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High resolution solid state ^{13}C NMR investigation of the deoxycholic acid / ferrocene inclusion compound

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Summary

The molecular mobility of deoxycholic acid (DCA) / ferrocene inclusion compound has been investigated by high resolution solid state ^{13}C NMR spectroscopy. Compared to the single crystal of ferrocene, the molecular mobility of the ferrocene in the inclusion compound is enhanced because it is included in the large cavity of DCA. It is found that the relaxation time measurement by solid state ^{13}C NMR can provide powerful evidence to confirm the formation of the inclusion compound.

Introduction

Chemistry of inclusion compounds attracts a great attention from the viewpoint of both technological and academic fields. Size fitness between host and guest molecules plays an important roll to recognize a particular guest molecule. Deoxycholic acid (DCA), which is known as the constituent of bile acid, constructs enough space for lots of guest molecules to form inclusion compounds.[1-5] Takemoto et al. found that DCA forms an inclusion compound with ferrocene molecules, that is the earliest investigation of inclusion compounds in which the arrangement of ferrocene molecules was uniquely determined in the channel lattice of DCA.[6] Recent developments of high resolution solid state ^{13}C NMR spectroscopy made possible to investigate not only molecular structure but also dynamic character of solid materials. The relaxation time measurements directly relate to the molecular mobility so that it is a powerful technique to make clear the mobility of ferrocene in the inclusion compound.

In this communication, we report the relationship between the crystal packing and the molecular mobility of ferrocene molecules by using high resolution solid state ^{13}C NMR spectroscopy.

Experimental

Samples of DCA and ferrocene were purchased from Wako Co. Ltd. The DCA/ferrocene inclusion compound was prepared by the recrystallization in methanol. Thermal analysis was performed by a RIGAKU TAS 200 differential scanning calorimeter (DSC). The samples were scanned at a heating rate of 10°C/min. The high resolution solid state ^{13}C NMR measurements were performed on a Bruker MSL 200 spectrometer under the magnetic field of 4.7 T. The magic angle spinning (MAS) of 4 kHz was achieved by the double bearing system. The ^{13}C resonance frequency was 50.3 MHz, and the $\gamma B_1/2\pi$

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used was 65 kHz for both ^{13}C and ^{1}H. ^{13}C spin-lattice relaxation times (T_{1C}) were measured by the saturation recovery method modified for solid-state measurements.

Results and Discussion

Figure 1 shows DSC curves of DCA crystals, ferrocene crystals and the DCA/ferrocene inclusion compound. The endothermic peaks of DCA and ferrocene were observed at 174.7°C and 176.0°C, respectively. Compared to these samples consisting of single components, the endothermic peak at 201.8°C for the inclusion compound is much higher. This indicates that the inclusion compound is crystallographically stabilized by making the complex between DCA and ferrocene. This is the evidence that the ferrocene molecule is included in DCA as a host molecule. By using these samples, the cross polarization / magic angle spinning (CP/MAS) ^{13}C NMR spectra of the DCA crystals, ferrocene crystals and DCA/ferrocene inclusion compound were measured as shown in Figure 2. The spectral shape of the DCA crystals is significantly different from that of the inclusion compound. This indicates that the molecular packing of DCA takes a unique structure by incorporating ferrocene into DCA channel. The spectrum of ferrocene crystals gives a single resonance line around 70 ppm which is the contribution from carbons of pentadienyl ring. The chemical shift of pentadienyl carbons in the inclusion compound was almost the same as that of the ferrocene crystals as shown in Figure 2(c). ^{13}C Longitudinal relaxation times of these peaks were measured by using the saturation recovery pulse sequence. Figure 3 shows a semilogarithmic plot of the peak intensity as a function of delay time.

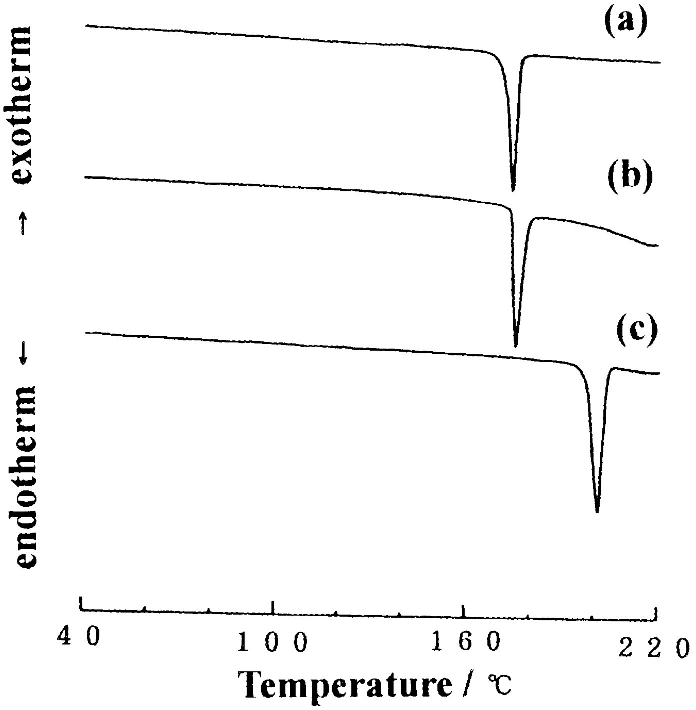

Figure 1: DSC curves for (a) DCA, (b) ferrocene and (c) their inclusion compound.

