

## ADSORPTION OF CITRIC ACID BY SYNTHETIC PSEUDOBOEHMITE

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**Abstract**—The adsorption of citrate, at  $10^{-4}$ – $10^{-3}$  M initial concentration, by pseudoboehmite suspended in 0.02 M NaClO<sub>4</sub> was investigated at varying pH. Citrate shows a strong affinity for the pseudoboehmite surface, as seen in the adsorption isotherm at pH 6. Adsorption envelopes of adsorbed citrate vs. pH for a given initial citrate concentration are characteristic for the adsorption of a polyprotic acid by a variable-charge mineral. The envelope data were fit well by the Constant Capacitance Model assuming a ligand-exchange adsorption mechanism, three monodentate surface species of citrate, and a reactive surface OH density of 0.4 mol kg<sup>-1</sup>. Aqueous speciation calculations suggest that solubility equilibrium with pseudoboehmite was attained at pH > 9 and that particulate or polymeric Al may have existed at 6 < pH < 9. Dissolved Al appeared to reduce the adsorption of citrate at pH < 5.5 via solution complexation reactions.

**Key Words**—Citrate, Pseudoboehmite, Adsorption reactions.

### INTRODUCTION

The adsorption of inorganic and organic anions by metal oxides has been investigated intensively because of applications in agronomic, environmental, and industrial sciences (Sposito, 1984; Stumm, 1987). The results of the many experimental equilibrium studies that have been published are characterized reasonably well by recent parametric models (Sposito, 1985; Schindler and Stumm, 1987; Barrow, 1987; Hayes *et al.*, 1988). Usually, these models are based on postulated chemical reactions controlling the equilibria between the adsorptive anion and an average hydroxyl group on the surface of a crystalline oxide, such as goethite, gibbsite or  $\alpha$ -alumina.

Because of its wide distribution in earth surficial materials, gibbsite [ $\gamma$ -Al(OH)<sub>3</sub>] has been the adsorbent of choice in studies of hydrous aluminum oxide reactions in soils (Hsu, 1989). However, evidence is accumulating that poorly-crystalline boehmite ( $\gamma$ -Al-OOH), or *pseudoboehmite*, may be an important adsorbent as well (Huang, 1988). Pseudoboehmite differs from boehmite because of smaller particle size, greater hydration, and lack of three-dimensional, long-range structural order (Hsu, 1989). Gastuche and Herbillon (1962) have shown that neutralization of aluminum chloride by sodium hydroxide and aging of the resulting solution favor the formation of a poorly-ordered boehmite, as compared to washing or dialyzing the precipitate, which favor gibbsite formation. High concentrations of chloride during the aging of Al-OH solutions (Hsu, 1967), and the presence of many other inorganic and organic ligands, including sulfate and

citrate, are known to stabilize pseudoboehmite (Huang and Violante, 1986; Huang, 1988; Hsu, 1989).

The present paper is intended to provide the first experimental data and chemical modeling of the adsorption of citrate by pseudoboehmite. Citrate is a highly reactive organic ligand that is common in soils (Huang and Violante, 1986), and that has been studied often in connection with mineral weathering, anion adsorption competition, and Al toxicity effects (Earl *et al.*, 1979; Bruckert, 1970; Violante and Huang, 1985; Huang and Violante, 1986; Traina *et al.*, 1987). Pseudoboehmite can persist in weathering environments if soluble anion concentrations and/or temperatures are high, and if alternate wetting and drying periods occur (Huang, 1988; Hsu, 1989). Under these conditions, pseudoboehmite could present an important reactive hydroxylated surface for citrate adsorption by the ligand exchange mechanism (Sposito, 1984).

