Polar Solvent Structure in the Debye-Hückel Theory of Strong Electrolytes

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A general formula is derived for the potential energy of an ion in an ionic solution using all assumptions of the Debye-Hückel theory except the assumption of constant permittivity. For the solvent the spatial correlation of polarization fluctuations is taken into account. The potential energy of an ion in it's ionic atmosphere is calculated for different models of the spatial correlation of polarization fluctuations and the corresponding excess free energy and activity coefficient of an ion is evaluated. It is concluded that the Debye-Hückel theory using a constant value of ε should only be valid for electrolyte concentrations lower than 10^{-7} mol·dm^{-3}. The paper intends to show the consequences of dropping the assumption of constant permittivity and so encourage further efforts towards a more exact treatment of the problem.

1. Introduction

The interest in electrolyte solutions dates back to the time of van't Hoff and Arhenius. The first statistical theory of electrolyte solutions is known as the Debye-Hückel [1] (DH) theory of diluted solutions of strong electrolytes, which has been shown [2] to be asymptotically valid for

$$\varkappa^3/c \rightarrow 0 \tag{1}$$

where c is the total number of ions per unit volume and $\varkappa$ the reciprocal Debye length

$$\varkappa = [4\pi e^2 c \sum_{\mathrm{a}} \nu_{\mathrm{a}} z_{\mathrm{a}}^2/(\varepsilon k T)]^{1/2} \tag{2}$$

where z_{a} and $\nu_{\mathrm{a}} = c_{\mathrm{a}}/c$ are the charge number and the fraction of the ionic species a, respectively, e is the electronic charge and ε the dielectric constant of the solvent. The range in which the DH theory is consistent with the principles of statistical mechanics has been estimated in different ways [2–6] to be

$$c^{1/2} \ll [\gamma \varepsilon k T/(e^2 \sum_{\mathrm{a}} \nu_{\mathrm{a}} z_{\mathrm{a}}^2)]^{3/2}, \tag{3}$$

i. e.

$$\varkappa \ll \gamma \varepsilon k T/(e^2 \sum_{\mathrm{a}} \nu_{\mathrm{a}} z_{\mathrm{a}}^2), \tag{4}$$

where $1/4\pi \leqq \gamma \leqq 2$. Thus for an aqueous solution of a uni-univalent electrolyte the largest upper bound (corresponding to $\gamma = 2$) gives $c \ll 10^{17}\,\mathrm{cm}^{-3}$ (i. e. $m \ll 10^{-4}$;mol·dm^{-3}) and $1/\varkappa \gg 100$ Å.

Even in the region of selfconsistency [i. e. where the inequality (3) is fulfilled] the DH theory was questioned because the solvent in the DH theory is treated as a structureless medium with the macroscopic dielectric constant ε. The continuous model was modified in different ways, e. g. in Ref. [8] the linearized Poisson-Boltzmann equation was solved for the permittivity (= microscopic dielectric constant) as an empirical function [9] depending on the potential of the ion according to the Malsch formula. The non-linearized Poisson-Boltzmann equation with use of a phenomenological interpolation formula for the permittivity as a function of the distance from the central ion was also solved [10]. These models may be of interest for their own sake [11], but they ignore the structure of the solvent. In fact, in the framework of local electrostatics, where the average polarization due to the outside electric field is proportional to the dielectric displacement $\boldsymbol{D}$

$$\langle \boldsymbol{P}(\boldsymbol{r}) \rangle = \left\{1 - \frac{1}{\varepsilon(\boldsymbol{r})}\right\} \boldsymbol{D}(\boldsymbol{r}) = -[\varepsilon(\boldsymbol{r}) - 1]\, \nabla \Phi \tag{5}$$

[where Φ is the potential of the electric field in the medium with the permittivity $\varepsilon(\boldsymbol{r})$ at a point $\boldsymbol{r}$] it is impossible to take into account the polar structure of the liquid which manifests itself through the correlations of polarization fluctuations at different points in space. The nonlocal electrostatics (or the electrostatics of media with space dispersion [12]) is

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based on the integral relationship

$$\langle P^\alpha(\boldsymbol{r})\rangle = \sum_\beta \int \mathrm{d}\boldsymbol{r}' \{\delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}') - \varepsilon^{-1}_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}')\}\, D^\beta(\boldsymbol{r}')$$
$$= \sum_\beta \int \mathrm{d}\boldsymbol{r}' \{\varepsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}') - \delta_{\alpha\beta}\,\delta(\boldsymbol{r}-\boldsymbol{r}')\}\nabla_\beta\, \Phi(\boldsymbol{r}') \quad (5\,\mathrm{a})$$

where the subscripts α, β denote the Cartesian components, $\varepsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}')$ is the tensor of generalized static field permittivity which takes into account the contributions of the electric field at different points $\boldsymbol{r}'$ to the average value of the polarization at a point $\boldsymbol{r}$ which are caused by spatial correlations of polarization fluctuations

$$S_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}') \equiv \langle P^\alpha(\boldsymbol{r})\, P^\beta(\boldsymbol{r}')\rangle \neq \delta(\boldsymbol{r}-\boldsymbol{r}')\,.$$

The model of a polar solvent based on linear electrodynamics of media with spatial dispersion was elaborated in [13, 14]. A detailed analysis of the physical principles and some applications of the model are presented in Ref. [15] where the theory of solvation is treated, and also in review articles [16, 17]. In Ref. [18] the energy of interaction of two ions in the polar solvent at large distance was studied (in fact the potential of an isolated ion) and it was shown that it becomes non-coulombic at a certain characteristic distance due to the dynamical structure of the solvent. In the present paper we treat the DH theory in its range of supposed validity taking into account the spatial dispersion of the solvent. [The effect of the spatial dispersion on the criterium of validity of the DH theory will be discussed in 4. At this point we use the estimates (3) and (4).] In the following the potential of an ion, the total electric work and the activity coefficient will be calculated under this assumption.

