

The concentration variation of the temperature of the maxima shown in Fig. 3 for potassium chloride may be explained by a relative increase in the number of associated species with increase in the electrolyte concentration. A similar explanation may be given for the descending branch of the curve for MgCl_2 and CaCl_2 , assuming that on association species such as MgCl^+ and CaCl^+ are mainly formed here. The subsequent increase in the temperature of the maxima with increase in concentration for MgCl_2 and CaCl_2 may be ascribed to the formation on association of more complex species which require a relatively smaller number of ions with high mobilities (for example, the formation of species of the type of MgCl_3^-).

The shape of the curve for CdSO_4 can be explained, similarly as that of the right-hand branch of the curve for MgCl_2 and CaCl_2 , by fact that initially CdSO_4 species are formed, followed by $[\text{Cd}(\text{SO}_4)_2]^{2-}$.

The authors thank Professor S. V. Gorbachev for his interest in the present work.

SUMMARY

1. Data have been obtained on the specific conductances of aqueous MgCl_2 , CaCl_2 , and SrCl_2 solutions at concentrations 0.05, 0.1, 0.25, 0.5, and 1 m and for 0.05 m BaCl_2 solution between 25° and 300°.
2. An equation of the type $\kappa = A c^k \exp[-B(T_M - T)^2/T]$ can be used for approximate calculations and interpolations for the salts investigated in the above temperature and concentration ranges.
3. Evidence is adduced in support of the hypothesis that the degree of dissociation of an electrolyte decreases with temperature.

THEORY OF THE ELECTRICAL DOUBLE LAYER IN CONCENTRATED SOLUTIONS. I. THE DIELECTRIC-SOLUTION INTERFACE

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Hitherto in setting up a theory of the electrical double layer at various interfaces, allowing for the discrete structure of the charge of specifically adsorbed ionic layers, it was assumed that the bulk concentrations of the electrolyte are either extremely high, when the fall in potential in the diffuse part of the double layer can be neglected, or very small, when the distribution of potential in the diffuse part may be described by a linearised Poisson-Boltzmann equation. Since in practice intermediate concentrations (of the order of 0.01–1 N) are encountered, it is of considerable interest to consider the diffuse part of the double layer with allowance for the effect of short-range interaction between ions at concentrations exceeding by several powers of ten those for which the Gouy-Stern theory is applicable. In the present work an attempt is made to do this for a dielectric-solution interface (a metal-solution interface will be examined in the next paper).

We shall find the distribution of potential $\psi(r)$ in the usual model of the double layer: region I ($x \leq -\beta$) is the dielectric; region II ($-\beta \leq x < \gamma$) is the dense part of the double layer; region III ($x > \gamma$) is the diffuse part of the double layer; the plane $x = 0$ contains the centres of the specifically adsorbed ions having the same charge z_0 . We shall solve the problem with the simplifying assumption that the space-charge density $\rho(r)$ in region III may be represented as the sum of the densities $\rho^{mn}(r)$ induced by each adsorbed ion separately. With this approximation

$$\psi(r) = \sum_{mn} \psi^{(mn)}(r),$$

where the potential $\psi^{(mn)}(r)$ satisfies the system of equations

$$\Delta \psi_1^{(mn)}(r) = 0; \Delta \psi_2^{(mn)}(r) = -\frac{4\pi e z_0}{D_2} \delta(x) \delta(y - y_{mn}) \delta(z - z_{mn});$$

$$\Delta \psi_3^{(mn)}(r) = -\frac{4\pi}{D_3} \rho^{(mn)}(r), \quad (1)$$

with the boundary conditions

$$|\psi_1^{(mn)}(-\infty, y, z)| < \infty; \psi_1^{(mn)}(-\beta, y, z) = \psi_2^{(mn)}(-\beta, y, z);$$

$$D_1 \frac{\partial \psi_1^{(mn)}}{\partial x}(-\beta, y, z) = D_2 \frac{\partial \psi_2^{(mn)}}{\partial x}(-\beta, y, z); \psi_2^{(mn)}(\gamma, y, z) = \psi_3^{(mn)}(\gamma, y, z);$$

$$D_2 \frac{\partial \psi_2^{(mn)}}{\partial x}(\gamma, y, z) = D_3 \frac{\partial \psi_3^{(mn)}}{\partial x}(\gamma, y, z); \psi_3^{(mn)}(\infty, y, z) = 0. \quad (2)$$

The subscripts 1, 2, 3 signify that the given quantity refers to regions I, II, and III respectively.

