Rotational Relaxation of Ionic Molecules in Electrolyte Solutions. Anisotropy Relaxation and Molecular Dynamics Study

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Abstract: Rotational diffusion of organic ions in electrolyte solution is studied via optically heterodyned polarization spectroscopy and molecular dynamics (MD) simulations. Significant differences between the behavior of organic cation and anion species were observed in the experiments. While the rotational relaxation time of the anion normalized by the viscosity of the solution increases with the electrolyte concentration, the normalized relaxation time of the cation decreases with increasing electrolyte concentration. The experimental data are analyzed by using a continuum theory approach and MD simulations. It is demonstrated that one must include ion pairs to describe the dynamics of the anion, but the analysis of the relaxation of the cation does not require ion pairing. MD simulations show that the difference in the dynamics of the anion and cation in electrolyte solution is caused by the different ability of free anion, free cation, and ion paired species to associate with the solvent (DMSO).

I. Introduction

Understanding molecular dynamics in liquids is an important goal of modern physical chemistry. The rotational relaxation of a solute molecule is influenced by its environment, especially for the case of ionic and polar solute species embedded in electrolyte solutions.[1−3] In such cases solute−solvent electrostatic interactions can significantly influence the behavior of the solute. Dramatic changes in the local solvent structure and the solute dynamics occur for ionic solute molecules. Both experimental[4−10] and theoretical[11−14] attempts have been made to describe the dynamics of systems in which the solute may associate with a counterion. Nevertheless, the current understanding of these systems is far from complete. The purpose of the present work is to characterize and compare the rotational relaxation properties of two organic solute molecules, the cation thionine and the anion resorufin, in electrolyte solutions. A combination of experimental studies, ab initio electronic structure, and molecular dynamics (MD) simulation is used to provide a realistic molecular description of these systems.

Recently, the rotation of the resorufin anion in DMSO and aqueous electrolyte solutions was studied experimentally.[8] It was found that the rotation time (τ_{or}) of resorufin increased substantially as the electrolyte concentration rose and that increase was correlated to the charge-to-size ratio of the cation. To explain the experimental observations it was proposed that an ion pair was formed between the resorufin and the metal cation. In turn, the cation was also coordinated with several DMSO molecules. Because such a solvent ion-pair complex is significantly bigger in size than the bare resorufin molecule, it experiences a larger mechanical friction that increases the observed rotational relaxation time of the resorufin in the electrolyte solution. This paper presents results which support the previous work's conclusions about ion-pair formation between resorufin and the metal cation. Conductivity measurements and ab initio electronic structure calculations are used to demonstrate the high probability for resorufin to form an ion pair with Li^+ in DMSO solution. Furthermore, a molecular dynamics simulation of the rotational relaxation of the resorufin−Li ion pair in DMSO solution is compared to a simulation of the rotational relaxation of the free resorufin in pure DMSO.[15] This comparison shows that the relaxation time of the resorufin−Li ion pair is longer than that of the free anion. These results support the contention that ion-pair formation is important under these conditions.

It is natural to ask, "To what extent is the observed behavior specific to the anionic nature of the solute?" The present study addresses this question. To identify general trends in the frictional mechanisms in solution and estimate how much structurally specific interactions change the general picture, two organic cations, thionine and cresyl violet, are studied. These cations are similar to resorufin in shape and size (see Figure 1). The rotational relaxation times of these cations in DMSO and methanol have been measured in concentrated electrolyte solutions, ranging from 0.0 to 1.0 M. Conductivity measurements as well as structural and energetic ab initio analysis of the possible ion-paired species are used to corroborate the rotational relaxation studies. MD simulations of thionine

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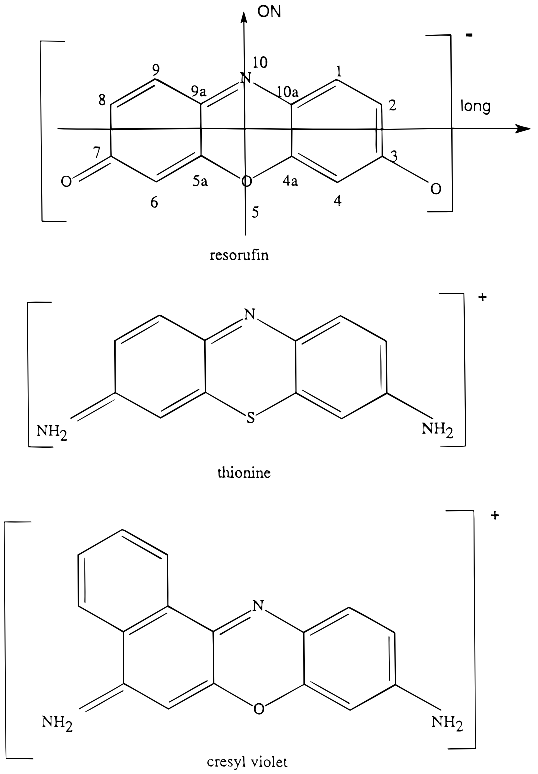

Figure 1. Molecular structures of resorufin, thionine, and cresyl violet are shown here. The number scheme on the carbon atoms is shown for the resorufin molecule (as an example).

chloride ion pairs in DMSO solution are performed to compare the rotational relaxation properties of the ion pair to that of the free cation. The comparison of the cation studies with those of the anion reveal two qualitatively different behaviors.

