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A quasielastic neutron scattering study of the self-diffusion coefficients for the homologous series of 4,4′-di-*n*-alkyloxyazoxybenzenes

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Incoherent quasielastic neutron scattering measurements performed with high resolution ($\sim 1\ \mu$eV) have provided the diffusion coefficients for translation of four members of the 4,4′-di-*n*-alkyloxyazoxybenzene series in their nematic phases. An odd–even effect in these coefficients was observed. The results were compared with those previously obtained by Noack via the NMR technique. There is fairly good agreement between his NMR and our QNS results.

1. Introduction

Diffusion coefficients for translation of 4,4′-dimethyloxyazoxybenzene (para-azoxyanisole, PAA) have been measured by various methods over the last twenty years. Several of these studies exploited the quasielastic neutron scattering technique (QNS) [1–4], in one case the tracer technique was applied [5], and the others have used a technique based upon NMR measurements [6, 7]. Some of the measurements were methodologically correct [4, 5], in others more or less arbitrary model assumptions were used [1–3]. It should be emphasised that for the QNS method it is essential to perform measurements at low neutron momentum transfer values, Q, and to use the $Q \to 0$ extrapolation, since only then do the diffusion coefficients correspond to the macroscopic scale, and, moreover, the molecular reorientation contribution is absent. Only [4] fulfils this condition. In any case a comparison of the various experimental techniques is probably a delicate matter.

Another aspect of the diffusion coefficient measurements is connected with comparison of results of several (first) members of a homologous series. For the 4,4′-di-*n*-alkyloxyazoxybenzene series such a comparison has been made by Noack [6], based upon his NMR results. An odd-even effect was obtained, the diffusion coefficients for substances with an even number of carbon atoms in the terminal alkoxy chains were relatively greater than for those with an odd number.

In consequence we decided to measure the average diffusion coefficients, $\bar{D}$, for four members of the alkyloxyazoxybenzene series (n-OAOB; $n = 1, 2, 3, 4$) by the QNS

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method. The measurements had two aims: to compare the results for PAA (1-OAOB) with previous results, and to verify the odd–even effect via the QNS method and to compare the results for this series with those of Noack's NMR measurements [6].

2. The experiment and the data analysis

The measurements were carried out on the IN10 neutron backscattering spectrometer at the Institute Laue-Langevin, Grenoble, France. The monochromatic neutron beam was obtained by Bragg reflection from the (1, 1, 1) planes of a perfect silicon crystal. This gives the incident neutron energy of 2·08 meV. The energy analysis of the scattered neutrons is obtained by (1, 1, 1) reflections from silicon single crystals at eight scattering angles: 8·60°, 15·50°, 23·80°, 34·70°, 61·0°, 94·0°, 112·0° and 138·0°. The respective neutron momentum transfers are: 0·150 Å^{-1}, 0·27 Å^{-1}, 0·413 Å^{-1}, 0·598 Å^{-1}, 1·017 Å^{-1}, 1·465 Å^{-1}, 1·661 Å^{-1} and 1·871 Å^{-1}. Only the four lowest angles provided results good enough for further analysis since the peaks broadened too much at higher Qs. The energy resolution was of the order of 1 μeV (FWHM). The instrumental function was obtained by scattering from a vanadium sample. All of the results were corrected for self-shielding effects and for neutron absorption in the sample. The analysis of the data proceeded via computer fittings of a convolution of a lorentzian lineshape and instrumental functions to the experimental data, after a computer subtraction of a linear neutron background.

