Kinetic polarization deficiency in electrolyte solutions

(dielectric relaxation/static permittivity/ion migration)

J. B. HUBBARD*, L. ONSAGER*†, W. M. VAN BEEK*, AND M. MANDEL‡

*Center for Theoretical Studies, P.O. Box 249055, University of Miami, Coral Gables, Florida 33124; and †Department of Physical Chemistry, Gorlaeus Laboratory, University of Leiden, Leiden, The Netherlands

Contributed by J. B. Hubbard, November 8, 1976

ABSTRACT The prediction and experimental confirmation of a previously unsuspected kinetic effect occurring in electrolyte solutions are presented herein. Kinetic polarization deficiency may be described as a reduction, with respect to the pure solvent, in the static permittivity of the solution; the decrement in ϵ_0 is shown to be proportional to the product of the dielectric relaxation time of the solvent and the low frequency conductivity of the solution. The kinetic ion-solvent interaction affects the capacitive admittance in two closely related ways: as an ion migrates, the surrounding volume elements of the liquid tend to rotate according to the laws of hydrodynamics, and although dielectric relaxation tends to restore an equilibrium polarization appropriate to the local electric field, this adjustment is not instantaneous; rather it lags behind by the dielectric relaxation time. Conversely, the force that an external field exerts on an ion does not develop its full strength instantly because the ion is driven partly by the external field and partly by the polarization that develops in response to the applied field, the polarization field evolving with a time constant that is the relaxation time for the orientation of solvent dipoles.

We wish to report the theoretical prediction and experimental confirmation of an effect occurring in electrolyte solutions for which we have coined the term "kinetic polarization deficiency." For the purpose at hand the phenomenon may be described as a reduction, with respect to the solvent, in the static permittivity of the solution. Assuming, as we shall, a simple Debye dispersion for the dielectric relaxation of the pure solvent, the decrement in ϵ_0 will be shown to be proportional to the product of the relaxation time of the solvent τ_D and the low frequency conductivity of the solution σ_0 .

The theoretical framework is as follows: we regard not only the polarization of the vacuum, but also the intrinsic polarization of molecules and ions as occurring on a much shorter time scale than τ_D , thereby contributing to the high frequency dielectric constant ϵ_∞ . On the other hand, since we are concerned only with ion-solvent interactions, the static and kinetic influences on the ionic atmosphere will also be neglected. The model we adopt is that of a symmetrically charged impenetrable sphere (the ion) moving in a viscous, incompressible, polarizable fluid continuum (the solvent) under the influence of a periodic external field. Of course, no continuum model that includes dielectric relaxation can avoid the following inconsistency: that a finite relaxation time implies finite dimensions for a fluid element.

If the ion is fixed with respect to the solvent, the latter supports a static polarization field $\vec{P}_D$, which is the vector sum of the field of the ion $\vec{P}_0$, plus the image charge-induced polarization emanating from the conducting planes which, we assume, enclose the system. The specification of the compensating image charges is absolutely necessary inasmuch as this insures the convergence of the integrals that determine the decrement in the permittivity (not that this is the first appearance of such

problems in the theory of dielectrics)[§]. Choosing the center of the ion as the origin of our coordinate system, and in accordance with the above considerations, we define

$$\vec{P}_0 = \kappa_D(e\vec{r}/\epsilon_0 r^3), \quad \kappa_D = [(\epsilon_0 - \epsilon_\infty)/4\pi], \quad [1]$$

where e is the ion charge and κ_D is the Debye susceptibility of the solvent. The dissipation function[¶] is constructed as the sum of the usual hydrodynamic term plus the "electrical" dissipation

$$2F_{el} = \frac{\tau_D}{\kappa_D} \left| \frac{\partial \vec{P}_D}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{P}_D + \frac{1}{2} \vec{P}_D \times [\vec{\nabla} \times \vec{v}] \right|^2, \quad [2]$$

which is the simplest form that allows no dissipation for rigid body motions of an inhomogeneously polarized dielectric. The local polarization deficiency corresponding to [2] is given by

$$\kappa_D \vec{E} - \vec{P}_D = \tau_D \left(\frac{d\vec{P}_D}{dt} + \frac{1}{2} \vec{P}_D \times [\vec{\nabla} \times \vec{v}] \right), \quad [3]$$

where $\vec{E}$ is the local electric field and the convective derivative is indicated. The volume integral of this expression with suitable boundary conditions on the velocity field $\vec{v}$ contributes to the polarization current and therefore to the permittivity.

