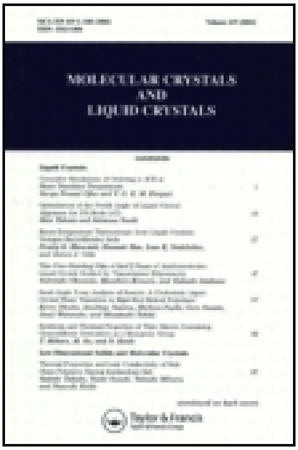

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Solid State NMR Studies of n-Alkane/urea Inclusion Compounds

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Solid State NMR Studies of n-Alkane/Urea Inclusion Compounds

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The molecular characteristics of n-alkane chains in urea inclusion compounds are examined over a large temperature range (100 K to 300 K) using dynamic ^2H NMR techniques. Particular emphasis is given to the guest properties in the vicinity of a solid-solid phase transition which is known to be accompanied by a distortion of the urea lattice. The analysis of the NMR data reveals several intra- and intermolecular motional processes which are responsible for spin relaxation in these systems. Likewise, it can be distinguished between conformational and overall chain order. Both the molecular dynamics and chain ordering are found to be strongly affected by the solid-solid phase transition. It is concluded that with respect to the guest components the phase transition can be assigned to a dynamic order-disorder transition.

Keywords: urea inclusion compounds; ^2H NMR spectroscopy

INTRODUCTION

Urea is well known to form inclusion compounds with a great number of guest components[1] which at room temperature can be described by hexagonal urea channels of "infinite" length. Due to the rather narrow urea channels, only n-alkanes and some derivatives can be used as guest components. X-ray studies have shown that the hexagonal symmetry of the urea channels, being stable at room temperature, is distorted upon cooling the samples below a solid-solid phase transition; the actual transition temperature varies with the guest species incorporated in the channels[2]. In the past, several studies have been performed, employing X-ray, calorimetry or spectroscopic techniques (IR, Raman or NMR), which were addressed to the molecular behaviour of the guest components in such systems[3-5]. The majority of these studies dealt with the behaviour in the high temperature (HT) phase. Here, it has been reported that the guest species possess a high molecular mobility which is accompanied with a large degree of orientational disorder[3]. However, the knowledge about the molecular behaviour of the guest components in the low temperature (LT) phase is very limited. In this contribution we present ^2H NMR investigations on urea inclusion compounds with selectively deuterated n-alkanes of different lengths (n = 15, 16, 19, 20). Particular emphasis is given to the behaviour in the LT phase and in the vicinity of the solid-solid phase transition.

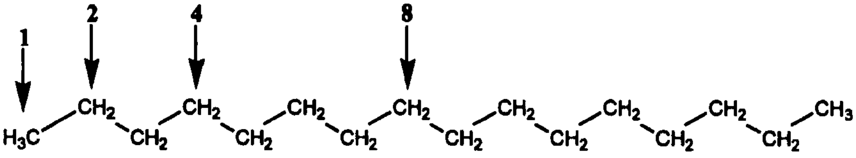

FIGURE 1 Deuterated positions in the n-hexadecane guest molecule.

EXPERIMENTAL

Selectively deuterated n-alkanes (see Fig. 1) were synthesized as described elsewhere[6]. Samples of inclusion compounds were prepared from a methanolic solution of urea and the desired selectively deuterated guest component according to standard procedures. NMR measurements were performed on a Bruker CXP 300 spectrometer which operates at a frequency of 46.07 MHz for deuterium. The ^2H NMR spectra were obtained using a 5 mm probe employing the quadrupole echo sequence with $\pi/2$-pulses of 2 μs width and a time interval between the pulses of 20-30 μs. Spin-lattice relaxation times were measured by the inversion recovery method. Simulations have been performed using a FORTRAN simulation package developed to simulate the various types of dynamic NMR experiments[6].

