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An Introduction to Clay Colloid Chemistry

Second Edition

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Clay Colloid Chemistry

For Clay Technologists, Geologists, and Soil Scientists

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PREFACE

It is not too surprising that the total research effort on clay systems is and has been tremendous: We live through the courtesy of plants grown on clayey soils; we eat our food from ceramic dinnerware; we live in buildings partly made of clay bricks which rest on clay-containing soils into which they sometimes tend to disappear. Part of our energy supply comes from petroleum, which often originates in clay-containing sedimentary rocks. Clays are used in many industrial products and processes. Outside the ceramic industry, clays are an essential part of paper, drilling fluids, and certain lubricating greases; they are applied in formulations of insecticides, adhesives, ointments, and rubber or synthetic plastics; they act as catalysts or catalyst supports in many processes, and they are used for clearing wine.

In almost every field of clay study, one has to deal at one time or another with dispersions of clay in water or in another fluid. Such dispersions, which are characterized by the large interfacial area between the extremely small clay particles and the surrounding liquid, are colloidal systems. Colloid chemistry therefore enters to some degree every technological problem involving clays and liquids, such as problems of soil consolidation, plant nutrition, molding of ceramic objects, and the circulation of drilling fluids in an oil well.

The purpose of this book is to familiarize those engaged in some phase of clay technology, in sedimentary geology, or in soil science, with the modern views of colloid science and its application to clay systems.

Colloid chemistry is a rather specialized branch of physical chemistry, and the colloid chemistry of clay systems is indeed a specialty within a specialty. Communication between the colloid chemist and the clay technologist or geologist is often hampered by differences in terminology. Although the technologist and the geologist frequently use terms not especially appealing to the colloid chemist, the latter must admit that he too uses a rather specialized jargon which is often misunderstood by the noncolloid chemist and which has led to many misconceptions. In this book, therefore, an attempt has been made to discuss the usage of terms very carefully.

Another communication barrier between the colloid chemist and technologist stems from a difference in point of view. The colloid chemist looks primarily at a system on a microscopic scale. He deals with the arrangement of ions and molecules on the surface of the submicroscopic particles and attempts to analyze the forces which act between these particles in a suspension. The technologist, on the other hand, is primarily interested in the bulk physical and mechanical properties of his systems.

The clay technologist is well aware that the bulk properties of the clay systems depend on the concentration as well as on the type of clay; but above all, he is familiar with—and often puzzled by—the remarkably strong dependence of these properties on the composition of the fluid phase. Comparatively minor changes in the composition of the liquid often have surprisingly large effects on the behavior of the system. Here is exactly the area where the colloid chemist and the technologist should get together, since the effects of small amounts of dissolved chemicals in the clay system are governed by the rules of colloid chemistry. A knowledge and an explanation of these rules should enable the technologist to understand the behavior of the systems and consequently to handle them more efficiently. Actually, in many applications he has a free hand to tailor the properties of the clay systems by the incorporation of comparatively small amounts of soluble additives.

The principal themes of this book are therefore a discussion of (*1*) the effect of changes in fluid composition on the forces acting between suspended clay particles, and (*2*) the consequences of such changes on the bulk physical and mechanical properties of the suspensions which are important in clay technology.

Item (*2*) will be illustrated with several examples from the field of clay and soil technology. Although in the choice of the examples emphasis will be on how to solve the problems in the manipulation of drilling fluids (with which the author is most familiar), problems of the same nature frequently arise in other fields where the same solutions can often be applied.

In the arrangement of the chapters, the specialized discussion of the colloid chemistry of clay systems will be preceded by the presentation of the general facts and modern theories of colloid chemistry. In the subsequent treatment of the clays, certain complications must be introduced which are inherent in the unusual structural features of clay particles.

