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INVESTIGATION OF BROWNIAN ROTATION OF NONSPHERICAL LIQUID MOLECULES BY NUCLEAR PARAMAGNETIC RESONANCE

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The characteristic rotation times of normal paraffin molecules dissolved in the weakly magnetic solvent CCl_4 are measured and computed. The experimental and theoretical results are compared. The comparison reveals that the most accurate of all theories of Brownian rotation of liquid molecules is the hydrodynamic theory in which a microfriction factor is taken into account. Temperature measurements show that the activation energy for reorientation of the investigated molecules is equal to the viscosity barrier of the solvent. The contributions of intermolecular dipole-dipole interactions to the measured spin-relaxation rates are investigated. It is found that such contributions decrease with increase of molecular size.

INTRODUCTION

THE spin-lattice relaxation rate in pure organic liquids is determined by the intermolecular and intramolecular dipole-dipole interactions modulated respectively by translational and rotational motions of the molecules, i.e., $T_1^{-1} = T_{1t}^{-1} + T_{1r}^{-1}$. The corresponding contributions to the total relaxation rate of the i-th nucleus are given by the equations (see [1])

$$(T_{1\,r})_i^{-1} = \hbar^2\gamma_i^2\left[\tfrac{3}{2}\gamma_i^2\sum_j r_{ij}^{-6} + \tfrac{4}{3}\gamma_f^2(I_f+1)\,I_f\sum_f r_{if}^{-6}\right]\tau_r, \quad (1)$$

$$(T_{1t})_i^{-1} = \pi^2\hbar^2\gamma_i^2\eta N_0\,\frac{a}{kT}\left[3\gamma_i^2\sum_j r_{ij}^{-1} + \tfrac{8}{3}\gamma_f^2\,(I_f+1)\,I_f\sum_f r_{if}^{-1}\right], \quad (2)$$

where γ is the gyromagnetic ratio of the nuclei, I their spin, τ_r the characteristic rotation time of the molecules, r_{ij} the internuclear separation, and the indices i and j pertain to nuclei of one kind and f to nuclei of another kind. The summation is carried out within the limits of one molecule in Eq. (1) and over neighboring molecules in Eq. (2); η is the viscosity of the solution, a the radius of the molecule, considered to be approximately spherical, and N_0 the number of molecules per unit volume.

In calculating the relaxation rate caused by intramolecular dipole-dipole interactions, taking the shape of the molecules into account,[2] the quantity $(T_{1r}^{-1})_{ij}$ is defined for each pair of nuclei separately in terms τ_r^{ij}. In this case τ_r^{ij} represents some average over the reciprocal rotation rates D_1, D_2, and D_3. A method for constructing this average was given by Valiev and Zaripov.[2] For molecules containing magnetic nuclei of only one kind with spin $I = 1/2$, we have

$$(T_{1\,r})_{ij}^{-1} = {}^3/_2\hbar^2\gamma^4 r_{ij}^{-6}\sum_{n=-2}^{2}\Omega_n/D_{mn}^{(2)}. \quad (3)$$

Here r_{ij} is the separation between the pairs of nuclei i and j, Ω_n (θ_{ij}, φ_{ij}) are factors that take into account the mutual arrangement of nuclei i and j in a coordinate system having principal axes D_{ij} (the angles θ_{ij} and φ_{ij} fix the orientation of the radius vector $\mathbf{r}_{ij}$ in this system), and $D^{(2)}_{mn}$ are combinations of the principal values of the tensors D_1, D_2, and D_3.

The rate of relaxation of an individual (the i-th) nucleus in the molecule is obtained from Eq. (3) by summing over the neighbors j: $(T_{1r})^{-1}_i = \sum_j (T_{1r})^{-1}_{ij}$.

We assume that the measured relaxation rate T_1^{-1} practically coincides with the arithmetic mean of the rates T_{1i}^{-1} for the different nuclei in the molecule:

$$T_1^{-1} = \frac{1}{N}\sum_i T_{1i}^{-1}, \qquad (4)$$

where N is the number of molecule nuclei in which resonance is observed.

For small concentrations of the investigated substance in a non-magnetic solvent, the measured spin-lattice relaxation rate is determined solely by the intramolecular dipole-dipole interactions, and this allows one to determine experimentally the characteristic time τ_r of Brownian rotation of the molecules.

