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Rotation of Aromatic Hydrocarbons in Viscous Alkanes. 2. Hindered Rotation in Squalane

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Time-resolved single-photon counting and the synchrotron radiation source at the CCLRC's Daresbury Laboratory have been used to measure the decay of fluorescence anisotropy of solutions in squalane of the aromatic hydrocarbons triphenylene, coronene, benzoperylene, perylene, anthracene, and tetracene. For the last four, extra information was obtained by exciting both parallel and perpendicular to the fluorescence transition. The results differ markedly from those obtained in methylcyclohexane (part 1 of the study) probably because the solute molecules are smaller than those of the solvent. Contrary to the predictions of hydrodynamic theory, decay rates appeared to change with excitation wavelength, and three decays were observed in some cases. Temperature effects (+20 to −70 °C) provided evidence for bifurcation of the molecular rotations into two stages: slow overall motion and faster rotation over a restricted angular range. This resembles the split into α and β processes observed in many relaxation studies of highly viscous liquids.

Introduction

Hydrodynamic theory has been widely used to describe the decay of fluorescence anisotropy, which results from molecular rotation in solution.[1−8] It is implied that the solvent can be treated as a continuum. This description breaks down when the solute molecule is smaller than those of the solvent.[9−13] This has been demonstrated in studies of series of *n*-alkanes where plots of rotation time against viscosity, η, show a change in slope when the solvent chain length exceeds the longest dimension of the solute. There are also indications of changes in the nature of the rotation, i.e., of the relative rates around different axes.[12−14]

Relaxation processes in very viscous liquids are described differently. Hydrodynamic theory predicts that rotational correlation times should be proportional to η/T. This relation is widely observed for individual systems, though the proportionality constant varies. However, this relation breaks down at high viscosities; as the glass transition temperature, T_g, is approached, the bulk viscosity rises rapidly. Some relaxations, e.g., α processes, follow the viscosity and disappear at or near T_g. Others, e.g., β-processes, show an Arrhenius dependence on temperature with no discontinuity at T_g.[15] Kivelson and Kivelson[16] have proposed that there are three rotational processes in viscous liquids: torsional oscillation, i.e., libration over a small range, and the β and α processes; diffusion over a restricted but reasonably large range; very infrequent, or very slow, jumps from one β range to another. β processes can be regarded as motion controlled by the cage potential, α as requiring relaxation of the cage, a process involving increasing numbers of molecules as T_g is approached.

Experimental observations of these three rotational processes are few, and to our knowledge, no probe studies of the bifurcation involving fluorescence anisotropy have been reported. Most workers requiring high viscosities near ambient temperature have used hydrogen-bonded liquids such as glycols. Alkanes might be expected to behave more simply, but most previous work has been restricted to *n*-alkanes.[9−13] Our aim is to study a wide range of temperatures and viscosities that are accessible for solvents that do not readily crystallize. In preliminary studies,[17] we used methylcyclohexane (MCH) and squalane (2,6,10,15,19,23-hexamethyltetracosane). Temperatures ranging from −60 to −130 and +20 to −80 °C, respectively, gave decay times in the range 0.5−500 ns, which is readily accessible. Paraffin oil has been used by other workers;[18,19] it is more viscous, but squalane has the advantage that its nature is better defined. It has been regarded as a model lubricant[20] and has been the subject of molecular dynamics calculations.[21]

Changing the temperature gave striking results for perylene solutions.[17] Two exponentials were needed to fit the decays, but their relative contributions were found to change with temperature, in disagreement with standard hydrodynamic behavior. This work has now been extended in two ways. Most of the solutes have been excited at two wavelengths: parallel and perpendicular to the emission axis. This provides further information about the rotational processes.[22,23] Second, a wider range of solutes has been used; triphenylene, benzo[*ghi*]perylene, and coronene are disk-shaped like perylene, tetracene is closer to rod-shape, and anthracene lies between those two shapes. The sizes of the solute molecules are between those of MCH and squalane, and results from solutions in MCH are reported in part 1 of the study[23] (referred to here as part 1). They can be understood if the ratios of the diffusion coefficients around different axes are allowed to vary with temperature. Solutions in squalane exhibit a new phenomenon, and they form the subject of this paper.

