The Influence of Chromophore Structure on Intermolecular Interactions. A Study of Selected Rhodamines in Polar Protic and Aprotic Solvents

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We have studied the linear optical response and orientational relaxation dynamics of a family of rhodamine dyes in which there is substantial variation in the chromophore structure. For these chromophores, the identity of a substituent at the center ring (1) position mediates the linear optical response of the chromophore, and semiempirical calculations provide agreement with experimental data. This phenomenon can be understood in terms of the extent of conjugation of the chromophore ring system. The reorientation data for these chromophores in several polar protic and aprotic solvents are nominally consistent with the predictions of the modified Debye–Stokes–Einstein (DSE) model. In several cases, polar aprotic solvents are found to interact more strongly than polar aprotic solvents with the rhodamine chromophores, despite the difference in the nature of intermolecular interactions in the two types of solvents. The terminal amino functionalities on the rhodamines exhibit stronger interactions with protic solvents than the analogous chromophores that have been structurally modified to constrain amino group rotation. The data point to the importance of both site-specific solvent–solute interactions and dipole–dipole interactions in mediating the solution phase dynamics of rhodamines.

Introduction

The interactions between molecules determine both the microscopic and bulk properties of essentially all solution phase systems. Achieving a detailed understanding of these interactions has proven to be an elusive task because of their strength and their characteristically short persistence time. The time scale of solvation phenomena in polar liquids is considered to be on the order of the longitudinal relaxation time of the solvent and can range from ~100 fs for polar aprotic solvents to hundreds of picoseconds for high viscosity solvents characterized by strong hydrogen bonding.[1,2] The process of measuring such phenomena usually requires the use of a chromophore that can be accessed using short light pulses, and the properties of the chromophore can have a substantial influence on the information obtained from the experiment. Owing to the complexity of these systems, much information in the literature must be considered valid for only a specific chromophore or, at best, a limited number of structurally similar systems.[3–11]

The rhodamines are a family of molecules that have been used extensively as dyes for fabrics, biological stains, water markers, probes for studies of molecular-scale processes in condensed phases and at interfaces, host–guest interactions, and laser dyes.[12–22] The utility of this family of dye molecules stems from their characteristically strong absorption in the visible combined with relatively high fluorescence quantum yields and several-nanosecond fluorescence lifetimes. There are a substantial number of rhodamines,[12] with most of the structural variations being made with the intent of controlling optical properties such as absorption energy or fluorescence lifetime. The various structural features of the rhodamines make systematic interpretation of experimental data difficult at best. We are interested in understanding the relationship between rhodamine structure, steady state spectroscopy, and solution phase dynamical properties. It is our ultimate intent to use this family of molecules in interfacial and other sterically restricted environments, such as lipid bilayers and micelles. A prerequisite for working in such environments is the development of an understanding of the role of chromophore structure on the experimental data we will acquire. For this reason we have undertaken a study of several rhodamines in selected polar protic and aprotic solvents.

Although the rhodamines are versatile probe molecules, their structural features serve to complicate the interpretation of experimental data in many cases. For example, several rhodamines possess a pendant *o*-substituted phenyl ring and both the substituents and ring orientation relative to the chromophore plane can influence the motional and spectroscopic properties of the molecule. The extent of structural freedom remains largely undetermined for this ring, as does its role in mediating excited-state relaxation and motional properties. We have studied the steady-state spectroscopy and orientational relaxation dynamics of five substituted rhodamines (Figure 1). Our data, in conjunction with semiempirical calculations, indicate that, for several of these rhodamines, dipolar solvent–solute interactions play at least as significant a role as hydrogen-bonding interactions in determining reorientation dynamics, despite the significantly different time scales that are characteristic for these interactions.

Experimental Section

Pump–Probe Laser System. The picosecond pump–probe laser spectrometer used in these reorientation measurements has been described in detail previously,[23] and we present only a brief synopsis of its operation here. A mode-locked continuous-wave (CW) Nd:YAG laser (Coherent Antares 76-S) produces 30 W of average power (1064 nm, 100 ps pulses, 76 MHz repetition rate). The output of this laser is frequency-doubled

