STRUCTURE AND CAPACITANCE OF THE METAL-FUSED SALT INTERFACE

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(Presented by Academician A. N. Frumkin, April 4, 1964)
Translated from Doklady Akademii Nauk SSSR, Vol. 157, No. 4, pp. 944-947, August, 1964
Original article submitted April 2, 1964

Experimental investigations of recent years have shown [1-3] that the capacitance of the electric double layer in fused salts possesses a number of interesting features. In the first place, the capacitance in melts ($\sim 40\ \mu F/cm^2$ at the point of zero charge) substantially exceeds the double-layer capacitance in solutions of electrolytes. Thus, the capacitance in melts in contrast to the capacitance in dilute solutions, * proves to be an increasing function of the temperature. Finally, the capacitance in melts, as a rule, is a symmetrical function of the potential.

The problem of the calculation of the capacitance reduces to finding the distribution of the concentration of ions or their unary correlative functions K_+, K_- † at the surface of the electrode, charged to a potential of φ_M. A rigorous step-by-step solution of this problem, in any case, is no easier than the well known problem of constructing the theory of a liquid. However, we can get around the difficulties related to a consideration of the Coulomb and short-range interactions between particles if we formulate the problem in the following way.

As is well known, the short-range order (microstructure) and volume properties of a liquid are characterized by a binary correlative function K_{12}, where the subscripts 1 and 2 correspond to the first and second particles. The character of this function is determined by the specific interaction in each concrete system. Assuming the binary function K_{12} to be set, let us attempt to express the unary correlative functions in the presence of an external field, K_+ and K_-, in terms of it. Let us consider on the whole an electrically neutral system of charged particles A^+ and B^- in a volume V between two planar electrodes, situated at a distance L. The unary function in the presence of an external field takes the form:

$$K_+ = \frac{V \cdot \int e^{-\beta U_N^0 + \beta \frac{\varphi M}{L} \Sigma e_i x_i} d2 \ldots dN}{\int e^{-\beta U_N^0 + \beta \frac{\varphi M}{L} \Sigma e_i x_i} d1 \ldots dN}, \quad (1)$$

where φ_M is the potential difference between electrodes, $\beta = 1/kT$, U_N^0 is the total energy of interaction of the particles at $\varphi_M = 0$. Resolving K_+ in a series with respect to $\beta e \varphi_M$, we obtain

$$K_+ = K_+^0 + \frac{\beta e \varphi_M x_1}{L} K_+^0 + \frac{\beta e \varphi_M \cdot \nu}{L} \int_{-L/2}^{+L/2} \int \int (K_{++}^0 - K_{+-}^0) x_2 d2, \quad (2)$$

where K_{++}^0, K_{+-}^0 are the binary functions when $\varphi_M = 0$, relating to the system contained in volume V; K_+^0 is the unary function when $\varphi_M = 0$. Function (2) in principle solves the problem posed above, of finding the concentrations of the ions according to binary functions when $\varphi_M = 0$. ‡ It should be mentioned that formula (2) permits the calculation

*The capacitance of a diffuse double layer in solutions, as experiments show, practically does not vary with the temperature, since the dependence of the Debye radius $1/\varkappa$ on T is compensated for by the dependence of the dielectric constant on T.

† The unary function is related to the concentration by the function $c_i(x) = K_i(x) \nu_i$, where ν_i is the volume concentration of the i-th component.

‡ These functions, strictly speaking, differ from the volume binary functions, since close to the electrode the distribution of the particles is not the same as in the volume.

of the capacitance only close to the point of zero charge, since it contains only first-order factors with respect to $\beta e\varphi_M$. A consideration of the following degrees of $\beta e\varphi_M$ leads to the appearance of higher and higher orders in the final formulas of the correlative functions.

Limiting ourselves to the case of particles identical in the sense of short-range action,* which differ only in electric charge, we can assume $K_+^0 = K_-^0 = 1$. Then from (2), it follows that $K_+ + K_- = K_+^0 + K_-^0$, i.e., in the first order with respect to $(\beta e\varphi_M)$, the density remains constant. In other words, the charge at the electrode arises as a result of a process of replacement of an anion by a cation, or vice versa. In the following orders along the field, this apparently no longer occurs. This conclusion of constancy of the density is not transferred directly to the case of particles of different dimensions.

