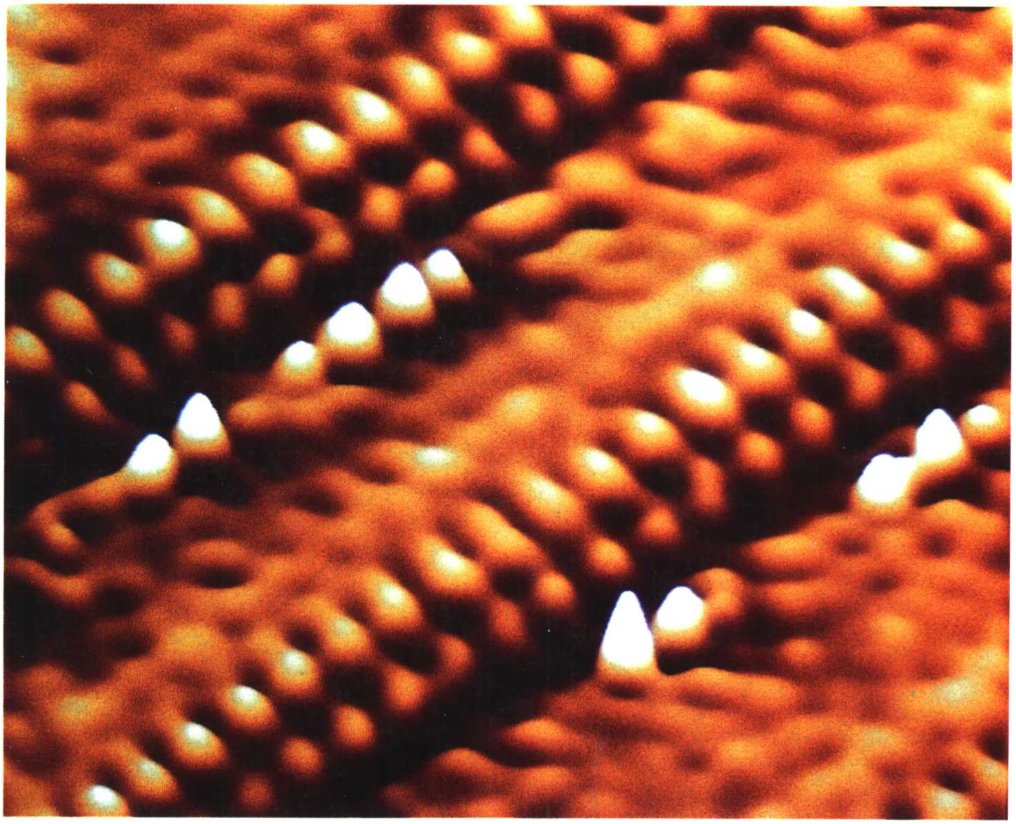
CHEMISTRY of the SOLID-WATER INTERFACE

PROCESSES AT THE MINERAL-WATER AND PARTICLE-WATER INTERFACE IN NATURAL SYSTEMS



WERNER STUMM

Chemistry of the Solid-Water Interface

Processes at the Mineral-Water and Particle-Water Interface in Natural Systems

WERNER STUMM
Professor, Swiss Federal Institute of Technology, ETH Zurich,
Institute for Water Resources and Water Pollution Control (EAWAG)

with contributions by
LAURA SIGG (Chapter 11)
BARBARA SULZBERGER (Chapter 10)

A Wiley-Interscience Publication
John Wiley & Sons, Inc.
New York / Chichester / Brisbane / Toronto / Singapore

Library of Congress Cataloging in Publication Data:

Stumm, Werner
Chemistry of the solid-water interface : processes at the mineral-water and particle-water interface in natural systems / Werner Stumm : with contributions by Laura Sigg (chapter 11), and Barbara Sulzberger (chapter 10).
p. cm.
"A Wiley-Interscience publication."
Includes bibliographical references and index.
ISBN 0-471-57672-7 (pbk.)
1. Water chemistry. 2. Surface chemistry. I. Sigg, Laura. II. Sulzberger, Barbara. III. Title.
GB855.S79 1992
551.46—dc20 92-9701
CIP

Printed in the United States of America

10 9 8 7 6 5

Preface

The aim of this book is to provide an introduction to the chemistry of the solid–water interface. Of primary interest are the important interfaces in natural systems, above all in geochemistry, in natural waters, soils, and sediments. The processes occurring at mineral–water, particle–water, and organism–water interfaces play critical roles in regulating the composition and the ecology of oceans and fresh waters, in the development of soils and the supply of plant nutrients, in preserving the integrity of waste repositories, and in technical applications such as in water technology and in corrosion science.

