Dependence of the dielectric constant of electrolyte solutions on ionic concentration

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We study the dependence of the static dielectric constant of aqueous electrolyte solutions upon the concentration of salt in the solution and temperature. The model takes into account the orientation of the solvent dipoles due to the electric field created by ions, the ionic response to an applied field, and the effect of thermal fluctuations. The analysis suggests that the formation of ion pairs by a small fraction of disassociated ions can have a significant effect on the static dielectric constant. The model predicts the dielectric has the functional dependence $\varepsilon(c) = \varepsilon_w - \beta L(3\alpha c/\beta)$ where L is the Langevin function, c is the salt concentration, ε_w is the dielectric of the pure water, α is the total excess polarization of the ions and β is the relative difference between the water dipole moment and the effective dipole moment of ion pairs as weighted by the density of ion pairs and their structural rigidity. The functional form gives an extremely accurate prediction of the dielectric constant for a variety of salts and a wide range of concentrations by fitting only the parameter β.

It is difficult to overstate the importance of aqueous electrolyte solutions in biological and electrochemical systems. There has been extensive study of physical properties of such solutions over the last 120 years. The first systematic experimental study of the dielectric properties of salt-water solutions was conducted in 1948 by Hasted et al. [1]. In this work, the static dielectric constant of a solution was observed to decrease with the salt concentration, a phenomena called *dielectric decrement*. Intuitively, the dielectric decrement stems from the fact that the local electric field generated by each ion dominates the external applied field. The polar water molecules tend to align with the local ionic field, creating a *hydration shell* around the ion, lowering the response of the water molecules to the external field and hence lowering the dielectric constant. In dilute solutions (typically salt concentrations less than 1.5M) the dielectric decrement is linear,

$$\varepsilon = \varepsilon_w - \alpha\, c, \tag{1}$$

where ε_w is the dielectric constant of pure water, c is the salt concentration, and α is a phenomenological ion-specific parameter, known as the total *excess polarization* of the ionic species. At higher salt concentrations significant deviations from linearity are observed and the dielectric decrement is observed to saturate [1].

Haggis et al. [2] modeled the observed linear dielectric decrement by considering the hydration shells as small spherical regions with a low dielectric constant, immersed in pure water medium with a high dielectric constant. The macroscopic dielectric constant of the solution was then computed by homogenization. The model was later refined by considering the variation of the local dielectric constant near the ions [3] and finite-size effects [4]. The treatment of hydration shells as spheres, however, is justifiable only for dilute solutions (typically less than 1M) for which the hydration shells do not overlap.

Only very recently, Levy, Andelman and Orland [5] presented a model for the dielectric decrement in concentrated solutions. Using a field-theory approach they calculated the average dielectric constant around each ion at the mean-field level, and accounted for ion-ion interactions and hydration shell overlap via a one-loop correction. The resulting prediction of the dielectric constant affords a good fit to data from a large range of concentrations of different salts using a single fit parameter related to the effective size of the ions.

In this letter, we develop a model for high salt concentrations (in excess of 1.5M) in which the solvation shells of the ions strongly overlap. The model is not based upon the field around a single ion. Rather, it assumes the water dipoles are influenced by an aggregate of ions, i.e., the local field acting on a water dipole arises from the net fields created by a surrounding ionic configuration. A key element in the analysis is based on the well known fact that a small fraction of the ions form ion pairs [6]. The analysis in this letter suggests that the propensity of even a small fraction of the ions to form pairs has a significant, even dominant, effect on the static dielectric constant of the solution. The key result is an analytic prediction for the solution dielectric constant as a function of salt concentration c,

$$\varepsilon(c) = \varepsilon_w - \beta L\left(\frac{3\alpha}{\beta}c\right), \tag{2}$$

where L is the Langevin function

$$L(v) = \coth(v) - \frac{1}{v},$$

ε_w is the dielectric of the pure solvent, α is the total excess polarization of the ions and β is the relative difference between an effective ion-pair dipole moment and the water dipole moment. This functional form gives

an extremely accurate prediction of the static dielectric constant over a large range of concentrations of different salts with a single fit parameter β for each mixture.

The static dielectric constant takes the functional form

$$\varepsilon(c) = \varepsilon_\infty + \left. \frac{\partial P(c, E_{\rm ex})}{\partial E_{\rm ex}} \right|_{E_{\rm ex}=0}, \qquad (3)$$

where $E_{\rm ex}$ is external field intensity, P is the orientational polarization of the medium, and ε_∞ is the contribution to the dielectric due to other effects such as molecular polarization. Assuming ε_∞ is independent of the ionic concentration c, the aim of this letter is to suggest a mechanism for the dependence of the orientational polarization P upon c.

