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Rotation of Aromatic Hydrocarbons in Viscous Alkanes. 1. Methylcyclohexane

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Time-resolved single-photon counting has been used to measure the decay of fluorescence anisotropy of a number of aromatic hydrocarbons in methylcyclohexane excited by synchrotron radiation. Changing the temperature (−60 to −140 °C) produces large changes in the viscosity, η. Most solutes were excited both parallel and perpendicular to the emission axis with the aim of determining all three principal rotational diffusion coefficients, D. The results are compared to predictions from hydrodynamic theory made using the "slip" and "stick" approximations and literature data for the *n*-alkanes and other solvents. Rotation times should be proportional to η/T, i.e., $D\eta/T$ should be constant. This is found to be approximately true for 9,10-disubstituted anthracenes; it does not hold for anthracene, perylene, and triphenylene for which $D\eta/T$ increases markedly on cooling. Also, against prediction, the ratios between D values for different molecular axes are found to change with temperature.

Introduction

Recent work on molecular relaxation in liquids has been concentrated in two areas—laser studies of mobile liquids on the picosecond time scale[1−7] and the use of a variety of techniques to study the changes in behavior of viscous liquids as the glass transition is approached (see Tanaka[8] for a convenient source and short review of the latter field). Decay of fluorescence polarization has been widely used partly because trace quantities of probe molecules or intrinsic fluorophors can be used to measure microscopic viscosities.[9] It has the disadvantages of limited time range (about 0.1−100 ns depending on the system) and of low precision. There is also the general problem of perturbation of its surroundings by the probe. On the other hand, anisotropy decay unambiguously measures solute rotation and, in principle, it is possible to separate the three principal components of the rotation tensor in suitable cases. In practice, the latter aim has seldom been achieved. The present paper describes a partly successful attempt to do so.

Early work on the decay of fluorescence anisotropy commonly made use of viscous liquids such as glycerol to slow the rotation rate to times of some tens of nanoseconds. The use of lasers has made possible measurements on the picosecond time scale and so of solutions in simple liquids such as *n*-alkanes.[2−4,7] However, the liquid range, and therefore the viscosity range, in any one *n*-alkane is quite small; less symmetrical alkanes give a much wider range, and some form glasses rather than crystallize, on cooling. Our aim in this and the following paper[10] has been to explore the opportunities afforded by two less symmetrical alkanes, methylcyclohexane (MCH) and squalane (2,6,10,15,19,23-hexamethyltetracosane). The melting point of MCH is −126.6 °C, and it is cf. +6 °C for cyclohexane. The methyl groups, which make crystallization more difficult, may also reduce the occurrence of specific interactions. These two papers form a considerable extension of the earlier work.[11]

Theory and Background

The fluorescence anisotropy, r, is defined by

$$r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence components parallel and perpendicular to the exciting light (vertically and horizontally polarized in most experiments). The decay of r is most commonly found to follow a single exponential. However, provided that the rotational diffusion coefficients, D_i, around the three principal axes differ substantially, it is quite easy to see biexponential decay:

$$r(t) = r_1 \exp(-t/\tau_1) + r_2 \exp(-t/\tau_2) \tag{2}$$

This condition is fulfilled by a number of aromatic compounds, notably perylene, for which Weber demonstrated that in-plane rotation is usually much faster than the out-of-plane motion.[12] Equation 2 is used to describe the experimental results in this paper.

To facilitate the description, the convention is adopted throughout this paper that the x axis is perpendicular to the molecular plane and that the emission dipole is parallel to the z axis. Chart 1 shows some of the molecules studied and the alignment of these axes. Other molecules used were coronene, tetracene, and the 9,10-disubstituted anthracenes (dichloro-, dimethyl-, and diphenylanthracenes are abbreviated DCA, DMA, and DPA, respectively). Coronene has D_{6h} symmetry; the others resemble anthracene. (Benzoperylene is included here and in Tables1 and 2 though it has been studied only in squalane.[10]) In most anisotropy experiments, the solute has been excited in the first absorption band so that transition axes for absorption and emission are parallel (z excitation). When two decays are present, analysis of the data is facilitated and more information can be obtained by comparing such results to those from excitation in a higher absorption band with its dipole oriented at an angle, usually a right angle, to the first[13] (y excitation).

The effect of changing the excitation wavelength is to change the relative importance of rotation around the three principal

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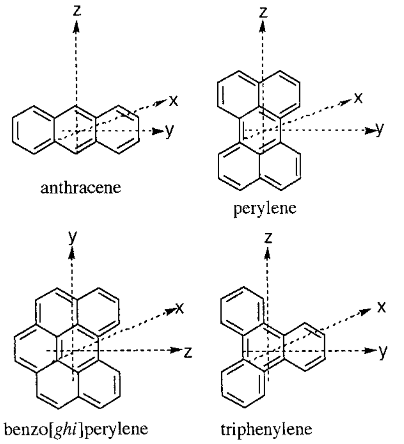
CHART 1: Structures of Some of the Solutes Used[a]



[a] Fluorescence is polarized along the *z* axis (in the molecular plane for triphenylene).

