# EFFECT OF INTERION INTERACTIONS ON ELECTROLYTE PROPERTIES NEAR A PHASE SEPARATION BOUNDARY

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The interaction of ions in solution and in the adsorbed state with themselves and with charges induced in the solid phase varies the isotherms of ion adsorption and the structure of the diffusion part of a double electric layer. This effect is treated within the Debye–Huckel approximation for a dilute solution of a strong electrolyte under conditions of local thermodynamic equilibrium.

The functioning of numerous electrochemical systems [1], the diversified electrokinetic effects and the processes based on them of electrofiltration, electrodialysis, direct and reverse electro-osmosis, electro-osmotic desalinification, the disintegration or consolidation of soils [2-4], widely used in contemporary technology – are ultimately determined by propulsive forces, depending on the equilibrium thermodynamic functions of components of electroactive fluid media in the presence of an evolving surface of contact with the solid phase. These functions in finely porous and colloid systems depend, in turn, substantially on the character of electrosurface effects, and primarily on the structure of Double Electric Layers (DEL) formed at phase boundaries. In that case the specific and nonspecific adsorption parts of solution ions lead not only to modification of this structure and to corresponding variations of the electrostatic interaction between pore walls or suspended particles, but also assist in depleting the solution of ions by shifting the equilibrium dissociation–recombination reactions in the solution and sorption–desorption of ions in adsorption layers [5]. Surface effects of nonelectric nature, considered in [6], can also have a similar effect on the thermodynamic properties of nondissociating solutions.

The Coulomb interaction of ions, both in an electrolyte solution and in adsorption layers, causes substantial variation in the thermodynamic functions of the solution components, and must therefore also affect the DEL properties and the rate of all electrokinetic processes depending on these properties. The difference in dielectric permittivity between the solution and the phase boundary with it also leads to appearance of an electrostatic interaction of ions with this phase (generating image forces), playing an important role in numerous electrochemical systems [1]. The mechanism of dielectric inclusion of ions caused by this interaction is also quite important for a number of electrokinetic effects, including reverse osmosis [3].

Taking into account interactions of ions with themselves and with induced charges in constructing models of dense and diffuse DEL parts requires generalization of the Guy–Chapman–Stern theory (see reviews in [7-9], as well as the discussion of the state of art of contemporary theory of ionic adsorption in [10]). Attempts of such generalization are usually based on numerical modeling or on the use of quite complicated methods of statistical physics, using, in particular, the Ornstein–Zernike equations along with the mean-spherical and hyperchain approximations (characteristic examples can be found in [7], as well as in [11-14]). Though these attempts have led to substantial improvement in the understanding of electric effects at interphase separation boundaries, the results are often difficult to review, and it is difficult to draw conclusions from them, except for most general ones. Therefore, in the present paper the problem is treated on the basis of consequences of the hypothesis of local thermodynamic equilibrium in the system, invoking a number of phenomenological considerations.

Consider below a completely dissociated electrolyte solution, containing J types of ions with valences $z_j$ in concentrations $n_j$ $(j = 1,\ldots,n)$, near a planar smooth molecular

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surface of the solid or fluid phase, or a boundary separating the solution from the gas phase. The quantities $n_j$ depend on the normal coordinate, whose origin of reference is selected on this surface. The deviations of $n_j$ from the corresponding $n_{j0}$ values, reached upon removal far from the surface, are assumed small, i.e., one puts $|n_j - n_{j0}|n_{j0}^{-1} \ll 1$, making it possible to linearize the Poisson–Boltzmann equation by means of the Debye–Huckel approximation, and at the same time simplify the calculations substantially. The number concentration $n_0$ of solvent molecules is assumed to be homogeneous. The electric neutrality condition leads to the requirement of vanishing density of the bulk electric charge upon removal from the surface of separation:

$$q = e\sum_{j=1}^{J} z_j n_j \xrightarrow[x\to\infty]{} q_0 = e\sum_{j=1}^{J} z_j n_{j0} = 0. \tag{1}$$

Ions of all kinds are capable of being adsorbed on the surface, so that the charged ionic centers of j-th type are located in the corresponding Helmholtz plane, found at a distance $x = \delta_j = d_j/2$ from the surface. For simplicity it is assumed that the characteristic sizes $d_j$ are identical for ions of all types, i.e., the corresponding Helmholtz planes coincide. (Situations are common in which only ions of one type practically posses the capability of specific adsorption. These ions are easily obtained if the corresponding energy of specific adsorption is much lower than the similar quantities for ions of all other types.) The surface density of the electric charge in the Helmholtz plane, caused by adsorption of ions, is expressed in the form

$$\sigma_a = e\sum_{j=1}^{J} z_j\Gamma_j = e\sum_{j=1}^{J} z_j\tau_j\Gamma,\quad \tau_j = \Gamma_j/\Gamma. \tag{2}$$

Besides, in the same plane with density $\sigma_e$ charges can be distributed, whose occurrence is related to dissociation of ionogenic groups, surface complex formation, etc. At the surface of separation x = 0 one also admits the presence of a charge distributed with density $\sigma_*$. The quantities $\sigma_e$ and $\sigma_*$ are further considered to be known. The elementary electric surface charges are, in principle, capable of being displaced and forming, as a result, short-range order. The problem of distribution and effective interaction of ions is quite complicated, and is discussed in detail in [10]. For simplicity it is phenomenologically assumed here that part of the ions is rigidly and randomly localized at certain fixed positions (i.e., without formation of short-range order), while the remaining part can be displaced completely freely, similarly to ions in the bulk of the solution. The fraction of ions of j-th type in the adsorption layer, capable of being displaced, is denoted below by $m_j$, while the fractions of free charges, forming densities $\sigma_e$ and $\sigma_*$, are denoted by $m_e$ and $m_*$, respectively. We note that the generalization to situations when the planes of adsorbed ions of different types and of charge of density $\sigma_e$ do not coincide – does not present any major difficulties, but it does complicate the calculations substantially.