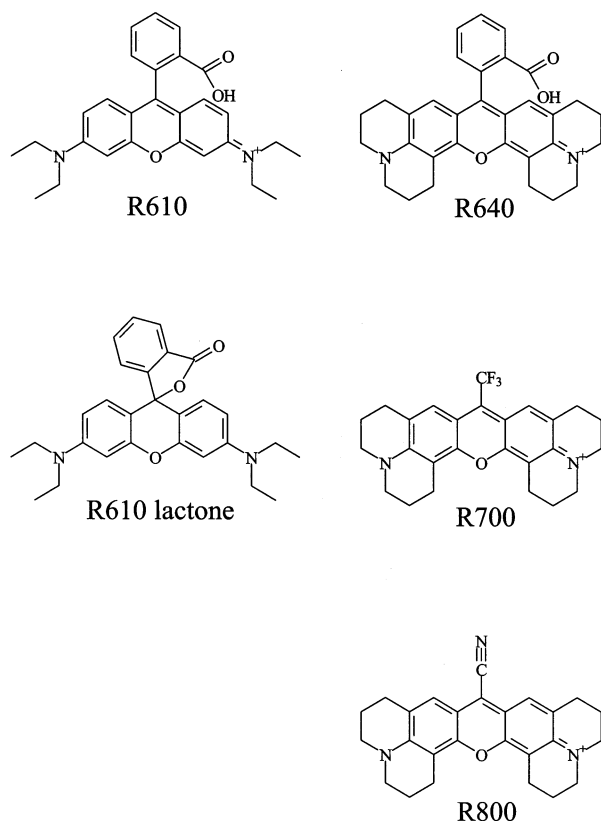* To whom correspondence should be addressed. E-mail: blanchard@chemistry.msu.edu.

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Figure 1. Structures of the five rhodamines studied here.

Figure 2. Absorption and emission spectra of (a) R610 and (b) R640, in methanol.

to produce ~3 W of average power at 532 nm. The second harmonic light is used to excite two cavity-dumped dye lasers (Coherent 702) synchronously, with the output of both lasers being ~70 mW average power at 8 MHz repetition rate, producing ~7 ps fwhm autocorrelation trace using a three plate birefringent filter. The pump dye laser was operated using Pyrromethene 567 dye (Exciton) at 549 nm (for R610 and ring-opened R610 lactone experiments) and 564 nm (for R640 experiments). For experiments on R700 and R800, the pump laser was operated using LDS698 dye (Exciton) (645 nm for R700, 682 nm for R800). The probe laser was operated with rhodamine 6G dye (Kodak) at 564 nm (for R610 and ring-opened R610 lactone experiments) and 580 nm (for R640 experiments). Kiton red dye (Exciton) was used in the probe laser for R700 and R800 chromophores (615 nm for R700, 622 nm for R800). The pump wavelength and probe wavelengths were chosen to access the $S_1 \leftarrow S_0$ transition of each chromophore to detect ground-state population recovery. The probe laser polarization was set to 0° and 90° relative to the pump laser polarization for individual scans of parallel and perpendicular polarization used in acquiring orientational relaxation data. The time resolution of this system, ~10 ps, is determined by the cross-correlation of the pump and probe laser pulses. Detection of the transient signals was accomplished using a radio and audio frequency triple-modulation scheme, with synchronous demodulation detection.[24−26] The reorientation time constants we report here are the average of six individual determinations, each composed of the average of 10−12 sets of $I_\parallel(t)$ and $I_\perp(t)$ scans.

Steady-Sate Spectroscopy. The steady-state absorption spectra of the chromophores used here were recorded with 1 nm resolution using a Cary 300 Bio UV−visible spectrophotometer. The spontaneous emission spectra for the same solutions were obtained with 1 nm resolution using a SPEX
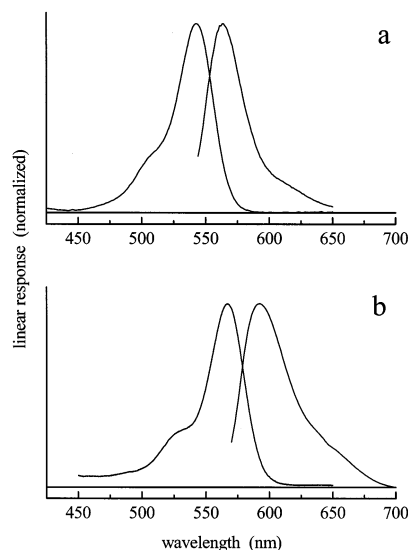
Fluorlog-3 spectrometer. These data were compared to semiempirical computational results (Hyperchem v. 6.0) and were used to determine the appropriate pump and probe wavelengths for each chromophore/solvent combination.

