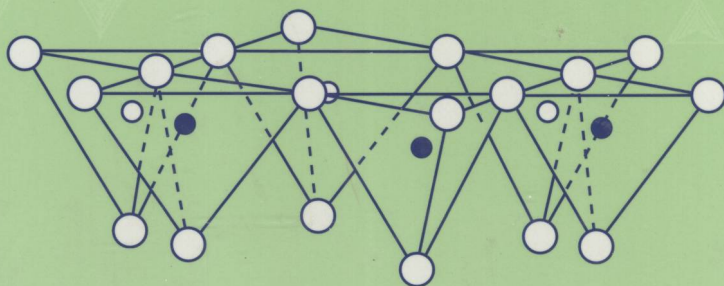


Organo-Clay Complexes and Interactions



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Organo-Clay Complexes and Interactions

Preface

Organo-clay complexes occur everywhere in nature, and the interaction between organic matter and clay minerals was one of the most important reactions in determining the history of our planet. Several theories attribute the origin of life to these kinds of interactions. The clay is thought to have served either as a catalyst in the synthesis of the first organic molecules or as a skeleton, taking part as an active component (see Chapter 11). The Bible states that God created Adam from clay. The Hebrew word *Adama* has the meanings of earth, soil, and clays, and the word Adam derives from it. Since we know today that the principal component of living creatures is organic matter, it appears that according to the Bible the origin of Adam involved clay-organic interactions.

The systematic scientific study of clay-organic interactions started at the beginning of the twentieth century. Among the pioneers in this study were I. D. Sedletsky, C. R. Smith, T. E. Gieseking, H. Jenny, U. Hoffmann, D. M. C. MacEwan, W. F. Bradley, S. B. Hendricks, R. E. Grim, W. H. Allaway, J. W. Jordan, and E. A. Hauser. The tools applied were mainly cation exchange, adsorption isotherms, x-ray, and DTA. Practical applications in different fields such as cleaning, purification treatments, thixotropy and rheopexy were studied even earlier (see, e.g., R. H. S. Robertson, *Fuller's Earth: A History of Calcium Montmorillonite*). In the past 60 years various advanced studies have been carried out and published. This book summarizes the progress made and examines various ideas and advanced techniques and their contributions to our knowledge of organo-clays.

Information on clay-organic interactions and organo-clay complexes is important to workers in many disciplines, including agricultural chemists, earth and soil scientists, geochemists, environmental scientists, and engineers in various industries in which both clays and organic matter are essential ingredients.

For this purpose we invited some leading scientists to contribute chapters to this collection. This book contains 11 chapters, covering the following subjects: Chapter 1 is a general description of clay minerals and their surface activity. Chapter 2 is a general introduction to organo-clay complexes and describes the

different types of complexes. Chapter 3 deals with a single mineral—it summarizes the available literature on the organo-vermiculite complexes. Chapters 4 and 5 are devoted to the physical chemistry of two specific surface phenomena of organo-clay complexes: organophilicity and hydrophobicity of these complexes and ion-exchange equilibria in these systems.

Four chapters are devoted to advanced investigative methods commonly used in the study of organo-clay complexes: nuclear magnetic resonance, differential thermal analysis and thermogravimetry, infrared and thermal-infrared spectroscopy, and visible spectroscopy of organo-clay complexes. These methods have contributed to the study of the fine structure of the complexes. Chapter 10 deals with the catalytic activity of clay minerals and their contribution to organic chemical reactions in nature and in the laboratory. Chapter 11 reviews the various ideas that relate clay minerals to the origin of life. We are grateful to all the authors for their contributions.

Today we can retrieve scientific information through computerized data banks. We therefore decided that this book should not be just a collection of articles summarizing the current literature but, rather, a critical review of the literature. The contributors were asked to follow this plan when writing their chapters.

Many important subjects in clay-organic systems have not been included in this volume or are merely mentioned in the introduction, for example, organo-sepiolite and palygorskite complexes, kaolin-like mineral intercalation complexes, x-ray study of organo-clays, electron microscopy study of organo-clays, adsorption of polyelectrolytes, and surfactants and their contribution to the colloidal behavior of organo-clay systems, organo-clay complexes in the environment and purification treatments, and organo-clay complexes in industrial applications. We hope to cover these and other subjects in a second volume.

We are grateful to the authors and publishers who granted us permission to reproduce illustrations from their books, articles, and journals. These sources are noted in the legends to the figures.

Thanks are also due to Mr. Leslie Weisenbaum for his valuable secretarial help and to Dr. Malcolm Schrader, Dr. Isaac Lapides, and Dr. Kirk H. Michaelian for their help and suggestions, and lastly to our wives for their forbearance during the long period of the book's preparation.

