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On the dielectric decrement of electrolyte solutions: A dressed-ion theory analysis

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Based on the dressed-ion theory and a simple physical argument regarding the conductivity of the solution, we derive a relation between the ionic strength and dielectric constant of an electrolyte solution. At its simplest, this model gives the dielectric constant at low ionic strength I as $\epsilon_r(I) = \epsilon_r(0)(1 + \alpha I)^{-1}$ where α (the excess polarization) is directly related to the dressed-ion charge. One contribution to the origin of the dielectric decrement is thus seen to stem from the electrostatic screening of the ions in solution, with no solvent contributions necessary.

1 Introduction

Many measurements and theories depend on the value of the dielectric constant. Part of the appeal of this macroscopic constant is doubtless its great use in theories of the equilibrium. Unlike the electrical conduction, the dielectric response ensures a thermodynamic equilibrium state in response to an external electric field. Biomolecular simulations and other large-scale computations can be drastically simplified by replacing the solvent with a so-called “dielectric continuum” and this approach is sometimes extended nowadays with the Debye-Hückel theory to take into account a nonzero ionic strength.¹ The phenomenon of the dielectric response is also interesting in its own right, ever since the foundations of electrostatics were laid in the 19:th century, but perhaps most important to the science of Physical Chemistry is the vital role that the so-called dielectric decrement plays in the theories and practice of Colloidal Science.^{2–5}

Electrolyte solutions are ubiquitous in Chemistry and it is an experimental fact that the static dielectric constant of a polar fluid decreases with increasing concentration of dissolved electrolytes.^{6–8} In the English-language literature, this is dubbed the “dielectric decrement” and may at first sight seem quite natural since the dielectric-conductor dichotomy is often taken to be a fundamental classification of media, but from the point of view of Physical Chemistry, it stands in need of a more satisfying explanation. Certainly, any medium that is subjected to an external electric perturbation can be considered, at its very simplest, as a capacitor and a resistor connected in parallel. There is no obvious reason on a macroscopic level why these two ideal electrical elements of the medium should have any direct connection. Furthermore, despite the large magnitude of the effect, it is not entirely trivial to model theoretically. The Debye-Hückel theory

does not predict it and a mesoscopic model by the present author and collaborators⁹ is too coarse-grained to capture it as well.

However, despite these apparent difficulties, explanations for this phenomenon are at least as old as the discovery of the phenomenon itself. Early reports in the German-language literature conflicted on the magnitude and sign of the dependence of the dielectric constant on the electrolyte concentration.^{10,11} Aware of these conflicting reports, Hückel¹² parametrized the dielectric constant as a function of the concentration in an effort to improve the Debye-Hückel theory for activity coefficients. The best fit was obtained with a decreasing dielectric constant with increasing salt concentration.

In the English-language literature, it was Hasted *et al.*⁶ who were the first to study systematically the behavior of the static dielectric constant in response to various added salts.* They found that at low salt concentrations, the dielectric constant was found to decrease linearly with the salt concentration (at a rate between 7 and 15 units per molar salt concentration), but it would eventually plateau at a limiting value. In their continued work, the same group¹⁴ modeled this phenomenon by assuming the electrolyte solution to constitute a two-phase system on the microscopic level.† In this model, the tightly bound hydration water around the ions exhibits a smaller dielectric constant than that of the bulk. The macroscopically homogeneous phase exhibits the volume-averaged dielectric constant of its microphase counterparts. This model was subsequently refined by taking into account more parameters.^{15,16} (More recently, ideas reminiscent of this model have been proposed as explanations for the unexpected concentration dependence of the far-infrared absorption of protein solutions,¹⁷ but this simplistic picture has met with

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* Already in 1927 Lowry gave 66 references, mostly in German, in his review of the matter.¹³

† This model was actually advanced partially already in Ref. 11.

criticism.¹⁸ We shall only concern ourselves with the static, equilibrium case in this paper.)

