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SOIL PHYSICAL CHEMISTRY

Donald L. Sparks

Soil Physical Chemistry

Editor

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DEDICATION

To my wife, Joy, with much love, admiration, and appreciation.

PREFACE

"There is nothing in the whole of nature which is more important or deserves as much attention as the soil. Truly it is the soil which makes the world a friendly environment for mankind. It is the soil which nourishes and provides for the whole of nature; the whole of creation depends on the soil which is the ultimate foundation of our existence."

Friedrich Albert Fallon, 1862

The quote above eloquently states the importance of soil to mankind. As we approach the 21st century, the management and care of soil will be extremely crucial to man's continued existence on earth.

The physical chemistry of soil is both fascinating and complex. It has been stated that soil itself is a transition state between the unstable mineral form of an ion and its most stable state, infinite dilution in water. Since the pioneering and elegant work of J. Thomas Way in the 1850s, whom many consider as the patriarch of soil chemistry, voluminous research has appeared on various aspects of soil physical chemistry. However, this information is scattered in numerous journal articles, books, and monographs. Additionally, the application of these investigations in solving practical agricultural problems is often not discussed.

In this book, every effort is made to synthesize information from many sources on each of the topics discussed, and to explain the theoretical aspects of each topic in a clear and lucid manner. This book should be of interest to students and professionals in soil science, marine studies, environmental engineering, chemistry, and geology.

The book is divided into five major chapters. Chapter 1 covers the electrochemistry of the double-layer, and the principles and applications of this topic are thoroughly presented. Topics include theory of the electrical double-layer and applications of electrical double-layer theory to a variety of soil-water systems. Chapter 2 discusses charge properties of soil colloids. Discussions on source of charge, types of charged sites, cation exchange and selectivity, ion adsorption models and processes, and zero point of charge theory are included. Chapter 3 involves kinetics of reactions on clay minerals and soils. This is a topic that is currently of great research interest to soil chemists. A definitive discussion on this topic as it applies to heterogenous systems has not previously appeared in any book. This chapter discusses theoretical aspects of chemical kinetics in homogeneous solutions, the effect of temperature on kinetics of reactions in clays and soils, rate-determining steps of ion exchange kinetics with clays and soils, methodologies used in kinetic studies, equations to describe the kinetics of reactions, kinetics of ionic reactions in clay minerals and soils, and kinetic modeling of soil reactions. Chapter 4 deals with thermodynamics of the soil solution. Topics that are covered include thermodynamic data in soil chemistry, variables of state and thermodynamic potentials, the chemical potential, chemical equilibria, and cation exchange equilibria. Chapter 4 gives a thorough overview of soil redox processes. Chapter 5 entitled "Hydrostatics of Water in Porous Media" describes: molecular aspects of water-solid interactions, macroscopic analysis of equilibrium water adsorption in rigid porous media, and macroscopic analysis of equilibrium water adsorption in deformable porous media. Each of the five chapters contains an extensive review of the literature.

I am deeply indebted to Professors D. F. Crossan, University of Delaware; C. R. Curtis, The Ohio State University; and D. C. Martens and L. W. Zelazny, Virginia Polytechnic Institute and State University, for their constant encouragement and support. I am also grateful to my parents, Elmer and Christine Sparks, and to my wife, Joy, for their love and support throughout the writing of this book. Immense appreciation is also expressed to graduate students Harris Martin, Phil Jardine, Clare Evans, Peter Galusky, Richard Ogwada,

THE EDITOR

Dr. Donald L. Sparks is Assistant Chairman of the Department of Plant Science and Associate Professor of Soil Physical Chemistry at the University of Delaware at Newark.

Dr. Sparks received his B.S. and M.S. degrees at the University of Kentucky, Lexington, and his Ph.D. degree in 1979 from the Virginia Polytechnic Institute and State University, Blacksburg. He served as Assistant Professor at the University of Delaware from 1979-1982 and was promoted to Associate Professor in 1983.

Dr. Sparks' research has centered on the kinetics and thermodynamics of potassium exchange in clay minerals and soils. He is the author of more than 60 published papers and abstracts, and of three book chapters on this topic. Dr. Sparks has presented his research findings at national and international symposia and has served as an invitational seminar speaker at universities throughout the United States and Canada.

Dr. Sparks has been the recipient of research grants from the Agency for International Development, Potash and Phosphate Institute, Department of the Interior, University of Delaware Research Foundation, and the United States Borax Corporation.

