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ROTATIONAL DIFFUSION MOTION OF PAA MOLECULES IN LIQUID CRYSTAL STATE

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Inelastic neutron scattering measurements were performed on PAA in liquid crystal state. Interpretation of the quasi-elastic results was by the circular random walk model with $N = 8$ sites and $K = 10^{10}\,\mathrm{sec}^{-1}$ rate constant.

THROUGHOUT the last few years inelastic neutron scattering measurements have been made on para-azoxy-anizol (PAA) in liquid crystal state.[1] The interpretation of the quasi-elastic neutron scattering data was based, at first, on the simple translational diffusion model, later on the basis of the continuous rotational diffustion model of Sears.[2,3] It was proved in references 1 and 3 that the continuous diffusion model is not suitable. It does not take into account properly the hindrance of rotation.

PAA i.e. $CH_3O{-}C_6H_4{-}N_2O{-}C_6H_4{-}OCH_3$ is nematic in the temperature range of 116–136°C its dielectric anisotropy $\epsilon_a = -0.21$. The liquid crystal material used in this experiment was synthesized in our department. The inelastic neutron scattering measurements at 121°C and various scattering angles were performed using a stochastic time of flight facility: reactor – single crystal – stochastic chopper – sample – detectors. The incident energy of neutron beam was $E = [4.26 \pm 0.07]$ meV.

The investigated material of 1 mm thickness was enclosed in a double-walled aluminium container by which the sample temperature was kept constant to within ± 0.1°C. The sample was not oriented by external magnetic or electric field and therefore the results correspond to the orientational average of the scattering over all molecular directions.

The interpretation of the results is based on the circular random walk[4] model. In this model the scattering particle (hydrogen) is located at the i-th site of a circle on whose circumference there are N sites. The particle is allowed to perform a random walk among these N sites. The probability that it will be found on the j-th site after t time is

$$P_{ij}(t) = \frac{1}{N}\sum_{l=1}^{N} e^{-t/\tau_l}\cos\frac{2\pi l\,(i-j)}{N} \tag{1}$$

where

$$\tau_l^{-1} = 4K\sin\frac{2\pi l}{N}. \tag{2}$$

K is a rate constant, and τ_l is the relaxation time. The scattering function, which is measured by neutron inelastic measurements is given by the equation

$$S(Q,\omega) = A_N(Q)\delta(\omega) + \frac{1}{\pi}\sum_{l=1}^{N} A_l(Q)\frac{\tau_l}{1+(\omega\tau_l)^2} \tag{3}$$

where

$$A_l(Q) = \frac{1}{N}\sum_{k=1}^{N} j_0\left(2Qa\sin\frac{\pi K}{N}\right)\cos\frac{2\pi lK}{N}$$

$$j_0(x) = \frac{\sin x}{x} \tag{4}$$

and d is the radius of the circle.

The measured quasi-elastic neutron spectra at different scattering angles compared with the calculated ones are shown in Fig. 1.

The folded ingoing spectra with the translational diffusion process,[1] $[D = (3.4 \pm 0.1) \times 10^{-6}]$ yield

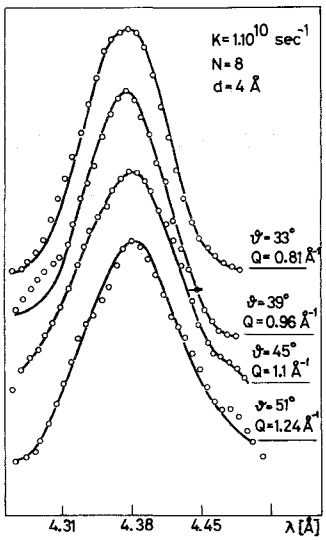

FIG. 1. Quasi-elastic spectra for PAA at 121°C in liquid crystal phase. ○; represents measured spectra. —; represents calculated spectra.

nearly elastic spectra, so the interpretation of the broadening is made on the circular random walk model with a single rate constant $K = 1.10^{10}\,\text{sec}^{-1}$ and parameters $d = 4$ Å, $N = 8$. At these parameters the fit was sensitive to K and N and not so sensitive to d. At four Q values the fit with the mentioned parameters (K, N, d) is shown in Fig. 1. With different K and N values there were spectra at certain Q values at which the fit was wrong.

From equation (2) we can calculate the relaxation times, and the values $\tau_4 = 2.5 \times 10^{-11}$ sec $\leqslant \tau \leqslant \tau_1 = 1.7 \times 10^{-10}$ sec are obtained. These values fit very well with the relaxation times determined from dielectric dispersion measurements,[5] where a distribution of relaxation times was found with the most probable values of $\tau_\perp = 2{,}5.10^{-11}$ sec, or $\tau_\parallel = 3.3 \times 10^{-11}$ sec. Supposing the Cole–Cole form[6] for the distribution of relaxation times with parameter $\beta \approx 0.18$ the fullwidth at half maximum is then $0.5\,\tau_\perp \lesssim \tau_\perp \lesssim 2\tau_\perp$. $\tau_\parallel$ and $\tau_\perp$ are connected with the rotation of the molecule around its short and long axes, respectively

It was found that the circular random walk model fits very well the experimental results obtained by quasi-elastic neutron scattering. The random rotation of the molecule around the nematic direction gives the important effect in quasi-elastic neutron scattering. The average radius for the rotation of protons around the nematic (preferred) direction is about $d = 4$ Å, the rate constant $K = 10^{10}$ sec, the most probable number of positions of the molecule around the nematic direction is $N = 8$; this value is understandable in that the molecule is asymmetric.

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