The samples of 4,4′-dimethyloxyazoxybenzene (PAA, 1-OAOB), 4,4′-diethyloxyazoxybenzene (2-OAOB), 4,4′-dipropyloxyazoxybenzene (3-OAOB) and 4,4′-dibutyloxyazoxybenzene (4-OAOB) were placed in standard, flat wall aluminium sample holders, whose upper part was in thermal contact with a furnace. The temperature gradient between the top and the bottom, evidently a nuisance, amounted to about 4°C. The average temperature was taken. All measurements were made in nematic phases. The melting and clearing points for the samples under study are: $T_{\mathrm{CN}}=118{\cdot}2$°C and $T_{\mathrm{NI}}=135{\cdot}5$°C for 1-OAOB; $T_{\mathrm{CN}}=136{\cdot}6$°C and $T_{\mathrm{NI}}=167{\cdot}5$°C for 2-OAOB; $T_{\mathrm{CN}}=115{\cdot}5$°C and $T_{\mathrm{NI}}=123{\cdot}6$°C for 3-OAOB; $T_{\mathrm{CN}}=102{\cdot}0$°C and $T_{\mathrm{NI}}=136{\cdot}7$°C for 4-OAOB, We decided to carry out measurements at a constant temperature of 121°C for samples 1-OAOB, 3-OAOB and 4-OAOB. For the 2-OAOB sample we made measurements at two temperatures, 144°C and 154°C. Figure 1 presents an example of QNS results obtained for 2-OAOB, together with the results obtained with a vanadium sample, corresponding to the instrumental function for this particular scattering angle.

3. Results and discussion

The fitting procedure described in § 2 provided the HWHM (Γ) values (see figure 2). They were plotted versus Q^2 for each sample; figure 3 presents an example of such a dependence (2-OAOB at 154°C). For all of the samples investigated the initial (low Q) dependence was found to be linear. Only for large Q^2 was a deviation from linearity observed. We interpret the linear part as corresponding to the Vineyard continuous diffusion theory [8] according to which

$$\Gamma=\hbar Q^2 D.$$

The diffusion coefficients D were obtained from this formula, by determining the slope in the limit $Q^2 \rightarrow 0$. We shall not discuss other theoretical models since they are more appropriate for longer Q values; in the limit $Q \rightarrow 0$ these models converge to that of Vineyard.

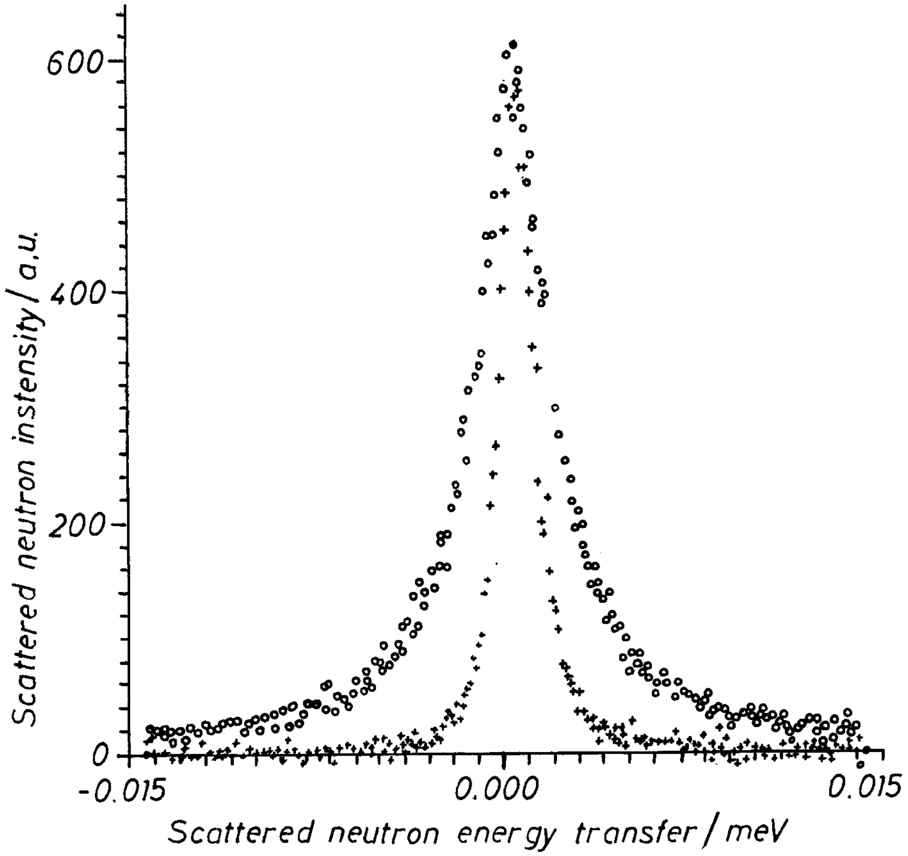

Figure 1. QNS patterns for 2-OAOB at 154°C (○) and for a vanadium sample (+). Scattering angle 8·6°. $Q = 0{\cdot}150\,\text{Å}^{-1}$.