Using the symmetry of the problem [Eqns. (1) and (2)] with respect to rotation about an axis passing through an

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adsorbed ion perpendicular to the $x = 0$ plane as well as the boundary conditions at infinity, we find the solution in the form

$$\psi_1^{(mn)}(r) = \int_0^\infty A_1(\lambda) e^{\lambda x} J_0(\lambda R_{mn}) \lambda d\lambda, \quad (3a)$$

$$\psi_2^{(mn)}(r) = \int_0^\infty \left\{ A_2(\lambda) e^{\lambda x} + B_2(\lambda) e^{-\lambda x} + \frac{e z_0}{D_2 \lambda} e^{-\lambda |x|} \right\} J_0(\lambda R_{mn}) \lambda d\lambda, \quad (3b)$$

$$\psi_3^{(mn)}(r) = \frac{1}{\pi D_2} \int_0^\infty \int_{-\infty}^\infty \frac{p^{(mn)}(k_x \lambda)}{k_x^2 + \lambda^2} e^{-i k_x x} J_0(\lambda R_{mn}) \lambda d k_x d \lambda, \quad (3c)$$

where $J_0(\lambda R_{mn})$ is a zero-order Bessel function of the first kind, $R_{mn}^2 = (y - y_{mn})^2 + (z - z_{mn})^2$, $p^{(mn)}(k_x \lambda)$ is the Fourier component of the charge density, and $A_1(\lambda)$, $A_2(\lambda)$, and $B_2(\lambda)$ are arbitrary functions. Below we shall derive the relation

$$\int_{-\infty}^\infty \frac{p^{(mn)}(k_x \lambda)}{k_x^2 + \lambda^2} e^{-i k_x x} d k_x = \pi D_2 A_3(\lambda) \{ a(\lambda) \exp[-\xi_1(\lambda)x] - b(\lambda) \exp[-\xi_2(\lambda)x] \}, \quad (4)$$

where $a(\lambda)$, $b(\lambda)$, $\xi_1(\lambda)$, and $\xi_2(\lambda)$ are known functions, and $A_3(\lambda)$ is an arbitrary function, the boundary conditions (2) permitting A_1 , A_2 , B_2 , and A_3 to be expressed in terms of a , b , ξ_1 , and ξ_2 :

$$A_1 = \eta e^{2\lambda\beta} (1 - \omega_1) (e^{2\lambda\gamma} - \omega_2) (\omega_1 \omega_2 - e^{2\lambda\delta})^{-1}, \quad (5)$$

$$A_2 = \eta \omega_2 (\omega_1 - e^{2\lambda\beta}) (\omega_1 \omega_2 - e^{2\lambda\delta})^{-1}, \quad (6)$$

$$B_2 = \eta \omega_1 (\omega_2 - e^{2\lambda\gamma}) (\omega_1 \omega_2 - e^{2\lambda\delta})^{-1}, \quad (7)$$

$$A_3 = \eta (1 - \omega_2) (e^{2\lambda\beta} - \omega_1) (\omega_1 \omega_2 - e^{2\lambda\delta})^{-1} [a e^{-\gamma(\lambda + \xi_2)} - b e^{-\gamma(\lambda + \xi_1)}]^{-1}, \quad (8)$$

where

$$\delta = \beta + \gamma; \quad \eta = -\frac{e z_0}{D_2 \lambda}; \quad \omega_1 = \frac{D_1 - D_2}{D_1 + D_2};$$

$$\omega_2 = \frac{a(D_2 \xi_1 - D_2 \lambda) \exp[\gamma(\lambda - \xi_1)] - b(D_2 \xi_2 - D_2 \lambda) \exp[\gamma(\lambda - \xi_2)]}{a(D_2 \xi_1 + D_2 \lambda) \exp[\gamma(\lambda - \xi_1)] - b(D_2 \xi_2 + D_2 \lambda) \exp[\gamma(\lambda - \xi_2)]}. \quad (9)$$

We shall seek the functions $a(\lambda)$, $b(\lambda)$, $\xi_1(\lambda)$, and $\xi_2(\lambda)$ by expanding the correlation functions, describing the statistical distribution of ions in the diffuse parts of the double layer, in power series in terms of parameters whose physical significance will be elucidated below. The main principles of this method were first laid down by Kirkwood *et al.*^{1,2}, but they used the ionic charge as the series expansion parameter, which made the correctness of the method doubtful and did not permit an assessment of its applicability.

