

COMPARISON OF ADSORPTION OF PHOSPHATE, TARTRATE, AND OXALATE ON HYDROXY ALUMINUM MONTMORILLONITE COMPLEXES

J.Z. HE,[†] A. DE CRISTOFARO, AND A. VIOLANTE

Dipartimento di Scienze Chimico-Agrarie, Università di Napoli Federico II, via Università 100, 80055 Portici, Napoli, Italy

Abstract—Competitive adsorption between phosphate, tartrate and oxalate was studied on two hydroxy aluminum montmorillonite complexes (AlMt1.6 and AlMt6), which were prepared by adding a base to pH 5.5 to samples containing 1.6 and 6.0 mol Al per kg clay. The quantities of phosphate, tartrate and oxalate adsorbed were more closely related to the amount of OH-Al species coatings on the montmorillonite than to the surface area of the complexes. The adsorption capacity of phosphate was much greater than that of tartrate or oxalate for both samples. Adding molar amounts of oxalate and tartrate resulted in an oxalate/tartrate adsorption ratio (Rf) of ~1. However, in the presence of phosphate, Rf values were <1.0, and the Rf values decreased with increasing amounts of added phosphate, indicating that tartrate competed with phosphate more effectively than oxalate. The presence of tartrate also reduced phosphate adsorption by the complexes. The efficiency of tartrate in reducing phosphate adsorption increased by increasing the initial tartrate/phosphate molar ratio and by adding tartrate 2 h before phosphate addition. Tartrate and oxalate added as a mixture in equimolar quantities were much more effective in inhibiting phosphate sorption than tartrate alone under the same organic ligand concentrations, probably because more sites with high affinity for both the organic ligands were occupied by tartrate and oxalate than by tartrate alone. The efficiency of tartrate alone, or combined with oxalate, in preventing phosphate adsorption was greater for the complex containing a lesser amount of OH-Al species coating the montmorillonite surfaces. This result may be attributable to a greater proportion of sites specific for organic ligands present on AlMt1.6 compared to AlMt6 complex.

Key Words—Competitive Adsorption, Hydroxyaluminum-Montmorillonite Complexes, Montmorillonite, Oxalate, Phosphate, Tartrate.

INTRODUCTION

Relatively large amounts of carbon assimilated in photosynthesis are exuded by plant roots. This carbon contains a significant fraction of low-molecular-weight organic acids, such as oxalic, citric, tartaric, malic and a series of amino acids (Rovira, 1969; Huang and Violante, 1986; Marschner, 1995). The concentration of organic acids in the soil solution is usually low (10^{-3} to 4×10^{-4} mol l⁻¹), but greater amounts are found in the rhizosphere of crop plants (Vance *et al.*, 1996). The area immediately surrounding a root is also a zone of intense biological activity, where most types of microorganisms thrive. The microorganisms in the rhizosphere are more active than are those located in bulk soil and synthesize many aliphatic organic acids and phenols.

The first studies on the influence of low-molecular-weight organic acids on the sorption and replacement of phosphate by clay minerals started years ago (Swenson *et al.*, 1949). Because hydrous oxides of aluminum and iron are largely responsible for the fixation of phosphate in soils, most of the investigations of the effect of organic ligands on the removal and sorption of phosphate were performed using Al or Fe oxides (Swenson *et al.*, 1949; Nagarajah *et al.*, 1970;

Hingston *et al.*, 1971; Earl *et al.*, 1979; Yuan, 1980; Sibanda and Young, 1986; Violante *et al.*, 1991, 1996). The results of these studies indicated that the most commonly occurring organic acids in soil, tri- and dicarboxylic acids were effective in reducing phosphate sorption, whereas monocarboxylic acids had little effect on phosphate fixation.

Hydroxy-Al interlayered smectites or vermiculites are widely distributed in several soil orders. Chemical interactions between plant roots and rhizosphere minerals include formation of noncrystalline Al precipitation products, which may coat the surfaces of phyllosilicates. The presence of OH-Al species on the surfaces of phyllosilicates significantly enhances the adsorption of anions on clay minerals (Barnhisel and Bertsch, 1989). Recently, Violante and Gianfreda (1993, 1995) studied the sorption of phosphate and oxalate and the competition in sorption between phosphate and oxalate on a hydroxy-Al montmorillonite complex. They reported that more phosphate than oxalate was adsorbed, even when the initial amount of oxalate was three times greater than that of phosphate. The order of addition of phosphate and oxalate strongly influenced the sorption of these ligands, and the maximum reduction in phosphate sorption occurred in acidic systems when oxalate was introduced before phosphate. Unfortunately, in spite of the fact that tartrate was identified in root exudates and aqueous extracts of forest litter, and is produced by bacteria in

[†] Permanent address: Department of Soil and Agrochemistry, Huazhong Agricultural University, Wuhan 430070, China.

the rhizosphere (Martell and Smith, 1977; Huang and Violante, 1986; Vance *et al.*, 1996), the competitive sorption of tartrate and phosphate on clay minerals and soils has received scant attention (Earl *et al.*, 1979; Violante and Gianfreda, 1995).

