PCCP

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Kinetic dielectric decrement revisited: phenomenology of finite ion concentrations

Marcello Sega,[*a] **Sofia Kantorovich,**[b,c] **and Axel Arnold**[d]

 With the help of a recently developed non-equilibrium approach, we investigate the ionic strength dependence of the Hubbard–Onsager dielectric decrement. We compute the depolarization of water molecules caused by the motion of ions in sodium chloride solutions from the dilute regime (0.035 M) up close to the saturation concentration (4.24 M), and find that the kinetic decrement displays a strong non monotonic behavior, in contrast to the prediction of available models. We introduce a phenomenological modification of the Hubbard–Onsager continuum theory, which takes into account the screening due to the ionic cloud at mean field level and, which is able to describe the kinetic decrement at high concentrations including the presence of a pronounced minimum.

More than thirty years ago, in what was one of the last articles written by L. Onsager, he and J. P. Hubbard made a captivating prediction that has eluded direct observation until now. They stated that in a saline solution, due to the motion of ions, polar solvent molecules should show a tendency to orient against any external, static electric field, in apparent contradiction with electrostatics.[1–3] According to the continuum model of Hubbard and Onsager, the rotational current induced in the solvent by ionic currents should generate a net solvent depolarization that survives in the zero frequency limit. As a consequence, a decrement of the *static* permittivity of the solution should be observed, even though the effect is purely *dynamic*, and as such can not be explained in terms of molecular configurations only. Systems containing free charges can be thought as being infinitely polarizable, since the positive and negative ions in a pair can be brought at infinite distance by a static electric field. The static dielectric permittivity of an electrolyte solution can not be strictly speaking measured, instead, the real part of the dielectric spectrum at low (but finite)

frequencies is used as a measure of the permittivity. To date, however, no direct experimental proof of the kinetic decrement exists, because its detection is complicated by the presence of dielectric saturation, from which it can not be easily separated.[4–8]

A quantitative picture of the kinetic contribution to the dielectric decrement is therefore key to the investigations of ion solvation properties, which rely on a correct estimate of the static contribution of the decrement.[9–11]

The continuum theory of the kinetic decrement predicts that the static permittivity ε_0 of a solvent should change upon addition of salt by an amount (in CGS units)

$$\Delta\varepsilon_{HO} = -4\pi p\sigma\tau(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0, \tag{1}$$

due to a subtle interplay between ion motion and rotational orientation of the solvent molecules. Here, σ denotes the conductivity of the solution and τ is the time constant of the Debye relaxation process that characterizes the dielectric susceptibility of the solvent, and ε_∞ is the infinite frequency dielectric constant.[1,2] The factor p can take values between 2/3 and 1, depending on the type of boundary condition at the surface of the ion (full slip and no slip, respectively). Strictly speaking, the continuum theory is valid only in the infinite dilution limit, and for large ionic radii.[3]

Despite these limitations, the formula for the decrement bears an enthralling elegance, and explains qualitatively the dependence of the dielectric permittivity of electrolyte solutions on their conductivity, even well within the concentrate solution regime.[12] However, the kinetic decrement is not the only effect that is expected to lower the dielectric permittivity of electrolyte solutions. The strong local electric field in the vicinity of the ions tends to polarize solvent molecules more than any external electric field in the linear regime. Such a high field saturates the dielectric response of solvent molecules next to ions, effectively reducing the dielectric permittivity of the solution. This effect depends on the salt concentration c and, implicitly, on the conductivity σ. For this reason it becomes hard, if not impossible, to separate the kinetic contribution from dielectric saturation experimentally.[4,5,7,8] This situation prevents not only a direct observation of the kinetic decrement, but also a precise evaluation of the effect of

---
[a] *University of Vienna, Department of Computational Biological Chemistry, Währinger Strasse 17, 1090 Vienna, Austria ; E-mail: marcello.sega@univie.ac.at*
[b] *University of Vienna, Faculty of Physics, Boltzmanngasse 5, 1090 Vienna, Austria*
[c] *Ural Federal University, Lenin av. 51, 620083 Ekaterinburg, Russia*
[d] *Institute for Computational Physics, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany*

saturation[6] and, consequently, a correct estimate of the number of solvent molecules coordinated by the ions.

Here, we use a non-equilibrium molecular dynamics approach to compute the kinetic decrement over an unprecedented wide range of concentrations, which is not accessible with conventional, equilibrium approaches.[13] Moreover, we present a simple phenomenological theory that gives a quantitative account of the features of the kinetic decrement at higher concentrations.