Theory and Background

The definition of fluorescence anisotropy and the basic theory[24] relating the decay parameters to the rotational diffusion coefficients, D_i, are set out in part 1. As before, it will be convenient to label the molecular axes according to the orientation of the absorption and emission dipoles. *z* is used for the emission direction (also that of absorption at long wavelengths), *x* is perpendicular to the molecular plane, and assignments for the molecules studied are given in Chart 1 of part 1. The symbols

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for the corresponding diffusion coefficients D_z, D_y, and D_x will also be used loosely to represent the corresponding rotational motion, e.g., D_x for rotation in the molecular plane. The symbols L_x, L_y, and L_z will be used similarly to denote the limited range rotation described above. Measured preexponential factors are labeled r_{1z}, r_{2y}, etc. for the first or second process observed for excitation along the *z* or *y* axis. The subscripts are numbered 1, 2, ... in order of increasing τ. To describe the experimental results, numbers are used empirically. They may not correspond to the theoretical components.

In part 1, the analysis of the results for MCH solutions in terms of three rotational diffusion processes was attempted despite the difficulty that the theoretical limits of +0.4 and −0.2 for parallel and perpendicular excitation are not observed. The slip approximation gave a qualitatively correct description at least at low viscosities. In the case of squalane, the breakdown of the theoretical description is much more serious; in particular, the decay rates appear to depend on wavelength and, even at one wavelength, three decay processes were observed in some cases in contradiction to prediction.

Effect of Restricted Rotation. One explanation for the loss of initial polarization is the occurrence of libration, i.e., free rotation over a limited range of angles.[25] Though this is not accepted as a general explanation,[26,27] the increase in $\sum r$ with viscosity observed for perylene in paraffin oil[18,19] is difficult to explain in other ways. For most of the molecules studied here the $\sum r$ values are essentially constant over a considerable range of temperature and viscosity. However, the results lead us to propose that limited range rotation (called L; see above), essentially equivalent to slow libration, is occurring with rates of $\sim$1 ns^{-1}. At such a rate, this must be a diffusional process, not free rotation.

Zinsli[18] showed that the effect of libration is equivalent to absorption and emission with axes chosen from a range of angles. The same formalism can be used for restricted range diffusion. For example, to describe the effect of limited rotation around the *x* axis, L_x, the emission vector was replaced by (0, sin θ, cos θ), the excitation vector by (0, sin θ, cos θ) for *z*-axis absorption or by (0, cos θ, sin θ) for *y*-axis absorption. These were inserted into eqs 6 and 7 of part 1, which were then integrated over the range $-\theta$ to $+\theta$. The results depend of course on the initial choice of *D* values. For the illustration in Figure 1, D_x, D_y, and D_z are in the ratios of 0.80:1:0.225. These are the values calculated for tetracene using the slip approximation (see part 1). Note that these calculations are for the individual axes taken in turn; simultaneous limited rotations around two or three axes present a much more difficult problem. Quantitative calculation has not been attempted.

Some generalizations about the effects are illustrated in Figure 1. (i) For *z* excitation, all orientations around *z* have an equal probability of excitation, so L_z has no effect. (ii) L_x is equivalent to mixing *y* and *z* excitation. For either excitation it changes $\sum r$ so that it approaches a limit of 0.1, the average of the *z* and *y* values of 0.4 and −0.2. (iii) L_y also reduces $\sum r$ for *z* excitation, ultimately to 0.1. (iv) Neither L_y nor L_z has any effect on $\sum r$ for *y* excitation, but r_1 and r_2 change.

Restricted rotation should be directly observable in some cases. For example, consider L_y for the case in Figure 1. For $\theta = 0°$, *r* is nearly equal to 0.4 and a single decay is observed. For $\theta = 30°$, r_{1z} is reduced from $\sim$0.4 to 0.3 and a new faster process with $r \approx 0.1$ appears. For *y* excitation, L_y reduces the magnitude of r_{1y} and increases that of r_{2y} but is not directly observable itself because the $\sum r_y$ does not change; i.e., the positive and negative contributions cancel out.

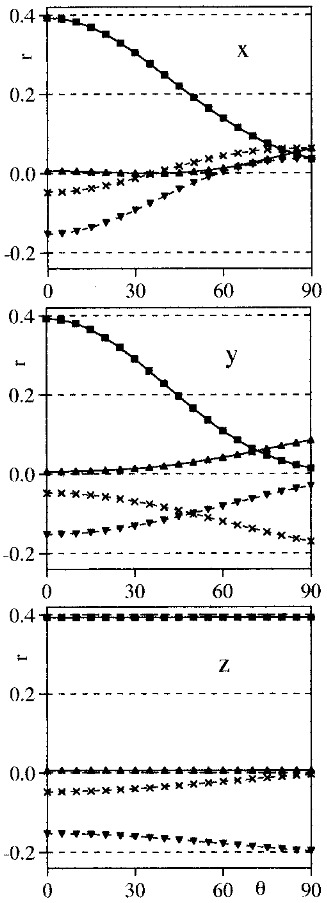

Figure 1. Calculated effect on anisotropy at zero time of libration or restricted rotation around the *x*, *y*, and *z* axes, where α is the half-angle of the libration range: (■) r_{1z}; (▲) r_{2z}; (▼) r_{1y} (×) r_{2y}.

