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THE MOLECULAR REORIENTATION OF FLUOROBENZENE AND THE INFLUENCE OF WEAK MOLECULAR INTERACTION — T_1-STUDY

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The dependence of orientational and angular momentum correlation times on weak molecular interaction is studied. It is shown that angular momentum correlation time can be the most interaction sensitive rotational parameter.

1. *Introduction*

Pecora et al. [1] have shown the reorientation times $\tau_{\theta,i}^{(2)}$ and the rotational diffusion coefficients R_i, respectively around the i-th axis to depend from viscosity η according to Eq. (1):

$$\tau_{\theta,i}^{(2)} = 1/6R_i = a_i^{(2)}\eta + \tau_{0,i}^{(2)}. \tag{1}$$

By setting $a_i^{(2)} = \lambda_i V_m/6kT$ in Eq. (1) (λ_i represents the shape-dependent dimensionless friction coefficient [2] and V_{m} the molecular volume) and taking $\tau_{0,i}^{(2)}$ to be the reorientation time of the free rotor [3]:

$$\tau_{0,i}^{(2)} \approx \tau_{\mathrm{free},i}^{(2)} = 2\pi\left(\tfrac{41}{360}\right)\left(\frac{I_i}{kT}\right)^{1/2}, \quad I_i = i \text{ th moment of inertia,} \tag{2}$$

it can be shown that the temperature dependence of the molecular reorientation can in the same way be described by Eq. (1) and Eq. (2); this has been proved right for chlorobenzene and toluene by the temperature dependence of the deuterium spin lattice relaxation times T_1^{Q} [4]. Here, the Woessner equations [5] used for transformation of T_1^{Q} into the rotation times $\tau_{\theta,i}^{(2)} = 1/6\ R_i$ have to be valid. This is right in the limit of rotational diffusion. The $\lambda_i V_{\mathrm{m}}$ have been assumed to be freely adjustable parameters and determined from the function $T_1^{\mathrm{Q}} = f(T)$ [4]. From the comparison of the $\lambda_i V_{\mathrm{m}}$ with the data of Pecora [1] determined in inert solvents and of Youngren and Acrivos [6] calculated

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from molecular shape it was guessed that the rotational behaviour of the molecules is possibly influenced by (specific) aromate-aromate interaction. In this paper for the special case of fluorobenzene the interaction of an aromatic molecule with dimethylformamide (DMFA) will be studied, which according to the predictions in [7, 8] ought to be stronger than the possible aromate-aromate interaction. The $\lambda_i V_\mathrm{m}$ having the characteristics of effective rotational volumes (around the i-th axis) were used as temperature-independent interaction parameters as was done in [4]. Because the determination of the $\lambda_i V_\mathrm{m}$ from the temperature dependence of T_1 requires a relatively wide temperature region (approx. 200 K), only toluene may be used as a "relatively inert" solvent. Except deuterons susceptible to the orientation correlation ($\tau_\theta^{(2)}$), fluorobenzene-d$_5$ contains ^{19}F, the relaxation of which depends on the angular momentum correlation (τ_J) in so far as ^{19}F–T_1 is governed by spin rotation (with simultaneous suppression of the competitive dipolar mechanism). This behaviour will be used in this paper to determine the "effective step width of the rotational jumps" $\langle\theta^2\rangle^{1/2}$ after O'Reilly [9] from the product $\tau_\theta \tau_J$.

