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# Solid State $^2$H NMR Studies of n-Alkanes Confined in Solid Matrices

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# Solid State $^2$H NMR Studies of n-Alkanes Confined in Solid Matrices

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$^2$H NMR spectroscopy is used to study the molecular behaviour of selectively deuterated n-alkanes of variable length that serve as guest molecules in channel-forming inclusion compounds, made from urea, cyclophosphazene or α-cyclodextrin. In the present study $^2$H NMR lineshape and relaxation experiments are performed which provide a deeper insight into the motional characteristics as well as the ordering behaviour of such spatially confined guest molecules. The analysis of these experiments reveals the presence of chain motions that are found to depend strongly on the particular host matrix.

*Keywords:* $^2$H NMR spectroscopy; inclusion compounds; n-alkanes

## INTRODUCTION

n-Alkanes are known to form inclusion compounds with various host components. Among these, the class of urea inclusion compounds is well known and has been studied in great detail. Urea inclusion compounds are characterized by the formation of hexagonal channels that are stabilized by the incorporation of suitable guest components. It is known that at room temperature the guest molecules are highly mobile displaying a substantial amount of orientational disorder.[1] More recently, $^2$H NMR investigations on the hexadecane/urea inclusion compounds have shown that the guest mobility can be frozen in on the NMR time scale upon cooling the sample down to about 100 K.[2] In the present work representative results are reported from a recent variable temperature $^2$H NMR study on the n-pentadecane/urea inclusion compound. In addition, complimentary $^2$H NMR studies on inclusion compounds from cyclophosphazene and α-cyclodextrin are presented, where again n-alkanes serve as guest molecules. Such investigations should provide further information about the specific influence of the host matrix on the molecular properties of the alkane guests.

## EXPERIMENTAL

Selectively deuterated n-alkanes were synthesized as described elsewhere[2]. Samples of inclusion compounds from urea, tris-(1,2-dioxyphenyl)-cyclotriphosphazene[3] and α-cyclodextrin[4] were

prepared according to literature procedures. NMR measurements were performed on a Bruker CXP 300 spectrometer which operates at a frequency of 46.07 MHz for deuterium. The $^2$H NMR experiments above 90 K were done using a home-built probe (5 mm coil) employing the quadrupole echo sequence (lineshapes, spin-spin relaxation studies) and a modified inversion recovery sequence[5] (spin-lattice relaxation studies) with a $\pi/2$-pulse width of 2.2 μs. The spectra were acquired with a fixed delay between the pulses of 20 μs. For the low temperature measurements a commercial Bruker low temperature probe was used. Here, the $\pi/2$-pulse width varied with temperature between 5.2 and 4 μs. Computer simulations were done with appropriate FORTRAN programs that consider various types of guest motions.[2] In the theoretical spectra the finite pulse widths – in particular during the low temperature experiments – has been taken into account by a correction described in Ref. [6].

## RESULTS AND DISCUSSION

Inclusion compounds from urea, cyclophosphazene and α-cyclodextrin with n-alkanes have been studied by $^2$H NMR spectroscopy. To begin with, we present results for the n-pentadecane/urea clathrate that has been studied between 100 K and room temperature. At room temperature hexagonal urea channels are formed. At 155 K a solid-solid phase transition is observed that is accompanied by a distortion of the hexagonal host lattice.[7] Fig. 1 contains experimental spectra that refer to four samples with n-pentadecane, deuterated at position C-1, C-

2, C-4 or C-8, respectively.

