# Recent developments of surface complexation models applied to environmental aquatic chemistry

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**Abstract**: Based on numerous latest references, the current developments in surface complexation, surface precipitation and the corresponding models (SCMs and SPMs), were reviewed. The contents involved comparison on surface charge composition and layer-structure of solid-solution interface for the classical 1-pK and 2-pK models. In addition, the fundamental concept and relations of the new models, i.e., multi-site complexation (MUSIC) and charge-distribution (CD) MUSIC models were described as well. To avoid misuse or abuse, it must be emphasized that the applicability and limitation for each model should be considered carefully when selecting the concerned model(s). In addition, some new powerful techniques for surface characterization and analysis applied to model establishment and modification were also briefly introduced.
**Keywords**: surface complexation models; environmental aquatic chemistry; geochemical circulation

## 1  Background

In geochemical circulation, various pollutants with adverse impacts (e.g., toxicity, mutagenicity and lethality) are usually associated with heterogeneous particles, predominantly clay minerals. Generally, the properties of these complex particles should be described using distribution functions based on related conceptual and mathematical models, rather than using physicochemical variables with a single well-defined value. Since most important reactions, e.g., acid/base chemistry, sorption/desorption and dissolution/precipitation, mainly occur in the region of solid-aqueous interfaces, the behavior, transport and ultimate fate of many contaminants are largely dependent on the corresponding interfacial processes (Buffle, 1993).

Acidity-basicity is of direct concern in many chemical processes, and it determines the pristine charging, and then the binding behavior of priority environmental contaminants, e.g., heavy metals and persistent organic compounds. After acid activation, some natural particles can act as cheap and efficient catalysts. Consequently, a quantitative understanding of the acid-base properties of the solid matrix is essential to further study the involved mechanisms and kinetics of many physiochemical processes, such as sorption/desorption, photocatalysis, photoredox or photodegradation. In addition, using batch adsorption experiments and the corresponding model description, we can investigate the conditions causing partitioning of pollutants between sediments and interstitial water. The reaction constants can then be derived (Du, 1997; 1999; Wen, 1998) and used to estimate the actual equilibrium partitioning coefficients, $K_p$s, which are critical for defining the numerical sediment quality criteria (SQC) in a specific region. The SQC are useful for indicating the distribution and extent of pollution, and for assessing potential ecological risks (Liu, 1999a; 1999b). Numerous studies have been devoted to different particle surfaces, such as (hydr)oxides (Ludwig, 1995; Koopal, 1996; Laiti, 1996; Au, 1998), clay minerals (Angove, 1997; Avena, 1998; Kraepiel, 1998; Ikhsan, 1999) and soils (Anderson, 1992). In addition, advances in simulation models (Hiemstra, 1996a; Charmas, 1999; Lützenkirchen, 1998a; 1998b; 1999a; 1999b), together with modification of experimental techniques (Turner, 1998; McGuire, 1999), have greatly expanded our knowledge of reaction kinetics and mechanisms during recent decades. However, it is still insufficient with respect to the complexity of the real world.

## 2  Surface charge of aqueous clay minerals

The chemical process of charge development on colloidal particles is generally determined by an excess of complex physicochemical properties of the particles' surfaces exposed to the aqueous environment, and the amount and strength of charged surface sites can be correlated with solid surface properties, such as catalytic efficiency (Schwartz, 1999). Composition and distribution of surface charge are both closely associated with the corresponding mechanisms of interactions between the solid surface sites and "xenobiotic" compounds, as well as the pathways of the weathering process.

Particle surfaces acquire electrical charge mainly by two means: permanently from isomorphic substitutions of component ions in the bulk structure of the solid, or conditionally from the reactions of surface functional groups with adsorptive ions in aqueous solution, e.g., surface hydroxyls at the basal planes or edge faces (Sposito, 1992; 1998; Stumm, 1992). The concerned surface charge balance can be expressed as follows:

$$\sigma_P = \sigma_{in} + \sigma_s, \tag{1}$$
$$\sigma_{in} = \sigma_0 + \sigma_H, \tag{2}$$
$$\sigma_S = \sigma_{IS} + \sigma_{0S}, \tag{3}$$
$$\sigma_P + \sigma_d = 0, \tag{4}$$
$$\Delta q = \sigma_{IS} + \sigma_{0S} + \sigma_d \text{ or } \Delta q = q_+ - q_-, \tag{5}$$

where $\sigma_P$, $\sigma_{in}$ and $\sigma_s$ are the net total particle-, the intrinsic- and the Stern layer-surface charge densities, respectively, $\sigma_0$ and $\sigma_H$ denote the net permanent structural- and the net proton- surface charge densities, respectively, the latter being proportional to the difference in the number of models between protons and hydroxide ions complexed by surface functional groups. $\sigma_{IS}$ and $\sigma_{OS}$ are inner- and outer-sphere complex surface charge densities, respectively. The

**Table 1    Definition and approach to the measurement of surface charge density**

| Symbol | Name | | | Description |
|---|---|---|---|---|
| PZNPC | Point of zero net proton charge | | | $\sigma_H = 0$ |
| PZNC | Point of zero net charge | | | $\sigma_{in} = 0$ |
| PZC | Point of zero charge | | | $\sigma_P = 0$ |
| Surface charge density | $\sigma_P$ | $\sigma_{ia}$ | $\sigma_0$ | $\sigma_H$ |
| Method of determination | Microscopic electrophoresis | Schofield method | Alkylammonium cation exchange | Electrometric titration |

diffuse-later surface charge density, represented by $\sigma_d$, is required to balance $\sigma_P$ for maintaining electrical neutrality. Finally $q_-$ and $q_+$ are the total relative amounts of adsorbed anions and cations, respectively.

Some definitions and routine methods for determining the particle surface charge density are listed in Table 1.

