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THEORY OF THE DIFFUSE PART OF THE DOUBLE LAYER IN SOLID ELECTROLYTES

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1. The distribution of the charge in the diffuse part of the double layer in solutions of electrolytes is usually described within the framework of the approximation of the self-consistent field of the Gouy-Chapman theory [1, 2] (Debye-Huckel [3]). In particular, the capacity of the region of the space charge C , calculated by means of this theory, is given by a familiar expression [1, 2], which in the simplest case of an I-I electrolyte has the form

$$C = C_0 \operatorname{ch} \psi_0/2, \quad C_0 = \epsilon/4\pi\kappa^{-1}. \quad (1)$$

Here, $\kappa^{-1} = (8\pi e^2 n_\infty / \epsilon kT)^{-1/2}$ is the Gouy (Debye) length, ϵ is the static dielectric constant, e is the charge of the electron, n_∞ is the concentration (in cm^{-3}) of ions of the same sign at a distance from the electrode in the depth of the solution, k is the Boltzmann constant, T is the absolute temperature, and ψ_0 is the potential of the boundary of the diffuse part of the double layer (the ψ' potential), measured in units of kT/e .

The aim of the present work was to examine the characteristic features of the diffuse part of the double layer in solid electrolytes. In particular, it is found that the capacity of the diffuse layer in this case differs from that given by Eq. (1). The physical reasons for this difference in the final analysis are determined by two features. Firstly, the concentration asymmetry of the charge carriers: The mobile species in solid electrolytes are generally charges of the same sign (usually cations), analogous to those in highly alloyed semiconductors with conductivity of the unipolar type [4]. Secondly, solid electrolytes should show the effect of lattice saturation, that is the concentration of carriers is limited by the fixed number of accessible positions (cells) in the crystal lattice.

2. We shall start from the expression for the free energy of unit volume of a solid electrolyte F , associated with cation disorder, under conditions where there is an external electric field.

$$F = E_1 n_1 + E_2 (N - n_2) + e\varphi (n_1 - n_2) - kT \ln \left\{ \frac{N!N'!}{(N - n_2)!n_2!(N' - n_1)!n_1!} \right\}. \quad (2)$$

Here, $n_1(x)$ is the number of cations situated in the interstices, and the total number of interstices in unit volume is equal to N' ; $n_2(x)$ is the number of vacant cation sites (vacancies), and the total number of such sites in unit volume is equal to N (usually, $N' \gg N$, see [5] for the case where $N' = N$); $E_1(E_2)$ is the energy of the introduction (or removal) of a cation into an interstice (from a site), and $E_1 - E_2 \equiv w > 0$ is the energy of formation of one Frenkel defect [6]; φ is the potential of the electrostatic field inside the crystal; the values of n_1 , n_2 , and φ depend on the coordinate x ; the x axis is taken as perpendicular to the plane of the crystal face, which corresponds to the coordinate $x = 0$, and is directed into the crystal (solid electrolyte). The last term in Eq. (2) corresponds to the configurational entropy [6, 7]; the expression under the logarithm sign is the number of ways in which n_1 cations and n_2 vacancies can be distributed among N' interstices and N sites.

In the region of the bulk charge there is no local electrical neutrality, and the quantities n_1 and n_2 are independent. We introduce the electrochemical (chemical in the terminology of [3]) potentials of the cations in the interstices μ_1 and the cation vacancies μ_2 .

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$$\begin{aligned}\mu_1 &= \partial F / \partial n_1 = E_1 + e\varphi + kT \ln[n_1 / (N' - n_1)], \\ \mu_2 &= \partial F / \partial n_2 = -E_2 - e\varphi + kT \ln[n_2 / (N - n_2)].\end{aligned}\quad (3)$$

The condition of "chemical" equilibrium, $\mu_1 + \mu_2 = 0$, which takes account of the effect of recombination of the cations and vacancies, makes it possible to rewrite Eq. (3) in the form

$$n_1 = n_\infty \frac{N' e^{-e\varphi/kT}}{n_\infty (e^{-e\varphi/kT} - 1) + N'}, \quad n_2 = n_\infty \frac{N e^{e\varphi/kT}}{n_\infty (e^{e\varphi/kT} - 1) + N}.$$
 (4)