Chemicals and Sample Handling. The probe molecules rhodamine 610 (R610), rhodamine 640 (R640), rhodamine 700 (R700), and rhodamine 800 (R800) were obtained from Exciton Chemical Co. and used as received. Rhodamine 610 lactone (R610 lactone) was obtained from Aldrich Chemical Co. and was used as received. All solvents except water were obtained from Aldrich (99+% purity) and were used without further purification. Distilled, deionized water was available in-house. The concentration of all solutions used for laser measurements was 10 μM. Measurements of R700 solutions were hampered by bleaching of the solution. This effect was mitigated by replacement with fresh solution on at least a daily basis, or as warranted. All measurements were taken using a flow cell with a 1 mm path length. Solution temperatures were maintained at 298 ± 0.5 K (Neslab EX100-DD).

Results and Discussion

We are interested in using rhodamines as probes of their local environment in a number of systems, such as bulk liquids, micelles, polymer matrixes, and interfacial adlayers. To make use of these chromophores, we must first understand their optical properties and the relationship(s) between chromophore structure and intermolecular interactions. We consider first the structure dependence of the linear optical response of rhodamines, with an eye toward understanding experimental trends in the data. With that understanding in place, we will consider the reorientation dynamics of several rhodamines in polar protic and aprotic solvents. Our data point to the importance of dipolar solvent−solute interactions, in systems where intuition would suggest the dominance of hydrogen bonding interactions.

Linear Optical Response. The normalized absorption and emission spectra of the chromophores studied here are shown in Figures 2−4. The absorption and emission spectra of R610 and R640 (Figure 2) are blue-shifted significantly from the spectra of R700 and R800 (Figure 3), and the experimental trend is mirrored in the results of semiempirical calculations performed with a PM-3 parametrization (Figure 5).[27−30] As has been indicated by Drexhage,[22] the *o*-benzoate ring at the 1 position
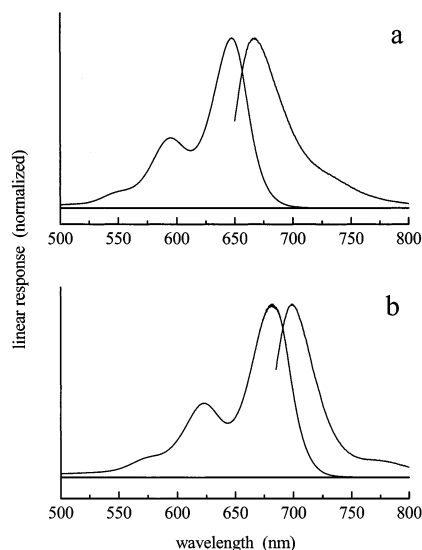
Figure 3. Absorption and emission spectra of (a) R700 and (b) R800, in *n*-propanol.
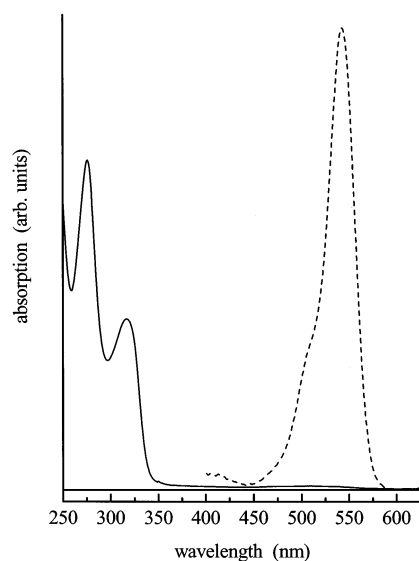

Figure 4. Absorption spectra of R610 lactone in acetonitrile (solid line) and ring-opened R610 lactone in methanol (dashed line).
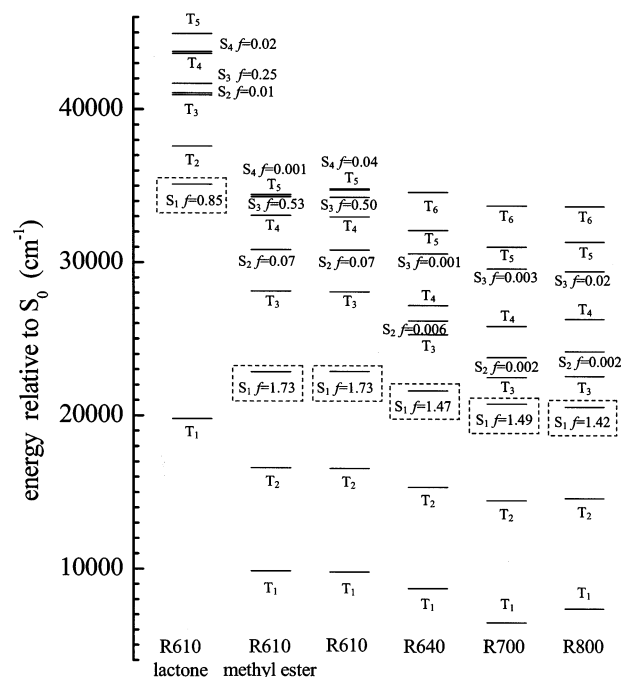