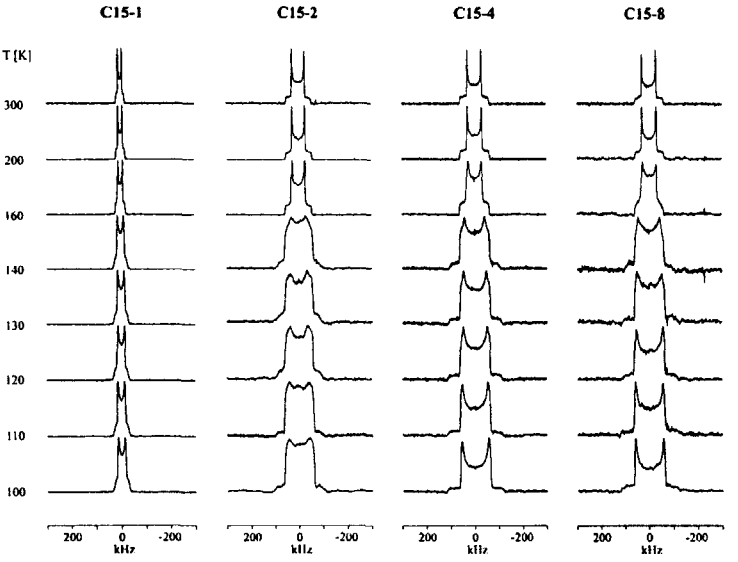


FIGURE 1 $^2$H NMR lineshapes of selectively deuterated n-pentadecane in urea at different temperatures.

It can be seen that the $^2$H NMR spectra change significantly upon going from the low to the high temperature phase. Generally, motionally averaged $^2$H NMR spectra (rate constant $k \geq 10^8$ $s^{-1}$) are observed. In the low temperature the spectra exhibit a biaxial pattern (asymmentry factor $\eta \neq 0$), whereas the high temperature phase is charactarized by the presence of axially symmetric $^2$H NMR spectra ($\eta = 0$). The variation of the experimental lineshapes implies a different pentadecane mobility in the two phases. The $^2$H NMR spectra of the sample with

pentadecane, bearing a deuterated methyl group (C-1), are further narrowed which can be attributed to the fast rotation of the methyl group ($k \geq 10^8\ s^{-1}$). Both the experimental $^2H$ NMR spectra and the spin-lattice relaxation data (see Fig. 2) have been analyzed with the same motional model that was also sucessfully applied to the description of hexadecane/urea.[2]

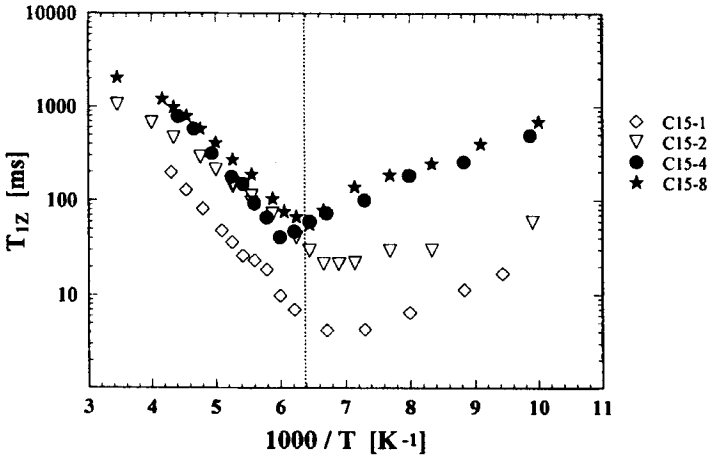


FIGURE 2 $T_{1Z}$ curves of selectively deuterated pentadecane in urea.

Thus, in the low temperature phase the pentadecane chains, with the interior part being in an almost all-trans conformation, undergo fast but highly restricted rotations around their long axes. This situation can be modelled by a fast two-site jump process ($k \geq 10^8\ s^{-1}$) between equally populated sites, where the jump angle increases linearly with temperature (see Fig. 3).

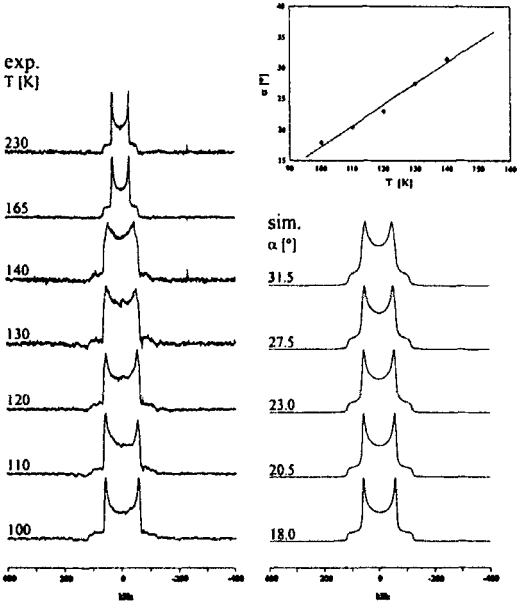


FIGURE 3 Experimental and theoretical $^2$H NMR spectra of n-pentadecane, deuterated at C-8, in urea.

