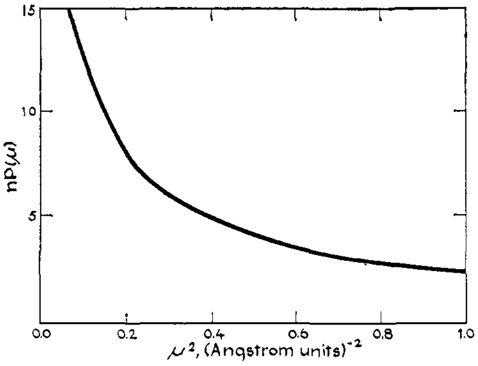

Figure 6. The relative intensity, $nP(\mu)$, per scattering element calculated by eq 33 for polymethylene in the limit $n \rightarrow \infty$, plotted against μ^2.

this case. It is again shown as curve 1; numeration of other curves corresponds to their designations in Figures 3 and 4. The Debye equation (16) with v defined by eq 14 (curve 3) offers the best approximation to curve 1. The series for $P^{-1}(\mu)$ is slightly less satisfactory for this longer chain; curves 2 and 6, representing this series truncated at its second and third terms, respectively, exhibit deviations setting in at small values of μ^2. Curve 10, representing eq 23, offers a much better approximation than the corresponding curve for $n = 10$ in Figure 4. It is to be observed that the range of v encompassed in these figures is large, going much beyond that normally covered in experiments on molecular scattering. Higher values of v were included in these calculations in order to accentuate differences between the various curves.

For very long chains measured at finite values of μ^2 such that $\mu^2\langle s^2\rangle \gg 1$, the pairs j,k which contribute appreciably to the scattering function are those for which $|j - k| \ll n$. The intensity $I(\theta)$ per scattering element observed at an angle $\theta > 0$ is proportional to $nP(\mu)$, and it is independent of the subdivision of the Nn scattering elements into separate molecules, subject to fulfillment of the conditions stated.

According to eq 9 with approximations appropriate in the limit $n \rightarrow \infty$

$$nP(\mu) = n^{-1}\sum_{j,k} \exp(-\mu^2\langle r_{jk}^2\rangle/6) = 2\sum_{m=1}^{\infty} \exp(-\mu^2\langle r_m^2\rangle/6) \quad (33)$$

This function, computed from the values of $\langle r_m^2\rangle$ for finite sequences as above, is plotted against μ^2 in Figure 6. Similar calculations for chain molecules other than polymethylene and comparisons with artificial models and with results of X-ray scattering by polymer solutions will be presented in a later paper.

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Relaxation Effects in Associating Electrolytes[1]

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Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut. *Received December 4, 1967*

Abstract: The dissociation–recombination kinetics in associating electrolytes are shown to provide an additional mechanism for the relaxation of the asymmetric charge distributions produced in the ionic atmospheres by migration of the ions in an external field. The relaxation effects are reduced significantly (the Onsager relaxation field by as much as 23%) when two conditions are satisfied: (1) the rate of ionic recombination is within two orders of magnitude of the diffusion-controlled rate, and (2) the lifetime of the associated species is at least comparable to the relaxation time of the ionic atmosphere. The theory of Debye and Falkenhagen for conductance and dielectric dispersion in alternating weak fields is modified to include this effect for associating binary electrolytes. The important limiting case of stationary weak fields is discussed in detail.

A weak electrolyte has been generally regarded as a solution of free ions in a solvent of neutral molecules, whereby the recombined ion pairs would function as another neutral component of the solvent for the remaining free ions and play no special role in electrolytic conduction. The theory of electrostatic interaction of ions has been applied in this spirit, assuming that the relaxation effects of the ionic atmospheres, as well as the electrophoretic effects and the modifications of chemical equilibrium, would be functions of the free ion concentrations only.

We have looked into the possibility that the recombination kinetics might provide an additional mechanism for the relaxation of the asymmetric charge distributions produced in the ionic atmospheres by migration of the ions. We find that the relaxation effects are significantly reduced when two conditions are fulfilled. First, the rate of recombination must be at least comparable to the fastest permitted by diffusion. Second, the lifetime of the associated species must be at least comparable to the relaxation time of the ionic

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[1] This paper is based on the dissertation submitted by S. W. Provencher to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree, June 1967. All computations were performed at the Yale Computer Center with funds provided by Yale University from National Science Foundation Grant No. GP 4774.

[2] National Science Foundation Graduate Fellow, 1964–1967.

atmosphere. The two conditions together imply a significant degree of association.

In this paper, we calculate to $O(c^{1/2})$ the conductivity and dielectric dispersion of associating binary electrolytes in weak alternating fields. The important limiting case of weak stationary fields is discussed in detail. The linearized equations of continuity are solved using three-dimensional Fourier transforms.[3] The results are expressed as a single complex integral, which is readily evaluated numerically.

Fundamental Equations

Chemical Kinetic Contribution to the Equation of Continuity. In developing the theory of conduction we assume a homogeneous field of force acting upon ions in a solution at rest. Therefore, the pair distribution functions depend only on the relative locations of the pair, and we may define the following set of symmetric distribution functions[4–6]

$$f_{ji} \equiv f_{ji}(\mathbf{r}) = n_j n_{ji}(\mathbf{r}) = n_i n_{ij}(-\mathbf{r}) = f_{ij}(-\mathbf{r}) \qquad (1)$$

where n_j is the macroscopic concentration of species j, and $n_{ji}(r)$ is the time-average concentration of species i at a directed distance $\mathbf{r}$ from a particular member of species j. Since we shall only consider binary electrolytes, we let the subscripts 1, 2, and 3 denote cation, anion, and associated species,[7] respectively. We define $n = n_1 = n_2$ and $\epsilon = e_1 = -e_2$, when e_i is the net charge (esu) on species i ($e_3 = 0$).