### MATERIALS AND METHODS

#### *Pseudoboehmite*

A sample of pseudoboehmite was prepared following the method of Gastuche and Herbillon (1962), and then used to investigate citrate adsorption at fixed pH. The sample contained a little gibbsite, and this more stable aluminum hydroxide developed further with time. Hsu (1989) has reviewed much of the evidence supporting the conversion of pseudoboehmite to gibbsite after prolonged aging in aqueous media under laboratory conditions. A second sample of pseudoboehmite was prepared by adapting the methods of Hsu (1967) and

Tettenhorst and Hoffmann (1980). Solutions of 0.4 M  $\text{AlCl}_3$  (standardized in Al concentration by atomic absorption analysis) and of 0.6 M NaOH in 4 M NaCl (standardized by titration with 0.5 M HCl commercial standard solution) were prepared. To the stirring solution of aluminum chloride, the base was added dropwise until a OH:Al molar ratio of 2.95 was achieved. The wet, solid residue obtained after centrifugation was aged in capped polyethylene bottles at 60°C for 20 hr. Afterward, it was washed with demineralized, organic carbon-free water, until a pH value near 6 was obtained, and dried at 60°C. The product was solely pseudoboehmite as determined by X-ray diffraction. Neither NaCl nor any other crystalline compound was detected. A test of dissolution by 1 M HCl for 20 min (Hsu, 1989) indicated the absence of amorphous aluminum hydroxide, within a limit of 1%. The total Al content of the product was 43% after drying at 110°C. The BET specific surface area determined after outgassing, either at room temperature (2 determinations), or at 110°C (2 determinations) was  $287 \pm 3 \text{ m}^2 \text{ g}^{-1}$ .

#### Adsorption experiments

A suspension of pseudoboehmite was prepared in 0.02 M  $\text{NaClO}_4$ , and kept at least 15 hr but no more than 2 days at laboratory temperature (22°C) before adsorption experiments were performed. This suspension was rapidly mixed in polypropylene centrifuge tubes with  $\text{NaClO}_4\text{-C}_6\text{H}_8\text{O}_7$  and NaOH, or  $\text{NaClO}_4\text{-HClO}_4$  solutions to achieve a selected pH value and citrate concentration, then shaken gently in a water bath at 25°C. The resulting solids concentration was  $4.9 \text{ g L}^{-1}$ . To reach the highest pH value desired after adsorption, some of the citric acid solutions were neutralized partially with NaOH before mixing. All solutions were maintained 0.02 M in Na. Nitrogen was bubbled into the basic solutions for at least 20 min to avoid excess carbonate formation. After shaking for a chosen time period (between 25 min and 16 hr for kinetics studies, and 2 or 4 hr for equilibrium studies), the mixtures were centrifuged at 35,000 g for 20 min. The supernatant solutions were pipetted into glass tubes containing small magnetic stirring bars. The pH value was measured immediately with a combination microelectrode. Concentrated nitric acid was added and the solutions stored at 5°C, if not analyzed immediately.

Chemical analyses were performed as described in detail by Cambier and Sposito (1991). Briefly, citrate concentrations were determined by total organic carbon analysis (TOC) with a Dohrman-Xertex carbon analyzer. We found consistency between TOC analyses and a standard citric acid solution prepared from analytical grade reagent dried overnight under vacuum over  $\text{P}_2\text{O}_5$ , assuming the formula  $\text{C}_6\text{H}_8\text{O}_7$ . Aluminum concentrations were measured by atomic adsorption or inductively-coupled argon plasma emission spec-

Table 1. Stability constants chosen for citrate (L) and aluminum speciation in solutions (values from the references cited were corrected to 0.02 M ionic strength using the Davies equation).

Species	log $K_{298}$	Reference
$\text{H}_3\text{L}$	13.734	Gregor and Powell (1986)
$\text{H}_2\text{L}^-$	10.722	Gregor and Powell (1986)
$\text{HL}^{2-}$	6.185	Gregor and Powell (1986)
$\text{AlLH}^+$	11.869	Gregor and Powell (1986)
$\text{AlL}$	9.207	Gregor and Powell (1986)
$\text{AlL}_2^{3-}$	14.249	Gregor and Powell (1986)
$\text{AlLLH}_{-1}^{4-}$	7.802	Gregor and Powell (1986)
$\text{AlLLH}_2^{2-}$	18.492	Gregor and Powell (1986)
$\text{Al}(\text{LH}_{-1})_2^{5-}$	0.239	Gregor and Powell (1986)
$\text{AlOH}_2^+$	-5.241	Nordstrom and May (1989)
$\text{Al}(\text{OH})_2^+$	-10.461	Nordstrom and May (1989)
$\text{Al}(\text{OH})_3$	-17.159	Nordstrom and May (1989)
$\text{Al}(\text{OH})_4^-$	-22.941	Nordstrom and May (1989)
$\text{NaL}^{2-}$	0.983	Martell and Smith (1977)

troscopy. Demineralized organic carbon-free water was used in all solutions. Glass and propylene vessels were washed with warm, 10% nitric acid and then with organic carbon-free water prior to use.