The natural evolution of research into the dependence of the static dielectric constant on the electrolyte concentration has culminated in more advanced models in the present day. For instance, Levy *et al.*¹⁹ write down field equations for a system of ions and dipoles that yield approximate analytical solutions for the local dielectric constant in the shell of an ion, and by extension the dielectric decrement of the solution. In the recent analysis by Gavish and Promislow²⁰, the ordering of water dipoles in the microfield stemming from an ensemble of ions is modeled at finite temperature. The thermal average of the water dipoles in the field of a single ion is computed analytically and under some simplifying assumptions the effect of the finite concentration of ions is taken into account. They too arrive at an analytical prediction of the dielectric decrement using only a single fitting parameter. Both Levy *et al.*¹⁹ and Gavish & Promislow²⁰ find good agreement with the experimental findings of the dielectric decrement even in the nonlinear regime for their respective expressions.

One may expect the dielectric decrement to be a consequence of the low polarizability of the ions in a picture where each individual ion and water molecule constitute a microphase analogous with, but physically distinct from, the model of Haggis *et al.*¹⁴ This view, formalized by Sack,^{21,22} is supported by the typically very low dielectric constants of the corresponding ionic crystals. However, even if the ions were completely unpolarizable, typically their partial molar volumes in dilute aqueous solutions are negative. Therefore, their dissolution should lead to an initial increase of the dielectric constant, since it is very accurately proportional to the density.²³ Moreover, if this were the only effect, the dielectric decrement would not deviate from linearity before the molecular volume of the solute approaches that of the crystal, which is likely to be at a point far past the solubility limit. This is why the reason just discussed in the preceding paragraphs is generally accepted: *viz.* that the hydration shell of each ion exhibits a greater reluctance to polarize, and hence a weaker dielectric response, than bulk water. When the ion concentration increases to the point where the hydration shells start to overlap, one expects a saturation of the dielectric decrement as a natural consequence of the ensuing geometrical restrictions. The “hydrated size” of an ion is likely much larger than the “bare size” calculated from its crystal structure so that this overlap effect occurs at concentrations below the solubility limit.

Here we wish to shed some light upon the issue from an angle that has so far not been covered, namely, the role of the electrostatic *ion* screening in reducing the dielectric constant of the solution. We employ arguments from the dressed-ion theory^{24,25} to derive an expression for the dielectric constant as a function of the ionic strength. Interestingly, we will find that also the electrostatic screening through ion correlations, manifested through a reduction of the magnitude of the apparent ionic charge, contributes to the dielectric decrement. For the benefit of the reader unfamiliar with this theory, a brief overview is given next. After that, we will present the dielectric model and the resulting equation for the salt-dependence of the dielectric constant.

2 Dressed-ion theory

The following presentation is not meant as a rigorous proof of the dressed-ion theory. The interested reader is advised to consult the original reference.²⁴ Here we give the main results with the important implications for the present paper. Most of the analysis will not rely on the fundamental details of the dressed-ion theory (which require extensive numerical simulations to apply), but rather borrow the physical concepts that it introduces. In essence, the dressed-ion theory can be considered a reformulation of the Ornstein-Zernike equation, which we will not attempt to solve.

We consider a set of ions with charges $\{q_i\}$ and concentrations $\{n_i\}$ and some unspecified but short-range repulsion to ensure thermodynamic stability at inverse thermodynamic temperature β . It is assumed that the system is wholly electroneutral, that is

$$\sum_i n_i q_i = 0 \quad (1)$$

The charge density at a distance r from an arbitrary ion i is given by,

$$\rho_i(r) = \sum_j n_j q_j e^{-\beta w_{ij}(r)} \quad (2)$$

where w_{ij} is the potential of mean force between ions i and j . The function $w_{ij}(r)$ is a complicated function of the system parameters and is generally not expressible in closed form. It describes all of the ion-ion correlations due to the interactions among the ions other than i among themselves. Poisson's equation provides a condition on eq. 2, *viz.*,

$$\epsilon_0 \nabla^2 \psi_i(r) = -\rho_i(r) \quad (3)$$

where ϵ_0 is the vacuum permittivity and $\psi_i(r)$ is the electrostatic potential at a distance r from i ; but solving this equation still requires knowledge of the $w_{ij}(r)$ function.

