Physical Chemistry

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1958

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Abstract

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ON THE THEORY OF THE SURFACE TENSION OF SOLUTIONS OF STRONG ELECTROLYTES

(Presented by Academician A. N. Frumkin, 10 I 1958)

The increase in the surface tension of solutions of inorganic salts in water (1,2) was first explained by Wagner (4) by the electrostatic repulsion of ions from the surface of the solution. Onsager and Samaras (5), simplifying Wagner' s differential equations, considered the case of solutions of strong uni-univalent electrolytes under the assumption that the dielectric constant ε' of the external medium is much smaller than the dielectric constant of the solvent ε. In the present work the result of Onsager–Samaras is developed in two directions: first, the case of solutions of multivalent electrolytes of asymmetric type is considered under the assumption $\varepsilon' \gg \varepsilon$, and, second, ε' is taken into account for the case of solutions of uni-univalent electrolytes.*

1. In the case of multivalent electrolytes of asymmetric type, the potential energy of ions of the i-th kind may be represented in the form

$$U_i = W_i + z_i e\varphi = \frac{z_i^2 e^2}{4\varepsilon x} e^{-2\chi x} + z_i e\varphi, \tag{1}$$

where W_i is the adsorption potential caused by the interaction of an ion with its electrostatic image, with allowance for the screening action of the surrounding ions; φ is the potential arising as a consequence of the asymmetry of the electrostatic picture and the violation of electroneutrality of each volume element. The expression for W_i, obtained by Onsager and Samaras (5) for uni-univalent electrolytes, is also applicable in the case of multivalent electrolytes, as follows from the Debye–Hückel theory (3), which is valid for electrolytes of any type. The potential φ satisfies the equation

$$\Delta\varphi = -\frac{4\pi}{\varepsilon} \sum_i z_i e n_i, \tag{2}$$

where

$$n_i = n_{0i} e^{-U_i/kT}. \tag{3}$$

If one restricts the consideration to solutions of sufficiently low concentrations, i.e., sets $\chi q \ll 1$ ($1/\chi$ is the Debye–Hückel radius, $q \sim e^2/\varepsilon kT$ is the distance at which the energy of Coulomb interaction is comparable with the mean energy of thermal motion), then the surface layer may be divided into two regions $x \lesseqgtr x_0$, where $q \ll x_0 \ll 1/\chi$. In region I ($x \ll x_0$), the term $z_i e\varphi$ may be neglected and $e^{-2\chi x} \simeq 1$ may be set in the expression for U_i, since in this region the action of the image forces is considerably stronger than the action of the other ions (the image is at a distance $x \ll 1/\chi$, whereas the effective charge of the ionic atmosphere is at a distance $\sim 1/\chi$).

* As in (^{5}), specific adsorption is not taken into account.

We find the potential $\varphi_I(x)$ from the equation

$$\frac{d^2\varphi_I}{dx^2} = -\frac{4\pi}{\varepsilon}\sum_i z_i e n_{0i}\left(\exp\left[-\frac{z_i^2 e^2}{4\varepsilon kTx}\right]-1\right) \tag{4}$$

with the boundary condition $(d\varphi_I/dx)_{x=0} = 0$ (continuity of the normal component of the electrostatic induction, on the assumption that $\varepsilon' = 0$). In region II ($x \geq x_0$), W_i/kT is small, since $x \gg q$. Consequently, bearing in mind that $z_i e\varphi \ll kT$, (3) can be expanded in a series in U_i/kT. In region II we find the potential from the equation

$$\frac{d^2\varphi_{II}}{dx^2} - \varkappa^2\varphi_{II} = \frac{\pi}{\varepsilon^2 kT}\sum_i (z_i e)^3 n_{0i}\frac{e^{-2\varkappa x}}{x} \tag{5}$$

under the boundary condition $\varphi_{II}(\infty) = 0$.

A consideration analogous to that carried out by Onsager and Samaras (^{5}) shows that in the present case also $\varkappa$ may be regarded as independent of x.

The solutions of equations (4) and (5), joined smoothly at the point $x = x_0$, uniquely determine the potential φ in the region from 0 to ∞.

To study the structure of the surface layer we introduce the quantity $\Delta n_i = n_i(x) - n_{0i}$, which differs from zero only in the surface layer. It is also convenient to introduce the following parameters: $p_i = n_{0i}/n$–the number of ions of the i-th kind formed upon dissociation of one molecule; u–distance in units of $1/\varkappa$; $h = e^2\varkappa/4\varepsilon kT$–a small parameter of the theory; $\ln z^* = \sum_i z_i^3 p_i \ln|z_i| / \sum_i z_i^3 p_i$. In these notations

$$\frac{\Delta n_i}{n} = p_i\left(\exp\left[-\frac{z_i^2 h}{u}\right]-1\right) \qquad \text{for } u \leq u_0;$$

$$\frac{\Delta n_i}{n} = -p_i z_i^2 h \frac{e^{-2u}}{u} - \frac{z_i p_i}{2}\, h \frac{\sum_k z_k^3 p_k}{\sum_k z_k^2 p_k} \left[e^{-u} \int_u^\infty \frac{e^{-v}}{v}\, dv - e^{-u} \int_{3u}^\infty \frac{e^{-v}}{v}\, dv - 2e^{-u} \left(\ln \frac{1}{\sqrt{3}\, h z^{*2}} - 1 + 2\gamma \right) \right] \tag{6}$$

for $u \geq u_0$.

