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Surface Reactions in Natural Aqueous Colloidal Systems**

Garrison Sposito*

Natural colloids are mixtures of inorganic and organic polymers resulting from weathering processes. These materials include layer-type aluminosilicates, hydrous oxides, and biodegraded organic matter. Regardless of their molecular structure, these polymeric constituents present reactive functional groups of two principal kinds at the colloid/aqueous solution interface: siloxane ditrigonal cavities and inorganic or organic hydroxy groups. The reactive proportion of each kind of functional group at a colloid surface depends on the extent of chemical weathering and the composition of the material cycling through the aqueous environment. – The principal mechanisms of reaction between surface functional groups and ions or molecules in aqueous solution, referred to generically as «adsorption», are (1) inner-sphere complexation, (2) outer-sphere complexation, and (3) association with a diffuse ion swarm. The role of these three mechanisms in diverse reactions, such as cation exchange, specific ion adsorption, and organic matter binding on colloids is discussed, as is the contribution these mechanisms make to surface charge development. The conceptual basis of surface charge variation for natural colloids is described in relation to the three adsorption mechanisms. – The formulation of the law of mass action for surface complexes on natural colloids involves stability constants analogous to those for aqueous complexes. The problem of determining the surface species activity coefficients in these stability constants is discussed along with recent activity coefficient models based on mean-field theory. Surface speciation models that incorporate both surface complexation and diffuse ion swarm association are reviewed and illustrated for adsorption phenomena in natural colloidal systems.

Garrison Sposito: Born 1939 in Los Angeles, California, USA. Studied soil physical chemistry at the University of Arizona and the University of California at Berkeley; Ph. D. 1965 with thesis in statistical mechanics of adsorbed water with Prof. Kenneth L. Babcock at Berkeley. Physics professor 1965–1974 at Sonoma State University; Professor of Soil Science 1974–1988 at the University of California, Riverside; appointed Professor of Soil Physical Chemistry at the University of California, Berkeley, in 1988. – Research prize of the Soil Science of America, 1982; John Simon Guggenheim Fellow, 1984. Fellow of the Soil Science Society of America and the American Geophysical Union. Author of five books, including «The Surface Chemistry of Soils» (Oxford, 1984), and editor of «The Environmental Chemistry of Aluminum» (CRC Press, 1989). – He thinks of himself as a chemical physicist who applies the methods of physical chemistry and molecular physics to study reactions in natural, aqueous porous media. His current research interests focus on the physical chemistry of soils in forested ecosystems.

1. Introduction

Natural colloids are heterogeneous mixtures of inorganic and organic polymers and polymer fragments. The more well-defined constituents in these colloids derive from aluminosilicates, hydrous oxides, and humus[1,2], the relative proportion of each solid material depending on the extent of chemical weathering and the composition of the substances which cycle through the natural aqueous environment. The surface reactivity of colloids also depends on these transformation and transport factors, but is more specifically influenced by the molecular structure of the colloid/aqueous solution interface itself. This latter topic has been the subject of intense investigation for nearly two decades[3–6], and a consensus has emerged that many of the data on natural surface reactions can be interpreted from the point of view of coordination chemistry[7].

1.1. Surface Functional Groups

The concept of functional group is perhaps most familiar in the study of organic molecules, both monomeric and polymeric. Humus is a collection of such molecules found in soil, sediment, and water bodies[8]. Of the variety of functional groups present in the organic compounds that polymerize to form humus (e. g. carboxy and phenolic hydroxy groups), some ultimately will come to reside on the interface between solid organic matter and the aqueous solution phase. These molecular units that protrude from the solid surface into solution are *surface functional groups*. In the case of organic matter, the surface functional groups are necessarily organic molecular units, but in general they can be bound to either organic or inorganic solids, and they can have any molecular structural arrangement that is possible for them were they bound to small molecules instead of polymeric materials like humus or clay minerals. Unlike the situation for small molecules, however, functional groups on surfaces cannot be diluted infinitely, even in aqueous suspension. Unless the substrate to which they are bound decomposes, surface functional groups remain separated by more or less fixed distances, regardless of how dilute a suspension of the substrate may be. Thus the groups remain closely associated and can influence one another in nearly all circumstances.

Because of the variety of natural colloid compositions, a broad spectrum of surface functional group reactivity is likely. Superimposed on this intrinsic variability is that created by the wide range of stereochemical and surface charge distribution characteristics possible in a heterogeneous matrix. For this reason, it is entirely conceivable that no particular surface functional group (e. g. hydroxy) possesses unique quantitative chemical properties, like the proton dissociation equilibrium constant, but instead can be characterized only by ranges of values for these properties. This «smearing-out» of their chemical behaviour is another important feature that distinguishes surface functional groups from functional groups bound to small organic molecules.

Metal hydrous oxides found in natural colloids react with water to create solvated metal cations at the colloid/aqueous solution interface[9]. This combination of metal cation and water molecule at an interface is a *Lewis acid site*, with the metal cation identified as the Lewis acid. Lewis acid sites exist, for example, on the edge surfaces of gibbsite (γ-Al(OH)$_3$) and goethite

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* *Correspondence:* Prof. Dr. G. Sposito
Department of Soil Science
University of California
Berkeley, CA 94720 (USA)

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(α-FeOOH; Fig. 1, bottom), as well as the edge surfaces of clay minerals like kaolinite ($Si_4Al_4O_{10}(OH)_8$). These surface functional groups are very reactive, since the positively-charged water molecule is quite unstable and is either deprotonated or exchanged readily for an organic or inorganic anion in aqueous solution.

The inorganic surface functional group of greatest abundance and reactivity in clay-sized colloids is the hydroxy group exposed on the outer periphery of a mineral. This kind of OH group is found on metal oxides, oxyhydroxides, and hydroxides, on clay minerals, and on amorphous silicate minerals like allophane ($Si_3Al_4O_{12} \cdot nH_2O$). Usually, more than one kind of surface OH group can be distinguished on the basis of stereochemistry. For example, in the case of goethite, part of whose molecular structure is shown in Fig. 1, the surface consists primarily of exposed planes of differing orientation, with the chemically distinguishable surface OH groups on these planes denoted A, B, and C. The type A hydroxy group is a former oxygen ion that is coordinated to one $Fe^{3\oplus}$ cation in the bulk mineral structure and has become protonated upon exposure to aqueous solution as a surface group. The type C hydroxy group is formed in the same way, except that it is coordinated to two $Fe^{3\oplus}$ cations. The type B hydroxy group is the same as a hydroxy moiety of the bulk structure coordinated to three $Fe^{3\oplus}$ cations, but is exposed on a surface. These three surface OH groups exhibit different reactivities: only the type A hydroxy groups are found to protonate, dissociate protons, complex metal cations and, upon protonation, to exchange with anions in aqueous solution.