In dressed-ion theory,²⁴ the effect of the ion-ion correlations on the distribution functions are *formally* taken into account by replacing the Coulomb potential between ions with the “dressed-ion” potential. The electrostatic scalar potential due to ion i at a distance r is then written

$$\psi_i(r) = \int d\mathbf{r}' \rho_i^*(r') \phi_{\text{Coul}}^*(|\mathbf{r} - \mathbf{r}'|) \quad (4)$$

where ρ_i^* is the “nonlinear part” of the charge density around ion i and ϕ_{Coul}^* is the “screened Coulomb potential”. The “nonlinear part” of the charge density is simply the error term that arises when linearizing eq. 2 for the charge density. Accordingly, ρ_i^* is less appreciable when ion correlations are weaker. However, the strong spatial nonlinearity in the charge density of a point ion means that

$$\rho_i^*(0) = \delta(\mathbf{r}) \quad (5)$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta-function, regardless of the presence of correlations. The restriction of eq. 3 is enforced but unlike the Debye-Hückel approximation, w_{ij} is not replaced by the Coulomb pair potential, instead it is given by

$$w_{ij}(r) = \int d\mathbf{r}' \psi_i(r') \rho_j^*(|\mathbf{r} - \mathbf{r}'|) \quad (6)$$

Although we will not make use of it, we note that the screened Coulomb potential satisfies,²⁵

$$-\epsilon_0 \nabla^2 \phi_{\text{Coul}}^*(r) - \int d\mathbf{r}' \phi_{\text{Coul}}^*(r') \chi^*(|\mathbf{r} - \mathbf{r}'|) = \delta(\mathbf{r}) \quad (7)$$

where

$$\chi^*(r) = -\beta \sum_j n_j q_j \rho_j^*(r) \quad (8)$$

an entity that Kjellander²⁵ calls the “polarization response function”. The integral in eq. 7 has units of charge density and the function χ^* may be thought of as “inducing” this charge density in response to the Coulombic field. For our purposes, we note that it includes no dipolar contributions from the solvent, a point that will be important in the later development.

The most important quantity in our treatment, apart from the function $\chi^*(r)$, will be the so-called “dressed-ion charge” defined for ion i by

$$q_i^* = \int d\mathbf{r} \rho_i^*(r) \quad (9)$$

which should be contrasted with the “bare-ion charge” q_i . The subtraction of the “linear part” of ρ_i from eq. 9 ensures that the integration is not trivially zero due to charge neutrality. At high temperature and/or low ion concentration, it follows from eq. 5 that $q_i^* \rightarrow q_i$, and the deviation of q_i^* from q_i is a direct consequence of the ion-ion correlations in the system. The magnitude of q_i^* is typically (except under very special circumstances which do not arise at low ion concentrations) smaller than that of q_i because of the dominance of counterions over coions in the “ionic atmosphere” around i . It is also important to note that the ions are themselves unpolarizable and so have a fixed charge density as per eq. 5.

3 Dielectric model

3.1 General considerations

In experiments, the static dielectric constant is defined as,

$$\epsilon_r = \frac{C}{C_0} \quad (10)$$

where C_0 is the capacitance of a reference vacuum capacitor and C is the capacitance of a capacitor with the vacuum replaced by a medium with dielectric constant ϵ_r . This capacitance is—however it is measured—always measured in response to an external electric perturbation.

