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1997 J. Phys.: Condens. Matter 9 L403

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LETTER TO THE EDITOR

Pressure dependence of the dynamics of an organic inclusion compound investigated by incoherent quasielastic neutron scattering

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Received 16 May 1997

Abstract. The nitroxide $C_9H_{16}NO_2$ (referred to as tano) forms channel inclusion compounds with linear hydrocarbons. At room temperature, both tano and chain molecules are dynamically disordered. When the temperature is decreased, one phase transition is observed. The pressure dependence of the temperature of transition and the evolution of the individual motions have been studied by incoherent quasielastic neutron scattering in the case of a tano–octane system. The transition temperature increases with the pressure with a slope $(dT_t/dP)_{P=0} = 24 \text{ K kbar}^{-1}$. The transition mechanism is connected to the lock-in of both tano (interconversion) and chain (reorientation) molecules, as a result of strong correlations between host and guest substructures. A residual disorder persists in the low-temperature phase confirming that all the tano molecules are not dynamically equivalent.

1. Introduction

The nitroxide 2, 2, 6, 6-tetramethyl-4-oxopiperidine-1-oxide ($C_9H_{16}NO_2$), referred to as tano, forms inclusion compounds with a wide range of linear chains (alkanes, alcohols, etc). These structures may be characterized by a framework of tano molecules with open parallel channels, in which the chains are embedded. At room temperature, all the tano inclusion compounds are monoclinic ($C2/c$, $Z = 24$) with similar crystallographic parameters ($a = 36 \text{ \AA}$, $b = 5.95 \text{ \AA}$, $c = 35.5 \text{ \AA}$, $\beta = 120^\circ$), revealing a similar organization of the whole tano matrix. There are four channels parallel to b in a cell, 18 \AA apart and 5 \AA in diameter (see figure and description of the structure in [1]).

X-ray rotating photographs revealed a system of periodic homogeneous diffuse layers, perpendicular to the b axis, characteristic of the nature of the guest species and typical of the diffraction by uncorrelated linear chains of molecules [2]. Projection of the structure parallel to the b axis evidenced an orientational disorder of the chains around their long axis [2]. This was also evidenced by quasielastic neutron scattering studies of alkyl [3] and mono-brominated alkyl [4] chains. In the latter case, the anisotropy of this motion was recently investigated with semi-oriented samples [5].

Moreover, in the high-temperature phase, tano molecules can adopt one of their two enantiomeric forms by a ring inversion process and 120° reorientation of the methyl groups occurs [3,4]. This highly disordered structure undergoes one or two phase transitions,

depending on the length of the included chains. When the temperature is decreased, diffuse layers disappear and a new superstructure appears indicating a 3D ordering of the alkanes [2, 6]. The b parameter is multiplied by an integer and becomes commensurable with the guest length.

The ordering mechanism can be related to the existence of different interactions between host–host, host–guest and guest–guest molecules. These competing temperature-dependent interactions are responsible for the existence of dynamical disorders and different phase transitions.

Although x-ray diffraction studies evidenced the development of orientational ordering of the alkane molecules, together with a reorganization of the tano matrix in the low-temperature phase, the mechanism of transition was not established. A detailed knowledge of the dynamical properties on both sides of the transition is necessary for a better understanding of the lock-in process. Studies under pressure can be an effective way to modify and tune the different interactions responsible for the dynamical properties, and thus to provide crucial information about the transition mechanism.

These considerations motivated the present work where we have investigated, through incoherent quasielastic neutron scattering (IQNS), the influence of hydrostatic pressure on tano inclusion compounds. In this paper, the evolution of the temperature of transition as a function of the pressure, and the change in the local motions encountered in the high- and low-temperature phases are presented, in the case of the tano–octane adduct.

2. Experimental details

Tano–octane adduct has been chosen for this study because its phase diagram at atmospheric pressure is quite simple, as shown by extensive previous results [3].