By scanning force microscopy (SFM), Brady et al. (Brady, 1996) studied the specific control of particle surface charge based on calculation of molecular electrostatic potential (MEP). Other reports have also offered the following valuable information: (1) theoretical prediction of the pH at the point of zero charge, $\text{pH}_{PZC}$ (Sverjensky, 1994; Eggleston, 1998); (2) evaluation of surface ionization parameters using atomic force microscopy (AFM) data (Zhmud, 1998); (3) molecular mechanical calculations of the relative proton binding energies for specific sites on oxide surfaces (Rustad, 1996); and (4) equilibrium constants for single-site surface protonation based on Born solvation theory, electrostatic interaction and intrinsic binding, in which the surface equilibrium constants for a series of complex silicates were considered to be determined by the underlying bulk crystal structure, instead of estimation from linear correlation with aqueous equilibrium constants (Sverjensky, 1996). In addition, the disk model containing spatial differentiation of permanent and pH-dependent charges, compared to the conventional infinite-plane model, may be more realistic in describing the electrical double layer (EDL) on 2:1 clay minerals (Chang, 1996).

# 3   Surface complexation and precipitation

## 3.1   Outline

The interfacial reactions of clay minerals can be separated into ion exchange and surface complexation. The former commonly occurs at the permanently-charged surface sites, resulting from isomorphous substitution leading to unspecified adsorption or outer-sphere complexation; whereas the latter is usually generated by ions binding to variably-charged surface sites, based on interactions with surface hydroxyl groups leading to specific adsorption, i.e., the formation of inner-sphere complexes (Sposito, 1992; Stadler, 1993). The surface complexation activity chiefly originates from the physicochemical behavior of the surface sites described above, their relative contribution depending on the system characteristics, such as pH and background electrolyte concentration (Davis, 1990).

As the ratio of adsorbate (e.g., cations) to sorbent gradually increases, the corresponding surface reactions probably undergo a smooth transition, from Langmuirian behavior with a saturated isotherm, to a Freundlich isotherm without apparent saturation in sorptive capacitance. Since it is difficult to strictly distinguish surface complexation from surface precipitation in many circumstances, a continuum has been suggested, from mononuclear adsorption to multinuclear complex formation, and finally to surface precipitation (Farley, 1985; Dzombak, 1986). The term of surface complexation is also extended to incorporate various hypothesized surface species or mechanisms, e.g., surface clusters, polymers and multinuclear complexes being the precursors to surface precipitates (Fendorf, 1992).

## 3.2   Surface complexation and precipitation models

Great developments in SCMs have been achieved since the initial form was introduced by Stumm and Schindler for interpreting heavy metal adsorption in simple suspension systems (Stumm, 1970; Schindler, 1972; 1981). Analogous to the formation of coordinated complexes in solution except for consideration of surface charge, the model formulation treats the solid surface as a polyelectrolyte carrying many charged surface hydroxyl groups, which can perform proton transition, and incorporate cations/anions or other ligands from solution phase. Consequently, the apparent surface reaction constant ($K^{app}$) is theoretically predicted as a product of the intrinsic surface reaction constant at zero surface charge ($K^{int}$) and an electrostatic (coulombic) term, which is in fact a surface activity coefficient for the long-range electrical effects of charged surface groups and calculated from the Gouy-Chapman theory of EDL:

$$K^{app} = K^{int} \cdot \exp(-\Delta z F \Psi / RT), \tag{6}$$

where $\Psi$ is the surface potential (V), $\Delta z$ denotes the change in the charge of the surface species for the considered reaction (C), $F$ represents the Faraday constant ($\text{Cmol}^{-1}$), $R$ is the molar gas constant ($\text{J}/(\text{mol} \cdot \text{K})$) and $T$ is the absolute temperature (K).

Several fundamental steps should be adopted in developing a surface complexation model (Davis, 1998): (1) the total number of surface sites should be determined experimentally or a value should be assigned on the basis of other studies; (2) an approach should be developed to describe surface site heterogeneity or the number of specific types of surface functional groups; (3) the mass action and mass balance equations that elucidate the equilibrium of surface reactions should be formulated, and the apparent stability constants for surface species should be measured; (4) a method should be developed or

assumed to quantify coulombic correction factors or rational activity coefficients to correct the equilibrium constants for surface acidity and complexation reactions.

The primary perceptions for various surface complexation models (SCMs) so far remain the same: (1) sorption on (hydr)oxides occurs at specific coordination sites; (2) sorption reactions on (hydr)oxides can be described quantitatively via mass law equations, and the $K^{app}$s determined for the mass law equations are empirical parameters related to thermodynamic constants via the rational activity coefficients, $\gamma$, or the surface species; (3) surface charge arises from the sorption reactions themselves; and (4) the effect of surface charge on sorption can be considered by embodying a correction factor from EDL theory into the mass law constants (Dzombak, 1990; Davis, 1992).

In mechanistic approach built on the knowledge of the underlying molecular binding mechanism, the binding models should at least account for the structures of the surface and adsorbate, and for the electrostatic outline and location of the ions in it. The advantage of electrostatic SCMs characterized by mechanistically oriented binding, is that they can, in principle, use the same formalism in all systems of interest, and enable the prediction of properties of the individual binding sites and complexes (Cernic, 1996). On the other hand, the application of SCMs is currently restricted by the uncertainty in the choice of the electrostatic geometry at the interface and the locations of the ions. Improvement of SCMs is often obstructed by the limited freedom of choice in the amount of involved surface sites and the number of different adsorbed species (Rietra, 1999).

Some frequently used SCMs include the constant capacitance model (CCM; Manning, 1997; Angove, 1998), the diffuse-layer model (DLM; Tessier, 1996; Bradbury, 1997; Avena, 1998), the triple-layer model (TLM; Righetto, 1995; He, 1997), as well as the four-layer model (FLM; Charmos, 1995; 1996; 1999). These models are based on the so-called 2-p$K$ approach characteristic of a diprotic acid reaction (Lützenkirchen, 1998b):

$$\equiv SOH_2^+ \leftrightarrow \equiv SOH + H_S^+ , \quad K_{a1}^{int} , \tag{7}$$

$$\equiv SOH \leftrightarrow \equiv SO^- + H_S^+ , \quad K_{a2}^{int} , \tag{8}$$

