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A test of continuum models for dielectric friction. Rotational diffusion of phenoxazine dyes in dimethylsulfoxide

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Rotational diffusion times for three mechanically similar phenoxazine dyes with differing electronic properties were measured. These studies probe the importance of dipole/dipole and ion/dipole couplings to the friction. The experimental results are compared with the predictions of available continuum theories of dielectric friction. Future directions for a more realistic model of dielectric friction are discussed.

INTRODUCTION

The appropriate description for the rotational relaxation of medium sized solute molecules (displaced volume of a few hundred cubic angstroms) in simple solvents remains an open issue. This size range probes the transition from a characteristically molecular regime to a continuum regime for the solvent. For weakly interacting fluids where the solute and the solvent are the same approximate size a kinetic description of the rotation is most appropriate.¹⁻³ When the solute is much larger than the solvent a diffusion based description is appropriate. In this limit the diffusion coefficient, and through the Einstein relation the friction, is adequately described by a continuum model of the fluid. The transition between these regimes and the relationship between molecular properties and the friction are less clearly understood.

Considerable experimental and theoretical effort has been focussed on the description of friction for solute molecules in this intermediate regime. Reviews of this work are available.⁴⁻⁶ The understanding of the experimental results is usually discussed in terms of hydrodynamics or other continuum based theories. Workers⁷⁻¹³ have shown that for a single solute in a single solvent the dependence of the rotational relaxation time on the solvent viscosity is as predicted by the hydrodynamic model, if physical parameters of the system (pressure and temperature) are varied. In contrast a wide range of observations are found when solute and solvent properties such as size, charge, and polarity are varied. Often specific molecular interactions are invoked to explain these observations. Noteworthy is recent progress toward understanding the role played by size and roughness of the solute on the rotational relaxation.¹⁴⁻¹⁶ The present work initiates a study of the influence of solute charge and solute dipole moment on the rotational relaxation rate and hence the friction.

In recent years workers^{11,35,47-49} have investigated the influence of dielectric friction on the rotational relaxation of medium sized molecules. Most of these studies have been performed with a single solute in a series of solvents, which changes the solute/solvent interaction potential. A test of continuum dielectric friction theories is needed in a single solvent where the solvent properties are changed by a change in temperature and/or pressure. Furthermore, all of the pre-

vious workers compare the relaxation of a charged solute with models developed for dipolar but uncharged solutes. Because of the uncertainty in defining a dipole moment for an ion (should the choice of origin be the center of mass or the center of hydrodynamic stress) and the different electrostatic fields for ions and dipoles, these models are not appropriate for comparison with the data. A better test of these models will be provided by the study of an uncharged, dipolar solute molecule.

The rotational relaxation of three mechanically similar solute molecules is studied in dimethylsulfoxide (DMSO) as a function of temperature. These three solute molecules possess distinct electrical properties (see Fig. 1). Resorufamine is uncharged but dipolar. By studying the rotational relaxation in both its ground and excited electronic states it is possible to quantitatively ascertain the influence of dipole moment strength on the hydrodynamic boundary condition. Resorufin is an anion and oxazine is a cation. Comparison of the rotational relaxation of these molecules addresses the importance of charge and in particular its sign to the friction. The experimental observations can be interpreted in two

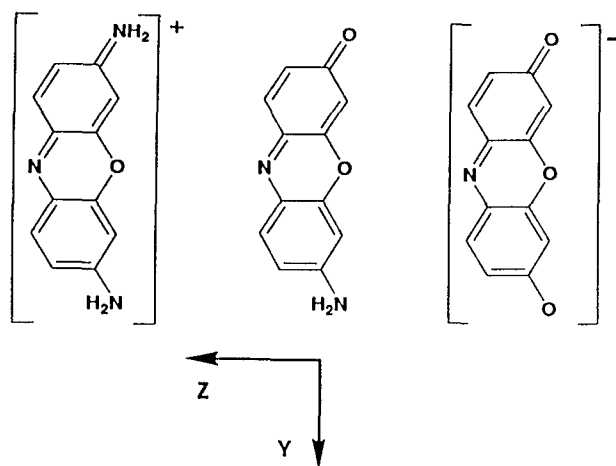


FIG. 1. Molecular structures for the three solute molecules is shown along with the definition of a molecular axis system. The cation is referred to as oxazine, the anion is resorufin and the uncharged compound is referred to as resorufamine.

ways, a changing hydrodynamic boundary condition and dielectric friction.

The remainder of this paper is organized as follows. First is background on currently available continuum theories which include both hydrodynamic and dielectric friction. The second section contains experimental details of the rotational diffusion studies undertaken, including the technique for measuring the second order orientational correlation function $r(t)$, the laser apparatus used for the pump/probe experiments, and the synthesis and characterization of the solutes and solvent. In the next section are presented the experimental results and their analysis in terms of continuum friction theories. Lastly, the conclusions of this work are drawn.

BACKGROUND THEORY

Hydrodynamic friction theory

The Debye–Stokes–Einstein (DSE) theory of rotational diffusion in liquids treats the solute as an ellipsoid immersed in a continuum solvent and uses hydrodynamics to calculate the rotational friction.^{5,6,16–19} This leads to the prediction that the reorientation time τ_{or} should be proportional to the solvent viscosity divided by absolute temperature, η/T . More specifically,

$$\tau_{or} = \frac{\eta V F C}{T}, \quad (1)$$

where V is the solute molecular volume, k is the Boltzmann constant, F is a parameter which accounts for the solute shape (axial ratios), and C is a parameter which is determined by the boundary condition assumed in the hydrodynamic calculation of the friction. It is through these two parameters that the continuum theory accounts for the intermolecular potential between the solute and the solvent molecules.

The boundary condition used in the calculation of the hydrodynamic friction ranges from “slip” to “stick.” The stick boundary condition requires zero relative velocity between the surface of an object and the first layer of solvent. This boundary condition is appropriate for macroscopic objects and macromolecules. The slip boundary condition is so named because it specifies that the solvent can exert no tangential stress on an object. This boundary condition is considered appropriate for small to medium sized molecules in nonpolar, noninteracting solvents. Recent theoretical and experimental work has shown that the use of a slip boundary condition in conjunction with a molecular shape that is rough, or bumpy (i.e., not a smooth ellipsoid), results in a friction coefficient which approaches the stick value for the corresponding smooth shape as the size and roughness increase. The amount of roughness and the relative solute to solvent size required to proceed from the slip to stick limits are still not resolved.¹⁵ Lastly, some theoretical work has attempted to relate the intermolecular potential to the boundary condition.²⁰

Dielectric friction theories

A variety of treatments of dielectric friction are available.^{21–29} Of these, two general types are discussed here. First are models which treat the solvent as a dielectric con-

tinuum and model the solute as a sphere containing a point dipole^{21–25} or a point charge.^{26,27} Second is a semiempirical approach to the dielectric friction. Van der Zwan and Hynes²⁸ have shown how the fluorescence Stokes shift of the solute in the solvent of interest is related to the dielectric friction. Although molecular models of dielectric friction are available,^{29–31} they have either been applied to translational motion and require some knowledge of the intermolecular potential or require solvent properties such as translational diffusion coefficients. Comparisons with such models may be possible in the future.