Selectively deuterated samples were used in order to investigate separately the motions of the chains and those of the tano molecules. Due to the large incoherent scattering cross-section of hydrogen ($\sigma_{inc} = 80 \times 10^{-24} \text{ cm}^2$), the main contribution to the scattered intensity arises from the hydrogen atoms in the specimen. By replacing hydrogenated molecules by deuterated ones ($\sigma_{inc} = 2 \times 10^{-24} \text{ cm}^2$), the motions of the tano molecules and of the alkyl chains can, in principle, be investigated separately.

Polycrystalline samples of hydrogenated tano–hydrogenated octane (TH/C8H) and deuterated tano–hydrogenated octane (TD/C8H) were obtained from rapid evaporation of tano–octane solution.

The IQNS experiments were performed at the Institut Laue–Langevin (ILL Grenoble France). The dynamics of the tano–octane system were investigated with the multichopper time-of-flight spectrometer IN5, at a wavelength of 7 Å, and with an instrumental energy resolution of 40 μeV . Spectra were simultaneously recorded at 89 angles, ranging from 11° to 136°. Other experiments were carried out with the high-resolution backscattering spectrometer IN16, with a wavelength of 6.28 Å and a resolution of 1.2 μeV .

Taking advantage of the different time-scales available on these two spectrometers (IN5: 10^{-10} s, IN16: 10^{-9} s), it was possible to analyse separately the effects of the pressure on the different types of motion.

The sample was placed in an aluminium alloy pressure cell (pressure range of 0–5 kbar) using gaseous helium as a pressure medium. All the experiments were carried out with an ILL-standard cryostat. Deviations in the temperature stability were less than half a degree.

3. Effect of hydrostatic pressure on the transition temperature

The phase transitions were evidenced by measuring the elastic intensity as a function of the temperature at constant pressure (IN16), or by inspecting carefully the variation of the elastic part of the spectra as a function of the pressure at constant temperature (IN5). The resulting phase diagram is represented in figure 1.

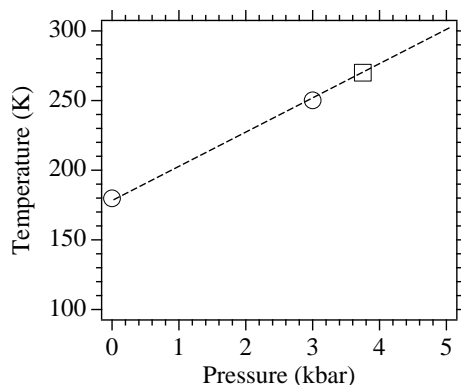


Figure 1. Evolution of the temperature of transition with pressure. ○, IN16 experiment; □, IN5 experiment.

The temperature of transition T_t increases with pressure in the range 0–5 kbar. As the transition is supposed to be related to the reorientational motions of both tano and chain molecules, one can intuitively understand that the effects of the pressure on the intermolecular separations would hinder these displacements, resulting in a higher T_t .

To the accuracy of our measurements, the transition temperature increases linearly with the pressure, with a slope $(dT_t/dP)_{P=0} = 24 \text{ K kbar}^{-1}$. The specific heat $(\Delta H_t)_{P=0}$ associated with the transition from the high- to the low-temperature phase is found to be equal to 2.4 cal g^{-1} using the Clausius–Clapeyron relation

$$\left(\frac{dT_t}{dP}\right)_{P=0} = T_t \frac{\Delta V_t}{(\Delta H_t)_{P=0}}$$

and considering the pressure derivative of 24 K kbar^{-1} and a molar volume variation $(\Delta V/V) = 1.65\%$ at the transition, deduced at $P = 0 \text{ kbar}$ from x-ray experiments. This value is in good agreement with that obtained from previous differential scanning calorimetry measurements: $\Delta H_t = 2.0 \pm 0.2 \text{ cal g}^{-1}$. The relative high value compared to the enthalpy of fusion ($\Delta H_t/\Delta H_f = 13\%$) was explained by the participation of the tano molecules in the phase transition mechanism (reconstructive first-order transition) [1].