The plane of oxygen atoms on the cleavage surface of a 2:1 layer aluminosilicate (Fig. 1, top) is called a *siloxane surface*[4]. This plane is characterized by a distorted hexagonal symmetry among the constituent oxygen ions, and the functional group associated with the siloxane surface is a roughly hexagonal cavity (Fig. 2) formed by the bases of six corner-sharing silica tetrahedra. This cavity has a diameter of about 0.26 nm and is bordered by six sets of «lone-pair» orbitals emanating from the surrounding ring of oxygen ions.

The reactivity of the siloxane cavity depends on the nature of the electronic charge distribution in the layer silicate structure[4]. If there are no neighboring isomorphic cation substitutions to create local deficits of positive charge in the underlying layer structure, the siloxane cavity will function as a very mild electron donor that can bind only neutral, dipolar molecules, such as water molecules. The complexes formed are not very stable, an example being the easily-reversed entrapment of a water molecule having one of its hydroxy groups directed into a cavity perpendicularly to the siloxane surface. If isomorphic substitution of $Al^{3\oplus}$ by $Fe^{2\oplus}$ or $Mg^{2\oplus}$ occurs deep in the layer, the resulting excess negative charge on a nearby siloxane cavity makes it possible to form reasonably strong complexes with cations as well as dipolar molecules. If isomorphic substitution of $Si^{4\oplus}$ by $Al^{3\oplus}$ occurs in the silica tetrahedra, the excess negative charge is located much nearer to the surface oxygen ions and much stronger complexes with cations and molecules become possible because of this greater localization of charge. Recent quantum chemical calculations using qualitative perturbation theory and the extended Hückel tight-binding method[10] have confirmed the greater delocalization of surface charge expected from cation substitutions deep in the phyllosilicate layer structure.

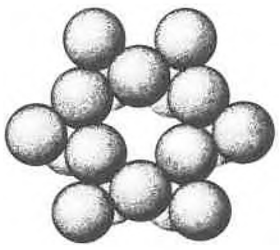
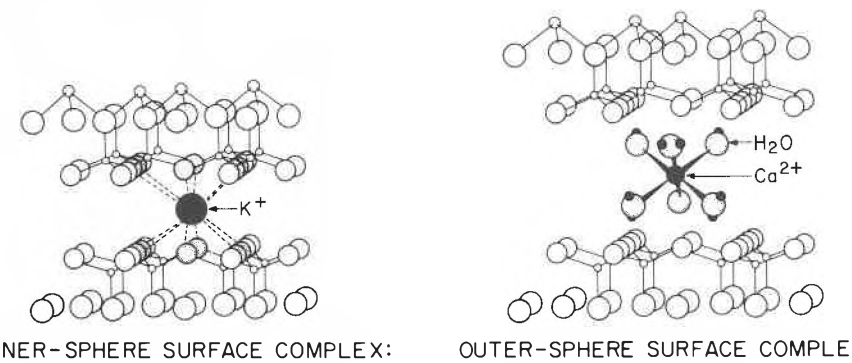
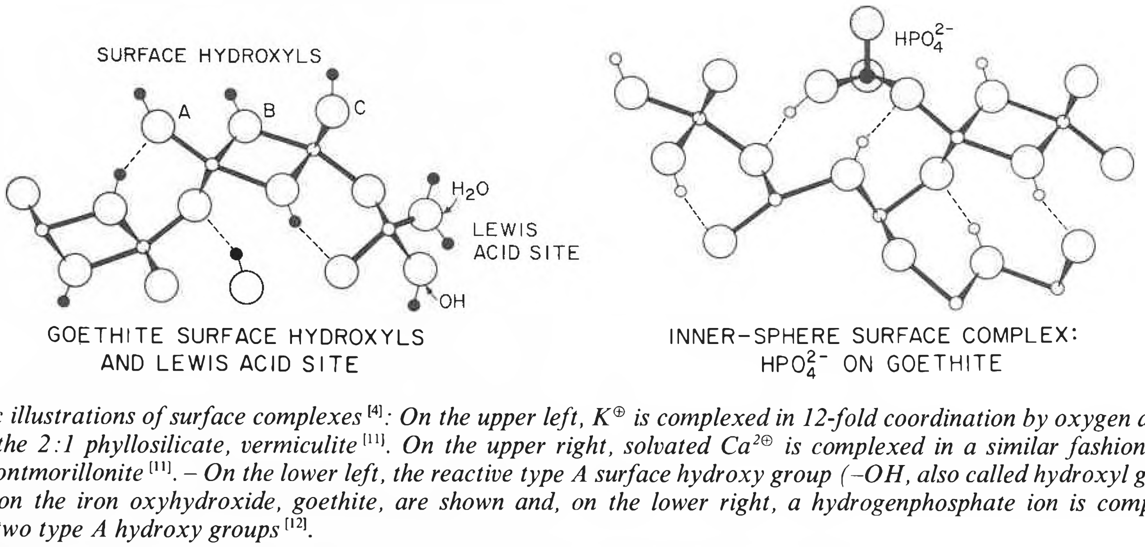


Fig. 2. The hexagonal cavity in a siloxane surface, such as occurs on the basal planes of the clay minerals, vermiculite and montmorillonite[4] *(cf. Fig. 1, top). The spheres denote oxygen ions.*



INNER-SPHERE SURFACE COMPLEX: K^+ ON VERMICULITE

OUTER-SPHERE SURFACE COMPLEX: $Ca(H_2O)_6^{2+}$ ON MONTMORILLONITE



GOETHITE SURFACE HYDROXYLS AND LEWIS ACID SITE

INNER-SPHERE SURFACE COMPLEX: HPO_4^{2-} ON GOETHITE

Fig. 1. Schematic illustrations of surface complexes[4]*: On the upper left, $K^{\oplus}$ is complexed in 12-fold coordination by oxygen anions in the basal planes of the 2:1 phyllosilicate, vermiculite*[11]*. On the upper right, solvated $Ca^{2\oplus}$ is complexed in a similar fashion by the 2:1 phyllosilicate, montmorillonite*[11]*. – On the lower left, the reactive type A surface hydroxy group (–OH, also called hydroxyl group) and a Lewis acid site on the iron oxyhydroxide, goethite, are shown and, on the lower right, a hydrogenphosphate ion is complexed after displacement of two type A hydroxy groups*[12].

1.2. Surface Complexes

The complexes formed between surface functional groups and constituents of an aqueous solution can be classified analogously to the complexes that form entirely among aqueous species[4,7]. For example, if no water molecule is interposed between the surface functional group and the ion or molecule it binds, the complex is *inner-sphere*. If at least one water molecule is interposed between the functional group and the bound ion or molecule, the complex is *outer-sphere*. As a general rule, outer-sphere surface complexes involve electrostatic bonding mechanisms and, therefore, are less stable than inner-sphere surface complexes, which usually involve either ionic or covalent bonding, or some combination of the two.