Experimental Section

The purification of squalane and the measurement of anisotropy decays have been described previously.[17,23,28] Data analysis has been described in part 1. The problems were greater for squalane. First, anisotropy decay times often appear to be different at the two exciting wavelengths. The fact that they were the same in most cases for MCH suggests that the effect is real. Attempts to transfer parameters or to use global analysis (simultaneous fitting of two data sets with common decay rates) were unsuccessful. Changes in wavelength cannot change decay rates, so the significance of the results must be that the decays are complex, i.e., consist of decays with lifetimes too close to be resolved, and that different components are emphasized at each wavelength (see further below). Second, three decay components could be distinguished in some cases. The longest of these was often too long to measure, with the advantage that one parameter could be used in the fit rather than two.

Results

The temperature dependences of the initial anisotropies, *r*, and decay times, τ, are presented in Figures 2 and 4−7, together with the values of η/T. Decay times became long enough to measure between +20 and 0 °C, depending on the solute. Some decay was still observable at the lowest temperatures used, about −70 °C; below that either the extent of the decay was too small or the rate too low to study. Because of the complicated nature of the results, it is easiest to present them in the order of the increasing complexity of their behavior rather than in the logical order of the change of shape, e.g., disk toward rod.

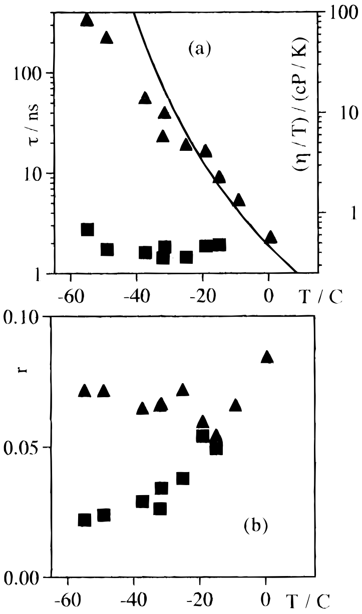

Figure 2. Triphenylene in squalane plots of temperature dependence of (a) anisotropy decay times and (b) anisotropy at $t = 0$: (- - -) η/T; (■) τ_1 and r_1; (▲) τ_2 and r_2.

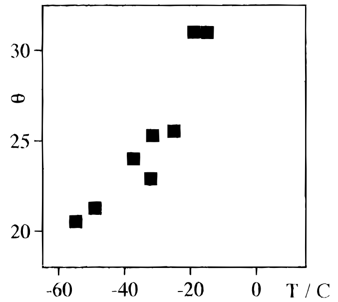

Figure 3. Triphenylene in squalane: temperature dependence of the range of limited diffusion.

Triphenylene. In MCH, the decay of the fluorescence anisotropy of this molecule fitted a single exponential. As explained in part 1, this is consistent with the molecular symmetry. The first electronic transition becomes weakly allowed by coupling with unsymmetrical in-plane vibrations. Since these are degenerate, there is no correlation in the molecular (yz) plane between the directions of absorption and emission. The decay corresponds to rotation out of plane. In squalane, a single exponential is observed down to −10 °C but the decay changes to biexponential as the temperature is reduced further. Figure 2 shows the temperature dependence of the values of r and τ. We propose that at low temperatures the slow process is overall rotation, the fast one a diffusive process taking place over a fairly well-defined angular range that decreases with temperature, leading to a corresponding decrease in r_1. In this case it is easy to estimate the angular range using the calculations described above; y and z are indistinguishable and L_x has no effect. The results are shown in Figure 3. This new process is distinct from libration, which is very much faster. $\sum r$ remains constant within the experimental error. Presumably at higher temperatures the range becomes less well-defined and the rates of the two processes converge so that the distinction between them disappears, leading to a single exponential.

Coronene. This molecule should behave like triphenylene. Some evidence of biexponential decay was found at lower temperatures, but it was not clear-cut. Useful measurements could only be made between +20 and −20 °C because of the wrap-around problem (see part 1).