Up to this time thorough studies had been made on molecules that are closely spherical in shape. We investigated the Brownian rotation of non-spherical molecules. In [3] we studied the Brownian rotation of an aromatic series of molecules dissolved in CCl_4; in the present work we study the rotation of molecules of a series of normal paraffins: hexane, octane, decane, dodecane, tetradecane, hexadecane, and octadecane.

The investigated molecules are strongly elongated ellipsoids whose major semi-axes vary in the series from 4.9 to 12.5 Å while the minor semi-axes are constant. It is known [4] that molecules of normal paraffins do not associate and are in unfolded form, i.e., in the form of linear chains, in the solid state. In the liquid state the molecules have a tendency to turn. Raman spectroscopy has shown [5] that right up to $C_{16}H_{34}$ the molecules in the liquid state exist in the unfolded form, and for hexadecane and octadecane the turnability is still weakly expressed.

Equation (1) is the result of a rather rigorous calculation of the rate of magnetic relaxation brought about only by intramolecular dipole-dipole interactions. Evidently, the discrepancy between experimental and theoretical results is associated with inaccuracy in calculating τ_r. Hence the goal of our investigations is the comparison of the rates of Brownian molecular rotation determined from experiment with those calculated on the basis of the various existing theories about the mechanism of molecular rotation in liquids. The principal ones are the hydrodynamical models of the rotating sphere [6] and ellipsoid, [2] and models that take into account "microfriction" [7] and "mutual viscosity." [8]

The hydrodynamical models consider the rotation of the molecules as a rotation of macroscopic solid bodies in a continuous viscous medium; they give the result

$$\tau_r = \frac{4\pi\eta a^3}{3kT} = \frac{1}{6D_{rot}}. \qquad (5)$$

Gierer and Wirtz [7] attempted to improve the equations for the characteristic time τ_r, by taking into account the discrete (molecular) character of the surroundings of the molecule under investigation. It can be assumed that discrepancies between the experimentally determined values of τ_r and those computed from the hydrodynamical formulas are due to just this assumption about the continuity of the medium surrounding the rotating molecule. Allowance for the discrete medium changes the Stokes formula (5) (for a sphere) to

$$\tau_r = \frac{4\pi\eta a^3}{3kT} f \qquad (5a)$$

where f is a microfriction correction factor:

$$f = \left[6\frac{a_s}{a} + \left(1 + \frac{a_s}{a}\right)^{-3}\right]^{-1}. \qquad (5b)$$

In Eq. (5b), a is the radius of the investigated molecule, and a_s is the radius of a solvent molecule.

Since the molecules we investigated have (approximately) ellipsoidal shapes, we introduced different microfriction factors for the rotation rates D_1, D_2, and D_3 ($6D_s = 1/\tau_r^{(s)}$) of the molecule about the principal axes ξ, η, and ζ of the tensor D_{ij}:

$$D_1 = kT\,(\beta_{\xi\xi} f_{\xi\xi})^{-1},$$
$$D_2 = kT\,(\beta_{\eta\eta} f_{\eta\eta})^{-1}, \quad D_3 = kT\,(\beta_{\zeta\zeta} f_{\zeta\zeta})^{-1}, \qquad (6)$$

where $\beta_{\xi\xi}$, $\beta_{\eta\eta}$, and $\beta_{\zeta\zeta}$ are the principal values of the viscous friction tensor for the rotation of an ellipsoid in a liquid, [9] while $f_{\xi\xi}$, $f_{\eta\eta}$, and $f_{\zeta\zeta}$ are the microfriction factors. In analogy to Eq. (5b), for $a > b \approx c$, we take for the microfriction coefficients

$$f_{\xi\xi} = \left[6\frac{a_s}{d} + \left(1 + \frac{a_s}{d}\right)^{-3}\right]^{-1},$$
$$f_{\eta\eta} = f_{\zeta\zeta} = \left[6\frac{a_s}{a} + \left(1 + \frac{a_s}{a}\right)^{-3}\right]^{-1}, \qquad (7)$$

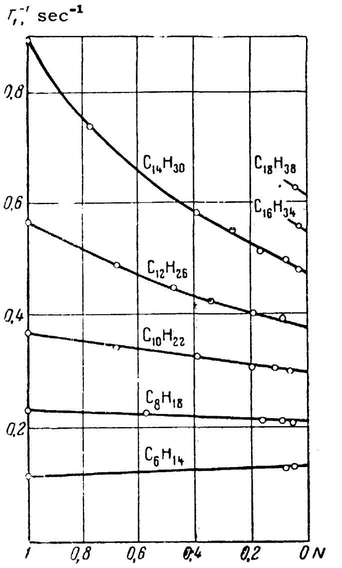

FIG. 1. Dependence of the relaxation rate on the relative concentration of the investigated molecules in CCl_4.

where d = ½(b + c), and a, b, c are the semiaxes of the molecule.