2. Experimental

Experimental details on the ^{2}D–T_1 measurement have already been reported [4]. The $\lambda_i V_\mathrm{m}$ were determined using Eqs. (1)–(3) [4].

$$1/T_1^\mathrm{Q} = \tfrac{3}{8}\left(\frac{e^2 qQ}{\hbar}\right)^2 \tau_\theta^\mathrm{eff}. \qquad (3)$$

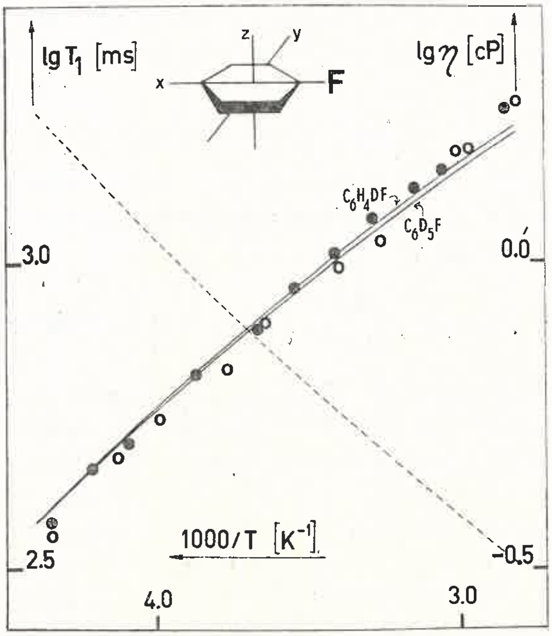

Fig. 1. $T_1^\mathrm{Q}(^2\mathrm{D})$ in neat fluorobenzene; open circles: C_6D_5F, full circles: para-C_6H_4DF, full lines: Eqs. (1)–(3), see Table I, broken line: viscosity (1cP = 10^{-2} g/cm · s) of C_6H_5F

The quadrupole coupling constant $e^2qQ/\hbar$ = 180 kHz was assumed to be independent from molecular position, temperature and medium [10, 11]. $\tau_\theta^{\mathrm{eff}} = f(\tau_{\theta,i}^{(2)})$ was determined from the Woessner equations [5], which will not be outlined in this paper. The geometrical limit of interest in this work (planar anisotropic rotator) is the same as in [4]. The effective relaxation times of C_6D_5F (ortho- and meta-^{2}D, respectively and para-^{2}D have different relaxation geometries) was expressed by the weighted sum of the various relaxation rates $(1/T_1(C_6D_5F) = (4/T_1(o, m)+1/T_1(p))/5)$. Considering the small difference between the relaxation times (Fig. 1) of neat C_6D_5F and neat para-C_6H_4DF this is an applicable procedure. T_1^Q in solutions of 15% C_6D_5F in DMFA and toulene is shown in Fig. 2. The solid curves lg T_1 vs $1/T$ have been calculated from the $\lambda_i V_m$ in Table I. In addition, Fig. 2

TABLE I

Effective rotational volumes $\lambda_i V_m$ of fluorobenzene

Parameter / Solution	$\lambda_x V_m$[a] [Å^3]	$\lambda_y V_m$[a] [Å^3]	$\lambda_z V_m$[a] [Å^3]
neat	86±12	110±15	12±12
15% in toluene	98±15	147±30	12±12
15% in DMFA	196±24	270±40	12±12

[a] $I_x = 186\times10^{-40}$ [gcm^2]; $I_y = 357\times10^{-40}$ [gcm^2], $I_z = 543\times10^{-40}$ [gcm^2], $V_m = 85$ [Å^3]