TABLE 1: Molecular Dimensions, Fluorescence Lifetimes at Ambient Temperature (from Refs 36 and 37), and Excitation Wavelengths

compound	*x*/Å	*y*/Å	*z*/Å	τ_F/ns	wavelength/nm *z*	 *y*
triphenylene	3.4	11.0	11.0	36.6	260	
coronene	3.4	12.04	12.04	~400	342	
anthracene	3.4	11.62	7.46	4.9	356	258
9,10-dichloroanthracene	3.4	11.62	10.0	8.5	382	265
9,10-dimethylanthracene	3.4	11.62	9.57	17.5	377	265
9,10-diphenylanthracene	6.71	11.62	17.02	9.4	355	270
perylene	3.4	9.13	11.68	6.4	430	255
benzo[*ghi*]perylene	3.4	11.66	10.39	180	365	303
tetracene	3.4	14.06	7.46	6.0	438	276

TABLE 2: Predicted Values of the Quantity, $D\eta/T$, Calculated Using the Stick and Slip Approximations, in Units of 10^{-4} kg m^{-1} s^{-2} K^{-1} as in the Figures

	stick			slip		
compound	D_x	D_y	D_z	D_x	D_y	D_z
triphenylene	0.284	0.361	0.361		0.652	0.652
coronene	0.226	0.28	0.28		0.459	0.459
anthracene	0.408	0.742	0.416	3.921	2.245	0.737
9,10-dichloroanthracene	0.302	0.421	0.344	32.97	0.815	0.596
9,10-dimethylanthracene	0.315	0.460	0.354	16.76	0.943	0.801
9,10-diphenylanthracene	0.1092	0.1157	0.1823	1.133	0.138	0.3235
perylene	0.332	0.361	0.503	9.99	0.627	1.089
tetracene	0.282	0.636	0.272	1.457	1.831	0.413
benzo[*ghi*]perylene	0.287	0.389	0.332	34.34	0.729	0.571

axes. For example, rotation round the *z* axis alone has no effect in the case of *z* excitation, but it does for *y* excitation. However, rotations around *x*, *y*, and *z* are not alternatives; all take place together. Mathematical analysis[14] leads to the following results. While in principle the decay of *r* may involve five components, only two are expected when the absorption and emission dipoles lie parallel to principal molecular rotation axes, which is the case for these molecules. Combination of eq 1 and the relevant terms of Chuang and Eisenthal's eq 12[14] gives

$$r(t) = 0.3\{(\beta + \alpha)\exp(-\overline{6D + 2\Delta t}) + (\beta - \alpha)\exp(-\overline{6D - 2\Delta t})\} \quad (3)$$

where *D* is the average rotational diffusion constant and Δ is related to the asymmetry of the diffusion tensor:

$$D = (D_x + D_y + D_z)/3 \quad (4)$$

$$\Delta = (D_x^2 + D_y^2 + D_z^2 - D_xD_y - D_yD_z - D_zD_x)^{1/2} \quad (5)$$

$$\beta = q_x^2\gamma_x^2 + q_y^2\gamma_y^2 + q_z^2\gamma_z^2 - 1/3 \quad (6)$$

$$\alpha = (D_x/\Delta)(q_y^2\gamma_y^2 + q_z^2\gamma_z^2 - 2q_x^2\gamma_x^2 + q_x^2 + \gamma_x^2) + (D_y/\Delta)(q_z^2\gamma_z^2 + q_x^2\gamma_x^2 - 2q_y^2\gamma_y^2 + q_y^2 + \gamma_y^2) + (D_z/\Delta)(q_x^2\gamma_x^2 + q_y^2\gamma_y^2 - 2q_z^2\gamma_z^2 + q_z^2 + \gamma_z^2) - 2D/\Delta \quad (7)$$

where γ and **q** are vectors describing the direction of the absorption and emission dipoles. If both are parallel to the *z* axis (both vectors (0,0,1)), $\beta = {}^2/_3$ and

$$\alpha = (D - D_z)/\Delta \quad (8)$$

For emission parallel to *z* and absorption parallel to *y*, $\beta = -{}^1/_3$ and

$$\alpha = (D - D_x)/\Delta \quad (9)$$

It follows that the maximum initial polarizations are 0.6β, i.e., +0.4 and −0.2 at time zero.

The same two decay rates should be observed regardless of excitation wavelength, but the relative values of r_1 and r_2 vary widely, depending on the relative values of the D_i. Simpler results are obtained if two of the D_i are assumed to be equal; this approximation has frequently been applied to perylene, for example.[12−14] There are some useful limiting cases, disks (approximated by perylene, cf. Table 1) for which $D_x > D_y = D_z$, rods with *y* as the long axis (approximated by tetracene) for which $D_y > D_x = D_z$, and rods with *z* as the long axis for which $D_z > D_x = D_y$. This last case is approximated by diphenylhexatriene, which is widely used to probe viscosity on the molecular scale. r_1 is zero in the extreme case; i.e., single-exponential decay is observed and no new information results from changing the excitation wavelength.

Even when both r_1 and r_2 can be measured, interpretation of the results is not straightforward because it is almost always found that $\sum r = r_1 + r_2 < 0.4$ (*z* excitation). The reasons for this are not easy to find.[15,16] A plausible explanation is the occurrence of libration (unhindered rotation over a limited range); while there is good evidence for this in some cases,[17,18] it does not provide a complete explanation.[15] The assumption that the solutes are planar with D_{2h} or higher symmetry may be invalid; this has been demonstrated for perylene.[16] Many other aromatics (coronene, triphenylene) have been shown to be nonplanar in the crystal; nothing is known of their structures in solution. In triphenylene and perylene, distortion may well result from steric interaction between hydrogen atoms. This will not occur for anthracene and tetracene. For them nonplanarity in solution is unlikely.

Though the transition dipoles of strong transitions in aromatics are parallel to the molecular axes for reasons of symmetry, weaker transitions may involve mixing with other excited states induced by coupling with unsymmetrical vibrations leading to mixed polarizations. If this happens for fluorescence alone, excitation at various wavelengths will be affected equally. More generally, absorption to the first and higher states will be affected to different extents, which alters the factor of −2 between the total initial polarizations.

