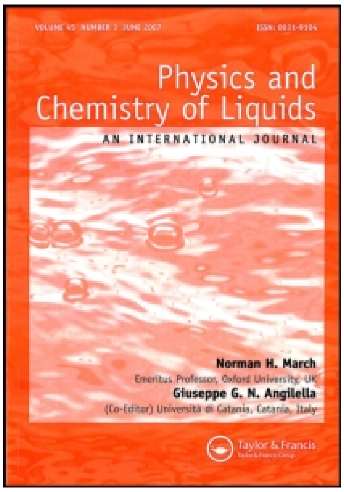

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Tosi, M. P. and March, N. H.(1978) 'Ion Migration and Frequency-Dependent Dielectric Loss', Physics and Chemistry of Liquids, 8: 3, 143 — 151
To link to this Article: DOI: 10.1080/00319107808084748
URL: http://dx.doi.org/10.1080/00319107808084748

Phys. Chem. Liq., 1978, Vol. 8, pp. 143-151

Printed in Holland

Ion Migration and Frequency-Dependent Dielectric Loss

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(*Received February 23, 1978*)

The frequency-dependent dielectric loss due to ion migration in a solvent with a given dielectric function $\varepsilon(\omega)$ is calculated explicitly within the following framework:

i) The solvent is treated in the dielectric continuum model

ii) The Navier–Stokes equation is solved for the velocity field

iii) The limiting cases of (a) large ion radius (weak coupling) and (b) point ions (strong coupling) are treated explicitly.

The most clearcut prediction of the theory is that the incremental frequency-dependent conductivity is proportional to $\omega^{1/4}$ at high frequencies, the power law being independent of the form of $\varepsilon(\omega)$. For arbitrary frequencies, in the limits (a) and (b) above, the incremental frequency-dependent conductivity can be calculated explicitly given the dielectric function of the solvent.

1 INTRODUCTION

The problem of the high-frequency conductivity $\sigma(\omega)$ in dielectric media remains of considerable interest. By now, there are numerous experimental situations where power law behaviour at high frequencies, i.e.

$$\sigma(\omega) \propto \omega^n \tag{1.1}$$

is found to represent the experimental data, n being often in the range 0.6–1.[1]

Earlier work of Glarum (Ref. 2; see also Ref. 3) leads to $n = \frac{1}{2}$ for a model of dipolar relaxation assisted by defect arrival at the relaxing site.

The purpose of the present paper is to report a calculation of the incremental frequency-dependent conductivity due to ion migration in a solvent

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with a given dielectric function $\varepsilon(\omega)$. We stress especially that, in contrast to earlier work in this area,[4–7] in all of which the solvent was assumed to be characterized by a single Debye relaxation process, the results presented below allow a given (e.g. measured) solvent $\varepsilon(\omega)$ to be used as input.

2 FIELD EQUATIONS AND NAVIER–STOKES EQUATION

Below, it is convenient to use the approach and notation of Hubbard and Onsager[7] (referred to below as HO), but their field equations for a simple Debye solvent will be generalized to apply to a given dielectric function $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$. This is achieved by writing the electrical dissipation function in the general form[8]

$$\begin{aligned} 2F_{el} &= -\frac{\omega}{4\pi}\varepsilon''(\omega)|\mathbf{E}|^2 \\ &= -\frac{4\pi}{\omega}\frac{\varepsilon''(\omega)}{|\varepsilon(\omega)-\varepsilon(\infty)|^2}\left|\frac{\partial \mathbf{P}_D}{\partial t}\right|^2 \end{aligned} \tag{2.1}$$

where $\mathbf{E}$ is the electric field while $\mathbf{P}_D$ is the polarization arising from motion of the solvent molecules and is given by

$$\mathbf{P}_D = \frac{1}{4\pi}[\varepsilon(\omega) - \varepsilon(\infty)]\mathbf{E}. \tag{2.2}$$

We follow HO by introducing the velocity field $\mathbf{v}$, when Eq. (2.1) requires the generalization

$$\frac{\partial \mathbf{P}_D}{\partial t} \to \frac{\partial \mathbf{P}_D}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{P}_D + \tfrac{1}{2}\mathbf{P}_D \times (\nabla \times \mathbf{v}). \tag{2.3}$$