Shmuel Yariv
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Organo-Clay Complexes and Interactions

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1

Structure and Surface Acidity of Clay Minerals

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1 INTRODUCTION

The term “clay minerals” is derived from the definition originally used by sedimentologists and soil scientists for the fraction of particles having very small size, with an equivalent diameter smaller than 2 μm , which is the “clay fraction.” Particles in this size range can include quartz, carbonates, metal oxides, and other minerals in addition to clay minerals, as well as amorphous materials. Although most clay minerals occur as particles too small to be resolved by an ordinary microscope, x-ray diffraction analysis shows that most of them, even in their finest size fraction, are composed of crystalline particles and that the number of crystalline minerals likely to be found is limited. Furthermore, a wide distribution of particle sizes is frequently present and certain clay deposits contain well-defined crystalline particles with diameters greater than 2 μm . In this book a distinction is made between clays and clay minerals. The former term is used for the small particles found in soils and sediments, including crystalline and amorphous oxides and hydroxides of various metals, whereas the latter is used for a certain group of layered crystalline silicate minerals (phyllosilicates and related minerals).

Clay minerals, hydrated oxides, and hydroxides, mainly of Si, Al, Fe, and Mn, and some geo-organic polymers are responsible for most surface and colloid

reactions in the earth, including adsorption of organic matter by its components. They are the most important components and exert the dominant influence on chemical and physical properties of a soil. A detailed examination of their ability to interact with organic matter and the nature and properties of the organo-soil component complexes is essential for a complete understanding of a soil's potential with respect to agricultural and engineering applications. Due to their great capacity for adsorption, these earth constituents in their natural form, and recently also as synthetic products, are used as components in organic-inorganic complexes for various purposes. They are widely used as catalysts in various organic reactions carried out in laboratories and in various industrial processes and are added to many organic industrial products as fillers or diluents. In the latter case the clay mineral determines the rheological properties of the system.

Among the various surface adsorption sites for organic compounds discussed in this chapter, adsorbed water molecules may also serve as such. Adsorption of organic compounds by clay minerals takes place in solid clay, in plastic clay, and in aqueous suspensions thereof. Consequently, in most studies of clay-organic interactions, one should take into consideration the presence of water and the important contribution of water molecules to the binding between clay minerals and organic materials. There are three different states that pertain to clay-water systems. The first state is the dry clay. To the touch, ground dry clay has a greasy feel. In this state water molecules are located on the surface of the solid clay in the adsorbed state, interacting with functional groups. The second state is plastic clay. Plasticity may be defined as a property of a material that permits it to be deformed under stress without rupturing and to retain the produced shape after the stress is removed. This is a colloid system in which microdrops of nonadsorbed free water (liquid phase with water clusters) are dispersed between solid clay particles. In other words, the solid clay serves as a continuous phase in which the liquid water microdrops are dispersed. The liquid water filling the voids between the clay particles serves as a lubricant that permits some movement between the particles under application of a deforming force, thus giving the system its plastic properties. The third state is an aqueous colloid solution or clay suspension. Here liquid water serves as a continuous phase in which solid clay particles are dispersed. In the first state the water and silicate together form a single solid phase, whereas in the second and third states liquid water forms a separate phase in addition to water molecules that are adsorbed on the clay surface and thereby belong to the silicate solid phase.

2 STRUCTURE AND COMPOSITION OF CLAY MINERALS

Mineralogists use the term "clay minerals" for a group of hydrous layered magnesium- or aluminosilicates (phyllosilicates). In many of these minerals vari-

ous metallic cations, such as lithium, magnesium, and aluminum, act as proxy wholly or in part for the magnesium, aluminum, or silicon, respectively, with alkali metal and alkaline earth metal cations present as exchangeable cations. Iron (di- or trivalent) is also a common substituent of aluminum and magnesium. Each magnesium- or aluminophyllosilicate is essentially composed of two types of sheets, octahedral and tetrahedral, designated O and T, respectively. Each sheet is composed of planes of atoms, arranged one above the other, a plane of hydroxyls and/or oxygens above a plane of aluminums and/or magnesiums or silicons, the latter above another plane of hydroxyls and/or oxygens, and so on. Variations among clay minerals and the differences in their physical and chemical properties arise from the various combinations of octahedral and tetrahedral sheets and the electrostatic effects that chemical substitutions have on the units.

The common groups of phylloclay minerals occurring in soils and sediments are listed in Table 1. They are presented by their ideal structural chemical formulas. An additional group includes those clay particles with more than one type of layer present, termed mixed-layered minerals. Apart from the phyllosilicates, chain-structure types of clay minerals also exist. These minerals belong to the sepiolite-palygorskite-attapulgite group. Modified amphibole double chains are linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms. Minerals of this group are widely used as adsorbing agents of different organic compounds.

