Evidence for Migration of Molecules into the Tunnel Structure of Urea Inclusion Compounds

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It is shown by high-resolution solid state ^{13}C NMR spectroscopy and optical microscopy that n-decane molecules can migrate from the liquid phase into the tunnel structure of the 1,8-dichlorooctane–urea inclusion compound without loss of single crystal integrity; this result provides strong evidence to suggest that urea inclusion compounds possess an open host structure, and has important implications with regard to potential applications of these inclusion compounds.

It is well established that urea can form inclusion compounds with a variety of appropriate organic molecules (such as sufficiently long n-alkanes). In these inclusion compounds urea forms an extensively hydrogen-bonded structure containing linear, parallel, essentially infinite tunnels (channels) within which the guest molecules are located.[1,2]

There are some important similarities between urea inclusion compounds and topologically-related zeolitic systems such as theta-1, mordenite and zeolite-L; these zeolites also contain uni-dimensional tunnels which can include appropriate guest species. However, there is a major difference between such zeolitic hosts and the urea inclusion compounds in the sense that the 'empty' zeolites can generally exist as stable structures, allowing a range of guest concentrations to be applied from zero (empty host) to a maximum value (saturation). As a consequence, one characteristic property of zeolitic materials is that guest molecules are able to migrate within the tunnels of these systems, and this property underlines many of the important industrial applications of these materials.[3] In contrast, both experimental evidence[4–7] and Monte Carlo simulation[8] have shown that removal of the guest molecules from urea inclusion compounds leads to collapse of the urea tunnel structure to produce the tetragonal crystal structure of pure urea, which does *not* contain 'empty' tunnels. Related to this is the fact that the urea inclusion compound containing a particular type of guest molecule is known to exist only at one specific host : guest ratio (corresponding, in principle, to saturation). Thus, there is always a dense packing of guest molecules within the tunnel structure of urea inclusion compounds.[2]

In this paper we report, for the first time, the migration of molecules into the tunnel structure of urea inclusion compounds, probed by high-resolution solid state ^{13}C NMR spectroscopy. This result provides strong evidence to suggest that the urea inclusion compounds possess an 'open' host framework. The particular system that we have studied is the migration of n-decane molecules from the liquid phase into the tunnels of the 1,8-dichlorooctane–urea inclusion compound. It is plausible that this kind of migration is a general phenomenon, which may also occur for other appropriate guest species.

The 1,8-dichlorooctane–urea and n-decane–urea inclusion compounds used in our study were prepared by conventional methods.[9] Single crystals of 1,8-dichlorooctane–urea were immersed in liquid n-decane inside a closed bottle and left at room temperature (24 ± 2 °C) for 5 days (sample I). During this period, the single crystals in this sample were regularly examined, *in situ*, by optical microscopy to monitor the crystal

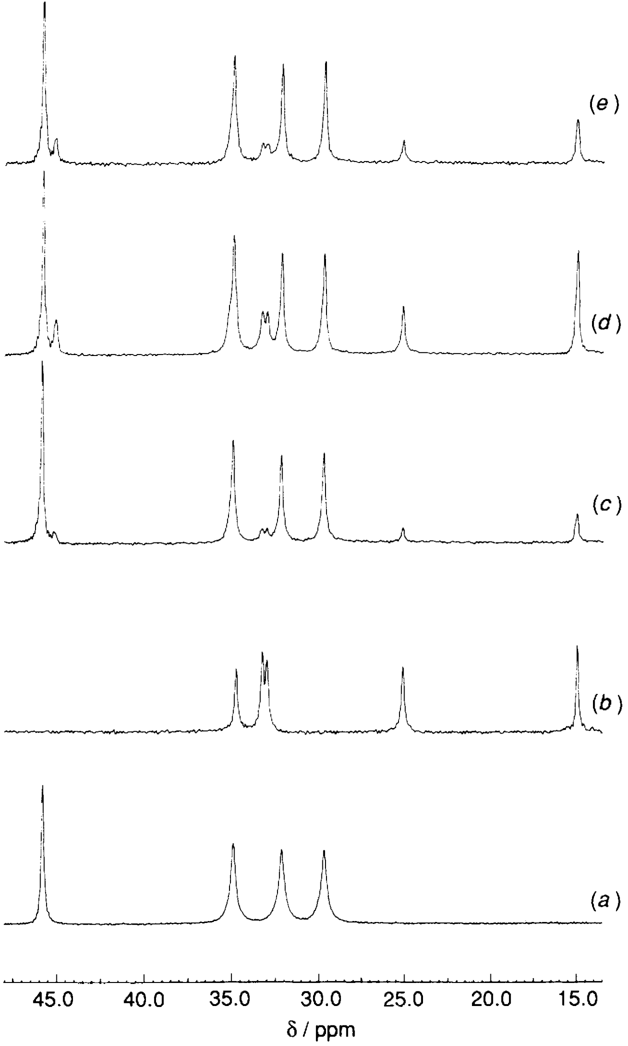

Fig. 1 High-resolution solid state ^{13}C NMR spectra of: (*a*) the 1,8-dichlorooctane–urea inclusion compound; (*b*) the n-decane–urea inclusion compound; (*c*) sample I; (*d*) sample II; (*e*) sample III

integrity as a function of time. Two other samples contained 1,8-dichlorooctane–urea crystals (0.35 g) which were ground thoroughly before being immersed in liquid n-decane (1.5 g) inside closed bottles. Sample II was left at room temperature (24 ± 2 °C) for 5 days and sample III was left at 0 °C for 5 days. (The 1,8-dichlorooctane–urea crystals used in all of these samples were from the same batch.) After the stated period of time, the solid materials were collected by filtration and then washed with 2,2,4-trimethylpentane to remove any molecules (particularly n-decane) adsorbed on their external surfaces.

