

PROTON SPIN-LATTICE RELAXATION AND MOLECULAR MOTION IN LIQUID TOLUENE

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The intra and intermolecular contributions of the spin-lattice relaxation times for the ring and methyl protons of toluene diluted in carbon tetrachloride at 20°C are separated, and rotational correlation times derived for the entire range of concentrations. Assuming the contributions to reorientation as proportional to the main moments of inertia, agreement is obtained between the experimental results and the Gutowsky-Woessner theory when the Nora Hill viscosity model is used.

1. Introduction

As shown by Nederbragt and Reilly [1], the spin-lattice relaxation time can be measured separately for chemically-shifted proton groups. Several years ago Powles and Neale [2, 3] pointed to the possibility of using distinct spin-lattice relaxation times, measured in function of temperature, for deducing correlation frequencies characterizing complex thermal motion of molecules in liquids. However, no extensive effort has since been made to the further development of such studies, and the results obtained to date for a limited number of liquids are of a more qualitative nature.

In the present report following the paper of Prichard and Richards [4] the problem of toluene is reconsidered in order to gain more precise information regarding complex thermal motion of this molecule in liquid. For the separation of intra and intermolecular contributions to the spin-lattice relaxation times, the dilution method was applied. The ensuing results are interpreted in terms of the Gutowsky-Woessner theory [5] using the Nora Hill viscosity model [6, 7]. The procedure described below seems to be applicable to the analysis of thermal motions of other molecules with chemically-shifted proton groups.

2. Experimental results

Separate spin-lattice relaxation times for the ring and methyl protons of toluene diluted in carbon tetrachloride at 20°C were determined for the entire range of concentrations with an accuracy better than 5 per cent. The measurements were performed using a "home made" conventional high resolution nuclear magnetic resonance spectrometer of the Bloch type

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operating at a frequency of 25 MHz. A selective null-method enabling the simple and rapid determination of the distinct relaxation times was worked out in this Laboratory [8].

Reagent grade liquids were thoroughly purified and dried (for toluene $n_{D20} = 1.4970$; b. p. 110.8°C; for carbon tetrachloride $n_{D20} = 1.4608$; b. p. 76.2°C). Samples were degassed

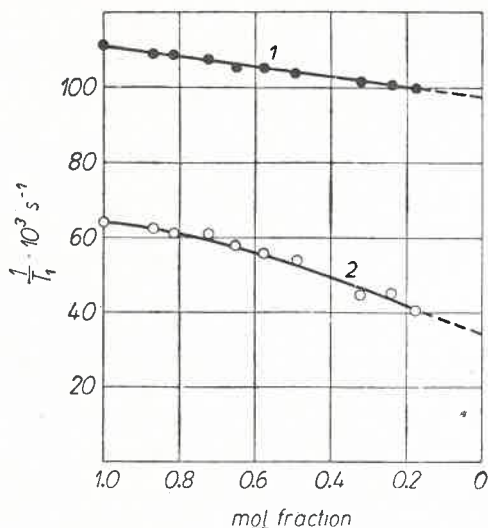


Fig. 1. Spin-lattice relaxation rates for the ring — 2 and methyl — 1 protons of toluene dissolved in CCl_4

by well-known freeze-pump-thaw technique. The viscosity of solutions was measured using an Ostwald viscosimeter; concentrations were determined by measuring the refractive index. The experimental results for relaxation rates are shown in Fig. 1.

Separate T_1 values for the pure liquid are 15.8 s (ring) and 9.0 s (methyl), in good agreement with the data published by others [1, 4, 9, 10]. Extrapolating the curves for infinite dilution one obtains two different values for rotational contributions to the relaxation times:

$$T_{1r}^{-1 \text{ ring}} = 34.7 \cdot 10^{-3} \text{ s}^{-1} \quad \text{and} \quad T_{1r}^{-1 \text{ methyl}} = 97.5 \cdot 10^{-3} \text{ s}^{-1}.$$

Using these values, one easily gets the ratio of the rotational correlation times as:

$$\frac{\tau_r^{\text{ring}}}{\tau_r^{\text{methyl}}} = \frac{T_{1r}^{-1 \text{ ring}} (\sum_j r_{ij}^{-6})^{\text{methyl}}}{T_{1r}^{-1 \text{ methyl}} (\sum_j r_{ij}^{-6})^{\text{ring}}} = \frac{5}{2}. \quad (1)$$