The first stage is to determine the contribution of a single water dipole to the orientational (dipolar) polarization, by introducing an ionic field to the standard Langevin dipole analysis, see, e.g., [7, sect. 4.6] or [8, p. 214] for details. Consider a water dipole $\mathbf{p}$ surrounded by point-like ions under an applied external field $\mathbf{E}_{\rm ex}$. The electric field due to the ions, in the absence of water dipoles, is denoted by $\mathbf{E}_{\rm ion}$. The potential energy W of the dipole $\mathbf{p}$ is given by

$$W = -\mathbf{p} \cdot (\mathbf{E}_{\rm ion} + \mathbf{E}_{\rm ex}).$$

The energy W is minimized when the dipole is aligned with the field $\mathbf{E}_{\rm ion} + \mathbf{E}_{\rm ex}$, hence the dipole orientation is a trade-off between the tendency of the dipole to align with the field $\mathbf{E}_{\rm ion} + \mathbf{E}_{\rm ex}$ and thermal fluctuations that disrupt this ordering. The contribution of a given dipole $\mathbf{p}$ to the polarization due to the external field $\mathbf{E}_{\rm ex}$ is $\mathrm{Proj}_{\mathbf{E}_{\rm ex}}(\mathbf{p} - \mathbf{p}_0)$ where $\mathbf{p}_0$ is the average orientation of the dipole $\mathbf{p}$ in the absence of an external field, i.e., in the direction of $\mathbf{E}_{\rm ion}$,

$$\mathbf{p}_0 = \frac{\mathbf{E}_{\rm ion}}{|\mathbf{E}_{\rm ion}|} |\mathbf{p}|.$$

The expectation of the contribution of the dipole $\mathbf{p}$ to the external field $\mathbf{E}_{\rm ex}$ is given by the Boltzmann average

$$P_{\rm local} = \frac{\int e^{-\frac{W}{kT}} \mathrm{Proj}_{\mathbf{E}_{\rm ex}}(\mathbf{p} - \mathbf{p}_0)}{\int e^{-\frac{W}{kT}}}, \qquad (4)$$

where $E_{\rm ion} = |\mathbf{E}_{\rm ion}|$, and $E_{\rm ex} = |\mathbf{E}_{\rm ex}|$. This integral can be explicitly evaluated following [9],

$$P_{\rm local} = pL\left(\frac{pE_{\rm ex}}{kT}\right)\left[1 - L\left(\frac{pE_{\rm ion}}{kT}\right)\right], \qquad (5)$$

where $p = |\mathbf{p}|$, see supplementary material for details.

Expression (5) quantifies the contribution of a single water dipole to the orientational polarization. The second stage of the derivation considers the aggregate contribution P of all water dipoles to the orientational polarization. Assuming the water dipoles are uniformly distributed in space, P is given by

$$P(c) = \int f(E_{\rm ion}; c) P_{\rm local}(E_{\rm ion}) dE_{\rm ion}, \qquad (6a)$$

where $P_{\rm local}$ is given by (5) and $f(E_{\rm ion}; c)$ is the probability density function of the ionic field intensity in the absence of water, given by [10],

$$f(E_{\rm ion}; c) = \frac{4}{\pi} \frac{1}{E_{\rm ion}^*} \frac{(E/E_{\rm ion}^*)^2}{[1 + (E/E_{\rm ion}^*)^2]^2}, \quad \frac{p}{kT}E_{\rm ion}^* = \alpha^* c. \qquad (6b)$$

Here, $E_{\rm ion}^*$ is the most probable ionic field intensity and $\alpha^*(M^{-1})$ is a dimensional constant of proportionality between the normalized ionic field intensity and the ionic concentration. The derivation of $f(E_{\rm ion})$ in [10] relates α^* to the electric field screening length.

The effect of water on the ionic field intensity is neglected in these calculations, i.e., the ionic field is considered as if the ions were in vacuum. The justification for this simplification is that in high concentrations, the water/ion ratio does not allow efficient screening by water molecules. For example, in 1M concentration, the average distance between ions and their counter-ions can not exceed 1.2nm. At this length scale, at most 3 water molecules can reside along the line segment connecting the ionic centers, hence the screening of electric field by the water is limited. In contrast, in 1mM solutions, ion separation distances can average 12nm, with hundreds of water molecules engaged in screening.

