

# A Chemical Model of Phosphate Adsorption by Soils: I. Reference Oxide Minerals<sup>1</sup>

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## ABSTRACT

The Constant Capacitance model is shown to provide a quantitative description of *o*-phosphate adsorption by a variety of aluminum and iron hydrous oxides, including the effect of varying pH values. This model, based on a ligand exchange mechanism for *o*-phosphate adsorption, comprises six adjustable parameters: two surface protonation-dissociation constants, three *o*-phosphate surface complexation constants, and a capacitance density parameter. The five surface equilibrium constants can be obtained from potentiometric titration data and *o*-phosphate adsorption data. These constants are independent of pH but, in principle, can depend on the composition of the background electrolyte solution. The capacitance density parameter cannot be obtained directly from experiment. A working value can be chosen on the basis of previous applications of the Constant Capacitance model and other model parameters are not sensitive to this choice.

**Additional Index Words:** anion adsorption, ligand exchange, surface chemistry, *o*-phosphate.

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THE REACTIONS between *o*-phosphates and soils often have been described mathematically with adsorption isotherm equations (Olsen and Watanabe, 1957; Syers et al., 1973; Holford et al., 1974; Fitter and Sutton, 1975; Barrow, 1978; Berkheiser et al., 1980;

Harter and Smith, 1981; Travis and Etnier, 1981; Mead, 1981). These equations usually are special cases of the expression:

$$q(c) = \sum_{i=1}^n \frac{b_i K_i^{\beta_i} c^{\beta_i}}{1 + K_i^{\beta_i} c^{\beta_i}} \quad [1]$$

where  $q(c)$  is the quantity of *o*-phosphate adsorbed per unit mass of soil solids,  $c$  is the concentration of *o*-phosphate in an aqueous solution phase equilibrated with the soil, and  $n$ ,  $b_i$ ,  $K_i$ , and  $\beta_i$  are empirical parameters. The best known special cases of Eq. [1] are the Langmuir equation ( $n = 1$ ,  $\beta_1 = 1$ ), the two-surface Langmuir equation ( $n = 2$ ,  $\beta_1 = \beta_2 = 1$ ), and the Freundlich equation ( $n = 1$ ,  $0 < \beta_1 < 1$ ,  $K_1^{\beta_1} c^{\beta_1} \ll 1$ ).

The application of any particular form of Eq. [1] to *o*-phosphate adsorption data commonly is predicated on goodness-of-fit criteria (Holford et al., 1974; Barrow, 1978; Berkheiser et al., 1980; Travis and Etnier, 1981; Mead, 1981), although derivations of the popular adsorption isotherm equations can be given in terms of surface chemical models (Brunauer et al., 1967; Sposito, 1981a, p. 160-165). The difficulty with the model derivations is that they are not unique (Brunauer et al., 1967). Therefore, a given set of model assumptions may be contradicted in a soil even though the equation derived from the assumptions provides a good fit to adsorption data for the soil (Berkheiser et al., 1980; Harter and Smith, 1981). The consensus drawn from recent studies of this nonuniqueness problem is that adsorption isotherm equations should be regarded as strictly empirical equations and that their use constitutes essentially a curve-fitting procedure (Veith and Sposito, 1977; Posner and Bowden, 1980; Berkheiser et al., 1980; Harter and Smith, 1981; Sposito, 1982).

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Besides its spurious relationship to the chemical mechanisms of *o*-phosphate adsorption, Eq. [1] suffers from the practical disadvantage that its parameters must be regarded as unknown functions of pH and ionic strength in the soil solution. The pH value in particular is a well established master variable for *o*-phosphate adsorption reactions (Berkheiser et al., 1980). Its explicit absence from Eq. [1] requires separate experimental determinations of the parameter  $b = \sum_{i=1}^n b_i$  as a function of pH (the "adsorption envelope") as well as the pH-dependence of the  $K_i$  and  $\beta_i$  ( $i = 1, \dots, n$ ). This limitation on the applicability of Eq. [1] has prompted the development of what may be termed *chemical models* of *o*-phosphate adsorption (Stumm et al., 1980; Bowden et al., 1980). These models are characterized by an explicit dependence on the master chemical variables of pH and *o*-phosphate concentration and by parameters that are related directly to an accepted mechanism of *o*-phosphate adsorption. In this respect, the models represent a conceptual advance over Eq. [1], but they are not regarded as definitive theoretical treatments of *o*-phosphate adsorption reactions.

