

Rotational Motion of a Solute Molecule in a Highly Viscous Liquid Studied by ^{13}C NMR: 1,3-Dibromoadamantane in Polymeric Chlorotrifluoroethene

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The viscosity-dependent retarding effect of a polymeric solvent on the rotation of small solute molecules is investigated by ^{13}C NMR relaxation measurements. It is found that the relaxation data of 1,3-dibromoadamantane in highly viscous polymeric chlorotrifluoroethene can be explained neither by isotropic nor by realistic anisotropic tumbling in a single environment. The experimental data are rationalized in terms of fast exchange between at least two environments with correlation times differing by up to two orders of magnitude. The study shows that a uniform retardation of molecular tumbling by a polymeric solvent, desirable for shifting the NMR observation window in studies of intramolecular mobility, is not always feasible. © 1998 Academic Press

Key Words: rotational correlation times; retardation of molecular rotation; distribution of correlation times; NMR ^{13}C relaxation; polychlorotrifluoroethene; polymeric solution properties.

1. INTRODUCTION

Nuclear magnetic resonance (NMR) is at present the most versatile and powerful tool for studying intramolecular dynamics both in the liquid phase and in solids (1–4). In principle, the NMR measurement parameters are sensitive to an extremely wide range of motional time scales, ranging from picoseconds to seconds (2). NMR relaxation measurements provide detailed information about reorientational motions of molecular axes and internuclear vectors (1, 5) and allow a critical assessment of motional models.

The inherent power of NMR relaxation spectroscopy for studying mobility in the liquid phase is hampered by the fact that only the composite effect of intramolecular and overall tumbling motion is sensed by the relaxation parameters. It is impossible to measure intramolecular mobility alone. This becomes apparent from a simple mathematical model where the intramolecular mobility is expressed in terms of an order parameter S^2 and a correlation time τ_i , leading, together with the overall tumbling correlation time τ_c , to the following expression for the relaxation-active motional correlation function (6, 7):

$$C(t) = [S^2 + (1 - S^2)e^{-t/\tau_i}]e^{-t/\tau_c}. \quad [1]$$

The rotational tumbling with the correlation time τ_c acts as a multiplicative “masking” process of the intramolecular mobility with correlation time τ_i that is of primary interest. As a result, τ_i can be determined with reasonable accuracy only in the interval $0.1\tau_c < \tau_i < 10\tau_c$ (8). This is a severe practical restriction in motional studies.

It would be highly desirable to shift the “observation window” for τ_i by a change of τ_c . Within the framework of classical hydrodynamic theory, the rotational correlation time for an interaction tensor of rank 2 in a spherical molecule obeys the Stokes–Einstein–Debye (SED) relationship (1, 9)

$$\tau_c = \frac{V\eta}{kT}, \quad [2]$$

where V is the effective spherical molecular volume, η is the shear viscosity, T is the absolute temperature, and k is the Boltzmann constant. This relation has frequently been used in NMR since the pioneering work of Bloembergen *et al.* (10). Based on Eq. [2], it is tempting to shift τ_c and the observation window of τ_i by varying the viscosity η of the solvent, while hoping that the intramolecular mobility of the solute is not significantly affected.

Williamson and Williams (11) used polychlorotrifluoroethene (PCTFE) as a polymeric solvent for NMR studies. Its viscosity can be varied in a large range by changing the temperature and by mixing fractions of different degrees of polymerization. PCTFE was subsequently used in a number of NMR investigations (12–15) for adjusting the viscosity in structural studies of solute molecules measuring the nuclear Overhauser effect (NOE) which depends on τ_c . However, according to our knowledge, no quantitative study of the dynamical aspects of solute molecules in PCTFE has been reported so far.