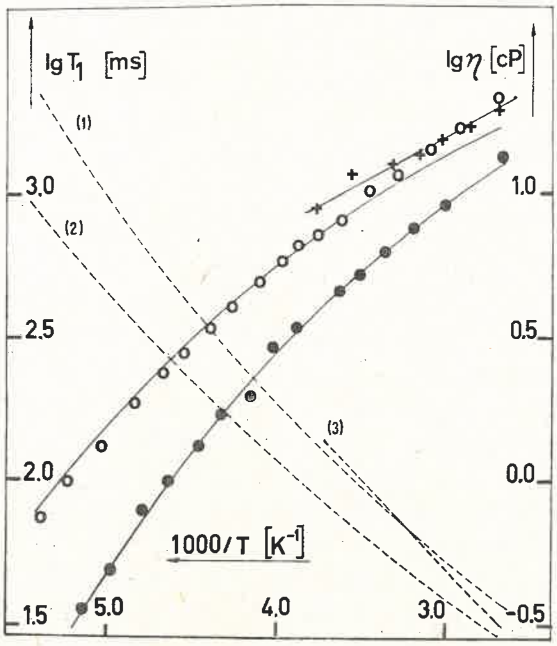

Fig. 2. T_1^Q of 15% C_6D_5F in toluene (open circles), DMFA (full circles) and cyclohexane (crosses); full lines: Eqs (1)–(3), see Table I, broken lines: viscosity of 15% C_6H_5F in (1) toluene, (2) DMFA and (3) cyclohexane

shows the straight line of lg T_1 vs $1/T$ in C_6H_{12} within a limited temperature region which renders impossible the determination of the $\lambda_i V_m$. The coarse description of the experimental variation of T_1^Q at temperatures above 50°C is attributed to the deviation from the diffusion limit [4].

The ^{19}F-relaxation times (Table II) have been determined with a Bruker SXP spectrometer at 84.7 MHz and 30°C with a pulse sequence of $180° - \Delta t - 90°$. Oxygen was removed before measurements by freeze-pump-thaw cycles down to 10^{-5} Torr. All samples were degassed simultaneously to maintain residual oxygen content on the same level. In an attempt to suppress the dipolar ^{19}F-relaxation mechanism competing with spin rotation, experiments were carried out with totally deuterated media only. The residual proton content was 5% in C_6D_5F (home-made) and 1% in DMFA-d_7 (Merck Darmstadt) and C_6D_{12} (Isocommerz Leipzig). The measured ^{19}F-relaxation times T_1^{exp} (Table II have to be corrected by the remaining small amount of the ^{19}F, ^{1}H and ^{2}D intermolecular and intramolecular dipolar coupling. The various intermolecular relaxation times ($^{19}F-{}^1H$, $^{19}F-{}^{19}F$, $^{19}F-{}^2D$) have been determined on the basis of the intermolecular proton relaxation time of benzene (23.7 sec.) [13]. Due to the motional similarity between benzene and fluorobenzene this seems to be more reasonable than using the relatively rough estimation of the translational correlation time from the Stokes-Einstein hydrodynamics [10]. $T_1^{inter}(C_6H_6)$ was then transformed to the different spin densities, gyromagnetic ratios and viscosities of the C_6D_5F solutions. In the case of intramolecular dipolar coupling ($^{19}F-{}^1H$, $^{19}F-{}^2D$) τ_θ^{eff} was calculated from the ^{2}D relaxation times using the Woessner equations and then — considering the different relaxation geometries — introduced into

TABLE II

Angular momentum correlation of C_6D_5F at 30°C

Parameter / Solution	η [cP]	$T_1^{exp}(^{19}F)$ [s]	T_1^{SR} [s]	τ_J[a] [ps]	τ_J[b] [ps]	τ_J[c] [ps]	τ_θ^{eff}[d] [ps]	$\langle\theta^2\rangle^{1/2}$ [°C]
neat	0.551	$21.{}_3$ $(22.{}_0)$[e]	$26.{}_2$ $(24.{}_8)$[e]	0.09_8 (0.10_4)[e]	0.100	0.151	1.7_5	$11.{}_5$
11.0% in DMFA-d_7	0.782	$26.{}_2$	$29.{}_9$	0.08_6	0.084	0.148	2.8_0	$20.{}_3$
22.6% in DMFA-d_7	0.747	$25.{}_0$	$28.{}_8$	0.09_0	0.086	0.149	2.6_5	$20.{}_0$
23.8% in C_6D_{12}	0.783	$16.{}_4$	$18.{}_0$	0.14_3	0.084	0.148	1.6_7	$20.{}_1$
45.0% in C_6D_{12}	0.710	$19.{}_2$	$21.{}_8$	0.11_8	0.088	0.150	1.7_0	$16.{}_0$