This chapter presents only a short description of the structures and properties of clay minerals and their surfaces. Further information can be found in the following books: Grim (1968); Yariv and Cross (1979); Barrer and Tinker (1984); Weaver (1989); and Velde (1992). X-ray diffraction data can be found in Brindley and Brown (1980), and data on chemical composition of clay minerals are given by Newman and Brown (1987).

2.1 The Tetrahedral Sheet

A continuous linkage of SiO_4 tetrahedra through sharing of three O atoms with three adjacent tetrahedra produces a sheet with a planar network (Fig. 1). In such a sheet the tetrahedral silica groups are arranged in the form of a hexagonal network, which is repeated indefinitely to form a phyllosilicate with the composition $[\text{Si}_4\text{O}_{10}]^{4-}$. A side view of the tetrahedral sheet shows that it is composed of three parallel atomic planes, which are composed of oxygens, silicons, and oxygens, respectively. The tetrahedra are arranged so that all of their apices point in the same direction with their bases in the same plane. The oxygens form an open hexagonal network in this plane, often referred to as the hexagonal or perforated oxygen plane (or O-plane). In reality the silica tetrahedra are slightly distorted, and consequently, the cavities bordered by six oxygens are ditrigonal rather than hexagonal (Radoslovich and Norish, 1962). This perforated oxygen

Table 1 Classification Scheme and Ideal Chemical Composition of Clay Minerals in Soils and Sediments

Type	Charge per formula unit	Group	Subgroup and minerals	Ideal chemical composition
TO (or 1:1)	0	Kaolin-serpentine	Nonexpanding.	
			Dioctahedral series	
			<i>Kaolin subgroup</i>	
			Kaolinite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Dickite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Nacrite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Nonexpanding.	
			Trioctahedral series	
			<i>Serpentine subgroup</i>	
			Chrysotile	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_8$
TOT (or 2:1)	0	Talc-pyrophyllite	Antigorite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Lizardite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Amesite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_8$
			Expanding.	$(\text{Mg},\text{Al}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_8$
			Dioctahedral series	
			<i>Kaolin subgroup</i>	
			Halloysite	$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$
			Nonexpanding.	
			Dioctahedral series	
			Pyrophyllite	$\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$
			Nonexpanding.	
			Trioctahedral series	$\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$
			Talc	

TOT (or 2:1)	0.25–0.6	Smectite	Expanding. Diocahedral series Beidellite	$[(Al_{4,00})(Si_{7,50-6,80}Al_{0,50-1,20})O_{20}(OH)_4]Na_{0,50-1,20}$
			Montmorillonite	$[Al_{3,50-2,80}Mg_{0,50-1,20})(Si_8)O_{20}(OH)_4]Na_{0,50-1,20}$
			Nontronite	$[(Fe_{4,00})(Si_{7,50-6,80}Al_{0,50-1,20})O_{20}(OH)_4]Na_{0,50-1,20}$
			Expanding. Triocahedral series Hectorite	$[(Mg_{5,50-4,80}Li_{0,50-1,20})(Si_{8,00})O_{20}(OH)_4]Na_{0,50-1,20}$
			Saponite	$[(Mg_{6,00})(Si_{7,50-6,80}Al_{0,50-1,20})O_{20}(OH)_4]Na_{0,50-1,20}$
TOT (or 2:1)	0.6–0.9	Vermiculite	Expanding. Diocahedral series Vermiculite	$[Al_{4,00})(Si_{6,80-6,20}Al_{1,20-1,80})O_{20}(OH)_4]Na_{1,20-1,80}$
			Expanding. Triocahedral series Vermiculite	$[(Mg_{6,00})(Si_{6,80-6,20}Al_{1,20-1,80})(OH)_4]Na_{1,20-1,80}$
		Illite	Nonexpanding. Diocahedral series Illite	$[(Al_{4,00})(Si_{7,50-6,50}Al_{0,50-1,50})O_{20}(OH)_4]K_{0,50-1,50}$
			Glauconite. Diocahedral illite rich in iron	
			Nonexpanding. Triocahedral series	
			Illites rich in magnesium and ferrous iron	

Table 1 Continued

Type	Charge per formula unit	Group	Subgroup and minerals	Ideal chemical composition
[TOT]O[TOT](or 2:1:1)	Variable	Chlorite	Nonexpanding. Dioctahedral series. There is some evidence for the existence of such a mineral, e.g., donbassite Nonexpanding. Trioctahedral series. Chlorites with structures related to $[(\text{Mg,Fe})_{3-x}(\text{Al,Fe})_x(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2]$ $[(\text{Mg,Fe,Al})_3(\text{OH})_6]$ e.g., clinochlore Nonexpanding. Dioctahedral series. Sudoite	