To avoid unnecessary confusion, it may help to clarify the physics of the arguments to be presented before we continue. Let us make a distinction between “bound” and “free” charges as follows: bound charges are trapped in a potential well and return to their original location after the external electric field that displaced them is removed; free charges do not. Hence, free charges are those that carry current in a conductor and bound charges are those responsible for the polarization in a dielectric. This distinction is phenomenological as it is clear that for any physical potential (*i. e.*, one that is bounded) *all* charges are free at finite temperature after infinite time. However, experiments are always conducted over a finite time. Strong ion associations, in the sense of the Bjerrum ion pair, clearly affect the dielectric response of

the concentrated electrolyte solution, in that the ion pair might be sufficiently strongly bound to withstand dissociation by the external field during the time period of the measurement. In this case, the pair behaves like an inducible dipole rather than two free charges.

3.2 Dielectric constant

Consider now the scalar electrostatic potential $\Psi(\mathbf{r})$ at a point \mathbf{r} inside the system. Let us assume that this region inside is separated physically from the *outside* whence originates an external potential $\Psi^{\text{ext}}(\mathbf{r})$.[‡] If this perturbation were not an external one, but rather a perturbation of the *intermolecular* potential, the total force in the fluid would vanish (Newton’s third law would be satisfied) at all times, even out of equilibrium. The perturbation could therefore not induce any macroscopic currents. After a relaxation period, an equilibrium state would be guaranteed, and we could write the total equilibrium potential²⁵

$$\Psi(\mathbf{r}) = \Psi^{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \rho^{\text{pol}}(\mathbf{r}') \phi_{\text{Coul}}(|\mathbf{r} - \mathbf{r}'|) \quad (11)$$

where ϕ_{Coul} is the Coulomb potential, and take a linear constitutive equation to relate $\rho^{\text{pol}}(\mathbf{r})$ (the bound charge density) with $\Psi(\mathbf{r})$,²⁵

$$\rho^{\text{pol}}(\mathbf{r}) = \int d\mathbf{r}' \Psi(\mathbf{r}') \chi^*(|\mathbf{r} - \mathbf{r}'|) \quad (12)$$

Inserting eq. 12 into eq. 11 and Fourier transforming, we would then have the dielectric constant (at any spatial wavelength) from the ratio (spatial Fourier transforms denoted by a tilde),²⁵

$$\tilde{\epsilon}(k) = \frac{\tilde{\Psi}^{\text{ext}}(\mathbf{k})}{\tilde{\Psi}(\mathbf{k})} \quad (13)$$

although this quantity would more correctly be denoted a “screening function” rather than “dielectric function” since it would not derive in response to an external perturbation.

However, since the perturbation to compute the actual dielectric constant is *external*, force symmetry is broken in the fluid, and there will be nonequilibrium currents. If the electric conductivity, σ , is nonzero, these will never disappear as long as Ψ^{ext} is present, and thermodynamic equilibrium will not exist. This is because the system is infinite and lacks boundaries where charge can accrue; or the boundaries act as current source and sink. This conduction current is proportional to $\sigma \nabla \Psi^{\text{ext}}$ and would, for a perfect conductor, be the only response to the perturbation. In this case, there is no microscopic polarization, which implies $\rho^{\text{pol}}(\mathbf{r}) \equiv 0$ instead of eq. (12). In actuality, the system may however exhibit *some* dielectric response, so that a more justifiable *Ansatz* for the constitutive equation is

$$\rho^{\text{pol}}(\mathbf{r}) = \int d\mathbf{r}' [\Psi(\mathbf{r}') - \lambda \Psi^{\text{ext}}(\mathbf{r}')] \chi^*(|\mathbf{r} - \mathbf{r}'|) \quad (14)$$

where the integrand represents only the part of the response which contributes to polarizing the fluid, after subtracting the part which is proportional to the induced current (only bound

[‡] Both Ψ and Ψ^{ext} are presumed to go to zero far away from their source charges.

charges contribute to ρ^{pol}). Here $\lambda \in [0, 1]$ is a parameter that interpolates between the purely conducting ($\lambda = 1$) and purely dielectric ($\lambda = 0$) cases, physically related to the balance between the free charge density (responsible for the current) and the bound charge density (responsible for the polarization).

