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Kusalik, P. G. and Patey, G. N. (1983). "Theoretical results for dielectric and structural properties of aqueous electrolytes. The influence of ion size and charge". *Journal of Chemical Physics*, Vol. 79(9): 4468-4474.

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# Theoretical results for dielectric and structural properties of aqueous electrolytes. The influence of ion size and charge

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(Received 7 June 1983; accepted 30 June 1983)

The present paper describes a theoretical investigation of aqueous electrolytes in the infinite dilution limit. The linearized hypernetted chain theory is applied to solutions of hard spherical ions in a waterlike solvent at 25 °C and the properties of solution are studied as a function of ion size and charge. We examine both dynamical and equilibrium contributions to the apparent "dielectric constant" of solution and compare with previous theoretical calculations as well as with experimental measurements. Ion-solvent correlation functions and ion-ion potentials of mean force for several common electrolytes are also presented and discussed.

## I. INTRODUCTION

In a recent article<sup>1</sup> we have presented theoretical results for model aqueous electrolytes in the infinite dilution limit. The waterlike solvent is a fluid of polarizable hard spheres with embedded point dipoles and tetrahedral quadrupoles and the ions are simply charged hard spheres. Integral equation theories such as the linearized hypernetted-chain (LHNC) approximation can be solved for this system<sup>1-3</sup> and in Ref. 1 1:1 electrolytes with ions and solvent molecules of equal diameter were studied with particular attention focused upon ion-ion potentials of mean force and the dielectric properties of solution.

It is now well known<sup>4,5</sup> that the experimentally measured dielectric constant of an ionic solution contains both equilibrium and dynamical contributions. The equilibrium part plays a role analogous to that of the usual static dielectric constant of nonconducting media and is often referred to as the solute-dependent dielectric constant denoted by  $\epsilon_p$  where  $\rho$  is the total ionic concentration. At low ionic concentration  $\epsilon_p$  is a linear function of concentration with a negative slope and in Ref. 1 it is shown that the present model and theory give results consistent with experimental data. A dynamical contribution which also tends to decrease the apparent (i.e., experimental) dielectric constant was first identified by Hubbard and Onsager<sup>6</sup> for a continuum model and has been further investigated on a molecular level by Hubbard, Colonomos, and Wolynes.<sup>4</sup> Following Hubbard, Colonomos, and Wolynes, we shall refer to this effect as the "kinetic dielectric decrement" (KDD). Although the magnitude of this contribution is uncertain, in the continuum theory of Hubbard and Onsager it appears to account for ~25% of the total dielectric decrement for typical 1:1 aqueous electrolytes.<sup>1,7</sup>

In the present paper we extend the work of Ref. 1 to ions of varying size and charge and investigate the influence of these parameters upon the dielectric and the structural properties of solution. Also we use the dynamical formalism of Hubbard, Colonomos, and Wolynes<sup>4</sup> together with our equilibrium theory in order to

study the kinetic dielectric decrement in more detail. The present theory is compared with previous theoretical work and where possible with experimental results.

The remainder of this paper is divided into three parts. In Sec. II we summarize the basic theoretical relationships, in Sec. III we discuss the numerical results and our conclusions are given in Sec. IV.

## II. FORMAL RELATIONSHIPS

### A. The model and ion-ion potentials of mean force

The details of the present model and theoretical approach have been described in Refs. 1 and 2 and we shall merely summarize the basic relationships here. We consider a solution of charged hard spheres in a polarizable hard sphere dipole-tetrahedral quadrupole solvent with waterlike parameters. The properties of this solvent according to the present theory are given in Ref. 2. The ion-ion and ion-solvent interactions,  $u_{ij}(r)$  and  $u_{is}(12)$ , respectively, are of the form

$$u_{ij}(r) = u_{ij}^{\text{HS}}(r) + q_i q_j / r \quad (1a)$$

and

$$u_{is}(12) = u_{is}^{\text{HS}}(r) + u_{is}^{011}(r) \Phi^{011}(12) + u_{is}^{022}(r) \Phi^{022}, \quad (1b)$$

where

$$u_{is}^{011}(r) = -q_i \mu / r^2, \quad (1c)$$

$$u_{is}^{022}(r) = q_i Q_T / \sqrt{6} r^3, \quad (1d)$$

$u_{\alpha\beta}^{\text{HS}}(r)$  represents the usual hard sphere interaction, the functions  $\Phi^{011}(12)$  and  $\Phi^{022}(12)$  depend upon the angles of orientation as previously defined,<sup>1-3</sup>  $r$  is the interparticle separation,  $q_i$  is the charge associated with the ionic species  $i$ ,  $\mu$  is an "effective" solvent dipole moment, and  $Q_T$  is the quadrupole moment of the solvent. The second and third terms in Eq. (1b) represent the charge-dipole and charge-quadrupole interactions, respectively, and the effective solvent dipole moment includes solvent-solvent polarization effects as discussed in Ref. 2. As in previous work<sup>1</sup> we make no attempt to take ion-solvent polarization effects into account.