4. Effect of hydrostatic pressure on the local motions

Previous experiments [3] focused on tano–heptane and tano–octane adducts at atmospheric pressure concluded that three different thermally activated processes exist: reorientation of the guest species, tano ring interconversion and 120° methyl rotation. At $T = 270 \text{ K}$, the correlation times were evaluated to be $9.4 \times 10^{-11} \text{ s}$, $6.6 \times 10^{-10} \text{ s}$ and $2.7 \times 10^{-11} \text{ s}$ respectively, with corresponding activation energies of 5, 31 and 13 kJ mol^{-1} . Thus, the

ring inversion yielded a quasielastic broadening of $2 \mu\text{eV}$ (FWHM) typically accessible to IN16 experiments (resolution $1.2 \mu\text{eV}$ FWHM), while the two others were easily observed on the IN5 spectrometer (resolution $40 \mu\text{eV}$ FWHM at 7 \AA). However, on decreasing the temperature near the phase transition (185 K), these motions are slowed down, and their observation was no longer possible on the time scale of the instruments. One could expect that the shift of the transition to higher temperature with increasing pressure would allow us to evidence more clearly the behaviour of the different motions involved during the lock-in process.

In this part, we present preliminary qualitative features of the observed spectra, as a function of pressure. A more precise analysis will be devoted to the quantitative evolution of the relevant parameters (elastic incoherent structure factor, correlation times, etc) and will be the object of a future publication.

4.1. Effects on the ring inversion (TH/C8H, IN16)

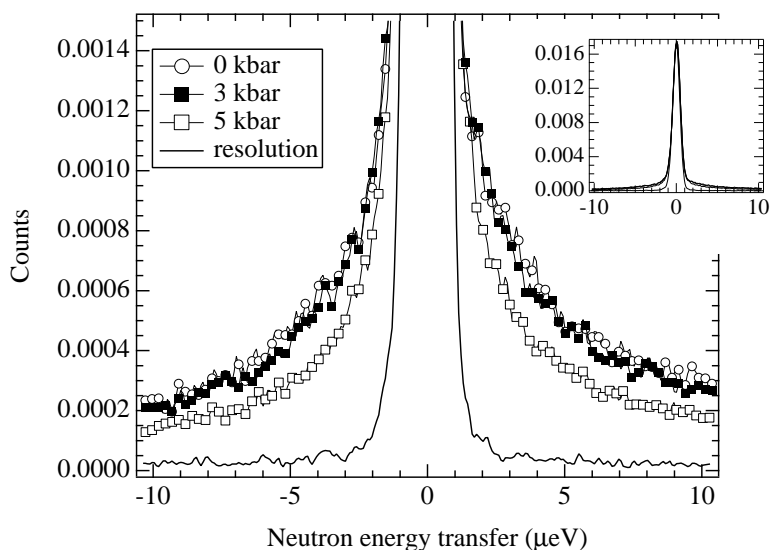


Figure 2. Typical spectra recorded at $T = 270 \text{ K}$, $Q = 1.6 \text{ \AA}^{-1}$, for different pressures (TH/C8H) from the IN16 experiment. The data at $P = 0$ and 3 kbar correspond to the high-temperature phase. At $P = 5 \text{ kbar}$, the system is in the low-temperature phase. The resolution of the instrument is also indicated. Only a third of the experimental points are represented.