Examples of surface complexes are shown schematically in Fig. 1. An inner-sphere surface complex involving $K^{\oplus}$ on the 2:1 phyllosilicate, vermiculite, appears in «exploded view» at the upper left in the figure. This surface complex requires the coordination of a potassium ion with 12 oxygen ions bordering two opposing siloxane cavities. The layer charge in vermiculite is large enough that each siloxane cavity in a basal plane of the mineral can complex a $K^{\oplus}$ cation. Moreover, the ionic radius of $K^{\oplus}$ is almost precisely equal to that of a cavity. This combination of charge distribution and stereochemical factors gives K-vermiculite surface complexes great stability[11]. An outer-sphere surface complex with a $Ca^{2\oplus}$ cation is illustrated on the upper right in Fig. 1. In this example, the two-layer hydrate of Ca-montmorillonite[11], two opposing siloxane cavities complex a $Ca^{2\oplus}$ cation solvated by six water molecules in octahedral coordination.

As mentioned in Section 1.1, the type A hydroxy group in goethite can be protonated to form a Lewis acid site. It can then be exchanged with, for example, $HPO_4^{2\ominus}$ to allow the formation of an inner-sphere surface complex, as illustrated on the lower right in Fig. 1. It consists of a $HPO_4^{2\ominus}$ bound through its oxygen ions to a pair of adjacent $Fe^{3\oplus}$ cations («binuclear surface complex»). The configuration of the orthophosphate unit is especially compatible with the grooved structure of the goethite surface, thus providing stereochemical enhancement of the stability of the inner-sphere complex[12]. Inner-sphere complexes also can form through the ligand exchange of other oxyanions (e.g. oxalate) with protonated OH groups on goethite.

2. Surface Speciation and the Development of Surface Charge

The perturbed molecular environment at colloid surfaces, caused by the loss of full coordination characteristic of the bulk colloid structure, leads to reactivity of the surfaces with solutes present in aqueous solution. This reactivity produces a net accumulation of matter at the colloid/aqueous solution interface. If a three-dimensional molecular structure («surface precipitate») does not develop, the process of accumulation is termed *adsorption*[2]. Given the existence of reactive functional groups and Lewis acid sites on natural colloidal surfaces, three mechanisms of adsorption can be identified for non-polymeric solutes. They are illustrated in Fig. 3 for the adsorption of a monovalent cation by the siloxane surface of a 2:1 phyllosilicate like the mica, muscovite, or the clay mineral, montmorillonite[4].

The inner-sphere surface complex shown in Fig. 1 involves the siloxane cavity, described in Section 1. The outer-sphere surface complex shown includes the cation solvation shell and is similar to that depicted in Fig. 1 for $Ca^{2\oplus}$. If a solvated ion does not form a complex with a charged surface functional group, but instead reacts with a surface only in a delocalized sense, it is said to be adsorbed in the *diffuse ion swarm*. This adsorption mechanism involves ions that remain fully dissociated from a surface and are, accordingly, free to move about nearby in aqueous solution. The diffuse-ion swarm and the outer-sphere surface complex mechanisms of adsorption involve almost exclusively electrostatic bonding, whereas inner-sphere complex mechanisms are likely to involve ionic as well as covalent bonding. Since covalent bonding depends significantly on electron configuration both at the surface and in the complexed ion, it is appropriate to consider inner-sphere surface complexation as the molecular basis of the generic term, *specific adsorption*. Correspondingly, diffuse-ion association and outer-sphere surface complexation are the molecular basis for the term, *non-specific adsorption*. The «non-specificity» implied by this definition refers to the weak dependence on electron configuration to be expected for the interaction of solvated species with a colloid surface. Solvated surface species, whether they be cations or anions, sometimes are referred to as *exchangeable ions*[2].

2.1. Surface Species

The experimental detection and quantitation of surface species on natural colloids is a difficult area of research because of sample heterogeneity, low surface concentrations, and the need to investigate solid materials in the presence of water[5,6,13].

Unambiguous information about the molecular structure and stability of species at the colloid/solution interface can only be obtained with in-situ surface spectroscopy. Invasive spectroscopic methods that require sample desiccation or high vacuum techniques (e.g., electron microscopy and microprobe analysis; X-ray photoelectron (XPS), IR-transmission, IR-ellipsometric, inelastic electron tunneling (IETS), and electron energy loss spectroscopies (EELS)) have contributed significantly to the understanding of adsorbate-surface interactions[14]. However, the sampling techniques required for these methods often annihilate or change irreversibly the surface species of interest. Molecular-level information about the mechanisms, orientation, or dynamics of surface species suggested by data obtained with these methods may bear little resemblance to the chemical mechanisms operating in a natural colloidal system.

Recent advances in the development of non-invasive, in-situ spectroscopic techniques have been applied successfully to study natural colloids in aqueous suspension. In-situ methods utilize molecular probes that have diagnostic properties sensitive to changes in short-range molecular environment. At the colloid/solution interface, the molecular environment around the probe species is perturbed and the diagnostic properties of the probe, which can be optical or magnetic, then «report back» on surface conditions. Examples of in-situ probes which have been used fruitfully include ESR spin-probe studies; NMR spin-probe studies; photochemical fluorescence

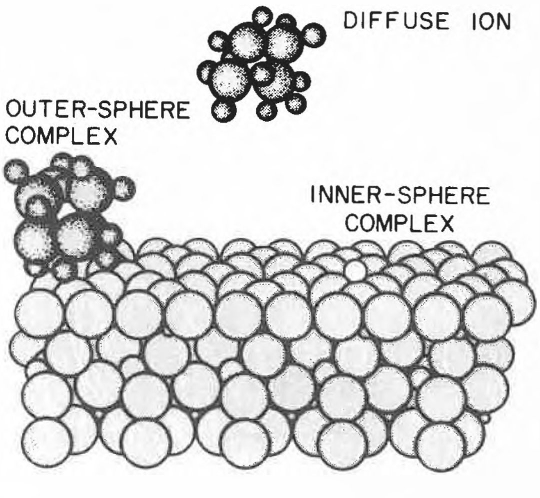


Fig. 3. The three mechanisms of adsorption, illustrated for a monovalent cation on the basal plane of a 2:1 phyllosilicate[2].

quenching investigations; perturbed vibration probe studies; and extended X-ray absorption fine structure investigations[5,6,15].