In the high temperature phase the overall chain motions are unrestricted. That is, the $^2$H NMR spectra and relaxation data can be described by pentadecane chains undergoing six-fold jumps (60° jumps). To sort out the kinetic parameters of these motions, we have analysed the spin-lattice relaxation data as well as the partially relaxed spectra from the inversion recovery experiments (data not shown). The derived motional correlation times are summarized in Fig. 4. It can be seen that both rotational processes follow the Arrhenius law, from which activation energies of 1.7 and 10.6 kJ/mol for the restricted rotation (low temperature phase) and unrestricted rotation (high

temperature phase), respectively, have been obtained. It should be noted that similar low values have been reported earlier for the rotational motions of hexadecane in urea.[2] The graph of Fig. 4 also contains the derived correlation times ($\tau$ = 1/k) for methyl group rotation. The rather low activation energies of 5.0 (low temperature phase) and 15.2 kJ/mol (high temperature phase) are typical for spatially less hindered methyl rotors. All in all, the results for the pentadecane/urea inclusion compound have shown a very similar behaviour of the pentadecane chains as reported before for hexadecane in urea. A typical odd-even effect, associated with the chain length, however cannot be derived from our present experimental data.

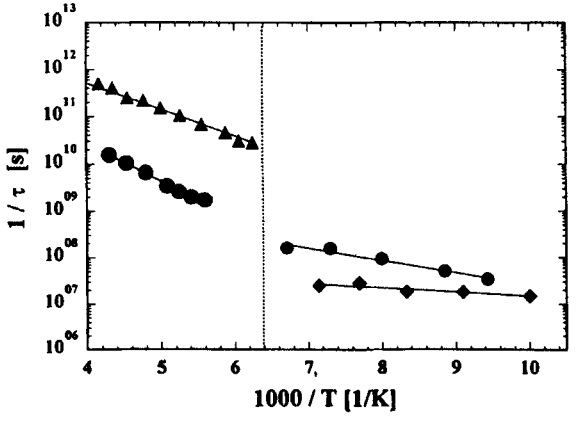


FIGURE 4 Arrhenius plot of the motions for pentadecane in urea.
◆ restricted chain rotation, ▲ unrestricted chain rotation,
● methyl group rotation.

In quite the same way, we have studied cyclophosphazene inclusion compounds, formed by tris-(1,2-dioxyphenyl)-cyclotriphosphazene with n-hexadecane, deuterated either at position C-8 or C-1. In Fig. 5 a series of experimental and theoretical $^2H$ NMR spectra is given that refers to the sample with hexadecane, deuterated at position C-8.

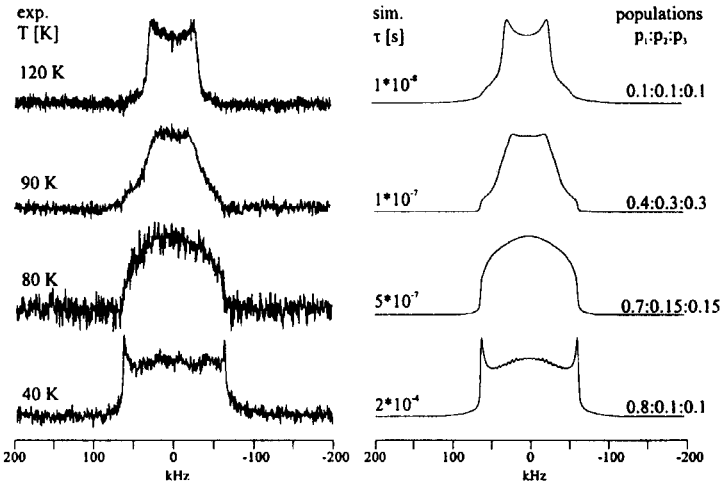


FIGURE 5 Experimental and theoretical lineshapes of the cyclophosphazene adduct with n-hexadecane, deuterated at C-8.