where $\equiv SOH$ represents a solid surface site, and the subscript S denotes the proton near the surface. One can differentiate the models depending on their treatment of the electrostatic profile at the solid-aqueous interface, in particular the locations and hydrated state of sorbed ions and the spatial distribution of solution counter ions (Fig.1). However, all the SCMs would reduce to a set of simultaneous equations that can be resolved numerically. These equations include: (1) mass law equations for all surface reactions under consideration; (2) a mole balance equation for surface species; (3) an equation for computation of surface charge, and (4) a set of equations representing the constraints imposed by the model of interfacial structure (Davis, 1992).
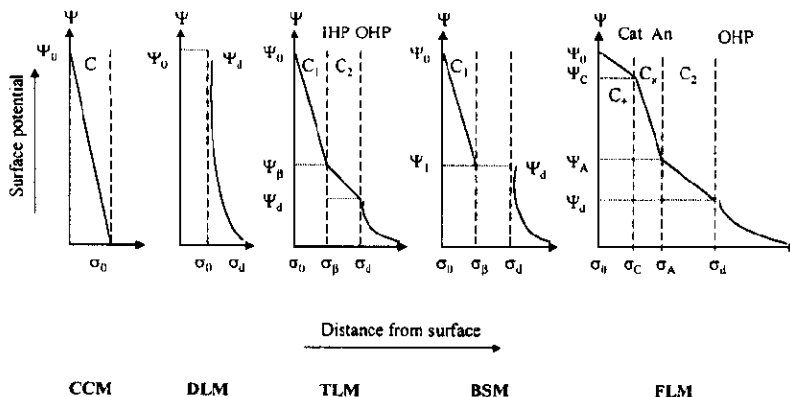


Fig.1    Presentations of the electrical double layer (EDL) in various surface complexation models, $\psi$ and $\sigma$ denote surface potential and surface charge, respectively, and $C$ is the specific capacitance. Subscripts indicate inner-sphere (0), outer-sphere ($\beta$), anion-(A), cation-(C) and diffuse (d) layers. IHP and OHP are inner- and outer- helmholtz planes, respectively

In the CCM, the thin EDL resembles a parallel plate capacitor, with only one plane in the interfacial region being considered. All surface complexes are regarded as inner-sphere complexes, while the background electrolyte ions are assumed to be inert. Although physically equivalent to the TLM near the PZC (Righetto, 1995), the ordinary CCM is not able to predict the variation of the isoelectric points (IEPs) with ionic strength in the opposite direction (Lützenkirchen, 1998b), because theoretical considerations presume the interfacial potential to be independent of ionic strength ($I$). However, the 2-p$K$ CCM has been substantiated as a good choice for the high $I$ and/or low surface potential cases, when experimental data allow a determination of unique parameters and if only the goodness-of-fit criterion is considered (Lützenkirchen, 1998b). In addition, the extended CCM (ECCM) has also been proposed to imbibe the contributions from electrostatic forces, i.e., the outer-sphere complexation reactions (Persson, 1996; 1998). An introduced total capacitance ($C_{tot}$) can be distributed over two specific capacitances, $C_1$ and $C_2$ (Eq. (9)), characterizing the inner- and outer-sphere complexation planes, respectively. To some extent, the ECCM is similar to the typical TLM with the exception that the diffuse layer is neglected.

$$\frac{1}{C_{tot}} = \frac{1}{C_1} + \frac{1}{C_2} . \tag{9}$$

The high ionic strength normally used in the corresponding potentiometric titration makes the CCM a physically realistic choice as an interfacial model (Lützenkirchen, 1999a). This succinct approach with fewer adjustable parameters is valid for constant ionic medium conditions (Lützenkirchen, 1998b, 1999a). Manipulation of multiple ionic strength data with one comprehensive parameter set is thus avoided. It allows data treatment on the concentration scale, and in principle involves strictly conditional parameters. The conditional character of the CCM with respect to ionic strength, in turn, avoids the quantification of electrolyte binding. More recently, however, Lützenkirchen (Lützenkirchen, 1999b) presented a critical evaluation of possible applications and applicability of the CCM. Some examples were listed, in which this model was misused or abused through its parameterization, especially for low ionic strengths, ascribed to the presence of a diffuse layer revealed by published surface force measurements and the interplay between low capacitance values and high $\Delta pK$. In addition, although the BSM or the TLM generally includes electrolyte binding constants, they are, in many cases, additional fitting parameters and difficult to corroborate experimentally. Furthermore, the goodness-of-fit is frequently utilized as a decision criterion in the modeling process, and in this respect, the 2-p$K$ CCM has been shown to be superior to the 1-p$K$ variant (Lützenkirchen, 1999a). On the whole, the 2-p$K$ CCM can be validated as a model for acid-base properties of a defined solid sample or for a defined medium, and applying the model in such a consequent way can avoid inconsistency (Lützenkirchen, 1998b; 1999a).

In a sense, the CCM is a special form of the DLM. The differences between the DLM and the CCM are that the former takes into account the dissociated counter-ions in the diffuse layer and surface capacitance is fixed by theory rather than a fitting parameter, therefore, the influence of background electrolyte on protolysis equilibria can be interpreted by the relationship between diffuse layer charge and ionic strength. The DLM is usually restricted to simulating low ionic strength conditions, attributable to an over-prediction of the diffuse-layer potential at high $I$ (Hayes, 1991). More recently, the DLM has been shown to be inferior to the CCM in the description of acid-base properties using the chosen experimental data and optimized procedure, though it would be the simplest model in 2-p$K$ formalism (Lützenkirchen, 1999a).