Dr. Sparks has also served as an invitational reviewer for numerous manuscripts in scientific journals and for grant proposals to the National Science Foundation and to the Agency for International Development. He is currently serving on the Editorial Board of the *Soil Science Society of America Journal*.

At the University of Delaware, Dr. Sparks has been very active in graduate education. He has served as Major Professor to a number of M.S. and Ph.D. students. He has also served as host to Visiting Scholars from around the world in soil science. In 1982, he was the recipient of the University of Delaware Sigma Xi Distinguished Scientist Award. In 1983, he was cited by the International Potash Institute for his outstanding research on soil potassium.

Dr. Sparks is a member of the American Society of Agronomy, Soil Science Society of America, Clays and Clay Minerals Society, and the honorary societies Gamma Sigma Delta and Sigma Xi.

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TABLE OF CONTENTS

Chapter 1

ELECTROCHEMISTRY OF THE DOUBLE-LAYER: PRINCIPLES AND APPLICATIONS TO SOILS

Upendra Singh and Goro Uehara

TABLE OF CONTENTS

This chapter is designed for students who are searching for a simple and complete mathematical explanation of double-layer theory. A thorough discussion of the strengths and weaknesses of double-layer theory has been sacrificed for completeness of theory and its derivation. Many steps that are omitted in advanced papers on the subject are included for clarity and continuity in this chapter. The aim of this chapter is to entice a larger number of scientists to adopt and apply the double-layer theory. Double-layer theory remains under utilized in aquatic chemistry and particularly in soil science because potential users have not learned the basic relationships that comprise it.

It is our premise that there exists a sizable group that is ready to use double-layer theory in its work. Soil science is a good case in point. In soil science, the use of double-layer theory is largely confined to soil chemists, soil physicists, and soil mineralogists. However, the greatest potential for practical application of double-layer theory is in the fields of soil fertility and pedology. Many soil scientists continue to operate on the assumption that a soil's cation exchange capacity is constant. They make soil fertility recommendations and classify soil on the basis of this assumption. Papers on soil classification that equate the sum of bases and extractable aluminum with permanent surface charge appear unabated in journals.

Double-layer theory has much to offer, but those who can profit from it cannot do so because they do not have access to an unabridged version of its derivation. This chapter alone will not convert nonusers to users, but it is an attempt to fill a critical need. It does so by providing the missing steps that so often discourage the neophyte from pursuing the subject to its logical conclusion.

I. INTRODUCTION

A particle or surface with acquired charge which is different from the surrounding solution accumulates counter charge in order to preserve electrical neutrality. The counter charge may consist simply of a diffuse atmosphere of counter-ions or it may take the form of a compact layer of bound charge and a diffuse atmosphere as well. The surface charge and the sublayers of compact and diffuse counter-ions are called the electrical double-layer.

Originally, the double-layer was assumed to be built up by the ''monoionic'' layer of opposite charges touching each other in the boundary plane. This very simple picture, which neglects the thermal agitation of the ions, is often ascribed to von Helmholtz (1835).[1] The true concept of electrical double-layer theory is due to Quincke (1861),[2] although he did not use the term. Gouy (1910) and Chapman (1913) independently described the diffuse distribution of counter-ions accumulated near the surface of mercury electrodes in response to an externally applied potential.[3]
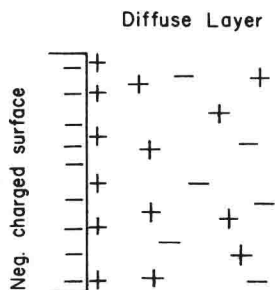
(a) Gouy–Chapman Model   (b) Stern Model
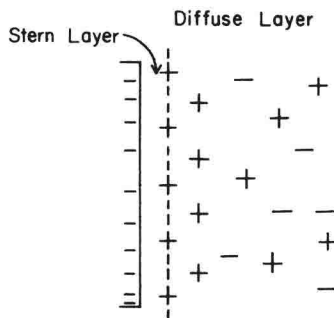
Charge distribution as related to distance.
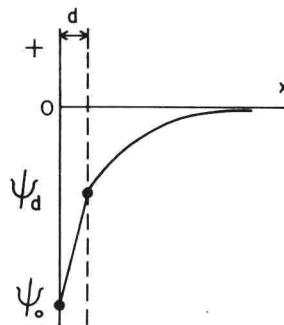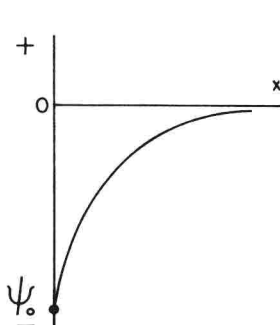
Potential distribution as related to distance.

