

Dynamics of some *n*-Alkanes Adsorbed in the Micropore of (\pm) -[Co(en)₃]Cl₃ as Studied by ²H NMR

Naomi Nagaoka, Takahiro Ueda, and Nobuo Nakamura

Department of Chemistry, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan

Reprint requests to Dr. T. U.; Fax: +81-6-6850-5785, E-mail: ueda@ch.wani.osaka-u.ac.jp

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The dynamic behavior of *n*-hexane-d₁₄ and *n*-decane-d₂₂, adsorbed in the micropore of [Co(en)₃]Cl₃ crystal was studied by ²H NMR at 144 - 345 K. The quadrupole coupling constants (QCC) are 160 kHz for the methylene group and 60 kHz for methyl group below 144 K for hexane and below 178 K for decane, suggesting that the molecular reorientation about the molecular long axis is frozen below these temperatures. The QCC of CD₂ group in hexane decreases from 160 kHz to 80 kHz on heating up to 170 K. Similar reduction of QCC of CD₂ observed above 280 K for decane. Assuming the three-site jump model of the guest molecule about its molecular long axis, we reproduced the experimental spectrum, and obtained the rate of the molecular motion in each guest. The temperature dependence of jump rates leads to the activation energies for the molecular reorientation of 20 kJ mol⁻¹ and 30 kJ mol⁻¹ for *n*-hexane and *n*-decane, respectively, suggesting that the length of the guest molecule influences greatly its dynamics in the micropore.

Key words: (\pm) -[Co(en)₃]Cl₃; ²H NMR; Micropore; Host-guest Interaction; Molecular Motion.

Introduction

Recently the structure and function of a variety of inclusion and intercalation compounds have been extensively studied. Among them were compounds based on micro- and meso-porous media. Various studies of the behavior of the guest molecules adsorbed in a variety of inclusion compounds [1, 2] and / or the zeolite family [3 - 8] were reported. The structure and dynamics of the guest molecules accommodated in these porous media depend strongly on the size and the shape of the pores as well as the kind of the host material.

(\pm) -[Co(en)₃]Cl₃·*n*H₂O crystallizes in a trigonal P $\bar{3}$ c1 unit cell of the dimension, $a = b = (1.150 \pm 0.002)$ nm and $c = (1.552 \pm 0.004)$ nm with $z = 4$ (290 K). The compound has a linear micropore along the crystallographic *c*-axis with 0.58 nm diameter. The micropore accommodates at most four crystal water molecules, which are known to be very mobile and behave like "zeolitic water" [9 - 11]. The dynamics of the accommodated water molecules has

been studied with respect to the local pore structure by dielectric measurements [12] and NMR [13]. We now attempted to substitute the crystallization water by small organic molecules such as *n*-alkanes, *n*-alkylamines, alcohols, and so on; since the micropore in the dehydrated (\pm) -[Co(en)₃]Cl₃ is straight and uniform, it may provide a highly restricted one-dimensional reaction field for a stereospecific organic reaction if such a substitution can be realized.

Straight-chain hydrocarbons have a molecular diameter of 0.49 nm, which is smaller than the pore diameter, 0.58 nm, in (\pm) -[Co(en)₃]Cl₃ and so can in principle enter the micropore with keeping its linear zigzag chain structure. It is expected therefore that the guest molecule undergoes a highly anisotropic molecular motion because it is accommodated in a narrow one-dimensional room.

²H NMR technique is useful in the study of the dynamic behavior of the guest organic molecules in the micropore. The line shape of ²H NMR is characterized by the mode and the rate of molecular motion [14 - 16]. Furthermore, we can examine the local

mode of motion individually by labeling the position of interest with deuterium. ²H NMR then greatly facilitates the study of dynamic processes and has been applied to study the dynamics of guest molecules adsorbed in the porous media [1, 2, 6 - 8].

In the present study we tried first to substitute some linear organic molecules for the crystallization water successfully. Next, we measured ²H NMR spectrum in the temperature range between 144 and 345 K to study the dynamic behavior of guest *n*-hexane-d₁₄ and *n*-decane-d₂₂ molecules in the pore of [Co(en)₃]Cl₃. We will discuss the influence of molecular length on the specific motion of the guest molecule on the basis of the spectral analyses.