The EDL is divided into three planes in the TLM, that is, two constant capacitance layers and one diffuse layer. The potential-determining ions, i.e., $H^+$, $OH^-$, and strongly-adsorbed ions, are assumed to form the inner Helmholtz plane (IHP), while the outer Helmholtz plane (OHP) is composed of the weakly-adsorbed ions, such as background electrolytes. The TLM can accommodate both inner- and outer-sphere complexes, and be applicable to systems with various ionic strengths. Nevertheless, the TLM requires the greatest number of adjustable parameters relative to the CCM and DLM. In contrast to some conventional means for the determination of the TLM parameters, such as linear/double graphic extrapolation and numerical methods, a possible alternative approach has been suggested on the basis of a simple equation for the IEP, in which the inner layer capacitance and the pristine point of zero charge (PPZC) were ascertained, and no knowledge of site density was required (Lützenkirchen, 1998a). In addition, the author indicated several shortcomings in previous work about TLM parameter estimation using solvation and electrostatic theory (Sahai, 1997a; 1997b), e. g., the demanded calibration involved high site density that was unable to explain the experimentally observed saturation phenomena. In Table 2, the main characters of the SCMs mentioned above are summarized.
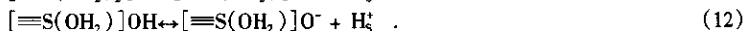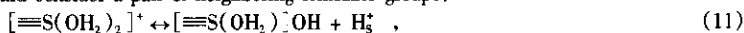
Since the presumption that anions and cations are located within the same layer is too coarse in many cases due to their different dimensions and electrostatic fields, some workers further put forward the four layer model (FLM) as a modification, in which anions are situated within the layer of potential $\psi_A$, whereas cations are gathered within the layer of potential $\psi_C$. This model develops the relationship between PZC and IEP. Obviously, more adjustable parameters are needed for the complex model description. A major stimulus for multiple-layer models is that the surface potentials calculated from the EDL theory are typically higher than the zeta potentials on particles measured by electrophoresis. However, fundamental difficulties are associated with the interpretation of electrophoresis experiments, furthermore, it is doubtful whether the average potential affecting the microscopic sorption of ions at the surface, should be equal or even simply related to the zeta potential affecting the macroscopic interaction of a particle with its viscous medium (Dzombak, 1990).

On the other hand, another concept of surface complexation modeling is currently referred to as the 1-p$K$ model based on the following reaction:

$$\equiv SOH^{-1/2} + H_s^+ \leftrightarrow \equiv SOH_2^{+1/2} \quad , \quad K = 10^{PPZC} . \tag{10}$$
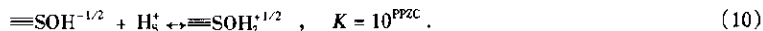
The presented charge in Eq.(10) should be considered as formal, attributed to the individual surface groups for a proper bookkeeping of charge in the model description. Compared to the 2-p$K$ models, a reduction in adjustable parameters is present, since the stability constant in Eq.(10) can be experimentally obtained as the PPZC of a solid and it will not rest on the electrostatic model (Lützenkirchen, 1998b). Both sufficient knowledge of the temperature dependence of PPZC and some available theories of PPZC prediction are in favor of the 1-p$K$ model.

Moreover, Borkovec (Borkovec, 1997) has studied the origin of 1-p$K$ and 2-p$K$ model based on statistical mechanics, and noted that an incorrect interpretation of consecutive surface protenation is presented in classical 2-p$K$ SCMs; that is, only one type of surface oxygen is reactive, two protons are assumed to bind sequentially to a single oxygen atom, being indicative of the large difference between the successive p$K$ values ( $\Delta pK > 10$), as indicated in Fig.2. Alternatively, an adequate expression of the given 2-p$K$ model should consider a pair of neighboring ionizable groups:

$$[\equiv S(OH_2)_2]^+ \leftrightarrow [\equiv S(OH_2)]OH + H_s^+ \quad , \tag{11}$$

$$[\equiv S(OH_2)]OH \leftrightarrow [\equiv S(OH_2)]O^- + H_s^+ \quad . \tag{12}$$

Such a mechanism can explain the small splitting of the consecutive p$K$ values, which were mostly derived from

Table 2 Comparison of basic properties between the different SCMs'

| Type | Parameters | Minimum number of parameters | Relation between surface charge ($\sigma$) and surface potential ($\psi$) |
|---|---|---|---|
| CCM | Capacitance ($C$), site density ($N_S$), specific area ($S_{BET}$), stability constants ($K_i$) | 5 | $$\sigma = C^{CCM} \times \psi$$ $$\text{or } \sigma = \left( C \times \frac{S_{BET} \times A}{F} \right) \times \psi$$ |
| DLM | Site density ($N_S$), specific area ($S_{BET}$), stability constants ($K_i$) | 4 | $$\sigma_0 + \sigma_d = 0$$ $$\psi_0 = \psi_d$$ $$\sigma_d = \frac{S_{BET} \times A}{F} \times \sqrt{8\varepsilon\varepsilon_0 RTI} \times \sinh \frac{zF\psi_0}{2RT}$$ |
| BSM | Capacitance ($C_1$), site density ($N_S$), specific surface area ($S_{BET}$), stability constants ($K_i$) | 7 | $$\sigma_0 + \sigma_1 + \sigma_d = 0$$ $$\sigma_0 = \frac{S_{BET} \times A}{F} \times C_1 \times (\psi_1 - \psi_0)$$ $$\sigma_1 = \frac{S_{BET} \times A}{F} \times C_i \times (\psi_1 - \psi_0) + \sqrt{8\varepsilon\varepsilon_0 RTI} \times \sinh \frac{zF\psi_0}{2RT}$$ $$\sigma_d = \frac{S_{BET} \times A}{F} \times \sqrt{8\varepsilon\varepsilon_0 RTI} \times \sinh \frac{zF\psi_0}{2RT}$$ $$\psi_1 = \psi_d$$ |
| TLM | Capacitance ($C_1$) and ($C_2$), site density ($N_S$), specific surface area ($S_{BET}$), stability constants ($K_i$) | 8 | $$\sigma_0 + \sigma_\beta + \sigma_d = 0;$$ $$\sigma_0 = \frac{S_{BET} \times A}{F} \times C_1 \times (\psi_0 - \psi_\beta);$$ $$\sigma_d = \frac{S_{BET} \times A}{F} \times C_2 \times (\psi_d - \psi_\beta);$$ $$\sigma_\beta = \frac{S_{BET} \times A}{F} \times [ C_1 \times (\psi_\beta - \psi_0) + C_2 \times (\psi_\beta - \psi_d) ]$$ $$\psi_0 - \psi_\beta = \frac{\sigma_P}{C_1}$$ $$\psi_\beta - \psi_d = \frac{\sigma_P + \sigma_\beta}{C_2} = \frac{\sigma_d}{C_2}$$ |