The outline of the manuscript is as follows. In the next section the experimental methods, the MD, and the electronic structure calculations are described. In section III the experimental results and a discussion of a continuum model description of the frictional coupling are presented. The analysis of the ion-pair formation for different systems is given in section IIIC. The results of the MD simulations are discussed in section IV.

II. Methods

A. Experiment Procedures. The time-resolved optical heterodyned polarization spectroscopy technique (OHPS) was used to study the rotational diffusion of thionine and cresyl violet in solution. This technique has been described in detail previously.[16,17] Briefly, a linearly polarized picosecond pulse excites molecules of a particular orientation and creates an anisotropy in the solution. Relaxation of the anisotropy as a function of time is detected by a second polarized light pulse that senses the sample dichroism. The measured relaxation represents the superposition of two processes, the anisotropy decay $r(t)$ and the population decay of the excited state $K(t)$, such that measured signal $T(t)$ has a time dependence

$$T(t) \propto r(t)\, K(t) \tag{1}$$

For the solutes studied here, the signal $T(t)$ and the excited-state population $K(t)$ are both well approximated as exponential decays. Hence the anisotropy decay is well described by a single exponential. In this case the measured decay time τ_m is given by

$$\frac{1}{\tau_m} = \frac{1}{\tau_{or}} + \frac{1}{\tau_f} \tag{2}$$

where τ_f is the decay time constant of the excited state and τ_{or} is the relaxation time constant of the anisotropy. Under the conditions used here the anisotropy decays by rotational relaxation.[16] The fluorescence lifetime τ_f was measured in a separate experiment with the time correlated single photon counting method. Equation 2 was used to extract the rotational relaxation time from the data.

The time-resolved polarization spectrometer has been described previously.[17,8] The instrument consists of a picosecond laser system [cw modelocked Nd:YAG laser (Spectra Physics Series 3000) and a home-built dye laser], Michelson interferometer for performing pump/probe experiments, and a data acquisition system. The dye laser was tuned to 590−600 nm. All experiments were performed at room temperature (296 K). The data were measured 5−10 times and the average value was calculated.

A conductivity meter with a glass electrode (YSI Model No. 35) was used to measure the equivalent conductance of thionine chloride salt in DMSO solution and to determine the association constant and therefore the fraction of ion pairs.

The viscosity and density values of each solution were measured. Density measurements were done with a pycnometer of capacity 10 mL (Thomas Scientific). Viscosity was measured in a water bath at 298 K with a calibrated Ubbelohde bulb viscometer (Thomas Scientific) and had an accuracy of 2−3%. Dielectric parameters for each solution were taken from the literature.[18,19]

Thionine (acetate salt) and cresyl violet (perchlorate salt) were used as received (from Aldrich). LiCl salt was dried for 24 h before use. DMSO (Aldrich, 99%) was treated with molecular sieves.

B. Molecular Dynamics and *ab Initio* Calculations. Electronic structure calculations were performed with Gaussian 94[20]. The geometry optimization and electron density calculations were performed at the Hartree−Fock level with a 3-21G basis set. The Tomasi algorithm[33] was used for the calculation of the electronic density in a continuum dielectric with a van der Waals cavity around the molecule. The atomic radii were taken from the OPLS force field.[21] Partial charges on the molecules in the DMSO were fitted by using the Merz−Singh−Kollman method.[22,23]

Molecular dynamics (MD) simulations of the resorufin-Li and thionine-Cl ion pairs in a model DMSO solvent were performed with AMBER4.1[24]. The simulation used an artificial ion pair (resorufin−

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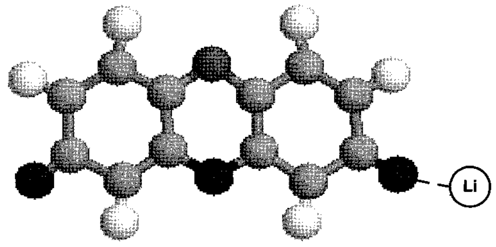
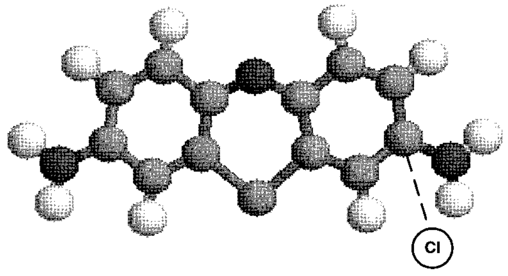


resorufin - Li



thionine - Cl

Figure 2. Molecular structures are shown for the ion paired species (thionine-Cl and resorufin−Li), excluding solvent.