FIGURE 1.   Distribution of electrical charges and potential in double layer according to (a) Gouy-Chapman theory and (b) Stern theory. ψ_o and ψ_d are surface and Stern potential, respectively, d is the thickness of the Stern layer.

Sterne and Grahame refined this, recognizing that counter-ions are unlikely to approach the surface more closely than the ionic radii of anions and the hydrated radii of cations.[2] They also introduced the concept of binding energy for specific adsorption. The historical background to the development of electrical double-layer is reviewed by Verwey,[1] Grahame,[2] and Overbeek.[4] A schematic representation of the Gouy-Chapman model and Stern-Grahame model is presented in Figure 1, to illustrate the fundamental difference between the two models. These and further modifications of Gouy-Chapman theory will be discussed in the later sections of this chapter.

II. ORIGIN OF SURFACE CHARGE IN SOILS

Three main types of colloidal charge constitute the mineral assemblage of soils. Based on origin of charge, these are categorized in the following ways: (1) isomorphic substitution or crystal lattice defects in the internal structure of the mineral; (2) ionic dissolution on surfaces of soil colloids; and (3) ionization of active organic functional groups.

FIGURE 2.   Schematic representation showing the charge reaction and zero point of charge of a colloid in which ion dissolution is the charge generating process.

A. Isomorphic Substitution

The most commonly acknowledged source of surface charge on soil colloids is from the structural imperfection in the interior of the crystal structure. Structural imperfections, due to ion substitution or site vacancies, frequently result in permanent charge on the soil colloi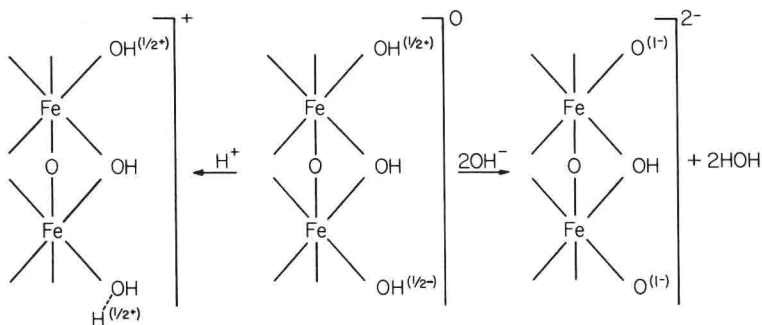dal particle. In theory, this charge may assume either a positive or negative value.[5] However, due to ion size limitation, the substitution is generally restricted to a lower valence element for one with a higher valency.[6,7] For example, Al^{3+} substituting for tetrahedral Si^{4+} and Mg^{2+} or Fe^{2+} substituting for octahedral Al^{3+} leads to a deficiency of positive charge on the crystal lattice. The resulting charge is generally negative on the clay structure.[8,9] Such colloids have permanent charge; however, they may not display nonamphoteric behavior because their edges may be amphoteric.

B. Ionic Dissolution

Surface charges also develop as a result of chemisorption of H_2O, i.e., water splitting into H^+ and OH^- during adsorption to form a hydroxylated surface. Establishment of charge on such a surface is then viewed as either an adsorption of H^+ or OH^- or as dissociation of surface sites which can then assume either a positive or a negative charge.[10] The sign and magnitude of the surface charge are determined solely by the ion that is adsorbed in excess onto the hydroxylated surface; such ions are termed potential determining ions. The sorption and eventually the surface charges are dependent on the activity of the potential determining ions in the bulk solution. The mechanism by which a colloid acquires its surface charge is schematically presented in Figure 2. Many minerals in soils typify this type of surface charge. The most notable of these are the oxides and/or the hydroxides of Al, Fe, Mn, Si, and Ti. Nevertheless, this type of charge is not confined to the oxides only. Equally illustrative is kaolinite which by its broken edges reflects similar charge behavior.

C. Ionization

Confined mainly to the organic fraction, ionization is viewed as a process by which a colloid acquired its charges either by dissociation of H^+ from or onto the active functional group. The charge generated could be either positive or negative:

$$R{-}COOH \xrightleftharpoons{H_2O} R \cdot COO^- + H^+$$

$$R{-}NH_2 + H_2O \xrightleftharpoons{H_2O} R \cdot NH_3^+ + OH^-$$
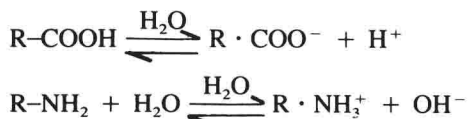
In some ways this is comparable to ion dissolution. The charge is dependent on the dissociation constant of each functional group and pH. Examples of functional groups generating this type of charge are the carboxyl, phenolic, and amino groups.