Typical spectra for a momentum transfer $Q = 1.6 \text{ \AA}^{-1}$ are presented in figure 2, at $T = 270 \text{ K}$ for $P = 0, 3$ and 5 kbar , where they are compared to the resolution curve. According to the phase diagram, the adduct is in its high-temperature phase at $P = 0$ and 3 kbar , while it is in the low-temperature phase at $P = 5 \text{ kbar}$. The quasielastic broadening measured in the two high-temperature phases ($P = 0$ and 3 kbar) show only slight difference. Nevertheless, the important point is the persistence of large-amplitude motions at $P = 5 \text{ kbar}$ (in the low-temperature phase) even if the quasielastic part is clearly reduced. The same phenomenon is still observed at $T = 250 \text{ K}$, between $P = 0 \text{ kbar}$ (high-temperature phase) and $P = 3 \text{ kbar}$ (low-temperature phase) where both quasielastic components differ from each other. Actually, from x-ray measurements, it was found that the transition mechanism is

related to the lock-in of the interconversion of the tano molecules. The dynamical behaviour of the ring interconversion confirms this assumption even if residual motions persist in the low-temperature phase. The determination of the nature of these displacements would require a more detailed analysis. One possible explanation would be to consider that all the tano molecules are not dynamically equivalent with respect to the octane chains.

4.2. Effects on methyl and guest molecule reorientations (TH/C8H, TD/C8H, IN5)

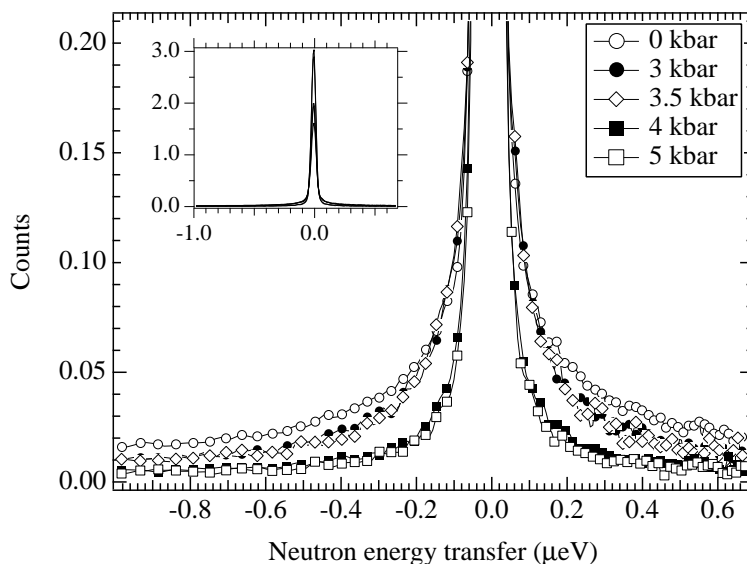


Figure 3. Typical spectra recorded at $T = 270$ K, $Q = 1.6 \text{ \AA}^{-1}$, for different pressures (TD/C8H) from the IN5 experiment. The data at $P = 0, 3$ and 3.5 kbar correspond to the high-temperature phase. At $P = 4$ and 5 kbar, the system is in the low-temperature phase. Only a third of the experimental points are represented.

In order to get information about the individual motions, the experiments were carried out with selectively deuterated samples. The chain reorientations were evidenced by a large quasielastic broadening (FWHM $15 \mu\text{eV}$ at $T = 270$ K) in the TD/C8H system. Spectra recorded at $P = 0, 3$ and 3.5 kbar (high-temperature phase) are presented in figure 3 and show a similar pressure dependence as that previously observed for tano ring inversion. Between 3.5 and 4 kbar, the transition occurs, and the quasielastic part considerably decreases, but still persists. Indeed, the transition process involves the lock-in of the chains, as previously suggested by x-ray studies. The residual motions observed in the low temperature phase cannot be identified at this stage, and would require the complete analysis of the scattering function. Nevertheless some information is provided by the analysis of the methyl reorientations in TH/C8H adduct (figure 4). In this case, the evolution of the quasielastic broadening is less pronounced at the phase transition. Thus these motions persist down to the transition and do not seem to be affected by the lock-in process. Because of the small amount of alkane with respect to the tano molecules (5% in weight), the contribution of the matrix to the incoherent scattering is still very important in the case of the TD/C8H system (about 29%) [3]. As the methyl reorientations occur

