KERR EFFECT OF CHARGED DIPOLAR MACROMOLECULES WITHOUT CONDENSED COUNTERIONS IN CONDUCTING SOLUTION

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ABSTRACT The theoretical treatment of the Kerr constant of rigid, dipolar, conducting ellipsoidal macromolecules of O'Konski and Krause (1970. *J. Phys. Chem.* **74**:3243) has been extended to very low ionic strength solutions for charged macromolecules. The O'Konski and Krause theoretical treatment postulated a surface conductivity directly on the surface of each macromolecule. For charged macromolecules, this surface conductivity was generally assumed to be caused by movement of condensed counterions on the macromolecules. In the present work, it has been assumed that, at very low ionic strength, the average counterion is at the Debye characteristic distance from the surface of each charged macromolecule and contributes to surface conductivity at that distance, with no additional surface conductivity on the true surface of the macromolecule. Essentially, these considerations change the calculated interaction energy of the macromolecule with an externally applied electric field via a change in both the internal field components and in the reaction field of the macromolecular dipole. The new interaction energy is used to calculate the orientation distribution function of the macromolecules in solution and this distribution function can, in principle, be used to calculate the steady state electric linear or circular dichroism, electric light scattering, anisotropy of conductivity, etc., using the appropriate theoretical treatment for each of these quantities.

INTRODUCTION

When placed in an electric field, all anisometric and/or electrically anisotropic molecules or particles tend to orient in the field. The extent of orientation for a set of independent identical particles can be described by an orientation distribution function $f(\theta, \psi, \phi)$, where θ, ψ, and ϕ are Eulerian angles as described, among others, by Morse and Feshbach (1). The Eulerian angles describe the orientation of mutually perpendicular molecular axes a, b, and c with respect to the direction of the applied electric field. When the molecules are ellipsoidal, as will be assumed here, then a, b, and c are the semiaxes of the ellipsoid. The angle θ is between the a axis and the electric field; if the molecule resembles an ellipsoid of revolution, then a is the symmetry semiaxis of the molecule. The angle ϕ measures the rotation of the macromolecule around the electric field direction, and ψ measures the rotation of the macromolecule about its a axis. The orientation distribution function per molecule, $f(\theta, \psi, \phi)$, is assumed to obey a Boltzmann distribution:

$$f(\theta, \psi, \phi) = e^{-U/kT}\left(\int e^{-U/kT}\mathrm{d}\Omega\right)^{-1}, \tag{1}$$

where $\mathrm{d}\Omega = \sin\theta\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}\psi$

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The limits of θ are 0 and π, while the limits of ϕ and ψ are 0 and 2π. The value of U is the interaction energy between each independent macromolecule and the applied electric field, k is the Boltzmann constant, and T is the absolute temperature. The fraction of molecules, $\mathrm{d}N/N$, with a particular orientation at equilibrium is

$$\frac{\mathrm{d}N}{N} = f(\theta, \psi, \phi)\mathrm{d}\Omega. \tag{2}$$

Eq. 2 must be used in any further evaluation of the properties of a set of molecules in an electric field. In this paper, only ellipsoidal macromolecules whose geometric axes are also the principal axes of various tensorial properties such as dielectric constant, conductivity, and refractive index will be considered. The macromolecules, to interact with the applied electric field independently, are assumed to be in dilute solution in a low molecular weight solvent.

In addition, only a single property, namely, the birefringence, which changes as the orientation distribution function varies, will be considered. This birefringence, $\Delta n = n_{\parallel} - n_{\perp}$, where Δn is the birefringence, and $n_{\parallel}$ and $n_{\perp}$ are the refractive indices of the macromolecular solution parallel and perpendicular to the applied electric field, respectively, has been found to be equal to (2)[1]

$$\Delta n = \frac{\pi\phi_v}{n}\left\{\int_0^{2\pi}\int_0^{\pi} [(g_a - g_b)(3\cos^2\theta - 1) + (g_c - g_b)(3\cos^2\psi - 3\cos^2\psi\cos^2\Theta - 1)]\, f(\theta, \psi)\sin\theta\mathrm{d}\theta\mathrm{d}\psi\right\}, \tag{3}$$

where n is the refractive index of the solution.

ϕ_v is the volume fraction of macromolecules in the solution

$$f(\theta, \psi) = \frac{e^{-U/kT}}{\int_0^{2\pi}\int_0^{\pi} e^{-U/kT}\sin\theta\mathrm{d}\theta\mathrm{d}\psi}, \tag{4}$$

where Eq. 4 is used for the orientation distribution function instead of Eq. 1 because the angle ϕ does not appear in the expression for U for those types of molecules considered here. Also (3)

$$g_i = \frac{n_i^2 - n_\ell^2}{4\pi[1 + (n_i^2 - n_\ell^2)A_i/n_\ell^2]} \tag{5a}$$

$$A_i = \frac{abc}{2}\int_0^{\infty}\frac{\mathrm{d}s}{(s + i^2)R_s} \tag{5b}$$

$$R_s = [(s + a^2)(s + b^2)(s + c^2)]^{1/2}, \tag{5c}$$

where $i = a$, b, or c. The A_i can be determined in closed form only for ellipsoids of revolution and must be evaluated numerically in the general case. In these equations, n_i and n_ℓ are the refractive indices of the macromolecule along its i axis and of the solvent, respectively, and a, b, and c are the semiaxes of the ellipsoid. The assumption that the principal axes of the

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[1] Our Eq. 3 is found in somewhat different form in reference 2.

refractive index tensor of the ellipsoid coincide with its geometrical axes is implicit in Eqs. 3 and 5a.

