Modeling the Permittivity of Electrolyte Solutions

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Solution of a strong electrolyte in a high-density polar fluid gives rise to a dielectric saturation that decreases the orientation polarizability of the solvent molecules in close proximity to the ions wherefore the relative permittivity in this region is determined solely by the atomic and electronic polarization. This causes a substantial decrease in the static permittivity of the solution. By considering the dielectric saturation, a model for the permittivity of an electrolyte solution have been developed and the parameters, the relative permittivities at dielectric saturation in close proximity to the ions, for 17 ions in water at 298.15 K were determined. By scaling these relative permittivities in proportion to the permittivity of the solvent, the model could be extended to calculate the permittivity of solutions of electrolytes in methanol and admixtures of water and ethanol. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2854–2860, 2015
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Introduction

In the theory of electrolyte solutions, the permittivity is of central importance because the solvent characteristics are temperature, volume, and permittivity. The relative permittivity, ε_r, is the permittivity of the continuum, ε, divided by the permittivity of free space, ε_0. The relative permittivity of a pure fluid depends on the temperature, and properties like the molar density, the optical polarizability, and the dipole moment. Onsager and Kirkwood[1–5] derived an expression for the relative permittivity of a pure fluid

$$\frac{(2\varepsilon_r+\varepsilon_\infty)(\varepsilon_r-\varepsilon_\infty)}{(2+\varepsilon_\infty)^2\,\varepsilon_r}=p=\frac{n}{V}\frac{N_A}{3\varepsilon_0}\left(\alpha+\frac{g\mu^2}{3k_BT}\right) \quad (1)$$

Here, n/V is the molar density of the fluid, p is the polarizability, N_A is Avogadro's number, k_B is Boltzmann's constant, ε_∞ is the relative permittivity at infinite frequency, and typically, it is replaced by the square of the refractive index or put to unity. α is the optical polarizability of the fluid that comprises the atomic and electronic polarization, μ is the dipole moment of an isolated molecule in the gaseous state, and T is the temperature. The frequency dependence of the permittivity is due to the frequency dependence of the optical polarizability and of the dipole moment.[5,6] The Kirkwood g-factor accounts for local dipolar correlations due to the fluid structure because the dipole moment in high-density polar fluids differs from that of an isolated molecule. $g\mu^2$ is the average of the product of the moment of the central molecule and the sum of the product of the moment of the central molecule and that of all the neighbors. This average is in general different in magnitude from the product of the moment of an isolated molecule,[3] that is, $g>1$. If i denotes a central molecule and j denotes molecules surrounding the central molecule i then[7]

$$g\mu^2=\mu_i^2+\left\langle\sum_{j\neq 1}\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j\right\rangle \quad (2)$$

The term in the brackets is the average of the contributions from the nearest neighbors.

For liquid mixtures, one can utilize the mixing rule

$$p_{\text{mixture}}=\sum_{\text{solvents}}\varphi_i p_i \quad (3)$$

where φ_i are the volume fractions, and p_i are the polarizabilities of the pure liquids. Harvey and Prausnitz[8] and more recently Wang and Anderko[9] discuss the application of the Onsager and Kirkwood model for pure and mixed solvents.

In a resent publication, Maribo-Mogensen et al.[7] showed that the relative permittivity at zero frequency of a pure fluid or a fluid mixture can be modeled simultaneously with the thermodynamic properties of the pure fluid or the fluid mixture. The thermodynamic properties were calculated using the cubic-plus association (CPA) equation of state model that includes the Soave–Redlich–Kwong equation of state and the Wertheim association model as formulated in the statistical associating fluid theory to account for hydrogen bonding molecules. The static permittivity was calculated from an extension of Eq. 1 to associating mixtures omitting the optical polarizability, that is

$$\frac{(2\varepsilon_r+\varepsilon_\infty)(\varepsilon_r-\varepsilon_\infty)}{(2+\varepsilon_\infty)^2\,\varepsilon_r}=\frac{N}{V}\frac{N_A}{9\varepsilon_0 k_BT}\sum_{\text{solvents}}x_i g_i\mu_i^2 \quad (4)$$

where x_i are the mole fractions. Maribo-Mogensen et al. showed that using a simple description of the geometry of

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the association, they were able to model the Kirkwood g-factor as a function of the probability of the hydrogen bond formation. Their model is

$$g_i=1+\sum_{j\neq 1}\frac{z_{ij}P_{ij}\cos\gamma_{ij}}{P_i\cos\theta_{ij}+1}\frac{\mu_j}{\mu_i} \tag{5}$$

where z_{ij} is the coordination number of molecule j around a central molecule i. P_{ij} is the probability of molecule i and j being associated. P_i is the probability of molecule i to be bonded to any molecule not belonging to the first shell. γ_{ij} is the angel between the dipole moments of molecule i and j, respectively, and θ_{ij} is the angle between the O—H bond of molecule i and the hydrogen bond between molecules i and j.