Table 1. Viscosity and Rotational Relaxation Time of Resorufin and Thionine in LiCl/DMSO and LiCl/Methanol Solutions

	τ_{or} (ps)	τ_{or}/η (ps/cP)	τ_{or} (ps)	τ_{or}/η (ps/cP)
	DMSO ($\eta = 1.99$ cP)		methanol ($\eta = 0.55$ cP)	
resorufin	91 ± 7	46 ± 4	70 ± 6	127 ± 11
thionine	302 ± 46	152 ± 23	84 ± 4	152 ± 8
	DMSO/1.0M LiCl ($\eta = 4.9$ cP)		Methanol/1.0M LiCl ($\eta = 0.94$ cP)	
resorufin	397 ± 15	81 ± 3	160 ± 14	170 ± 15
thionine	502 ± 8	124 ± 2	115 ± 13	122 ± 14

Li in one case and thionine−Cl in the other) as the solute. The structure of the ion pair and the atomic partial charges were taken from an ab initio geometry optimization calculation. The resorufin−Li ion pair contained an O^-−Li^+ bond to keep the resorufin and the Li^+ in the paired configuration during the course of the simulation. Similarly, thionine and Cl^- were connected by an artificial C−Cl^- bond as shown in Figure 2. Nonbonded interactions were calculated by using a pairwise potential consisting of a Lennard-Jones term, Coulombic term, and reaction potential term within a 10-Å cutoff radius (to account for the long-range electrostatic interactions[25]). The partial charges on the atoms of the solute molecules are provided in Table 1 of the Supporting Information. The solvent consisted of 324 DMSO molecules contained in a cubic box, 35 Å on a side. Parameters used to model the DMSO molecule were taken from ref 26.

MD simulations were carried out as follows. First, an energy minimization of 10 000 steps was performed. Then a 10 ps constant pressure MD trajectory with a gradual rise of temperature up to 298 K was performed. Third, a 40 ps constant pressure, constant temperature, equilibration MD was computed. Last, equilibrium MD trajectories were collected at $T = 300$ K and a constant volume, for about 2 ns.

III. Results and Discussion

A. Rotational Relaxation of Cations and Its Analysis in Continuum Representation. The rotational relaxation of the cations in DMSO and methanol electrolyte solutions was measured for concentrations from 0.0 to1.0 M. A complete set of data is provided in Table 2 of the Supporting Information. In all cases the observed signal was well characterized by a single exponential decay law. Figure 3 shows the dependence of the rotational relaxation time of thionine and cresyl violet on salt concentration. The rotational relaxation time increases as the concentration of the salt increases for all the systems studied. This effect is qualitatively similar in both DMSO and methanol solutions. The rotation time of both cation solutes increases by 70% between pure DMSO and 1.0 M LiCl/DMSO solution, and by 36% between pure methanol and 1.0 M LiCl/methanol solution. However, this increase in relaxation time is smaller than that observed for the resorufin,[8] where the relaxation time increased by over 300% between pure DMSO and 1.0 M LiCl/DMSO solution and by over 115% between pure methanol and 1.0 M LiCl/methanol solution.

Table 2. Ion Pair Fraction Y_{ip} for Lithium Resorufin and Thionine Chloride DMSO Solutions

	c (mol/L)				
	0.1	0.25	0.5	0.75	1
thionine chloride	0.05	0.09	0.13	0.17	0.25
resorufin lithium	0.58	0.72	0.79	0.82	0.86

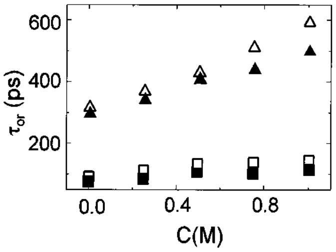


Figure 3. The rotational relaxation times are shown for thionine (solid triangles) and cresyl violet (open triangles) in LiCl/DMSO and thionine (solid squares) and cresyl violet (open squares) in LiCl/methanol.

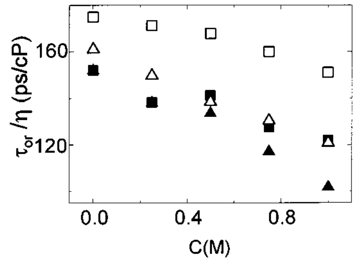


Figure 4. Dependence of the viscosity normalized relaxation time is plotted versus electrolyte concentration. The code for the symbols is given in the caption for Figure 3.

For many solutes in a wide range of solvents the rotational relaxation time is observed to be proportional to the viscosity η of the solution. Such dependence is predicted by the hydrodynamic Debye−Stokes−Einstein (DSE) model[34,35]

$$\tau_{or} = \frac{CV}{6kT}\eta \tag{3}$$

where C is the appropriate boundary condition coefficient and V is the hydrodynamic volume of the solute. A linear correlation between the relaxation time and the solution viscosity is often observed, even in a size regime (i.e. relative solute to solvent size) where the DSE model might be expected to fail.[35] Figure 4 shows the concentration dependence of the viscosity normalized relaxation time versus concentration of electrolyte for DMSO and methanol solution. If the relaxation time were controlled only by the viscosity, then no concentration depen-

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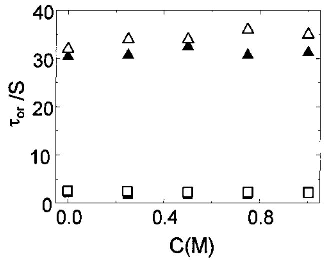

Figure 5. The relaxation times normalized by the dielectric parameters are plotted against the electrolyte concentration for thionine (solid triangles) and cresyl violet (open triangles) in LiCl/DMSO and thionine (solid squares) and cresyl violet (open squares) in LiCl/methanol. (Note that the solid squares are nearly hidden by, i.e., indistinguishable from, the open squares.)