Figure 5. Calculated state energy levels for the rhodamines studied here. Calculations were performed at the semiempirical level with PM-3 parametrization. State energies and oscillator strengths for $S_n \leftarrow S_0$ transitions were calculated using the configuration interaction.

of R610 and R640 is effectively decoupled from the 3-ring chromophore system. For R800, we understand the red-shift in the context of an effective increase in the extent of the π-system to include the $-C\equiv N$ group. R700 is red-shifted from R610 and R640 because the fluorine 3p atomic orbitals on the $-CF_3$ group at the 1 position can interact with the chromophore π-system.[31-33] The π-interaction with the F 3p atomic orbitals is not on the same order as that for the $-C\equiv N$ π orbitals of R800, and the spectral response of R700 is not shifted as far to the red.

The linear optical response of R610 lactone is qualitatively different from that of the other rhodamines by virtue of the presence of the lactone ring.[34-38] Closure of the lactone ring at the 1 position breaks the conjugation of the chromophore system, giving rise to an absorption spectrum that is blue shifted by ~250 nm relative to R610 (Figure 4). In protic solvents, such as the primary *n*-alcohols used in this study, hydrolytic ester formation proceeds efficiently with the resultant formation of the rhodamine chromophore, and a steady-state optical response identical to R610 (Figure 3). This is an expected and well-documented result.[36,39-42] With this understanding of the steady-

state optical properties of the rhodamines, we turn to an examination of the dynamical behavior of these chromophores.

Conversion of the experimental data ($I_{\parallel}(t)$ and $I_{\perp}(t)$) to the induced orientation anisotropy function, $R(t)$, is accomplished using

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (1)$$

The functionality of the $R(t)$ decay provides important information on the dynamics of the chromophores. In this work, we find that all of the chromophores exhibit single-exponential anisotropy decays and the $S_1 \leftarrow S_0$ transitions accessed spectroscopically are polarized along the rhodamine chromophore long axis. These pieces of information, taken together, indicate that all of the rhodamine probe molecules we use reorient as prolate rotors in the solvents studied. Because of the observed single-exponential decay functionality, we can interpret our data in the context of the modified DSE equation. For all data, the reported zero-time anisotropies are derived from the regression of the data for times greater than 15 ps after excitation, and the uncertainties reported for each quantity are the standard deviations for six or more individual determinations. We report the quantities $R(0)$ and τ_{OR} in Table 1 for the several rhodamines and solvents used. The values of $R(0)$ are reflective of the angle between the excited and interrogated transition moments. If these transition moments were parallel, $R(0) = 0.40$. ($R(0) = \frac{2}{5}P_2(\cos \delta)$, where $\delta =$ angle between the transition moments.) We observe $R(0) \sim 0.25$ in our measurements and ascribe the existence of a nonzero angle between these transition moments to vibronic coupling. This is a typical result for polar chromophores in solution.

The intermolecular interactions of most interest to us are between polar organic chromophores and associative solvents and systems that can exhibit spontaneous self-assembly phenomena.[43-48] For such studies, some spectroscopic property of the chromophore is monitored as a function of a systematic

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TABLE 1: Reorientation Times and Zero-Time Anisotropies for the Rhodamine Chromophores in Protic and Aprotic Solvents[a]