The integral of the convective term is easily shown to vanish if use is made of the assumption that the system is bounded by equipotential conducting surfaces, so that the total induced image charge is the negative of the ion charge, and if the fluid far from the ion is undisturbed by the ion's motion. If we consider an ion moving at a steady velocity $\vec{u}$, then for the case of perfect adherence at the ion-fluid interface, we have

$$\frac{1}{2} \int \vec{P}_D \times [\vec{\nabla} \times \vec{v}] dV = -\frac{e\vec{u}}{2} \left[\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \right] \quad [4]$$

and so

$$\Delta\epsilon_0(\text{dipole}) = -2\pi \left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \right) \tau_D \sigma_0, \quad [5]$$

where we have assumed additivity of the various "rotation currents" defined by [4].

The total kinetic decrement in ϵ_0 is not, however, given simply by [5], but has an additional contribution due to the finite time (about τ_D) required for the ion to reach the steady velocity $\vec{u}$; this delay manifests itself as an apparent decrease in susceptibility. It can be shown that an electrical stress tensor of the form

$$S_{el} = \frac{1}{8\pi} [\vec{D}\vec{E} + \vec{E}\vec{D} - \vec{E} \cdot \vec{D} \mathbf{I}] \quad [6]$$

[§] The Clausius-Mosotti derivation of the cavity field is a classic example. See H. A. Lorentz, *Theory of Electrons* or P. Debye (1929) *Polar Molecules* (Dover, New York), pp. 9-12.

[¶] The dissipation function equals one half the local rate of dissipation of energy (1).

[†] Deceased.

($\mathbf{I}$ is the unit tensor) is consistent^{||} with the dissipation function defined by [2], where the local induction $\vec{D} = \epsilon_\infty \vec{E} + 4\pi \vec{P}_D$. With the assumption that inertial effects are negligible, the electrical driving force acting on the ion, $\vec{K}_{el}$, must always balance the viscous retarding force, so that $\vec{K}_{el}$ may be obtained most simply by calculating the total electrical force transfer to an indefinitely large spherical shell centered on the ion. Given a periodic external field $\vec{E}_{ex}$ of circular frequency ω , we have, for sufficiently large values of r ,

$$\begin{aligned}\vec{E} &= \vec{E}_{ex} + (e/\epsilon_0) (\vec{r}/r^3), \\ \vec{D} &= \epsilon(\omega) \vec{E}_{ex} + e (\vec{r}/r^3), \\ \vec{K}_{el} &= e \vec{E}_{ex} [\epsilon_0 + \epsilon(\omega)]/2\epsilon_0,\end{aligned}\quad [7]$$

whatever the form of $\epsilon(\omega)$, which is the dispersion law for the solvent. Now in the absence of dielectric friction the ion mobility A is a real number, so that at non-zero frequency part of the ion velocity, which we shall call $\vec{u}^*$, is $\pi/2$ radians out of phase with $\vec{E}_{ex}$ and must, therefore, be considered as part of the "effective" polarization current. If we choose the Debye form for $\epsilon(\omega)$, then equating driving and retarding forces yields

$$\vec{u}^* = -[Ae\vec{E}_{ex}] \left[\frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau_D^2} \right] \left[\frac{\omega\tau_D}{2\epsilon_0} \right] \quad [8]$$

so that the corresponding conductivity may be expressed as

$$\sigma_\omega^*(\text{ion}) = -\sigma_0 \left[\frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau_D^2} \right] \left[\frac{\omega\tau_D}{2\epsilon_0} \right]. \quad [9]$$

Considering the relation between conductivity and permittivity** in the limit of zero frequency, we arrive at

$$\begin{aligned}\Delta\epsilon_0(\text{ion}) &= 4\pi \lim_{\omega \rightarrow 0} \left[\frac{\sigma_\omega^*(\text{ion})}{\omega} \right], \\ &= -2\pi \left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \right) \tau_D \sigma_0,\end{aligned}\quad [10]$$

which is identical to [5]. The total decrement in the static dielectric constant is therefore given by

$$\begin{aligned}\Delta\epsilon_0 &= \Delta\epsilon_0(\text{ion}) + \Delta\epsilon_0(\text{dipole}), \\ &= -4\pi \left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0} \right) \tau_D \sigma_0.\end{aligned}\quad [11]$$

It should be emphasized that the preceding result is independent of ion size only if dielectric friction is negligible compared to viscous friction; the more general case will be treated in a later publication.

