INVESTIGATION OF THE ROTATIONAL MOTION OF MOLECULES OF A LIQUID BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

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Measurements and calculations have been made of the characteristic times of rotation of molecules of benzene, naphthalene and anthracene dissolved in CCl_4. The results of the calculations are compared with experiment. It is found that if the shape of the molecule is taken into account some improvement is obtained in the agreement between theory and experiment.

1. INTRODUCTION

THE magnetic relaxation time T_1 for protons in pure organic liquids is determined by intramolecular and intermolecular dipole-dipole interactions $T_1^{-1} = T_{1\,tr}^{-1} + T_{1\,rot}^{-1}$ perturbed respectively by the rotational (characteristic time $T_{1\,rot}$) and the translational (characteristic time $T_{1\,tr}$) Brownian motion of the molecules. If the molecules under investigation are dissolved in a nonmagnetic (CS_2) or in a weakly magnetic (CCl_4) liquid, and if the concentration of the solution is not very great, then we can neglect the contribution to the relaxation made by the time $T_{1\,tr}$ due to intermolecular interactions. This makes it possible to calculate with the aid of the measured values of T_1, and consequently of $T_{1\,rot}$, the frequencies of the Brownian rotation of the molecules and to compare them with those calculated on the basis of some definite assumptions about the process of rotation of molecules.

The formula most widely used for the calculation of the characteristic time of rotation of molecules τ is Stokes' formula (2) (cf. below) obtained on the basis of a hydrodynamic model. Considerable disagreement is found in comparing the calculated values of τ with those obtained experimentally. This shows that the concept of the rotation of molecules in a liquid being similar to a rotation of a macroscopic solid body in a continuous viscous medium describes the actual situation only approximately.

Often experiments are carried out using molecules whose shape is far from spherical, while in calculations based on Stokes' formula the molecule is assumed to be spherical. Therefore, there remains the possibility of ascribing the observed discrepancy between theory and experiment to the approximation made in treating a nonspherical molecule as a spherical one.

A theory which enables one to take into account the effect of the shape of the molecule on the magnetic relaxation time has been developed by Valiev and Zaripov. [1] In this paper the rotational diffusion tensor with principal values D_1, D_2, D_3 is introduced for the description of Brownian molecular rotation; these principal values can be calculated using different assumptions about the mechanism of the interaction of the rotating molecule with its surroundings.

In order to check the hydrodynamic model we have calculated the values of D_1, D_2, D_3 with the aid of hydrodynamic formulas by approximating the shape of the molecules which we have investigated (benzene, naphthalene, anthracene) by ellipsoids, and we have compared the values of the characteristic rotation times of the molecules found experimentally with the theoretical values obtained utilizing models based on a sphere and an ellipsoid rotating in a viscous medium, and also the model in which the concept is introduced of the mutual viscosity of the solvent-solute system. [2]

2. EXPERIMENTAL ARRANGEMENT AND RESULTS OF MEASUREMENTS

Measurements of the relaxation times T_1 were carried out at a temperature of 24°C by the spin echo method at a frequency of 16.365 MHz by using a 90-90-180° sequence of pulses. The last pulse was the sampling one, i.e., the magnitude of the restored magnetization was measured by means of the amplitude of the echo. Such a method

enables one to obtain a better signal-to-noise ratio by narrowing the acceptance band of the receiver, and to increase the accuracy of measurement in the case of a low concentration of protons in the solvent. The time interval between the first 90° pulse and the following pair of pulses was measured with an accuracy of 0.02 sec. The time interval between the 90° and the 180° pulses was fixed and was equal to 2×10^{-4} sec.

The relaxation time $T_{1\,rot}$ was determined by measuring the relaxation times T_1 for different concentrations of the substance in the weakly magnetic solvent CCl_4 and by extrapolating to zero concentration[2]. Owing to the poor solubility of anthracene in CCl_4 the measurements were carried out at a concentration of 0.015—0.02 mole/liter. The viscosity of the solvent was measured by an Ostwald viscosimeter in a thermostatically controlled bath and was equal to 0.904 cP. The samples were prepared from materials of chemical and analytic purity. After deoxidation they were sealed into ampoules of 13 mm diameter. Deoxidation was carried out by means of several cycles of repeated freezing, pumping out and melting. The pumping out was carried out down to a pressure of 6×10^{-3} mm Hg. The working volume of the sample was equal to 2 cm³. During measurements the temperature of the samples was kept constant to ±1°C.

