ROLE OF POLAR SOLVENT STRUCTURE IN THE STATISTICAL MECHANICS OF STRONG ELECTROLYTE SOLUTIONS

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In preceding papers we have discussed a dynamical model of polar solvents [1], and on this basis deduced an equation for the free energy of pairwose interaction of ions dissolved in the polar medium [2]. Using this result and a technique developed in recent years [3, 4] one can obtain the form of the distribution function for a system of charged particles in a polar medium at distances of separation which are much larger than the particles' own dimensions. The pair potential $\Phi_{ab}(|\mathbf{r}-\mathbf{r}'|)$ of [4], which according to [2] is formulated as*

$$\Phi_{ab}(R)=z_a z_b e^2\frac{2}{\pi}\int_0^\infty \frac{dk}{\varepsilon_\parallel(k)}\frac{\sin kR}{kR}\frac{\sin kr_a}{kr_a}\frac{\sin kr_b}{kr_b},\quad R\gg r_a, r_b, \tag{1}$$

(where z_a, z_b and r_a, r_b are the charges and radii of ions of sorts a and b, and $\varepsilon_\parallel(k)$ is the static dielectric permittivity of the solvent as function of the wave vector), makes it possible, moreover, to explicitly distinguish the role of the polar solvent's own structure in the theory of electrolyte solutions. It is known [6] that in the electrodynamics of dielectrics, it is their structure, i.e., the degree and character of correlation of the polarization fluctuations in space, which determines the spectrum of spatial dispersion of the dielectric permittivity, or its dependence on k. As an illustration of the solvent's role, we shall investigate the form of the binary distribution function of the ions at distances of separation which are much larger than their own dimensions; we shall use the Born-Green-Bogolyubov method [7, 3].

One can show by extending the method of [4, 8] to the case being considered here that the binary correlation function $F_{ab}(R)$ at distances $R \gg r_a, r_b$, which corresponds to the potential (1), is determined by the integral equation

$$\ln F_{ab}(\mathbf{r}-\mathbf{r}')+\frac{1}{Tv}\sum n_c\int \Phi_{ac}(\mathbf{r}-\mathbf{r}'')\ln F_{cb}(\mathbf{r}''-\mathbf{r}')\cdot d\mathbf{r}''=-\Phi_{ab}(\mathbf{r}-\mathbf{r}')/T \tag{2}$$

($n_a = N_a/N$, N_a is the total number of particles of sort a, $N=\sum_a N_a$, v is the specific volume, and T is the temperature in units of energy), with an accuracy to first-order terms with respect to the modified Debye parameter $d=v^{-1/2}\left(\frac{4\pi e^2}{T}\sum_a n_a z_a^2\right)^{3/2}$†. Its solution by the Fourier method can readily be obtained when the pair poten-

* In deducing (1) the Born model of ions (metallic spheres) [5, 2] and the model of cut-off spheres [2] were used, i.e. the assumption was made that within the ions the medium retains the dielectric properties of the pure liquid.

† In contrast to the usual Debye parameter $d \equiv v/r_D^3$, where $1/r_D=\sqrt{\frac{4\pi e^2}{\varepsilon Tv}\sum_a n_a z_a^2}$, the static dielectric permittivity ε in the modified parameter has been replaced by unity. It follows from the results of [2] that such a majorant criterion is required. It follows from the sufficient condition $\tilde{d} \ll 1$ that the starting equation (2) is correct for

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tial, in the region where it applies, is rewritten in an approximate form as

$$\Phi_{ab}(R)=z_a z_b e^2 \frac{2}{\pi}\int_0^\infty \frac{dk}{\varepsilon_\parallel(k)}\frac{\sin kR}{kR}\equiv z_a z_b \Phi(R). \tag{3}$$

Then the solution of (2) is of the form

$$F_{ab}(R)=\exp\{-z_a z_b G(R)\}, \tag{4a}$$

$$G(R)=\frac{v}{2\pi^2\sum_c n_c z_c^2}\int_0^\infty dk\,\frac{\sin kR}{kR}\frac{k^2}{1+\varepsilon_\parallel(k)\tilde{r}_D^2 k^2}, \tag{4b}$$

where $\tilde{r}_D = r_D/\sqrt{\varepsilon}$.