This book is a teaching book; it progresses from the simple to the more complex and applied. It is addressed to students and researchers (geochemists, oceanographers, limnologists, soil scientists and environmental engineers). Rather than providing descriptive data, this book tries to stress surface chemical principles that can be applied in the geochemistry of natural waters, soils, and sediments, and in water technology.

Interface and colloid science has a very wide scope and depends on many branches of the physical sciences, including thermodynamics, kinetics, electrolyte and electrochemistry, and solid state chemistry. Throughout, this book explores one fundamental mechanism, the interaction of solutes with solid surfaces (adsorption and desorption). This interaction is characterized in terms of the chemical and physical properties of water, the solute, and the sorbent. Two basic processes in the reaction of solutes with natural surfaces are: 1) the formation of coordinative bonds (surface complexation), and 2) hydrophobic adsorption, driven by the incompatibility of the nonpolar compounds with water (and not by the attraction of the compounds to the particulate surface). Both processes need to be understood to explain many processes in natural systems and to derive rate laws for geochemical processes.

The geochemical fate of most reactive substances (trace metals, pollutants) is controlled by the reaction of solutes with solid surfaces. Simple chemical models for the residence time of reactive elements in oceans, lakes, sediment, and soil systems are based on the partitioning of chemical species between the aqueous solution and the particle surface. The rates of processes involved in precipitation (heterogeneous nucleation, crystal growth) and dissolution of mineral phases, of importance in the weathering of rocks, in the formation of soils, and sediment diagenesis, are critically dependent on surface species and their structural identity.

The dynamics of particles, especially the role of particle–particle interactions (coagulation) is critically assessed. The effects of particle surfaces on the catalysis of redox processes and on photochemically induced processes are discussed, and it is shown that the geochemical cycling of electrons is not only mediated by microorganisms but also by suitable surfaces, and is thus of general importance at particle–water interfaces.

The chemical, physical, and biological processes that are analyzed here at the micro level influence the major geochemical cycles. Understanding how geochemical cycles are coupled by particles and organisms may aid our understanding of global ecosystems, and on how interacting systems may become disturbed by civilization.

Acknowledgements

Chemistry of the Solid-Water Interface covers many subjects where I have been involved in my own research. This research has been stimulated by many colleagues. Regretfully, only casual recognition of some of their papers can be made because this book does not review the literature comprehensively; but I should like to acknowledge the great influence of Paul W. Schindler (University of Berne) on the ideas of surface coordination, and the significant contributions of Garrison Sposito to the surface chemistry of soils. My own research could not have been carried out without the help and the enthusiasm of a number of doctoral students. My own scientific development owes a great deal to Elisabeth Stumm-Zollinger. The prolonged association with James J. Morgan (California Institute of Technology, Pasadena), Charles R. O'Melia (Johns Hopkins University, Baltimore), and Laura Sigg (Swiss Federal Institute of Technology, EAWAG, Zurich) has been of great inspiration.

I greatly acknowledge my colleagues Laura Sigg and Barbara Sulzberger for contributing the two last chapters in this book.

In the preparation of this book I am greatly indebted to Lilo Schwarz who skillfully carried the manuscript through its many revisions to camera-readiness. Heidi Bolliger drew and redrew most of the illustrations. I am also grateful to Sonja Rex and Gerda Thieme.

Many of my colleagues, including M. Blesa, J. J. Morgan, F. M. M. Morel, C. R. O'Melia, Jerry L. Schnoor, L. Sigg, and B. Sulzberger, have made valuable suggestions for corrections and improvements. Rolf Grauer (Paul Scherrer Institute, Switzerland) deserves special credit for giving critical and constructive advice on many chapters.

December 1991 Werner Stumm

We are indepted to Peter R. van der Linde, Utrecht (NL), who called our attention to numerous errors and inconsistencies; many of these could be corrected in the reprinted edition.