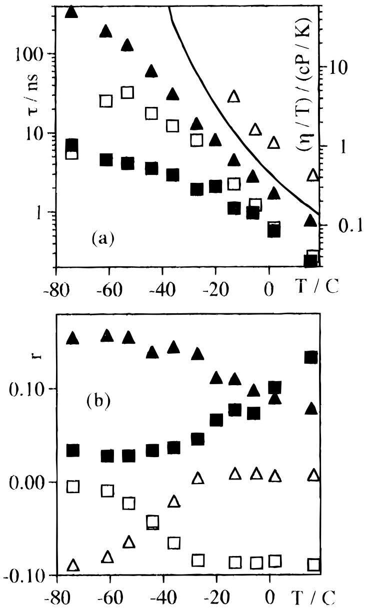

Figure 4. Tetracene, as in Figure 2: (filled symbols) z excitation; (open symbols) y excitation.

Tetracene. The alignment of the axes is the same as for anthracene (see part 1, Chart 1). Results are shown in Figure 4. τ_{2y} becomes too long to measure below −20 °C, and over a limited range it is proportional to η/T. This is not true of any other process. In direct contradiction to hydrodynamic theory, the two processes observed at each exciting wavelength are not the same. τ_{1y} is essentially equal to τ_{1z} at the highest temperatures and is probably indistinguishable from τ_{2z} around −30 °C. Elsewhere, the differences are very large, much greater than the experimental uncertainty.

Such behavior cannot be explained in terms of rotation alone. In part, it can be in terms of restricted rotation. It appears likely that this is occurring over the whole temperature range in this case. First, suppose that the rates of overall rotation, the D processes, are such that r_{2z} is too small to be easily measured. This requires $D_z < D_x \sim D_y$, in fair agreement with the slip calculations. Second, suppose that restricted rotation occurs only around the long y axis (plausible given the shape of the molecule) to an extent that decreases with temperature. Then, as Figure 1 shows, the relative importance of the two y-excited decays changes with the extent of L_y, as is observed. L_y itself is not observable with y excitation, but it can be seen with z excitation; i.e., we ascribe τ_{1z} to restricted, not overall, rotation, the change in relative magnitudes of r_{2z} and r_{2z} paralleling the changes seen for triphenylene (Figure 2).

The description is incomplete of course. τ_{2z} and τ_{1y} should be identical, which is certainly not true at the lower temperatures. Also, attempts at quantitative fitting were unsuccessful. However, it should be recalled that the relative values of the D_i probably change with temperatue as they do for MCH (part 1). Also, the limitation of restricted rotation to a single axis must be too simple; the occurrence of L_x and L_z will introduce further decay processes. The presence of these may account for some of the apparent changes with wavelength of the decay rates. Further, the r values are much less than the maximum values and less than found for other solvents, including MCH, suggesting that extensive libration is also occurring.

Perylene. Results are shown in Figure 5. The behavior is quite similar to that of tetracene, notably in the crossover of r_{1z}

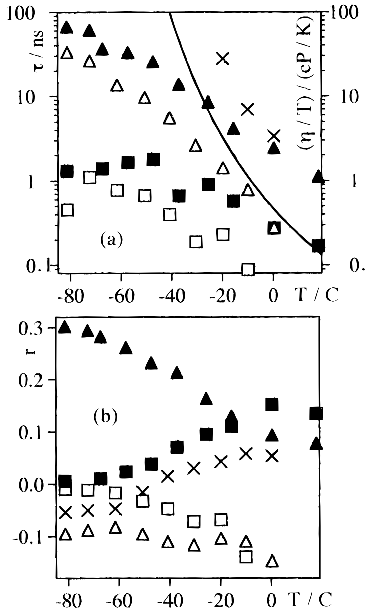

Figure 5. Perylene, as in Figures 2 and 4: (×) y excitation, third process.

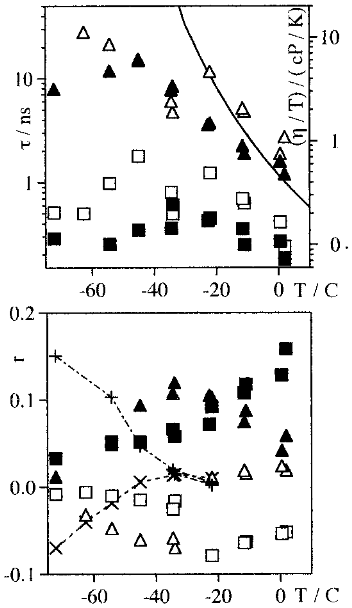

Figure 6. Anthracene, as in Figures 2 and 4: (×) y excitation; (+) z excitation, third process. Dotted lines are for guidance only.

and r_{2z}; however, three decays are seen in the y excitation data, the lifetime of the slowest becoming too long to measure below −20 °C. At short times, $r(t)$ is negative, and it rises to become positive and then decays toward zero at long times. This reversal of direction of the decay helps considerably in providing evidence that the three processes are real, not artifacts of the analysis. The z-excitation data can be fit with two exponentials. When the anisotropy is all positive, it might well be possible to fit three decays with two exponentials, so an attempt was made to fit the z data using three τ values derived from y excitation held fixed. An acceptable, though less good, fit was obtained for the early fast decay, but this was not true at longer times. The slowest decays at the two wavelengths are clearly distinct, i.e., there appear to be four, possibly five, distinct decay processes, not two.