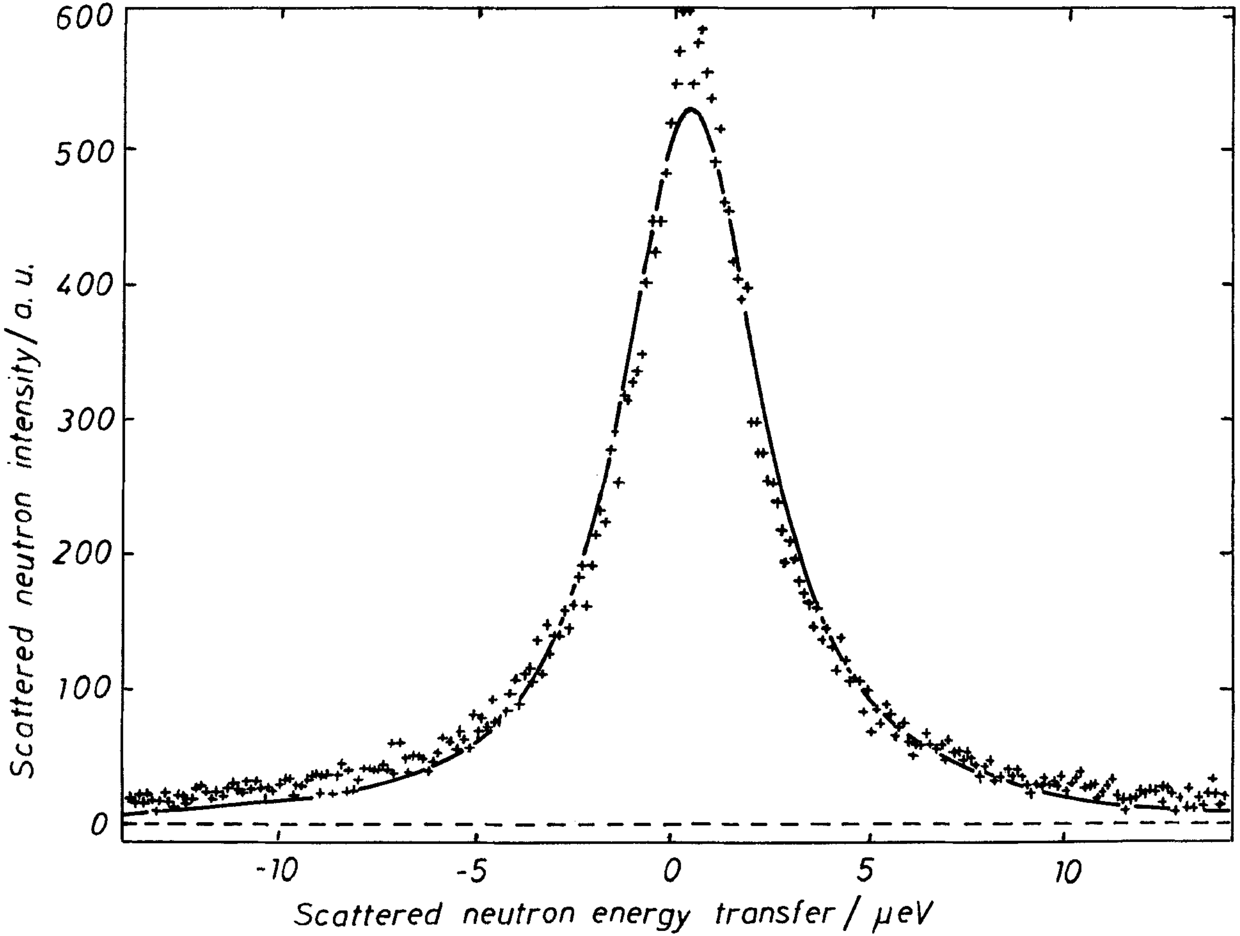

Figure 2. Example of curve fitting. Sample 2-OAOB (+) at 154°C. Solid curve: a fitted lorentzian convoluted with the instrumental function. Broken curve: background containing various motions faster than diffusion. $\Gamma = 1{\cdot}49\ \mu$eV corresponds to HWHM. $Q = 0{\cdot}150$ Å.