The present experimental study explores the potential of PCTFE as a solvent to control the overall tumbling correlation time of a simple solute molecule by varying the viscosity. We selected the rigid and symmetrical molecule 1,3-dibromoadamantane as a probe and focused on the relaxation properties of its methine carbon-13 spins with the goal of developing a

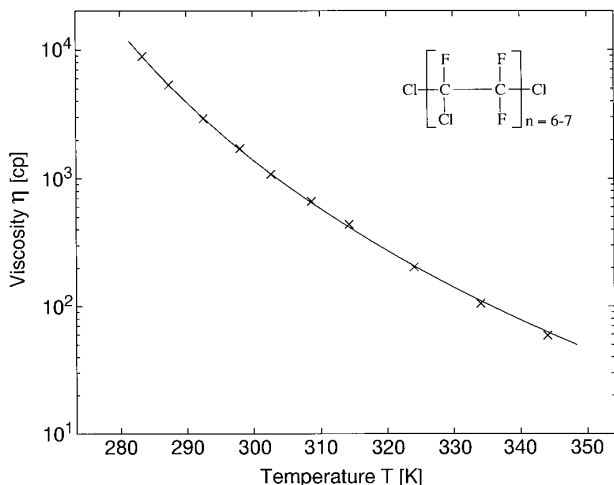


FIG. 1. Temperature dependence of the viscosity of PCTFE. The experimental data points measured at a shear rate of 1 s^{-1} are given for a temperature range from 283 to 344 K. The curve corresponds to the fitted power law of Eq. [3].

motional model for this solute in the accessible temperature-dependent viscosity range between 10^2 and 10^5 cP.

2. MATERIALS AND MEASUREMENTS

Solvent system and sample. Voltalef 10S (Atochem, France) is a highly viscous, nonpolar, aprotic oil consisting of polychlorotrifluoroethene with 6 to 7 monomer units and a molecular mass of approximately 800 Da. Viscosity measurements were performed using a dynamic stress rheometer (Rheometrics) with a Couette geometry (concentric cylinders). At temperatures above 282 K, the viscosity of PCTFE is within experimental accuracy not dependent on the shear rate in the range from 10^{-2} to 10^2 s^{-1} . The shear viscosity at a shear rate of 1 s^{-1} , given in Fig. 1, covers more than two orders of magnitude from 59 cP at 344.1 K to 8920 cP at 283.3 K. In this range a small but systematic deviation from an Arrhenius temperature dependence is found, similar to other highly viscous liquids (16, 17), with an activation energy varying from $E_a \approx 87 \text{ kJ mol}^{-1}$ at 283 K to $E_a \approx 55 \text{ kJ mol}^{-1}$ at 344 K. The measured temperature dependence is shown in Fig. 1. On the other hand, the temperature dependence can be fitted within experimental accuracy by a power law (17),

$$\eta(T) = c(T - T_0)^q, \quad [3]$$

where $c = 7.119 \times 10^{12} \text{ cP K}^{-q}$, $T_0 = 241.8 \text{ K}$, and $q = -5.501$. Below 282 K, PCTFE becomes opaque and the viscosity dependent on the shear rate. At 281 K, for example, we measured viscosities of $\eta = 1.25 \times 10^5 \text{ cP}$ at a shear rate of 10^{-2} s^{-1} and $\eta = 3.7 \times 10^4 \text{ cP}$ at a shear rate of 10 s^{-1} (see Table 1).

It is known that fluorinated organic compounds have ex-

ceptional abilities to dissolve oxygen (18, 19), which could cause paramagnetic relaxation of guest molecules. Therefore, the polymeric oil was degassed under high vacuum and handled in an argon atmosphere. 1,3-Dibromoadamantane (Aldrich) was dissolved in PCTFE with a concentration of 85 mM. Benzene- d_6 , enclosed in a coaxial capillary, was used for field-frequency locking.

NMR measurements. The NMR measurements were performed on Bruker DMX-400 and AMX-600 spectrometers, operating at 400 and 600 MHz proton resonance frequency, respectively. T_1 , NOE, $T_{1\rho}$, and T_2 have been measured for the methine carbons in 1,3-dibromoadamantane at temperatures of 274, 281, 290, 300, 324, and 339 K and a proton resonance frequency of 600 MHz. Additional measurements with 400 MHz proton resonance were carried out at a temperature of 300 K.

The ^{13}C spin–lattice relaxation times T_1 were measured by the standard inversion-recovery method, after an initial polarization transfer from protons by refocused INEPT and with proton decoupling during mixing and acquisition times. Eight or more mixing times τ_m in the range $3 \mu\text{s} \leq \tau_m \leq 5T_1$ were used. The inversion-recovery data were fitted by a three-parameter monoexponential function, employing the simplex algorithm from the toolbox of MATLAB (20). The covariance matrix of the fitted parameters was calculated for uncorrelated measurement errors of equal variance.