Experimental

(\pm) -[Co(en)₃]Cl₃·*n*H₂O was synthesized according to literature [9] and dehydrated by keeping it at 120 °C for 3 days. The adduct was prepared by exposing the powdered dehydrated complex compound to the atmosphere of the suitable organic solvent, *i. e.*, *n*-hexane-d₁₄ or *n*-decane-d₂₂, at room temperature. The amount of guests adsorbed was estimated by measuring the change of the weight by the above treatment. The number of molecules per one formula unit of [Co(en)₃]Cl₃ complex was 0.22 and 0.20 for *n*-hexane-d₁₄ and *n*-decane-d₂₂, respectively. Each sample was sealed in a 5 mm ø glass NMR tube under equilibrium pressure of the guest compounds for the NMR measurements.

²H NMR measurements were carried out by a Bruker DSX-200 spectrometer operating at 30.72 MHz in the temperature range 144 - 345 K. The temperature of the sample was controlled to within 1 K by flowing heated N₂ gas and monitored by Cu-Constantan thermocouples. The complete line shape was measured with no distortion using the solid-echo sequence (90°-τ-90°-τ-acq) with 90° pulse length of 2.9 μsec and a pulse delay τ of 20 μsec over the spectral width of 500 kHz. The repetition time for the data accumulation was 4.0 sec. The spectra were analyzed using the simulation program MXQET for quadrupolar powder patterns taking account of exchange among *n*-sites, which was supplied by Greenfield *et al.* [17].

X-ray powder diffraction patterns were measured by a Rigaku Rotaflux RINT 2000 on HP 9000 S712/60 over the range of 2θ from 5 to 30°. The scan rate was 0.5°/min and the step 0.01°.

Table 1. The desorption temperature, the desorbed and the absorbed amounts of guest molecules in the micropore of (\pm) -[Co(en)₃]Cl₃ crystal measured by TG-DTA.

Guest molecule	DTA (°C)	desorption (%)	adsorption (%)
Water ^a	100	-23	-
CH ₃ (CH ₂) ₄ CH ₃	79	-9	10
CH ₃ (CH ₂) ₅ CH ₃	82	-7	10
CH ₃ (CH ₂) ₆ CH ₃	77	-9	10
CH ₃ (CH ₂) ₈ CH ₃	68	-8	10

^a The sample obtained by recrystallization from the aqueous solution is used in the present measurement.

TG-DTA diagram was measured by a SEIKO I SSC-5020M II TG/DTA 200 in the temperature range 25 - 200 °C. The heating rate is 10 °C/min. The temperature of sample was monitored by referring to Al₂O₃.

¹³C CP/MAS NMR measurements were carried out by a Bruker DSX-200 spectrometer operating at 50.32 MHz at room temperature. The contact time was 1 msec and the 90° pulse length 4.7 μsec.

Result and Discussion

Adsorption of Guest Molecules in the Micropore

The linear organic molecules such as *n*-alkanes, *n*-alcohols, and *n*-alkylamines can be substituted for the hydration water in (\pm) -[Co(en)₃]Cl₃ by exposing the dehydrated sample to the atmosphere of the organic solvent. The adsorption processes of several guests were monitored by measuring the increase in the weight of the sample. All samples show a gain of 10% of the initial weight, as listed in Table 1. The process of desorption was monitored by TG-DTA [11], and the desorbed amounts in relation to the absorbed amounts are listed in Table 1, suggesting that the adsorption and desorption processes of the guests are reversible. Furthermore, the X-ray powder diffraction pattern of each specimen confirmed that the original trigonal unit cell is kept unchanged before and after the substitution. In order to identify the guest molecular species we carried out ¹³C CP/MAS NMR experiments. The peak due to ethylenediamine in the host lattice appeared at 46 ppm. In the case of the sample which has been exposed to *n*-hexane vapor, the spectrum consists of peaks at 17 ppm, 26 ppm and 36 ppm, which can be certainly assigned to the methyl-, α- and β-carbons of hexane. For the specimen including *n*-decane, the peaks of spectrum appear