[a] $C_{xx}^2 I_x + C_{yy}^2 I_y + C_{zz}^2 I_z = (2\pi)^2(3.92 \pm 0.69) \pm 10^{-31}$ [gcm²/s²] [10];
[b] with $\lambda_x V = 86$ [Å³], $\lambda_y V = 110$ [Å³], $\lambda_z V = 24$ [Å³];
[c] with $\lambda_x V = 86$ [Å³], $\lambda_y V = 110$ [Å³], $\lambda_z V = 0$ [Å³];
[d] real, not fitted values; [e] Assink and Jonas Ref. [10].

the equations of the intramolecular dipolar coupling [14]. Table II shows the spin rotational relaxation times thus obtained in comparison with the data of Assink and Jonas [10] (Our somewhat lower value of $T_1^{\exp}$ in neat C_6D_5F must be attributed to the higher proton content of the substance used here.) The viscosities were measured with a modified Ubbelohde viscosimeter, the deviations from the viscosity curves (broken lines in Fig. 1 and 2) being less than 2%.

3. Discussion

The rotational behaviour of fluorobenzene is very similar to that of benzene but less similar to that of toluene and chlorobenzene [4]. This similarity is indicated by the close similarity of the relaxation times of all deuterons in the whole range of fluid state. This is a further evidence for the contribution of molecular shape to rotation. Therefore, the difference between $\lambda_x V_m$ and $\lambda_y V_m$ is considerably smaller than in the case of toluene and chlorobenzene [4] (molecular geometry of benzene almost not disturbed by fluorine incorporation). The $\lambda_i V_m$ of neat fluorobenzene are identical to those in toluene solution. When the z-rotation is assumed to be independent from the interaction $C_6H_5F-DMFA$ [8], by reason of the $\lg T_1^Q - 1/T$ dependence (Fig. 2) one obtains for the x, y-rotations doubled $\lambda_i V_m$-values in comparison to the aromatic media (Table I). This unambiguously supports the existence of specific aromate-DMFA complexes. In cyclohexane solution the $\lambda_i V_m$ cannot be analyzed, with the T_1 — values almost not much differing from those of toluene solution. The only hint for a possible aromate-aromate interaction comes from the weak $T_1^Q(C_6D_5F)$-activation in C_6H_{12} -solution despite of higher activation of viscosity of the C_6H_{12}-system. Therefore, in addition to the $\tau_{\theta,i}$-investigations, we studied the correlation time τ_J of the angular momentum in C_6D_5F/C_6D_{12} and $C_6D_5F/DMFA\text{-}d_7$ solutions which have been calculated from T_1^{SR} (Eq. (4)):

$$1/T_1^{SR} = \frac{2kT}{3\hbar^2} \sum_i C_{ii}^2 I_i \tau_J . \tag{4}$$

Moment of inertia data and elements of the spin rotation tensor of ^{19}F in C_6D_5F have been taken from [10].

The comparison of τ_J-data in different media is surprising: Despite the higher cyclohexane viscosity the C_6D_5F molecule introduced into the cyclohexane "lattice" suffers considerably less collisions by surrounding molecules than in the pure substance (τ_J increases with increasing time between "collisions" τ_{BC} and often exists a simple proportionality between the two times [3, 10, 15].). For an anisotropic rotator the change of τ_J to be expected with respect to neat fluorobenzene may be determined from Eq. (5) [9]:

$$\tau_J = \frac{\sum I_i^2 R_i}{2kT \sum I_i} . \tag{5}$$

The $\tau_{\theta,i}$ have been calculated using the $\lambda_i V_m$ from Table I; an increase in viscosity effects a reduction of the resulting τ_J (Table II). The discrepancy between Eq. (3) and the experimental results must be attributed to the disregard of the diffusion limit: A theory of O'Reilly [9] takes into account the influence of small finite step intervals on to the product $\tau_\theta^{(2)}\tau_J$. To realize different "reorientational mechanism" in the various media and with respect to the coarse description of the $\tau_{\theta,i}$ by Eqs. (1) and (2) above room temperature it is only used in the approximation of isotropic reorientation:

$$\tau_\theta^{\mathrm{eff}}\tau_J = \frac{I_{\mathrm{AV}}}{6kT}\langle\theta^2\rangle/(1-\exp(-\langle\theta^2\rangle)); \quad \langle\theta^2\rangle = \sum\langle\theta_i^2\rangle. \tag{6}$$