The results showed that it was possible to predict the static permittivity of complex mixtures over wide temperature and pressure ranges simultaneously with the calculation of the thermodynamic properties of the mixture.

Correlations of Relative Permittivities of Electrolyte Solutions

Solution of a strong electrolyte in a high-density polar solvent decreases the relative permittivity of the electrolyte solution because the addition of ions alters the electric configuration of the solvent molecules. The effect of ions is caused by a kinetic dielectric decrement and a decrement due to the dielectric satiation. A recent exploration of the kinetic dielectric decrement is given by Sega et al.[10] Now, for real systems it seems nearly impossible to disentangle saturation effects from the kinetic dielectric decrement. Therefore, it is reasonable to use a saturation model as a complete description of the electrolyte effect on the permittivity although not entirely physical correct.

Maribo-Mogensen et al.[11] utilized a modification of the Onsager and Kirkwood model. Following the concepts used in models for the static permittivity incorporating ion solvation, they assume that the polar molecules in the first hydration shell surrounding an ion will associate with the ion and, therefore, not contribute to the projected dipole moment due to the alignment of dipoles in the electrical field surrounding an ion. This effect entails a reduction in the static permittivity due to cancellation of the oppositely directed dipole moments. By assuming cancellation of the dipole moments of molecules in the first hydration shell, they arrived at the following model

$$\frac{(2\varepsilon_r+\varepsilon_\infty)(\varepsilon_r-\varepsilon_\infty)}{(2+\varepsilon_\infty)^2\,\varepsilon_r}=\frac{n}{V}\frac{N_A}{3\varepsilon_0}\sum_{\text{solvents}}\frac{x_i\Theta_i g_i\mu_i^2}{3k_BT} \tag{6}$$

in which x_i is the mole fraction of solvent component i and Θ_i is the fraction of component i that is not associated with an ion j. Θ_i is calculable as

$$\Theta_i=1-\sum_{\text{ions}}P_{ij} \tag{7}$$

where P_{ij} is the probability that a molecule i is associated with an ion j. The thermodynamic properties were calculated using the CPA electrolyte equation of state model including the Wertheim association model. Further details are given in Ref. 11. Maribo-Mogensen et al., in addition to their own developments, also presented a review of theoretical principles and models for permittivities including some empirical models as well.

A Simple Model for the Influence of Dielectric Saturation

To account for the decrease in the orientation polarizability of the solvent molecules, we utilize the theoretical development from Refs. 11–14. The decrease is of course continuous, as model calculations presented in Figure 2 in Ref. 11 show, but we assume the following approximate model to be valid. Each ion together with the surrounding water, which does not contribute fully to the orientation polarizability, is considered to form a sphere of radius r_i consisting of a homogeneous dielectric medium with the relative permittivity ε_{sat}. These spheres all together occupy the fraction, θ, of the total volume of the solution. The solvent between these spheres is considered as a homogeneous dielectric medium with the relative permittivity of the pure solvent, ε_S.

According to Giese et al.,[12] Brown[13] presented a relation between the relative permittivity of the electrolyte solution, ε_E, the relative permittivity of the pure solvent, ε_S, and the fraction of spheres of fluid, θ, having a relative permittivity of, ε_{sat}, from which θ is calculable according to the equation

$$\theta=\frac{2\varepsilon_S+\varepsilon_{\text{sat}}}{\varepsilon_S-\varepsilon_{\text{sat}}}\Bigg/\frac{2\varepsilon_S+\varepsilon_E}{\varepsilon_S-\varepsilon_E} \tag{8}$$

Giese et al. utilized this equation to calculate θ from experimental measurements.