A key feature of the model is that α^*, which relates ionic concentrations to screening length, particularly ionic screening, is independent of ionic concentrations above 1.5-2M. At these concentrations inter-ionic distances relate weakly to the concentration, and the ability of ions to redistribute to improve effective screening becomes limited due to finite size effects and thermal fluctuations. As a result, the effective screening length saturates.

The Langevin function can be approximated by

$$L(v) \approx 1 - 1/v \qquad (7)$$

for $v \gg v_L = 0.2$. Using (7) to simplify (5) in the integral (6) yields,

$$P(c) \approx pL\left(\frac{pE_{\rm ex}}{kT}\right)\frac{2}{\pi\alpha^* c}. \qquad (8)$$

Although the primary goal of this derivation is to obtain a prediction for $P(c)$ in the high concentration regime, it is still helpful to obtain an approximation that is compatible with known results in the dilute regime. Relation (1) implies that the orientational polarization is linear for low concentrations. Using (7) in (8) to obtain an approximation of P that is linear for $\alpha^* c \ll 1$ yields

$$P(c) \approx pL\left(\frac{pE_{\rm ex}}{kT}\right)\left[1 - L\left(\frac{\pi\alpha^* c}{2}\right)\right]. \qquad (9)$$

The resulting expression (9) well approximates the tail of P in (6) and in addition complies with the observed linear decrement of the orientational polarization at low concentrations where (6) is invalid, see Figure 1.
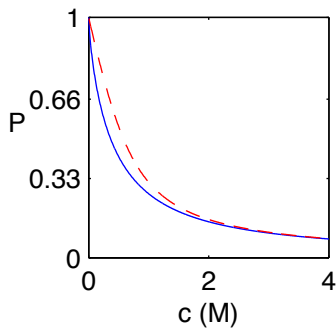
FIG. 1. (color online) Orientational polarization (6) for $\alpha^* = 2$ (-) and the approximation (9) (- -).

Expression (9) quantifies the aggregate contribution of all water dipoles to the orientational polarization P. As expected, $P \to 0$ as $c \to \infty$ (or $E_{\text{ion}} \to \infty$), since the water dipoles become 'immobilized' by the strong ionic field. Experimental data, however, suggests that the dielectric constant of many electrolyte solutions approaches a limiting value, in some instances as high as $\varepsilon = 20$, as the ionic concentration increases, see, e.g., Figure 2B. This observation supports the idea that water dipoles are not the sole contributors to the orientational polarization, but that ionic pairs may also contribute to the orientational polarization. This line of thought is supported by the study of molten salts in the absence of a solvent, in which orientational polarization is significant and the static dielectric constant is relatively high, e.g., $\varepsilon \cong 20$ for Ethylammonium Nitrate [11].

To form an effective dipole, ions need to tightly paired. Molecular dynamics simulations and small angle X-Ray scattering experiments conducted in a wide range of concentrations, $0.01M \le c \le 20M$, consistently show that the locations of the peaks of the anion-cation radial distribution functions are independent of concentration, see, e.g., [12–17]. These anion-cation radial distribution functions suggest that for $c > 0.01M$, a portion of the anions and cations associate into ion-pairs with ion-specific distances of $r = 2.5 - 3.5A°$ for contact pairs or $r = 4.5 - 5.5A°$ for looser pairs. A fundamental assumption of the model is that these ion pairs act as dipoles and consequently contribute to the orientational polarization of the medium. As a first approximation, the effect of the ion-pairs is modeled by a local effective dipole moment $p_{\text{ion}}^{\text{effective}}$ of uniform magnitude which is aligned in the direction of the local ionic field

$$\mathbf{p}_{\text{ion}}^{\text{effective}}(\mathbf{x}) = \frac{\mathbf{E}_{\text{ion}}(\mathbf{x})}{|\mathbf{E}_{\text{ion}}(\mathbf{x})|} \underbrace{p_{\text{ion}} f_{\text{ion}} s_{\text{ion}}}_{p_{\text{ion}}^{\text{effective}}}.$$

Here, p_{ion} is the dipole moment of an ion-pair, f_{ion} is the fraction of ions that form ion-pairs and $0 < s_{\text{ion}} \le 1$ is the structural rigidity of the dipole assumed to be high for contact pairs, and lower for looser pairs.