solvent	rhodamine 610		rhodamine 640		ring-opened rhodamine 610 lactone		rhodamine 700		rhodamine 800	
	$R(0)$	τ_{OR}	$R(0)$	τ_{OR}	$R(0)$	τ_{OR}	$R(0)$	τ_{OR}	$R(0)$	τ_{OR}
acetonitrile	0.26 ± 0.02	57 ± 3	0.25 ± 0.05	50 ± 3			0.20 ± 0.01	42 ± 1	0.22 ± 0.02	47 ± 5
methanol	0.26 ± 0.03	87 ± 6	0.24 ± 0.02	68 ± 2	0.29 ± 0.04	95 ± 5	0.17 ± 0.02	48 ± 4	0.22 ± 0.02	50 ± 4
DMF	0.26 ± 0.03	138 ± 5	0.28 ± 0.02	125 ± 2			0.21 ± 0.01	97 ± 7	0.27 ± 0.01	101 ± 7
water	0.23 ± 0.03	141 ± 6	0.24 ± 0.06	121 ± 3	0.2 ± 0.01	129 ± 10	0.26 ± 0.02	110 ± 10	0.25 ± 0.02	122 ± 11
ethanol	0.29 ± 0.03	143 ± 4	0.25 ± 0.02	135 ± 6	0.22 ± 0.01	154 ± 9	0.23 ± 0.01	89 ± 3	0.24 ± 0.04	94 ± 6
n-propanol	0.27 ± 0.01	229 ± 5	0.25 ± 0.02	227 ± 12	0.27 ± 0.01	310 ± 11	0.19 ± 0.02	152 ± 6	0.22 ± 0.04	156 ± 7
DMSO	0.32 ± 0.03	271 ± 15	0.24 ± 0.04	264 ± 18			0.26 ± 0.03	213 ± 15	0.24 ± 0.02	217 ± 10

[a] The data are the best fit results of the data to the function $R(t) = R(0) \exp(-t/\tau_{OR})$. Time constants are in picoseconds, and the uncertainties are standard deviations ($\pm 1\sigma$) for at least six determinations of each quantity. Some data for R610 lactone were not obtained; see text for explanation.

change in the system, such as viscosity or polarity.[49–53] In many cases, collecting information in the time domain is most instructive, with orientational relaxation measurements being perhaps the most information-rich for our purposes. The starting point for the interpretation of molecular reorientation measurements is usually the modified Debye–Stokes–Einstein (DSE) equation.[54–56]

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \qquad (2)$$

This simple model has proven to be remarkably successful in providing at least a semiquantitative model for the rotational motion of molecules in solution. In this model, η is the solvent bulk viscosity, V is the solute hydrodynamic volume,[57] and the terms f and S are frictional boundary condition[56] and molecular shape factors, respectively.[55] The frictional boundary condition and molecular shape factors arise from modifications of the original theory, which described the reorientation of spheroidal particles in a microwave cavity. The DSE model assumes a continuum solvent and it has been shown to model reorientation data quantitatively in the limit that the individual solvent molecules are smaller than the solute.[43–45,51,58–68] Discrepancies between the modified DSE model and experimental data are often expressed in terms of the molecular-level breakdown of the notion of viscosity or in terms of variations in the friction coefficient, f, that are related to the interactions between solvent and solute molecules. The main limitation of the DSE model in the prediction of solute reorientation lies with the molecular-scale definition of the solute–solvent boundary condition. Indeed, this model treats the solvent as a continuum and is thus incapable of accounting for specific chemical interactions. For solvent–solute interactions with a substantial frictional component, the so-called "stick limit" is used,[5,7,51,53,66,69–72] and for cases where frictional interactions are expected to be less significant, e.g., reorientation of nonpolar solutes in nonpolar solvents, the "slip" limit is used. In this limit, f can range in value from 0 to 1, with its exact value being determined by the effective shape of the volume swept out by the reorienting molecule. For some ionic solutes in polar solvents, the reorientation times measured experimentally exceed those predicted by the modified DSE equation in the stick limit, and such systems are termed "superstick". The central issue for such systems is determining the dominant contribution(s) to the solvent–solute boundary condition, with dielectric friction[73] and hydrogen bonding[60,61] being proposed to account for the experimental data.

The data we present in this paper are predicted reasonably well by stick-limit reorientation, save for one case. The ring-opened form of R610 lactone reorients more slowly than R610,

TABLE 2: Calculated Dielectric Friction Times for Rhodamine 610 (R610) and 640 (R640)[a]

solvent	R610 (ps)	R640 (ps)
acetonitrile	0.1	0.1
methanol	0.9	0.8
DMF	0.4	0.3
water	0.1	0.0
ethanol	2.2	2.1
n-propanol	10.9	10.2
DMSO	0.2	0.2

[a] The times reported are intended to be additive contributions to the reorientation time calculated using the modified DSE model. Values are calculated from Nee and Zwanzig.[73] Some values necessary for completion of the calculation are taken from Table 4 and references contained therein.

and we understand this behavior on the basis of the formation of an alkyl ester by reaction of the R610 lactone with the alcohol solvent (vide infra). We find that the reorientation of rhodamines in polar aprotic solvents is consistent with stick or slightly "superstick" limit behavior, whereas the reorientation of these same chromophores in alcohols is slightly substick. We examine these data in terms of solvent–solute interactions and the internal structural freedom available to the chromophores, an effect that can influence the effective rotor shape of the reorienting moiety and, under some circumstances, can affect its apparent hydrodynamic volume.[47]