2. The Debye-Hückel Ionic Atmosphere in a Solvent With Spatial Dispersion

We assume an ion a to lie at the origin of the coordinate system and to be surrounded with a spherically symmetric ionic atmosphere. We neglect the size of ions and assume the solvent to be a medium with spatial dispersion of permittivity [see Equation (5 a)]. In the self-consistent field approximation the equation for the effective potential Φ_a of an ion of type a in an electrolytic solution [1, 7, 19] (the so called Poisson-Boltzmann equation) can be written as

$$-\operatorname{div}\boldsymbol{D}_\mathrm{a} = \sum_{\alpha\beta} \frac{\partial}{\partial r_\alpha} \int \mathrm{d}\boldsymbol{r}'\, \varepsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}')\, \frac{\partial}{\partial r_\beta{}'}\, \Phi_\mathrm{a}(\boldsymbol{r}') \quad (6)$$
$$= -4\pi e\,[z_\mathrm{a}\,\delta(\boldsymbol{r}) + c \sum_{\mathbf{b}} z_\mathrm{b}\,\nu_\mathrm{b} \exp\{-e\, z_\mathrm{b}\, \Phi_\mathrm{a}/k T\}]\,.$$

Strictly speaking, $\varepsilon_{\alpha\beta}$ is a function [11] of $(\boldsymbol{r},\boldsymbol{r}')$. We will however treat sufficiently diluted solutions. To describe these it is sufficient to know the field at a distance from the ion where we can assume the medium to be homogeneous and isotropic so that we can set $\varepsilon_{\alpha\beta}(\boldsymbol{r},\boldsymbol{r}') = \varepsilon_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}')$. In this way we neglect the difference of the structure in the vicinity of the ion and in the pure solvent which corresponds to neglecting the short range forces in the DH theory. In addition to the self-consistent field approximation in the DH theory the linearization of Eq. (6) by an expansion of the exponential to the first two terms is a further major approximation. (It has been shown that using the DH-treatment only the linearized Poisson-Boltzmann equation leads to results consistent [7] with the principles of statistical mechanics.) Under these assumptions and using the condition of electroneutrality $\sum_\mathrm{a} \nu_\mathrm{a}\, z_\mathrm{a} = 0$ we get the following equation for the potential $\Phi = \Phi_\mathrm{a}/z_\mathrm{a}$

$$\sum_{\alpha\beta} \frac{\partial}{\partial r_\alpha} \int \mathrm{d}\boldsymbol{r}'\, \varepsilon_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r}')\, \frac{\partial}{\partial r_\beta{}'}\, \Phi(\boldsymbol{r}') \quad (7)$$
$$= -4\pi e\,\delta(\boldsymbol{r}) + \frac{8\pi e^2}{k T}\, I\, \Phi$$

where $I = c \sum_\mathrm{a} \nu_\mathrm{a}\, z_\mathrm{a}{}^2/2$ is the ionic strength. This equation can be solved using e. g. a Fourier transformation, and its solution is

$$\Phi(r) = \frac{e}{\varepsilon\, r}\, S_\varkappa(r) \quad (8)$$

where the function $S_\varkappa(r)$, which we shall call the shielding factor, is given as

$$S_\varkappa(r) = \frac{2}{\pi} \int\limits_0^\infty \frac{k \sin k r}{\varkappa^2 + k^2\, F(k)}\, \mathrm{d}k\,. \quad (9)$$

The function $F(k)$ is given (cf. also the Ref. [15]) as

$$F(k) = \frac{1}{\varepsilon} \sum_{\alpha\beta} \frac{k_\alpha\, k_\beta}{k^2} \int \mathrm{d}\boldsymbol{r}\, e^{-i\boldsymbol{k}\boldsymbol{r}}\, \varepsilon_{\alpha\beta}(\boldsymbol{r}) \equiv \frac{\varepsilon_{||}(k)}{\varepsilon}\,. \quad (10)$$

When spatial dispersion is absent, i. e. $\varepsilon_{||}(k) = \varepsilon$, the permittivity of the solvent is $\varepsilon_{\alpha\beta} = \delta_{\alpha\beta}\,\delta(r)\,\varepsilon$ and $F(k) = 1$; in this case the shielding factor is the same as in the DH theory, i. e. $S_\varkappa(r) = \exp\{-\varkappa r\}$. For the other limiting case, i. e. the case of infinitely diluted solution ($\varkappa = 0$), the formulae (8) and (9) give the potential of an isolated point ion in a medium with spatial dispersion [11, 18].