Strong evidence exists in support of the hypothesis that the principal mechanism of *o*-phosphate adsorption in noncalcareous, nonallophanic mineral soils is ligand exchange with hydroxyl groups (Parfitt, 1978; Mott, 1981; White, 1981). The result of this exchange reaction is the formation of an inner-sphere surface complex (Sposito, 1981b) between an *o*-phosphate group and a metal cation which was bound to the hydroxyl group. Two models based on inner-sphere complex formation have been developed to describe *o*-phosphate adsorption on hydrous oxide surfaces. Bowden et al. (1980) have adapted the model of Barrow et al. (1980a) to describe the adsorption of *o*-phosphate by synthetic goethite ( $\alpha$ -FeOOH). In this model, surface charge resides in four planes, each of which is associated with an electric potential determined through classical electrostatic theory and the Poisson-Boltzmann equation. Adsorbed protons and hydroxide ions (i.e., protonated and dissociated surface hydroxyl groups) reside in an *s*-plane closest to the periphery of the bulk adsorbent. Adsorbed phosphate ions are considered to form inner-sphere surface complexes in an *a*-plane located a short distance out from the *s*-plane. Cations and anions in the background electrolyte solution are permitted to form outer-sphere surface complexes (Sposito, 1981b) in a  $\beta$ -plane still farther out from the *s*-plane. The last plane is the *d*-plane, which indicates the boundary of the diffuse ion swarm. Besides the electric potentials in each plane, the model parameters include "affinity constants" for each adsorbed species, capacitance densities for each pair of consecutive planes, and maximum adsorption densities for the *s*- and *a*-planes. All of these parameters are adjustable and emphasis in the model is placed on parameter optimization (Sposito, 1984). Ten independent parameters must be adjusted to describe the adsorption of a single *o*-phosphate species (e.g.,  $\text{HPO}_4^{2-}$ ) from a background solution of NaCl. This fitting is done with potentiometric titration data taken in the absence of *o*-phosphate and with *o*-phosphate adsorption data. Surface charge balance (Sposito,

1981b) is employed as a constraint on parameter adjustment, but surface mass balance is not. The model successfully describes both pH and background electrolyte effects on *o*-phosphate adsorption by goethite (Bowden et al., 1980; Barrow et al., 1980b).

Stumm et al. (1980) adapted the Constant Capacitance model of Schindler and Stumm (Westall and Hohl, 1980; Hohl et al., 1980; Schindler, 1981) to describe the adsorption of *o*-phosphate by synthetic goethite. The Constant Capacitance model differs from the model of Bowden et al. (1980) in that it assigns adsorbed protons, hydroxide ions and *o*-phosphate species to the *s*-plane and takes no explicit account of the background electrolyte ions. The protonation and dissociation of the surface hydroxyl groups, as well as the adsorption of *o*-phosphate species, are described in terms of explicit surface chemical reactions. The adjustable model parameters include the conditional equilibrium constants for these reactions and a capacitance density defined as the ratio of surface charge density to surface electric potential. The maximum adsorption density for *o*-phosphate is assumed to equal the maximum density of protonatable surface hydroxyls determined experimentally. Surface mass balance thus serves as a constraint in model applications, whereas surface charge balance is used only to calculate the surface electric potential. As with the model of Bowden et al. (1980), potentiometric titration data and *o*-phosphate adsorption data are required to determine the model parameters. Four independent parameters must be adjusted to describe the adsorption of a single *o*-phosphate species. The Constant Capacitance model successfully describes pH effects on *o*-phosphate adsorption by goethite (Stumm et al., 1980; Sigg and Stumm, 1981). The model also can describe the effect of changing total *o*-phosphate concentration in the aqueous solution phase without changes in the model parameters.

Both of the models discussed represent idealized conceptions of the surface chemistry of hydrous oxides. Despite their differing treatments of the background electrolyte solution, both models give quantitative descriptions of potentiometric titration data (Westall and Hohl, 1980). The ways in which the two models employ inner- and outer-sphere surface complexes differentiate them on the molecular level (Sposito, 1983, 1984), but this difference has no effect on goodness-of-fit to proton titration data or *o*-phosphate adsorption data. Since the *o*-phosphate ion is larger than the proton or the hydroxide ion, it seems more correct to visualize the phosphate ion farther out from the surface (Bowden et al., 1980). However, this increases the complexity of the model since an adjustable parameter is added for each additional plane of adsorbed charge.