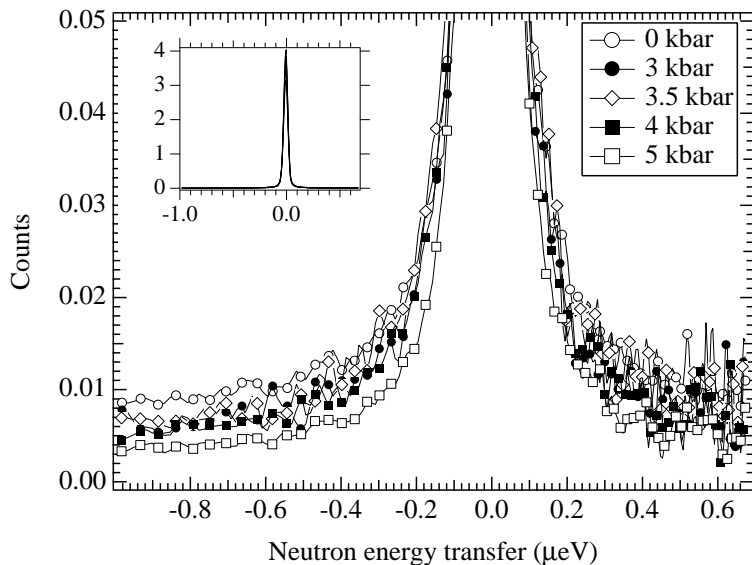


Figure 4. Typical spectra recorded at $T = 270$ K, $Q = 1.6 \text{ \AA}^{-1}$, for different pressures (TH/C8H) from the IN5 experiment. The data at $P = 0, 3$ and 3.5 kbar correspond to the high-temperature phase. At $P = 4$ and 5 kbar, the system is in the low-temperature phase. Only a third of the experimental points are represented.

even in the low-temperature phase, the residual broadening observed in figure 3 could arise from the deuterated methyl groups and it seems reasonable to state that the motion of the included chains is frozen at the phase transition.

5. Conclusions

In this letter, we have presented the main effects of hydrostatic pressure on the dynamics of the highly disordered tano–octane adduct.

The temperature–pressure phase diagram was roughed out in the 120–300 K and 0–5 kbar ranges. In spite of a restricted set of data, a linear variation of T_t as a function of the pressure was established, the slope $(dT_t/dP)_{P=0}$ being equal to 24 K kbar^{-1} . This value yielded an enthalpy of transition of 2.4 cal g^{-1} , in accordance with a previous calorimetric study.

So, by increasing the pressure, the transition was shifted to higher temperature. Thus, it turned out that the residual motions in the low temperature phase occurred with faster characteristic correlation times, and could be observed within the resolution of the two instruments. Under the assumption that the nature of these motions is not changed under pressure, we could in particular observe to what extent these different involved molecular motions were affected by the lock-in process occurring at the phase transition.

Although an accurate description of the dynamical disorder would certainly require a more quantitative analysis, the most interesting features of the pressure dependence of the motions were qualitatively evidenced, i.e.:

(i) the chain reorientation and the tano interconversion are dramatically reduced during the lock-in process;

(ii) the methyl reorientation does not change when crossing the transition;
(iii) some quasielastic broadening is still measured on IN16 in the low-temperature phase, due to the persistence of large-amplitude motions. That could be a consequence of the existence of non-equivalent tano molecules, with respect to the octane chains during the lock-in process. Indeed, x-ray experiments evidenced a very unequal residual disorder persisting in the ordered low-temperature phase [1].

The authors thank B Frick and J L Mélési at the Institut Laue–Langevin for their technical assistance during the experiments.

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