In order to get an analytical expression for the shielding factor $S_\varkappa(r)$ it is necessary to know the function $F(k)$. The main contribution to the value of the integral (9) is due to $k \lesssim 1/r$, and therefore it is sufficient to know $F(k)$ for $k \lesssim 1/r$. It is an accordance with our assumption that we neglect short range effects, and therefore it is sufficient to know the function $F(k)$ in the range $k < 1/l_s$. l_s is a length characteristic for the size of the ion with its first coordination shell. Therefore we can use the equation (Fourier transform variable corresponding to space coordinate r in spherical coordinates)

$$F(k) = [\xi - (\xi - 1)\, f(k\Lambda)]^{-1}, \quad \xi = \varepsilon/\varepsilon^* , \quad (11)$$

which has been derived[13, 14] for k sufficiently smaller than the reciprocal of the characteristic length of the solvent molecules and where $\varepsilon^* \equiv \varepsilon(\omega, k=0)$, ω corresponding to the frequency which separates the rotational Debye and infrared frequencies of the degrees of freedom of the solvent, i. e. ε^* is the so called intermediate permittivity (for detailes see[13, 15]). The value of ε^* is usually taken to be 4.9 for water, 6 for methanol, and 4.4 for ethanol and does not depend markedly on temperature[20, 21, 15]. The function $f(x)$ is the so called spectral function[13, 14] $[f(0) = 1, f(x \gg 1) \ll 1]$ and Λ is the characteristic length of the spatial correlation range of the polarization fluctuations caused by excitations of hindered Debye rotation of dipoles (in liquids with hydrogen bonds it is connected with the characteristic length of the hydrogen bonding chains).

The form of the spectral function depends on the character of the correlations of fluctuations in r-space:

$$f(x) = (1 + x^2)^{-2} \quad (12\,a)$$

corresponds[13, 14] to the exponential approximation of the correlation function in r-sprace,

$$f(x) = \exp\{-x^2/4\} \quad (12\,b)$$

corresponds to the gaussian and

$$f(x) = \frac{3}{x^2}\left(\frac{\sin x}{x} - \cos x\right) \quad (12\,c)$$

to the step correlation. However, one general result can be obtained without specifying the function $F(k)$ [or $f(x)$]. In order to obtain this result we make the only assumption that $F(k)$ changes substantially at the characteristic value k^* $(\sim 1/\Lambda)$ and that the concentration of the solution is such as to fulfil[25] $\varkappa\Lambda \ll 1$. Then (see Appendix A)

$$S_\varkappa(r) \cong \exp\{-\varkappa r\} + S_0(r) - 1 \quad (13)$$

where $S_0(r) \equiv S_{\varkappa=0}(r)$ is the shielding factor of an isolated ion in the absence of other ions. In this way the shielding factor is substancially different from that of Debye $(\exp\{-\varkappa r\})$ in the $r \lesssim \Lambda$, i. e. where the Debye shielding factor is $\cong 1$.

Using the approximation (11) and the spectral functions (12 a), (12 b) and (12 c) we get

$$S_0(r) = 1 + (\xi - 1)\,[1 + r/(2\Lambda)]\,\exp\{-r/\Lambda\} \quad (14\,a)$$

$$S_0(r) = 1 + (\xi - 1)[1 - \operatorname{erf}(r/\Lambda)] \quad (14\,b)$$

$$S_0(r) = \begin{cases} \xi - (\xi - 1)\,[r/(2\Lambda)]\,[3 - (r/\Lambda)^2]\,, & \text{for } r \leqq \Lambda \\ 1, \text{ for } r \geqq \Lambda \end{cases} \quad (14\,c)$$

respectively (cf. Figures 1 – 4).

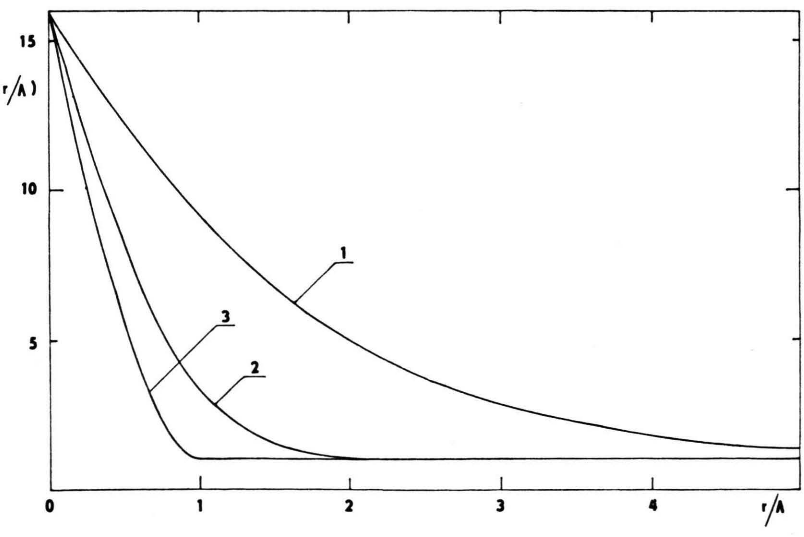

Fig. 1. The shielding factor for an ion in pure solvent $S_0(r/\Lambda)$ (i. e. $\varkappa\Lambda = 0$, see Eq. (9)) vs. r/Λ for three different models of the correlation of polarization fluctuations according the Eqs. (14a), (14 b) and (14 c) — curves 1, 2 and 3 respectively; $\xi = 78/4.9 = 15.92$.