The dielectric constant $\varepsilon_*$ of the boundary phase is assumed homogeneous (for conductors $\varepsilon_* \to \infty$, and for a gas $\varepsilon_* \approx 1$). The dielectric constant of the solution, depending strongly on the distance from the surface, is described phenomenologically, assuming that it acquires the values $\varepsilon$ and $\varepsilon_1$ in the regions $x > \delta$ and $0 < x < \delta$, respectively (usually $\varepsilon_1$ is much smaller than $\varepsilon$).

The mean electric potential is determined within the approximations adopted by solving the equations:

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi e}{\varepsilon}\sum_{j=1}^{J} z_j n_j(x),\quad \delta < x < \infty; \tag{3}$$
$$d^2\varphi_1/dx^2 = 0,\quad 0 < x < \delta;\quad \varphi_* = \text{const},\quad -\infty < x < 0$$

with boundary conditions:

$$\varphi \to 0,\ x \to \infty;\quad \varphi = \varphi_1,\ \varepsilon\frac{d\varphi}{dx} - \varepsilon_1\frac{d\varphi_1}{dx} = -4\pi(\sigma_a + \sigma_e),\ x = \delta; \tag{4}$$
$$\varphi_1 = \varphi_*,\ \frac{d\varphi_1}{dx} = -\frac{4\pi}{\varepsilon_1}\sigma_*,\ x = 0.$$

For closure of this boundary value problem it is necessary to determine the adsorbed charge density according to (2) and the distributions $n_j(x)$, tending to $n_{j0}$ for $x \to \infty$ and satisfying condition (1).

In principle, the quantities indicated above can be found on the basis of the concept of local thermodynamic equilibrium of ions of all types from the homogeneity requirement of the corresponding total chemical (electrochemical) potentials. The basic difficulty of calculating the latter is related to estimating the contributions due to ion interactions with themselves and with charges induced in the phase boundary. It is first necessary to determine the effective electric potential created by all ions and charges except one, at the location of whose center an ion is isolated. This can be done by means of the classical Debye procedure by using the mean field approximation.

Consider the electrostatic field around an ion with charge $ez_j$ and centered at a point at distance h from the interphase surface. This ion forms an ionic cluster consisting of other ions in the solution, generates a polarization of the mobile parts of the surface charges, and induces charges at the phase boundary. This leads, in particular, to the appearance of perturbed surface charge densities and electric potential in different regions. Using the definitions of the coefficients $m_j$, $m_e$, and $m_*$, the Boltzmann distribution for ions, and the Debye-Huckel approximation, we have:

$$q' \approx -\frac{e^2}{kT}\left(\sum_{j=1}^{J} z_j^2 n_j\right)\varphi'(x),$$

$$\sigma_a' \approx -\frac{e^2}{kT}\left(\sum_{j=1}^{J} m_j z_j^2 \Gamma_j\right)\varphi'\Big|_{x=\delta},$$

$$\sigma_e' \approx -\frac{ez_j}{kt} m_e \sigma_e \varphi'\Big|_{x=\delta}, \quad \sigma_*' \approx -\frac{ez_j}{kT} m_* \sigma_* \varphi_1'\Big|_{x=0}.$$

Taking into account these expressions in equations of type (3) for the total potentials $\phi + \phi'$, $\phi_1 + \phi_1'$ and $\phi_* + \phi_*'$, and evaluating (3) from them, we obtain:

$$\Delta\varphi' - \varkappa^2\varphi' = 0, \quad \varkappa^2 = \frac{4\pi e^2}{\varepsilon kT}\sum_{j=1}^{J} z_j^2 n_j, \quad \delta < x < \infty;$$
$$\Delta\varphi_1' = 0, \quad 0 < x < \delta; \quad \Delta\varphi_*' = 0, \quad -\infty < x < 0. \tag{5}$$

Proceeding similarly with the boundary conditions (4), we have:

$$\varphi' \to 0, \quad x \to \infty; \quad \varphi' \to \frac{ez_j}{\sqrt{\varepsilon}\,(x-h)^2 + r^2}, \quad x \to h, \quad r \to 0;$$
$$\varphi' = \varphi_1', \quad \partial\varphi'/\partial x - (\varepsilon_1/\varepsilon)\,\partial\varphi_1'/\partial x = \gamma\varphi', \quad x = \delta;$$
$$\varphi_1' = \varphi_*', \quad (\varepsilon_1/\varepsilon)\,\partial\varphi_1'/\partial x - (\varepsilon_*/\varepsilon)\,\partial\varphi_*'/\partial x = \gamma_*\varphi_1', \quad x = 0; \tag{6}$$
$$\varphi_*' \to 0, \quad x \to -\infty;$$
$$\gamma = \frac{4\pi e^2}{\varepsilon kT}\left(\sum_{j=1}^{J} m_j z_j^2 \Gamma_j + \frac{m_e \sigma_e}{e}\right), \quad \gamma_* = \frac{4\pi e}{\varepsilon kT} m_* \sigma_*.$$

