Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 157, No. 4

PHYSICAL CHEMISTRY

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STRUCTURE AND CAPACITANCE OF THE METAL–MOLTEN SALT INTERFACE

(Presented by Academician A. N. Frumkin, 4 IV 1964)

Experimental studies of recent years have shown ([1–3]) that the capacitance of the electrical double layer in molten salts possesses a number of interesting features. First, the capacitance in melts (~ 40 μF/cm^2 and so on) considerably exceeds the capacitance of the double layer in electrolyte solutions. Further, the capacitance in melts, unlike the capacitance in dilute solutions *, turns out to be an increasing function of temperature. Finally, the capacitance in melts is, as a rule, a symmetric function of the potential.

The problem of calculating the capacitance reduces to finding the distribution of the ion concentrations or their unary correlation functions K_+, K_- ** near the surface of an electrode charged to the potential φ_M. A rigorous, consistent solution of this problem is, in any case, no easier than the well-known problem of constructing a theory of liquids. However, the difficulties associated with taking into account the Coulomb and short-range interactions between particles can be avoided if the problem is formulated as follows.

As is known, the short-range order (microstructure) and bulk properties of a liquid are characterized by the binary correlation function K_{12}, where the indices 1 and 2 correspond to the first and second particles. The character of this function is determined by the specificity of the interactions in each particular system. Assuming the binary function K_{12} to be given, we shall try to express through it the unary correlation functions in the presence of an external field K_+ and K_-. Let us consider, as a whole, an electroneutral system of charged particles A^+ and B^- in a volume V between two plane electrodes separated by a distance L. The unary function in the presence of an external field has the form:

$$K_+ = \frac{V \cdot \int e^{-\beta U_N^0 + \beta \frac{\varphi_M}{L} \sum e_i x_i} \, d2 \ldots dN}{\int e^{-\beta U_N^0 + \beta \frac{\varphi_M}{L} \sum e_i x_i} \, d1 \ldots dN}, \tag{1}$$

where φ_M is the potential difference between the electrodes, $\beta = \frac{1}{kT}$, and U_N^0

is the total interaction energy of the particles at $\varphi_M = 0$. Expanding K_+ in a series in $\beta e\varphi_M$, we obtain

$$K_+ = K_+^0 + \frac{\beta e\varphi_M x_1}{L} K_+^0 + \frac{\beta e\varphi_M \cdot v}{L} \iint_{-L/2}^{+L/2} (K_{++}^0 - K_{+-}^0)\, x_2\, d2, \qquad (2)$$

* The capacitance of the diffuse double layer in solutions, as experiment shows, practically does not change with temperature, since the dependence of the Debye radius $1/\chi$ on T is compensated by the dependence of the dielectric constant on T.

** The unary function is related to the concentration by the relation $c_i(x) = K_i(x)v_i$, where v_i is the bulk concentration of the i-th component.

where K_{++}^0, K_{+-}^0 are binary functions at $\varphi_M = 0$, referring to the system enclosed in the volume V; K_+^0 is the unary function at $\varphi_M = 0$. Relation (2) solves, in principle, the problem posed above of finding the ion concentrations in terms of the binary functions at $\varphi_M = 0$.* It should be noted that formula (2) makes it possible to calculate the capacitance only near the p.z.c., since it contains only first-order terms in $\beta e\varphi_M$. Taking into account subsequent powers of $\beta e\varphi_M$ leads to the appearance, in the final formulas, of correlation functions of ever higher orders.

Restricting ourselves to the case of particles identical in the sense of short-range interaction,** which differ only in electric charge, one may put $K_+^0 = K_-^0 = 1$. Then it follows from (2) that $K_+^0 + K_-^0 = K_+^0 + K_-^0$, i.e., to first order in $(\beta e\varphi_M)$ the density remains constant. In other words, the charge at the electrode arises as a result of the process of replacing an anion by a cation, or conversely. In the following orders in the field this, apparently, is no longer the case. This conclusion about the constancy of the density is not carried over directly to the case of particles of different sizes.

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

$$\rho_e = -\beta e^2 \varphi_M \cdot v - \beta e^2 \varphi_M v^2 \cdot \int_0^\infty \iint \Delta K_{12}^0\, d2, \qquad (3)$$

where $v = N/2V$ is the volume concentration of anions (cations), $\Delta K_{12}^0 = (K_{++}^0 - K_{+-}^0)$. It should be noted that if in (2) the coordinate x was measured from the middle of the interelectrode space, then in (3) the origin is at the left electrode. By the condition of electroneutrality,

$$v \cdot \int_V \Delta K_{12}^0 d2 = -1, \qquad (4)$$

so that for sufficiently large x_1 the integral in (3) is equal to a constant, which exactly compensates the first term, and the charge density at such x becomes zero. Relation (3) is applicable to solutions of any concentration 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):

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

as well as an expression for the binary functions near the electrode at $\varphi_M = 0$:

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

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

Substitution of expression (5′) into formula (3) leads to the correct value of the capacitance $C_d = \chi/4\pi$, whereas (5) gives $C_d = \chi/8\pi$. Thus, the use of volume binary functions that do not take into account changes in the charge distribution near the electrode leads, in the case of a dilute solution, to a capacitance value half as large as the true one.