Here, $n_\infty \equiv n_1(\infty) \equiv n_2(\infty)$, where $n_1(\infty)$ and $n_2(\infty)$ are the concentrations of the cations and vacancies in the depth of the crystal, that is at $\varphi = 0$ they are equal to one another as a consequence of the electrical neutrality condition. The value of n_∞ , according to Eq. (3) is related to the parameters of the system by the following expression

$$n_\infty = N' / [1 + e^{(E_1 - \mu_1)/kT}] = N / [1 + e^{-(E_2 + \mu_1)/kT}], \quad n_\infty^2 / (N - n_\infty)(N' - n_\infty) = e^{-w/kT}.$$
 (5)

3. We can now take account of the fact that, from the complete analogy with the Gouy-Chapman theory, the potential $\varphi(x)$ and the values of $n_1(x)$ and $n_2(x)$ "tune" one another. This leads to a self-consistent equation of the form

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi}{\varepsilon} e[n_1(\varphi) - n_2(\varphi)]$$
 (6)

(ε is the static dielectric constant of the crystal) with the boundary conditions $\varphi|_{x=0} = \varphi_0$, $\varphi|_{x=\infty} = 0$.

It should be noted that with allowance for Eq. (4), the self-consistent equation (6) differs from the Poisson-Boltzmann equation usually obtained (see [1-3, 5, 7]). The dependence of the concentrations n_1 and n_2 on φ obtained in the problem being considered (see Eq. (4)) is described not by a Boltzmann distribution but by a distribution of the Fermi type, which is at the same time physically related to the effect of lattice saturation, as can be seen from Eq. (3). It may also be noted that the parameters of the distributions (4) of the Fermi type for the cations in the interstices and the vacancies are different; this is a reflection of the concentration asymmetry mentioned above.

By integrating Eq. (6) and taking account of the boundary conditions, we obtain the charge of the diffuse layer Q :

$$Q = e \int_0^\infty (n_1 - n_2) dx = \int_{\varphi_0}^0 \frac{(n_1 - n_2) d\varphi}{(d\varphi/dx)},$$
 (7)

where

$$\frac{d\varphi}{dx} = -(\operatorname{sgn} \varphi_0) \left[\frac{8\pi e}{\varepsilon} \int_{\varphi_0}^0 d\varphi (n_2 - n_1) \right]^{1/2}.$$
 (8)

Using the definition of the differential capacity of the diffuse layer $C = -dQ/d\varphi_0$, we obtain from Eqs. (7) and (8)

$$C = \frac{C_0}{2} \frac{\{e^{\psi_0} [1 + \gamma(e^{\psi_0} - 1)] - e^{-\psi_0} [1 + \gamma'(e^{-\psi_0} - 1)]\} \operatorname{sgn} \psi_0}{\{\gamma^{-1} \ln[\gamma(e^{\psi_0} - 1) + 1] + \gamma'^{-1} \ln[\gamma'(e^{-\psi_0} - 1) + 1]\}^{1/2}}.$$
 (9)

Here, $C_0 \equiv \varepsilon/4\pi\kappa^{-1}$ (see Eq. (1)), $\psi_0 \equiv e\varphi_0/kT$ is the dimensionless potential, $\gamma = n_\infty/N$, $\gamma' = n'_\infty/N'$, $0 \leq \gamma' \leq \gamma \leq 1$. Equation (9) is exact within the framework of the model adopted.

4. We can now calculate approximately the nature of the $C(\psi_0)$ relationship in different ranges of change in the potential ψ_0 , assuming that $\gamma^{-1} \gg 1$ and $\gamma'^{-1} \gg 1$.