A seminal example of a molecular probe used extensively to study the colloid/solution interface is the ESR spin-probe, Cu$^{2\oplus}$[5,6], whose spectroscopic parameters are sensitive to changes in ligand-field properties. Since water does not interfere significantly with Cu^{II} ESR spectra, they may be recorded in situ for natural colloidal suspensions. Detailed molecular-level information about coordination and orientation of both inner-and outer-sphere Cu$^{2\oplus}$ surface complexes has resulted from ESR studies of clay minerals and hydrous metal oxides[5]. In addition, ESR techniques have been coupled with other spectroscopic methods, like electron-spin-echo modulation (ESEM) and electron nuclear double resonance (ENDOR), to provide complementary information about transition metal ion behavior near colloid surfaces[6]. In a novel application of diverse spectroscopic methods, *Hipps* et al.[16] combined ESR spectroscopy with IETS and Fourier transform infrared (FT-IR) spectroscopy to characterize the adsorbate-surface redox reactions of diphenyl(picryl)-hydrazyl on δ-alumina. The level of sophistication of these kinds of surface speciation studies is expected to increase in the future, such that the heterogeneous colloidal systems found in soils and sediments can be investigated accurately.

2.2. Surface Charge

Solid particle surfaces can develop electrical charge in two principal ways: either from isomorphic substitutions in minerals or from the reactions of surface functional groups with ions in aqueous solution. Four different types of surface charge contribute to the *net total particle charge* on a colloid, denoted σ_p[4]. The *permanent structural charge,* denoted σ_0, is created by isomorphic substitutions in minerals. These substitutions occur in both primary and secondary minerals, but they produce significant surface charge only in the 2:1 phyllosilicates. The contribution to σ_0 from isomorphic substitution in hydrous oxides and 1:1 layer silicates (like kaolinite) typically is less than 0.02 mol kg^{-1}. On the other hand, the micas and the clay minerals, illite, vermiculite, and smectite, can contribute permanent structural charge up to 100 times larger. The *net proton charge* of a soil, denoted σ_H, is the difference between the moles of protons and the moles of hydroxide ions complexed by surface functional groups:

$$\sigma_H = q_H - q_{OH} \qquad (1)$$

where q_i is moles of ion i complexed by surface groups. Diffuse-swarm protons are not included in σ_H. The most important surface functional groups that complex protons are on colloidal humus, hydrous oxides, and 1:1 aluminosilicates (e.g., kaolinite). Values of σ_H on these adsorbents can be measured as a function of pH in titration experiments[3]. Measured values of σ_H range from -9 to $+1$ mol kg^{-1} for humus and from -0.7 to $+0.4$ mol kg^{-1} for minerals bearing surface OH groups[4].

Besides σ_H, natural colloidal surfaces bear the *inner-sphere complex charge,* σ_{IS}, and the *outer-sphere complex charge,* σ_{OS}. Contributing to σ_{IS} is the net total charge of the ions, other than H$^\oplus$ or OH$^\ominus$, which are bound into inner-sphere surface complexes. Similarly, σ_{OS} is the net total charge of the ions, other than H$^\oplus$ or OH$^\ominus$, which are bound into outer-sphere surface complexes. The net total particle charge now can be represented mathematically by the equation:

$$\sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS} \qquad (2)$$

Both σ_p and its components are the resultant of contributions from a variety of adsorbents or surface species, both inorganic and organic.

Although colloid particles bear electrical charge, colloidal systems are always electrically neutral. Thus σ_p in Equation (2) must be balanced, when it is non-zero, by another kind of surface charge. This balancing charge arises from the ions in the diffuse swarm, which move about freely in solution while remaining near enough to colloid surfaces to create the effective surface charge σ_D that balances σ_p. On the molecular scale, this effective surface charge can be apportioned to each diffuse-swarm ion according to the equation:

$$\sigma_{Di} = \frac{Z_i}{m_s} \int_V [c_i(x) - c_{0i}]\, \mathrm{d}V \qquad (3)$$

where Z_i is the valence of the ion, $c_i(x)$ is its concentration at the point x in solution, and c_{0i} is its concentration in solution far enough from any colloid particle surface to avoid adsorption in the diffuse ion swarm. The integral in Equation (3) is over the entire volume V of aqueous solution contacting the mass m_s of solid adsorbent. Thus Equation (3) represents the excess charge of ion «*i*» in aqueous solution: if $c_i(x) = c_{0i}$ uniformly, there would be no contribution of ion *i* to σ_D. Note that Equation (3) applies to all ions in the solution, including H$^\oplus$ and OH$^\ominus$, and that σ_D is the sum of all σ_{Di}. This sum is required to balance σ_p to maintain electrical neutrality:

$$\sigma_D + \sigma_D = 0 \qquad (4)$$

Equation (4) expresses the balances of surface charge. It applies both to an individual colloid in suspension and to an entire colloidal mass.

3. Points of Zero Charge

Points of zero charge are *pH values* at which one or more of the surface charge components in Equation (2) vanishes. The four most important points of zero charge are summarized in Table 1[4]. A standard nomenclature for points of zero charge has not been established. For example, the PZC when measured electrokinetically often is termed the isoelectric point (IEP) and the PZNPC is also called the zero point of charge (ZPC)[3]. In much of the surface chemistry literature concerning natural colloids, the PZSE has been called the point of zero charge, as has the PZNC[17]. Irrespective of this variability in terminology, agreement exists on the importance of the points of zero charge to colloidal phenomena despite their operational nature.

3.1. Experimental Significance

The PZC is the pH value at which the net total particle charge vanishes: $\sigma_p = 0$. At this pH value, there is no net surface charge neutralized by ions adsorbed in the diffuse swarm, according to Equation (3). This condition can be ascertained experimentally by measuring the pH value at which colloidal particles do not move in an applied electric field (electrophoretic mobility measurement, Fig.4) or at which settling occurs in a suspension of colloids (flocculation measurement). The PZC thus signals the absence of freely-moving adsorbed ions and the dominance of interparticle forces that produce coagulation. The PZC plays an important role in aggregate formation and in the retention of adsorbed ions against leaching losses.

The PZNPC is the pH value at which σ_H vanishes (Fig. 4). Note the general property of σ_H, that it decreases as the pH value increases (i.e., $\Delta\sigma_H/\Delta\,\mathrm{pH}$ is always negative). This stability criterion exists regardless of the composition or ionic strength of the aqueous solution, and independently of the nature of the colloidal particles.

The PZNC is the pH value at which the net adsorbed ion charge, *other* than that represented by σ_H, vanishes. If q_+ and q_- represent the moles of adsorbed cation and anion charge, respectively, then $q_+ = q_-$ at the PZNC. It is common practice to utilize «index ions», like Na$^\oplus$ and Cl$^\ominus$, in the measurement of the PZNC. Evidently the value of the PZNC will depend on the choice of index ions, although experience shows that this dependence is very small if the ions chosen are adsorbed non-specifi-

Table 1. Points of zero charge.

Symbol	Name	Defining Conditon[a)]
PZC	point of zero charge	$\sigma_p = 0$
PZNPC	point of zero net proton charge	$\sigma_H = 0$
PZNC	point of zero net charge	$q_+ = q_-$
PZSE	point of zero salt effect	$\partial\sigma_H/\partial I = 0$

[a)] q_+ = moles of adsorbed cation charge per unit mass; q_- = moles of adsorbed anion charge per unit mass; I = ionic strength of a swamping background electrolyte.