To keep this presentation within the scope of an introduction, it will be elementary, and the mathematical formulations of modern colloid science will be avoided in the main text. However, for the benefit of those readers who plan to engage in physicochemical clay research a brief survey of electric double-layer computations as they apply to clay systems is given in an appendix. In the main text, only the gist of the theoretical approach is discussed, and a sufficiently detailed account is given of the practical results to supply the technologist with a workable background knowledge. The highlights of each chapter have been included in a relatively extensive *Synopsis* following Chapter Twelve.

Selected references at the end of each chapter furnish a good entry to the literature. In addition, a bibliography of books and publications on clay literature is presented in Appendix V. References to this bibliography are prefixed by the letter B to indicate books or by the letter P to indicate periodicals.

Since the appearance of the first edition of this book in 1963, developments in clay research have been substantial, particularly through intensive application of X-ray and electron diffraction, nuclear magnetic resonance, electron spin resonance, infrared absorption, and other tools of physics. The scanning electron microscope has provided detailed pictures of clay agglomerates. Various physicochemical studies have improved our understanding of the mobility and position of ions and adsorbed molecules on clay surfaces. Considerable advances have been made in understanding the reactivity of clay surfaces and catalysis—a subject that is, however, outside the scope of this book. In general, research of the last decade has not made our previous basic concepts obsolete, but our knowledge of clay structure and clay behavior has become more refined. The same is true for the relevant concepts of colloid science, but in both fields some new phenomena were discovered and some new concepts were developed. In colloid science, discreteness of charge effects in electrical particle interaction, and the so-called "hydrophobic bonding" mechanism of stability have received much attention. In clay science, the phenomenon of expansion of the kaolinite structure by potassium acetate and certain other salts ("intersalation"), as well as by hydrogen bonding compounds, (briefly mentioned in the first edition) has been intensively studied in the past decade.

In the present edition both the text and the literature references have been updated to recognize these new developments. Furthermore, recent international recommendations on terminology for both colloid science (IUPAC) and clay mineralogy (AIPEA) have been adopted in this edition (see Appendix V). Also, SI units are used with some convenient exceptions—with due apology. Thus, equivalents were not altogether discarded: the Angstrom unit has been maintained, and electrical double-layer calculations are primarily presented in terms of the electrostatic unit system (esu), rather than the rationalized four quantity system which is part of the SI system. The reason for the latter is that the use of the esu system provides easier access to the now classic literature on the electrical double layer. However, in a few cases, formulas and calculations are presented in both rationalized units and in electrostatic units, to demonstrate the differences between the two systems.

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CONTENTS

CHAPTER ONE

Clay Suspensions and Colloidal Systems in General

I. THE COLLOIDAL SOLUTION OF A CLAY IN WATER

Clays as found in nature are often light to dark grey and are sometimes greenish or bluish owing to organic and inorganic impurities, although certain ion constituents of the clays themselves may cause some coloration. In the purified form, most clays are white. We shall consider a pure white clay powder, for example, a bentonitic clay, and describe what happens when a small amount of the powder is stirred with a large volume of water.

A. Observations with the Naked Eye

The powdered clay seems to dissolve in water, just like common salt. However, some unusual optical effects are observed which are not displayed by a salt solution. When one looks *through* the clay "solution" against the light, the solution appears to be perfectly transparent, but it is brownish in color. When one looks *at* the illuminated clay "solution" from the side, against a dark background, the solution appears bluish white and seems to be slightly turbid. This optical effect is known as the *Tyndall effect.* It is explained as follows:

The clay "solution" is actually a dispersion of very small clay particles. These tiny particles scatter part of the incident light in all directions. According to the theory of light scattering, the intensity of the scattered light increases with decreasing wavelength. Therefore, when the incident light is white, the scattered light has a bluish color, and the transmitted light, which has lost a relatively larger portion of the smaller wavelengths, shows a complementary yellowish to brownish color. Of course, for a non-white clay, certain colors are preferentially absorbed by the clay particles, and a different color distribution between scattered and transmitted light is observed.