The model of Bowden et al. (1980) contains twice as many adjustable parameters as the Constant Capacitance model. Chemical significance suffers when parameters whose values are available from independent experiments are adjusted. Two such parameters in the model of Bowden et al. (1980) are the maximum surface charge density and the maximum adsorption density. Equilibrium constants obtained for the *o*-phosphate surface species from the Constant Ca-

capacitance model should be more meaningful chemically than the "affinity constants" in the model of Bowden et al. (1980) because the former parameters are defined for definite surface species and are independent of pH. The accuracy of the surface chemical speciation carried out in the model of Bowden et al. (1980) is reduced by the lack of imposed mass balance for the surface hydroxyl group. On the basis of these considerations, the Constant Capacitance model was used in the present study. In this paper, the nonlinear least-squares optimization program, FITEQL (Westall, 1982), is applied to fit the Constant Capacitance model to data on *o*-phosphate adsorption by reference iron and aluminum oxides. Phosphate adsorption by noncalcareous, nonallophanic soils often has been correlated with their aluminum and iron oxide content (Udo and Uzu, 1972; Ballard and Fiskell, 1974; Juo and Fox, 1977; Kanabo et al., 1978; Berkeiser et al., 1980; McLaughlin et al., 1981). These oxide minerals are considered to be the principal phosphate-reactive fraction providing surfaces for *o*-phosphate adsorption (Parfitt, 1978). The parameters determined through an application of the Constant Capacitance model to these prototypical surfaces are expected to provide data on protonation-dissociation reactions and *o*-phosphate surface complexes that will be of direct value in the application of the model to soils. The application of the model to noncalcareous soils is the subject of Part II of this study.

## DATA AND METHODS

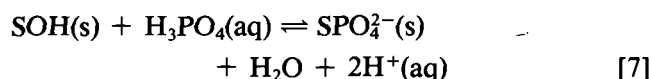
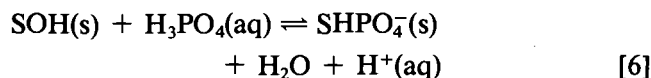
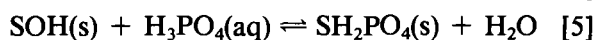
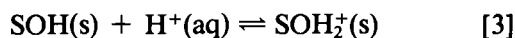
### Constant Capacitance Model

The Constant Capacitance model (Stumm et al., 1980) has four essential characteristics as a chemical model of *o*-phosphate adsorption: (i) adsorption is based on a ligand exchange mechanism; (ii) all surface complexes are inner-sphere complexes; (iii) no complexes with ions in the background electrolyte are considered; (iv) the relationship between net surface charge,  $\sigma$ , expressed in moles of charge per cubic meter of aqueous solution, and surface potential,  $\psi$ , expressed in volts, is given by the equation:

$$\sigma = (CSa/F)\psi \quad [2]$$

where  $C$  ( $F\ m^{-2}$ ) is a capacitance density parameter,  $S$  ( $m^2\ kg^{-1}$ ) is the specific surface area,  $a$  ( $kg\ m^{-3}$ ) is the concentration of the solid in aqueous suspension, and  $F$  ( $C\ mol^{-1}$ ) is the Faraday constant. As a result of assumptions (i) and (iii), the surface charge density is equal to the density of net proton charge plus the charge density contributed by the formation of inner-sphere surface complexes (Sposito, 1981b).

In the application of the Constant Capacitance model to phosphate adsorption, the following chemical reactions are defined:



where  $SOH(s)$  represents 1 mole of reactive surface hydrox-

yls bound to a metal ion, S, in an oxide mineral. The intrinsic conditional equilibrium constants for these reactions are defined by the equations:

$$K_+(int) = \frac{[SOH_2^+]}{[SOH][H^+]} \exp(F\psi/RT) \quad [8]$$

$$K_-(int) = \frac{[SO^-][H^+]}{[SOH]} \exp(-F\psi/RT) \quad [9]$$

$$K1(int) = \frac{[SH_2PO_4]}{[SOH][H_3PO_4]} \quad [10]$$

$$K2(int) = \frac{[SHPO_4^-][H^+]}{[SOH][H_3PO_4]} \exp(-F\psi/RT) \quad [11]$$

$$K3(int) = \frac{[SPO_4^{2-}][H^+]^2}{[SOH][H_3PO_4]} \exp(-2F\psi/RT) \quad [12]$$

where  $R$  is the molar gas constant,  $T$  is the absolute temperature, and square brackets indicate concentrations ( $mol\ m^{-3}$ ). The intrinsic conditional equilibrium constants can be obtained by extrapolating ordinary conditional equilibrium constants to zero net surface charge (Stumm et al., 1980). Conditional equilibrium constants are defined by equations of the form:

$$c_{K+} = [SOH_2^+]/[SOH][H^+] \quad [13]$$

and so on for the other reactions represented in Eq. [9] to [12]. Unlike the intrinsic constants, the ordinary conditional equilibrium constants are dependent on surface charge (Stumm et al., 1980).