Using the Hankel transform, the solution of boundary value problem (5), (6) can be represented in integral form:

$$\varphi' = \int_0^\infty \left\{\frac{ez_j}{\varepsilon}\,\frac{\exp[-|h-x|\sqrt{\omega^2+\varkappa^2}]}{\sqrt{\omega^2+\varkappa^2}} + C(\omega)\exp\left(-x\sqrt{\omega^2+\varkappa^2}\right)\right\} \times$$
$$\times J_0(\omega r)\,\omega d\omega, \quad \varphi_1' = \int_0^\infty \left\{C_1^+(\omega)\,e^{x\omega} + C_1^-(\omega)\,e^{-x\omega}\right\} J_0(\omega r)\,\omega d\omega, \tag{7}$$
$$\varphi_*' = \int_0^\infty C_*(\omega)\,e^{x\omega} J_0(\omega r)\,\omega d\omega,$$

where the following algebraic equations follow for the unknown coefficients in the integrand functions of (6) and (7):

$$\frac{ez_j}{\varepsilon}\frac{\exp[-(h-\delta)\sqrt{\omega^2+\varkappa^2}]}{\sqrt{\omega^2+\varkappa^2}}+C\exp(-\delta\sqrt{\omega^2+\varkappa^2})=$$
$$=C_1^+e^{\delta\omega}+C_1^-e^{-\delta\omega},\quad (ez_j/\varepsilon)\exp[-(h-\delta)\sqrt{\omega^2+\varkappa^2}]-$$
$$-\sqrt{\omega^2+\varkappa^2}\,C\exp(-\delta\sqrt{\omega^2+\varkappa^2})-$$
$$-\frac{\varepsilon_1}{\varepsilon}\omega(C_1^+e^{\delta\omega}-C_1^-e^{-\delta\omega})=\gamma\frac{ez_j}{\varepsilon}\frac{\exp[-(h-\delta)\sqrt{\omega^2+\varkappa^2}]}{\sqrt{\omega^2+\varkappa^2}}+$$
$$+\gamma C\exp(-\delta\sqrt{\omega^2+\varkappa^2}),\quad C_1^++C_1^-=C_*,$$
$$(\varepsilon_1/\varepsilon)(C_1^+-C_1^-)=(\varepsilon_*/\varepsilon+\gamma_*/\omega)C_*.$$

It hence follows, in particular, that

$$C(\omega)=\frac{ez_j}{\varepsilon}\frac{\exp[-(h-2\delta)\sqrt{\omega^2+\varkappa^2}]}{\sqrt{\omega^2+\varkappa^2}}\times$$
$$\times\frac{(1-B)(\sqrt{\omega^2+\varkappa^2}-\gamma)-\alpha(1+B)\omega}{(1-B)(\sqrt{\omega^2+\varkappa^2}+\gamma)+\alpha(1+B)\omega},\tag{8}$$
$$B(\omega)=\frac{\varepsilon_*-\varepsilon_1+\varepsilon\gamma_*/\omega}{\varepsilon_*+\varepsilon_1+\varepsilon\gamma_*/\omega}e^{-2\omega\delta},\quad \alpha=\frac{\varepsilon_1}{\varepsilon}.$$

It must be noted that in integrating the first of Eqs. (5) the reciprocal Debye length x was considered to be a constant, in determining which $n_j$ were replaced by $n_{j0}$. This can be done within the assumption of small deviations of $j_j(x)$ from their asymptotic values far from the surface of interphase separation.

The effective potential of the mean field, created at the center position of the isolated ion by all other charges, is determined as follows:

$$\varphi_j(h)=\lim_{x\to h,\ r\to 0}[\varphi'(x,r)-\lim_{\varkappa\to 0}\varphi'(x,r)],\tag{9}$$

where the second term describes the mean field of the isolated ion in the absence of all others. According to (7) and (8) the potential (9) can be expressed in the form of a quite complicated integral, considered in the Appendix. Below we study for simplicity the special case, when there exists no polarization of all surface charges ($\gamma = \gamma_* = 0$), corresponding to the concept of localized adsorption. If the electrolyte solution is adjacent to the dielectric material ($\varepsilon_* < \infty$), then for $\alpha \ll 1$ we obtain the following asymptotic equations:

$$\varphi_j(h)\approx-\frac{ez_j}{\varepsilon}\left[1-\frac{\beta}{2\varkappa h}(1-e^{-2\varkappa h})-\frac{\alpha N}{\varkappa h}\left(1-\frac{\sqrt{\pi}}{2\varkappa h}\right)e^{-2\varkappa h}\right]\varkappa,\quad \varkappa h>1,\tag{10}$$

$$\varphi_j(h)\approx-(ez_j/\varepsilon)[1-\beta-(\pi-2)\alpha N]\varkappa,\quad h=\delta,\tag{11}$$

where the following notations have been introduced:

$$N=\frac{1+\beta_1}{1-\beta_1},\quad \beta=\frac{\varepsilon_*-\varepsilon}{\varepsilon_*+\varepsilon},\ \beta_1=\frac{\varepsilon_*-\varepsilon_1}{\varepsilon_*+\varepsilon_1}.\tag{12}$$