Dipolar solute

The Nee–Zwanzig theory²¹ generates a frequency dependent friction coefficient by calculating the torque exerted on a point dipole rotating at the center of a spherical cavity in a continuous dielectric. The torque arises because the direction of the dipole’s reaction field lags behind the dipole’s orientation as a result of the frequency dependence of the dielectric constant. The friction coefficient is calculated in the limit of zero frequency for a medium exhibiting Debye relaxation behavior. This leads to the following expression for the reorientation time of a solute molecule with dipole moment μ :

$$\tau_{or} = \tau_{slip} + \frac{\mu^2}{kTa^3} \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)^2} \tau_D, \quad (2)$$

where a is the radius of the cavity in the dielectric occupied by the solute molecule, ϵ_s is the static dielectric constant, τ_D is the Debye relaxation time, T is the temperature, and μ is the dipole moment of the solute in vacuum. In this model a slip boundary condition between the solute and the solvent is implicitly assumed for the mechanical friction, and the high frequency dielectric constant is taken to be one.

More recently Hubbard and Wolynes²² employed a different method to calculate the friction. A rotational Smoluchowski equation with fluctuating torques is solved to obtain an expression for the dipole correlation time. In the limit that the torques arising from the polarization of the dielectric fluctuate much more rapidly than the dipole reorients, the Nee–Zwanzig expression is obtained. This regime is appropriate for the experimental studies presented here.

Hubbard²³ has derived an expression for the friction on a spherical dipole with a variable hydrodynamic boundary condition, which ranges from zero for slip to one for stick. The friction is determined by calculating the energy dissipation as the polar solute rotates within the frequency dependent dielectric. The resulting expression is

$$\tau_{or} = \tau_{\sigma} + \left(\frac{2}{3} - \frac{4\sigma}{3} + \frac{61\sigma^2}{60} \right) \frac{3\mu^2}{2kTa^3} \frac{(\epsilon_s - 1)\tau_D}{(2\epsilon_s + 1)^2} \quad (3)$$

and contains both mechanical and dielectric contributions to the friction. The time constant τ_{σ} is given as

$$\tau_{\sigma} = \frac{\eta V \sigma}{kT}. \quad (4)$$

Lastly, Felderhof²⁴ and Nowak²⁵ have developed models for the friction on a dipole which not only allows for an

arbitrary hydrodynamic boundary condition but generalizes this concept to an electrohydrodynamic boundary condition. Their method is to solve the hydrodynamic equation of motion where the stress tensor is modified to account for polarization from the dipole. The resulting expression for the time constant is

$$\tau_{or} = \tau_{\sigma} + \frac{3}{2} \frac{\mu^2 \tau_D}{kT a^3} \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)^2} \left[\left(\frac{2}{3} - \frac{4\sigma}{3} + \frac{61\sigma^2}{60} \right) + (\lambda - 1)(1 - \sigma) \left(\frac{2}{3} - \frac{103\sigma}{60} \right) \right], \quad (5)$$

where $\lambda = \lambda_{EL}/\lambda_H$ is the ratio of the electrohydrodynamic boundary condition, λ_{EL} , to the hydrodynamic boundary condition, λ_H which is given by

$$\sigma = \frac{a}{a + 3\lambda_H}. \quad (6)$$

Ionic solute

In a similar manner Felderhof²⁶ and Nowak²⁵ have treated the case of a point charge rotating in a spherical cavity. The expression for the friction is found to be

$$\tau_{or} = \tau \{ 1 - \sigma J(\alpha') + (1 - \sigma)(\lambda - 1)[\alpha'/(1 + \alpha')] \}^{-1} \quad (7)$$

where α' is given by

$$\alpha' = \frac{Q^2 \tau_D}{16\pi\eta} \frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_s^2} \frac{1}{a^4} \quad (8)$$

and the function $J(x)$ is

$$J(x) = 1 - 3 \int_1^{\infty} dy \frac{1}{y^4 + x} \quad (9)$$

and has been tabulated by Felderhof.²⁶

Semiempirical model

Van der Zwan and Hynes²⁸ relate the dielectric friction experienced by a solute in a solvent to the correlation time for solvation τ_s and the solute Stokes shift S in the solvent. S is given as $v_A - v_F$, where v_A is the energy of the zero-zero transition for absorption and v_F is the energy of the zero-zero transition for fluorescence. Their result is

$$\zeta_D(\Delta\mu) = S\tau_s, \quad (10)$$

where $\Delta\mu$ is the change in dipole moment upon excitation. Numerous studies of solvation dynamics³²⁻³⁴ indicate that the solvation time τ_s is approximately given by $\tau_i[\tau_D(\epsilon_{\infty}/\epsilon_s)]$ and relatively independent of the solute properties. This relationship holds to within a factor of 2 or 3, despite the fact that the model which predicts τ_i for the characteristic solvation time also predicts single exponential relaxation for the solvent response whereas the observed dynamics is nonexponential. The expression for the dielectric friction in electronic state i is given by

$$\zeta_D(\mu_i) = \mu_i^2 S \tau_s / (\Delta\mu)^2 \quad (11)$$

which is just a rescaling of Eq. (10) from a dipole strength of $\Delta\mu$ to one of μ_i . Following Simon,³⁵ if one assumes that the total friction is a sum of mechanical and dielectric contribu-

tions then the rotation time is given by

$$\tau_{or} = \tau_{hyd} + \frac{1}{6kT} \frac{\mu^2}{(\Delta\mu)^2} S \tau_s. \quad (12)$$

EXPERIMENT

Optically heterodyned polarization spectroscopy

The technique of optically heterodyned polarization spectroscopy (OHPS) was used to measure the second order orientational correlation function in a state specific manner,

$$r(t) = \frac{1}{2} \langle P_2[\mu(0) \cdot \mu(t)] \rangle, \quad (13)$$

where μ is the transition moment and $P_2(x)$ is the second Legendre polynomial. This pump/probe technique has been described in detail earlier,³⁶ and more recent refinements will be described here. Briefly, a linearly polarized pump pulse creates anisotropic distributions of both ground and excited state molecules. The transmission (T) of a copropagating, noncollinear probe pulse, linearly polarized 45° from the pump polarization, is monitored through an analyzer polarizer. If δ_D is the angle (radians) between the analyzer transmission axis and its crossed position, then the fraction of probe light transmitted is

$$T = \frac{1}{4} \exp\left(\frac{-\sigma_0 dK}{3}\right) \left| \frac{dK^{(1)}(t)r(t)}{2} + i\phi(t) + \delta_D \left(2 + \frac{d\sigma_0 K^{(1)}(t)}{3} + \frac{dK^{(1)}(t)r(t)}{6} \right) \right|^2, \quad (14)$$

where σ_0 is the absorption cross section, K is the total dye concentration, d is the sample thickness, $K^{(1)}(t)$ is the excited state concentration, and $\phi(t)$ is the birefringent part of the signal. Expansion of this expression results in terms which are constant, linear, and quadratic with respect to δ_D . The dichroic part of the signal, which varies linearly with δ_D is the term of interest in this experiment.