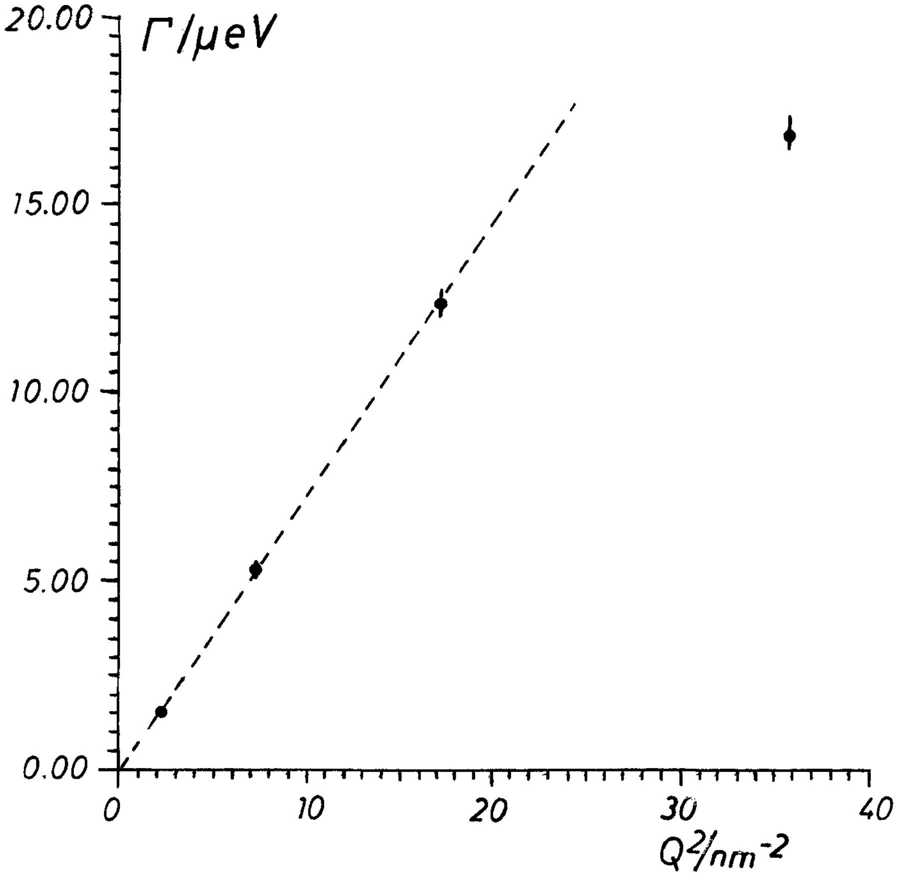

Figure 3. HWHM of the lorentzian curves obtained from the fitting, versus Q^2 for 2-OAOB at 154°C.

QNS obtained diffusion coefficients for nematic *n*-OAOBs.

Substance	Temperature/°C	$\bar{D}$/cm^2 s^{-1}	Substance	Temperature T_{NI}/°C	$\bar{D}$/cm^2 s^{-1}
1-OAOB	121	$5{\cdot}9\times10^{-6}$	1-OAOB	135·5	$10{\cdot}0\times10^{-6}$
2-OAOB	extrap. to 121	$6{\cdot}8\times10^{-6}$	2-OAOB	167·5	$14{\cdot}2\times10^{-6}$
3-OAOB	121	$6{\cdot}1\times10^{-6}$	3-OAOB	123·6	$6{\cdot}3\times10^{-6}$
4-OAOB	121	$5{\cdot}3\times10^{-6}$	4-OAOB	136·7	$8{\cdot}0\times10^{-6}$