The equations defining the LHNC integral equation theory for this ion-solvent mixture are given in Ref. 1. In this approximation the ion-solvent pair and direct correlation functions, denoted by  $h_{is}(12)$  and  $c_{is}(12)$ , respectively, are of the form

$$h_{is}(12) = h_{is}^{000}(r) + h_{is}^{011}(r)\Phi^{011}(12) + h_{is}^{022}(r)\Phi^{022}(12) \quad (2)$$

and the theory consists of a set of closed integral equations for the coefficients  $h_{is}^{mnl}(r)$  and  $c_{is}^{mnl}(r)$ . The integral equations can be solved numerically and the  $h_{is}^{mnl}(r)$  and  $c_{is}^{mnl}(r)$  are sufficient to determine ion-ion correlation functions at infinite dilution. The ion-ion potential of mean force  $w_{ij}(r)$  is given by

$$\beta w_{ij}(r) = -\ln g_{ij}(r) \approx \beta u_{ij}(r) - \eta_{ij}(r), \quad (3a)$$

where  $g_{ij}(r) = h_{ij}(r) + 1$ ,  $\eta_{ij}(r) = h_{ij}(r) - c_{ij}(r)$ ,  $\beta = 1/kT$ , and the approximate expression on the right follows from the HNC closure. We note that as  $r \rightarrow \infty$ ,

$$w_{ij}(r) \rightarrow q_i q_j / \epsilon_0 r, \quad (3b)$$

where  $\epsilon_0$  is the dielectric constant of the pure solvent.

### B. The dielectric constant of solution

As mentioned earlier the apparent dielectric constant of solution  $\epsilon_{\text{sol}}$  contains both equilibrium and dynamical contributions. The equilibrium part  $\epsilon_p$  is now well defined and formally understood.<sup>8-10</sup> For the present model at low ionic concentrations  $\epsilon_p$  is given by

$$\epsilon_p = \epsilon_0 + \sum_i \epsilon_{(i)} \rho_i + \dots, \quad (4a)$$

where

$$\epsilon_{(i)} = \frac{(\epsilon_0 - 1)^2}{9y} \rho_s \delta_i \tilde{c}_{ss}^{110}, \quad (4b)$$

$$\delta_i \tilde{c}_{ss}^{110} = \left. \frac{\partial}{\partial \rho_i} \tilde{c}_{ss}^{110}(k) \right|_{k=0, \rho=0}. \quad (4c)$$

$y = 4\pi\beta\mu^2\rho_s/9$ ,  $\rho_s$  is the solvent density,  $\rho_i$  is the density of ionic species  $i$ ,  $\rho = \sum_{i \in \text{ions}} \rho_i$  and  $\tilde{c}_{ss}^{110}(k)$  is the Fourier transform of  $c_{ss}^{110}(r)$  which is a coefficient occurring in the solvent-solvent direct correlation function (cf. Ref. 2). We note that in Ref. 1 the  $\rho_s$  now included explicitly in Eq. (4b) was absorbed into the definition of  $\delta_i \tilde{c}_{ss}^{110}$ . Applying cluster expansion methods Friedman<sup>10</sup> showed that in the HNC theory infinite dilution results for  $h_{is}(12)$  and  $h_{ss}(12)$  are sufficient to determine  $\delta_i \tilde{c}_{ss}^{110}$  and hence the coefficient of the linear term in Eq. (4a). For the present model and theory one obtains<sup>1</sup>

$$\delta_i \tilde{c}_{ss}^{110} = I_{00}^{00110} + \frac{1}{3} I_{00}^{11000}, \quad (5a)$$

where

$$I_{mm'}^{ll' MNL} = \frac{1}{2\pi^2} \int_0^\infty k^2 dk \tilde{h}_{si, m0}^{l0l}(k) \tilde{h}_{is, 0m'}^{l'l'}(k) \tilde{h}_{ss, -m-m'}^{MNL}(k) \quad (5b)$$

and the tilde denotes appropriate Hankel transforms as defined elsewhere.<sup>11</sup>

There are two known dynamical contributions to  $\epsilon_{\text{sol}}$ . These are the Debye-Falkenhagen (DF) effect<sup>4,5,7</sup> which tends to increase the apparent dielectric constant and the previously mentioned kinetic dielectric decrement of Hubbard and Onsager. At low ionic concentrations the DF contribution can be estimated and subtracted

from the experimental results (cf. Ref. 7). In the present paper we consider the microscopic theory of Hubbard *et al.*<sup>4</sup> for the kinetic dielectric decrement which we shall denote by  $\Delta\epsilon_i^{\text{KDD}}$ .

