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^2H nuclear magnetic relaxation study of the rotation of adamantane in n -alkanes

Bernard Ancian, Bernard Tiffon, and Jacques-Emile Dubois

Institut de Topologie et de Dynamique des Systèmes de l'Université Paris VII, associé au C.N.R.S., 1 rue Guy de la Brosse, 75005 Paris, France

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Deuteron spin-lattice relaxation time has been measured for adamantane- d_1 in several n -alkane solutions at variable temperature. It is found that solvent viscosity plays only a minor role in adamantane reorientation. This latter involves an activated Arrhenius process with a solvent-independent activation energy (1.3 kcal/mole in the 183–423 °K temperature range). It follows that adamantane rotation is mainly governed by microscopic collisional motions rather than by collective hydrodynamic effects and can be pictured by the concept of transient solvent cavities in which the solvent molecule reorients.

Considerable experimental^{1–4} and theoretical investigations^{5–8} have recently been devoted to molecular reorientation in the liquid phase in order to test the applicability of macroscopic hydrodynamics to microscopic motion. In this context, the study of highly symmetrical molecules in solution is undoubtedly pertinent, since it eliminates anisotropy in the solute rotation, and should therefore lead to better agreement between experimental reorientational correlation times and the theoretical values obtained using Debye's model with various modifications: introduction of the "slip" boundary condition,⁶ microviscosity,⁹ mutual viscosity,¹⁰ or anisotropy of the intermolecular potentials.¹¹

Adamantane, a globular molecule belonging to the molecular point group T_d , is an especially suitable model for rotational motion studies in solvents covering a wide range of viscosity. Indeed, Kuhlmann *et al.*'s pioneer work¹² on ^{13}C relaxation and ^{13}C – ^1H nuclear Overhauser effect has shown that adamantane tumbles isotropically in CS_2 . Wasylishen and Pettitt¹³ and McGaughey, Wu, and Fung¹⁴ independently conducted deuteron relaxation measurements on this molecule in solution; both research groups concluded that adamantane should rotate rather freely in n -hexane and chloroalkanes ("slip" boundary conditions), but that it should reorient by small-step diffusion in the more highly viscous CHBr_3 and CH_2I_2 .¹³ However, they also concluded, in complete disagreement with predictions by Kivelson *et al.*¹¹ and results by Fury and Jonas,³ that the solute rotation-translation coupling parameter should be solvent independent,¹³ but temperature dependent.¹⁴

In keeping with the previous work in this laboratory on CCl_4 and CS_2 in alkanes,¹⁵ this striking behavior prompted a reexamination of the rotation of adamantane by a ^2H spin-lattice relaxation study in inert solvents of comparable size: n -hexane, n -octane, n -decane, n -dodecane, n -tetradecane, and n -hexadecane. The viscosity and temperature dependence of reorientational correlation times of adamantane- d_1 are reported here; the viscosity of the different solvents at constant temperature varies by an order of magnitude, whereas when temperature is varied the viscosity varies by a factor of 6–8 (Table I). Experiments were also run in a carbon tetrachloride solution for comparison with results from the literature.

EXPERIMENTAL

Adamantane- d_1 (99% enriched) was obtained by reduction of 1-chloro adamantane (Aldrich) with an excess of LiAlD_4 (Fluka) in n -butylether at reflux.

^2H relaxation times were measured at 30 MHz on a Bruker WP-200 FT NMR spectrometer by the inversion recovery method. The $\pi/2$ pulse, which was measured for each sample at each temperature, ranged from 51 to 115 μsec . Single scan measurements were performed using a 1 kHz spectral width, 8 K data point acquisition, complete ^1H decoupling, and a 1 Hz S/N enhancement exponential window. Relaxation times were measured twice on each adamantane- d_1 solution in n -alkanes (2.5% w/w) and in CCl_4 (1% w/w) at each temperature ($\pm 1^\circ\text{K}$). T_1 values were computed using a two-parameter exponential curve fitting (equilibrium magnetization and relaxation time) developed in our laboratory and described elsewhere.¹⁶ It leads to better agreement with T_1 values obtained by the null signal in the inversion recovery method; it is therefore preferred to a three-parameter exponential curve fitting which gives systematically larger relaxation times.