The Constant Capacitance model can be interpreted as a special case of the van der Waals model in statistical mechanics (Sposito, 1983). In this model, charged surface species create a long-ranged, mean electric field through their mutual interaction. The exponential terms in Eq. [8], [9], [11], and [12] represent the contribution of this mean electric field to the ratio of rational activity coefficients of the surface species. In practical terms, the exponential term can be considered as a solid-phase activity coefficient that corrects for the charge of a surface species.

With the addition of mass balance and charge balance equations, the chemical equilibrium problem formulated above can be solved. The mass balance equation for the surface functional group, SOH, is:

$$[SOH]_T = [SOH] + [SOH_2^+] + [SO^-] + [SH_2PO_4] + [SHPO_4^-] + [SPO_4^{2-}] \quad [14]$$

where again square brackets indicate concentrations ( $mol\ m^{-3}$ ). The corresponding charge balance equation is:

$$\sigma = [SOH_2^+] - [SO^-] - [SHPO_4^-] - 2[SPO_4^{2-}] \quad [15]$$

### Parameter Determination and Surface Speciation

In order to solve the set of Eq. [2], [8] to [12], [14], and [15], a computer program is necessary. The computer program MICROQL (Westall, 1979) computes chemical speciation in aqueous systems containing surface species and can be amended to include the Constant Capacitance model for describing adsorption processes. The use of MICROQL requires values of intrinsic surface protonation-dissociation constants and intrinsic surface complexation constants. The computer program, FITEQL (Westall, 1982), can be utilized to obtain these parameters. FITEQL employs a nonlinear least squares method to determine equilibrium constants

from experimental data and can be amended to include the Constant Capacitance model to describe surface complexation reactions.

In the present study, FITEQL was used to fit the Constant Capacitance model to phosphate adsorption isotherm data on metal oxides and to obtain optimal values of the phosphate surface complexation constants. The intrinsic equilibrium constants thus obtained were employed in MICROQL to check goodness-of-fit for the model at each point of the adsorption isotherms.

Values assigned to the intrinsic protonation-dissociation constants,  $K_+(int)$  and  $K_-(int)$ , were obtained from a literature compilation of experimental data for aluminum and iron oxides (Table 1). There was no statistically significant ( $P = 0.05$ ) linear relation between the compiled values of these two constants and the ionic strength of the background electrolyte. The values of intrinsic surface protonation-dissociation constants are calculated from potentiometric titration curves determined in the absence of specifically-adsorbing ions other than  $H^+$  or  $OH^-$ . In analyzing these data, the assumption is made that  $\sigma$ , the net surface charge density, is equal to  $[SOH_2^+]$  below the point of zero charge (PZC) and is equal to  $-[SO^-]$  above the PZC. (The PZC is the pH value at which  $\sigma = 0$ ; Sposito, 1981b). A plot of the common logarithm of the conditional equilibrium constant vs.  $\sigma$  will yield the common logarithm of the intrinsic equilibrium constant upon extrapolation to  $\sigma = 0$ . The intrinsic surface protonation constant,  $K_+(int)$ , for example, is obtained as follows. By combining Eq. [8] and [13], one can relate the intrinsic and conditional protonation constants:

$$K_+(int) = {}^cK_+ \exp(F\psi/RT) \quad [16]$$

Substituting for  $\psi$  from Eq. [2], taking the common logarithms of both sides, and solving for  $\log {}^cK_+$ , one transforms Eq. [16] into:

$$\log {}^cK_+ = \log K_+(int) - \frac{\sigma F^2}{CSaRT(\ln 10)} \quad [17]$$

Therefore plotting the titration data as  $\log {}^cK_+$  vs.  $\sigma$  provides an estimate of  $\log K_+(int)$  from the  $y$ -intercept, where  $\sigma = 0$  (Stumm et al., 1980).

The capacitance density,  $C$ , cannot be determined exper-

Table 1—Compiled surface protonation-dissociation constants for aluminum and iron oxides.

