

ION DISTRIBUTION IN CONCENTRATED ELECTROLYTES

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Communicated by Raymond M. Fuoss, May 24, 1968

Although many years have passed since the appearance of the classic Debye-Hückel work on dilute electrolytes,¹ theory has yet to provide an adequate account of concentrated electrolyte properties. Doubtless this is due in part to current ignorance of the details of solvent behavior at the molecular level, especially in the case of water. But also the Coulomb interaction between ions itself provides a second difficulty, since it is generally unknown what role this potential's extreme range must play in reliable statistical-mechanical theory of the high concentration regime.

It is the purpose of this note to summarize a strategy which minimizes the second of these difficulties,² and to report some computations based on that strategy.

The general approach is initiated by redefinition of the basic "particles" of the problem. Conventionally, the individually charged ions play this role, but now we group the ions into uncharged sets of minimum size. In the case of a symmetrical electrolyte, this amounts to pairing off all ions, two by two, into "diatomic molecules" of zero net charge comprising one anion and one cation. These polar "molecules," or ion pairs, can have quite variable length, and can be individually oriented at random.

Of course the idea of pairing up ions is far from new.^{3, 4} However, the demand that *all* ions in a symmetrical electrolyte be formally paired makes it especially important to understand the logical structure and implications of the pairing process. We therefore specify that the pairing be carried out in the following manner:

(1) In a vessel containing N anions and N cations, arrange the set of instantaneous anion-cation distances in order of ascending size (without ultimate error they may be presumed distinct).

(2) Select the smallest of these distances and designate the ions it connects as the first ion pair.

(3) Consider next only the remaining $2N - 2$ unpaired ions, and arrange their anion-cation distances in ascending order.

(4) Choose the new smallest distance, and define its endpoint ions to be the second ion pair.

(5) Continue the process of selecting the smallest anion-cation distance for remaining unpaired ions at any intermediate stage to provide a next ion pair until all ions have been exhausted.

The final result is that all ions have been assigned unique partners of opposite charge; equivalently, no one ion simultaneously serves as partner to more than one other ion. Though we shall not enter into full details here, it is clear that the pairing process could be generalized to accommodate unsymmetrical electrolytes in such a way as to divide ions uniquely into uncharged "molecules" with minimal internal distances.

The starting ion positions in the symmetrical electrolyte quite obviously determine precisely which anions pair with which cations. As thermal agitation moves the ions about in the solution, all $N!$ distinct pairings will eventually obtain. However, all anions are identical to one another, as are all cations, so these distinct pairings (regarded merely as the result of ion permutations) are structurally equivalent. If interest is confined only to equilibrium properties of the electrolyte, it is therefore convenient to restrict attention merely to one possible pairing, say anion 1 with cation 1, . . . , anion N with cation N .

There are two basic implications of this restriction to a single pairing. First, only $1/N!$ of the entire electrolyte phase space is admitted, so that the actual electrolyte partition function is precisely $N!$ times the partition function for non-exchangeable ion pairs. Secondly, the ions must be prevented from moving into positions which violate the postulated pairing. In calculation of any property of the electrolyte (such as ion atmosphere charge density) which is independent of absolute entropy, the first of these implications is irrelevant, but the second requires very careful attention.

It is helpful to imagine that the partners in each ion pair are connected by a "bond." In order to maintain a given set of bonds, or ion pairs, we must prevent any anion of one pair from approaching cations of larger pairs more closely than its own partner, for if it did, the corresponding smaller anion-cation distance or bond would have been drawn in the above pairing process. By symmetry the same is true of cation approaches to anions belonging to larger pairs.

In chemical terminology, the ion pairs are subject to steric hindrance. Any bonded pair with fixed length and centroid position will have available to it only certain orientations, so as to avoid unallowed approaches to neighboring pairs. The entire set of configurational restrictions on the pairs may in fact be precisely cast into a set of "steric hindrance" potentials $u(i,j)$ acting between pairs i and j . The function $u(i,j)$ will depend upon the entire set of configuration variables for the four ions involved, and it will be zero if their positions are consistent with the postulated pairing, and infinitely large otherwise. Thus the set of steric hindrance potentials will force the ion pairs to remain in the correct $1/N!$ fraction of the original phase space.

