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Rotational Diffusion in Electrolyte Solutions

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Abstract: Rotational diffusion of the dye molecule resorufin in both aqueous and DMSO solutions of $LiNO_3$ is used to assess the importance of ion atmosphere friction and ion pairing on the solute/solvent frictional coupling. Rotational diffusion times for resorufin in aqueous $LiNO_3$ follow the solution viscosity and dielectric parameters as $LiNO_3$ concentration increases, while rotation times for resorufin in DMSO solutions of $LiNO_3$ show a much larger increase than can be accounted for by either of these factors. Evidence for ion pairing is presented, and its effect on the hydrodynamic component of the friction is evaluated. The experimental rotational diffusion times are compared with diffusion times calculated by incorporating terms for hydrodynamic, dielectric, and ion atmosphere friction. The term resulting from the ion pairing is the largest, and its inclusion is able to reproduce the experimentally measured relaxation times to within 15%.

Introduction

The influence of solute/solvent interactions on reaction rates has been the subject of much study.[1-4] This area of investigation is very complex, however. For example, the potential energy surface controlling the reaction may be strongly affected by the choice of solvent, both dynamically and statically. Changes in other physical properties, such as molecular size, shape, orientation, and position of the species involved in a reaction, will also affect the dynamics and be influenced by solvent. Isolating the role of the solvent from the role of the intramolecular potential is a complicated task and not always possible. One simplifying approach is to limit the number of processes which occur during the investigation. Rotational diffusion studies provide a method for examining the interaction of a species with its solvent without the complicating factors introduced by a reaction.

The suitability of a rotational diffusion model for describing the relaxation of medium-sized molecules (a few hundred cubic angstroms) is well established. The relationship between the friction ζ and the rotational diffusion time τ_{or} is also well-known[2,5] and for a spherical solute is given by

$$\tau_{or} = \frac{\zeta}{6kT} \qquad (1)$$

where T is the temperature and k is Boltzmann's constant. For nonspherical solutes the relationship is similar but more complicated.[2,6,7] Early rotational diffusion studies focused on the validity of a hydrodynamic model of the friction,[7-10] while more recent work has explored the effects of the electrostatic nature of the solute and the dielectric properties of the solvent on this friction.[11-16] Studies have been performed in a wide range of solvents as well as solvent mixtures;[2,11-16] however, many important molecular aspects relating to the friction remain unclear.

The magnitude of the friction on a rotating solute molecule ultimately has its origins in the intermolecular potential. While not rigorous, it is helpful to regard the friction as comprised of a mechanical, or hydrodynamic, component ζ_{hyd} and a dielectric friction component ζ_{diel}. The mechanical contribution to the friction depends on the shape and volume of the solute molecule and has its origins in the repulsive part of the intermolecular potential. The dielectric contribution to the friction arises from the electrostatic coupling between the solute's charge distribution and the induced polarization in the solvent and has its origins in the attractive part of the intermolecular potential. The total friction is expressed as a sum of the hydrodynamic and dielectric components,

$$\zeta = \zeta_{hyd} + \zeta_{diel} \qquad (2)$$

Recent work from this laboratory[17-21] has focused on the dielectric component of friction. In these studies, mechanically similar but electrostatically different molecules have been studied in a variety of solvents. Point source models of dielectric friction have been found to underestimate the friction by up to 100 times, whereas an extended charge distribution model for the solute molecule works quite well. These studies have been performed in a number of pure polar and nonpolar solvents and some solvent mixtures as well. The studies reported here extend this previous work to electrolyte solutions.

Recent studies of the solvation dynamics of dye molecules in electrolyte solutions are relevant to the studies reported here. Huppert and co-workers[22] have measured the solvation times of

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probe molecules over a wide range in electrolyte concentration (0.01–2.0 M) and have observed a strong inverse dependence on electrolyte concentration. Experiments have been conducted in a variety of solvents, and at equimolar electrolyte concentrations the rates appear to correlate with the solution viscosity. Chapman and Maroncelli[23] have also reported studies of solvation dynamics in electrolyte solutions. Their results are interpreted in terms of an ion-paired species formed with the solute and the electrolyte cation. The unusually long relaxation times (nanosecond time scale) which they observe are taken to arise from the formation and dissociation of the ion pair. These conclusions are in general agreement with the conclusions of this study on the rotational diffusion of resorufin in $LiNO_3$ solutions.

A few rotational diffusion studies of solute ions have been performed in electrolyte solutions. An early report by Spears and co-workers[24] showed an increase of 50% in the rotational relaxation time for resorufin in DMSO when Mg^{2+} counterion was added to the solution. G. Kenney-Wallace and co-workers studied the anion resorufin in aqueous solutions of LiCl[15] and found that reduced rotational diffusion times (τ/η) changed very little with electrolyte concentration. This study included similar measurements in methanol, where the reduced rotation times were reported to decrease with increasing electrolyte concentration, at high concentrations. Competition between the probe and the Li^+ ion for the solvating molecules was proposed to explain the data. L. Phillips[13] made similar measurements of Rhodamine 6G (cation) and *p*-terphenyl (neutral) in ethanolic LiCl over a similar concentration range and observed a comparable decrease in τ/η. The experiments described in this paper examine the friction on resorufin reorienting in aqueous and DMSO solutions of the electrolyte $LiNO_3$ over a concentration range similar to that in these earlier studies. The measurements in the aqueous solutions, in agreement with the Kenney-Wallace work, resulted in a nearly constant value for τ/η, while in DMSO the corresponding values of τ/η more than doubled (see Figure 2A). These results are compared further in the Conclusion section.

The rest of this paper is structured in the following manner. The first section describes the apparatus and procedure used in gathering the data and also outlines sample preparation. Following this section, the experimental results are presented. A third section provides background for several friction models and analyzes the data in light of these models. The Discussion section which follows presents an interpretation of the data and places it in the context of previous data. The last section summarizes the conclusions of this work.

Experimental Section

Optically Heterodyned Polarization Spectroscopy. In these experiments, optically heterodyned polarization spectroscopy (OHPS) is used to determine the rotational diffusion times τ_{or}. This method is described in detail in earlier publications from this laboratory;[18,24] however, the principal features will be outlined here.