We assume that we can describe the chemical kinetic process on the microscopic scale by a mass action rate law. Therefore, if

$$A = f^2 k_a$$

where k_a is the rate constant for association (particles^{-1} cm^3 sec^{-1}) and f^2 is the ion activity coefficient product,[8] and $K = n^2/n_3$ is the stoichiometric dissociation constant, then the chemical kinetic contribution to the equations of continuity may be written as

$$\left(\frac{\partial f_{ji}}{\partial t}\right)_{\text{kin}} = \mp n_j A n_{j1}(\mathbf{r}) n_{j2}(\mathbf{r}) \pm n_j K A n_{j3}(\mathbf{r}) - n_i A n_{i1}(-\mathbf{r}) n_{i2}(-\mathbf{r}) + n_i K A n_{i3}(-\mathbf{r}) = \mp (A/n) f_{j1} f_{j2} \pm K A f_{j3} - (A/n_i) f_{1i} f_{2i} + K A f_{3i} \qquad (2)$$

$$j = 1, 2 \qquad i = 1, 2, 3$$

where we take the upper signs for $i = 1, 2$ and the lower signs for $i = 3$. The first two terms on the right give, respectively, the recombination and dissociation rates in the atmospheres of the j species. The last two terms on the right give the rates of the respective processes in the atmospheres of the i species.

In order to linearize eq 2, we define the perturbed distribution functions,[4] $f_{ji}' = O(\epsilon^2)$, by

$$f_{ji} = f_{ji}' + f_{ji}^\circ \qquad (3)$$

where f_{ji}° is the equilibrium distribution in the absence of an external field[5,6,9]

$$f_{ji}^\circ(\mathbf{r}) = n_j n_i \left(1 - \frac{e_i e_j}{DkT} \frac{e^{-\kappa r}}{r}\right) + O(\epsilon^4) \qquad (4)$$

where, for binary electrolytes

$$\kappa = \left(\frac{8\pi\epsilon^2 n}{DkT}\right)^{1/2}$$

Substituting eq 3 into eq 2 and dropping[10] all terms $O(\epsilon^4)$, we obtain

$$\left(\frac{\partial f_{ji}}{\partial t}\right)_{\text{kin}} = An[\mp(f_{j1}' + f_{j2}') - (f_{1i}' + f_{2i}') + (K/n)(f_{3i}' \pm f_{j3}')] \qquad (5)$$

$$j = 1, 2 \qquad i = 1, 2, 3$$

where we take the upper signs for $i = 1, 2$ and the lower signs for $i = 3$. To $O(\epsilon^2)$, f_{ji}' has the well-known symmetry properties[5–7]

$$f_{ji}'(\mathbf{r}) = -f_{ji}'(-\mathbf{r}) \qquad (6a)$$

$$f_{jj}'(\mathbf{r}) = 0 \qquad (6b)$$

Equation of Continuity. The derivation of the equation of continuity valid to $O(c^{1/2})$ in the conductance function for weak fields is well known,[4–6] and we shall not repeat it here. For binary electrolytes, it may be written in terms of the f_{ji}' as[11] shown in eq 6c, where ω_j

$$\frac{\partial f_{ji}}{\partial t} = kT(\omega_i + \omega_j)\nabla^2 f_{ji}' + (e_j\omega_j - e_i\omega_i) X \frac{\partial f_{ji}^\circ}{\partial x} - \frac{4\pi\epsilon}{D}[e_i\omega_i n_i(f_{j1}' - f_{j2}') + e_j\omega_j n_j(f_{1j}' - f_{2i}')] + \left(\frac{\partial f_{ji}}{\partial t}\right)_{\text{kin}} \qquad (6c)$$

is the absolute mobility of species j, and the x axis is parallel to the applied weak alternating field, which we represent by

$$X = |X| e^{i\omega t} \qquad (7)$$

where ω is the angular frequency. For weak applied fields, the perturbations f_{ji}' will be directly proportional to the applied force field X, and we may write[12]

$$f_{ji}'(\mathbf{r}) = g_{ji}(\mathbf{r}_0) e^{i\omega t} \qquad (8)$$

where $g_{ji} \equiv g_{ji}(\mathbf{r}_0)$ is independent of time and retains the symmetry properties of f_{ji}

$$g_{ji}(\mathbf{r}_0) = -g_{ji}(-\mathbf{r}_0) = g_{ij}(-\mathbf{r}_0) \qquad (9a)$$

$$g_{jj} = 0 \qquad (9b)$$

For convenience, we have defined g_{ji} in terms of the dimensionless variable $\mathbf{r}_0(x_0, y_0, z_0)$

$$\mathbf{r}_0 = \kappa\mathbf{r} \qquad \nabla = \kappa\nabla_0 \qquad (10)$$

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(3) L. Onsager and S. K. Kim, *J. Phys. Chem.*, **61**, 198 (1957).

(4) L. Onsager, *Physik. Z.*, **28**, 277 (1927); L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958.

(6) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(7) In this paper we make no distinction between ion pairs and molecules.

(8) The activity coefficient of the associated species is usually assumed to be unity.

(9) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

(10) The terms $O(\epsilon^4)$ do not affect terms $O(c^{1/2})$ in the conductance equation; see ref 4 and 6.