If the adjacent phase is a conductor, the corresponding expressions are formally obtained from (10) and (11) for $\alpha = 0$ and $\beta = 1$; in this case the requirement $\alpha \ll 1$ is not needed in deriving the equations (see Appendix). We stress that the potential $\phi_j(\delta)$ for ions adsorbed at the surface of the conductor vanishes within the approximation considered. The first term in the square brackets in (10) corresponds to the ionic field in an unbounded solution, the second term describes the interaction with the dielectric material in the region $x < 0$, and the third describes the effect of a thin layer with a reduced dielectric constant. The terms in (11) have a similar meaning.

We calculate the electrochemical potential of ions in the solution by means of a standard procedure [15]. For ions of the j-th type we have

$$\mu_j=\psi_j(T)+kT\ln(v_0n_j)+ez_j\varphi+\mu_j^{(e)},\quad v_0=n_0^{-1},\tag{13}$$

where $\psi_j(T)$ is the standard chemical potential, and the last term describes the contribution due to Coulomb interion interactions. According to (10), we write down the energy of these interactions in a calculation per unit volume in the form

$$E(x) = \frac{1}{2}\sum_{j=1}^{J} ez_j n_j(x)\,\varphi_j(x) \approx -\frac{e^2\varkappa}{2\varepsilon}\left(\sum_{j=1}^{J} z_j^2 n_{j0}\right) \times$$
$$\times\left[1-\frac{\beta}{2\varkappa x}\left(1-\mathrm{e}^{-2\varkappa x}\right)-\frac{\alpha N}{\varkappa x}\left(1-\frac{\sqrt{\pi}}{2\varkappa x}\right)\mathrm{e}^{-2\varkappa x}\right],$$

where $n_j$ is replaced by $n_{j0}$ according to the assumptions made above (the quantity $\kappa$ introduced in (5) is also considered as a function of $n_{j0}$). Assuming for simplicity that $\kappa x \gg 1$ and neglecting the last term in this equation, we calculate the corresponding contribution to the free energy by means of the Gibbs–Helmholtz relation, i.e.,

$$F(x) = T\int_T^{\infty}\frac{E(x)}{T^2}\mathrm{d}T \approx -\frac{e^2\varkappa}{2\varepsilon}\left(\sum_{j=1}^{J} z_j^2 n_{j0}\right)\times$$
$$\times\left\{\frac{2}{3}-\frac{2(\beta+2\alpha N)}{(2\varkappa x)^3}\left[1-(1+2\varkappa x)\,\mathrm{e}^{-2\varkappa x}\right]-\frac{\beta}{2\varkappa x}\right\}$$

(it is assumed that the contribution mentioned vanishes for $T \to \infty$). Hence one obtains

$$\mu_j^{(e)}(x) = \frac{\partial F(x)}{\partial n_{j0}} + \frac{\partial F(x)}{\partial \varkappa}\,\frac{\partial \varkappa}{\partial n_{j0}} =$$
$$= -\frac{e^2 z_j^2 \varkappa}{2\varepsilon}\left[1-(\beta+2\alpha N)\frac{\mathrm{e}^{-2\varkappa x}}{2\varkappa x}-\frac{\beta}{2\varkappa x}\right], \qquad (14)$$

which reduces to the classical result for $x \to \infty$ and finally determines the potential (13).

The electrochemical potential of ions in the adsorbed layer can be calculated quite similarly. Introducing the electric potential value $\phi_\delta$ in the Helmholtz plane, we write down

$$\mu_{a,j} = \chi_j(T) + kT\ln\left[\tau_j\left(1-\sum_{j=1}^{J}\tau_j\right)^{-1}\right] + ez_j\varphi_\delta + \mu_{a,j}^{(e)}, \qquad (15)$$

while the second term describes entropy effects, related to the multiplicity of methods of arranging $\Gamma_j$ ions in a lattice consisting of $\Gamma$ allowed adsorption positions. Using (11) and the previously defined electrostatic contributions due to interion interactions, we subsequently obtain for the energy and the free energy

$$E_a = \frac{1}{2}\sum_{j=1}^{J} ez_j\Gamma_j\varphi_j(\delta) = -\frac{e^2\varkappa}{2\varepsilon}\left[1-\beta-(\pi-2)\,\alpha N\right]\sum_{j=1}^{J} z_j^2\Gamma_j,$$
$$F_a = -\frac{e^2\varkappa}{3\varepsilon}\left[1-\beta-(\pi-2)\,\alpha N\right]\sum_{j=1}^{J} z_j^2\Gamma_j$$

and, finally,

$$\mu_{a,j}^{(e)} = \frac{\partial F_a}{\partial \Gamma_j} = -\left[1-\beta-(\pi-2)\,\alpha N\right]\frac{e^2 z_j^2\varkappa}{3\varepsilon}, \qquad (16)$$

which finally determines the potential of ions appearing in the compound of adsorption layers. We note that Eqs. (13)-(16) make it possible to also obtain expressions for all other thermodynamic functions of ions.