In the earlier characterization of this technique, this linear term had been isolated by chopping the pump beam, which eliminated the $4\delta_D^2$ term, and making δ_D large enough that the linear term dominated the constant term, but not so large that the remaining quadratic terms became significant. This procedure was inexact, and typically led to systematic errors of up to 5% in the measurement of decay times. A refinement of the technique has since been developed to isolate the linear term in an unambiguous way.

In the improved procedure, two decays are collected in rapid succession, one with the analyzer at $+\delta_D$ and the other at $-\delta_D$. These two decays are subtracted, which cancels the constant and quadratic terms, leaving only the linear term (Fig. 2).

$$T = \frac{\delta_D}{2} \exp\left(\frac{-\sigma_0 dK}{3}\right) \times \left[dK^{(1)}(t)r(t) + \frac{d^2(K^{(1)}(t))^2}{6} \left(\sigma^0 + \frac{r(t)}{2} \right) \right]. \quad (15)$$

In this expression $r(t)$ is defined as

$$r(t) = \sigma_{01} r^{(0)}(t, \mu^{01}) - \sigma_{12} r^{(1)}(t, \mu^{12}) - \sigma_{10} r^{(1)}(t, \mu^{10}). \quad (16)$$

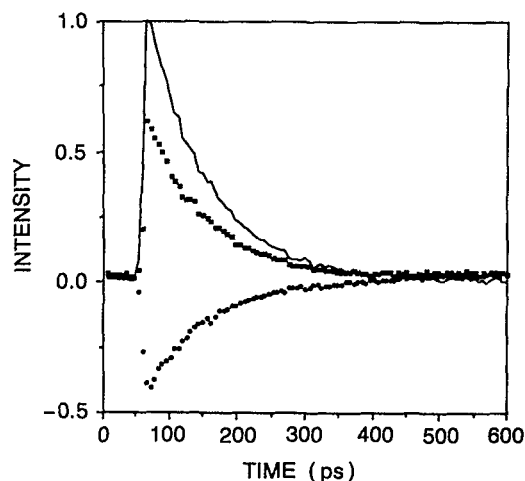


FIG. 2. Decay curves for resorufin in DMSO at $T = 294$ K are shown. The points are measured decays obtained with the analyzer at 0.83° and -0.83° . The solid curve results from subtracting these two curves, as described in the text.

When $\sigma_{01} \gg \sigma_{12}$, σ_{10} only the ground state anisotropy is probed. Correspondingly when σ_{12} , $\sigma_{10} \gg \sigma_{01}$, the excited state anisotropy is probed. The second term in Eq. (15) depends on the excited state population squared and is much smaller than the first term. Since the only change in experimental configuration required for the two measurements is the rotation of the analyzer through a few degrees, no extensive normalization procedure is required before subtraction of the two decays. This technique has the added advantage that it also discriminates against any stray signals due to birefringence, since these signals do not change sign with δ_D . Figure 3 shows the variation of the measured decay time with analyzer angle for OHPS both with and without the subtraction scheme, and clearly shows the advantage of this refinement of the OHPS technique.

Pump/probe apparatus

The pump/probe apparatus has been described earlier.³⁶ The laser source consists of a cw mode-locked Nd:YAG laser which is frequency doubled to 532 nm and used to synchronously pump two independently tunable Rhodamine 6G dye lasers. These dye lasers provide the pump and probe pulses. Cross correlation measurements are used to determine the time resolution, and are typically 8–9 ps FWHM. Pump and probe beams are chopped at 1600 and

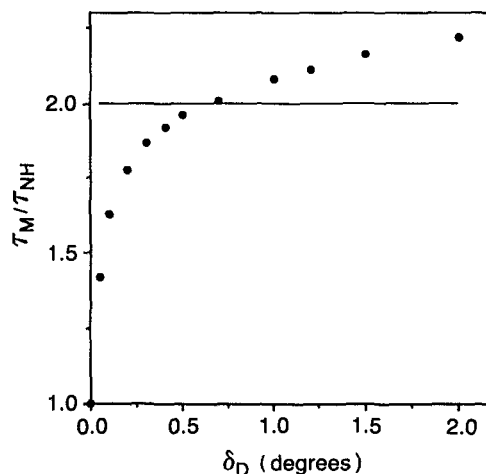


FIG. 3. The value of the measured decay time is plotted versus the angle of the analyzer. The optically heterodyned regime corresponds to the plateau region. The subtraction scheme gives the line and the standard heterodyned method the circles. τ_{NH} is the nonheterodyned decay time [the decay time from equation 14 with $\delta_D = 0$ (Ref. 36)].

900 Hz, respectively, and the signal from the photomultiplier is detected at the sum frequency by a lock-in amplifier. A microcomputer controls the variable pathlength and stores the signal from the lock-in.

The decays, given by Eq. (15), are fit to a single exponential to yield a decay time τ_M . Excited state lifetimes (τ_F) are measured using a time correlated single photon counting apparatus,³⁷ and the rotation time is computed as

$$\tau_{or} = (\tau_M^{-1} - \tau_F^{-1})^{-1}. \quad (17)$$

The excited state anisotropy decays simply with the rotational diffusion in the excited state and the population relaxation of the excited state. The ground state anisotropy has a more complicated dependence on the samples time evolution. The two factors which contribute to the anisotropy relaxation are ground state rotational diffusion and rotational diffusion in the excited state, followed by population relaxation to the ground state and the subsequent rotational diffusion in the ground state. These effects have been treated by Cross *et al.*³⁸ and can be found in their Eq. (54). For the molecules studied here the effect of the excited state relaxation is small because the population lifetime of the excited state is long. The actual changes in ground state diffusion coefficients from the simple analysis described in the previous paragraph is a 1 or 2% reduction, far below the experi-

TABLE I. Solute properties.^a

Solute	Axial radii (\AA)	Volume (\AA^3)	F	C_{slip}	Charge (e)	μ_g (D)		μ_e (D) Spec
						Spec.	Calc	
Resorufin	$6.5 \times 3.5 \times 2$	190	2.32	0.25	-1	3.3	2.6(z)	4.8
Resorufamine	$6.5 \times 3.5 \times 2$	190	2.32	0.25	0	3.2	5.6(y)	7.0
Oxazine	$6.5 \times 3.5 \times 2$	190	2.32	0.25	+1	3.7	-2.0(z)	6.1

^aNote: $\sigma = FC$.

mental error. The simple procedure for obtaining the relaxation rates was therefore used.

Samples

The molecules studied are three phenoxazine dyes, resorufin (anionic), resorufamine (neutral), and oxazine 118 (cationic). They were chosen because their similar structures should eliminate effects of solute size and shape on reorientation rates (Fig. 1). Their volumes and hydrodynamic parameters, F and C , are given in Table I. The volume was computed as that of the corresponding ellipse using the axial radii. The axial radii were found via standard bond lengths and atomic radii.³⁹ The variation in volume caused by a 10% variation in the axial radii is 20%. The shape factor F changes by $\sim 13\%$ with a 10% change in the axial ratios.

The diffusion coefficients were obtained by approximating the molecules as asymmetric ellipsoids and computing the friction for rotation about each axis in the principal axis system. The slip boundary coefficients were obtained from Youngren and Acrivos.¹⁷ Because the molecule is treated as an asymmetric ellipsoid the anisotropy is in general a double exponential. The decay time was found as the correlation time of this double exponential function. In fact, one of the two exponentials dominates the decay and this approximation is quite good.