(11) Equation 6 is eq (4–5–2) of ref 5 except that the chemical kinetic contribution has now been included.

(12) P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 401 (1928); for English translation see "The Collected Papers of Peter J. W. Debye," Interscience Publishers, Inc., New York, N. Y., 1954, p 395.

Substituting eq 7, 8, and 10 into eq 6c we obtain

$$\nabla_0{}^2 g_{ji} - \frac{1}{2}\, i\omega\tau\gamma_{ji} g_{ji} - \frac{1}{2}(e_i/\epsilon)\omega_{ij}(g_{j1} - g_{j2}) - \frac{1}{2}(e_j/\epsilon)\omega_{ji}(g_{1i} - g_{2i}) + \frac{1}{2}\, \gamma_{ji}\tau \mathrm{e}^{-i\omega t}\left(\frac{\partial f_{ji}}{\partial t}\right)_{\mathrm{kin}} = -a_{ji}\mathrm{e}^{-i\omega t}\, \frac{\partial f_{ji}{}^{\circ}}{\partial x_0} \quad (11)$$

where we have defined

$$\gamma_{ji} \equiv \frac{\omega_1 + \omega_2}{\omega_j + \omega_i} \qquad \omega_{ji} \equiv \frac{\omega_j}{\omega_j + \omega_i}$$

$$a_{ji} \equiv \frac{(\omega_j e_j - \omega_i e_i)X}{(\omega_j + \omega_i)\kappa kT} \quad (12)$$

and τ is the Maxwell relaxation time of the ionic atmosphere about an ion[12]

$$\tau = \frac{2}{\kappa^2 kT(\omega_1 + \omega_2)} \quad (13)$$

Substituting eq 4 and 5 into eq 11 and making use of eq 9, we obtain the independent equations

$$\left(\nabla_0{}^2 - \mu - \frac{1}{2} - \frac{1}{2}\, i\omega\tau\right)g_{12} + (K\mu/2n)(g_{13} - g_{23}) = -n^2(2\beta q)\, \frac{\partial}{\partial x_0}\left(\frac{e^{-r_0}}{r_0}\right) \quad (14a)$$

$$\left[\nabla_0{}^2 - \frac{1}{2}\omega_{j3} - \frac{1}{2}\, \gamma_{j3}(K\mu/n + \mu + i\omega\tau)\right]g_{j3} + \frac{1}{2}(\omega_{j3} - \gamma_{j3}\mu)g_{i3} + \frac{1}{2}(e_j/\epsilon)\gamma_{j3}\mu g_{12} = 0 \quad (14b)$$

$$j, i = 1, 2 \qquad i \neq j$$

where we have defined

$$\beta \equiv |X|\epsilon/2kT \qquad q \equiv \epsilon^2/2DkT \quad (15)$$

and μ is the ratio of An^2, the actual rate of association, to $A_{\mathrm{L}}n^2$, the Langevin limiting rate[13,14] for the diffusion-controlled recombination of point charges at infinite dilution

$$\mu = \frac{A}{A_{\mathrm{L}}} = A\, \frac{D}{4\pi\epsilon^2(\omega_1 + \omega_2)} = An\tau \quad (16)$$

General Solution

Complex Relaxation Field. Equations 14 have homogeneous boundary conditions at large r_0. Therefore, the Fourier transforms G_{ji} should exist

$$G_{ji}(\boldsymbol{\lambda}) = (2\pi)^{-3/2}\int g_{ji}(\mathbf{r}_0)e^{-i(\boldsymbol{\lambda}\cdot\mathbf{r}_0)}\mathbf{d}^3\mathbf{r}_0 \quad (17a)$$

where the spherical polar coordinates of $\boldsymbol{\lambda}$ are λ, θ, and φ. By the Fourier inversion theorem[15]

$$g_{ji}(\mathbf{r}_0) = (2\pi)^{-3/2}\int G_{ji}(\boldsymbol{\lambda})e^{i(\boldsymbol{\lambda}\cdot\mathbf{r}_0)}\mathbf{d}^3\boldsymbol{\lambda} \quad (17b)$$

Equations 14 transform into the linear algebraic equations

$$-\left(\lambda^2 + \mu + \frac{1}{2} + \frac{1}{2}\, i\omega\tau\right)G_{12} + (K\mu/2n)(G_{13} - G_{23}) = -n^2(2\beta q) \times (2/\pi)^{1/2} i\lambda(\lambda^2 + 1)^{-1}\cos\theta \quad (18a)$$

$$\frac{1}{2}(e_j/\epsilon)\gamma_{j3}\mu G_{12} - \left[\lambda^2 + \frac{1}{2}\, \omega_{j3} + \frac{1}{2}\, \gamma_{j3}(K\mu/n + \mu + i\omega\tau)\right]G_{j3} + \frac{1}{2}\, (\omega_{j3} - \gamma_{j3}\mu)G_{i3} = 0 \quad (18b)$$

$$j, i = 1, 2 \qquad i \neq j$$

Since $f_{12}{}^{\circ}$, the symmetric part of the ionic atmosphere, will not produce any field at the central ion, the x component of the ionic field at a j ion ΔX_j may be written as

$$\Delta X_j = -\frac{\partial}{\partial x}\, \psi_j{}'(\mathbf{r})|_{r=0} \qquad j = 1, 2, 3 \quad (19)$$

where $\psi_j{}'(\mathbf{r})$ is the (average) electrostatic potential due to the perturbed part of the ionic atmosphere $f_{ji}{}'$. Using eq 6a and 6b, we may write Poisson's equation as

$$\nabla^2\psi_j{}'(\mathbf{r}) = (4\pi\epsilon/nD)f_{12}{}'(\mathbf{r}) \qquad j = 1, 2 \quad (20)$$