3. Discussion

The spin-lattice relaxation time for a nonviscous liquid can be described following the well-known BPP theory [11] generalized by Gutowsky and Woessner [5] for multispin systems as:

$$T_1^{-1} = \frac{3}{2} \gamma^4 \hbar^2 \left(\sum_j r_{ij}^{-6} \right) \tau_r + \frac{1}{2} \pi \gamma^4 \hbar^2 \rho \left(\sum_j r_{ij}^{-1} \right)_0 D^{-1} \quad (2)$$

where ρ denotes the spin concentration and D the diffusion coefficient. The ratio of Eq. (1) can be used for separating the rotational (intra) and translational (inter) contributions, by solving the following set of equations:

$$T_1^{-1 \text{ ring}} = \frac{15}{4} \gamma^4 \hbar^2 \left(\sum_j r_{ij}^{-6} \right)^{\text{ring}} \cdot \tau_r^{\text{methyl}} + T_{1t}^{-1}$$

$$T_1^{-1 \text{ methyl}} = \frac{3}{2} \gamma^4 \hbar^2 \left(\sum_j r_{ij}^{-6} \right)^{\text{methyl}} \cdot \tau_r^{\text{methyl}} + T_{1t}^{-1} \quad (3)$$

leading to $\tau_r^{\text{methyl}} = 1.4 \cdot 10^{-12}$ s and $T_{1t}^{-1} = 38 \cdot 10^{-3}$ s⁻¹ for the pure liquid. Similarly, the concentration dependence of the contributions can be obtained; the result of this separation is shown in Figs 2 and 3 as experimental points — common for the translational part

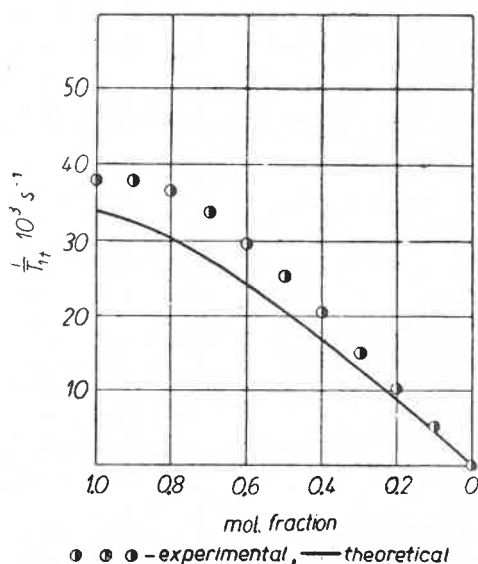


Fig. 2. Translational part of relaxation rate in function of concentration

and separate for the rotational correlation times of methyl and ring protons.

Independently, the same relations can be derived theoretically using the Nora Hill [6, 7] mutual viscosity model. The concentration dependence of τ_r and D for molecules B dissolved in molecules A can be expressed as:

$$\tau_r = (6kT)^{-1} [6f_A \eta_{AB} \sigma_{AB} K_A^2 + 3(3 - \sqrt{2}) f_B \eta_B \sigma_B K_B^2] \quad (4)$$

$$D = kT [6(f_A \eta_{AB} \sigma_{AB} + f_B \eta_B \sigma_B)]^{-1} \quad (5)$$

where f 's are mole fractions, σ 's intermolecular distances, η 's viscosities and

$$K_B^2 = \frac{I_{BB} \cdot I_B}{I_{BB} + I_B} \cdot \frac{2m_B}{m_B^2}$$

The mutual viscosity η_{AB} can be found from the equation:

$$\eta_m \sigma_m = f_A^2 \eta_A \sigma_A + f_B^2 \eta_B \sigma_B + 2 f_A f_B \eta_{AB} \sigma_{AB} \quad (6)$$

where η_m is the viscosity and σ_m the internuclear distance of a mixture.

Fig. 2 shows satisfactorily good agreement between the theoretical curve and experimental points for the common translational part of relaxation time. The theoretical curves I,

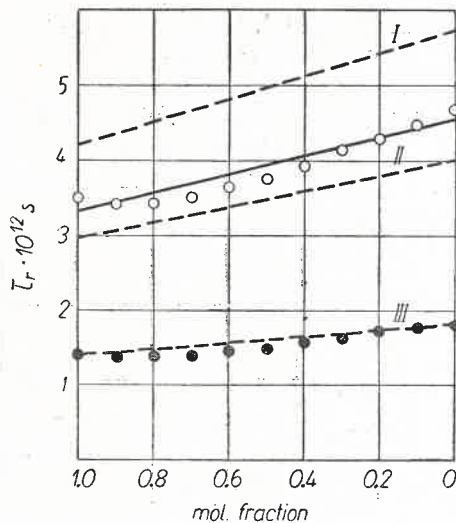


Fig. 3. Rotational correlation times in function of concentration: $\circ\circ\circ$ experimental-ring, $\bullet\bullet\bullet$ experimental-methyl; ——— theoretical complex motion; I, II, III — theoretical single reorientations about main axes of inertia moments