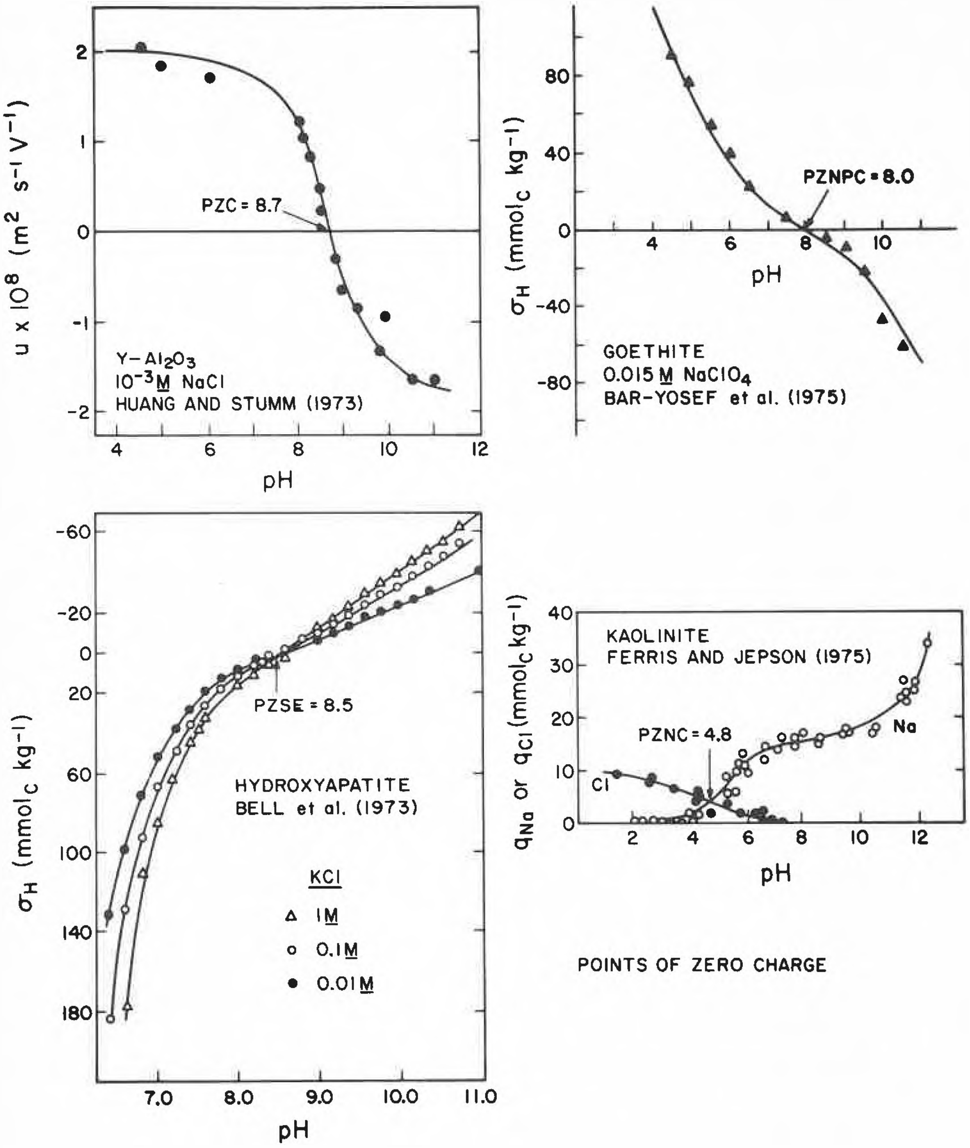


Fig. 4. Experimental data illustrating four different points of zero charge[4] *(cf. Table 1): PZC (C.-P. Huang, W. Stumm, J. Colloid Interface Sci. 43 (1973) 409); PZNPC (B. Bar-Yosef, A.M. Posner, J.P. Quirk, J. Soil Sci. 26 (1975) 1); PZNC (A.P. Ferris, W.B. Jepson, J. Colloid Interface Sci. 51 (1975) 245); PZSE (L.C. Bell, A.M. Posner, J.P. Quirk, J. Colloid Interface Sci. 42 (1973) 250).*

cally («indifferent electrolyte»). Ions such as $Li^{\oplus}$, $Na^{\oplus}$, $Cl^{\ominus}$, $ClO_4^{\ominus}$, and $NO_3^{\ominus}$ are examples. Note that

$$q_+ - q_- \equiv \sigma_{IS} + \sigma_{OS} + \sigma_D \qquad (5)$$

vanishes at the PZNC (although σ_{IS} will not contribute if the colloid reacts with an indifferent electrolyte). Thus mobile adsorbed ions exist at the PZNC, whereas they do not at the PZC. Representative values of the PZNC for important minerals in natural colloids are listed in Table 2.

The PZSE is an unusual point of zero charge in that it is defined by an invariance condition on σ_H instead of the vanishing of a surface charge component. Thus the relationship of the PZSE to surface speciation is indirect and generally it is necessary to appeal to some model of the colloid/aqueous solution interface in order to interpret it without ambiguity.

3.2. The PZC Theorems

Since each of the definitions in Table 1 is operational, there is no necessary conceptual relationship among them. It turns out, however, that a set of general statements about points of zero charge can be proved using only Equations (2) and (3) along with the stability criterion, $\partial\sigma_H/\partial pH < 0$[18]. These statements, the *PZC Theorems*, thus do not depend on the details of chemical speciation at the colloid/aqueous solution interface and so may be applied to validate molecular models or to examine speciation data for internal consistency.

Theorem 1: Let q_+ be the moles of «index» cation charge adsorbed per unit mass and let q_- be the moles of «index» anion charge adsorbed per unit mass. If $(\partial\sigma_H/\partial pH) < 0$, then:

$$\sigma_0 = -\frac{F}{S}(q_+ - q_-) \quad (pH = PZNPC) \qquad (6)$$

(F = Faraday constant; S = specific surface area)

$$\sigma_0 \gtreqless 0 \text{ if PZNC} \gtreqless \text{PZNPC} \qquad (7)$$

Proof: Equation (6) is the result of combining Equations (2)–(5) and setting $\sigma_H = 0$. The expression in Equation (7) is derived after noting that

$$\sigma_H\,(pH = PZNC) \gtreqless 0 \text{ if PNZC} \lesseqgtr \text{PZNPC} \qquad (8)$$

since $\sigma_H(pH = PZNPC) \equiv 0$ and $\partial\sigma_H/\partial pH < 0$. Because $\sigma_0 = -\sigma_H$ at the PZNC, Equation (7) follows. Equation (7) shows that PZNPC = PZNC when $\sigma_0 = 0$ (oxides, organic matter, kaolinite). Thus the PZNC can be used to determine the absolute value of σ_H measured by titration[19].

