

H. van Olphen

An Introduction to Clay Colloid Chemistry

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Clay Colloid Chemistry

For Clay Technologists, Geologists,
and Soil Scientists

H. van Olphen

*National Academy of Sciences
Washington D.C.*

Second Edition

A Wiley-Interscience Publication

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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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H. VAN OLPHEN

CONTENTS

Chapter One—Clay Suspensions and Colloidal Systems in General . . .	1
I. The Colloidal Solution of a Clay in Water	1
A. Observations with the Naked Eye	1
B. Observations with the Ordinary Light Microscope	2
C. Observations with the Ultramicroscope	2
D. Observations with the Electron Microscope	5
E. X-Ray Diffraction Patterns of Clays	6
F. Electron Diffraction Patterns of Clay Particles	9
II. Particle Interaction	9
III. Terminology in Colloid Chemistry	12
IV. Classification of Colloidal Systems	13
References	15
 Chapter Two—Properties of Hydrophobic Sols	 16
I. Settling, Aging, and Flocculation	16
A. Settling	16
B. Aging	16
C. Flocculation (Particle Agglomeration)	17
II. The Origin of the Electric Charge of the Particles	17
III. The Preparation of a Stable Hydrophobic Sol	20
A. Condensation Method	20
B. Dispersion Method	21
C. Cleaning of the Sols	22
IV. Flocculation of Sols by Electrolytes	22
V. Reversal of Particle Charge—Irrregular Flocculation Series	24
VI. Counter-Ion Exchange	26
VII. Gelation—A Special Case of Flocculation	27
References	28
 Chapter Three—The Theory of the Stability of Hydrophobic Sols	 29
I. Configuration of the Electric Double Layer	29
II. Effect of Electrolytes on the Configuration of the Electric Double Layer	34

III. The Balance of Repulsive and Attractive Forces on Particle Approach	35
A. The Electric Double-Layer Repulsion	35
B. The van der Waals Attraction	36
IV. The Summation of Repulsion and Attraction	38
V. The Net Interaction Curve and Sol Stability	40
References	42
 Chapter Four—Successes of the Theory of Stability—Further Theories and Refinements	45
I. Stability, Flocculation, and the Schulze-Hardy Rule	45
II. Limits of Particle Size	46
III. Flocculation by Water-Miscible Organic Solvents	47
IV. Direct Evidence of Long-Range Particle Interaction: Schiller Layers and Tactoids	47
A. Schiller Layers	47
B. Tactoid Formation	48
V. Counter-Ion Exchange	49
VI. Stern's Model of the Double Layer and Other Refinements	49
VII. The Hydration Theory of Stability and Its Fallacies	52
VIII. The "Critical Zeta Potential"	53
IX. "Entropy" Stabilization	54
References	55
 Chapter Five—Clay Mineralogy	57
I. Structural Principles	57
II. Montmorillonites (Expanding 2:1 Layer Clays)	64
III. Illites (Nonexpanding 2:1 Layer Clays)	68
IV. Kaolinites (1:1 Layer Clays)	69
V. Chlorites	70
VI. Attapulgite (Palygorskite)	71
VII. Mixed-Layer Clays	71
VIII. Thermal and Spectral Analysis of Clays	71
A. Thermal Analysis	71
B. Spectral Analysis	73
IX. Genesis and Diagenesis of Clay Minerals—Synthetic Clays	73
X. Conclusions	75
References	76