All viscosities were taken from the Landolt-Börnstein tables.¹⁷

RESULTS AND DISCUSSION

In the extreme narrowing condition, the quadrupolar contribution T_1^Q to the deuteron spin-lattice relaxation time T_1 of adamantane- d_1 can be expressed by^{18,19}

$$\frac{1}{T_1^Q} = \frac{3\pi^2}{2} \left(1 + \frac{\eta^2}{3} \right) \left(\frac{e^2 q Q}{h} \right)^2 \tau_c, \quad (1)$$

where η is the asymmetry parameter, $e^2 q Q/h$ is the quadrupole coupling constant (QCC), and τ_c is the reorientational correlation time of the principal axis of the field gradient tensor, i.e., that of the C–D bond axis. Other contributions to the ^2H relaxation rate ($0.2 \text{ s} < T_1 < 2 \text{ s}$) are extremely negligible and $T_1 = T_1^Q$: e.g., even in the highly protonated n -hexadecane at room temperature, the ^2H – ^1H intermolecular dipole-dipole term, calculated using a continuous translation diffusion model,²⁰ does not exceed $3 \times 10^{-3} \text{ sec}^{-1}$. Moreover, the ^2H – ^1H intramolecular dipole-dipole contribution ($\sim 0.34 \times 10^{-3} \text{ sec}^{-1}$) is also highly negligible. Since the C–D bond axis is a

TABLE I. Deuteron spin-lattice relaxation times T_1 and shear viscosities η of adamantane- d_1 in *n*-alkanes and CCl_4 solutions at variable temperatures (T_1 in $s \pm 3\%$, η in cP from Ref. 17).