We will use this relation to develop a model for calculation of ε_E. The fraction, θ_i, for each ion is calculable from the radius of the spheres, r_i, encircling the homogeneous dielectric medium with the relative permittivity, $\varepsilon_{\text{sat},i}$, the number of the ions of species i, N_i, and the volume of the solution, V. That is

$$\theta_i=\frac{4\pi}{3}r_i^3N_i/V=\frac{4\pi}{3}N_Ar_i^3c_i \tag{9}$$

where c_i is the molar concentration of the ion. Applying Eq. 8 for each ion fraction and solving for the relative permittivity of the electrolyte solution, ε_E, the eventual result is

$$\frac{\varepsilon_E}{\varepsilon_S}=1-3\sum_{\text{ions}}\frac{\theta_i}{D_i} \tag{10}$$

where

$$D_i=\frac{2\varepsilon_S+\varepsilon_{\text{sat},i}}{\varepsilon_S-\varepsilon_{\text{sat},i}}+\theta_i \tag{11}$$

To apply this model for the calculation of the relative permittivity of an electrolyte solution, ε_E, we must derive an equation for the calculation of r_i.

The mean dipole moment and, therefore, the polarization, depends on a competition between the aligning influence of the field, E, and the randomizing influence of thermal motion. The average dipole moment of a fluid sample is evaluated using the Boltzmann distribution for a sample at a temperature T, and is[5,6]

$$\langle\mu\rangle=\mu\text{L}(\mu E/k_BT)=\mu\text{L}(y) \tag{12}$$

$\text{L}(y)$ is the Langevin function, $\text{L}(y)=\coth(y)-1/y$, where $\text{L}(y)=y/3$ for y << 1 and $\lim_{y\to\infty}\text{L}(y)=1$.

Table 1. Estimated Relative Permittivity Ratios at Dielectric Saturation at 298.15 K

Cations	$\omega_{\mathrm{sat},i}=\frac{\varepsilon_{\mathrm{sat},i}}{\varepsilon_{\mathrm{S}}}$	$(r_{0,i}/\boldsymbol{m})10^{10}$ in water	Anions	$\omega_{\mathrm{sat},i}=\frac{\varepsilon_{\mathrm{sat},i}}{\varepsilon_{\mathrm{S}}}$	$(r_{0,i}/\boldsymbol{m})10^{10}$ in water
H^+	0.0471	3.68	OH^-	0.0427	3.87
Li^+	0.0588	3.29	F^-	0.0741	2.93
Na^+	0.0700	3.02	Cl^-	0.0653	3.13
K^+	0.0863	2.72	Br^-	0.0570	3.35
Cs^+	0.105	2.47	I^-	0.0495	3.59
Mg^{2+}	0.0783	4.04	NO_3^-	0.0690	3.04
Ca^{2+}	0.108	3.43	SO_4^{2-}	0.286	2.11
Ba^{2+}	0.146	2.95			
Zn^{2+}	0.116	3.32			
Ni^{2+}	0.128	3.16			

In a weak field, that is, for $E << k_{\mathrm{B}}T/\mu$, $\langle\mu\rangle=\mu y/3=\mu^2E/3k_{\mathrm{B}}T$ wherefore the orientation polarizability, $<\mu>/E$, attains its maximum value

$$\langle\mu\rangle/E=\mu^2/3k_{\mathrm{B}}T \tag{13}$$

In a very strong field where $E >> k_{\mathrm{B}}T/\mu$, $\mathrm{L}(y)=1$, and $\langle\mu\rangle=\mu$, the orientation polarizability vanishes, that is, $<\mu>/E \to 0$ and ε_{r} is determined solely by the atomic and electronic polarization, α. That is, the last term in the bracket on the right hand side of Eq. 1, vanishes, that is, $\varepsilon_{\mathrm{r}} \to \varepsilon_{\infty}$.

When the field is caused by the charge of an ion in solution, spherical regions are formed around each ion[11] where ε_{r} increases from a very low value denoted $\varepsilon_{\mathrm{sat}}$ to the permittivity of the pure solvent, ε_{S}, as one moves away from the centre of an ion. To simplify the calculations one can, as mentioned, take recourse to an approximate model where ε_{r} changes discontinuously from $\varepsilon_{\mathrm{sat}}$ to ε_{S}. This change takes place at a distance r_1 from the centre of the ion, and at $r=r_1$ the value of y is y_1. When changing over to the approximate model, one must substitute the Langevin function L(y) by a function where $<\mu>/E=0$, that is, $\varepsilon_{\mathrm{r}}=\varepsilon_{\mathrm{sat}}$ (strong field) for $r \le r_1$, but $\langle\mu\rangle/E=\mu^2/3k_{\mathrm{B}}T$, that is, $\varepsilon_{\mathrm{r}}=\varepsilon_{\mathrm{S}}$ (weak field) for $r>r_1$. The value of y_1 can be determined from the condition that the average electric moment is preserved, that is the area under the Langevin function from 0 to y_1 equals the area between 1 (value of L in a strong field) and the Langevin function from 0 to y_1

$$\int_0^{y_1} \mathrm{L}(y)dy=\int_0^{y_1}[1-\mathrm{L}(y)]dy \tag{14}$$

or

$$\ln(\sinh y_1)-\ln y_1-y_1/2=0 \tag{15}$$

Solving Eq. 15 yields a value of $y_1=4.31$.