Most of the time, both experimentally and theoretically, using most formulations of the interaction energy, U, it turns out that the birefringence is directly proportional to the square of the applied electric field when the applied field is small, i.e., when $U \ll kT$. Under those conditions, a specific Kerr constant, K_{sp}, may be defined for the macromolecules:

$$K_{sp} = \frac{\Delta n}{nE^2\phi_v}, \tag{6}$$

where E is the applied electric field.

In general, if one assumes that each macromolecule has a permanent dipole moment with components along the molecular axes μ_a, μ_b, and μ_c, and that, in addition, it has a non-time-dependent induced moment or polarizability, one finds a relationship of the sort (2–4):

$$\begin{aligned} K_{sp} = (\pi/15\, n^2)[(g_a - g_b)(P_a - P_b + Q_{ab}) \\ + (g_b - g_c)(P_b - P_c + Q_{bc}) + (g_c - g_a)(P_c - P_a + Q_{ca})], \end{aligned} \tag{7}$$

where the P_i are permanent dipole terms and the Q_{ij} are induced dipole terms that depend on the assumptions used to determine the interaction energy, U.

When one considers nonconducting but electrically anisotropic ellipsoids with permanent dipole moments immersed in a nonconducting isotropic solvent with dielectric constant ϵ_ℓ, one may obtain, by combining the ideas of Peterlin and Stuart (3), O'Konski et al. (5), and Holcomb and Tinoco (2):

$$P_i = B_i^2(\epsilon)\mu_i^2/k^2T^2 \tag{8}$$

$$Q_{ij} = \frac{V\epsilon_o}{kT}[B_i(\epsilon)(\epsilon_i - \epsilon_\ell) - B_j(\epsilon)(\epsilon_j - \epsilon_\ell)], \tag{9}$$

where ϵ_o = the permittivity of vacuum, V = the volume of the ellipsoid

$$B_i(\epsilon) = \left[1 + \left(\frac{\epsilon_i}{\epsilon_\ell} - 1\right)A_i\right]^{-1}, \tag{10}$$

and the A_i are defined by Eq. 5b. Eq. 8 and other equations are written to conform with SI units; in previous publications c.g.s.-e.s.u. were used, giving a number of the equations a somewhat different appearance.

Since these equations for insulating systems predicted a specific Kerr constant two orders of magnitude below the experimental value for a strain of tobacco mosaic virus (TMV) that appeared to have no permanent dipole moment (6), and since these equations could not explain the observed variations of K_{sp} with pH (molecular charge) and with ionic strength (6), O'Konski and Krause (4) devised a theoretical treatment suitable for conducting ellipsoids in conducting solutions. Specifically, they derived equations for the interaction energy of a dipolar ellipsoid with an anisotropic dielectric constant and an anisotropic volume conductivity in an isotropic dielectric and conducting solvent. Most macromolecules have no true volume conductivity, but O'Konski (7) had shown earlier that a surface conductivity, which must exist around any macromolecule in conducting solution, is theoretically equivalent to an anisotropic volume conductivity in the macromolecule. These considerations led to the following equations for P_i and Q_{ij}:

$$P_i = B_i^2(\kappa)\mu_i^2/k^2T^2 \tag{11}$$

$$Q_{ij} = \frac{V\epsilon_\ell\epsilon_o}{kT}\left[\left(\frac{\kappa_i}{\kappa_\ell} - \frac{\epsilon_i}{\epsilon_\ell}\right)B_i^2(\kappa) - \left(\frac{\kappa_j}{\kappa_\ell} - \frac{\epsilon_j}{\epsilon_\ell}\right)B_j^2(\kappa) + \left(\frac{\kappa_i}{\kappa_\ell} - 1\right)B_i(\kappa) - \left(\frac{\kappa_j}{\kappa_\ell} - 1\right)B_j(\kappa)\right], \tag{12}$$

where κ_ℓ = the conductivity of the solvent and, κ_i = principal value of the effective conductivity of the ellipsoid along its i axis.

The value of $B_i(\kappa)$ is defined in the same way as $B_i(\epsilon)$ in Eq. 9, except that κ is substituted for ϵ in every place where it appears. According to O'Konski (7)

$$\kappa_i = \kappa_i^0 + \kappa_i', \tag{13}$$

where κ_i^0 = true volume conductivity along the i axis, κ_i' = volume conductivity along the i axis equivalent to the surface conductivity of the ellipsoid.

