

Chemical Modeling of Arsenate Adsorption on Aluminum and Iron Oxide Minerals¹

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ABSTRACT

The constant capacitance model was used to describe arsenate adsorption on goethite, gibbsite, and amorphous Al hydroxide. Because the model assumes a ligand exchange mechanism it is appropriate for describing the specific adsorption of arsenate anions. Arsenate surface complexation constants were fitted to the experimental data using a nonlinear least squares optimization technique. The constant capacitance model was able to represent arsenate adsorption over the pH range 4.5 to 9 on each oxide using the same set of surface complexation constants. However, the values of the surface complexation constants varied with the mineral considered. The model was able to describe arsenate-phosphate competition on gibbsite quantitatively over the pH range 4.5 to 9 using the same set of anion surface complexation constants. A set of surface complexation constants obtained for one ternary system could be used to predict competitive phosphate and arsenate adsorption on the same material for other ternary systems containing different amounts of total anions in solution.

Additional Index Words: phosphate adsorption, ligand exchange, surface chemistry, constant capacitance model, FITEQL.

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ARSENIC IS TOXIC to both plants and animals and can accumulate in agricultural soils. Previous researchers have studied the adsorption of As by soil materials (Jacobs et al., 1970; Livesey and Huang, 1981). Jacobs et al. (1970) suggested that As was adsorbed preferentially by the oxalate-extractable amorphous Al and Fe compounds in 24 Wisconsin soils. Livesey and Huang (1981) also found significant correlation between these materials and As adsorption maxima of four soils from Saskatchewan, Canada.

Various researchers have previously investigated the adsorption of arsenate on Al oxides (Hingston et al., 1971; Anderson et al., 1976; Malotky and Anderson,

1976; Anderson and Malotky, 1979) and Fe oxides (Hingston 1970; Hingston et al., 1971; Harrison and Berkheiser, 1982; Lumsdon et al., 1984). Arsenate adsorption on goethite, gibbsite, and amorphous Al hydroxide exhibited a maximum in the pH range 3 to 4 followed by a gradual decline with increasing pH (Hingston, 1970; Hingston et al., 1971; Anderson et al., 1976). Hingston et al. (1971) described their adsorption data using the Langmuir equation and obtained good fits.

The mechanism of specific arsenate adsorption on Al and Fe oxides is considered to be ligand exchange with surface hydroxyls and/or surface aquo groups (Hingston et al., 1971; Anderson et al., 1976; Anderson and Malotky, 1979; Harrison and Berkheiser, 1982; Lumsdon et al., 1984). Direct evidence for ligand exchange of arsenate using infrared spectroscopy has been provided by Lumsdon et al. (1984) for goethite, and by Harrison and Berkheiser (1982) for hydrous Fe oxide. Specific anion adsorption produces a shift in the zero point of charge (ZPC) of the adsorbent. Such a shift was observed by Anderson et al. (1976) and by Anderson and Malotky (1979) for arsenate adsorption on amorphous Al hydroxide indicating that specific adsorption had taken place.

The constant capacitance model (Stumm et al., 1970; Schindler and Gamsjager, 1972; Stumm et al., 1976; Stumm et al., 1980) describes adsorption using a ligand exchange mechanism. It is a chemical model that explicitly defines surface complexes and chemical reactions and includes the effect of the pH variable on adsorption. The model has been used previously to describe the specific adsorption of fluoride, phosphate, silicate, selenite, and borate anions by Al and Fe oxide minerals (Sigg and Stumm, 1981; Goldberg and Sposito, 1984a; Goldberg, 1985; Goldberg and Glaubig, 1985).

Since arsenic acid is a triprotic acid whose dissociation constants are very similar to those of phosphoric acid and since both anions adsorb via ligand exchange it is reasonable to expect similar amounts of adsorption for both anions. Indeed, Hingston et al. (1971) observed a close correspondance in both the

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shape of the curve relating adsorption to pH and the amounts of these anions adsorbed on goethite. Livesey and Huang (1981) found that the presence of phosphate substantially reduced arsenate adsorption in their soil system.