It should be emphasized that Eqs. (7) are in fact the result of an "extrapolation" of Eq. (5b) to the ellipsoidal case. A more systematic calculation is required for the exact coefficients f_{ii}.

We also determined the activation energy for the reorientation of our molecules and investigated the contributions of intermolecular dipole-dipole interactions to the measured relaxation rates.

EXPERIMENTAL RESULTS AND DISCUSSION

The intermolecular magnetic interactions between the investigated molecules will equal zero when their concentration in a nonmagnetic solvent is infinitely small, i.e., when N = 0. Therefore we carried out measurements of the spin-lattice relaxation rate T_1^{-1} as a function of the concentration of the investigated molecules in the weakly magnetic solvent CCl_4. By extrapolating the dependence of T_1^{-1} on N to N = 0 (Fig. 1), we obtained the value of the magnetic relaxation rate T_{1r}^{-1} due only to the intramolecular dipole-dipole interactions modulated by the Brownian rotational motion of the molecules.

In using the weakly magnetic solvent CCl_4 it is necessary to consider the intermolecular magnetic interactions between the molecules of the solvent and the investigated substance. An estimate of this contribution according to Eq. (2) shows that it can be neglected within the limits of accuracy of the experiment.

The measurements of T_1 were carried out in a "spin-echo" spectrometer[10] using a pulse sequence 90—90—180°. The samples were prepared for the measurements in the manner described earlier.[3] The samples were pumped to a pressure of 2×10^{-5} Torr to remove oxygen. The temperature measurements of T_1 were carried out by blowing a copious stream of air of suitable temperature on the sample. The temperature was regulated to ± 1°C.

For the molecules we investigated, which contain magnetic nuclei of only one kind (protons) with spin I = ½ and consist of repeating segments, the majority of the nuclei are equivalent in the sense of having the same relaxation rates; from Eqs. (1) and (4) we have:

$$T^{-1}_{1r} \approx (T_{1r})^{-1}_i = {}^3/_2\hbar^2\gamma^4 \sum_i r_{ij}^{-6}\tau_r\,. \qquad (8)$$

From the values of T_{1r}^{-1} found from Fig. 1, using Eq. (8), we computed the characteristic times of rotation of the molecules of hexane, octane, decane, dodecane, tetradecane, hexadecane, and octadecane. The values of τ_r determined from the data for T_{1r}^{-1} are presented in Table I. In this table there are also given the values of τ_r calculated on the basis of various theories of molecular rotation in a viscous medium. From the theory of magnetic relaxation [2] with account taken of the shape of the molecules it is possible

Table I

	$\tau_r \times 10^{12}$, sec					
	Experi-ment	Sphere	Ellipsoid	Mutual viscosity	Sphere*	Ellipsoid*
C_6H_{14}	3,0	17,2	24,3	6,7	2,2	3,8
C_8H_{18}	4,7	21,7	33,0	14,0	3,0	5,9
$C_{10}H_{22}$	6,9	26,0	46,5	29,4	3,8	11,2
$C_{12}H_{26}$	8,5	30,5	65,0	41,5	4,7	17,5
$C_{14}H_{30}$	10,8	35,0	77,6	63,7	5,7	26,2
$C_{16}H_{34}$	12,4	39,3	101,0	92,6	6,6	40,0
$C_{18}H_{38}$	13,9	43,7	122,0	130,2	7,6	47,0

*Calculated taking the microfriction factor into account.

to calculate only T_{1r}. In this case τ_r was determined by substitution of the calculated values of T_{1r} into Eq. (8).