The field strength around a point charge falls off according to an exponential law[3,5]

$$E=-\frac{\partial\phi}{\partial r}=\frac{ez_i(1+\kappa r)\exp(-\kappa r)}{4\pi\varepsilon_0\varepsilon_{\mathrm{sat}}r^2}=\frac{ez_i}{4\pi\varepsilon_0\varepsilon_{\mathrm{sat}}r^2}\left(1-\frac{\kappa^2r^2}{2}+\frac{\kappa^3r^3}{3}-\cdots\right) \tag{16}$$

where ϕ is the electric potential of the ion, z_i is the valance of the ion, e is the proton charge, and $1/\kappa$ is the Debye length where

$$\kappa^2=\frac{e^2N_{\mathrm{A}}}{\varepsilon_0\varepsilon_{\mathrm{sat}}k_{\mathrm{B}}TV}\sum_j n_jz_j^2 \tag{17}$$

For the determination of E at low ionic strength, Eq. 16 can be limited to the first term of the expansion, that is

$$y=\frac{\mu E}{k_{\mathrm{B}}T}=\frac{\mu}{k_{\mathrm{B}}T}\frac{ez_i}{4\pi\varepsilon_0\varepsilon_{\mathrm{sat},i}r_i^2} \tag{18}$$

and at $y=y_1$ we obtain the desired equivalent radius, $r_{0,i}$, at low ionic strength

$$r_{0,i}^2=\frac{\mu}{k_{\mathrm{B}}T}\frac{ez_i}{17.24\pi\varepsilon_0\varepsilon_{\mathrm{sat},i}} \tag{19}$$

However, as shown in Eq. 16, when the ionic strength increases, the field strength becomes dependent on the ionic strength. We account for this by lumping the higher order terms into a single term having one adjustable parameter, β_i, that is

$$y_1=\frac{\mu E}{k_{\mathrm{B}}T}=\frac{\mu}{k_{\mathrm{B}}T}\frac{ez_i}{4\pi\varepsilon_0\varepsilon_{\mathrm{sat},i}r_i^2}\left(1-\beta_i\kappa^2r_i^2\right) \tag{20}$$

Combining Eqs. 19 and 20 provides the eventual result where

$$r_i^2=\frac{r_{0,i}^2}{1+\beta_i\kappa^2r_{0,i}^2} \tag{21}$$

The model parameters are $\varepsilon_{\mathrm{sat},i}$ and β_i.

The Debye length accounts for the contribution of all ions in the solution to the field strength in the proximity of a picked ion. In Eq. 21, the curvature of the r_i function is determined by the product, $\beta_i\kappa^2$, and in this product β_i is an adjustable parameter inversely proportional to $\varepsilon_{\mathrm{sat}}$ that must be a number common to all ions. Therefore, to avoid a direct correlation between the two parameters we decided to use the value $\varepsilon_{\mathrm{sat}}=1$ in Eq. 17.

We have investigated if it was possible to extend the model to nonaqueous solvents and mixed solvents without fitting any new parameters. It is likely that the size of the relative permittivity of a solvent at dielectric saturation, $\varepsilon_{\mathrm{sat},i}$, must depend on the size of the relative permittivity of the pure solvent, ε_{S}, because the atomic and electronic polarization for different fluids are not alike, wherefore $\varepsilon_{\mathrm{sat},i}$ cannot be a universal parameter. However, if we assumed that the relative decrease in the permittivity, that is, the ratio of the permittivity of a solvent at dielectric saturation to the permittivity of the pure solvent

$$\omega_{\mathrm{sat},i}=\varepsilon_{\mathrm{sat},i}/\varepsilon_{\mathrm{S}} \tag{22}$$

is a universal ion specific parameter, we were able extend the model to include methanol, and water with an admixture of ethanol, as solvents. For physical reasons, it is required that $\varepsilon_{\mathrm{sat},i} \ge 1$. That limits the model to solvents or solvent mixtures where $\varepsilon_{\mathrm{S}} \ge 20$.