In order to calculate the capacitance in a melt, it is necessary to specify a definite function $(K_{++}^0 - K_{+-}^0)$, i.e., the distribution of charge density around an arbitrary ion. X-ray diffraction methods used to study the structure of liquids make it possible to determine, strictly–

* Strictly speaking, these functions differ from the volume binary functions, since near the electrode the distribution of particles is not the same as in the bulk.

** In particular, in the hard-sphere model this means that all particles have the same size. The theory can also be generalized to the case of particles of different sizes.

generally speaking, only the distribution of the density of matter $(K_{++}^0 + K_{+-}^0)$, and not of charge. The corresponding radial distribution function has an oscillatory, damped character (Fig. 1). It may be assumed that the binary charge-distribution function has an analogous form. This assumption is physically justified, since it means that the microstructure in the melt is analogous to the structure of the corresponding crystal. X-ray diffraction patterns of salts of the NaCl type show [4] that the coordinates of the first two maxima are close to the distances Na^+–Cl^- and Na^+–Na^+(Cl^-–Cl^-) in crystals. Therefore it is usually assumed that the first coordination sphere around Na^+ consists of Cl^-, and the second of Na^+. Consequently, the volume function ΔK_{12} may be chosen in the form

Fig. 1 Fig. 2

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$$\Delta K_{12} = \begin{cases} \dfrac{1}{2\nu d^2} \dfrac{e^{-\lambda r}}{r} \cos \dfrac{\pi}{d} r, & r \geq \dfrac{d}{2}, \\ 0, & r \leq d/2, \end{cases} \tag{6}$$

where d is the distance to the first maximum, and $1/\lambda$ is the correlation length, which characterizes the size of the region of short-range order ($1/\lambda > d$). As experiment shows [5], d is practically independent of temperature, whereas λ increases with temperature. The latter is connected with the fact that an increase in temperature disrupts the short-range order [6] and thereby reduces the correlation radius $1/\lambda$. To calculate the charge distribution we shall use the volume function (6), neglecting the distortions introduced by the electrode. Some justification for this is provided by the fact that, in the Debye case, such an approximation does not affect the qualitative character of the results, changing only a numerical coefficient. The distribution of the charge density in a melt characterized by the function (6) has, according to (3), the form (Fig. 2):

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

where $x' = x - d/2$, $\varkappa^2 = 8\pi e^2 n\beta$. Thus, the charge distribution in the melt has an oscillatory, damped character, analogous to the behavior of the binary fraction 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 opposite in sign, and so on. Such a charge distribution can be explained physically. Suppose that 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 a strong correlation between anion and cation leads to the second layer being positively charged, the third negatively charged, and so on. As far as we know, qualitative considerations on the possibility of this kind of charge distribution in a solution were first expressed by O. A. Esin [7]. In discussing the experimental data obtained, E. A. Ukshe, N. G. Bukun, D. I. Leikis, and A. N. Frumkin [3] pointed to the possibility of the existence of an oscillatory charge distribution in the solu-

melts, by which some observed facts can be explained. On the other hand, distributions of this type in moderately concentrated solutions have been obtained theoretically [8,9]. However, the degree of reliability of these theoretical results is not high, since a number of crude approximations were made in the calculations. According to [6], the capacitance is equal to

$$C = \frac{\varkappa^2 \lambda d^2}{8\pi^4}. \tag{8}$$

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

The dependence of the capacitance on temperature is connected with $1/T$ from $\varkappa^2$ and with the dependence $\lambda(T)$. As noted above, $\lambda(T)$ increases with temperature, and the charge distribution becomes less diffuse. This may explain the observed increase of capacitance with temperature. Our treatment of X-ray diffraction patterns [10] relating to liquid cesium at different temperatures showed that $\lambda_1 = 0.22$ at $t_1 = 30°$, and $\lambda_2 = 0.33$ at $t_2 = 300°$, i.e., λ increases with T. The absence of similar data for salt melts deprives us of the possibility of carrying out a quantitative comparison of the theory with experimental data concerning the dependence of capacitance on temperature. Moreover, in a real melt the anions and cations have different sizes. It follows from experiment [2] that the nature of the components of the melt, which can be roughly characterized by the sizes of the corresponding ions, has 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 kind of ions. It should also be noted that the approximation of the true binary function by expression (6), which contains only two parameters—λ and d—is too crude for describing the dependence on the nature of the particles.

We are grateful to Academician A. N. Frumkin, Corresponding Member of the Academy of Sciences of the USSR V. G. Levich, D. I. Leikis, and E. A. Ukshe for useful discussions.

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Received
2 IV 1964

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