Using eq 17, 19, and 20, we can write ΔX_j in terms of an inverse Fourier transform

$$\frac{\Delta X_j}{X} = \left(\frac{2}{\pi}\right)^{1/2}\frac{\epsilon}{nD\kappa|X|}\int i\lambda^{-1}(\cos\theta)G_{12}(\boldsymbol{\lambda})\mathbf{d}^3\boldsymbol{\lambda} \quad (21)$$

$$j = 1, 2$$

Solving eq 18 for G_{12} by Cramer's rule and substituting the solution into eq 21, we obtain, after trivial integrations over θ and φ.

$$\Delta X_j/X = -({}^4/_3)\kappa q\chi(\mu,\omega\tau) \qquad j = 1, 2 \quad (22)$$

where

$$\chi(\mu,\omega\tau) = -\frac{1}{\pi}\int_0^{\infty}\frac{\lambda^2 \mathrm{d}\lambda}{(\lambda^2 + 1)[d(\lambda^2)/C(\lambda^2)]} \quad (23)$$

$d(\lambda^2)$ is the determinant of the coefficient matrix of eq 18, and $C(\lambda^2)$ is the cofactor of the element in the first row and first column

$$d(\lambda^2)/C(\lambda^2) = -\left(\lambda^2 + \mu + \frac{1}{2} + \frac{1}{2}\, i\omega\tau\right) + R(\lambda^2) \quad (24a)$$

$$R(\lambda^2) = (K\mu^2/4n)[(\gamma_{13} + \gamma_{23})\lambda^2 + \gamma_{13}\gamma_{23} \times (K\mu/n + 2\mu + i\omega\tau)]/C(\lambda^2) \quad (24b)$$

$$C(\lambda^2) = b_1 b_2 - \frac{1}{4}(\omega_{13} - \gamma_{13}\mu)(\omega_{23} - \gamma_{23}\mu) \quad (24c)$$

$$b_j = \lambda^2 + \frac{1}{2}\omega_{j3} + \frac{1}{2}\gamma_{j3}(K\mu/n + \mu + i\omega\tau) \quad (24d)$$

$$j = 1, 2$$

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(13) P. Langevin, *Ann. Chim. Phys.*, 28, 433 (1903).

(14) L. Onsager, *J. Chem. Phys.*, 2, 599 (1934).

(15) R. Courant and D. Hilbert, "Methods of Mathematical Physics," Interscience Publishers, Inc., New York, N. Y., 1953, p 79.

For unassociated electrolytes $\mu = 0$, and eq 23 reduces to

$$\chi(0,\omega\tau) = \frac{1}{\pi}\int_0^\infty \frac{\lambda^2 d\lambda}{(\lambda^2 + 1)\left(\lambda^2 + \frac{1}{2} + \frac{1}{2}\, i\omega\tau\right)} = \frac{{}^1/_2}{1 + ({}^1/_2 + {}^1/_2 i\omega\tau)^{{}^1/_2}} \quad (25)$$

This is the result first obtained by Debye and Falkenhagen[12] for unassociated binary electrolytes. At the other extreme, in the limit of negligible degree of dissociation, $K/n = 0$, and we easily obtain in a similar manner

$$\chi(\mu,\omega\tau) = \frac{{}^1/_2}{1 + (\mu + {}^1/_2 + {}^1/_2 i\omega\tau)^{{}^1/_2}} \qquad K/n = 0 \quad (26)$$

For intermediate cases, eq 23 is most easily evaluated numerically, and the necessary details of the procedure used in this work are given in the Appendix.

Complex Conductivity. To $O(c^{{}^1/_2})$ the x component of the average velocity of a j ion is given by

$$v_j = \omega_j e_j X + \omega_j e_j \Delta X_j + \Delta v_j \quad (27)$$

where Δv_j is the additional velocity of the j ion due to the electrophoretic flow of the medium surrounding the ion. Since Δv_j is due entirely to the symmetric part of the ionic atmosphere,[3,4] in weak fields $\Delta v_j/X$ is independent of frequency and is given by the Debye–Hückel expression[4,9]

$$\Delta v_j/X = -(e_j\kappa/6\pi\eta_0) \quad (28)$$

where η_0 is the viscosity of the solvent.

According to Maxwell's electromagnetic theory, the total current density of j ions, J_j, is equal to the sum of the conduction and displacement currents

$$J_j = \lambda_j X + (D_j'/4\pi)(\partial X/\partial t) \quad (29a)$$

where λ_j is the ionic conductivity of species j, and D_j' is the dielectric constant of the solvent plus the contribution due to the displacement current of the j ions. Substituting eq 7 into 29a, we get

$$J_j/X = \lambda_j + (i\omega/4\pi)D_j' \quad (29b)$$

Equations 29 were derived by considering the electrolyte solution as a whole. Applying Maxwell's theory to the interionic attraction theory model of point charges in a continuum of dielectric constant D, we obtain

$$J_j = ne_j v_j + (i\omega/4\pi)D \quad (30a)$$

Substituting eq 27 into eq 30a, we get

$$J_j/X = n\epsilon^2\omega_j + n\epsilon^2\omega_j(\Delta X_j/X) + ne_j(\Delta v_j/X) + (i\omega/4\pi)D \quad (30b)$$

Equating the real and imaginary parts of eq 29b and 30b and using eq 22 and 28, we obtained for $j = 1, 2$

$$\lambda_j(\mu,\omega\tau) = n\epsilon^2[\omega_j - ({}^4/_3)\omega_j\kappa q\chi_R(\mu,\omega\tau) - \kappa/(6\pi\eta_0)] \quad (31a)$$

$$D_j'(\mu,\omega\tau) - D = -(16\pi/3\omega)n\epsilon^2\omega_j\kappa q\chi_I(\mu,\omega\tau) \quad (31b)$$

where the subscripts R and I denote real and imaginary parts, respectively. Equation 31b gives the contribution of the antisymmetric atmosphere about the j ion to the dielectric constant.