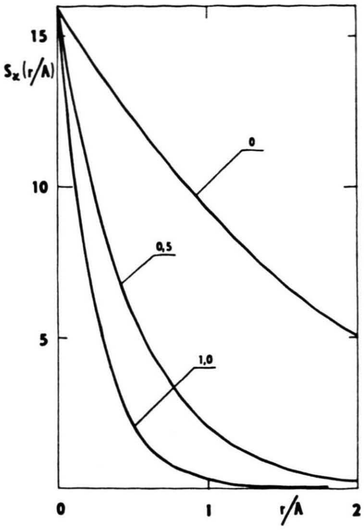

Fig. 2. The shielding factor (see Eq. (9)) vs. r/Λ for the indicated values of $\varkappa\Lambda$ (model (12 a)); $\xi = 15.92$.

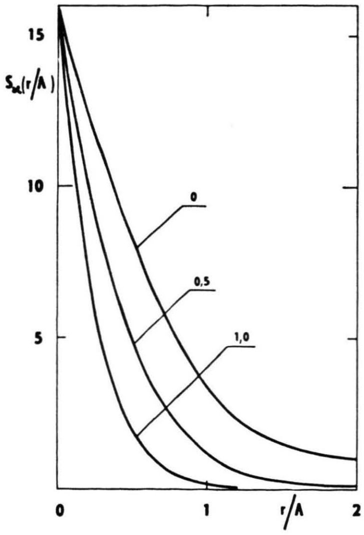

Fig. 3. The shielding factor (see Eq. (9)) vs. r/Λ for the indicated values of $\varkappa\Lambda$ (model (12 b)); $\xi = 15.92$.

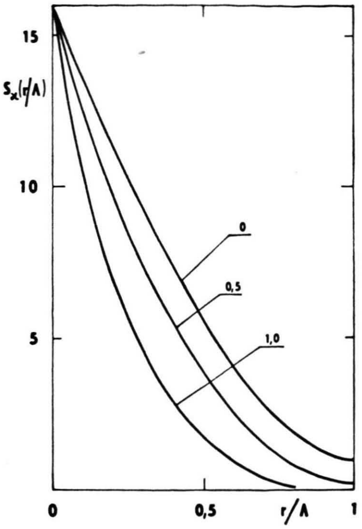

Fig. 4. The shielding factor (see Eq. (9)) vs. r/Λ for the indicated values of $\varkappa\Lambda$ (model (12c)); $\xi = 15.92$.

3. Thermodynamics of Diluted Solutions

The fundamental quantity of diluted electrolyte solutions is W^E – the free energy of the long-range forces (the change of the energy of the system due to the so called Debye charging process[23, 19]). In the range of low concentrations [(3), (4)] the free energy of charging per unit volume of the electrolyte, $w = W^E/V$ can be calculated by means of the following approximate[19] formula

$$w = \frac{c^2}{2}\int_0^1 \mathrm{d}s \int \mathrm{d}\mathbf{r} \sum_{a,b} e\,\{\Phi(r)|_{\varkappa=0}\}\, z_a z_b \nu_a \nu_b \cdot \left[1 - \frac{s\,e}{k\,T}\{\Phi(r)|_{\varkappa\to\varkappa\sqrt{s}}\}\, z_a z_b\right] \tag{15}$$
$$= -8\pi\,[I^2 e^4/(\varepsilon^2 k\,T)] \int_0^1 \mathrm{d}s\, s \int_0^\infty \mathrm{d}r\, S_0(r)\, S_{\varkappa\sqrt{s}}(r)\,.$$

Using (9) for S and performing the integration over s and r taking into account the identity

$$\pi^{-1}\int_{-\infty}^{\infty} \mathrm{d}r \sin(k_1 r)\sin(k_2 r) = \delta(k_1 - k_2) - \delta(k_1 + k_2)$$

we get

$$\frac{w}{w_{\mathrm{DH}}} = \frac{3}{\pi}\int_0^\infty \frac{\mathrm{d}k}{\varkappa}\left\{\frac{1}{F(k)} - \frac{k^2}{\varkappa^2}\ln\left[1 + \frac{\varkappa^2}{k^2 F(k)}\right]\right\} \tag{16}$$

where $w_{\mathrm{DH}} \equiv -k\,T\varkappa^3/(12\pi)$ is the "long-range forces" free energy per unit volume in the DH theory. The activity coefficient can be expressed by means of the free energy

$$k\,T \ln f_a = \frac{\partial w}{\partial(c\,\nu_a)} = \frac{z_a{}^2 \varkappa^3}{2I}\,\frac{\partial w}{\partial \varkappa^2}\,. \tag{17}$$

We substitute into this equation from the Eq. (16) and get

$$\frac{\ln f_a}{(\ln f_a)_{\mathrm{DH}}} = \frac{2\varkappa}{\pi}\int_0^\infty \frac{\mathrm{d}k}{F(k)\,[k^2 F(k) + \varkappa^2]} \tag{18}$$

where

$(\ln f_a)_{\mathrm{DH}} \equiv -z_a{}^2\varkappa^3/(16\pi I) = -z_a{}^2 e^2 \varkappa/(2\varepsilon k\,T)$

is the expression for $\ln f_a$ in the DH theory.