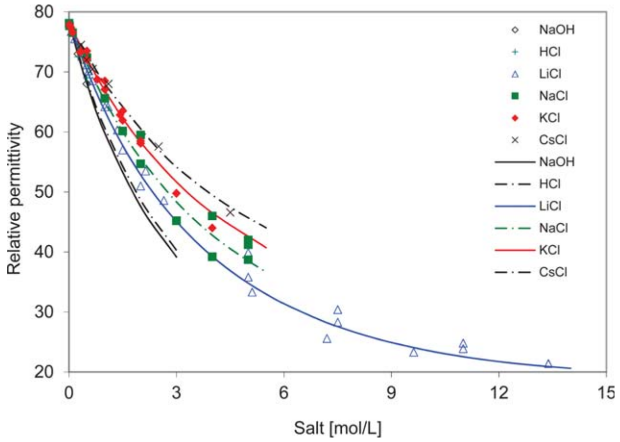

Figure 1. Relative permittivity of aqueous solutions of chloride salts, HCl, and NaOH at 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results

Electrolytes in water

Relative permittivities at 298.15 K of aqueous solutions of the salts LiCl, NaCl, KCl, CsCl, LiBr, KBr, CsBr, $LiNO_3$, $NaNO_3$, KNO_3, Na_2SO_4, $NiCl_2$, $CaCl_2$, $ZnCl_2$, and $MgCl_2$ from Ref. 15, HCl, NaOH, LiCl, KCl, $BaCl_2$, Na_2SO_4 from Ref. 16 and $CaCl_2$ from Ref. 17 were included in the database. The dipole moment of water was 6.17×10^{-30} C·m from Ref. 6, and the relative permittivity of water at 298.15 K, $\varepsilon_S = 78.44$ from Ref. 18. 140 data points were utilized to determine 17 ion parameters by minimizing the residual sum of squares between the experimental and the calculated relative permittivities of the electrolyte solutions. The result of the parameter estimation showed that a good agreement between calculated and experimental data were obtained with $\beta_i = 1.17 \times 10^{-3}$ for all monovalent ions and $\beta_i = 1.17 \cdot 10^{-3}/4$ for divalent ions. The values of $\omega_{\mathrm{sat,i}}$ and $r_{0,i}$ are reported in Table 1. Figures 1–4 show comparisons between the experimental data and the model. The model calculations were extended to the solubility limit of the salts.

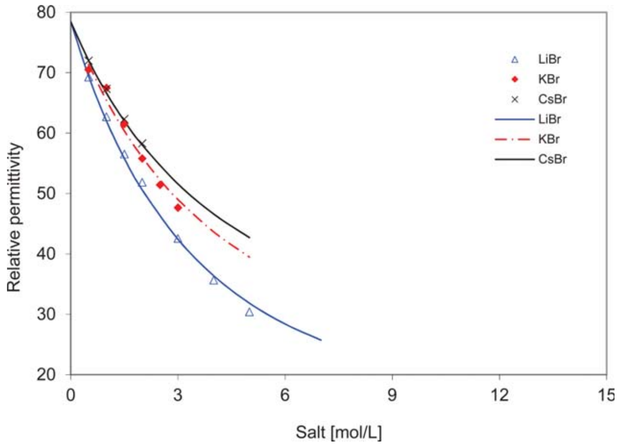

Figure 2. Relative permittivity of aqueous bromide salt solutions at 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

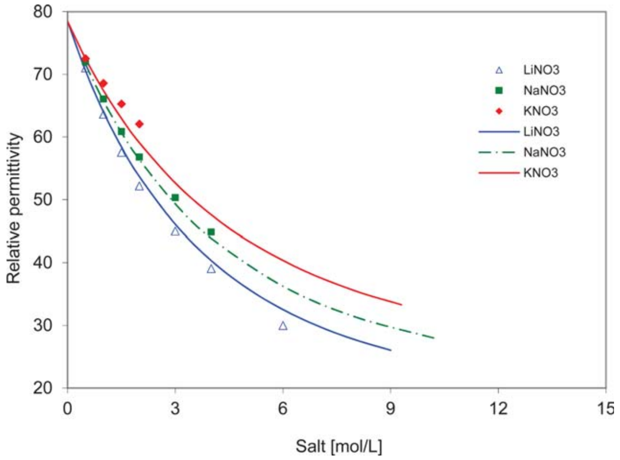

Figure 3. Relative permittivity of aqueous nitrate salt solutions at 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrolytes in methanol

To test the validity of the assumption that the $\omega_{\mathrm{sat},i}$ values are solvent independent parameters, we calculated the relative permittivity of four 1:1 salts dissolved in pure methanol[15,17,19–21] at 298.15 K. We have utilized a dipole moment of 5.70×10^{-30} C·m from Ref. 6, a relative permittivity of 31.5 for methanol,[22] and the ω-parameters given in Table 1, that is for methanol

$$\varepsilon_{\mathrm{sat},i} = 31.5\omega_{\mathrm{sat},i} \tag{23}$$

Not to introduce new adjustable parameters, we simply used $\beta_i = 1.17 \cdot 10^{-3}$ for monovalent ions. No divalent ions were involved in the test calculations. The calculations are shown in Figure 5.