Then we obtain

$$\tilde{\Psi}(\mathbf{k}) = \tilde{\Psi}^{\text{ext}}(\mathbf{k}) + [\tilde{\Psi}(\mathbf{k}) - \lambda \tilde{\Psi}^{\text{ext}}(\mathbf{k})] \tilde{\chi}^*(k) \tilde{\phi}_{\text{Coul}}(k) \quad (15)$$

which implies the static dielectric constant,

$$\tilde{\epsilon}(k) = \frac{1 - \tilde{\chi}^*(k) \tilde{\phi}_{\text{Coul}}(k)}{1 - \lambda \tilde{\chi}^*(k) \tilde{\phi}_{\text{Coul}}(k)} \quad (16)$$

If $\lambda \neq 0$, this function remains finite as $k \rightarrow 0$, in agreement with experiment. In fact, λ is the reciprocal of the static dielectric constant of the fluid: $\lambda = 1/\epsilon_r$, a result which is physically conditioned on $\sigma > 0$.

Since $\tilde{\phi}_{\text{Coul}}(k) = 1/(\epsilon_0 k^2)$, neglecting the weak k -dependence of $\tilde{\chi}^*(k)$ and expanding eq. (16) for small k , we have[§]

$$\tilde{\epsilon}(k)^{-1} \approx \lambda + \frac{\epsilon_0(\lambda - 1)k^2}{\tilde{\chi}^*(0)} \quad (17)$$

The reciprocal dielectric function is related to the charge-charge structure factor \tilde{S}_{QQ} ,²⁶

$$\tilde{\epsilon}(k)^{-1} = 1 - \frac{\beta}{\epsilon_0 k^2} \tilde{S}_{\text{QQ}}(k; \lambda) \quad (18)$$

The limit of this equation is zero for $k \rightarrow 0$ if all charges are included in the structure factor. However, we wish to restrict it only to the bound charges, in which case it should equal λ in the limit $k \rightarrow 0$. In order to bring consistency and only consider bound charges, we define

$$\tilde{S}_{\text{QQ}}(k; \lambda) = (1 - \lambda) \tilde{S}_{\text{QQ}}(k; 0) \quad (19)$$

which is seen to ensure the correct limit to eq. 18. The next higher-order term in k is also consistent with eq. 17, as seen from the expansion of $\tilde{S}_{\text{QQ}}(k; \lambda)$ for small k ,²⁵

$$\frac{\tilde{S}_{\text{QQ}}(k; \lambda)}{1 - \lambda} = \frac{\epsilon_0 k^2}{\beta} - \frac{\epsilon_0^2 k^4}{\beta^2} \left(\sum_i n_i q_i q_i^* \right)^{-1} + \dots \quad (20)$$

The consistency of eqs 17 and 18 mean that they impose no constraints on λ . Let us for the moment assume that the dielectric constant is only weakly dependent on the ion concentration. In this case, we may let $\sum n_i \rightarrow 0$, so that $\lambda \rightarrow 0$ and $q_i^* \rightarrow q_i$, in either one of the two equations and they should both agree as $k \rightarrow 0$ as long as they are not evaluated at values of the ionic strength that differ too much. We may then determine λ by matching coefficients between eqs 17 and 18, and we obtain

$$\lambda = \epsilon_r^{-1} = 1 - I^{-1} \sum_i n_i q_i q_i^* \quad (21)$$

where $I = \sum_i n_i q_i^2$ is the ionic strength and we have used the relation,

$$\tilde{\chi}^*(0) = -\beta \sum_i n_i q_i q_i^* \quad (22)$$

apparent from eqs 8 and 9. In other words, by assuming that the dielectric constant is a weak function of the ionic strength, we somewhat inconsistently find a concentration dependence. It is important to stress that we obtain the same result independently of which equation for which we choose the limit $\lambda \rightarrow 0$. Eq. 21 provides the value of λ (and hence ϵ_r) that ensures consistency between eqs 17 and 18 when one is evaluated at infinite dilution and the other at a finite concentration.