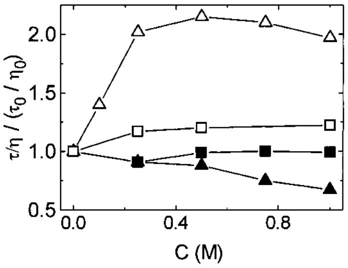

Figure 6. The renormalized relaxation times of thionine and resorufin are plotted versus the concentration of LiCl electrolyte solution (thionine (solid triangles) and resorufin (open triangles) in DMSO; thionine (solid squares) and resorufin (open squares) in methanol.

dence would be found. It is clear from the data, however, that an increase in the electrolyte concentration causes a decrease in the normalized relaxation time of the cation. This result stands in contrast to the case of the resorufin where the relaxation time normalized to the solution viscosity increases in DMSO and methanol solutions (see Figure 6).

These results show that the change in the rotation time is not controlled by the viscosity of the solution alone. Other factors contribute to the observed dependence of τ_{or} on the salt concentration. In electrolyte solution electrostatic interactions can play an important role.[1] The dielectric properties of the solution (Debye relaxation time τ_D and the dielectric constant ϵ_s) and local structure ($g(r)$) depend on the salt concentration and so the solute dynamics will be affected by their change. One approach to describing the dependence of the solute dynamics on the dielectric properties of the solvent is to use a dielectric continuum model for the frictional coupling. Such a model for the rotational relaxation time τ_{or} leads to an explicit dependence of the relaxation time on the dielectric parameters of the solution. This dependence is approximately given by[27-29]

$$\tau_{or} \propto \frac{\epsilon_s - 1}{(2\epsilon_s + 1)^2}\tau_D \equiv S \tag{4}$$

A continuum model is expected to be reasonable when the local solute−solvent interactions are weak compared to kT and the solvent does not have long-range structure. Figure 5 plots the rotational relaxation times normalized by S (see eq 4). It can be seen from this plot that the relaxation time of cations correlates well with the dielectric parameters. This observation suggests that electrostatic interactions dominate the dynamics of the cationic solute in electrolyte systems. On the contrary, the rotational relaxation time of resorufin normalized by the dielectric parameters increases with the electrolyte concentration,[7] hence the anion requires a more complicated analysis to describe its rotational dynamics.

B. Comparison of the Resorufin Anion and the Thionine Cation. The difference in the rotational relaxation behavior of resorufin and thionine must lie with their different intermolecular interaction with the solvent. Because the size, shape, and magnitude of the charge on the molecules is similar one would expect, based on continuum models, similar rotational relaxation behavior in the electrolyte solution. The difference in the behavior of the two solutes indicates that molecular considerations are needed. The solutes differ by the sign of the charge and the nature of the functionalities on the chromophore, NH_2 for thionine and O for resorufin.

For comparison, the rotational relaxation times of resorufin and thionine are presented in Table 1 for the case of pure solvent and 1.0 M LiCl electrolyte solutions. The thionine ion exhibits a longer relaxation time than resorufin ion in pure DMSO. A recent extensive MD and experimental study of resorufin and thionine in pure DMSO solvent[15] reveals that the slower dynamics of the thionine can be explained by the stronger local coupling with DMSO molecules. By contrast, resorufin does not show any DMSO association features in that study.[15] Table 1 shows that the rotational relaxation time τ_{or} increases as the concentration of salt increases for both the cation and the anion solutes. However, this increase is smaller for the thionine cation than for the resorufin anion. While the τ_{or} of resorufin increases four times from pure DMSO to 1.0 M LiCl/DMSO solution, the τ_{or} of thionine increases only one and a half times from pure DMSO to 1.0 M LiCl/DMSO solution. The same but less pronounced trend was observed for thionine and resorufin in LiCl/methanol solution.

Figure 6 plots a renormalized rotational relaxation time versus electrolyte concentration. In this graph the viscosity normalized relaxation time τ/η is divided by the viscosity normalized relaxation time in the pure solvent τ_0/η_0. This renormalization scales the data so that resorufin and thionine may be directly compared. The renormalized relaxation time **increases** by a factor of 2 for the resorufin anion and **decreases** by over 40% for thionine cation. Thus, the trends for the normalized relaxation times of the cation and the anion are in opposite directions. This trend is similar for all the DMSO electrolyte solutions studied. These trends are smaller for the data in the methanol solvent, but still evident. The same trends can also be identified in the data obtained in earlier work.[5,6] Clearly, a continuum based model will not be able to account for this qualitative difference in behavior. Rather, a model that includes structural features of electrolyte and/or solvent is required.

An earlier study for resorufin in salt solution attributed the increase in the rotational relaxation time to the formation of resorufin−Li ion pairs, which exhibit much longer relaxation times than the free solute.[7,8] By choosing a cavity radius that accounted for the size of the ion pair−DMSO complex, the continuum model provided reasonable agreement with the experimental observations. Because of the importance of ion pairing in the resorufin system, and its possible importance for the thionine studies, the role of ion pairs was investigated for the thionine.