Electrolytes in ethanol–water mixtures

A test of a possible extension to mixed solvents was done as follows. We calculated the relative permittivities of the solutions with the electrolytes dissolved in the pure solvents, water, and ethanol, respectively, and utilized a mixing rule similar to Eq. 3

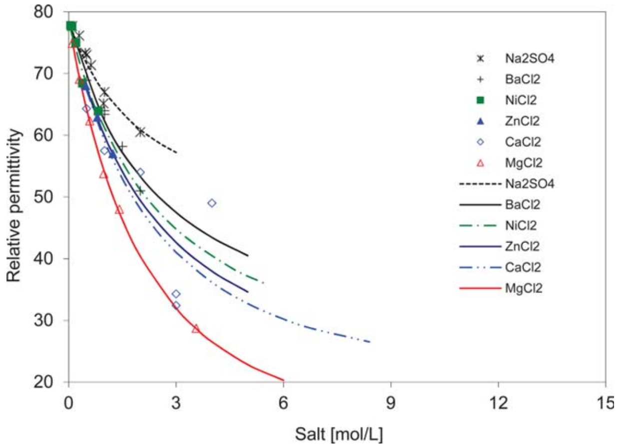

Figure 4. Relative permittivity of aqueous salt solutions containing divalent ions at 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

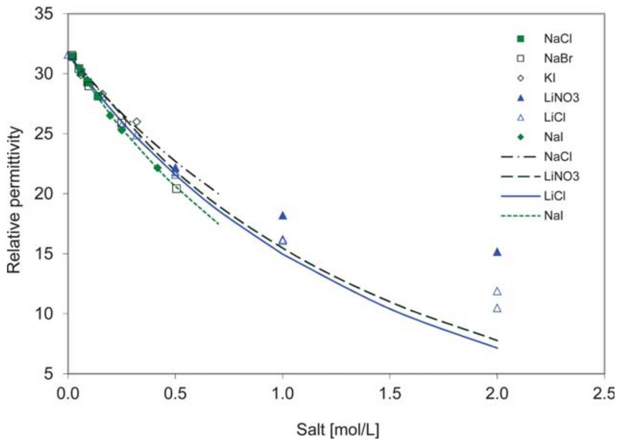

Figure 5. Relative permittivity of solutions of various salts in pure methanol at 298.15 K.

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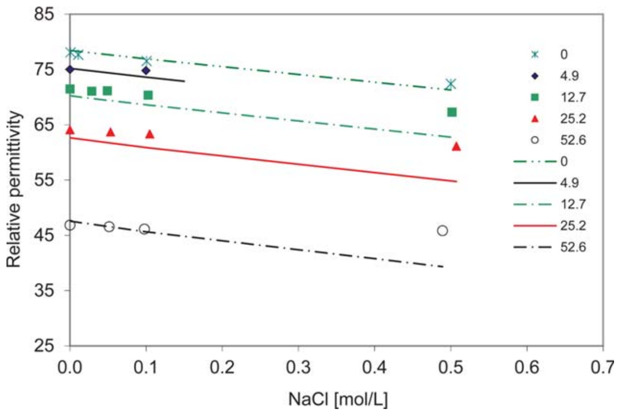

Figure 6. Relative permittivity of solutions of NaCl in pure water and aqueous ethanol at 298.15 K.

The numbers in the legend indicate the weight percent of ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$p_{\mathrm{E}}=\sum_{\text{solvents}} \varphi_i p_{\mathrm{E},i} \tag{24}$$

and $\varepsilon_\infty = 1$ to calculate the relative permittivity of the mixture. Figure 6 shows experimental and calculated relative permittivities of solutions of NaCl in admixtures of water and ethanol[15,21] at 298.15 K. The pure component densities from Ref. 23 were used for the conversion from weight fractions to volume fractions, the dipole moment of ethanol, 5.64×10^{-30} C·m, was from Ref. 6, the relative permittivity, 25.7, was from Ref. 22, $\beta_i = 1.17 \cdot 10^{-3}$ for monovalent ions, and for ethanol

$$\varepsilon_{\mathrm{sat},i}=25.7\omega_{\mathrm{sat},i} \tag{25}$$

No divalent ions were involved in the test calculation.

