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Abstract

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ON THE INFLUENCE OF IMAGE FORCES ON THE DISTRIBUTION OF CHARGE IN THE ELECTRIC DOUBLE LAYER

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As is well known, the Wagner–Onsager–Samaras theory of the surface tension of electrolyte solutions assumes that there is no jump of potential at the interface between two media, and that the entire change in the concentration of ions near the surface is due only to the influence of "image" forces (i.e., to the different polarizability of the solvent and the external medium) and to the presence of distorted "Debye" atmospheres (^{1,2}). On the other hand, the Gouy–Chapman theory of the electric double layer assumes that the change in the concentration of ions near the surface is caused only by the jump of potential ψ_0 at the interface between two media; image forces, as well as the presence of "Debye" atmospheres in the double layer, are not taken into account in it at all. It is of interest to try to combine both these theories and to take image forces into account for $\psi_0 \neq 0$. This is all the more important because, as the simplest estimates show, in the case of multicharged ions or solutions of weak electrolytes the correction due to the influence of image forces may change the result of the Gouy–Chapman theory severalfold (^{3}).

The Gouy–Chapman theory of the electric double layer is based on the Poisson equation $\varphi''(z) = -\frac{4\pi}{\varepsilon} \sum_a e_a v_a(z)$ for the potential $\varphi(z)$, in which the concentration $v_a(z)$ of ions of kind a in the plane z is expressed in terms of the potential $\varphi(z)$ by means of the Boltzmann formula

$$v_a(z) = v_{a0} e^{-U_a(z)/\theta}, \qquad U_a = e_a \varphi(z), \qquad \theta = kT. \tag{1}$$

It follows from (1) that for $\varphi = 0$ the energy of ions near the interface between two media is also equal to zero. However, if the image forces and the presence of spherically asymmetric Debye atmospheres are taken into account, then U_a will differ from zero even for $\varphi = 0$. Therefore the more accurate expression is $U_a = e_a\varphi + \chi_a$, where $\chi_a(z)$ is the additive term to the ion energy caused by the indicated effects. As a result, instead of the usual Poisson–Boltzmann equation we obtain

$$\varphi''(z) = -\frac{4\pi}{\varepsilon} \sum_a e_a v_{a0} \exp\left[-\frac{e_a\varphi(z) + \chi_a(z)}{\theta}\right], \qquad \varphi(0) = \psi_0, \quad \varphi(\infty) = 0. \tag{2}$$

In the general case the function χ_a is very difficult to determine. However, for small $e_a\psi_0 \ll \theta$ it may be assumed, with a high degree of accuracy, that χ_a differs little from the value it has for $\psi_0 = \varphi(z) = 0$. As was shown by Bravina by solving the three-dimensional Poisson—Boltzmann equation, for $\psi_0 = 0$ the function χ_a for symmetric electrolytes has the form

$$\chi(z) = k^2 \frac{e^2}{2\varepsilon} \int_0^\infty \frac{\exp\left[-2z\sqrt{\varkappa^2+\lambda^2}\right]}{\sqrt{\varkappa^2+\lambda^2}} \, \frac{\varepsilon\sqrt{\varkappa^2+\lambda^2} - \varepsilon'\lambda}{\varepsilon\sqrt{\varkappa^2+\lambda^2} + \varepsilon'\lambda} \, \lambda \, d\lambda, \qquad \varkappa^2 = \frac{8\pi e^2 k^2 v_0}{\varepsilon\theta}, \tag{3}$$

where ke is the ion charge, k its valence, and ε and ε' are the dielectric constants of the solvent and the external medium, respectively.