Chapter Six—Particle Size and Shape, Surface Area, and Density of Charge	83
I. Size and Shape of Clay Particles	83
A. Direct Method—Ultramicroscopical Counting	83
B. Indirect Methods	84
II. Determination of the Surface Area of Clays	87
A. Computation from the Particle Dimensions	87
B. Computation from the Crystallographic Cell Dimensions	87
C. Direct Determination from Adsorption Data	87
III. Density of Charge of the Surface	89
References	89
 Chapter Seven—Electric Double-Layer Structure and Stability of Clay Suspensions	92
I. Electric Double-Layer Structure	92
A. The Double Layer on the Flat Layer Surfaces	92
B. The Double Layer on the Edge Surfaces of Clay Plates	93
II. Flocculation and Gelation	95
A. Modes of Particle Association	95
B. Clay Flocculation and the Schulze-Hardy Rule	98
C. Particle Association and Flow Properties	99
D. Argumentation	103
E. Further Experimental Support	105
1. The Structure of the Pure Gel	105
2. Criterion for Face-to-Face Association (“Aggregation”)	105
F. Particle Association in Dilute Sols and Spontaneous Swelling of Montmorillonites	106
1. Particle Association in Dilute Sols	106
2. Spontaneous Swelling of Montmorillonites	107
G. Deflocculation of Clay Suspensions	107
References	108
 Chapter Eight—Peptization of Clay Suspensions	111
I. Peptization (Deflocculation) by Special Inorganic Salts	111
II. The Mechanism of Peptization	113
III. Activity Reduction and Ion Exchange in Clay Peptization	117
A. Cation Activity Reduction	117
B. Ion Exchange	118

IV. Peptization by Alkali	119
References	120
Chapter Nine—Technological Applications of Stability Control: Sedimentation, Filtration, and Flow Behavior	121
I. Sedimentation and Stability	121
A. Principles	121
B. Applications	124
1. Separation of Dispersed Solids from a Suspension	124
2. Sedimentation Geology	125
3. Paints	125
4. Preparation of Thin Surface Coatings	125
5. Soils	125
II. Filtration of Suspensions and Stability	125
A. Principles	125
B. Applications	126
1. Analytical Chemistry	126
2. Management of Clay-Containing Soils	126
3. Permeability of Porous Formations	127
4. Conditioning of Drilling Fluids	128
5. Ceramics	129
III. Rheology and Stability of Suspensions	130
A. Terminology	130
1. Newtonian Flow	130
2. Non-Newtonian Flow	131
3. Time-Dependent Phenomena	133
4. Turbulent Flow	133
B. Measurements of Flow Properties	134
C. Rheological Properties of Suspensions	136
1. Dilute Sols and Suspensions	136
2. Effect of Particle Interaction on the Flow Properties of Suspensions	137
3. Thixotropy and Rheopexy	138
D. Applications	140
1. Drilling Fluids	140
2. Paints	144
3. Paper Fillers and Coatings	144
E. Rheological Properties of Sediments	145
F. Mechanical Properties of Soils	146
References	147

Chapter Ten—Interlamellar and Osmotic Swelling—Applications	150
I. Clay-Water Relationships: Swelling and Compaction in Soil Engineering and Sedimentary Geology	150
A. Short-Range Particle Interaction—Swelling Due to Hydration Energy	151
1. Thermodynamic Analysis of Intracrystalline Swelling	152
2. Infrared Absorption Spectra of Hydrated Clay Minerals	154
B. Long-Range Particle Interaction—“Osmotic Swelling” or Electrical Double-Layer Repulsion	155
References	158
Chapter Eleven—Interaction of Clays and Organic Compounds	162
I. Introduction	162
A. Terminology—Surface Activity	162
B. Wetting	163
C. Classification	163
D. X-Ray Observations and Infrared Absorption Spectra	164
E. Adsorption Measurements	166
II. Compounds with Low to Moderate Molecular Weights	167
✓ A. Organic Anions—Specifically Tannates	167
1. Effect of Tannates on Clay Suspensions	167
2. Application of Tannates in “Red Muds” and “Lime Red Muds”	168
B. Organic Cations—Specifically Amine Salts	171
C. Polar Organic Compounds	173
III. Macromolecular Compounds	174
A. Polyelectrolytes	174
1. Effect of Polyelectrolytes on Clay Suspensions	176
2. The Mechanism of the Protective and Sensitizing Action	176
3. Applications	179
B. Nonionic Polymers	181
1. Interaction with Clay Suspensions	181
2. Applications	181
IV. Emulsions Containing Dispersed Clays	182
A. Applications	183
V. Clay Dispersions in Oil	183
A. Applications	184
VI. Intercalation and Intersalation in Kaolinites	186
VII. Summary of Particle Interaction	187
A. Factors Promoting Deflocculation	187
1. Electric Double-Layer Repulsion	187