The relationship between κ_i' and the surface conductivity, λ, is given by O'Konski (7) for ellipsoids, rods, and disks.

For a highly charged macromolecule, one may assume as a first approximation that the surface conductivity λ arises mainly from the movement of mobile counterions on the surface of the macromolecule. This assumption should be reasonable under two conditions: (*a*) at ionic strengths at which the Debye radius is small, i.e., at ionic strengths so large that the average counterion is close to the surface of the macromolecule, and (*b*) if the charge density is so large that at least some of the counterions are condensed onto the macromolecular surface even at low ionic strength (8, 9).

Assuming the presence of mobile counterions directly on the surface of the macromolecules (4),

$$\lambda = n_c uZe/S, \tag{14}$$

where n_c = number of mobile ions on the surface of the macromolecule, generally assumed equal to the charge on the macromolecule divided by Z as a first approximation, Z = charge of each mobile ion on the surface, e = electron charge, u = mobility of mobile ions on surface, generally assumed to equal the mobility in the bulk of the solution as a first approximation, and, S = surface area of the ellipsoidal macromolecule.

VERY LOW IONIC STRENGTH TREATMENT

One cannot assume the presence of a layer of counterions on the surface of a macromolecule with low surface charge density in solutions of very low ionic strength. In such a case, the counterions are distributed throughout the solution, more or less in accord with Debye-Hückel theory, at least when the concentration of macromolecules is low.

In this work, an attempt is made to calculate a first approximation to the interaction energy, U, between macromolecule and applied electric field for such cases, assuming that the average counterion moves around the macromolecule at a distance from the surface equal to the Debye radius in the solution. All the surface conductivity, λ, in this model, exists at a distance equal to the Debye length, d, away from the macromolecule.

$$d = \left[\frac{\epsilon_o \epsilon_\ell kT}{2N_o e^2 I}\right]^{1/2}, \tag{15}$$

where N_o = Avogadro's number, and $I = \Sigma(1/2) Z_i^2 m_i$, the ionic strength of the solution, and m_i = molality of the ion with charge Z_i.

This model is mathematically tractable, while the more realistic model in which the whole extent of the counterion atmosphere is considered is not tractable by the methods of electrostatic theory used in this paper. The present model will probably be at its most unrealistic at the lowest possible ionic strengths where, in addition, the counterion atmospheres from different macromolecules overlap even at low concentrations of macromolecules. Therefore, the present model will probably fail at the lowest possible ionic strengths. There is another reason why the present model must fail at the lowest possible ionic strengths, namely, this model does not transform smoothly into the Peterlin-Stuart electrostatic model (discussed above) as the ionic strength goes to zero. It would be interesting, in the future, to fill this gap in the theory.

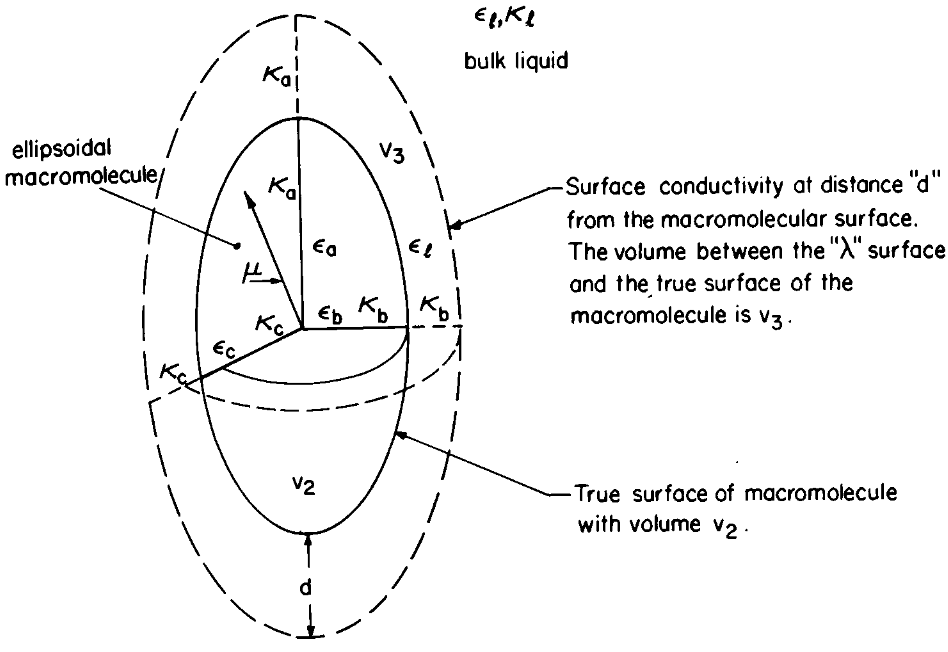
Since we are discussing charged macromolecules in this work, it is obvious that electrophoresis of these molecules is taking place at the same time as rotation and one must worry about coupling between the two types of motion. Hydrodynamic coupling has not worried previous workers in this subject because Perrin (10) concluded over forty years ago that translation will affect rotational diffusion only when there are fairly large concentration gradients in the solution. Benoit (11) later stated that such concentration gradients do not exist in the solutions subjected to electric fields in electro-optic experiments except perhaps very close to the electrodes where no experimental measurements are made. It should be noted, however, that Perrin's conclusions (10) were based on calculations involving field-free translational diffusion; Perrin (10) also noted that a centrifugal or gravitational field could affect the rotational distribution function. In the same way, relatively rapid electrophoresis would probably affect the rotational distribution function of the macromolecules. In the low field region in which the Kerr law (Eq. 6) holds, electrophoresis is slow and is not expected to affect rotational diffusion to a noticeable extent. There is one calculation in the literature (12) that indicates the relative magnitudes of electrophoretic and rotational motions for the muscle protein paramyosin at low field; this calculation shows that electrophoresis is relatively slow with respect to rotation for this very asymmetric macromolecule (>1,000 Å long and 20 Å in diameter). In high electric fields, the effect of electrophoresis on the rotational distribution function has yet to be calculated. Such calculations have not been done in this paper; the macromolecules discussed in the present paper are not very highly charged and are, therefore, not expected to have even as large an electrophoretic velocity as paramyosin at pH 3.2.