In the theory of Hubbard *et al.*<sup>4</sup>  $\Delta\epsilon_i^{\text{KDD}}$  is given by the expression [cf. Eq. (35) of Ref. 4]:

$$\Delta\epsilon_i^{\text{KDD}} = \frac{-8\pi}{3} \left( \frac{\sigma_i \tau_D}{q_i} \right) N_s r_{(\text{ST})i} \left\langle \frac{\mu \cdot \hat{r}}{r^2} \right\rangle, \quad (6)$$

where  $\sigma_i$  is the conductivity of species  $i$ ,  $\tau_D$  is the Debye relaxation time of the solvent,  $N_s$  is the number of solvent particles, the angular brackets denote an equilibrium average and  $r_{(\text{ST})i}$  is the Stokes radius of species  $i$  obtained assuming slip boundary conditions.<sup>4</sup> Using Eq. (2) together with the relationship  $\mu \cdot \hat{r} = \mu \Phi^{011}(12)$  it is not difficult to show that for a sample of volume  $V$ ,

$$\left\langle \frac{\mu \cdot \hat{r}}{r^2} \right\rangle = \frac{4\pi}{3} \frac{\mu}{V} \int_{d_{is}}^\infty h_{is}^{011}(r) dr \quad (7a)$$

and hence

$$\frac{\Delta\epsilon_i^{\text{KDD}}}{\sigma_i \tau_D} = \frac{8\pi}{3} \frac{r_{(\text{ST})i}}{q_i^2} \left( \frac{U_{\text{CD}}}{N_i} \right), \quad (7b)$$

where

$$\frac{U_{\text{CD}}}{N_i} = \frac{-4\pi}{3} \rho_s q_i \mu \int_{d_{is}}^\infty h_{is}^{011}(r) dr, \quad (7c)$$

$d_{is} = (d_i + d_s)/2$  and  $N_i$  is the number of ions of species  $i$ . In the infinite dilution limit  $U_{\text{CD}}/N_i$  is just the average charge-dipole interaction energy for a single ion. It is important to note that according to the theory of Hubbard *et al.*<sup>4</sup> two different ionic radii enter into the calculation of  $\Delta\epsilon_i^{\text{KDD}}/\sigma_i \tau_D$ . These are the Stokes radius which enters through the inverse of the diffusion constant<sup>4</sup> and the bare ionic or crystal radius which enters into the calculation of  $U_{\text{CD}}/N_i$ . Of course, these radii become equal in the limit of infinitely large ions. It is possible to show that if the long-range asymptotic form for  $h_{is}^{011}(r)$  (cf. Ref. 11) is used to evaluate the integral in Eq. (7c) then as  $d_s/d_i \rightarrow 0$ ,  $\Delta\epsilon_i^{\text{KDD}}/\sigma_i \tau_D \rightarrow 8\pi(\epsilon - 1)/3\epsilon$  which, if we take the high frequency dielectric constant to be one, agrees with the continuum result for slip boundary conditions.<sup>4</sup> In the present paper we calculate  $\Delta\epsilon_i^{\text{KDD}}$  using the LHNC theory for  $h_{is}^{011}(r)$  and compare with previous results of Hubbard *et al.*<sup>4</sup>

### III. RESULTS AND DISCUSSION

At infinite dilution our system is totally characterized by the reduced parameters  $\rho_s^* = \rho_s d_s^3$ ,  $\mu^* = (\beta\mu^2/d_s^3)^{1/2}$ ,  $Q_T^* = (\beta Q_T^2/d_s^5)^{1/2}$ ,  $q_i^* = (\beta q_i^2/d_s)^{1/2}$ , and  $d_i^* = d_i/d_s$ . The solvent diameter is  $d_s = 2.8 \text{ \AA}$  and at 25 °C,  $\rho_s^* = 0.732$ ,  $Q_T^* = 0.94$ , the effective dipole moment (cf. Ref. 2)  $\mu^* = 2.751$ ,  $\epsilon_0 = 77.47$ , and the reduced charge  $q_i^* = 14.1527z_i$ , where  $|z_i|$  is the number of elementary charges associated with the ion. In the following discussion we refer extensively to the alkali halides taking  $d_i/2$  to be the crystal radii obtained from x-ray electron density measurements as described by Morris.<sup>12</sup> The values of  $d_i^*$  for various ions are summarized in Table I. We note that for cations these values are somewhat larger and for anions somewhat smaller than those obtained using

TABLE I. Reduced diameters ( $d_i^* = d_i/d_s$ ) for alkali metal and halide ions. The values of  $d_i$  are from Ref. 12 and  $d_s = 2.8 \text{ \AA}$ . The values of  $d_i^*$  used in the numerical calculations were rounded to the nearest 0.04 in order to accommodate a grid width of  $0.02d_s$ .

Ion	$d_i^*$
Li <sup>+</sup>	0.66
Na <sup>+</sup>	0.84
K <sup>+</sup>	1.06
Rb <sup>+</sup>	1.17
Cs <sup>+</sup>	1.31
F <sup>-</sup>	0.83
Cl <sup>-</sup>	1.17
Br <sup>-</sup>	1.29
I <sup>-</sup>	1.49

the more familiar Pauling<sup>13</sup> radii. The electron density measurements appear to be a less arbitrary and physically more realistic method of defining ionic radii.