The ^{13}C NOEs were measured after presaturation of the protons by a series of 120° pulses with 10-ms interpulse delays, applied for at least $5 T_1$ (21). The peak areas were integrated and the NOEs were calculated as ratios with and without proton saturation. The experimental error was estimated by repeating the measurement for some of the NOEs.

The ^{13}C spin–spin relaxation times T_2 were determined by the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence after an initial INEPT transfer. ^{13}C rotating-frame relaxation times $T_{1\rho}$ were measured for a ^{13}C spin-locking field of 1.2 kHz. It proved unnecessary to eliminate the cross correlation between dipolar and chemical shift anisotropy relaxation by applying pulses to the protons during the mixing time. A quantitative estimate of the cross-correlated cross-relaxation effect, using an experiment similar to the one of Ref. (22), showed that the contribution to T_2 or $T_{1\rho}$ is below 1%, indicating a negligible anisotropy of the CH carbon shift. This is in agreement with quantum chemical calculations of the CSA tensor based on density functional theory (DFT) which showed that $\Delta\sigma < 10 \text{ ppm}$. In the T_2 and $T_{1\rho}$ measurements, the carrier frequency was set 100 Hz off resonance. The magnetization decays were fitted by a two-parameter monoexponential function. It was found that at 300 K and 600 MHz $T_{1\rho}$ is independent of the spin-locking field strength set to 0, 0.6, 1.2, 1.8, and 2.8 kHz. This shows that no slow exchange processes with $\tau_{\text{exch}} > 10 \mu\text{s}$ occur.

Decoupling of the ^{19}F spins of the solvent by strong RF

TABLE 1

Experimental ^{13}C Relaxation Data for ^{13}CH Groups in 1,3-Dibromoadamantane Dissolved in PCTFE and Viscosity η of the Solvent PCTFE at the Corresponding Temperatures

$\omega_{\text{H}}/2\pi$ [MHz]	T [K]	η [cP]	T_1 [ms]	T_2 [ms]	NOE
600	274	—	791 ± 16^d	—	1.62
	281	$125,000^a$	771 ± 9^d	32 ± 2^d	1.66
		$50,000^b$			
		$37,000^c$			
	290	$3,928^b$	731 ± 14^e	78 ± 3^e	1.75 ± 0.02^e
300	$1,392^b$	750 ± 3^e	196 ± 1^e	1.82 ± 0.02^e	
400	324	208^b	1058 ± 5^d	784 ± 4^e	2.19
	339	83^b	1515 ± 13^d	1334 ± 8^d	2.43
	300	$1,392^b$	535 ± 3^e	188 ± 2^d	1.91 ± 0.02^e

^a Viscosity measured at a shear rate of 0.01 s^{-1} .

^b Viscosity measured at a shear rate of 1 s^{-1} .

^c Viscosity measured at a shear rate of 10 s^{-1} .

^d Error is the standard deviation obtained from fitting the time course of the peak integrals.

^e Error is the standard deviation obtained by repeating the experiment.

irradiation during the mixing time of NOESY and ^1H T_1 inversion-recovery experiments did not noticeably affect relaxation, verifying that there is no measurable cross relaxation between the ^{19}F spins of PCTFE and the spins of the guest molecules. However, a small contribution of ^{19}F to dipolar T_1 and T_2 relaxation of ^{13}C , not exceeding a few percent, cannot be excluded.

We observed a monoexponential relaxation behavior at all temperatures (even at 281 and 274 K where the solvent is very viscous and opaque). The measured ^{13}C relaxation parameters are listed in Table 1. The errors for T_1 and T_2 vary between 0.5 and 6%, and the standard deviations for the heteronuclear NOEs at 290 and 300 K were found to be 1%.