Rotation rates of solute molecules are commonly discussed in terms of the hydrodynamic theory developed by Einstein and Perrin for spheres[19] and ellipsoids.[20] The rotational diffusion coefficient around axis *i* is given by

$$D_i = \frac{kT}{\eta V f_i} \tag{10}$$

where η is the viscosity, V the volume of the solute molecule, and f_i a friction coefficient that depends on the shape of the molecule and on the interaction between solute and solvent. The corresponding rotation time τ_i is

$$\tau_i = \frac{1}{6D_i} + \tau_{iI}; \qquad \tau_{iI} = \frac{2\pi}{9}\sqrt{\frac{I_i}{kT}} \tag{11}$$

where I_i is the corresponding moment of inertia and the second term corresponds to free (inertial) rotation. For these molecules, the τ_I are a few picoseconds and can be neglected here. Hydrodynamic theory treats the solvent as a continuum, implying that a thin layer rotates with the solute ("stick approximation"). This works quite well for molecules much larger than the solvent molecules, but smaller molecules rotate more rapidly.[21−23] Such behavior is described as "slip".[12,21,24,25] In the limiting case, rotation does not depend on friction. For example, a spheroid can rotate freely about its principal axis, but rotation about other axes is slower because of the need to displace solvent. Hydrodynamic theory has been extended to cover this behavior in the case of spheroids[26] and ellipsoids.[27,28]

At very high viscosities, saturation is observed;[29] i.e., D rises more slowly than η/T. Rotation faster than slip is described as "subslip". Such behavior in alcohol solutions[30] has been ascribed to the formation of a large cavity round the solute as a result of hydrogen-bonding in the solvent. However, the phenomenon is also seen in the alkanes.[2−4,7,22,31,32] These studies further illustrate the importance of relative molecular size; rotation times rise less steeply with viscosity once the length of the solvent molecule exceeds that of the solute. Solutions of aromatic hydrocarbons in alkanes might appear to be particularly simple because of the weakness of solute−solvent interactions, but studies of vibrational relaxation in such solutions provide evidence of local structure around the solute even in this case.[33,34]

An earlier paper[11] described studies of solutions in two glass-forming liquids: MCH and squalane. Changing the temperature gave striking results for perylene solutions; two exponentials were needed to fit the decays but their relative contributions were found to change with temperature, in marked contrast to standard hydrodynamic behavior. We have now found considerable differences in behavior between the two solvents, probably the result of their sizes relative to the solutes. In MCH, most, though not all, of the data can be described qualitatively by hydrodynamic theory. These results are reported here and compared to data for the same solutes in other solvents. In squalane, new phenomena are found that can be described in terms of limited range rotation and the α and β processes used to intepret relaxation near the glass transition; these are reported in the following paper.[10] The earlier work has been extended in two ways: solutes have been excited at two different wavelengths and a wider range has been used.

For comparison with experimental results, theoretical values of the diffusion coefficients have been calculated using the stick and slip approximations for ellipsoids and are listed in Table 2. Molecular dimensions (Table 1) were taken from the crystal structures. As before,[11] the molecules were first regarded as rectangular blocks and then the dimensions rescaled to obtain ellipsoids with the same volume and the same axial ratios. Alternative procedures can be used,[2] but in any case the ellipsoid approximation is likely to introduce considerable errors. In particular, it is hardly realistic for the substituted anthrancenes. The substituted anthracenes were treated as follows. The van der Waals radii of chlorine atoms (1.8 Å) and methyl groups (2.0 Å) are only slightly greater than the half-thickness of the aromatics (1.7 Å), so these differences have been ignored in preference to using the larger values for the whole molecule. In the case of DPA, the phenyl groups were assumed to lie at an angle of 30° to the plane of the anthracene. For the stick approximation, friction coefficients were then calculated from Perrin's equations for ellipsoids.[20] In the case of slip, the dimensions were used to obtain f values by interpolation in the table given by Sension and Hochstrasser,[28] which corrects the original work of Youngren and Acrivos.[27] Relative values of the diffusion coefficients are very sensitive to the dimensions, but the differences between theory and experiment are such that errors in the absolute values are not important.

Experimental Section

Purification of the solvents and the experimental procedure have been described previously.[11,35] In brief, ultraviolet and visible light from the synchrotron radiation source (SRS) at the CCLRC's Daresbury Laboratory was used to excite samples and the luminescence decays recorded using single-photon counting. The pulse width is approximately 160 ps; the instrument response (fwhm of 300 ps) was determined by scattering from Ludox suspensions. This is larger than in laser experiments and limits the short decay times that can be measured. It is partly due to the jitter of the photomultiplier transit time and partly to the pulse width of the SRS. For most light sources, both are wavelength-dependent; however, synchrotron radiation has the advantage that pulse shape is independent of wavelength so that the response function can be determined accurately by observing the scattering from Ludox suspensions at the mean fluorescence wavelength. Determination of longer decay times depends on the fluorescence lifetime. These were usually maximized by deoxygenating the samples. Satisfactory agreement between measured and literature values[36,37] (Table 1) was obtained in all cases.

Care was taken to ensure that no scattered incident light reached the photomultiplier. It could be detected by its short apparent lifetime and its high polarization (greater than the theoretical maxima of 0.4 and −0.2 for fluorescence). To ensure separation of fluorescence and exciting light, a variety of glass cutoff and band-pass filters were used; a chlorine gas filter (5 cm path length, 1 atm) was very useful when exciting at short wavelengths, since it absorbs near-ultraviolet wavelengths. Excitation wavelengths are listed in Table 1.

The light level was too low to permit spectral resolution of the fluorescence. The operation of the facility is regularly checked by us and other workers. We have found limiting polarizations as high as 0.38, suggesting that there is no loss of polarization in the equipment. Bias in the detection optics was checked in each experiment by looking at the long-time value of r, which decays to zero at low viscosities. Small departures from zero were found in some cases, due probably to strain in Dewar vessels, and a correction was applied. The cryostat was regularly checked for condensation on the windows, which would cause depolarization and shift the zero. It did occur but could be prevented by circulating dry nitrogen through the apparatus.