### A. The dielectric constant of solution

The equilibrium contribution to the total dielectric decrement can be written in the form

$$\Delta\epsilon_p = \epsilon_p - \epsilon_0 = \sum_i \epsilon_{(1)i}^* \rho_i^* + \dots, \quad (8a)$$

where

$$\epsilon_{(1)i}^* = \frac{\epsilon_{(1)i}}{d_s^3} = \frac{(\epsilon_0 - 1)^2}{9y} \rho_s^* (I_{00}^{00110*} + \frac{1}{3} I_{00}^{11000*}), \quad (8b)$$

$\rho_i^* = \rho_i d_s^3$  and  $I_{mm}^{11' MNL*} = I_{mm}^{11 MNL} / d_s^6$ . If we consider salts of the general form  $A_\nu B_\nu C_\nu \dots$  and assume complete dissociation then

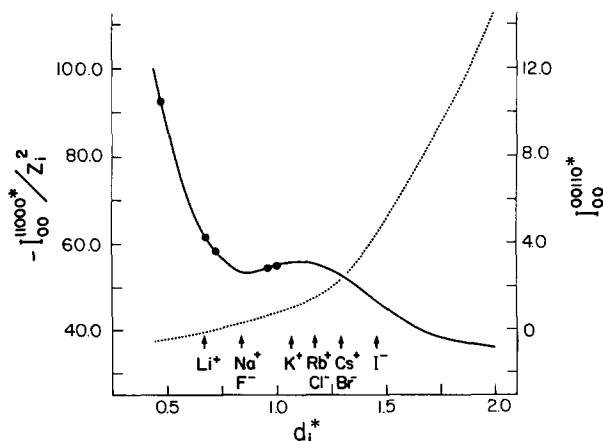


FIG. 1. The terms contributing to  $\epsilon_{(1)i}^*$  at 25 °C [cf. Eq. (8b)] as a function of ion diameter. The solid line represents  $-I_{00}^{11000*}/z_i^2$  for univalent ions and the solid dots are results for the divalent case. The dashed line represents  $I_{00}^{00110*}$  which in the present theory does not depend upon the ionic charge. Note that two scales are used in the plot.

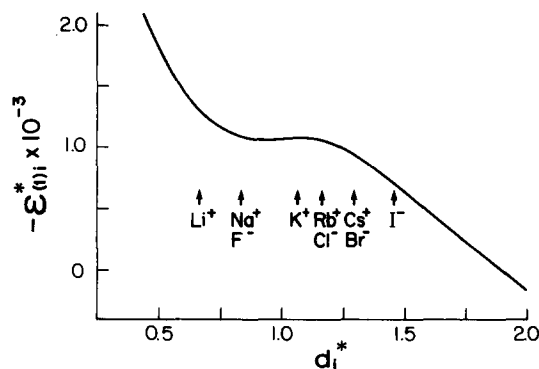


FIG. 2. The diameter dependence of  $\epsilon_{(1)i}^*$  for univalent ions at 25 °C.

$$\Delta\epsilon_p = \left( \frac{N_A d_s^3}{10^{27}} \sum_i \epsilon_{(1)i}^* \nu_i \right) C_{\text{SALT}}, \quad (9)$$

where  $C_{\text{SALT}}$  is the concentration of salt in mol  $l^{-1}$ ,  $N_A$  is Avogadro's number, and  $d_s^3$  must be expressed in cubic angstroms.

The variation of  $I_{00}^{11000*}$  and  $I_{00}^{00110*}$  with ion diameter is shown in Fig. 1 and  $\epsilon_{(1)i}^*$  is plotted in Fig. 2. We emphasize that for the present model these functions depend only upon the magnitude and not upon the sign of the ionic charge. We see from Fig. 1 that  $I_{00}^{11000*}$  is relatively large and negative and exhibits some structural features with a local maximum occurring at  $d_i^* \sim 1.1$ . At first sight this structure may appear surprising but it can be understood physically by considering two contributing factors which vary with ion size. As  $d_i^*$  is increased the decreasing strength of the charge-dipole interaction tends to decrease the magnitude of  $I_{00}^{11000*}$  but this will be offset to some extent by the increasing number of solvent neighbors around the larger ion. It is likely that these competing effects give rise to the structural features in  $I_{00}^{11000*}$ . It is also interesting to observe that to an excellent approximation  $I_{00}^{11000*}/z_i^2$  is independent of the value of  $z_i$  and thus the contribution of  $I_{00}^{11000*}$  to  $\epsilon_p$  simply scales with the square of the ionic charge.

In the LHNC theory  $I_{00}^{00110*}$  does not depend upon the ionic charge but does vary with  $d_i^*$ . From Fig. 1 it can be seen that the values obtained are relatively small and negative for small ions but become larger and positive as  $d_i^*$  is increased. We observe (cf. Fig. 2) that  $\epsilon_{(1)i}^*$  decreases in magnitude with increasing  $d_i^*$ , actually becoming positive for values of  $d_i^* > 1.9$ . However, for the alkali metal and halide ions  $I_{00}^{11000*}$  makes the most important contribution to  $\epsilon_{(1)i}^*$  which is in fact nearly constant in the range  $\text{Na}^+ \rightarrow \text{Rb}^+$  or  $\text{F}^- \rightarrow \text{Cl}^-$ .  $\epsilon_{(1)i}^*$  does increase in magnitude for  $\text{Li}^+$  and shows a marked decrease for the larger ions  $\text{Cs}^+$  and  $\text{I}^-$  where  $I_{00}^{00110*}$  begins to have a significant effect and  $I_{00}^{11000*}$  decreases more rapidly.