C. Characterizing the Ion Pair. The conductivity of thionine chloride solution and its dependence on salt concentration were measured to determine the association constant of the salt. Using the Ostwald Dilution law and Kolrausch's law[30] one can estimate the association constant K_1 for the association reaction $thn^+ + Cl^- = thnCl$. Both these models are appropriate over the concentration range of $10^{-3}-10^{-4}$ M. The fraction of free thionine, Y_{fr}, and ion-paired thionine, Y_{ip}, were estimated assuming coupled equilibria for Cl^- in the solution ($Li^+ + Cl^- = LiCl$ and $thn^+ + Cl^- = thnCl$, see Table 2). By using an association constant for LiCl of 10 M^{-1}, the conductivity data show that the association constant for the thionine−Cl ion pair is 5 M^{-1}. This equilibrium constant predicts about 25% ion pairs at a 1.0 M concentration of LiCl. A lower limit on the lifetime of the ion-paired thionine was evaluated by using the Smoluchowski model, which assumes that the ion pair forms without any activation barrier when ions encounter each other.[7,31] The estimated lifetime of the ion-paired thionine is about 300 ps, which is comparable to the rotational relaxation time of the free thionine. Hence conductivity measurements show that a noticeable ion pairing occurs for the thionine case and could play a role in the rotational relaxation.

The ion pairs were also studied via electronic structure ab initio calculations. To find the possible ion-pair configuration, the potential energy landscape for the thionine−Cl complex was explored in *vacuo*. These calculations revealed the existence of a global energy minimum. The geometry of the corresponding complex was further refined by standard geometry optimization. The association energy of the thionine−Cl and resorufin−Li complexes in DMSO solution were estimated as

$$\Delta G_{ass} = \Delta G_{cmplx}^{vac} + \Delta G_{cmplx}^{DMSO} - \Delta G_{solute}^{DMSO} - \Delta G_{ion}^{DMSO} \quad (5)$$

where ΔG_{cmplx}^{vac} (with cmplx being the complex thionine−Cl or resorufin−Li) is the free energy change for the creation of the ion pair in a vacuum and

$$\Delta G_{cmplx}^{DMSO},\ \Delta G_{solute}^{DMSO},\ \text{and}\ \Delta G_{ion}^{DMSO}$$

are the corresponding solvation energies for the complex, the solute, and the ion. The ion pairs free energy ΔG_{cmplx}^{vac} was estimated by an ab initio electronic structure calculation in a vacuum at the Hartree−Fock level with a 6-311G basis set. The solvation energies were calculated with the DelPhi program.[32] This program uses a continuum dielectric and numerically solves the Poisson equation for the electrostatic potential. The solvent was modeled as a continuum dielectric medium with the dielectric constant $\epsilon = 47$. The other parameters in the model were the radius of a solvent molecule ($r_s = 2.4$ Å) and the van der Waals radii of the solute's constituent atoms ($R_C = 2.3$ Å, $R_H = 1.25$ Å, $R_O = 1.7$ Å, $R_S = 1.9$ Å, $R_N = 1.9$ Å, $R_{Li} = 1.25$ Å, $R_{Cl} = 2.4$ Å).

The free energy ΔG_{ass} was found to be 7 kT for the thionine−Cl and was found to be −17 kT for the resorufin−Li ion. Despite the low level of the computational methods and the poor quantitative agreement with experiment, these calculations agree qualitatively with the experimental observation. Namely, the association constant measured for the lithium−resorufin ion pair is larger than that measured for the thionine−chloride ion pair. Therefore the fraction of ion pairs formed by resorufin is greater than the fraction of ion pairs formed by thionine at the same electrolyte concentration. For comparison, the measured association constants predict that the fractions of the ion pairs formed by thionine and resorufin in 1.0 M LiCl/DMSO solution are 25% and 88%, respectively. Thus, the dynamics of the solute is determined largely by the rotation of the ion pairs in the resorufin case, while it is less clear how important ion pairing is for the rotational relaxation of the thionine.

IV. Molecular Dynamics Analysis of the Resorufin and Thionine Rotational Relaxation

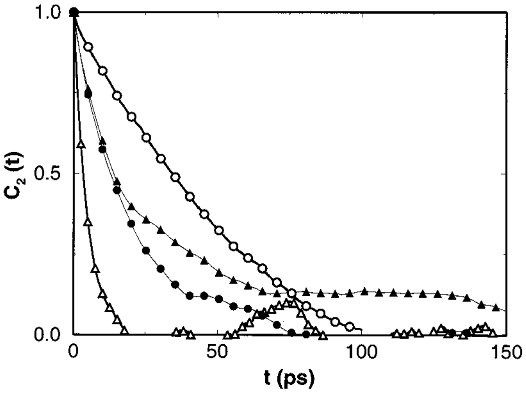

Figure 7. Rotational correlation functions $C_2(t)$ are shown for thionine (solid triangles), thionine−Cl (solid circles), resorufin (open triangles), and resorufin−Li (open circles).

Table 3. Rotational Relaxation Times Calculated from MD Simulations in DMSO Solvent

solute	τ_{or} (ps)
resorufin	6
resorufin lithium	40
thionine	50
thionine chloride	20

Molecular dynamics simulations provide a means to explore the molecular details of the solute−solvent interactions. Several possible geometries and stoichiometries of the solute molecule with the salt ions and the solvent molecules may exist simultaneously in the solution. Each of these species can have different relaxation times. While the OHPS experiment probes an effective rotational relaxation that is averaged over all the species, the MD method may be exploited to study relaxation properties of the free and ion-paired molecules in DMSO solution separately from each other.