Here, the guest mobility differs significantly from that in the urea clathrates. Firstly, the overall chain motions can be followed down to about 40 K. Secondly, for the lineshape simulations, given in Fig. 5, a chain rotational motion has been assumed that is described by a three-fold jump process (120° jumps) of the n-hexadecane chains, being in

the all-trans conformation. The populations of the jump sites are found to vary with temperature. Thus, at 40 K an highly unequal population ($p_1 = 0.8$, $p_2 = p_3 = 0.1$) exists that changes continuously with temperature until at 120 K fast jumps between equally populated sites occur. From the analysis of the derived rate constants an activation energy for chain rotation of 6.2 kJ/mol has been obtained which is very similar to the activation energies for chain rotation in urea inclusion compounds (see above). The above findings of unequally populated jump sites strongly suggests that the hexagonal symmetry of the cyclophosphazene channels is distorted at lower temperatures. It should be noted that recent studies on other cyclophosphazene inclusion compounds also have indicated the presence of distorted cyclophosphazene channels at lower temperatures.[8]

As a last example, we present results from an $^2H$ NMR study on α-cyclodextrin inclusion compounds with n-hexadecane, again deuterated at positions C-8 or C-1. Here, all chain motions – except for the methyl group rotation – again can be frozen in at about 100 K. In this respect the α-cyclodextrin clathrates resemble the urea inclusion compounds, presented above. The motion of the hexadecane chains at higher temperatures, however, is found to be quite different. Thus, up to 250 K the best agreement between the theoretical spectra could be achieved with the assumption that very restricted rotational motions of all-trans chains occur. In this case the chain rotation is modelled by rotational jumps between two sites whose relative populations are given by $p_1 = 0.6$ and $p_2 = 0.4$. In addition, a Gaussian distribution of jump angles ($\sigma = 1.0$) has been used with a mean opening angle of 75°, reflecting a

certain degree of heterogeneity of the hexadecane motions in α-cyclodextrin. The theoretical $^2H$ NMR spectra, given in Fig. 6, clearly demonstrate that this model is able to reproduce the experimental $^2H$ NMR spectra. The derived activation energy of the hexadecane chain rotation in α-cyclodextrin was found to 7.1 kJ/mol which resembles the values reported for other systems (see above).

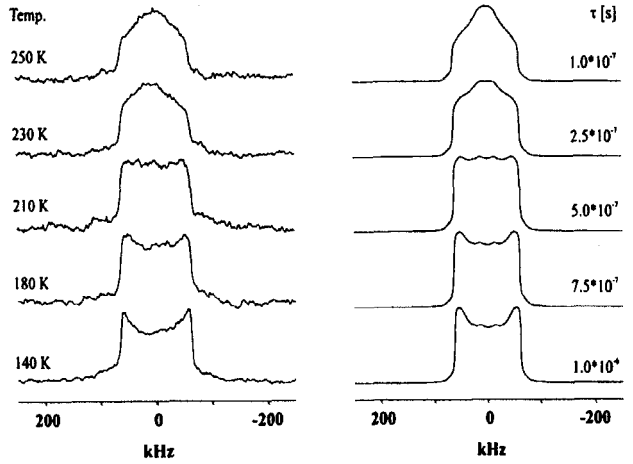


FIGURE 6 Experimental and simulated lineshapes of n-hexadecane in α-cyclodextrin.

## CONCLUSION

It has been shown that n-alkanes in channel-forming inclusion compounds are highly mobile displaying a high degree of rotational disorder. The n-alkane chains were found to exist in an almost all-trans

conformation undergoing rotational motion around their long axes being parallel to the host channel main axis. The type and time scale of this process, however, were found to depend strongly on the particular host matrix, sample temperature or host phase. Thus, for the above systems unhindered chain rotation as well as hindered motions have been discussed. So far, there was no evidence for the existence of chain fluctuations perpendicular to the channel axis which might reflect the large spatial restrictions imposed by the surrounding host lattice.



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