Again, the results can be qualitatively understood in terms of restricted rotation, in this case L_x, taking place over the whole range of temperatures, its angular range decreasing with temperature. As Figure 1 shows, this makes both r_{1y} and r_{2y} less negative, so τ_{1y} can be ascribed tentatively to L_x, the two others to overall rotations. The predicted values of r_{1z} and r_{2z} are ~0.3 and 0.1, respectively, so one would expect three decays with z excitation. In fact, perylene appears to behave like tetracene where the D processes are concerned. This is in agreement with other work on alkanes.[14,23] The real situation must be complex, of course. The concept of restricted rotation does not immediately explain the differences in decay rates between y and z excitation.

Anthracene. This molecule is intermediate in shape between tetracene and perylene. Figure 6 shows effects that can be ascribed to the occurrence of both L_x and L_y. The data are somewhat scattered, probably owing to the need to fit to three exponentials, for both y and z excitation in this case. The y excitation appears to give larger lifetime values as in the case of tetracene. The behavior between 0 and −30 °C resembles that of tetracene; there are crossings of r_{1y} and r_{2y} and of r_{1z} and r_{2z}. At lower temperatures, a third process appears (lifetime too long to measure). This suggests a role for L_x as in the case of perylene.

One difference is that three processes are observed at both wavelengths. This suggests that the D values are such that two overall rotation processes are observable for z excitation, together with the L processes. Slip calculations give $D_x > D_y > D_z$ and a somewhat larger r_{2z}. A value of 0.03 in place of 0.007 for tetracene is predicted. Possibly the ratios of the D values change on cooling (cf. part 1) in such a way as to increase the theoretical r_{2z}.

Benzo[*ghi*]perylene. The fluorescence anisotropy of this molecule does not appear to have been studied previously. It was chosen of course because of its similarity in shape to perylene. However, it differs in its photophysics. In perylene the first absorption is the fairly strong ^1L_a absorption polarized parallel to the long axis. For benzoperylene, the weak ^1L_b lies some 1275−1400 cm^{-1} below ^1L_a.[29] The former probably has mixed polarization due to coupling with unsymmetrical vibrations, but we observe differences in the fluorescence anisotropy between 303 and 365 nm, suggesting the main polarizations of the two transitions are at right angles. Hückel calculations suggest that ^1L_a is polarized along the long axis as in perylene, so we assign ^1L_b as short-axis-polarized (see part 1, Chart 1). These excitation wavelengths were chosen to give adequate signals. In fact, both could be exciting the ^1L_a state according to Dawson and Kropp's[29] assignment, but the observed behavior (Figure 7) is consistent with y and z excitation, respectively.

At high temperatures, >0 °C, only one decay was seen (the faster decay seen at lower temperatures is probably too fast for measurement) and the results were the same for both wavelengths. This is to be expected because most of the emission comes from the ^1L_a state, which is thermally excited from the first excited state.[29] At low temperatures, in addition to the two decays on the nanosecond time scale there is a very fast decay; its lifetime is probably ~0.1 ns and appears to be independent of temperature. Satisfactory fits could not be obtained, not surprising given the instrumental fwhm of 0.3 ns and the small number of points involved. This does appear to be a real phenomenon rather than an artifact. Scattered incident light passing through the filters would give similar results, but tests with different filters showed no change. Also, scattered light can have a much larger anisotropy than fluorescence. In the raw data before deconvolution, the largest values were fairly constant, −0.14 ± 0.02 and 0.33 ± 0.03 for y and z, respectively, and in no case were they larger than the theoretical limits of

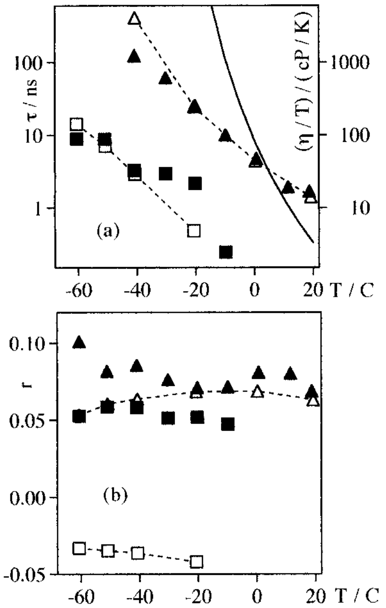

Figure 7. Benzoperylene, as in Figures 2 and 4. dotted lines are for guidance only.