In the rhizosphere, many different organic ligands may interact with nutrients for adsorbing sites on clay minerals. However, there is no information about the competitive sorption behavior of phosphate (or other nutrients) and organic ligands on clay minerals or soils when two or more organic acids are introduced to the system. This paper describes an investigation of the sorption of phosphate, tartrate, or oxalate and the competitive sorption between phosphate and tartrate, oxalate and tartrate, and among phosphate, tartrate and oxalate on two hydroxy-Al-montmorillonite complexes containing different amounts of OH-Al species adsorbed on the surfaces of the montmorillonite.

MATERIALS AND METHODS

Preparation of Al(OH)_x-montmorillonite complexes

The <2 μm fraction of Na-montmorillonite from Crook County, Wyoming was separated by sedimentation after ultrasonic dispersion in water. The Al(OH)_x-montmorillonite (chlorite-like) complexes (AlMt1.6 and AlMt6) were prepared by adding 0.5 mol l⁻¹ NaOH at the rate of 1 ml min⁻¹ to Na-montmorillonite suspensions containing 1.6 and 6.0 mol AlCl₃ per kg clay, respectively, until a pH of 5.5 was reached (Barnhisel and Bertsch, 1989; Violante and Gianfreda, 1993). The suspensions were thoroughly stirred during the titration. The final suspensions (2 l) were aged for 24 h and then centrifuged at 10,000 g for 30 min. The supernatants were filtered through Millipore M.F. filters (pore size <0.2 μm, Millipore Co., Bedford, Massachusetts) and used for Al determination. The sedimented pellets were washed two times with water, dialysed until Cl⁻ free, and then freeze-dried. The samples were lightly ground to pass a 0.25 mm sieve. The specific surface area was determined gravimetrically using the retention of ethylene glycol monoethyl ether (EGME) (Eltanawy and Arnold, 1973). Exchangeable Al was extracted using 1.0 mol l⁻¹ KCl and determined as described below. The X-ray diffraction patterns of the oriented K-saturated minerals were obtained with a Rigaku diffractometer (Rigaku Co., Tokyo) with Ni-filtered CoKα radiation generated at 40 kV and 30 mA.

Adsorption isotherms of phosphate, tartrate and oxalate

One hundred milligrams of the complexes were shaken for 24 h at 20°C with a series of 25 ml of 0.02 mol l⁻¹ KCl solutions containing different amounts (0–3.2 mmol l⁻¹) of phosphate, tartrate, or oxalate. The final pH of the suspensions, previously adjusted to 5.5,

was recorded. The suspensions were centrifuged and filtered, and phosphate, tartrate, and oxalate concentrations in the solutions were then determined.

Competitive adsorption between tartrate and oxalate

One hundred milligrams of the complexes were shaken for 24 h at 20°C with a series of 25 ml of 0.02 mol l⁻¹ KCl solutions containing different amounts (0–1.6 mmol l⁻¹) of tartrate and oxalate. The total amount of tartrate and oxalate added to the clay was kept constant at 400 mmol kg⁻¹ with the oxalate/tartrate molar ratio (Ri) ranging from 0.2 to 5.0. Some samples were prepared by adding 50, 100, 150 mmol kg⁻¹ of tartrate and oxalate while keeping Ri = 1. The suspensions were centrifuged and filtered, and tartrate and oxalate concentrations in the solutions were then determined.

Competitive adsorption between phosphate and tartrate

One hundred milligrams of the complexes were shaken for 24 h at 20°C with a series of 25 ml of 0.02 mol l⁻¹ KCl solutions containing different amounts of phosphate and tartrate. The amounts of phosphate initially added to the clay were 150 or 400 mmol kg⁻¹ for AlMt1.6 and 150 or 500 mmol kg⁻¹ for AlMt6, which resulted in nearly maximum phosphate adsorption. The molar ratio of tartrate/phosphate ranged from 0.25 to 3.0. To investigate the effect of sequence of anion addition on phosphate adsorption, tartrate was introduced either simultaneously with phosphate (P + T systems), or 2 h before phosphate (T/P systems). The suspensions were centrifuged and filtered, and phosphate and tartrate concentrations in the solutions were then determined.