2. "Entropic" Repulsion	187
3. Short-Range Hydration or "Lyosphere" Repulsion	188
4. Born Repulsion	188
B. Factors Promoting Flocculation	188
1. van der Waals Attraction	188
2. Electrostatic Attraction	188
3. Bridging of Particles by Polyfunctional Long-Chain Compounds	189
4. Bridging of Particles by a Second Immiscible Liquid Component	189
VIII. Chemical Reactions between Clays and Organic Compounds	190
IX. Clays and the Origin of Life	192
References	193

Chapter Twelve—Electrokinetic and Electrochemical Properties of Clay—Water Systems	201
I. Electrokinetic Phenomena	202
A. Surface Conductance	202
B. Electrophoresis	204
C. Electrosmosis	205
D. Streaming Potentials	206
E. Electrokinetic Phenomena in Porous Media	207
II. Electrochemistry of Dispersed Systems	208
A. Ion Activities and pH Measurements	208
1. Degree of Dissociation and Ion Activity in Electrolyte Solutions	209
2. Determination of Ion Activities in Solutions	210
3. The pH Scale and Measurements of pH in Electrolyte Solutions	210
4. Measurement of pH in Sols and Suspensions	211
5. "Degree of Dissociation" and "Cation Activities" in Clay Suspensions	214
B. Membrane Potentials	217
References	219

Synopsis	222
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Appendix I—Note on the Preparation of Clay Suspensions	249
References	252

Appendix II—Miscellaneous Computed Data for Montmorillonites . . .	254
A. Total Layer Surface Area and Surface Charge Density	254
B. Average Particle Distance in Suspensions of Clays for Parallel and Cubic Stacking of the Plates	255
1. Bentonite	256
2. Illite	256
C. Formula Computation from Chemical Analysis	258
References	259
 Appendix III—Electric Double-Layer Computations	 260
A. The Single Flat Double Layer	261
1. Potential and Charge Distribution in a Single Flat Double Layer According to the Gouy Theory	261
2. Potential and Charge Distribution in a Flat Double Layer According to the Stern Model	269
3. Corrections of the Gouy Theory According to Bolt	272
B. Interacting Flat Double Layers	273
1. Potential and Charge Distribution between Interacting Flat Double Layers According to the Gouy Model	273
2. Potential and Charge Distribution between Interacting Surfaces with Stern-Type Double Layers	275
C. Force and Energy of Interaction of Two Flat Double Layers	276
1. Repulsive Energy of Double Layers of Constant Potential Derived from the Free-Energy Change	276
2. Direct Computation of the Interaction Force between Flat Double Layers	277
3. Interaction Energy of Stern Double Layers	278
D. Cation-Exchange Capacity and Negative Adsorption	280
E. Cation-Exchange Equilibrium	283
1. Monovalent Cation Exchange	283
2. Monovalent-Divalent Ion Exchange	284
F. Summary of Gouy Double-Layer Formulas	285
1. Symbols and Values	285
2. Single Gouy Double Layer	285
3. Interacting Gouy Double Layers	287
4. Interaction Force and Energy	288
G. Short-Range Electrostatic Interaction between Layers of a 2:1 Layer Clay	288
1. Counter Ions Associated with Silica Sheets—Calculation of the Repulsive Electrostatic Energy	288

2. Counter Ions in Midway Position between the Layers— Calculation of the Attractive Electrostatic Energy	290
References	290
Appendix IV—van der Waals Attraction Energy between Two Layers .	292
Appendix V—Clay Literature	294
Current	294
Terminology, Symbols, Units	294
Books, Monographs, Reviews	294
References Clays	297
Periodic Publications	298
Author Index	303
Subject Index	311

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.