Let us note two special cases of formula (3). If the electrolyte borders

with the metal and, consequently, $\varepsilon \ll \varepsilon' = \infty$, then

$$\chi(z) = -\theta\kappa^2 \frac{z^*}{2z} e^{-2\kappa z}, \qquad z^* = \frac{e^2}{2\varepsilon\theta}; \tag{4}$$

whereas if $\varepsilon \gg \varepsilon'$, then

$$\chi(z) = \theta\kappa^2 \frac{z^*}{2z} e^{-2\kappa z}. \tag{5}$$

Substituting (5) into the Boltzmann formula (1), we obtain the well-known Onsager—Samaras expression for the distribution of the ion concentration near the boundary of an aqueous electrolyte solution with a gaseous medium ([2]). From (4) and (5) it is seen that for $\varepsilon \ll \varepsilon'$ positive adsorption of ions takes place, and for $\varepsilon \gg \varepsilon'$, negative adsorption.

Since the form of the function $\chi(z)$ is known only for the case of small potentials, it is expedient in (2) to expand the exponential in a series in powers of $e\varphi/\theta$ and to retain the first terms of the series. As a result we obtain

$$\varphi''(z) - \kappa^2 e^{-\chi(z)/\theta}\varphi(z) = 0, \qquad \varphi(z_0) = \psi_0, \qquad \varphi(\infty) = 0, \tag{6}$$

where z_0 is the shortest distance to which the centers of ions can approach the interface. We note that equations (2)—(6) can be obtained in an entirely rigorous way from Bogolyubov' s equations for correlation functions, which are a direct consequence of the Gibbs canonical distribution ([3]).

Figure 1

Figure 1: Figure 1

Fig. 1. Dependence of the potential φ/ψ_0 on the distance κz:
a—according to equation (6),
b—according to the formula $\varphi = \psi_0 \exp(-\kappa z)$.

Equation (6) is a special case of a Riccati equation with a very complicated right-hand side. As is known, the solution of equations of this type cannot be obtained in the class of known functions. Therefore the system (6) was solved by us numerically. But even in the numerical solution we encountered great difficulties, since (6) is posed on a semi-infinite axis (^{6}). In order to eliminate the difficulties connected with the boundary condition at infinity, it is expedient first to consider the equation

$$y'(t) = F^2(t) - y^2(t), \qquad \text{where } F^2(t) = \exp\left[-\frac{\chi(t)}{\theta}\right], \qquad t = \kappa z, \quad (7)$$

which is obtained from (6) as a result of the substitution $y = \varphi'/\varphi$, under the condition

$$\int_{t_0}^{\infty} y(a)\, da = -\infty,$$

following from the boundary conditions (6). From (7) one finds y with any preassigned degree of accuracy.* After this, (6) can be

* By investigating (7) for various $y(t)$, one can show that the desired solution of (7) lies between the curve $y = -F(t)$ and the straight line $y = -1$, which it asymptotically approaches. Since the approach to the asymptote occurs rapidly, already at comparatively small t the desired solution turns out to be “clamped”in a very narrow region. If now one integrates (7) from right to left in the interval $\{t_0, t_m\}$, where t_m is determined from the inequality $F(t_m) - 1 < \delta$, and at the point t_m the initial condition is prescribed in the form $y_m = -1$, then the obtained $y(t_0)$ will differ from the true one certainly by less than δ. This is connected with the fact that, when integrating in the direction from large t to small, the error arising from the inaccuracy in specifying the boundary condition at $t = t_m$ decays. Indeed, denoting the solution obtained in the above way by $y_m(t)$, and the desired one by $y(t)$, it follows from (7) that when $\tau = t_m - t$ changes from $\tau_0 = 0$ to $\tau_m = t_m - t_0$, the quantity $(y_m - y)'_\tau = (y_m + y)(y_m - y)$. Since $y < 0$, $y_m < 0$, $0 \le y_m(t_m) - y(t_m) \le \delta$, the derivative of the error $\Delta y = y_m - y$ will be negative over the entire interval of integration and, consequently, $\Delta y(t_0) < \delta$.

integrated by ordinary methods as a Cauchy problem, since the boundary condition at infinity is replaced by the value of the derivative φ' at the point z_0 found from (7), since $y(t_0) = \frac{1}{\chi\psi_0} \frac{\partial\varphi}{\partial z}\Big|_{z_0}$.

