Ionic motion and Disordered Structure in the Rotator Phase of Butylammonium Chloride Studied by Temperature Dependences of ^{35}Cl and ^{2}H NMR *

Mineyuki Hattori
Electrotechnical Laboratory, Tsukuba 305, Japan

Yoshito Onoda
National Institute for Research in Inorganic Materials, Tsukuba 305, Japan

Tomoki Erata
Department of Applied Physics, University of Tsukuba, Tsukuba 305, Japan

M.E. Smith
Bruker Analytische Messtechnik, GMBH, Silberstreifen, D-7512, Rheinstetten 4, Germany

Masakazu Hattori, Hiroshi Ohki and Ryuichi Ikeda
Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan

Z. Naturforsch. **49 a,** 291–296 (1994); received July 23, 1993

Temperature dependences of ^{35}Cl and ^{2}H quadrupole coupling constants and ^{35}Cl NMR spin-lattice relaxation times in polycrystalline samples were measured in the rotator phase of the butylammonium chlorides $C_4H_9NH_3Cl$ and $C_4H_9ND_3Cl$, obtainable above the phase transition temperature of 241 K. A rapid decrease of the quadrupole coupling constants of both nuclei upon heating is attributed to increasing dynamic disorder formed around the polar head. The presence of self-diffussion of Cl^- ions was revealed from the spin-spin relaxation time and resonance line-width in single crystals, and confirmed by measuring the dc electrical conductivity.

Key words: Solid NMR; Quadrupole coupling constant; Spin-lattice relaxation time; Self-diffusion; Rotator phase.

1. Introduction

Butylammonium chloride ($C_4H_9NH_3Cl$) forms a rotator phase (241–487 K) consisting of axially rotating rod-like cations and spherical anions stacked alternately in a double-layered lamellar-type structure [1, 2]. We have shown [3] that anisotropic cationic diffusion takes place in the 2D layers in this phase by measuring ^{1}H NMR spin-lattice relaxation times, T_1 and $T_{1\varrho}$ and the ac electrical conductivity. From this microscopic motional state and the marked plasticity we may call the rotator phase to be a "low-dimensional plastic crystal". In our previous study [4] of ^{1}H NMR on several alkylammonium chlorides (C_6-C_{10}) having isomorphous crystal structure with the present salt, we suggested the presence of anionic self-diffusion in this phase from ^{1}H $T_{1\varrho}$ data analysis. In the present study we intend to get more information on the anionic self-diffusion by measuring ^{35}Cl NMR on polycrystalline and single-crystal $C_4H_9NH_3Cl$, and also to know disordered molecular arrangements around the polar head by observing ^{2}H NMR spectra on powdered $C_4H_9ND_3Cl$ in the rotator phase.

2. Experimental

Polycrystalline $C_4H_9NH_3Cl$ and $C_4H_9ND_3Cl$, and single crystals of $C_4H_9NH_3Cl$ were prepared according to [3]. ^{35}Cl NMR spectra and relaxation times, T_1^*, T_2, and T_2^* for the central transition ($m_I = -1/2 \rightarrow +1/2$) in the rotator phase were measured at Larmor frequencies of 29.4 and 39.2 MHz using Bruker MSL-

---

* Presented at XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, Switzerland, July, 19–23, 1993.

Reprint requests to Prof. R. Ikeda, Department of Chemistry, University of Tsukuba, Tsukuba 305, Japan.

0932-0784 / 94 / 0100-0291 $ 01.30/0. – Please order a reprint rather than making your own copy.