The kinetic decrement can be seen as the sum of two complementary contributions: the first is the depolarization due to the moving ions, which exerts a torque on the solvent molecules; the second, more subtle effect, is a change in the imaginary part of the ion conductivity, a lag in the response of ions induced by the rotation of solvent molecules which are orienting along the external electric field. The two contributions must have exactly the same value, as a consequence of Onsager reciprocal relations. A straightforward way to see this is through the Green–Kubo expression for the kinetic decrement. The change in solvent polarization current $\mathbf{J}_p$ due to the ionic one $\mathbf{J}_i$ leads to a contribution to the conductivity spectrum $\Delta\sigma_{pi}(\omega) = \beta/(3L^3) \int_0^\infty \exp(i\omega t) \langle \mathbf{J}_p(t)\mathbf{J}_i(0)\rangle \, dt$, where β is the inverse thermal energy, L^3 the simulation box volume, and $\langle \cdot \rangle$ is a suitable ensemble average. This change in conductivity reflects a change in permittivity, since $\varepsilon(\omega) - 1 = i4\pi\sigma(\omega)/\omega$,[14] and results in the first contribution to the kinetic decrement $\Delta\varepsilon_{pi} = \lim_{\omega\to 0} 4\pi i\Delta\sigma_{pi}(\omega)/\omega$. Owing to the symmetry of the current cross-correlation function, the second contribution , which originates from the action of the rotating solvent molecules on the ions, is $\Delta\varepsilon_{ip} = \Delta\varepsilon_{pi}$. The total kinetic decrement is therefore twice the first contribution, $\Delta\varepsilon = 2\Delta\varepsilon_{pi}$.

However elegant, the Green–Kubo expression is not very much suited for the computation of the kinetic decrement, because the signal-to-noise ratio at extreme dilutions would be too small for any practical purposes. A much more efficient way to compute $\Delta\varepsilon_{pi}$ consists instead in applying an external fictitious field $\mathbf{E}_f$, that couples to the ions only, and in calculating the resulting polarization of the solvent $\mathbf{P}$, so that $\Delta\varepsilon_{pi} = 4\pi P/(L^3 E_f)$.[15] This is evidently the out-of-equilibrium counterpart of the Green-Kubo formula for $\Delta\varepsilon_{pi}$, because $\mathbf{J}_i$ is the current that couples to the external field $\mathbf{E}_f$, and $\mathbf{J}_p$ the one generating the polarization $\mathbf{P}$.

We applied this non-equilibrium calculation to an aqueous solution of sodium chloride at 11 different salt concentrations. In our simulations we model water molecules using the three-sites SPC/E potential[16] and sodium and chloride ions using the thermodynamics consistent Kirkwood–Buff potential.[17] The salt concentration c varies from 0.035 to 4.24 M, keeping the water content fixed at 1621 molecules per simulation box and changing the number of salt pairs from 1 to 140. We kept constant temperature (300 K) and pressure (1 atm) using the Nosé–Hoover[18,19] and Parrinello–Rahman[20]
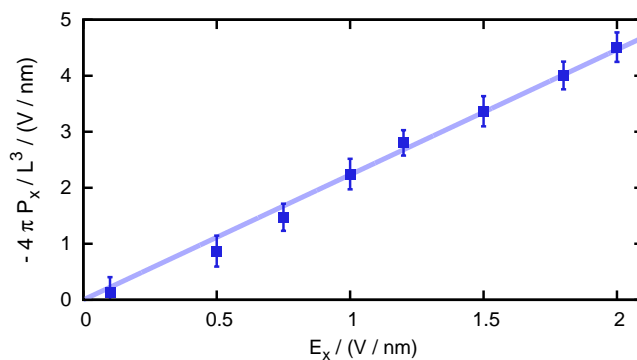

Fig. 1 Calculated water depolarization as a function of the applied fictitious field (points) and linear fit (line).

algorithms with relaxation times of 5 ps. Electrostatic interactions were computed using the smooth particle mesh Ewald method[21] with tin-foil boundary conditions, a 4-th order interpolation spline on a grid with spacing not larger than 0.12 nm and a relative interaction strength of 10^{-5} at 0.9 nm. We switched the short range part of the electrostatic interaction and the Lennard-Jones smoothly to zero between 0.9 to 1.2 nm using a fourth-degree polynomial. Simulations were performed with an in-house modified version of gromacs[22] for the on-line calculation of the currents associated to the different species, and used an integration time step of 1 fs.