Solid	Ionic medium	log $K_+$ (int)	log $K_-$ (int)	Source of data
Al-oxides				
$\gamma$ - $Al_2O_3$	0.005M NaNO <sub>3</sub>	6.78	-7.95	Stumm et al. (1970)
	0.01M NaNO <sub>3</sub>	6.73	-8.18	Stumm et al. (1970)
	0.1M NaNO <sub>3</sub>	6.51	-8.43	Stumm et al. (1970)
	0.1M NaCl	7.90	-9.10	Huang and Stumm (1973)
	0.1M NaClO <sub>4</sub>	7.20	-9.50	Hohl and Stumm (1976)
	0.1M NaClO <sub>4</sub>	7.40	-9.24	Westall and Hohl (1980)
	0.1M NaClO <sub>4</sub>	7.40	-10.00	Stumm et al. (1980)
	1M KCl	7.83	-9.36	Sadek et al. (1970)
	0.1M KCl	7.52	-9.39	Sadek et al. (1970)
	0.1M NaCl	8.50	-9.70	Yopps and Fuerstenau (1964)
		Average log $K_+$ (int) = 7.38 ± 0.61		
		Average log $K_-$ (int) = -9.09 ± 0.68		
Fe-oxides				
$\alpha$ -FeOOH	0.1M KCl	6.99	-8.40	Atkinson et al. (1967)
	0.1M NaClO <sub>4</sub>	6.40	-9.25	Sigg (1979)
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	0.1M KCl	8.85	-9.75	Atkinson et al. (1967)
	0.1M KCl	8.05	-8.95	Breeuwsma and Lyklema (1971)
Fe <sub>3</sub> O <sub>4</sub>	0.1M KCl	6.28	-7.66	Ahmed and Maksimov (1968)
		Average log $K_+$ (int) = 7.31 ± 1.11		
		Average log $K_-$ (int) = -8.80 ± 0.80		

imentally and so is treated as an empirical, adjustable model parameter. In this study,  $C$  was fixed at 1.06 F m<sup>-2</sup>, the value which was optimal for  $\gamma$ - $Al_2O_3$  (Westall and Hohl, 1980).

Phosphate adsorption isotherm data for various aluminum and iron oxides were obtained from published literature. Additional, nonadjustable parameters, such as the specific surface area,  $S$ , the concentration of the solid,  $a$ , and the maximum adsorption density,  $[SOH]_T$ , had been determined experimentally by the authors of the articles used.

## RESULTS AND DISCUSSION

Common logarithms of the three phosphate surface complexation constants resulting from the application of FITEQL are given in Tables 2 and 3 for aluminum

Table 2—Phosphate surface complexation constants for aluminum-oxides.

Solid	Ionic medium	log $K_1$ (int)	log $K_2$ (int)	log $K_3$ (int)	Source of data
$\gamma$ - $Al_2O_3$	0.01M NaClO <sub>4</sub>	10.34	4.30	-2.81	Anderson and Malotky (1979)
$\gamma$ - $Al_2O_3$	0.1M NaCl				
	(pH = 4 to 7)	8.50	2.21		Huang (1975)
	(pH = 8, 9)	9.78		-3.61	
$\alpha$ -alumina	0.01M NaCl	8.69	2.89	-4.78	Chen et al. (1973)
Hydrous alumina	0.01M KCl	7.79	2.19		Rajan et al. (1974)
Gibbsite	0.1M NaCl	9.46	5.26	0.62	Parfitt et al. (1977)
Gibbsite	1M, 0.05M, 0.001M NaCl	11.11	3.98	-3.75	Hingston et al. (1974)
	(pH = 9.0)				
Gibbsite	0.002M, 0.02M KCl	9.01	2.56		Helyar et al. (1976)
Average values		9.34 ± 1.07	3.34 ± 1.19	-2.87 ± 2.07	

Table 3—Phosphate surface complexation constants for iron-oxides.