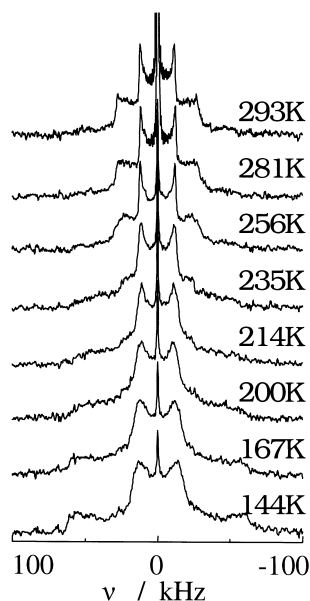


Fig. 1. Temperature dependence of the ^2H NMR spectrum of (\pm) -[Co(en)₃]Cl₃·0.22C₆D₁₄

at 17 ppm, 26 ppm, 36 ppm and 34 ppm, being consistent with the structure of *n*-decane. These aspects suggest strongly that the micropore of (\pm) -[Co(en)₃]Cl₃ crystal can accommodate some small linear organic molecules without undergoing any distortion of the crystal lattice.

Temperature Dependence of ^2H NMR Spectrum

Figures 1 and 2 show the temperature dependence of ^2H NMR spectra for *n*-hexane-d₁₄ and *n*-decane-d₂₂, respectively, adsorbed in the micropore of [Co(en)₃]Cl₃. The ^2H NMR spectrum of each guest compound consists of superposition of two Pake doublets corresponding to two different quadrupole coupling constants (QCC) due to the methyl and the methylene groups, and depends conspicuously on temperature in the range between 144 and 345 K.

For (\pm) -[Co(en)₃]Cl₃·0.22C₆D₁₄, the separation of the Pake doublets is 160 kHz for the broad component and 60 kHz for the narrow one at 144 K, which lead to the QCC values of 160 kHz and 60 kHz, respectively, on the assumption that the asymmetry parameter (η) of each electric field gradient (EFG) tensor is zero. The QCC values indicate that the CD₃ group undergoes rapid reorientation about its

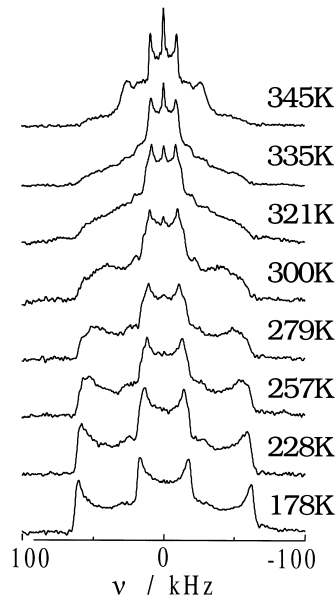


Fig. 2. Temperature dependence of the ^2H NMR spectrum of (\pm) -[Co(en)₃]Cl₃·0.20C₁₀D₂₂

C₃-axis and the CD₂ group is rigid at this temperature. The sharp component at the center of the spectrum may come from the guest molecule adsorbed on the surface of the powdered sample. The QCC of the CD₂ group suddenly decreases to 80 kHz at 170 K on heating, whereas the QCC of the CD₃ group gradually decreases on heating and reaches 32 kHz at 298 K.

The reduction of the QCC value for the CD₂ group suggests that the *n*-hexane-d₁₄ molecule undergoes an anisotropic motion in the micropore. Since the size of the cross section of the chain molecules is comparable to the pore diameter (0.58 nm), the micropore can accommodate *n*-alkanes only with all-*trans* conformation. Therefore it is reasonable to consider that the “linear” guest molecule undergoes rapid reorientation about its molecular long axis, *i. e.*, about the crystallographic *c*-axis.

The spectrum of (\pm) -[Co(en)₃]Cl₃·0.20C₁₀D₂₂ observed at 170 K gives similar QCC values for the CD₂ and CD₃ groups to those for *n*-hexane-d₁₄. For *n*-decane-d₂₂, the QCC value for CD₂ group decreases at much higher temperature than for *n*-hexane-d₁₄. The spectrum at 178 K shows that the molecular reorientation about the molecular long axis has not been excited at that temperature. The QCC's of the CD₂ and CD₃ groups reduce gradually to 75 kHz and 26 kHz,