To check that we are performing calculations in the linear regime, we applied our non-equilibrium approach for the system of 100 ion pairs using an applied external fictitious fields of magnitude varying from 0.1 to 2 V/nm, sampling the resulting depolarization of water $-4\pi P_x/L^3$ during 500 ps long simulation runs (Fig. 1) as a function of the applied field. The linear behavior holds even for rather high fields, and this allows to collect meaningful statistics also for very dilute solutions with relatively short simulation runs, making this non-equilibrium approach the key to calculating the kinetic decrement over an unprecedented broad range of concentrations.

Using an external fictitious field of 0.5 V/nm we proceeded to calculate the kinetic decrement for different salt concentrations in 1 ns long runs, obtaining the values of dielectric decrement presented in Figure 2. The kinetic decrement shows a marked non monotonic dependence on the concentration, with a clear minimum right before $c = 2$ M. To test the Hubbard–Onsager formula, Eq. (1), we calculated also the molar conductivity Λ of the solution at the different concentrations, as reported in Figure 3. A best fit to the Kohlrausch law, $\Lambda(c) = \Lambda_0 - K\sqrt{c}$, allows us to extrapolate the molar conductivity to infinite dilution, and estimate the limiting molar conductivity Λ_0 separately for the sodium and chloride ions. Therefore, we can write the Hubbard–Onsager decrement for the mixture of sodium and chloride in the form
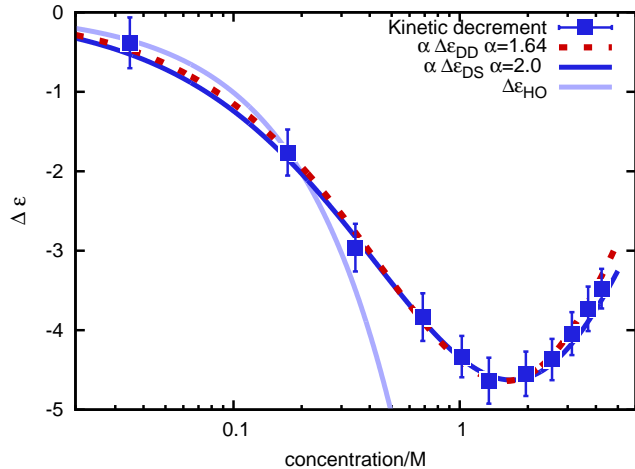
Fig. 2 Kinetic contribution to the static dielectric permittivity. Squares: simulation result; light line: Hubbard–Onsager theory, $\Delta\varepsilon_{HO}(c)$; dark line: $\alpha\Delta\varepsilon_{DS}(c)$, with $\alpha = 2$; dashed line: $\alpha\Delta\varepsilon_{DD}(c)$, with $\alpha = 1.64$
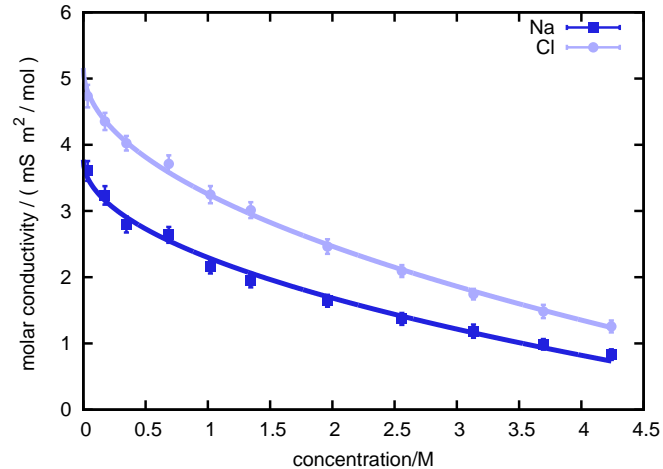

Fig. 3 Molar conductivity of sodium and chloride ions, as a function of the concentration. Squares: sodium; Circles: chloride; Solid lines: best fit to Kohlrausch law.

$\Delta\varepsilon_{HO} = -4\pi p\tau(\Lambda_0^{Na} + \Lambda_0^{Cl})c(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0$. The Hubbard–Onsager decrement so calculated (Fig.2, light line) is not compatible with the simulation data above a concentration of 0.2 M. The presence of a pronounced minimum and the subsequent increase of $\Delta\varepsilon$ can not be explained even qualitatively with the continuum Hubbard–Onsager theory.

