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PROJECT NO. I-461-82

**Sorption and Desorption of Ortho-Phosphate from
Reference and Soil Clay as Influenced by Chemical
Factors Existent Near Plant Roots**

U. Kafkafi, G. Sposito, S. Traina, B. Bar-Yosef

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Abstract

The effect of citric, formic and tartaric acids and their anions, sodium bicarbonate and amino carboxylate on the adsorption and dissolution of phosphate from soil clay mineral separates and pure clay minerals, was studied. The purpose of that study was to investigate the effect of organic compounds, known to be excreted from roots of various crops, on the reactions of P with surfaces of clay minerals.

It was shown that organic compounds containing one or more OH groups displace adsorbed P from clay particles. Amino compounds increase the affinity of the phosphate to 2:1 clay surfaces, even if they contain OH groups in their molecule. The systematic study of P adsorption as a function of pH, ionic strength and organic ligand concentration have led us to suggest a unified explanation of the phenomena of phosphate adsorption. Maximum P adsorption occurs at pH 5.1 on kaolinite and at pH 6.2 on montmorillonite. These values are very close to the PZC of these clays. At dilute suspension of 2:1 smectite minerals no phosphate interacted with the clay. When the clay collapsed due to high ionic strength or to H-bonding due to amino acid adsorption the broken edges of the mineral expose active aluminum sites that are capable to bind phosphate.

This work has put forward explanations and clarified the mechanism of phosphate binding to clay minerals. The major practical outcome of this research is that it was shown that high salt concentration increases the phosphate binding to the clay.

It suggests that under saline soil conditions higher phosphate application will be needed to supply enough phosphate to plant growth.

3. Objectives and Significance of Research

3.1. Objectives

1. To describe quantitatively the concentration of o-phosphate in aqueous solution, when the conditions for both adsorption and precipitation reactions exist simultaneously, as a function of: pH value, the concentration competing anions, and phosphate-precipitating cations, adsorbing surface characteristics, ionic strength, and the adsorbent-aqueous solution ratio.

2. To study the effects of the above-mentioned factors on the kinetics of adsorption and desorption processes for o-phosphate.

3. To develop and compare reasonably simple, chemically-based models of o-phosphate adsorption and precipitation reactions in the presence of root excretion products.

Effects of pH and Organic Acids on Orthophosphate Solubility in an Acidic, Montmorillonitic Soil¹

SAMUEL J. TRAINA, GARRISON SPOSITO, DEAN HESTERBERG, AND U. KAFKAFI²

ABSTRACT

The effects of pH and organic acid addition on residual orthophosphate (*o*-phosphate) solubility in an acidic, montmorillonitic soil separate suspended in 20 mol NaCl m⁻³ were investigated. In the absence of added organic acid, the solubility of residual *o*-phosphate in the soil decreased as the pH value was increased from 4 to 7. With *o*-phosphate additions that resulted in low aqueous-solution *o*-phosphate concentrations, the soil sorbed more *o*-phosphate at pH 7 than at 5.5. The solubility data appeared consistent with the presence of an Al-phosphate solid whose formation was initiated through the hydrolysis of exchangeable Al³⁺ and subsequent reaction of the hydrolytic product with *o*-phosphate in aqueous solution. Additions of citric, tartaric, or formic acid at low concentrations (<0.1 mol m⁻³) produced a drop in residual *o*-phosphate solubility at pH 5.5 and 7.0. In the case of citric acid, *o*-phosphate solubility gradually returned to its value in the absence of organic ligand as the ligand concentration was increased to 0.6 mol m⁻³, whereas no such increase occurred in the case of tartaric or formic acid. This behavior was rationalized as the outcome principally of two competing reactions: (i) the reaction of adsorbed, polymeric hydroxy-Al with organic ligand to form an exchangeable Al species that combined with *o*-phosphate to reduce its solubility, and (ii) the complexation of adsorbed Al to form a soluble Al-organic complex that did not subsequently combine with *o*-phosphate. The latter reaction was important only for citric acid. The former reaction, favored by a large stability constant for Al-organic acid adducts, produced *o*-phosphate solubility decreases in the order citrate > tartrate > formate.