RESULTS AND DISCUSSION

Samples of n-alkane/urea inclusion compounds have been studied with dynamic ^2H NMR techniques. To begin with, we discuss the results for the n-hexadecane/urea system which is known to undergo a phase transition at 156 K.

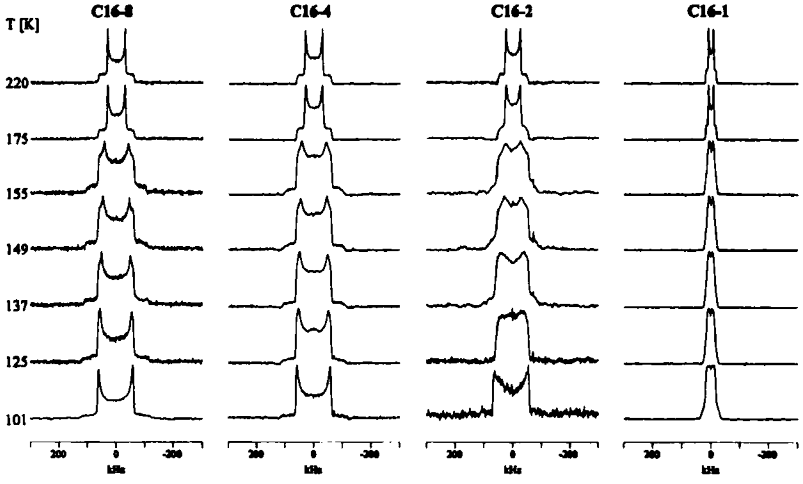

FIGURE 2 Variable temperature ^2H NMR spectra of the different selectively deuterated n-hexadecane molecules in urea.

Fig. 2 exhibits representative ^2H NMR spectra which were obtained from four different samples. Each of them refers to a different selectively deuterated hexadecane (see Fig. 1). It is quite obvious that the experimental ^2H NMR spectra depend on the actual deuterated position within the hexadecane chains, temperature and phase (i.e. LT or HT phase). Model simulations have shown that the molecular dynamics of the hexadecane chains can be described by the assumption of the following motional contributions: (i) overall chain rotation about the chain long axis which is restricted (LT phase) or almost unrestricted (HT phase), (ii) trans-gauche isomerization of the C2-C3-bonds, (iii) methyl group rotation. For the chain order it is found that the chains are perfectly aligned within the urea channels, i.e. there is no evidence for a wobbling motion of the chain perpendicular to the long axis. At the same time, the inner parts of the hexadecane chains exist exclusively in the trans-conformation, while the outer segments also contain some amount of gauche-conformers (see below). The data analysis has shown that the molecular motions already occur in the fast motional limit. Spin-lattice (T_1) relaxation experiments therefore have been performed in order to quantify the timescale of the various motional contributions.

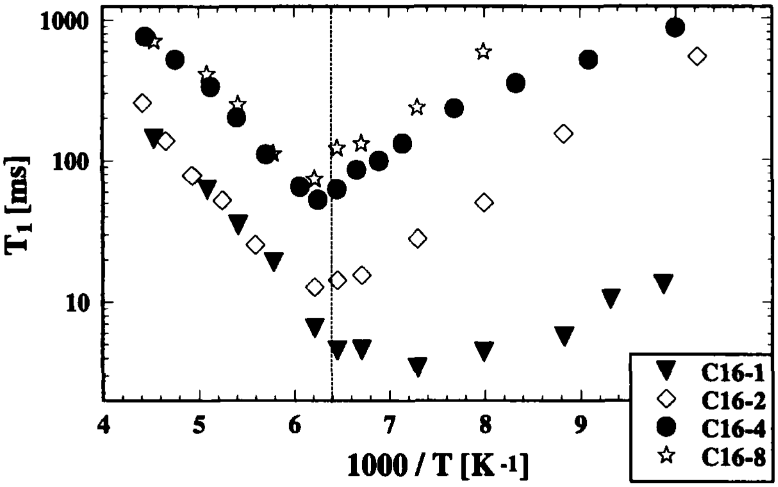

FIGURE 3 T_1 relaxation data for n-hexadecane/urea.

