

MEASUREMENT OF T_1 —RELAXATION TIME IN 1,2-DICHLOROETHANE DISSOLVED IN CARBON TETRACHLORIDE

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The measurements of proton spin-lattice relaxation time T_1 have been carried out in 1,2-DCE vs its concentration in CCl_4 . The results are compared with Gutowsky and Woessner theory where, in place of correlation times, the formulas of Hill are introduced. It is shown, that the 1,2-DCE molecule rotates on the average about an axis with respect to which its mean moment of inertia amounts to $I = \frac{1}{3}(I_x + I_y + I_z)$, where I_x, I_y, I_z are the moments of inertia with regard to the three principal axes of the molecule.

1,2-dichloroethane (1,2-DCE)—a substance exhibiting internal rotation—has been the topics of various papers [1–9]. Dielectric studies [4–7] showed the relaxation times and electric dipole moment of 1,2-DCE molecules to depend on the choice of solvent. Measurements [2–3] of nuclear magnetic relaxation times in pure 1,2-DCE between 80° and 313°K permitted the determination of the activation energy for internal rotation. Linder [3] showed relaxation in solid 1,2-DCE to occur by way of internal rotation about the C—C axis with a single activation energy of 1.5 kcal/mole, in contradiction to the results of Gutowsky and Pake [9] who, in NMR studies, found two changes in linewidth between 80° and 230°K pointing to a change in the mechanism of the nuclear relaxation process. Refs [3] and [9] report a sharp change in linewidth and a change in activation energy at melting point. Linder [3] evaluates the activation energy for relaxation in liquid phase at 0.6 kcal/mole; his results, however, are subject to doubt, as his relaxation time measured in liquid 1,2 DCE is too short (0.6–0.8 s) and has since been invalidated by the results of Bock and Tomchuk [1]. Linder [3] moreover performed measurements of T_1 in function of the concentration of 1,2-DCE in solution in CCl_4 , but refrained from publishing his results. He reports, however, that the relaxation time T_1 and the rotational part T_{1ro} , calculated from BPP theory [10] are in agreement with experiment. IR measurements [8] revealed the presence of two rotational isomers (*trans* and *gauche*) at thermodynamical equilibrium in liquid 1,2-DCE.

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A very thorough investigation, clarifying the dependence of the dielectric relaxation time and the NMR — measured correlation time on the choice of solvent is due to Bock and Tomchuk [1], who measured the longitudinal relaxation time T_1 in solutions of 1,2-DCE in 6 distinct solvents and found viscous motion in dipolar medium to be affected by the electric moment and polarizability of the solvent molecules. The difference in activation energy calculated by them as between viscous motion without and with dipole-dipole interaction taken into account is equal to the energy of the two electric dipoles those of the solvent and solute. Bock and Tomchuk based their calculations on a $\left(\frac{1}{T_1}\right)_0$ value corresponding to infinitely low concentration of 1,2-DCE in proton-less solvents extrapolated by drawing a straight line through the experimental T_1 — points plotted in accordance with the formula:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_0 + cx, \quad (1)$$

where T_1 is an experimental value, c a constant, and x — the concentration of 1,2-DCE in CCl_4 .

The authors of Ref. [1] state that the mean square deviation from linearity in the case of 1,2-DCE in CCl_4 amounted to $7.1 \cdot 10^{-3} \text{ s}^{-1}$, and give a value of $\left(\frac{1}{T_1}\right)_0 = 0.0527 \text{ s}^{-1}$.

The present paper contains results for the thermal nuclear relaxation time T_1 in 1,2-DCE *vs* its concentration in CCl_4 measured by the spin echo method, together

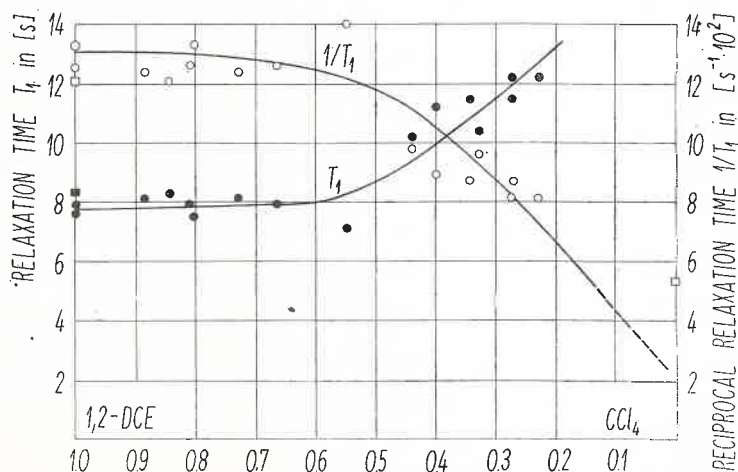


Fig. 1. Measurements of thermal relaxation time in solutions of 1,2-DCE in CCl_4 . Squares denote results of Bock and Tomchuk [1]

with an attempt at their theoretical interpretation. The T_1 values measured in thoroughly purified samples are shown in Fig. 1, where experimental points from Ref. [1] are plotted also. The relaxation time of pure 1,2-DCE is in agreement, to within experimental error, with the data of Bock and Tomchuk. However, a straight line as given by Eq. 1 cannot

be drawn through our results. Moreover, our extrapolated value of $\left(\frac{1}{T_1}\right)_0$ diverges strongly from the value of [1], and amounts to $0,02 \text{ s}^{-1}$ only.