Resorufin was obtained commercially (sodium salt, Aldrich) and used as received. Oxazine (chloride salt) and resorufamine were not available and had to be synthesized.^{40,41} The synthesis proceeded by nitration of phenoxazine at the 3 and 7 positions, followed by catalytic hydrogenation of the nitro groups to amines. Acidic workup resulted in oxazine 118 chloride. Acid hydrolysis of the oxazine yielded resorufamine. All three dyes yielded single spots upon TLC analysis, and their identities were confirmed by visible⁴² and NMR spectra. Absorption and fluorescence spectra are shown in Fig. 4, along with the wavelengths used for pump and probe pulses. These and all other spectra were obtained on an IBM Model 9420 spectrophotometer and an SLM 8000C fluorimeter.

Dimethylsulfoxide (DMSO) was chosen as a polar aprotic solvent. The solvent was 99.9% pure (from Fisher) and used without further purification. Temperature dependent viscosity and dielectric constant data were taken from the literature.^{43,44}

Solute electrical properties

The electrical properties of all three solute molecules were studied by electronic structure calculations and by steady state spectroscopy. The calculations were performed on the departmental FPS 500 computer using the GAUSSIAN 86 software package. First, the molecular geometries were optimized using the MNDO algorithm, and then a Hartree-Fock electronic structure calculation was performed. The molecules were restricted to be planar and the ionic dyes were constrained to have a plane of symmetry perpendicular to the molecular frame. The ground state (S_0) dipole moment was calculated by the program, which also listed all molecular orbital coefficients in terms of the atomic orbitals,

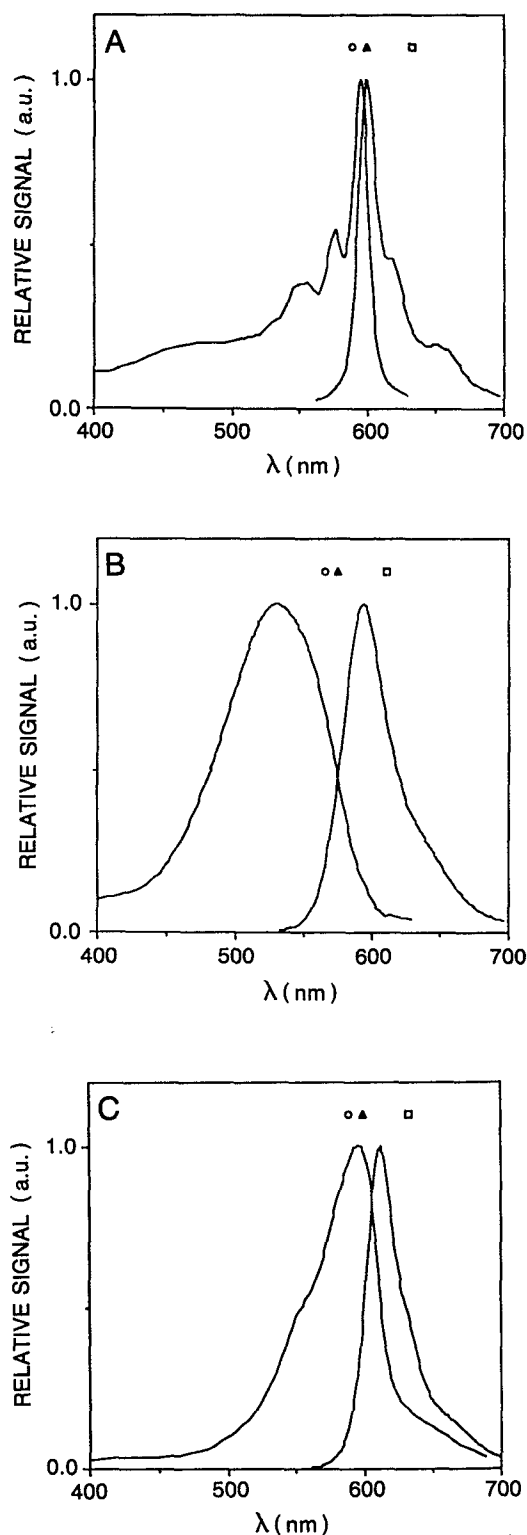


FIG. 4. Fluorescence and absorption spectra are shown for the three dye molecules (A is resorufin, B is resorufamine, and C is oxazine) in DMSO. The wavelengths of the pump laser (▲), and the probe for the ground state (○) and excited state (□) are indicated.

and also the overall charge distribution of the three solutes. The results of these calculations are summarized in Table I.

The ground state dipole moment and dipole moment change upon electronic excitation were also estimated from

solvent induced shifts in absorption and fluorescence spectra. Following the notation used by van der Zwan and Hynes,²⁸ the absorption energy is $\hbar\omega_{\text{abs}}$

$$\hbar\omega_{\text{abs}} = U_{0,e} - U_{0,g} - \frac{1}{2}B_{\text{op}}(\mu_e^2 - \mu_g^2) + B_{\text{or}}\mu_g \cdot (\Delta\mu), \quad (18)$$

and the Stokes shift S is

$$S = B_{\text{or}}(\Delta\mu)^2, \quad (19)$$

where $U_{0,g}$ is the ground state energy of the isolated solute molecule, $U_{0,e}$ is the excited state energy of the isolated solute molecule, μ_g is the ground state dipole moment, and μ_e is the excited state dipole moment. The quantities B_{op} and B_{or} are response functions which when multiplied by the instantaneous solute dipole moment squared give the solvents' contribution to the solute free energy. B_{op} is the optical response function related to the electronic degrees of freedom of the solvent and B_{or} is the orientational response function which describes the contribution of solvent molecule nuclear arrangements (primarily through dipole moment orientation). If B_{op} and B_{or} are modeled using the Lippert–Mataga theory then

$$B_{\text{op}} = \frac{2}{a^3} \frac{(\epsilon_\infty - 1)}{(2\epsilon_\infty + 1)} \quad (20)$$

and

$$B_{\text{or}} = \frac{2}{a^3} \left(\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1} \right), \quad (21)$$

where the solute's polarizability is ignored.

If the variation in the optical response between solvents is ignored in Eq. (17) then a plot of the absorption energy versus B_{or} gives a slope of $\mu_g(\mu_g - \mu_e \cos \theta)$, where θ is the angle between the ground and excited state dipole moments. A plot of S vs B_{or} gives a slope of $(\Delta\mu)^2$. These two slopes, knowledge of θ , and the relation $\mu_g = \mu_e + (\Delta\mu)$ can be used to find μ_g and μ_e . The results of these plots for all the dye molecules are summarized in Table I. The adequacy of the Lippert–Mataga model (a continuum model) is not clear and the results obtained depend on the specific solvents used. Effects such as hydrogen bonding may preclude the validity of this method. The results presented (see Fig. 5) were obtained in a homologous series of solvents, for resorufin and oxazine the normal alcohols and for resorufamine the alkyl nitriles. In the absorption spectrum of resorufamine in normal alcohols a red-shifted peak appears, perhaps a hydrogen bonded complex, which makes assignment of the peak energy difficult. Unfortunately the ions are not very soluble in the alkyl nitriles and the spectral studies had to be performed in a different homologous series.