Measured were the permittivities of solutions of various chlorides in water and methanol at concentrations between 10^{-3} and 10^{-1} mole-liter⁻¹, temperature 25°, and frequency range 5–20 MHz, which is well outside the dispersion region for these solvents.

Previous experimental studies (2, 3) dealt with more concentrated solutions at frequencies above 1 GHz, so that ϵ_0 could be obtained only by long extrapolations of the experimentally determined impedances to zero frequency. It was observed that the static permittivities so obtained exhibit a strong tendency to decrease with increasing concentration. We have succeeded in measuring permittivities at such low frequencies that, for the

concentrations considered, the dispersions due to relaxation of the solvent and ionic atmosphere are negligible (4), and in fact, no frequency dependence was found in the region explored. The ϵ_0 values presented here are averages of measured values at different frequencies.

Our measurements were performed with the help of an RX Meter, type 250-A (Boonton Radio Co.), in combination with a coaxial cell of variable liquid column height. The balance equations of the RX Meter were generalized to take into account parasitic effects which become important for systems with nonnegligible conductivity (5). This necessitates standardization of the admittance bridge and introduces the possibility of systematic errors in ϵ_0 , the maximum value of which may be estimated. Comparison with results obtained independently by another experimental method at 500 KHz and below (6, 7) with concentrations up to 6×10^{-2} M shows that both experimental approaches yield identical values for ϵ_0 within experimental accuracy. This suggests that systematic errors in our data are well below these theoretical estimates.

The coaxial measuring cell is a modification of the displacement cell described by Lovell and Cole (8). As expected, both the conductance and the capacitance of the cell displayed parabolic variations with the height of the liquid column. The cell has been calibrated with liquids of known specific conductivity σ_0 (aqueous KCl solutions) and electric permittivity (water-methanol mixtures).

All the experimental results, collected in Table 1, show the same pattern for the dependence of ϵ_0 on concentration: at concentrations up to 2.5×10^{-2} M ϵ_0 is larger than the measured value of the static permittivity of the solvent (78.60 ± 0.05 for water and 32.66 ± 0.05 for methanol), while at higher concentrations ϵ_0 decreases with increasing concentration and falls below the value of ϵ_0 (solvent). The striking difference between the electric permittivity of aqueous HCl and other chloride solutions at comparable concentrations, particularly in the higher concentration ranges, should be noted. The decrements with respect to the permittivity of water are much larger for HCl than, for example, LiCl or NaCl at the same concentration. This is not predicted by current theories, which attribute decrements of the electric permittivity with respect to the solvent to dielectric saturation effects in the solvation layers around the ions; for example, according to Glueckauf's theory (9) a 0.05 M solution of HCl should have an ϵ_0 that is only 0.3 lower than for NaCl, whereas here a difference larger than 5 was found.

For practically all chlorides in water the increments $\epsilon_0 - \epsilon_0$ (solvent) observed at concentrations less than 2.5×10^{-2} M were in fair agreement with the predictions of the Debye-Falkenhagen theory, according to which $\Delta\epsilon_{DF} = B c^{1/2}$, with B a constant depending on the type of electrolyte, the solvent, and the temperature (see Table 1). The only aqueous solutions that showed considerable and always negative deviations with respect to $\Delta\epsilon_{DF}$ up to this concentration were HCl and CuCl_2 , both characterized by large specific conductivities. On the other hand, solutions of some chlorides in methanol also had dielectric increments that were smaller than the values predicted by the Debye-Falkenhagen theory, in contrast to the situation in water. Here no large specific conductivities could be involved, but it should be noted that in methanol dielectric relaxation is slower than in water.

