Influence of Viscosity and Temperature on Rotational Reorientation. Anisotropic Absorption Studies of 3,3'-Diethylxocarbocyanine Iodide

David H. Waldeck and Graham R. Fleming

Department of Chemistry and James Franck Institute, The University of Chicago, Chicago, Illinois 60637 (Received: February 4, 1981; In Final Form: May 1, 1981)

The rotational diffusion of a single probe molecule, 3,3'-diethylxocarbocyanine iodide (DODCI), has been studied in various normal alcohols by the anisotropic absorption method. At room temperature an apparent saturation of the reorienting influence of viscosity is observed for the higher alcohols. Temperature-dependent studies in single solvents over the same viscosity range show no such saturation, which is therefore ascribed to specific effects associated with increasing solvent size. The activation energies obtained for the reorientation rate are generally identical with the solvent viscosity activation energy. When temperature and viscosity variations are studied in a single solvent, hydrodynamics with a stick boundary condition gives an accurate and consistent description of our data.

Introduction

The measurement of rotational reorientation dynamics in solution by picosecond spectroscopic techniques has attracted a number of workers in recent years.1-5 Studies have been performed on a range of dye molecules in a series of solvents in order to test the predictions of Stokes–Einstein hydrodynamic theory. The results of these studies can be summarized as follows. Molecules with a single positive charge in hydrogen-bonding solvents of low to medium viscosity seem to follow the predictions of hydrodynamics with a stick boundary condition.6 The situation with anions in hydrogen-bonding solvents is more complex. The dianion fluorescein derivatives in hydrogen-bonding solvents rotate at about half the speed expected from a stick boundary condition, and solvent attachment has been suggested as the likely explanation.4 Spears and Cramer5 showed that the rotation time of the fluorescein derivative rose bengal was a factor of 2 shorter in polar aprotic solvents than in alcohols of similar viscosity. A similar trend was observed recently by Spears and co-workers6 for the monooanion resorufin, but here there was a much larger ratio between alcohol and aprotic solvents (5:1 vs. 2:1 for rose bengal). In higher-viscosity solvents, workers have seen deviations from hydrodynamic predictions for both cations and anions.7,9 These deviations have been attributed to a saturation of the reorienting influence of the viscosity8 to specific solvent effects, such as increasing size of the solvent molecule.5 To test these conclusions in detail, we have chosen to study the rotational reorientation of a "singly positively charged" molecule, DODCI, over a wide viscosity range and as a function of temperature. Although there are considerable uncertainties in the molecular shape and volume, the use of a single probe molecule in a wide range of solvents should minimize these difficulties. Varying the ratio $\eta/\zeta$ over the same range for a single solvent by temperature change and for a series of different solvents at constant temperature should help to distinguish specific effects (e.g., increasing solvent size) from those that merely depend on the viscosity. In addition, if the energy of interaction (or "lifetime") of the solvent–solute complex is important,4 changes in temperature may alter the observed boundary condition. Temperature-dependent studies will also enable the activation energy for the reorientation dynamics to be obtained and compared with the activation energy of the solvent viscosity.

The technique which we have used is the anisotropic absorption method of Shank and Ippen.10 We have recently shown that in this technique both induced dichroism (caused by differing absorption cross sections $S_0$ and $S_1$) and induced birefringence (caused by a change in the anisotropy of the polarizability between $S_0$ and $S_1$) contribute to the signal.11 In that study, these effects and the influence of any external birefringence were described in a Jones matrix formalism. The change in polarizability anisotropy was obtained for two molecules. We have also shown that, when high-quality (strain-free) optics are used, very precise and accurate reorientation times are obtained.11 One reason for the choice of DODCI as the probe molecule is that the change in the polarizability anisotropy is quite small (~4 $A^2$) and signals are less likely to be influenced by external birefringence than in a number of other molecules. The anisotropic absorption technique measures the signal $I(t) = \langle r_1(t) K(t) \rangle$, where $r_1(t) = \langle \mu(0) \mu(t) \rangle$ is the rotational correlation function and $K(t)$ is the excited-state decay law.2

In the present work we have also measured fluorescence lifetimes for DODCI in all of the solvents and at each temperature. The results of this study will be presented elsewhere.12

Experimental Section

The excitation source for all of the experiments reported

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1 Exxon Predoctoral Fellow, 1980.
2 Alfred P. Sloan Foundation Fellow.