Under conditions of local thermodynamic equilibrium the electrochemical potential of ions of any kind in the diffusion parts of DEL must be homogeneous and must coincide with the potential of the same ions in the adsorbed state. Requiring that the quantity (13) be independent of x, with account of (14) we obtain the distribution of ions of the j-th type in the form

$$n_j(x) = n_{j0} \exp\left(-\frac{ez_j\varphi}{kT}\right) g_j(x),$$

$$g_j(x) \approx \exp\left\{-\frac{e^2 z_j^2 \varkappa}{2\varepsilon kT}\left[(\beta + 2\alpha N)\frac{e^{-2\varkappa x}}{2\varkappa x} + \frac{\beta}{2\varkappa x}\right]\right\}, \quad \varkappa x \gg 1, \tag{17}$$

where the function $g_j(x)$ describes the deviation of the real distribution from that ordinarily used in the theory following from Boltzmann's law without including interion interactions. The presence of phase boundaries distorts the interactions mentioned in comparison with situations in the bulk of the solution far from the surface of interphase separation, and it is precisely this distortion which affects the field of ion concentration in the DEL diffuse part. In that case the effect mentioned can be interpreted as an additional repulsion from the surface of separation (which is characteristic of boundaries with conductors) or as an effective attraction of ions to it (characteristic of boundaries with the gas phase).

The adsorption isotherm of ions of the j-th type is found by equating the electrochemical potential (15) of adsorbed ions to the potential (13) for ions in the solution:

$$\tau_j\left(1 - \sum_{j=1}^{J}\tau_j\right)^{-1} = v_0 n_{j0} \exp\left(-\frac{u_j + ez_j\varphi_\delta}{kT}\right) f_j,$$

$$f_j = \exp\left(-\frac{e^2 z_j^2 \varkappa}{2\varepsilon kT}\left\{1 - \frac{2}{3}\left[1 - \beta - (\pi - 2)\alpha N\right]\right\}\right), \quad u_j = \chi_j - \psi_j, \tag{18}$$

where the factor $f_j$ describes the deviation form the classical isotherm obtained by Stern. The two terms in the curly brackets in the exponent in the definition of $f_j$ correspond, respectively, to the effect of interion interactions in the solution far from the surface of separation and in the adsorption layer. If the adjacent phase is a conductor, then only the first of the interactions mentioned play a role, while the second ones do not contribute in this case to the electrochemical potential (15) of adsorbed ions (the quantity (16) vanishes), which was already noted in connection with the discussion of Eq. (11) for the electric potential. The interion interactions in the solution undergo filling of the adsorption layer, at the same time that the effect of these interactions for adsorbed ions can have an arbitrary sign, depending on the dielectric properties of the solution itself, the adjacent phase, and the thin layer near its surface. The difference $u_j$ of standard chemical potentials in the adsorbed and free ion states is usually derived from the specific adsorption energy.

We determine now the electric potential in the Helmholtz planes appearing in (18), as well as (15). For this it is necessary to solve the problem (3), (4) for the Poisson–Boltzmann equation, using for its closure the distribution (17) for ions in the diffuse DEL part, as well as Eq. (2) for the surface adsorbed charge density with account of (18). As a result, in using the Debye–Huckel approximation the first equation in (3) reduces in the region $\kappa x \gg 1$ to the form

$$\frac{d^2\varphi}{dx^2} - \varkappa^2\varphi = R_1\frac{e^{-2\varkappa x}}{2\varkappa x} + \frac{R_2}{2\varkappa x},$$

$$R_1 = \frac{2\pi e^3}{\varepsilon^2 kT}\varkappa(\beta + 2\alpha N)\sum_{j=1}^{J} z_j^3 n_{j0}, \quad R_2 = \frac{2\pi e^3}{\varepsilon^2 kT}\varkappa\beta\sum_{j=1}^{J} z_j^3 n_{j0},$$

where $\kappa$ has been determined by Eq. (5) with $n_j$ replaced by $n_{j0}$. The solution of this boundary value problem is

$$\varphi \approx \left\{\varphi_\delta e^{\varkappa\delta} + \frac{R_1}{2\varkappa^2}\int_{\varkappa\delta}^{\varkappa x}\left[\mathrm{Ei}(-3y) - \mathrm{Ei}(-3\varkappa\delta)\right]e^{2y}dy + \frac{R_2}{2\varkappa^2}\int_{\varkappa\delta}^{\varkappa x}\left[\mathrm{Ei}(-y) - \mathrm{Ei}(-\varkappa\delta)\right]e^{2y}dy\right\}e^{-\varkappa x}, \tag{19}$$

$$\varphi_1 = \varphi_* - (\varphi_* - \varphi_\delta)(x/\delta), \quad \varphi_* = \varphi_\delta + (4\pi/\varepsilon_1)\sigma_*\delta,$$

where $\mathrm{Ei}(x)$ is the exponential integral function, and the connection between $\phi_\delta$ and the extent of filling of the adsorption layer $\tau_j$ is given by the relation

$$\varphi_\delta = \frac{4\pi}{\varepsilon\varkappa}\left(\sigma_* + \sigma_e + e\Gamma\sum_{j=1}^{J} z_j\tau_j\right). \tag{20}$$

