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Abstract

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ON THE DOUBLE ELECTRIC LAYER IN MOLTEN SALTS AND CONCENTRATED ELECTROLYTE SOLUTIONS

In investigating the capacitance of the double electric layer in molten salts ([1]), it was found that the dependence of the capacitance C on the potential φ is, in character, very close to that observed in dilute solutions, since the curves $C = C(\varphi)$ for salts with the same charge of the anion and cation are completely symmetric with respect to the point of zero charge and do not depend on the type of cation and anion. As is known, in dilute solutions the symmetry of the curve $C = C(\varphi)$ is explained by the presence of a diffuse part of the double layer, whose capacitance is much smaller than the capacitance of the compact part. It is natural to suppose that in very concentrated solutions and in molten salts a diffuse electric layer also arises, whose capacitance is less than that of the compact part, and whose dimensions are so large that the specific features of individual ions* (for example, their diameter) no longer play any substantial role. Calculations confirm this supposition.

Let us consider a system of hard spheres interacting with one another according to Coulomb' s law and occupying the half-space $z > 0$. Let the plane $z = 0$ carry an electric charge uniformly distributed with density η. We shall start from Bogolyubov' s chain of equations ([2]) for distribution functions, which, as is known, is exactly equivalent to the canonical Gibbs distribution. Consider the equation for the singlet function $G_a = g_a$, in which we represent the binary function G_{ab} in the form

$$G_{ab} = g_a g_b \exp\left[-\frac{\Phi_{ab}^{(s)}}{kT}\right] \cdot (1 + g_{ab}), \quad \text{where } \Phi_{ab}^{(s)} =$$

$$= \begin{cases} +\infty, & 0 \le r_{ab} < r_0, \\ 0, & r_0 < r_{ab} \le \infty \end{cases}$$

is the energy of Born repulsion of ions a and b, and g_{ab} is a correlation function taking into account, chiefly, the presence of "Debye atmospheres" in the double layer. In a first approximation the quantity g_{ab} may be neglected, after which, to determine $g_a(z_a)$, we obtain the closed equation

$$kT\nabla_a \ln g_a + \nabla_a U_a + \frac{1}{v}\int_{z_c \geq 0} \sum_c n_c g_c e^{-\Phi_{ac}^{(s)}/kT} \nabla_a \Phi_{ac}\, d^3 r_c = 0, \qquad \text{(A)}$$

where $U_a = \dfrac{2\pi\eta e_a}{\varepsilon} z_a$ is the energy of ion a in the field of a uniformly charged plane, $\Phi_{ac} = \Phi_{ac}^{(s)} + \Phi_{ac}^{(coul)}$, and $\Phi_{ac}^{(coul)} = \dfrac{e_a e_c}{\varepsilon}\dfrac{1}{r_{ac}}$ is the energy of Coulomb interaction of ions a and c. The remaining notation is the same as in ([2]). A complete investigation of equation (A) is given in ([3]); here we shall confine ourselves only to a brief presentation of the results obtained in ([3]).

Put $g_a = \exp[-e_a\varphi/kT]$, where $\varphi(z_a)$ has the dimension of potential. It can be shown that, for small η, the quantity $e_a\varphi \ll kT$ and, consequently, $g_a \simeq 1 - e_a\varphi/kT$. Substituting this expression into (A) and taking into account,

* In molten salts the Stern molecular condenser may be absent altogether.

that, because of the neutrality of the system far from the interface, $\sum_c e_c n_c = 0$, we obtain for the region

$$r_0 < z \leq \infty, \quad \varphi'(z) = \frac{\chi^2}{2r_0}\int_{z-r_0}^{z+r_0} dt \int_t^\infty \varphi(\tau)\, d\tau, \quad \chi^2 = \frac{4\pi \sum_c n_c e_c^2}{v\varepsilon kT}. \qquad \text{(B)}$$

In deriving (B) we neglected the term with $\nabla_a \Phi_{ac}^{(s)}$, since it is much smaller than the term with $\nabla_a \Phi_{ac}^{(coul)}$. Differentiating (B) twice, we transform it to the form