Solutes were used as received. Fluorescence spectra and lifetime measurements were used to check purity. In some cases, weak emission from an impurity was observed; except in the case of coronene, these could be avoided by choosing excitation

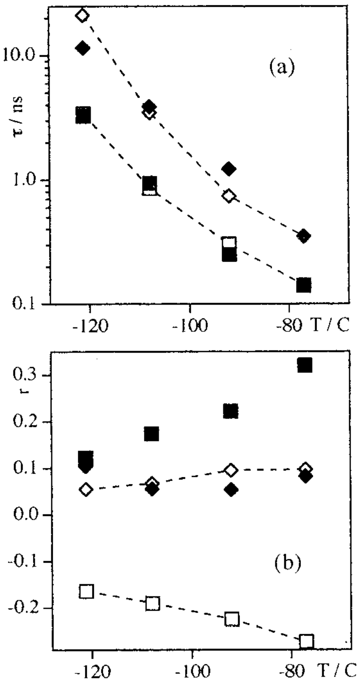


Figure 1. Temperature dependence of anisotropy decay of 9,10-dimethylanthracene in MCH: (a) τ; (b) r; (■, ◆) fast and slow decays, respectively, with z excitation; (□, ◇) fast and slow decays, respectively, with y excitation. Lines are for guidance only.

wavelengths corresponding to strong solute absorptions. Because the spacing of the synchrotron pulses is fixed at 320 ns, substrates with fluorescence lifetimes of $\lesssim$40 ns are most easily studied; triphenylene is ideal in this respect. Pyrene (450 ns) was not studied for this reason, but coronene is of special interest because of its shape. In this case, the lifetime was reduced by bubbling oxygen through the samples; despite this, serious "wraparound" problems were encountered at low temperatures. Photooxidation of this or other solutes is not likely to have caused any problems because of the low light levels. It is estimated that the number of photons on the sample was of the order of 10^{11} in an experiment while the number of molecules in the exposed volume was 10^{15}. Further, there would be diffusion out of this region (~0.3 mL into the bulk of the cell whose volume is 3−4 mL).

The decay of the anisotropy was fitted to one or two exponentials using standard nonlinear least-squares procedures, the reduced χ^2 (usually in the range 0.95−1.05) and the residuals being used to judge the fit. In the case of two exponentials, it is difficult to estimate the errors because the parameters are strongly linked. If the decay times are very different, it is a simple matter to measure the longer one separately by selecting an appropriate range of times. Then it can be held constant while the whole range is used. Closer decay rates are more difficult; a considerable range of pairs of values can give quite satisfactory fits. Here, the use of two excitation wavelengths is very useful, especially when y-axis excitation gives a positive r_2 and a negative r_1. In principle, the τ values are independent of wavelength, so in Figures1 and 2 results for two wavelengths are shown to give a measure of the errors. Calculations were then repeated, linking the two sets of data measured at the same temperature, i.e., forcing the τ's to agree. These data were used to calculate the three individual D_i. These calculations usually gave equally satisfactory fits; i.e., the change in χ^2 was small. Exceptions are detailed below.

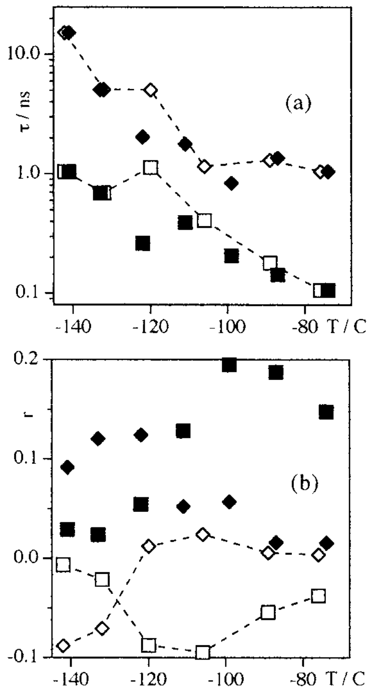


Figure 2. Temperature dependence of anisotropy decay of anthracene in MCH. Symbols are as in Figure 1.

Small drifts of the electronic timing system were unavoidable because the instrument response could only be measured before and after each series of experiments; it was not feasible to remove the sample from the cold cryostat. Drifts (in the range 10−100 ps) between response function and data could be obtained from the fitting procedure. Constant values or values changing smoothly with time were regarded as acceptable, and data with large or erratic shifts were discarded. This procedure introduces some uncertainty in the time zero and therefore in the r values, especially in r_1 when τ_1 is short.

Results

Temperatures below about −60 °C were found to give decay times long enough for convenient measurement. Rapid cooling with liquid nitrogen converts MCH to a glass, but attempts to supercool the liquid below its melting point of −126.6 °C usually led to crystallization, easily recognized by the apparent loss of anisotropy and formation of a white solid. Occasionally, it was possible to make observations on the supercooled liquid, and a few results are reported down to −140 °C. This behavior was erratic; some samples could not be supercooled.