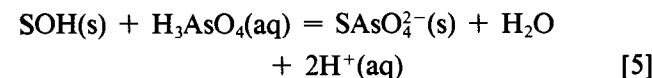
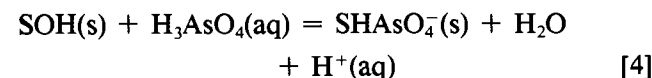
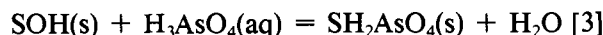
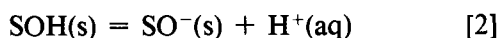
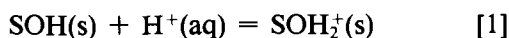
The ability of the constant capacitance model to predict competitive anion adsorption on goethite from aqueous solutions containing two anions using the surface complexation constants obtained from single anion systems has been tested previously (Goldberg, 1985). The model could describe phosphate-selenite and phosphate-silicate competition qualitatively by reproducing the shape but not the magnitude of the adsorption curves. Site heterogeneity was suggested to explain the inability of the model to describe these anion competition data. Chu and Sposito (1981) have shown that ternary exchange systems cannot in principle be predicted based solely on binary exchange data.

The purpose of this study is to test the ability of the constant capacitance model to describe arsenate adsorption on Al and Fe oxide minerals. In addition, direct optimization of the ternary data will be carried out to test whether the model can describe arsenate-phosphate competition in ternary systems.

DATA AND METHODS

The constant capacitance model (Stumm et al., 1980) was used to describe the arsenate adsorption data. The computer program FITEQL (Westall, 1982) was used to fit the intrinsic surface complexation constants to the experimental arsenate adsorption data using the model assumptions given in Goldberg and Sposito (1984a). The modeling procedure for arsenate was identical to that used in this previous study for describing phosphate adsorption reactions on oxide minerals.

Analogous to the application of the model to phosphate adsorption on Al and Fe oxides (Goldberg and Sposito, 1984a), the following surface reactions are defined for arsenate adsorption:



where SOH(s) represents 1 mol of reactive surface hydroxyls bound to a metal ion S (Al^{3+} or Fe^{3+}) in the oxide mineral. These reactions are represented by the following intrinsic conditional equilibrium constant expressions:

$$K_+(\text{int}) = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+]} \exp(F\psi/RT) \quad [6]$$

$$K_-(\text{int}) = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp(-F\psi/RT) \quad [7]$$

$$K^1_{\text{As}}(\text{int}) = \frac{[\text{SH}_2\text{AsO}_4]}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \quad [8]$$

$$K^2_{\text{As}}(\text{int}) = \frac{[\text{SHAsO}_4^-][\text{H}^+]}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \exp(-F\psi/RT) \quad [9]$$

Table 1. Numerical values of model parameters.†

	C = 1.06 F m ⁻²			
	Goethite-A‡	Goethite-C§	Gibbsite‡	am-Al-hydroxide¶
Temperature	20°C	23°C	20°C	25°C
Ionic strength	0.1 M NaCl	0.1 M NaCl	0.1 M NaCl	0.01 M NaClO ₄
Specific surface area, 10 ⁴ m ² kg ⁻¹	6.0	3.2	3.1	69.0
Suspension density, kg m ⁻³	3.72	4.64	2.12	0.13
Maximum adsorption density, mol m ⁻²	0.588	0.433	0.302	0.207
K ₊ (int)	7.31	7.31	7.38	7.38
K ₋ (int)	-8.80	-8.80	-9.09	-9.09
K ¹ _{As} (int)	10.10	10.87	9.72	9.89
K ² _{As} (int)	5.80	6.52	3.41	3.32
K ³ _{As} (int)	-0.63	0.29	-3.58	-4.52
K ¹ _{As} (int)#			6.59	
K ² _{As} (int)#			0.96	
K ³ _{As} (int)#			-5.66	
K _p ¹ (int)#			7.69	
K _p ² (int)#			1.92	
K _p ³ (int)#			-4.68	

† All intrinsic surface complexation constants were obtained using concentrations in mol L⁻¹.

‡ Experimental data from Hingston et al. (1971).

§ Experimental data from Hingston (1970).

¶ Experimental data from Anderson and Malotky (1979).