3. RESULTS AND DISCUSSION

The relaxation of the ^{13}CH carbon spins is governed by the ^{13}C – ^1H dipolar interaction with the following standard relations for T_1 , T_2 , and NOE (I),

$$\frac{1}{T_1} = \frac{1}{20} \left(\frac{\mu_0 \cdot \hbar \gamma_{\text{C}} \gamma_{\text{H}}}{4\pi r_{\text{CH}}^3} \right)^2 \times \{3J(\omega_{\text{C}}) + J(\omega_{\text{H}} - \omega_{\text{C}}) + 6J(\omega_{\text{H}} + \omega_{\text{C}})\}, \quad [4]$$

$$\frac{1}{T_2} = \frac{1}{40} \left(\frac{\mu_0 \cdot \hbar \gamma_{\text{C}} \gamma_{\text{H}}}{4\pi r_{\text{CH}}^3} \right)^2 \times \{4J(0) + 3J(\omega_{\text{C}}) + J(\omega_{\text{H}} - \omega_{\text{C}}) + 6J(\omega_{\text{H}}) + 6J(\omega_{\text{H}} + \omega_{\text{C}})\}, \quad [5]$$

$$\text{NOE} = 1 + \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}} \cdot \frac{\sigma}{T_1^{-1}}, \quad [6]$$

with the cross-relaxation rate constant

$$\sigma = \frac{1}{20} \left(\frac{\mu_0 \cdot \hbar \gamma_{\text{C}} \gamma_{\text{H}}}{4\pi r_{\text{CH}}^3} \right)^2 \times \{6J(\omega_{\text{H}} + \omega_{\text{C}}) - J(\omega_{\text{H}} - \omega_{\text{C}})\}, \quad [7]$$

where γ_{H} and γ_{C} are gyromagnetic ratios, ω_{H} and ω_{C} are Larmor frequencies, and r_{CH} is the internuclear distance. $J(\omega)$ is the power spectral density of the ^{13}C – ^1H dipolar interaction.

For simplicity it is often assumed that the correlation function of the random process causing relaxation is monoexponential with the correlation time τ_{c} (I). This is justified for a rigid molecule tumbling isotropically in a homogeneous medium which leads to the Lorentzian spectral density function

$$J(\omega) = \frac{2\tau_{\text{c}}}{1 + (\omega\tau_{\text{c}})^2}. \quad [8]$$

However, an analysis of the experimental data shows that the three ^{13}C parameters T_1 , T_2 , and NOE contradict each other if a Lorentzian spectral density is assumed. This is illustrated in Fig. 2 for the experimental values at 300 K and 600 MHz. The measured T_1 and T_2 values were corrected by subtracting the $\sim 10\%$ contribution of intramolecular dipolar relaxation induced by remote protons, assuming isotropic tumbling and internuclear distances $r_{\text{CH}} = 1.08 \text{ \AA}$, $r_{\text{CC}} = 1.54 \text{ \AA}$, and tetrahedral bond angles as geometric parameters. The observed T_1 value may be rationalized by one of the two correlation times $\tau_{\text{c}} \approx 60 \text{ ps}$ or $\tau_{\text{c}} \approx 7 \text{ ns}$. Both are in contradiction with the value $\tau_{\text{c}} \approx 400 \text{ ps}$ deduced from the measured T_2 and NOE values.

Fitting of the experimental data by a non-axially symmetric rotational diffusion tensor and by applying the Woessner equations (23) would lead to an anisotropy of rotational tumbling of at least two orders of magnitude. This is however in contrast to the moment of inertia tensor of 1,3-dibromoadamantane whose principal values have a ratio of 1:2.6:3.1, rendering this interpretation unlikely.

Distribution of correlation times. It is attempted to rationalize the experimental data by a distribution of rotational correlation times ($I6, 24$) which may be the result of an exchange between environments with different effective microviscosities or rotational hindering potentials. The strictly exponential time course in the relaxation experiments suggests rapid exchange on time scales much shorter than T_2 . If each environment has a characteristic correlation time τ_{c} and an occupational probability $p(\tau_{\text{c}})$, the mean relaxation rate constants are given by