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here was a synchronously pumped rhodamine 6G dye laser operating at 580 nm. The characteristics of the laser have been described previously, as has the optical arrangement for anisotropic absorption. Briefly, the pump and probe beams polarized at 45° to each other are focused into the sample, and the intensity of the probe beam is monitored, as a function of time delay, through an analyzer polarizer oriented to extinguish the probe light in the absence of pump beam excitation. The observed decay time is very sensitive to the purity of the linearly polarized probe beam through the interaction of the transient birefringence and any strain birefringence in the lens, polarizers, etc. Hence, very high-quality optics are required for this technique. Our polarizers are quality E Glan Taylor from Karl Lambrecht. The focusing and recollimating lenses are 10-cm focal length either from Optics for Research or especially fabricated by Karl Lambrecht Corp. from Schott superannealed glass. In all of our experiments, the extinction ratio (ratio of the intensity transmitted with polarizers crossed to intensity transmitted with polarizers parallel) was <5 × 10⁻⁷. In our previous work we showed that this extinction ratio is adequate to obtain correct reorientation times for DODCI.

Fluorescence decay times were obtained by the time-correlated, single-photon counting method, again using a synchronously pumped dye laser as the excitation source. The experimental setup is similar to that described by Robbins et al. with the exception that an Amperex PM31000 was used to detect the fluorescence. The instrument function was ~270 ps. Both anisotropic absorption and fluorescence decay curves were fit to single exponential decays by least-squares fitting on a VAX 11-780 computer. For the fluorescence data the method of iterative convolution was used in the fitting. The precision of both the observed decay time of the anisotropic absorption signal (τₐ, see eq 1) and the fluorescence lifetime is estimated to be ±5%. In the case of decanol solutions, particularly at the lower temperatures, the τₐ values may be less precise because of systematic errors arising from misalignment of the translation stage during the long (~6 in.) translations required and from the inability to fit the decay over more than two lifetimes.

DODCI (3,3'-diethyloxadicarbocyanine iodide) (Eastman, laser grade) was used in various normal alcohols (analytical grade) at concentrations of ≤2 × 10⁻⁴ M. No evidence for a contribution to the anisotropic absorption decay from Förster energy transfer was observed in hexanol at concentrations ranging from 5 × 10⁻⁵ to 10⁻³ M. The sample was flowed through a standard dye laser nozzle. This simple technique avoids the problem of sample heating, troublesome reflections from the windows of optical cells, and the interference of any strain birefringence in the cell window. For the temperature-dependent studies the sample circulated through a coil immersed in a temperature-controlled ethylene glycol–water bath. The temperature controller was a Neslab RTE-4. Sample temperatures were measured by a thermometer in the sample reservoir.

Results

A typical anisotropic absorption result is shown in Figure 1, along with the fitted exponential curve.

\[ 1/\tau_{\text{ref}} = 1/(2\tau_{\text{M}}) - 1/\tau \]  

where \( \tau_{\text{M}} \) is the measured decay time and \( \tau \) is the excited-state lifetime obtained from the fluorescence lifetime measurements. The results of an extensive temperature- and solvent-dependent study of \( \tau \) for DODCI will be presented elsewhere.

**Solvent Study.** Figure 2 shows the dependence of \( \tau_{\text{ref}} \) on viscosity (η) at room temperature (23 °C) for DODCI dissolved in normal alcohols. After butanol the points became more scattered; the general trend is for \( \tau_{\text{ref}} \) to be smaller in the higher alcohols than would be expected by extrapolation of the linear dependence observed for the lower alcohols. In other words, an apparent saturation effect is observed.

The first six normal alcohols fall on a smooth curve, but the \( \tau_{\text{ref}} \) observed for 2-propanol lies below this curve presumably pointing to a specific influence of the solvent shape. In their study of the reorientation dynamics of rhodamine 6G, von Jena and Lessing observed the influence of different butanol isomers. In their study the normal isomer gave the shortest reorientation time in contrast to our result with the two propanol isomers. Clearly more comprehensive studies are required before attempting to interpret these findings.