According to the dynamical model of polar liquids [1] (cf., also [9]), several degrees of freedom of the system contribute to the polarization. If the spectrum of the optical eigenfrequencies of the medium, which can be determined from the absorption spectrum of electromagnetic waves, has a shape where absorption zones in the form of smeared-out peaks are separated by zones of transparency, then each absorption zone can be identified with a particular mode of motion corresponding to its polarization. The total polarization of the medium presents itself as a superposition of the polarizations of the individual modes (subsystems). The assumption that the polarizations of the individual subsystems are uncorrelated is more accurately satisfied the wider the zones of transparency. The polarizations in the different points of space in a structured liquid correlate with one another, the correlation function being

$$S_{\alpha\beta}(\mathbf{r}-\mathbf{r}')=\langle P^\alpha(\mathbf{r})P^\beta(\mathbf{r}')\rangle=\sum_n\langle P_n^\alpha(\mathbf{r})P_n^\beta(\mathbf{r}')\rangle \quad (\alpha,\beta=x,y,z),$$

where $P_n(\mathbf{r})$ is the polarization of the subsystem n. To each subsystem n one can ascribe a characteristic correlation radius λ_n such that at

$$\{|\mathbf{r}-\mathbf{r}'|/\lambda_n\}\to\infty, \quad \langle P_n^\alpha(\mathbf{r})P_n^\beta(\mathbf{r}')\rangle\to\langle P_n^\alpha(\mathbf{r})\rangle\langle P_n^\beta(\mathbf{r}')\rangle=0\,*.$$

It has been shown in [9] that

$$\varepsilon_\parallel(k)=\left\{1-\sum_n\left(\frac{1}{\varepsilon_{n+1}}-\frac{1}{\varepsilon_n}\right)\mathcal{F}_n(k\lambda_n)\right\}^{-1},$$

where ε_n is the long-wave dielectric permittivity (k = 0) in the zone of transparency which separates the absorption zones n and (n−1) ($\varepsilon_{n=0}=\varepsilon_0$ coincides with the dielectric constant $\varepsilon\equiv\varepsilon(k=0)$), $\mathcal{F}_n(0)=1$, $\mathcal{F}_n(\infty)=0$, $\mathcal{F}_n(x)$ has a characteristic radius of subsidence of x = 1.

According to (5), $\varepsilon_\parallel(k)$ in Eq. (4b) can approximately be replaced by ε at distances R which are much larger than all correlation radii λ_n. Putting the result of integration into (4a) we obtain

$$F_{ab}(R)=\exp\left\{-\frac{z_a z_b e^2}{\varepsilon T}\frac{1}{R}e^{-R/r_D}\right\}. \tag{6}$$

For $R \gg r_D$, (6) goes over into the equation of Debye [10] and Bogolyubov [3]:

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electrolytes with a mean interionic distance $\bar{r}\equiv\sqrt[3]{v}\gg\frac{4\pi e^2}{T}\sum_a n_a z_a$, which for univalent electrolytes at room temperatures gives $\bar{r}\gg 10^4$ Å.

*The approximation of a single correlation radius for a subsystem n should yield not only qualitative but also quantitative results, provided that the absorption zone lacks fine structure, i.e., does not consist of overlapping resonances.

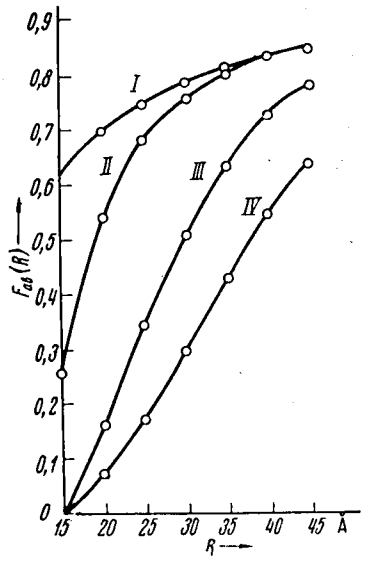

Fig. 1. The radial distribution function of ions of like charge in the aqueous solution of a univalent electrolyte at 25°C over the range from 15 to 45 Å. Calculated according to Eq. (10) with $\varepsilon = 78$, $\varepsilon_* = 4.9$, and the following choices of the unknown parameter Λ: I) $\lambda = 0$ [distribution (8)], II) $\lambda = 5$ Å, III) 10 Å, IV) 15 Å.