Among the factors that can contribute to stick or superstick reorientation behavior is dielectric friction.[64,69,70,73–76] Dielectric friction impedes rotational motion of molecules in solution on the basis of the strength of dipole–induced dipole interactions. The transient polarization of the solution arising spontaneously from solvent molecule fluctuations will couple to the solute permanent dipole moment, with the strength of coupling scaling as r^{-6}. The interaction of the solvent fluctuations with the solute dipole moment induces a torque on the rotating molecule that acts to slow its motion. This contribution to the solvent–solute boundary condition is expected to operate in addition to the frictional terms considered in the DSE treatment and several methods have been used to evaluate the contribution of dielectric friction to solute reorientation.[65,73,74,77] For the rhodamines and solvents we use here, this effect is found to be a minor factor relative to frictional interactions (see Table 2).

In protic solvents, both solvent–solvent and solvent–solute hydrogen bonding can play a significant role in mediating solute motion. The characteristic persistence time of these interactions in long-chain alkanols is similar to the reorientation times seen for polar solutes in the size range of the rhodamines.[60] Hydrogen bonding interactions are known to play a significant role in determining solvent bulk viscosity, and the Blanchard group has reported previously on evidence for strong solvent–solute
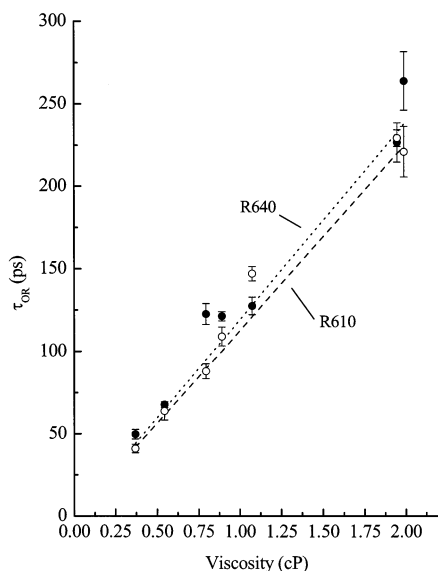
Figure 6. Reorientation time constants of R610 (solid circles) and R640 (open circles) as a function of solvent viscosity. The calculated DSE stick-limit line is shown for each chromophore, with a dashed line for R610 and a dotted line for R640.

TABLE 3: Calculated Molecular Volumes and S_0 Permanent Dipole Moments for the Rhodamines Examined Here[a]

probe	vol (Å^3)	μ (D)
R610	418	2.7
R640	443	2.6
R610 lactone	415	6.7
R700	375	5.7
R800	364	3.7

[a] Volumes were calculated from ref 57. Dipole moments were calculated using Hyperchem v. 6.0 with PM-3 parameterization.

hydrogen bonding interactions in alcohols and their effect on the reorientation dynamics observed for these systems.[43,60,61] In cases where H-bonding can play a role, the interaction is typically between the solvent alcohol proton and a specific functionality on the solute, such as an amine group. These interactions persist for sufficient time, on average, that the effect is to increase the hydrodynamic volume of the reorienting moiety (solute plus attached solvent), an effect that can be modeled effectively within the framework of the modified DSE equation.

We show the solvent viscosity dependence of R610 and R640 reorientation in Figure 6, along with the dependence predicted from eq 2 (lines). The data show that, with minor exceptions, both R610 and R640 reorient in the DSE stick limit, for both polar protic and aprotic solvents. Using the finding that the rhodamines reorient as prolate rotors, we calculate a shape factor of $S = 0.9$ for both R610 and R640 using Perrin's equations.[55,56] The reorientation dynamics of these two rhodamines are expected to be similar on the basis of their hydrodynamic volumes, 418 Å^3 for R610 and 443 Å^3 for R640 (see Table 3).[57] It is well established that polar solutes such as rhodamines reorient more slowly in polar protic solvents than the DSE model would predict whereas in polar aprotic solvents they are modeled well by the (modified) DSE equation.[50,58,66−68]

This trend can be understood to a significant extent on the basis of the characteristic persistence time of solvent−solute interactions. This interaction time has been shown to correlate with the longitudinal relaxation time, τ_L, of the solvent, at least for polar aprotics.[1−3,62] The longitudinal relaxation times for