(16) and (18) can be simplified by assuming that the characteristic value k^* is much larger than $\varkappa$ (see Appendix B):

$$w \cong w_{\mathrm{DH}}\,[1+(3/4)\,\varkappa\, L] \tag{19}$$

$$\ln f_{\mathrm{a}} \cong (\ln f_{\mathrm{a}})_{\mathrm{DH}}\,[1+\varkappa\, L] \tag{20}$$

where

$$L \equiv -\frac{4}{\pi}\int\limits_0^\infty \frac{\mathrm{d}k}{k}\,\frac{F'}{F^3}\,. \tag{21}$$

The integral L is convergent because $F'_{k\to 0} \sim k$ and $k\,F'_{k\to\infty} \to 0$ (these properties of the function $F(k)$ were obtained in References[13, 14]). The second terms in the square brackets on the r.h.s. of the Eqs. (19) and (20) correspond to the correction of the DH theory due to the effect of spatial correlation of the solvent. The characteristic length parameter L describes the effect of the solvent dynamical structure. For the calculation of the length L we can use the approximation (11). Then

$$L = \Lambda\, U(\xi) \tag{22}$$

where

$$U(\xi) = -\xi(\xi-1)\,\frac{4}{\pi}\int\limits_0^\infty \frac{\mathrm{d}x}{x}\,f'(x) + (\xi-1)^2\,\frac{4}{\pi}\int\limits_0^\infty \frac{\mathrm{d}x}{x}\,f'(x)\,f(x)\,. \tag{23}$$

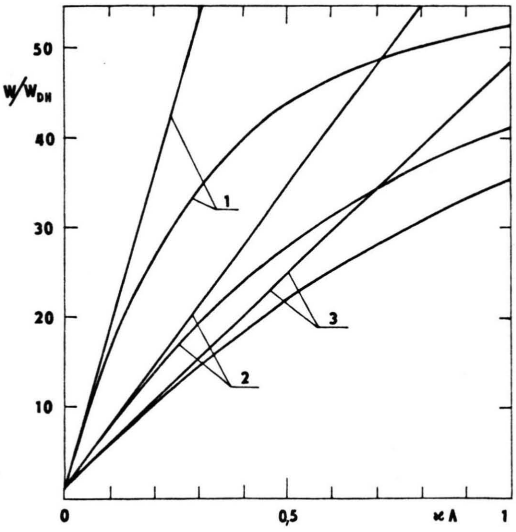

Fig. 5. The excess free energy in "units" of the DH theory excess free energy vs. $\varkappa\Lambda$ (see Eq. (16)). The curves 1, 2 and 3 correspond to (12 a), (12 b) and (12 c), respectively. The straight lines correspond to the asymptotic formula (19); ξ = 15.92.

Using now the approximation of the spectral function $f(x)$ (12 a) we get

$$U(\xi) = A(\xi) \equiv 13(\xi-1)^2/16 + 3(\xi-1)\,. \tag{24 a}$$

Analogically we get

$$U(\xi) = B(\xi) \equiv 2\,\pi^{-1/2} \cdot [(\xi-1)^2(1-2^{-1/2}) + \xi - 1] \tag{24 b}$$

and

$$U(\xi) = C(\xi) \equiv 6(\xi-1)\,[\xi/8 - 3(\xi-1)/35] \tag{24 c}$$

from (12 b) and (12 c), respectively. Curves for the excess free energies and activity coefficients are shown in Figures 5 and 6.

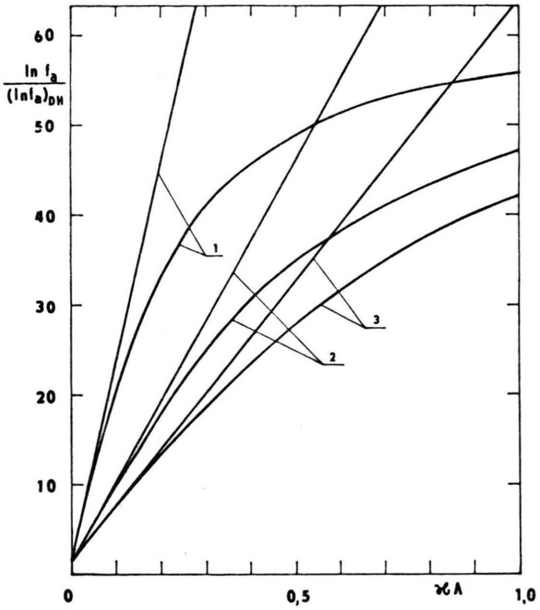

Fig. 6. The natural logarithm of the activity coefficient divided by that of the DH theory vs. $\varkappa\Lambda$ according to formula (18); 1, 2 and 3 correspond to models (12 a), (12 b) and (12 c) respectively. The lines correspond to the asymptotic formula (20); ξ = 15.92.