Solid	Ionic medium	log $K_1$ (int)	log $K_2$ (int)	log $K_3$ (int)	Source of data
Amorphous iron hydroxide	0.01M NaClO <sub>4</sub>	11.84	5.60	-0.65	Anderson and Malotky (1979)
Iron oxide gel	0.125M NaClO <sub>4</sub>	10.78	3.86	-3.67	Ryden et al. (1977)
	1M NaClO <sub>4</sub> (pH = 7)	11.75	4.22	-0.27	
	0.1M NaClO <sub>4</sub> (pH = 7)	10.72	4.63	-1.63	
	0.01M NaClO <sub>4</sub> (pH = 7)		3.39	-4.57	
	0.1M NaClO <sub>4</sub>	10.54	7.25	2.94	Sigg (1979)
Goethite-C	0.1M NaCl	10.47	6.58	0.50	Hingston et al. (1972)
Goethite-E	0.1M NaCl	11.19	7.37	1.12	Hingston et al. (1972)
Hematite		7.43	2.06	-4.23	Breeuwsma and Lyklema (1973)
Average values		10.59 ± 1.38	5.00 ± 1.85	-1.16 ± 2.58	

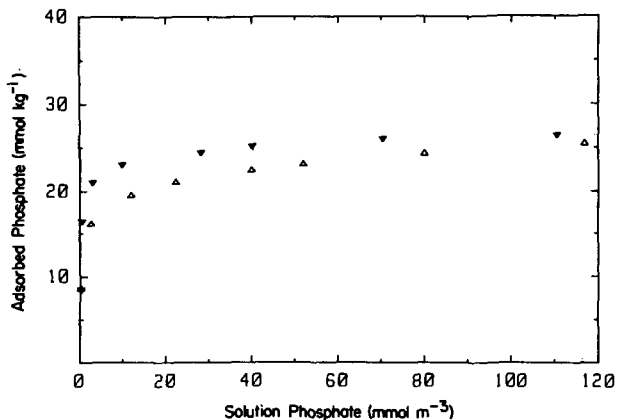
**Table 4—Effect of variability in the protonation-dissociation constants on the average phosphate surface complexation constants for iron-oxides.†**

log $K_+$ (int)	log $K_-$ (int)	log $K_1$ (int)	log $K_2$ (int)	log $K_3$ (int)
7.31	-8.80	10.59	5.00	-1.16
6.20	-9.60	9.97	5.28	-0.31

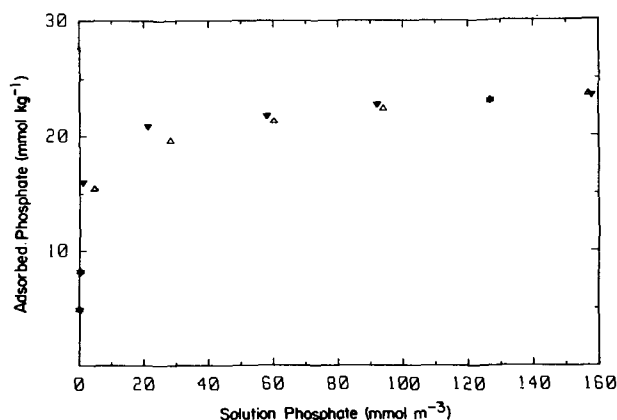
† It was impossible to change log  $K_+$  (int) and log  $K_-$  (int) by plus one standard deviation as this would have given a log  $K_-$  (int) value larger in absolute magnitude than log  $K_+$  (int), which is chemically impossible.

and iron oxides, respectively. The standard deviations of the common logarithms of these constants are larger than those for the logarithms of the compiled protonation-dissociation constants (Table 1). The parameter log  $K_3$ (int) for the formation of the species  $\text{SPO}_4^{2-}$ , has a much larger standard deviation than the other two log formation constants because log  $K_3$ (int) was the most difficult parameter to fit. Most of the adsorption isotherm data used were determined at pH values below 8, where the surface species  $\text{SPO}_4^{2-}$  is present at very small concentrations (see Fig. 5). It is difficult, sometimes impossible, to obtain convergence of the fitting program for species present at very small concentrations.

Common logarithm values of the protonation-dissociation constants used were averages obtained from a literature compilation. Thus, a sensitivity analysis of the FITEQL program results for these two pa-



**Fig. 1—Phosphate adsorption on  $\alpha$ -alumina at pH 5.6. Experimental data (filled triangles) from Chen et al. (1973). Model results are represented by open triangles.**



**Fig. 2—Phosphate adsorption on  $\alpha$ -alumina at pH 6.3. Experimental data (filled triangles) from Chen et al. (1973). Model results are represented by open triangles.**

**Table 5—Effect of varying the capacitance density on phosphate surface complexation constants for iron-oxides.**

$C$ ( $\text{F m}^{-2}$ )	log $K_1$ (int)	log $K_2$ (int)	log $K_3$ (int)
Amorphous iron hydroxide†			
1.06	13.14	5.91	-1.89
1.8	13.19	5.81	-2.18
Goethite‡			
1.8	9.10	5.47	-0.26
2.33	8.90	5.01	-0.68
4.52	8.59	4.06	-1.59

† Anderson and Malotky (1979).