Notes: $C$ is the capacitance density (F/m$^2$); $S_{BET}$ is the specific surface area (m$^2$/g); $A$ is the suspension concentration of solid (g/L); $\psi$ is the surface potential (V); $\sigma$ is the surface charge (mol$_c$/L, $I$ is the ionic strength (mol/L); $\varepsilon$ is the dielectric constant; $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-12}$ C$^2$/(N·m$^2$); $F$ is the Faraday constant (96487 C/mol); $T$ is the absolute temperature (K); and $R$ is the ideal gas constant

experimental oxide data ($\Delta pK \approx 2$—$4$). In most cases, the 1-p$K$ model can provide a sufficiently accurate illustration of the titration behavior of the solid-water interface. In some particular situations where the 1-p$K$ simulation fails, e.g., when the surface is composed of small groups of sites which mutually interact to a greater extent than with all other neighboring sites within the lattice (Borkovec, 1997), the application of 2-p$K$, or even 3-p$K$ or 4-p$K$ models, may become essential. Similar conclusions were drawn in another comparative study as well, in which the 1-p$K$ basic Stern model (BSM) and the 2-p$K$ CCM were recommended with respect to the fitting efficiency and the uniqueness of estimated parameters. The 2-p$K$ BSM and the TLM, as well as the more complex FLM, were subordinate due to the large number of adjustable parameters involved (Lützenkirchen, 1998b).

In view of chemical thermodynamics, however, there seems to be no difference in nature between the two types of models, and in this sense, an appropriate choice of different standard states (i.e., hypothetical states) is at the heart of the comparison (Tao, 1998). On the other hand, since the different crystal planes may have different PPZCs, and the significance of the individual planes will decide the
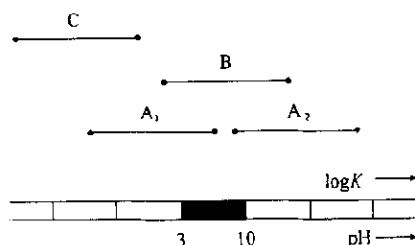


Fig. 2 The schematic interposition of the log$K$ values of consecutive protonation reactions of one surface group with respect to the pH range of titration (pH = 3 – 10)
Position A: one of the log$K$ values of a certain surface group in or near the pH range (for example, A$_1$: SiOH, A$_2$: AlOH); Position B: both values are more or less symmetrical around, but outside the pH range of titration (for example, Fe$_2$OH); Position C: both log$K$ values are far outside the pH range of titration like in the case of SiO$_2$ or Ti$_3$O surface groups

overall PPZC of a certain sample, Sverjensky's prediction (Sverjensky, 1994) appears to be adopted only in specific cases where actual measurements are not possible (Lützenkirchen, 1998b). Based on the situations mentioned above, it should be emphasized that any simplified approach, e.g., 1-p$K$ and 2-p$K$ models, necessarily introduces some kinds of approximation or simplification, the quality of which has seldom been properly tested (Borkovec, 1997).

Furthermore, both the classical 1-p$K$ and the 2-p$K$ models can be treated as special cases of the multisite complexation (MUSIC) model, proposed according to the crystallographic principle and physicochemical considerations, e.g., Pauling's concept of bond valence (Hiemstra, 1989). The model deems that protonation reactions involve different types of surface groups. One of the main differences in intrinsic proton affinity of surface groups is due to the number of metal-coordinated oxo groups, and the difference in affinity between two consecutive protons binding to the same type of oxygen is very large ($\Delta pK$ > 14; Hiemstra, 1996b). Consequently, the MUSIC model relies on detailed crystallographic characterization of solid samples, such as in terms of the contribution of different crystal planes, to calculate the proton affinity constants for individual types of surface groups.

In this model, including multiple surface groups with singly, doubly and triply metal-coordinated oxygen atoms, exhibiting different proton affinities, the concerned surface charge can be described by one proton adsorption and one discrete $K$ for each type of surface group (Hiemstra, 1989; Venema, 1998; Nagashima, 1999). The basic concept and relationship can be briefly described as follows:

$$v = z / CN, \tag{13}$$

$$\log K_H = \text{function}(nv), \tag{14}$$

where, the Pauling bond valence ($v$) is defined as the charge ($z$) of the central cation divided by its coordination number ($CN$), $K_H$ represents the proton affinity of a surface group, $n$ denotes the coordination number of the surface (hydr)oxide group. The overall chemical formula for simple (hydr)oxides and the typical protonation reactions of metal(hydr)oxide surface groups are expressed respectively by:

$$\text{MeO}_{((1-f)\cdot CN/n)}\text{OH}_{(f\cdot CN/n)}, \tag{15}$$

$$\text{Me}_n\text{O}^{n\cdot v-2} + 2\text{H}_S^+ \leftrightarrow \text{Me}_n\text{OH}^{n\cdot v-1} + \text{H}_S^+ \leftrightarrow \text{Me}_n\text{OH}_2^{n\cdot v}. \tag{16}$$

Here, $f$ is the fraction of anions in the structure, present as OH ions.

The framework of the MUSIC model is, however, still relatively simple, since it is based primarily on electrostatic considerations and assumes that the same site types have the same p$K$ values independent of the surface face or structure. The conventional MUSIC model contains some drawbacks as well: (1) it does not yet predict any actually observed saturation in proton adsorption; (2) since provision of surface protonation equilibrium constants must take into account the difference in both the Pauling bond strengths per Å and the dielectric constants of the solids, forecasting solely from the former is inherently defective (Sverjensky, 1996); and (3) for some environmentally important sorbents, an accurate estimation of the crystallographic representation is virtually impossible and, therefore, surface complexation modeling will rather be based on the simple approaches, though it can not be expected to provide a mechanically realistic interpretation in such situations (Lützenkirchen, 1998b).