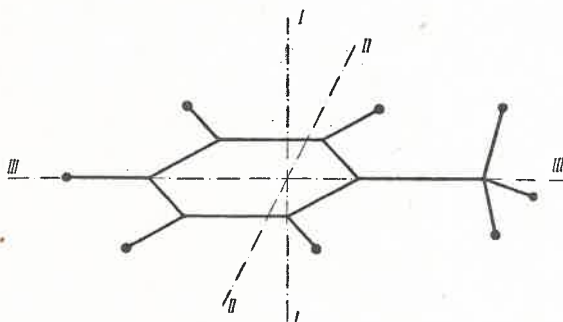


Fig. 4. Main axes of inertia moment for toluene molecule

II, III shown in Fig. 3 correspond to the single reorientations of the toluene molecule about the three main axes of its inertia moment (see Fig. 4).

The respective moments of inertia are:

$$I_I = 480 \cdot 10^{-40} \text{ gcm}^2$$

$$I_{II} = 338 \cdot 10^{-40} \text{ gcm}^2$$

$$I_{III} = 150 \cdot 10^{-40} \text{ gcm}^2.$$

Assuming only that the contributions to the rotational correlation time of the molecule are proportional to the respective moments of inertia, which seems reasonable,

$$\tau_r^{\text{ring}} = p_I \tau_I + p_{II} \tau_{II} + p_{III} \tau_{III} \quad (7)$$

where $p_I = 0.50$; $p_{II} = 0.35$; $p_{III} = 0.15$; one obtains the theoretical concentration dependence for τ_r^{ring} describing the complex motion of the molecule. There is striking agreement, visible in Fig. 3, between the experimental points for the ring protons and the theoretical curve. The slight deviation at higher concentrations is probably attributable to the weak dipolar association. Noteworthy is the coincidence of the experimental correlation times for methyl protons with the theoretical curve for single reorientation of the molecule about the *III*-axis.

3. Conclusions

From the results presented above it follows that the translational and rotational contributions to the spin-lattice relaxation times for liquid toluene are comparable and that the proposed method of separation makes it possible to find the respective contributions for the entire range of concentrations. The single reorientations about main axes of the inertia moment compose to yield the effective complex motion of the molecule proportionally to the respective moments of the molecule. Reorientation of the methyl group coincides with the reorientation of the molecule about the *III*-axis. Thus it can be stated that at the temperature considered the molecule reorients as a rigid one and one can neglect the intramolecular motion of the methyl group. This result confirms the suggestion made by Powles [2] that at temperatures higher than melting point the methyl group reorientation becomes inextricably mixed with the rapid reorientation of the molecule as a whole. The complex motion of the molecule can be characterized by the effective rotational correlation time which for the pure liquid equals $\tau_r^{\text{ring}} = 3.5 \cdot 10^{-12}$ s and $4.6 \cdot 10^{-12}$ s for infinite dilution.

REFERENCES

- [1] E. W. Nederbragt, C. A. Reilly, *J. Chem. Phys.*, **24**, 1110 (1956).
- [2] J. G. Powles, D. J. Neale, *Proc. Phys. Soc.*, **77**, 737 (1961).
- [3] J. G. Powles, D. J. Neale, *Proc. Phys. Soc.*, **78**, 377 (1961).
- [4] A. M. Pritchard, R. E. Richards, *Trans. Faraday Soc.*, **62**, 1388 (1966).
- [5] H. S. Gutowsky, D. E. Woessner, *Phys. Rev.*, **94**, 630 (1956).
- [6] N. E. Hill, *Proc. Phys. Soc.*, **B67**, 149 (1954).
- [7] N. E. Hill, *Proc. Phys. Soc.*, **B68**, 209 (1955).
- [8] Z. Pająk, K. Jurga, J. Jurga, *Acta Phys. Polon.*, **A38**, 263 (1970).
- [9] J. G. Powles, *Ber. Bunsenges.*, **67**, 328 (1963).
- [10] G. Bonera, L. Chiodi, G. Lanzi, A. Rigamonti, *Nuovo Cimento*, **17**, 198 (1960).
- [11] N. Bloembergen, E. M. Purcell, R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).