The MD simulations of the ion-paired resorufin and ion-paired thionine in DMSO are compared with MD data on the free resorufin and thionine which are reported in detail in ref 15. Figure 7 shows the rotational correlation functions

$$C_2(t) = \langle P_2(\vec{\mu}(t)\cdot\vec{\mu}(0))\rangle$$

calculated from the MD data on free and ion-paired solutes. $P_2(x)$ denotes the second rank Legendre function and $\vec{\mu}(t)$ is the solute's dipole moment vector. The analysis of the correlation functions revealed that the resorufin correlation function decays exponentially with time, while the rest of the solutes exhibit multiexponential relaxation. It was shown in ref 15 that free resorufin does not experience prolonged solvent attachment in DMSO solution but free thionine attracts several DMSO molecules by its NH_2 groups. The thionine−DMSO complex had a lifetime comparable with the characteristic time of the thionine relaxation in the MD simulation.

The relaxation times of the four species were calculated from the MD trajectories as

$$\tau_{or} = \int C_2(t)\, dt$$

The calculated values of τ_{or} are provided in Table 3. The relaxation times obtained from the simulations are several times smaller than those measured experimentally. The reasons for this difference in absolute value and a discussion of the MD method's deficiency in the quantitative description of the collective dynamical properties of the system are discussed elsewhere.[15] A comparison of the t_{or} values from the MD with the experimental values demonstrates that the simulation reproduces the correct trend in the rotational relaxation times

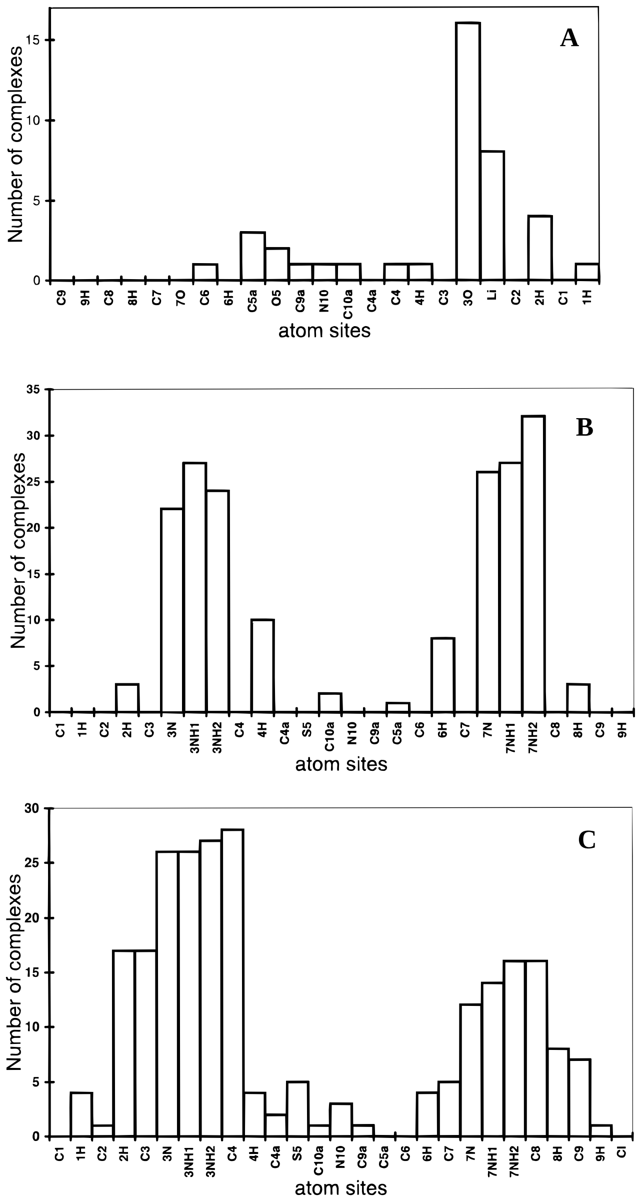

Figure 8. Distributions of the DMSO−solute complexes with different solute atoms: (A) for resorufin−Li, (B) for thionine, and (C) for thionine−Cl.

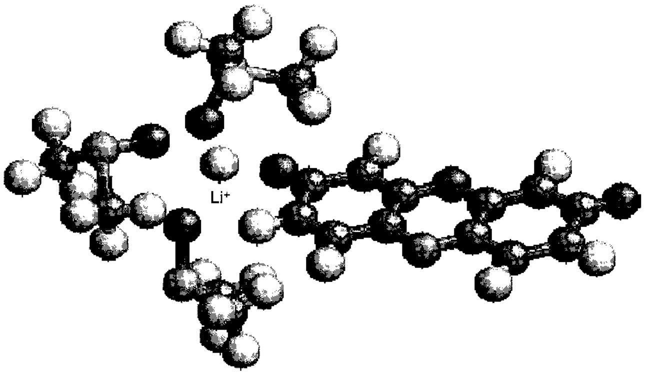

Figure 9. A resorufin−Li/DMSO complex is shown.