March 1996

Contents

Chapter 9 **Redox Processes Mediated by Surfaces** **309**

Chapter 10 **Heterogeneous Photochemistry** **337**

Chapter 11 **Regulation of Trace Elements by the Solid-Water Interface in Surface Waters** **369**

Chapter 1

Introduction
Scope of Aquatic Surface Chemistry

The various reservoirs of the earth (atmosphere, water, sediments, soils, biota) contain material that is characterized by high area to volume ratios. Even the atmosphere contains solid-water-gas interfaces. There are trillions of square kilometers of surfaces of inorganic, organic and biological material that cover our sediments and soils and that are dispersed in our waters. Very efficient interface chemistry must occur to maintain appropriate atmospheric chemistry and hydrospheric chemistry. Mineral-based assemblages and humus make up our soil systems that provide the supply of nutrients and support our vegetation. The action of water (and CO_2 and organic matter) on minerals is one of the most important processes which produce extremely high surface areas and reactive and catalytic materials in the surface environments. The geological processes creating topography involve erosion by solution and particle transport. Such processes provide nutrient supply to the biosphere. The mass of material eroded off the continents annually is thus of an order of magnitude similar to that of the rate of crust formation and subduction (Fyfe, 1987). Human activity is greatly increasing erosion; and soil erosion has become a most serious world problem. The oceanic microcosmos of particles – biological particles dominate the detrital phases – plays a vital role in ocean chemistry.

The actual natural systems usually consist of numerous mineral assemblages and often a gas phase in addition to the aqueous phase; they nearly always include a portion of the biosphere. Hence natural systems are characterized by a complexity seldom encountered in the laboratory. In order to understand the pertinent variables out of a bewildering number of possible ones it is advantageous to compare the real system with idealized counterparts, and to abstract from the complexity of nature.

Adsorption

Adsorption, the accumulation of matter at the solid-water interface, is the basis of most surface-chemical processes.

1) It influences the *distribution of substances* between the aqueous phase and particulate matter, which, in turn, affects their transport through the various reservoirs of the earth. The affinity of the solutes to the surfaces of the "conveyor belt" of the settling inorganic and biotic particles in the ocean (and in lakes) regulate their (relative) residence time, their residual concentrations and their

ultimate fate (Fig. 1.1). Adsorption has a pronouced effect on the speciation of aquatic constituents.