From the preceding observations it may be inferred that for the concentrations considered, two quite different and opposing effects determine the electric permittivity of electrolyte solutions: (a) the Debye-Falkenhagen effect, which tends to increase the permittivity of the solution with respect to the pure solvent,

^{||} This is a general form for the electrical stress tensor associated with a moving anisotropic fluid in which the free energy is independent of the rate of deformation.

** The electrical conductivity and dielectric dispersion are related by $\sigma(\omega) - \sigma_0 = (i\omega/4\pi) \epsilon(\omega)$, where σ_0 defines a finite steady current.

Table 1. Static permittivities ϵ_0 and conductances σ_0 for various electrolyte solutions at 25°*

Electrolyte	Solvent	c (mole-liter ⁻¹)	ϵ_0	σ_0 ($\Omega^{-1} \text{ m}^{-1}$)	$\Delta\epsilon_0$	$\Delta\epsilon_{\text{DF}} = B c^{1/2}$
HCl	H ₂ O	0.025	77.2 ± 0.20	1.014	-1.4 ± 0.21	0.59
		0.0375	76.1 ± 0.54	1.509		
		0.05	73.4 ± 0.39	1.991		
LiCl	H ₂ O	0.025	79.2 ± 0.11	0.258	0.6 ± 0.12	0.59
		0.05	78.3 ± 0.11	0.497		
		0.075	77.8 ± 0.14	0.726		
		0.1	77.0 ± 0.14	0.948		
NaCl	H ₂ O	0.025	79.2 ± 0.15	0.288	0.6 ± 0.16	0.59
		0.05	78.6 ± 0.20	0.558		
		0.075	77.3 ± 0.17	0.814		
		0.1	76.2 ± 0.15	1.072		
KCl	H ₂ O	0.001	78.7 ± 0.12	0.015†	0.1 ± 0.13	0.12
		0.01	79.0 ± 0.11	0.0140	0.4 ± 0.12	0.37
		0.025	79.12 ± 0.08	0.344	0.52 ± 0.09	0.59
		0.05	78.5 ± 0.15	0.667		
		0.075	77.3 ± 0.18	0.984		
NH ₄ Cl	H ₂ O	0.1	76.7 ± 0.17	1.286	0.6 ± 0.19	0.59
		0.025	79.2 ± 0.18	0.342		
		0.05	78.3 ± 0.32	0.669		
		0.075	76.7 ± 0.36	0.983		
		0.1	76.9 ± 0.31	1.293		
(C ₂ H ₅) ₄ NCl	H ₂ O	0.025	79.0 ± 0.16	0.238	0.4 ± 0.17	0.59
		0.1	77.2 ± 0.15	0.874		
CuCl ₂	H ₂ O	0.0125	79.8 ± 0.27	0.270	1.2 ± 0.27	1.20
		0.025	79.5 ± 0.29	0.510	0.9 ± 0.29	1.70
		0.0375	78.6 ± 0.25	0.736		
		0.05	77.2 ± 0.28	0.951		
		0.1	74.8 ± 0.51	1.736		
LiCl	CH ₃ OH	0.025	32.9 ± 0.10	0.161	0.2 ± 0.11	0.92
		0.05	32.3 ± 0.10	0.289		
		0.075	31.5 ± 0.13	0.400		
		0.1	30.5 ± 0.13	0.502		
(C ₂ H ₅) ₄ NCl	CH ₃ OH	0.025	32.9 ± 0.13	0.190	0.3 ± 0.14	0.92
		0.1	31.3 ± 0.15	0.615		

* The "net" deviation $\Delta\epsilon_0 = \epsilon_0(\text{solution}) - \epsilon_0(\text{solvent})$; the Debye-Falkenhagen increments are presented in the last column. (ϵ_0 values are averages of measurements at different frequencies with standard deviations in the average values; number of measurements per concentration between 2 and 6.)

† Literature value at 25°.

and (b) the kinetic polarization deficiency effect, which tends to decrease the permittivity, the decrement increasing with solvent relaxation time and conductance of the solution.