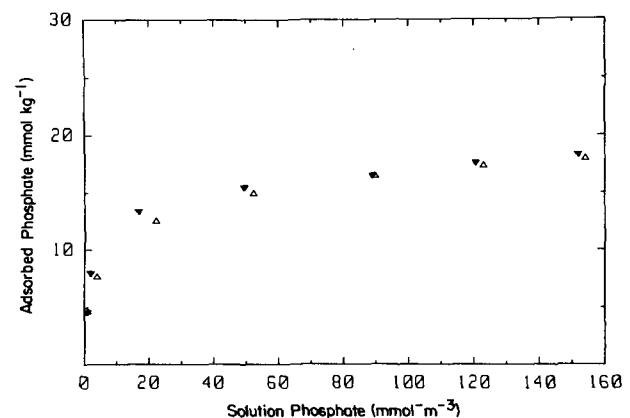
‡ Sigg (1979).

rameters was conducted. The values of log  $K_+$ (int) and log  $K_-$ (int) were varied by plus or minus one standard deviation with minimal change in the PZC. In the Constant Capacitance model, the PZC is given by the equation (Stumm et al., 1980):

$$\text{PZC} = 1/2 [\log K_+(\text{int}) - \log K_-(\text{int})] \quad [18]$$

Table 4 shows the effect of varying log  $K_+$ (int) and log  $K_-$ (int) on the average log  $K_i$ (int) ( $i = 1,2,3$ ) values for  $\alpha$ -phosphate adsorption by nine iron-oxide minerals. Given the standard deviations in Table 3, the two resulting sets of phosphate surface complexation constants are not significantly different ( $P = 0.05$ , Student's  $t$ -test). The variability of log  $K_+$ (int) and log  $K_-$ (int) is masked by the larger variability of log  $K_i$ (int) ( $i = 1,2,3$ ).

The sensitivity of the model to the capacitance density parameter also was tested (Table 5). Capacitance density values can be obtained from the slope of a plot of log  $^cK_+$  or log  $^cK_-$  vs.  $\sigma$ , as indicated in Eq. [17]. This method was applied to potentiometric titration data obtained by Sigg (1979) for goethite. The capacitance density values obtained were  $C = 2.33 \text{ F m}^{-2}$  and  $C = 4.52 \text{ F m}^{-2}$ . The value,  $C = 1.8 \text{ F m}^{-2}$ , listed in Table 5, was considered optimum by Sigg (1979) for modeling phosphate adsorption on goethite. The values obtained with FITEQL for the phosphate surface complexation constants with these different capacitance densities are given in Table 5. Even a doubling of the capacitance density produced changes in log  $K_i$ (int) ( $i = 1,2,3$ ) that were within the standard deviation range reported in Table 3 for these constants. Table 5 also indicates that a reduction in the



**Fig. 3—Phosphate adsorption on  $\alpha$ -alumina at pH 7.5. Experimental data (filled triangles) from Chen et al. (1973). Model results are represented by open triangles.**

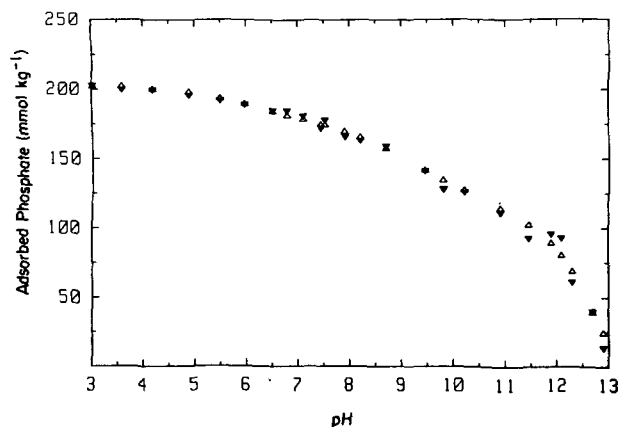


Fig. 4—The “adsorption envelope” for phosphate on goethite. Experimental data (filled triangles) from Hingston et al. (1972). Model results are represented by open triangles.

capacitance density from  $1.8 \text{ F m}^{-2}$  to  $1.06 \text{ F m}^{-2}$  causes a negligible change in the  $\log Ki(\text{int})$  ( $i=1,2,3$ ). The capacitance density is strictly an empirical parameter and, therefore, the relative insensitivity of the model to changes in its value is fortunate. For this reason, the value of  $1.06 \text{ F m}^{-2}$  could be used uniformly for modeling  $\alpha$ -phosphate adsorption by both aluminum and iron oxides.

