + \rho_i \Phi. \quad (2.9)$$

We shall find the expression for the double-layer capacity. Since

$$C = dq/d\varphi, \quad (2.10)$$

we obtain from (2.5) and (2.6),

$$C = C_0 - \frac{\mu}{\delta} \sum_i \rho_i \frac{\partial n_i}{\partial \varphi_i} = C_0 + \frac{\mu^2 n}{\delta^2 kT} \frac{d^2}{d\Phi^2} \left(\ln \sum_i e^{-W_i} \right). \quad (2.11)$$

Let us compare these relations with the experimental results of Payne for the double-layer capacity at the mercury electrode in dimethylsulfoxide [16]. In this work the potential dependence of capacity is given by a bell-shaped curve* (Fig. 1; the points are experimental results). Such a curve can be obtained when assuming the existence of merely two adsorbed states. Then the capacity is given by

$$C = C_0 + \frac{\mu^2 n (\rho_1 - \rho_2)^2 \exp(-W_1 - W_2)}{\delta^2 kT (e^{-W_1} + e^{-W_2})^2}. \quad (2.12)$$

Introducing the dimensionless quantity

$$\psi = \frac{U_1 - U_2}{2} + \frac{(\rho_1 - \rho_2)\mu}{2kT\delta} \varphi = \frac{\Delta U}{2} + \frac{\Delta \mu \varphi}{2kT\delta}, \quad (2.13)$$

*Sometimes one discusses the dependence, not on potential φ but on electrode charge q , which are linked by relation (2.6).

where

$$\Delta U = U_1 - U_2, \quad \Delta \mu = \mu_1 - \mu_2, \quad (2.14)$$

we can rewrite the expression for capacity as

$$C = C_0 + \frac{n(\Delta\mu)^2}{4\delta^2 kT} \frac{1}{\cosh^2 \psi}. \quad (2.15)$$

Figure 1 presents the theoretical potential dependence of capacity. The bell shape is defined only by the pseudopotential ψ . Function $1/\cosh^2 \psi$ changes from 1 to 0 when ψ changes from 0 to $\pm\infty$, and has a value of 1/2 for $\psi_{0.5} = \pm 0.9$. Experiment does not yield the absolute value of potential φ , so that we can only determine the potential shift. The potential, φ_m , of maximum capacity corresponds to $\psi_m = 0$. The curve falls off symmetrically on both sides of the maximum. Hence the dimensional half-decay potential $\varphi_{0.5}$ is related to $\psi_{0.5}$ as follows:

$$\psi_{0.5} = \frac{\Delta\mu}{2kT\delta} (\varphi_{0.5} - \varphi_m). \quad (2.16)$$

In Payne's experiment [16] $|\varphi_{0.5} - \varphi_m| = 0.3$ V. Substituting this value into the foregoing equality we obtain

$$\Delta\mu = 0.15e\delta, \quad (2.17)$$

where e is the electronic charge and δ is double-layer thickness.

Moreover, the point of zero charge is known from experiment:

$$\varphi_{zc} - \varphi_m = -0.26 \text{ V}. \quad (2.18)$$

Then

$$\psi_{zc} = \frac{\Delta\mu}{2kT\delta} (\varphi_{zc} - \varphi_m) = -0.8 \text{ V}. \quad (2.19)$$

From Eq. (2.6) we obtain electrode charge as

$$q = C_0 \varphi - \frac{\mu_1 n_1 + \mu_2 n_2}{\delta}. \quad (2.20)$$

Setting $q = 0$ we obtain an expression for φ_{zc} . Together with equalities (2.5) this gives,

$$\frac{\delta C_0}{n} \varphi_{zc} = \frac{\mu_1}{1 + e^{2\psi_{zc}}} + \frac{\mu_2}{1 + e^{-2\psi_{zc}}}. \quad (2.21)$$

For further computations we make the model somewhat more specific. We shall assume that in the first state the dipole moment has no projection onto the normal to the surface, i.e., $\mu_1 = 0$. Then

$$\mu_2 = -0.15 e\delta. \quad (2.22)$$

For a determination of the other parameters we shall make use of experimental data:

$$C_0 = 8 \text{ } \mu\text{F/cm}^2, \quad C_m = 33 \text{ } \mu\text{F/cm}^2. \quad (2.23)$$