300 and 400 spectrometers, respectively. Spectra were obtained by Fourier transformation of the echo observed after the quadrupole-echo pulse sequence, in which the pulse-width was reduced to one half of the 90° pulse-width for the non-selective irradiation [5, 6]. Since almost an exponential recovery of magnetization after the signal saturation was observed, we determined the probable spin-lattice relaxation time for the central transition T_1^* by measuring the spectrum intensity calculated from the echo recovered after the saturation pulse train. The values of T_2 together with T_2^* in single crystals were determined from the decay curve of the echo height and the spectrum linewidth, respectively. We measured ^{1}H-decoupled ^{35}Cl NMR spectra for a single crystal at 270 K using the MSL-300 spectrometer. ^{2}H NMR spectra were measured on a powdered sample by the quadrupole echo method at 61.4 MHz using the MSL-400 spectrometer in a temperature range from 140 to 370 K. The dc electrical resistivity was measured by a Takeda Riken TR8652 electrometer on fine crystals pressed into a pellet of 1 cm diameter and ca. 1 mm thickness, using platinum plates as blocking electrodes, and then a pressed mixture of graphite and benzyltrimethylammonium tetrachloroiodate(III) $[C_6H_5CH_2(CH_3)_3N][ICl_4]$ as the cathode for supplying ions.

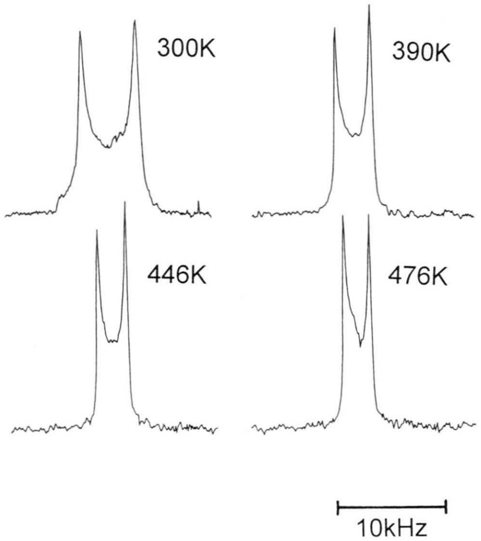

Fig. 1. ^{35}Cl NMR spectra for the central transition $m_I = +1/2 \leftrightarrow m = -1/2$ in the rotator phase of powdered $C_4H_9NH_3Cl$ observed at the Larmor frequency $\nu_L = 39.2$ MHz.

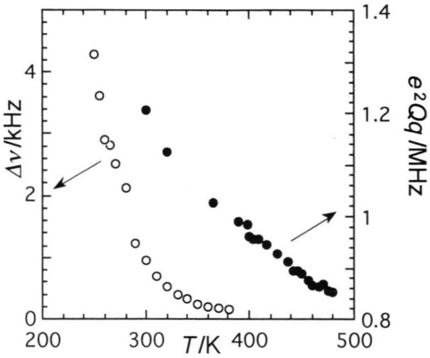

Fig. 2. Temperature dependences of ^{35}Cl e^2Qq(●), and half-height-widht $\Delta\nu$(○) ^{35}Cl NMR spectra observed on single crystals with the magnetic field $\boldsymbol{B}_0$ perpendicular to the tetragonal c-axis at $\nu_L = 39.2$ MHz in the rotator phase of $C_4H_9NH_3Cl$.

3. Results and Discussion

Chlorine NMR

^{35}Cl NMR spectra for the central transition between $m_I = -1/2$ and $+1/2$ observed in a range 300–476 K are shown in Figure 1. These spectra show a marked narrowing upon heating. The quadrupole coupling constant, e^2Qq, was derived from the spectra by assuming a vanishing asymmetry parameter η. This assumption is supported by the crystal symmetry of the rotator phase in which Cl$^-$ ions are located on the C$_4$-axis. ^{35}Cl e^2Qq values were determined using the relation [7]

$$e^2Qq = 2[(48/25)\,\nu_L\,\Delta\nu^{(2)}]^{1/2}, \tag{1}$$

where ν_L and $\Delta\nu^{(2)}$ are the Larmor frequency and the second-order quadrupole splitting, respectively. The obtained temperature dependence of ^{35}Cl e^2Qq is shown in Figure 2. This result is quite analogous to the value observed in the rotator phase of $C_6H_{13}NH_3Cl$ by Seliger et al. using double resonance technique [8]. The rapid decrease of e^2Qq in the present compound from ca. 1.2 to 0.85 MHz on heating from 300 to 480 K is unexplainable by a simple model of lattice vibration or thermal expansion of crystals, but attributable to considerable dynamic disorder of the ionic arrangement taking place around the polar end of the cation. The expected marked disorder at high temperatures is supported by the fact [9] that an e^2Qq of 630 kHz, close to the value in the present system, has been observed in a lamellar mesophase of