| T (K) | <i>n</i> -C ₆ H ₁₄ | | <i>n</i> -C ₈ H ₁₈ | | <i>n</i> -C ₁₀ H ₂₂ | | <i>n</i> -C ₁₂ H ₂₆ | | <i>n</i> -C ₁₄ H ₃₀ | | <i>n</i> -C ₁₆ H ₃₄ | | CCl ₄ | |
|---------|--|--------|--|--------|---|--------|---|--------|---|--------|---|--------|------------------|--------|
| | T_1 | η | T_1 | η | T_1 | η | T_1 | η | T_1 | η | T_1 | η | T_1 | η |
| 183 | 0.36 | 1.84 | ... | ... | | | | | | | | | | |
| 193 | 0.46 | 1.39 | ... | ... | | | | | | | | | | |
| 213 | 0.64 | 0.894 | 0.53 | 2.48 | | | | | | | | | | |
| 217 | ... | ... | 0.55 | 2.18 | | | | | | | | | | |
| 223 | ... | ... | 0.62 | 1.85 | | | | | | | | | | |
| 233 | 0.81 | 0.635 | 0.68 | 1.45 | ... | ... | | | | | | | | |
| 243 | ... | ... | ... | ... | 0.69 | 2.53 | | | | | | | | |
| 247 | ... | ... | ... | ... | 0.73 | 2.27 | | | | | | | | |
| 253 | 0.94 | 0.481 | 0.86 | 0.968 | 0.81 | 1.94 | | | | | | | | |
| 263 | ... | ... | ... | ... | 0.87 | 1.55 | 0.75 | 2.90 | | | | | 0.66 | 1.675 |
| 268 | ... | ... | ... | ... | ... | ... | 0.81 | 2.55 | | | | | 0.70 | 1.491 |
| 273 | 1.15 | 0.400 | 0.99 | 0.703 | 0.93 | 1.298 | 0.83 | 2.26 | | | | | 0.74 | 1.349 |
| 278 | ... | ... | ... | ... | ... | ... | 0.86 | 1.99 | 0.82 | 3.29 | | | ... | ... |
| 279 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | | | 0.77 | 1.202 |
| 282 | 1.24 | 0.360 | ... | ... | ... | ... | ... | ... | ... | ... | | | ... | ... |
| 283 | ... | ... | ... | ... | ... | ... | 0.90 | 1.81 | 0.83 | 2.92 | | | 0.79 | 1.121 |
| 285 | ... | ... | 1.08 | 0.594 | ... | ... | ... | ... | ... | ... | | | ... | ... |
| 288 | ... | ... | ... | ... | 1.06 | 0.987 | ... | ... | 0.89 | 2.58 | | | ... | ... |
| 293 | ... | ... | ... | ... | ... | ... | 0.97 | 1.504 | 0.98 | 2.18 | 1.01 | 3.44 | 0.85 | 0.961 |
| 295 | 1.34 | 0.312 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 296 | ... | ... | 1.15 | 0.520 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 298 | ... | ... | ... | ... | 1.15 | 0.841 | ... | ... | ... | ... | 1.04 | 3.08 | ... | ... |
| 303 | 1.43 | 0.290 | ... | ... | 1.21 | 0.784 | 1.01 | 1.228 | ... | ... | 1.06 | 2.76 | 0.91 | 0.836 |
| 306 | ... | ... | 1.23 | 0.463 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 310 | 1.50 | 0.270 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 313 | ... | ... | ... | ... | ... | ... | ... | ... | 1.12 | 1.465 | 1.16 | 2.25 | 0.96 | 0.738 |
| 317 | ... | ... | 1.34 | 0.411 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 318 | ... | ... | ... | ... | ... | ... | 1.17 | 0.969 | ... | ... | ... | ... | ... | ... |
| 323 | ... | ... | ... | ... | 1.37 | 0.601 | ... | ... | 1.17 | 1.259 | 1.21 | 1.862 | 1.00 | 0.655 |
| 328 | ... | ... | 1.38 | 0.367 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 333 | ... | ... | ... | ... | ... | ... | 1.32 | 0.786 | 1.28 | 1.105 | 1.32 | 1.57 | 1.02 | 0.585 |
| 339 | ... | ... | 1.47 | 0.328 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 343 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.35 | 1.343 | 1.07 | 0.524 |
| 351 | ... | ... | 1.58 | 0.296 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 353 | ... | ... | ... | ... | 1.59 | 0.452 | 1.47 | 0.636 | 1.45 | 0.832 | 1.48 | 1.164 | ... | ... |
| 363 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.51 | 1.017 | ... | ... |
| 373 | ... | ... | ... | ... | 1.65 | 0.357 | 1.57 | 0.512 | 1.58 | 0.67 | ... | ... | ... | ... |
| 383 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.62 | 0.801 | ... | ... |
| 398 | ... | ... | ... | ... | ... | ... | ... | ... | 1.71 | 0.532 | ... | ... | ... | ... |
| 403 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.80 | 0.647 | ... | ... |
| 423 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1.87 | 0.534 | ... | ... |

threefold symmetry axis for the molecule, η equals zero. Through lack of an available numerical value for the QCC of adamantane- d_1 , it is assumed in this work to be the same as that of cyclohexane²¹ (174 kHz), in accordance with other workers.^{13,14} For the isotropic rotation of the spherical adamantane- d_1 , τ_c is the rotational correlation time of the solute. Deuteron spin-lattice relaxation times of adamantane- d_1 , and shear viscosities of the solutions at variable temperature are listed in Table I.

Generally, in liquid phase, the reorientational correlation times τ_c of rigid molecules are interpreted in terms of hydrodynamic transport phenomena; i.e., they are assumed to be linearly related to the shear viscosity, as expressed by the well-known Debye-Stokes-Einstein equation¹⁻⁴

$$\tau_c = \frac{4}{3} \frac{\pi r_0^3 \eta}{k_B T} \times c + \tau_0, \quad (2)$$

in which r_0 is the hydrodynamic radius of the solute, k_B is Boltzmann's constant, T is the absolute temperature, and η is the shear viscosity. The coefficient c and the intercept τ_0 are not predicted by the hydrodynamic theory of a large hard sphere rotating randomly in a continuous medium with "stick" boundary conditions.