Theorem 2: PZC = PZNC if and only if $\sigma_{IS} + \sigma_{OS} = 0$ when pH = PZNC.
Proof: This result is demonstrated by applying the definitions of PZC and PZNC simultaneously to Equations (2) and (3). Sufficiency follows from setting $\sigma_{IS} + \sigma_{OS} = 0$ in the two equations and using the definitions, whereas necessity follows from inserting the definition of PZC into that of PZNC. Note that Theorem 2 is an identity if only the diffuse-ion swarm mechanism of adsorption is assumed to operate. Otherwise, the surface complexation of cations and anions must be such as to produce a zero net particle charge contribution.

Theorem 3: If $\sigma_{IS} + \sigma_{OS}$ decreases (increases), then the PZC decreases (increases).
Proof: Theorem 3 is an application of surface charge balance and the condition $\partial\sigma_H/\partial pH < 0$. At the PZC, Equations (2) and (3) can be combined and solved for σ_H:

$$\sigma_H = -(\sigma_0 + \sigma_{IS} + \sigma_{OS}) \quad (pH = PZC) \qquad (9)$$

The pH value at which Equation (9) holds must increase (decrease) as the sum $\sigma_{IS} + \sigma_{OS}$ increases (decreases) since $\partial\sigma_H/\partial pH < 0$. Thus the surface complexation of cations increases the PZC, whereas the surface complexation of anions decreases the PZC. *Note that these shifts in the PZC do not require specific adsorption, but only surface complexation.* Equation (9) thus may be used to determine whether surface complexes are forming at the colloid/aqueous

Table 2. Representative values of PZNC for colloidal minerals.

Mineral	PZNC	Mineral	PZNC
Quartz and silica	2.0–3.0	Goethite	7.0–8.0
Birnessite	1.5–2.5	Hematite	8.0–8.5
Kaolinite	4.0–5.0	Gibbsite	8.0–9.0

solution interface, but not to claim that ions are specifically adsorbed.

Theorem 4: If $\partial(q_+ - q_-)/\partial I = 0$ at the PZNC, then PZSE = PZNC. If $\sigma_0 = 0$ as well, then PZSE = PZNPC also. If $\sigma_{IS} + \sigma_{OS} = 0$ as well, then PZSE = PZC also.
Proof: Theorem 4 follows immediately from combining Equations (2)–(5) and calculating the derivative of each term with respect to I, noting that this derivative vanishes identically for σ_0. If in fact $\sigma_0 = 0$, then Equation (7) can be used to show that PZSE = PZNC = PZNPC. If $\sigma_{IS} + \sigma_{OS} = 0$, then Theorem 2 applies and PZSE = PZC. These results appear to be the only *model-independent* relationships between the PZSE and other points of zero charge. They make it clear that there is no *necessary* condition of vanishing surface charge to be associated with the «crossover point» determined through potentiometric titration experiments carried out at different background ionic strengths (Fig. 4). If the adsorbed ions contributing to q_+ and q_- are monovalent and do not tend to be adsorbed specifically, the PZSE may approximate the PZNC reasonably well.

4. Chemical Models

Chemical models of the colloid/aqueous solution interface differ from empirical models by their dependence on specific reactions assumed to describe the process of adsorption. Empirical models of adsorption may be strictly macroscopic optimization algorithms, like adsorption isotherm equations[2], or they may indroduce molecular speciation concepts, like the «four-plane model»[17]. In either case they remain parametric correlation treatments of the colloid surface without a direct relationship to chemical reactions. Chemical models, on the other hand, must postulate reactions and, if they are molecular in nature, adsorption mechanisms.

4.1. Structure of Chemical Models

The past decade has witnessed great advances in the development and understanding of chemical models of natural colloidal surfaces[4-6,9,20]. On the macroscopic level, the chemical model of adsorption equilibria is simply chemical thermodynamics. Consider, for example, the reaction of an hydroxylated surface with an aqueous solution containing the electrolyte M_aL_b. If SOH(s) denotes 1 mol of dissociable hydroxy groups bound to a substrate S, then a general adsorption reaction can be expressed:

$$\begin{aligned}\mathrm{SOH(s)} + \mathrm{pM^{m\oplus}(aq)} + \mathrm{qL^{l\ominus}} + \mathrm{nH^{\oplus}(aq)} + \mathrm{rOH^{\ominus}(aq)} &\rightleftarrows \\ \mathrm{SOM_p(OH)_rH_nL_q^{\delta}(s)} + \mathrm{H^{\oplus}(aq)}\end{aligned} \tag{10}$$

where $\delta = \mathrm{pm + n - l - ql - r}$. The thermodynamic equilibrium constant is:

$$K = \mathrm{(SOC)(H)^{1-n}/(SOH)(M)^m(L)^q(OH)^r} \tag{11}$$

where ( ) is a thermodynamic activity and C represents the adsorbed complex, $\mathrm{M_p(OH)_rH_nL_q}$. The evaluation of K can be achieved experimentally with data on the composition of the solid and aqueous phases after separating the soil species activities into rational activity coefficients and mole fractions and applying standard chemical thermodynamics to calculate the activity coefficients from composition data[21]. This approach requires no mechanistic assumptions other than those implicit in Equation (10) and the conventions of chemical thermodynamics for charged species. Applications of the results to interpret colloidal surface behavior follow along lines well established for heterogeneous chemical systems[4].

Table 3. Molecular models of adsorption.

Molecular Model	Surface Species Assumed	Rational Activity Coefficients
Modified Gouy-Chapman	diffuse swarm of hard-sphere ions	based on modified Poisson-Boltzmann equation
Triple Layer	inner-sphere or outer-sphere complexes (cations); outer-sphere complexes (anions); diffuse ion swarm	$f_i = f_{i\lambda}^0 \exp(Z_i F \psi_\lambda / RT)$ for a complexed ion i where ψ_λ is surface potential in plane λ
Constant Capacitance	inner-sphere complexes	$f_k = f_k^0 \exp(Z_k F \psi_S / RT)$ for a surface complex k where ψ_S is surface potential

A deeper perception of the mechanistic implications of Equation (10) can be had if the rational activity coefficients are described on the molecular level using the methods of statistical mechanics. This approach is the analog of the statistical mechanical theory of activity coefficients for species in aqueous solution[22]. Fundamental to it is the prescription of surface speciation and the dependence of the rational activity coefficient on surface characteristics. Three leading molecular models of adsorption following this paradigm are summarized in Table 3. Each has been applied with success to describe the surface reactions of natural colloids[4-6,9,20,23].