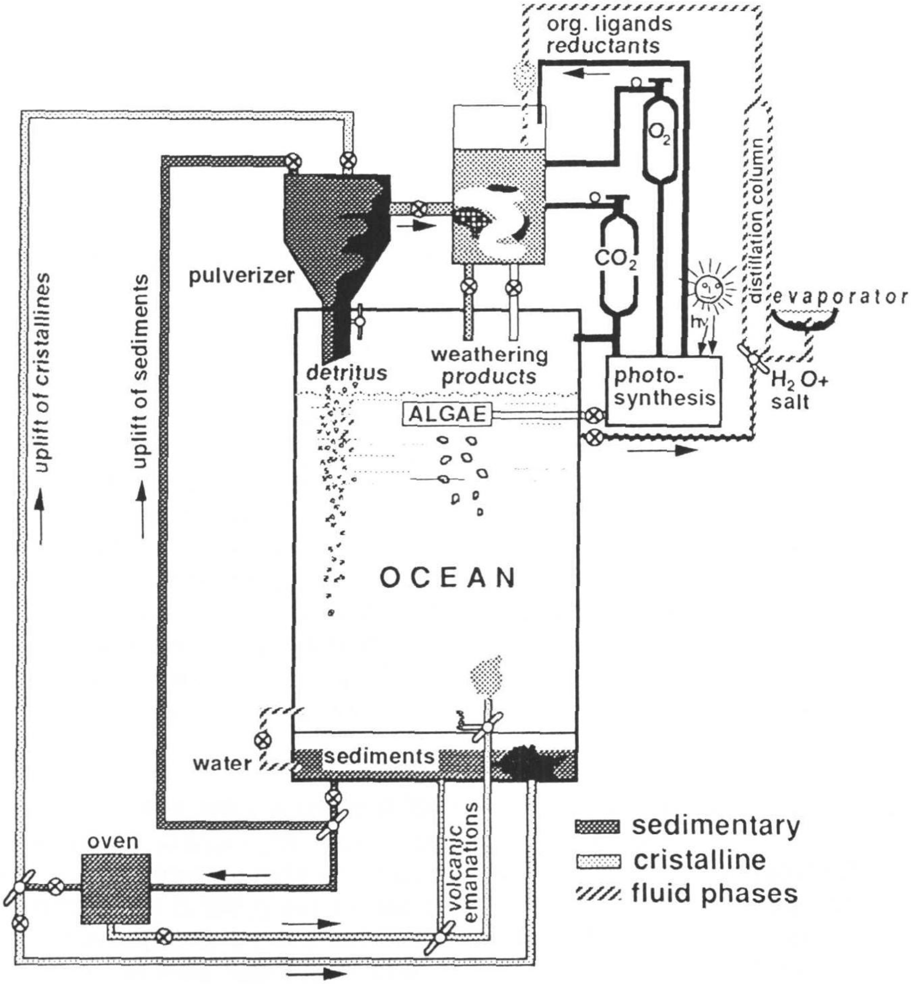


Figure 1.1

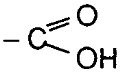
Circulation of rocks, water and biota. Steady state model for the earth's surface geochemical system likened to a chemical engineering plant. The interaction of water with rocks in the presence of photosynthesized organic matter continuously produces reactive material of high surface area in the surface environment. This process provides nutrient supply to the biosphere and, along with biota, forms the array of small particles (soils). Weathering imparts solutes to the water and erosion brings particles into surface waters and oceans. A large flux of settling detrital and biogenic particles continuously runs through the water column. The steady state conveyor belt of settling particles which are efficient sorbents of heavy metals and other trace elements regulates their concentrations in the water column. The sediments are the predominant sink of trace elements.

(Modified from Siever, 1968)

2) Adsorption affects the *electrostatic properties* of suspended particles and colloids, which, in turn, influences their tendency to aggregate and attach (coagulation, settling, filtration).
3) Adsorption influences the reactivity of surfaces. It has been shown that the rates of processes such as precipitation (heterogeneous nucleation and surface precipitation), dissolution of minerals (of importance in the weathering of rocks, in the formation of soils and sediments, and in the corrosion of structures and metals), and in the catalysis and photocatalysis of redox processes, are critically dependent on the properties of the surfaces (surface species and their structural identity).

Atoms, molecules and ions exert forces upon each other at the interface. In this book, adsorption reactions are discussed primarily in terms of intermolecular interactions between solute and solid phases. This includes: 1) *Surface complexation reactions* (surface hydrolysis, the formation of coordinative bonds at the surface with metals and with ligands). 2) The *electric interactions* at surfaces, extending over longer distances than chemical forces. 3) *Hydrophobic expulsion* (hydrophobic substances) – this includes non-polar organic solutes – which are usually only sparingly soluble in water, tend to reduce the contact in water and seek relatively non-polar environments and thus may accumulate at solid surfaces and may become absorbed on organic sorbents. 4) *Adsorption of surfactants* (molecules that contain a hydrophobic moiety). (interfacial tension and adsorption are intimately related through the Gibbs adsorption law; its main message – expressed in a simple way – is that substances that tend to reduce surface tension, tend to become adsorbed at interfaces). 5) *The adsorption of polymers* and of polyelectrolytes – above all humic substances and proteins – is a rather general phenomenon in natural waters and soil systems that has far-reaching consequences for the interaction of particles with each other and on the attachment of colloids (and bacteria) to surfaces.

Surface Coordination

One of the more important generalizations emphasized in this book is that the solids can be considered as inorganic and organic polymers, the surfaces of which can be looked at as *extending structures* bearing surface functional groups. These functional groups contain the same donor atoms which are found in functional groups of solute ligands such as –OH, –SH, –SS,  $-\mathrm{C}\overset{\displaystyle\mathrm{O}}{\diagup\!\!\!\!\diagdown}_{\mathrm{OH}}$ etc. Such functional groups provide a diversity of interactions through the formation of *coordinative bonds*. Fig. 1.2 illustrates three possible adsorption mechanisms of metal ions on an oxide-water interface as well as sorption through the formation of a surface precipitate. In a similar way ligands can replace surface OH groups (ligand exchange) to form ligand surface complexes. The concept of active sites has been a highly