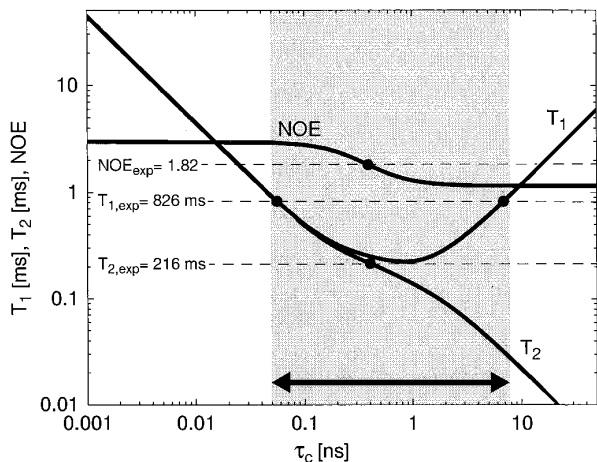


FIG. 2. Illustration of the failure of a single-correlation-time model. The theoretical dependencies of ^{13}C T_1 , T_2 , and NOE on a single correlation time τ_c according to Eqs. [4] to [8] are plotted, assuming $r_{\text{CH}} = 1.08 \text{ \AA}$ and $\omega_{\text{H}}/2\pi = 600 \text{ MHz}$. The experimental values for the data at 300 K, corrected for the dipolar relaxation by remote protons, are given as solid circles. It is not possible to find a single correlation time τ_c for which all three experimental values lie on the corresponding theoretical curves. The τ_c “uncertainty range” is marked in gray.

$$\langle T_x^{-1} \rangle_{\tau_c} = \int_0^{\infty} p(\tau_c) \frac{1}{T_x} d\tau_c, \quad \langle \sigma \rangle_{\tau_c} = \int_0^{\infty} p(\tau_c) \sigma d\tau_c, \quad [9]$$

with $x = 1, 2$, or 1ρ ; and the mean NOE is given by

$$\langle \text{NOE} \rangle_{\tau_c} = 1 + \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}} \cdot \frac{\langle \sigma \rangle_{\tau_c}}{\langle T_1^{-1} \rangle_{\tau_c}}. \quad [10]$$

Because of the linear dependence of the relaxation rate constants on $J(\omega)$, it is possible to express them by a mean spectral density function

$$\langle J(\omega) \rangle_{\tau_c} = \int_0^{\infty} p(\tau_c) \frac{2\tau_c}{1 + (\omega\tau_c)^2} d\tau_c. \quad [11]$$

Based on this equation, the relaxation data of Table 1 measured at 300 K for 400 and 600 MHz proton resonance were fitted by various distribution functions $p(\tau_c)$.

We explore at first models with $n = 2$ or 3 discrete environments (25, 26) with the mean spectral density function

$$\langle J(\omega) \rangle_{\tau_c} = \sum_{k=1}^n p_k \frac{2\tau_{c,k}}{1 + (\omega\tau_{c,k})^2}. \quad [12]$$

At first, we assume $n = 2$. Prior to fitting, the experimental values were corrected as described below Eq. [8]. The

corrected values are given in Table 2. The resulting fit parameters $p_1 = 1 - p_2$, τ_{c1} , and τ_{c2} and the back-calculated relaxation parameters T_1 , T_2 , and NOE are included in Table 2 (row A). As expected, the fit is significantly better than that for a single correlation time. But the differences between the back-calculated values and the corrected experimental values are still significantly larger than the estimated measurement errors. It is remarkable that the two resulting correlation times $\tau_{c1} = 37 \text{ ps}$ and $\tau_{c2} = 3.3 \text{ ns}$ differ by nearly two orders of magnitude and indicate two vastly different environments. Environment 1 with a population of 76% seems to approximate freely moving solute molecules, while environment 2 with a population of 24% suggests strong association with PCTFE molecules or rotational hindrance by the PCTFE molecules. Interestingly, for certain parameters $p_1 = 1 - p_2$, τ_{c1} , and τ_{c2} of the bimodal model the calculated NOE parameters show an anomalous field dependence where, in contrast to the single-correlation-time model, the NOE may increase with increasing magnetic field strength. This contradicts the experimental findings. In a further attempt to improve the fit for all six relaxation parameters, an adjustable r_{CH} bond length was used. Although the error of the fit (not shown) is reduced to $\chi^2 = 53$, this led to a physically unreasonable bond length of $r_{\text{CH}} = 1.28 \text{ \AA}$.

The inclusion of a third environment ($n = 3$ in Eq. [12]) with correlation time τ_{c3} significantly improved the fitting quality. The fit, documented in Table 2 (row B), leads to three correlation times that differ from each other by more than an order of magnitude. Such a fitting procedure should be considered rather as an attempt of mathematically modeling the measured data than to imply a specific physical model. Nevertheless, it shows that the environment experienced by the solute molecules is highly inhomogeneous, requiring more than just two discrete correlation times.