Surface complexation constants for the ternary system.

$$K^3_{\text{As}}(\text{int}) = \frac{[\text{SAsO}_4^{2-}][\text{H}^+]^2}{[\text{SOH}][\text{H}_3\text{AsO}_4]} \exp(-2F\psi/RT) \quad [10]$$

where F is the Faraday constant, ψ is the surface potential (V), R is the molar gas constant, T is the absolute temperature, and square brackets represent concentrations (mol m⁻³). Similar intrinsic conditional equilibrium constant expressions for ligand exchange with the surface aquo group, SOH_2^+ , can be obtained upon subtracting Reaction [1] from Reactions [3], [4], and [5], respectively.

The mass balance for the surface functional group, SOH, is

$$[\text{SOH}]_T = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] + \sum_{i=1}^n [\text{SH}_2\text{A}] + \sum_{i=1}^n [\text{SHA}^-] + \sum_{i=1}^n [\text{SA}^{2-}] \quad [11]$$

where A is the completely dissociated form of the acid (AsO_4^{3-} or PO_4^{3-}), and n is the number of adsorbing anions in the system. The charge balance equation is defined as:

$$\sigma = [\text{SOH}_2^+] - [\text{SO}^-] - \sum_{i=1}^n [\text{SHA}^-] - 2 \sum_{i=1}^n [\text{SA}^{2-}] \quad [12]$$

Arsenate adsorption isotherm data for goethite, gibbsite, and amorphous Al hydroxide were obtained from the literature (Hingston, 1970; Hingston et al., 1971; Anderson and Malotky, 1979). Numerical values for the intrinsic protonation-dissociation constants $K_+(\text{int})$ and $K_-(\text{int})$ used in this study were averages obtained from a literature compilation of experimental values for Al and Fe oxide minerals (see Table 1, Goldberg and Sposito, 1984a). Values for the model parameters $\log K_+(\text{int})$ and the capacitance density, C , were fixed at identical values as in previous modeling studies of phosphate (Goldberg and Sposito, 1984a), selenite, silicate (Goldberg, 1985), and borate (Goldberg and Glaubig, 1985) anion adsorption on oxides. Experimental values of additional necessary model parameters: specific surface area, s , concentration of the solid, a , and the max-

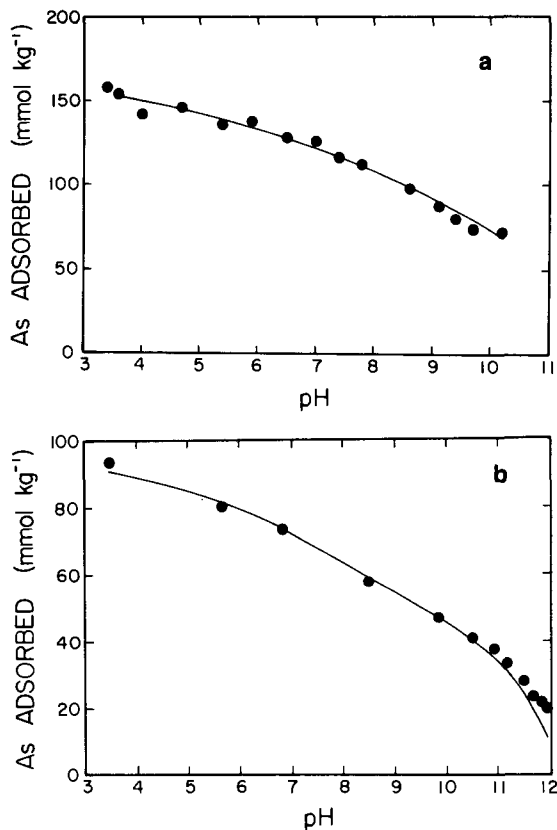


Fig. 1. Arsenate adsorption on Fe oxides: (a) goethite-A ($As_T = 1.07 \text{ mol m}^{-3}$; experimental data, represented by circles, from Hingston et al., 1971); (b) goethite-C ($As_T = 0.534 \text{ mol m}^{-3}$; experimental data, represented by circles, from Hingston, 1970). Model results are represented by solid line.

