INTRAMOLECULAR AND INTERMOLECULAR CONTRIBUTIONS TO THE SPIN-LATTICE RELAXATION OF PROTONS IN BENZENE AND CYCLOHEXANE

N. K. Gaisin

UDC 539.1.01

Temperature dependences are found for the intramolecular and intermolecular contributions to the spin-lattice relaxation of protons in benzene and cyclohexane by dilution in deuterated analogs. The intermolecular contribution in benzene is discussed on the basis of the model for the molecular distribution found from x-ray diffraction studies. The Hubbard correction to the intermolecular contribution is calculated on the basis of the experimental parameters corresponding to rotation and translation. The results imply discontinuous translational motion of molecules in both liquids.

1. It is important to distinguish between the intramolecular and intermolecular contributions, T_{1i}^{-1} and T_{1e}^{-1} respectively, to spin-lattice relaxation, because these contributions can reveal characteristic features of and can be used to determine the parameters of rotational and translational motion of the molecules.

We report here a study of these types of motion in liquid benzene and cyclohexane. The contributions were separated through a progressive dilution of these compounds in their deuterated analogs.

Benzene has been studied on several occasions by the NMR method. In [1-4] the contributions to the relaxation were distinguished by dissolution of benzene in deuterobenzene. We carried out another study of the spin-lattice relaxation of protons in this substance in an attempt to make a more accurate check of the equations decribing the intermolecular contribution.

Fewer NMR studies have been made of cyclohexane; the intramolecular and intermolecular contributions to the relaxation were distinguished in [3, 5], but these results refer only to room temperature.

2. The samples consisted of C_6H_6 in C_6D_6 (molar fractions of 1.0, 0.75, 0.5, 0.17, 0.1) and of C_6H_{12} in C_6D_{12} (1.0, 0.83, 0.75, 0.5, 0.375, 0.23, 0.1). The samples were degassed at a pressure on the order of 10^{-5} torr by repeated freezing-evacuation and thawing cycles. The spin-lattice relaxation time T_1 was measured on a spin-echo spectrometer [6] having a working frequency of 16.365 MHz with a sequence of 90 – 90 – 180° pulses. The T_1 values were measured for benzene from the melting point to +115°C, and they were measured for cyclohexane from room temperature to +130-140°C. The temperature regulation and measurement were described in [7]. The average error in the T_1 measurements was about 3% for the samples having high proton concentrations and about 8% for samples having low proton concentrations. The same apparatus was used to measure the self-diffusion coefficients of the molecules of these substances; the error in these measurements was about 5%.

The deuterated substances were furnished by the Leningrad Office of the Isotop enterprise. The degree of deuteration for C_6D_6 was 96.6%, and that for C_6D_{12} was 98.4%. The "cp" C_6H_6 and C_6H_{12} were subjected to additional drying under metallic sodium and a double dissolution.

The intermolecular and intramolecular contributions were resolved in the concentration dependence of the T_1^{-1} values for the protons by the method of least squares. In the calculations we took into account the intermolecular contribution due to the interaction of protons with deuterons of surrounding molecules and with those protons remaining among the solid molecules because of the incomplete deuteration.

Kazan' State Pedagogical Institute. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii Fizika, No. 3, pp. 116-121, March, 1971. Original article submitted January 19, 1970.

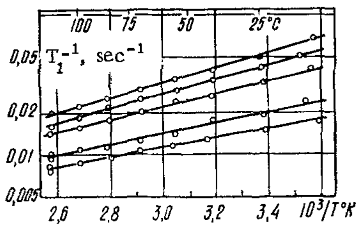

Fig.1

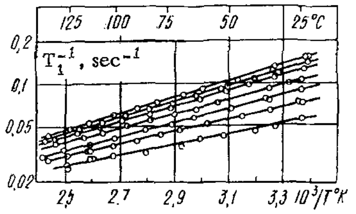

Fig.2

Fig. 1. Temperature dependence of the spin-lattice relaxation rate in $C_6H_6-C_6D_6$ mixtures. The curves corresponds to different concentrations, as explained in the text.