The field equations then take the form, with

$$\mathbf{P}^* = \frac{\varepsilon(0) - \varepsilon(\infty)}{4\pi}\mathbf{E} - \mathbf{P}_D, \tag{2.4}$$

$$\mathbf{P}^* = \frac{1}{i\omega}\frac{\varepsilon(0) - \varepsilon(\omega)}{\varepsilon(\omega) - \varepsilon(\infty)}\left[\frac{\partial \mathbf{P}_D}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{P}_D + \tfrac{1}{2}\mathbf{P}_D \times (\nabla \times \mathbf{v})\right]. \tag{2.5}$$

Adding the hydrodynamic dissipation function to F_{el} leads to the Navier–Stokes equation, which in linearized form reads

$$\eta\nabla^2\mathbf{v} = \nabla p - \tfrac{1}{2}[\mathbf{E}_0 \times (\nabla \times \mathbf{P}^*) + \mathbf{E}_0(\nabla\cdot\mathbf{P}^*)], \tag{2.6}$$

where η is the shear viscosity of the solvent, p is the hydrodynamic pressure while $\mathbf{E}_0$ is

$$\mathbf{E}_0 = -\frac{e}{\varepsilon(0)}\nabla\left(\frac{1}{r}\right). \tag{2.7}$$

2.1 Description of velocity field

At this stage, we return to the formalism of HO by expressing the velocity field $\mathbf{v}$ in terms of a scalar function $f(r)$ defined by

$$\mathbf{v} = \tfrac{1}{2}\nabla \times [f(r)(\mathbf{r} \times \mathbf{u})]. \tag{2.8}$$

The underlying reason for the form (2.8) is that it expresses the most general divergence free vector field $\mathbf{v}$ that is proportional to a specified constant vector $\mathbf{u}$ in a spherically symmetrical system, $-\mathbf{u}$ being the velocity of the ion when $f(r)$ is normalized to be unity as $r \to \infty$.

The Navier–Stokes equation (2.6) then leads to a differential equation for $F(z) = \mathrm{d}f/\mathrm{d}r$, namely

$$z\left[z\frac{\mathrm{d}}{\mathrm{d}z} - \alpha_0\right]\left[z\frac{\mathrm{d}}{\mathrm{d}z} - \beta_0\right]F(z) - \left[z\frac{\mathrm{d}}{\mathrm{d}z} - \alpha_1\right]\left[z\frac{\mathrm{d}}{\mathrm{d}z} - \beta_1\right]F(z) = \gamma z^{1/2} \tag{2.9}$$

where $z = -r^4/a$ and γ is an arbitrary constant of integration. The constants appearing in Eq. (2.9) are defined by:

$$a = \frac{e^2}{16\pi\eta}\frac{\varepsilon(0) - \varepsilon(\omega)}{i\omega\varepsilon^2(0)}, \tag{2.10}$$

$\alpha_0 = -1$, $\beta_0 = \frac{1}{4}$ and

$$\begin{aligned} \alpha_1 &= \frac{1}{8}\left\{1 + \left[49 + 8\frac{b}{a}\right]^{1/2}\right\} \\ \beta_1 &= \frac{1}{8}\left\{1 - \left[49 + 8\frac{b}{a}\right]^{1/2}\right\} \end{aligned} \tag{2.11}$$

b being given by

$$\frac{b}{a} = \frac{\varepsilon(0)}{\varepsilon(\omega)}. \tag{2.12}$$

Eqs. (2.9)–(2.12) constitute the generalization of the results of HO to a general dielectric function for the solvent, the form of the equation (2.9) being identical to theirs, provided the quantities a and b are redefined according to Eqs. (2.10) and (2.12).

One wishes now to solve for $f(r)$ subject to the boundary conditions, for a migrating ion of radius R,

$$\lim_{r\to\infty} f(r) = 1, \qquad f(R) = 0. \tag{2.13}$$

The third boundary condition depends on an assumption about the tangential velocity at the surface of the migrating ion. Below we restrict ourselves to the case when the tangential velocity is zero at the ion surface $r = R$, which leads to

$$F\left(\frac{-R^4}{a}\right) = 0, \tag{2.14}$$

this being the appropriate boundary condition for the case of point ions ($R \to 0$) which is our major interest here.

As pointed out by HO, the homogeneous form of Eq. (2.9), i.e. $\gamma = 0$, can be solved in terms of hypergeometric functions, the mathematical detail being given in the Appendix for the limiting cases of (a) large ionic radii (weak coupling) and (b) point ions (strong coupling).