However, a great deal of experimental data^{1-4,13-15} has shown that $c < 1$ is needed to account for the shear viscosity dependence of most nonassociating molecular liquids. Parameter c was recently interpreted by Hu and Zwanzig⁶ who solved the Navier-Stokes hydrodynamic equation using "slip" boundary conditions. This correction has been successfully applied to rotational diffusion of many ellipsoids in low viscosity molecular liquids and solvents.¹⁻⁴ Nevertheless, this modified theory predicts a dependence of slip rotation only with the solute molecular shape, but not with the solvent one.

In contrast, the Gierer-Wirtz microviscosity theory⁹

TABLE II. Comparison of experimental reorientational correlation times τ_c (expt) with theoretical Gierer-Wirtz τ_c (G-W) and Hill τ_c (H) values for adamantane- d_1 in *n*-alkanes at 303 °K.

| Solvent | τ_c (expt) (ps) | τ_c (G-W) (ps) | τ_c (H) (ps) |
|-----------------------|-------------------------|------------------------|----------------------|
| <i>n</i> -Hexane | 1.56 | 2.80 | 3.41 |
| <i>n</i> -Octane | 1.85 | 3.91 | 4.76 |
| <i>n</i> -Decane | 1.84 | 5.61 | 6.96 |
| <i>n</i> -Dodecane | 2.21 | 7.99 | 10.20 |
| <i>n</i> -Tetradecane | 2.08 | 10.96 | 14.35 |
| <i>n</i> -Hexadecane | 2.10 | 15.74 | 21.23 |

as well as the Hill mutual viscosity theory¹⁰ assumes a strong influence of the relative sizes of the solution-constituent molecules. Although the Hill theory has been applied with some success in dielectric and nuclear magnetic relaxation of molecular liquids and dilute solutions,²²⁻²⁴ it is very difficult to apply and does not predict the correct solvent mass and temperature dependence.^{11,22} The rotational microviscosity of Gierer and Wirtz, based on the rotation of the surrounding layers of a spherical solute molecule, has also been severely criticized. O'Reilly and Peterson²⁵ have pointed out that the time required for the establishment of the equilibrium between the various layers is much longer than the reorientational correlation time of the solute so that the equilibrium state can never be achieved. McClung and Kivelson¹¹ have also noticed that the microviscosity factor of the ClO_2 radical in two distinct solvents differs largely from the expected ratio of the solvent molecular radii. Finally, Glaser²⁶ and Sandhu²⁷ have shown that, even in a molecular liquid, agreement between experimental and theoretical τ_c values is obtained when a microviscosity factor of about 1/12 instead of 1/6 is used.

Adamantane rotation in *n*-alkanes and in carbon tetrachloride further stresses the shortcomings of these two models. For example, results in Table I show that, at 303 °K, ^2H spin-lattice relaxation time decreases only by about 30%, while the viscosity of the *n*-alkanes from *n*-hexane to *n*-hexadecane increases by an order of magnitude. According to the Gierer-Wirtz microviscosity theory,⁹ the c factor in Eq. (1) can be expressed in terms of f_r by $f_r^{-1} = 6r_s/r_0 + 1/(1 + r_s/r_0)^3$, where r_s and r_0 , respectively, are the solvent and solute radii estimated from molecular volumes by assuming hexagonally close-packed pure liquid ($r_0 = 3.47$ Å). Application of the Hill theory of mutual viscosity to an infinitely dilute solution gives

$$\tau_c(\text{H}) = \frac{2\eta r_s I}{\mu kT} + \tau_0, \quad (3)$$

in which I is the moment of inertia of the solute ($I = 49.61 \times 10^{-39}$ g cm²) and μ is the reduced mass of the solvent-solute system. By estimating τ_0 from the classical free rotor theory⁵ equation

$$\tau_0 = \frac{2\pi}{9} \left(\frac{I}{kT} \right)^{1/2}, \quad (4)$$

the rotational correlation times τ_c (G-W) and τ_c (H) cal-

culated by both methods can be compared to the experimental values $\tau_c(\text{expt})$ for adamantane- d_1 in each *n*-alkane at 303 °K (Table II). Neither the correlation times calculated using the Gierer-Wirtz microviscosity theory nor those calculated using the Hill mutual viscosity theory agree with the experimental correlation times. Both methods fail to account for the solvent viscosity "saturation" effect. Work carried out in this laboratory on rotational motion of the quasispherical CCl_4 and the rodlike CS_2 in alkanes had already detected this failure in the Gierer-Wirtz microviscosity theory.¹⁵