The kinetic dielectric decrement for particle  $i$  can be written in the form

$$\Delta\epsilon_i^{KDD} = A \left( \frac{\Delta\epsilon_i^{KDD}}{\sigma_i \tau_D} \right) \sigma_i, \quad (10)$$

where  $\Delta\epsilon_i^{KDD}/\sigma_i \tau_D$  is the dimensionless ratio given by Eq. (7b). If we express  $\sigma_i$  in  $\Omega^{-1} m^{-1}$  then  $A = \tau_D/4\pi\epsilon'$  = 0.07415  $\Omega m$ , where  $\epsilon'$  is the permittivity of free space and we have used the value  $\tau_D = 8.25 \times 10^{-12}$  s for the Debye relaxation time of water.<sup>14</sup> At low ionic concentrations  $\sigma_i = C_{SALT} \nu_i \lambda_i^0$ , where  $\lambda_i^0$  is the molar ionic conductance at infinite dilution and hence the total kinetic contribution to the dielectric decrement  $\Delta\epsilon^{KDD}$  is given by

$$\Delta\epsilon^{KDD} = \left[ A \sum_i \left( \frac{\Delta\epsilon_i^{KDD}}{\sigma_i \tau_D} \right) \nu_i \lambda_i^0 \right] C_{SALT}. \quad (11)$$

The ratio  $(\Delta\epsilon^{KDD}/\sigma_i \tau_D) r_i / r_{(ST)i}$  where  $r_i$  is the crystal radius is shown in Fig. 3. This quantity is a continuous function of ion diameter and we note that essentially the same values are obtained for monovalent and divalent ions. Thus differences in  $\Delta\epsilon^{KDD}/\sigma_i \tau_D$  for divalent and monovalent ions of the same size enter only through differing values of the Stokes radius. In Fig. 3 we also plot values of  $\Delta\epsilon_i^{KDD}/\sigma_i \tau_D$  for several ions and comparisons are made with previous results of Hubbard *et al.*<sup>4</sup> [cf., Fig. 2 of Ref. 4]. In the present calculations the Stokes radii were taken to be the values given in Ref. 15 corrected for slip boundary conditions. From Fig. 3 it can be seen that fair agreement is obtained between the present and previous calculations. This is particu-

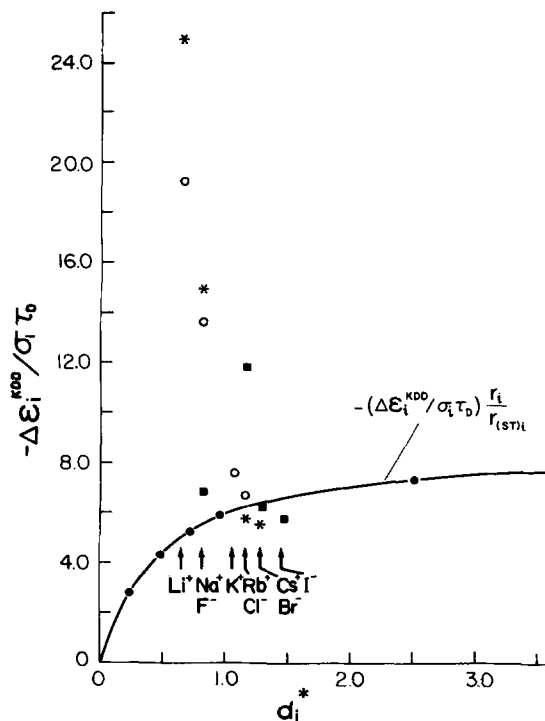


FIG. 3. The kinetic dielectric decrement at 25 °C. The solid line and dots are the present results for  $(\Delta\epsilon_i^{KDD}/\sigma_i \tau_D) r_i / r_{(ST)i}$  for univalent and divalent ions, respectively. The present results for  $\Delta\epsilon_i^{KDD}/\sigma_i \tau_D$  for several positive and negative ions are represented by open circles and solid squares, respectively. From left to right the stars are the previous results of Hubbard *et al.*<sup>4</sup> for  $Li^+$ ,  $Na^+$ ,  $Cl^-$ , and  $Cs^+$ .

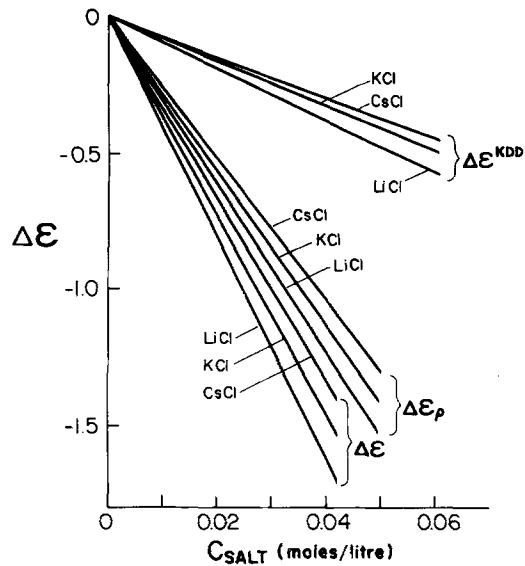


FIG. 4. Comparing theoretical results for the equilibrium and dynamical contributions ( $\Delta\epsilon_p$  and  $\Delta\epsilon^{KDD}$ , respectively) to the total dielectric decrement,  $\Delta\epsilon$ , for LiCl, KCl, and CsCl solutions at 25 °C. The ion diameters are given in Table I.

larly true for the larger ions with the largest discrepancy occurring for the relatively small  $Li^+$ . This agreement is rather encouraging in view of the fact that quite different approximations for the ion-dipole correlation functions were used in the calculations.