2.2 Friction coefficient and ion mobility

At this point, we must consider how the friction coefficient and the frequency-dependent ion mobility are related to the asymptotic form of the solution for $F(z)$. As HO point out, the velocity field will resemble the Stokes form $\mathbf{v}_0(\infty) + \mathbf{v}_1(\infty)/r$ far from the ion. Thus, the coefficient of $1/r$ in the large r expansion of $f(r)$ is related to the friction coefficient, ζ, by

$$\zeta = +4\pi\eta \operatorname*{Lt}_{r\to\infty} rf(r). \tag{2.15}$$

The frequency-dependent ion mobility $\mu(\omega)$, related directly to the incremental conductivity $\Delta\sigma(\omega)$, is given in terms of the friction coefficient by

$$\mu(\omega) = \frac{\varepsilon(0) + \varepsilon(\omega)}{2\varepsilon(0)\zeta(\omega)}. \tag{2.16}$$

To establish Eq. (2.16) the hydrodynamic force $\zeta(\omega)\mathbf{u}$ is equated to the electrical force on the ion $[\varepsilon(0) + \varepsilon(\omega)]e\mathbf{E}_{\text{ext}}/2\varepsilon(0)$, and the mobility is defined as usual through $\mathbf{u} = \mu\mathbf{E}_{\text{ext}}$.

3 LIMITING CASES OF LARGE IONIC RADIUS AND POINT IONS

3.1 Large ionic radius ($|a/R^4| \ll 1$)

As discussed in the Appendix, the differential Eq. (2.9) has solution in the range $|z| > 1$ of the form

$$F_>(z) = A_2F_2(z) + g_>(z) \tag{3.1}$$

where both $F_2(z)$ and $g_>(z)$ can be represented by descending series in $1/z$, these forms being given in the Appendix. For large ionic radius, i.e. such that

$|R^4/a| \gg 1$, the leading terms in these series are all that is required to impose the boundary conditions (2.13) and (2.14).

The friction coefficient is then determined through

$$\frac{1}{\zeta(\omega)} = \frac{1}{6\pi\eta R}\left[1 - \frac{a}{R^4}\frac{(47 + 4(b/a))}{315} + \left(\frac{a}{R^4}\right)^2 P\left(\frac{b}{a}\right) + 0\left(\left\{\frac{a}{R^4}\right\}^3\right)\right] \tag{3.2}$$

where P is polynomial of the second degree, which is given in the Appendix.

The structure of the series (3.2) makes it clear that the friction coefficient, in this dielectric continuum model has a form such that

$$\frac{1}{\zeta(\omega)} = \frac{1}{6\pi\eta R} H\left(\frac{a}{R^4}; \frac{b}{a}\right). \tag{3.3}$$

This represents already some considerable simplification in that ζ involves three reduced quantities rather than five original quantities. Clearly comparison of Eqs. (3.2) and (3.3) yields the precise form of H in the limit of weak coupling $|a/R^4| \ll 1$.

Though, as we shall see below, the most interesting high-frequency results come from the strong coupling limit, we note here that for sufficiently large ω, $(b/a) \to [\varepsilon(0)/\varepsilon(\infty)]$ and $a \to (e^2/16\pi\eta)[\varepsilon(0) - \varepsilon(\infty)]/[\varepsilon^2(0)i\omega]$, so that in this limit the friction coefficient is independent of the detailed form of $\varepsilon(\omega)$ for the solvent.

3.2 Point ions ($R \to 0$)

For the point ion limit, we require not only the solution (3.1) of Eq. (2.9) for $|z| > 1$, but also the solution for $|z| < 1$

$$F_<(z) = A_1 F_1(z) + g_<(z), \tag{3.4}$$

which is regular at the origin. In the Appendix, forms of $F_1(z)$ and $g_<(z)$ are given as ascending power series in z. In the outer region $|z| > 1$, the solution (3.1) must be the analytic continuation of (3.4), which fixes the constants A_1 and A_2 in terms of γ.

One next integrates Eq. (3.4) to obtain $f(r)$, which, according to (2.13), must satisfy $f(0) = 0$ in this point ion limit, while its analytic continuation must satisfy $f(\infty) = 1$. This latter condition suffices to determine γ. The friction coefficient is found to again take the form of Eq. (3.3), with H now given, as $R \to 0$, by

$$H\left(\frac{a}{R^4}; \frac{b}{a}\right) = \frac{9}{8\sqrt{2}}\left(\frac{a}{R^4}\right)^{-1/4}\left[\frac{\Gamma(\frac{1}{4} + \alpha_1)\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{2} + \alpha_1)}\right]^2 \tag{3.5}$$

where α_1 is given in Eq. (2.11).