Under the combined influence of the original real forces acting between ions, and the mathematically convenient steric hindrance forces, the ion pairs will establish some size distribution. This distribution $p(r)$ may be defined by the statement that the probability for two volume elements dV_1 and dV_2 in the solution, separated by distance r , to be simultaneously occupied by the two members of one pair is $p(r)dV_1dV_2$. As a result of finite ion size, $p(r)$ will vanish near $r = 0$. We also can reasonably expect that $p(r)$ will rapidly go to zero when r exceeds the inverse cube root of concentration, since such very large ion pairs will suffer considerable steric hindrance repulsion.

Once symmetrical electrolytes have been transcribed into equivalent fluids of diatomic polar molecules, it is natural to describe the new system in terms of its dielectric properties. Any externally applied static electric field may be resolved into separate Fourier sinusoidal components, and for those with wave-vector \mathbf{k} , the bulk linear response of the polar fluid defines a dielectric function $\epsilon(k)$. W

know of course that the solution macroscopically behaves as a conductor, that is, it tends to shield completely any electric field source. Hence, we know that in the long-wavelength limit:

$$\lim_{k \rightarrow 0} \epsilon(k) = +\infty. \quad (1)$$

However, this complete shielding property will obtain only in that limit, and for arbitrary nonzero k we must expect a finite $\epsilon(k)$ indicative of only partial shielding.

The k dependence of $\epsilon(k)$ amounts to nonlocal dielectric response, and is intimately connected with the distribution of charge in the electrolyte's ion atmospheres. The precise connection is established by the fact that static linear response of fluids to external fields may be expressed in terms of the system's doublet correlation functions. In the case of the "primitive model" symmetrical electrolyte, which specifies rigid spherical ions all of diameter a and charges $\pm Z|e|$ suspended in a dielectric continuum solvent, one finds

$$\frac{\epsilon_0}{\epsilon(k)} = 1 - \frac{\kappa^2}{k^2} \left\{ 1 + \frac{4\pi c}{k} \int_0^\infty r \sin(kr) [g_{+-}^{(2)}(r) - g_{++}^{(2)}(r)] dr \right\}. \quad (2)$$

Here ϵ_0 is the solvent dielectric constant, c is the electrolyte concentration, $g_{++}^{(2)}$ and $g_{+-}^{(2)}$ are the two independent ionic correlation functions (normalized to unity at large r), and κ is the usual Debye-Hückel inverse length:

$$\kappa^2 = \frac{8\pi(Z|e|)^2 c}{\epsilon_0 k_B T}. \quad (3)$$

The particular combination of $g^{(2)}$'s appearing in equation (2) is precisely the one which gives the radial dependence of ion-atmosphere charge density. Therefore the Fourier transform inverse to expression (2) allows us to represent the ion-atmosphere charge density as an integral of the equivalent polar fluid dielectric function:

$$Z|e|c [g_{+-}^{(2)}(r) - g_{++}^{(2)}(r)] = - \frac{Z|e|}{2\pi^2 r} \int_0^\infty k \sin(kr) \left\{ \frac{k^2}{\kappa^2} \left[\frac{\epsilon_0}{\epsilon(k)} - 1 \right] + 1 \right\} dk. \quad (4)$$

The complete shielding property expressed in equation (1) implies that the right member of equation (2) must vanish as k goes to zero. In order for that to occur, two conditions are required:

$$1 = 4\pi c \int_0^\infty r^2 [g_{+-}^{(2)}(r) - g_{++}^{(2)}(r)] dr; \quad (5)$$

$$6/\kappa^2 = 4\pi c \int_0^\infty r^4 [g_{+-}^{(2)}(r) - g_{++}^{(2)}(r)] dr. \quad (6)$$

The former is the familiar local electroneutrality condition stating that the total diffuse ion-atmosphere charge exactly cancels the central ion's charge. The second condition, however, is new, and if $\kappa a > \sqrt{6}$, it is easy to show that the two

are compatible only if the diffuse atmosphere consists of concentric regions of both charge signs.

