

ROTATIONAL CORRELATION TIMES OF AROMATIC AND HETEROAROMATIC MOLECULES BY PROTON SPIN-LATTICE RELAXATION

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Rotational correlation times for aromatic (phenol, aniline, nitrobenzene, toluene) and heteroaromatic (pyrrole, pyridine, furan, thiophen) molecules dissolved in carbon tetrachloride are determined and compared with calculated theoretical values. The Nora Hill model is found to be a good approximation for describing the molecular motions and interactions of different kinds in liquids.

The thermal reorientational motion of molecules in liquids can be characterized by a rotational correlation time determined by dielectric absorption, sound absorption, light scattering or nuclear magnetic resonance. The last method enables the deduction of the rotational correlation times when measuring the spin-lattice relaxation time T_1 of the liquid diluted in a nonmagnetic solvent in function of concentration. Extrapolation for infinite dilution ($f_B = 0$) gives the rotational contribution to the spin-lattice relaxation time defined as:

$$\frac{1}{T_1} = \left(\frac{1}{T_1} \right)_{\text{rot}} + f_B \left(\frac{1}{T_1} \right)_{\text{trans}},$$

where f_B denotes the molar fraction of the investigated liquid. The experimental value of the rotational correlation time τ_{rot} can be defined from the Gutowsky-Woessner formula [1] describing, for a multispin system, the rotational part of the relaxation time as:

$$\left(\frac{1}{T_1} \right)_{\text{rot}} = \frac{3}{2} \hbar^2 \gamma^4 \left(\sum_j r_{ij}^{-6} \right) \tau_{\text{rot}}.$$

In the course of an extensive study of molecular motions by NMR carried out at this Laboratory, the reorientational thermal motions in liquids with similar structure in a set of aromatic (phenol, aniline, nitrobenzene, toluene) and heteroaromatic (pyrrole, pyridine, furan, thiophen) molecules have been investigated. Reagent grade compounds were thoroughly purified and dried. Measurements of the spin-lattice relaxation times were performed by the stationary Hennel-Hryniewicz method [2] using a "home made" NMR spectro-

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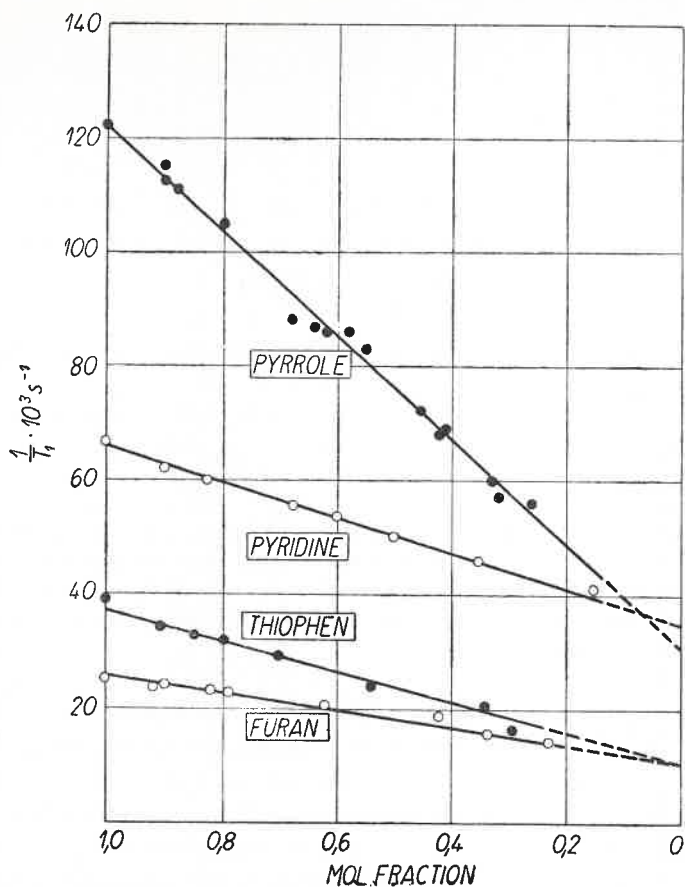


Fig. 1. Spin-lattice relaxation rates for heteroaromatic compound — carbon tetrachloride solutions

meter (medium resolution) operating at 16.5 MHz [3]. The results obtained for the solutions at 20°C are presented in Figs 1 and 2. The samples of carbon tetrachloride solutions were conventionally degassed.

The experimentally determined relaxation rates reveal a linear concentration dependence for heteroaromatic compounds whereas in the aromatic group a distinct deviation in the case of aniline and nitrobenzene is visible. The linear relations found for toluene, furan and thiophen, similarly as for the case of benzene [4], are mainly related to the gradual disappearance with dilution of the translational contribution to the relaxation time, which vanishes at $f_B = 0$. The weak interactions due to the small dipole moments of these molecules are unimportant. The deviations observed for aniline and nitrobenzene, probably relevant to the dipolar interaction at higher concentrations, may be caused by the weak association of molecules disappearing quickly with dilution at $f_B = 0.6$. The lack of such deviations in the case of phenol, pyridine and pyrrole can be explained by taking into account the hydrogen bonding occurring in the investigated range of concentrations. Strong association existing in pure liquids and even in diluted solutions [5] diminishes the effective dipole moments of multimers making the dipolar interaction unimportant.