The r and τ data shown in Figure 1 for dimethylanthracene are fairly typical. The anisotropy decay is easy to represent by two exponentials; at short wavelengths the net polarization is negative, as expected. The observed values of τ show some differences between the wavelengths, but we believe this to be an artifact, since satisfactory though slightly less good fits can be obtained using common values. These have been used to calculate individual D_i (below). Similar data for anthracene itself are shown in Figure 2. In this case measurements below the melting point of MCH were possible. They show striking differences from those at higher temperatures. In particular, at short wavelengths r_2 changes sign. Around −120 °C, the behavior changed very rapidly and attempts at fitting the data at both wavelengths with common decay constants were unsuccessful using just two exponentials. There was some evidence of a third decay process, but the precision of the data was not adequate to characterize it. Such behavior has been observed for anthracene and a number of other solutes in

TABLE 3: Experimental Total Anisotropies

compound	$\sum r_z$[a]	$\sum r_y$[a]	solvent	ref
triphenylene	0.07 ± 0.01		MCH	*b*
coronene	~ 0.07		MCH	*b*
anthracene	$0.20-0.12$	-0.03_4 to -0.09_4	MCH	*b*
	0.340 ± 0.003	-0.179 ± 0.002	glycerol	40
9,10-dichloroanthracene	$0.26-0.22$	-0.13_4 to -0.10_5	MCH	*b*
9,10-dimethylanthracene	$0.27-0.23$	-0.18 to -0.12	MCH	*b*
	$0.19-0.28$		tripropionin	39
	0.345 ± 0.002	-0.183 ± 0.002	glycerol	40
9,10-diphenylanthracene	0.247 ± 0.006	-0.101 ± 0.004	MCH	b
perylene	0.203 ± 0.03	-0.061 ± 0.025	MCH	b
	0.370		various	41
		-0.157	glycerol−water	33, *c*
	0.326 ± 0.005		MTHF	37
tetracene	0.134 ± 0.005	-0.084 ± 0.003	MCH	*b*
	0.26		1-octanol	24
	0.31		1-dodecanol	24
	0.219 ± 0.13		MTHF	37

[a] Where $\sum r$ is constant within the experimental error, the mean value and standard deviation are quoted. Where it changes with temperature, the range of values is given (high temperatures first). [b] This work. [c] Averaged over three glycerol−water mixtures.

squalane and will be discussed in more detail in the following paper.[10] As there, we tentatively ascribe it to a bifurcation of the rotation process into a slow overall rotation and a faster diffusion over a limited angular range, which decreases with temperature. Similar behavior, but less marked, was observed for perylene but in no other cases.

Values of the total anisotropy at zero time are given in Table 3 together with selected values from the literature. $\sum r$ is invariably less in MCH than in the polar solvents, and this suggests that extensive libration is occurring. Other effects, such as vibronic mixing or molecular distortion, are unlikely to be solvent-dependent. The effects of libration are described in more detail in part 2 of this study. They are very complicated unless one assumes that it only occurs about one axis, which is unlikely. It produces partial averaging of the diffusion processes, so reducing their differences, for example, libration around *x* plus rotation around *y*, mimics rotation around *z*.

Thus, the discrepancies between experimental and theoretical $\sum r$ values probably arise from several causes simultaneously. This poses a serious problem. Two procedures for calculating the individual D_i values were tested. First, D and Δ were calculated from the mean experimental decay times and eq 3, and α values were calculated from Δ and $(r_1 - r_2)$ at the two wavelengths. D_z and D_x were then calculated from eqs 6 and 7, and D_y was calculated from eq 4. This implies that the polarization "losses" only affect the quantity β. The values of D_x and D_z may be expected to be too small and D_y too large. Therefore, for comparison, it was asumed that α and β are affected equally and the *r* values were scaled up so that $(r_1 + r_2) = 0.4$ or -0.2. In terms of the relative magnitudes of the *D* values, the results were qualitatively similar. However, it was clear that D_x and D_z were now too large. D_y was often very small and sometimes negative, so the first procedure was adopted. Though the results must be regarded as semiquantitative at best, it appears reasonable to attempt to separate the D_i with the proviso that the differences between them may be too small because of the effects of libration. However, we believe the analysis to be worthwhile; at the very least, it provides a framework for rationalizing the striking effects of temperature, which is not possible from studying the original data.

An alternative approach is to fit the data using the angle between absorption and emission as a variable. This may be useful in some cases, but it is not valid when several factors contribute to the difference between experimental and theoretical $\sum r$ values.

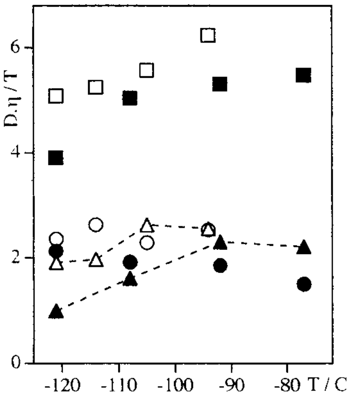


Figure 3. Variation of $D\eta/T$ with temperature for 9,10-substituted anthracenes in MCH: (filled symbols) dimethyl; (open symbols) dichloro. Here and later figures, squares represent D_x, triangles D_y, circles D_z. Units are 10^2 ns^{-1} cP K^{-1} (10^{-4} kg m^{-1} s^{-2} K^{-1}). Lines (D_y) are for guidance only.

Hydrodynamic theory predicts proportionality between rotational diffusion constants and T/η; i.e., $D\eta/T$ should be constant. To demonstrate departures from the theory and to facilitate comparisons, this quantity is plotted in the remaining figures. Where analysis into three components was not possible, mean D values equal to $(6\tau)^{-1}$ were used. These of course are independent of the uncertainties in the analysis discussed above. Note that a linear scale is used for Figure 3 where the variations are small. A log scale is needed in Figures4−6 because of the very large changes in some of the diffusion coefficients with temperature.