RESULTS AND DISCUSSION

Comparison with the DSE expression

Dipole case

Rotational diffusion times for resorufamine (both S_0 and S_1) in DMSO were measured over a range of temperatures from 294 to 355 K, and a DSE plot of τ_{or} vs η/T is shown in Fig. 6(a), along with calculated lines for slip and stick boundary conditions. The results of fitting these points

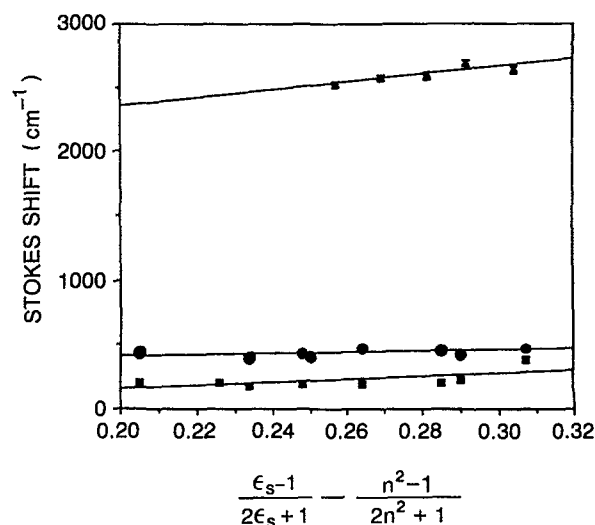


FIG. 5. Lippert–Mataga plots for the three solute molecules are shown. Resorufin (●) and oxazine (■) are in normal alcohols. Resorufamine (▲) is in the alkyl nitriles.

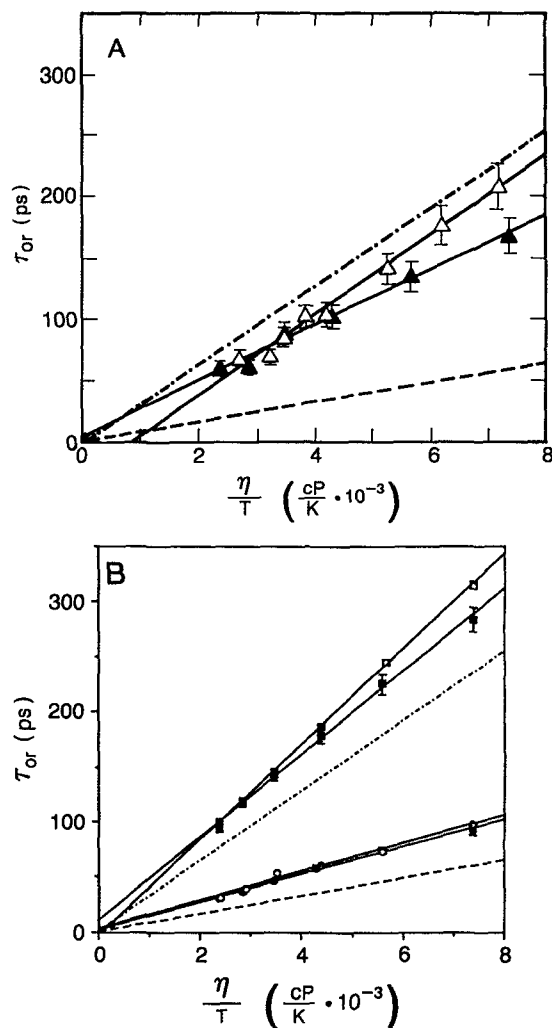


FIG. 6. Debye–Stokes–Einstein plots for the molecules are shown with the expected stick and slip lines. Figure 6(A) shows the resorufamine data in ground (▲) and excited (△) states. Figure 6(B) shows the oxazine data in ground (■) and excited (□) states and resorufin in ground (●) and excited (○) states.

TABLE II. Debye–Stokes–Einstein fitting parameters.^a

Solute	Slope $\left(\frac{\text{ns K}}{\text{cp}}\right)$	Intercept (ps)	$T = 294 \text{ K}$		$\Delta\tau/\tau$	$E_{\text{act}} \left(\frac{\text{kcal}}{\text{mol}}\right)$
			τ_{or} (ps)	$r(0)$		
Resorufin (gr)	13.0 ± 0.4	-0.5 ± 1.5	95	0.36^b	0.04	3.3
Resorufin (ex)	13.1 ± 0.7	1.2 ± 2.5	98	0.35	0.06	3.0
Resorufamine (gr)	22.7 ± 2.0	2.4 ± 7.2	170	...	0.11	3.1
Resorufamine (ex)	31.6 ± 2.3	-24.5 ± 9.2	209	0.33	0.09	3.6
Oxazine (gr)	38.5 ± 1.0	5.9 ± 3.8	290	0.36^c	0.04	3.1
Oxazine (ex)	43.4 ± 0.4	-4.3 ± 1.4	316	0.35	0.01	3.4
Slip	8.0	0.0	59
Stick	31.9	0.0	235

^aNote: Assuming $\eta = \eta_0 \exp(E_\eta/RT)$ yields $E_\eta = 3.2 \text{ kcal/mol}$ for DMSO.

^bFrom Ref. 47(c), measured in 2-methyl-2-butanol at $T = 300 \text{ K}$.

^cFrom Ref. 47(c), measured in 2-butanone at $T = 300 \text{ K}$.

to straight lines are given in Table II. The excited state slope is very close to the stick prediction, while the ground state slope is about 20% smaller. This qualitative trend is expected based on the larger dipole moment in the excited state, which would increase the solute/solvent coupling. The intercept for the ground state line is very close to zero which is predicted by the simple DSE model, whereas the excited state line has a negative intercept. Some workers have interpreted a finite intercept as a free rotor time for the solute molecule^{45,46} which is clearly not the case here. It is quite likely that as the temperature is raised the excited state line will curve and coalesce with the ground state line since at high temperatures the significance of the dipole/dipole coupling with respect to the available kinetic energy decreases.

Ion case

The rotational diffusion of oxazine and resorufin was studied in both ground and excited states over the same temperature range as resorufamine. The DSE plot and fitting parameters are shown in Fig. 6(b) and Table II. The diffusion time is not state dependent for resorufin, and the state dependence is small for oxazine. The fitted line for resorufin falls between the slip and stick lines, while the oxazine line exceeds the stick line. This trend is evident from previous work^{47,48} where the solvent viscosity was varied by changing the solvent molecules chemical identity or by the use of binary solvent mixtures. The continuum theories do not explain this trend. The origin of this change in boundary condition in terms of electrostatic interactions is discussed later.

Arrhenius plots

An analysis of the activation energy for solute molecule rotation was performed. Over the range of temperatures studied the shear viscosity of DMSO can be fit to an Arrhenius expression with an activation energy of 3.2 kcal/mol. The DSE equation (1) predicts that a plot of $\ln(\tau_{\text{or}} T)$ vs $1/T$ should yield an activation energy for solute rotation that is similar to the solvent viscosity. The activation energies obtained from this procedure are given in Table II and are in

quite good agreement with that of the solvent viscosity. This behavior is another manifestation of the linear dependence of τ_{or} on η/T shown in Fig. 6, and, more importantly, shows that the rotation is activated as the viscosity is activated. The difference in rotation times between solutes results from the parameters V , F , and C .