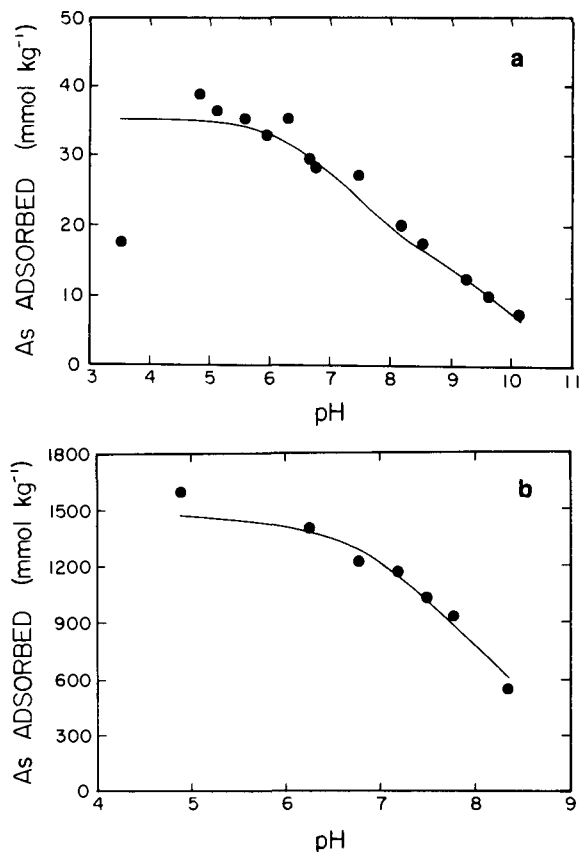


Fig. 2. Arsenate adsorption on Al oxides: (a) gibbsite ($As_T = 0.27 \text{ mol m}^{-3}$; experimental data, represented by circles, from Hingston et al., 1971); (b) amorphous Al hydroxide ($As_T = 0.40 \text{ mol m}^{-3}$; experimental data, represented by circles, from Anderson and Malotky, 1979). Model results are represented by solid line.

imum adsorption density, $[SOH]_T$, were obtained by the respective authors and are listed in Table 1. This table also provides the ionic strength and temperature conditions under which the experiments were carried out.

Modeling of the ternary data was done in identical fashion as for the single anion systems. Surface complexation constants for phosphate and arsenate adsorption were determined for a system in which both anions were present in approximately equimolar amounts. The surface complexation constants obtained from modeling this system were then used to predict arsenate and phosphate adsorption from systems dominated by one of the anions.

RESULTS AND DISCUSSION

Plots of the maximum amount of arsenate adsorption vs. pH, adsorption envelopes, are shown in Fig. 1 for two goethites. The constant capacitance model produces a close fit to the experimental data over the entire pH range studied. Figure 2 shows arsenate adsorption data for gibbsite and amorphous Al hydroxide. The model was able to represent the data well over the pH range 4.5 to 10, fitting a smooth curve through the data. The model was unable to describe the drop in adsorption exhibited on gibbsite at pH 3.5. It is emphasized that the only parameters optimized by the computer program were the three arsenate surface complexation constants. The constant capacitance model is able to describe changes in adsorption as a function of solution pH using only one more ad-

justable parameter than the Langmuir and Freundlich adsorption isotherms.

Arsenate and phosphate adsorption envelopes for the competitive system are shown in Fig. 3. Figure 3b demonstrates the ability of the model to describe ternary adsorption data. The model produced a close fit to the experimental data for both anions in the pH range 3.5 to 9. Some underestimation in phosphate adsorption occurs at pH values >9 . In the model simulations of arsenate-phosphate competition shown in Fig. 3a and 3c no constants were fitted, all anion surface complexation constants were fixed at the values obtained previously from fitting the ternary system of Fig. 3b, and the program used solely to obtain chemical speciation. The model quantitatively predicts arsenate and phosphate adsorption over the pH range 4.5 to 9. Above pH 9 the model prediction underestimates adsorption. The model is unable to describe adsorption below pH 4 quantitatively. It is noteworthy that the predictive fit of the model in Fig. 3a and 3c is similar in quality to that obtained by direct optimization of the data in Fig. 3b.

