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Abstract

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THEORY OF THE DOUBLE ELECTRIC LAYER IN CONCENTRATED SOLUTIONS

In a number of previous works ($^{1-3}$), devoted to a quantitative account of the discrete structure of the charge of specifically adsorbed ionic layers at various interphase boundaries, it was assumed that the bulk concentrations of the electrolyte are either extremely high, in which case the potential drop in the diffuse part of the double layer may be neglected, or extremely low, in which case the potential distribution in the diffuse part can be described by the linearized Poisson—Boltzmann equation. Since in practice intermediate concentrations are most often encountered (of the order of $0.01 \div 1$ mole/liter), a quantitative treatment of the diffuse part of the double layer, taking into account electrostatic correlations and short-range effects between ions at bulk concentrations several orders of magnitude higher than those for which the Gouy—Stern theory is applicable, is of considerable interest. In the present work an attempt at such a treatment is made on the basis of the statistical theory of correlation functions, developed earlier in a series of papers ($^{4-8}$). Kirkwood et al. (^{5,6}) proposed a method for finding correlation functions for the distribution of ions in the bulk of a solution and in the diffuse region of the double layer, based on expansion of these functions in power series, with the charge of an arbitrary ion chosen as the expansion parameter; this cast doubt on the correctness of the method and did not make it possible to estimate its range of applicability.

In the present work it is shown that if the diffuse part of the double layer is a medium with a comparatively high value of the dielectric permittivity, while the compact part contains a discrete layer of adsorbed ions of one sign, then Kirkwood' s method makes it possible to obtain results valid in the zeroth approximation with respect to the parameter $\varepsilon_1 = cr_0^3$ (c is the mean electrolyte concentration, r_0 is the mean effective radius of short-range interaction between electrolyte ions) and in the first approximation with respect to the parameters $\varepsilon_2 = e^2c^{1/3}/D_3kT$ and $\varepsilon_3 = |e|\psi_3(\gamma)/kT$ (D_3 is the dielectric constant of the diffuse region, $\psi_3(\gamma)$ is the mean potential of the plane of closest approach of the ions of the diffuse region to the phase boundary). If the degree of filling of the surface adsorbed layer is denoted by θ, then for aqueous solutions of 1—1-valent electrolytes at an uncharged interphase boundary the above approximation is valid for $c \lesssim 0.5$ mole/liter, $\theta \lesssim 0.1$. If the interphase boundary is charged with density q, and the adsorbed ions have valence z_0, then, in addition, the condition

$|q + ez_0\theta/\sqrt{3}\gamma^2| \lesssim 5$ μcoul/cm^2 must be satisfied, where γ is the half-thickness of the compact part of the double layer.

Having calculated in this approximation the bulk charge density in the diffuse region of the double layer and assuming that the adsorbed ions are located in fixed positions, we can find the potential distribution in all space.

Let the electrolyte solution occupy the region $x \geq -\beta$, let the dense part of the double layer have thickness $\delta = \beta + \gamma$ and dielectric constant D_2, and let the centers of the adsorbed ions lie in the plane $x = 0$. The potential distribution in such a system has the form

$$\psi_1(\mathbf{r}) = \begin{cases} \sum\limits_{mn} \int_0^\infty A_1(\lambda) e^{\lambda x} J_0(\lambda R_{mn})\, \lambda\, d\lambda & \text{(dielectric–solution boundary),} \\ \psi_0 = \text{const} & \text{(metal–solution boundary);} \end{cases} \qquad (x \leq -\beta)$$

$$\psi_2(\mathbf{r}) = \begin{cases} \sum\limits_{mn} \int_0^\infty \left\{ A_2^{(1)}(\lambda) e^{\lambda x} + B_2^{(1)}(\lambda) e^{-\lambda x} + \dfrac{ez_0}{D_2\lambda} e^{-\lambda|x|} \right\} J_0(\lambda R_{mn})\, \lambda d\lambda & \text{(dielectric–solu} \\ \sum\limits_{mn} \int_0^\infty \left\{ A_2^{(2)}(\lambda) e^{\lambda x} + B_2^{(2)}(\lambda) e^{-\lambda x} + \dfrac{ez_0}{D_2\lambda} e^{-\lambda|x|} \right\} J_0(\lambda R_{mn})\, \lambda d\lambda + M(x+\beta) + \psi_0 & \text{(metal–solutio} \end{cases}$$

$$\psi_3(\mathbf{r}) = \begin{cases} \sum\limits_{mn} \int_0^\infty A_3^{(1)}(\lambda) \{a(\lambda) e^{-\xi_1(\lambda)x} - b(\lambda) e^{-\xi_2(\lambda)x}\} J_0(\lambda R_{mn})\, \lambda d\lambda & \text{(dielec} \\ \sum\limits_{mn} \int_0^\infty A_3^{(2)}(\lambda) \{a(\lambda) e^{-\xi_1(\lambda)x} - b(\lambda) e^{-\xi_2(\lambda)x}\} J_0(\lambda R_{mn})\, \lambda d\lambda + C\{a(0) e^{-\xi_1(0)x} - b(0) e^{-\xi_2(0)x}\} & \text{(metal} \end{cases}$$