$$\varphi'''(z) = \frac{\chi^2}{2r_0}\{\varphi(z + r_0) - \varphi(z - r_0)\}.$$

The solution of this equation has the form

$$\varphi(z) = \sum_{k=1}^{\infty} A_k e^{-a_k z},$$

where a_k are the roots of the transcendental equation $w^3 = (\chi r_0)^2 \operatorname{sh} w,\ w = a r_0$. The constants A_k can be determined from the equation obtained from (A) for the constants $0 \leq z \leq r_0$. Since, with increasing term number k, the real part of a_k increases and, consequently, the contribution of this term to φ decreases sharply, in a first approximation one may restrict oneself to the first two terms of the series $\varphi = A_1 e^{-w_1 \xi} + A_2 e^{-w_2 \xi}$, $\xi = z/r_0$. Put $w_k = \lambda_k + i\omega_k$, $k = 1, 2$, and consider the dependence $w_k = w_k(\chi r_0)$. It can be shown that for $0 \leq \chi r_0 \leq 1.642$ the quantities $\omega_{1,2} = 0$, and as $\chi r_0 \to 0$ the value $\lambda_1 \to \chi r_0$, while $\lambda_2 \to \infty$. Therefore, in dilute solutions, when χr_0 is small, one may with a high degree of accuracy put $\varphi \simeq A_1 e^{-\chi z}$, which coincides with the solution of the self-consistent Gouy–Chapman equation. As $\chi r_0 \to 1.642$, the quantities $\lambda_1 \to \lambda_2 \to 2.984$, and, consequently, the effective thickness of the diffuse part of the double layer $L \simeq r_0/\lambda_1$ becomes very small.

Let us now consider the region $\chi r_0 > 1.642$, in which $w_{1,2}$ become complex conjugates. Therefore φ takes the form $\varphi \simeq A e^{-\lambda\xi} \cos(\omega\xi + \Omega)$, where the period of oscillations $T = 2\pi r_0/\omega$ changes from $T = \infty$ at $\chi r_0 = 1.642$ to $T = 1.451\, r_0$ at $\chi_0 = 9.167$, while the effective thickness of the diffuse part of the double layer L increases from $0.335\, r_0$ at $\chi r_0 = 1.642$ to $L = \infty$ at $\chi r_0 = 9.167$. The point $\chi r_0 = 9.167$ is limiting for a system of hard spheres interacting with one another according to Coulomb' s law. This means that at $\chi r_0 \geq 9.167$ a system of hard spheres can exist only in the form of a crystal; the liquid and gaseous phases in this region of concentrations and temperatures are absolutely unstable.

We note that analogous results, although by another method, were obtained in work ([4]). However, the calculation of the capacitance of the diffuse part of the double layer C in ([4]) was carried out not by means of the complete series

$$\varphi = \sum_{k=1}^{\infty} A_k e^{-w_k \xi},$$

but using only its first two terms. This led to a meaningless result: the capacitance went to infinity at $\chi r_0 = 1.46$, i.e., at a time when the thickness of the double layer L still remained of order r_0. Therefore the authors did not consider the region $\chi r_0 > 1.46$, in which the main increase in the dimensions of the double layer occurs.

It can be shown that the exact expression for the capacitance of the double layer has the form

$$C = \frac{\varepsilon\chi}{4\pi} h, \quad \text{where } h = \sum_{k=1}^{\infty} A_k \frac{\chi r_0}{w_k}, \tag{C}$$

and the series in (C) converges for any values of χr_0. In the limit, as $\chi r_0 \to 0$, the quantity $h \to 1$; in all other cases $h > 1$.

Thus, in sufficiently concentrated systems the existence of a diffuse double layer of large thickness is indeed possible. In this respect they are analogous to dilute systems. However, in

···in contrast to the latter, in concentrated systems the potential decreases with distance in an oscillatory manner, and not smoothly.

It is easy to show that, in the case of a thin film formed from a very concentrated electrolyte solution, the overlap of diffuse ionic layers, just as in dilute systems, must lead to the appearance of repulsive forces capable of ensuring the stability of colloids; moreover, because of the oscillatory character of the forces, this type of stabilization must possess interesting special features.

The effect of an increase in the thickness of the double layer should exist not only in melts and very concentrated aqueous solutions, but also in solutions of weak electrolytes of medium and low concentration, for which χr_0 is large because of the small dielectric constant of the solvent ε. It is therefore possible that in some solutions of weak electrolytes lyophobic colloids will be stable not only at small but also at large χr_0, since in both cases they will be stabilized by diffuse layers of great extent; at intermediate values of χr_0, however, they should be unstable.

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REFERENCES

1. E. A. Ukshe, N. G. Bukun, D. I. Leikis, *ZhFKh*, No. 11, 2322, 1962.
2. N. N. Bogolyubov, *Problems of Dynamical Theory in Statistical Physics*, 1946.
3. G. A. Martynov, Collection: *Studies in the Field of Surface Phenomena*, Publishing House of the USSR Academy of Sciences, 1963.
4. F. H. Stillinger, G. G. Kirkwood, *J. Chem. Phys.*, 33, 1960, No. 5, 1282.

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