The value of the polar-molecule point of view consists largely in the manner of calculating $\epsilon(k)$ that it suggests, namely, that this dielectric response function should be accessible through analysis of the orientation perturbation of ion pairs resulting from an applied field. This program must be carried out in a self-consistent way: the mean torque potential acting on an ion pair (when the system is linearly perturbed by a single wave vector- κ external field) not only determines the induced sinusoidal charge density, but is in turn partly determined by that induced charge. The relevant picture to bear in mind is that of a single ion pair moving in the mean charge and the mean potential field inside the electrolyte, but excluding induced charge from the two radius- a spherical regions about its two ends.

The steric hindrance potentials complicate this otherwise simple picture of mean torque in a self-consistent potential. As a result of the repulsion between their unlike ends, neighboring ion pairs will tend to line up side by side and parallel. This tendency will persist under the influence of external fields to the extent that reorientation of one ion pair will tend to drag along its neighbors into the new position. It is fortunate that this local tendency toward cooperative reorientation may be accounted for in calculation of $\epsilon(k)$ by means of a torque-potential renormalization factor:

$$\lambda(k) = \left\{ \frac{4\pi}{c} \int_0^\infty s^2 \left[1 - \frac{\sin(ks)}{ks} \right] p(s) ds \right\}^{-1}. \quad (7)$$

Use of $\lambda(k)$ as a simple multiplier for the self-consistent fields acting on a given ion pair permits one to proceed as though the pair were independent of further steric hindrance.

The evaluation of $\lambda(k)$ clearly depends on the form of ion-pair size distribution p . In dilute solution p may be determined by a variety of techniques.² However, in very concentrated solutions or molten salts $p(r)$ should be strongly compressed into a narrow range of r values just exceeding the distance of closest approach a . Replacement of $p(r)$ by a suitable constant times the Dirac delta function then is reasonable, and equation (7) undergoes trivial reduction. The dielectric function calculation likewise proceeds in straightforward fashion to yield ultimately the following explicit result:

$$\frac{\epsilon_0}{\epsilon(k)} = 1 - \frac{\kappa^2}{k^2 + \kappa^2 [\cos(ka) + H(ka)]}; \quad (8)$$

$$H(x) = \frac{\sin(x) + \sin(2x) - 3x \cos(x)}{4[x - \sin(x)]}. \quad (9)$$

To illustrate application of the theory to specific electrolytes, we have selected saturated aqueous KCl for numerical analysis. The equal-ion-size presumption utilized by the primitive model seems superficially vindicated by the near-equality of transport numbers for this salt at all concentrations. At 20°C the saturated solution is 4.65 moles per liter, and from the dielectric measurements on

electrolytes performed by Hasted, Ritson, and Collie⁵ we may reasonably infer that $\epsilon_0 \cong 50$. Furthermore, the effective ion size a has been reported as 3.63 angstroms.⁶ Accordingly, one computes $\kappa^2 a^2 = 10.6$, well in excess of the value 6 for which alternating atmosphere charge sign necessarily occurs.

Figure 1 presents the dielectric response function for saturated KCl, obtained from equation (8). For comparison, the linear point-ion Debye-Hückel theory response function

$$\left(\frac{\epsilon_0}{\epsilon(k)}\right)_{DH} = 1 - \frac{\kappa^2}{k^2 + \kappa^2}$$

(which may be obtained as the $a \rightarrow 0$ limit of expression (8)) has been plotted as well. The most important feature of the concentrated salt's response function is the fact that it goes negative for a range of k 's, indicating charge overcompensation for external fields of those wavelengths.