Recently, as a consistent extension of the MUSIC approach, a model combined with Pauling's concept of charge distribution (CD-MUSIC) has been forwarded, and applied to the formation of surface complexes (Hiemstra, 1996a), such as protons (Hiemstra, 1996b; Venema, 1996; 1998) and other ions (Hiemstra, 1999a; 1999b; Rietra, 1999). In this new model, surface complexes are regarded as having a spatial distribution of charge in the interfacial regions, rather than point charges, and surface oxygen atoms are neutralized by both Me ions belonging to the solid and a variable number of adsorbed protons. In the case of inner-sphere complex formation, only part of the complex is incorporated into the surface by a ligand exchange reaction, while the other part is located in the Stern layer (Hiemstra, 1996a). The model can depict, within a single conceptual scope, all significant experimental adsorption procedures, by considering the chemical compositions of the crystal surface. Some important properties are given in Fig.3.

Since the charge distribution and neutralization are actually related to Me-O bond length which is unequal due to electrostatic Me-Me repulsion, a smaller length/distance will contribute more to the neutralization of charge than a bond with a larger Me-O distance (Hiemstra, 1996b). Accordingly, a refinement has also been developed using an alterative actual bond valence(s) related to the bond length (Hiemstra, 1996b; Venema, 1998). It is different from the conventional Pauling's bond valence rule based on equal charge distribution and can be interpreted with the Me-O distance ($R$; Eq. (17)). Fig.4 illustrates an example of charge distribution and its factor ($f$).

$$s = e^{\frac{R-R_0}{b}}. \tag{17}$$

In this relation, $R$ and $R_0$ are bond distance and element-specific distance, respectively, and $b$ is a constant (usually

0.37 Å).

These advances partially address the deficiency in the conventional MUSIC model, i.e., p$K$ values independent of surface faces and structures (Felmy, 1998).

In their treatise, Dzombak and Morel (Dzombak, 1990) have indicated that, the proof of the model adequacy is found *a posteriori* in its ability to account for all available sorption data, and in coherence of the resulting parameters, additional complexity can be added when required and justified by new data. The authors also emphasized that a clear understanding of what the constraining data are, is necessary to evaluate the validity of the model. Different assumptions regarding the data that
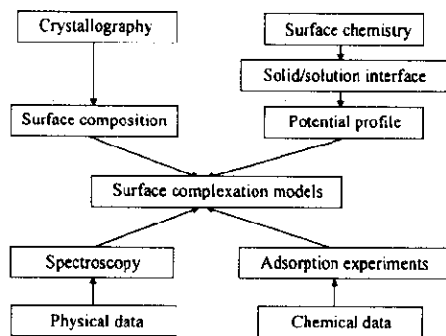


Fig.3   Diagram of the important properties of the CD-MUSIC model. Data on the surface composition are obtained from crystallography. The model of the surface/solution interface should be in agreement with surface chemistry. The features of adsorption complexes can be specified using spectroscopic results. The model is calibrated with records from adsorption experiments
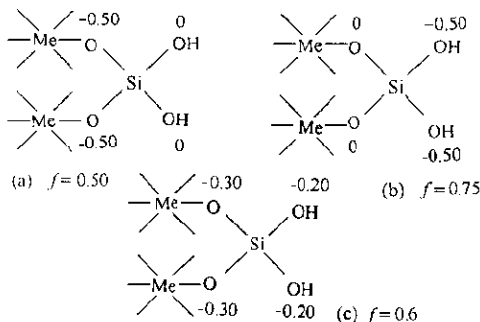


Fig.4   A schematic representation of a bidentate silicon oxo complex bound to a Me hydroxide with trivalent Me ions in a sixfold coordination ($v_{Me} = 3/6 = 0.5$). The charge of the various ligands is given for various choices of the value of the charge distribution factor $f$. (a) equal distribution of the charge of the central ion over the surrounding ligands; (b) an asymmetric distribution with neutral surface/solid oxygens; (c) the possible actual distribution with $f = 0.6$, the value can be considered as a compromise between the two opposing tendencies described in (a) and (b)

a sorption model must be capable of fitting, have been in part responsible for the multitude of SCMs that have been proposed. However, in many cases, it seems particularly difficult to find a reasonable solution with respect to the number of adjustable parameters, in term of the choice of the actual interfacial model (basic charging) and in terms of the surface species (ion adsorption). The quality of the different models is not the same when they are applied to different sorbent data, and general conclusions are at present impossible (Lützenkirchen, 1998b). If the goal is to find an accurate physical-chemical description of the surface reactions, not confined to a successful mathematical fitting, the foundational assumption of the SCMs must be tested for validity over a variety of conditions. Otherwise, it is unavoidable that methodologies not equipped to explore molecular structure will produce ambiguous results in the study of surface speciation (Sposito, 1995). The method of choice for investigating molecular structure is spectroscopy. Some authors advocate that there is generally a guiding criterion for the selection of scientific methods, referred as to Ockham's Razor (or the rule of parsimony). This states that, of all the possibilities to explain the observed facts, the simplest one is preferred (McBride, 1997). It has been argued that simpler hypotheses are more likely to be correct *a priori* and tend to provide better defined, more testable predictions.

During the simulation using SCMs, the surface site density undoubtedly plays as a critical role. The main problem with the site density is the discrepancy between experimental measurements and crystallographic estimation. Whenever densities of proton active sites are determined by titration with excess acid, it is observed that the measured saturation values are far below the crystallographically calculated ones or the numbers acquired by tritium exchange. Even the advanced MUSIC model does not explain the actual values (Lützenkirchen, 1998b). For this reason, another new idea has been given for portraying the saturation phenomena on the basis of crystallography, in which the concept of site includes one proton and one hydroxyl ion exchange group, the site densities for each being equal, and the maximum adsorption corresponds to half of the number of water molecules physically adsorbed in the first monolayer (Eq. (18)). Both protonation and depotonation occur in the first hydration layer surrounding the particles, rather than on surface hydroxyls. Meanwhile, it still allows the use of current SCMs with more complicated forms to delineate the acid-base behavior of oxides (Pivovarov, 1997).

$$D_s \text{ (site density) } = d/(2nV), \tag{18}$$

where $d$ is the lattice spacing or average lattice spacing, $V$ is the volume per cation (the volume of the elementary cell, divided by the number of cations), 2 is a coefficient, in which the doubling of the surface area of the crystallographic plane by its two faces is taken into account, and $n$ is the number of cations per site.