The high-frequency behaviour in this limit is of considerable interest. As noted above, a $\alpha(i\omega)^{-1}$, and $b/a \to \varepsilon(0)/\varepsilon(\infty)$ for sufficiently large ω. Thus, Eq. (3.5) shows that H, and hence the inverse friction coefficient, goes like $\omega^{1/4}$. Thus, the incremental high-frequency conductivity $\Delta\sigma(\omega)$ takes the form (1.1) with $n = \frac{1}{4}$. We stress that this result is independent of the detailed form of $\varepsilon(\omega)$ for the pure solvent.

4 DISCUSSION AND SUMMARY

The main conclusions of this model based on a dielectric continuum assumption are:

i) For all coupling strengths, the frequency-dependent ion mobility has the form

$$\mu(\omega) = \frac{\varepsilon(0) + \varepsilon(\omega)}{12\pi\eta R\varepsilon(0)} H\left(\frac{a}{R^4}, \frac{b}{a}\right) \tag{4.1}$$

where a and b are determined in terms of pure solvent properties by Eqs. (2.10) and (2.12). The form of Eq. (2.10) makes it clear that the quantity a/R^4 plays the role of an electrical coupling parameter between the ion and the solvent. The two limiting cases of large ionic radius and point ions thus correspond to weak and strong coupling respectively, the weak coupling results given being for the "no slip" type of boundary condition.

ii) For strong coupling, and suitably high frequencies, the incremental high-frequency conductivity $\Delta\sigma(\omega)$ has the power law form (1.1) with $n = \frac{1}{4}$. Since this exponent is different from that of Debye relaxation assisted by defect arrival at the relaxing site, when $n = \frac{1}{2}$ (see Refs. 2 and 3) the exponent clearly depends on the mechanism operating.

It would seem of considerable interest to undertake an experimental programme to test whether the predictions of the dielectric continuum model apply to real liquid systems with ions migrating. One or two cautionary remarks seem called for. First, the exponent $n = \frac{1}{4}$ seems low compared with the values currently obtained on many dielectric materials. Therefore the separation of solvent contribution will have to be done with great care. Secondly, it would clearly be simplest if one type of ion only migrates. Two cases come to mind as possibilities here. The first is that in water as solvent, when dilute concentrations of ammonium halides are introduced, the ammonium ions are believed to replace water molecules in the structure with relatively small local distortion. In contrast the halogen ions have a very marked effect on the structure as seen by X-ray diffraction and may well be more mobile. The second possibility is in superionic conductors, where above the transition temperature, say in CaF_2, the anions show marked mobility. It is not clear to us presently, whether the assumptions of the model adopted here will be validated in these systems, but we consider that investigation of this point may well be of interest.

Appendix

DETERMINATION OF VELOCITY FIELD

The solution of the differential Eq. (2.9) for $|z| < 1$, which is regular at the origin, is

$$F_<(z) = A_1 F_1(z) + g_<(z) \tag{A.1}$$

where A_1 is an arbitrary constant and

$$F_1(z) = z^{\alpha_1} \sum_{n=0}^{\infty} \frac{\Gamma(\alpha_1 - \alpha_0 + n)\Gamma(\alpha_1 - \beta_0 + n)}{n!\,\Gamma(\alpha_1 - \beta_1 + n + 1)} z^n, \tag{A.2}$$

$$g_<(z) = -\gamma z^{1/2} \frac{\Gamma(\frac{1}{2} - \alpha_1)\Gamma(\frac{1}{2} - \beta_1)}{\Gamma(\frac{1}{2} - \alpha_0)\Gamma(\frac{1}{2} - \beta_0)} \sum_{n=0}^{\infty} \frac{\Gamma(\frac{1}{2} - \alpha_0 + n)\Gamma(\frac{1}{2} - \beta_0 + n)}{\Gamma(\frac{3}{2} - \alpha_1 + n)\Gamma(\frac{3}{2} - \beta_1 + n)} z^n. \tag{A.3}$$