Competitive adsorption among phosphate, tartrate, and oxalate

One hundred milligrams of the complexes were shaken for 24 h at 20°C with a series of 25 ml of 0.02 mol l⁻¹ KCl solutions containing different amounts of phosphate, tartrate, and oxalate. The amounts of phosphate initially added to the clays ranged from 100 to 500 mmol kg⁻¹, whereas those of tartrate and oxalate ranged from 50 to 375 mmol kg⁻¹. In most samples, the total amount of phosphate, tartrate and oxalate was kept constant at 600 mmol kg⁻¹. The oxalate/tartrate molar ratio was 1 in all the samples, but the (tartrate + oxalate)/phosphate molar ratio ranged from 0.2 to 5. Tartrate and oxalate were introduced either simultaneously with phosphate (P + T + OX systems) or 2 h before phosphate (T + OX/P systems). The suspensions were centrifuged and filtered, and phosphate, tartrate, and oxalate concentrations in the solutions were then determined.

Analytical methods

Freshly prepared tartrate and oxalate solutions, in which a few drops of toluene were initially added to

Table 1. Chemical and physico-chemical properties of Al(OH)_x-montmorillonite complexes.

Sample ¹	Added Al mol kg ⁻¹	Sorbed Al mol kg ⁻¹	<i>d</i> (001)-values, nm			Exchangeable Al, mmol kg ⁻¹	Surface area m ² g ⁻¹
			20°C	300°C	550°C		
Mt ²	0	0	1.170	0.968	0.964	0	800
AlMt1.6 ²	1.6	1.6	1.405	1.307	1.137	94	566
AlMt6 ²	6.0	3.1	1.577	1.476	1.379	23	313

¹ K-saturated.

² Mt = montmorillonite; AlMt1.6 and AlMt6 = hydroxy aluminum-montmorillonite complexes prepared by adding 1.6 or 6 mol kg⁻¹ of clay.

inhibit microbial activity, were used in all experiments. The final pH of the suspensions was recorded at the end of the reaction period. The final pH of most of the suspensions was between 6.4–6.6 when the total initial amount of phosphate, tartrate, and/or oxalate was 300 mmol kg⁻¹ or more. The equilibrated suspensions were centrifuged at 10,000 g for 30 min and the supernatants filtered through Millipore M.F. filters (pore size <0.2 μm). The amounts of phosphate, tartrate and/or oxalate in the supernatants were determined by ion chromatography. A Dionex ion chro-

matograph (Model 2000i/SP, Dionex Co., Sunnyvale, CA) was used with an AS4A separator column connected to a conductivity cell. The eluent was 0.75 mmol l⁻¹ NaHCO₃ + 2 mmol l⁻¹ Na₂CO₃ at a flow rate of 2 ml min⁻¹. The amounts of phosphate, tartrate, and oxalate adsorbed were calculated as the difference between the initial and final concentrations of the ligands in the solutions. The adsorption experiments were conducted in duplicate. The average error in the determination of the ligands was <5%. The amount of Al in the final solutions was determined by atomic adsorption spectrophotometry (Perkin-Elmer 3030B, Norwalk, Connecticut).

RESULTS AND DISCUSSION

Properties of the hydroxy-Al montmorillonite complexes

Table 1 summarizes some characteristics of the synthetic hydroxy-Al montmorillonite complexes obtained by adding 1.6 or 6.0 mol of Al per kg of clay (AlMt1.6, AlMt6). The AlMt1.6 and AlMt6 complexes retained 1.6 and 3.1 mol of Al kg⁻¹ clay, respectively. Negligible quantities of OH-Al species (<6%) of the adsorbed Al were exchanged by 1 mol l⁻¹ KCl solutions. The K-saturated montmorillonite showed a *d*(001)-value at 1.170 nm at 20°C, which collapsed to 0.968 and 0.964 nm after heating at 300 and 550°C. The AlMt1.6 and AlMt6 complexes showed *d*(001)-values, respectively, at 1.405 and 1.577 nm, which indicate interlayering (Huang and Violante, 1986; Barnhisel and Bertsch, 1989). After heating to 300 and 550°C, the complexes showed *d*(001)-values at 1.307 and 1.137 nm for AlMt1.6 and 1.476 and 1.379 nm for AlMt6, providing evidence that greater amounts of hydroxy aluminum polymers were present in the interlayer of montmorillonite in the AlMt6 sample. The surface area of AlMt6 (313 m² g⁻¹) was much smaller than that of AlMt1.6 (566 m² g⁻¹), evidently because of the greater interlayering of the OH-Al species in the AlMt6 (Barnhisel and Bertsch, 1989).

Adsorption isotherms

The adsorption isotherms for phosphate, tartrate, and oxalate on AlMt1.6 and AlMt6 are presented in Figure 1, which shows the quantities of each ligand