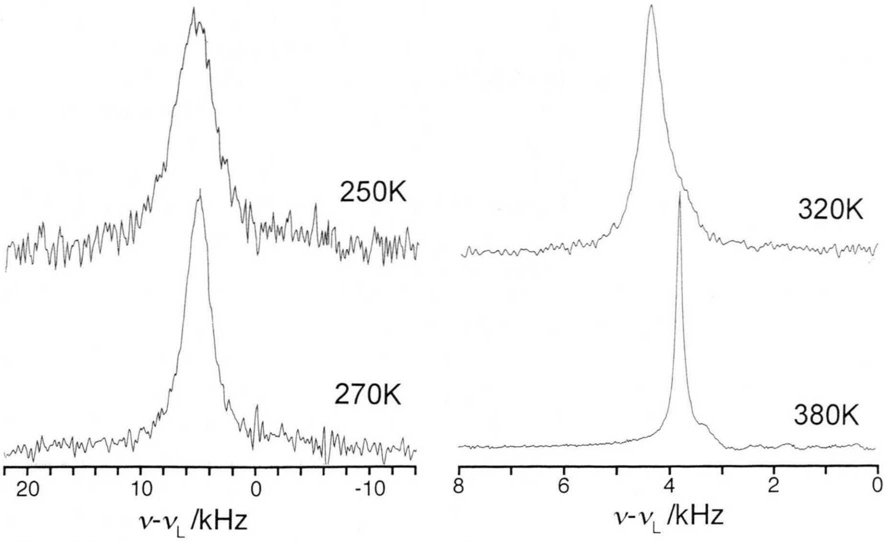

Fig. 3. Temperature dependence of ^{35}Cl NMR spectra for the transition between $m_I = +1/2$ and $-1/2$ observed for single crystals of $C_4H_9NH_3Cl$ with $\boldsymbol{B}_0$ perpendicular to the tetragonal *c*-axis.

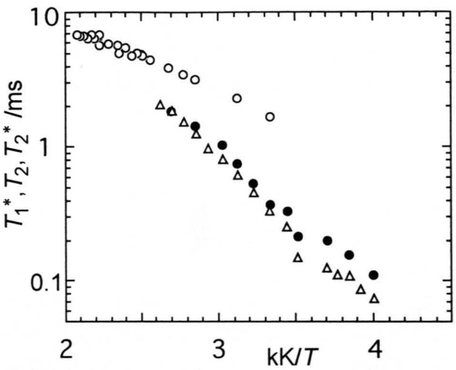

Fig. 4. Temperature dependence of ^{35}Cl NMR spin-spin relaxation times T_2 (●) and T_2 (△) on single crystals with $\boldsymbol{B}_0$ perpendicular to the tetragonal *c*-axis, and the probable spin-lattice relaxation time for the central transition T_1^* (○) on powdered $C_4H_9NH_3Cl$ in the rotator phase at $\nu_L = 39.2$ MHz.

an octylammonium chloride (80%) – water (20%) system, which forms a highly fluid state.

To get more information about anionic motions, we measured the ^{35}Cl NMR line-width for a single crystal with the static magnetic field perpendicular to the crystallographic C_4-axis in the rotator phase. The temperature dependences of the observed spectrum and the evaluated half-height width $\Delta\nu$ are shown in Figs. 3 and 2, respectively.