To obtain a more detailed knowledge of the adsorption reactions, chemical speciation calculations were done using the computer program MICROQL-UCR (Coves and Sposito, 1986). The stability constants needed were taken from Nordstrom and May (1989) for  $\text{AlOH}_n$  species; from Gregor and Powell (1986) for citric acid dissociation and Al-citrate complexes; and from Martell and Smith (1977) for a  $\text{NaL}^{2-}$  species (L = citrate; see Table 1). Polymeric Al species were not considered. Corrections for an ionic strength of 0.02 M were applied using the Davies equation (Sposito, 1981).

## RESULTS AND DISCUSSION

#### Adsorption data

Figure 1 shows an adsorption isotherm for citrate on the pseudoboehmite sample prepared by the method of Gastuche and Herbillion (1962). The circles represent data obtained after a 4-hr shaking period. The x's represent data obtained after shaking times varying from 25 min to 16 hr (centrifugation time excluded) and final pH between 5.86 and 6.11. No significant differences in citrate adsorption behavior were observed over this range of shaking times. Monitoring pH, however, was a sensitive way to observe that the sorption process actually reached a quasi-equilibrium only after about 80 min. Some mineral dissolution occurred (see discussion below) and slow attainment of equilibrium between citrate-aluminum complexes in solution is well known (Öhman and Sjöberg, 1983). The isotherm in Figure 1 for the 4-hr shaking time is H-type (Sposito, 1984), which indicates a high affinity between citrate and the pseudoboehmite surface at  $\text{pH } 5.97 \pm 0.07$ .

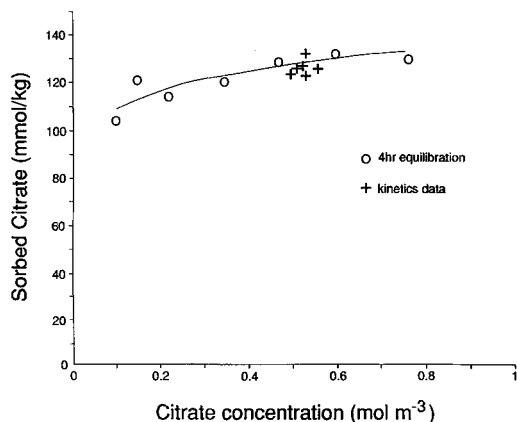


Figure 1. Adsorption isotherm of citric acid on pseudo-boehmite at pH 6.  $\circ$  equilibration for 4 hr;  $+$  kinetics study between 0.4 and 16 hr ( $1 \text{ mol m}^{-3} = 1 \text{ mmol L}^{-1}$ ).

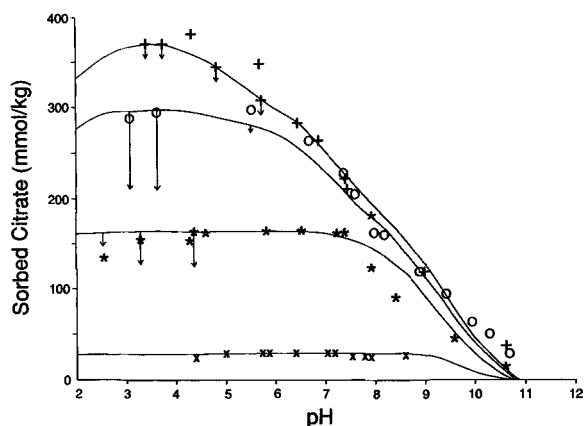


Figure 2. Adsorption envelopes for citrate on pseudo-boehmite. Discrete symbols: experimental data for different initial citrate concentrations ( $C_i$ ):  $+$   $C_i = 2.08 \text{ mmol L}^{-1}$ ;  $\circ$   $C_i = 1.49 \text{ mmol L}^{-1}$ ;  $*$   $C_i = 0.80 \text{ mmol L}^{-1}$ ;  $\times$   $C_i = 0.13 \text{ mmol L}^{-1}$ . Continuous lines: calculated with the Constant Capacitance Model. Arrows: calculated effects of soluble Al (concentration data from Table 2) on sorbed citrate (see text).