From (2.15) we have

$$C_m - C_0 = \frac{n(\Delta\mu)^2}{4\delta^2 kT}. \quad (2.24)$$

Hence one can determine the number of solvent molecules on the electrode surface:

$$n = \frac{4\delta^2 kT (C_m - C_0)}{(\Delta\mu)^2} = 6.9 \cdot 10^{14} \text{ cm}^{-2}. \quad (2.25)$$

It follows from the definition (2.7) of C_0 that

$$\delta/\epsilon = 1.1 \cdot 10^{-8} \text{ cm}. \quad (2.26)$$

Now we can "link up" the potential scales:

$$\varphi_{zc} = - \frac{0.15en}{C_0(1 + e^{-2\psi_{zc}})} = -0.36 \text{ V}. \quad (2.27)$$

Further we can calculate the difference in adsorption energies:

$$U_1 - U_2 = 2\psi_{zc} - \frac{\Delta\mu}{\delta kT} \varphi_{zc} = 0.56. \quad (2.28)$$

The desired difference is given in units of kT .

Thus, with the two-state model one can describe a simple potential dependence of capacity, and determine the model parameters. However, this is achieved only in the simple case where the curve has the shape of a single bell. In other cases one must use a more detailed model. The physically reasonable values of the parameters indicate that the model selected for the compact double-layer part is suitable for a description of capacity, and now we can proceed to examine nonequilibrium phenomena.

2.2. The Frequency Dependence of Capacity. We shall now assume that a constant potential, and on top of it a small harmonic signal, are applied to the electrode:

$$\Phi = \Phi_0 + \alpha e^{i\omega t}. \quad (2.29)$$

Then the molecules will make transitions between the different states. We shall write $\nu_{jk}(\Phi)$ for the transition constant between states j and k . The equations for the occupation numbers of the different states are of the form of

$$\frac{dn_i}{dt} = \sum_k' \nu_{ki}(\Phi) n_k - n_i \sum_k' \nu_{ik}(\Phi), \quad (2.30)$$

where the dash signifies that terms with identical suffixes are missing from the sum. Because of the principle of microscopic reversibility, the dependence of the transition constants on the energies of the particles in different states is of the form of

$$\nu_{jk}/\nu_{kj} = \exp(W_j - W_k). \quad (2.31)$$

Since the energy depends on potential Φ , the transition constants will also depend on potential in accordance with relation (2.9). For further computations we must specify the potential dependence of the constants in somewhat greater detail. We shall assume that

$$\nu_{jk}(\Phi) = \nu_{jk}(\Phi_0) \exp \left[\frac{\alpha(\rho_j - \rho_k)}{2} e^{i\omega t} \right]. \quad (2.32)$$

Assuming that α is small we expand the exponential into a series:

$$\nu_{jk}(\Phi) = \nu_{jk}(\Phi_0) \left[1 + \frac{1}{2} \alpha(\rho_j - \rho_k) e^{i\omega t} \right]. \quad (2.33)$$

If now we substitute this expression into the system of Eqs. (2.29), we obtain the final formulation of the problem. We shall solve it without starting conditions, i.e., for the fully established mode. After elementary but tedious computations we obtain the occupation numbers n_k of the individual states. Then we use the relation for electrode charge,

$$q = C_0 \varphi - \left(\sum_k \mu_k n_k \right) / \delta, \quad (2.34)$$

from which we obtain the current by differentiating with respect to time:

$$I = C_0 \frac{d\varphi}{dt} - \left(\sum_k \mu_k \frac{dn_k}{dt} \right) / \delta. \quad (2.35)$$

