Chemical Modeling of Anion Competition on Oxides Using the Constant Capacitance Model–Mixed-ligand Approach[1]

SABINE GOLDBERG AND SAMUEL J. TRAINA[2]

ABSTRACT

The constant capacitance model was used to describe selenite-*o*-phosphate and silicate-*o*-phosphate competition on synthetic goethite (α-FeOOH) and synthetic gibbsite ($Al(OH)_3$) by direct optimization of mixed-ligand adsorption data. The model assumes ligand exchange mechanisms for selenite, *o*-phosphate, and silicate adsorption on oxide surfaces. The computer program, FITEQL, was used to fit intrinsic surface complexation constants to the competitive adsorption data. Values for the intrinsic protonation-dissociation constants, surface capacitance density, surface site density, and specific surface area had been determined previously. The constant capacitance model was able to represent competitive anion adsorption for selenite–*o*-phosphate over the pH range of 4 to 10 and for silicate–*o*-phosphate from pH 5.5 to 9.5. The fit to the experimental data using the mixed-ligand approach was much better than that obtained by prediction from single anion systems. The intrinsic surface complexation constants for *o*-phosphate adsorption were found to be dependent upon the surface composition of the adsorbent oxide. We suggest that this composition dependence is due to heterogeneity of surface adsorption sites. Our findings suggest the utility of mixed-ligand modeling for describing anion competition reactions using direct optimization of competitive adsorption data.

Additional Index Words: **o-phosphate adsorption, selenite adsorption, silicate adsorption, ligand exchange, FITEQL.**

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THE CONSTANT CAPACITANCE MODEL (Stumm et al., 1980) is a chemical model that describes anion adsorption by a solid phase, explicitly defines surface complexes and chemical reactions, and includes the effect of the pH variable on adsorption. Previously, this model has been used to describe specific adsorption of orthophosphate (*o*-phosphate), silicate, selenite, and arsenate anions by Al and Fe oxide minerals (Sigg and Stumm, 1981; Goldberg and Sposito, 1984a; Goldberg, 1985, 1986).

Implicit to the use of the constant capacitance model is the assumption that anion adsorption occurs as an exchange reaction between an aqueous ligand and a surface hydroxyl group which can be described as

$$\mathrm{SOH(s)} + \mathrm{H}_x\mathrm{L}^0\mathrm{(aq)} = \mathrm{SH}_y\mathrm{L}^{(-x+y+1)}\mathrm{(s)} + \mathrm{H_2O} + (x - y - 1)\mathrm{H^+(aq)} \qquad [1]$$

where $0 \leq y \leq x$, SOH(s) represents 1 mol of reactive surface hydroxyl groups bound to a metal ion S, and L represents the adsorbing ligand of interest. In the simplest application of the model, the stoichiometric coefficient $x = 1$, and Eq. [1], along with a description of the protonation and deprotonation reactions of SOH(s), is adequate to describe the experimental system. In the case of a polyprotic ligand $x > 1$, the adsorption of the ligand can no longer be thought of as a binary exchange reaction since the adsorption of each species of $\mathrm{H}_y\mathrm{L}^{(-x+y)}$, for $0 \leq y \leq x$ must be considered. In principle, the adsorption of the anion $\mathrm{H}_y\mathrm{L}^{(-x+y)}$ represents a competitive exchange reaction between x species of anion and the hydroxyl groups bound to the mineral surface for a total of $x + 1$ anionic components. In practice, the adsorption of a polyprotic ligand will be limited to a binary or at most a ternary exchange reaction since no more than two species of a given polyprotic ligand are generally present in solution at any specific pH value.

Recent analyses have tested the ability of the constant capacitance model to predict competitive adsorption by goethite in *o*-phosphate-selenite, *o*-phosphate-silicate (Goldberg, 1985), and *o*-phosphate-arsenate systems (Goldberg, 1985, unpublished results), by using model parameters obtained from separate studies of *o*-phosphate, selenite, silicate, and arsenate adsorption alone. Whereas the model was able to describe qualitatively the adsorption competition between each set of polyprotic anions, quantitative prediction was lacking in that *o*-phosphate adsorption was overestimated considerably while adsorption of the competing polyprotic ligand was underestimated. Goldberg (1985) suggested that the inability of the model to describe these anion competition data might be due to site heterogeneity. However, Chu and Sposito (1981) have shown that the exchanger-phase activity coefficients for $n + 1$ component exchange systems

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[2] Soil Scientist (Riverside) and Assistant Professor Soil Physical Chemistry (Columbus), respectively. OSU-OARDC Journal Article no. 43-87.