TABLE 4: Selected Properties for the Solvents Used[a]

solvent	viscosity (cP)	vol (Å^3)	μ (D)	τ_D (ps)	n	ϵ_0	τ_L (ps)[b]
acetonitrile	0.369	47.1	3.92	3.9	1.34	37.5	0.2
methanol	0.544	36.1	1.70	55.6	1.328	32.6	3.0
DMF	0.794	76.6	3.82	27.4	1.43	36.7	1.5
water	0.89	20.6	1.85	8.2	1.333	78.5	0.2
ethanol	1.074	53.1	1.69	105	1.361	24.3	8.0
n-propanol	1.945	70.1	1.68	435	1.386	20.1	41.6
DMSO	1.987	76.8	3.96	20.6	1.478	4.7	9.6

[a] Values for τ_D are from refs 45 and references therein. Volumes are calculated from ref 50. Viscosity values are from refs 60 and 78. Solvent dipole moments (vapor phase) are taken from ref 78. [b] $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D$, $\epsilon_\infty = n^2$.
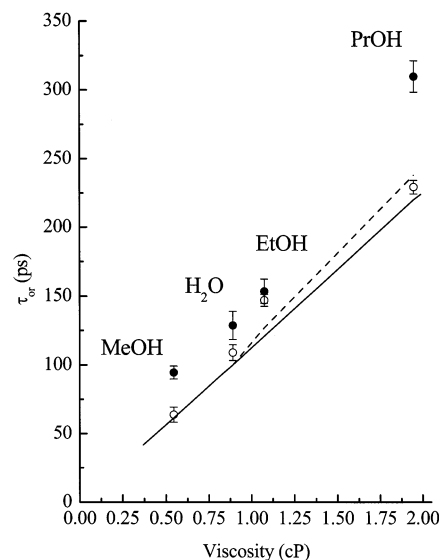

Figure 7. Reorientation time constants of ring-opened R610 lactone (solid circles) and R610 (open circles) as a function of solvent viscosity. The reorientation data for some solvents was not obtained. See text for explanation. The calculated DSE stick-limit lines are shown for each chromophore. For the ring-opened lactone, the calculated hydrodynamic volume reflects an increase due to ester formation.

the solvents used here (τ_L, Table 4) show that the dielectric relaxation times for the low viscosity protic and aprotic solvents are very similar and all are fast on the time scale of reorientation. Thus, the results for this system are substantially in keeping with the DSE model and there is little distinction between reorientation in polar protic and aprotic solvents because the reorientation time constants for the two chromophores are much longer than the longitudinal relaxation times for the solvents studied.

Figure 4 shows the absorption spectra of both the lactone and ring-opened forms of R610 lactone. R610 lactone undergoes a ring-opening reaction in alcohols to form the alkyl ester of R610. This reaction does not proceed in polar aprotic solvents and the reorientation data are available only for the ring-opened R610 lactone only in alcohols. We show these data in Figure 7, along with the reorientation data for R610 for comparison. The reorientation of the ring-opened R610 lactone and R610 are measurably different, with the exception of reorientation in ethanol, and we ascribe this difference to the added volume of the alkyl ester. We note that the addition of the aliphatic tail to the R610 chromophore yields reorientation behavior that is consistent with the "superstick" limit. We believe that this phenomenon is the result of relatively strong interactions between the (alkyl) ester functionality and the solvent. This argument is equivalent to the assertion that the interactions
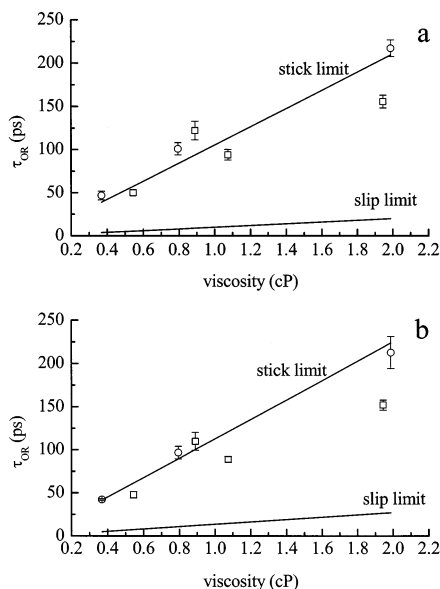
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Figure 8. Reorientation time constants of (a) R700 and (b) R800 as a function of solvent viscosity. Aprotic solvents are shown with open (○) circles and protic solvents are shown with open (□) squares. For each chromophore the calculated DSE stick and slip-limit lines are shown.

between the R610 aliphatic ester moiety and the surrounding solvent is of the same order as solvent−solvent interactions that give rise to the relatively high viscosity of the alkanols.

