Chapter 1

Introduction

Layered clay minerals have two-dimensionally expanded spaces between their layers. Many kinds of species such as alkaline metal ions, water, organic ammonium ions and alcohols, etc., can be intercalated into the interlayer space of the clays without collapse of the layer structure. Especially, organocations such as alkylammonium ions can be easily intercalated by the simple cation exchange method.

A lot of investigations to determine structures intercalated organocations have been performed. For example, it was found that n-alkylammonium ions form a characteristic layer structure depending on their length and charges in clay walls [1]: In clays with high layer charges, e.g., vermiculite, densely packed alkylammonium ions form mono- or bilayer structures, and with the increase of the carbon number in alkyl groups, the basal spacing between layers is expanded by a constant increment per carbon atom, indicating that long chains are inclined by 50-60° to the clay sheet [2]. On the other hand, in smectites with low layer charges, alkylammonium ions are arranged with their long axes parallel to the clay layer and form mono- to trilayers according to their chain lengths [3].

The structures and arrangements of the intercalated organocations so far have been presumed to be solid or crystal-like in the interlayer spaces. This is because only averaged structures of intercalated ions have been studied on the assumption that they

are in the rigid state, so systematic studies on dynamics of intercalated organocations have been insufficient. To deepen the understanding of physical features of the organocation-clay series, the author thinks it important that dynamic properties of intercalated organocations are clarified. At present organo-clay complexes have applicatons for various fields such as rheological control agents, chemical sensors, reinforced plastics, and so on [4]. If dynamic properties of intercalated organocations are fully investigated, it is expected to explore new applications of organo-clay composites, e.g., new ionic conductors, new catalysts or fields for organic reactions.

Motional states of organocations, moreover, are of interest from the viewpoint of the fundamental physical chemistry: In organocation-clay compounds, a two dimensional (2D) aggregate made up of only organocations is formed between clay sheets, as is impossible to achieve in usual three dimensional (3D) crystals. In such a 2D phase, intercalated cations are expected to exhibit unique dynamic properties of 2D ionic systems such as 2D phase transitions and 2D diffusion, etc.

The first purpose in this study is to understand arrangements and dynamic behavior of organocations intercalated in interlayer spaces of the layered clay minerals by X-ray powder diffraction, elemental analysis, and solid state NMR measurements. In the present study, it is investigated the influence to the motional state of intercalated ions from the cationic shape, cationic size (or length), and the number of positive charges per a cation. For this purpose, various kinds of organocations are employed: (1) bar-like n-alkylmono- and diammonium ions with the carbon number of three, four, and eight, (2) plate-like guanidinium and trimethylammonium ions, and (3) spherically

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symmetric tetramethylammonium ions.

In this study, two species of clays, saponite and tetrasilicicfluormica are employed as host clays, because these clays, which contain only trace amounts of paramagnetic impurity, can be synthesized artificially and obtained easily. Both clays belong to 2:1 structural groups in which two silicate sheets made of vertex sharing SiO_4 tetrahedra are linked to sheets of cations X, which octahedrally coordinate to oxygens and hydroxyls or fluorides (refer to Fig. 1.1). The classification of 2:1 type clays is shown in Table 1.1. Saponite expressed by the ideal formula of $A^{n+}_{x/n}Si_{4-x}Al_xMg_3O_{10}(OH)_2$ belongs to smectite group with a small layer charge, and tetrasilicicfluormica by the ideal formula of $A^{n+}_{2x/n}Si_4Mg_{3-x}O_{10}F_2$ to mica group with a high layer charge. In saponite which is categolized into the trioctahedral subgroup, a part of Si^{4+} sites is replaced by Al^{3+} in the tetrahedral site, and negative charges appear in the outer layers. In tetrasilicicfluormica, having an intermediate structure between dioctahedral and trioctahedral subgroups, there are vacancies at some magnesium sites, and negative charges are generated inside the mica layers. In addition to the positions of charge defects, morphologies in saponite and mica have also differences. The averaged width of saponite layers is about 40-50 nm, whereas that of tetrasilicicfluormica is about 1000-5000 nm. Although saponite and tetrasilicicfluormica have similar structures, they have different characters as mentioned above. So, it is likely that the dynamic behavior of intercalated organocations is different from each other in these clays.