As a result of the reduction of the measured values of T_1 the following values of $T_{1\,rot}$ were obtained: benzene—54.0 sec, naphthalene—24.8 sec, anthracene—12.5 sec.

3. CALCULATION OF THE CHARACTERISTIC ROTATION TIMES OF THE MOLECULES

According to [1-3] in the case of molecules containing nuclei of one kind of spin I = ½ the magnetic relaxation time for the i-th nucleus can be calculated[1] by means of the formula

$$(T_{1rot})_i^{-1} = 1.5\, \hbar^2 \gamma^4 \sum_j r_{ij}^{-6} \tau. \qquad (1)$$

The formulas for the calculation of τ differ depending on the model adopted for the rotation of molecules. We introduce the notation τ_s, τ_e and τ_m for the characteristic times of rotation of molecules respectively for the models of the rotating sphere and ellipsoid[1,4], and for the model involving mutual viscosity[2]. Then we have

$$\tau_s = 4\pi\eta a^3/3kT, \qquad (2)$$

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1)Under the condition $\omega\tau_s \ll 1$, $\omega\tau_m \ll 1$ and $\omega \ll D_{mn}^{(2)}$, where ω is the angular frequency for the transition.

$$\tau_m = 2J\eta a/\mu kT, \qquad (3)$$

$$\tau_e = \sum_{n=2}^{-2} \Omega_n/D_{mn}^{(2)}, \qquad (4)$$

where η is the viscosity of the solvent, a is the average radius of the molecule, J is the average value of the moment of inertia of the molecule, μ is the reduced mass of the molecules of the solvent and of the solute, Ω_n are factors taking into account the relative position of the nuclei with respect to the principal axes of the diffusion tensor, $D_{mn}^{(2)}$ are combinations of the principal values D_1, D_2, D_3 of the rotational diffusion tensor determined in accordance with [5] in terms of the principal values of the viscous friction tensor[6]:

$$D_1 = kT\beta_{\xi\xi}^{-1}, \qquad D_2 = kT\beta_{\eta\eta}^{-1}, \qquad D_3 = kT\beta_{\zeta\zeta}^{-1};$$

$$\beta_{\xi\xi} = 16\pi\eta\,(b^2 + c^2)/3\,(b^2 B + c^2 C),$$

$$\beta_{\eta\eta} = 16\pi\eta\,(a^2 + c^2)/3\,(a^2 A + c^2 C),$$

$$\beta_{\zeta\zeta} = 16\pi\eta\,(a^2 + b^2)/3\,(a^2 A + b^2 B), \qquad (5)$$

where a, b and c are the semi-major axes; A, B, and C are coefficients which we have expressed in terms of elliptic integrals (cf. tabulated values in [7]). For a > b > c

$$A = 2\,[F\,(\alpha, \varphi) - E\,(\alpha, \varphi)]\,[(a^2 - b^2)\,(a^2 - c^2)^{1/2}]^{-1},$$

$$B = 2\,(a^2 - c^2)^{1/2} E\,(\alpha, \varphi)\,[(a^2 - b^2)\,(b^2 - c^2)]^{-1}$$

$$- 2F\,(\alpha, \varphi)\,[(a^2 - b^2)\,(a^2 - c^2)^{1/2}]^{-1} - 2c\,[ab\,(b^2 - c^2)]^{-1},$$

$$C = 2b\,[ac\,(b^2 - c^2)]^{-1} - 2E\,(\alpha, \varphi)\,[(b^2 - c^2)\,(a^2 - c^2)^{1/2}]^{-1};$$

$$F\,(\alpha, \varphi) = \int_0^\varphi \frac{dx}{\sqrt{1 - \alpha^2 \sin^2 x}}, \qquad E\,(\alpha, \varphi) = \int_0^\varphi \sqrt{1 - \alpha^2\sin^2 x}\; dx;$$

$$\alpha = \arcsin\left(\frac{a^2 - b^2}{a^2 - c^2}\right)^{1/2}, \qquad \varphi = \arcsin\frac{(a^2 - c^2)^{1/2}}{a}. \qquad (6)$$