Let region III occupy a volume V and contain N ions belonging to classes $a_1, a_2, \dots, a_m$. We shall describe the statistical properties of these ions by the set of correlation functions $F_{a_1 \dots a_S}(r_1, \dots, r_S)$ related to Gibbs' distribution in the following way:

$$F_{a_1 \dots a_S}(r_1, \dots, r_S) = \frac{V^S \int \exp(-U_N(r_1, \dots, r_N)/kT) dr_{S+1} \dots dr_N}{\int \exp(-U_N(r_1, \dots, r_N)/kT) dr_1 \dots dr_N},$$

where $U_N(r_1, \dots, r_N)$ is the potential energy of all the ions. For the purposes of our problem, it is sufficient to know the unary functions $F_a(r)$, since the latter are related to the space charge density: if c_a is the bulk concentration of ions of type a , then $\rho(r) = e \sum_a c_a z_a F_a(r)$. We shall write the potential energy in the following form:

$$U_N(r_1, \dots, r_N) = \sum_{i < k} \{ \Phi_{a_i a_k}^{(e)}(r_i, r_k) + \Phi_{a_i a_k}^{(s)}(r_i, r_k) \} + \sum_i \{ U_{a_i}^{(e)}(r_i) + U_{a_i}^{(s)}(r_i) \},$$

where the first sum represents the potential energy of interionic interaction, and the second the energy of ions in the

external field; the superscript s denotes short-range interactions and the superscript e electrostatic interactions. Let us consider the electrostatic energy of an arbitrary ion of class a_1 with charge z_1 located in the vicinity of point r_1 , and let us denote this energy by $e z_1 \varphi_1$:

$$e z_1 \varphi_1 = U_{a_1}^{(e)}(r_1) + \frac{e^2 z_1}{D_2} \sum_{k=2}^N \frac{z_k}{|r_1 - r_k|}.$$

The quantity φ_1 represents the electrostatic potential at point r_1 due to the external field and all the ions in region III with the exception of the ion under consideration. We shall show how this quantity is related to the external field and the average bulk concentration of the electrolyte c . We shall denote by r_0 the mean effective radius of interionic short-range interaction, by $\bar{r} = c^{-1/3}$ the mean distance between the ions, and we shall assume that the parameter $\epsilon_1 = (r_0/\bar{r})^3$ is small. We shall further assume that short-range interaction between ions can be described with adequate accuracy in terms of the rigid sphere model, *i.e.*

$$\Phi^{(s)}(r_1, r_2) = \begin{cases} \infty & |r_1 - r_2| < r_0, \\ 0 & |r_1 - r_2| > r_0. \end{cases} \quad (10)$$

Then, as shown by approximate calculation (see, for example, Ref. 3), when the conditions

$$\epsilon_2 = \frac{e^2 |z_1 z_2|}{D_2 k T} c^{1/2} \ll 1 \text{ and } r_0 \gg \frac{e^2 |z_1 z_2|}{2 D_2 k T}$$

hold in the bulk of the solution, where the unary functions may be regarded as equal to unity, the probability of finding an ion with charge z_2 at a distance r from the nearest ion with an opposite charge z_1 is a maximum when $r \sim c^{-1/3}$. This means that with the assumptions made above the electrostatic energy of any ion in the bulk of the solution may be estimated by means of the relation

$$|e z_1 \varphi_1|_{|r_1| \gg r_0} \ll \frac{e^2 |z_1|^2}{D_2} c^{1/2}.$$

The external field has a significant influence on the electrostatic energy of the ions located near the plane $x = \gamma$, and if the potential $\psi_3(\gamma, y, z)$ changes little in this plane, retaining its order of magnitude, then

$$|e z_1 \varphi_1|_{|x_1 \sim \gamma} \sim |e z_1 \bar{\psi}_3(\gamma)|,$$

where $\bar{\psi}_3(\gamma)$ is the mean potential of the plane $x = \gamma$. If we introduce into the problem a third small parameter $\epsilon_3 = |e z_1 \bar{\psi}_3(\gamma)|/kT$, then the following condition will hold over the entire region III:

$$\frac{|e z_1 \varphi_1|}{kT} \ll 1.$$

For aqueous uni-univalent electrolyte solutions at $T = 300^\circ \text{K}$ and $r_0 = 4.2 \text{ \AA}$, the parameters ϵ_1 and ϵ_2 have the following values: $\epsilon_1 = 0.04 c'$ and $\epsilon_2 = 0.6 c'^{1/3}$, where $c' = 10^3 c/N_0$ is the molar concentration and N_0 the Avogadro number. It should be noted that the Bogolyubov parameter⁴, in terms of which the first-approximation linearised Poisson-Boltzmann equation is obtained, is in this case given by $\epsilon_4 = \kappa^3 c^{-1} = 54 c'^{1/2}$, *i.e.* in order that it be small it is necessary that the order of magnitude of the concentration should not exceed 10^{-4} M . Starting with the above estimates of the parameters and assuming that $\epsilon_2 \sim \epsilon_3 \gg \epsilon_1$, we shall solve the problem with an accuracy determined by retention of terms in ϵ_2 and ϵ_3 of the first order of smallness and terms in ϵ_1 of the zero order of smallness. Expanding the unary function in series in powers of $e z_1 \varphi_1/kT$,

