

Chapter 2

Experimental

2.1 Sample Preparations

n-Octylammonium chloride ($\text{CH}_3(\text{CH}_2)_7\text{NH}_3\text{Cl}$), octamethylenediammonium dichloride ($\text{NH}_3(\text{CH}_2)_8\text{NH}_3\text{Cl}_2$), *n*-butylammonium chloride ($\text{CH}_3(\text{CH}_2)_3\text{NH}_3\text{Cl}$), and tetramethylenediammonium dichloride ($\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{Cl}_2$) were prepared by neutralizing ethanol solutions of *n*-octylamine (Wako Pure Chemical Industries. LTD.), octamethylenediamine (Tokyo Chemical Industry Co., LTD.), *n*-butylamine (Wako Pure Chemical Industries. LTD.), tetramethylenediamine (Tokyo Chemical Industry Co., LTD.) with hydrochloric acid diluted with ethanol by 1:1 and evaporating solvent. Obtained crude salts other than *n*-octylammonium chloride were recrystallized from a mixed solvent of ethanol and diethylether. Crystals of *n*-octylammonium chloride were obtained by adding diethylether to the benzene solution of the crude salts.

The synthetic clay minerals used for preparation of intercalation compounds were sodium-saponite (abbreviated to Na-SP) expressed by the formula of $\text{Na}_{0.53}\text{Si}_{4-x}\text{Al}_x\text{Mg}_3\text{O}_{10}(\text{OH})_2$, $x=0.4$, the reference clay of the Clay Society of Japan, (synthesized in Kunimine Ind. Co.) and sodium-tetrasilicicfluormica (Na-MC) $\text{Na}_{0.76}\text{Mg}_{3-x}\text{Si}_4\text{O}_{10}\text{F}_2$, $x=0.3$, (CO-OP Chemical Co. Ltd.). The cation exchange capacities (CEC) of these clays were 70-80 meq / 100 g.

n-Octylammonium, octamethylenediammonium, *n*-butylammonium, and tetramethylenediammonium ions were intercalated into the interlayer space of saponite and tetrasilicicfluormica by a conventional ion exchange method as follows: fine powder of clays was immersed into each of aqueous solutions of the above mentioned alkylammonium chlorides whose concentrations were adjusted to twice the CEC of clays. After the exchange, products were filtered (or centrifuged) and washed with pure water repeatedly until the negative AgNO₃ test was obtained. The intercalated clays are hereafter called C81-SP for the *n*-octylammonium-saponite, C41-SP for *n*-butylammonium-saponite, and C42-SP for tetramethylenediammonium-saponite, C81-MC for *n*-octylammonium-tetrasilicicfluormica, C41-MC for *n*-butylammonium-tetrasilicicfluormica, C82-MC for octamethylenediammonium-tetrasilicicfluormica, and C42-MC for tetramethylenediammonium-tetrasilicicfluormica. The neutralizations of octamethylenediamine and trimethylenediamine and the intercalations of their corresponding diammonium ions (NH₃⁺(CH₂)₈NH₃⁺ or NH₃⁺(CH₂)₃NH₃⁺) into saponite were simultaneously carried out by adding 18 % hydrochloric acid into aqueous suspension of each of these amines and saponite, where the concentration of diamine is twice the CEC of the clay. The obtained intercalated compounds abbreviated to C82-SP or C32-SP were filtered and washed. The intercalation of guanidinium ion into saponite or tetrasilicicfluormica and of tetramethylammonium and trimethylammonium into tetrasilicicfluormica were performed by a similar aqueous ion exchange method as described above using guanidinium chloride (Wako Pure Chemical Industries, LTD.), tetramethylammonium chloride (Wako Pure Chemical Industries, LTD.), and

trimethylammonium chloride (Wako Pure Chemical Industries, LTD.), respectively. Obtained guanidinium-saponite (or tetrasilicicfluormica), tetramethylammonium-tetrasilicicfluormica, and trimethylammonium-tetrasilicicfluormica are abbreviated to Gu-SP (MC), M4-MC, and M3-MC.

Deuteration of ammonium or amino groups in intercalated cations was carried out by keeping the specimens in the saturated vapor of 99.5 atom % heavy water (Aldrich) at room temperature for two days. Deuterated C81-SP(MC), C82-SP(MC), C41-SP(MC), C42-SP(MC), C32-SP, GD-SP(MC), and M3A-MC are denoted hereafter as C81 d_3 -SP(MC), C82 d_6 -SP(MC), C41 d_3 -SP(MC), C42 d_6 -SP(MC), and C32 d_6 -SP, GD d_6 -SP(MC), M3A d -MC respectively. All samples treated in this study and their abbreviations are tabulated in Table 2.1.1.

Table 2.1.1. All samples used in this study and their abbreviations.

cation	clay	
	saponite	tetrasilicicfluormica
<i>n</i> -octylammonium	C81-SP	C81-MC
<i>n</i> -butylammonium	C41-SP	C41-MC
octamethylenediammonium	C82-SP	C82-MC
tetramethylenediammonium	C42-SP	C42-MC
trimethylenediammonium	C32-SP	-
guanidinium	Gu-SP	Gu-MC
trimethylammonium	-	M3-MC
tetramethylammonium	-	M4-MC

2.2 Measurements

Measurements of X-ray powder diffraction were performed for Na-SP, Na-MC, and all intercalated compounds with a PHILIPS X pert PW 3040/00 diffractometer using Cu ($K\alpha$) radiation. The data were collected at ca. 300 and ca. 400 K.

^1H NMR spectra were taken in C81-SP and C81-MC. These measurements were performed at a Larmor frequency of 300.1 MHz with a Bruker MSL-300 NMR system equipped with a Bruker B-VT 1000 temperature controller. The spectra were obtained by Fourier transformation of signals after the echo top observed by the solid echo method [5].