TABLE 1: Quantity $D\eta/T$ (Units of 100 ns^{-1} cP K^{-1}): Comparison of Theory and Experiment[a]

	fast decay				slow decay			
			squalane				squalane	
compound	theory	MCH	z	y	theory	MCH	z	y
triphenylene					0.65	0.85	2.3	
coronene					0.46	0.66	1.12	
benzoperylene	23		18.1		0.65		1.41	
perylene	7.0	5.4	18.1	25	0.86	1.30	3.3	2.1
anthracene	3.2	5.1	37	20	1.38	0.512	5.2	2.8
tetracene	1.7	3.0[b]	11.4	9.4	0.81	2.5[b]	3.6	0.86
BTBP					0.20		0.20	

[a] D is the mean rotational diffusion coefficient (=(1/6)τ). [b] Only one exponential was observed for tetracene in MCH (see part 1). These are the values at short and long wavelengths, respectively.

−0.2 and +0.4. Given the shape of the molecule and the perylene results, it is plausible to ascribe this very fast process to L_x. Over the limited range accessible (−20 to −60 °C), its extent does not change significantly, but it appears to be large. As Figure 1 shows, this gives a positive $\sum r_y$ as is observed.

Temperature Dependence of Decay Times. Hydrodynamic theory predicts that rotation times will be proportional to η/T. For MCH,[23] it was found that the quantities $D_i\eta/T$ were not in fact constant. For the unsubstituted aromatics, they increased, very rapidly in some cases, with falling temperature. The plots of η/T in Figures 2 and 4−7 show that the same is true here. Viscosity measurements on squalane only extend to −20 °C; therefore, direct comparisons between the two solvents and with theoretical predictions (Table 1) have been limited to the rotation rates at the upper ends of the temperature ranges. Temperatures selected were −60 °C for MCH and 0 °C for squalane. The latter value required short extrapolations in some cases, using the relations described below. This procedure necessarily alters relative values derived from τ_1 and τ_2 slightly, but the interest here is in the orders of magnitude of the data. Since analysis into x, y, and z components was not feasible in this case, mean values of D (=(1/6)τ), both calculated and experimental, are used in Table 1.

As the figures show, below about −45 °C the shorter decay times tend to level off or even decrease; at higher temperatues, all the decays can be fitted to Arrhenius equations within the experimental error. The activation energies obtained, i.e., R d(ln τ)/d(1/T), are collected in Table 2. Their precision varies considerably; only a few points could be measured for the slowest processes, and in some other cases, there is considerable scatter; the results for anthracene are suspect (cf. Figure 6). However, the table shows clear trends, the slower processes giving larger activation energies than fast, and y excitation larger than z.

TABLE 2: Energies of Activation (kJ mol^{-1}) for the Rotational Processes

compound	E_{1z}	E_{2z}	E_{1y}	E_{2y}
coronene		45.5 ± 8.0		
triphenylene	3.2 ± 2.6	44.0 ± 2.1		
benzoperylene	28.5 ± 7.5	43.1 ± 1.5	38.2 ± 2.6	53.4 ± 4.6
perylene	14.2 ± 7.7	26.9 ± 2.2	21.1 ± 7.9	36.8 ± 3.0[a]
anthracene	25.0 ± 4.1	26.2 ± 2.2	29.4 ± 3.8	17.0 ± 3.2
tetracene	21.1 ± 2.6	40.1 ± 0.4	39.8 ± 2.4	47.2 ± 4.7

[a] And 60.7 ± 10.7 for the slowest decay in perylene.

Discussion

The bifurcation on cooling of relaxation processes in viscous liquids is well-known.[15,16,30,31] For α processes the rates are proportional to η/T and approach zero at the glass transition temperature, T_g. In contrast, β processes follow the Arrhenius law. This was first observed for polymers where the β processes were ascribed to segmental motions, but it was later found in glass-forming small molecules and appears to be a characteristic, though not a universal, property of the glassy state.[15] The nature of the β relaxation has been much discussed. Given the wide variety of materials, there may be a number of such processes. The association of the bifurcation with viscous flow suggests that the occurrence of the β process reflects inhomogeneities, i.e., the formation of regions of different mobility.[15] This seems unlikely at temperatures well above T_g, and recent work suggests it is not a general explanation.[16,30,32] Kivelson and Kivelson[16] explained the β process in molecular liquids as limited range diffusional rotation, but actual measurements are few. Hinze and Sillescu[33] made NMR measurements on the β process in supercooled toluene below the glass transition (T_g of 117 K), which they interpreted as rotation, over 9° at 75 K and 13° at 115 K.