The temperature dependence of $\omega_{\mathrm{sat,i}}$

Using the assumptions that $\omega_{\mathrm{sat},i}$ is a universal parameter, means that the temperature dependence of $\varepsilon_{\mathrm{sat},i}$ is similar to the temperature dependence of the relative permittivity of the solvent, that is

$$\varepsilon_{\mathrm{sat},i}(T)=\omega_{\mathrm{sat},i}\varepsilon_{\mathrm{S}}(T) \tag{26}$$

A few sample calculations showed that the results were unacceptable and that much better results were obtained using the values of $\varepsilon_{\mathrm{sat},i}$ calculated at 298.15 K. The experimental data at temperatures other than room temperature are sparse and the experimental errors are sometimes large, wherefore we have mainly used the selected data from the compilation of Barthel et al.[15]

Figure 7 shows the relative permittivity of a solution of NaI in methanol at 298.15 K, 255.15 K, and 244.5 K. The data are from Ref. 15 and the relative permittivities of pure methanol are from Ref. 22. The dashed (244.5 K) and dashed-dotted (255.15 K) lines are the predictions using temperature dependent $\varepsilon_{\mathrm{sat},i}$, Eq. 26, and the full lines are the correlation using the values of $\varepsilon_{\mathrm{sat},i}$ calculated at 298.15 K. That is, assuming that $\varepsilon_{\mathrm{sat},i}$ is independent of the temperature.

Figure 8 shows data of the relative permittivity of a solution of NaCl in water at 274.65 K, 294.15 K, and 298.15 K. The data at 274.65 K, filled diamonds, and 294.15 K, open triangles, are from Ref. 16 and the data at 298.15 K, open squares, are from Ref. 15. The relative permittivities of pure water are from Ref. 18. Hasted et al.[16] have estimated the uncertainty of their data to ±2. The temperature dependence of the data at 294.15 K does not conform to the temperature dependence of the data at 298.15 K wherefore we only show the correlation of the data at 274.15 K. The dashed-dotted line is the correlation of the data at 298.15 K, the dashed line is the prediction at 274.15 K using temperature dependent $\varepsilon_{\mathrm{sat},i}$, Eq. 26, and the full line is the correlation using the value of $\varepsilon_{\mathrm{sat},i}$ calculated at 298.15 K.

Discussion

There is a reasonable agreement between the correlation and the data when water is the solvent, Figures 1–4. The model is limited to electrolyte solutions where the permittivity decreases with increasing salt concentration. Cadmium salts, for example, are reported to increase the permittivity.[15] Generally, the water structure in a solution becomes more ordered by dissolving smaller ions and disordered by dissolving larger ions and this effect may be related to the distance

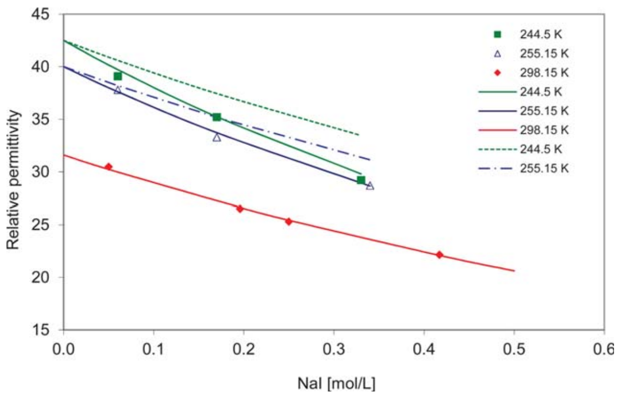

Figure 7. Relative permittivity of solutions of NaI in pure methanol at 244.5 K, 255.15 K, and 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

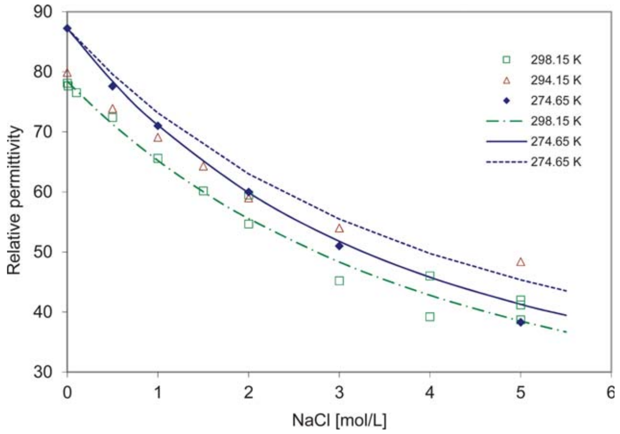

Figure 8. Relative permittivity of solutions of NaCl in pure water at 274.65 K, 294.15 K, and 298.15 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between the dipole moment of water and the charge on the ion.[24]

The parameters in Table 1 for the hydrated cations of the elements in groups IA and IIA of the periodic table of elements show that the radius of the low-permittivity sphere decreases with increasing molecular weight. In contrast, the parameters for anions of the elements in group VIIB show that the radius of the low-permittivity sphere increases with increasing molecular weight.