We have decided to present two ways of comparing our results for the compounds investigated. In the first we determine the diffusion coefficients at a constant temperature of 121°C. In the case of 2-OAOB the values are extrapolated to this temperature using the results obtained at 144°C and 154°C. In the second method, we extrapolate the diffusion coefficients to the nematic–isotropic transition for each substance, using the activation energies obtained by Noack [6]. Such an extrapolation procedure seems to be fully justified, since the activation energy for 2-OAOB obtained from our measurements at just two temperatures is in good agreement with Noack's value ($22{\cdot}3\times10^3$ and $21{\cdot}4\times10^3$ J mole^{-1}, respectively). Both ways of treating the data provide diffusion coefficients for nematic phases and non-oriented samples. (The result for 121°C in the case of 2-OAOB corresponds to the extrapolated nematic phase.) The table presents these results.

The average diffusion coefficient, $\bar{D}$, obtained by us for 1-OAOB at 121°C, of $5{\cdot}9\times10^{-6}$ cm^2 s^{-1}, is a little larger than that obtained by Töpler *et al.* [14] in a similar neutron experiment at low Q, which provided the value of $4{\cdot}1\times10^{-6}$ cm^2 s^{-1}. The tracer method applied by Yun *et al.* [5] gave a value of about $3{\cdot}5\times10^{-6}$ cm^2 s^{-1}. Noack's (NMR) value is $6{\cdot}9\times10^{-6}$ cm^2 s^{-1} [6]. All of these data certainly differ beyond estimated experimental accuracies. We have to take into consideration the methodological difficulties in the determination of D, which no doubt lead to certain discrepancies.

A comparison of our QNS results for all four compounds with the NMR results obtained by Noack [6] was made after calculation of the $\bar{D}$ values from his values for $D_{\parallel}$ and $D_{\perp}$; $\bar{D}$ was calculated from

$$\bar{D}=\tfrac{1}{3}D_{\parallel}+\tfrac{2}{3}D_{\perp}.$$

Figures 4 and 5 present the comparison; the agreement between the two sets of data is fairly good. As we can see, the odd–even effect for the diffusion coefficients in the alkyloxyazoxybenzene series, previously obtained by Noack, has been reproduced in these QNS measurements, after their extrapolation to the nematic–isotropic transition. The odd–even effect at the constant temperature of 121°C is considerably reduced, but still visible in particular via the significantly larger $\bar{D}$ value for 2-OAOB.

It is worth mentioning that not only are the translational motions of molecules less hindered in the even members of the alkyloxyazoxybenzene series, but the same is valid for the reorientational motions [9–12]. We believe that for these two types of motions the same general explanation is valid: the motions are less hindered in compounds which are more orientationally ordered in the nematic phases, since the steric obstacles are smaller. If this is true, we should expect a relatively greater nematic order parameter in even members as compared to the odd ones. Indeed, an odd–even effect of the order