The total dielectric decrement,  $\Delta\epsilon = \Delta\epsilon_p + \Delta\epsilon^{KDD}$ , as a function of salt concentration for LiCl, KCl, and CsCl solutions is shown in Fig. 4. Also included in the figure are  $\Delta\epsilon_p$ , as given by Eq. (9) and  $\Delta\epsilon^{KDD}$  which is obtained from Eq. (11) using literature values<sup>16</sup> for  $\lambda_i^0$ . We see that the three salts give very similar results as is indeed the case for all alkali halides. For the alkali halides the present results are consistent with the available experimental data<sup>7</sup> and provide further support for the conclusions reached in Ref. 1.

In Fig. 5 we compare theoretical and experimental<sup>7</sup> results for dilute  $CuCl_2$  solutions. As in Ref. 1 the experimental points represent

$$\Delta\epsilon_{EXPT} = \epsilon_{SOL} - \Delta\epsilon_{DF} - \epsilon_0, \quad (12)$$

where  $\Delta\epsilon_{DF}$  is the estimated Debye-Falkenhagen contribution. The theoretical calculations assume that the radius of  $Cu^{+2}$  is 0.73 Å and  $\lambda_{Cu^{+2}}^0$  is as given in Ref. 16. We note that if we assume that the experimental points obey a linear law then the theoretical and experimental slopes are reasonably close. However, the experimental points appear to be shifted upward and a linear plot does not extrapolate to zero. Similar effects are apparent in the alkali halide data<sup>1,7</sup> and at present there does not appear to be an explanation for this unexpected behavior.

### B. Potentials of mean force and correlation functions

Potentials of mean force at infinite dilution for unlike and like ion pairs with ions of varying size are shown in Figs. 6 and 7, respectively. The results in-

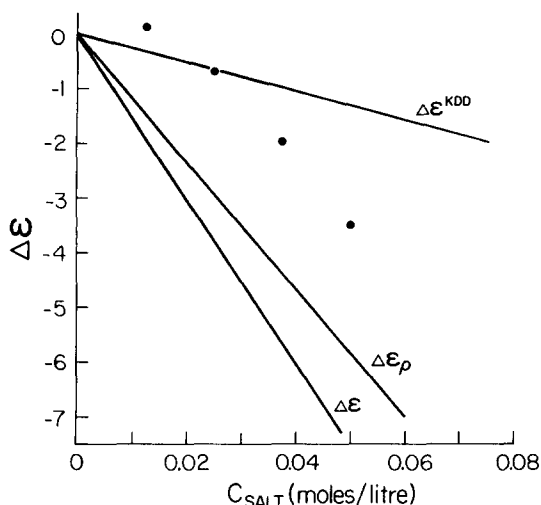


FIG. 5. Comparing experimental and theoretical results for  $\text{CuCl}_2$  at 25 °C. The solid dots represent  $\Delta\epsilon_{\text{EXPT}}$  as obtained from Ref. 7 and Eq. (12).

cluded were chosen such as to span a realistic range of ion diameters. From both figures we see that pairs of relatively small ions exhibit the most distinctive structural features. This is perhaps not surprising since the smaller ions interact more strongly with the solvent molecules and hence will have larger ordering or disordering effects upon the solvent-ion and solvent-solvent structures.

For the unlike pairs it is interesting to observe (cf. Fig. 6) that as the ion size is increased the second minimum decreases in depth and occurs at larger separations. For example, for  $\text{Li}^+/\text{F}^-$  and  $\text{Cs}^+/\text{I}^-$  pairs this minimum occurs at  $(r - d_{ij})/d_s \sim 0.75$  and 1.0, respec-

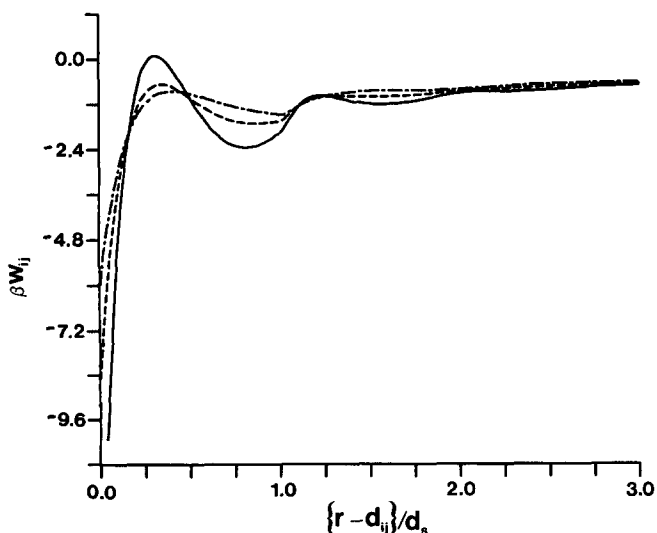


FIG. 6. Comparing  $\beta w_{ij}(r)$  for pairs of oppositely charged ions at 25 °C. The solid, dashed, and dash-dot lines are for  $\text{Li}^+/\text{F}^-$ ,  $\text{Li}^+/\text{I}^-$ , and  $\text{Cs}^+/\text{I}^-$ , respectively. The ion diameters are given in Table I.