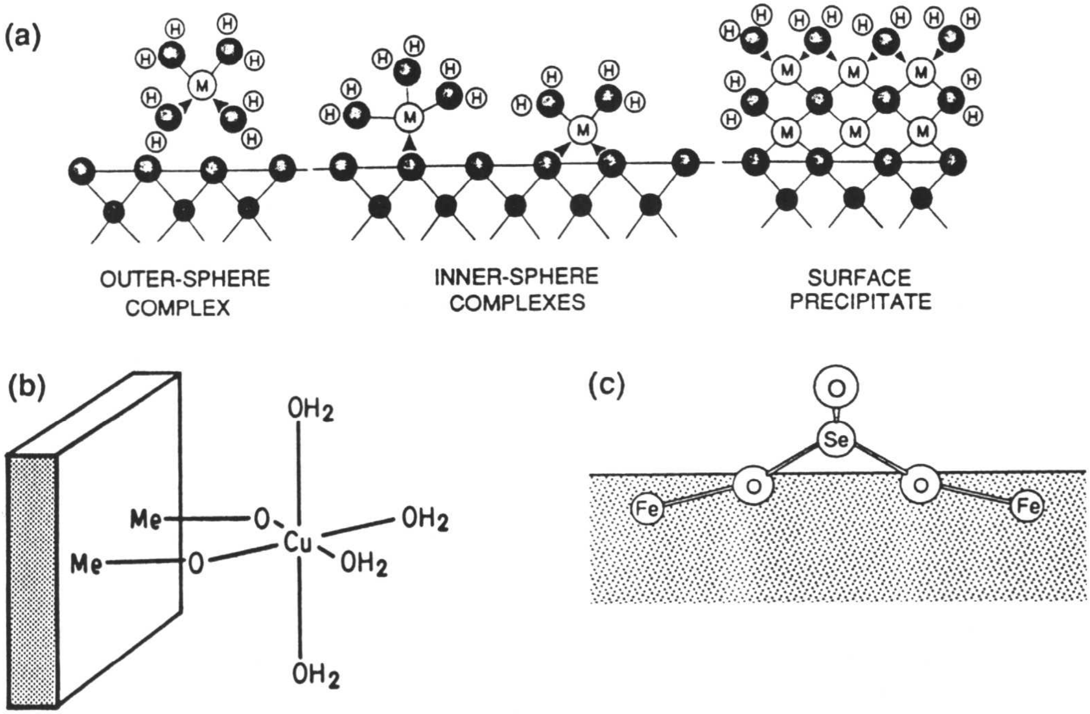


Figure 1.2

Structural arrangements in surface complexes at an oxide surface.

a) Definition of possible sorption complexes at the solid/water interface, which is represented by the horizontal line. The solid substrate is below the line and the solution is above the line. The circles labeled M represent sorbed metal atoms in various types of sorption complexes. The larger shaded spheres in the solid substrate and surrounding the metal in the solution phase are oxygens. The smaller dark spheres in the solid substrate are metal ions, as are the spheres labeled M in the sorption complexes and surface precipitate. (From Brown, 1990)

b) Surface complex of Cu(II) on δ–Al_2O_3 (structure inferred from EPR measurements). (From Motschi, 1987)

c) Proposed structure for SeO_3^{2-} coordinated with Fe atoms of goethite based on Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. (From Hayes, Roe, Brown, Hodgson, Leckie, and Parks, 1981)

productive one in understanding catalysis by enzymes and coenzymes. Although surface functional groups at solid-water interfaces are often characterized by less specificity than that of enzymes, they form an array of surface complexes, whose reactivities determine the mechanism of many surface controlled processes. We know from research on nucleation and biomineralization that the specific surface sites can extent "molecular recognition"; they determine in nucleation not only what allotropic modification of the solid phase is formed but also the morphology of the new phase. It is only today that we are discovering some of the basic mechanistic steps. Many mechanisms can readily be described in terms of Brønsted acid sites

Table 1.1 Coordination Chemistry of the Solid-Water Interface: Concepts and important Applications in natural and technical Systems