neglecting short-range interaction between the external field and the ions in solution (with the condition $\gamma - r_0 > 0$) and assuming that the electrolyte is binary and symmetrical, we obtain as the initial approximation

$$F_a(r) = 1 - \frac{ez_1}{kT} H(r), \quad (11)$$

where the function $H(r)$ satisfies the equation

$$\Delta \left\{ H(r) + \frac{\kappa^2}{4\pi} \int_{\kappa > r} G(|r-r'|) H(r') dr' \right\} = 0, \quad (12)$$

where

$$G(|r-r'|) = \frac{\exp\{-\Phi^{(s)}(|r-r'|)/kT\}}{|r-r'|}; \quad \kappa^2 = \frac{4\pi e^2}{D_0 kT} \sum_b c_b z_b^2.$$

In the derivation of Eqn. (12) it was assumed that the nature of short-range interaction between ions in solution is independent of their type and that the correlation between two ions in region III, one of which has lost its charge, may be described by a binary function with "superposition" approximation:

$$F_{ab}(r_1, r_2) = F_a(r_1) F_b(r_2) F_{ab}^{(0)}(|r_1 - r_2|),$$

where the function $F_{ab}^{(0)}(|r_1 - r_2|)$ describes the correlation of ions in the bulk of the solution, due solely to their short-range interaction. From Eqn. (11), it follows that

$$\rho(r) = -\frac{D_0 \kappa^2}{4\pi} H(r). \quad (13)$$

The linearity of Eqn. (12) makes it possible to represent the charge density induced in region III as the sum of densities induced by each of the adsorbed charges separately, as has been done from the very beginning.

We shall now denote by $H^{(mn)}(r)$ the function related to $\rho^{(mn)}(r)$ by Eqn. (13). This function must satisfy Eqn. (12), tending to zero when $|r| \rightarrow \infty$ and when $z_0 \rightarrow 0$, and also must satisfy the condition of electroneutrality of the double layer. We shall now obtain a mathematical expression for this last condition. If the average surface density of the adsorbed charges in the plane $x = 0$ is given by

$$\sigma = ez_0 \lim_{S \rightarrow \infty} \frac{1}{S} \iint_{-\infty}^{\infty} dy dz \sum_{mn} \delta(y - y_{mn}) \delta(z - z_{mn}),$$

the condition of electroneutrality of the double layer can be written as follows:

$$-\sigma = -\frac{D_0 \kappa^2}{4\pi} \lim_{S \rightarrow \infty} \frac{1}{S} \iint_{-\infty}^{\infty} dy dz \sum_{mn} \int_{\gamma}^{\infty} H^{(mn)}(r) dx.$$

Since $H^{(mn)}(r) = H^{(mn)}(x, R_{mn})$, the Fourier integral of this function can be represented in the following form:

$$H^{(mn)}(r) = \int_0^{\infty} H(x, \lambda) J_0(\lambda R_{mn}) \lambda d\lambda.$$

Using the definition of the density σ , it can be readily shown that the following relation holds for any function $Q(x, \lambda)$ (see, for example, Refs. 5 and 6):

$$\lim_{S \rightarrow \infty} \frac{1}{S} \iint_{-\infty}^{\infty} dy dz \sum_{mn} \int_0^{\infty} Q(x, \lambda) J_0(\lambda R_{mn}) \lambda d\lambda = \frac{2\pi\sigma}{ez_0} Q(x, 0). \quad (14)$$

Using Eqn. (14), we now obtain the following expression for the electroneutrality condition:

$$\int_{\gamma}^{\infty} H(x, 0) dx = \frac{2ez_0}{D_0 \kappa^2}. \quad (15)$$

The functions $H^{(mn)}(r)$ will be sought on the assumption that short-range interaction between ions is described by Eqn. (10). In order to solve Eqn. (12), we shall additionally define the functions $H^{(mn)}(r)$ over the entire space, putting them in the form

$$H^{(mn)}(r) = H_p^{(mn)}(r) + H_n^{(mn)}(r);$$

$H_p^{(mn)}(r) = 0$ when $x < \gamma$, and when $x \geq \gamma$ the function satisfies the same condition as does $H^{(mn)}(r)$; $H_n^{(mn)}(r) = 0$ when $x > 0$ and tends to zero quite rapidly when $x \rightarrow -\infty$ [in view of Eqn. (13), the physical significance of $H^{(mn)}(r) = 0$ in the range $0 < x\gamma$ is that there are no charges in this range]. Eqn. (12) then assumes the form