NMR relaxation times in highly viscous liquids have previously been successfully fitted by assuming a Cole–Davidson spectral density function (27, 28),

$$\langle J(\omega) \rangle_{\tau_c} = \frac{2}{\omega} \cdot \left(\frac{\sin(\beta_{\text{CD}} \text{atan}(\omega\tau_{\text{CD}}))}{(1 + (\omega\tau_{\text{CD}})^2)^{\beta_{\text{CD}}/2}} \right), \quad [13]$$

with the distribution parameter β_{CD} , $0 < \beta_{\text{CD}} \leq 1$, and the effective correlation time τ_{CD} . For $\beta_{\text{CD}} = 1$, the spectral density merges into the one for a single correlation time. A simple physical interpretation of this empirical spectral density function is not apparent. Fitting the relaxation data by the Cole–Davidson spectral density function leads to the results in Table 2 (row C). The fitting error lies between the ones for two and three discrete correlation times (Table 2, rows A and B). The very low value $\beta_{\text{CD}} = 0.094$ indicates a significant deviation from a single-environment situation. The fitted Cole–Davidson spectral density function is compared with those of the bimodal and trimodal models in Fig. 3. While the values $\langle J(0) \rangle_{\tau_c}$ are nearly identical for the three

TABLE 2

Model Parameters Obtained by Fitting Various Motional Models to the Experimental Data and Back-Calculated Relaxation Data for 1,3-Dibromoadamantane at 300 K and $\omega_{\text{H}}/2\pi = 400$ and 600 MHz

Motional model	$\omega_{\text{H}}/2\pi$ [MHz]	T [ms]	T_2 [ms]	NOE	Model parameters ^c	χ^{2b}
A Bimodal model	400	560	202	1.81	$p_1 = 0.757 \pm 0.002$ $p_2 = 0.243 \pm 0.002$ $\tau_{c1} = (36.7 \pm 0.5)\text{ps}$ $\tau_{c2} = (3.32 \pm 0.03)\text{ns}$	325
	600	843	217	2.10		
B Trimodal model	400	590	201	1.90	$p_1 = 0.693 \pm 0.012$ $p_2 = 0.181 \pm 0.010$ $p_3 = 0.126 \pm 0.012$ $\tau_{c1} = (16.9 \pm 2.2)\text{ps}$ $\tau_{c2} = (528 \pm 44)\text{ps}$ $\tau_{c3} = (5.75 \pm 0.30)\text{ns}$	8
	600	825	217	1.83		
C Cole–Davidson model	400	560	200	1.72	$\beta_{\text{CD}} = 0.094 \pm 0.001$ $\tau_{\text{CD}} = (8.90 \pm 0.06)\text{ns}$	249
	600	846	218	1.70		
Experimental data at 300 K ^a	400	589 ± 3	207 ± 2	1.91 ± 0.02		
	600	826 ± 3	216 ± 1	1.82 ± 0.02		

^a The values are experimental measurements corrected for dipolar relaxation by remote protons (see text).

^b Fitting error

$$\chi^2 = \frac{(T_{1\text{calc}} - T_{1\text{exp}})^2}{(\Delta T_{1\text{exp}})^2} + \frac{(T_{2\text{calc}} - T_{2\text{exp}})^2}{(\Delta T_{2\text{exp}})^2} + \frac{(\text{NOE}_{\text{calc}} - \text{NOE}_{\text{exp}})^2}{(\Delta \text{NOE}_{\text{exp}})^2}$$

with the standard deviations $\Delta T_{1\text{exp}}$, $\Delta T_{2\text{exp}}$, and $\Delta \text{NOE}_{\text{exp}}$.

^c The error limits of the model parameters are determined by a Monte Carlo procedure consisting of 100 fits with random errors corresponding to the experimental standard deviations added to all relaxation parameters.

spectral density functions, their forms differ at the other relevant frequencies (see Eqs. [4] to [7]), particularly for 300 and 750 MHz.