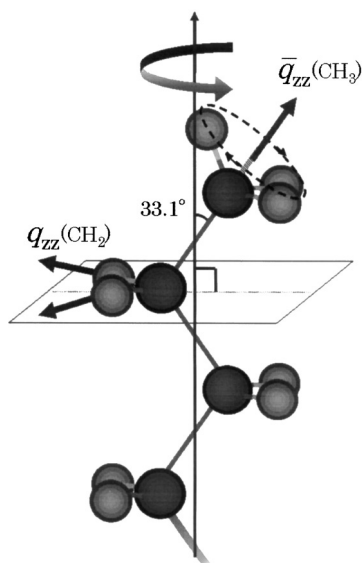


Fig. 3. Model of molecular motion; q_{zz} indicates the direction of the principal z -component of the EFG tensor.

respectively, with increase in the temperature from 279 to 345 K. That the temperature at which the line narrowing takes place is higher in *n*-decane-d₂₂ than that in *n*-hexane-d₁₄ indicates that *n*-decane-d₂₂ interacts more strongly with the wall of the pore than *n*-hexane-d₁₄.

Model of Molecular Motion

In order to derive a quantitative information on the guest dynamics from the temperature dependence of the ²H NMR spectrum for both specimens, we carried out spectral simulations in the presence of (1) 180° flip of the guest molecule, (2) 60° flip of the guest molecule, and (3) 3-site jump of the guest molecule about the molecular long axis. In the simulation, we adopted the following assumptions about the direction of the EFG tensor as shown in Figure 3: Since the CD₃ group is rotating rapidly about its three-fold axis at low temperatures, the direction of the motion-averaged principal z -axis of the EFG tensor is assumed to coincide with its C_3 -axis. Thus the angle between the molecular long axis and the apparent principal z -axis of the EFG tensor is 33.1°. For the CD₂ group, the principal z -axis of the EFG tensor coincides with the axis of the C-D bond. Then, the angle between the molecular long axis and the EFG tensor is 90°. Under these conditions, we simulated the ²H NMR spectrum for the CD₂ group and the CD₃ group independently,

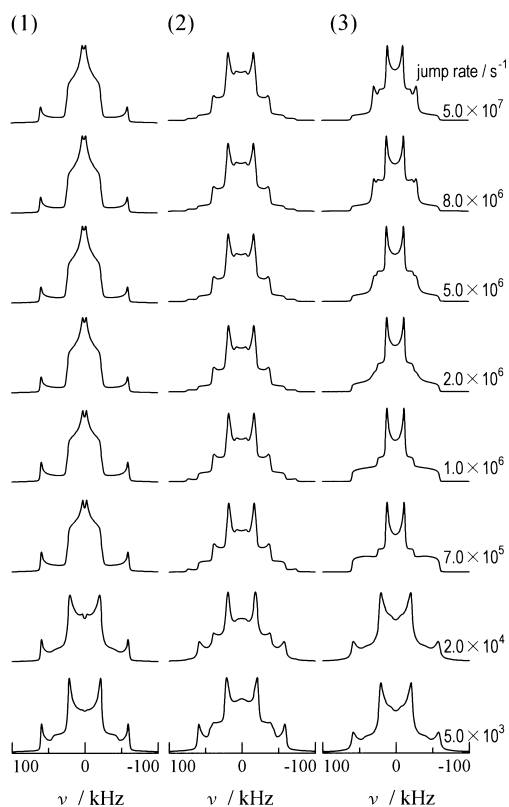


Fig. 4. Calculated ²H NMR spectra for *n*-hexane-d₁₄ assuming (1) 180° flip of guest molecule, (2) 60° flips of the guest molecule, and (3) a three-site jump of the guest molecule about the molecular long axis.

and superimposed each other with the appropriate weights to reproduce the experimental spectrum.

Figures 4 and 5 show the simulated spectra of *n*-hexane and *n*-decane, respectively, with different jump rates. In the case of model (1) above, the peaks of the CD₃ group give a characteristic spectral pattern with $\eta = 0.9$ at a jump rate larger than $7.0 \times 10^5 \text{ s}^{-1}$ [18]. Conversely, in the case of model (2), the CD₂ group also gives a characteristic spectral pattern with $\eta = 0.9$ at a jump rate larger than $7.0 \times 10^5 \text{ s}^{-1}$. These models can not interpret the experimental spectrum with $\eta \sim 0$. On the other hand, model (3) can reproduce the experimental spectrum for *n*-hexane-d₁₄ very well, as shown in Figure 4. In the case of *n*-decane-d₂₂, model (3) again reproduces the experimental spectrum as shown in Figure 5. This suggests that the *n*-alkane confined in the micropore of (\pm) -[Co(en)₃]Cl₃ undergoes molecular reorienta-