Some of these molecules have been studied previously in DMSO, in particular resorufin at room temperature.^{12,48} In all cases the observed decay times here are in good agreement with previous results.

Comparison with dielectric friction models

Dipole case

The inclusion of dielectric friction explains the qualitative trend in the data for resorufamine, however quantitative agreement is lacking. Fits of the data to the Nee–Zwanzig/Hubbard–Wolynes model (see Fig. 7) yield ground and excited state dipole moments of 44 and 57 D, respectively. These values are much larger than the estimates of 3–5 and 7–10 D. If the ground state dipole is assumed to be 5 D, the difference in slopes yields an excited state dipole of 29 D, which is still too large. This previous analysis uses τ_{slip} as a measure of the mechanical contribution to the relaxation time. The boundary condition can also be estimated¹⁵ from the size of the solute yielding $\sigma = FC = 1.1$, and subtraction of τ_σ from τ_{or} gives the dielectric contribution to the decay time. This data is plotted in Fig. 7(a) and the results of the fits are given in Table III. Although the dipole moments decrease compared to the slip case, they are still quite large. Although the dielectric friction increases with the increase in dipole moment, this model appears to underestimate the friction.

The Hubbard model which allows for a nonslip boundary condition was no more successful. There was some uncertainty as to how this theory should be applied since the molecules studied are not spherical. Two approaches were used. For the first, τ_σ was evaluated for $\sigma = 1.1$. This procedure led to estimates of 40 and 62 D for the ground and excited states. The second approach was to constrain the

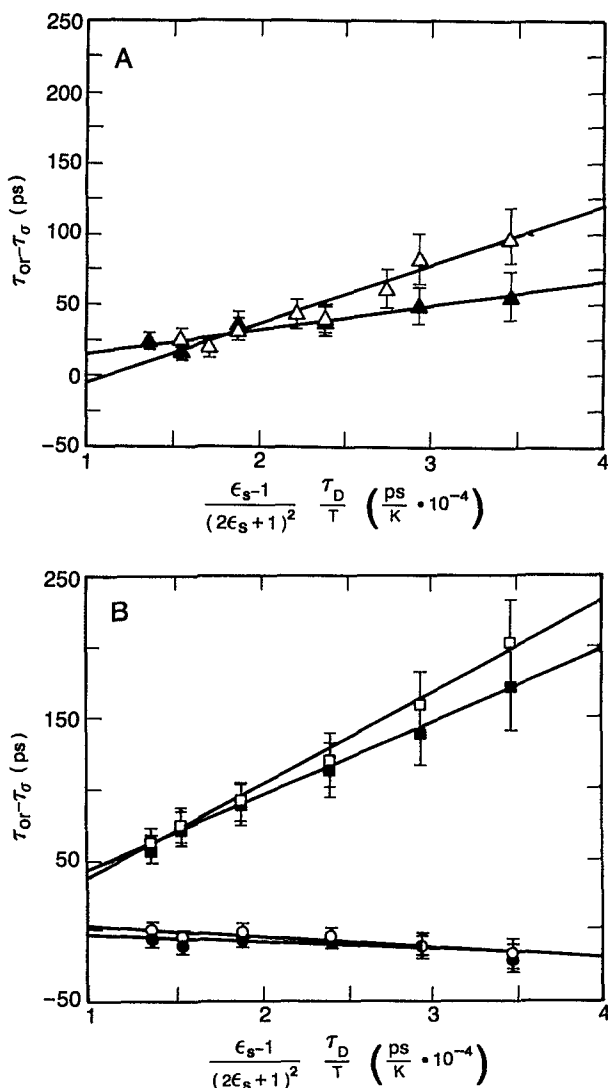


FIG. 7. Nee-Zwanzig plots of the rotation relaxation times are given in (A) for resorufamine [ground state (Δ), excited state (\square)] and in (B) for oxazine [ground state (\blacksquare), excited state (\square)] and resorufin [ground state (\bullet), excited state (\circ)].

dipole moments of the ground (3.2 D) and excited states (7.0 D) and vary the boundary condition parameter σ . This latter case gave reasonable fits with a boundary condition parameter of $\sigma = 1.8$. The appropriateness of the values used

in these fits is not clear. The models are derived for spherical particles in which σ ranges from zero to one.

Equation (5), given by Nowak, can be used to fit the data when the dipole moments and the hydrodynamic boundary conditions are constrained. These fits are as good as those shown in Fig. 7. The good fit results from the presence of another parameter, the electrohydrodynamic boundary condition. In these latter fits a σ value of 1.1 is used and the ratio of the electrohydrodynamic to hydrodynamic boundary condition is found to be 564 for the excited state and 168 for the ground state. The increase of this ratio for the excited state over that of the ground state indicates that the excited state has a more sliplike electrohydrodynamic boundary condition than does the ground state. The use of a hydrodynamic boundary condition in the range from 0.3884 to 1 results in very poor fits because the electrohydrodynamic term becomes negative unless $\lambda < 1$. Since λ must be greater than zero, the extra term is unable to compensate. As with the Hubbard model, the meaning of a σ value greater than 1 in the context of this model is not clear.

Ion case

Fitting the ion data to the Nee-Zwanzig/Hubbard-Woynes model yields dipole moments of 27 and 66 D for resorufin and oxazine, respectively (Table III). These values stand in contrast to the ground state moments of 2–3 D. More importantly, it is incorrect to apply the Nee-Zwanzig result to a charged solute as has been done by previous workers.^{11,35,48,49} The dipole moment of a charged particle is not a well defined quantity, but depends on the origin of the coordinate system, which is arbitrary. Furthermore, the derivation by Nee and Zwanzig explicitly includes the field of a point dipole, which falls off as r^{-3} , and it is this field which polarizes the dielectric and gives rise to the friction. The field of a charge goes as r^{-2} , producing a different dielectric polarization, and necessarily a different amount of friction.

Nowak²⁵ and Felderhof²⁶ have both treated the case of a point charge rotating in a fluid. From their expression, Eqs. (7) and (8), it is clear that the friction depends on the square of the charge and should therefore be sign independent. The factor of 3 difference in rotation times for the cation and anion is in clear disagreement with this expectation. The use of dielectric and viscosity data for DMSO gives a value of α' in the range of $10/a^4$, where a is the radius of the ion in

TABLE III. Parameters from fits to continuum dielectric friction models.