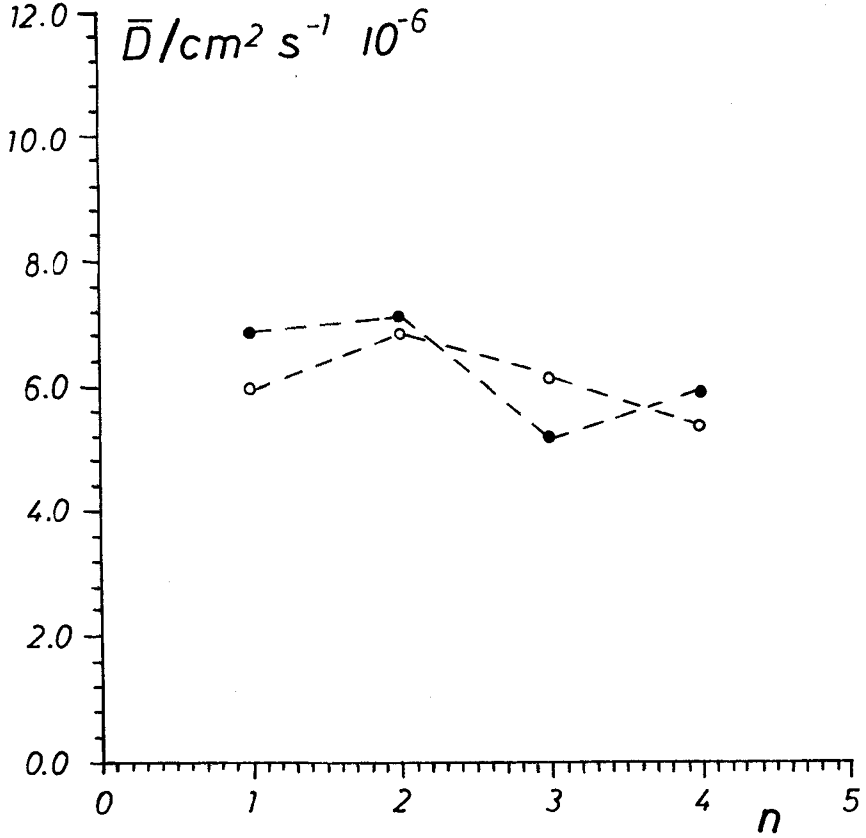

Figure 4. A comparison of our (QNS ○) and Noack's (NMR ●) diffusion coefficients for four members of the alkyloxyazoxybenzene series ($n = 1, 2, 3, 4$) in the nematic phases at 121°C. The results for 2-OAOB were extrapolated to this temperature. The broken curves are guides to the eye.

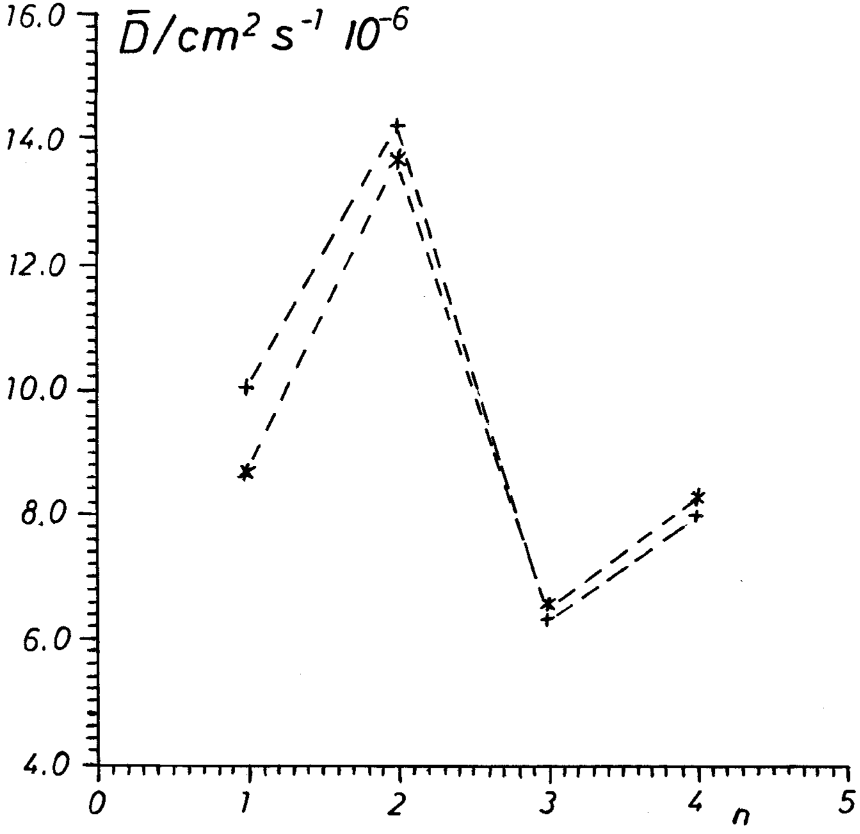

Figure 5. A comparison of our (QNS *) and Noack's (NMR +) diffusion coefficients for four members of the alkyloxyazoxybenzene series ($n = 1, 2, 3, 4$) in the nematic phases extrapolated to T_{NI} by using the activation energies determined by Noack. The broken curves are guides to the eye.

parameter has been obtained experimentally by Lippmann and Weber [13], and explained theoretically by Marcelja [14], for members of the alkyloxyazoxybenzene series.

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