In polarization spectroscopy,[2,25] a polarized pump pulse resonant with the molecule of interest interacts with the ground-state population according to $\vec{\mu}\cdot\vec{E}_{pump}$. Thus, solute molecules with their transition moment orientation parallel to the pump polarization field are preferentially excited and an orientational anisotropy is created. In dilute solutions where these experiments were performed ($<10^{-4}$ M), this anisotropy decays by solute rotation ($r(t)$) and excited-state population decay ($K(t)$). A probe pulse with a variable delay time monitors this decay, providing a direct measure of the orientational correlation function for the solute,

$$r(t) = {}^2/_5\langle P_2(\hat{\mu}(0))\cdot\hat{\mu}(t)\rangle \qquad (3)$$

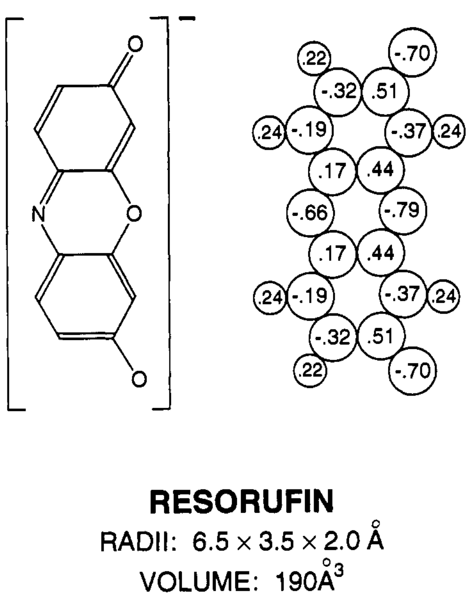

Figure 1. (Left) Molecular structure of resorufin. (Right) The charge distribution used in the model calculations. Note that the net charge in the figure suffers from rounding error.

Because the orientational anisotropy may generate transient birefringence as well as dichroism, the signal can reflect relaxation in multiple electronic states. Optically heterodyned polarization spectroscopy[26] is a modification of this method which overcomes this limitation by selectively enhancing the component of the signal originating in either sample dichroism or birefringence. The component enhanced depends on whether the probe is polarized linearly or elliptically. If a linearly polarized probe is used and is resonant with only one electronic state, the method becomes selective for an electronic state. In addition, enhancement of the signal increases the sensitivity of the original technique by at least an order of magnitude.

As described above, the decay of the signal observed using OHPS results from both the randomization of solute orientation and also the relaxation of the excited-state population, which is measured in an independent experiment. The measured decay time (τ_M) includes the fluorescence decay time τ_F as well as the rotational relaxation time τ_{or}. When the rotational relaxation and the population relaxation are exponential, the reorientation time is given by

$$\tau_{or}^{-1} = \tau_M^{-1} - \tau_F^{-1} \qquad (4)$$

In these experiments, the fluorescence lifetime showed no discernible dependence on electrolyte concentration. In DMSO the fluorescence lifetime is 4758 ± 69 ps, and in water the fluorescence lifetime is 2778 ± 34 ps.

Pump/Probe Apparatus. The system used for determining the measured decay time (τ_M) is described in detail in earlier papers.[18–20,25] Briefly, the acousto-optically mode-locked 1064-nm output from a Nd:YAG laser is frequency doubled and used to synchronously pump a Rhodamine 6G dye laser. The 590-nm output is split to form the pump (fixed path length) and probe (variable path length). Autocorrelation of the pump and probe pulses typically gives a full width at half-maximum (FWHM) of 6 ps. The pump and probe, chopped at different frequencies, are focused into the sample, which is flowed through a dye jet and recirculated in a constant temperature bath. The resulting signal from the photomultiplier is read by a lock-in amplifier at the sum frequency. The output from the lock-in is stored by a computer which also controls the probe path length.

Other Instrumentation. The fluorescence decay time was determined by the time correlated single photon counting (TCSPC) method using an apparatus described elsewhere.[27,28] Conductivity measurements were made on a Radiometer Copenhagen CDM83 conductivity meter. Infrared spectra were measured on a Nicolet 800-FTIR spectrophotometer using CaF_2 cell windows. A Hewlett-Packard Model 8450A diode array

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Table I. Experimental Rotational Diffusion Times

	water			DMSO		
$[LiNO_3]$ (M)	τ_{or} (ps)	η (cP)	$\frac{\tau_D(\epsilon_s - 1)}{(2\epsilon_s + 1)^2} \times 10^{14}$ s	τ_{or} (ps)	η (cP)	$\frac{\tau_D(\epsilon_s - 1)}{(2\epsilon_s + 1)^2} \times 10^{14}$ s
0.00	74	0.95	2.58	83	1.99	9.93
0.10		0.96	2.61	126	2.10	10.4
0.25	77	0.97	2.79	175	2.37	11.0
0.5	76	1.00	2.80	281	2.89	12.7
0.75		1.03		363	3.54	14.3
1.00	85	1.06	2.86	406	4.35	16.8
1.25		1.09		569	5.38	20.3
1.50		1.16		726	6.65	27.2
2.00	102	1.20	3.05	827	10.30	31.2

spectrophotometer was used for the absorbance spectra, and emission profiles were taken on an SLM 8000 fluorimeter.

Samples. Resorufin (Figure 1) was used as the probe molecule and was studied in both aqueous and DMSO solutions of the electrolyte $LiNO_3$. Decays were measured in solutions of $LiNO_3$ ranging from 0.1 to 2.0 M and in the pure solvent. Resorufin (sodium salt) and $LiNO_3$ were obtained commercially from Aldrich. Resorufin was used as received. The $LiNO_3$ was dried for 24 h in a vacuum oven before use. DMSO (Fisher, 99.9%) was treated with molecular sieves, and aqueous solutions were prepared using 17 MΩ water purified by ion exchange.

Preparation of Lithium Salt. The lithium salt of resorufin used in the conductivity measurements was prepared as follows. A methanol solution of the sodium salt was acidified with HCl. The resulting insoluble protonated form of resorufin was filtered, washed with methanol, and dried overnight in a vacuum oven at 50 °C. A stoichiometric amount of LiOH (Aldrich) dissolved in methanol was added to the protonated resorufin with just enough methanol to dissolve the resulting lithium salt. This solution was precipitated by adding acetonitrile and allowing the solution to stand overnight. After being filtered and washed with acetonitrile, the salt was dried overnight in a vacuum oven. Atomic emission detected no sodium and clearly indicated lithium as the cation. The proton NMR spectrum of the product dissolved in DMSO was identical to that of the sodium salt in DMSO.

Computational Information. The partial charges (see Figure 1) used for the charge distribution model of dielectric friction were obtained with the Gaussian 90 program for electronic structure calculations using a 3-21g basis set.[29] The OHPS experiment was controlled by a program written using Asyst software, which was also used for the data-fitting programs.

Results

Rotational Diffusion Data. The rotational diffusion times for resorufin in both water and DMSO at several $LiNO_3$ concentrations are given in Table I. Data points were measured an average of five times, and the error is estimated to be ±7%.

The relaxation times, and therefore the friction, increase by only 30% in aqueous solutions for an increase from 0.0 to 2.0 M $LiNO_3$ concentration. In contrast the relaxation times increase by an order of magnitude over the same electrolyte concentration range in DMSO. The rotational diffusion time is a function of solvent viscosity and the dielectric properties of the solution, i.e., dielectric constant and Debye relaxation time.[12,21,30-32] Figure 2A shows relaxation times normalized to viscosity and plotted against $LiNO_3$ concentration. In Figure 2B, the relaxation times are normalized to the dielectric parameter *E*, given by

$$E = \frac{(\epsilon_s - 1)\tau_D}{(2\epsilon_s + 1)^2} \tag{5}$$

From these plots it can be seen that in the aqueous solutions the increase in rotation times with concentration follows both the viscosity and the dielectric parameters, but in DMSO the increase is far too large to be accounted for by these effects. In the solvents used herein, the shear viscosity and the dielectric parameter *E* are found to be nearly linearly related, and this relationship is reflected in the similar trends for τ_{OR}. Other friction mechanisms, particularly ion atmosphere friction and ion pairing, must be considered in order to account for the observed increase of the friction in DMSO solutions.