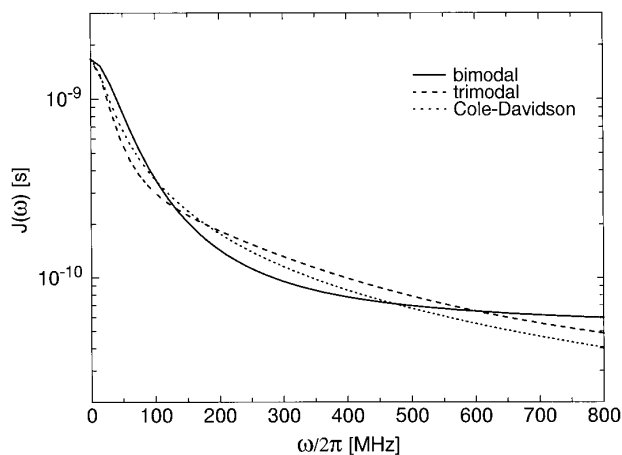


FIG. 3. Comparison of three model spectral density functions fitted to the experimental ^{13}C data T_1 , T_2 , and NOE at 300 K, measured at $\omega_{\text{H}}/2\pi = 400$ and 600 MHz. Solid line, bimodal spectral density function; dashed line, trimodal spectral density function; dotted line, Cole–Davidson spectral density function.

Finally, the temperature-dependent relaxation data of Table 1 were used to study the viscosity dependence of the dynamical behavior of the solute molecules. At 290 K and 600 MHz a T_1 minimum with $T_{1,\text{min}}^{\text{obs}} = 731$ ms is found. A comparison with the theoretical value of $T_{1,\text{min}}^{\text{theor}} = 224$ ms for a single-correlation-time model and $r_{\text{CH}} = 1.08$ Å provides another indication for a multiple-site dynamics of 1,3-dibromoadamantane. Because we are hesitant to relate the deduced correlation times to a specific physical model of the inhomogeneous polymer environment of the solute molecules, we felt it to be sufficient to analyze the data at a single proton-resonance frequency of 600 MHz in terms of the bimodal model. The three model parameters $p_1 = 1 - p_2$, τ_{c1} , and τ_{c2} were deduced from the three measurements T_1 , T_2 , and NOE, again corrected for the dipolar relaxation of remote protons. They are given in Table 3. The slight discrepancy between the values at 300 K in Tables 2 and 3 is caused by the fact that additional 400-MHz measurements are used in the fitting procedure, leading to the values in Table 2. Throughout the viscosity range investigated, two significantly different correlation times result which monotonously increase for increasing viscosity. It is remarkable that at the highest measured viscosity (281 K) the environment with the longer correlation time is populated to 78%, whereas

at the lowest measured viscosity (339 K) the environment with the shorter correlation time dominates with 95% population. It appears that the equilibrium is shifted toward the “free” form of the solute at high temperature.

In Fig. 4, the products $\tau_{c1}T$ and $\tau_{c2}T$ are plotted in a double logarithmic form against the viscosity η . Based on the SED relationship of Eq. [2], a linear dependence with unit slope is expected. For both components the slope is significantly smaller than 1, following a relationship

$$T\tau_{ci} = \text{const} \cdot \eta^{m_i}, \quad i = 1, 2. \quad [14]$$

A least-squares fit leads to the values $m_1 = 0.12$ for the rapidly tumbling population and $m_2 = 0.45$ for the slowly tumbling population. The functional form of Eq. [14] is in agreement with earlier findings for other systems using NMR and dielectric relaxation measurements (29, 30). The violation of the SED relation implies that the motion of the solute molecules is less influenced by the solvent viscosity than expected. This is not unreasonable for the rapidly tumbling population as the small molecules may move with little hindrance in cavities formed by the polymeric solvent. For the derivation of the SED relation, on the other hand, it was assumed that the solute molecules move in a homogeneous environment of very small solvent molecules which can be approximated to be a continuum (31) where obviously the formation of long-lived cavities is unlikely. An Arrhenius-type approximation of the correlation times τ_{c1} and τ_{c2} , $\tau_{c1,2} = k \exp(E_{a1,2}/(RT))$, leads to the activation energies $E_{a1} = 11 \text{ kJ mol}^{-1}$ and $E_{a2} = 33 \text{ kJ mol}^{-1}$.