Table 1. Numerical values of intrinsic surface complexation constants.†

	Goethite-C	Goethite-E	Gibbsite-B
	Selenite–*o*-phosphate competition		
log K^1_{Se}(int)	9.72	9.64	
log K^2_{Se}(int)	5.98	5.51	
log K^1_{p}(int)	9.01	9.13	
log K^2_{p}(Int)	6.37	5.98	
log K^3_{p}(int)	−0.75	−0.21	
	Silicate–*o*-phosphate competition		
log K^1_{Si}(int)		6.96	3.53
log K^2_{Si}(int)			−4.62
log K^1_{p}(int)		10.29	9.43
log K^2_{p}(int)		8.91	3.01
log K^3_{p}(int)		0.93	−2.26

† All intrinsic surface complexation constants were obtained using concentrations in mol L^{-1}. Experimental data from Hingston (1970).

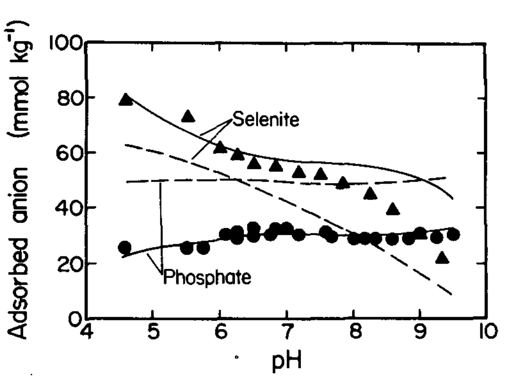

Fig. 1. *o*-Phosphate and selenite adsorption on goethite-C from a mixed-ligand system. Experimental data *o*-phosphate (circles) and selenite (triangles) from Hingston (1970). Model results mixed-ligand approach (solid lines) and single anion approach (dashed lines from Goldberg, 1985). P_T = 0.65 mol m^{-3} and Se_T = 0.99 mol m^{-3}.

cannot in principle be described exclusively with data obtained from *n* component exchange experiments. Since the electric potential terms within the constant capacitance model can be considered as exchanger-phase activity coefficients that correct for the charges of the adsorbed species (Goldberg and Sposito, 1984a), it is apparent that the model, in principle, must be fit directly to competitive sorption data to describe competitive ligand adsorption. Goldberg (1986) successfully described *o*-phosphate–arsenate competition on gibbsite in this manner.

In this study we test the ability of the constant capacitance model to describe *o*-phosphate–selenite and o-phosphate–silicate competition data by direct optimization of the mixed-ligand data previously used by Goldberg (1985).

DATA AND METHODS

The modeling procedure was identical to that used in the previous study (Goldberg, 1985) except that surface complexation constants for both anions were fit simultaneously. Experimental adsorption data were obtained from Hingston (1970). Model parameter values for the goethites including specific surface area, solid concentration, and maximum adsorption density, determined experimentally by Hingston (1970), were presented in Table 1 of Goldberg (1985) where K_i(int) are actually log K_i(int). Model parameter values for the gibbsite were log K_+(int) = 7.38, log K_-(int) = −9.09, C = 1.06 F m^{-2}, maximum adsorption density = 1.46 mol m^{-3}, specific surface area = 5.8 × 10^4 m^2 kg^{-1}, and solid concentration = 5.92 kg m^{-3}. Background electrolyte concentration for all systems was 0.1 *M* NaCl. Table 1 presents values of the intrinsic surface complexation constants for the mixed-ligand systems obtained with the FITEQL (Westall, 1982) program.