Hereafter, the charged colloids will be considered as permanent or variable charged or permanent-variable charged mixtures.

III. THEORY OF THE ELECTRICAL DOUBLE-LAYER

Irrespective of the origin of the surface charge on the colloidal surface, electrical neutrality demands that an equal amount of charge of the opposite sign must accumulate in the liquid phase near the charged surface. For a negatively charged surface, this means that positively charged cations are thus, by electrostatic forces, attracted to the charged surface.

At the same time, due to diffusion forces, the cations are also drawn back towards the equilibrating solution. An "atmospheric" distribution of cations in a "diffuse layer" is established where the concentration of cation increases towards the surface, the concentration increasing from a value equal to that of the equilibrating solution to a higher value principally determined by the magnitude of the surface charge. On the contrary, ions of equal sign (anions) are repelled by such a surface with diffusion forces acting in an opposite direction, such that there is a deficit of anions near the surface. Based on such a theory, different models are formulated relating the density of charge on the surface and the distribution of counter-ions in the diffuse layer.

A. Gouy-Chapman Theory for a Single Flat Double-Layer

The assumptions involved in the Gouy-Chapman model are that the charge is uniformly spread over the surface. The space charge in the solution is considered to be built up by unequal distribution of point charges. The solvent is treated as a continuous medium, influencing the double-layer only through its dielectric constant which is assumed invariant with position in the double-layer.[4] Further, it is assumed that ions and surface are involved only in electrostatic interactions. The present derivation is for a flat surface infinite in size and at an infinite distance from the surface. The double-layer theory applies equally well to rounded or spherical surfaces.[4] The derivation that follows is based on van Olphen,[7] Overbeek,[4] Bolt,[11] and El-Swaify.[12]

At equilibrium between any point in the double-layer and the bulk solution for ionic species i:

$$\overline{\mu}_i = \overline{\mu}_{oi} \tag{1}$$

Here $\overline{\mu}_i$ and $\overline{\mu}_{oi}$ are electrochemical potentials for species i in the double-layer and in the bulk solution, respectively. The electrochemical potential is defined as

$$\overline{\mu}_i = \mu_i + Z_i F \psi_i \tag{2}$$

where μ_i is the chemical potential, z_i is the valence, ψ_i is the electrical potential in the double-layer, and F is the Faraday constant. One could relate the chemical potential, μ_i, to activity, a_i, as

$$\mu_i = \mu_i' + RT \ln a_i \tag{3}$$

where μ_i' is the standard chemical potential, R is the gas constant, and T is the absolute temperature. Thus, Equation 1 can be rewritten as

$$\mu_i' + RT \ln a_i + zF \psi_i = \mu_i' + RT \ln a_{oi} + zF \psi_{oi} \tag{4}$$

Therefore,

$$\psi_i - \psi_{oi} = \frac{RT}{zF} \ln \frac{a_{oi}}{a_i} \tag{5}$$

If ψ_{oi} is assumed to be zero and activity is assumed to be equal to molar concentration,[6] then Equation 5 becomes Boltzmann's equation

$$c_i = c_{oi} \exp - \left(\frac{z_i F \psi}{RT}\right) \tag{6a}$$

$$c_- = c_{o-} \exp \left(\frac{z_- F \psi}{RT}\right) \tag{6b}$$

$$c_+ = c_{o+} \exp - \left(\frac{z_+ F \psi}{RT}\right) \tag{6c}$$

where c_+ and c_- are the local molar concentration of the cations and anions, c_{o+} and c_{o-} are their molar concentration far away from the surface in the equilibrium liquid, concentration is expressed as $kmol/m^3$, z_+ and z_- are the valence of cations and anions, respectively, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. Thus, when equilibrium is established in the double-layer, the average local concentration of ions can be expressed as a function of the average electrical potential, ψ, at that distance according to the Boltzmann theory.[4,13,14]