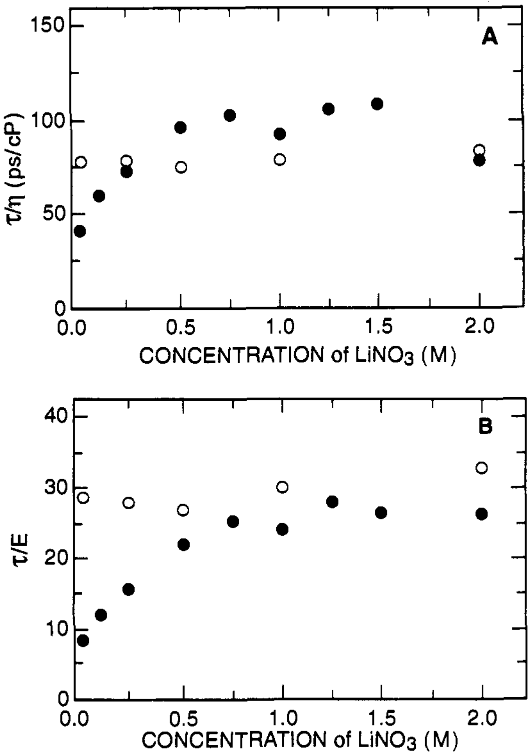

Figure 2. Rotational diffusion times normalized by (A) viscosity and (B) dielectric parameter *E* are plotted versus electrolyte concentration. Open circles represent water, and solid circles DMSO.

Conductivity Experiments. Association of electrolytes in solution results in deviation from a linear relationship of conductivity with concentration.[33] Measurement of the conductivity's dependence on salt concentration allows an association constant for the salt to be determined. The lithium salt of resorufin was used in conductivity measurements, and this data appears in Table II. Analysis of this data shows that ion pairing occurs at a lower salt concentration in DMSO than in water.

A quantitative indication of the degree of ion pairing is given by the equilibrium constant, K_D, for the dissociation of the lithium salt according to

$$Li^{\delta+}[\text{resorufin}]^{\delta-} \rightleftarrows Li^+ + [\text{resorufin}]^-$$

K_D be calculated from the conductivity data using the Ostwald

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Table II. Conductivity Data and Ion Pair Concentrations for Lithium Resorufin Solutions

[LiRes] (M)	κ_{H_2O} (μS/cm)	κ_{DMSO} (μS/cm)	Y_{IP} (DMSO)	Y_{IP} (H_2O)
0.0010	52.5	20.3		
0.0025	134	49.5		
0.0050	261	92.6		
0.0075	400	134		
0.010	535	170		
0.025	1260	369		
0.050	2500	636		
0.075	3570	841		
0.100	4450	1039	0.594	0.226
0.25	8400	1670	0.694	0.388
0.50	10620		0.783	0.527
0.75			0.822	0.607
1.00			0.847	0.624
1.25			0.865	0.676
1.50			0.878	0.729
2.00			0.895	0.771

Table III. Shift of C═O Stretch with Electrolyte Concentration in DMSO

[$LiNO_3$] (M)	C═O stretch (cm^{-1})	peak width FWHM (cm^{-1})
0.0	1584	9.8
0.1	1585	10.7
1.0	1587	12.5
2.0	1588	12.9

dilution law:[34]

$$\frac{1}{\Lambda_M} = \frac{1}{\Lambda_M{}^\circ} + \frac{\kappa}{K_D(\Lambda_M{}^\circ)^2} \qquad (6)$$

In this expression, the conductivity is given by κ, the molar conductivity by Λ_M, and the limiting conductivity by $\Lambda_M{}^\circ$. The dissociation constant K_D is calculated from the slope of a plot of $1/\Lambda_M$ versus κ. The limiting conductivity needed to extract K_D from the slope of this plot is obtained by plotting Λ_M against the concentration according to Kolrausch's law,[34]

$$\Lambda_M = \Lambda_M{}^\circ - Gc^{1/2} \qquad (7)$$

so that the intercept gives $\Lambda_M{}^\circ$. The K_D value obtained thus for the lithium salt in DMSO is 4.27×10^{-2} M and in water is 0.251 M. The dissociation constant is then used with activities calculated using the extended Debye–Hückel law to determine the fraction of resorufin that is ion paired, Y_{IP}, and the fraction that is free, $Y_{FR} = 1 - Y_{IP}$. The values for Y_{IP} are also given in Table II.

Spectral Studies. Further evidence for ion pairing was obtained spectroscopically. Infrared spectra of resorufin in pure DMSO as well as several concentrations of $LiNO_3$ solution were measured. Table III shows the change in resonance frequency as well as peak width for the C═O stretch. The overall shift in frequency is about 4 cm^{-1}.

The electronic spectrum is sensitive to both solvent and electrolyte. The absorbance maximum of resorufin in water is blue shifted from that in DMSO and shows less structure. The Stokes shift (measured as the energy difference between the absorption maximum and the emission maximum) is 361 cm^{-1} in water and 822 cm^{-1} in DMSO. As electrolyte is added, the absorption peak in DMSO blue shifts (from 594 to 588 nm). In contrast the water spectrum does not change as electrolyte is added.

Analysis Using Continuum Models

In this section different mechanisms for the friction on the free solute (i.e., assume no ion pairing is present) are evaluated by comparison of the data with theoretical models. First, hydrodynamic and dielectric models are evaluated. Subsequently, ion atmosphere friction is examined. In evaluating components of the friction and determining their relative importance, several methods of modeling the data were used. In each case the rotation times corresponding to the various friction components were estimated in a systematic way, summed, and compared with the experimental results.

Hydrodynamic Friction. The hydrodynamic component of the friction is determined by the size and shape of the solute, the viscosity of the solvent, and the strength of the solute/solvent coupling, or boundary condition. Two different boundary conditions, known as "slip" and "stick", have been used to solve the hydrodynamic equations.[2,35] The stick boundary condition is defined as having a zero difference in angular velocity between the surface of the rotating molecule and the solvent at the solute/solvent interface, i.e., the solvent "sticks" to the solute. For the slip boundary condition no tangential force is exerted on the rotating molecule by the solvent, and thus, for a spherical molecule, the slip friction is 0. For a nonspherical molecule friction arises from the displacement of volume in the solvent, i.e., solvent must be pushed aside as the molecule rotates. The expression which describes the friction includes two model parameters, a factor F, which depends on the solute nonsphericity, and the boundary condition factor, C. The factor $\sigma \equiv FC$ for the slip boundary condition can be calculated from tabulated values[9] if the molecule is assumed to be ellipsoidal and the axial ratios of the ellipsoid are known. For a nonspherical molecule having a volume V rotating in a solvent of viscosity η, the friction about axis i is given by

$$\zeta_i = 6\eta V\sigma_i \qquad (8)$$

The solute molecule, resorufin, is modeled as an asymmetric ellipsoid with axial ratios of 6.5:3.5:2.0, and the volume is 190 Å^3. As in previous studies from this group,[17-21,32] the hydrodynamic boundary condition is taken to be slip. In this case the characteristic relaxation time for the orientational correlation function would be 26 ps/cP at room temperature, if no other friction mechanism were present. This estimate of the friction is a lower bound on the actual mechanical friction, since the roughness features of the resorufin will increase the friction coefficient somewhat.[36]