Magnitudes and Mechanisms for the Chemical Kinetic Effect

Limiting Case of Stationary Fields. The simplest and most important case of a staionary (or low frequency) field merits the most detailed discussion. Figure 1 shows the per cent decrease in the relaxation field (*i.e.*, the in-phase or real part of the ionic field) due to the chemical kinetic effect.[16] In order to explain the results, we first note using eq 4 that, in the absence of an external field, the microscopic distribution functions satisfy the macroscopic equilibrium condition[17]

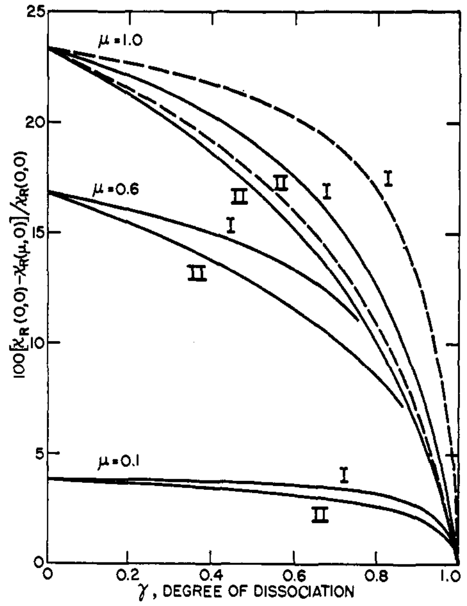

Figure 1. Per cent decrease in the relaxation field due to the chemical kinetic effect in weak stationary fields: ——, $p_3 = 1.0$; – – –, $p_3 = 10.0$; I, $\omega_1/\omega_2 = 1.0$; II, $\omega_1/\omega_2 = 10^{\pm 2}$.

$$f_{12}^\circ f_{11}^\circ / f_{13}^\circ = n^3/n_3 + O(\epsilon^4) \quad (32)$$

Thus, as expected, there is no chemical kinetic effect in the absence of an external field. In the presence of a weak applied field, the ion moves on the average parallel to the applied force, and the asymmetric perturbation f_{12}' results from the inability of the gegenion atmosphere to instantaneously re-form itself ahead of the central ion as it moves and to instantaneously destroy itself behind the ion. Therefore, ahead of the ion, $f_{12}f_{11}/f_{13} < n^3/n_3$, and there will be a stronger tendency for dissociation to occur in an attempt to reestablish chemical equilibrium. Likewise, behind the ion there will be a stronger tendency toward association. Thus, the chemical kinetic effect results in an increased ability of the ionic atmosphere to relax back toward its unperturbed equilibrium state, and hence results in a decrease in the relaxation field.

Clearly the magnitude of the effect should increase as the chemical kinetic rates increase. From Figure

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(16) See Appendix for the details of the numerical evaluation of eq 23.

(17) If the complete Boltzmann expression is used for f_{ji}°, eq 32 becomes valid to all orders of ϵ.

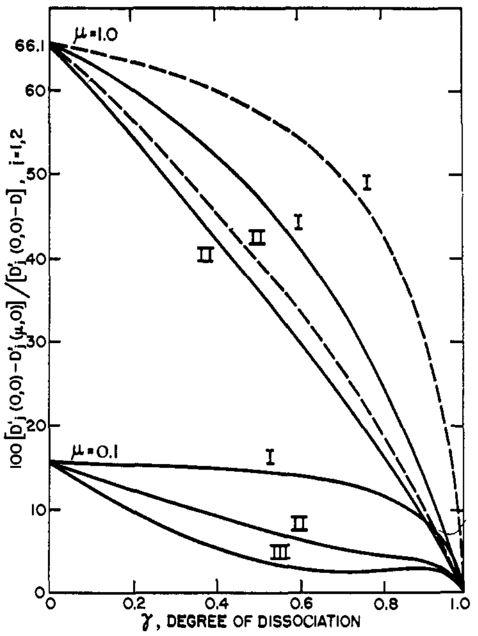

Figure 2. Per cent decrease (due to chemical kinetic effect only) in the contribution of the ionic atmosphere to the dielectric constant in weak stationary fields: ——, $p_3 = 1.0$; - - -, $p_3 = 10$; I, $\omega_1/\omega_2 = 1.0$; II, $\omega_1/\omega_2 = 10^{\pm 2}$; III, $\omega_1/\omega_2 = 10^{\pm 3}$.

1 we see that, for a diffusion-controlled recombination rate ($\mu \approx 1$), the effect can be quite large, resulting in as much as a 23% decrease of the relaxation field. The effect is very strongly dependent on μ, dropping to only a 3.8% maximum decrease of the relaxation field for $\mu = 0.1$ and to a 0.48% maximum decrease for $\mu = 0.01$.