For the theoretical calculation of $\left(\frac{1}{T_1}\right)$ vs concentration, we assumed the formulas of Gutowsky and Woessner [11] where, in place of the correlation times for rotational and translational interactions, the formulas of Hill [12, 13] are introduced. The relaxation time T_1 of a liquid 1,2-DCE sample at room temperature can be described by the relation:

$$\frac{1}{T_1} = \left\langle \frac{1}{T_1^{\text{rot}}} \right\rangle + \left\langle \frac{1}{T_1^{\text{trans}}} \right\rangle, \quad (2)$$

the brackets $\langle \rangle$ denoting averaging over all protons of a 1,2-DCE molecule. In Gutowsky and Woessner's [11], neither the radius of the molecule nor the mean distance between interacting nuclei of neighbouring molecules is stated. The correlation time formulas

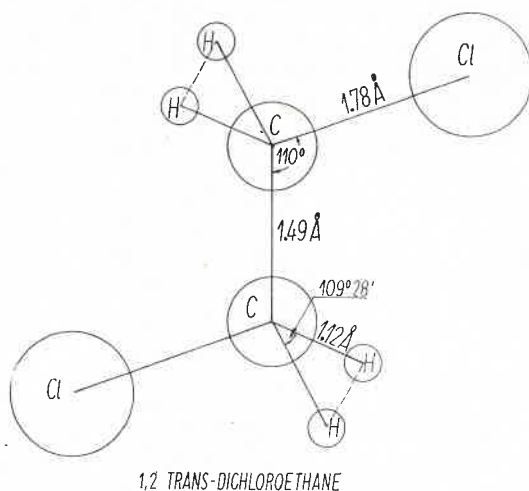


Fig. 2. Structure of 1,2-DCE molecule

proposed by Hill contain undefined minimal intermolecular distances, of which use is made in calculating expressions for K_A^2 and K_B^2 [12, 13]. We attempted to circumvent these inconveniences by establishing a program of numerical computations providing for variational adjustment of the radii of the interacting molecules.

In calculating the distances between nuclei in the 1,2-DCE molecule, we resorted to structural data for the *trans* form (Fig. 2). On the other hand, the quantity $\eta_{AB} \sigma_{AB}$ occurring in Hill's correlation time formula (and referred to as the mutual viscosity parameter) was determined by measuring the viscosity of the solutions. Fig. 3 contains

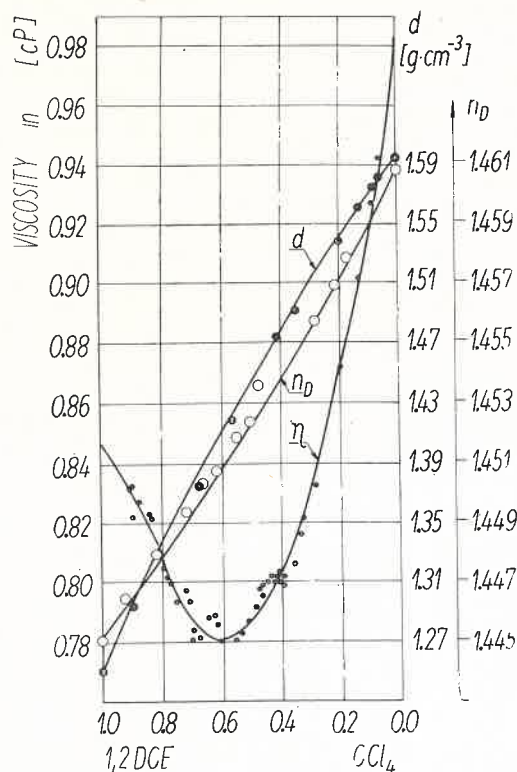


Fig. 3. Measurements of macroscopic viscosity, refractive index and density for solutions of 1,2-DCE in CCl_4

the results of these measurements, together with those of refractive index and density. With these values, the following relation due to Hill:

$$\eta_m = f_A^2 \eta_A \frac{\sigma_A}{\sigma_m} + 2f_A f_B \frac{\eta_{AB} \sigma_{AB}}{\sigma_m} + f_B^2 \eta_B \frac{\sigma_B}{\sigma_m} \quad (3)$$

permits the calculation of $\eta_{AB} \sigma_{AB}$. In Eq. (3), η_m is the viscosity of the solution, η_A and η_B respectively the viscosities of CCl_4 and 1,2-DCE, f_A and f_B their molar concentrations σ_A and σ_B their mean molecular diameters from the density on the assumption of closest packing, and σ_m the mean distance between the molecules of the solution calculated from the formula:

$$\sigma_m = f_A \sigma_A + f_B \sigma_B \quad (4)$$

Fig. 4 shows the results of $\eta_{AB} \sigma_{AB}$ calculations, as well as the mean square deviation of the theoretical curve of $\eta_m = \eta_m(f_B)$, plotted with the $\eta_{AB} \sigma_{AB}$ parameter calculated for the given concentration, from the experimental curve. Thus, e.g., Fig. 5 contains three theoretical shapes of $\eta_m = \eta_m(f_B)$ calculated with the values of $\eta_{AB} \sigma_{AB}$ obtained for the concentrations $f_B = 0.95$, 0.45 and 0.05 , as well as the experimentally determined curve.