Dielectric Friction. Dielectric friction on a reorienting solute molecule results from the inability of the solvent to adjust instantaneously to a new solute orientation. Earlier work from this laboratory included the testing of several models of dielectric friction. Nee and Zwanzig[30] used the torque generated by the interaction of the solute dipole moment with the reaction field to develop an expression for the friction,

$$\zeta = \frac{6\mu^2}{a^3}\frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)^2}\tau_D \qquad (9)$$

where μ is the magnitude of the solute's dipole moment, a is the solute radius, ϵ_S is the static dielectric constant, and τ_D is the Debye relaxation time. This model is limited because of its reliance on a point dipole to describe the electronic character of the solute molecule. An improvement over this model was recently proposed by Alavi and Waldeck[21] and incorporates the charge distribution on the solute into the expression for the dielectric friction,

$$\zeta_{DF} = \frac{8(\epsilon_s - 1)\tau_D}{a(2\epsilon_s + 1)^2}\sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{L=1}^{L_{MAX}}\sum_{M=1}^{L}\left(\frac{2L+1}{L+1}\right)$$

$$M^2 q_i q_j\left(\frac{r_i}{a}\right)^L\left(\frac{r_j}{a}\right)^L P_L{}^M(\cos\theta_i)P_L{}^M(\cos\theta_j)\cos M\phi_{ji} \qquad (10)$$

where $P_L{}^M(x)$ are Legendre polynomials, a is the cavity radius,

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N is the number of partial charges, q_i is the partial charge on atom i, the position of atom i is given by (r_i,θ_i,ϕ_i), and $\phi_{ji} = \phi_j - \phi_i$. This model provides a much more realistic description of the electronic properties of the solute. Other studies from this laboratory have compared several models of dielectric friction with the charge distribution model and find that while point source models predict rotational relaxation times that differ from experiment by more than an order of magnitude, the charge distribution model provides reasonable quantitative agreement with experiment.[17-21,32] Therefore, this model was chosen for calculating the dielectric friction in this work.

In this analysis the cavity radius about the solute molecule is varied until the measured rotational relaxation time in pure solvent matches the model. This best fit radius is then used to calculate the dielectric friction on resorufin in the electrolyte solutions. In the case where the slip boundary condition is used to model the mechanical friction, the best fit radius is found to be 6.87 Å in DMSO and 5.98 Å in water. The best fit radius in DMSO is quite realistic; however, that in water is not. The origin of this inconsistency could lie with either the modeling of the mechanical friction (DMSO and water are quite different in size) or the modeling of the dielectric friction. A more realistic model may be used to estimate the mechanical component of the friction. A "quasihydrodynamic" model proposed by Dote et al.[7] appears to capture effects arising from the relative solute/solvent size.[36] This model depends on the particular properties of not only the solute but the solvent since it accounts for the free volume in the solution (related to the solute/solvent size). The difference in effective boundary condition is predicted to be only 10–20% between DMSO and water. This small difference reflects only the size effects; hence, it is likely that the electrostatic differences between resorufin/water and resorufin/DMSO contribute significantly to the observed relaxation times.

The inability to model the absolute value of the rotational relaxation time of resorufin in water is troublesome, but does not affect the major focus of this study, the influence of electrolyte on the rotational relaxation. It is likely that for resorufin in water the electrostatic model fails to describe the friction because the solvent is "attached" to the solute for times comparable to the rotational period. In fact an increase in the molecular volume to 230 Å^3 models the observed times well and would correspond to the attachment of two to three water molecules to the solute. The modeling of the magnitude of the friction in water is given more attention in the Discussion. It is useful to note here that temperature studies for the relaxation of resorufin in water[37] and the electrolyte studies reported here are in full agreement (see Figure 3). This observation indicates that the addition of salt does not significantly affect the rotational relaxation of resorufin in water, other than its influence on the solution's viscosity.

From Figure 2 it is clear that the modeling of the friction in DMSO, although appropriate for the neat solvent, fails to describe the dependence of the measured relaxation time on the concentration of electrolyte. However, an additional contribution to the friction is present in electrolyte solutions, ion atmosphere friction. The reason for this mechanism's possible importance in DMSO, compared to water, is the difference in dielectric parameters for these two solvents. The rapid dielectric relaxation of water and its high dielectric constant lead to a small dielectric friction and correspondingly small ion atmosphere friction.

Ion Atmosphere Friction. The friction on a solute rotating in an electrolyte solution will be larger than that in a pure solvent. The presence of the electrolyte increases the viscosity of the solution, and this will be reflected in an increased hydrodynamic friction component since the viscosity is included in the friction expression. In addition, the presence of electrolyte ions in solution changes the dielectric character of the system. First, it alters the ability of the solvent to shield the charges on the rotating solute, which is reflected in a decreasing dielectric constant with increasing electrolyte concentration. Since the friction has its origin in the interaction between the rotating dipole and the reaction field created in the cavity occupied by the dipole, the decrease in the dielectric constant results in an increase in friction. Both of these contributions are included in the previous modeling of the hydrodynamic and dielectric friction because the viscosity, dielectric constants, and Debye relaxation times of the electrolyte solutions were used in modeling the data.

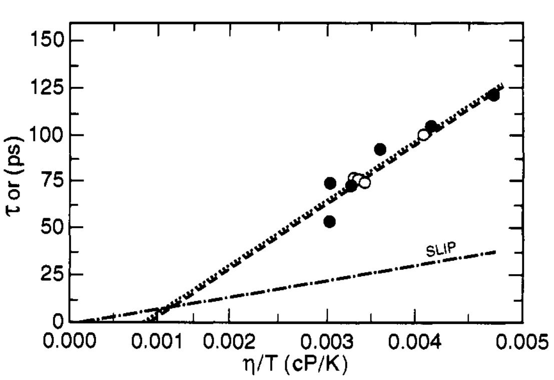

Figure 3. Debye–Stokes–Einstein plot for resorufin in pure water at different temperatures (solid circles) and in aqueous LiNO$_3$ (open circles). The dotted line shows the slope for measurements in pure water, and the dashed line for those in LiNO$_3$ solutions, while the dot/dash line gives the slope for slip hydrodynamics.