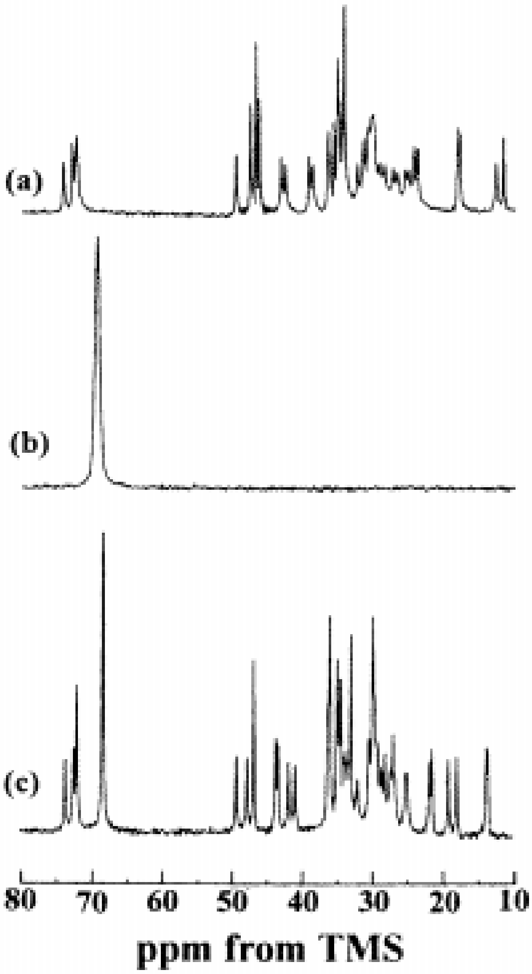

Figure 2: CP/MAS ^{13}C NMR spectra : (a) DCA crystal; (b) ferrocene crystal; (c) DCA/ferrocene inclusion compound.

A significant difference between the inclusion compound and the ferrocene crystal was observed in the T_{1C} values; 14s for the ferrocene crystal and 3.4s for ferrocene in the inclusion compound. According to the single-correlation-time theory,[7] the longer T_{1C} corresponds to less mobility under this experimental condition. It can be, therefore, concluded that the motion of the ferrocene molecule is much more hindered in the crystal lattice than that in the inclusion compound due to tight packing. Since the channel structure makes a little larger space for ferrocene molecules, the motional fluctuation around the average position will be enhanced. Therefore, the ferrocene molecules in the DCA channel is suggested to be intermediate state between rigid crystal and mobile liquid. It leads to the fact that the ferrocene molecules do not flow out from the DCA channel unlike liquid, but they are not stabilized in the DCA channel for a long period unlike rigid crystals. As a result, the enhancement of molecular mobility connects to the phenomenon that the ferrocene molecules gradually emerge from the host channel.

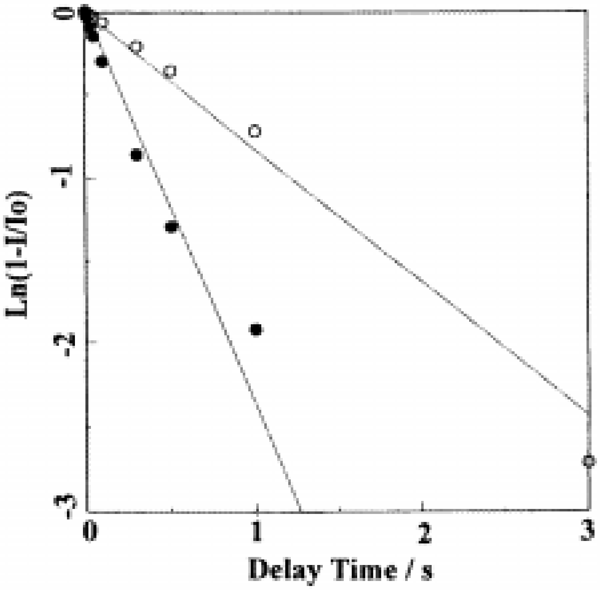

Figure 3: Semilogarithmic plot of the peak intensity of cyclopentadienyl carbons as a function of delay time. ○ : ferrocene crystal; ● : DCA / ferrocene inclusion compound.

As shown in Figure 2, there exists a large difference in the line width of cyclopentadienyl carbons observed around 70 ppm for the inclusion compound and the ferrocene crystals. The half width of the inclusion compound is estimated to be 14 Hz, which is much narrower than 39 Hz in the ferrocene crystals. The extreme narrowing for the inclusion compound is regarded as the effect of enhanced molecular mobility. Then, the half width of resonance line can be correlated to the spin-spin relaxation time (T_{2C}); the narrower peak corresponds to the longer T_{2C} associated with the fast molecular mobility. Therefore, this result supports the conclusion of the T_{1C} analysis

Conclusion

DSC measurements are one of the most useful methods to confirm whether the guest molecules are included in the host molecules or not. However, the DSC peak for the inclusion compound is in accord with that for the host molecule in certain cases. In the case of solid state ^{13}C NMR, the environment around the guest molecule in the inclusion compound is sensitively reflected on molecular mobility. Therefore, the nuclear magnetic relaxation time measurement is a simple and accurate method to characterize the guest molecule included in the host molecule. This method will be applied to the confirmation for the formation of other inclusion compounds.

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