For the charge-density distribution ρ we find:

$$\frac{\rho}{en} = \sum_i z_i p_i \left(\exp\left[-\frac{z_i^2 h}{u} \right] - 1 \right) \qquad \text{for } u \leq u_0;$$

$$\frac{\rho}{en} = -\sum_i z_i^3 p_i h \frac{e^{-2u}}{u} - \frac{h}{2} \sum_i z_i^3 p_i \left[e^{-u} \int_u^\infty \frac{e^{-v}}{v}\, dv - e^{-u} \int_{3u}^\infty \frac{e^{-v}}{v}\, dv - 2e^{-u} \left(\ln \frac{1}{\sqrt{3}\, h z^{*2}} + 1 - 2\gamma \right) \right] \tag{7}$$

for $u \geq u_0$,

where $\gamma = 0.577\ldots$ is Euler’ s constant.

In contrast to uni-univalent electrolytes, the charge density is not identically zero; however, as can be shown, the surface layer as a whole is electrically neutral.

The dependences ρ/en and $\Delta n_i/n$ for solutions of electrolytes of the type MgJ_2 are shown in Figs. 1 and 2.

The change in surface tension is related to the adsorption quantity (6) Λ in the following way:

$$\Delta\sigma = -kT \sum_i \int \Lambda_i \, d \ln a_i. \tag{8}$$

The calculations lead to the following results:

$$\Lambda_i = -\frac{n_{0i}(z_i e)^2}{4\varepsilon kT} \left(1 - 2\gamma + \ln \frac{2\varepsilon kT}{z_i^2 e^2 \varkappa} \right) +$$
$$+ \frac{\pi n_{0i} z_i e}{\varepsilon^2 (kT)^2 \varkappa^2} \sum_k (z_k e)^3 n_{0k} \left(1 - 2\gamma + \ln \frac{2\varepsilon kT}{\varkappa (z_k e)^2} \right); \tag{9}$$

$$\Delta\sigma = \frac{kT\varkappa^2}{16\pi} \left(\frac{3}{2} - 2\gamma + \ln \frac{2\varepsilon kT}{e^2 \varkappa} \right) - \frac{kT\varkappa^2}{16\pi} \frac{\sum_i (z_i e)^2 n_{0i} \ln (z_i e)^2}{\sum_i (z_i e)^2 n_{0i}}. \tag{10}$$

In practice, formula (10) is convenient in the form

$$\Delta\sigma = 39.7 \left(\sum_i z_i p_i\right) \frac{m}{\varepsilon} \lg \left[2.28 \cdot 10^{-13} \frac{(\varepsilon T)^3}{z_0^4 \sum_i z_i^2 p_i m}\right], \tag{11}$$

where m is the concentration in moles per liter.

In the case of uni-univalent electrolytes this result coincides with the limiting law of Onsager–Samaras (^{5}). As can be shown, the general formula obtained by them has no meaning, since the correction to the limiting law contained in it is of the same order as the terms neglected by the authors.

2. Let some ion with charge e be located at the origin. We take the plane $z = z_0 > 0$ to be the boundary of separation electrolyte–external medium. The potential φ created by the ion and its atmosphere in a medium with dielectric constant ε, and the potential φ' in the external medium, are determined by the following equations and boundary conditions:

$$\Delta\varphi = -\frac{4\pi}{\varepsilon}\rho; \qquad \Delta\varphi' = 0; \tag{12}$$

$$[\varphi - \varphi']_{z=z_0} = 0; \qquad \left[\varepsilon\frac{\partial\varphi}{\partial z} - \varepsilon'\frac{\partial\varphi'}{\partial z}\right]_{z=z_0} = 0. \tag{13}$$

Fig. 1. $\rho\, du = \rho'\, d\lg u$

For the charge density one may write $\rho = e\delta(r) + \sum_i e_i n_i$, where $\delta(r)$ is the delta function. Following the Debye–Hückel method, we reduce equation (12) to the form

$$(\Delta - \varkappa^2)\varphi = -\frac{4\pi}{\varepsilon} e\delta(r). \tag{12'}$$