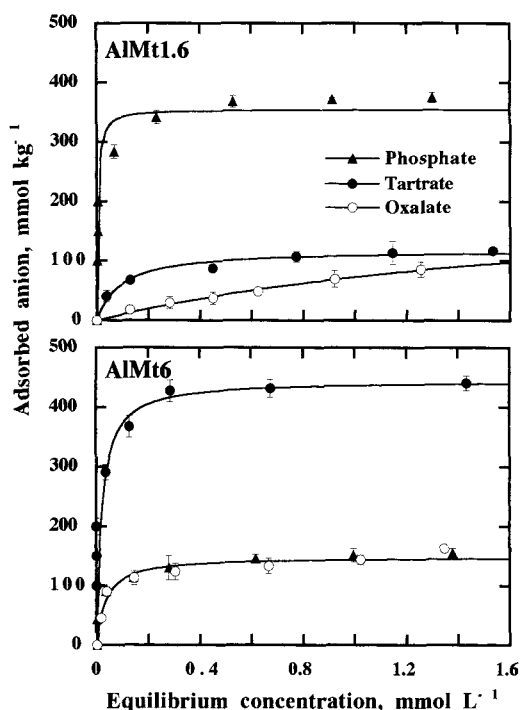


Figure 1. Isotherms for the sorption of phosphate, tartrate, and oxalate on the AlMt1.6 and AlMt6 complexes. The respective Langmuir parameters and *r*² of the equations were: AlMt1.6, Phosphate *S*_m = 384.6 mmol kg⁻¹, *K* = 0.113 and *r*² = 0.999; Tartrate *S*_m = 125 mmol kg⁻¹, *K* = 0.008 and *r*² = 0.997; Oxalate *S*_m = 166.6 mmol kg⁻¹, *K* = 0.007 and *r*² = 0.916; AlMt6, Phosphate *S*_m = 454 mmol kg⁻¹, *K* = 0.105 and *r*² = 0.999; Tartrate (Oxalate) *S*_m = 166 mmol kg⁻¹, *K* = 0.025 and *r*² = 0.999. The standard deviation for the adsorbed anions values ranged from 2.82 to 19.8 for AlMt1.6 and from 2.3 to 18.4 for AlMt6.

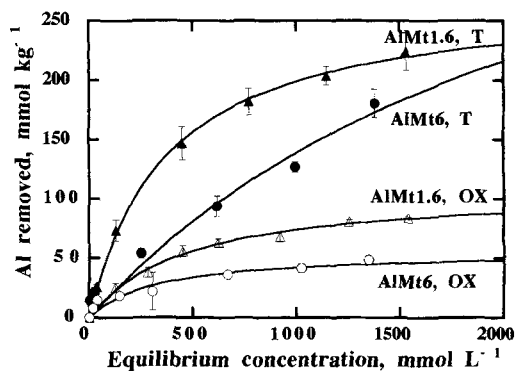


Figure 2. Aluminum removed from the AIMt1.6 and AIMt6 complexes vs. the concentrations of tartrate (T) or oxalate (OX) in the final solutions. The standard deviation for the solubility of Al values ranged from 1 to 15.8.

adsorbed against the final ligand concentration in equilibrium solutions. The data are in agreement with the Langmuir equation

$$S = S_m KC / (1 + KC)$$

where S is the amount of ligand adsorbed (mmol kg^{-1}), S_m is the maximum amount of ligand adsorbed (mmol kg^{-1}), C is the equilibrium solution concentration of the adsorbate, both free and complexed with aluminum (mmol l^{-1}), and K is a constant related to the adsorption energy (Giles *et al.*, 1974; Parfitt, 1978). The adsorption data for phosphate, tartrate, and oxalate were also plotted according to the linear form of the Langmuir equation (double reciprocal; not shown) to obtain the phosphate, tartrate, and oxalate adsorption maxima and K constant values (legend of Figure 1).

Figure 1 and the Langmuir constants suggest: (1) the adsorption capacity (S_m) of the complexes for phosphate was much greater than that for tartrate or oxalate; (2) the bonding energy for phosphate was much higher than for tartrate and oxalate on both AIMt1.6 and AIMt6; (3) the adsorption capacity of the AIMt6 complex for the organic ligands was similar, but on the AIMt1.6 complex at a final ligand concentration $<1.2 \text{ mmol l}^{-1}$ more tartrate than oxalate was adsorbed; (4) the bonding energy for tartrate was slightly higher than for oxalate on the AIMt1.6 complex; and (5) the complex AIMt6 adsorbed greater quantities of phosphate, tartrate, or oxalate than the complex AIMt1.6. On the basis of the mmol of ligands adsorbed per kg of clay, the amounts of phosphate, tartrate, and oxalate adsorbed on AIMt6 in the range of concentrations used were 1.2–1.5 times greater than those adsorbed on AIMt1.6. In contrast, on the basis of the quantities of ligands adsorbed per m^2 of clay, the amounts of anions adsorbed on AIMt6 were 1.8–2.4 times greater than those adsorbed on AIMt1.6. Given that the exposed surfaces of the complex AIMt6 were much lower than those of the complex AIMt1.6

Table 2. Amounts of tartrate (T) and oxalate (OX) sorbed by $\text{Al}(\text{OH})_x$ -montmorillonite complexes (AIMt1.6 and AIMt6) when $400 \text{ mmol T} + \text{OX kg}^{-1}$ clay were added at different initial OX/T molar ratio (R_i).