$$\Delta \left\{ H_p^{(mn)}(r) + H_n^{(mn)}(r) + \frac{\kappa^2}{4\pi} \int G(|r-r'|) H_p^{(mn)}(r') dr' \right\} = 0$$

with integration over the entire space, and can be readily solved by means of Fourier transforms:

$$H_p^{(mn)}(r) = \int_0^{\infty} H_p(x, \lambda) J_0(\lambda R_{mn}) \lambda d\lambda, \quad (16)$$

where

$$H_p(x, \lambda) = -\frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{k^2 h_n(k) \exp(-ik_x x)}{k^2 + \kappa^2 \cos(kr_0)} dk_x \quad (-\infty < x < \infty); \quad (17)$$

$$h_n(k) = 2\pi \int_0^{\infty} J_0(\lambda R) R dR \int_{-\infty}^0 H_n^{(mn)}(x, R) \exp(ik_x x) dx. \quad (18)$$

Since $H_n^{(mn)}(r)$ decreases fairly rapidly when $x \rightarrow -\infty$, then in the lower half-plane of the complex variable k_x the function $h_n(k)$ has no poles and uniformly tends to zero when $|k_x| \rightarrow \infty$. According to Jordan's lemma, integral (17) is proportional to the sum of the residues of the integrand at the point k_{xj} ($j = 1, 2, 3, \dots$), which represent zeros of the denominator, located in the lower half-plane. Using the condition $H_p^{(mn)}(r) = 0$ when $x < \gamma$ and introducing the notation

$$C_j = \frac{ih_n(k_{xj}, \lambda)}{2\pi k_{xj}} (k_{xj}^2 + \lambda^2) \left[2 - \frac{\kappa^2 r_0}{\sqrt{k_{xj}^2 + \lambda^2}} \sin(r_0 \sqrt{k_{xj}^2 + \lambda^2}) \right]^{-1},$$

we obtain

$$\sum_j C_j \exp\left(-y_j \frac{x}{r_0}\right) = \begin{cases} H_p(x, \lambda) & \gamma \leq x < \infty, \\ 0 & 0 < x < \gamma, \end{cases} \quad (19)$$

where $y_j = y_j(\lambda, \kappa, r_0)$ are the roots of the equation

$$y^2 - (\lambda r_0)^2 - (\kappa r_0)^2 \cosh \sqrt{y^2 - (\lambda r_0)^2} = 0 \quad (20a)$$

located in the right half-plane. We shall leave in the sum (19) only two terms, containing y_1 and y_2 with the minimum real components (for given λ , κ , and r_0). This approximation, which is fairly satisfactory for $x \geq r_0$ ($\text{Re } y_2 - \text{Re } y_1$)⁻¹ makes it possible to find the relation between the coefficients C_1 and C_2 . Denoting by $C_1^{(0)}$ and $C_2^{(0)}$ the values of these coefficients at $\lambda = 0$, we obtain the approximate equality

$$H_p(x, 0) \approx \sum_{j=1}^2 C_j^{(0)} \exp\left(-y_j^{(0)} \frac{x}{r_0}\right) \quad (\gamma \leq x < \infty). \quad (19^*)$$

where $y_j^{(0)}$ are the roots of the equation

$$y^2 - (\kappa r_0)^2 \cosh y = 0, \quad (20b)$$

located in the right half-plane and having the minimum real components (for given κ and r_0). These roots were found by Stillinger and Kirkwood². On the other hand, according to Eqn. (17),

$$H_p(x, 0) = -\frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{k_x^2 h_n(k_x) \exp(-ik_x x)}{k_x^2 + \kappa^2 \cos(k_x r_0)} dk_x \quad (\gamma \leq x < \infty).$$

A direct check readily shows that the last expression is a solution of the equation

$$\frac{d^2}{dx^2} \{H_p(x, 0) + H_n(x, 0)\} = \frac{\kappa^2}{2} \int_{-\infty}^{\infty} \{\delta(x-x'+r_0) + \delta(x-x'-r_0)\} H_p(x', 0) dx'. \quad (21)$$

On carrying out the integration on the right-hand side of Eqn. (21), we obtain the following condition for $H_p(x, 0)$:

$$\left. \frac{d^2 H_p(x, 0)}{dx^2} \right|_{x=\gamma} = \frac{\kappa^2}{2} H_p(x, 0) \Big|_{x=\gamma+r_0}, \quad (22)$$

which together with Eqn. (15) defines $C_1^{(0)}$ and $C_2^{(0)}$:

$$C_1^{(0)} = \frac{2\epsilon_3 y_1^{(0)} y_2^{(0)} \exp[y_2^{(0)} + (\gamma/r_0) y_1^{(0)}]}{D_3 \kappa^2 r_0 (y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)})}, \quad (23a)$$

$$C_2^{(0)} = -\frac{2\epsilon_3 y_1^{(0)} y_2^{(0)} \exp[y_1^{(0)} + (\gamma/r_0) y_2^{(0)}]}{D_3 \kappa^2 r_0 (y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)})}. \quad (23b)$$