CONCLUSIONS

Arsenate adsorption on goethite, gibbsite, and amorphous Al hydroxide can be described quantitatively with the constant capacitance model. For each

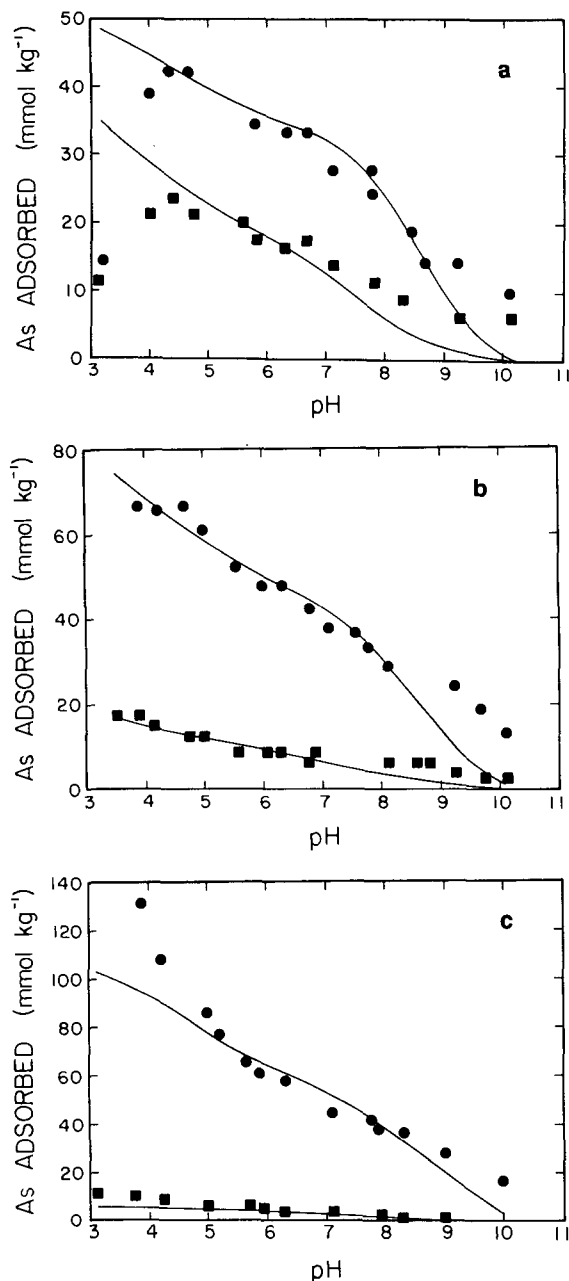


Fig. 3. Arsenate and phosphate adsorption on gibbsite from a ternary system. Experimental data arsenate (circles) and phosphate (squares) from Hingston et al. (1971). Model results are represented by solid lines. $As_T = 0.27 \text{ mol m}^{-3}$. (a) $P_T = 0.13 \text{ mol m}^{-3}$; (b) $P_T = 0.26 \text{ mol m}^{-3}$; (c) $P_T = 0.65 \text{ mol m}^{-3}$.

oxide the model is able to represent arsenate adsorption behavior over the pH range 4.5 to 10 using the same set of intrinsic surface complexation constants. However, the values of these constants are specific to the material studied. In previous modeling studies of phosphate (Goldberg and Sposito, 1984a) and B adsorption (Goldberg and Glaubig, 1985), Al and Fe oxide minerals exhibited similar adsorption behavior. That is, the common logarithms of the anion surface complexation constants for the two types of oxides were not significantly different. This comparison was not possible in the present study because only two data sets for each type of oxide were available. If upon

the inclusion of additional data sets no significant differences in arsenate surface complexation constant values were found for these two types of oxides, the model could be extended readily to arsenate adsorption on soils using the method of Goldberg and Sposito (1984b).

The constant capacitance model is able to describe arsenate-phosphate competition on gibbsite quantitatively over the pH range 4.5 to 9 using the same set of anion surface complexation constants. Anion surface complexation constants obtained for one ternary system could be used to predict competitive anion adsorption for other ternary systems on the same material containing different amounts of total anions in solution. Additional research is necessary to determine whether this procedure is applicable to other ternary adsorption systems and other adsorbents.

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All surface constant values given in Table 1 in both papers are for $\log K_i(\text{int})$ not $K_i(\text{int})$.