The monotonic increase in the effect with decreasing degree of dissociation γ is also reasonable. A smaller γ simply means that there is a greater probability of finding an associated species available to dissociate in an ion-poor region. Therefore, the time lag for diffusion of the associated species into these ion-poor regions is reduced, and the relaxation process is more complete. However, the dependence of the effect on γ is weaker than the μ dependence; a considerable effect remains in an 80% dissociated system.

For convenience, we express the mobility of the associated species in terms of the quantity p_3 as

$$p_3 \equiv \omega_3\left(\frac{1}{\omega_1} + \frac{1}{\omega_2}\right) \tag{33}$$

If the two ions were spheres, and the associated species were a sphere whose radius was the sum of the two ionic radii, p_3 would be unity if all three species obeyed Stokes' law for the motion of spheres in a viscous fluid. The dependence of the chemical kinetic effect on p_3 (see Figure 1) is closely related to the γ dependence discussed above. As p_3 increases, the time lag for diffusion of the associated species into ion-poor regions (and out of ion-rich regions) decreases, and the relaxation field decreases. For the same reason, the γ dependence becomes weaker as p_3 increases.

From eq 21 it is clear that the effect is invariant to interchange of ω_1 and ω_2. The effect is maximum when $\omega_1 = \omega_2$ and slowly decreases monotonically as the two mobilities differ more from each other. In Figure 1, curves II ($\omega_1/\omega_2 = 10^{\pm 2}$) represent nearly the lower limit of this variation.

From eq 31a we see that the relative increase in the observed conductivity due to the chemical kinetic effect will be proportional to κq, *i.e.*, to ϵ^3, $n^{1/2}$, and $(DT)^{-3/2}$. For a 10^{-4} M ionic concentration of a 1:1 electrolyte in water at 25°, the effect can produce at most only a 0.05% increase in λ_j. However, under the same conditions in methanol ($D = 31.5$), in acetone ($D = 19.1$), and in 20% water-80% dioxane ($D = 10.7$), the maximum possible increases in λ_j are 0.21, 0.45, and 1.1%, respectively. Similarly, increases in n, $1/T$, and especially ϵ will produce larger effects.

The curves in Figure 2 show the per cent decrease (due to the chemical kinetic effect only) of the contribution of the ionic atmosphere to the dielectric constant.[16] Since this contribution is also due to the ionic field, the qualitative similarity of the curves in Figures 1 and 2 is not surprising, and the discussion given above of the origin and mechanism of the chemical kinetic effect on the relaxation field applies to this case as well. The main quantitative differences are the larger per cent decreases and the stronger dependence on ω_1/ω_2 in Figure 2. For $\mu = 1.0$, curve II represents nearly the lower limit of the variation of the effect with ω_1/ω_2; for $\mu = 0.1$, curve III represents nearly the lower limit.

General Case of Alternating Weak Fields. In alternating fields the average motion of the ion is oscillatory. If the frequency of the applied field is high enough so that the period of oscillation of the ion is comparable to the relaxation time of its atmosphere, the asymmetry of the charge distribution around the ion will not be fully developed; as the frequency increases, the ionic field decreases in amplitude and lags in phase. In the limit of infinite frequency, the ionic atmosphere approaches its unperturbed spherically symmetric distribution, and the ionic field disappears.

We saw in the preceeding section that the chemical kinetic effect helps the ionic atmosphere keep up with the central ion. We would therefore expect that the ionic field would decrease more slowly with increasing frequency in the case of associating electrolytes. This is clearly seen in Figures 3 and 4, where the results of the Debye-Falkenhagen theory[12] for unassociated electrolytes (curves I) may be compared with some typical results for associating electrolytes. Only curves I start at the origin because in stationary fields the ionic field is smaller for associating electrolytes (see preceding section). However, as expected, the effect of increasing frequency is greater for unassociated electrolytes; curves I increase more rapidly and even cross some of the curves for associating electrolytes.

Discussion

Our computations have revealed a small but significant effect which complicates the quantitative interpretation of conductivity in terms of ionic association. It should be recognized as a possible source of small discrepancies between the dissociation constants inferred from conductivity and those determined from thermodynamic or optical studies. In some cases we may expect the chemical kinetic effect to exceed reasonable estimates for other complicating effects such as the "viscosity correction." Of course, we must not forget that the very concept of "association" is inherently

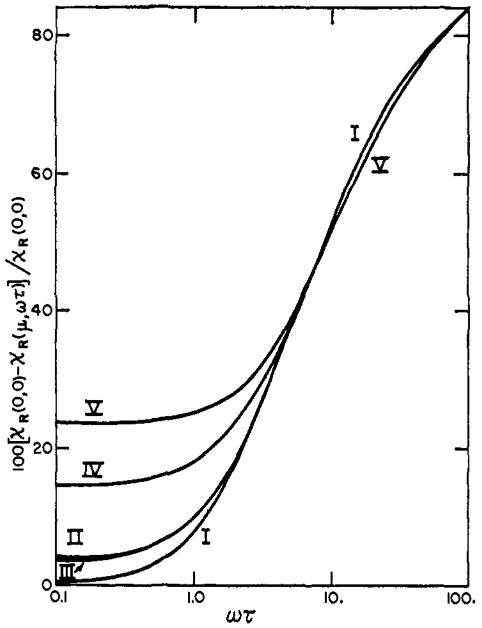

Figure 3. Per cent decrease in the relaxation field in alternating weak fields: I, $\mu = 0$ (Debye–Falkenhagen dispersion curve); II, $\mu = 0.1$, $\gamma = 0.5$, $\omega_1/\omega_2 = p_3 = 1.0$; III, same as II except that $\omega_1/\omega_2 = 10^{\pm 4}$; IV, same as II except that $\mu = 0.6$; V, $\mu = 1.0$, $\gamma = 0$.

somewhat unsharp and that the relations between the best pragmatic conventions for thermodynamic and transport properties are not yet clearly understood, although recent work by Onsager and Fuoss[18] has thrown some light on such questions. Nevertheless, it seems unlikely that the chemical kinetic effect would masquerade perfectly as a combination of other things, and we recommend that it be taken into account.