Surface Complex Formation	Applications: Distribution of Solutes between Water and Solid Surface	Applications: Rates depend on Surface Speciation
Interaction with – H^+, OH^- – Metal ions – Ligands (ligand exchange) **Thermodynamics of Surface Complex Formation** – K (mass law constants, corrected for electrostatic effects) – ΔG, ΔH **Kinetics of Surface Complex Formation** Rates of sorption and desorption **Structure of Surface Compounds** (Surface Speciation) – Inner-sphere versus outer-sphere – Monodentate versus binuclear – Monodentate versus bidentate **Establishment of Surface Charge** **Structure of Lattice** – Defect sites – Adatoms, kinks, steps, ledges – Lattice statistics **Microtopography**	**Binding of Reactive Elements to Aquatic Particles in Natural Systems** – Regulation of metals in soil, sediment, and water systems – Regulation of oxyanions of P, As, Se, Si in water and soil systems – Interaction with phenols carboxylates and humic acids – Transport of reactive elements including radio-nuclides in soils and aquifers **Binding of Cations, Anions and Weak Acids to Hydrous Oxides in Technical Systems** – Corrosion; passive films – Processing of ores, flotation – Coagulation, flocculation, filtration – Ceramics, cements – (Photo)electrochemistry (electrodes, oxide electrodes and semiconductors) **Surface Charge resulting from the Sorption of Solutes** – Particle-particle interaction; coagulation, filtration	**Natural Systems** **Dissolution of Oxides, Silicates and other minerals** – Weathering of minerals – Proton and ligand promoted dissolution – Reductive dissolution of Fe(III) and Mn(III, IV) oxides **Formation of Solid Phases** – Heterogeneous nucleation – Surface precipitation, crystal growth – Biomineralization **Surface Catalyzed Processes** – (Photo)redox processes – Hydrolysis of esters – Transformations of organic matter by Fe and Mn (photo)redox-cycles – Oxygenation of Fe(II), Mn(II), Cu(I) and V(IV) **Technical Systems** – Passive films (corrosion) – Photoredox processes with colloidal semiconductor particles as photo-catalyst, e.g. degradation of refractory organic substances – Photoelectrochemistry, e.g. photoredox processes at semiconductor electrodes

or Lewis acid sites. Of course, the properties of the surfaces are influenced with the properties and conditions of the bulk structure and the action of special surface structural entities will be influenced by the properties of both surface and bulk. Table 1.1 gives an overview of the major concepts and important applications. Emphasis is on surface chemistry of the oxide-water interface not only because the oxides are of great importance at the mineral-water (including the clay water) interface but because its coordination chemistry is much better understood than that of other surfaces. Experimental studies on the surface interactions of carbonates, sulfides, disulfides, phosphates and biological materials are only now emerging. The results of these studies show, that the concepts of surface coordination chemistry can also be applied to these interfaces.

Some emphasis is given in the first two chapters to show that complex formation equilibria permit to predict quantitatively the extent of adsorption of H^+, OH^-, of metal ions and ligands as a function of pH, solution variables and of surface characteristics. Although the surface chemistry of hydrous oxides is somewhat similar to that of reversible electrodes the charge development and sorption mechanism for oxides and other mineral surfaces are different. Charge development on hydrous oxides often results from coordinative interactions at the oxide surface. The surface coordinative model describes quantitatively how surface charge develops, and permits to incorporate the central features of the *Electric Double Layer* theory, above all the *Gouy-Chapman* diffuse double layer model.

The Hydrophobic Effect

The hydrophobic effect, due to the incompatibility of the hydrophobic substance with water, plays an important role in the adsorption of non-polar organic substances (Tanford, 1980). The sorption of hydrophobic substances to solid materials (particles, soils, sediments) that contain organic carbon may be compared with the partitioning of a solute between two solvents – water and the organic phase. It is possible to characterize the sorption of a wide range of the organic compounds based on a single property of the compound, i.e., its octanol-water partition constant, K_{OW}, (Fig. 1.3) and the property of the sorbent, i.e., the fraction of the sorbent that is organic carbon (Westall, 1987). Many organic substances, such as fatty acids, detergents, contain a hydrophobic part and a hydrophilic polar or ionic group; they are amphipathic. Such substances may, depending on the configuration, become adsorbed either by hydrophobic effect or by coordinative interaction.

Colloids

Colloids will receive attention throughout this book. They are usually defined on the basis of size; they are entities having at least in one direction a dimension between 1 nm and 1 μm (Lyklema, 1991). Colloids are ubiquitous in seawater, in fresh surface waters, in soils and sediments and in groundwaters and are typically present at substantial concentrations (usually more than 10^6 colloids cm^{-3}). A renewed research interest concerns the *stability of colloids*, their genesis and dissolution, their coagulation and attachment and their role in the transport of reactive elements, of radionuclides and other pollutants. The presence of colloids causes major operational difficulties in distinguishing between dissolved and particulate matter. All what we learn about interfaces is applicable to the colloid surface; because of the small size of the colloids they have relatively large area per given volume.