Anions added			Anions sorbed				
T	OX	R_i^1	OX	T + OX	Al^2	R_f^3	
			mmol kg^{-14}				
AIMt1.6							
400	0	0	114	0	114	203	0
333	67	0.2	67	5	72	168	0.07
267	133	0.5	58	21	79	156	0.37
200	200	1.0	36	36	72	136	1.01
133	267	2.0	29	57	86	124	2.01
67	333	5.0	15	65	80	92	4.30
0	400	∞	0	86	86	81	∞
AIMt6							
400	0	0	152	0	152	127	0
333	67	0.2	102	26	128	130	0.26
267	133	0.5	81	43	124	118	0.53
200	200	1.0	68	66	134	98	0.97
133	267	2.0	49	81	130	86	1.66
67	333	5.0	32	110	142	57	3.43
0	400	∞	0	144	144	42	∞

¹ R_i = Initial oxalate/tartrate molar ratio in solution.

² Al = Al removed from the complexes.

³ R_f = Final oxalate/tartrate molar ratio on the surface of mineral.

⁴ Average error $<5\%$.

(Table 1), the quantities of ligands adsorbed on the clay minerals were primarily related to the amount of OH-Al species covering the surfaces of montmorillonite, which tremendously promote the adsorption of anions (Parfitt, 1978; Huang and Violante, 1986; Hsu, 1989; Barnhisel and Bertsch, 1989; Violante and Gianfreda, 1995).

Much more Al can be placed in solution by tartrate than oxalate (Stumm *et al.*, 1985) and, surprisingly, more from the complex AIMt1.6 than AIMt6 (Figure 2). These results may be related to a greater quantity and proportion of OH-Al species which were adsorbed into the interlayer of montmorillonite in the AIMt6 complex (Table 1). Consequently, the hydrolytic products of Al were more protected and thus less soluble in the presence of organic ligands. Additionally, it is possible that the much greater amount of OH-Al species present on the surfaces of the AIMt6 complex promoted stronger aggregation between the clay particles (Huang and Violante, 1986), thus decreasing the rate of Al solubility. No or negligible quantities of Al were found in the solutions in the presence of phosphate.

Competitive adsorption between tartrate and oxalate

Results from the competitive adsorption between tartrate and oxalate on AIMt1.6 and AIMt6 at different oxalate/tartrate molar ratios (R_i) ranging from 0.2 to 5 are shown in Table 2. The total amount of oxalate

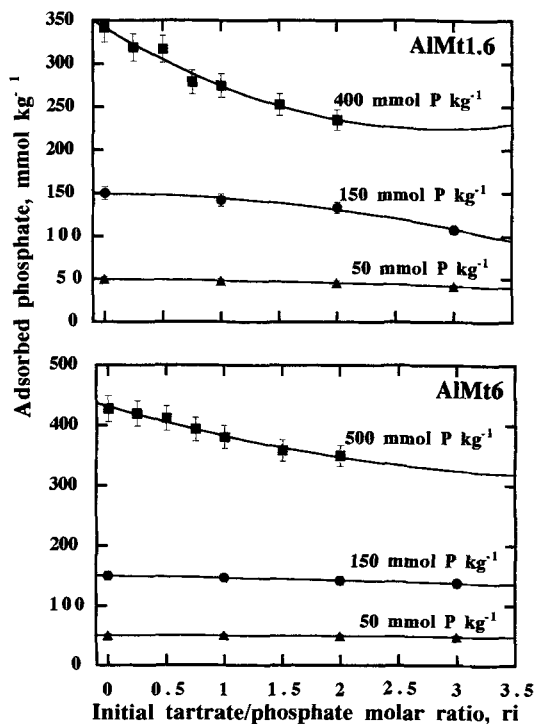


Figure 3. Added tartrate/added phosphate molar ratios (r_i) vs. adsorbed phosphate (mmol P kg^{-1}) on AlMt1.6 and AlMt6 complexes. Tartrate was added together with phosphate.

+ tartrate was kept constant at 400 mmol of added ligands kg^{-1} clay. It was previously found that by adding 300–400 mmol oxalate or tartrate kg^{-1} clay, the adsorbed quantity of each ligand was close to the maximum amount that may be bound by the clay minerals (Figure 1).

The presence of one organic ligand strongly reduced the adsorption of the other. By increasing R_i from 0.2 to 5 the final oxalate adsorbed/tartrate adsorbed molar ratios (R_f) were usually close to or lower than R_i . However, when the same amount of oxalate and tartrate were added (50–200 mmol of each ligand kg^{-1} , $R_i = 1$), R_f was practically 1.