**Temperature Studies.** Figure 3, a-c, shows the dependence of \( \tau_{\text{ref}} \) on η/T for ethanol, butanol, and decanol solutions. Here the dependence is linear with η/T; no sat-
Table I: Reorientation Times ($\tau_{or}$) as a Function of Temperature and Viscosity

<table>
<thead>
<tr>
<th>solvent</th>
<th>$10^{3}$ (slope) $^a$</th>
<th>slope at $T = 298$ K, $^{a}$</th>
<th>intercept $^a$</th>
<th>exp. vol.$^b$</th>
<th>$^A^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>46.7 ± 2.2</td>
<td>157 ± 7.4</td>
<td>-24 ± 9</td>
<td>374 ± 18</td>
<td></td>
</tr>
<tr>
<td>1-butanol</td>
<td>43.9 ± 3</td>
<td>147 ± 10</td>
<td>-18 ± 22</td>
<td>352 ± 24</td>
<td></td>
</tr>
<tr>
<td>1-decanol</td>
<td>39.2 ± 4</td>
<td>132 ± 15.4</td>
<td>-99 ± 66</td>
<td>314 ± 32</td>
<td></td>
</tr>
<tr>
<td>normal alcohols</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(n = 1-4)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>normal alcohols</td>
<td>39.4 ± 3</td>
<td>132 ± 10</td>
<td>16 ± 9</td>
<td>316 ± 24</td>
<td></td>
</tr>
<tr>
<td>$(n = 1-6, 8, 10)$</td>
<td>33.8 ± 1.6</td>
<td>112 ± 4</td>
<td>33 ± 6</td>
<td>271 ± 13</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Slope and intercept obtained from weighted least-squares fit of $\tau_{or}$ vs. $\eta/T$. Weighting factor $1/\sigma^2$ derived from $\sigma_M^2 = 0.025\eta_M, \sigma_T = 0.025\tau$. Errors quoted are ±2 standard deviations.

Slope and intercept obtained from weighted least-squares fit of $\tau_{or}$ vs. $\eta/T$. Weighting factor $1/\sigma^2$ derived from $\sigma_M^2 = 0.025\eta_M, \sigma_T = 0.025\tau$. Errors quoted are ±2 standard deviations.

Discussion

The slopes and the intercepts for the plots of $\tau_{or}$ vs. $\eta/T$ show a remarkable agreement among the three solvents in which temperature studies were performed and the first four normal alcohols at room temperature. Within our experimental precision the intercept is always very close to zero as should be the case for simple Stokes hydrodynamics. The free rotor time for DODCI is 4 ps, and thus an empirical equation of the form$^{16}$ suggested by Bauer et al.$^{16} r_0 C \eta + \tau_0$ where $\tau_0$ is the free rotor reorientation time—would have an intercept within our experimental error. We do not believe that our data are precise enough to attach significance to the small decrease in slope through the series ethanol, butanol, decanol.

The final entry in Table I shows the influence of including the higher alcohols in the fit for the normal alcohols; the slope is lowered and the intercept raised by their inclusion. It seems clear that specific solvent effects (see Figure 2) occur for alcohols larger than butanol and that studies of viscosity-dependent phenomena in a series of different solvents do not represent an unambiguous method of testing hydrodynamic predictions. This remark should also apply to radiationless processes involving viscosity-hindered, large-amplitude motion such as stilbene trans-cis photoisomerization.$^{17,18}$


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Table II: Activation Energies for the Reorientation Rate ($\Delta E(k_{\alpha})$) and Solvent Viscosity ($\Delta E(\eta)$)

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\Delta E(k_{\alpha})$, kcal/mol</th>
<th>$\Delta E(\eta)$, kcal/mol</th>
<th>$A$, $\text{s}^{-1} \text{K}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>$4.2 \pm 0.2$</td>
<td>$3.4$</td>
<td>$(2.64 \pm 0.13) \times 10^{10}$</td>
</tr>
<tr>
<td>1-butanol</td>
<td>$4.9 \pm 0.3$</td>
<td>$4.6$</td>
<td>$(3.95 \pm 0.1) \times 10^{10}$</td>
</tr>
<tr>
<td>1-decanol</td>
<td>$7.4 \pm 0.7$</td>
<td>$6.3$</td>
<td>$(58.8 \pm 70) \times 10^{10}$</td>
</tr>
</tbody>
</table>

$^a$ Calculated from data in ref 15.  $^b$ Preexponential factor in eq 2. $A = \phi k T / (V \nu_0)$. Errors quoted are $\pm 2\sigma$.

The temperature-variation studies give more consistent data and should provide less ambiguous tests of hydrodynamic predictions. It is well-known empirically that the mobility ($\eta^{-1}$) of many solvents exhibits Arrhenius-type behavior, i.e., $\eta^{-1} = \eta_0^{-1} \exp(-\Delta E(\eta)/kT)$.

Figure 4a shows a plot of $\ln (\eta^{-1})$ vs. $1/T$ for butanol. Excellent straight lines are obtained for the three solvents over the temperature range of interest. Viscosity data were obtained from Landolt-Börnstein.