Fig. 2. Temperature dependence of the spin-lattice relaxation rate in $C_6H_{12}-C_6D_{12}$ mixtures.

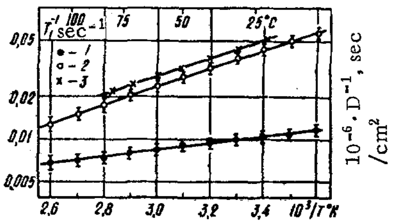

Fig.3

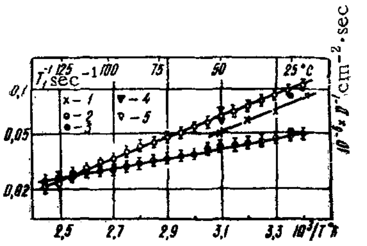

Fig.4

Fig. 3. Temperature dependence of the intramolecular (1) and intermolecular (2) contributions to the rate of spin-lattice relaxation in benzene; value of D^{-1} (3).

Fig. 4. Temperature dependence of the intramolecular (○) and intermolecular (●) contributions to the rate of spin-lattice relaxation in cyclohexane. 1) D^{-1}; 2, 3) T_{1i}^{-1} and T_{1e}^{-1}, respectively [3]; 4, 5) T_{1i}^{-1} and T_{1e}^{-1}, respectively [5].

3. Figures 1 and 2 show the temperature dependences for $C_6H_6-C_6D_6$ and $C_6H_{12}-C_6D_{12}$ mixtures. Figures 3 and 4 show the temperature dependences of the intramolecular and intermolecular contributions.

Our values of T_{1i} and T_{1e} for benzene agree better with the results of Powles and Figgins [4] than with those of Bonera and Rigamonti [2]; at 25°C, e.g., our values and T_{1i} = 99.5 sec and T_{1e} = 25 sec, those of [4] are T_{1i} = 26 sec, and those of [2] (at 22°C) are T_{1i} = 60 sec and T_{1e} = 25 sec. The apparent activation energies for the temperature dependences of T_{1i}^{-1} and T_{1e}^{-1}, 1.2 ± 0.2 and 2.9 ± 0.2 kcal/mole, are also approximately equal to the values reported in [4]. The contributions of intermolecular dipole–dipole and spin-rotational interactions were distinguished in [4] for benzene. Since our measurements were carried out over a narrow temperature range, we cannot make this distinction. We will not discuss the intramolecular contribution in benzene here.

The ln $(T_{1i}^{-1}) = f(10^3/T\,°K)$ dependence for cyclohexane is linear; it follows that spin-rotational interactions does not make an appreciable contribution to the relaxation of cyclohexane protons in the temperature range studied.

We also note that in cyclohexane there may be an important contribution to the proton relaxation due to the conversion of one chair-shaped configuration into another [8, 9] without any change in the position of the molecular center of gravity. These conversions involve a change in both the orientation and the length of the radius vector connecting the protons. For example, a change in the orientation of the vector between the axial and equatorial protons of some vertex with respect to the plane passing through the center of the C–C bond is 54°45', and the change in the length of the vector between the protons is the orthopositions 0.56 Å. It would be plausible to assume that the correlation time τ_c found from the expression

$$T_{1i}^{-1} = 3/2\hbar^2\gamma^4 n^{-1}\sum_{i}^{n}\sum_{j}^{n} r_{ij}^{-6}\tau_c \qquad (1)$$

TABLE 1. Effective Correlation Times τ_c for Certain Temperatures for Protons in Cyclohexane

t°C	20	40	60	80	100	120
$\tau_c \cdot 10^{12}$ sec	1,16–0,12	0,97–0,1	0,83–0,08	0,72–0,08	0,64–0,07	0,57–0,07