Additional Index Words: Al-organic complexes, Al phosphates, exchangeable Al, phosphate sorption reactions.

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THE MAGNITUDE of organic acid production in the rhizosphere and its influence on the availability of *o*-phosphate to higher plants remain controversial issues in the literature of soil-plant relations (see e.g., Tinker, 1981; Hedley et al., 1982; 1983; Whipps and Lynch, 1983; Whipps, 1984, and the references cited in these papers). From the perspective of soil chem-

istry, the issue can be focused on the processes that affect the concentration of *o*-phosphate in a soil solution to which carboxylic or amino acids have been introduced (Nagarajah et al., 1968; Hale and Moore, 1979; Tinker, 1980; Olsen and Khasawneh, 1980, and the references cited therein). Much research has been published over the past 35 yr concerning the effects of organic acids on *o*-phosphate sorption (Swenson et al., 1949; Deb and Datta, 1967a,b; Nagarajah et al., 1968; 1970; Chen et al., 1973a; Kuo and Lotse, 1974; Earl et al., 1979; Lopez-Hernandez et al., 1979) and three principal categories of organic acid-*o*-phosphate interaction have been identified. These are: (i) competitive sorption reactions (Nagarajah et al., 1968; Lopez-Hernandez et al., 1979), (ii) dissolution of *o*-phosphate adsorbents by organic ligands (Chen et al., 1973a; Earl et al., 1979), and (iii) modification of the surface charge on *o*-phosphate adsorbents by organic ligand adsorption (Nagarajah et al., 1968; Kwong and Huang, 1979). Category (i) refers to the breaking and forming of metal *o*-phosphate bonds in either surface complexes or precipitates; category (ii) refers to the well known chemical weathering of soil inorganic materials by organic acids (Robert et al., 1979; Stevenson, 1982, Chap. 18), and category (iii) refers to an indirect effect of organic ligand adsorption on *o*-phosphate adsorption.

In acidic soils, all three categories of *o*-phosphate-organic acid interaction are mediated by protons and the effect of pH alone on *o*-phosphate solubility must be appreciated clearly. This topic has been reviewed recently by Haynes (1982) and by White (1981; 1983), who point out that most studies of acidic soils in which aluminosilicates are the dominant adsorbents show that *o*-phosphate solubility either decreases with increasing pH or exhibits no significant change. The chemical basis for this common observation appears to be the hydrolysis of exchangeable (i.e., KCl-extractable) Al(III) and the subsequent reaction of the newly-formed surface hydrolytic species with *o*-phosphate from the soil solution (Haynes, 1982; White, 1983). If Al(III) on a soil adsorbent is already hydrolyzed extensively at low pH values, increasing the pH will not decrease *o*-phosphate solubility (White and Thomas, 1981; Haynes, 1982). White (1983) has suggested that any soil in which the exchangeable Al(III) content exceeds 20 mmol kg⁻¹ at low pH will show a decrease in soluble *o*-phosphate with increasing pH up to 7.0, whereas any soil in which the exchangeable Al(III) content falls below 2 mmol kg⁻¹ will not.

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The pioneering studies of Wild (1953) and Coleman et al. (1960) on *o*-phosphate sorption reactions with montmorillonite can be taken as the basis for a detailed application of the concepts discussed above to *o*-phosphate solubility in acidic, montmorillonitic soils. Coleman et al. (1960) demonstrated that: (i) montmorillonite without exchangeable Al(III) does not react significantly with *o*-phosphate at low pH and ionic strength, (ii) Al-montmorillonite can react with *o*-phosphate at low pH to form $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4(\text{s})$ once the exchangeable Al(III) has been displaced by the metal cations in an added electrolyte, and (iii) Al-montmorillonite can react with *o*-phosphate at $\text{pH} < 7$ to form the amorphous solid $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4(\text{s})$ after hydrolysis of the exchangeable Al(III). The solid-phase Al-phosphate product was shown by Coleman et al. (1960) to have a pK_{so} ($= \text{pAl}^{3+} + 2\text{pOH}^- + \text{pH}_2\text{PO}_4^-$) of 27.8 ± 0.1 . Other studies of *o*-phosphate sorption reactions with aluminosilicates or Al-bearing solid organic matter under acidic conditions also have suggested this Al-phosphate product and have served to bracket its pK_{so} value between 27 and 29 (Cole and Jackson, 1950; Taylor and Gurney, 1962; Chen et al., 1973b; Gebhardt and Coleman, 1974; Veith and Sposito, 1977; Bloom, 1981). Robarge and Corey (1979) have simulated *o*-phosphate sorption behavior using an Al-saturated sulfonic resin to mimic a constant-charge, Al-bearing adsorbent. Their data for P/Al molar ratios > 0.5 in the Al-hydroxy polymers adsorbed by the resin were consistent with the precipitation of Al-phosphate as described above with a pK_{so} value of 28.2 ± 0.1 (Corey, 1981).