The total amount of oxalate + tartrate adsorbed on the clays was slightly lower than the quantities of tartrate or oxalate adsorbed when 400 mmol of each ligand was added alone to the clays. Al removed from the complexes in the presence of a mixture of the organic ligands was generally lower than Al removed in the presence of tartrate alone, but was greater than Al going into solution in the presence of oxalate alone, further indicating that the hydroxy-Al polymers were more soluble in tartrate than in oxalate (Figure 2). The greater the quantity of Al that goes into solution, the lower the total amounts of oxalate + tartrate adsorbed on AlMt1.6 and AlMt6, probably because some sites were removed by Al going into solution (Earl *et al.*, 1979).

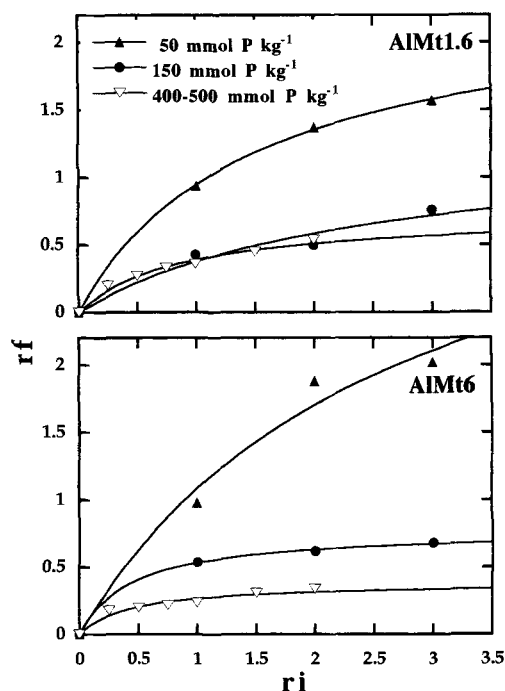


Figure 4. Added tartrate/added phosphate molar ratios (r_i) vs. adsorbed tartrate/adsorbed phosphate molar ratios (r_f) in experiments of tartrate adsorption on AlMt1.6 and AlMt6 in systems containing 50, 150 and 400 or 500 mmol P kg^{-1} . Tartrate was added together with phosphate.

Competitive adsorption of phosphate and tartrate

The amounts of phosphate adsorbed on the complexes in systems containing 50, 150, 400 (complex AlMt1.6) or 500 mmol kg^{-1} (complex AlMt6) of phosphate and different quantities of tartrate to have an initial tartrate/phosphate molar ratio (r_i) ranging from 0.25 to 3 are shown in Figure 3. The amount of Al removed from AlMt1.6 was always greater than that removed from AlMt6, and ranged from 0 to 107 and from 0 to 84 mmol kg^{-1} , respectively (not shown).

Phosphate adsorption generally decreased with increasing tartrate concentration. No evidence of competitive adsorption was observed when low quantities of phosphate (50 mmol kg^{-1}) were added to the complexes in the presence of tartrate. This may result because there were sufficient sites available for both the anions. Only at an initial tartrate/phosphate molar ratio (r_i) of 3 did the tartrate sorption decrease by 3–15% (data not shown), but phosphate adsorption did not decrease significantly (Figure 3).

By adding 150–500 mmol phosphate kg^{-1} clay, more phosphate than tartrate was adsorbed on the complexes even when the initial r_i was 3. The tartrate adsorbed/phosphate adsorbed molar ratios (r_f) are plotted vs. the initial tartrate/phosphate molar ratios (r_i) in the systems containing 50, 150, and 400 or 500 mmol phosphate kg^{-1} in, Figure 4. In the presence of 50

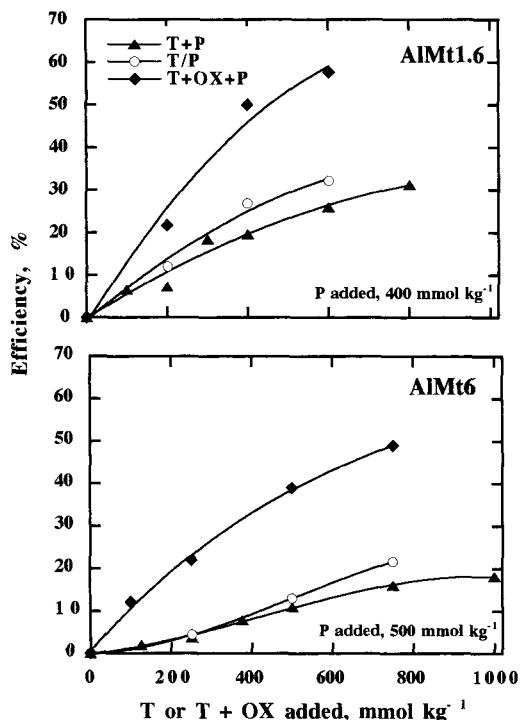


Figure 5. Efficiency of different amounts of tartrate (T) and tartrate + oxalate (T + OX) in decreasing phosphate (P) sorption on AlMt1.6 and AlMt6 complexes, when the organic ligands were introduced together with P (T + P or T + OX + P systems) or 2 h before P (T/P systems).

mmol phosphate kg^{-1} the rf values increased significantly with increasing r_i , because there are many sites on the complexes available for tartrate (clearly more on AlMt6 than AlMt1.6; Figure 1). However, rf was always lower than r_i . In the presence of 150–500 mmol phosphate kg^{-1} , the rf values were much lower than r_i and only slightly increased at $r_i > 1.0$, evidently because many sites became inaccessible for tartrate. Even in the presence of high concentrations of tartrate ($r_i = 3$), from 56 to 79% of the anions adsorbed on the complexes were phosphate.