The feature of the electrolyte solutions not incorporated above is the screening of the solute molecule charge distribution by the electrolyte ions and the finite response time of this "ion atmosphere". The parameter κ^{-1}, the Debye length,[33,34] measures this screening length and is given by

$$\kappa^{-1} = \left(\frac{\epsilon_s kT}{4\pi q_i^2 c_i}\right)^{1/2} \qquad (11)$$

where q_i is the charge on ion i and c_i is the concentration of ion i. Increasing electrolyte concentration decreases the Debye length so that the potential of the solute drops off more quickly, resulting in less electrostatic interaction between the rotating dipole and the solvent, thus lowering the friction. A final variable D, the diffusion constant for the ions of the electrolyte, while independent of concentration, affects the magnitude of the ion atmosphere friction, since the ion atmosphere responds to the rotating charge distribution by translational diffusion of the ions. This constant may be determined using the Nernst–Einstein relation[34] if one assumes that $D = D_+ = D_-$

$$\Lambda_M{}^\circ = \frac{F^2}{RT}(\nu_+ z_+{}^2 D_+ + \nu_- z_-{}^2 D_-) \qquad (12)$$

where F is Faraday's constant, ν_i is the stoichiometric coefficient, and z_i is the magnitude of the charge. These quantities are used by van der Zwan and Hynes[38] to write the ion atmosphere friction,

$$\zeta_u = \frac{3\mu^2}{2a^2}\,\frac{\epsilon_s y}{D(2\epsilon_s + 1)(2\epsilon_s + 1 + \epsilon_s y)\kappa} \qquad (13)$$

where

$$y = \frac{(\kappa a)^2}{1 + \kappa a} \qquad (14)$$

The effects of the change in dielectric constant and in Debye length on ion atmosphere friction oppose one another (see Figure

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(38) van der Zwan, G.; Hynes, J. T. *Chem. Phys.* **1991**, *152*, 169.

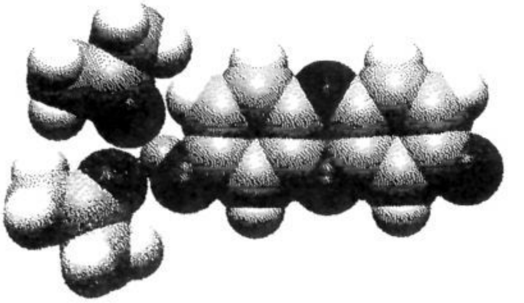

Figure 4. Resorufin–lithium ion pair in DMSO.

3 of ref 38). At lower concentrations, the effect of decreasing dielectric constant is more important and the ion atmosphere friction increases, while at higher concentrations, the decreasing Debye length becomes the governing factor, resulting in a decreasing ion atmosphere friction. The ion atmosphere friction for resorufin was calculated following the van der Zwan and Hynes expression given above. The results were quite small, on the order of a picosecond. The calculated ion atmosphere friction was then scaled to reflect the more realistic picture of the solute molecule afforded by the charge distribution method of calculating dielectric friction. Using data for resorufin in pure DMSO, a ratio of the dielectric friction calculated from the Nee and Zwanzig expression (eq 9) to that calculated using the expression of Alavi and Waldeck (eq 10) was used to scale the ion atmosphere friction obtained using the van der Zwan and Hynes expression (eq 13). This modification is intended as an estimate of the effect of including a realistic charge distribution into the model as opposed to the point dipole used in the other models. However, even with the ion atmosphere friction adjusted to reflect the solute charge distribution, the calculated increase in relaxation time with electrolyte concentration is not nearly large enough to account for the data.

The inability of these continuum models to describe the friction experienced by the solute indicates that a more molecular treatment of the solute/solvent interaction should be considered. This observation in combination with the conductivity and spectral data on these solutions suggests that an ion-paired species exists in DMSO solutions and the lifetime of this species is similar to or longer than the characteristic time scale of rotational relaxation.

Analysis Using Ion Pair Species and Continuum Models

In this section the data is analyzed with the assumption that two distinct species are present in solution, a free solute and an ion-paired species. Figure 4 shows a sketch of a possible ion-paired species. This sketch is used to estimate a shape and a volume for the ion-paired species in DMSO. Clearly the structure of the ion pair, its lifetime, and its rigidity are not known. The calculations presented here are intended to be illustrative only. The analysis proceeds in three steps: (1) only hydrodynamic friction is considered, (2) both hydrodynamic friction and dielectric friction are considered, and (3) ion atmosphere friction is considered with dielectric and hydrodynamic friction.

Hydrodynamic Friction. In the first calculation, the friction is assumed to be totally hydrodynamic, with one component coming from the free species and one from the ion-paired species. Since the ion-paired species has a larger volume, its hydrodynamic contribution is larger. With this information, it is possible to calculate an ion-paired version of $V\sigma$. The value of σ is 0.57 and the volume is 190 Å^3 for the free anion, whereas σ is 0.88 and the volume is 370 Å^3 for the ion-paired form in DMSO. This gives

$$\frac{(V\sigma)_{\mathrm{IP}}}{(V\sigma)_{\mathrm{FR}}} = \frac{(370\ \text{Å}^3)(0.88)}{(190\ \text{Å}^3)(0.57)} = 3.0 \tag{15}$$

Analogous calculations for resorufin in water lead to

$$\frac{(V\sigma)_{\mathrm{IP}}}{(V\sigma)_{\mathrm{FR}}} = \frac{(244\ \text{Å}^3)(0.97)}{(190\ \text{Å}^3)(0.57)} = 2.2 \tag{16}$$

In the following analysis the experimental rotational diffusion times are used to calculate a factor denoted as G, which is the experimental analogue to $V\sigma$, for both the ion-paired and the free species. The ratio of these G factors, $G_{\mathrm{IP}}/G_{\mathrm{FR}}$, is then compared to the corresponding ratio calculated directly from the volume and hydrodynamic parameters, $(V\sigma)_{\mathrm{IP}}/(V\sigma)_{\mathrm{FR}}$, for both DMSO and water.

The factor G_{FR} (or correspondingly $G_{\mathrm{H_2O}}$) is determined from the rotation time in the pure solvent:

$$G_{\mathrm{FR}} = \frac{\tau_{\mathrm{pure}}}{\eta_{\mathrm{pure}}} \tag{17}$$

The corresponding factor G_{IP} was determined by calculating g_{IP} for each concentration of the electrolyte[30,31] according to

$$g_{\mathrm{IP}} = \frac{(\tau_{\mathrm{or}} - \tau_{\mathrm{FR}})}{Y_{\mathrm{IP}}\eta_{\mathrm{sol}}} \tag{18}$$

where η_{sol} is the shear viscosity[43,44] of the solution and $\tau_{\mathrm{FR}} \equiv G_{\mathrm{FR}}Y_{\mathrm{FR}}\eta_{\mathrm{sol}}$. The mean value of g_{IP} is taken to be G_{IP}. Since the solute species are independent,

$$\tau_{\mathrm{total}} = \tau_{\mathrm{FR}} + \tau_{\mathrm{IP}} \tag{19}$$

and a rotation time is predicted for each concentration using

$$\tau_{\mathrm{total}} = G_{\mathrm{FR}}Y_{\mathrm{FR}}\eta_{\mathrm{sol}} + G_{\mathrm{IP}}Y_{\mathrm{IP}}\eta_{\mathrm{sol}} \tag{20}$$

Figure 5A compares the experimental rotation times to those computed with this model. The free ion and ion pair contributions to the total calculated relaxation time are shown here as well. The dotted curve shows the contribution of the ion-paired form to the total relaxation time, and it clearly dominates the friction. The dot/dash curve indicates the contribution of the free species, which decreases at high concentrations of electrolyte because the population of free species decreases. Although not obvious from this plot, at larger concentrations the rotational relaxation time of the free species increases with concentration of electrolyte, because of the increase in solution viscosity. The experimental data is approximated rather well, and comparison of the ratio $(V\sigma)_{\mathrm{IP}}/(V\sigma)_{\mathrm{FR}} = 3.0$ to the ratio $G_{\mathrm{IP}}/G_{\mathrm{FR}} = 2.4$ indicates a reasonable correspondence.