The viscosity of MCH is known accurately down to the melting point:[38]

$$\eta \text{ (in cP)} = 0.01084 \exp(1226.04K/T) + (1.377 \times 10^{-6}) \exp(2742.37K/T) \quad (12)$$

To facilitate comparison with other solvents, it is convenient to list some numerical values, 3.9, 8.2, 23, and 115 cP at −60, −80, −100 and −120 °C, respectively. Use of eq 12 at lower temperatures is likely to give values that are too low. The glass transition temperature, T_g, of MCH is ~90 K, and by use of $\eta = 10^{13}$ P as a criterion of glass formation, eq 12 gives $T_g = \sim 57$ K, which is much too low. The extrapolation might be improved by fitting values from eq 12 betweeen −60 and −120

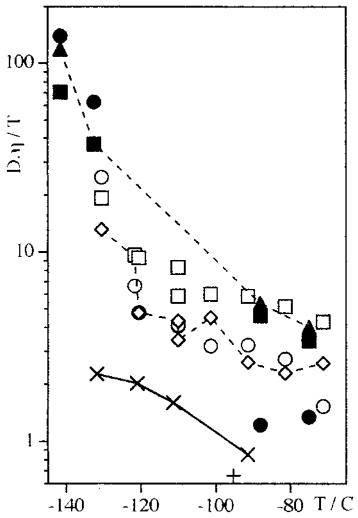


Figure 4. Variation of $D\eta/T$ with temperature for anthracene (filled symbols) and perylene (open symbols). Notation and units as in Figure 3. The symbol $\times$ is for out-of-plane motion of triphenylene, and $+$ is for out-of-plane motion of coronene.

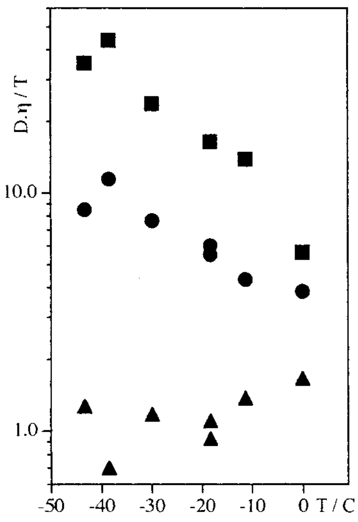


Figure 5. Variation of $D\eta/T$ with temperature for dimethylanthracene in tripropionin calculated from data in ref 41. Notation is as in Figure 3.

°C to a Williams–Landel–Ferry equation[39]

$$\eta = \eta_0 \exp(B/(T - T_0)) \tag{13}$$

A very good fit was obtained with $T_0 = 78.5$ K and $T_g = 94$ K; however, the difference at -140 °C was only a factor of 1.5, so eq 12 was retained for Figures 3–6, since the observed changes in $D\eta/T$ are much larger.

Results for the substituted anthracenes are described first. Figure 3 shows data for DMA and DCA. That the quantity $D\eta/T$ is not constant is shown unambiguously by considering the mean D values derived directly from the decay times. For example, for DMA, the fast process decreases by some 20%, which alone would not be very significant, but for the longer decay time the decrease is ~45%. The results for DCA are similar to those for DMA, though the changes are less striking. Again, $D\eta/T$ values decrease slightly with temperature by some 20–25%. The change in ratios of the D_i are well-defined for DMA. For DCA, they are smaller and may not be real, but they do parallel those for DMA.

For DPA, single-exponential decay of the anisotropy was observed at both wavelengths. This implies that $D_z > D_x \sim D_y$.

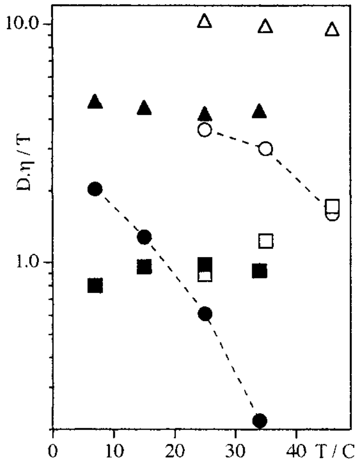


Figure 6. Variation of $D\eta/T$ with temperature for tetracene in primary alcohols calculated from data in ref 30. Notation is as in Figure 3. Full symbols represent results for 1-octanol, and open symbols represent results for 1-dodecanol.

The longest dimension is z not y as in the other anthracenes, so this result is not surprising. The mean value of $D\eta/T$, 0.59 ± 0.02, appears to be independent of temperature down to -120 °C, in contrast to the behavior of the other two substituted anthracenes. It then rises slightly to 0.7 at -130 °C. (Samples containing the other substituted anthracenes crystallized and could not be studied at this temperature.)

In the case of anthracene, values of the $D_i\eta/T$ could be calculated only for the extremes of temperature. These are shown in Figure 4. It is clear that major changes occur in the relative values of the D_i. Though all increase on cooling, unlike the substituted anthracenes, there are common changes in the relative values, e.g., D_z increasing relative to D_x and D_y. The whole range could be used for perylene (Figure 4) except for the data around -120 °C, which were not easily fitted with the same exponents for the two excitation wavelengths. Original data for r and τ are given in the earlier paper.[11] Again, there is a change in the nature of the rotation on cooling, rotation around the z axis being favored at low temperatures and around x at high temperatures.

Given its behavior in squalane[10] and in alcohols,[30] it is surprising that tetracene only showed single-exponent decays in MCH. Mean $D\eta/T$ values increased smoothly by some 30% between -60 and -130 °C. However, the decay rates could not be fitted to common values; they differed by about 25%, a very significant difference for single exponentials. It would be possible to take r_1 and r_2 as zero at long and short wavelengths, respectively, implying $D_x \gtrsim D_z \gg D_y$. This seems unlikely. It may be that there are two close decay times that cannot be distinguished in our data.