If there exists a value of κ_1 satisfying the inequalities $r_0(\operatorname{Re} y_3 - \operatorname{Re} y_1)^{-1} \leq \kappa_1 < \gamma$, then according to Eqn. (19), the following approximate equality holds:

$$\sum_{j=1}^2 C_j \exp(-y_j \frac{x_1}{r_0}) = 0,$$

whence

$$C_2 = -C_1 \exp\left\{(y_2 - y_1) \frac{x_1}{r_0}\right\}. \quad (24)$$

From the condition

$$\lim_{\lambda \rightarrow 0} \frac{C_2}{C_1} = \frac{C_2^{(0)}}{C_1^{(0)}}$$

we find by means of Eqn. (23) that $\kappa_1 = \gamma - r_0$.

On substituting in Eqn. (4) the Fourier component $P^{(mm)}(\mathbf{k})$, related to $h_p(\mathbf{k})$ by Eqn. (13), and using Eqn. (24), we obtain

$$a(\lambda) = \left(\frac{\kappa r_0}{y_1^{(0)}}\right)^2, \quad (25)$$

$$b(\lambda) = \left(\frac{\kappa r_0}{y_2^{(0)}}\right)^2 \exp\left\{(y_2 - y_1) \left(\frac{\gamma}{r_0} - 1\right)\right\}, \quad (26)$$

$$r_0 \xi_j(\lambda) = y_j, \quad (j = 1, 2), \quad (27)$$

where y_j and $y_j^{(0)}$ are respectively the roots of Eqns. (20a) and (20b), located in the right-hand half-plane and having the minimum real components (for the given λ , κ , and r_0). Then, as can be readily verified, the right-hand side of Eqn. (8) becomes identical with the right-hand side of Eqn. (23a) at the limit $\lambda \rightarrow 0$. Let the roots of Eqn. (20b) have the form

$$y_j^{(0)} = x_j + i\beta_j \quad (j = 1, 2, \dots).$$

Putting $y_j = p_j + iq_j$, we obtain

$$p_j^2 = \frac{1}{2} \{V(x_j^2 - \beta_j^2 + \lambda^2 r_0^2) + 4x_j^2 \beta_j^2 + (x_j^2 - \beta_j^2 + \lambda^2 r_0^2)\}, \quad (28)$$

$$q_j^2 = \frac{1}{2} \{V(x_j^2 - \beta_j^2 + \lambda^2 r_0^2) + 4x_j^2 \beta_j^2 - (x_j^2 - \beta_j^2 + \lambda^2 r_0^2)\}. \quad (29)$$

As shown by the calculations of Stillinger and Kirkwood², in the region $\kappa r_0 \leq 1.03$ the roots $y_j^{(0)}$ are real, i.e. $\beta_j^2 = \alpha_j^2 + \lambda^2 r_0^2$ and $q_j^2 = 0$. In this case the minimum α_1 and α_2 unambiguously determine the solution of the problem. In the region $\kappa r_0 > 1.03$ each α_j corresponds to two complex conjugate roots $y_j^{(0)} = \alpha_j + i\beta_j$. Since at the limit $\lambda \rightarrow 0$ the coefficients A_1 , A_2 , B_2 , and A_3 must be determined by the root $y_j^{(0)}$, in order to find p_j and q_j it is sufficient to take two complex conjugate roots $y_{1,2}^{(0)} = \alpha_1 \pm i\beta_1$ with the minimum α_1 (for the given κr_0) and find by means of Eqns. (28) and (29) the corresponding two complex conjugate roots $y_{1,2} = p_1 \pm iq_1$.