Method	Resorufamine		Resorufin		Oxazine	
	E.S.	G.S.	E.S.	G.S.	E.S.	G.S.
Nee-Zwanzig						
(1) $\sigma = 1.1$	50 D	32 D	65 D	58 D
(2) $\sigma = 0.58$ (slip)	57 D	44 D	27 D	27 D	71 D	66 D
van der Zwan/Hynes						
(1) $\sigma = 0.58$ (slip)	24 D	19 D	18 D	18 D	39 D	36 D
(2) $\tau_{es} - \tau_{gs}$	34 D	30 D	39 D	37 D
Hubbard						
(1) $\sigma = 1.1$	62 D	40 D	σ fixed and dipole moments varied			
(2) $\sigma = 1.8$	7 D	3.2 D	Dipole moments fixed and σ varied			

angstroms. Choosing the radius of the solute from its volume as if it were a sphere gives $a = 3.6$ and a value of $\alpha' < 0.06$. This parameter, a reduced charge, gauges the significance of dielectric friction and is quite small here. This model predicts that the anion and cation should not only have the same friction but that it should be predominantly (95%) hydrodynamic. For such a small α' the contribution of $J(\alpha')$ in Eq. (7) can be ignored. Furthermore the value $\alpha'/(1 + \alpha')$ is approximately α' and constant over the temperature range, leading to an approximate proportionality of τ_{or} on η/T . The small difference in volume of oxazine and resorufin cannot account for this difference in slopes. To quantitatively model the observed DSE slopes requires different hydrodynamic boundary conditions. Requiring $\lambda > 0$ leads to the criterion that $\sigma > 0.61$ for resorufin, and $\sigma > 1.9$ for oxazine which is close to the hydrodynamic stick value. The unreasonable parameters most likely result from the fact that the solute molecules are not spherical and by no means have their charges located at the center of the sphere.

Semiempirical approach

The Stokes shift energy and correlation time can be used to gauge the magnitude of the dielectric friction for the solute molecule in DMSO. Presumably this semiempirical approach should include any specific solute/solvent interactions in an effective manner. This procedure was used with some success³⁵ in evaluating the dielectric friction of oxazine 725 in *n*-alcohols, which has diethylamines as opposed to the amine groups in Fig. 1. In order to properly model the dielectric friction via Eq. (12), the Stokes shift must be determined which requires assignment of the zero-zero transition energy. In solution this assignment is nontrivial to perform. So instead it is common to compute the difference in energy of the absorption and fluorescence maxima in both polar and nonpolar solvents. By subtracting the nonpolar solvent's energy shift from the polar solvent's one the dipolar part of the solvation energy can be isolated. In any case the energy difference between the absorption and fluorescence maxima of the solute provides an upper bound on the solvation energy. For the case of resorufin in DMSO the difference in the energy of the absorption and fluorescence maxima is only 112 cm^{-1} , suggesting that the use of peak maxima will result in an error of 100 cm^{-1} or less for the Stokes shifts of these similar molecules (for oxazine $S = 378 \text{ cm}^{-1}$ and for resorufamine $S = 2022 \text{ cm}^{-1}$).

The semiempirical model provides a prescription for computing the dielectric friction, but does not indicate how it can be used to model the friction for a molecule undergoing rotational diffusion. The combination of mechanical and dielectric effects is not always simple.^{23–26} The model was applied in two ways, both of which assume that the mechanical and dielectric contributions to the friction are independent and model the Stokes shift as the difference in energy of the absorption and fluorescence maxima. First a slip boundary condition ($\sigma = 0.58$) was used for the hydrodynamic part of the friction and the residual was attributed to dielectric friction. The results of this procedure are given in Table III and the dipole moments are larger than expected, but

more reasonable than those found using the Nee-Zwanzig model.

Second, the dipole moments can be found in a manner employed by Simon³⁵ where the difference between ground and excited state rotation times are used to find the change in the dielectric friction. With an independent determination of $\Delta\mu$, from spectral shifts, it is possible to determine the dipole moments in each state. The advantage of this procedure is that it requires no knowledge of the mechanical friction (i.e., sidesteps the need to model the hydrodynamic boundary condition). For this case

$$\tau_e - \tau_g = \frac{1}{6kT} \frac{\mu_e + \mu_g}{\mu_e - \mu_g} S\tau_s, \quad (22)$$

where τ_e and τ_g are the orientational relaxation times for the excited and ground states, respectively. The temperature dependence of the steady state Stokes shift was found to be weak over the range studied and the room temperature value was used in this analysis. Because the solvation time τ_s (3 ps) is only available in DMSO at room temperature the tem-

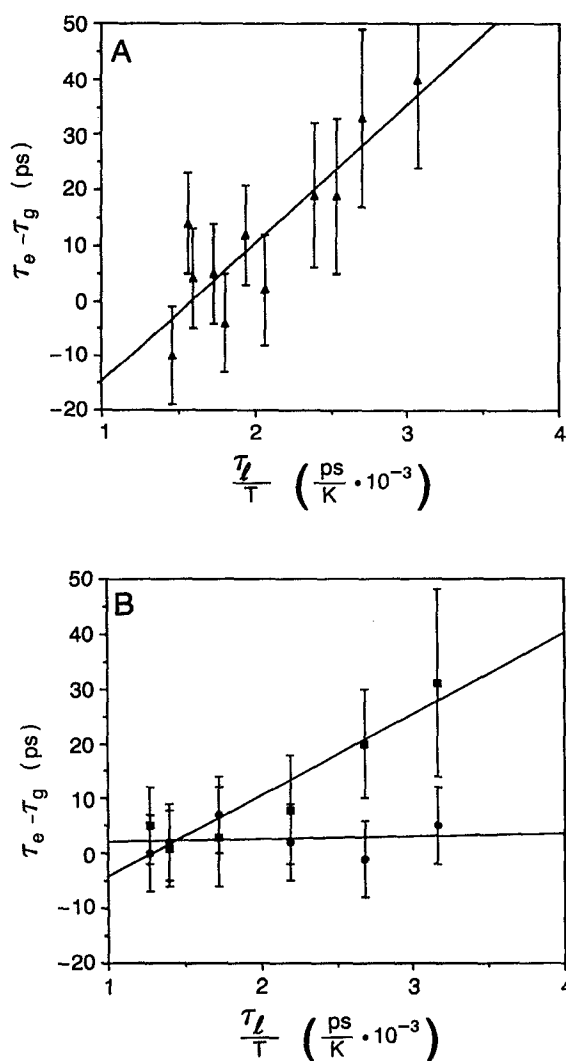


FIG. 8. Shown are van der Zwan and Hynes plots of the difference in rotation times between excited and ground state [(\blacktriangle) resorufamine, (\blacksquare) oxazine, (\bullet) resorufin].

perature dependence of the solvation time was modeled as that of the longitudinal relaxation time of the solvent τ_l . The results of this analysis are given in Table III and Fig. 8. Although this model is superior to the simple continuum models of the solvent, the dipole moments obtained remain unrealistic. This failure suggests that more emphasis needs to be placed on more realistically modeling the solute electrical properties rather than using the approximation of a point dipole. It is important to realize that the magnitude of the dipole moments depend on the quality of modeling S and τ_s . Better modeling of these parameters could change the dipole moments by a factor of 2, perhaps more. This semiempirical model may give results superior to the continuum models because of the empirical determination of the solute/solvent interaction strength via S .

Failure of dielectric friction models

Clearly these theories fail to correctly model the friction for the systems studied here. The most obvious pieces of evidence are (1) the factor of 5–10 or more overestimate of the solute dipole moments, and (2) the factor of 3 difference in decay times between anion and cation, when the sign of the ionic charge should have no effect in a dielectric continuum. Several possible reasons for the inadequacy of these models exist, each of which may point toward improvements in the modeling of the solute/solvent friction.