We shall limit ourselves to the case of three states in order to obtain perspicuous relations (the three-state model). The system's admittance is given by

$$A = \frac{I}{\alpha e^{i\omega t}}. \quad (2.36)$$

Substituting the expression obtained for I we obtain

$$A = i\omega C_0 - \frac{i\omega \mu^2 \xi}{kT \delta \eta}, \quad (2.37)$$

where

$$\begin{aligned} \xi = & -(\rho_1 - \rho_2)^2 (\nu_{12}\nu_{32} + \nu_{12}\nu_{31} + \nu_{13}\nu_{32}) n_1 - (\rho_2 - \rho_3)^2 (\nu_{23}\nu_{12} + \\ & + \nu_{23}\nu_{13} + \nu_{13}\nu_{21}) n_2 - (\rho_3 - \rho_1)^2 (\nu_{31}\nu_{21} + \nu_{32}\nu_{21} + \nu_{31}\nu_{23}) n_3 - \\ & - i\omega [(\rho_1 - \rho_2)^2 n_1 \nu_{12} + (\rho_2 - \rho_3)^2 n_2 \nu_{23} + (\rho_3 - \rho_1)^2 n_3 \nu_{31}], \end{aligned} \quad (2.38)$$

$$\begin{aligned} \eta = & -\omega^2 + i\omega (\nu_{12} + \nu_{13} + \nu_{23} + \nu_{21} + \nu_{31} + \nu_{32}) + \\ & + (\nu_{12}\nu_{23}e^{W_2} + \nu_{31}\nu_{12}e^{W_1} + \nu_{23}\nu_{31}e^{W_1}) (e^{-W_1} + e^{-W_2} + e^{-W_3}). \end{aligned} \quad (2.39)$$

The impedance is resolved in a series equivalent circuit. Then

$$C = 1/\operatorname{Re} \left(\frac{i\omega}{A} \right). \quad (2.40)$$

Substituting (2.37) to (2.39) into (2.40) we obtain

$$C = C_0 - \frac{\mu^2}{\delta^2 k T} \frac{\xi_1 (\beta \eta_1 - \zeta_1) - \zeta_2 (\beta \eta_2 - \zeta_2)}{\eta_1 (\beta \eta_1 - \zeta_1) + \eta_2 (\beta \eta_2 - \zeta_2)}. \quad (2.41)$$

Here the notations

$$\beta = \frac{\epsilon k T \delta}{4 \pi \mu^2} = \frac{C_0 \delta^2 k T}{\mu^2}, \quad (2.42)$$

$$\xi_1 = \operatorname{Re} (\zeta), \quad \xi_2 = \operatorname{Im} (\zeta), \quad \eta_1 = \operatorname{Re} (\eta), \quad \eta_2 = \operatorname{Im} (\eta) \quad (2.43)$$

have been used. Relation (2.41) is found to be rather cumbersome. Hence we shall examine its particular form for the case of two states. Then we obtain

$$C = C_0 + \frac{(\Delta \mu)^2 n e^{-W_1 - W_2}}{\delta^2 k T (e^{-W_1} + e^{-W_2})^2} \frac{1}{1 + (\omega/\omega_0)^2}. \quad (2.44)$$

This can also be written down as

$$C = C_0 + \frac{(\Delta \mu)^2 n}{4 \delta^2 k T \cosh^2 \psi} \frac{1}{1 + (\omega/\omega_0)^2}. \quad (2.45)$$

Quantity ψ has been defined before (2.13), while the characteristic frequency ω_0 is given by

$$\omega_0^2 = v^2 [4 \cosh^2(\Delta W) + \Delta \rho^2 n / \beta], \quad (2.46)$$

where

$$\Delta W = W_1 - W_2, \quad \Delta \rho = \rho_1 - \rho_2, \quad v^2 = v_{12} v_{21}. \quad (2.47)$$

With the notation

$$C_1 = \frac{(\Delta \mu)^2 n}{4 \delta^2 k T \cosh^2 \psi}, \quad (2.48)$$

expression (2.36) for the capacity becomes,

$$C = C_0 + \frac{C_1}{1 + (\omega/\omega_0)^2}. \quad (2.49)$$

We shall try to apply the theory developed above to a specific system, viz., the Ga electrode in dimethylsulfoxide examined in [13]. It has been shown there that at frequencies of 0.4, 2, and 10 kHz, the capacity is 93, 45, and 35 $\mu\text{F}/\text{cm}^2$, respectively. By comparing the theory with this experiment one can determine the model parameters: $C_0 = 34.7 \mu\text{F}/\text{cm}^2$, $C_1 = 72.0 \mu\text{F}/\text{cm}^2$, and $\omega_0 = 824 \text{ Hz}$.