Shilov and co-workers (13, 14) have performed some calculations which indicate that ion atmosphere polarization should not be neglected when considering the energy of interaction of rod-shaped particles having a low charge density with an electric field. Since some of their assumptions do not coincide with ours, it is not possible for us to use their results quantitatively. In the future, if possible, we plan to incorporate the polarization of the diffuse ion atmosphere into the present theoretical treatment.

Using the usual ellipsoidal model for the macromolecule, it is thus assumed that the counterions, on the average, move on an ellipsoidal surface whose semiaxes are $a' = a + d$, $b' = b + d$, and $c' = c + d$. The volume of the ellipsoid whose semiaxes are a, b, c is designated v_2 and the volume of the ellipsoid whose semiaxes are a', b', c' is designated as $v_2 + v_3$. Therefore, the volume of solution between the actual physical ellipsoid and the ellipsoidal surface at the Debye radius (to be designated the "λ" surface) is v_3. Values of bulk conductivities equivalent to the surface conductivity λ inside the "λ" surface are now calculated using a', b', and c' instead of a, b, and c for the semiaxes of the ellipsoid.

As shown in Fig. 1, the region within and near an ellipsoidal macromolecule is now divided into three parts: one is the bulk liquid with isotropic dielectric constant ϵ_ℓ and isotropic conductivity κ_ℓ; the second is the volume, v_3, between the "λ" surface and the true surface of the macromolecule, with isotropic dielectric constant ϵ_ℓ and equivalent bulk conductivities along the major axes $\kappa_a, \kappa_b, \kappa_c$; and the third is the volume within the macromolecule, v_2, with anisotropic dielectric constants $\epsilon_a, \epsilon_b, \epsilon_c$, and equivalent bulk conductivities $\kappa_a, \kappa_b, \kappa_c$ along the molecular axes. The mathematical constraints of the problem with the surface conductivity, λ, situated out in the solution surrounding the macromolecule, result in the same equivalent bulk conductivities κ_a, κ_b, and κ_c everywhere within the "λ" surface, both within volume v_2 and within volume v_3. The molecule in Fig. 1 is shown with a dipole moment, μ, in an arbitrary direction with respect to the molecular axes.

As discussed previously by O'Konski and Krause (4), the dipole moment, μ, is assumed to be the permanent dipole moment of the solvated macromolecule in the particular solvent system. It includes contributions from charge anisotropy within the macromolecule as well as any other contributions which may be assumed to be field-independent. The interaction



Surface conductivity at distance "d" from the macromolecular surface. The volume between the "λ" surface and the true surface of the macromolecule is V_3.

True surface of macromolecule with volume V_2.

FIGURE 1 The ellipsoidal macromolecule and its surroundings in the very low ionic strength theoretical treatment.

energy of the dipole moment with the applied electric field is

$$U_1 = -\mu \cdot E = -\mu_a E_a - \mu_b E_b - \mu_c E_c, \tag{16}$$

where μ_a, μ_b, μ_c are the components of the dipole moment along the molecular axes and E_a, E_b, E_c are the components of the applied electric field in the same directions, as modified by the reaction field of the dipole:

$$E_a = B_a(\kappa) E \cos\theta \tag{17a}$$

$$E_b = -B_b(\kappa) E \sin\theta \cos\psi \tag{17b}$$

$$E_c = B_c(\kappa) E \sin\theta \sin\psi. \tag{17c}$$

These equations are formally identical to those given previously (4), except that now the $B_i(\kappa)$ are calculated using conductivities within the "λ" surfaces, as discussed above.

