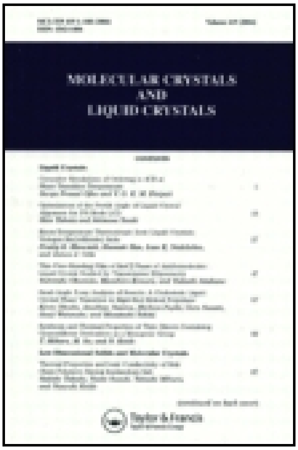

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Quasielastic Neutron Scattering to Determine Self-Diffusion Constants in Liquid p-Azoxyanisol

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Quasielasric scattering experiments on nematic p-azoxyanisol have been performed at relatively small scattering vectors ($K < 0.3 Å^{-1}$) and with a correspondingly high energy resolution ($4 \cdot 10^{-7}$ eV), using a backscattering neutron spectometer. The observed quasielastic width can be interpreted in terms of self-diffusion, and the resulting diffusion constant ($D = 4{,}1.10^{-6}$ cm^2/sec) agrees quite well with results from tracer experiments (Yun and Fredrickson). The quasielastic width measured by several other authors at relatively large K-values (several $Å^{-1}$) should be interpreted by rotational motions of the molecule with an estimated rotational diffusion constant of $D_r = 10^{10} .. 10^{11}$ sec^{-1}.

INTRODUCTION

In several papers (Blinc and Dimic,[1] Janik et al.,[2] Otnes et al.[3]) the self-diffusion of the molecules in the nematic phase of p-azoxyanisol (PAA) has been investigated by the method of quasielastic scattering of slow neutrons. The self-diffusion coefficients, as extracted from the widths of the quasielastic spectra, have been found to be several times larger than the values from C^{14}-tracer experiments (Yun and Fredrickson[4]). The aim of our work was to study the origin of this discrepancy with the help of the backscattering crystal spectrometer[5] whose energy resolution is about two orders of magnitude higher than that applied in the previous measurements. As will be seen the discrepancy can be understood and a general insight has been obtained with respect to the interpretation of such quasielastic scattering experiments on molecular liquids.

Theoretical background

The interaction of neutrons with an organic molecule is predominantly determined by incoherent scattering on the proton. As a consequence, the energy spectrum of the scattered intensity consists of a superposition of the spectra from the *different protons within one molecule*; each of these spectra is, in its term, determined by a convolution of the spectra due to the *various kinds* of motion imposed on this proton; this statement holds, if these motions are independent from each other. For simplicity, let us assume that a certain proton of the PAA molecule (e.g. one of the benzene ring) rotates around the long axis of the molecule, and, at the same time, performs a translational diffusion connected with the molecule as a whole. Formally, the timedependent intermediate scattering function for incoherent neutron-interaction reads then (see e.g. [6] [7])

$$I_s(K,t) \simeq I_s^{(t)}(K,t) \cdot I_s^{(r)}(K,t). \tag{1}$$

assuming independent motions; $I_s^{(t)}$ and $I_s^{(r)}$ are the intermediate scattering functions for translational (diffusive) and rotational motions, respectively. $\hbar K = \hbar (k_0 - k_1)$ denotes the momentum transfer during this scattering process. As a consequence of (1), the incoherent scattering law $S_{inc}(K,\omega)$ is a convolution of the scattering law $S_{inc}^{(t)}(K,\omega)$ for the diffusive motion with $S_{inc}^{(r)}(K,\omega)$ for the rotational motion. In an oriented nematic phase, the diffusion constant is a tensor (D_{ij}) which, in its diagonal form, has three components $D_{11} = D_{22} = D_\perp$, and $D_{33} = D_\parallel$. The corresponding scattering law reads then[8]

$$S_{inc}^{(t)}(K,\omega) = \frac{1}{\pi} \frac{D_\parallel K_z^2}{(D_\parallel K_z^2)^2 + \omega^2} \tag{2}$$

if K is choosen parallel to the nematic axis in z-direction. For K perpendicular to this direction, $D_\parallel$ must be replaced by $D_\perp$. For the non-oriented state of the nematic liquid, the anisotropic scattering law has to be averaged over all directions of K (and not D_{ij}!) with respect to the axis introduced before. As has been demonstrated[8] one can approximate this scattering law as follows

$$< S_{inc}^{(t)}(K,\omega) > \simeq \frac{1}{\pi} \frac{\bar{D} K^2}{(\bar{D} K^2)^2 + \omega^2} \tag{3}$$

where $\bar{D}$ is an effective diffusion constant; $\bar{D}$ approaches the diffusion constant for the isotropic medium

$$<D>_{orient} = \frac{1}{3} D_\parallel + \frac{2}{3} D_\perp \tag{4}$$

if the anisotropy is small. The full width at half maximum (fwhm) of the Lorentzian-shaped spectrum is then

$$\Delta E = 2\hbar K^2 D \tag{5}$$

where D stands for $D_{\parallel}$, $D_{\perp}$, and $\bar{D}$ or $\langle D \rangle$.