TABLE 2*

Substance	t°C	A	$F_3(A)\cdot 10^3$	$F_4(2A)\cdot 10^3$	$F_4(3A)\cdot 10^3$	f
Benzene	25	22,85	4,68	1,67	1,25	1,08
Cyclohexane	20	63,25	2,20	0,78	0,55	1,03
	30	53,80	2,50	0,89	0,63	1,03
	40	51,40	2,59	0,92	0,66	1,03
	50	44,05	2,92	1,04	0,75	1,04

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*For benzene we have a = 2.82 Å, and b = 2.47 Å and for cyclohexane we have a = 3.15 Å and b = 2.23 Å.

is some effective parameter which characterizes both the rotational motion of the molecule and this internal motion. Here n is the protons in the molecule; and r_{ij} is the difference between a selected pair of protons.

The distance between the protons in a chair-shaped molecule were calculated on the basis of standard data [10]. Table 1 shows the value of τ_c for certain temperatures. The apparent activation energy for T_{1i}^{-1} is 1.6 ± 0.2 kcal/mole.

4. Theories of the intermolecular contribution to the overall rate of nuclear spin-lattice relaxation in liquids differ in how the nature of the translational motion of the molecules and the local structure of the liquid are taken into account.

Torrey's theory [11] treats the liquid as a set of hard spherical particles undergoing random jumps. The distance of closest approach between nuclei is the diameter of these particles. From this theory for the case $\omega\tau_c \ll 1$ we have

$$T_{1e}^{-1} = \frac{2\pi}{5}\hbar^2\gamma^4\frac{N}{Dd}\left(1+\frac{5}{12}\frac{<r^2>}{d^2}\right), \tag{2}$$

where N is the number of nuclei per unit volume; $<r^2>^{1/2}$ is the rms jumping distance of the molecules; and D is the self-diffusion coefficient.

In contrast with Torrey, Oppenheim and Bloom [12] treat the translational motion of the molecules as due to continuous diffusion and take into account the nonuniformity of the molecular distribution; their result can be written as

$$T_{1e}^{-1} = \frac{6\pi}{5}\hbar^2\gamma^4\frac{1}{D}\left[\int_0^\infty dx\cdot\frac{\rho^{1/2}(x)}{x^4}\int_0^x dy\,\rho^{1/2}(y)\,y\right], \tag{3}$$

which is a form more convenient for applications. Here $\rho(r)$ is the radial distribution function of the molecules.

Khazanovich [13] found a correction to the intermolecular contribution which takes into account the cooperative nature of the translational motion of the molecules. This account reduces essentially to the replacement in (3) of the self-diffusion coefficient by some parameter D_e, an effective diffusion coefficient. For simplicity, we will use the correction obtained for the hard-sphere model: $D_e = 0.81\,D$.

The generalized Hubbard correction [14], which takes into account the noncentral nature of the magnetic nuclei in the molecule, can be written as

$$f = 1 + (b/a)^2F_3(A) + (b/a)^4\{5F_4(2A) + 3F_4(3A)\}, \tag{4}$$

where $A = 2a^2 2D'/D_e$, a is the radius of a molecule; b is the distance from the nucleus to the center of the molecule; D' is the rotational-diffusion coefficient ($D' = 1/6\tau_c$);

$$F_L(g) = C_L \int_0^\infty du\, [J_{L-1/2}(u)]^2/u\,(u^2 + g)$$

and $C_3 = 75/4$ and $C_4 = 35/8$ ($J_{L-1/2}$ is a spherical Bessel function). Table 2 shows the values of A, $F_L(g)$, and f; these f values are much smaller than those found on the basis of the hydrodynamic relations (1.267 for benzene and 1.154 for cyclohexane).

For large A we can obviously assume that the spins lie at the centers of the molecules and that their closest-approach distance is equal to the effective diameter of the molecules.