Passing to the limit $L \to \infty$, we obtain an expression for the charge density

$$\rho = -\beta e^2\varphi_M \cdot \nu - \beta e^2\varphi_M \nu^2 \cdot \int_0^\infty \int \int \int \Delta K_{12}^0 d2, \tag{3}$$

where $\nu = N/2V$ is the volume concentration of anions (cations), $\Delta K_{12}^0 = (K_{++}^0 - K_{+-}^0)$. We should mention that although in (2) the coordinate $\underline{x}$ was counted from the middle of the space between the electrodes, in (3), the beginning of the count is situated at the left-hand electrode. According to the condition of electrical neutrality,

$$\nu \cdot \int_V \Delta K_{12}^0 d2 = -1, \tag{4}$$

so that at sufficiently large x_1, the integral in (3) is equal to a constant, which exactly compensates for the first component, and the charge density at such $\underline{x}$ becomes zero. Function (3) is applicable to solutions of any concentrations and to melts.

It is of interest to apply formula (3) to dilute solutions, for which there is a theoretically derived expression for the volume function ΔK_{12} (the Debye-Hückel distribution):

$$\Delta K_{12} = -2e^2\beta \frac{e^{-\varkappa r}}{r}, \tag{5}$$

as well as an expression for binary functions close to the electrode when $\varphi_M = 0$

$$\Delta K_{12}^0 = -2e^2\beta \left(\frac{e^{-\varkappa r}}{r} - \frac{e^{-\varkappa r^*}}{r^*} \right), \tag{5'}$$

where r^* is the coordinate of the "image."

Substituting expression (5') into formula (3) leads to the proper value of the capacitance $C_d = \varkappa/4\pi$, while (5) gives $C_d = \varkappa/8\pi$. Thus, the use of the volume binary functions, without considering the change in the charge distribution around the electrode, leads to a value of the capacitance half the true value in the case of a dilute solution.

In order to calculate the capacitance in a melt, it is necessary to set a definite function $K_{++}^0 - K_{+-}^0$), i.e., the distribution of charge density around an arbitrary ion. X-ray diffraction methods, used to investigate the structure of liquids, make it possible to determine, strictly speaking, only the distribution of the density of matter $K_{++}^0 + K_{+-}^0$), and not of charge. The corresponding radial distribution function possesses an oscillating, quenching character (Fig. 1). It can be assumed that the binary charge distribution function takes an analogous form. This hypothesis is physically justified, since it means that the microstructure in a melt is analogous to the structure of the corresponding crystal. X-ray diffraction pictures of salts of the type of NaCl show [4] that the coordinates of the first two maxima are close to the distances $Na^+ - Cl^-$ and $Na^+ - Na^+(Cl^- - Cl^-)$ in the crystals. Hence, it is usually assumed that the first coordination sphere around Na^+ consists of Cl^-, and the second of Na^+. Consequently, we can take the volume function ΔK_{12} in the form.

*In particular, in the model of solid spheres, this means that these particles possess the same dimensions. The theory can also be generalized for the case of particles of different dimensions.

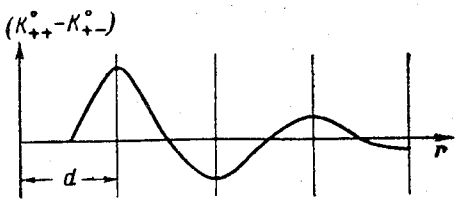

Fig. 1.