We perform a Fourier transformation with respect to the variables x, y. For the Fourier component $\varphi_k(z)$ we obtain the equation

$$\left(\frac{d^2}{dz^2} - k_1^2 - k_2^2 - \varkappa^2\right)\varphi_k =$$

$$= -\frac{e}{\varepsilon\pi}\delta(z).$$

Fig. 2. $\delta n_1\, du = \delta n_1'\, d\lg u$; $\quad \delta n_2\, du = \delta n_2'\, d\lg u$;
I–$\delta n_1'/n$; $\quad II$–$\delta n_2'/n$

The presence of the δ-function leads to the fact that, for $z \neq 0$,

$$\frac{d^2\varphi_k}{dz^2} - (k^2 + \varkappa^2)\varphi_k = 0 \quad (k^2 = k_1^2 + k_2^2), \tag{14}$$

and at the point $z = 0$ there is a discontinuity of the first derivative

$$\left.\frac{d\varphi_k}{dz}\right|_{-0}^{+0} = -\frac{e}{\varepsilon\pi}. \tag{15}$$

The function $\varphi_k(z)$ itself is continuous at zero.

For $\varphi'_k(z)$ we similarly find:

$$\frac{d^2\varphi'_k}{dz^2} - k^2\varphi'_k = 0. \tag{16}$$

Boundary conditions

$$[\varphi_k - \varphi'_k]_{z=z_0} = 0, \qquad \left[\varepsilon\frac{d\varphi_k}{dz} - \varepsilon'\frac{d\varphi'_k}{dz}\right]_{z=z_0} = 0. \tag{17}$$

The potential φ_e, produced by the electrostatic image of the ion with account of screening, at the position of the given ion is equal to

$$\varphi_e = \left[\varphi - (\varphi)_{z_0=\infty}\right]_{x=0,\ y=0,\ z=0}. \tag{18}$$

The term $(\varphi)_{z_0=\infty}$ corresponds to the potential produced by the ion and its atmosphere far from the surface.

Expressing φ and $(\varphi)_{z_0=\infty}$ through Fourier components, we obtain

$$\varphi_e = \left[\int_{-\infty}^{+\infty}\int \varphi_k(z)e^{i(k_1x+k_2y)}\,dk_1dk_2 + \right.$$

$$\left. + \int_{-\infty}^{+\infty}\int \{-[\varphi_k(z)]_{z_0=\infty}e^{i(k_1x+k_2y)}\,dk_1dk_2\}\right]_{x=0,\ y=0,\ z=0}. \tag{19}$$

Let us note that here one cannot set x, y, z equal to zero in each term of the sum, since they become infinite. This can, however, be done after adding the expressions under the integrals. As a result, after certain transformations we find

$$\varphi_e = \frac{e}{\varepsilon}\int_{\chi}^{\infty}\frac{\lambda\varepsilon - \varepsilon'\sqrt{\lambda^2-\chi^2}}{\lambda\varepsilon + \varepsilon'\sqrt{\lambda^2-\chi^2}}e^{-2\lambda z_0}\,d\lambda \qquad (\lambda = \sqrt{\chi^2 + k^2}). \tag{20}$$

The adsorption potential $W(z) = e\varphi_e/2$ is not expressible in elementary functions. In calculating the adsorption quantity Λ, taking into account the smallness of the parameter χq, in the region $z \ll 1/\chi$ the function $W(z)$ can be substantially simplified; in the region $z \gg q$, the exponential containing $W(z)$ can be expanded in a series. This makes it possible to express Λ in elementary functions.

The calculations give:

$$\Delta\sigma = \frac{e^2(\varepsilon-\varepsilon')n}{2\varepsilon(\varepsilon+\varepsilon')}\left[\ln\frac{2\sqrt{2}\,\varepsilon kT(\varepsilon+\varepsilon')}{\chi e^2(\varepsilon-\varepsilon')}+\right.$$

$$\left.+\frac{3}{2}-2\gamma-\frac{1}{2}\left(\frac{\varepsilon+\varepsilon'}{\varepsilon-\varepsilon'}\right)\ln 2+\frac{2\varepsilon^2}{(\varepsilon-\varepsilon')^2}\ln\frac{\varepsilon+\varepsilon'}{\varepsilon^2}\right]. \tag{21}$$

For $\varepsilon' = 0$ this expression is in complete agreement with the results of Onsager –Samaras (^{5}).

In conclusion I express my gratitude to Prof. V. G. Levich for suggesting the problem and to Prof. E. M. Lifshitz for a number of valuable comments.

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Received
9 I 1958

References Cited

1. A. Heydweiller, Ann. Phys., **33**, 145 (1910).
2. G. Schwenker, Ann. Phys., **11**, 525 (1931).
3. P. Debye, E. Hückel, Phys. Zs., **24**, 185 (1923).
4. G. Wagner, Phys. Zs., **25**, 474 (1924).
5. L. Onsager, N. T. Samaras, J. Chem. Phys., **2**, 528 (1934).
6. G. Harned, B. Owen, *Physical Chemistry of Electrolyte Solutions*, IL, 1952.

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