4. Discussion

From formulae (19) and (20) it can be seen that the DH limits for $\varkappa \to 0$ remain valid. We will estimate now the magnitude of the correction terms in the Eqs. (19) and (20) which take into account the spatial dispersion of the solvent at finite values of $\varkappa$. For that purpose we consider a 1 – 1 electrolyte in water at 25 °C. Assuming further[15] $\xi = 16$, $\Lambda = 10$ Å, $\varepsilon = 78$ we get $A = 226$, $B = 90$ and $C = 64$ [see Eqs. (24 a), (24 b) and (24 c)]. If we express

$\varkappa$ by the ionic strength I^* (in moles·dm^{-3}) we get

$$A(\xi)\varkappa\Lambda \sim 744\sqrt{I^*}\,, \qquad (25\text{ a})$$

$$B(\xi)\varkappa\Lambda \sim 298\sqrt{I^*}\,, \qquad (25\text{ b})$$

$$C(\xi)\varkappa\Lambda \sim 210\sqrt{I^*}\,. \qquad (25\text{ c})$$

From this we see that even in the region of the presumptive validity of the self-consistent field approach[1] $c \cong 10^{-5}$ mol·dm^{-3}, $\varkappa \ll 10^{-2}$ Å^{-1}, [26] the correction terms may be of the order of one (i. e. 100%) because $A(\xi)\varkappa\Lambda \ll 25$. According to this the DH theory (using a constant value of ε) should only be valid for concentrations lower than or equal to approximately 10^{-7} mol·dm^{-3}.

Without a careful examination it would have been difficult to predict[24] the effect of the spatial dispersion of the permittivity of the solution with a correlation length Λ (~ 10 Å) on the thermodynamic properties of electrolyte solutions with concentrations 10^{-6} mol·dm^{-3} (i. e. with interionic distances of the order 1000 Å). It has turned out that the increase of the electric interaction at a distance of the order of Λ (see Fig. 1) is so substantial (for sufficiently large value of ξ) that its contribution to the thermodynamic properties is significant.

The analysis of the problem presented in this paper has obviously all drawbacks of the DH theory. It is not aimed, however, at obtained exact quantitative results but at bringing some light in to the effects of the solvent structure on the thermodynamic properties of diluted electrolyte solutions. In our opinion the results obtained justify further attempts towards an exact theory (including "short range forces") which would take into account the spatial dispersion of the permittivity of the solvent.

Appendix

A Derivation of Equation (13)

Putting $k \equiv x/\Lambda$ we obtain (9) in the form

$$S_\varkappa(r) = \frac{2}{\pi}\int_0^\infty \frac{x\sin(x\,r/\Lambda)}{\mu^2 + x^2 H(x)}\,\mathrm{d}x \qquad (\text{A }1)$$

where $\mu \equiv \varkappa\Lambda$ and $H(x) \equiv F(x/\Lambda)$.

The identity

$$(\mu^2 + x^2 H)^{-1} = (x^2 H)^{-1} - \mu^2[x^2 H(\mu^2 + x^2 H)]^{-1} \qquad (\text{A }2)$$

is easy enough to verify. If we set $H = 1$ (A 2) takes the form

$$0 = (\mu^2 + x^2)^{-1} - x^2 + \mu^2[x^2(\mu^2 + x^2)]^{-1}\,. \qquad (\text{A }3)$$

We multiply both identities by $x\sin(x\,r/\Lambda)$, integrate over x and add the equations. We get

$$S_\varkappa(r) = S_0(r) + \exp\{-\mu\,r/\Lambda\} - 1 + \mu^2(2/\pi)\,K(\mu, r/\Lambda) \qquad (\text{A }4)$$

with

$$K(\mu, r/\Lambda) \equiv \int_0^\infty L(\mu, x)\,x^{-1}\sin(x\,r/\Lambda)\,\mathrm{d}x \qquad (\text{A }5)$$

where

$$L(\mu, x) \equiv [H(x)(\mu^2 + x^2 H(x))]^{-1} - [\mu^2 + x^2]^{-1}\,. \qquad (\text{A }6)$$

Now we estimate the integral $K(\mu, r/\Lambda)$ for μ sufficiently small. Let x^* be such a value of x that $x^* \gg \mu\,\xi$ (note that $\xi > 1$) and $H(x^*) \approx H(0) = 1$, i. e. the function $H(x)$ does not change substantially on $[0, x^*]$; (note that $x^* \ll 1$). We split the integral (A 5) into the two integrals

$$K_1 \equiv \int_0^{x^*} L(\mu, x)\,x^{-1}\sin(x\,r/\Lambda)\,\mathrm{d}x\,, \qquad (\text{A }7)$$

$$K_2 \equiv \int_{x^*}^\infty L(\mu, x)\,x^{-1}\sin(x\,r/\Lambda)\,\mathrm{d}x\,. \qquad (\text{A }8)$$

We find first the bound for the integral K_1. By assumption, $H(x) \approx 1$ on $[0, x^*]$, hence

$$L(\mu, x) \approx g(x)\,, \quad x \in [0, x^*] \qquad (\text{A }9)$$

where

$$g(x) \equiv [1 - H(x)]\;(\mu^2 + 2\,x^2)\,(\mu^2 + x^2)^{-1}\,. \qquad (\text{A }10)$$