RESULTS AND DISCUSSION

Plots of anion adsorption vs. pH, adsorption envelopes, for the *o*-phosphate–selenite system are shown in Fig. 1 and 2 for two goethites. The constant capacitance model produces a reasonable fit to the experimental data on goethite-C over most of the pH range studied. The model is able to fit the experimental adsorption data on goethite-E for four different total *o*-phosphate concentrations using the same set of surface complexation constants (Fig. 2). The fit for all four total *o*-phosphate concentrations is equally good. This result is in marked contrast to the results of Goldberg (1985) where a reasonable fit was obtained only at very low total *o*-phosphate concentration. Statistical analyses of the goodness-of-fit of the model to the experimental data could not be carried out because the standard deviations for the adsorption isotherm analyses were not available.

Figures 3 and 4 show anion adsorption envelopes for the silicate–*o*-phosphate system. The model optimization of the surface complexation constants did not converge for the silicate–*o*-phosphate competition data on goethite-B shown in Fig. 6 of Goldberg (1985). We suspect that this was due to the absence of any data below pH 7. The model was able to represent the silicate–*o*-phosphate competition data on goethite-E over the pH range 5.5 to 9.5, fitting a smooth curve through the data. However, the model was unable to describe silicate adsorption below pH 5.5 and above pH 9.5. Figure 4 shows a good fit by the model for silicate–*o*-phosphate competition on an Al oxide, gibbsite-B. However, the model underestimates silicate adsorption below pH 7.

CONCLUSIONS

The constant capacitance model is able to describe selenite–*o*-phosphate competition on two goethites and silicate–*o*-phosphate competition on one goethite and one gibbsite by direct optimization of the competitive adsorption data. The fit to the experimental data using the mixed-ligand approach is much closer than that obtained by prediction from single anion systems, indicating the utility of the mixed-ligand modeling approach using the constant capacitance model.

The constant capacitance model is based on the premise that the intrinsic surface protonation-dissociation constants are independent of surface composition (Sposito, 1984). Fundamental to this hypothesis is the assumption that ion adsorption occurs at only one type of surface site. However, the constant capacitance model has been successful in describing *o*-phosphate (Goldberg and Sposito, 1984b) and B (Goldberg and Glaubig, 1986) sorption in soils which are complex, multi-site mixtures. Clearly in the case of whole soils, the values obtained for the intrinsic

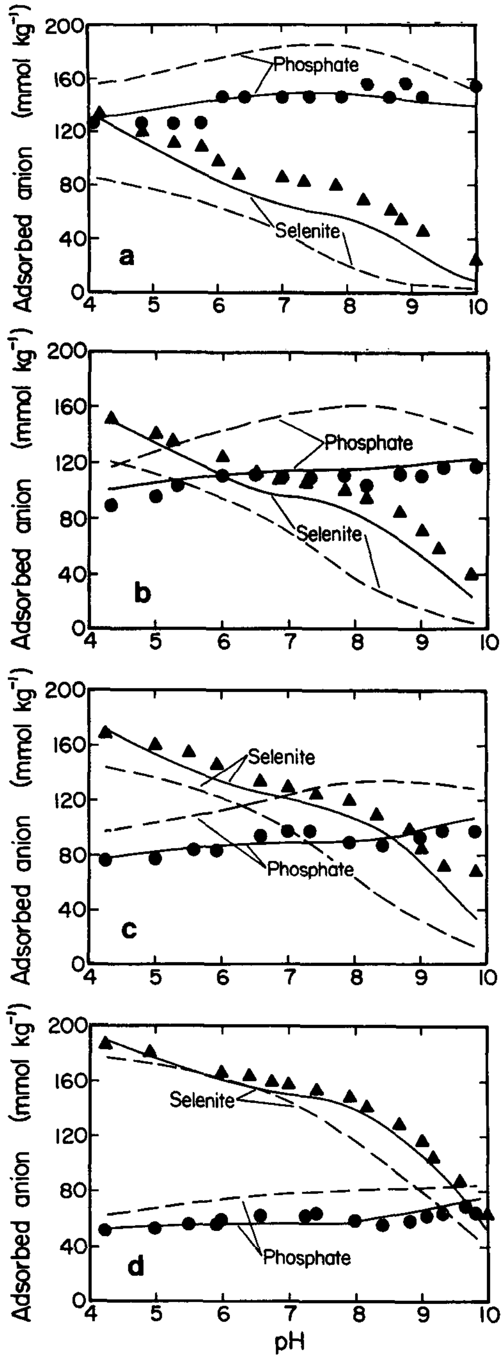

Fig. 2. *o*-Phosphate and selenite adsorption on goethite-E from a mixed-ligand system. Experimental data *o*-phosphate (circles) and selenite (triangles) from Hingston (1970). Model results mixed-ligand approach (solid lines) and single anion approach (dashed lines from Goldberg, 1985). Se_T = 1.0 mol m^{-3}. (a) P_T = 2.6 mol m^{-3}, (b) P_T = 1.3 mol m^{-3}, (c) P_T = 0.77 mol m^{-3}, and (d) P_T = 0.39 mol m^{-3}.