Molecular perspective

One possibility is that the assumption of no specific interactions between solute and solvent could be in error. Although DMSO is a polar aprotic, it possesses lone pairs which could possibly form hydrogen bonds with solute amino groups. This interaction would explain the qualitative trend between the three dyes, with resorufin (no amino groups) reorienting fastest, resorufamine (one group) more slowly, and oxazine (two groups) slowest. If such interactions occurred, then an explicit treatment of at least the first solvation shell would be necessary to explain the observed reorientation behavior. Pair potentials for these three solutes and DMSO could be generated and these in turn may be used in several ways.

One approach would involve a more sophisticated hydrodynamic calculation of the friction, either using the potential to determine a variable boundary condition, or simply using the potential directly in the calculation of the hydrodynamic friction, instead of a boundary condition. The latter procedure has been investigated previously²⁰ for simple repulsive potentials and a relatively crude model for the fluid. Unfortunately, even this relatively simple calculation resorts to numerical evaluation, suggesting that the more complicated potential for these solutes would present a considerable challenge.

One could also use the pair potentials to determine the orientational correlation function. Alternatively, the diffusion constant could be found from the mean squared angular displacement divided by a characteristic timescale during which the angular velocity is randomized, $D = \langle \theta^2 \rangle / 2\Delta t$. A perturbation theory approach, similar to that used by Steele¹ for modeling the correlation functions of smaller spherical

and symmetric top molecules, might be adaptable to these more complex systems. Knowledge of the intermolecular potential from quantum calculations could be used to determine the mean square torques and hence the rotational relaxation times. Such a model was discussed qualitatively some years ago by Spears and Cramer.⁵⁰

Viewing the rotational relaxation in this manner suggests a marriage of molecular and continuum theories.²⁷ One could construct a complex consisting of a solute molecule surrounded by a solvation shell of solvent molecules. The diffusion could then be decomposed into two parallel components: (1) reorientation of the entire complex, which could be adequately described by hydrodynamics, and (2) diffusion of the solute within the complex, modeled with the potential of the solute molecule within the solvation shell. These methods are not particularly straightforward or practical, but they would produce a more realistic calculation of the observed rotation times based on specific solute/solvent interactions.

Continuum perspective

The search for an adequate continuum model has as its primary rewards simplicity and the inclusion of relevant molecular interactions in terms of accessible solute and solvent properties. Two important assumptions in the theoretical treatments discussed are the use of point dipoles and charges and the use of a spherical cavity for the solute molecule. Although this simplifies the mathematics involved, it can be shown that localization of the charges at the center of the cavity leads to a significant underestimation of the dielectric friction. The use of a spherical cavity can also significantly effect the calculation of the friction, since an ellipsoidal cavity would more accurately describe the environment of the molecule.

A more general form of a Nee–Zwanzig type theory would calculate the dielectric friction for an arbitrary collection of point charges rotating within an ellipsoidal cavity. A first step toward this goal, the calculation of the friction on a collection of point charges within a spherical cavity, has been performed and will be presented in a forthcoming paper.⁵¹ This generalization allows the Nee–Zwanzig theory to be applied to charged as well as neutral species, and gives improved agreement between observed and predicted decay times.

CONCLUSIONS

The overall trend in rotation rates, oxazine slower than resorufamine slower than resorufin, can be understood on a qualitative level from the partial charge distributions expected for the solute and solvent. Because DMSO has its most electropositive atom in the center of the molecule, it is primarily the negatively charged regions which interact with neighboring molecules. This accounts for the well known observation that DMSO solvates cations much better than anions.⁵² The partial charge distributions for the three solutes is given in Fig. 9. Clearly when the molecule possesses an amine substituent that end of the molecule is predominantly positively charged, whereas the presence of a car-

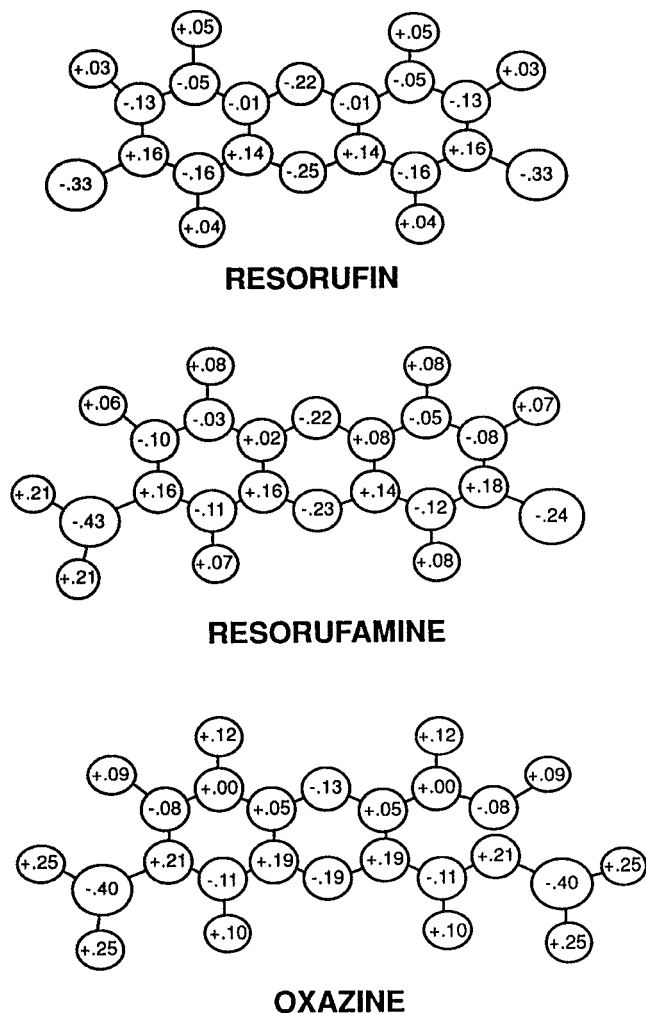


FIG. 9. Shown are ball and stick models of the solute molecules with the partial charge (Mulliken charge) of each atom indicated.

bonyl group leads to less net charge on the ends of the molecule. The experiment measures the rotational relaxation of the molecule for motion perpendicular to the transition moment direction which for these molecules lies approximately along the long axis. Therefore when the solute has a large amount of positive charge on its outer rim the drag from the solvent is increased. Since oxazine has two amine ends it relaxes most slowly and since resorufin has only carbonyl ends it experiences less friction. Correspondingly resorufamine is intermediate between these two extremes.

A quantitative study of the effect of dielectric friction on molecular rotation in liquid solutions was performed by studying three mechanically similar dye molecules with differing electrical properties in the polar aprotic solvent dimethylsulfoxide. Current theories of dielectric friction fail to quantitatively account for the experimental data. A major reason for this failure is believed to be the oversimplification of the molecular charge distribution by the use of a point dipole or point charge. A generalization of these continuum theories to account for an arbitrary charge distribution will lead to improvement of the Nee-Zwanzig theory, and will be

presented in a later paper, along with its application to the rotational diffusion of these phenoxazine dyes.

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