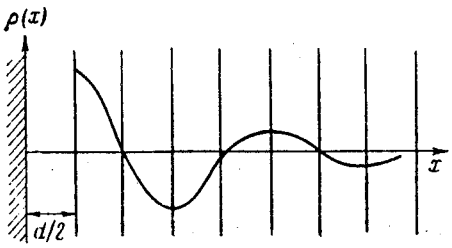

Fig. 2.

$$\Delta K_{12} = \begin{cases} \frac{1}{2\nu d^2} \frac{e^{-\lambda r}}{r} \cos \frac{\pi}{d} r, & r \geqslant \frac{d}{2}, \\ 0, & r \leqslant d/2, \end{cases} \qquad (2)$$

where d is the distance to the first maximum, $1/\lambda$ is the length of correlation, which characterizes the dimensions of the region of short-range order ($1/\lambda > d$). As experiments show [5], d is practically independent of the temperature, while λ increases with the temperature. The latter is related to the fact that increasing temperature disturbs the short-range order [6] and thereby reduces the radius of correlation $1/\lambda$. To calculate the charge distribution, we shall use the volume function (6), neglecting the distortions introduced by the electrode. A certain justification is the fact that in the Debye case, such an approximation has no effect on the qualitative character of the results, changing only the numerical coefficient. The distribution of charge density in a melt, characterized by function (6), according to (3), takes the form (Fig. 2):

$$\rho = -\frac{\varkappa^2 \cdot \varphi_M}{8\pi^2} e^{-\lambda x'} \cos \frac{\pi}{d} x', \qquad (7)$$

where $x' = x - d/2$, $\varkappa^2 = 8\pi e^2 \nu \beta$. Thus, the distribution of charge in the melt possesses an oscillating quenching character, analogous to the behavior of the binary function in Fig. 1. In the first layer the charge is opposite in sign to the charge of the electrode and exceeds it in magnitude; in the second layer the charge is smaller in magnitude than in the first and is opposite in sign, etc. Such a charge distribution can be explained physically. Let us assume at $\varphi_M = 0$, the concentrations of anions and cations at the electrode are equal, and $\rho = 0$. As the electrode is charged ($\varphi_M > 0$), an excess of anions arises in the first layer. The presence of strong correlation between the anion and cation leads to the fact that the second layer proves to be positively charged, the third negatively, etc. Insofar as we know, qualitative considerations of the possibility of a charge distribution of this type in solution were first expressed by O. A. Esin [7]. In a discussion of the experimental data obtained, E. A. Ukshe, N. G. Bukun, D. I. Leikis, and A. N. Frumkin [3] indicated the possibility of the existence of an oscillating charge distribution in melts, by which certain observed facts can be explained. On the other hand, distributions of this type were obtained theoretically in moderately concentrated solutions [8, 9]. However, the degree of reliability of these theoretical results is low, since a number of rough approximations were made in the calculations. According to [6], the capacitance is equal to

$$C = \frac{\varkappa^2 \lambda d^3}{8\pi^4}. \qquad (8)$$

Numerical estimates show that when $\nu \sim 2 \cdot 10^{22}$, $d \sim 2$ A, $\lambda \sim 1/6 \cdot 10^{-8}$ cm^{-1}, the capacitance is rather great and comprises approximately 50 μF/cm^2.

The dependence of the capacitance on the temperature is related to $1/T$ from $\varkappa^2$ and to the function $\lambda(T)$. As was noted above, $\lambda(T)$ increases with the temperature, while the charge distribution becomes less blurred. This can explain the observed increase in the capacitance with the temperature. The treatment of X-ray diffraction pictures [10] pertaining to liquid cesium at various temperatures, which we performed, showed that $\lambda_1 = 0.22$ when $t_1 = 30°$, while $\lambda_2 = 0.33$ when $t_2 = 300°$, i.e., λ increases with T. The absence of similar data for melts of salts deprives us of the possibility of conducting a quantitative comparison of the theory with the experimental data pertaining to the temperature dependence of the capacitance. Moreover, in a real melt, the anions and cations possess different dimensions. It follows from the experimental data [2] that the nature of the components of the melt, which can be roughly characterized by the dimensions of the corresponding ions, exerts a substantial influence on the capacitance. A quantitative description of the dependence of the capacitance on the nature of the components is difficult, since there are no reliable data on the dependence of λ on the type of ion. It should also be mentioned that the approximation of the true binary function by expression (6), which contains only two parameters – λ and d, is too rough for a description of the dependence on the nature of the particles.

We should like to thank Academician A. N. Frumkin, Corresponding Member of the Academy of Sciences USSR V. G. Levich, D. I. Leikis, and E. A. Ushke for their useful discussions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