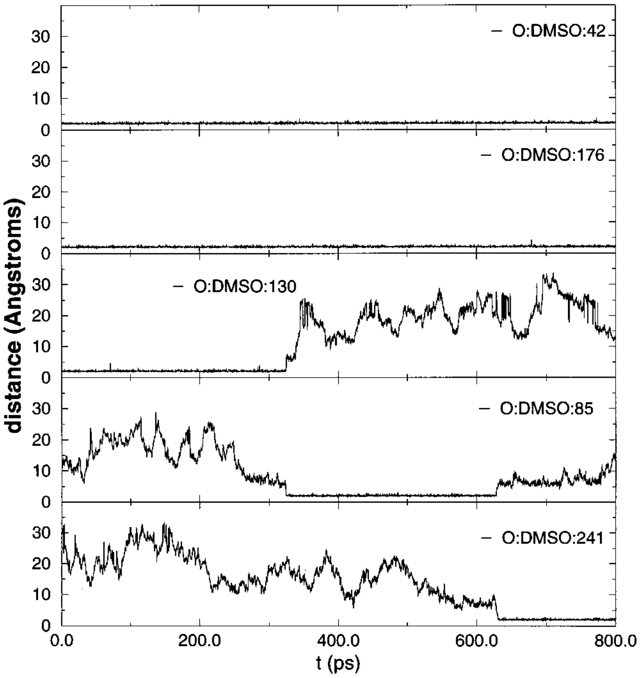

Figure 10. The time evolution of the distance between the Li^+ ion and the O atom of different associated DMSO molecules is shown over an 800 ps span of an MD trajectory. Label numbers of the DMSO molecules are indicated on the corresponding plots.

of the dyes in pure DMSO. Resorufin has the smallest rotational relaxation time. Thionine rotates much more slowly than resorufin. Furthermore, the relaxation time of the resorufin−Li ion pair is significantly longer than that of free resorufin. In contrast, the relaxation time of the thionine chloride ion pair is smaller than that of free thionine.

The origin of these trends in the normalized relaxation time becomes evident upon performing a detailed analysis of the solute−solvent interactions. In each case pronounced differences in the ability of the solute molecules to associate with DMSO are revealed. To perform a detailed analysis it is necessary to define a solute−solvent complex. The criterion chosen to define a solute−solvent complex is that the oxygen atom of a DMSO molecule must reside in close proximity (less than 4 Å) to an atom of the solute for a time longer than 20 ps during the course of the MD trajectory. Figure 8 shows a histogram of the number of such solvent association events as a function of the solute atom site.

It is clear from Figure 8A that the resorufin−lithium ion pair attracts DMSO molecules via the Li^+ ion; i.e., the Li^+ of the ion pair serves as an association site. It is this feature of the resorufin ion pair that causes the large increase in its rotational relaxation time over that for resorufin in DMSO. A characteristic geometry of the resorufin−lithium/DMSO complex is shown in Figure 9. Three DMSO molecules arrange themselves into the indicated geometry during the MD run. For any particular DMSO molecule the residence lifetime in the complex ranged from 200 to 1000 ps. The time evolution of the distance between the O atom of the associated DMSO molecules and the Li^+ ion is shown over an 800 ps time span in Figure 10. The typical distance between the oxygen atom of an associated DMSO molecule and Li^+ was about 2 Å. Two sites in the complex were continuously occupied by the same DMSO molecules throughout the trajectory. The third site in the ion pair−solvent complex was occupied by three DMSO molecules interchangeably (see Figure 10). The dramatic increase in rotation time of resorufin in the presence of the LiCl salt was explained earlier[7,8] in terms of the ion pairing of resorufin and Li^+ in Rf/LiCl/DMSO solution. The MD results support the idea that the complexation of DMSO around the resorufin−Li ion pair results in a dramatic increase in the rotational relaxation time (40 ps for the ion pair vs 6 ps for the free resorufin

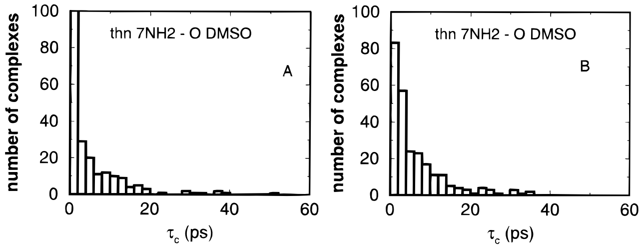

Figure 11. Plots of the distribution of lifetimes of the DMSO−solute complexes: (a) for thionine and (b) for thionine-Cl.

in the MD solvent). This static regime for the effect of solvent association is consistent with ideas concerning the use of a hydrodynamic volume to account for the size of the rotating body and hence its enhanced friction in associating systems.[36]

In the case of the thionine and thionine−Cl ion pair, the effect of the thionine and Cl^- association is opposite to the resorufin−Li case. The thionine−Cl ion pair rotates somewhat faster than the free solute. Figure 8B shows that two DMSO association sites are supplied by the thionine molecule. These sites are the NH_2 side groups. The Cl^- ion by itself does not interact strongly with DMSO solvent. Moreover, when it occupies the side adjacent to one of the two NH_2 thionine side groups to form an ion pair, it blocks the DMSO molecules from associating at the site. In Figure 8C the peak on the right-hand side is lower than the one on the left-hand side, which indicates that the NH_2 group occupied by the Cl^- associates less strongly with DMSO than does the vacant site. Thus, the Cl^- ion reduces the extent of local solute−solvent attractive interactions.

The character of thionine's interaction with the solvent is very different from that of the resorufin ion pair. Figure 11 presents the distribution of the lifetimes for DMSO molecules associated with thionine and the thionine−Cl complex. In this case, a complex was defined as present when the O atom of the DMSO was within 4 Å of the solute atom. Although the decay of the histogram is nearly exponential, several long-lived complexes can be identified. Even considering these few longer lifetime complexes, it is evident that the time scale for the dissociation of a solvent complex is shorter than the 50 ps time scale for the thionine's rotational relaxation. In short, a dynamical equilibrium exists between the solvent associated thionine and the free thionine on the rotational time scale.