The rotational part $S_{inc}^{(r)}$ from (1) is more difficult to formulate. For a simple qualitative understanding, we describe it by an isotropic diffusive rotation of the molecule where one gets[6,9]

$$S_{inc}^{(r)}(K, \omega) = \delta(\omega)\, j_0^2\, (Kd) + \sum_{\ell=1}^{\infty} j_\ell^2\, (Kd)\, (2\ell+1) \frac{\ell(\ell+1)\, D_r/\pi}{[\ell(\ell+1) D_r]^2 + \omega^2} \tag{6}$$

D_r is the rotational diffusion constant[9,10]. d is the distance of the rotating proton from the center of gravity. Eq. (6) has to be averaged over all protons in the molecule. For large K-values (Kd>1), the quasielastic part of the spectrum (sum in Eq. (6)) dominates over the purely elastic term. The full width at half maximum of the resulting composite spectrum can be taken from numerical calculations as given in figure 3 of reference[9]; here the K-dependence can be approximately represented by the relation

$$\Delta E \simeq 0{,}4\, (Kd)^2\, D_r h \tag{7}$$

up to $(Kd)^2 \approx 15$.

By the convolution of $S_{inc}^{(r)}$ with $S_{inc}^{(t)}$, the $\delta(\omega)$-term in (6) reproduces directly the diffusive quasielastic spectrum (2) or (3). Obviously, a reliable separation of the rotational from the diffusive part of the spectrum is possible if

$$K^2 D < D_r$$

and if the first term in Eq. (6) is sufficiently large compared to the quasielastic part. This is the case for Kd<1. Obviously, a combination of measurements at large and at small *K* may allow a separate evaluation of the rotational and the translational diffusion constants.

Experiments and results

The PAA sample material had a purity of 99.67% (Merck Comp.). It has been filled into a flat aluminum container with a wall distance of 0.5 mm and an area of 3 cm². To orient the molecules, an electric voltage has been applied to the container walls, producing an electric field E ≈ 1 KV/cm. All scattering experiments have been performed in "transmission geometry" so that, with field, one had $E \perp K$. The energy spectra have been measured by means of the backscattering crystal spectrometer. Its resolution curve has been determined by scattering on a vanadium foil, and, as well, on a solid PAA sample at room temperature where diffusive broadening is supposed to be negligible (figure 1a). The experimental resolution (fwhm) varies from 3 to 7.10^{-7} eV, depending on the scattering angle. A typical quasielastic spectrum is shown in figure 1b. The spectra have been numerically corrected with respect to resolution, by fitting the measured quasielastic spectra and the resolution curves with Lorentzians. Figure 2 shows the corrected quasielastic widths ΔE, measured with and without field.

DISCUSSION.

In the introduction, a great discrepancy between quasielastic scattering experiments at large K^2, and tracer experiments[4] has been stated. On this basis, we interprete the width of the large -*K* experiments essentially in terms of a *rotational* motion of the molecule, and not by diffusion,† and we argue that our width at small *K* (figure 2) is due to translational diffusion.

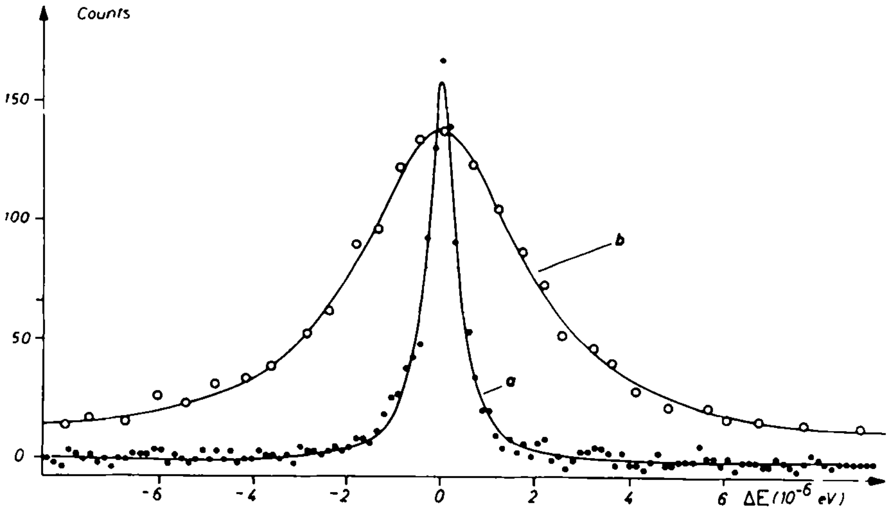

FIGURE 1 Typical energy spectrum of neutrons scattered on solid PAA (22°C, curve a; counts per 18 h) and nematic PAA (122°C, curve b, counts per 67 h) at $K = 0.27$ Å^{-1}, after background subtraction.