This perspective on the role of exchangeable Al(III) in *o*-phosphate solubility is broadened, in the context of the present study, by the recent experiments of Kwong and Huang (1979) and Goh and Huang (1984) concerning the influence of organic acids on Al(III) hydrolysis. Kwong and Huang (1979) have shown that the progress of normal Al(III) hydrolysis is perturbed increasingly by an organic acid (at a given concentration) the greater is the stability of its Al(III) complexes. Thus, for example, the order of increasing hindrance of Al(III) hydrolysis among the three organic acids, citric (2-hydroxypropane-1,2,3-tricarboxylic acid), tartaric (*D*-2,3-dihydroxybutane acid), and formic (methanoic acid), would be formic $<$ tartaric $<$ citric because this is the order of the stability constants for their 1:1 complexes with Al(III) (Martel and Smith, 1977; Kwong and Huang, 1979). Complementary to this insight, Goh and Huang (1984) have shown that citric acid additions to montmorillonite suspensions equilibrated with solutions containing hydrolyzed Al(III) reduce the adsorption of Al(III) hydrolytic species in favor of exchangeable Al(III). Moreover, if the concentration of citric acid is large enough, exchangeable Al(III) is displaced in favor of the formation of soluble Al(III)-citric acid complexes. These results suggest that metal-complexing organic acids tend to augment exchangeable Al(III) on montmorillonite because they inhibit hydrolysis and that, at sufficiently high concentrations, they solubilize exchangeable Al(III). The former effect should decrease *o*-phosphate solubility at a given pH value because it increases the quantity of potentially hydrolyzable adsorbed Al(III), whereas the latter effect should increase

Table 1. Chemical properties of the Altamont soil separate.

| pH _e | Exchangeable Na | Organic C | Total P† | Extractable Al | |
|-----------------|----------------------|-----------|------------|-----------------------|---------|
| | | | | CDB‡ | oxalate |
| | mol kg ⁻¹ | | | mmol kg ⁻¹ | |
| 6.6 ± 0.1 | 0.60 ± 0.01 | 2.9 ± 0.8 | 13.5 ± 0.3 | 49 ± 5 | 82 ± 11 |

† By HF digestion.

‡ Citrate-dithionite-bicarbonate.

o-phosphate solubility because it decreases the quantity of potentially hydrolyzable adsorbed Al(III).

In this paper, the conceptualizations summarized above concerning *o*-phosphate solubility in model systems containing Al-montmorillonite and organic acids will be tested for an acidic, montmorillonitic soil separate (Fletcher et al., 1984). The objective of the present investigation is to determine the effects of pH and added organic acid concentration on the solubility of residual *o*-phosphate in the soil. The organic acids selected were citric, tartaric, and formic acid, representing tri-, di-, and mono-carboxylic ligands for metal binding. The choice of organic acids and of their range of concentration were considered representative of rhizosphere conditions (W.M. Jarrell, 1983, personal communication) and of the spectrum of differing stability for Al(III)-organic acid complexes. The largest organic acid concentration used (0.6 mol m^{-3}) was small enough to preclude massive soil mineral dissolution during the solubility experiments (Robert et al., 1979; Earl et al., 1979).