Possibly the phenomenon most sensitive to the chemical kinetic effect is the dispersion of conductivity in high-frequency fields. The total increment of the conductivity due to this dispersion equals the low-frequency relaxation effect, and we have seen that this may be quite significantly reduced by the chemical kinetics. Moreover, an inspection of Figure 3 reveals characteristic modifications of the dispersion curve. The low frequency end is flattened, and accordingly the Debye–Falkenhagen increment of the dielectric constant is more drastically reduced than is the in-phase relaxation field.

The chemical kinetic effects entail corrections of varying magnitude for all or nearly all theories of transport processes in associating electrolytes. We have ascertained that these corrections become fairly important for the detailed understanding of the Wien effect.[5,19] Appropriate computations are well advanced; in view of the greater complexity we defer these for separate publication.

Limitations of Superposition Principle. Certain consequences of our computations expose a mild inconsistency in the underlying mathematical approximations; this may help to define the problems which must be solved at the first or second stage of further refinement. As we look into these matters, we shall find among our results a tentative solution to an amusing paradox: the superposition principle requires that the atmospheric field on a neutral species equal the sum of the atmospheric fields which act on the two ions separately

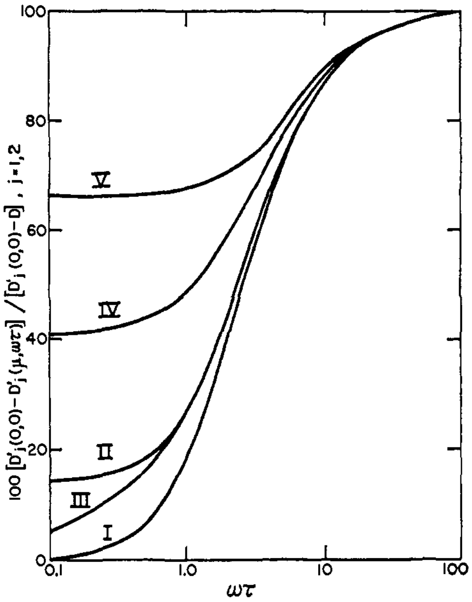

Figure 4. Per cent decrease in the contribution of the ionic atmosphere to the dielectric constant in alternating weak fields. The Roman numerals have the same meaning as in Figure 3.

$$\Delta X_3 = \Delta X_1 + \Delta X_2 = 2\Delta X_1 \qquad (34)$$

We shall see that our results imply a relaxation of that requirement. In the same way that we derived eq 21, we obtain

$$\frac{\Delta X_3}{X} = \left(\frac{2}{\pi}\right)^{1/2} \frac{\epsilon}{n_3 D\kappa|X|} \times \int i\lambda^{-1}(\cos\theta)[G_{13}(\lambda) - G_{23}(\lambda)]\mathrm{d}^3\lambda \qquad (35)$$

For simplicity we specialize to the case $\omega_1 = \omega_2$; then, by subtracting one of eq 18b from the other, we immediately obtain

$$\gamma_{13}\mu G_{12} = \left[\lambda^2 + \frac{1}{2} + \frac{1}{2}\gamma_{13}(K\mu/n + i\omega\tau)\right] \times (G_{13} - G_{23}) \qquad (36)$$

Combining eq 35 and 36, we can write

$$\frac{\Delta X_3}{X} = \left(\frac{2}{\pi}\right)^{1/2} \frac{\epsilon}{nD\kappa|X|} \int i\lambda^{-1}(\cos\theta) \times \left[\frac{K\gamma_{13}\mu/n}{\lambda^2 + \frac{1}{2} + \frac{1}{2}\gamma_{13}(K\mu/n + i\omega\tau)}\right] G_{12}(\lambda)\mathrm{d}^3\lambda \qquad (37)$$

We can get a simple physical interpretation of this result by the following considerations. The average lifetime, τ_3, of an associated species is the macroscopic concentration n_3 divided by the dissociation rate n_3KA; hence

$$\tau_3 = 1/KA \qquad (38)$$

The lifetime of the composite atmospheres about a

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(18) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **66**, 1722 (1962); **67**, 621, 628 (1963); **68**, 1 (1964); R. M. Fuoss, L. Onsager, and J. F. Skinner, *ibid.*, **69**, 2581 (1965).

(19) L. Onsager and C. T. Liu, *Z. Physik. Chem.* (Leipzig), **228**, 428 (1965); C. T. Liu, Ph.D. Thesis, Yale University, 1965.