Both eqs 17 and 21 erroneously predict an infinite dielectric constant of the pure solvent. This error appears in the truncated expansions.[¶] In order to rectify it, we normalize eq. 21 by its (infinite) pure solvent value to obtain in principle a finite limit of unity for this ratio in this limit. Thus, we write

$$\frac{\epsilon_r(I)^{-1}}{\epsilon_r(0)^{-1}} = A(I) - I^{-1} \sum_i n_i q_i q_i^* \quad (23)$$

where $A(I)$ is a function that fulfills $A(0) = 2$ as required by mathematical consistency. For $I > 0$, the right-hand side vanishes if the dielectric constant of the pure solvent actually is infinite, but this is the unphysical result that we want to avoid. For simplicity, we take $A = 2$ as a constant, thereby rescaling the equation to an appropriate range of values for all I that is assuredly appropriate in the limit $I \rightarrow 0$. Interestingly, this procedure leads to a limiting value, in the opposite limit when $I \rightarrow \infty$, of $\frac{1}{2} \epsilon_r(0)$ which coincidentally turns out to be close to the high-concentration limit found experimentally, whereas here it is a device to obtain the correct limiting behavior in the dilute limit.

Eq. 23 constitutes the main result of this paper. However, it is unwieldy to use as the dressed-ion charges are expensive to compute, something which cannot be done by hand. To proceed and obtain something usable, we therefore consider the limiting behavior of eq. 23 at low ionic strength. The electrostatic screening causes $|q_i^*|$ to decrease with increasing ionic strength. At low ion concentrations, we may expand q_i^* in a truncated power series in the ionic strength and write $q_i^* = q_i - \text{sgn}(q_i) a_i I + \dots$, where $a_i > 0$ is a constant. In this regime, eq. 23 hence simplifies to

$$\epsilon_r(I)^{-1} \approx \epsilon_r(0)^{-1} (1 + \alpha I) \quad (24)$$

where $\alpha > 0$ is a system-specific constant.^{||} This reproduces by Taylor expansion to first order the empirical law of Hasted *et al.*⁶ The “excess polarization” of their model, corresponding to the constant α , is thus seen to stem from the concentration behavior of the dressed-ion charge. Unlike the original equation (eq. 23), the high-concentration limiting value of ϵ_r is now zero. However, that is far outside the range of the equation’s applicability.

A comparison with the experiments of Hasted *et al.*⁶ is given in Fig. 1. The erroneous limiting behavior at high concentration is

[§] In eq. 16, $\tilde{\chi}^*(k) \rightarrow 0$ as the ion concentration vanishes and so $\tilde{\epsilon}(0)$ remains finite.

^{||} For a symmetric electrolyte $\sum_i q_i = 0$, $q \equiv |q_i| = |q_j|$ for all i, j , $\alpha = |q|^{-1} \sum_i a_i$. The expression for α becomes more complicated in the general case.

[§] For length scales larger than the correlation length, the polarization response function quickly decays. This is not true of the Coulomb potential whose integral is divergent.

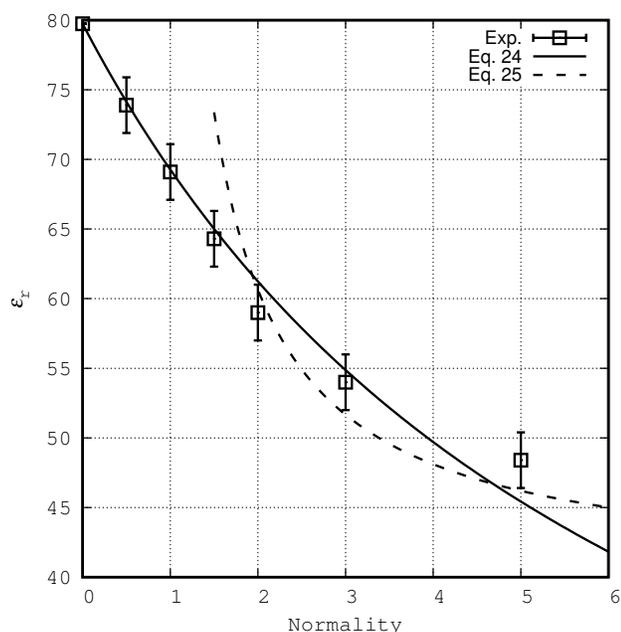


Fig. 1 Static dielectric constant as a function of aqueous NaCl solution normality. Experimental data taken from Refs 6 and 27. Full line corresponds to least-squares fit of eq. 24; dashed line to fit of eq. 25.