TABLE 3

Parameters of the Bimodal Model Computed from the Experimental Values of T_1 , T_2 , and NOE (Corrected for Dipolar Relaxation by Remote Protons) at Various Viscosities and $\omega_H/2\pi = 600 \text{ MHz}$

T [K]	η^a [cP]	Populations ^b	Correlation times ^b
281	—	$p_1 = 0.221 \pm 0.023$ $p_2 = 0.779 \pm 0.023$	$\tau_{c1} = (74.2 \pm 10.7)\text{ps}$ $\tau_{c2} = (7.80 \pm 0.30)\text{ns}$
290	3928	$p_1 = 0.505 \pm 0.012$ $p_2 = 0.495 \pm 0.012$	$\tau_{c1} = (35.9 \pm 1.6)\text{ps}$ $\tau_{c2} = (4.79 \pm 0.13)\text{ns}$
300	1392	$p_1 = 0.709 \pm 0.003$ $p_2 = 0.291 \pm 0.003$	$\tau_{c1} = (27.6 \pm 0.8)\text{ps}$ $\tau_{c2} = (2.84 \pm 0.03)\text{ns}$
324	208	$p_1 = 0.909 \pm 0.002$ $p_2 = 0.091 \pm 0.002$	$\tau_{c1} = (22.5 \pm 0.5)\text{ps}$ $\tau_{c2} = (1.11 \pm 0.03)\text{ns}$
339	83	$p_1 = 0.953 \pm 0.003$ $p_2 = 0.047 \pm 0.003$	$\tau_{c1} = (18.2 \pm 0.4)\text{ps}$ $\tau_{c2} = (748 \pm 56)\text{ps}$

^a Viscosity measured at a shear rate of 1 s^{-1} . The viscosity at 281 K depends on the shear rate (see Table 1) and was not used.

^b The error limits of the model parameters are determined by a Monte Carlo procedure consisting of 100 fits with random errors corresponding to the experimental standard deviations added to all relaxation parameters.

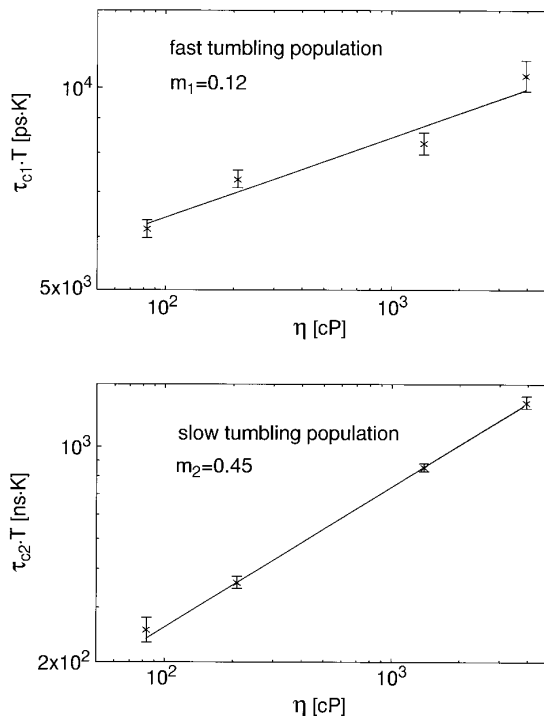


FIG. 4. Viscosity dependence of $\tau_{c1}T$ for the fast and $\tau_{c2}T$ for the slow tumbling population in the bimodal model. Only data points with shear-rate-independent viscosities are included (see Table 3). The linear fits correspond to Eq. [14] with the fitting parameters m_i .

4. CONCLUSION

This study demonstrates that 1,3-dibromoadamantane experiences PCTFE as an inhomogeneous solvent medium. The observations can formally be modeled by a rapid exchange between at least two different environments. Similar situations have been found for solutes in other highly viscous solvents (16, 28, 32). For the bimodal model, the apparent correlation times differ by two orders of magnitude, one environment corresponding to virtually free guest molecules, and the other environment exhibiting a strong solute–solvent interaction. The temperature and viscosity dependence of the tumbling correlation times of the two populations is much weaker than would be expected from the Stokes–Einstein–Debye relationship. The exchange of the guest molecules between the different environments appears to be rapid, but is difficult to quantify based on NMR measurements alone, as no RF field strength dispersion is observed in $T_{1\rho}$ experiments. The results presented in this paper show that the tumbling behavior of small solute molecules in solvents such as PCTFE is not as simple as desired for shifting the rotational correlation time in view of NMR studies of intramolecular motion.

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