High-resolution solid state ^{13}C NMR spectra[†] were recorded for these samples and for the n-decane–urea and 1,8-dichlorooctane–urea inclusion compounds (Fig. 1). For all the samples I–III, the spectra indicate the existence of n-decane *in addition to* 1,8-dichlorooctane, with the relative amount of n-decane different in the different samples. It should be noted (*vide infra*) that in the spectra of these samples there are two peaks (at δ 45.2 and 45.7) due to the CH_2Cl carbon whereas in the spectrum of 1,8-dichlorooctane–urea [Fig. 1(*a*)] there is only one peak (at δ 45.7) due to the CH_2Cl carbon.

We attribute the existence of n-decane in samples I–III to the migration of the n-decane molecules from the liquid phase into the tunnel structure of the inclusion compound. This migration is clearly more rapid for the ground sample (sample II) than for unground single crystals (sample I) under identical conditions [compare Figs. 1(*d*) and 1(*c*)], presumably because of the larger contact area between the liquid and solid phases for the ground samples. Furthermore, the results for samples II and III suggest that the migration is slower at lower temperature [compare Figs. 1(*d*) and 1(*e*)].

It is conceivable that the existence of n-decane molecules in these samples could alternatively result from partial decomposition or partial dissolution of the 1,8-dichlorooctane–urea inclusion compound, followed by recrystallization as n-decane–urea. However, the *in situ* optical microscopic investigation of the single crystals of sample I indicated that there was no loss of crystal integrity or decomposition of the crystals during the experiment.

It could be argued that surface adsorption of n-decane might explain the detection of n-decane in the ^{13}C NMR spectra of samples I–III. While it is possible that small amounts of n-decane could indeed be adsorbed on the surface of the crystals, washing the collected materials with 2,2,4-trimethylpentane will ensure that the amount of surface-adsorbed n-decane on the materials used in the NMR experiments is negligible.

Finally, we recall that two peaks are observed for the CH_2Cl carbon in the ^{13}C NMR spectra of samples I–III. As demonstrated elsewhere,[10] this phenomenon arises from the presence of two different intermolecular environments (specifically, $-CH_2Cl\cdots Cl$ and $-CH_2Cl\cdots CH_3$) for the CH_2Cl group in these inclusion compounds. [Note that there is only one type of environment ($-CH_2Cl\cdots Cl$) for the CH_2Cl group in the 1,8-dichlorooctane–urea inclusion compound, and a single peak is observed for the CH_2Cl carbon in the ^{13}C NMR spectrum of this sample.] The existence of these two environments for the CH_2Cl group in samples I–III provides further strong evidence to support the exchange mechanism proposed above, since it proves directly that 1,8-dichlorooctane and n-decane molecules are both located within the *same* tunnels.

The results reported here provide the first conclusive evidence which proves that it is possible to carry out an exchange of the guest molecules in a urea inclusion compound without loss of integrity of the inclusion compound single crystal. This has two important and immediate implications. First, the occurrence of the exchange process suggests that the host framework in urea inclusion compounds could indeed, in a manner similar to zeolitic and other microporous inorganic hosts, serve as a medium within which chemical (or other) transformations of guest species could be carried out with continuous removal of product molecules and insertion of fresh reactant molecules [without requiring to destroy the host framework (*e.g.* by dissolution) in order to recover the product molecules]. This conclusion is of fundamental importance with regard to the development of potential applications of urea inclusion compounds. Second, the occurrence of the exchange process provides evidence, albeit circumstantial, that the 'ends' of the urea tunnels are 'open', allowing the migration of guest molecules into (and out of) the tunnels. In view of the fact that the guest molecules within urea inclusion compounds are always closely packed along the tunnel, the entry of external molecules into the tunnel should be associated with the concommitant loss of guest molecules from this structure (*via* the other end of the tunnel). To our knowledge, there have been no reported studies of the surface structure of urea inclusion compounds; however, if there were some type of surface reconstruction on the (001) crystal faces,[2] it is probable that this would effectively 'close' the ends of the tunnels.

[†] High-resolution solid state ^{13}C NMR spectra were recorded at 125.7 MHz on a Brüker MSL500 spectrometer. A 'single pulse' ^{13}C pulse sequence was used, with high power ^1H decoupling applied during acquisition of the spectrum and with the sample subjected to magic angle spinning (typically *ca.* 7 kHz). A recycle delay of 5 s was used. Chemical shifts are given relative to tetramethylsilane, *via* the use of tetrakis(trimethylsilyl)silane (δ 3.50) as an internal standard.

Further experiments aimed towards developing a fundamental understanding of the mechanism of the exchange process are currently in progress. These include studies of the time dependence, temperature dependence, particle size dependence and thermodynamic aspects of this process, together with studies of other combinations of guest species with urea and other organic host solids.

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