I. We assume that $|\psi_0| \ll 1$. It then follows from Eq. (9) that

$$C_I = C_0 \left[1 - \frac{\gamma + \gamma'}{4} - \frac{\gamma - \gamma'}{2} \psi_0 + \frac{5\psi_0^2}{4} \right].$$
 (10)

It follows from Eq. (10) that the minimum value of $C(\psi_0)$ is reached at $\psi_0^{\min} = 6(\gamma - \gamma')/5$ and is equal to $C^{\min} = C_0[1 - (\gamma + \gamma')/4 - 3(\gamma - \gamma')^2/10]$, so that $C^{\min} < C_0$ (Fig. 1).

II. We assume that $1 \ll \psi_0 \ll \ln \gamma^{-1}$ and $\ln \gamma' \ll \psi_0 \ll -1$ (this is possible, if $\gamma, \gamma' \ll 1$). We then obtain from Eq. (9)

$$C_{II} = \begin{cases} C_0 \operatorname{ch}(\psi_0/2) [1 - 3/4 \gamma e^{\psi_0}] & \text{for } \ln \gamma^{-1} \gg \psi_0 \gg 1; \\ C_0 \operatorname{ch}(\psi_0/2) [1 - 3/4 \gamma' e^{-\psi_0}] & \text{for } \ln \gamma' \ll \psi_0 \ll -1. \end{cases}$$
 (11)

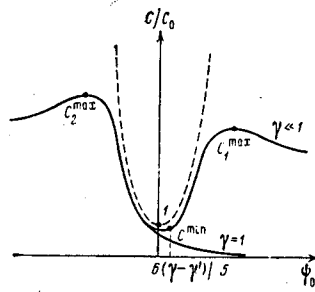


Fig. 1

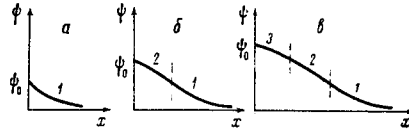


Fig. 2

Fig. 1. Schematic form of the dependence of the capacity of the diffuse layer in a solid electrolyte on the potential - continuous curves; broken line - capacity of the diffuse layer in a liquid electrolyte (see Eq. (1)).

Fig. 2. Schematic form of the coordinate distribution of the potential in the diffuse layer in a solid electrolyte.

In this range C_{II} , with an accuracy up to the small corrections given in the square brackets, is an even function (the asymmetry is slight) and coincides with Eq. (1).

III. We assume that $\psi_0 \gg \ln \gamma^{-1} > 0$ or $\psi_0 \ll \ln \gamma' < 0$. We then have

$$C_{III} = \begin{cases} C_0 \frac{1}{\{\gamma (\ln \gamma + \psi_0)\}^{1/2}}, & \psi_0 \gg \ln \gamma^{-1}; \\ C_0 \frac{1}{\{\gamma' (\ln \gamma' + |\psi_0|)\}^{1/2}}, & \psi_0 \ll \ln \gamma'. \end{cases} \quad (12)$$

It should be noted that the quantity $C(\psi_0)$ increases rapidly in region II and begins to decrease slowly in region III (Fig. 1).*

From Eq. (9) for $\gamma e^{\psi_0} \gg 1$ we readily obtain

$$C_1^{max} = 0.319 C_0 / \sqrt{\gamma}, \quad \psi_{01}^{max} = \ln 2.75 / \gamma; \quad C_2^{max} = 0.319 C_0 / \sqrt{\gamma'}, \quad \psi_{02}^{max} = -\ln 2.75 / \gamma'.$$

5. From Eq. (8) it is possible to obtain in implicit form the distribution of the potential in the diffuse layer of a solid electrolyte

$$\kappa x = (\text{sgn } \psi_0) \cdot \int_{\psi_0}^{\psi} d\psi \{ \gamma^{-1} \ln [\gamma (e^{\psi} - 1) + 1] + \gamma'^{-1} \ln [\gamma' (e^{-\psi} - 1) + 1] \}^{-1/2}. \quad (13)$$

We can now examine the nature of the distribution of the potential $\psi(x)$ along the coordinate x (to be definite, we shall assume that $\psi_0 > 0$; the distribution for $\psi_0 < 0$ is analogous).