The solution for $|z| > 1$, which is regular at infinity, is immediately found by the transformation $z \to 1/z$ in the differential equation, and reads

$$F_>(z) = A_2 F_2(z) + g_>(z) \tag{A.4}$$

where A_2 is another arbitrary constant, and

$$F_2(z) = z^{\alpha_0} \sum_{n=0}^{\infty} \frac{\Gamma(\alpha_1 - \alpha_0 + n)\Gamma(\beta_1 - \alpha_0 + n)}{\Gamma(\beta_0 - \alpha_0 + n + 1)n!} z^{-n}, \tag{A.5}$$

$$g_>(z) = \gamma z^{-1/2} \frac{\Gamma(\frac{1}{2} + \alpha_0)\Gamma(\frac{1}{2} + \beta_0)}{\Gamma(\frac{1}{2} + \alpha_1)\Gamma(\frac{1}{2} + \beta_1)} \sum_{n=0}^{\infty} \frac{\Gamma(\frac{1}{2} + \alpha_1 + n)\Gamma(\frac{1}{2} + \beta_1 + n)}{\Gamma(\frac{3}{2} + \alpha_0 + n)\Gamma(\frac{3}{2} + \beta_0 + n)} z^{-n}. \tag{A.6}$$

1 Large ionic radius

The boundary condition (2.14) yields

$$A_2 = -g_>(-R^4/a)/F_2(-R^4/a) \tag{A.7}$$

while the boundary conditions (2.13) can be used to determine γ through

$$\int_R^\infty \mathrm{d}rF_>(-r^4/a) = 1. \tag{A.8}$$

Equation (2.15) yields the friction coefficient as

$$\begin{aligned}\zeta &= -\frac{4\pi i\eta\gamma(a)^{1/2}}{(\alpha_0+\frac{1}{2})(\beta_0+\frac{1}{2})}\\ &= 6\pi\eta R\left[1+\frac{47+4b/a}{315}\frac{a}{R^4}-\frac{2602828+342592b/a-1328(b/a)^2}{315\cdot 385\cdot 377}\left(\frac{a}{R^4}\right)^2\right.\\ &\qquad\left.+\cdots\right]\end{aligned} \tag{A.9}$$

This reduces in the limit $\omega = 0$ to the result reported by HO to order a/R^4.

2 Point ions

The solution (A.1) for $|z| < 1$ already satisfies the boundary condition (2.14). The two arbitary constants A_1 and A_2 are determined by requiring that the external solution (A.4) coincide with the analytic continuation of the internal solution (A.1). The latter is calculated by the Barnes contour integral method,[10] with the result

$$\begin{aligned}F_<(z) &= g_>(z) + (-1)^{\alpha_0}\frac{\sin[\pi(\beta_1-\alpha_0)]}{\sin[\pi(\alpha_0-\beta_0)]}\\ &\quad\times\left[(-1)^{-\alpha_1}A_1 + i\gamma\frac{\Gamma(\frac{1}{2}-\alpha_1)\Gamma(\frac{1}{2}-\beta_1)\Gamma(\frac{1}{2}+\alpha_0)}{\Gamma(\frac{1}{2}-\beta_0)\Gamma(\alpha_1-\alpha_0)\Gamma(\alpha_0-\alpha_1+1)}\right]F_2(z)\\ &\quad+\frac{\Gamma(\beta_0-\alpha_0)}{\Gamma(\beta_0-\beta_1+1)}\left[(-1)^{-\alpha_1}A_1\Gamma(\alpha_1-\beta_0) + i\gamma\right.\\ &\quad\left.\times\frac{\Gamma(\frac{1}{2}-\alpha_1)\Gamma(\frac{1}{2}-\beta_1)\Gamma(\frac{1}{2}+\beta_0)}{\Gamma(\frac{1}{2}-\alpha_0)\Gamma(\beta_0-\alpha_1+1)}\right]\\ &\quad\times(-z)^{\beta_0}F(\alpha_1-\beta_0,\beta_1-\beta_0;\alpha_0-\beta_0+1;1/z)\end{aligned} \tag{A.10}$$

where we have used the standard symbol for the hypergeometric function. Therefore,

$$A_1 = -(-1)^{\alpha_1} i\gamma \frac{\Gamma(\frac{1}{2}-\alpha_1)\Gamma(\frac{1}{2}-\beta_1)\Gamma(\frac{1}{2}+\beta_0)}{\Gamma(\frac{1}{2}-\alpha_0)\Gamma(\alpha_1-\beta_0)\Gamma(\beta_0-\alpha_1+1)} \qquad \text{(A.11)}$$

A similar analytic continuation of $f(r)$ and use of the boundary conditions (2.13) yields the value of the arbitrary constant γ:

$$\gamma a^{1/4} = -\frac{i}{\sqrt{2}}\left[\frac{\Gamma(\frac{1}{2}+\alpha_1)}{\Gamma(\frac{3}{4})\Gamma(\frac{1}{4}+\alpha_1)}\right]^2. \qquad \text{(A.12)}$$

The value (3.5) of the friction coefficient follows by using Eq. (A.9).

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