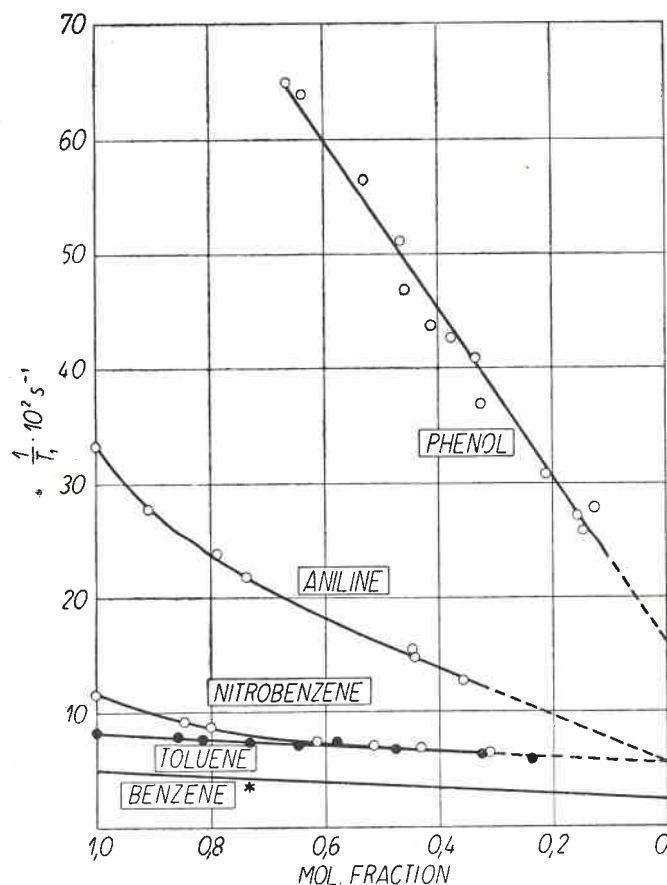


Fig. 2. Spin-lattice relaxation rates for aromatic compound — tetrachloride solutions; * results of Mitchell and Eisner [4]

Experimental correlation times τ_{rot} deduced by extrapolation are compared in Table I with the theoretical values.

Theoretical correlation times were calculated on the one hand using the Nora Hill mutual viscosity model [6]. For infinite dilution:

$$\tau_{\text{rot}}^{\text{NH}} = \frac{2I_B \eta_A a_B}{kT} \cdot \frac{m_A + m_B}{m_A \cdot m_B},$$

where I_B is the moment of inertia of the solute molecule B , m_A and m_B are the respective solvent and solute masses.

On the other hand, the theoretical correlation times were obtained when the Gierer-Wirtz microviscosity model [7] was applied:

$$\tau_{\text{rot}}^{\text{GW}} = \left[6 \frac{a_A}{a_B} + \left(1 + \frac{a_A}{a_B} \right)^{-3} \right]^{-1} \cdot \tau_{\text{rot}}^D,$$

where $\tau_{\text{rot}}^D = 4\pi\eta a^3/3kT$ and a are the respective molecular radii.

TABLE I

Substance	n_D^{20}	μ Debye	a Å	$T_{1\text{rot}}^{-1}$ $\times 10^3 \text{ s}^{-1}$	Correlation time $\times 10^{12} \text{ s}$		
					τ_{rot}	$\tau_{\text{rot}}^{\text{NH}}$	$\tau_{\text{rot}}^{\text{GW}}$
Benzene		0	2.9	18*	2.3*	2.6	3.7
Thiophen	1.5283	0.54	2.8	10	2.4	2.2	3.3
Furan	1.4218	0.63	2.7	10	2.2	1.9	2.8
Toluene	1.4970	0.37	3.0	59	4.6	4.8	4.3
Aniline	1.5783	1.68	3.05	60	4.1	4.1	4.6
Nitrobenzene	1.5520	4.3	3.14	60	8.2	7.8	5.2
Pyridine	1.5101	2.2	2.85	35	5.2	3.1	3.4
Pyrrole	1.5043	1.83	2.65	31	6.2	2.0	2.7
Phenol	—	1.4	2.98	130	28.8	4.4	4.2

* R. W. Mitchell, M. Eisner, *J. Chem. Phys.*, **33**, 86 (1960).

The comparison of the correlation times shows that the Nora Hill model correctly describes the reorientational thermal motion of the investigated molecules in liquid. The distinct differences occurring in the case of pyridine, pyrrole and phenol, however, can be explained assuming that the experimental τ_{rot} values correspond to the associates of the hydrogen-bond type existing in the investigated range of concentrations and not to the respective monomers. This assumption can be confirmed for the case of pyridine. The theoretical value $\tau_{\text{rot}}^{\text{NH}}$ calculated for a dimer is $5.5 \times 10^{-12} \text{ s}$ comparable to the experimental value $5.2 \times 10^{-12} \text{ s}$. Measurements of the spin-lattice relaxation times in diluted solutions would thus be valuable.

It should be mentioned that the experimental value τ_{rot} given for toluene in Table I is taken from our paper [8], where an analysis of the complex thermal motion of this molecule is performed.

It can thus be concluded that the Nora Hill model appears to be a good approximation for the study of molecular motions in liquids. Rotational correlation times of aromatic and heteroaromatic compounds are of the same order of magnitude, what is reasonable considering the structural similarity of these molecules. The mass of the ring substituents may be decisive for the elongation of the determined correlation times. Measurements of the spin-lattice relaxation times can moreover be useful in studying hydrogen bonding in liquids and the ratio $\tau_{\text{rot}}/\tau_{\text{rot}}^{\text{NH}}$ may well represent a measure of the degree of association in such liquids.

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