The efficiency of tartrate in preventing phosphate adsorption on AlMt1.6 or AlMt6, calculated according to the expression of Deb and Datta (1967): Efficiency of tartrate (%) = $(1 - \text{phosphate adsorbed in the presence of tartrate/phosphate adsorbed when applied alone}) \times 100$ ranged, in systems containing 400 (AlMt1.6) or 500 (AlMt6) mmol phosphate kg^{-1} , from 5.3 to 31.3% or from 2.0 to 18.2%, respectively. The efficiency of tartrate increased when the organic ligand was added before phosphate (T/P systems; Figure 5).

The efficiency of tartrate in preventing phosphate retention was greater on AlMt1.6 than AlMt6. A possible explanation for this result is that the two complexes, which differed substantially in degree of interlayering and surface properties (Table 1) might also

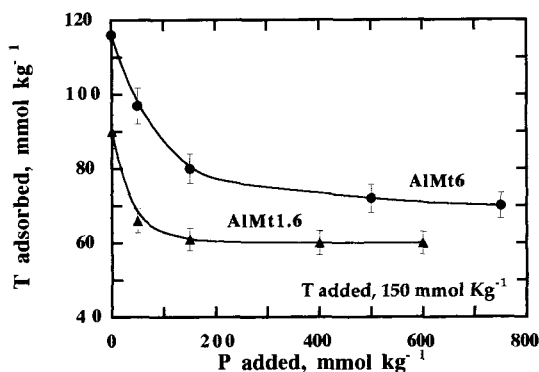


Figure 6. Adsorption of tartrate (T) on the Al(OH)_x -montmorillonite complexes (AlMt1.6 and AlMt6) by adding 150 mmol T kg^{-1} and different quantities of phosphate (P) (from 50 to 150 mmol P kg^{-1}). The standard deviation for the adsorbed tartrate ranged from 2 to 17.

have different proportions of “site-types”. Differences in the competition between tartrate and phosphate on the two clays could be due, at least partly, to differences in the relative proportion of sites having a high affinity for phosphate or tartrate. A greater proportion of sites specific for the organic ligand were likely present on AlMt1.6 than on the AlMt6 complex.

The above results indicate that many sites on clay minerals were specific for phosphate (Figure 1), whereas many other sites, common to both the ligands, showed a higher affinity for phosphate than for tartrate. However, some sites appeared more specific for tartrate than for phosphate. In fact, the adsorption of tartrate on the complexes decreased to a minimum amount in the presence of increasing concentrations of phosphate. Tartrate concentration remained practically constant even in the presence of large quantities of phosphate (Figure 6). For example, by adding 150 mmol tartrate kg^{-1} to the AlMt6 complex, 116 mmol tartrate kg^{-1} were adsorbed in the absence of phosphate. However, in the presence of increasing quantities of phosphate (50–200 mmol phosphate kg^{-1}) the amounts of adsorbed tartrate decreased to 80–75 mmol kg^{-1} , but remained practically constant even when adding greater amounts of phosphate (to 600 mmol phosphate kg^{-1}). A similar trend was observed for the AlMt1.6 complex (Figure 6).

Competition in adsorption of phosphate, tartrate, and oxalate

The quantities of phosphate, tartrate, and oxalate adsorbed on the complexes AlMt1.6 and AlMt6, when all the ligands were added as a mixture (P + T + OX systems) and when tartrate + oxalate were added to the clay minerals 2 h before phosphate (T + OX/P) are summarized in Table 3. The total amount of phosphate + tartrate + oxalate added to the clays and the oxalate/tartrate molar ratios were kept constant at 600

Table 3. Amounts of phosphate (P), tartrate (T) and oxalate (OX) sorbed on the $\text{Al}(\text{OH})_x$ -montmorillonite complexes (AlMt1.6 and AlMt6) when P was added together with T and OX (T/OX molar ratio = 1) (P + T + OX systems) or 2 h after T and OX addition (T + OX/P systems).