The ability of the Constant Capacitance model to fit adsorption isotherm data is illustrated in Fig. 1 to 3. The experimental data in these figures were obtained by Chen et al. (1973) for phosphate adsorption on  $\alpha$ -alumina at three different pH values. The actual data points and the corresponding model fits to these points are plotted in the form of a standard adsorption isotherm. The model is able to represent the experimental data well at all three pH values. The model points for pH 5.6, 6.3, and 7.5 were calculated using the same set of phosphate surface complexation constants.

Figure 4 illustrates a model fit of phosphate adsorption data for an iron oxide. In this case, the experimental data obtained by Hingston et al. (1972) for phosphate adsorption on goethite were plotted as the maximum amount of phosphate adsorbed vs. pH (the “adsorption envelope”). The graph shows the typical result, that phosphate adsorption steadily decreases as the pH value increases. The model produces a close fit to the experimental data.

Figure 5 shows the effect of pH on the distribution of phosphate surface species predicted by the model for an iron oxide mineral. It is apparent upon comparison of Fig. 5 with the well known corresponding distribution of phosphate species in aqueous solution (e.g., Lindsay, 1979, Fig. 12.1) that there is no direct relationship between solution speciation and surface speciation. Thus the dominance of a certain ionic species in aqueous solution may not be used to predict the dominant surface species present.

## CONCLUSIONS

Phosphate adsorption by aluminum and iron oxide minerals can be described with the Constant Capacitance model. This model assumes a ligand exchange adsorption mechanism and is therefore an appropriate

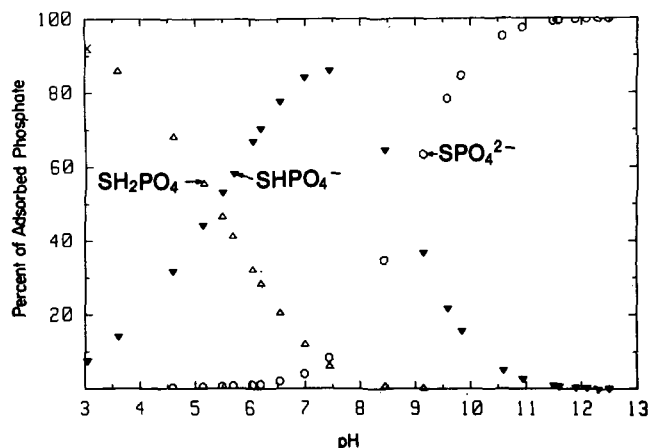


Fig. 5—Calculated phosphate surface speciation on goethite vs. pH based on the adsorption data of Hingston et al. (1972):  $\text{SH}_2\text{PO}_4$ , open triangles;  $\text{SHPO}_4^-$ , filled triangles;  $\text{SPO}_4^{2-}$ , open circles.

representation of the surface complexation behavior of specifically adsorbed  $\alpha$ -phosphate ions. The charge of both the adsorptive ion and the adsorbent surface are considered. Thus the model uses the same set of surface complexation constants to describe adsorption at different pH values and predicts the well known decrease in  $\alpha$ -phosphate adsorption with increasing pH value. This predictive ability constitutes an advantage of the model over the Langmuir and Freundlich adsorption isotherm equations. Aluminum and iron oxide minerals were found to have similar phosphate adsorption behavior, in that the protonation-dissociation constants and the phosphate surface complexation constants for the two types of oxide were not significantly different. This result will prove useful in extending the model to soils because aluminum and iron oxides need not be distinguished with respect to their phosphate adsorption behavior. The model calculations also illustrate the point that the dominance of a certain phosphate species in aqueous solution can not be used generally to predict the major phosphate surface species. The aqueous solution phosphate speciation is determined by the dissociation constants of  $\alpha$ -phosphoric acid, whereas the surface  $\alpha$ -phosphate speciation depends on the magnitudes of the three phosphate surface complexation constants.

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# ERRATA

## **A Chemical Model of Phosphate Adsorption by Soils: I. Reference Oxide Minerals; II. Noncalcareous Soils**

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All surface constants in Tables 1-5 of Part I and Table 2 of Part II were obtained using concentrations in mol L<sup>-1</sup>. We would like to thank Dr. N. J. Barrow for pointing out this oversight.