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† For simplicity, we neglect that the width at large K includes a diffusive contribution; it is small in view of the results from the tracer experiments.[4]

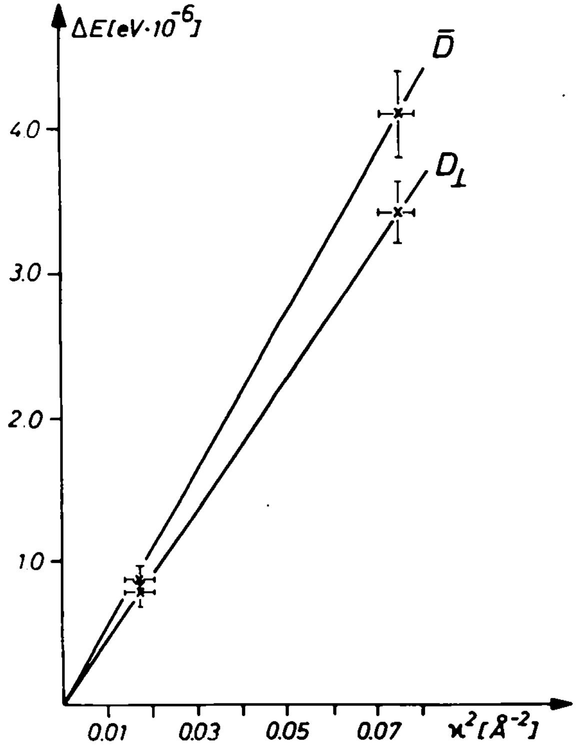

FIGURE 2 Full widths at half maximum ΔE of the quasielastic spectrum at 122°C, after resolution correction; D̄: Without electric field, and $D_\perp$: With field $E \perp K$.

Assuming, for simplicity, an isotropic rotation, we introduce the width at large *K* into Eq. (7) and obtain

$$D_r = 2{,}2 \cdot 10^{10}\ \text{sec}^{-1}\ (d = 6 \cdot 1\ \text{Å})\ \text{and}\ D_r = 9 \cdot 10^{10}\ \text{sec}^{-1}\ (d = 3\ \text{Å}).$$

(In the PAA molecule there are 6 protons with d = 6.1 Å, 4 with D = 5.1 Å and 4 with d = 3 Å). Unfortunately the neutron scattering experiment cannot find out what type of rotation this means; this question could be answered by partly deuterating the molecules, thus making certain protons "invisible".

For the small *K*-value as applied in our experiments, the spectral width due to rotation is essentially given by the $\ell = 1$ term in Eq. (6), namely

$$\Delta E_{\ell=1} = 4\hbar D_r = 0{,}6.10^{-4}\ \text{eV or}\ 2{,}4.10^{-4}\ \text{eV}$$

for d = 6 Å and 3 Å, respectively. This is much larger than our measured width which is, at $K = 0.27$ Å^{-1}

$$\Delta E = 4 \cdot 10^{-6} \text{ eV}.$$

Therefore, our width cannot be understood in terms of the rotational motion which has been taken from the experiments at large K. This rotational motion will only produce a "background" beneath the quasielastic spectrum; it must be very small because $\Delta E_{\ell = 1} \gg \Delta E$, and because, at the same time, the intensity of the rotational spectrum is of the same order of magnitude as its translational part, as can be calculated from Eq. (6). We should point out that in our argumentation we assumed a fully isotropic rotation. Actually, this will not be the case and D_r may come out still larger.

Interpreting now the quasielastic widths from figure 2 according to Eq. (5), we obtain the self-diffusion constants (table 1). The agreement with the tracer experiments confirms our interpretation. For comparison, the results as given in[2] (which are not "true" diffusion constants) are also included. The values for $D_\perp$ should be taken with certain precautions since the molecular orientation (which was produced by an electric field) may have been affected by molecular flow.

TABLE I

Self-diffusion constants of PAA at 122°C (in cm^2/sec).

	this experiment	tracer measurements$^{(4)}$	large K-experiments $^{(2)}$ "apparent D"
$\bar{D}$	$(4.1 \pm 0.3) \cdot 10^{-6}$	$(3.4 \pm 0.1) \cdot 10^{-6}$	$(14 \pm 1) \cdot 10^{-6}$
$D_\perp$	$(3.4 \pm 0.2) \cdot 10^{-6}$	$(3.1 \pm 0.1) \cdot 10^{-6}$	$(10 \pm 1) \cdot 10^{-6}$

Finally we point out the following: Assume one would, alternatively, try to interprete the width at small K in terms of a rotational motion which happens to fall into the proper frequency region of our experiment ($D_r \approx 10^9$ sec^{-1}). To be able to observe such a rotation, the corresponding quasielastic intensity must be sufficiently large. One can show that this would only be the case if the molecule performs a completely isotropic rotation; an amplitude as suggested by the fluctuation of the order parameter would not be sufficient.

The present results have demonstrated that, by combining experiments at relatively large and at small K-values, one is able to separate two different kinds of molecular motion of the PAA molecules. The results at small K can be understood in terms of ordinary diffusion.

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