The only work on excited probes in highly viscous hydrocarbons appears to be that of Ediger et al., who studied polyisoprene[34] and o-terphenyl[32,35] as matrices. Though biexponential decays were observed, details are not given. There appears to be no evidence of restricted rotation in the data, but β processes are said to be weak in polyisoprene while o-terphenyl is a smaller molecule than the probes used.

Measurements of the viscosity of squalane have only been reported for temperatures above −20 °C.[36−38] The data are plotted in Figure 8 together with a curve put forward previously, based partly on the glass transition temperature, which is ∼180 K.[17]

$$\log(\eta/\mathrm{cP}) = -1.071 + \frac{312}{T/K - 175} \qquad (1)$$

The intermolecular forces in alkanes are weak, so one may expect squalane to form a "fragile glass";[30,39] however, the expected curvature in Figure 8 is not very marked. Recently, Kivelson et al.,[40] extending their earlier work, have been able to reduce viscosity data for a wide variety of glass formers to a single curve. An attempt to apply their equation to the viscosity

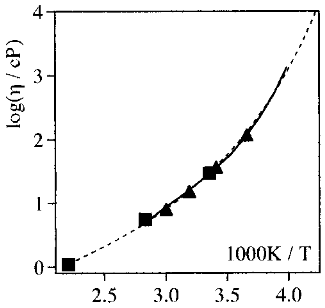

Figure 8. Temperature dependence of the viscosity of squalane: (—) ref 39; (■) ref 40; (▲) ref 41; (- - -) fitted curve, eq 1.

of squalane was unsatisfactory possibly because the available data are too far above T_g.

The α process should correlate with viscous flow. The slowest rotations observed here do indeed run parallel to η/T down to -40 to -50 °C, below which they are usually too slow to measure. Differentiation of eq 1 gives apparent activation energies of 46, 65, and 101 kJ mol^{-1} at 0, -20, and -40 °C, comparable with the highest values in Table 2. The idea that translational diffusion may depend on $(\eta/T)^a$, where $0 < a < 1$, has long been familiar and is readily explained by free volume theory.[41] The same relation is found for internal rotation (photoisomerization)[28,42,43] and for overall rotation.[44] In an attempt to extend the curve fits to lower temperatures, log(τ) was plotted against log(T). As expected, values of a were obtained ranging from 0.2 to 1; however, the precision of the data is not adequate to distinguish these fits from the simple Arrhenius plots and the extension of the range of fit was not significant. This confirms that there is a change in the nature of the process at lower temperatures. One can only speculate that this is connected with the range of angles involved. In the description above (Figure 1) it was assumed that all rotation angles were equally probable up to a limit. It is more likely that diffusion over a small range requires less energy than a larger one. This may account for the triphenylene data (Figure 2) where, at first sight, the lack of dependence of the rate on temperature appears to be inconsistent with the proposed hindered motion.

Literature measurements on these molecules were discussed in part 1 together with the data for MCH. There is considerable variation with both solute and solvent, but some generalizations were possible. Some molecules, such as substituted anthracenes in MCH, are found to behave simply. In other cases, usually for the unsubstituted compounds, rotation times rose less rapidly than η/T on cooling and the ratios of the D_i changed considerably. Rotation in *n*-alkanes has been studied extensively, more than in branched ones, but their liquid range is limited. Beyond C_{16} they are solid at ambient temperature. It has been demonstrated for a number of molecules[9−13] that their rotation time is proportional to viscosity in small *n*-alkanes, but the times shorten relatively when the length of the alkane exceeds that of the probe. Measurements of fluorescence anisotropy in squalane are few, but 9,10-diphenylanthracene rotates almost twice as fast in squalane as in the *n*-alkanes if the viscosities are scaled.[10] The relative sizes of solute and solvent are 17 × 11.6 Å for DPA and 33 Å for squalane in the all-trans conformations of the main chain. Ben-Amotz and Drake[45] have made use of an exceptionally large fluorescent molecule BTBP (*N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide, whose overall length is ∼26 Å). In the *n*-alkanes (C_6-C_{16}), its rotation time increased in proportion to viscosity and was 85% of the value calculated from the "stick" approximation. However, McLure et al.[48] find that τ_r for BTBP in squalane is only 54% of the stick value and in fact happens to coincide with the slip prediction. Table 1 shows that the smaller aromatics studied here rotate much faster than predicted and faster than they do in MCH.