Since $|x^{-1}\sin x| \leqq 1$, it follows that

$$|K_1| \lesssim \int_0^{x^*} |g(x)\;\mathrm{d}x \lesssim (r/\Lambda)\,[(1.5/\mu) \qquad (\text{A }11)$$
$$\arctan(x^*/\mu) - 0.5\,x^*/(\mu^2 + x^{*2})]\max_{x\in[0,x^*]}|1 - H(x)|\,.$$

Using the supposed inequality $\mu \ll x^*$ we get

$$|K_1| \lesssim (3\,\pi/4)\,(r/\Lambda)\,\mu^{-1}\max_{x\in[0,x^*]}|1 - H(x)|\,. \qquad (\text{A }12)$$

Obviously this estimate is suitable for $\mu\,r/\Lambda$ not too large. Let the function $g(x)/x$ be differentiable on $[0, x^*]$. Then we can get another estimate of the integral K_1, integrating (A 7) by parts and using (A 9) and (A 10)

$$|K_1| \lesssim 2\,A/(r/\Lambda)\,, \qquad (\text{A }13)$$
$$A = \max\left\{|g(x^*)/x^*|,\; \int_0^{x^*} |\mathrm{d}[g(x)/x]/\mathrm{d}x|\,\mathrm{d}x\right\}$$

provided that $g(x)/x \to 0$ for $x \to 0$. Taking into account that[13] the spectral function can be expressed as $f(x) \approx 1 - a\,x^2$ (for $x \to 0$) we can approximate $[1 - H(x)]/x \approx C\,x$. By the same procedure we get for this case the following estimate

$$|K_1| \lesssim 1.6\, C/(\mu\, r/\Lambda) \tag{A 14}$$

where we have used again the assumption $x^* \gg \mu\,\xi$.

To estimate the integral K_2 let us observe that by the assumption

$$L(\mu, x) \approx x^{-2} H^{-2}(x) - x^{-2}, \quad \text{for} \quad x \geqq x^*, \tag{A 15}$$

using the inequality $|\sin x| \leqq 1$ and assuming $H(x)$ to have its range on $[1/\xi, 1]$, we get

$$|K_2| < (\xi^2 - 1)\, x^{*\,-2}/2\,. \tag{A 16}$$

Thus we conclude that $\mu^2 K(u, r/\Lambda)$ can be neglected against 1 (using $\mu\,\xi \ll x^*$) and the approximation (13) is proved.

B Deviation of Equation (20)

We put $k \equiv x/\Lambda$ in (18) and get

$$K \equiv (\ln f_{\mathrm{a}})/(\ln f_{\mathrm{a}})_{\mathrm{DH}} \tag{B 1}$$
$$= (2\,\mu/\pi) \int_0^\infty \{H(x)\,[\mu^2 + x^2 H(x)]\}^{-1}\, \mathrm{d}x$$

where $\mu \equiv \varkappa\,\Lambda$ and $H(x) = F(x/\Lambda)$.

We use the identity

$$[H(\mu^2 + x^2 H)]^{-1} = [\mu^2 + x^2]^{-1} + [1 - H] \tag{B 2}$$
$$\cdot\, [\mu^2 + x^2(1 + H)]\, [H(\mu^2 + x^2 H)\, (\mu^2 + x^2)]^{-1}$$

and get

$$K = 1 + (2\,\mu/\pi) \int_0^\infty k(x)\, \mathrm{d}x \tag{B 3}$$

where

$$k(x) \equiv (-H(x))\, [\mu^2 + x^2\, (1 + H(x))] \tag{B 4}$$
$$\cdot\, [H(x)\, (\mu^2 + x^2 H(x))\, (\mu^2 + x^2)]^{-1}\,.$$

Now we split the domain of integration into two intervals: $[0, x^*]$ and $[x^*, \infty]$. The same procedure as in part A of the appendix [cf. (A 7), (A 10), (A 11) and (B 4)] leads us to

$$\left|(2\,\mu/\pi) \int_0^{x^*} k(x)\, \mathrm{d}x\right| \lesssim 3 \max_{x \in [0, x^*]} |1 - H(x)|/2 \tag{B 5}$$

where we have used the assumption $\mu = \varkappa\,\Lambda \ll x^*$, $H(x^*) \approx 1$. Using the assumption $\mu \ll x^*$ for the integral on the interval $[x^*, \infty]$ and neglecting μ^2 against x^2 or $x^2 H(x)$ we get

$$\int_{x^*}^\infty k(x)\, \mathrm{d}x \approx \int_{x^*}^\infty [G^2(x) - 1]\, x^{-2}\, \mathrm{d}x \tag{B 6}$$

where $G(x) \equiv 1/H(x) \equiv 1/F(x/\Lambda)$. We integrate now the last integral by parts and get

$$\int_{x^*}^\infty [G^2(x) - 1]\, x^{-2}\, \mathrm{d}x = [G^2(x^*) - 1]/x^* \tag{B 7}$$
$$+ 2 \int_{x^*}^\infty G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x\,.$$

Now we write

$$\int_{x^*}^\infty G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x = \int_0^\infty G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x \tag{B 8}$$
$$- \int_0^{x^*} G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x\,.$$

We note that both integrals on the r.h.s. of this equation are convergent. The ratio $G(x)/x < C$ is bounded because $G'(x) = 0(x)$[13, 14] and thus the last integral can be estimated

$$\int_0^{x^*} G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x < C\, x^*\,. \tag{B 9}$$

Therefore for sufficiently small x^* the second integral on the r.h.s. of (B 8) can be neglected against the first integral and finally we have

$$K \approx 1 + (4\,\mu/\pi) \int_0^\infty G(x)\, G'(x)\, x^{-1}\, \mathrm{d}x \tag{B 10}$$

where we have neglected the term $\mu[G^2(x^*) - 1]/x^*$ against 1 in accordance with our assumption that $\mu \ll x^*$.