Following the same method of calculation for the data in water, a value of 1.0 is obtained for the ratio $G_{\mathrm{IP}}/G_{\mathrm{H_2O}}$. This indicates that the friction for the ion-paired species is effectively the same as for the free species. This result is discussed more later.

Inclusion of Dielectric Friction. Somewhat better results are achieved by incorporating a dielectric friction component into the calculation of the friction for the free solute, in addition to the hydrodynamic components. First, a component of the rotation time for dielectric friction is determined for each concentration using the charge distribution model with values for ϵ_{S} and τ_{D} specific to each concentration,[39] according to eq 10. The hydrodynamic component for the free species is determined in a manner similar to the first calculation, where

$$G_{\mathrm{FR}} = \frac{\tau_{\mathrm{pure}} - \tau_{\mathrm{diel}}}{\eta_{\mathrm{pure}}} \tag{21}$$

Again, a corresponding G_{IP} is determined from the mean value of g_{IP}, given in this case by

$$g_{\mathrm{IP}} = \frac{\tau_{\mathrm{or}} - \tau_{\mathrm{diel}} - \tau_{\mathrm{FR}}}{Y_{\mathrm{IP}}\eta_{\mathrm{sol}}} \tag{22}$$

and the predicted rotation time is a sum of three components,

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(39) Barthel, J.; Behret, H.; Schmithals, F. *Ber. Bunsen-Ges. Phys. Chem.*; **1971**, *75*, 305.

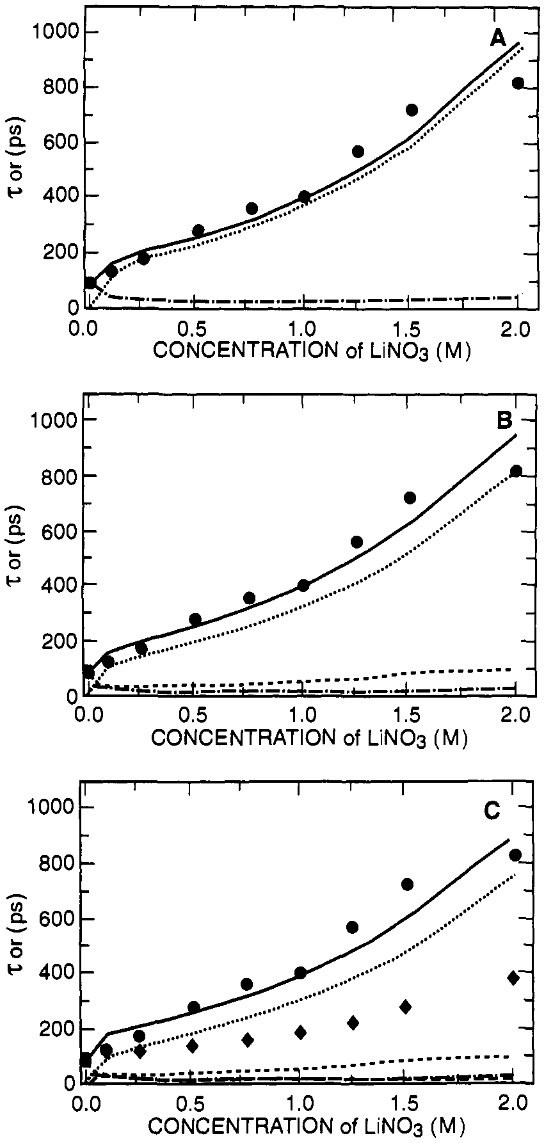

Figure 5. Experimental rotation times (solid circles) in DMSO/$LiNO_3$, with (A) hydrodynamic components only (dot/dash line, free anion contribution; dotted line, ion paired contribution; solid line, total); (B) dielectric friction included (dashed line indicates the dielectric component); (C) ion atmosphere friction included (long dashes indicate the ion atmosphere component); without ion pairing (◆).

$$\tau_{total} = \tau_{diel} + G_{FR}Y_{FR}\eta_{sol} + G_{IP}Y_{IP}\eta_{sol} \qquad (23)$$

While the fit of the experimental data to the predicted rotation times (see Figure 5B) is not noticeably better, the correspondence of the experimental ratio of $G_{IP}/G_{FR} = 3.4$ to $(V\sigma)_{IP}/(V\sigma)_{FR} = 3.0$ is improved. In this calculation, the values used for ϵ_S and τ_D are those for the electrolyte solutions and not the pure solvents, so the resulting values for dielectric friction reflect the presence of the electrolyte, even without a term specifically attributed to ion atmosphere friction. However, dielectric friction which may also contribute to the rotational relaxation of the ion-paired species is not included. This additional friction term would reduce the value of $(V\sigma)_{IP}$ and might lead to better correspondence.

Hydrodynamic, Dielectric, and Ion Atmosphere Friction. The third calculation includes an ion atmosphere friction term for the free solute species, and it has been scaled to reflect the extended charge distribution of the solute. This term is given by

$$\tau_{IA} = \frac{\zeta_{IA}}{kT}\frac{\zeta_{diel(AW)}}{\zeta_{diel(NZ)}} \qquad (24)$$

The calculation follows the general pattern of the previous one, and the expression for g_{IP} differs by the addition of the ion atmosphere term,

$$g_{IP} = \frac{\tau_{or} - \tau_{diel} - \tau_{IA} - \tau_{FR}}{Y_{IP}\eta_{sol}} \qquad (25)$$

Again, the mean value of g_{IP} is used for G_{IP}, but the value is somewhat smaller in this calculation, since some of the friction is being attributed to the ion atmosphere term. As in the previous calculation, a predicted value for the rotation time is obtained by summing the various contributions, according to

$$\tau_{total} = \tau_{diel} + \tau_{FR} + \tau_{IP} + \tau_{IA} \qquad (26)$$

In this calculation, the (experimental) ratio G_{IP}/G_{FR} of 3.1 gives excellent correspondence with the calculated ratio of 3.0 for $(V\sigma)_{IP}/(V\sigma)_{FR}$. Figure 5C shows contributions to the calculated relaxation time with the ion atmosphere friction incorporated into the model.