Table 2. Speciation of the supernatant solutions related to three adsorption envelopes in Figure 2.

$C_i$ (mmol L <sup>-1</sup> )	$Q_{\text{ads}}$	pH	$C_e$	$Al_T$	log IAP <sup>1</sup>	$[Al]_{\text{free}}^2$ (%)	Free citrate <sup>3</sup>	
							(mmol L <sup>-1</sup> )	(%)
2.076	1.825	3.43	0.250	0.222	-36.82	12.0	22.0	0.05
2.077	1.814	3.74	0.262	0.181	-36.75	2.1	32.0	0.08
2.069	1.862	4.33	0.208	0.136	-36.09	0.2	31.0	0.07
2.061	1.695	4.84	0.365	0.143	-35.89	0.0	46.0	0.16
2.061	1.705	5.70	0.357	0.093	-35.03	0.0	50.0	0.18
2.078	1.504	5.74	0.574	0.195	-34.75	0.0	35.0	0.20
2.075	1.288	6.86	0.788	0.055	-34.38	0.0	75.0	0.59
2.089	1.081	7.42	1.009	0.218	-32.66	0.6	48.0	0.48
2.077	0.883	7.95	1.193	0.193	-32.29	5.5	5.0	0.69
2.079	0.573	8.97	1.506	0.008	-33.57	72.0	84.0	1.27
2.087	0.169	10.6	1.918	0.285	-33.54	100.0	84.0	1.61
1.506	1.406	3.10	0.101	2.90	-35.80	97.0	1.3	0.001
1.499	1.445	3.64	0.054	0.725	-34.81	93.0	0.4	$2 \times 10^{-4}$
1.474	1.455	5.54	0.020	0.03	-31.71	34.0	0.3	$5 \times 10^{-5}$
1.468	1.291	6.72	0.178	0.04	-33.14	0.3	49.0	0.09
1.463	1.116	7.40	0.348	0.035	-32.88	2.2	68.0	0.24
1.503	0.784	8.05	0.720	0.107	-32.12	18.0	63.0	0.45
1.505	0.770	8.23	0.734	0.08	-32.21	30.0	71.0	0.52
1.496	0.578	8.91	0.919	0.045	-32.69	85.0	83.0	0.76
1.501	0.303	9.96	1.198	0.08	-33.42	100.0	84.0	1.01
1.499	0.239	10.30	1.260	0.19	-33.38	100.0	84.0	1.06
1.499	0.129	10.70	1.370	0.30	-33.59	100.0	84.0	1.15
0.808	0.657	2.55	0.150	8.40	-36.98	98.0	6.8	$1 \times 10^{-2}$
0.809	0.755	3.30	0.053	3.07	-35.17	98.0	0.5	$3 \times 10^{-4}$
0.795	0.750	4.28	0.044	2.85	-32.30	98.0	0.0	$3 \times 10^{-6}$
0.806	0.799	4.38	0.007	0.28	-33.02	97.0	0.1	$4 \times 10^{-6}$
0.806	0.804	6.54	0.003	0.002	-32.15	43.0	49.0	$1.5 \times 10^{-3}$
0.802	0.789	7.40	0.014	0.002	-32.52	90.0	82.0	0.01
0.807	0.441	8.43	0.366	0.015	-32.73	78.0	82.0	0.30
0.801	0.218	9.59	0.583	0.05	-33.25	100.0	84.0	0.49
0.795	0.061	10.60	0.734	0.38	-33.38	100.0	84.0	0.62

<sup>1</sup> IAP  $\equiv (Al^{3+})(OH^-)^3$ , where ( ) = activity in aqueous solution.

<sup>2</sup> Al not complexed by citrate.

<sup>3</sup> Citrate not bound to Al or Na.

$C_i$  = initial citrate concentration;  $Q_{\text{ads}}$  = adsorbed citrate concentration;  $C_e$  = equilibrium citrate concentration;  $Al_T$  = total Al concentration in supernatant solution.