Physical intuition suggests that the local field of the ions, which determines the torque on water molecules, should be screened by the presence of oppositely charged ions in its vicinity. To formalize this, we introduce a mean-field correction to the Hubbard–Onsager theory, along the lines of the Debye–Hückel theory. The crucial step in the Hubbard–Onsager theory is the calculation of the rotational current $\mathbf{J}_R$ induced in the polar medium by an ion travelling with a speed $\mathbf{u}$. The coupling between electrostatics and Navier–Stokes equations allows to express the rotational current as a functional of the local field generated by the ion, $\mathbf{E}_0$, as $\mathbf{J}_R = \int(\chi/2\varepsilon_0)\mathbf{E}_0 \times (\nabla \times \mathbf{v})\,d\mathbf{r}$, where $\mathbf{v}$ is the velocity field of the solvent surrounding the ion and χ its dielectric susceptibility.[1] For large ionic radii R, the velocity field can be approximated (in the low salt concentration limit) by Stokes' solution, $\mathbf{v}(\mathbf{r}) = (3R/4r^3)[r^2\mathbf{u} + (\mathbf{r}\cdot\mathbf{u})\mathbf{r}]$. If, instead of using the Coulomb field, we use the Debye–Hückel one, $\mathbf{E}_0 = (q/\varepsilon_0 r^3)\exp(-\kappa r)(1 + \kappa r)\mathbf{r}$, the rotational current can be evaluated analytically as $\mathbf{J}_R = (2\pi/\varepsilon_0)\mathbf{u}\chi q\exp(-\kappa R)$. Here $\kappa = \sqrt{\beta c e^2/(2\pi\varepsilon_0)}$ is the inverse Debye screening length.

Since the ratio between the ion speed u and the driving electric field E_x is $u/E_x = \sigma/q$, it is possible express the dielectric decrement (which we denote here as $\Delta\varepsilon_{DS}$, and where the suffix hints at the use of the Debye–Hückel field and of the

Stokes' flow solution) in terms of the rotational current

$$\Delta\varepsilon_{DS} = \lim_{\omega\to 0} 4\pi\frac{\sigma''}{\omega} = \lim_{\omega\to 0}\frac{4\pi}{\omega}J_R''/E_x. \qquad (2)$$

Here, the imaginary part of a quantity is denoted by double-primes. The susceptibility of the dipolar medium is assumed to be characterized by a single Debye relaxation, so that $4\pi\chi(\omega) = (\varepsilon_0 - \varepsilon_\infty)(1 + i\omega\tau_D)$, from which one derives

$$\Delta\varepsilon_{DS} = -4\pi\sigma\tau\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0}e^{-\kappa R}p. \qquad (3)$$

The solution resembles the classical Hubbard–Onsager one, but features an additional factor $\exp(-\kappa R)$ which depends on the (effective) ion size. This difference is an important one, because it shows that even at the mean field level there is an additional length scale, the screening length κ^{-1}, that governs the non-monotonic behaviour of the kinetic decrement. The screening, however, affects not only the electric field generated by the ion, but also the velocity of the fluid around it, so that at finite concentrations the Debye–Hückel-corrected velocity field reads[23] $\mathbf{v}(\mathbf{r}) = (3R/4r^3)\exp(-\kappa r)\{(4/3)r^2\mathbf{u} + 2\kappa^{-2}[1 + \kappa r + \kappa^2 r^2/3 - \exp(\kappa r)][\mathbf{u} - 3(\mathbf{r}\cdot\mathbf{u})\mathbf{r}/r^2]\}$. This flow can be integrated in a similar way to the Stokes' one, yielding the decrement

$$\Delta\varepsilon_{DD} = -2\pi\sigma\tau\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0}e^{-\kappa R}(\kappa R + 2)p, \qquad (4)$$

where the subscript underlines that the Debye–Hückel approximation has been used both for the electric field and for the flow solution.

In Figure 2 we compare the simulation results with the mean field results Eq. (3) and Eq. (4), summed over the contributions of the two ionic species, and multiplied by a phenomenological scaling factor α, that takes into account the effect of ionic correlations arising at high salt concentration. The relaxation time τ has been computed from a fit of the Debye process $\chi(\omega)$ to the spectrum of the pure solvent, and the solution conductivity has been calculated from the limiting molar ones as for the Hubbard–Onsager case. The relaxation of water is not described by a single Debye process, and often a Cole-Cole relaxation or two Debye processes[24] are used to fit experimental data. However, the dominant water contribution at lower frequencies comes from the main Debye relaxation, which is the one we are using here to calculate the decrement.