As before (4), the polarization energy of the ellipsoidal macromolecule in the applied electric field is calculated from the integral

$$U_2 = (1/2) \int D \cdot E \, dv \tag{18}$$

over all space. If a homogeneous field E exists everywhere at large distances from the macromolecule, then insertion of a single macromolecule with a known orientation in space causes the energy change

$$U_2 = \frac{\epsilon_o}{2} \int (\epsilon_a E_a^2 + \epsilon_b E_b^2 + \epsilon_c E_c^2 - \epsilon_\ell E^2) dv_2 + \frac{\epsilon_o \epsilon_\ell}{2} \int (E_a^2 + E_b^2 + E_c^2 - E^2) \, dv_3 + \frac{\epsilon_o \epsilon_\ell}{2} \int (E_1^2 - E^2) \, dv_1, \tag{19}$$

where the first integral, I_2, is taken over the actual volume of the ellipsoidal macromolecule, the second integral, I_3, is taken over the volume between the macromolecule and the "λ" surface (see Fig. 1), and the third integral, I_1, is taken over all space outside the "λ" surface. E is the magnitude of the applied electric field in the absence of the ellipsoid, E_1 is the magnitude of the field outside the "λ" surface with the ellipsoid in place, and E_a, E_b, and E_c are internal field components which are defined by Eqs. 17a, b, and c.

Integrals I_2 and I_3 can be evaluated by direct integration, while integral I_1 can be evaluated by the same indirect method used previously (4). The result is:

$$\begin{aligned} U_2 = -(\epsilon_o \epsilon_\ell E^2/2) \Bigg(\cos^2\theta & \left\{ \left[\frac{\kappa_a}{\kappa_\ell}(v_2 + v_3) - \frac{\epsilon_a}{\epsilon_\ell} v_2 - v_3 \right] B_a^2(\kappa) + (v_2 + v_3) \left(\frac{\kappa_a - \kappa_\ell}{\kappa_\ell} \right) B_a(\kappa) \right\} \\ + \sin^2\theta \cos^2\psi & \left\{ \left[\frac{\kappa_b}{\kappa_\ell}(v_2 + v_3) - \frac{\epsilon_b}{\epsilon_\ell} v_2 - v_3 \right] B_b^2(\kappa) + (v_2 + v_3) \left(\frac{\kappa_b - \kappa_\ell}{\kappa_\ell} \right) B_b(\kappa) \right\} \\ + \sin^2\theta \sin^2\psi & \left\{ \left[\frac{\kappa_c}{\kappa_\ell}(v_2 + v_3) - \frac{\epsilon_c}{\epsilon_\ell} v_2 - v_3 \right] B_c^2(\kappa) + (v_2 + v_3) \left(\frac{\kappa_c - \kappa_\ell}{\kappa_\ell} \right) B_c(\kappa) \right\} \Bigg) \end{aligned} \tag{20}$$

The total electric energy change on inserting the macromolecule is now

$$U = U_1 + U_2, \tag{21}$$

which can be used in Eq. 1 to find the orientation distribution function for the system assuming only that the solution is so dilute that the orientation of each macromolecule with respect to the applied electric field is uncorrelated with that of neighboring macromolecules.

The birefringence of the solution is calculated according to Eq. 3, and, at small fields, the specific Kerr constant still looks like Eq. 7. The only change in the P_i (Eq. 11) that occurs in this approximation is in the calculation of $B_i(\kappa)$ for which a', b', and c' must be used in place of a, b, and c, both in the calculation of λ and κ_i and in the calculation of $B_i(\kappa)$ itself. In the calculation of Q_{ij}, the same change is made in $B_i(\kappa)$ and

$$\begin{aligned} Q_{ij} = \frac{\epsilon_o \epsilon_\ell}{kT} \Bigg\{ & \left[\frac{\kappa_i}{\kappa_\ell}(v_2 + v_3) - \frac{\epsilon_i}{\epsilon_\ell} v_2 - v_3 \right] B_i^2(\kappa) + (v_2 + v_3) \left[\frac{\kappa_i - \kappa_\ell}{\kappa_\ell} \right] B_i(\kappa) \\ & - \left[\frac{\kappa_j}{\kappa_\ell}(v_2 + v_3) - \frac{\epsilon_j}{\epsilon_\ell} v_2 - v_3 \right] B_j^2(\kappa) + (v_2 + v_3) \left[\frac{\kappa_j - \kappa_\ell}{\kappa_\ell} \right] B_j(\kappa) \Bigg\} \end{aligned} \quad (22)$$

ELLIPSOIDS OF REVOLUTION

Many macromolecules can be approximated by ellipsoids of revolution, and, for predictive purposes, equations are much simplified in such cases. For example, Eq. 7 becomes

$$K_{sp} = \frac{2\pi}{15n^2}(g_a - g_b)(P_a - P_b + Q_{ab}), \quad (23)$$

where a is the symmetry axis of the molecule and the molecular dipole moment, if present and not oriented in the direction of the molecular symmetry axis, is situated so that it has equal components along the b and c axes. In addition, there must be no anisotropy of the molecular tensor properties in directions perpendicular to the symmetry axis for Eq. 23 to hold.