In these formulas $J_0(\lambda R_{mn})$ is a Bessel function of the first kind; $R_{mn}^2 = (y - y_{mn})^2 + (z - z_{mn})^2$; the indices m, n determine the positions of the centers of the adsorbed ions in the plane $x = 0$; the functions $A_1(\lambda)$, $A_2(\lambda)$, $B_2(\lambda)$, and $A_3(\lambda)$ are expressed in a fairly simple, though cumbersome, way in terms of the quantities $a(\lambda)$, $b(\lambda)$, $\xi_1(\lambda)$, and $\xi_2(\lambda)$:

$$a(\lambda) = \left(\frac{\varkappa r_0}{y_1^{(0)}} \right)^2; \qquad b(\lambda) = \left(\frac{\varkappa r_0}{y_2^{(0)}} \right)^2 \exp\left\{ (y_2 - y_1) \left(\frac{\gamma}{r_0} - 1 \right) \right\};$$

$$r_0 \xi_j(\lambda) = y_j \qquad (j = 1, 2),$$

where $\varkappa$ is the inverse Debye radius; $y_j^{(0)}$ are the complex roots of the equation $y^2 - (\varkappa r_0)^2 \operatorname{ch} y = 0$, lying in the right half-plane and having the smallest (for the given $\varkappa r_0$) real part. To each $y_j^{(0)} = \alpha_j + i\beta_j$ there must be assigned a value $y_j = p_j + iq_j$ according to the formulas

$$p_j^2 = \frac{1}{2}\left\{\sqrt{(\alpha_j^2 - \beta_j^2 + \lambda^2 r_0^2)^2 + 4\alpha_j^2\beta_j^2} + (\alpha_j^2 - \beta_j^2 + \lambda^2 r_0^2)\right\};$$

$$q_j^2 = \frac{1}{2}\left\{\sqrt{(\alpha_j^2 - \beta_j^2 + \lambda^2 r_0^2)^2 + 4\alpha_j^2\beta_j^2} - (\alpha_j^2 - \beta_j^2 + \lambda^2 r_0^2)\right\}.$$

The constants ψ_0, M, and C depend on $y_j^{(0)}$ and other characteristics of the double layer. We shall not give the corresponding formulas, owing to their cumbersomeness.

In complete agreement with the results of works $^{(1-3)}$, it has been found that, for an arbitrary character of the charge distribution in the adsorbed layer,

the average jump of potential in the dense part of the double layer is equal to:

$$\delta\psi = \begin{cases} \dfrac{4\pi\sigma\gamma}{D^2} & \text{(dielectric—solution boundary)}, \\ \dfrac{4\pi\sigma\gamma}{D_2} + \dfrac{4\pi q(\beta+\gamma)}{D_2} & \text{(metal—solution boundary)}, \end{cases}$$

where σ denotes the average density of the adsorbed charge.

In this work the behavior of the averaged potential was investigated

$$\overline{\psi}_3(x) = \lim_{S\to\infty} \frac{1}{S} \iint_{-\infty}^{\infty} \psi_3(\mathbf{r})\, dy\, dz$$

and it was shown that, at moderate volume concentrations of electrolyte (~ 0.5 mole/liter), this potential decreases with distance into the solution more sharply than according to the Gouy—Stern theory. This is clearly seen in the graphs of the dependences (see Fig. 1)

$$Z^{(0)}(x^*) = \frac{\overline{\psi}_3^{(0)}(x)}{\overline{\psi}_3^{(0)}(\gamma)}, \qquad Z(x^*) = \frac{\overline{\psi}_3(x)}{\overline{\psi}_3^{(0)}(\gamma)},$$

where

$$\overline{\psi}_3^{(0)}(x) = \overline{\psi}_3^{(0)}(\gamma)\exp\{-\varkappa(x-\gamma)\}$$

is the potential varying according to the Gouy—Stern law,

Fig. 1. Graphs of the dependences $Z^0(x^*)$ and $Z(x^*)$. 1 –Gouy–Stern law ($\varkappa r_0 = 1.03$); 2 –$\varkappa r_0 = 1.03$; 3 –$\varkappa r_0 = 1.15$.

Figure 1: Fig. 1. Graphs of the dependences $Z^0(x^*)$ and $Z(x^*)$. 1 –Gouy–Stern law ($\varkappa r_0 = 1.03$); 2 –$\varkappa r_0 = 1.03$; 3 –$\varkappa r_0 = 1.15$.

$$x^* = \frac{x - \gamma}{r_0} \geqslant 0.$$

Fig. 1. Graphs of the dependences $Z^0(x^*)$ and $Z(x^*)$. 1 –Gouy–Stern law ($\varkappa r_0 = 1.03$); 2 –$\varkappa r_0 = 1.03$; 3 –$\varkappa r_0 = 1.15$.

In the case $\varkappa r_0 = 1.03$, already at $x^* = 3$, $Z(x^*)$ amounts to 0.5% of its value at the point $x^* = 0$ and is an order of magnitude smaller than the corresponding value of the function $Z^{(0)}(x^*)$. In the case $\varkappa r_0 = 1.15$, the function $Z(x^*)$ oscillates weakly, first becoming zero at $x^* \sim 2$. At $x^* \sim 5$ the function $Z(x^*)$ becomes zero a second time; however, the maximum deviation from zero in the interval $2 < x^* < 5$, where $Z(x^*) < 0$, amounts to 0.7% of the value at the point $x^* = 0$, so that it may be assumed that, in this case, the potential drop in the diffuse region of the double layer occurs over a distance of the order of two ionic diameters.

In the case of infinitely large and infinitely small volume concentrations, all the results of the present work reduce to already known results ($^{1-3}$).

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

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