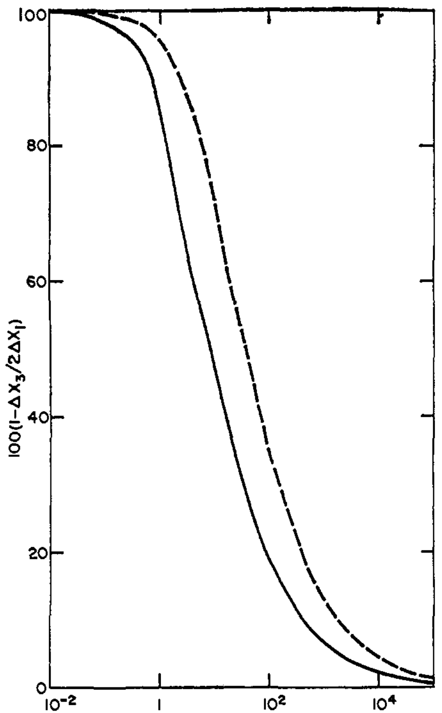

Figure 5. Per cent deviation of the ionic field at an associated species from that required by the superposition principle: ——, $p_3 = 1.0$; - - -, $p_3 = 10.0$; for both curves, $\omega\tau = 0$, $\omega_1 = \omega_2$, and $\mu = 1$.

nascent ion pair is of the order of τ, the Maxwell relaxation time of the atmospheres. Combining eq 38 and 16

$$\tau/\tau_3 = K\mu/n = \gamma\mu/(1-\gamma) \qquad (39)$$

When $\tau_3 \gg \tau$, the associated species outlives its inherited atmosphere, and $\Delta X_3 \sim 0$. This is confirmed by eq 39 and 37, since $\Delta X_3 \sim 0$ as $K\mu/n \sim 0$. In this case we have the greatest deviation from the superposition principle (eq 34). When $\tau_3 \ll \tau$, the association of the two central ions ends before the atmosphere has time to get away, and then, as described by eq 37, the deviations from the superposition principle remain small, and eq 21 and 37 become consistent with eq 34.

For intermediate cases, the right side of eq 37 is easily evaluated numerically. Figure 5 shows some typical results for the stationary field limit, $\omega\tau = 0$. Although the curves are for the case $\mu = 1$, they represent, to within the accuracy of the figure, all cases for $\mu < 1$. This emphasizes the fundamental significance of the ratio τ/τ_3. The increased deviations from the superposition principle with an increase in p_3 results from the increased ability of the associated species to diffuse out of its atmosphere. The factors γ_{13} in eq 37 show this dependence explicitly.

Of course, the ionic field acting on a neutral species produces no drift velocity and affects the current only through the related anisotropy of union and parting. It still seems quite likely that when we compute the fields which act on the ions, the errors incurred by assuming superposition will lead to terms of order higher than $c^{1/2}$, as has been demonstrated for the computation of the thermodynamic properties.[20]

Appendix

Numerical Evaluation of the Integral in Eq 23. From eq 24 we see that

$$|R(\lambda^2)| = O(\lambda^{-2}) \qquad \lambda \gg 1$$

Therefore, using Simpson's rule, we evaluate the integral in eq 23 from 0 along the λ axis until a point λ_0 is reached for which the following relations hold

$$\left|\frac{R_R(\lambda_0^2)}{\lambda_0^2 + \mu + \frac{1}{2}}\right|, \quad \left|\frac{R_I(\lambda_0^2)}{\frac{1}{2}\omega\tau}\right| < 10^{-6}$$

where the subscripts R and I denote real and imaginary parts, respectively. The rest of the integral is then evaluated by eq 40a–d. Equation 40c is used for small

$$I(\lambda_0) \equiv \frac{1}{\pi}\int_{\lambda_0}^{\infty} \frac{\lambda^2 d\lambda}{(\lambda^2+1)\left(\lambda^2 + \mu + \frac{1}{2} + \frac{1}{2}i\omega\tau\right)} \qquad (40a)$$

$$= \frac{-1}{\pi(\nu^2+1)}\left[\frac{\nu}{2}\ln\left(\frac{\lambda_0 - \nu}{\lambda_0 + \nu}\right) - \arctan\left(\frac{1}{\lambda_0}\right)\right]$$

$$\left|\frac{\nu}{\lambda_0}\right|^2 \geq 0.05 \qquad (40b)$$

$$= \frac{1}{\pi(\nu^2+1)}\left\{\frac{\nu^2}{\lambda_0}\left[1 + \frac{1}{3}\left(\frac{\nu}{\lambda_0}\right)^2 + \frac{1}{5}\left(\frac{\nu}{\lambda_0}\right)^4 + \frac{1}{7}\left(\frac{\nu}{\lambda_0}\right)^6\right] + \arctan\left(\frac{1}{\lambda_0}\right)\right\} + O(10^{-6}I)$$

$$\left|\frac{\nu}{\lambda_0}\right|^2 < 0.05 \qquad (40c)$$

$$\nu = \left(-\mu - \frac{1}{2} - \frac{1}{2}i\omega\tau\right)^{1/2} \qquad (40d)$$

$|\nu/\lambda_0|$ because computer evaluation of the log term in eq 40b becomes inaccurate due to cancellation of terms of nearly equal magnitude and opposite sign. By using an equal interval quadrature formula like Simpson's rule, it is possible to simultaneously perform a second quadrature with twice as coarse partitioning by taking only alternate points along the λ axis. The difference between the two results gives a good idea of their accuracy.

For the limiting case of stationary fields ($\omega\tau = 0$), results accurate to well within 1% may be obtained by using the above procedure with $\omega\tau = 10^{-4}$. The only exception is that one cannot take $\mu = 0.5$; for $\omega\tau \ll 1$ and this particular value of μ, computer evaluation of eq 40b or 40c becomes inaccurate due to cancellation of terms of equal magnitude and opposite sign.

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[20] L. Onsager, *J. Am. Chem. Soc.*, 86, 3421 (1964).