We shall now find for regions I and III the distribution of potential averaged with respect to the coordinates y and z . From Eqn. (5), it follows that

$$A_1(0) = \frac{\epsilon_3}{D_3} \lim_{\lambda \rightarrow 0} (2\gamma - \frac{\partial \omega_3}{\partial \lambda}).$$

From Eqn. (9), we find

$$\frac{\partial \omega_3}{\partial \lambda} \Big|_{\lambda=0} = -2 \frac{D_3 r_0}{D_3} \frac{a(0) \exp[-(\gamma/r_0) y_1^{(0)}] - b(0) \exp[-(\gamma/r_0) y_2^{(0)}]}{a(0) y_1^{(0)} \exp[-(\gamma/r_0) y_1^{(0)}] - b(0) y_2^{(0)} \exp[-(\gamma/r_0) y_2^{(0)}]}. \quad (30)$$

Eqn. (23a), which defines the quantity $A_3(0)$, and Eqns. (14), (25), and (26) make it possible to find the average potentials

$$\bar{\psi}_1(x) = \frac{4\pi\sigma}{D_1} \left\{ \gamma + \frac{D_3 r_0}{D_3 y_1^{(0)} y_2^{(0)}} \frac{(y_2^{(0)})^2 \exp y_2^{(0)} - (y_1^{(0)})^2 \exp y_1^{(0)}}{y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}} \right\}, \quad (31)$$

$$\bar{\psi}_2(x) = \frac{4\pi\sigma r_0}{D_3 y_1^{(0)} y_2^{(0)}} \frac{(y_2^{(0)})^2 \exp[y_2^{(0)} + \frac{\gamma-x}{r_0} y_2^{(0)}] - (y_1^{(0)})^2 \exp[y_1^{(0)} + \frac{\gamma-x}{r_0} y_1^{(0)}]}{y_2^{(0)} \exp y_2^{(0)} - y_1^{(0)} \exp y_1^{(0)}}. \quad (32)$$

The jump of the average potential in region II is given by

$$\bar{\psi}_1(-\beta) - \bar{\psi}_2(\gamma) = \frac{4\pi\sigma\gamma}{D_3}. \quad (33)$$

In the limiting case $\kappa r_0 \ll 1$ Eqn. (20b) has two real roots: $y_1^{(0)} = \kappa r_0$ and $y_2^{(0)} = \ln[2/(\kappa r_0)^2]$, and Eqns. (31) and (32) assume respectively the following forms:

$$\bar{\psi}_1^{(0)} = \frac{4\pi\sigma}{D_1} \left(\gamma + \frac{D_3}{D_3 \kappa} \right); \quad \bar{\psi}_2^{(0)}(x) = \frac{4\pi\sigma}{D_3 \kappa} e^{-\kappa(x-\gamma)}.$$

The same result would have been obtained by putting in the initial system of Eqns. (1)

$$\rho^{mn}(r) = -\frac{D_3 \kappa^2}{4\pi} \psi_3^{(mn)}(r).$$

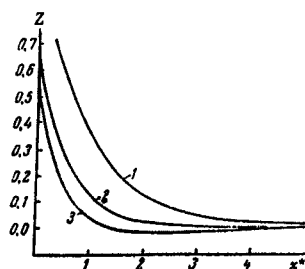
Consequently, when $\kappa r_0 \ll 1$ the distribution of potential in region III is described by a linearised Poisson-Boltzmann equation.

We shall now show what limitation is imposed on the external field by the condition that the parameter $\epsilon_3 = |e\bar{\psi}_3(\gamma)|/kT$. When $\kappa r_0 \ll 1$, we have $\bar{\psi}_3^{(0)}(\gamma) = 4\pi\sigma/D_3 \kappa$. When $\kappa r_0 > 1$, the two roots of Eqn. (20b) closest to the imaginary axis are conjugate complexes: $y_{1,2}^{(0)} = \alpha_1 \pm i\beta_1$, and from Eqn. (32) it follows that

$$\bar{\psi}_3(\gamma) = \bar{\psi}_3^{(0)}(\gamma) \frac{\kappa r_0}{\alpha_1^2 + \beta_1^2} \frac{(\alpha_1^2 - \beta_1^2) \sin \beta_1 + 2\alpha_1 \beta_1 \cos \beta_1}{\alpha_1 \sin \beta_1 + \beta_1 \cos \beta_1},$$

and, as shown by numerical calculation, the modulus of the multiplier of $\bar{\psi}_3^{(0)}(\gamma)$ is less than unity, so that the condition $\epsilon_3 \sim \epsilon_2 \ll 1$ signifies that

$$|\sigma| \leq \frac{\epsilon \kappa}{4\pi} c/\lambda.$$



For aqueous solutions of uni-univalent electrolytes at room temperature, we obtain

$$|\sigma| \leq 4.7 (c')^{1/2} \mu\text{C cm}^{-2}.$$

It is interesting to compare the behaviour of the potential (32) with that of the potential $\bar{\Psi}_3^{(0)}(x)$, which obeys the Gouy-Stern law. In order to demonstrate the sharp difference in the behaviour, we shall examine two relatively large numerical values of the parameter κr_0 : 1.03 and 1.15, which for $r_0 = 4.2 \text{ \AA}$ and $T = 300^\circ\text{K}$ correspond to the concentrations 0.59 and 0.75 M. From Ref. 2, we find that

$$y_{1,2}^{(0)} = \alpha_1 \pm i\beta_1; \quad \begin{array}{ll} \alpha_1 = 2.07; & \beta_1 = 0 \quad \text{when } \kappa r_0 = 1.03; \\ \alpha_1 = 1.92; & \beta_1 = 0.89 \quad \text{when } \kappa r_0 = 1.15. \end{array}$$