Other derived SCMs have been also suggested, such as a two-phase model for interpreting proton and metal ion interactions with charged polyelectrolyte gels and their linear analog (Marinsky, 1987), the component additivity approach and the generalized composite approach for complex mineral assemblage (Davis, 1998), a hybrid surface complexation and the Scheutjens-Fleer model (Au, 1998).

Since the sorption of cations at high sorbate/sorbent ratios follows a Freundlich, rather than a Langmuir isotherm, experimental results for the adsorptive capacity do not demonstrate an achievement of saturation. Therefore, a gradual transition of cation sorption has been proposed to occur from mononuclear adsorption to multinuclear adsorption, and finally to surface precipitation. Two categories of thermodynamic model, for explaining the phenomenon of surface precipitation, have been proposed corresponding to the changes in solution properties in the vicinity of the interface and in the precipitating solid (Towle, 1997). In contrast to the conventional adsorption isotherms where the adsorption density $\Gamma$ was regarded as a state variable, a new metastable-equilibrium adsorption (MEA) theory was proposed recently and provided a possible way to modify some existing theories into MEA model. In this theory, an equilibrium inequality revealed a simple relationship between the real metastable-equilibrium constant and the ideal equilibrium constant, and indicated that $\Gamma$ did not represent a definite state of adsorbate on the solid surface (Pan, 1998a; 1998b).

An important challenge in SCMs/SPMs is to combine the molecular, or even atomic, microscopic reality with macroscopic complexation phenomena, because SCMs/SPMs alone provide insufficient insight into the surface binding mechanisms (Hiemstra, 1999). In contrast, modern surface spectroscopic methods, both optical and magnetic (Johnston, 1993), can afford more discriminative results to scrutinize and confirm the assumed chemical reactions on surface (e.g., the occurrence of surface precipitates), together with model illustration. These powerful tools contain $X$-ray absorption spectroscopy (XAS; Papelis, 1996), extended $X$-ray absorption fine structure (EXAFS; O'Day, 1994; Bargar, 1997; Manning, 1998; Korshin, 1998), $X$-ray absorption near edge structure (XANES), polarized EXAFS (Schlegel, 1999) and grazing-incidence EXAFS (Towle, 1999). Accordingly, the SCMs accounting for the related processes have been extended to the surface precipitation models, SPMs (Farley, 1985; Dzombak, 1986; Towle, 1997). The strategy for different types of SPM for modeling polymerization and precipitation was also proposed, such as solid solution-, polymer-and continuum-models (Katz, 1995). In addition, several distinct steps of surface precipitate formation were suggested in kinetic studies (Comans, 1987; Wersin, 1989), i.e., rapid initial adsorption, followed by slower kinetics, which could be regarded as (1) diffusion into a hydrated surface layer; (2) dehydration and formation of surface complexation bonds; or (3) nucleation, and eventually final precipitation of a solid solution layer or of a pure phase.

During the past decade, the SCMs/SPMs have been applied to not only pure metal (hydr)oxides (Lövgren, 1990; Robertson, 1998) and sulfides (Sun, 1991), but also to clay minerals (Bradbury, 1999; Wang, 1998; Angove, 1998), amorphous aluminosilicate (Avena, 1996), municipal solid waste incinerator ashes (Meima, 1998), natural soils (Chorover, 1995), sediments (Wang, 1997; Wen, 1998; Westall, 1999), humic acids (Westall, 1995) and bacterial surfaces (Daughney, 1998; Fowle, 1999). The studied sorbates include metal cations (Lofts, 1998), anions (Ioannou, 1997; He, 1997; Rietra, 1999) as well as organic compounds (Stone, 1993; Evanko, 1999), polymers (Furrer, 1992) and natural organic matter (Au, 1999). Moreover, many computer simulation programs have been developed, e.g., FITEQL, HYDRAQL, MINTEQ, MINEQL, MICROQL and SOLGASWATER. Generally, the specific surface area of sorbent ($A_{BET}$) and the total surface site concentration (SSC), are assigned as the fixed parameters, since both can be obtained by corresponding experimental measurements. The specific capacitance ($C$) and the intrinsic surface reaction constants ($K^{int}$s) may act as adjustable parameters in the computer-assisted model calculations. It should be noted that the coherence of the parameters is more important than their absolute values. The computation is often implemented by tuning the input of $C$ so as to optimize the $K^{int}$ values. In some cases, one should take caution to justify some of the parameters to avoid co-optimizing site concentrations and equilibrium constants, due to the presence of high correlation between adjustable parameters, and thus it is preferable to use an alternative estimation of site concentration (Lützenkirchen, 1999a).
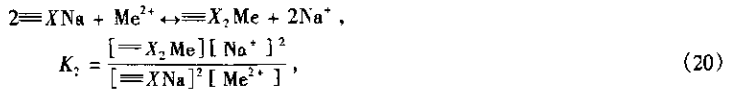
### 3.3  Model fitting of surface reactions

In general, a comprehensive description of clay-metal interactions should take both ion exchange and surface complexation into account (Stadler, 1993; Lu, 1996; Angove, 1998; Avena, 1998). In Table 3, some surface processes frequently involved are listed.

For instance, in a typical system of aqueous clay minerals, ion exchange at permanently-charged surface sites ($\equiv\!XH$) may occur in the following way:

$$\equiv\!X\mathrm{Na} + \mathrm{H}^+ \leftrightarrow \equiv\!X\mathrm{H} + \mathrm{Na}^+ ,$$

$$K_1 = \frac{[\equiv\!X\mathrm{H}][\mathrm{Na}^+]}{[\equiv\!X\mathrm{Na}][\mathrm{H}^+]}, \tag{19}$$

$$2\equiv X\mathrm{Na} + \mathrm{Me}^{2+} \leftrightarrow \equiv X_2\mathrm{Me} + 2\mathrm{Na}^+ ,$$

$$K_2 = \frac{[\equiv X_2\mathrm{Me}][\mathrm{Na}^+]^2}{[\equiv X\mathrm{Na}]^2[\mathrm{Me}^{2+}]} , \tag{20}$$

where $\mathrm{Na}^+$ and $\mathrm{Me}^{2+}$ denote the specific background electrolyte ions and adsorptive cations, respectively; [ ] in formulae is designated as species concentration. In formulating the relevant equilibria, the presence of a constant ionic medium would permit the replacement of activities by concentrations for dissolved species. In addition, activity coefficients of surface species and species involved an ion exchange equilibria are neglected (Stadler, 1993).