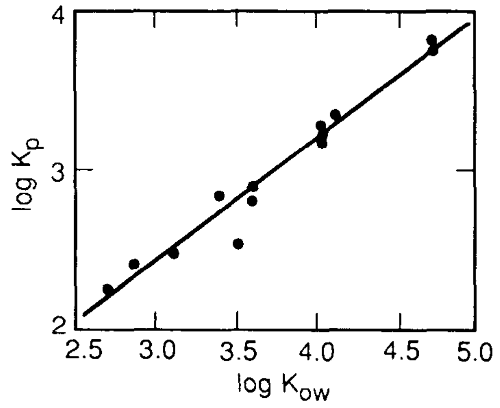


Figure 1.3

Partition constant for the distribution of various aromatic substances (mono-, di-, tri-, and tetramethyl, and chlorobenzenes) between water and an aquifer material (0.15 % organic carbon) as a function of the octanol-water partition coefficient, K_{ow}. The values of log K_p have been adjusted to be correct for a sorbent of 100 % organic carbon. K_{ow} is defined for the partition of a substance A between octanol water: $K_{ow} = [A_{oct}]/[A_{aq}]$. (For additional information see Chapter 4.8.)
(Modified from Westall, 1987)

With a chapter on particle-particle interaction (coagulation) the characteristics of particles and colloids as chemical reactants are discussed. Since charge, and in turn the surface potential of the colloids is important in coagulation, it is illustrated how in simple cases the modelling of surface complex formation permits the calculation of surface charge and potential. The role of particle-particle interaction in natural water and soil systems and in water technology (coagulation, filtration, flotation) is exemplified.

Surface Structure and Surface Reactivity

Three applications in geochemistry, in soil science and sediment chemistry are of importance:

1) Dissolution (weathering) of minerals;
2) The formation of the solid phase (nucleation, precipitation, crystal growth, biomineralization);
3) Redox processes at the solid-water interface.

In analyzing the kinetics of surface reactions, it will be illustrated that many of these processes are rate-controlled at the surface (and not by transport). Thus, the surface structure (the surface speciation and its microtopography) determine the kinetics. Heterogeneous kinetics is often not more difficult than the kinetics in homogeneous systems; as will be shown, rate laws should be written in terms of concentrations of surface species.

Because surfaces can adsorb reductants and oxidants and modify redox intensity, the solid-solution interface can *catalyze many redox reactions.* The geochemical cycling of electrons is not only mediated by microorganisms but is of importance at particle-water interfaces (especially at the sediment-water interface due to strong redox gradients) and in surface waters due to *heterogeneous photo-chemical processes.* Many of the naturally occurring solid phases, such as Fe(III) oxides, TiO_2, CdS, have electronic structures with semiconductor properties. Light can induce – as in biological photosynthesis – transformations that are important in the cycling of elements; such light-catalyzed redox processes are also of importance in prebiotic geochemistry. Applications of heterogeneous photochemical redox processes include the catalytic degradation of toxic inorganic and organic substances in waters and wastes, and, of course, the exploration of the possibility of using semiconducting minerals in the splitting of water.

The Bonding between Solids and Solutes; The Need for a better Understanding

The structural identity of the surface species, the geometry of the coordinating shell of surface sites and of reactants at surfaces need to be known. The overlapping orbital of the *inner-sphere surface complex* interconnects the solid phase (metal, ionic or covalent solid, polymer) with the aqueous solution phase; it is a key to understanding of the reactivity of the solid-water interface (dissolution and formation of solids, heterogeneous catalysis). The mechanism of most surface controlled processes depend on the coordinative environment at the solid-water interface. We lack sufficient knowledge on the ways molecules, atoms and ions interact at solid-water interfaces, above all, on the electronic structure of the bonding between solids and solutes. The recent book by R. Hoffmann on *Solids and Surfaces; a Chemist's View of Bonding in Extended Structures* (1988) shows how chemistry and physics come together in the solid state and on surfaces and how the basic mechanistic steps in heterogeneous catalysis can be understood. Although *water* at the interface of the solid is not considered in Hoffmanns book, it gives us an idea in which direction we should go. A better understanding on the electronic structure of the bonding between solids and aquatic solutes would push the boundaries of aquatic surface chemistry.