In calculating τ_r according to the various theories, we kept the volume constant in each model, i.e., when approximating the molecule as a sphere, we took its radius as $(abc)^{1/3}$. The semi-axes a, b, and c of the molecule were determined from the Van der Waals radii for the protons; the distances between the nuclei and the angles θ_{ij} and φ_{ij} were determined graphically from the data of Volkenshteĭn.[11]

From the comparison of the experimental data and the values of τ_r calculated according to the different formulas it can be seen (see Table I) that the hydrodynamical theory for rotation of both spheres and ellipsoids, as well as the theory with "mutual viscosity," describes the Brownian rotation of molecules only approximately. Note that in the hydrodynamical theory (with the molecules represented as spheres) the discrepancy between theory and experiment gradually decreases (by a factor from 5.7 to 3) as the dimensions of the molecules increase, whereas for the "mutual viscosity" theory the discrepancy increases from 2.2 to 9.3 times. For the accurate hydrodynamical model (with the shape taken into account) the discrepancy remains almost constant (by a factor 7.8 on the average). This is evidence that the hydrodynamical theory of molecular rotation describes the real situation in a qualitatively better way. And if the microfriction factors f are introduced, it is possible to achieve a completely satisfactory agreement between the calculated and experimental values.

To determine the activation energy for reorientation of the molecules, we carried out temperature measurements of the quantity T_{1r} for octadecane, dodecane, and hexane (for the largest, average and smallest molecules of the series). The measurements were carried out in the temperature interval 273—343°K (the boiling point of CCl_4 is 349°K).

Figure 2 shows the experimentally obtained temperature dependence of the characteristic time τ_r for the molecules of hexane, dodecane, and octadecane. As can be seen from the figure, we obtained a linear plot of $\ln \tau_r$ vs. $1/T$, within the limits of experimental error. This means a constant activation energy over the temperature interval and an exponential temperature dependence of τ_r: $\tau_r = \tau_0 \exp(U_r/kT)$.

Figure 2 also shows the temperature dependence of the viscosity of the solvent, constructed from the data of [12]. Comparisons of the dependences $\ln \tau_r$ and $\ln \eta$ on $1/T$ show that the activation energies for reorientation for the molecules of hexane, dodecane, and octadecane in the solvent CCl_4 are determined by the viscosity barrier of the latter. Calculations showed that $U_{vis} = U_r = 2.88$ kcal/mole. It should be noted that for hexane at temperatures above 315°K two relaxation rates are observed; one of these belongs to the protons on the methyl groups, and the other to the protons on the CH_2 group. At 341°K, for a sample with relative concentration of hexane in CCl_4 equal to 0.052, the relaxation rates were equal to 0.5 and 0.08 sec^{-1} respectively for CH_3 and CH_2.

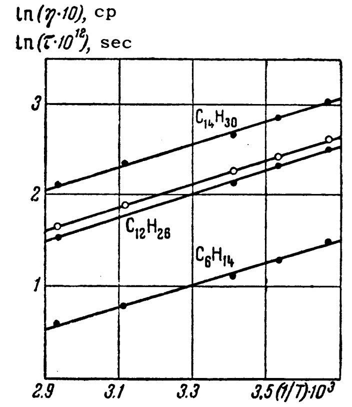

FIG. 2. Dependence of the time τ_r (solid circles) and the viscosity of the CCl_4 solvent (open circles) on temperature.

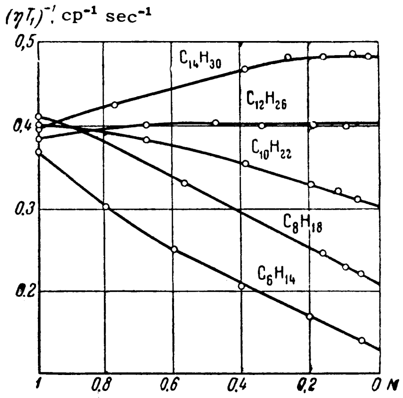

FIG. 3. Dependence of the quantity $(\eta T_1)^{-1}$ on the relative concentration of the investigated molecules in CCl_4.

No difference in relaxation rates was observed at room temperature. It is possible that at this temperature the additional rotation of the methyl group of the molecule is completely stopped or the existing rotation gives a difference in relaxation time by a factor less than 3. The latter circumstance is occasioned by the difficulty in distinguishing clearly by the spin echo method two relaxation times that differ by a factor of less than 3. In those cases when the relaxation rates were different, we used only the relaxation of the CH_2 group as the starting point in the calculation of τ_r, since this group constitutes the "skeleton" of the molecule.

We now discuss the concentration dependence of T_1. The quantity T_1^{-1} is proportional to the viscosity of the solution η and depends on the concentration of the investigated molecules in the solvent. Obviously, the product $(\eta T_1)^{-1}$ will more directly characterize the contribution of the intermolecular dipole-dipole interactions to the total rate of magnetic relaxation.