Figure 1 shows the classical plot of the reorientational correlation time τ_c of adamantane- d_1 versus the solvent viscosity function η/T . The dependence of τ_c upon η/T is clearly nonlinear for *n*-alkanes, as previously reported by McGaughey, Wu, and Fung¹⁴ for adamantane- d_{18} in *n*-hexane. All the curves in Fig. 1 have the same intercept, $\tau_0 \approx 0.8$ ps, which is very close to the free rotor correlation time [Eq. (4)] at 303 °K. Indeed, for each alkane, the temperature range can be divided into two parts in each of which the variation of τ_c is roughly linear. The corresponding c values calculated by Eq. (2) (i.e., Kivelson's κ values), which are actually temperature dependent, are listed in Table III. For comparison, results in CCl_4 are listed in both Fig. 1 and Table III. In agreement with results reported by Wasylishen and Pettitt,¹³ adamantane- d_1 does not display the

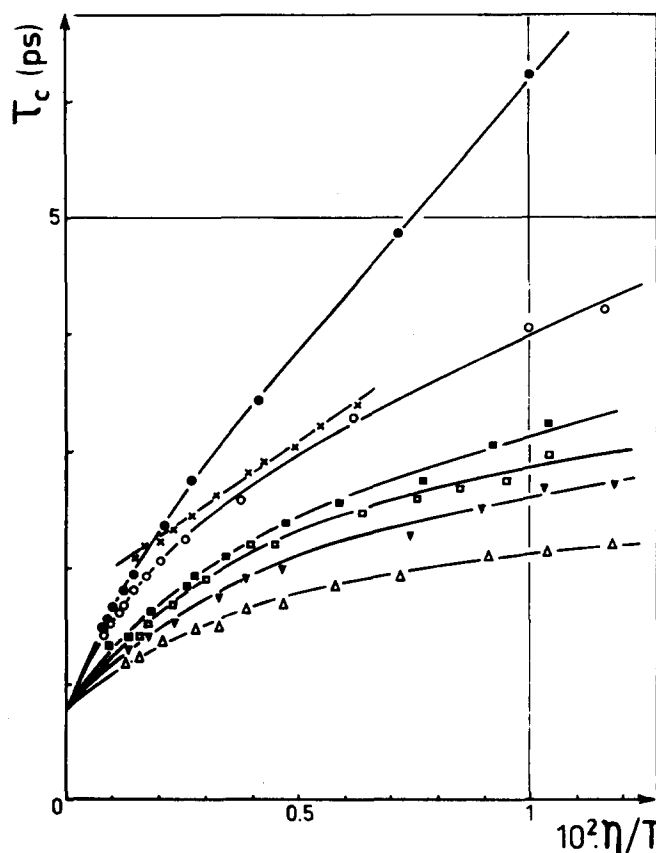


FIG. 1. Adamantane- d_1 rotational correlation times τ_c as a function of viscosity times reciprocal temperature η/T . Solvents are: ●, *n*-C₆H₁₄; ○, *n*-C₈H₁₈; ■, *n*-C₁₀H₂₂; □, *n*-C₁₂H₂₆; ▲, C₁₄H₃₀; △, *n*-C₁₆H₃₄; ×, CCl₄.

