# *LIMITING LAWS FOR SURFACE TENSION OF SOLUTIONS OF STRONG ELECTROLYTES*

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I. Multivalent electrolytes of the asymmetrical type. In the surface layer of multivalent electrons of the asymmetrical type, unlike in those of the mono-monovalent electrolytes, the electric neutrality of each volume element is destroyed. This makes it necessary to take into account not only the potential due to the electrostatic representation of the ion with allowance for the screening action of the surrounding ions, but also the additional field due to the asymmetry of the electrostatic pattern. The potential of this field satisfies the equation

$$\Delta\varphi = -(4\pi/\varepsilon)\sum_i z_i e n_i, \tag{1}$$

where

$$n_i = n_{0i}\exp\{-U_i/kT\} \tag{2}$$

is the density of the ions of the i-th type in the surface layer. The potential energy $U_i$ of the ions is

$$U_i = \frac{(z_i e)^2}{4\varepsilon kT}e^{-2\varkappa x} + z_i e\varphi \tag{3}$$

($z_i$ are positive and negative integers, e the electron charge, and $1/\kappa$ the Debye-Hückel radius[1]).

The distribution of the ions and of the charge density is determined by the following formulas

$$\frac{\delta n_i}{n} = \begin{cases} P_i\left(e^{-z_i^2 h|u} - 1\right) & \text{for } u \leqslant u_0 \\ -P_i z_i^2 h\frac{e^{-2u}}{u} - \frac{z_i P_i}{2}h\frac{\Sigma z_k^3 P_k}{\Sigma z_k^2 P_k}\left[e^{-u}\int\limits_u^\infty \frac{e^{-v}}{v}dv - \right. & \\ \left. -e^u\int\limits_{3u}^\infty \frac{e^{-v}}{v}dv - 2e^{-u}\left(\ln\frac{1}{\sqrt{3hz^{*2}}} + 1 - 2\gamma\right)\right] & \text{for } u \geqslant u_0 \end{cases} \tag{4}$$

$$\frac{\rho}{en} = \begin{cases} \sum\limits_i z_i P_i\left(e^{-z_i^2 h/u} - 1\right) & \text{for } u \leqslant u_0 \\ -\sum\limits_i z_i^3 P_i h\frac{e^{-2u}}{u} - \frac{h}{2}\sum\limits_i z_i^3 P_i\left[e^{-u}\int\limits_u^\infty \frac{e^{-v}}{v}dv - \right. & \\ \left. -e^u\int\limits_{3u}^\infty \frac{e^{-v}}{v}dv - 2e^{-u}\left(\ln\frac{1}{\sqrt{3hz^{*2}}} + 1 - 2\gamma\right)\right], & \text{for } u \geqslant u_0, \end{cases} \tag{5}$$

where $\delta n_i = n_i(x) - n_{0i}$ are the deviations of the ion density in the surface layer from the density inside the electrolyte, and n is the density of the dissociated molecules. For convenience let us write $P_i = n_{0i}/n$ for the number of ions of the i-th type, formed upon dissociation of one molecule; u, for the distance in $1/\kappa$ units,

$$\ln z^* = \sum_i z_i^3 P_i \ln|z_i| \Big/ \sum_i z_i^3 P_i, \quad h = \frac{e^2}{4\varepsilon kT}\varkappa,$$

h is the small parameter of the theory (the ratio of the energy of the electrostatic interaction to the mean energy of thermal motion).

We note that the surface layer as a whole is electrically neutral, since the regions of positively and negatively charged cancel each other.

The following limiting law is derived for the change in the surface tension

$$\Delta\sigma = \frac{kT\varkappa^2}{16\pi}\left(\frac{3}{2} - 2\gamma + \ln\frac{2\varepsilon kT}{e^2\varkappa}\right) - \frac{kT\varkappa^2}{16\pi}\,\frac{\sum\limits_i (z_ie)^2 n_{0i}\ln(z_ie)^2}{\Sigma(z_ie)^2 n_{0i}} \tag{6}$$

($\gamma = 0.577$, the Euler constant). In practice it is more convenient to use this formula in the following form

$$\Delta\sigma = 39.7\left(\sum_i z_iP_i\right)\frac{m}{\varepsilon}\log[2.28\cdot 10^{-13}(\varepsilon T)^3/mz_0^4\,\Sigma z_i^2P_i], \tag{7}$$

where m is the concnetration in moles/liter.

In the case of mono-monovalent electrolytes the resultant limiting law becomes the Onsager-Samaras limiting law.[2] The general formula they derived has no meaning, since the correction to the limiting law, contained in this formula, is of the same order as the quantities neglected by these authors.

2. Allowance for the dielectric constant of the external medium. In the case of mono-monovalent electrolytes the potential of the electrostatic field, produced by a fixed ion in its atmosphere, with allowance for the separation surface between the two dielectrics, is determined by the following equation

$$(\Delta - \varkappa^2)\varphi = -(4\pi/\varepsilon)\,e\delta(\mathbf{r}). \tag{8}$$

The solution of this equation is substantially more complicated than that for the case considered by Onsager and Samaras, owing to the fact that the dielectric constant of the external medium is not assumed to be zero. The adsorption potential (the potential energy of the interaction of the ion with its electrostatic image, with allowance for screening) turns out to be

$$W(z) = \frac{e^2}{2\varepsilon}\int_{\varkappa}^{\infty}\frac{\lambda\varepsilon - \varepsilon'\sqrt{\lambda^2-\varkappa^2}}{\lambda\varepsilon + \varepsilon'\sqrt{\lambda^2-\varkappa^2}}\,e^{-2\lambda z}\,d\lambda. \tag{9}$$

In spite of the fact that it is necessary to calculate an integral of a non-elementary function (9), which is furthermore in exponential form, it is possible, using the smallness of the parameter of the theory, to obtain an expression for the change in surface tension $\Delta s$ in terms of elementary functions

$$\Delta\sigma = \frac{e^2(\varepsilon-\varepsilon')n}{2\varepsilon(\varepsilon+\varepsilon')}\left[\ln\frac{2\sqrt{2}\cdot\varepsilon kT(\varepsilon+\varepsilon')}{\varkappa e^2(\varepsilon-\varepsilon')} + \frac{3}{2} - 2\gamma - \frac{1}{2}\left(\frac{\varepsilon+\varepsilon'}{\varepsilon-\varepsilon'}\right)^2\ln 2 + \frac{2\varepsilon^2}{(\varepsilon-\varepsilon')^2}\ln\frac{\varepsilon+\varepsilon'}{\varepsilon}\right]. \tag{10}$$

When $\epsilon' = 0$, Eq. (10) goes into the limiting Onsager-Samaras law.[2]

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[1] P. Debye and F. Hückel, Phys. Z. 24, 1085 (1929).

[2] L. Onsager and N. T. Samaras, J. Chem. Phys. 2, 528 (1934).

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# *REFINEMENT OF THE APPROXIMATION FOR SMALL ANGLES IN MULTIPLE-SCATTERING PROBLEMS*

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To analyze the scattering of beams of charged particles by metallic foils it is necessary to solve the problem of the spatial and angular distribution of the density produced in the beam as a result of a large number of collisions. At a depth $\tau$, the particle density in a monoenergetic (E > 10 Mev) beam $\psi(\mu, \tau)$