The temperature dependence of second moment (M_2) of ^1H NMR line-width was measured in C81-SP at 35 MHz, C81-MC at 41 MHz with a BRUKER SXP-100 spectrometer using the solid-echo method [5]. M_2 values were determined by the curve fit of obtained echo signals, $I(t)$, using

$$I(t) = 1 - \frac{M_2}{2!} t^2 + \frac{M_4}{4!} t^4,$$

where M_4 is the fourth moment of ^1H NMR line-width. In this measurement, the sample temperature was controlled by a Chino DB-1000 temperature controller and measured by a digital multimeter with a chromel-constantan thermocouple within ± 1 K.

Temperature dependences of ^1H NMR spin-lattice relaxation time (T_1) were measured for C81-SP(MC), C81 d_3 -SP(MC), C82-SP(MC), C82 d_6 -SP, C41-SP(MC), C41 d_3 -SP(MC), C42-SP(MC), C42 d_6 -SP, C32-SP, Gu-MC, and M4-MC with a home-made apparatus, as shown in Fig. 2.2.1, using the 180° - τ - 90° pulse sequence in a

temperature region of 100-500K. The employed Larmor frequencies were 50.4-15.0 MHz. The sample temperature was controlled by a Chino SU10-2121LNN temperature controller and measured by a digital multimeter with a chromel-constantan thermocouple within ± 1 K.

^2H NMR spectra were taken for all deuterated samples at a Larmor frequency of 46.1 MHz with the foregoing MSL-300 instrument using the quadrupole-echo method [6] in a temperature range 100-500K. ^2H spectra were recorded after the accumulation of echo signal by 200-10000 times. The sample temperature was controlled by a BRUKER VT-1000 controller.

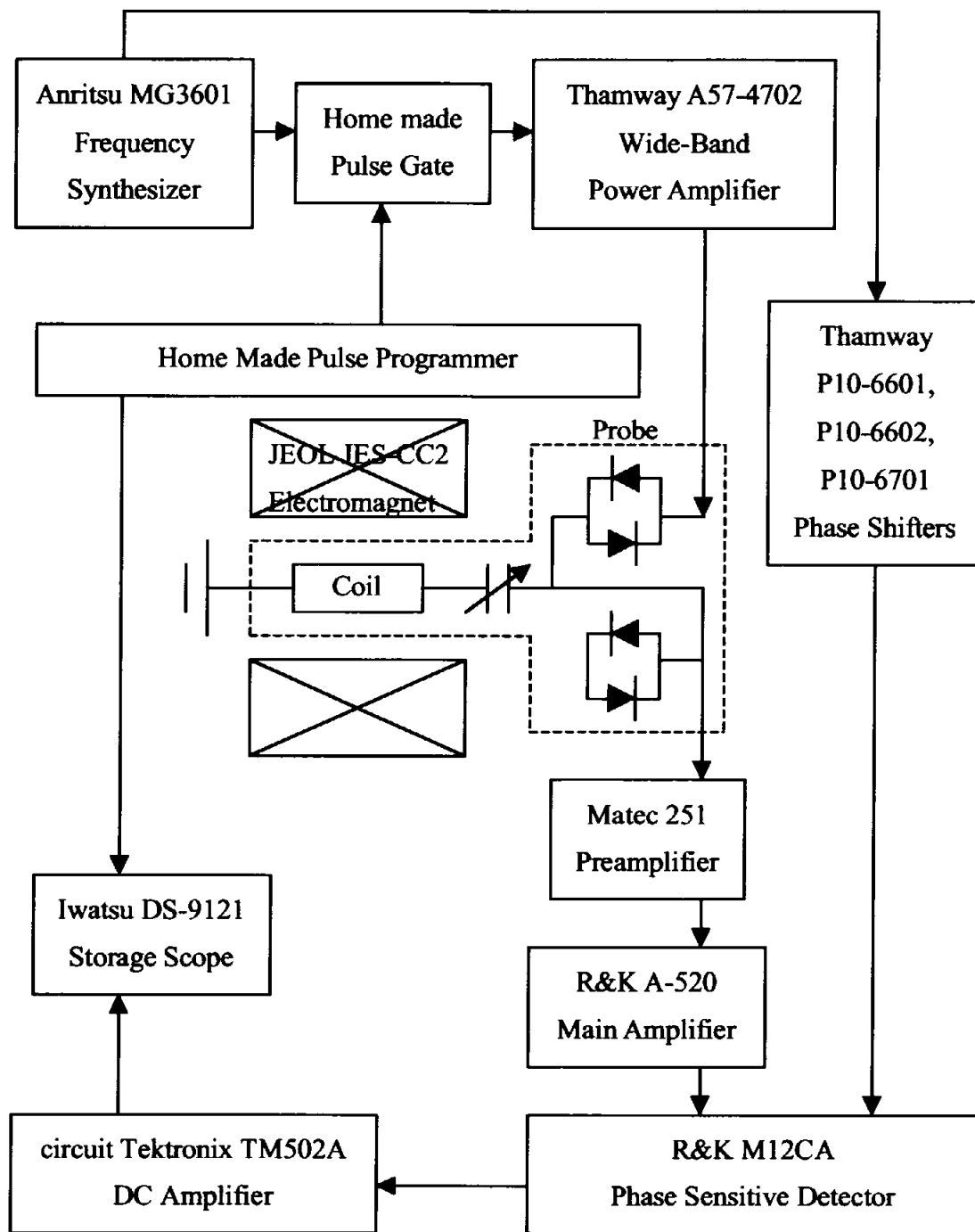


Fig. 2.2.1. A homemade NMR apparatus.