Substituting the expression for $\tau_j$ following from (18), we obtain a transcendental algebraic equation for the potential $\phi_\delta$. Restricting ourselves to situations with low extents of filling, corresponding to replacement of Stern isotherms by Henry isotherms, from (18) and (20) we have the equation

$$\varphi_\delta \approx \frac{4\pi}{\varepsilon\varkappa}\left\{\sigma_* + \sigma_e + v_0 e\Gamma\sum_{j=1}^{J} f_j z_j n_{j0}\exp\left(-\frac{u_j + e z_j\varphi_\delta}{kT}\right)\right\}, \tag{21}$$

whose solution, with the use of the Debye—Huckel approximation, is:

$$\begin{aligned}\varphi_\delta \approx \frac{4\pi}{\varepsilon\varkappa}\left\{\sigma_* + \sigma_e + v_0 e\Gamma\sum_{j=1}^{J} f_j z_j n_{j0}\exp\left(-\frac{u_j}{kT}\right)\right\} \times \\ \times\left\{1 + \frac{4\pi v_0 e^2}{\varepsilon\varkappa kT}\Gamma\sum_{j=1}^{J} f_j z_j^2 n_{j0}\exp\left(-\frac{u_j}{kT}\right)\right\}^{-1}\end{aligned} \tag{22}$$

If ions of one type only are capable of specific absorption, the corresponding equations for $\phi_\delta$, as well as for the corresponding extent of filling, can be obtained from (21) or (22) and from (18), formally assuming that for all other ions $u_j$ tend to infinity. Thus, if a 1—1-valence electrolyte is adjacent to the surface of a conductor and only anions are adsorbed, we have

$$\frac{\tau}{1-\tau} = v_0 n_{20}\exp\left(-\frac{u_2 - e\varphi_s}{kT}\right) f,\ f = \exp\left(-\frac{e^2\varkappa}{2\varepsilon kT}\right). \tag{23}$$

Exactly the same is obtained by changing the sign of $e\phi_\delta$ and replacing $u_2$, $n_{20}$ by $u_1$, $n_{10} = n_{20}$, and for adsorption of cations only. In either case the interion interactions, characteristic of an unbounded electrolyte solution, leads to reduced adsorption in comparison with the requirements of Stern's theory. Image forces due to absorption are generally not inferred in the given case. Usually the interaction between ions is not included in a theory based on the Poisson—Boltzmann equation and on Langmuir's adsorption theory. However, inclusion of ion—ion electrostatic correlations in the analysis is unavoidable in contemporary statistical theories. For example, in the theory of [12], based on using the hyperchain approximation, the conclusion has also been drawn of reduction of the effective surface charge due to adsorption, though no simple equation has been obtained for describing this effect.

To estimate the effect discussed from a quantitative point of view, consider Grahame's clasical experiments [16] of measuring the capacity of a DEL, formed on the surface of a mercury electrode in a solution of sodium fluoride, as well as their interpretation in [17]. The device measured the total capacity C of the whole DEL, including the dense and diffuse parts, for various solution concentrations $c_0$. The capacity $C_1$ of the molecular condenser, forming the electrode surface and parallel to its Helmholtz plane, was estimated from these data and from the capacity value of the diffuse DEL part $C_2$, calculated from the Guy—Chapman—Stern theory for minimum concentration $c_0 = 0.001$ mol/liter. Proceeding by the equation $C_2 = CC_1(C_1 - C)^{-1}$ for serial combination of both capacities under the assumption of independence of $C_1$ of the solution concentration and with using the experimental C values, the capacity $C_2$ was found for varying concentrations; these values can be referred to conditionaly as "experimental". On the other hand, the $C_2$ value was calculated from the Guy—Chapman—Stern theory. The deviation between these values was estimated by means of the ratio K of the first term to the second for each concentration $c_0$. In that case the functional dependence $(c_0)$ of [18] was used in the calculations. For $c_0 = 0.01$ and 0.1 mol/liter K = 0.906 and 0.689, respectively, were obtained, i.e., the theory gives for $C_2$ an estimate which is too high, getting worse with increasing concentration. However, the variable $C_2$ must be approximately linear in the adsorbed charge. Using Eq. (23) to estimate this quantity, and not the Stern isotherm, we obtain that the effect of interion interactions is reduced to the necessity of dividing the K values obtained by the coefficient f of (23). The corresponding calculation gives for K at these concentrations the 1.018 and 1.002 values, respectively (it is assumed that T = 300 K). Thus, there is very good agreement between the theoretical values of the capacity of the diffuse DEL part, obtained by the ordinarily used theory, but by using the modified isotherm (23), and the values found by the method described of recalculating the experimental values. Though the results of Grahame's experiments with account of their errors can be explained on the basis of the standard DEL theory (see the detailed discussion in [8]) and by other methods [19], the agreement obtained can be considered a sound basis of claiming adequacy of the arguments suggested in the present study.

Quantitatively the effect of interion interactions on the electric potential of the Helmholtz plane is approximately the same as on the adsorbed charge; in the case of contact with a conductor it leads to a decrease in the potential. However, the shape of the potential distribution for given $\phi_\delta$ in the diffuse DEL part depends on these interactions and on the image forces, vanishing weakly everywhere, except for a region directly adjacent to the Helmholtz planes.