surface complexation constants must in reality represent average composite values of the intrinsic surface complexation constants for all soil surfaces undergoing net anion sorption reactions.

Ample experimental evidence exists to suggest that even synthetic oxide surfaces contain more than one type of surface site which may undergo anion adsorption reactions (Parfitt, 1978; Rochester and Topham, 1979a, b; Benjamin and Leckie, 1980, 1981). Thus even

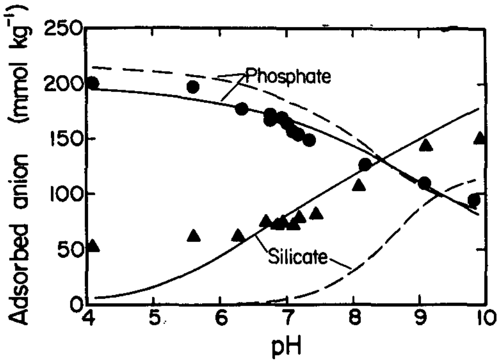

Fig. 3. *o*-Phosphate and silicate adsorption on goethite-E from a mixed-ligand system. Experimental data *o*-phosphate (circles) and silicate (triangles) from Hingston (1970). Model results mixed-ligand approach (solid lines) and single anion approach (dashed lines from Goldberg, 1985). P_T = 0.77 mol m^{-3} and Si_T = 2.5 mol m^{-3}.

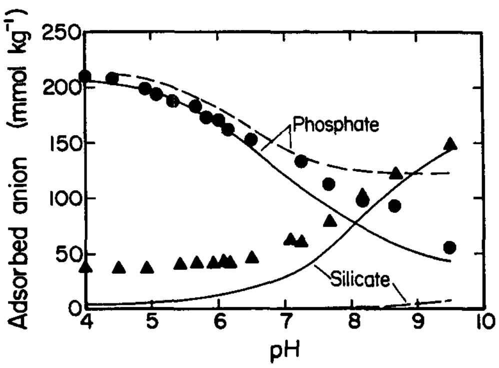

Fig. 4. *o*-Phosphate and silicate adsorption on gibbsite-B from a mixed-ligand system. Experimental data *o*-phosphate (circles) and silicate (triangles) from Hingston (1970). Model results mixed-ligand approach (solid lines) and single anion approach (dashed lines, K^1_P(int) = 11.15, K^3_P(int) = 2.85, K^1_{Si}(int) = 3.24, K^2_{Si}(int) = −4.06). P_T = 1.3 mol m^{-3} and Si_T = 2.5 mol m^{-3}.

intrinsic surface complexation constants determined in pure mineral systems are most likely average composite values. If, in the presence of two or more competing anions, the site heterogeneity of oxide surfaces manifests itself as selective anion adsorption by some fraction of the total adsorption sites, the resulting surface complexation constants for each anion will exhibit some surface composition dependence being average values based on only a fraction of the surface functional groups. Such composition dependence was found for *o*-phosphate adsorption on goethite-E (values of log K^1_P(int) differ in the presence of selenite and silicate, see Table 1), suggesting the presence of heterogeneous anion adsorption sites for this material.

In the absence of highly selective, heterogeneous anion adsorption sites, it may be possible to use adsorption data collected from single anion experiments to predict the results of competitive anion adsorption reactions. Our findings suggest that without knowledge of the molecular nature of the specific anion adsorption reactions in question, predictions of anion competition based on single anion systems may not be valid, and that incorporation of surface complexation constants obtained from such systems into chemical speciation programs such as GEOCHEM (Sposito and Mattigod, 1979) or MINEQL (Westall et al., 1976) with the intent to model anion adsorption in mixed-ligand electrolytes is premature.

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