While perylene is oftened studied as a typical disk-shaped molecule, coronene and triphenylene are closer to a true disk. Unfortunately, the first transition in these molecules is symmetry-forbidden and becomes allowed by coupling with unsymmetrical in-plane vibrations. Regardless of excitation wavelength, emission can take place in any direction in the yz plane; only the out-of-plane rotation, $D_y = D_z$, is detectable. On the other hand, in this simple situtation, there is no ambiguity in interpretation. Results for triphenylene are shown in Figure 4. Again, $D\eta/T$ increases with falling temperature. Coronene should behave in the same way. Despite the use of oxygen to reduce the fluorescence lifetime, we were unable to make satisfactory measurements at low temperatures where the effective lifetime lengthened rapidly. One data point is shown in Figure 4. As expected, $D\eta/T$ is slightly smaller than for triphenylene.

For perylene we recorded the excitation spectrum of the anisotropy. As expected from previous work,[13,40] the sign changed from positive to negative below 280 nm. The possibility that local heating, much larger of course at short wavelengths, by excess excitation energy leads to fast initial rotation is often discussed, but we could find no difference between MCH and ethanol solutions, which suggests that this can be ruled out.

Discussion

Comparison to Predicted Values (Table 2). The "stick" approximation not only gives values that are much too small, but it predicts the wrong order for D_x, D_y, and D_z in almost all cases. The "slip" approximation performs better. It gives the correct order at higher temperatures in most cases. Exceptions are DMA in tripropionin, anthracene in MCH, and tetracene in *n*-octanol. The predicted values are again generally too low, though the discrepancies are less than for "stick" and the exceptions are worth considering. Theory gives very high values for D_x for DCA and DMA. This reflects the shortcomings of treating the molecule as an ellipsoid; as the *y* and *z* dimensions approach equality, D_x rises toward the inertial value regardless of the actual shape of the molecule. Numerical calculations based on the actual molecular shape would be a considerable improvement on the ellipsoid approximation, but this appears to have been done only for benzene.[27]

More interesting is the finding that the experimental D_x for perylene is below the "slip" value over most of the temperature range. The ellipsoid approximation should be better in this case, but it is not surprising that it exaggerates the effect of slip. Elsewhere, D_x for anthracene is close to the slip value at high temperatures and so is D_y for DMA at low temperatures. More puzzling is that the slip approximation predicts an observable biexponential decay for both DPA and tetracene. This is not observed in either case in MCH; it is for tetracene in alcohols[27] and squalane (part 2). In MCH the mean tetracene values are higher than the slip prediction, but Wirth and Chou find D_x less than slip over most of their range.

In general the predicted differences among *x*, *y*, and *z* are much too large, but the discrepancies may well be exaggerated. As noted above, libration is likely to reduce the apparent differences.

Comparison to Literature Data. Viovy[41] made a detailed study of the motion of dimethylanthracene over a range of temperatures in the ester, tripropionin (glyceryl tripropanoate). Values of $D_i\eta/T$ have been calculated from his data and are shown in Figure 5. The viscosity range covered is 2700−24 cP (cf. ~120 to 8 cP for MCH). Mean values for $i = x$ and y are comparable with theory (slip); D_z values are much higher. Hyde and Ediger[42] report measurements in polyisoprene at 35 °C (well above the glass transition) with values of $\log(D/\mathrm{s}^{-1})$ of 8.9, 8.0, and 7.4 for *x*, *y*, and *z* (this is our notation; theirs reverses *x* and *z*). This order agrees with our findings at higher temperatures. The extent of the change in the relative values of D_y and D_z in MCH may be exaggerated by the approximations made in the calculation, but it appears to be real and the low-temperature order in MCH is the same as in tripropionin. Closer comparison shows good agreement between $D_y\eta/T$ values in the two solvents at the same viscosity where the ranges overlap. This is probably an accidental result; it is not true of D_x and D_z.

There appears to be no previous work on dichloroanthracene, but the rotation of diphenylanthracene in a number of alkanes at 22 °C has been studied by Ben-Amotz and Scott.[2] Given the difference in time scale, agreement is good. Their results give $D\eta/T$ values of 0.66 for *n*-decane, 0.74 for *n*-dodecane, 0.65 for *n*-tetradecane, 0.77 for *n*-hexadecane, 0.90 for heptamethylnonane, and 1.56 for squalane. In *o*-terphenyl it is 0.63.[43] Surprisingly, there appear to be no other observations of biexponential decays for anthracene itself in normal liquids. In polyisoprene, remarkable changes with temperature in relative values of the diffusion coefficients have been reported:[42] at +40 °C, $\log(D)$ values are 9.0, 8.0, and 8.1 for *x*, *y*, and *z*; at −40 °C, the values are 4.1, 4.6, and 0.8. The relative fall in D_z is in the opposite direction to our finding.

Our results for perylene are somewhat scattered (the similarity of D_y and D_z is one reason), but this appears to the first report of all three diffusion constants. This molecule has been studied by a number of authors, but it has been invariably treated as a spheroid, i.e., $D_y = D_z$. For example, Christensen et al.[15] found values of $D\eta/T$ (units of 100 ns^{-1} cP K^{-1}, as in Figures 3−6) of 9−12 for rotation in plane and 1.4−1.8 out of plane in water−glycerol mixtures. Paraffin oil gives more spectacular results. From Zinsli's data[17] one can estimate corresponding values of ~240 and 24 at −20 °C (where $\eta = 4370$ cP), both a factor of almost 50 smaller at +50 °C ($\eta = 32$ cP). Later work by Kalman et al.[18] gave qualitatively similar results for the same solvent: $D_x\eta/T$ falling with increasing temperature but $D_y(D_z)\eta/T$ approximately constant. There is evidence for extensive libration in this solvent, which complicates the interpretation.