We stress that the calculations performed refer only to describing the effect of ion–ion interactions and, naturally, do not exhaust the complex problems of DEL structure and the shapes of ionic thermodynamic functions. Dwelling on the aspect of obvious possible generalizations, related with accounting for charge polarization, the disagreement of planar locations of charges of different occurrence, and the nonlinear response of the diffuse DEL part, we mention the necessity of analyzing the polarization of dipolar solvent molecules and accounting for charge discreteness, making it possible to explain the well-known Esin–Markov effect (see the detailed discussion in [10]).

Finally, one must recall the most important problem of finding the parameters of thermodynamic equilibrium of components of electrolyte solutions in finely porous membranes of different structure and in concentrated colloidal systems, required to calculate many electrochemical processes. In this context account of interion interactions is very important. Indeed, even in bodies with wide pores and in colloids in which one can neglect DEL overlap on separate particles, the adsorbed ions parts and the localization parts of counter ions can lead to substantial ion combination of the main mass of the solution, unavoidably related to driving forces of diverse technological processes.

## APPENDIX

Equation (9) is written in expanded form as:

$$\varphi_j(h) = (ez_j/\varepsilon)(P_1 - P_2),$$

$$P_1 = \lim_{r\to 0}\int_0^\infty \left\{ 1 + \frac{(1-B)\sqrt{\omega^2+\varkappa^2} - \alpha(1+B)\omega}{(1-B)\sqrt{\omega^2+\varkappa^2} + \alpha(1+B)\omega}\, e^{-2(h-\delta)\sqrt{\omega^2+\varkappa^2}} \right\} \frac{\omega J_0(\omega r)\, d\omega}{\sqrt{\omega^2+\varkappa^2}},$$

$$P_2 = \lim_{r\to 0}\int_0^\infty \left\{ 1 + \frac{1-\beta_1-\alpha(1+\beta_1)}{1-\beta_1+\alpha(1+\beta_1)}\, e^{-2(h-\delta)\omega} \right\} J_0(\omega r)\, d\omega,$$

where in deriving these relations we have taken $\gamma = \gamma_* = 0$, have used Eqs. (7) and (8), and have introduced $B = \beta_1 e^{-2\omega\delta}$, where $\beta_1$ is defined in (12). This expression can also be represented in the form (we take into account here that the quantity dependent on $\beta_1$ in the representation for $P_2$ is identically equal to $-\beta$, where $\beta$ is also defined in (12))

$$P_1 - P_2 = G_1 + G_2 + G_3,$$

$$G_1 = -\int_0^\infty \left( 1 - \frac{\omega}{\sqrt{\omega^2+\varkappa^2}} \right) d\omega = \lim_{\Omega\to\infty}\left(-\Omega + \sqrt{\Omega^2+\varkappa^2} - \varkappa\right) = -\varkappa,$$

$$G_2 = \beta\int_0^\infty \left[ e^{-2(h-\delta)\omega} - \frac{\omega}{\sqrt{\omega^2+\varkappa^2}}\, e^{-2(h-\delta)\sqrt{\omega^2+\varkappa^2}} \right] d\omega =$$

$$= \frac{\beta}{2(h-\delta)}\left(1 - \exp[-2\varkappa(h-\delta)]\right)$$

and, finally,

$$G_3 = \int_0^\infty \left[ \frac{(1-\beta_1)\sqrt{\omega^2+\varkappa^2} - \alpha(1+\beta_1)\omega}{(1-\beta_1)\sqrt{\omega^2+\varkappa^2} + \alpha(1+\beta_1)\omega} + \beta \right] e^{-2(h-\delta)\sqrt{\omega^2+\varkappa^2}}\ \frac{\omega d\omega}{\sqrt{\omega^2+\varkappa^2}}$$

(due to the smallness of $\omega\delta$ we have taken $B \approx \beta_1$). The integral $G_3$ is calculated for small $\alpha = \varepsilon_1/\varepsilon$, using the expansion

$$\frac{(1-\beta_1)\sqrt{\omega^2+\varkappa^2}-\alpha(1+\beta_1)\omega}{(1-\beta_1)\sqrt{\omega^2+\varkappa^2}+\alpha(1+\beta_1)\omega}=\frac{\sqrt{\omega^2+\varkappa^2}-\alpha\omega}{\sqrt{\omega^2+\varkappa^2}+\alpha\omega}\times$$

$$\times\left(1-\beta_1\frac{\sqrt{\omega^2+\varkappa^2}+\alpha\omega}{\sqrt{\omega^2+\varkappa^2}-\alpha\omega}\right)\sum_{k=0}^{\infty}\beta_1^k\left(\frac{\sqrt{\omega^2+\varkappa^2}-\alpha\omega}{\sqrt{\omega^2+\varkappa^2}+\alpha\omega}\right)^k\approx$$

$$\approx(1-\beta_1)\sum_{k=0}^{\infty}\beta_1^k-2\alpha\left[(1-\beta_1)\sum_{k=0}^{\infty}k\beta_1^k+\sum_{k=0}^{\infty}\beta_1^k\right]\frac{\omega}{\sqrt{\omega^2+\varkappa^2}}.$$