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[1] P. Debye and W. Hückel, Physik. Z. **24,** 185, 305 [1923].

[2] N. N. Bogoliubov, Problems of Dynamic Theory in Statistical Physics (in Russian), Gostekhizdat, Moscow 1946.

[3] A. E. Glauberman, in Thermodynamics and Structure of Solutions, Izdatelstvo AN SSSR, 1959, p. 5–15.

[4] H. Falkenhagen, Electrolytes, English ed. in Intern. Ser. Monographs, Oxford 1934; V. K. Semenchenko, Physical Theory of Solutions (in Russian), GITTL, Moscow 1941.

[5] H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold Publ. Corp., New York 1950.

[6] R. H. Fowler, Proc. Camb. Phil. Soc. **22,** 861 [1925].

[7] J. G. Kirkwood, J. Chem. Phys. **2,** 767 [1934]; L. Onsager, Chem. Rev. **13,** 73 [1938]; J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. **58,** 591 [1954].

[8] E. Glueckauf, Trans. Farady Soc. **60,** 776 [1964].

[9] J. Malsch, Physik. Z. **29,** 770 [1928]; ib. **30,** 837 [1929].

[10] R. A. Goldstein and J. J. Kozak, J. Chem. Phys. **62,** 276 [1975]; R. A. Goldstein, P. F. Hay, and J. J. Kozak, ib. **62,** 285 [1975].

[11] Yu. I. Kharkatz, A. A. Kornyshev, and M. A. Vorotyncev, J. Chem. Soc. Faraday Trans. II, **72,** 361 [1976].

[12] V. P. Silin and A. A. Rukhadze, Electromagnetic Properties of Plasma and Plasmatic Media (in Russian), Atomizdat, Moscow 1961.

[13] R. R. Dogonadze, A. A. Kornyshev, and A. M. Kuznetsov, Teor. Mat. Fiz. **15,** 127 [1973].

[14] R. R. Dogonadze and A. A. Kornyshev, Phys. Stat. Sol. (b) **53,** 439 [1972]; ib. **55,** 843 [1973].

[15] R. R. Dogonadze and A. A. Kornyshev, J. Chem. Soc. Faraday Trans. **II 70,** 1121 [1974].

[16] R. R. Dogonadze and A. M. Kuznetsov, Progress in Surface Sci. **6,** 1 [1975].

[17] R. R. Dogonadze and A. M. Kuznetsov, Kinetics of Chemical Reactions in Polar Solvents (in Russian), VINITI, Moscow 1973, Chapter 2.

[18] R. R. Dogonadze, A. A. Kornyshev, Dokl. Akad. Nauk SSSR **207,** 896 [1972].

[19] P. M. V. Résibois, Electrolyte Theory, Harper & Row, New York, Evanston, London 1968.

[20] J. A. Saxton, Proc. Roy. Soc. London **A 213,** 473 [1952].

[21] N. V. Chekalin and M. I. Shakhparonov, in: Physics and Physical Chemistry of Liquids (in Russian), ed. M. I. Shakhparonov, Moscow State Univ., Moscow 1972, p. 151.

[22] P. L. Kudrin, Statistical Physics of Plasma (in Russian), Atomizdat, Moscow 1974.

[23] P. Debye, Physik. Z. **25,** 97 [1924].

[24] R. R. Dogonadze, V. A. Kirianov, and A. A. Kornyshev, Dokl. Akad. Nauk SSSR **212,** 904 [1973].

[25] The estimate (4) can be rewritten as $\varkappa \Lambda \ll \varepsilon k T \Lambda / (4 \pi e^2 \sum_{\mathrm{a}} \nu_a z_{\mathrm{a}}^2)$. For the room temperature and for a 1−1 electrolyte we get $\varkappa \Lambda \ll \Lambda(\text{Å})/(28 \pi)$. If we use the estimate[15] $\Lambda \sim 10$ Å we get $\varkappa \Lambda \ll 1/9$. The case $\varkappa \Lambda \sim 1$ (when $1/\varkappa$ is of the order of l_{S}) should be treated taking into account the finite size of ions and short range forces and using methods of statistical mechanics (see e.g. Ref.[22]) which will be the subject of another paper.

[26] It seems that the spatial dispersion does not affect the parameter of asymptotic expansion (1) because at large distance from an isolated ion ($r \to \infty$) the potential remains coulombic. An estimate by the Fowler method[6] leads to the conclusion that in the region $\varkappa^{-1} \gg \Lambda$ the inclusion of spatial dispersion does not affect the criteria (3), (4) (the criterion proposed in paper[24] is too strong without proper foundation). For distances $\varkappa^{-1} \sim \Lambda$ the problem requires special treatment.