From (2) and (8) it is easy to obtain the equation

$$(\eta T_1)^{-1} = A + BN_0, \tag{9}$$

where A and B are constants for each considered liquid:

$$A = (\eta T_{1r})^{-1}, \qquad B = 3\pi^2\hbar^2\gamma^4 a/kT \sum_j r_{ij}^{-1}. \tag{10}$$

For rough estimates of B we take r_{ij}^{-1} equal to $(2a)^{-1}$, where a is the radius of the sphere equivalent to the molecule.

At first sight it would seem to follow from Eq. (9) that the contribution of the intermolecular dipole-dipole forces to the measured relaxation rate should increase with an increase in the number of magnetic nuclei in the molecule (i.e., with an increase in the size of the investigated molecules). However, the dependence of $(\eta T_1)^{-1}$ on the relative concentration of the investigated molecules N in CCl_4 (see Fig. 3), constructed from the data of Table II and Fig. 1, shows that as the dimensions of the molecules increase, the effect of the term BN_0 in Eq. (9) is diminished. This means that the intermolecular contributions to the total relaxation rate decrease with increasing molecular size.

Evidently, the observed discrepancy between the values of B measured experimentally and calculated from Eq. (10) means that Eq. (10) is inaccurate for calculating the contributions of intermolecular dipole interactions to the relaxation rate, particularly when the molecules are nonspherical. In our opinion, B should decrease for nonspherical molecules, since the major part of collisions of nonspherical molecules occur in such a way that the sum $\Sigma_j r_{ij}^{-1}$ is small, for example, in those cases when the major axes of the colliding molecules are parallel or perpendicular to each other. Thus, the more the molecule differs from a sphere, the less will be the value of B. This is indeed manifest in our experiments.

From the experimental dependence of $(\eta T_1)^{-1}$ on N for the molecules dodecane and tetradecane it is seen that Eq. (9) will qualitatively correctly describe these dependences only for negative values of B, which in our case has no physical meaning. This can be reconciled if we introduce the microfriction factors f from Eq. (5b) into the term A. On the basis of Eq. (5b) it is easy to show that if the molecules of the investigated substance and the solvent are not the same size, then the microfriction factor will vary with the concentration of the investigated molecules in the solvent. For pure liquid f = 0.147 and, depending on the ratio a_s/a, f will increase or decrease as the sample is diluted with nonmagnetic solvent. Note that in calculating f from Eq. (5b) it is necessary to define a as $(a + b + c)/3$, since this determines the moment of the forces of microfriction more accurately than in the calculation starting from the volume of the ellipsoid. The factor f attains values corresponding to the case in which the investigated molecules are completely surrounded by solvent molecules at finite concentrations. If from the experimental data for tetradecane and dodecane we take B = 0, then the increase in $(\eta T_1)^{-1}$ with decreasing N (Fig. 3) finds a natural explanation in the growth of the microfriction factor by 1.35 and 1.23 times respectively.

For the remaining liquids (decane, octane, hexane), the microfriction factor does not change significantly (from 1.1 to 0.85 times) as the solution is diluted, and the behavior of $(\eta T_1)^{-1}$ is explained mainly on the basis of the change in intermolecular magnetic dipole-dipole interactions.

Table II. Dependence of the viscosity of solutions of normal paraffins in CCl_4 on the relative concentration N at 20°C

Substance	*N*					
	1	0,8	0,6	0,4	0,2	0
C_6H_{14}	0.32	0.39	0.48	0.59	0.75	0.97
C_8H_{18}	0.54	0.59	0.66	0.74	0.84	0.97
$C_{10}H_{22}$	0.9	0.89	0.89	0.91	0.93	0.97
$C_{12}H_{26}$	1.49	1.28	1.16	1.08	1.00	0.97
$C_{14}H_{30}$	2.26	1.76	1.48	1.25	1.09	0.97

Thus, a comparison of the experimental and theoretical dependences of $(\eta T_1)^{-1}$ on N for the investigated liquids shows that the effect of the B term in Eq. (9) diminishes with increasing molecular size. This points to a decrease in the contribution of the intermolecular magnetic dipole-dipole interactions to the total relaxation rate as the dimensions of these molecules increase.

In conclusion, the author takes this opportunity to express his thanks to K. A. Valiev for his leadership and constant interest in the work.

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