$$F_{ab}(R) = 1 - \frac{z_a z_b e^2}{\varepsilon T}\frac{1}{R} e^{-R/r_D}.$$

It is easy to show that the initial term of the asymptote $R \ll r_D$ of expression (4b) is of the form

$$G(R) \simeq \frac{e^2}{T}\frac{2}{\pi}\int_0^\infty \frac{dk}{\varepsilon_\parallel(k)}\frac{\sin kR}{kR} = \frac{\Phi(R)}{T}, \qquad (7a)$$

$$F_{ab}(R) = \exp\{-z_a z_b \Phi(R)/T\}, \qquad (7b)$$

i.e., the binary distribution function is in this case determined by a Boltzmann factor with the potential (3). For $R \gg$ all λ_n this potential does not differ from the coulombic, and

$$F_{ab}(R) = \exp\{-z_a z_b e^2/\varepsilon RT\}. \qquad (8)$$

For $R \sim \lambda_n$, i.e., when $\Phi(R)$ is of a substantially noncoulombic form [2], $F_{ab}(R)$ is substantially different from (8).

It must be stressed that in the concentration range where the starting equation (2) holds, one has $r_D \gg 4\pi e^2 \sum_a n_a z_a^2/\varepsilon T$, which, e.g., for a univalent electrolyte in water under normal conditions, gives $r_D \gg 100$ Å. It is clear, at the same time, that the largest correlation radius, $\max\{\lambda_n\}$, in water surely does not exceed 100 Å, i.e., in the region where the theory applies to aqueous solutions, $r_D \gg \max\{\lambda_n\}$. Hence for $R \sim r_D$ the binary function is always of the form (6), i.e., the dynamical structure of the polar solvent has no effect over such distances. At distances where it is effective, the distribution function is of the Boltzmann form.

A single analytical expression for the really interesting case $\lambda_n \ll r_D$ can be obtained by approximating $\varepsilon_\parallel(k)$. In polar liquids there usually exist three types of mode, corresponding to the Debye, infrared, and electronic zones of absorption; it appears that the correlation radii of the quantum-type subsystems (the infrared and the electronic ones) are $\leqslant r_a, r_b$. For the Debye mode (that of hindered rotation of the molecules), one can use the approximation $\mathcal{F}_n(x) = (1 + x^2)^{-2}$ proven in [1]. Substituting into (4) the relation

$$\varepsilon_\parallel(k) = \left\{\frac{1}{\varepsilon_*} - \left(\frac{1}{\varepsilon_*} - \frac{1}{\varepsilon}\right)\frac{1}{(1+k^2\Lambda^2)^2}\right\}^{-1}, \qquad (9)$$

where ε_* is the dielectric permittivity at the frequencies of the zone of transparency separating the Debye absorption zone from the others,* and $\Lambda \equiv \lambda_D$ is the correlation radius of "orientational" polarization, we have

$$F_{ab}(R) = \exp\left\{-\frac{z_a z_b e^2}{RT}\left[\frac{1}{\varepsilon}e^{-R/r_D} + \left(\frac{1}{\varepsilon_*} - \frac{1}{\varepsilon}\right)\left(1 + \frac{R}{2\Lambda}\right)e^{-R/\Lambda}\right]\right\}. \qquad (10)$$

Figure 1 illustrates the decrease of the distribution function with "increasing" Λ. The physical significance of this decrease is obvious: It will be more difficult to turn the dipoles around according to the field of the ion, i.e.,

* In water and alcohols, the first resonance of the infrared region partly overlaps with the Debye absorption region (cf. [11]), i.e., there is no zone of transparency. In this case we shall use the following values for ε_*, by making use of the procedure proposed in [11] for superimposing the regions: 4.9 for water, 6.0 for methanol, 4.4 for ethanol, etc.

the screening of the ion by the solvent will be weaker the stronger the spatial correlation of the orientation of the dipoles. This leads to an increase in the energy of ionic interaction (here, of repulsion, so that the probability of an approach decreases).

As indicated above, the distribution functions obtained hold for dilute solutions ($\bar{r} \gg 10^4$ Å). Hence the dynamical structure of the solvent has no effect upon the shape of the distribution functions in the region of distances corresponding to the average distances between the ions in such solutions. The new results obtained are of interest in those problems where distances of the order of magnitude of the correlation radii of the solvent are important, e.g., when calculating the probability of approach of the ions of a dilute solution to small distances of separation, which is an important quantity in kinetics. In solutions of higher concentrations ($c \geq 0.1$ mole/liter) ($\bar{r} \sim \Lambda$), the correlation functions must be substantially dependent on the character of the dynamical structure of the solvent at distances $R \sim \bar{r}$, i.e., it must be taken into account when calculating the thermodynamic functions.

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