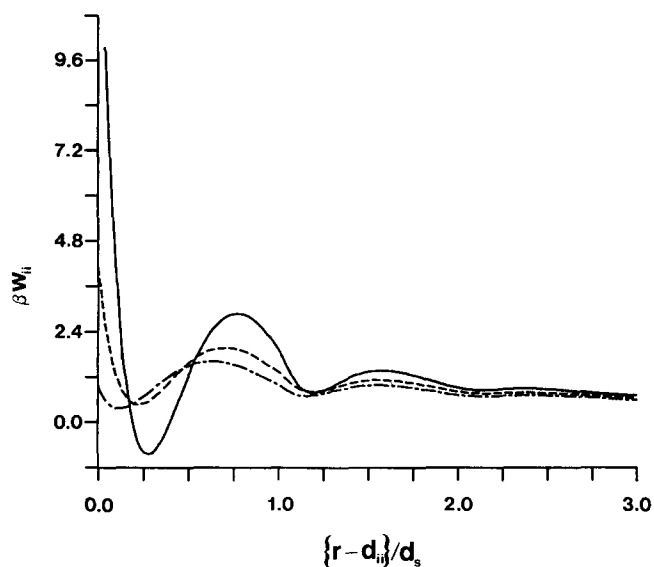


FIG. 7. Comparing  $\beta w_{ii}(r)$  for ions of like charge at 25 °C. The solid, dashed, and dash-dot lines are for  $\text{Li}^+/\text{Li}^+$ ,  $\text{K}^+/\text{K}^+$ , and  $\text{I}^-/\text{I}^-$ , respectively. The ion diameters are given in Table I.

tively. This behavior is likely due to the fact that the charge-quadrupole interaction (which is proportional to  $1/r^3$ ) decreases in importance relative to the charge-dipole interaction (which is proportional to  $1/r^2$ ) as the ion size is increased. Indeed, for  $\text{Cs}^+/\text{I}^-$  the second minimum occurs in the same position as that observed for purely dipolar fluids.<sup>1,9</sup> For ions of like charge (cf. Fig. 7) we see that the repulsion at contact decreases very rapidly with ion size and that the location of the first minimum shifts to smaller separations. We note that for smaller ions such as  $\text{Li}^+$  the minimum at

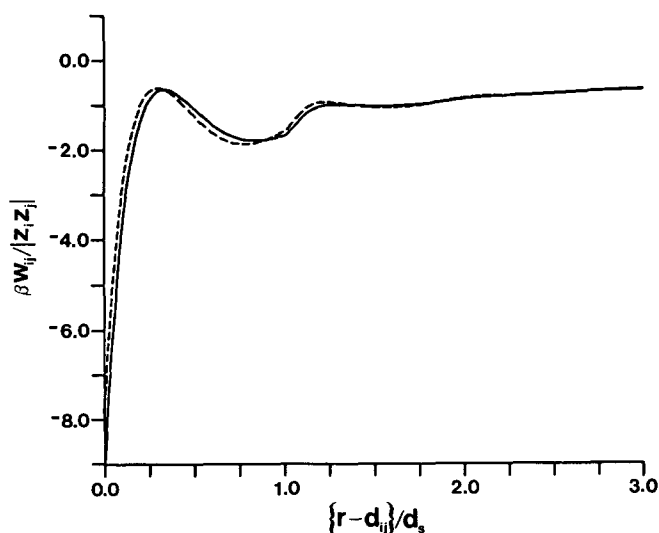


FIG. 8. Comparing  $\beta w_{ij}(r)/|z_i z_j|$  at 25 °C for pairs of univalent and divalent ions of opposite charge. The solid and dashed lines represent univalent and divalent pairs, respectively. The ions and solvent particles are of the same diameter.

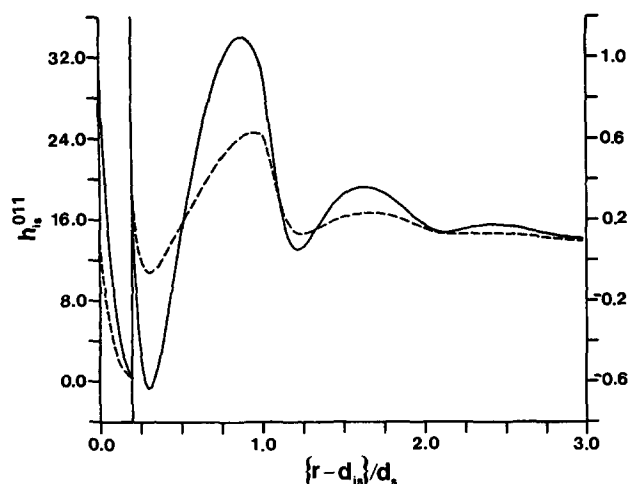


FIG. 9. Comparing  $h_{is}^{011}(r)$  for  $\text{Li}^+$  and  $\text{I}^-$  at 25 °C. The solid line is  $h_{is}^{011}(r)$  for  $\text{Li}^+$  and the dashed line is  $-h_{is}^{011}(r)$  for  $\text{I}^-$ . The ion diameters are given in Table I.