The reorientation dynamics of R700 and R800 are shown in Figure 8 as a function of solvent viscosity, along with the DSE predictions. Included with the data are two lines, the upper being the DSE predicted reorientation in the "stick" limit and the lower the DSE predicted "slip" limit. These values of the boundary conditions were obtained using the "stick" limit ($f = 1$) or the calculated "slip" limit ($f \sim 0.1$) for a prolate rotor with shape factors $S = 0.81$ (R700) and 0.84 (R800).[56] The shape factor was calculated according to Perrin,[55] and the slip-limit frictional term was determined using the method of Hu and Zwanzig.[56] The reorientation data for these two molecules show a clear distinction between polar protic and aprotic solvents. In the solvents methanol, ethanol, and propanol, both R700 and R800 exhibit slightly substick reorientation times, whereas in water and the polar aprotic solvents, we observe stick-limit behavior. The reorientation dynamics measured in the alcohols are not consistent with slip-limit predictions, but there are two clearly discernible groups of data (Figure 8).

The data for R610 and R640 reorientation differ qualitatively from that seen for R700 and R800. For the first two chromophores, there is not a clear distinction between their reorientation dynamics in polar protic and aprotic solvents, whereas there is clear distinction for R700 and R800. It is tempting to ascribe this difference in behavior to differences in the structures of these two groups of molecules, and indeed, several distinctions can be made on the basis of structure. The first distinction is that the calculated permanent ground-state dipole moments of R610 and R640 are smaller than those for R700 and R800 (Table 3). This finding is consistent with the experimental data in the sense that, for R610 and R640, we observe little discernible difference between their reorientation behavior in the alcohols and in polar aprotic solvents. For R700 and R800, we observe stronger solvent−solute interactions for polar aprotic solvents than for the alcohols or water. The larger permanent dipole moment of these two chromophores serves

to interact with solvents characterized by large permanent dipole moments (Table 4).

Another structural feature that is worthy of examination is the shape of the chromophores. R610 and R640, by virtue of their *o*-benzoate group at the 1 position, are expected to sweep out volumes that are substantially more spherical than those seen for R700 and R800. This effect is seen in the calculated shape factors for these two groups of molecules; $S \sim 0.9$ for R610 and R640 and $S \sim 0.8$ for R700 and R800. In the stick limit, such a distinction would not matter, but in the slip limit, the frictional term f would be larger for R700 and R800 than for R610 and R640. We are not implying that the rhodamines behave in the slip limit for the solvents we have studied here, but if there is any slip-like component to frictional solvent−solute interactions, we assert that such contributions would be more prominent in systems with a more anisotropic rotor shape, hence the more pronounced solvent dependence for R700 and R800.

In comparing the reorientation dynamics of R610 and R640, we would expect R610 to be slightly faster than R640 on the basis of the (small) difference in hydrodynamic volume. Instead, we find that R610 exhibits reorientation times equal to or longer than those of R640 in all of the solvents studied. This effect is especially pronounced in the solvents water, methanol, and ethanol (Table 1). We understand this behavior in terms of the motional freedom of the terminal amines in R610 and their restricted motion in R640. Semiempirical calculations show that, when free to rotate, the amino groups are capable of stabilizing a partial positive charge, making them more amenable to strong solvent−solute interactions. When both dipolar and structural contributions to the reorientation and linear response of the rhodamines are considered, we can understand the behavior of these chromophores within the framework of a single system.

Conclusion

We have examined the linear optical response and reorientation dynamics of several rhodamines in a series of polar protic and aprotic solvents. The reorientation data are all qualitatively consistent with the modified DSE model in the stick limit. At a quantitative level, several trends emerge. The first is that dipolar solvent−solute interactions are at least as important in determining reorientation dynamics as are H-bonding interactions for the rhodamines, and the distinction between polar protic and aprotic solvents is most clear for rhodamines with small polar substituents at the 1 position. We also find that H-bonding interactions with the chromophore terminal amino groups are more prominent in chromophores where the amino groups are free to rotate, and we understand this phenomenon in the context of the ability of the free and locked amino groups to stabilize charge. In the case of reactive systems, such as R610 lactone, only polar protic solvents are capable of participating in a lactone ring-opening reaction to form an ester. Our reorientation data reflect the formation of the ester and, for the esters, we observe stronger solvent−solute interactions than are seen for the native chromophore, R610. The basis for this finding requires further investigation.

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