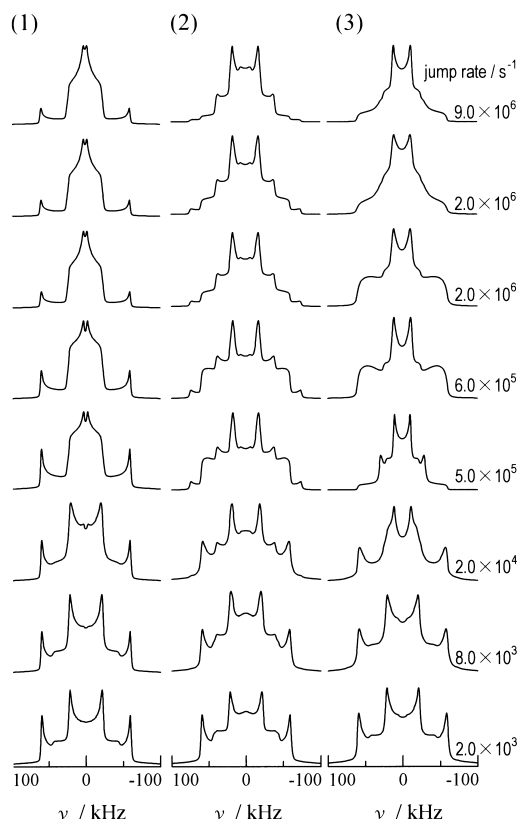


Fig. 5. Calculated ^2H NMR spectra for *n*-decane- d_{22} assuming (1) 180° flip of guest molecule, (2) 60° flips of the guest molecule, and (3) a three-site jump of the guest molecule about the molecular long axis.

tion about the long molecular axis, and the molecular motion can be approximated very well by the three-site jump model.

Figure 6 shows the Arrhenius plot of the jump rate obtained by comparing the experimental spectrum with the simulated one against the reciprocal temperature. The activation energies (E_a) are deduced to be $(20 \pm 2) \text{ kJ mol}^{-1}$ for *n*-hexane and $(30 \pm 2) \text{ kJ mol}^{-1}$ for *n*-decane. The E_a value for *n*-decane is 1.5 times

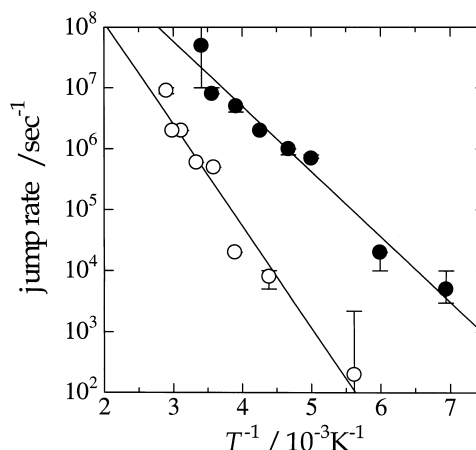


Fig. 6. The Arrhenius plot of the jump rate determined for *n*-hexane (●) and *n*-decane (○).

greater than that for *n*-hexane. This ratio of 1.5 is very close to the ratio of the number of carbon atoms between *n*-decane and *n*-hexane ($\text{C}_{10} / \text{C}_6 \sim 1.7$). This fact implies that the molecular interaction increases almost linearly with the molecular length. The interaction with the wall of micropore is estimated to amount to about 3 kJ mol^{-1} for a single CH_2 or CH_3 group in the guest molecule.

Conclusion

We can account for the temperature dependence of experimental ^2H powder spectra for *n*-hexane and *n*-decane in the micropore in (\pm) -[Co(en)₃]Cl₃ by the three-site jump model about the molecular long axis. Accordingly, we found that each guest molecule assumes an extended all-*trans* configuration and undergoes reorientation about the molecular long axis. The activation energies for *n*-hexane and *n*-decane were estimated to be $(20 \pm 2) \text{ kJ mol}^{-1}$ and $(30 \pm 2) \text{ kJ mol}^{-1}$, respectively, suggesting that the interaction energy between the CD_3 or CD_2 group and the pore wall amounts to about 3 kJ mol^{-1} .

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