Dynamics of Ferrocene Enclathrated in Deoxycholic Acid as Studied by SASS (Switching-angle Sample Spinning) NMR Spectroscopy

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A ^{13}C chemical-shift powder pattern for ferrocene enclathrated in the deoxycholic acid channel selectively observed by SASS NMR reveals that the included ferrocene molecule is rotating around its five-fold axis; moreover, the axis is rotating on a cone with a half-angle of 18° at ambient temperature.

Recently, Miki *et al.*[1] reported an X-ray diffraction study of the deoxycholic acid (DCA)–ferrocene (2 : 1) inclusion compound: the ferrocene molecule was concluded to be fixed in the DCA channel. Various types of molecular motion have, however, been found for ferrocene enclathrated in other host molecules such as thiourea[2–4] and cyclodextrins[3,5] by NMR spectroscopy. We therefore investigated the existence of molecular motion of ferrocene in the DCA inclusion compound using the SASS (switching-angle sample spinning) NMR method,[6,7] by which the ^{13}C powder pattern of ferrocene can be observed independently from the overlapping patterns of DCA.

The inclusion compound was prepared by the reported procedure.[1] The ^{13}C cross-polarisation magic-angle-spinning (CPMAS) NMR spectrum[†] [Fig. 1(*a*)] shows a sharp single resonance line at δ 68.9 for the ferrocene carbons. Many of the DCA resonance lines split into doublets with equal intensities, demonstrating the existence of two noncongruent DCA molecules in the inclusion compound. At about 50 °C, however, such splittings were not observed. On the other hand, the X-ray study[1] showed the crystallographic equivalence of all the DCA molecules. These NMR and X-ray results suggest the existence of a phase transition around ambient temperature.

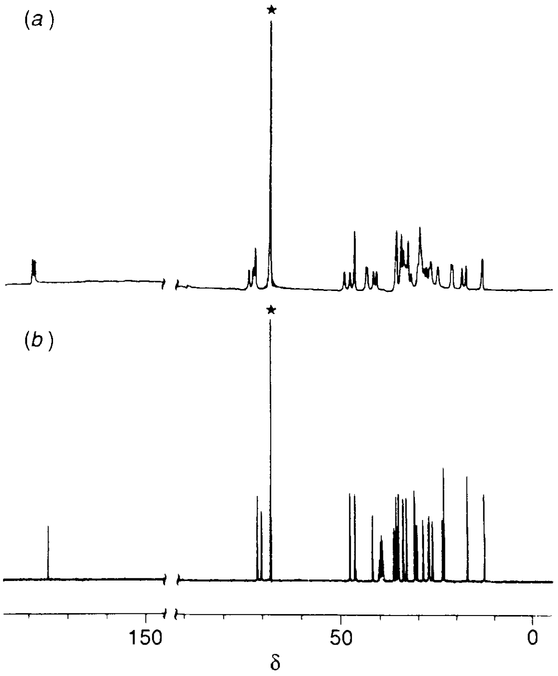

Fig. 1 ^{13}C CPMAS NMR spectra for the deoxycholic acid–ferrocene (2 : 1) inclusion compound. Strong peaks, marked with an asterisk, are assigned to ferrocene. (*a*) Solid state. (*b*) $(CD_3)_2SO$ solution. A septet peak at δ 39.6 is due to $(CD_3)_2SO$.

[†] NMR spectra were measured at room temperature with a home-built spectrometer operating at 22.6 MHz for ^{13}C with a sample-spinning rate of *ca.* 3 kHz, a mixing time of 5 ms, and a repetition time of 4 s. The evolution time t_1 was increased in steps of 300 μs from 0 to 36 ms. Eighty scans were accumulated for each t_1 value.

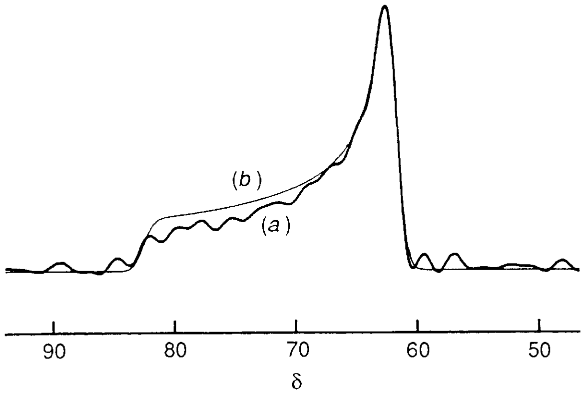

Fig. 2 ^{13}C Chemical-shift powder pattern for ferrocene in the deoxycholic acid inclusion compound (*a*, experimental; *b*, calculated). The spectrum is scaled by a factor of −0.303 around the isotropic shift due to the off-magic angle spinning.

Fig. 2 shows the ^{13}C chemical-shift powder pattern selectively obtained for the included ferrocene molecules using the SASS NMR method:† it clearly indicates that the chemical shift tensor is axially symmetric. The off-magic angle θ_{off} of the sample spinning axis during the evolution period in SASS 2D NMR was set to be 68.74° so that the ^{13}C powder pattern in Fig. 2 is scaled down by a factor of $P_2(\cos\theta_{off}) = -0.303$ around the isotropic shift. The anisotropy of the tensor is calculated to be 68 ppm by scaling up the observed anisotropy by this spinning-induced scaling factor.

In solid ferrocene, the ^{13}C chemical shift tensor has been shown to be axially symmetric owing to rapid rotation of ferrocene around its five-fold molecular axis[8] with an anisotropy of 79 ppm.[5] The ^{13}C chemical shift anisotropy for ferrocene in the DCA channel is smaller by a factor of 0.86 than that for solid ferrocene. This reduction of the anisotropy in the DCA channel shows the existence of further molecular motions other than the rotation around the five-fold axis. If we assume that the five-fold axis rotates on a cone with a half-angle β_o, the motion-induced scaling factor for the chemical shift anisotropy is given by $(3\cos^2\beta_o - 1)/2$. Equating it to the experimental value of 0.86, we have $\beta_o = 18°$.‡ Thus, we conclude that the ferrocene molecule included in the DCA channel undergoes a composite molecular motion: the rotation of the ferrocene molecule around its five-fold axis and the rotation of the five-fold axis on a cone with a half-angle of 18° at ambient temperature.

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‡ The error for β_o is at most 1°, since that for the anisotropies of the tensors is less than 1 ppm.