If, in addition, the molecular dipole can be assumed to lie along the symmetry axis, then the strong field birefringence equations of O'Konski et al. (5) will hold using

$$\beta = P_a^{1/2} E \quad (24a)$$

and

$$\gamma = Q_{ab} E^2 / 2kT \quad (24b)$$

in their equations.

DISCUSSION

Applicability

Eqs. 19–24 should be applicable to macromolecules and colloids that are roughly ellipsoidal in conducting solution. The macromolecules or colloids must be charged, and should have no counterions condensed on their surfaces. Eqs. 11 and 12, on the other hand, should be applicable when an appreciable number of counterions is condensed on the macromolecular surface. It is not easy to decide which set of equations is most reasonable for a highly charged macromolecule with only a small number of condensed counterions; in this case, the macromolecule still carries a rather large net charge, but, in addition, a large number of counterions are situated in the ion atmosphere. In fact, both sets of counterions should be considered in this case, but this is not possible with the existing theoretical treatments.

The case of the uncharged macromolecule in conducting solution has also not been adequately described by existing theoretical treatments. It may be possible to describe the surface conductivity of isoelectric polyampholytes by means of the movement of protons, such as carboxyl protons, along the surface of the macromolecule (15). On the other hand, it may be necessary to consider the effects of charge fluctuations at the isoelectric point in the following manner: molecules with different net changes will have different numbers and kinds of counterions in the ion atmosphere, and, thus, an average surface conductivity on the "λ" surface will have to be calculated using the calculated distribution of differently charged macromolecules.

Other influences on the interaction energy between macromolecule and electric field have also been neglected in this theoretical treatment. As mentioned earlier, ion atmosphere polarization is one of these influences. Frequency-dependent effects, which are not considered in this paper, may legitimately be neglected in a steady-state theory. One of these frequency-dependent effects, for example, may involve slow motions of counterions in and out of the counterion atmosphere around the macromolecule. Other small ion diffusion processes, both inside and outside the double layer around the macromolecule, will eventually have to be considered; we hope to incorporate some of these ideas, possibly as summarized by Dukhin and Shilov (16) and by Dukhin (17), into this theoretical treatment in the future.

Ionic Strength and Conductivity

Since the value of the ionic strength of the solution is needed for calculation of the Debye radius which is necessary for the evaluation of a', b', κ_a, κ_b, κ_c, v_3, $B_a(\kappa)$ and $B_b(\kappa)$, and $B_c(\kappa)$, and since the bulk conductivity of the same solution is needed in the evaluation of $B_a(\kappa)$, $B_b(\kappa)$, $B_c(\kappa)$, and the Q_{ij}, both quantities must be known for any solution of interest. Ionic strength

TABLE I

EXPERIMENTAL COMPARISON OF IONIC STRENGTH WITH CONDUCTIVITY

In absence of macromolecules (handbook values)				In Presence of Macromolecules					
Electrolyte	I	κ_t	$(\kappa_t/I) \times 10^3$	Macromolecule	pH	Electrolyte	$I \times 10^4$	$\kappa_t \times 10^3$	$(\kappa_t/I) \times 10^3$
	(mol dm^{-3})	*($\Omega^{-1}m^{-1}$)*	*($m^2\Omega^{-1}mol^{-1}$)*				*(mol dm^{-3})*	*($\Omega^{-1}m^{-1}$)*	*($m^2\Omega^{-1}mol^{-1}$)*
$KHC_8H_4O_4$	0.024	0.20	8.3	TMV*	7.0	Phosphate	3.3	1.92	5.8
KH_2PO_4	0.036	0.30	8.3	TMV*	7.0	Phosphate	3.3	2.68	8.2
K_2HPO_4	0.063	0.52	8.3	TMV*	7.0	Phosphate + KCl	4.9	4.62	9.4
NaCl	0.017	0.17	10.3	TMV*	7.0	Phosphate + KCl	8.5	10.2	12.0
NaCl	0.085	0.82	9.6	TMV*	5.6	Phthalate	12.8	7.17	5.6
$Na_3C_6H_5O_7$	0.102	0.74	7.2	BSA‡	5.2	KCl	5.0	18.0	36.0
Citric acid	0.023	0.12	5.2	BSA‡	5.3	KCl	25.0	52.6	21.0
HCl	0.012	4.51	34.0	BSA‡	5.0	$ZnCl_2$	75.0	62.6	8.3
				BSA‡	5.1	$ZnCl_2$	7.5	7.55	10.3
				Paramyosin§	3.2	Citrate	3.6	30.0	83

*Tobacco Mosaic Virus (see reference 6).