Modified Gouy-Chapman theory[24] has been applied to natural colloids for many years[25]. It postulates only one adsorption mechanism – the diffuse ion swarm – and effectively prescribes surface species activity coefficients through the surface charge-inner potential relationship contained implicitly in the Poisson-Boltzmann equation[4]. Closed-form equations for these activity coefficients have been worked out[26]. They show that the counter-ion activity coefficient decreases with increasing absolute value of σ_D, whereas the co-ion activity coefficient shows the opposite trend. The modified Gouy-Chapman model has had predictive success in describing colloidal dispersion behaviour that depends principally on long-range surface forces (e.g., colloidal dispersion or negative adsorption); but it is inadequate to describe even qualitatively the structure of the diffuse ion swarm in concentrated 1:1 electrolytes or in multivalent-ion electrolytes like $CaCl_2$[4,24].

The triple layer model[27,28] assigns adsorbed $H^{\oplus}$ and $OH^{\ominus}$ to inner-sphere complexes and the diffuse ion swarm, while assigning adsorbed cations to either inner-sphere or outer-sphere complexes and the diffuse ion swarm. Adsorbed anions are assigned to outer-sphere complexes and the diffuse ion swarm. The activity coefficients of surface-complexed ions are assumed to factor into a part that does not depend on surface charge ($f_{i\lambda}^0$ in Table 3) and is the same for all complexed ions, together with a part that depends on the valence of the complexed ion (Z_i in Table 3) and the inner potential in a plane (designated λ) that contains the ion: $\exp(Z_i F \psi_\lambda / RT)$, where F is the Faraday constant, R is the molar gas constant, and T is absolute temperature. For inner-sphere complexes, λ indexes the surface of the colloid, whereas for outer-sphere complexes, λ indexes a single plane assumed to pass through the centers of the complexes. Since the inner potential ψ_λ cannot be measured[4], a surface charge-potential relationship must be postulated to obtain physical closure in the model. In the triple layer model, this is done by analogy with the theory of parallel-plate capacitors[27]:

$$\sigma_H = C_1(\psi_S - \psi_{OS}) \tag{12}$$

$$\sigma_D = C_2(\psi_D - \psi_{OS}) \tag{13}$$

where C is a capacitance density, and S, OS, and D refer to planes at the colloid surface, through the outer-sphere complexes, and at the interface between outer-sphere complexes and the diffuse ion swarm, respectively. The surface charge density σ_D also is related to ψ_D through a standard diffuse double layer relationship, which then provides three independent equations for the three inner potentials in Equations (12) and (13). The capacitance densities are regarded as adjustable parameters in the model.

The constant capacitance model[29] assigns all adsorbed ions to inner-sphere complexes. Since this model also employs the constant ionic medium reference state for activity coefficients, the swamping background electrolyte is not considered and no diffuse ion swarm appears in the model structure. Activity coefficients of surface species are assumed to factor, as in the triple layer model, but the charge-dependent part is a function of the overall valence of the surface complex (Z_k in Table 3) and the inner potential at the colloid surface: $\exp(Z_k F \psi_S / RT)$. Closure in the model is achieved with the surface charge-potential relation:

$$\sigma_p = C\psi_S \qquad (14)$$

where C is an adjustable capacitance density. The left side of Equation (14) does not include σ_{OS}, according to the constant capacitance model. Charge balance as in Equation (4) cannot be invoked in this model because $\sigma_D \equiv 0$ through the choice of the constant ionic medium reference state. It follows that the PZC Theorems which make use of Equation (4) generally cannot be applied to the constant capacitance model. An exception is Theorem 3, however, since Equations (9) (without σ_{OS}) can be derived from the definition of the PZC by stetting the left side of Equation (2) equal to zero. Theorem 2 is also valid, with the proviso that the net adsorbed ion charge is taken proportional to σ_{IS} alone. The constant capacitance model by hypothesis does not provide a decription of non-specific adsorption.

4.2. Applications to Natural Colloids

Applications of surface complexation models, like the triple layer and constant capacitance models, to colloids in natural water systems have been described in a number of recent reviews[4 6,20,23]. In each application, a computational scheme is defined by *constraint equations,* which develop from mass and charge balance along with the conditions for chemical equilibrium (surface complex stability constants), and by *molecular hypotheses,* which prescribe the kinds and numbers of surface species and generate expressions for their activity coefficients. Conceptual differences among models derive principally from differences in their respective molecular hypotheses, but the number of model parameters often is large enough to allow a good fit to adsorption data irrespective of these differences[30]. This fact implies that the criterion of goodness-of-fit to such macroscopic data is intrinsically insensitive to molecular phenomena and cannot be interpreted to obtain unequivocal molecular-level information. Before models of surface speciation can be accepted, their molecular assumptions must be verified by direct examination of adsorbed species at the colloid/aqueous solution interface using non-invasive, in-situ surface spectroscopic methods[13].

The characteristic features of an application of a molecular model of adsorption are illustrated in Table 4, taking a simple example of the constant capacitance model as applied to an hydrous oxide colloid. Given the assumption of an average surface hydroxy group, there are just two chemical reactions involved (recall that the «background» electrolyte is not considered explicitly). The constraint equations prescribe mass and charge balance (in terms of mole fractions, x) and two complex stability constants. Parameter estimation then requires the determination of the two stability constants and the capacitance density simultaneously from experimental measurements of the species mole fractions as functions of pH. The linear expressions at the bottom of Table 4, which result from the combination of the five equations just above them, reveal that the constant capacitance model is a special case of «mean-field theory», well known in statistical mechanics[21].

Model applications to ion adsorption by heterogeneous colloids, such as those in soils, follow the same format as in Table 4, but with additional parameters. An illustrative example is provided by a recent study of selenite adsorption by alluvial soils using the constant capacitance model[31]. This model was chosen because of spectroscopic evidence that $SeO_3^{2\ominus}$ forms inner-sphere complexes on hydroxylated surfaces[15]. In addition to the acid-base reactions in Table 4, the chemical reactions describing adsorption (in a NaCl background) were:

$$SOH(s) + 2H^{\oplus}(aq) + SeO_3^{2\ominus}(aq) \rightleftharpoons SHSeO_3(s) + H_2O(l) \qquad (15)$$

$$SOH(s) + H^{\oplus}(aq) + SeO_3^{2\ominus}(aq) \rightleftharpoons SSeO_3^{\ominus}(s) + H_2O(l) \qquad (16)$$

$$2SOH(s) + 2H^{\oplus}(aq) + SeO_3^{2\ominus}(aq) \rightleftharpoons S_2SeO_3(s) + 2H_2O(l) \qquad (17)$$

where SOH(s) represents 1 mol of reactive surface hydroxy groups bound to a Lewis acid site, S, in a soil. Equations (15)–(17) are ligand exchange reactions whose product surface species are either monodentate or binuclear bidentate complexes of selenite. With chosen values of the acid-base equilibrium constants and an experimental estimate of the total number of moles of surface sites, model optimization consisted of evaluation of the three equilibrium constants for the reactions (15)–(17) simultaneously with the capacitance density parameter, C[31]. This was done with data on selenite adsorption as a function of pH for a single alluvial soil («adsorption envelope»). The model then was applied to *predict* selenite adsorption on four other soils of similar composition, without changing the value of any model parameter except the number of moles of surface sites, which was obtained experimentally. The results (Fig. 5) indicated that the model had reasonable predictive capability under the conditions of its application.