**Table 3    Summary of major surface reactions at the solid-solution interface**

| Reaction type | Reaction equation |
| --- | --- |
| Ion exchange | $\equiv X\mathrm{Na} + \mathrm{H}^+ \leftrightarrow \equiv X\mathrm{H} + \mathrm{Na}^+ , K_1$ |
| | $2\equiv X\mathrm{Na} + \mathrm{Me}^{2+} \leftrightarrow \equiv X_2\mathrm{Me} + 2\mathrm{Na}^+ , K_2$ |
| Surface complexation of proton | $\equiv \mathrm{SOH}_2^+ \leftrightarrow \equiv \mathrm{SOH} + \mathrm{H}_S^+ , K_{a1}^S$ |
| | $\equiv \mathrm{SOH} \leftrightarrow \equiv \mathrm{SO}^- + \mathrm{H}_S^+ , K_{a2}^S$ |
| Surface complexation of cation | $\equiv \mathrm{SOH} + \mathrm{M}_S^{+z} \leftrightarrow \equiv \mathrm{SOM}^{+(z-1)} + \mathrm{H}_S^+ , K_{1M}^S$ |
| | $2\equiv \mathrm{SOH} + \mathrm{M}_S^{+z} \leftrightarrow 2(\equiv \mathrm{SO})_2 \mathrm{M}^{+(z-2)} + 2\mathrm{H}_S^+ , \beta_{2M}^S$ |
| | $\equiv \mathrm{SOH} + \mathrm{M}_S^{+z} + \mathrm{H}_2\mathrm{O} \leftrightarrow \equiv \mathrm{SOMOH}^{+(z-2)} + 2\mathrm{H}_S^+ , K_{2M}^S$ |
| Surface complexation of ligands (anions and weak acids) | $\equiv \mathrm{SOH} + \mathrm{L}^{-n} \leftrightarrow \equiv \mathrm{SL}^{-n+1} + \mathrm{OH}_S^- , K_{1L}^S$ |
| | $2\equiv \mathrm{SOH} + \mathrm{L}^{-n} \leftrightarrow \equiv \mathrm{S}_2\mathrm{L}^{-n+2} + 2\mathrm{OH}_S^- , \beta_{2L}^S$ |
| Ternary surface | $\equiv \mathrm{SOH} + \mathrm{M}_S^{+z} + \mathrm{L}^{-n} \leftrightarrow \equiv \mathrm{SLM}^{-n+z+1} + \mathrm{OH}_S^- , K_{LM}^3$ |
| | $\equiv \mathrm{SOH} + \mathrm{M}_S^{+z} + \mathrm{L}^{-n} \leftrightarrow \equiv \mathrm{SOLM}^{-n+z-1} + \mathrm{H}_S^+ , K_{ML}^3$ |
| General forms of surface coordination[*] | $a(\equiv \mathrm{SOH}) + p\mathrm{M}^{m+} + q\mathrm{L}^l + x\mathrm{H}^+ + y\mathrm{OH}^- \leftrightarrow (\equiv \mathrm{SO})_a \mathrm{M}_p(\mathrm{OH})_y \mathrm{H}_x \mathrm{L}_q^\delta + a\mathrm{H}^+$ |
| | $b(\equiv \mathrm{SOH}) + q\mathrm{L}^{-l} + x\mathrm{H}^- \leftrightarrow \equiv \mathrm{S}_b \mathrm{H}_x \mathrm{L}_q^\zeta + b\mathrm{OH}^-$ |

* . $\delta = pm + x - a - ql - y$ and $\zeta = x + b - ql$ are vlaences of the surface complexes formed (whole numbers)

On the other hand, the complexation at amphoteric surface hydroxyl sites ($\equiv\mathrm{SOH}$) can be modeled by a classical 2-p$K$ SCM:

$$\equiv \mathrm{SOH}_2^+ \leftrightarrow \equiv \mathrm{SOH} + \mathrm{H}^+ , \tag{21}$$

$$K_{a1}^{int} = \frac{[\equiv \mathrm{SOH}][\mathrm{H}^+]}{[\equiv \mathrm{SOH}_2^+]}\exp(-F\psi/RT) ,$$

$$\equiv \mathrm{SOH} \leftrightarrow \equiv \mathrm{SO}^- + \mathrm{H}^+ , \tag{22}$$

$$K_{a2}^{int} = \frac{[\equiv \mathrm{SO}^-][\mathrm{H}^+]}{[\equiv \mathrm{SOH}]}\exp(-F\psi/RT) ,$$

$$n\equiv\mathrm{SOH} + m\mathrm{Me}^{2+} + (p-n)\mathrm{H}_2\mathrm{O} \leftrightarrow (\equiv\mathrm{SO})_n\mathrm{Me}_m(\mathrm{OH})_{(p-n)}^{(zm-p)+} + p\mathrm{H}^+ ,$$

$$k_{n,m,-p}^{int} = \frac{\left[(\equiv\mathrm{SO})_n\mathrm{Me}_m(\mathrm{OH})_{(p-n)}^{(zm-p)+}\right][\mathrm{H}^+]^p}{[\equiv\mathrm{SOH}]^n[\mathrm{Me}^{2+}]^m}\exp((zm-p)F\psi/RT) . \tag{23}$$

Where $K^{int}$ is the intrinsic surface reaction constant; $n$, $m$ and $p$ represent, respectively, the quantities of surface sites, adsorptive cations and protons. The introduced Boltzmann distribution factor (i.e., the exponential term) relates the surface concentration to the concentration in the bulk solution.

Moreover, several SPMs have introduced some additional complex procedures for describing the discrepancies in distribution and binding affinity, details pertaining to these can be found elsewhere (Farley, 1985; Katz, 1995).

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