Fig. 3 summarizes the T_1-data observed for the various samples, while Figure 4 shows representative partially relaxed spectra from the T_1-experiment (LT and HT phase) of sample C16-8 together with their best simulations. It has been shown that such partially relaxed spectra (which reflect the T_1-anisotropy) are very useful for the determination of the type and timescale of the underlying molecular motions responsible for spin relaxation[6].

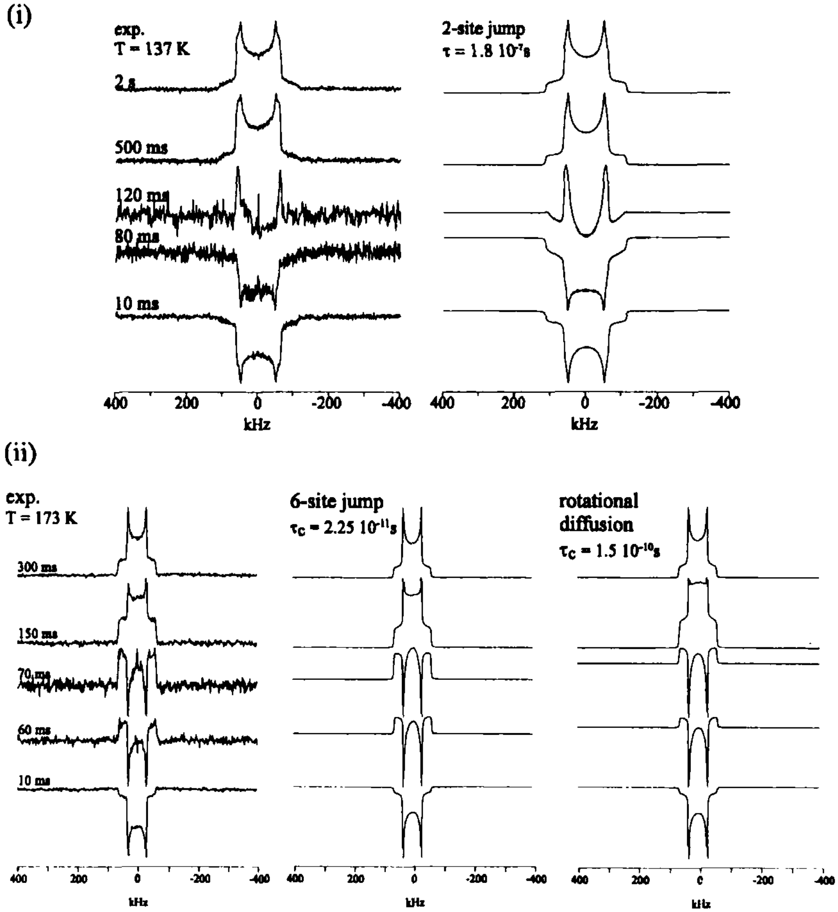

FIGURE 4 Partially relaxed spectra of C16-8/urea: (i) LT and (ii) HT phase. To emphasize the T_1 anisotropy all spectra are plotted to the same height.

The analysis of these relaxation data has shown that in the LT phase the hexadecane chains are only allowed to undergo restricted overall rotations which can be described by a two-site jump process. The jump angle varies almost linear with temperature reaching an upper limit of 39° close to the phase transition. The rate constant for this process is in the order of 10^{-7} s^{-1} with an activation energy of E_a = 6.2 kJ/mol. At the phase transition this overall motional process is significantly altered. In the HT phase the chains are able to undergo almost unrestricted chain rotation which can be modelled by either six-fold jumps or by a rotational diffusion process. In addition, the timescale has changed by almost three orders of magnitude. Hence, the rate constants for overall rotation are found in the order of 10^{-10} s^{-1} with an activation energy of 12.5 kJ/mol. It therefore is concluded that the solid-solid phase transition can be assigned to a (dynamic) order-disorder transition. The hexadecane molecules are rotationally disordered in the HT phase.