apparent in the fit, although some nonlinearity is captured. The complete expression in eq. 23 requires numerical simulation, but on the hypothesis that the dressed-ion charge approaches a constant value, we may write

$$\epsilon_r(I)^{-1} \approx \epsilon_r(0)^{-1} \left(2 - \frac{\alpha'}{I} \right) \quad (25)$$

where α' is another (hypothetical) constant. A fit of this equation, hypothetically valid in the high-concentration regime, to the last three experimental data points is shown by the dashed line in Fig. 1. One should not hastily conclude from the bad quality of the fit in this case that the assumption that the dressed-ion charge becomes constant at high concentration is a poor one, because it is also likely that the high-concentration limit has not actually been fully reached.

4 Conclusion

In this paper, we have derived an equation relating the dielectric constant of an electrolyte solution to its ionic strength. We have shown how in the limit of low concentration, it reduces to the empirical law found by Hasted *et al.*⁶ The physical origin of the “excess polarization” lies in our model in the electrostatic screening caused by the ion-ion correlations which reduce the dressed-ion charge magnitude from its infinite dilution value. The corresponding results in the Debye-Hückel theory indicate no effect of the ion concentration on the dielectric constant (as is seen by replacing q_i^* by q_i throughout). It is interesting to note that no solvent contributions are necessary for the dielectric decrement. This sets our model apart very particularly from the common explanations^{14–16,19,20} that all crucially rely on the concept of the hydration shell.

The objective has not been to obtain the most accurate prediction of the dielectric decrement. This is a task that is best suited for molecular simulations. Rather, I wanted to prove physical insight into the dielectric decrement and to see to what extent simple physical assumptions could explain the phenomenon. In reality, one expects the “excess polarization” constant α to have contributions (of varying magnitude and sign) not only from the hydration shell and from the intrinsic ion polarizability but also, as in our derivation, from the ion-ion correlations. Treating the parameter α as a fitting parameter, as we have done for the sake of expediency, naturally confounds all of these contributions. Their separate magnitudes (to the extent that they can be decoupled) could in principle be established in careful calculations that avoid such an empirical reinterpretation. Nevertheless, the penultimate empirical equation that we have derived somewhat surprisingly captures both the linear regime at low ionic strength, as well as part of the nonlinearity that appears at higher concentration, hinting at a possible importance of the role of nonlocal electrostatics in the dielectric decrement.

Just like no material is ever fully electrically insulating, it should be clear that the primitive model electrolyte solution should have the same dielectric constant as the medium. This follows because at finite temperature, no ion pair has an infinite lifetime and so all charges should be considered free. This view has experimental support. The measurements by Barthel *et al.*⁷ of the static dielectric constant of NaCl solutions were improved upon by Buchner *et al.*⁸ who managed measurements at about five times lower frequencies. The resulting value of the static dielectric constant was also lower in their improved measurements. However, the parameter λ that we have introduced is phenomenological and should, strictly interpreted, be frequency dependent. The question then remains how, for a given frequency, the ion correlations reduce the dielectric constant. Although this is expected according to the empirical inverse relation between the dielectric constant and conductivity of materials¹³ – as it is almost certain that increasing the ion concentration will increase the conductivity at almost all frequencies – a more direct physical explanation could be that the screening of the ion charges (as evidenced by the decrease of the magnitude of the dressed-ion charges) lead to weaker “long-range” cohesiveness between the ions, which offsets whatever gains there are in “short-range” ion pairing of the Bjerrum type.

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