‡Bovine Serum Albumin (see reference 18).

§See reference 19.

can be calculated from the composition of the solution, but the conductivity must be measured. Table I gives a comparison of conductivity and ionic strength for various solutions, both in the absence and in the presence of macromolecules. In Table I, ionic strength has been calculated in terms of molarity, i.e., mol dm^{-3}, instead of molality as expected from the definition of ionic strength given just below Eq. 15.

It can be seen from Table I that the experimental ratio of κ_ℓ to I varies within the same limits both in the absence and in the presence of macromolecules. The higher values of this ratio are generally found in the solutions in which appreciable conductivity is due to hydrated protons. In solutions in which other charge carriers predominate, an average value of $\kappa_\ell/I = 8 \times 10^{-3}\ m^2\Omega^{-1}\ mol^{-1}$ seems reasonable for predictive calculations. Because κ_ℓ/I is not really a constant, and because it is κ_ℓ and not I that appears as one of the major independent variables in this theoretical treatment, the predictions made below and the abscissas in Figs. 2 and 3 are in terms of κ_ℓ and not I. The highest values of κ_ℓ in Figs. 2 and 3 usually refer to solutions with ionic strengths of the order of 1 mol dm^{-3}.

Theoretical Predictions

Fig. 2 shows some theoretical predictions of specific Kerr constant of a fictitious protein in aqueous solution. This protein is represented by a prolate ellipsoid of revolution with the dimensions shown in the figure, with $g_a - g_b = 0.006$, $\epsilon_a = \epsilon_b = 2.5$, $\epsilon_\ell = 78.5$, and with monovalent counterions whose number equals the charge given for each calculated curve and whose mobility equals that of K^+. For these calculations, $\kappa_\ell/I = 8 \times 10^{-3}\ m^2\Omega^{-1}\ mol^{-1}$ was used.

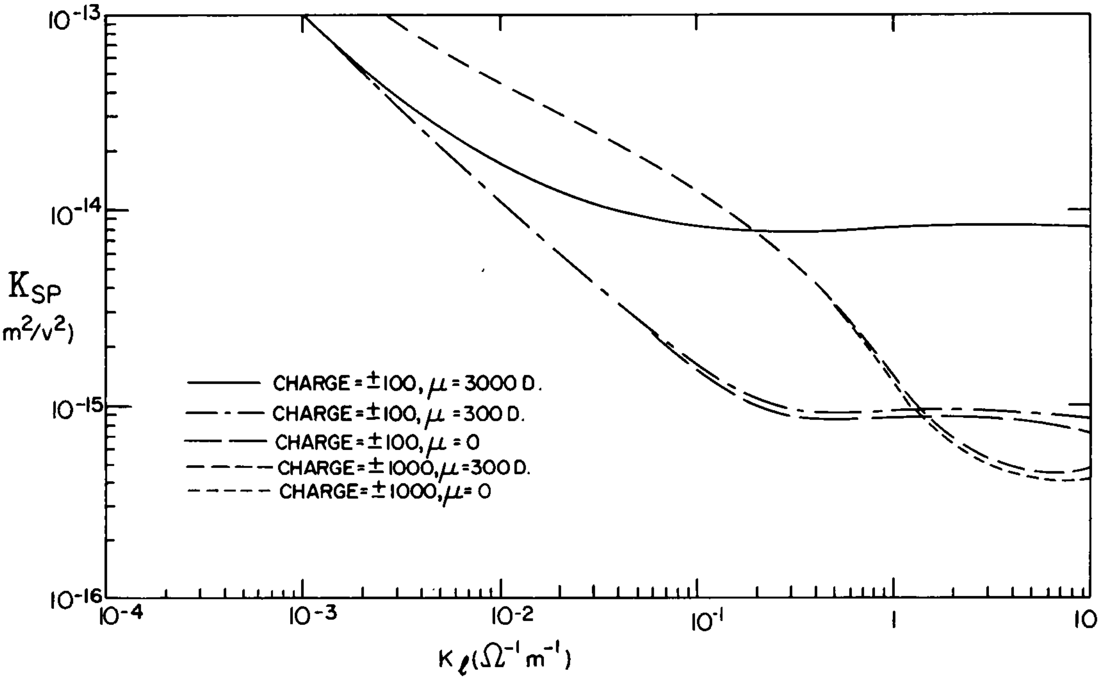


FIGURE 2 Ellipsoid of revolution, this work. Specific Kerr constant vs. solution conductivity calculated using the present theoretical treatment for a hypothetical prolate ellipsoid. $a = 300$ Å; $b = 50$ Å.