The only comparable work on long-chain alkanes is that of Zinsli[18] and Johansson[19] who studied perylene in paraffin oil. Whereas r_2 is approximately constant, ∼0.1, r_1 falls quite rapidly with increasing temperature. They propose that this is the result of fast libration in the molecular plane; the extent was calculated as 15° at -20 °C increasing to 42° at 50 °C[18] and as 40° at -8 °C, 90° at 52 °C.[19] The precise composition of paraffin oil is not known; its high viscosity suggests the alkane chains are considerably longer than alkane chains of squalane. The difference between the two solvents is considerable; diffusive limited range rotation, if present in paraffin oil, must be very fast. A plot of Johansson's τ_2 values against $1/T$ shows that they fit the Arrhenius law with an activation energy of 47.0 ± 1.8 kJ mol^{-1}, in excellent agreement with that of the viscosity, 45.3 kJ mol^{-1}.[19] τ_1 may be less steeply dependent on temperature, but the difference, if any, is small.

A complete quantitative description of the data is not feasible; it would require 15 parameters—range and rate of libration about each axis, the same for restricted rotation, and three rates of overall rotation. Further, restricted rotation may occur in several stages. However, a qualitative description has been given that appears plausible in terms of the shapes of the molecules. The differences in decay rates between y and z excitation are a particular problem. The precision of the data is such that two or three exponentials suffice to represent the decays. In fact, the decays may well be more complicated; i.e., each decay may contain components of both restricted and overall rotation. As Figure 1 shows, overall rotation will predominate for y excitation because only L_x will introduce a faster decay. Both L_x and L_y do this for z excitation. This view is supported by data in Table 2; the derived Arrhenius parameters are always larger for y excitation.

The differences between MCH and squalane are very striking, though it should be noted that the results are not directly comparable. The highest viscosities in MCH correspond approximately to the lowest ones in squalane. While restricted rotation may occur in MCH, we found no clear-cut evidence for it except over a limited range of temperatures for anthracene and possibly perylene. The effect of relative molecular sizes of solvent and solute is well-known. The differences may result from differences in geometry, but relative rates of translation and rotation must also be important. Small solvent molecules rotate faster than the solutes, but the overall rotation of squalane will be considerably slower. Limited rotation of the solute may require movement of sections of the solvent molecule, overall rotation of the solute, and larger-scale movements, which require cooperative motions of other molecules. This distinction does not arise for small solvent molecules.

Concluding Remarks

In his pioneering work on α and β processes, Johari[15] found evidence only for a single β process. Our results provide clear evidence for the role of rotation, and most strikingly, the bifurcation is found to differ among the molecular axes. However, it should be recalled that most relaxation studies are made on pure materials, not solutions. Quantitative studies of restricted-range rotation are few. At one extreme are the NMR studies of toluene[33] mentioned above; at the other, in picosecond laser studies,[47] aniline in alkanes was found to rotate in times only about double that expected for inertial rotation and modeling suggested libration over 38°. The faster times found here are ∼100−1000 times the inertial value of a few picoseconds. While the triphenylene data can be treated simply because of its symmetry, attempts at a quantitative description of the results for other molecules in the same way were unsuccessful. More sophisticated modeling techniqes are required, and we hope the present results will be the subject of such studies.

Fluorescence anisotropy has the advantage that rotations around different axes are readily distinguished; squalane is useful in this respect (compared to, for example, *o*-terphenyl) because it is transparent to the short wavelengths needed to excite higher electronic states. The time range available here is very limited, but shorter times are accessible using laser excitation. Ediger et al.[32,34,35] have been able to extend it by many orders of magnitude by studying excited triplet states of anthracenes. Their method has the potential to give results for different axes. The fluorescence of anthracene is short-axis-polarized, while the triplet−triplet absorption they used is oriented along the long axis. Studies of phosphorescence would add to this, since it is polarized out of plane for aromatic hydrocarbons.

Our overall aim was to use alkanes with a wide liquid range to fill a gap between studies of mobile liquids on one hand and highly viscous liquids on the other. The former has now reached very short rotation times thanks to the use of picosecond lasers, but the choice of liquids has been rather limited; for the latter, fluorescence anisotropy, which has the potential to give detailed information about rotation, has hardly been used previously.

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