$(r - d_i)/d_s \sim 0.25$  is actually attractive and would give a relatively high probability of finding pairs of like ions at quite small separations. It will be interesting to see if this holds true at finite concentrations.

In Fig. 8 we compare potentials of mean force for 1:1 and 2:2 electrolytes where the ions are oppositely charged and the ions and solvent molecules are of equal diameter. Here we have plotted  $w_{ij}(r)/|z_i z_j|$  and it is obvious that to a fair approximation the potentials of mean force simply scale with the square of the ionic charge (recall  $q = z_i e$ ). Physically, this means that even for univalent ions the system must be approaching structural saturation.

The projection  $h_{is}^{011}(r)$  which essentially describes the charge-dipole part of the ion-solvent pair correlation function is plotted in Fig. 9 for  $\text{Li}^+$  and  $\text{I}^-$ . It can be seen that the contact value is much greater in magnitude and that the structural features are more important for  $\text{Li}^+$ . This clearly shows the greater tendency of smaller ions to order the solvent particles. Although it is not included in the figure, we have also examined the charge dependence of  $h_{is}^{011}(r)$ . It is found that to a very good approximation (i.e., <1%) the function for divalent ions can be obtained by simply scaling the univalent result by the charge ratio (i.e., a factor of 2). Again this indicates that for the present model and theory the ion-solvent structure is effectively saturated for univalent ions. We do not include an illustration of the projection  $h_{is}^{022}(r)$  since its dependence upon size and charge is very similar to that described for  $h_{is}^{011}(r)$ .

#### IV. SUMMARY AND CONCLUSIONS

In the present paper we have studied the dielectric properties of model aqueous electrolytes as a function of ion size and charge. Both equilibrium and dynamical contributions,  $\Delta\epsilon_p$  and  $\Delta\epsilon^{\text{KDD}}$ , respectively, to the apparent dielectric constant of solution have been examined in the infinite dilution limit. It is shown that for the present model and theory  $\Delta\epsilon_p$  decreases in magnitude with increasing ion size and can actually change sign

becoming positive for very large ions. However, for common alkali metal and halide ions  $\Delta\epsilon_p$  is relatively constant. Physically, it appears that for ions in this diameter range the decrease in  $|\Delta\epsilon_p|$  due to diminishing charge-solvent interactions is offset by the increasing number of solvent neighbors about an ion.

We also have used the LHNC ion-solvent pair correlation function in order to numerically evaluate an expression for  $\Delta\epsilon^{\text{KDD}}$  given by Hubbard *et al.*<sup>4</sup> The agreement between the present calculations and previous estimates of Hubbard *et al.* depends to some extent upon the ion size. The agreement is better for the larger ions with the largest discrepancy (~24%) occurring for the relatively small  $\text{Li}^+$ .

It is possible to compare the present theory with experimental data although as discussed in Ref. 1 such comparisons remain somewhat ambiguous since the magnitude of the Debye-Falkenhagen effect is not known with certainty. For alkali halide solutions we find that ion size effects are not very important and similar results are obtained for a number of common salts. This is consistent with experimental data<sup>1,7</sup> and for simple 1:1 electrolytes the present calculations corroborate the conclusions reached in Ref. 1. Also in this paper we have compared theoretical and experimental results for the 2:1 electrolyte  $\text{CuCl}_2$ , which for comparable salt concentrations gives a decrement about four times larger than that obtained for alkali halides. Again it is found that if at low concentrations the experimental  $\Delta\epsilon$  is assumed to be a linear function of  $C_{\text{SALT}}$  than the experimental and theoretical slopes are very similar. However, the results differ in that a linear extrapolation of the experimental points to zero concentration does not give the dielectric constant of pure water. This behavior is also observed for alkali halide solutions and deserves further experimental and theoretical investigation.

In this paper we have also studied ion-solvent correlation functions and ion-ion potentials of mean force as functions of ion size and charge. It is found that although the ion-solvent correlations are quite sensitive to ion diameter the charge effects are rather simple. For example, for divalent ions with physically reasonable diameters the projections  $h_{is}^{011}(r)$  and  $h_{is}^{022}(r)$  can be obtained by simply multiplying the univalent results by the charge ratio. This "scaling" indicates that even for univalent ions the ion-solvent interactions are strong enough to effectively saturate the orientational structure. The ion-ion potentials of mean force are also interesting with the short-range behavior being strongly influenced by ion size. Again, however, the charge dependence is relatively simple since to a fair approximation the potentials scale as the square of the ionic charge.

This investigation of aqueous electrolytes is currently being extended to finite ion concentrations. This will allow for more extensive comparisons with available experimental data for the thermodynamic and dielectric properties of various solutions. In addition, we are developing a theory for the dynamical behavior of dilute ionic systems which relies upon average potentials ob-

tained as described in the present paper. This will provide further tests of the model and theory.

#### ACKNOWLEDGMENTS

We thank Peter Wolynes for clarifying our understanding of the KDD theory and the financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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