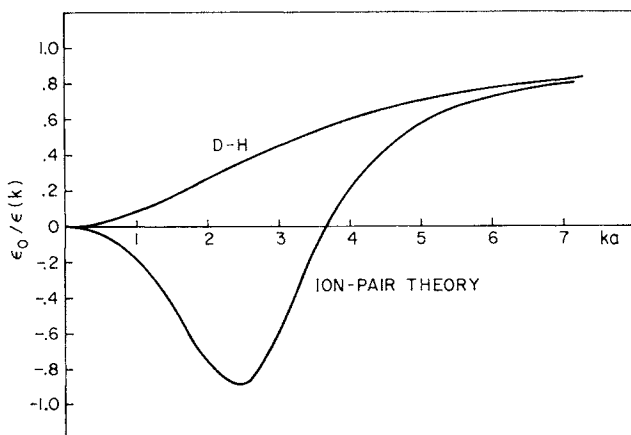


FIG. 1.—Dielectric response function of saturated aqueous KCl (20°C) for various wavelengths of the external field. The ion-pair theory curve predicts overshielding of the sinusoidal external field when $0 < ka < 3.66$, though this never occurs in the linear point-ion Debye-Hückel (*D-H*) approximation.

Equation (4) has been used in turn to evaluate the ion atmosphere radial charge density, with results displayed in Figure 2. The existence of concentric shells of alternating average charge is very obvious out to several ionic diameters, and detailed analysis shows that this mean charge and potential damped oscillation extends to infinity. Doubtless the ions have started sorting themselves into the precursor of a regular lattice, even though considerable short-range disorder still persists.⁷ The successive shells shown in Figure 2 have charges corresponding roughly to $+1.6, -0.7, +0.2, -0.05, \dots$ ionic charges.

The calculation just presented should be considered merely exploratory. Ideally, the ion-pair theory should also predict $p(r)$, and not rely on the crude delta-function presumption. Indeed, the theory may be set up variationally with the free energy serving as a functional of $p(r)$; minimization of that func-

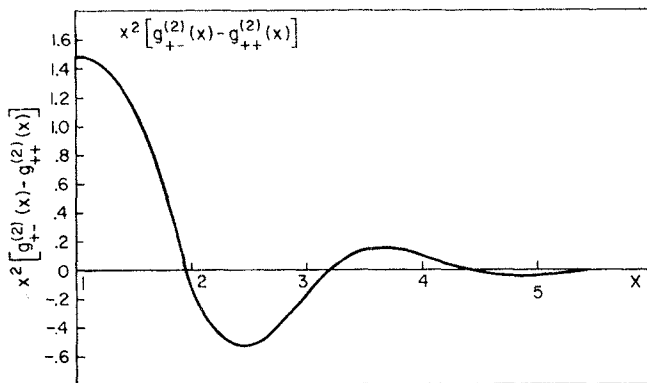


FIG. 2.—Ion atmosphere charge for saturated aqueous KCl at 20°C, as predicted by the ion-pair theory. With the sign convention chosen, the curve refers to charge about an anion; for cations a sign change is required. The damped oscillations persist to infinity.

tional then would produce the correct $p(r)$ and serve as the basis for an improved version of our ion-pair theory. In particular such a variational theory should be valuable in quantitative description of ionic order in molten salts.

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¹ Debye, P., and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

² Detailed derivations of results quoted here may be found in Stillinger, F. H., Jr., and R. Lovett, *J. Chem. Phys.*, **48**, 3858 (1968), and the paper immediately following it.

³ Bjerrum, N., *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **7**(9), 1 (1926).

⁴ Fuoss, R. M., *Trans. Faraday Soc.*, **30**, 967 (1934).

⁵ Hasted, J. B., D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

⁶ Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions* (New York: Academic Press, 1959), p. 246.

⁷ The first suggestion of this possibility in concentrated electrolytes seems to have been made in Kirkwood, J. G., *Chem. Revs.*, **19**, 275 (1936).