The small number of experimental data for capacity dispersion available up to now does not allow us to verify theory more thoroughly at this point. The values found for parameters C_0 and C_1 are physically reasonable. The low value of ω indicates that the characteristic transition constants ν_{12} and ν_{21} are low. This implies that the different dipole states are separated by a high energy barrier. These results can only find a complete explanation in a microscopic theory, which is beyond the scope of our exposition.

3. NONLINEAR EFFECTS WITH THE HARMONIC SIGNAL

As in the previous section, we shall examine a harmonic signal applied to the electrode on top of some constant signal, but unlike the previous section, we shall not restrict ourselves to linear terms in the expansion of the transition rate constants relative to the applied harmonic signal.

In looking for nonlinear effects we shall replace the usual expression

$$\Phi = \Phi_0 + \alpha e^{i\omega t} \quad (3.1)$$

by the more exact formulation

$$\Phi = \Phi_0 + \alpha \operatorname{Re} (e^{i\omega t}) = \Phi_0 + \alpha \cos \omega t. \quad (3.2)$$

The potential dependence of the transition rate constants is of a form analogous to expression (2.32):

$$\nu_{jk}(\Phi) = \nu_{jk}(\Phi_0) \exp \left[\frac{\alpha (\rho_j - \rho_k)}{2} \cos \omega t \right]. \quad (3.3)$$

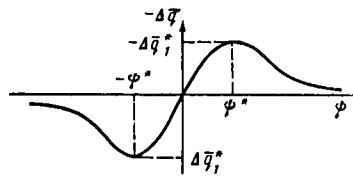


Fig. 2

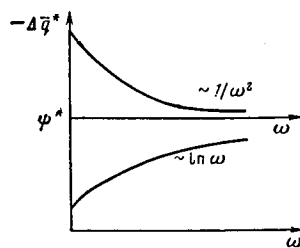


Fig. 3

Fig. 2. The change in average electrode charge found when nonlinear effects are included.

Fig. 3. The maximum average change, $\overline{\Delta q^*}$, of electrode charge and the potential, ψ^* , of the maximum average change of charge as functions of frequency ω of the harmonic signal.

In order to allow for nonlinear effects we shall expand expression (3.3) into a series retaining the required terms, without restricting ourselves to the linear approximation. The further calculating procedure is similar to that described in the previous section. For the sake of simplicity we shall limit ourselves to the case of two different adsorption states of the solvent on the electrode. Then the occupation number of the first state is given by

$$n_1 = n_1^0 + \tilde{n}_1 + \xi_1 e^{i\omega t} + \xi_2 e^{-i\omega t} + \xi_3 e^{2i\omega t} + \xi_4 e^{-2i\omega t}, \quad (3.4)$$

which is accurate to terms of second-order smallness in α , and where n_1^0 is the equilibrium value of n_1 (for $\alpha = 0$),

$$\tilde{n}_1 = - \frac{\alpha^2 \mu^2 \Delta \rho^2 n \tanh \psi}{4 \delta^2 [4 \cosh \psi + (\omega/\nu)^2]}, \quad (3.5)$$

$$\xi_1 = \frac{\alpha n}{\cosh \psi [2 \cosh \psi + i\omega/\nu]}, \quad (3.6)$$

$$\xi_2 = \frac{\alpha n}{\cosh \psi [2 \cosh \psi - i\omega/\nu]}, \quad (3.7)$$

$$\xi_3 = - \frac{\alpha^2 n \sinh \psi}{2 \cosh \psi [2 \cosh \psi + i\omega/\nu] [\cosh \psi + i\omega/\nu]}, \quad (3.8)$$

$$\xi_4 = - \frac{\alpha^2 n \sinh \psi}{2 \cosh \psi [2 \cosh \psi - i\omega/\nu] [\cosh \psi - i\omega/\nu]}, \quad (3.9)$$

$$\nu = \sqrt{\nu_{12} \nu_{21}}, \quad \psi = (W_2^0 - W_1^0)/2. \quad (3.10)$$

One can see from expressions (3.4) to (3.9) that in addition to the harmonically varying component which is of first order with respect to α and is analogous to that obtained in the previous section, there is a time-invariant displacement proportional to α^2 .