TABLE III. Kivelson's κ values for adamantane- d_1 in *n*-alkanes and in CCl_4 .

| Solvent | <i>n</i> -C ₆ H ₁₄ | <i>n</i> -C ₈ H ₁₈ | <i>n</i> -C ₁₀ H ₂₂ | <i>n</i> -C ₁₂ H ₂₆ | <i>n</i> -C ₁₄ H ₃₀ | <i>n</i> -C ₁₆ H ₃₄ | CCl_4 |
|--------------------------|--|--|---|---|---|---|----------------|
| Temp. interval 1 (°K) | 183–253 | 213–285 | 243–288 | 263–303 | 278–323 | 293–343 | 263–343 |
| | 0.0370 | 0.0179 | 0.0123 | 0.0085 | 0.0086 | 0.0058 | 0.0211 |
| Temp. interval 2 | 253–310 | 285–351 | 288–373 | 303–373 | 323–398 | 343–423 | ... |
| | 0.0662 | 0.0417 | 0.0249 | 0.0181 | 0.0182 | 0.0131 | ... |

same behavior in CCl_4 as in alkanes and the plot of τ_c vs η/T is linear, at least in the temperature range where CCl_4 is liquid. In contrast, the same plot is nonlinear in CH_2Cl_2 .¹⁴

Hynes, Kapral, and Weinberg⁸ recently concluded that "observed linearity of τ_c with η/T does not necessarily imply any significant hydrodynamic component of the motion and ... the precise value of the intercept has no particular fundamental significance." They further postulated that it is likely that the rotation of a small spherical molecule is mainly governed by microscopic collisions rather than by hydrodynamic (collective) properties of the liquid unless the solute particle size is over a hundred times larger than that of the solvent.⁸ The present work, in which the solute and the solvents are comparable in size (i.e., 3.5–4.5 Å), largely upholds this view. Reorientation of adamantane- d_1 in *n*-alkanes as well as in CCl_4 ¹³ or other halomethanes (CH_2I_2 , CHBr_3 , CHCl_3 , and CH_2Cl_2)^{13,14} is a near "slip" condition. Nevertheless, there is a fundamental difference between its behavior in alkanes and in halomethanes. Wasylishen and Pettitt¹³ observed that at room temperature the reorientational correlation time τ_c of adamantane- d_1 is roughly equal to that of the solvent molecule (1.7 ps at 296°K for pure CCl_4). In contrast, in *n*-alkanes at a given temperature, the τ_c of adamantane- d_1 remains roughly constant, whereas the τ_c of each carbon of the solvent molecule varies noticeably^{28,29} from ~1.4–16 ps. Likewise, depolarized Rayleigh linewidths, which mainly depend on overall molecular reorientation, yield very high and very variable correlation times for *n*-alkanes (e.g., 200 ps for *n*-dodecane at 273°K).³⁰ This indicates that the coupling of the motion of solute and solvent molecules is less important in *n*-alkanes than in halomethanes, although Kivelson's κ values are greater in the shortest *n*-alkanes (*n*-hexane to *n*-decane) than in CCl_4 (Table III). Thus, the physical meaning of these κ values, which assumedly represent the ratio between the mean-square intermolecular torques on the solute molecules and the mean-square intermolecular forces on the solvent molecules,¹¹ can be questioned, at least in the case of *n*-alkane solvents. Furthermore, theoretical decomposition of the κ parameter in terms of the slip coefficient β and of the shear viscosity η leads to $\kappa = [1 + (3\eta/\beta)]^{-1}$, thereby indicating that κ should vary with viscosity for sufficiently low and high viscosity values,⁸ in accordance with our results (Table III).

As a tendfold increase in solvent viscosity from *n*-hexane to *n*-hexadecane induces only a 30% increase in τ_c values at 303°K, it is clear that the main factor gov-

erning τ_c variation is temperature, whereas solvent shear viscosity plays only a minor role. Therefore, the rotational motion of adamantane- d_1 in *n*-alkanes and CCl_4 should be essentially inertial. However, a plot of τ_c vs $T^{-1/2}$ according to Eq. (4) is not linear, whatever the solvent. This is not surprising since the free rotor theory is certainly irrelevant to dense liquids such as *n*-alkanes or halomethanes.