Incorporating the contribution, $\text{Proj}_{\mathbf{E}_{\text{ex}}} \mathbf{p}_{\text{ion}}^{\text{effective}}$, of the ion-pair dipole to the orientation polarization into the

Boltzmann averaging (4) and evaluating the integral yields

$$P_{\text{local}} = pL\left(\frac{pE_{\text{ex}}}{kT}\right)\left[1 - \beta^* L\left(\frac{pE_{\text{ion}}}{kT}\right)\right], \quad (10)$$

where $\beta^* = \frac{p - p_{\text{ion}}^{\text{effective}}}{p}$. As before, using (7) to simplify (10) in the integral (6) yields

$$P(c) = pL\left(\frac{pE_{\text{ex}}}{kT}\right)\left[1 - \beta^* L\left(\frac{\pi \alpha^* c}{2}\right)\right]. \quad (11)$$

Finally, substituting (11) into (3) gives the functional form (2) where the empirical parameters in (1) take the form

$$\alpha = \frac{\pi}{6}\beta \alpha^* \quad \beta = (\varepsilon_w - \varepsilon_\infty)\beta^*.$$

The functional relation (2) is validated against six different sets of experimental data, where the parameter β is fitted separately for type of electrolyte. Figure 2A presents the experimental data of Hasted et al. [1] for an NaCl solution at $21°$. Prediction (2) agrees very well with the experimental data over the full range of $0 \le c \le 6M$. Figure 2B presents the experimental data of Wei et al. [18] for LiCl, RbCl and CsCl solutions at $25°$. The predicted dielectric (2) remains accurate for LiCl data at concentrations as high as 13M. Finally, Figure 2C shows data taken from [18], which were complied and presented in [5], together with the prediction obtained using the field-theory approach [5] (solid black). The functional form (2) for the dielectric permits a resolution of the differing high-concentration dielectrics of the KCl and KF salts, implying that KCl has a greater predilection to form ion-pairs than KF.

The model naturally incorporates the dependence of the dielectric constant upon temperature T, in which case all parameters become a function of temperature. The validity of functional relation (2) is validated against four different sets of experimental data, due to Buchner et al. [19], for NaCl at various temperatures, where the parameters α and β are fitted separately for each temperature, see Figure 3.

In conclusion, we have derived a model which gives an extremely accurate prediction for the static dielectric constant of aqueous electrolyte solutions. The key parameters arising from the model are the constant of proportionality between the most probable ionic field intensity and the ionic concentration α^* and the parameter β related to the relative difference between the water dipole moment and the effective ionic dipole moment $f_{\text{ion}}^{\text{effective}}$. Assuming that only rigid contact ion-pairs contribute to the orientational polarization, the fitted values of β in Figure 2 imply that $f_{\text{ion}} = 0.024 - 0.073$, i.e., $2.4\% - 7.3\%$ of the ions associate into ion-pairs, excluding the KF salt for which data suggests a weak propensity for K^+-F^- to form ion pairs in water. These values are compared with an approximate of 8% ion-pairs in molten salt Ethylammonium Nitrate [11]. The fitted values of β in Figure 3
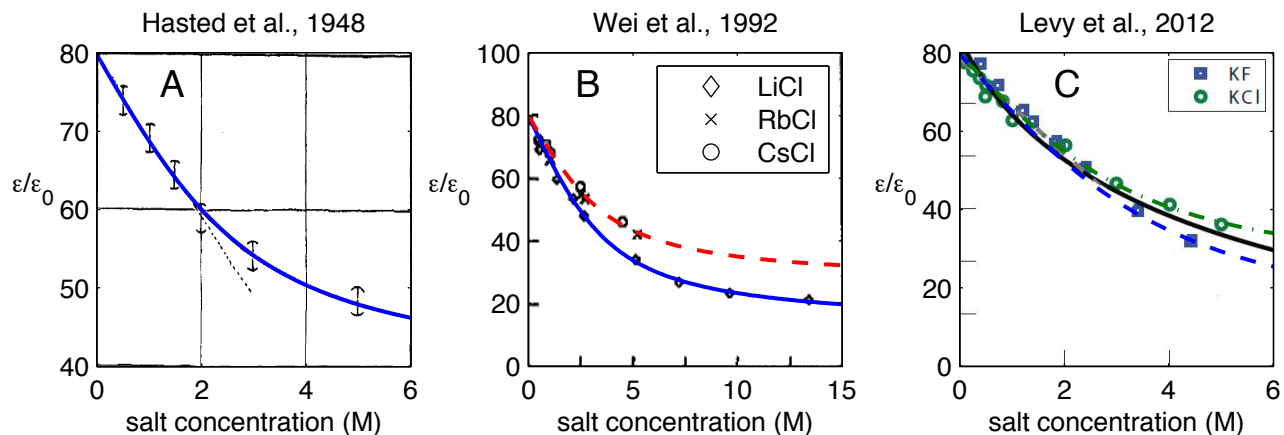
FIG. 2. (color online) Comparison of the predicted dielectric constant (2), with experimental data as function of ionic concentration c for various salts. The theoretical prediction was calculated using β as a fitting parameter. A: Data for NaCl salt from [1], compared to (2) with $\beta = 42.07$. B: Data from [18], where fit for RbCl and CsCl salt ($--$) is obtained with $\beta = 67.20$ and for LiCl ($-$) with $\beta = 53.22$. C: Figure 2(b) from [5] where fit for KF ($--$) is obtained with $\beta = 75$ and with $\beta = 60$ for KCl ($.-$). Solid black curve is the prediction obtained using the field-theory approach [5].
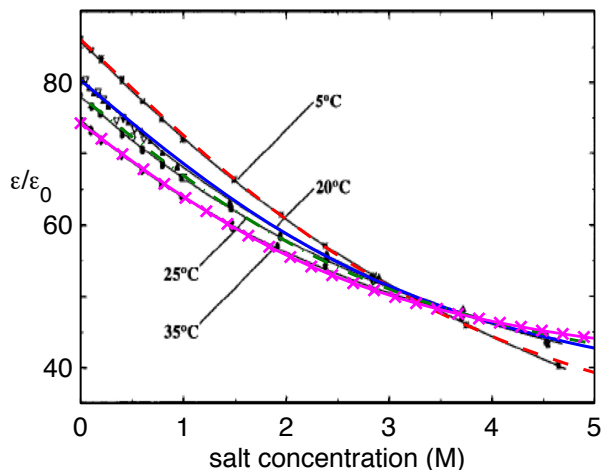