We also determined the ^{35}Cl spin-spin relaxation time T_2 of single crystals, and the probable spin-lattice relaxation time for the central transition T_1^* for the powder sample. The obtained temperature dependences of T_1^* and T_2 are given in Figure 4. The gradual increase of T_1^* with temperature, quite analogous to that of ^{1}H NMR T_1 already reported [3], suggests that ^{35}Cl T_1^* stems mainly from the fluctuation of the electric field gradient (EFG) caused by the axial reorientation of cations which dominantly contributes to ^{1}H T_1. The observed T_2 also increases with temperature, but $T_2 < T_1^*$ indicates that the spin-lattice relaxation contributes only little to the T_2 mechanism. Using the relationship $T_2^* \approx 1/\pi\Delta\nu$, we evaluated T_2^* from the observed $\Delta\nu$ and plotted it in Figure 4. The agreement between T_2 and T_2^* is quite good, implying that the line-width $\Delta\nu$ is attributable to ^{35}Cl · · · ^{1}H magnetic dipolar interaction and not to the broadening due to the distributed EFG made by lattice imperfections such as impurities and vacancies.

The above explanation could be confirmed by measuring ^{1}H decoupled ^{35}Cl NMR spectra on the single crystal with the magnetic field perpendicular to the C_4-axis. The spectra with and without the decoupling observed at 270 K and a Larmor frequency of 29.4 MHz, are shown in Figure 5. The marked spectrum narrowing obtained by the ^{1}H decoupling implies that the linewidth is mostly due to ^{35}Cl · · · ^{1}H magnetic dipolar interaction.

We evaluated the theoretical T_2 due to ^{35}Cl · · · ^{1}H dipolar interaction using the structural data of the rotator phase [1], where uniaxial rotation of the cation with C_3-reorienting CH_3 and NH_3^+ groups was assumed. The calculated approximate value became ca.

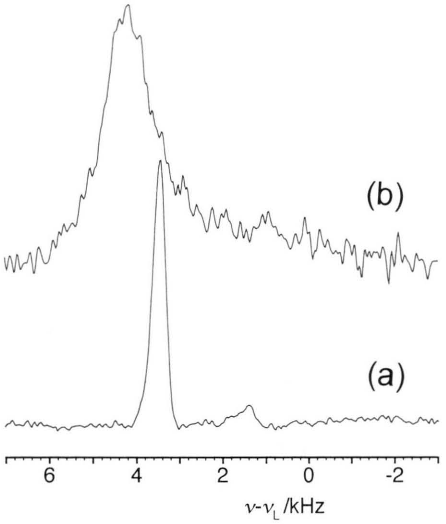

Fig. 5. ^{35}Cl NMR spectra with (a) and without (b) ^{1}H decoupling for a single crystal of $C_4H_9NH_3Cl$ observed with $\boldsymbol{B}_0$ perpendicular to the crystallographic *c*-axis and at a Larmor frequency of 29.4 MHz.

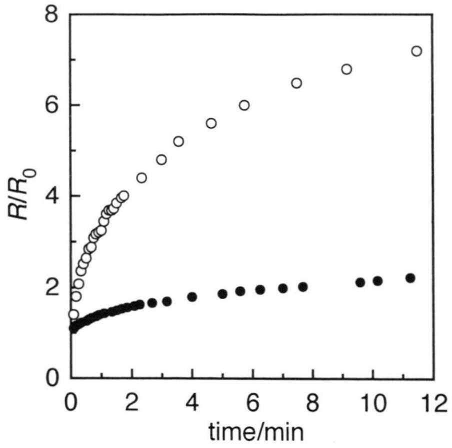

Fig. 6. Time dependence of reduced resistance (R/R_0) (R_0: resistance at $t=0$) measured for powdered $C_4H_9NH_3Cl$ with the Pt blocking electrode (○), and with the cathode of benzyltrimethylammonium tetrachloroiodate(III) + graphite (●).

0.1 ms, being one order of magnitude shorter than observed around 350 K. This result indicates that the averaging of the dipolar interactions is caused by some new motional process of the cations or anions excited at about room temperature. The long T_2 of the order of 1 ms can only be realized by averaging most of the dipolar interactions including the intermolecular origin. We assinged this motion to the anionic self-diffusion because it has been shown by ^{1}H NMR [3] that the cationic diffusional jump at room temperature takes place in the order of 10 Hz, which is too slow to affect T_2.