In contrast, Fig. 2 shows that the Arrhenius plot of $\ln \tau_c$ for adamantane- d_1 in *n*-alkanes is linear, whereas it is nonlinear in CCl_4 . Moreover, all the slopes are nearly identical. Table IV gives the activation energies of adamantane- d_1 rotation in *n*-alkanes and in CCl_4 . For comparison, activation energies of η/T are also listed. It should be noted that these two activation energies largely differ: $E_a(\tau_c) \approx 1.27 \pm 0.13$ kcal/mole whatever the solvent, whereas $E_a(\eta/T)$ ranges from 2.15 kcal/

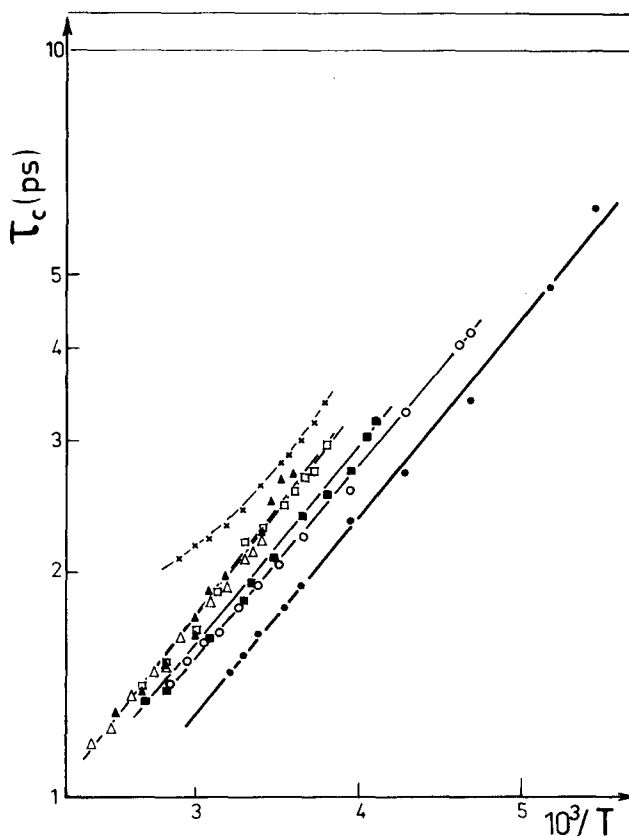


FIG. 2. Temperature dependence of adamantane- d_1 rotational correlation times τ_c in *n*-alkanes and in CCl_4 . Solvent code as in Fig. 1.

TABLE IV. Activation energies of adamantane-*d*₁ rotational correlation time $E_a(\tau_c)$ in *n*-alkanes and of viscosity times reciprocal temperature $E_a(\eta/T)$.

| Solvent | <i>n</i> -C ₆ H ₁₄ | <i>n</i> -C ₈ H ₁₈ | <i>n</i> -C ₁₀ H ₂₂ | <i>n</i> -C ₁₂ H ₂₆ | <i>n</i> -C ₁₄ H ₃₀ | <i>n</i> -C ₁₆ H ₃₄ |
|------------------------------|--|--|---|---|---|---|
| $E_a(\tau_c)$ (kcal/mole) | 1.23 | 1.17 | 1.24 | 1.34 | 1.40 | 1.21 |
| $E_a(\eta/T)$ (kcal/mole) | 2.15 | 2.80 | 3.29 | 3.72 | 4.05 | 4.25 |

mole for *n*-hexane to 4.25 kcal/mole for *n*-hexadecane. This again confirms that rotational motion of adamantane-*d*₁ in *n*-alkanes has nothing to do with the shear viscosity of the solvent, i.e., with collective hydrodynamic processes. The slight shift of the *n*-hexane plot and, to a lesser extent, that of *n*-octane and *n*-decane compared to the (quasi) unique straight line obtained for *n*-dodecane, *n*-tetradecane, and *n*-hexadecane may be related to a more important chain length effect for the first three *n*-alkanes.