Table 3. Modeling of adsorption data: Constant Capacitance Model (L = citrate).

$[\text{SOH}_2^+] = K_1[\text{SOH}][\text{H}^+] \exp(-F\psi/RT)$	$\log K_1$	=	8.2
$[\text{SO}^-] = K_2[\text{SOH}][\text{H}^+]^{-1} \exp(F\psi/RT)$	$\log K_2$	=	-10.4
$[\text{SLH}_2^{\text{OH}}] = K_3[\text{SOH}][\text{L}^-][\text{H}^+]^2$	$\log K_3$	=	23.78
$[\text{SLH}^-] = K_4[\text{SOH}][\text{L}^-][\text{H}^+] \exp(F\psi/RT)$	$\log K_4$	=	19.71
$[\text{SL}^-] = K_5[\text{SOH}][\text{L}^-][\text{H}^+] \exp(2F\psi/RT)$	$\log K_5$	=	12.80

$$S_T = [\text{SOH}_2^+] + [\text{SOH}] + [\text{SO}^-] + [\text{SLH}_2] + [\text{SLH}] + [\text{SL}] = C_S D_S$$

$$\sigma = C\psi; C_S = 4.9 \text{ kg m}^{-3}; D_S = 0.4 \text{ mol kg}^{-1}; C = 1.5 \text{ Farad m}^{-2}.$$

$F = 96485 \text{ C mol}^{-1}$ ;  $\psi$  = surface potential;  $C_S$  = solid suspension concentration.  $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\sigma$  = surface charge density;  $D_S$  = total site density.  $T = 298.15 \text{ K}$ ;  $C$  = density capacitance;  $[ ]$  = concentration of species.

Figure 2 shows adsorption envelopes for citrate on the pseudoboehmite samples prepared following the method of Hsu (1967) and Tettendorf and Hoffmann (1980). The reaction time was 2 hr in these experiments, with the initial citrate concentration ( $C_i$ ) taking on four different values:  $2.078 \pm 0.012$ ,  $1.494 \pm 0.015$ ,  $0.801 \pm 0.006$ ,  $0.130 \pm 0.001 \text{ mmol L}^{-1}$ . The two lower curves show plateaus that correspond to adsorption of virtually the total amount of citrate provided initially. For example, the equilibrium concentrations ( $C_e$ ) related to the third curve ( $C_i = 0.8 \text{ mmol L}^{-1}$ ) were found, between pH 4 and pH 7, to be of the order of  $1 \mu\text{mol L}^{-1}$ . The  $C_e$  for the fourth curve was very low and is not known with accuracy. The uppermost curve, on the other hand, corresponds to adsorption that left around 10% of the added citrate in solution.

Table 2 lists the values of  $C_i$ , and of adsorbed citrate ( $Q_{\text{ads}}$  in  $\text{mmol L}^{-1}$ ), pH,  $C_e$ , and the total Al concentration ( $\text{Al}_T$ ) corresponding to the upper three adsorption envelopes in Figure 2. Listed also are the results of the speciation calculations, including the ion activity product for  $\text{Al}(\text{OH})_3$ , the percentage of inorganic soluble Al, and the percentage and concentration of citrate free of Al or Na.

At  $\text{pH} > 9$ , the log IAP values were relatively stable ( $-33.5 \pm 0.2$ ) and the species of aluminum were limited to the inorganic aluminate ion. A recently reported log ion activity product for well-crystallized, acid-washed boehmite is  $-34.5$  (Peryea and Kittrick, 1988). Small particle size and surface defects could increase this value significantly (Peryea and Kittrick, 1988; Hemingway and Sposito, 1989). Thus, at  $\text{pH} > 9$ , when little adsorption of citric acid occurs and when the aqueous ligands alone are responsible for aluminum dissolution (Table 2), solubility equilibrium with pre-existing pseudoboehmite can be reached quickly and is characterized by a log IAP value of about  $-33.5$ .