While the inclusion of ion atmosphere and dielectric friction components improves the correspondence of the calculated with the experimental times, it is the incorporation of ion pairing that allows the modeling to work at all. To illustrate this point, rotation times were calculated incorporating hydrodynamic, dielectric, and ion atmosphere terms *without* ion pairing. These times are included in Figure 5C (◆) and show a very poor correspondence with the experimental data. These calculations demonstrate the ability to model the increase in relaxation time with electrolyte concentration in DMSO solution if an ion-paired species is present. Clearly it is difficult to talk quantitatively about the elements of the friction which each species in this solution experiences. However, the ability to model the data with an ion-paired species stands in stark contrast to the analysis for the free solute which was unable to reproduce the data.

Discussion

As the concentration of $LiNO_3$ in DMSO increases, the rotation time for resorufin shows a much larger increase than would be expected from the changing viscosity and dielectric parameters. In contrast, as the concentration of $LiNO_3$ in water increases, the rotation time for resorufin follows the viscosity and dielectric parameters quite closely. Clearly some factor in addition to changes in viscosity and dielectric parameters is affecting the motion in the DMSO solutions, and this factor does not appear to be significant in the aqueous solutions.

The ion atmosphere friction is greater by an order of magnitude in DMSO solutions than in aqueous solutions. The addition of ion atmosphere friction to the calculated rotation times is qualitatively correct. This friction term is larger in DMSO than in water; however, the magnitude of this increase in friction is not large enough to account for the observed increase in rotation time with electrolyte concentration. Available models for the ion atmosphere friction do not use an extended charge distribution, and inclusion of an extended charge distribution is likely to increase the ion atmosphere friction over that found via point source models.

The large increase in resorufin rotation times in $LiNO_3$/DMSO solutions can be accounted for by proposing the formation of an ion-paired species which then rotates as a unit. Evidence for this ion pairing in DMSO is provided by FTIR studies, as well as conductivity measurements. The conductivity measurements for the lithium salt of resorufin in DMSO show a larger deviation from linearity in the plot of conductance versus concentration than does the aqueous solution. These measurements result in a dissociation constant for the lithium resorufin in DMSO that is smaller by a factor of 5 than is the dissociation constant for the same salt in water. This supports the hypothesis that ion pairing is a large contributor to the slower than expected rotation time and makes less of a contribution to the friction in the aqueous solutions.

The values for K_D were used to calculate the fraction of resorufin that is ion paired at each electrolyte concentration where the rotation times were measured (see Table II). As expected, the fractions were higher in DMSO than in water, but still indicated significant ion pairing in aqueous solutions. However, the values for G_{IP}/G_{FR} in water are approximately 1, which corresponds to an unchanging value of $V\sigma$ for the ion-paired species. The ratio $(V\sigma)_{IP}/(V\sigma)_{FR} = 2.2$ is smaller in water than the corresponding value of 3.0 in DMSO, but it is still much larger than the experimentally observed G_{IP}/G_{FR} of 1.0. Thus, in water the increase in τ_{OR} calculated using the larger (ion paired) volume would be much larger than the increase observed. The model, which accounts for the data in DMSO, initially appears to do less well in water. Two explanations can be used to account for this observation: (1) the relative lifetimes of the ion-paired species in the two solvents are quite different and (2) the ion-paired species in water has a similar relaxation time to "hydrated" resorufin.

Ion Pair Dynamics. In order to estimate the lifetime of the ion-paired species, the following equilibrium is considered:

$$\mathrm{Li}^{\delta+}[\mathrm{resorufin}]^{\delta-} \underset{k_U}{\overset{k_P}{\rightleftarrows}} \mathrm{Li}^+ + [\mathrm{resorufin}]^- \qquad (27)$$

where k_p is the rate of ion pairing and k_u is the rate of dissociation of the ion pairs. The lifetime of the ion-paired species is given by

$$\tau_{IP} = k_u^{-1} = \frac{1}{K_{Diss}k_P} \qquad (28)$$

where

$$K_{Diss} = \frac{k_u}{k_P} \qquad (29)$$

By assuming that the ions pair when they encounter one another and that there is no activation barrier, one can calculate a lower limit to the ion pair lifetime by using an expression given by Smoluchowski[1] for the frequency of encounters, Z_E, where

$$Z_E = \frac{8\pi N_A q(D_A + D_B)}{1 - e^{-2q/\sigma_{AB}}} \qquad (30)$$

and

$$q = \frac{-Z_A Z_E e^2}{2\epsilon_s kT} \qquad (31)$$

In this expression, D_A and D_B are the translational diffusion constants for ions A and B, Z_A and Z_B are the magnitudes of the ionic charges, e is the charge on an electron, and σ_{AB} is the distance between ion centers in the ion-paired species. Letting $k_p = Z_E$ and incorporating the previously determined values for K_D into eq 29, one obtains an ion paired lifetime of 1.87 ns in DMSO and 172 ps in water. These lifetimes are only estimates, but the long lifetime in DMSO suggests that the ion pair is bound on the rotational diffusion time scale and longer. Also, the relative values of the ion pair lifetime in DMSO and water indicate that the ion pair in DMSO is much longer lived than that in water. These estimations support the model that the resorufin in DMSO electrolyte solutions forms an ion pair which undergoes rotational motion, whereas in water the ion pair is likely to dissociate and the resorufin may rotate as a free, i.e., not ion-paired, species.

Resorufin Hydration. An alternative explanation to that provided above is that resorufin never reorients as a "free" species in aqueous solution. Previous studies of resorufin in DMSO solvent[18] and in 2-propanol solvent[19] could be well modeled by a friction coefficient which was a sum of two components, a mechanical friction using a slip boundary condition and a dielectric friction using an extended charge distribution to model the solute/solvent coupling. By contrast the relaxation time of resorufin in water solvent is too long to be modeled adequately in this manner. A more realistic model for the mechanical friction which accounts for the change in size between water and the other two solvents increases the mechanical friction by 20% or less, which is not enough to model the data. The view proposed as an explanation for this failure is that water molecules are hydrogen bonded to the resorufin and increase the effective volume of the molecule as it reorients. A number of studies provide support for this hypothesis. Molecular dynamics studies of tryptophan zwitterion[40] rotating in water indicate that water molecules are strongly correlated with the charged sites on the solute, for times of 90 ps. Resorufin is a charged species, and it is not unlikely to expect it to reflect similar dynamics. Secondly, the hydrogen bond strength between water and dimethylacetamide is 3.2 kcal/mol,[41] whereas that of 2-propanol is 2.4 kcal/mol. This difference is consistent with the decreased effect of hydrogen bonding in the 2-propanol solvents. In addition, recent studies by Moog, Bankert, and Maroncelli[42] provide further support for the solvent attachment hypothesis. They obtained rotational diffusion times for coumarin 102 consistent with the attachment of the strongly hydrogen bonding trifluoroethanol (TFE) both in pure TFE and in nonpolar decalin doped with small amounts of TFE. Lastly, Dutt and Doraiswamy[16] found that solvent attachment is necessary to model their rotational diffusion times for resorufin in alcohol/water mixtures.