Another aspect of the system's properties is that the neutral thionine−Cl complex experiences weaker long-range interactions with the polar solvent than does the positively charged thionine. For example, the dielectric friction term calculated by the AW formula[29] is smaller for thionine−Cl than for thionine. Both effects, short-range solute−DMSO interactions and the long-range collective relaxation, contribute to a faster rotational relaxation for the thionine−Cl as compared to thionine. This change in the long-range interactions also applies when comparing the resorufin−lithium ion pairs with resorufin. However, the impact of this effect on the rotational relaxation time is smaller because of the large increase in the rotational relaxation time that results from the high mechanical friction of the large resorufin−lithium/DMSO complex.

These insights from the MD studies provide an answer to the question, "Why does the experimentally observed salt dependence of the rotation relaxation time for the thionine correlate with the solution's dielectric parameters, but that for resorufin does not?" For thionine, the change in the local solvent−solute interactions as salt is being added to the DMSO solvent does not dramatically change the rotational relaxation time. First, it is clear that fewer ion pairs are formed as compared to resorufin at similar electrolyte concentrations. Second, the association of Cl^- with thionine occurs at a DMSO association site. For this reason (the ion pair displaces a DMSO molecule), the rotational relaxation of the ion pair is not that different from the thionine associated with DMSO. A change in the longer range solute−solvent interaction with electrolyte concentration also occurs, but the change in dielectric parameters is able to mimic this effect reasonably well. The resorufin case is qualitatively different. The free resorufin in the pure DMSO does not associate with the DMSO. When LiCl is added to the solution, the resorufin strongly associates with the Li^+ ion. The subsequent strong attachment of several DMSO molecules to the ion pair creates a long-lived structure in the solution. The addition of the salt into the solvent causes a qualitative change in the character of the solute−solvent interactions. To successfully apply a continuum model formalism to resorufin in DMSO/electrolyte solution, one must consider the resorufin−Li^+/DMSO complex as a whole entity because its lifetime is long compared to the rotational time scale.

V. Conclusions

In this work, spectroscopic experiments, conductivity measurements, and MD simulations of the rotation of ionic molecules in electrolyte solutions have been used to investigate the mechanisms of solute−solvent interactions. The experimental data show that the solute rotational relaxation time increases as the salt concentration rises, in the case of both thionine and resorufin. The increase of the relaxation time τ_{or} is more significant for the anions than the cations. A plot of the normalized rotational relaxation time vs electrolyte concentration (Figure 6) reveals significant differences between the behavior of the organic cations and anion studied. While the normalized relaxation time increases dramatically with the electrolyte concentration for resorufin anion, it decreases with electrolyte concentration for the cations, thionine and cresyl violet.

Theoretical analyses of the experimental data were performed with both continuum and molecular models. It was concluded that the formation of an ion pair for resorufin causes a change in the local structure of the solvent around the solute, in particular the strong coordination of the DMSO molecules with the resorufin−Li ion pair. The continuum model, appropriate for the case when the local interactions are weak, fails to describe the dynamics of the anion in DMSO/electrolyte solution. The slow relaxation of the resorufin−Li ion pair can be satisfactorily explained if the molecular complex formed in the solution is treated as one rotating unit of a size larger than that of the free molecule, as done in ref 8. For thionine, the situation is different. In pure DMSO solution, the MD simulations reveal that the DMSO−thionine association is significant and it causes an increase in friction relative to the free resorufin in DMSO. This observation is consistent with the longer τ_{or} values measured for thionine. The experimentally observed decrease in the normalized relaxation time with electrolyte concentration reflects a correlation of the rotational relaxation time on the dielectric properties of the solution. This trend occurs despite the presence of thionine−Cl ion pairs in solution. The MD simulations show that the rotational relaxation of the thionine−Cl ion pair is faster than that of the free thionine (Figure 7 and Table 3). Both the change in dielectric parameters with electrolyte concentration and ion pairing contribute to a decreasing normalized relaxation time for the thionine in LiCl/DMSO solution.

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(36) (a) Spears K. G.; Steinmetz K. M. *J. Phys. Chem.* **1985**, *89*, 3623. (b) Zwanzig, R.; Harrison, A. K. *J. Chem. Phys.* **1985**, *83*, 5861.

This study compared the relaxation dynamics of a cation and an anion (thionine and resorufin) in DMSO solution. A combination of MD simulation and experiment was used to elucidate the mechanisms responsible for the observed differences in their behavior. For the resorufin anion the formation of an ion-paired species (resorufin−Li^+) increases the coupling with the solvent and hence the rotational relaxation time. In contrast, for the thionine cation the formation of an ion-paired species (thionine−Cl^-) decreases the coupling with the solvent and hence the rotational relaxation time. This behavior underscores the subtleties present when considering specific solute−solvent interaction and their impact on dynamics. On a more general level, this study demonstrates that ion-paired species may exist as discrete entities for times long compared to the rotational time scale of the solute molecules.

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Supplementary Information Available: List of partial charges for the solute molecules used in the MD simulations and experimental data on the dielectric and viscous properties of the solvents (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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