The quantity $\beta$ can be represented in the form of the same expansion with a negative sign at $\kappa = 0$. If $\kappa h > 1$ we have, using the Laplace method and summing the series:

$$G_3\approx 2\alpha\int_0^{\infty}\left[\frac{1+\beta_1}{1-\beta_1}\right]\frac{\omega}{\varkappa}\left(1-\frac{\omega}{\varkappa}\right)\exp\left(-2\varkappa h-\frac{h}{\varkappa}\omega^2\right)d\omega=$$

$$=\alpha N\left(1-\frac{\sqrt{\pi}}{2\varkappa h}\right)\frac{e^{-2\varkappa h}}{h},\quad N=\frac{1+\beta_1}{1-\beta_1}.$$

If $h = \delta$, we have

$$G_3\approx 2\alpha\int_0^{\infty}\left[\frac{1+\beta_1}{1-\beta_1}\right]\frac{\omega}{\sqrt{\omega^2+\varkappa^2}}\left(1-\frac{\omega}{\sqrt{\omega^2+x^2}}\right)d\omega=2\alpha N\times$$

$$\times\lim_{\Omega\to\infty}\left(\sqrt{\Omega^2+\varkappa^2}-\varkappa-\Omega+\varkappa\,\mathrm{arctg}\,\frac{\Omega}{\varkappa}\right)=2\alpha N\left(\frac{\pi}{2}-1\right)\varkappa.$$

Equations (10) and (11) are hence easily obtained. If the adjacent phase is a conductor ($\beta_1 = 1$), the integral $G_3$ vanishes identically.

## NOTATION

Here d denotes the characteristic ion diameter; C are the coefficients in (7); E is the energy of interion interactions; e is the electron charge; F is the free energy of interion interactions; f and g are correction coefficients in (17) and (18); h is the distance between the center of an isolated ion and the surface of interphase separation; J is the number of ion types; k is the Boltzmann constant; m is the fraction of surface ions capable of free displacement; N is a parameter in (12); $n_0$ and $n_j$ are the number concentrations of molecules of the solvent and of ions of the j-th kind; q is the bulk charge density; r is the radial coordinate in the plane of separation; T is temperature; u is the specific adsorption energy; $v_0$ is the specific volume of a solvent molecule; x is the normal coordinate; z is the valence of an ion; $\alpha$, $\beta$ are coefficients introduced in (8) and (12); $\Gamma$ is the density of adsorption centers; $\Gamma_j$ is the number of ions of j-th type on a single Helmholtz plane; $\gamma$ are parameters introduced in (6); $\delta$ is the distance between the Helmholtz plane and the surface of separation; $\varepsilon$ is the dielectric constant; $\mu$ is the electrochemical potential; $\sigma$ is the surface charge density; $\tau$ is the extent of filling of an adsorption layer; $\phi$ is the electric potential; and $\psi$, $\chi$ denote standard chemical potentials. Subscripts: 1, j, a, e, * refer, respectively, to the layer between the surface of separation and the Helmholtz plane, the ion type, the adsorption layer, the charge side in the Helmholtz plane, and the phase boundary.

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# DIFFUSION ENTROPY AND THEORETICAL SEPARATIVE WORK FOR GAS MIXTURES WITH VARIABLE CONCENTRATION

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The entropy of mixing and the minimum separative work of a gas mixture with fixed composition per kmole of a component are studied. The entropy of diffusion and the theoretical separative work per kmole of a component in the concentration range of the component are determined for a limited mass of the mixture, when the separation process proceeds with variable concentration.

Entropy of mixing and separative work per kmole of the mixture. In technology it is often necessary to separate gas mixtures. Thus oxygen and nitrogen as well as inert gases (neon, krypton, and xenon) present in them with low (up to $z = 10^{-6}$) concentrations are obtained from air. The development of nuclear power has raised the problem of separating uranium isotopes for enrichment of nuclear fuel. Helium is produced by extraction from natural gas.

The minimum separative work of a mixture of gases is determined from the increase in the entropy accompanying irreversible mixing of ideal gases under identical pressure and temperature. According to Gibbs, the increase in entropy accompanying irreversible mixing is equal to the entropy of mixing per kmole of the mixture [1]:

$$\Delta s^{\mathrm{m}}_{\mathrm{mixing}} = R(z_B \ln 1/z_B + z_A \ln 1/z_A). \tag{1}$$

Hence the minimum separative work of a gas mixture with a constant composition at temperature T (in K) is

$$l^{\mathrm{m}}_{\mathrm{mixing}} = T\Delta s^{\mathrm{m}}_{\mathrm{mixing}} \tag{2}$$

For a two-component mixture the entropy of mixing and the minimum separative work, which is proportional to the entropy of mixing, are usually given as functions of the concentration z, as done in Fig. 1 (dashed curve). It should be noted that the actual separative work of a mixture is, as a rule, several times greater than the indicated minimum. This indicates that other irreversible losses are also present. This dependence also gives the impression that for low concentration of one component the separative work of a mixture decreases appreciably and approaches zero, though in reality at low concentrations of the component the separation work which must be performed in order to obtain the component increases sharply. This impression results from the fact that the dashed curve in Fig. 1 is always constructed per kmole of the mixture, even though when substances are obtained from

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