FIG. 3. (color online) Comparison of the predicted dielectric constant (2), with experimental data from [19] as a function of ionic concentration c for NaCl at various temperatures. Data for $T = 5°$ fit with $\alpha = 13.7$ and $\beta = 70.25$ ($--$), for $T = 20°$ with $\alpha = 12$ and $\beta = 52.94$ ($-$), for $T = 25°$ with $\alpha = 11.5$ and $\beta = 47.91$ ($.-$) and for $T = 35°$ with $\alpha = 10.7$ and $\beta = 40.12$ ($\times-$).

show that β decreases with temperature, which is attributed to a decrease in the structural rigidity of the ionic pairs as temperature increases.

A key implication of this work is a reinterpretation of the excess polarization parameter as the constant of proportionality between the most probable ionic field intensity and the ionic concentration, weighted by β. This interpretation is consistent with the data showing an anomalously high excess polarization of H^+ ions. The value $\alpha = 20$ for HCl [1], compared to $\alpha = 11 - 14$

for the various salt solutions of Figure 2, reflects the high entropic cost associated with the localization of protons [20, 21], leading to higher value of both α^* and β. Indeed, this delocalization inhibits effective pairing of the ions, and also inhibits the effectiveness of protons in the screening of counter ions, as compared to K, Li, and Na. This suggests that the constant of proportionality α^* between the ionic field intensity and the ionic concentration should be significantly higher in salts which disassociate into H^+. Similarly, we observe that the dimensional constant of proportionality between the ionic field intensity and the ionic concentration $kT\alpha^*/p$ increases with temperature, since thermal fluctuations reduce the effectiveness of electric field [22].

Electrolyte solutions are highly complex mixtures, and the model neglects numerous structural elements: water/water interactions, water/ion-pair interactions, finite size effects, reaction field effects, influence of the hydrogen bond network, and the decrease in water molarity as ionic concentration increases. While a systematic study of these effects is clearly important, it is plausible that they will contribute perturbatively.

Finally, utilizing the explicit evaluation of the Boltzmann average (4), the model is readily extendable to the case of a strong applied field. In addition, although the model is validated only with 1:1 electrolytes for which relevant experimental data is avaliable, it is also expected to be valid for 2:2 electrolytes. In this case, the anticipated higher tendency to form ion-pairs, would be manifested in small values of β^*, leading to a high dielectric constant $\varepsilon = \varepsilon_w(1 - \beta^*)$ at high concentrations. Furthermore, β^* may become negative [23] leading to a non-monotonic dependence of the dielectric constant upon concentration.

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[22] The non-dimensional parameter α is rescaled with temperature, see (6b), and therefore may decrease with temperature as, indeed, observed in Figure 3.

[23] In the case of $\beta^* < 0$, approximation (9) may not be valid for $\alpha^* c \ll 1$ and a different matching between the tail and solution near $c = 0$ would be required .