From the slope of log T_2 vs T^{-1} plots we obtained an activation energy of 25 ± 5 kJ mol^{-1} for the anionic self-diffusion. This value agrees quite well with the activation energy evaluated from the shallow minimum of ^{1}H $T_{1\varrho}$ [3], which we recently assigned to the anionic diffusion for alkylammonium chlorides with longer chains [4] having isomorphous structure with the present salt in the rotator phase.

We confirmed the presence of anionic diffusion by measuring the dc current in the pressed powder sample. Time dependences of the reduced resistance between the electrodes observed at room temperature are shown in Figure 6. When we used platinum plates as the electrodes, which act as blocking electrodes, the resistivity rapidly increased to ca. six times of the initial value R_0 observed at $t=0$. When a graphite mixture with benzyltrimethylammonium tetrachloroiodate(III) is used as the cathode, Cl^- ions are expected to be supplied at the cathode by the reaction [10]:

$$\mathrm{ICl_4^- + 2e^- \rightarrow ICl_2^- + 2Cl^-}\,. \qquad (2)$$

The ionic conduction continues via Cl^- ions, if Cl^- self-diffusion occurs in the crystals. In fact, the observed resistance R was very close to R_0, and its increase with time was much gentler than in the measurement using Pt electrodes. This result clearly shows the onset of rapid anionic diffusion around room temperature.

^{2}*H NMR Spectra*

^{2}H NMR spectra for powdered $C_4H_9ND_3Cl$ observed on cooling from 270 to 140 K are shown in Figure 7. By assuming the asymmetry parameter $\eta=0$, we evaluated e^2Qq in the low-temperature phase below the transition temperature T_{tr} (241 K on cooling) and the high-temperature rotator phase as shown in Figure 8. Two kinds of e^2Qq values, ca. 160 and 45 kHz observed below T_{tr} imply the presence of two nonequivalent cations in the specimen having different hindrances for the ND_3^+ reorientation. The site of large e^2Qq can be assigned to the cation with the rigid ND_3^+ because this e^2Qq is close to the reported values 168–177 kHz for the rigid ND_3^+ observed in $C_2H_5ND_3Cl$ [11]. This assignment is supported by our ^{1}H NMR T_1 measurement for the annealed crys-

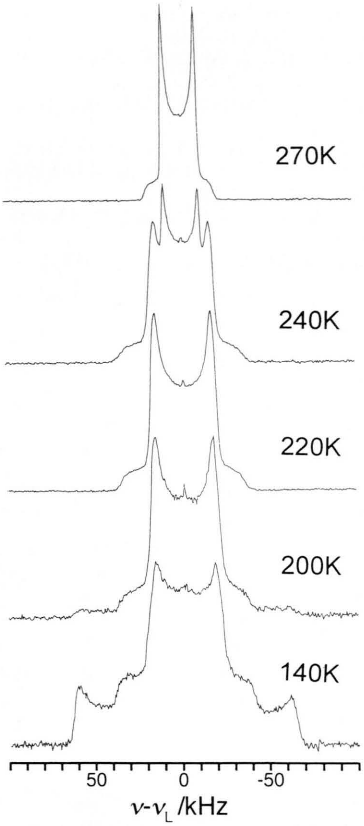

Fig. 7. Temperature dependence of ^{2}H NMR spectra of powdered $C_4H_9ND_3Cl$ at a Larmor frequency of 61.4 MHz measured with decreasing temperature.