At pH values between 9 and about 6, some of the values of log IAP were significantly greater than  $-33.5$  (Table 2). This result suggests that the  $\text{Al}_T$  values were affected partly by solid Al particles or polymeric Al species in the supernatant solutions. At  $\text{pH} \leq 6$ , the log IAP values are generally lower than  $-33.5$ , indicating that adsorption equilibrium, but not solubility equilibrium, was attained. The free citrate activity was reduced considerably by complexation with aluminum

at  $\text{pH} < 7$  (Table 2, last two columns). The percentage of complexed citrate is less at a pH near 7, and is even more so if soluble Al has been overestimated. At  $\text{pH} > 7$ , the activity is uniform and corresponds to  $\text{NaL}^{2-}$  (L = citrate).

#### Adsorption modeling

To model our adsorption data, we needed a simple surface ligand-exchange model so as to have few model parameters to fit. We used the Constant Capacitance Model (Stumm *et al.*, 1970; Sposito, 1984). The model conditions are summarized in Table 3. The conditional constants for acid-base surface site reactions with the aqueous ions were deduced from proton titration experiments following the method presented by Sposito (1984, p. 171). For the total surface OH density, we used values that have been published for aluminum oxides and hydroxides (Rajan, 1977; Parfitt *et al.*, 1977; Kummert and Stumm, 1980; Pulfer *et al.*, 1984). Our experimental adsorption maximum fell in the published range. We also tried different values for the capacitance density between 0.1 and  $3.0 \text{ F m}^{-2}$ .

To fit the adsorption envelopes within the whole range of pH investigated, it was necessary to consider the three surface citrate species indicated in Table 3, all of which are monodentate. The three corresponding stability constants ( $K_1$ ,  $K_2$ ,  $K_3$ ) were fitted using a modification of the MICROQL-UCR program and least squares criteria. Because solubility equilibrium for Al was not attained at  $\text{pH} < 5.5$ , no  $\text{Al}_T$  data were entered into the speciation calculation. All data points of the three upper curves in Figure 2 were considered, except for the two points located above the uppermost curve. The good quality of the resulting model fits is indicated in Figure 2 (solid lines).

Instead of using the values shown in Table 2, a lower capacitance density permitted only a slight improvement of the fitting for  $\text{pH} > 7$ . The values for  $K_1$ ,  $K_2$ ,  $K_3$  were then higher and led to impossibly low calculated values of  $C_e$  when  $C_i = 0.8 \text{ mmol L}^{-1}$  at  $\text{pH} < 7$ . Obviously, an equilibrium concentration in a range  $10^{-5}$ – $10^{-8} \text{ M}$  does not influence the adsorption envelope. However, the quantities of citrate that remained in solution were the experimental values actually determined. The final fitting was a compromise, taking

into account not only the adsorbed quantities of citrate but also the magnitude of  $C_c$ .

Other species are available if one assumes a more complex structure of the surface (Pulfer *et al.*, 1984), but the modeling approach we have taken is known to be insensitive to the detailed molecular structure of the adsorbate (Westall and Hohl, 1980). McBride (1982) has shown by electron spin resonance spectroscopy the existence of strong carboxylate bonds on aluminum hydroxide surfaces reacted with a carboxylated nitroxide spin probe. This is consistent with the ligand exchange model assumed here.

Although it was not possible to include soluble Al data when fitting the ligand-exchange model, we applied the model to estimate the effect of reintroducing Al into solution. The arrows in Figure 2 provide examples of the calculated decrease in adsorbed citrate using the experimental values of Table 2 for the total Al concentration in the supernatant solutions. The effect was nil for  $\text{pH} > 5.5$ , but at lower pH solubilized Al is able to compete with the surface sites for citrate, and thus decrease the amount adsorbed. Therefore, part of the scatter in the adsorption data at low pH can be related to scatter in Al concentrations, since equilibrium was not reached with respect to mineral dissolution. We may conclude that the envelopes are explained reasonably well by our simple model without taking dissolved aluminum into account, but the possibility exists that this aluminum might well explain the observed decrease in citrate adsorption at more acid pH values.

In another model application we observe that the global equilibrium between solution and surface species at  $\text{pH} \leq 7$  involves a high fraction of bound citrate, even when the free citrate activity is very low in solution. This means that solution aluminum-citrate species react with the surface sites to give surface citrate species. Thus, one cannot exclude the existence of ternary surface (aluminum)-citrate-aluminum species on pseudoboehmite.

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