From Figs 4 and 5 it follows that, for concentrations f_B ranging from 0.8 to 0.2, the parameter $\eta_{AB} \sigma_{AB}$ is constant and, at the same time, the mean square deviation of the theoretical curve from experiment is the smallest. Basing on this result, we took $\eta_{AB} \sigma_{AB} = 3.51 \text{ cP} \cdot \text{\AA}$ when calculating T_1 .

The model of Nora Hill requires moreover that the moment of inertia of the rotating molecules be known. From the geometry of the 1,2-DCE molecule, the three moments

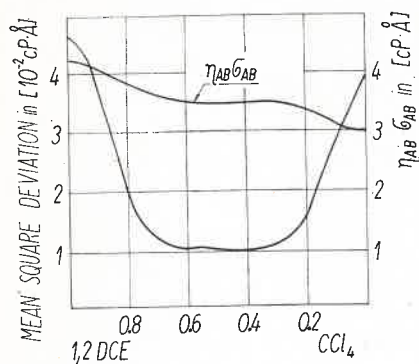


Fig. 4

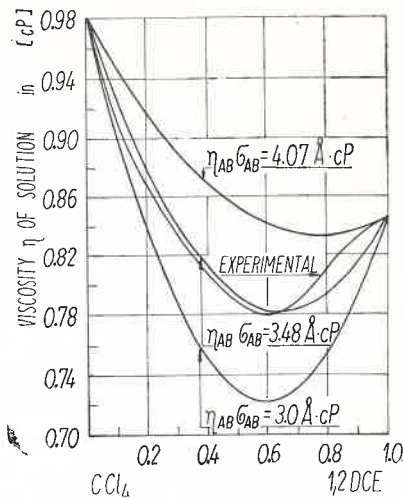


Fig. 5

Fig. 4. Calculated values of the parameter $\eta_{AB} \sigma_{AB}$, and mean square deviations for the $\eta_{AB} \sigma_{AB}$ matched curve

Fig. 5. Shapes of functions matching the macroscopic viscosity

of inertia with regard to the three principal axes can be calculated, and so can that of spherical CCl_4 . Calculations of T_1 for the various moments of inertia of the 1,2-DCE molecule lead to the values shown in Fig. 6, which gives the minimal and maximal moments as well as a "mean" moment defined as the arithmetical average of the three principal moments.

For this "mean" moment, we give graphs of $\frac{1}{T_1}$ calculated for various assumed values of the "radius" r_A of the CCl_4 molecule and of that of the 1,2-DCE molecule. It is found that on going over from a 1,2-DCE "radius" of 2 Å to one of 4 Å the reciprocal relaxation time $\frac{1}{T_1}$ remains *grosso modo* unaffected and within error. However, the value of $\frac{1}{T_1}$ is highly sensitive to the moment of inertia. It results from a comparison of the experimental and calculated data that the molecule rotates on the average about an axis with respect to which its mean moment amounts to $I = \frac{1}{3}(I_x + I_y + I_z)$. Another conclusion to be drawn from such a comparison is that, for high concentrations, the phenomenon is adequately described by the BPP longitudinal magnetic relaxation model generalized by Gutowsky

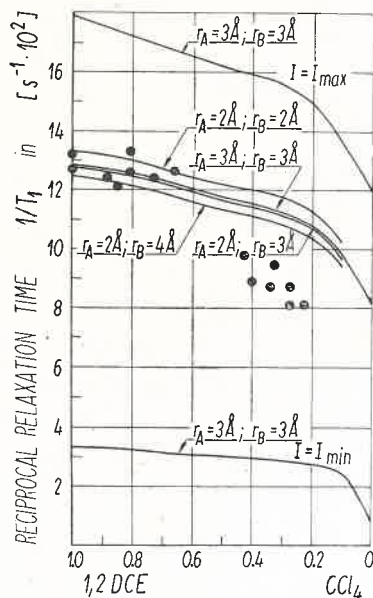


Fig. 6. Results of theoretical calculations of $1/T_1$ vs concentration of 1,2-DCE in CCl_4 :
 $I_{\max} = 5.77 \cdot 10^{-38} \text{ g} \cdot \text{cm}^2$, $I_{\min} = 0.37 \cdot 10^{-38} \text{ g} \cdot \text{cm}^2$, $I = 3.85 \cdot 10^{-38} \text{ g} \cdot \text{cm}^2$

and Woessner with correlation time according to Hill. This model fails to account for the discrepancies found in the dilute case.

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