For single exponential $r(t)$, stick hydrodynamics gives $k_{\alpha} (=r_{\alpha}^{-2}) = \phi k T / V \nu_0$, where $V$ is the molecular volume and $\phi$ is a geometric factor.

For the solvents studied here, we can then write

$$k_{\alpha} = \frac{k T}{V \nu_0} \exp(-\Delta E(\eta)/kT)$$

Thus, plots of $\ln (k_{\alpha}/T)$ vs. $1/T$ should be linear with slope $\Delta E(\eta)/k$. Figure 4b shows a representative plot for DODCI in 1-butanol. The data for the three solvents studied are collected in Table II. The reorientation rate’s activation energy, $\Delta E(k_{\alpha})$, parallels the viscosity’s activation energy, $\Delta E(\eta)$. For butanol and decanol, $\Delta E(k_{\alpha})$ and $\Delta E(\eta)$ are equal within our experimental error. For ethanol $\Delta E(k_{\alpha})$ is $\sim 1$ kcal larger than $\Delta E(\eta)$. In their study of the reorientation dynamics of rhodamine 6G in glycerol, Rice and Kenny-Wallace found $\Delta E(k_{\alpha}) \leq 2.15$ kcal/mol as compared with $\Delta E(\eta)$ of 16.2 kcal/mol. It was suggested that the solute is relatively unhindered in its rotation within a solvent cage and that simple hydrodynamics was therefore inappropriate. In the smaller, lower-viscosity solvents studied in this work, the results show that simple hydrodynamics gives a remarkably accurate description of the reorientation dynamics of DODCI and that the macroscopic solvent viscosity is an appropriate measure of the friction on the rotating probe molecule.

Implications on Molecular Shape of DODCI

Our conclusions so far have not depended on a theoretical value for the reorientation time in a given solvent. In a previous fluorescence depolarization study of DODCI, it was concluded that the normal form of DODCI has a compact configuration (cis,cis-1,5-DODCI) and approximates an oblate rotor. The calculation of $\tau_{\alpha}$ gave $\sim 138 \pm 14$ ps/cP at 298 K assuming a stick boundary condition. The calculation was for an oblate rotor with semiaxes $6.5 \times 6.5 \times 2 \text{ Å}$ ($V = 354 \text{ Å}^3$) as obtained from space-filling models. The values in Table I for $\tau_{\alpha}$ (ps/cP) at 298 K are very similar to both this value and the previous measurements of 160 ps in ethanol. However, given the rather large errors associated with approximating DODCI as a smooth ellipsoid, too great a significance should not be attached to the numerical agreement of the slope calculated for a symmetric rotor with stick boundary conditions and the measured slopes. The experimental volumes are also listed in Table I.

A compact rather than extended form of DODCI is also consistent with the small polarizability anisotropy change observed between $S_0$ and $S_1$. An extended (trans) conformation should have one component of the polarizability (the one along the long axis) significantly larger than the others. This dominant component should become significantly larger in $S_1$ if the transition moment lies (as expected) along the long axis. Thus, a significant increase in anisotropy is expected. The compact form, on the other hand, will have significant polarizability in at least two directions, and for comparable absolute changes in polarizability the anisotropy change will be much less for the compact form than for the extended form.

Concluding Remarks

For a fairly large, positively charged, molecule like DODCI dissolved in interacting (e.g., H-bonding) solvents, a simple hydrodynamic description (including the empirical temperature dependence of solvent viscosity) gives a remarkably accurate and consistent description of the rotational diffusion, provided temperature and viscosity variations are studied in a single solvent.

No evidence for a “saturation effect” at high viscosity was found in the single-solvent studies, nor was there any influence of temperature on the boundary condition (or apparent molecular volume). A possible implication of the present work is that, where solvent–solute interactions are strong, the strength of interaction and the lifetime of the solvent–solute complex can be varied over quite large ranges without influencing the detailed form of the rotational diffusion coefficient. It will be interesting to see whether these phenomena are observed with smaller nonpolar molecules in noninteracting solvents.

Acknowledgment. This work was supported by NSF Grant CHE-80-09216 to Graham R. Fleming. David H. Waldeck was an Exxon predoctoral fellow 1979–80. We thank Mr. Stephan Velsko for access to his lifetime data and for numerous helpful discussions.

(20) Landolt-Börnstein, "Zahlenwerte und Funktionen", Springer-Verlag, New York, Band II, Teil 5.