If the experimental values of ϵ_0 could be corrected for the Debye-Falkenhagen effect, it would be possible to determine the magnitude of effect (b), assuming in a first approximation that dielectric saturation could be neglected at the concentra-

tions considered here. Unfortunately the Debye-Falkenhagen effect has only been evaluated for sufficiently diluted solutions for the Debye model to hold. For concentrations up to 10^{-1} M, where deviations with respect to such a theoretical calculation can be expected, $\Delta\epsilon_{\text{DF}} = B c^{1/2} f(c)$, where $f(c)$ is a correction factor which tends to unity as $c \rightarrow 0$. An estimate for $f(c)$ can be found by speculating that deviations of the Debye-Falken-

FIG. 1. The kinetic polarization deficiency effect is exhibited by a plot of permittivities, corrected for the Debye-Falkenhagen effect, against the specific conductivity σ_0 at 25°. Values of the corrected permittivities in water: ordinate at the left-hand side; in methanol: ordinate at the right-hand side. (○) HCl; (▽) LiCl; (□) NaCl; (Δ) KCl; (▲) KCl (independent method); (▼) NH₄Cl; (×) (C₂H₅)₄NCl; (+) CuCl₂. Curve 1, straight line calculated with a weighted least-squares fit for results in water. Curve 2, straight line calculated with a weighted least-squares fit for results in methanol.

hagen effect with respect to its theoretical value will occur with increasing concentration in nearly the same way as deviations observed in the experimental molar conductivities Λ_{exp} occur with respect to the theoretical values derived by Onsager: $\Lambda = \Lambda_{\infty} - \beta c^{1/2}$, i.e., $f(c) \sim (\Lambda_{\infty} - \Lambda_{\text{exp}}) \beta^{-1} c^{1/2}$. Here Λ_{∞} is the molar conductivity at infinite dilution.

If $(\epsilon_0 - \Delta\epsilon_{\text{DF}}) = [\epsilon_0 - B c^{1/2} f(c)]$ is plotted against conductivity for all electrolytes studies in a given solvent, all the points seem to be around a single straight line (Fig. 1), the intercept and slope of which have been determined by a weighted least-squares fit. In water the intercept and slope have been found to be 79.1 ± 0.11 and $-2.7 \pm 0.2 \Omega \text{ m}$, respectively; in methanol, 33.2 ± 0.41 and $-6.0 \pm 1.1 \Omega \text{ m}$, respectively. The two intercepts are in fair agreement with the experimental values of the electric permittivities of the pure solvents; the slopes are somewhat larger than predicted by the theory of kinetic polarization deficiency; i.e., $-0.86 \Omega \text{ m}$ and $-4.50 \Omega \text{ m}$ for water and methanol, respectively.

Thus, our estimates account for a substantial fraction of the observed polarization deficiencies. The remainder might indicate a measure of dielectric saturation; but we should bear in mind that the continuum model describes a fairly severe idealization of a real liquid, and also that we have not looked into the consequences of viscous relaxation, although the viscous

and the dielectric relaxation times are presumably comparable.

More complete descriptions of the experimental procedures and details of the mathematical analysis will be given elsewhere.

This research was supported by National Institutes of Health Grant GM 20284-04, National Science Foundation Grant CHE 75-17533, and the Army Grant DAHCO-04-76G00002.

1. Onsager, L. (1931) *Phys. Rev.* **38**, 2265-2279.
2. Hasted, J. B. (1973) *Aqueous Dielectrics* (Chapman and Hall, London), pp. 136-175.
3. Pottel, R. (1966) in *Chemical Physics of Ionic Solutions*, eds. Conway, B. E. & Barradas, R. G. (Wiley, New York), pp. 581-596.
4. Falkenhagen, H. (1971) *Theorie der Elektrolyte* (Hirzel, Leipzig), pp. 168-222.
5. van Beek, W. M. (1975) Ph. D. Dissertation, University of Leiden.
6. van der Touw, F. & Mandel, M. (1971) *Trans. Faraday Soc.* **67**, 1336-1342.
7. van der Touw, F., Mandel, M., Honijk, D. D. & Verhoog, H. G. F. (1971) *Trans. Faraday Soc.* **67**, 1343-1354.
8. Lovell, S. E. & Cole, R. H. (1959) *Rev. Sci. Instrum.* **30**, 361-362.
9. Glueckauf, E. (1964) *Trans. Faraday Soc.* **60**, 1637-1645.