The calculations of the relative permittivity of four 1:1 salts in methanol are shown in Figure 5. There is a good agreement between the data and the calculated results up to 0.5 M. The upper dashed-dotted line and the lower short-dashed line both extending to 0.7 M are the models for NaCl and NaI, respectively, and all other model predictions for the salts listed are within these two lines. The prediction of the relative permittivity of LiCl and $LiNO_3$ dissolved in pure methanol at high ionic strength is off by a factor of 2–3. The model over-estimates the effect of the lithium salt.

The temperature dependence of $r_{0,i}$, Eq. 19, is due to the temperature dependence of $T\varepsilon_{\text{sat},i} = T\omega_{\text{sat},i}\varepsilon_{\text{S}}$. According to the Kirkwood-Onsager model, Eq. 1, p is inversely proportional to Tv and for $\varepsilon_{\text{r}} >> 1$, ε_{r} is inversely proportional to Tv. That is, $T\omega_{\text{sat},i}\varepsilon_{\text{S}}$ becomes almost independent of T. The molar volume, v, at atmospheric pressure has weak temperature dependence. In agreement with this analysis, it is observed that the dashed and the dashed-dotted lines in Figure 7 are parallel to the full line representing the correlation at 298.15 K. That explains why temperature independent values of $\varepsilon_{\text{sat},i}$ gives better results.

The extension of the correlation to mixed solvents of water and ethanol, Figure 6, shows that the correlation predicts the right trend. We calculated the relative permittivities of the electrolyte solutions with the electrolytes dissolved in the pure solvents and utilized the mixing rule, Eq. 24, to calculate the relative permittivity of the mixture, ε_{E}. Alternatively, we calculated the relative permittivity of the mixed solvent, $\varepsilon_{\text{mixed solvent}}$, utilizing the mixing rule for the polarizability, p, given in Eq. 2, and calculated the relative permittivity at dielectric saturation for each ion using

$$\varepsilon_{\text{sat},i} = \varepsilon_{\text{mixedsolvent}}\omega_{\text{sat},i} \tag{27}$$

The average dipole moment of the mixed solvent, required in Eq. 19, was calculated as the volume fraction average of the dipole moments of the single solvents. In the present case, it made little difference.

In Kirkwood's theory[25] of solutions of charged macromolecules, like proteins, the complex ion is regarded as a spherical molecule of radius r having not only a net charge but also multipoles. The chemical potential of the complex ion in solution comprises the Born potential, a potential due to the mutual interactions of the ions similar to but not identical with the Debye–Hückel potential, and a potential caused by the interaction between the dipole of the macro ion and the simple ions in solution.[25] Kirkwood's model has been utilized to calculate the chromatographic adsorption equilibria of Lysozyme in hydrophobic interaction chromatography.[26,27] Because of the high electric field inside the complex ion, the relative permittivity inside the ion, ε_{sat}, is less than the permittivity of the bulk solution. Kirkwood assumed $\varepsilon_{\text{sat}} = 1$; however, the model, given in Eq. 21, provides a relationship between r and ε_{sat} that can be utilized to improve Kirkwood's model and similar electrostatic models.

Concluding Remarks

We have developed a model for the permittivity of electrolyte solutions that takes into account that the ions alter the molecular configuration of solvent dipoles and, thus, decrease the orientation polarizability of the solvent molecules in close proximity of the ions. Furthermore, we have demonstrated that the model can be applied to other high-density polar fluids than water simply by scaling the relative permittivities at dielectric saturation in proportion to the permittivity of the solvent, that is, by assuming that the permittivity ratios $\omega_{\text{sat},i} = \varepsilon_{\text{sat},i}/\varepsilon_{\text{S}}$ are universal solvent independent parameters. However, due to the limited amount of data for relative permittivities of salts in nonaqueous solvents and mixed solvents included in this investigation, we hesitate to conclude that the model is applicable to any mixed solvent in general.

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