In the case of an ellipsoid of revolution with a = b > c

$$A = B = (a^2 - c^2)^{-3/2}\left[\frac{\pi}{2} - \operatorname{arc\,tg}\sqrt{\frac{c^2}{a^2 - c^2}}\right] - \frac{c}{a^2\,(a^2 - c^2)},$$

$$C = \frac{2}{c\,(a^2 - c^2)} - (a^2 - c^2)^{-3/2}\left[\frac{\pi}{2} - \operatorname{arc\,tg}\sqrt{\frac{c^2}{a^2 - c^2}}\right];$$

and for a > b = c

$$A = -\frac{2}{a\,(a^2 - c^2)} + (a^2 - c^2)^{-3/2}\ln\frac{a + \sqrt{a^2 - c^2}}{a - \sqrt{a^2 - c^2}},$$

$$B = C = \frac{a}{c^2\,(a^2 - c^2)} - \frac{1}{2}\,(a^2 - c^2)^{-3/2}\ln\frac{a + \sqrt{a^2 - c^2}}{a - \sqrt{a^2 - c^2}}.$$

$$(7)*$$

With the aid of formulas (2)—(7), and of formulas from the paper of Valiev and Zaripov[1], we have calculated the characteristic rotation times τ for the molecules of benzene, naphthalene, and anthra-

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*arc tg = $\tan^{-1}$.

cene. The dimensions of the molecules, the internuclear distances and the angles θ_{ij} and φ_{ij}, which determine the values of Ω_n, were obtained graphically from the data of Vol'kenshteĭn[8]. The experimental values for the characteristic rotation times of the molecules were calculated with the aid of (1) by substituting the measured values of $T_{1\,rot}$. The results both of the calculations and of the measurements are summarized in the table where in brackets we have shown the values of τ calculated taking into account the van der Waals radii of the hydrogen atoms.

Molecule	$\tau \times 10^{12}$, sec			
	τ_s	τ_e	τ_m	τ_{exp}
C_6H_6	9(18.5)	6.7(17)	2.2(2.7)	2.45
$C_{10}H_8$	16(25)	15.5(26)	5.9(7.1)	5.26
$C_{14}H_{10}$	24(36.4)	27.7(41)	13.6(15.8)	10.43

4. DISCUSSION OF RESULTS

From the comparison of the experimental values for the characteristic rotation times of the molecules with those calculated on the basis of the different models it is seen that a much better agreement between theory and experiment is obtained in the case when the dimensions of the molecules are determined without taking into account the van der Waals radii of the hydrogen atoms. Apparently, it is more correct to determine the dimensions of the molecules which we have investigated using the outermost protons in the molecule, since the electron shell of a hydrogen atom forming a covalent chemical bond has small external dimensions.

If the hydrodynamic model is used for a discussion of molecular rotation and account is taken at the same time of the deviation of molecular shape from spherical, the agreement between theory and experiment is somewhat improved. Nevertheless, the remaining discrepancy (by a factor of 2.6—2.9) is still great. Evidently this indicates that hydrodynamic formulas are not sufficiently accurate for the description of Brownian rotation of the small molecules investigated by us. Reasonably good agreement between measured and calculated values of the characteristic rotation times of molecules is obtained if we make our calculations on the basis of a model in which the concept of mutual viscosity of the solvent-solute system[2] is introduced. By comparing formulas (2) and (3) it can be easily established that the effective size of a molecule in the mutual viscosity model has been decreased almost down to the dimensions defined by the distances between the heavy atoms in the molecule (for the molecules investigated here— the distances between carbon atoms). These conclusions are a consequence of taking into account the moment of inertia of the molecule in formula (3). Calculations show that the contribution made by the protons to the total moment of inertia for the molecules investigated amounts to only 20%.

Rakov[9] has calculated the effective dimensions of the molecules using characteristic rotation times of the molecules determined by the methods of Raman scattering and infrared absorption; for benzene he obtained an effective radius of 1.4×10^{-8} cm, i.e., the radius of the benzene ring measured in terms of the carbon nuclei, while the radius of the ring measured in terms of the hydrogen nuclei amounts to 2.47×10^{-8} cm.

Thus, hydrodynamic models for the rotation of molecules in a liquid lead to low effective dimensions of the molecules. Physically this means that the actual angular velocities of rotation of the molecules are greater than predicted by the hydrodynamics of a viscous fluid. One may expect that in the case of molecules of larger size (of the order of several tens of Å) the hydrodynamic model will give a more satisfactory description of the rotational motion.

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