As can be seen from the $\langle\theta^2\rangle$ values (Table II), the mean step interval of fluorobenzenes is reduced due to aromate — aromate interaction; on the other hand, the $\langle\theta^2\rangle$ -effect is largely compensated by the increased number of collisions per unit time and the resulting τ_J-reduction (compared to the ideal state of rotation at the same viscosity). As a result, τ_θ and $T_1(\tau_\theta)$ are the same for "interacting" (fluorobenzene) and "non-interacting" (cyclohexane) media. Another mechanism influencing the rotation is found in the DMFA-aromate interaction: τ_θ is increased by the value of τ_J reduction, the mean step width remaining unchanged.

Application of Eq. (4) deserves some critical comment (although widely used in nuclear relaxation theory [10, 12, 16]): Line shape analysis of molecular vibrations [15] and the molecular dipole vector absorption in the far infrared [17] of molecules similar to fluorobenzene show a negative overshoot in the angular momentum correlation function. Under these circumstances the definition of τ_J as the time integral of the correlation function should be questionable. Due to the lack of a more sophisticated theory of angular momentum correlation in liquids to describe spin rotational relaxation times we have to work with this uncertainty. For the *comparisons* given above this fact should be of minor importance and it can be concluded, that in certain cases (beyond the diffusion limit!) the angular momentum correlation should be more sensitive for weak molecular interaction than orientational correlation. More profound insights can be obtained by the methods mentioned above desregarding the fact that they are complicated in mixtures.

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REFERENCES

[1] D. R. Bauer, G. R. Alms, J. I. Brauman, R. Pecora, *J. Chem. Phys.* **61**, 2255 (1974).
[2] C.-M. Hu, R. Zwanzig, *J. Chem. Phys.* **60**, 4354 (1974).
[3] F. J. Bartoli, T. A. Litovitz, *J. Chem. Phys.* **56**, 404, 413 (1972).
[4] G. Rudakoff, K.-L. Oehme, *Chem. Phys. Lett.* **54**, 342 (1978).
[5] D. E. Woessner, *J. Chem. Phys.* **37**, 647 (1962).
[6] G. K. Youngren, A. Acrivos, *J. Chem. Phys.* **63**, 3846 (1975).
[7] G. Rudakoff, R. Radeglia, P. Junghans, T. Ha-Phuong, W. Köhler, *Z. Chem.* **2**, 307 (1971).
[8] S. Brownstein, V. Bystrov, *Can. J. Chem.* **48**, 243 (1970).
[9] D. E. O'Reilly, *Mol. Phys.* **32**, 891 (1976).
[10] R. A. Assink, J. Jonas, *J. Chem. Phys.* **57**, 3329 (1972).
[11] J. P. Jacobsen, K. Schaumburg, *J. Magn. Res.* **28**, 1 (1977).

[12] R. E. D. McClung, *Advan. Mol. Relax. Proc.* **10**, 83 (1977).
[13] H. G. Hertz, B. Kwatra, R. Tutsch, *Z. Phys. Chem.* NF **103**, 259 (1976).
[14] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford 1961 .
[15] J. F. Dill, T. A. Litovitz, J. A. Bucaro, *J. Chem. Phys.* **62**, 3839 (1975).
[16] T. E. Bull, *J. Chem. Phys.* **62**, 222 (1975).
[17] M. Evans, *J. Chem. Soc. Faraday Trans. II* **71**, 2051 (1975).