Katzoff [15], Bochinskii [16], and Narten [17] have reported x-ray diffraction curves of the radial distribution for benzene, but these curves do not yield a direct estimate of the intermolecular contribution: the centers of intense x-ray scattering in benzene are the carbon atoms, so the curves actually describe the distribution, not of the molecules, but of the carbon atoms of neighboring molecules around one of the carbon atoms of a selected molecule.

Narten described a model for the distribution of molecules in liquid benzene at 25°C. According to this model, each molecule of liquid benzene, like each molecule in solid benzene, is surrounded by 12 neighboring molecules. The centers of four of these neighboring molecules lie at an average distance of $r_1 = 5.63$ Å from the center of the selected molecule, those of four others lie at $r_2 = 5.92$ Å, while the centers of the four others lie at $r_3 = 6.64$ Å. This distribution can be described approximately by

$$\rho(r) = \begin{cases} 0, & \text{for} \quad r \leqslant r_{\mathrm{I}} \\ \dfrac{4}{4/3\,\pi\,(r_{\mathrm{II}}^3 - r_{\mathrm{I}}^3)} & r_{\mathrm{I}} \leqslant r \leqslant r_{\mathrm{II}} \\ \dfrac{4}{4/3\,\pi\,(r_{\mathrm{III}}^3 - r_{\mathrm{II}}^3)} & r_{\mathrm{II}} \leqslant r \leqslant r_{\mathrm{III}} \\ \dfrac{4}{4/3\,\pi\,(l^3 - r_{\mathrm{III}}^3)} & r_{\mathrm{III}} \leqslant r \leqslant l \\ N & l \leqslant r, \end{cases} \tag{5}$$

where

$$r_{\mathrm{I}} = r_1 - \frac{r_2 - r_1}{2}; \quad r_{\mathrm{II}} = \frac{r_1 + r_2}{2};$$

$$r_{\mathrm{III}} = r_2 + \frac{1}{2}\left(\frac{r_2 - r_1}{4} + \frac{r_3 - r_2}{4}\right)$$

and $l = r_3 + (r_3 - r_{\mathrm{III}})$ is the distance adopted as the boundary of the uniform molecular distribution.

Substituting (5) into (3), and using the corrections given above, we find

$$T_{1e}^{-1} = \frac{6\pi\hbar^2\gamma^4}{4.05\,D}\left[0.960\cdot 10^{29} + \frac{N}{3l}\right]\cdot f. \tag{6}$$

Let us compare the experimental value of T_{1e}^{-1} for 25°C, equal to 4.0, with that calculated from (6), equal to 3.67, and that found from

$$T_{1e}^{-1} = \frac{2\pi}{4.05}\hbar^2\gamma^4\frac{N}{Dd}f, \tag{7}$$

in which Eqs. (2) and (3) convert into a uniform molecular distribution for $\langle r^2 \rangle \ll d^2$; this value is equal to 3.02.

The discrepancy between the value calculated from (3) and the experimental T_{1e}^{-1} values can be explained on the basis of Torrey's jump model. From the difference between the experimental and theoretical intermolecular contributions we find $\langle r^2 \rangle^{1/2} = 0.86\,d$.

No information is available on the molecular distribution for liquid cyclohexane. If the effective diameter of this molecule is evaluated from the condition for hexagonal close packing of hard spheres, $(\pi/6)d^3 \cdot N = 0.74\ V_m$ (where V_m is the molar volume), we have $d = 6.3\ \mathring{A}$ at 25°C, and Eq. (7) yields $T_{1e}^{-1} = 7.0 \cdot 10^{-2}\ \mathrm{sec}^{-1}$. The experimental value of T_{1e}^{-1} at 25°C is $10^{-1}\ \mathrm{sec}^{-1}$. The rms jumping distance for the cyclohexane molecules is appreciably shorter than that for benzene.

We see from Figs. 3 and 4 that the temperature dependences of D^{-1} are parallel to the T_{1e}^{-1} curves; this result means that the rms jumping length for the molecules does not undergo any noticeable changes with changing temperature.

In conclusion the author thanks T. N. Khazanovich for useful advice.

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