The rotational relaxation time of resorufin in water can be adequately represented by a hydrated molecule, consisting of two to three water molecules and one resorufin. The relaxation time of such a hydrated species is not that different from the relaxation time computed for resorufin ion paired to $\mathrm{Li(H_2O)_2}^+$. Hence, as one increases the electrolyte concentration in water, an ion pair is formed but its formation is not reflected in an increase in the rotational relaxation time of the solvent. A calculation analogous to that shown in eq 16 comparing the hydrodynamic parameters $V\sigma$ for the ion-paired and "hydrated" resorufin gives

$$\frac{V\sigma_{IP}}{V\sigma_{H_2O}} = \frac{(244\ \text{Å}^3)(0.97)}{(227\ \text{Å}^3)(1.08)} = 0.97 \qquad (32)$$

This shows excellent correspondence with the empirical ratio $G_{IP}/G_{H_2O} = 1.0$.

In contrast to the studies in water, for DMSO the component of the friction arising from ion pairing is the largest, and the experimental values of τ_{or} in DMSO cannot be even roughly approximated without considering the contribution from the ion-paired species to the hydrodynamic friction. Comparison of the three methods of calculating τ_{or} shows that it is difficult to determine which elements of the friction are important. However, when one includes the dielectric and ion atmosphere friction terms in the modeling, the best fit parameters for the mechanical component of the friction are in good agreement with one's expectations based on the size and shape of the solute species.

Connection with Previous Studies. Kenney-Wallace and coworkers[14,15] also measured the rotational relaxation of resorufin in electrolyte solutions. Their results in water agree with those reported here, and their results in methanol solvent are plotted in Figure 6 (note that the salt used in these earlier studies was LiCl, not $\mathrm{LiNO_3}$). Figure 6 shows a plot of the data reported here in water and DMSO along with the data in methanol reported

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(41) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974.

(42) Moog, R. S.; Bankert, D. L.; Maroncelli, M. *J. Phys. Chem.*, in press.

(43) Viscosities of $\mathrm{LiNO_3}$/DMSO solutions are given in the following: Kodejs, Z.; Novak, J.; Slama, I. *Chem. Zvesti* **1984**, *38*, 455.

(44) Viscosities of aqueous $\mathrm{LiNO_3}$ solutions are given in the following: Landolt-Börnstein *Zahlenwerte und Functionen*; Springer-Verlag: New York, 1967; Band II, Teil 5.

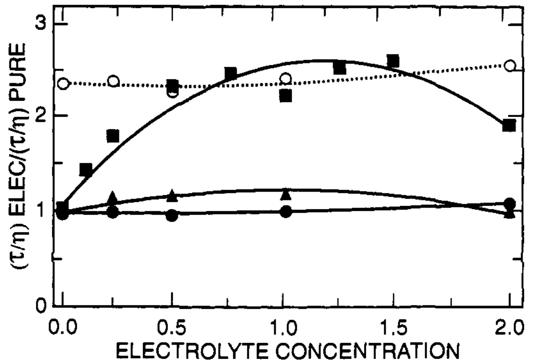

Figure 6. Plot of the experimental τ_{or}/η in water/$LiNO_3$ (solid circles), DMSO/$LiNO_3$ (solid boxes), and methanol/LiCl (solid triangles), all normalized by the τ_{or}/η values for pure solvent versus the concentration of electrolyte (in M). The open circles represent τ/η for water normalized by the value of τ/η calculated from the charge distribution dielectric friction and the slip hydrodynamic friction.

by Kenney-Wallace and co-workers,[15] all plotted against concentration of electrolyte. The ordinate is the reduced rotation time in water, τ_{or}/η, which is rescaled by dividing with its value in the pure solvent, i.e., $(\tau/\eta)/(\tau/\eta)_{pure}$. Such a plot shows the relative increase in relaxation time for each solvent and begins necessarily at 1 for the pure solvent. A second plot of the data in water shows it rescaled using a calculated relaxation time for "free" resorufin in water instead of the measured τ_{OR} in the pure solvent. That is, the relaxation time for resorufin in water was computed using a slip boundary condition for the mechanical friction and an extended charge distribution model for the dielectric friction, and this number, $\tau_{slip+DF}/\eta$, was used to rescale the relaxation times measured in water.

Clearly the data reported here and previous data are in accord. As the concentration of electrolyte increases in both DMSO and methanol, the relaxation time increases until a plateau is reached. The increase in relaxation time can be associated with ion pair formation. Conductivity measurements for resorufin in methanol were performed and yield a dissociation constant of 6.68×10^{-2} M, which is intermediate to the values measured for resorufin in water and in DMSO. Also, an ion paired lifetime in methanol was calculated and found to be 350 ps, which falls between the values for water and DMSO. When the water data is rescaled to the free solute relaxation time, it shows a reduced relaxation time similar to that observed in DMSO. This behavior is consistent with the view that the hydrated resorufin and the ion-paired resorufin have similar relaxation times in water, so that the formation of the ion pair is not evident in the raw data. At higher concentrations where the mole fraction of electrolyte is significant, the measured rotation time appears to decrease somewhat. This decrease may reflect decreasing solvation of the solute from the competition for solvent between the resorufin and the electrolyte.[15] The similarity of the trends in these very different solvents, methanol and DMSO, may be indicative of the general nature of this result.

Conclusion

In summary, these data suggest that, at these electrolyte concentrations in DMSO, ion pairing is significant, and the increase in hydrodynamic friction arising from ion pair formation is the major contributor to the long rotation times observed. It appears that the increase in rotation time arising from the ion atmosphere contribution is overshadowed by the large increase in rotation time from ion pair formation. These conclusions are consistent with previous data for resorufin in methanol.

In contrast, the results in water are inconclusive; the rotation time does not increase significantly between pure water and concentrated electrolyte solutions. The modeling of resorufin's relaxation time in pure water requires that a hydrated solute molecule be invoked, which would have a relaxation time similar in size to that of the ion-paired species. Because of this difficulty, the presence of the ion pair is not evident in this measurement. Additionally, the estimates of the lifetime of the ion paired complex in water are comparable to the observed rotational time scale of the solute, and it is not clear that the ion pair would rotate as a unit.

The analysis of this data with continuum models is unsatisfactory. The explanation offered for the increase in rotation time is the formation of an ion pair; however, this ion-paired species is not expected to be rigid or to have a clearly defined geometry. The calculations presented are intended only as guides for discussion. It appears that a model which accounts for the local structure about the solute molecule may be necessary for a quantitative description of these results. However, the ion atmosphere friction captures essential physical aspects of the observations reported here. This friction results from the time lag between the motion of the solute molecule and the response of the ion atmosphere, which reflects the time for the ions to diffuse. When the electrolyte ions diffuse rapidly compared to the solute molecule orientation and are weakly coupled to the solute, the friction is small. As the time lag increases, i.e., the diffusion of the electrolyte ions is small, the friction increases. However, if the solute and the ion are strongly coupled, as with the ion pair, and the diffusion of the ions is slow, then the solute motion could become limited by the ion diffusion. This latter case is similar to the ion-pairing limit. The similar behavior represented in Figure 6 for these different solvents is suggestive. Whether a continuum-based model is capable of capturing these features remains unclear.

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