A very good qualitative agreement is already achieved by using the Stokes' flow based solution, Eq. (3), and $\alpha = 2$ (dark curve in Figure 2), taking as a value for the effective ionic radius R the size of the first hydration shell of the ion, defined as the sum of the position of the first minimum in the ion-water radial distribution function and of the Lennard-Jones diameter of a water molecule. Taking into account also the screening of the flow due to the counterion clouds introduces a qualitative difference in the formula for the decrement, Eq. (4), which is characterized by the presence of an additional term proportional to κ. In fact the smaller scaling factor $\alpha = 1.64$ is sufficient to obtain an equivalently good fit, if at the same time the value of both effective ionic radii is increased by 1.5 Å. Both models are thus able to give a qualitatively correct picture of the concentration dependence of the kinetic dielectric decrement at finite concentrations, underlining the importance of the screening induced by the counterion clouds in determining the effective water-ion interaction in the hydrodynamic regime.

As a final remark, we note that due to the presence of the scaling factor α, both curves do not converge, for $\kappa R \ll 1$, to the solution of Hubbard and Onsager, the latter being a better approximation at low concentrations. Nevertheless, the simulation data shows that the applicability range of the Hubbard–Onsager theory is limited to concentrations smaller than approximately 0.2 M, a condition which has been often not fulfilled when searching for experimental evidences of the kinetic decrement.[12] Our simulation results thus resolve the doubts which were cast on the attribution of the measured dielectric decrement[5] in favor of the hypothesis of a static effect arising from dielectric saturation,[7] which is definitely the largest contribution to the dielectric decrement.

References

1 J. B. Hubbard and L. J. Onsager, *J. Chem. Phys.*, 1977, **67**, 4850.

2 J. B. Hubbard, *J. Chem. Phys.*, 1978, **68**, 1649.

3 J. B. Hubbard, P. Colonomos and P. G. Wolynes, *J. Chem. Phys.*, 1979, **71**, 2652–2661.

4 P. Winsor IV and R. H. Cole, *J. Chem. Phys.*, 1982, **86**, 2491–2494.

5 Y.-Z. Wei, P. Chiang and S. Sridhar, *J. Chem. Phys.*, 1992, **96**, 4569.

6 K. Nörtemann, J. Hilland and U. Kaatze, *J. Phys. Chem. A*, 1997, **101**, 6864–6869.

7 U. Kaatze, *J. Solution Chem.*, 1997, **26**, 1049–1112.

8 U. Kaatze, *J. Mol. Liq.*, 2011, **162**, 105–112.

9 K. Tielrooij, N. Garcia-Araez, M. Bonn and H. Bakker, *Science*, 2010, **328**, 1006–1009.

10 R. Buchner, G. T. Hefter and P. M. May, *J. Chem. Phys. A*, 1999, **103**, 1–9.

11 N. Nandi, K. Bhattacharyya and B. Bagchi, *Chem. Rev.*, 2000, **100**, 2013–2046.

12 J. Hubbard, L. Onsager, W. Van Beek and M. Mandel, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 401–404.

13 A. Chandra, *J. Chem. Phys.*, 2000, **113**, 903.

14 J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, London, 1986.

15 M. Sega, S. Kantorovich, C. Holm and A. Arnold, *J. Chem. Phys.*, 2014, **140**, 211101.

16 H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269–6271.

17 S. Weerasinghe and P. E. Smith, *J. Chem. Phys.*, 2003, **119**, 11342–11349.

18 S. Nosé, *Mol. Phys.*, 1984, **52**, 255–268.

19 W. G. Hoover, *Phys. Rev. A*, 1985, **31**, 1695–1697.

20 M. Parrinello and A. Rahman, *J. Appl. Phys.*, 1981, **52**, 7182–7190.

21 U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. Pedersen, *J. Chem. Phys.*, 1995, **103**, 8577.

22 B. Hess, C. Kutzner, D. Van Der Spoel and E. Lindahl, *J. Chem. Theory Comput.*, 2008, **4**, 435–447.

23 D. Long and A. Ajdari, *Eur. Phys. J. E*, 2001, **4**, 29–32.

24 J. Barthel, K. Bachhuber, R. Buchner and H. Hetzenauer, *Chemical physics letters*, 1990, **165**, 369–373.