Although such linear Arrhenius plots have often been reported,³¹ the physical meaning of the activated process is not yet clear. The important point here is that the activation energy of adamantane-*d*₁ in *n*-alkanes [$E_a(\tau_c) \approx 1.27$ kcal/mole] is much lower than those of the end chain methyl rotation²⁸ (~2.6 kcal/mole), of the reorientational correlation times for methine and methylene of 10-methyl nonadecane²⁹ (5.0 kcal/mole for *n*-dodecane); this last value is highly comparable to that of the internal rotation barrier between a *trans* and a *gauche* state.³⁰ It can be concluded that adamantane-*d*₁ rotation in *n*-alkanes is only a slightly hindered motion which only depends on local (microscopic) solvent chain rotation, i.e., segmental or crankshaft motion.

We previously pictured the rotation of small spherical (CCl₄) or small rodlike molecules (CS₂) in alkanes as that of a solute in a "hole" of the flexible solvent chain.¹⁵ In the study of cyanoacetylene³² and dicyano-

acetylene⁴ in hydrocarbon solutions, Vold *et al.* have proposed a similar concept of transient cavities formed by solvent molecules in which the solute molecule reorients, provided the cavity lifetime is greater than the solute rotational correlation time. These two models provide a qualitatively better physical interpretation of the activation energy which is nearly independent from the *n*-alkane chain length. It seems likely that the existence and lifetime of the transient cavities of the solvent are related to the overall as well as to the crankshaft, segmental, or internal rotations of the *n*-alkane chain (cf. above). This concept is strongly supported by the monotonic dependence of the cyanoacetylene and dicyanoacetylene rotational correlation times on the solvent isothermal compressibility observed by Vold, Vold, and Szeverenyi.⁴ Figure 3 shows the plot of adamantane-*d*₁ τ_c^{-1} versus the isothermal compressibility of *n*-alkanes at 298 °K.³³ As expected, τ_c tends to decrease as the solvent isothermal compressibility increases due to a corresponding increase of void volumes between solvent molecules. It is noteworthy that this dependence is weaker—by a factor of 10—for the globular adamantane-*d*₁ than for the rodlike dicyanoacetylene.⁴ Reorientation of the long axis of the latter molecule would require cavities larger than the smaller adamantane; moreover, it would also displace more solvent. In contrast, as previously shown by intermolecular ¹³C-¹H nuclear Overhauser measurements²⁰ of CS₂ and CCl₄ in *n*-alkanes, translational diffusion of small molecules remains closely related to shear viscosity. Similar conclusions have been drawn by Amu³⁴ in the diffusion of the nearly spherical cyclohexylbromide in *n*-alkanes.

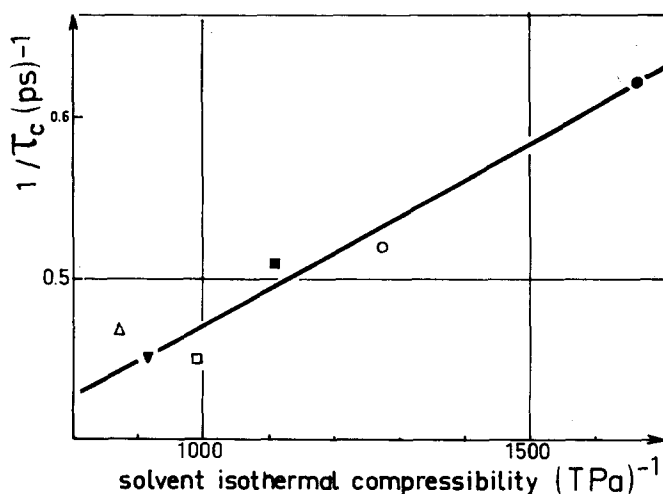


FIG. 3. Correlation between adamantane-*d*₁ rotational reorientation rates $1/\tau_c$ and solvent isothermal compressibility. Solvent code as in Fig. 1.

CONCLUSION

The herein described results indicate that rotational reorientation of adamantane in *n*-alkanes cannot be related to solvent shear viscosity and therefore cannot be interpreted by means of the classical hydrodynamic (collective) theory. The slipping rotation of adamantane obeys an activated Arrhenius process in which the activation energy (~1.3 kcal/mole) is nearly independent of alkane chain length. The globular adamantane undergoes slightly hindered rotation in solvent transient cavities with lifetimes much longer than the solute reorientational correlation time.

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