Starting from the expression (2.34) for electrode charge, and from expressions (3.4) to (3.10), we obtain

$$q = C_0 \varphi - \frac{\mu_2 N}{\delta} + \frac{\Delta \mu}{\delta} (n_1^0 + \tilde{n}_1 + \xi_1 e^{i\omega t} + \xi_2 e^{-i\omega t}). \quad (3.11)$$

Averaging over time we obtain the value of average charge on the electrode:

$$\bar{q} = C_0 \varphi_0 - \frac{\mu_2 N}{\delta} + \frac{\Delta \mu}{\delta} (n_1^0 + \tilde{n}_1), \quad (3.12)$$

which differs from the charge q_0 found on the electrode in the case of $\alpha = 0$:

$$\bar{q}_0 = C_0 \varphi_0 - \frac{\mu_2 N}{\delta} + \frac{\Delta \mu}{\delta} n_1^0, \quad (3.13)$$

$$\overline{\Delta q} = \bar{q} - \bar{q}_0 = \frac{\Delta \mu}{\delta} \tilde{n}_1 \quad (3.14)$$

or

$$\overline{\Delta q} = - \alpha^2 N \frac{\Delta \mu^3 \tanh \psi}{4 \delta^3 (kT)^2 [4 \cosh \psi + (\omega/\nu)^2]}.$$

The change in average electrode charge is a measurable quantity and has the ψ -dependence shown in Fig. 2, where

$$\psi^* = \frac{1}{2} \ln [2a - 1 + 2\sqrt{a(a-1)}], \quad (3.15)$$

$$a \equiv \frac{3 + \sqrt{9 + 2(\omega/\nu)^2}}{4}. \quad (3.16)$$

For $\omega \rightarrow 0$, quantity ψ^* is shifting in the direction of zero but has the finite value

$$\psi^*(0) = \frac{1}{2} \ln(2 + \sqrt{3}) \approx 0.658,$$

while

$$\overline{\Delta q^*}(0) = -0.024 \frac{\alpha^2 \Delta \mu^3 N}{4\delta^3}.$$

For $\omega \rightarrow \infty$ one has

$$\overline{\Delta q^*} \sim 1/\omega^2, \quad \psi^* \sim \ln \omega.$$

These dependences are shown in Fig. 3.

Let us discuss the results obtained. The electrode charge fluctuates around some average value when a constant potential shift and an alternating harmonic signal are applied to the electrode. In linear systems the average value of charge corresponds to the average value of potential. But such a simple connection no longer exists in nonlinear systems such as that of our model. The average value of charge changes relative to the original level as a function of amplitude of the applied alternating signal [relation (3.12)]. For instance, when the constant part of potential is selected so that it corresponds to zero charge of the electrode, then the additional alternating component of potential has the effect that the average charge is no longer zero. To bring it back to zero one must change the constant component of potential, i.e., change the zero-charge potential by $\Delta \varphi_{zc}$:

$$\Delta \varphi_{zc} = - \frac{C_0 \varphi_{zc}^0 + \frac{\Delta \mu}{\delta} [n_1^0(\varphi_{zc}) + \bar{n}_1(\varphi_{zc}^0)]}{C_0 + \frac{\Delta \mu}{\delta} \frac{\partial n_1^0}{\partial \varphi_{zc}}}, \quad (3.17)$$

where φ_{zc}^0 is the zero-charge potential in the equilibrium mode, and φ_{zc} is the constant potential upon which the harmonic component $\alpha \cos \omega t$ has been superimposed and at which the average electrode charge $\bar{q}$ is zero.

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