5. Concluding Remarks and Outlook

Adsorption phenomena at the soil colloid-soil solution interface can be interpreted on the molecular level as the result of surface complex formation and the development of a diffuse ion swarm. The diffuse-swarm ions and those bound in outer-sphere surface complexes may be termed «exchangeable», whereas ions bound in inner-sphere surface complexes are termed «specifically adsorbed». Spectroscopic methods can be used to detect and quantitate the surface species.

Although the application of invasive spectroscopic techniques has contributed much to the understanding of the chemical mechanisms of surface interactions, in-situ techniques represent the only experimental approach which can provide truly unambiguous molecular information relevant to natural colloids. Electron spin resonance methods have been uniquely successful in

Table 4. Application of the constant capacitance model.

Surface Acid-Base Reactions	$SOH_2^{\oplus}(s) = SOH(s) + H^{\oplus}(aq)$ $SOH(s) = SO^{\ominus}(s) + H^{\oplus}(aq)$	
Mass Balance	$x_{SOH_2^{\oplus}} + x_{SO^{\ominus}} + x_{SOH} = 1$ x = mole fraction	
Surface Charge	$\sigma_H = \frac{F}{S} N_T (x_{SOH_2^{\oplus}} - x_{SO^{\ominus}})$ N_T = total moles of SOH(s) per unit mass S = specific surface area	
Equilibrium Constants	$K_{a1}^s\,(\text{int}) = \frac{(SOH)(H^{\oplus})}{(SOH_2^{\oplus})}$	$K_{a2}^s\,(\text{int}) = \frac{(SO^{\ominus})(H^{\oplus})}{(SOH)}$
Activity Coefficients	$f_{SOH} = f^0_{SOH_2^{\oplus}} \exp(F\psi_S/RT)$ $f_{SO^{\ominus}} = f^0_{SO^{\ominus}} \exp(-F\psi_S/RT)$ $f_{SOH} = f^0_{SOH} = f^0_{SOH_2^{\oplus}} = f^0_{SO^{\ominus}}$	ψ_S = surface potential
Charge-Potential Relationship	$\sigma_H = C\psi_S$	C = capacitance density [$F\,m^{-2}$]
Parameter Estimation	$-\lg\left[\frac{x_{SOH}(H^{\oplus})}{x_{SOH_2^{\oplus}}}\right] = -\lg K_{a1}^s(\text{int}) - \frac{F}{(\ln 10)\,CRT}\,\sigma_H$ $-\lg\left[\frac{x_{SO^{\ominus}}(H^{\oplus})}{x_{SOH}}\right] = -\lg K_{a2}^s(\text{int}) - \frac{F}{(\ln 10)\,CRT}\,\sigma_H$	

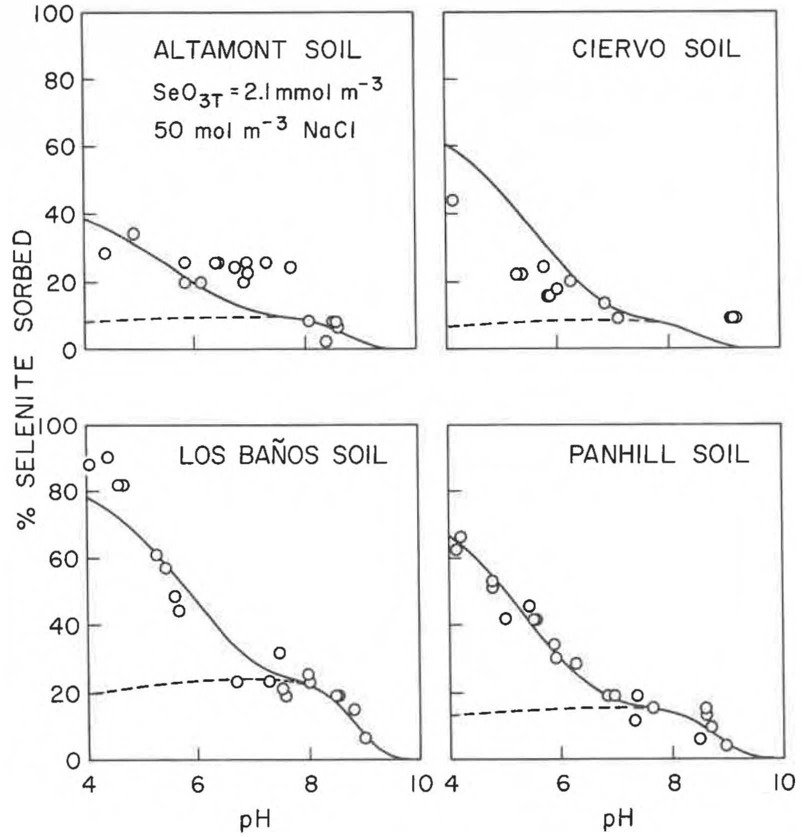


Fig. 5. Selenite adsorption envelopes (open circles) and predictions *of the constant capacitance model (solid curve) for four alluvial soils*[31]*. The dashed curve shows the contribution of the binuclear surface complex (Equation (17)). Model parameters used in the predictions for all four soils were:*

C	2.7 $F\,m^{-2}$	lg K_{SSeO_3} (int)	10.4
lg K^s_{a1} (int)	−7.35	lg K_{SHSeO_3} (int)	16.9
lg K^s_{a2} (int)	−8.95	lg $K_{S_2SeO_3}$ (int)	29.6

providing in-situ molecular level information during the past 15 years. Recent technological advances, however, have significantly extended the in-situ sampling capabilities of other spectroscopic methods, vibrational and X-ray spectroscopies in particular. Although these methods and their associated sampling techniques are not yet fully developed, combined application of several spectroscopies offers a powerful experimental approach to studying molecular structure at the colloid/solution interface.

Surface charge balance formulated according to molecular concepts can be applied to derive model-independent results concerning the points of zero charge investigated commonly for natural colloids. In particular, general relationships among the points of zero charge can be established along with general rules about the effects of ion adsorption on them. The most significant points of zero charge appear to be the pH value at which the net colloid particle charge vanishes (PZC) and the pH values at which the net adsorbed ion charge vanishes (PZNC or PZNPC).

Chemical models of adsorption based on the surface complexation concept show promise in describing reactions at the colloid-solution interface for a broad variety of natural systems. These models, which account for surface speciation in a relatively uncomplicated manner, appear to be of significant predictive value in applications.

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