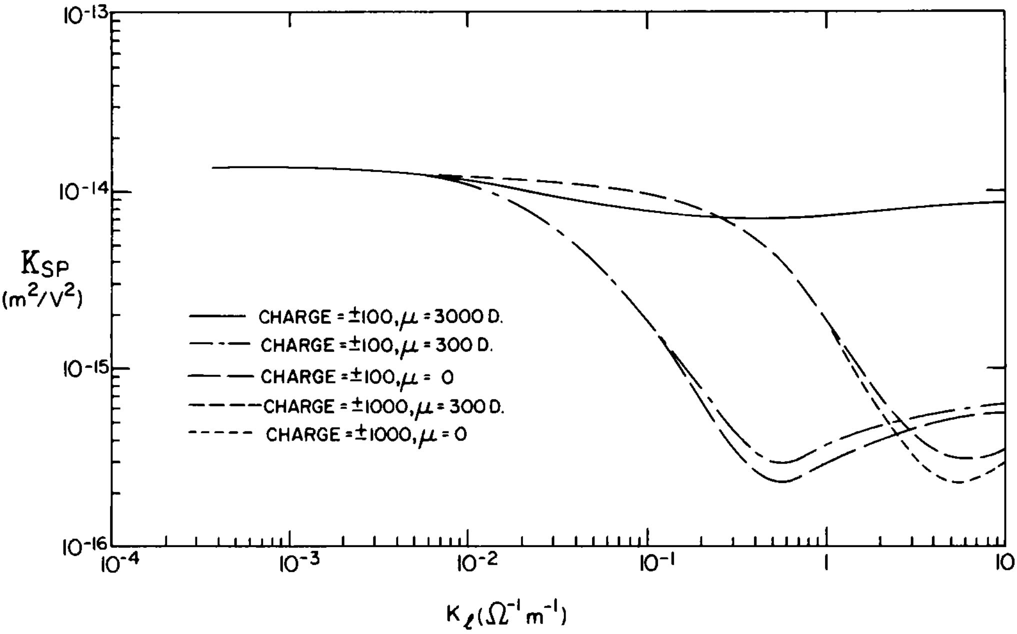


FIGURE 3 Ellipsoid of revolution, O'Konski-Krause theory. Specific Kerr constant vs. solution conductivity calculated using the O'Konski-Krause (4) theoretical treatment for the same hypothetical prolate ellipsoid used for the calculations in Fig. 2. a = 300 Å; b = 50 Å.

Fig. 2 exhibits the general features of this theoretical treatment for all prolate ellipsoids. At very low solvent conductivity, the K_{sp} is high, but it drops rapidly as the conductivity, κ_ℓ, increases until it reaches a minimum, after which it rises again. The lower the charge on the macromolecule, the lower the value of κ_ℓ at which the minimum in K_{sp} is expected to occur. The higher the dipole moment of the macromolecule, the higher the value of K_{sp} at which the minimum is expected. Let us note, however, that a charge of ± 1,000 on a molecule of this size, which has an average surface area of 150 Å^2/charge, is probably high enough to result in a large number of condensed counterions (9); in that case, the O'Konski-Krause (4) theoretical treatment should be used.

Fig. 3 shows the results of calculations of K_{sp} for the same hypothetical molecule shown in Fig. 2 using the O'Konski-Krause theoretical treatment. In this treatment, as shown in Fig. 3, the macromolecule is expected to have a constant value of K_{sp} at low ionic strength (low values of κ_ℓ), independent of charge, dipole moment, or solvent conductivity. This is the major difference in the prediction of K_{sp} vs. κ_ℓ in the two theoretical treatments represented by the calculations in Figs. 2 and 3. This difference arises from the fact that the $B_i(\kappa)$ in Eq. 22 are evaluated for a much larger volume (that within the "λ" surface instead of the volume of the actual ellipsoidal molecule) than are those in Eq. 12. It is expected that the molecule with charge ±1,000 would be more likely to follow the prediction shown in Fig. 3, while the macromolecule with charge ±100 would be more likely to follow the predictions shown in Fig. 2.

One interesting difference between the predictions of K_{sp} from the two theoretical treatments not visible in Figs. 2 and 3 concerns macromolecules with small charges, very large dipole moments, and shapes that are not overly anisometric (a prolate ellipsoid with axial ratio 1.5, for example). In such cases, the O'Konski-Krause equations predict a drop of K_{sp} at very small values of κ_ℓ, while the present theoretical treatment predicts a rise of K_{sp} at very low κ_ℓ.

Let us note that the range of κ_ℓ reported in the electric birefringence literature up to this time is $\sim 10^{-3}$–$1\ \Omega^{-1}\ \mathrm{m}^{-1}$. The predictions discussed here and shown in Figs. 2 and 3 have been extended an order of magnitude on each side of this range.

Attempts at correlating theoretical predictions with data on real macromolecules are difficult and will be discussed in some detail in a later publication. At this point, we may note that literature data generally indicate a decrease in specific Kerr constant with increasing ionic strength for both charged (6, 20) and uncharged (21) macromolecules. The minimum in K_{sp} predicted in Figs. 2 and 3 has not yet been observed. It would be of great interest if a macromolecule could be found for which this minimum could be observed.

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