It is the second purpose to clarify how clay minerals affect molecular motions of intercalated ions by comparing motional states of organocations intercalated in these

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clays. Generally, clays called "-mica" have a high layer charge (1e per unit formula), but synthetic tetrasilicicfluormica employed in this study does not (0.6e per unit formula). Because the layer charge of tetrasilicicfluormica is close to that of saponite (0.4e per unit formula), it is convenient to compare the motional states of intercalated ions in two clays.

In this dissertation, structures of intercalated organocations investigated by measurements of X-ray powder diffraction and elemental analysis will be mentioned in Chapter 3. In Chapters 4 and 5, motional states of organocations intercalated in interlayer spaces of saponite and tetrasilicicfluormica are discussed. The comparison of dynamic properties of intercalated organocations in saponite and tetrasilicicfluormica will be made in Chapter 6.

Table 1.1. Classification and generalized structural formulae of 2:1 type layered clay minarals.

mineral group	layer charge per clay unit	dioctahedral	trioctahedral
pyrophyllite, talc	0	pyrophyllite $Si_4Al_2O_{10}(OH)_2$	talc $Si_4Mg_3O_{10}(OH)_2$
smectite	0.25-0.6	montmorillonite $A_xSi_4(Al_{2-x}Mg_x)O_{10}(OH)_2$ beidellite $A_x(Si_{4-x}Al_x)Al_2O_{10}(OH)_2$	hectorite $A_xSi_4(Mg_{3-x}Li_x)O_{10}(OH)_2$ saponite $A_x(Si_{4-x}Al_x)Mg_3O_{10}(OH)_2$
vermiculite	0.6-0.9	$Mg_{x/2}(Si_{4-x}Al)Al_2O_{10}(OH)_2$ muscovite	$Mg_{x/2}(Si_{4-x}Al_x)Mg_3O_{10}(OH)_2$ phlogopite
mica	~1	$K_x(Si_{4-x}Al_x)Al_2O_{10}(OH)_2$ tetrasilicicfluormica $NaSi_4Mg_{2.5}F_2O_{10}$	$K_x(Si_{4-x}Al_x)Mg_3O_{10}(OH)_2$

exchangeable cations
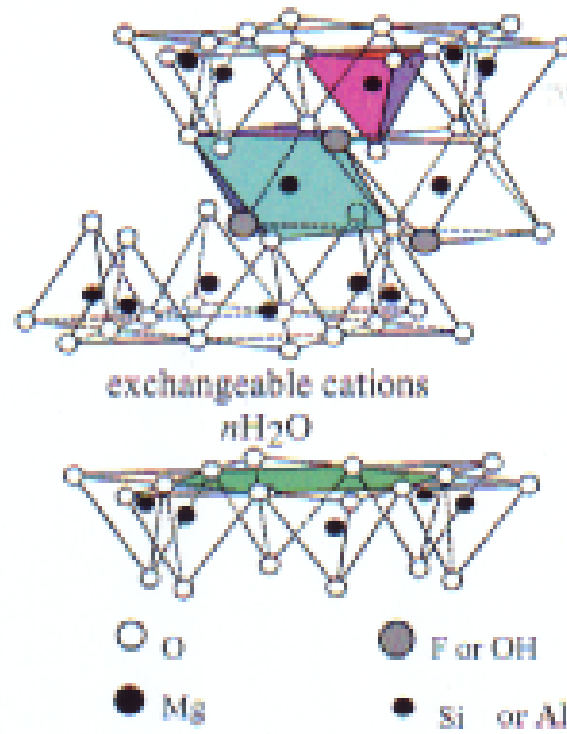
$n\mathrm{H_2O}$

○ O   ⬤ F or OH

● Mg   • Si   or Al

Fig. 1.1. The structure of 2:1 type layered clay minerals.