For convenience we shall now introduce the following notation:

$$Z^{(0)}(x) = \frac{\bar{\Psi}_3^{(0)}(x)}{\bar{\Psi}_3^{(0)}(\gamma)}; \quad Z(x) = \frac{\bar{\Psi}_3(x)}{\bar{\Psi}_3^{(0)}(\gamma)}; \quad x^* = \frac{x - \gamma}{r_0} > 0.$$

With this notation, the Gouy-Stern law and Eqn. (32) assume the following forms respectively:

$$\begin{aligned} Z(x^*) &= \exp(-\kappa r_0 x^*); \\ Z(x^*) &= \frac{\kappa r_0 (2 + \alpha_1 + \alpha_1 x^*)}{\alpha_1 (1 + x^*)} \exp(-\alpha_1 x^*) \quad (\kappa r_0 = 1.03); \\ Z(x^*) &= \frac{\kappa r_0 [(\alpha_1^2 - \beta_1^2) \sin(\beta_1 + \beta_1 x^*) + 2\alpha_1 \beta_1 \cos(\beta_1 + \beta_1 x^*)]}{(\alpha_1^2 + \beta_1^2) (\alpha_1 \sin \beta_1 + \beta_1 \cos \beta_1)} \exp(-\alpha_1 x^*) \quad (\kappa r_0 > 1.03). \end{aligned}$$

The Figure shows that $Z(x^*)$ decreases on going into the bulk of the solution much more rapidly than does $Z^{(0)}(x^*)$. When $\kappa r_0 = 1.03$, we find that even with $x^* = 3$ the function $Z(x^*)$ amounts to 0.5% of its value at the point $x^* = 0$, which is smaller by a power of ten than the corresponding value of the function $Z^{(0)}(x^*)$. When $\kappa r_0 = 1.15$, the function $Z(x^*)$ oscillates weakly, becoming zero first when $x^* \sim 2$ and then again when $x^* \sim 5$, but the maximum deviation from zero in the range $2 < x^* < 5$, where $Z(x^*) < 0$, amounts to only 0.7% of the value at the point $x^* = 0$, so that we may assume that the fall in potential in the diffuse part of the double layer occurs in this case over a distance of the order of two ionic diameters.

SUMMARY

1. Conditions have been deduced for the applicability of the method proposed by Kirkwood *et al.*^{1,2} for finding approximate correlation functions for the distribution of ions in the bulk of the solution and in the diffuse part of the double layer, allowing for short-range interaction between the ions. This method makes it possible to find important characteristics of the double layer at bulk electrolyte concentrations greater by 2-3 powers of ten than the concentrations at which the linearised Poisson-Boltzmann equation is valid.
2. For the rigid sphere model, the above method has been used to find the distribution of potential in the electrical double layer at the dielectric-solution interface when layers of specifically adsorbed ions are present, allowance being made for the discrete structure of the layers. At moderate bulk electrolyte concentrations (0.1-0.5 M) the potential in the diffuse part of the double layer falls on going into the bulk of the solution more rapidly than predicted by the Gouy-Stern theory.

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Received 12th November 1961

KINETIC RELATIONS IN THE DEHYDROGENATION OF COMPOUNDS WITH SIX-MEMBERED RINGS. II†

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The previous communication presented our experimental results for the dehydrogenation of methylcyclohexane and its binary mixtures with toluene, hydrogen, and argon over a Pt/asbestos catalyst. The present paper discusses these results.

If pure methylcyclohexane or its binary mixtures are passed over the catalyst, then from the general kinetic equation for monomolecular reactions in a flow we obtain

$$(4 + \delta_1 + \delta_1 b_1 + b_2 + 3b_3) A_1 \ln \frac{A_1}{A_1 - m} - (3 - b_1 + b_2 + 3b_3) m = b_1 K, \quad (1)$$

where $\delta_i = A_i/A_1$ (A_i is the rate of supply to the reactor of the reaction product or a substance not involved in the reaction; $\delta_1 = 0$ in the latter case), $b_i = a_i P$, and a_i is the

† In the Russian original Parts I and II of this paper have been transposed. This order has been retained in the translation. Part I begins on p. 59 (Ed. of Translation).