The space charge density (C/m^3) is given by

$$\rho = \Sigma c_i z_i F$$

$$= c_+ z_+ F - c_- z_- F \tag{7}$$

The coulombic interaction between the charges present in the system is described by the Poisson equation

$$\Delta \psi = \frac{-4\pi\rho}{\epsilon} \tag{8}$$

where ψ is the potential which changes from a certain value ψ_o at the colloid-water interface to zero in the bulk solution, and ρ is the space charge density, ϵ is the dielectric constant, and Δ is the Laplace operator which in Cartesian coordinates is equal to $d^2/dx^2 + d^2/dy^2 + d^2/dz^2$.[10]

At an infinitely large interface (flat surface), Δ, simplifies to d^2/dx^2. Thus, Equation 8 becomes:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\rho}{\epsilon} \tag{9}$$

Substituting Equation 7 into 9 one obtains:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon} (c_+ z_+ F - c_- z_- F) \tag{10}$$

Using the assumption for a symmetrical electrolyte ($z_+ = z_- = z_i$, then $c_{o+} = c_{o-} = c_o$) and substituting Equation 6b and 6c, respectively for c_+ and c_- in Equation 10 one obtains:

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon}\left[zFc_o \exp\left(\frac{-zF\psi}{RT}\right) - zFc_o \exp\left(\frac{zF\psi}{RT}\right)\right] \tag{11}$$

$$= -\frac{4\pi}{\epsilon} zFc_o\left[\exp\left(\frac{-zF\psi}{RT}\right) - \exp\left(\frac{zF\psi}{RT}\right)\right] \tag{12}$$

By rearrangement Equation 12 becomes:

$$\frac{d^2\psi}{dx^2} = \frac{4\pi}{\epsilon} zFc_o\left[\exp\left(\frac{zF\psi}{RT}\right) - \exp\left(\frac{-zF\psi}{RT}\right)\right] \tag{13}$$

By definition:

$$\sinh x = \frac{\exp(x) - \exp(-x)}{2}$$

Therefore,

$$\frac{\exp\left(\frac{zF\psi}{RT}\right) - \exp\left(\frac{-zF\psi}{RT}\right)}{2} = \sinh\frac{ze\psi}{RT} \tag{14}$$

Thus, by substituting the sinh term in Equation 13, the basic Poisson-Boltzmann differential equation, the basis of the diffuse double-layer theory is obtained:

$$\frac{d^2\psi}{dx^2} = \frac{8\pi zFc_o}{\epsilon} \sinh\left(\frac{zF\psi}{RT}\right) \tag{15}$$

It is convenient to rewrite this equation in terms of the following dimensionless quantities:[7]

$$y = \frac{zF\psi}{RT} \tag{16}$$

$$\xi = \kappa_x \tag{17}$$

Here,

$$\kappa^2 = \frac{8\pi z^2 F^2 c_o}{\epsilon RT} m^{-2} \tag{18}$$

Then Equation 15 becomes simply:

$$\frac{d^2y}{d\xi^2} = \sinh y \tag{19}$$

The steps involved in arriving to Equation 19 are based on El-Swaify,[12] and Overbeek[4] and are shown to be:

$$\frac{dy}{dx} = \frac{zFd\psi}{RTdx} \tag{20}$$

Thus:

$$\frac{d^2y}{dx^2} = \frac{zF}{RT}\frac{d^2\psi}{dx^2} \tag{21}$$

Substituting Equation 15 into 21:

$$\frac{d^2y}{dx^2} = \frac{zF}{RT}\left[\frac{8\pi zFc_o}{\epsilon}\sinh\left(\frac{zF\psi}{RT}\right)\right] \tag{22}$$

Further substitution of Equations 16 and 17 gives:

$$\frac{d^2y}{dx^2} = \kappa^2 \sinh y \tag{23}$$

Differentiating Equation 17 with respect to distance x and substituting, one obtains the following relationships:

$$\frac{d\xi}{dx} = \kappa \tag{24}$$

$$\frac{dy}{dx} = \frac{dy}{d\xi}\cdot\kappa \tag{25}$$

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left[\frac{dy}{d\xi}\cdot\kappa\right] \tag{26}$$

$$= \kappa\frac{d^2y}{d\xi}\cdot\frac{1}{dx} \tag{27}$$

from Equation 24:

$$1/dx = \kappa/d\xi \tag{28}$$

Substituting into Equation 27 we obtain:

$$\frac{d^2y}{dx^2} = \kappa^2\frac{d^2y}{d\xi^2} \tag{29}$$

Thus:

$$\frac{d^2y}{d\xi^2} = \frac{1}{\kappa^2}\frac{d^2y}{dx^2} \tag{30}$$