From Jiang and Blanchard's[4] results for perylene, one can calculate average $D\eta/T$ values, which rise from 1.5 for *n*-pentane to 3.8 for hexadecane. These values are similar to those for MCH (Figure 4), but the comparison involves a long extrapolation; the *n*-alkane measurements were made at 300 K and the rotation times were a few tens of picoseconds. If $D\eta/T$ continues to fall with rising temperature in MCH, then rotation will be slower in MCH than in the *n*-alkanes. This might be simply a function of density (compare MCH, 0.769 g cm^{-3}, with *n*-heptane, 0.684 g cm^{-3}, at 20 °C).

Both perylene and tetracene show only a single-exponential decay in methyltetrahydrofuran (MTHF);[35] the mean $D\eta/T$ values are 1.53 and 1.68, respectively. This could be an indication of the formation of weak complexes, but a sufficient explanation may be that solute−solvent interaction is stronger relative to the solvent−solvent forces than in alkanes or alcohols. This is consistent with the observation that the decay rate appears to follow the viscosity in MTHF.

Wirth and Chou[30] observed biexponential decay for tetracene in both *n*-octanol and *n*-dodecanol over a range of temperatures. Their data have been plotted as $D_i\eta/T$ in Figure 6, and theoretical slip values are 1.46, 1.83, and 0.41 for *x*, *y*, and *z*. The viscosities range from 5 to 13 cP for octanol and 8 to 17 cP for dodecanol. The pattern of results shows some resemblance to that for anthracene in MCH (Figure 4); however, the spectacular fall in $D_z\eta/T$ in octanol should be noted. D_z itself appears to decrease with temperature, an unlikely result.

For triphenylene, only its total limiting anisotropy, ~0.08_4, measured in a rigid solution, appears to have been reported previously[44] (cf. our value in Table 3). As is usual, it lies a little below the theoretical limiting anisotropy, which in the case of molecules of C_{3v} or higher symmetry is +0.1. For coronene, a value of 0.20_6 was found, and vibrational distortion of the molecule was put forward to explain the high value;[44] an alternative is the presence of less symmetrical impurities, such as benzo[*ghi*]perylene, which absorb more strongly in the near-ultraviolet.

General Remarks. The data reported here show once again that molecular rotation in solution is very sensitive to the properties of both solvent and solute. Hydrodynamic theory does not account for this, but it has been widely used because of its simplicity. In particular, it explains the proportionality often found between rotational diffusion times and η/T ($D\eta/T$ is constant), which is obeyed surprisingly well given that viscosity is a bulk property.[21] However, in MCH, the substituted anthracenes show a small decrease in $D\eta/T$ on cooling. One might regard them as becoming more sticky, the substituents engaging the solvent molecules increasingly as the density increases, though the rotation rates are still very fast. In contrast, anthracene itself, triphenylene, and perylene rotate much more rapidly than expected at low temperatures, $D\eta/T$ rising by a factor of 10 or more over the accessible range. In particular the spectacular increase found for anthracene is very remarkable and deserves more work. Explanation of this "subslip" behavior in terms of a solvent cavity[30] is not easy to accept for alkane solvents.

The changes with temperature in relative rates of rotation around different axes are particularly interesting. Comparisons with other solvents where available show some measure of consistency of behavior. Explanations are not easy to find. Ediger et al.[42] suggested that rotation around the axis requiring the least displacement of solvent would be favored at low temperatures, e.g., the y axis for anthracene and tetracene, the x axis for perylene. NMR measurements[45] on several glass formers suggest that rates of rotation around different axes tend to equalize near the glass transition because of the need for cooperative motion of a large number of solvent molecules. Neither criterion is obeyed here probably because the temperatures are too far above the glass transition. It is a matter of concern that D_z increases relative to the other diffusion coefficients on cooling both in our work and in that of Wirth and Chou. Since z is the emission axis, this suggests an artifact, but it is difficult to see why it should be temperature-dependent.

In their very interesting study of perylene, Jiang and Blanchard[4] found not only a change in rate as the chain length of the alkane is increased but also some evidence for a change in the nature of the rotation. They propose that the long-chain aliphatic solvents constrain the perylene rotation to be predominantly about its long axis (z). This is intriguing because our limited low-temperature data suggest a similar change. (Remarkably, 1-methylperylene[33] shows a similar change in the opposite direction!) One should also bear in mind that overall rotation and translation of large solvent molecules is relatively slow; their internal motions are faster. On the time scale of the rotation of a small solute, relaxation of the solvent cage can involve only internal motions of the solvent. This may be one factor explaining the change in behavior with solvent size. An apparently similar change with viscosity in the alcohols and even in MCH suggests that overall motion of the solvent becomes increasingly restricted at low temperatures. In the following paper on motion in squalane, these arguments will be carried further. There is evidence that the motion of the solutes themselves splits into a two-stage process: diffusion over a limited range and overall rotation.

Very recently, Pauls et al.[46] have used two-photon excitation with both linearly and circularly polarized light to study the fluorescence anisotropy decay of perylene. Potentially, this technique can provide more information about the anisotropy of rotational relaxation. It is somewhat surprising that they only observed single-exponential decays, but the same is true of the more conventional study of perylene in the n-alkanes[4] at ambient temperature. Their work confirms that though in-plane rotation is much the fastest process in alcohols, this is less true, or untrue, in the alkanes.

In conclusion, we have found a clear-cut difference in η/T dependence between the various unsubstituted aromatics and the substituted anthracenes. The analysis of the data to give individual D_i is uncertain, but the results are fairly self-consistent and consistent with the behavior found by other authors. Hydrodynamic theory and its extensions appear to be inadequate to explain the results. At present, it seems that more detailed study does not lead to generalizations but uncovers more complex phenomena. Computer simulation may eventually lead to deeper understanding. We hope the data reported in this and in part 2 of the study will prove useful for the development of detailed molecular dynamics models.

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