Equations (7) and (6) were solved by us on an IPT-5 continuous-action machine installed at the Department of Permafrost Studies of Moscow University, for cases in which χ is specified in the form (4) and (5). The accuracy of the solution is $\pm 0.1\%$. Table 1 gives the values $\Delta\eta = (\eta - \eta_0)/\eta_0$, where $\eta_0 = -\varepsilon\chi\psi_0/4\pi$ is the total charge of the double layer, calculated according to the Gouy theory (i.e., for $\chi = 0$), $y(z_0) = \frac{1}{\psi_0} \frac{\partial\varphi}{\partial(\varkappa z)}\Big|_{z_0}$ is the correction factor arising because $\chi \neq 0$. The calculation was carried out for an aqueous electrolyte solution for which $z^* = 3.57$ Å, and for simplicity it was assumed that $2z_0 = z^*$. From the data presented in the table it is seen that, in the case of monovalent solutions, the influence of image forces can practically always be neglected, since the correction nowhere exceeds 10%; in the case of divalent electrolytes, however, the error is of the order of 100% over a very wide concentration range. In other words, already for $k = 2$ the Gouy–Chapman theory leads to values of η differing from the true ones by approximately a factor of 2. In this connection one may suppose that for $k > 2$ the error increases by several more times.

Table 1

v_0, mol/l	$\Delta\eta \cdot 100$, %, $\varepsilon'/\varepsilon = 0$, $k = 1$	$\Delta\eta \cdot 100$, %, $\varepsilon'/\varepsilon = \infty$, $k = 1$	v_0, mol/l	$\Delta\eta \cdot 100$, %, $\varepsilon'/\varepsilon = \infty$, $k = 2$
$7.7 \cdot 10^{-5}$	-1.1	0.5	$1.2 \cdot 10^{-6}$	23
$3.1 \cdot 10^{-4}$	-3.9	1.7	$4.8 \cdot 10^{-6}$	35
$7.7 \cdot 10^{-3}$	-7.8	7.4	$1.2 \cdot 10^{-4}$	82
$3.1 \cdot 10^{-2}$	-9.0	10.4	$4.8 \cdot 10^{-4}$	86
$7.2 \cdot 10^{-2}$	-9.9	10.7	$1.1 \cdot 10^{-3}$	102
0.123	-9.5	11.2	$1.9 \cdot 10^{-3}$	92
0.279	-1.8	9.8	$4.4 \cdot 10^{-3}$	71

$$\eta = \int_{z_0}^{\infty} \rho(z)\, dz = -\frac{\varepsilon}{4\pi} \frac{\partial\varphi}{\partial z}\Big|_{z_0} = \eta_0 y(z_0), \tag{8}$$

Figure 1 gives the curve $\varphi = \varphi(z)$, calculated according to the Gouy–Chapman theory and according to equation (6) for the case $k = 2$ and $v_0 = 1.1 \cdot 10^{-3}$ mol/l. From this graph it is seen that taking image forces into account leads to a more rapid decrease of the potential. In calculating the curve in Fig. 1 we did not take into account the potential drop in the molecular capacitor. If this effect is also taken into account, the difference between the two curves will become still greater. All this means that the Gouy–Chapman theory is completely inapplicable to solutions of polyvalent ions.

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REFERENCES

1. C. Wagner, Phys. Zs., **25**, 474 (1924).
2. L. Onsager, N. N. T. Samaras, J. Chem. Phys., **2**, 528 (1934).
3. G. A. Martynov, *Collection: Studies in Surface Phenomena*, Publishing House of the Academy of Sciences of the USSR, 1963.
4. G. R. Kruyt, *Science of Colloids*, Foreign Literature Publishing House, 1955.
5. V. E. Bravina, *Vestn. Mosk. Univ.*, Ser. Math.-Mech., No. 2, 85 (1958).
6. Yu. A. Klokov, DAN, **139**, No. 4, 799 (1961).

Note: Figure translations are in progress. See original paper for figures.

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