tals of $C_4H_9NH_3Cl$ [3], revealing that NH_3^+ reorientation is almost frozen in below ca. 200 K. The small e^2Qq of 45 kHz in the low-temperature phase seems to be attributed to a metastable state formed in the cooling process through T_{tr}. This e^2Qq is reasonably assigned to the C_3-rotating ND_3^+ group using the reduction factor R of e^2Qq given by [12]

$$R = (1/2)(3\cos^2\phi - 1), \qquad (3)$$

where ϕ is the angle between the N–D bond and rotation axis. In the rotator phase, a Pake doublet with $\eta = 0$ was again observed, but its e^2Qq (26.1 kHz at 240 K) was smaller than those observed below T_{tr}. Upon heating to 370 K in this phase, this spectrum kept the same shape but showed a continuous decrease of e^2Qq from 26.1 to 20.5 kHz. These results indicate the onset of a new motion of the ND_3^+ group and an increase in amplitude with temperature. This new motion is attributable to the cationic reorientation about the long axis by referring to ^{1}H NMR data [3]. The decrease of e^2Qq upon heating can be understood as increasing randomness of the direction of the averaged EFG principal axis which is roughly along the cationic long axis above T_{tr}. This random reorientation can be schematically expressed by the precession of this axis about the *c*-axis. The precession angle ϕ can be determined by (3). Tentatively, if we assume the e^2Qq before the onset of precession to be 45 kHz, as observed in the low-temperature metastable state, the increase of precession angle on increasing the temperature from 240 to 370 K can be evaluated to be 6°. This dynamically disordered orientation seems to be connected with the onset of diffusional jumps of the cations and anions, which result in diffused positions of the center of gravity for both ions.

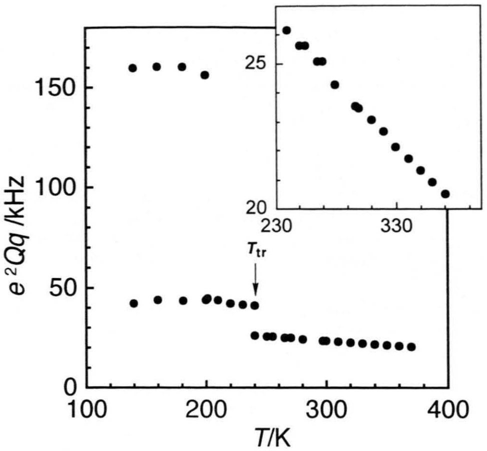

Figure 8. Temperature dependence of e^2Qq observed for powdered $C_4H_9ND_3Cl$. The phase transition temperature of 241 K obtained on heating is shown by T_{tr}.

[1] S. B. Hendricks, Z. Kristallogr. **68,** 189 (1928); R. W. G. Wyckoff, Crystal Structures, Wiley Interscience, 2nd Edn., New York 1966, Vol. **5,** Chapter 14A.

[2] S. Iwai, R. Ikeda, and D. Nakamura, Can. J. Chem., **66,** 1961 (1988); A. Müller, Proc. Roy. Soc. London. Ser. A **138,** 514 (1932).

[3] M. Hattori, S. Fukada, D. Nakamura, and R. Ikeda, J. Chem. Soc. Faraday Trans. **86,** 3777 (1990).

[4] S. Iwai, M. Hattori, D. Nakamura, and R. Ikeda, J. Chem. Soc. Faraday Trans. **89,** 827 (1993).

[5] S. Jurga, G. S. Harbison, B. Blümich, H. W. Spiess, F. Fujara, and A. Olinger, Ber. Bunsenges. Phys. Chem. **90,** 1153 (1986).

[6] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, Oxford 1961.

[7] M. H. Cohen and F. Reif, Solid State Phys. **5,** 321 (1957).

[8] J. Seliger, V. Zagar, R. Blinc, R. Kind, H. Arend, G. Chapuis, K. J. Schenk, and F. Milia, Z. Phys. B **69,** 379 (1987).

[9] G. Lindblom, H. Wennerström, and B. Lindman, Chem. Phys. Lett. **8,** 489 (1971).

[10] J. Coetzee, Standard Potentials in Aqueous Solution, Ed. A. J. Bard, R. Parsons and J. Jordan, Marcel Dekker, Inc., New York 1985, Chapter 5.

[11] M. J. Hunt and A. L. Mackay, J. Mag. Reson. **15,** 402 (1974).

[12] L. W. Jelinski, Ann. Rev. Mater. Sci. **15,** 359 (1985).