I. If $|\psi_0| \ll 1$, we obtain from Eq. (13) $\psi_1 = \psi_0 \exp(-\kappa x)$. The characteristic length n_1 at which the potential changes is here equal to κ^{-1} (Fig. 2a).

II. If $\ln(1/\gamma) \gg \psi_0 \gg 1$, the coordinate distribution $\psi(x)$ has two characteristic sections (Fig. 2b). In the first, $\psi \ll 1$ and decreases exponentially with the characteristic length l_1 . In the second, $\psi_0 \gg \psi \gg 1$ and we obtain from Eq. (13) $\kappa x = \ln [(e^{\psi_0} - 1)(e^{\psi_{II}} + 1) / (e^{\psi_0} + 1)(e^{\psi_{II}} - 1)]$. The characteristic length l_2 for the decrease in ψ is given in this section by the expression $l_2 = \kappa^{-1} / 2 \text{sh}(\psi_0/2)$.

III. If $\psi_0 \gg \ln \gamma^{-1}$, the distribution of the potential has three characteristic sections (Fig. 2c): 1) $\psi \ll 1$; 2) $1 \ll \psi \ll \ln \gamma^{-1}$; 3) $\ln \gamma^{-1} \ll \psi \ll \psi_0$. In section (3) we obtain from Eq. (13) $\psi_{III} = \psi_0 - \sqrt{\psi_0 \kappa} / \sqrt{\gamma} + x^2 \kappa^2 / 4 \gamma$, $l_3 = \sqrt{\psi_0 \gamma} \cdot \kappa^{-1}$. The other two sections are analogous to those considered above.

It should be noted that l_2 decreases with increase in ψ_0 , and $l_2 < l_1$, whereas l_3 increases together with ψ_0 , and $l_3 > l_2$. This naturally corresponds to the dependence of C on ψ_0 found above, with allowance for the fact that we always have $C \sim C_0 \kappa^{-1} l^{-1}$, where l gives the dimensions of the region of the bulk charge.

*It should be emphasized that the "inflections" on the $C(\psi_0)$ curves are here related to the effect of lattice saturation, and not to the influence of the capacity of the compact part of the double layer (see, for example, [8]); the last effect, in particular, does not determine the dependence of C on ψ_0 at high values of $|\psi_0|$.

6. We shall deal separately with the case where $n_{\infty}/N \equiv \gamma = 1$, which may correspond to solid electrolytes with an extremely high bulk concentration of mobile carriers. Since usually $N' \gg N$, it follows that $\gamma' \ll 1$. The asymmetry noted above is here revealed most strongly. Thus at $\psi_0 > 0$, the region II, which corresponds to $1 \ll \psi_0 < \ln \gamma^{-1}$, is "compressed", so that region I in fact adjoins region III. At the same time, for $\psi_0 < 0$, as before, there exist three characteristic regions. As γ approaches unity, the quantity $C_1^{\max}$ decreases, and the curve $C(\psi_0)$ in the range $\psi_0 > 0$ is flattened. In the limit $\gamma = 1$, a maximum is not observed (see Fig. 1). If in addition we have, formally, $N'/N \rightarrow \infty$ (or $\gamma' \rightarrow 0$), then $C(\psi_0)$ decreases monotonically for all values of ψ_0 and is given by the expression

$$C(\psi_0) = \frac{C_0}{2} \frac{(1 - e^{-\psi_0})}{[\psi_0 + e^{-\psi_0} - 1]^{1/2}}, \quad (14)$$

which coincides with the expression for the capacity of alloyed semiconductors having conductivity of the unipolar type [9]. Thus the limit $\gamma = 1$, $\gamma' = 0$ corresponds to the unipolar model of solid electrolytes. The symmetrical case $\gamma = \gamma'$ was examined in [10].

In conclusion it should be emphasized that although the details of the behavior of the capacity examined in the present work are related to the choice of model, the main results obtained, namely the effect of lattice saturation and the asymmetry of the dependence of the capacity on potential, are evidently sufficiently general in character. These effects should also be revealed in the kinetics of charge transfer through the boundary of a solid electrolyte.

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