At the same time, the data analysis has shown that near the chain ends (C2-C3-bond) trans-gauche isomerizations occur which again are on the fast timescale for both the LT and HT phases. The rather small T_1-values observed for the sample with hexadecane, deuterated at the methyl group, can be attributed to the methyl group rotation which dominates spin relaxation in the LT phase (rate constant in the order of 10^{-10} s^{-1} at 140 K, E_a = 8.3 kJ/mol). This latter observation is very general and has been observed also for urea inclusion compounds with n-alkanes of other lengths (n = 15, 19, 20) bearing deuterated methyl groups.

Concerning the chain ordering, it has been mentioned earlier that the chains are perfectly aligned within the channels throughout the whole temperature range studied here. That is, the chains are unable to undergo wobble motions perpendicular to their long axes which would cause some degree of orientational disorder. An interesting behaviour is found for the conformational order of the alkane chains. While the inner parts of the chains exist in the trans-conformation, for the C2-C3-bond near the chain ends the amount of trans-conformers is less than unity. Moreover, the actual number depends on the phase and on the length of the aliphatic chains. In Fig. 5 representative ^{2}H NMR spectra are given for samples containing deuterated methyl groups.

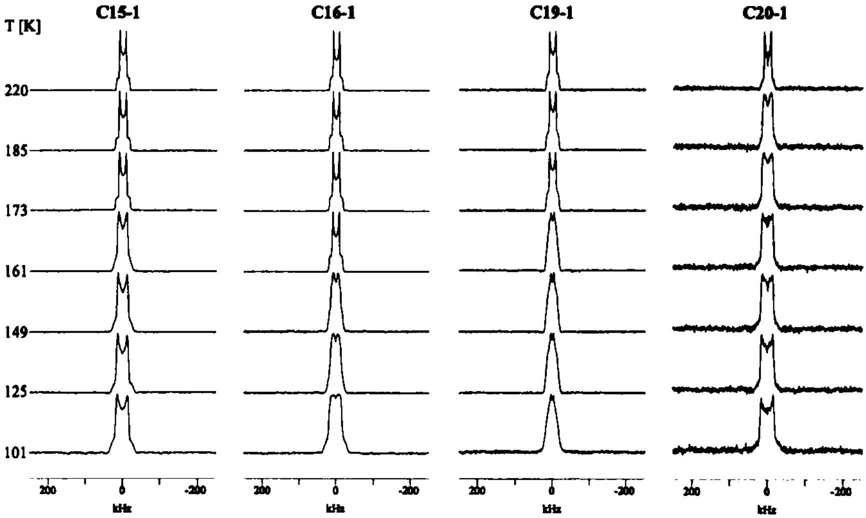

FIGURE 5 Variable temperature ^{2}H NMR spectra of n-alkanes (C_nH_{2n+2}, n = 15, 16, 19, 20) deuterated at the terminal methyl group.

Generally, it is found that the amount of trans-conformers increases significantly upon passing from the LT to the HT phase. Thus, for n-hexadecane the amounts of trans-conformers are given to $p_t = 0.7$ and $p_t = 0.95$ in the LT and HT phase, respectively. A similar trend has been observed for the other systems as well. At present, the reasons for this observation are unknown. One might, however, speculate whether sterical effects due to a stronger interaction of the chain ends in the LT phase are responsible for this unusual phenomenon.

CONCLUSION

It has been shown that n-alkanes in urea are highly mobile displaying a high degree of rotational disorder in the high temperature phase. The solid-solid phase transition is accompanied by a distortion of the hexagonal symmetry of the host channels. As a direct consequence, in the LT phase the alkane overall motion becomes highly restricted (order-disorder transition). Furthermore, the conformational properties at the chain ends also are affected by the solid-solid phase transition. This molecular property seems to be unusual in the sense that in the LT phase the conformational order near the chain ends is significantly lower than in the HT phase.

Acknowledgments

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