Anions added			Anions sorbed							Al ²	E ³	Rf ⁴
P	T	OX	P ¹	P	T	OX	Total	mmol kg ⁻¹⁵				
AlMt1.6												
P + T + OX systems												
100	250	250	100	67	69	46	182	128	33.5	0.67		
200	200	200	200	114	67	43	224	116	42.9	0.64		
300	150	150	284	186	65	39	289	98	34.4	0.60		
400	100	100	342	234	60	28	322	72	31.7	0.47		
500	50	50	368	307	43	17	367	6	16.6	0.39		
T + OX/P systems												
200	200	200	200	98	75	47	220	174	51.3	0.63		
300	150	150	284	157	68	40	255	128	44.6	0.59		
400	100	100	342	199	62	31	292	105	41.8	0.50		
AlMt6												
P + T + OX systems												
100	250	250	100	87	65	59	211	68	12.7	0.91		
200	200	200	200	172	60	50	282	42	13.9	0.83		
300	150	150	283	247	59	48	354	24	12.7	0.81		
400	100	100	361	311	43	30	384	12	13.8	0.70		
500	50	50	428	351	38	19	407	2	18.1	0.50		
T + OX/P systems												
200	200	200	200	165	65	55	285	76	17.5	0.85		
300	150	150	283	230	60	48	338	51	18.7	0.80		
400	100	100	361	299	47	31	377	12	17.2	0.66		

¹ P = P adsorption amount in the absence of organic acids.

² Al = Al removed from the complexes.

³ E = Efficiency of organic acids to reduce P adsorption.

⁴ Rf = Final OX/T molar ratio.

⁵ Average error <5%.

mmol kg⁻¹ and 1, respectively, whereas the tartrate + oxalate/phosphate molar ratio ranged from 5 to 0.5.

The total amount of the adsorbed ligands increased by increasing phosphate concentration (Table 3), apparently because many sites, as discussed before, were specific for phosphate. The final oxalate adsorbed/tartrate adsorbed molar ratios (Rf) were always <1 and decreased by increasing the amount of phosphate initially added. In the absence of phosphate, by adding equimolar quantities of tartrate and oxalate, the Rf values were practically equal to 1.0 (Table 2). Evidently, tartrate competed with phosphate more than oxalate for the sites common to all the ligands, so that more tartrate than oxalate was adsorbed in the presence of phosphate. Probably, when mixtures of equimolar amounts of tartrate and oxalate were added before phosphate, oxalate initially adsorbed was replaced by phosphate more easily than tartrate.

The Rf values were lower when the ligands were added to AlMt1.6 than AlMt6. These results are expected because tartrate was adsorbed on AlMt1.6 more easily than oxalate (Figure 1). In addition, mixtures of

tartrate and oxalate were much more effective at inhibiting phosphate fixation than tartrate alone (Figure 5) and, as found for tartrate, were more effective for AlMt1.6 than AlMt6.

Many sites on the $\text{Al}(\text{OH})_x$ -montmorillonite complexes were probably specific only for phosphate (Figure 1), whereas many others, common to phosphate, tartrate, and oxalate, had a greater affinity for phosphate than for oxalate or tartrate. However, some surface sites of the complexes have a very high affinity for tartrate and others for oxalate. Evidently, when a mixture of ligands was added to the complexes, their effectiveness in preventing phosphate adsorption was greater, because more sites at high affinity for both the organic ligands were occupied by tartrate and oxalate than by tartrate alone. Finally, it was also confirmed that the efficiency of tartrate + oxalate in preventing phosphate adsorption was higher when these ligands were added to the clay minerals before phosphate.

In conclusion, the data show that: 1) the quantities of phosphate, tartrate, and oxalate adsorbed on the hydroxy aluminum montmorillonite complexes were related to the amounts of OH-Al species covering the montmorillonite surfaces, more than to the surface area of the complexes; 2) more phosphate than tartrate (or oxalate) was adsorbed on the clay minerals even when the initial concentration of the organic ligands was particularly high; 3) by adding the same amounts of oxalate and tartrate to the complexes, the final oxalate adsorbed/tartrate adsorbed molar ratio (Rf) was practically 1; 4) in the presence of phosphate the Rf values were always <1 and decreased with increasing phosphate, indicating that tartrate competed with phosphate more than oxalate for the sites common to all the ligands; 5) the efficiency of tartrate in preventing phosphate adsorption on AlMt1.6 and AlMt6 increased by increasing the initial tartrate/phosphate molar ratio (ri) and when tartrate was added 2 h before phosphate; 6) tartrate and oxalate added as a mixture were much more effective in inhibiting phosphate sorption than tartrate or oxalate alone; and 7) the efficiency of tartrate alone or in mixture with oxalate in preventing phosphate adsorption was greater on the complex containing a lower amount of OH-Al species coating the montmorillonite surfaces (AlMt1.6), probably because a greater proportion of sites specific for the organic ligands was present on AlMt1.6 than on AlMt6 complex.

In the rhizosphere, the release of many different low-molecular weight organic ligands by roots of plants and microorganisms may play an important role in phosphate availability by preventing phosphate adsorption on variable charge minerals which usually are formed in rhizosphere soils.

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