MATERIALS AND METHODS

Soil Separate

A sample of the 0- to 0.15-m depth of Altamont clay loam (fine, montmorillonitic, thermic Typic Chromoxererts) was used in this study. The pH value of the saturated soil paste (pH_{sp}) is 5.7 and the content of organic C is $29 \pm 1 \text{ g kg}^{-1}$ soil. The method of preparation of a Na-saturated soil separate which comprises principally silt and clay has been described in detail by Fletcher et al. (1984). Stock suspensions of the Na-saturated separate in $20 \text{ mol NaCl m}^{-3}$ were prepared following this method and then stored under refrigeration in polyethylene bottles. Some chemical properties of the separate determined by standard procedures (Page et al., 1982) are listed in Table 1. The NaHCO_3 -extractable P in the separate amounted to $3.0 \pm 0.1 \text{ mmol kg}^{-1}$ and the KCl-extractable Al was $5.2 \pm 0.8 \text{ mmol kg}^{-1}$. To the extent that these results characterize "exchangeable" chemical species, it may be inferred that the pool of exchangeable *o*-phosphate in the separate is relatively large (Olsen and Sommers, 1982, p. 422) whereas that of exchangeable Al is relatively small in respect to its potential effect on *o*-phosphate solubility (White, 1983).

Solubility Experiments

Sorption Isotherms

A quantity of the stock soil separate suspension containing $0.40 \pm 0.02 \text{ g}$ solids was placed into a tared 250-mL polycarbonate centrifuge bottle and approximately 0.2 kg of $20 \text{ mol NaCl m}^{-3}$ solution was added. The pH of the NaCl solution had been adjusted previously with HCl or NaOH to provide a final value of either 5.5 or 7.0 in the soil suspension. Aliquots of $1 \text{ mol H}_3\text{PO}_4 \text{ m}^{-3}$ in $20 \text{ mol NaCl m}^{-3}$ at pH 5.5 or 7.0 were added to give initial *o*-phosphate concentrations between 0 and 100 mmol m^{-3} . The suspension

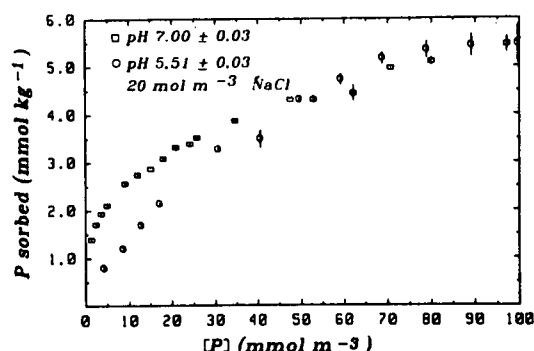


Fig. 1. Sorption isotherms for *o*-phosphate on the Na-Altamont soil separate at 298 K. Vertical bars denote one standard deviation.

density was 2.00 ± 0.05 g oven-dry soil separate kg^{-1} for all experiments, which were conducted in duplicate. The reaction bottles were shaken at 298 K for 24 h, then centrifuged (19 745 RCF) at 295 K for 30 min. A subsample of the supernatant solution was removed for pH measurement while the remainder of the solution was passed through a Nucleopore 0.2- μm polycarbonate filter membrane and saved for chemical analysis.

The control samples (i.e., those not reacted with added *o*-phosphate) for the pH 5.5 and 7.0 sorption experiments were reacted with Cl-saturated exchange resin (Olsen and Sommers, 1982) to estimate residual sorbed *o*-phosphate. The total residual sorbed *o*-phosphate in the soil-separate suspension, taken equal to the sum of the resin-extractable P and the total solution P in the control samples, was 2.85 ± 0.07 and 2.02 ± 0.03 mmol kg^{-1} soil at pH 5.5 and 7.0, respectively.

The total sorbed *o*-phosphate in each experiment was calculated from the difference between the initial and final solution concentrations of *o*-phosphate, corrected for the amount of residual sorbed *o*-phosphate in the control samples.

Residual *o*-phosphate Solubility at Varying pH Values

A quantity of the stock soil separate suspension containing 0.40 ± 0.02 g solids was placed into a tared 250-mL polycarbonate centrifuge bottle and approximately 0.2 kg of 20 mol NaCl m^{-3} solution was added. The pH of the NaCl solution had been adjusted with HCl or NaOH to provide a final pH value between 4 and 9 in the soil separate suspension. Duplicate samples were prepared for each experiment. The suspension density was 2.00 ± 0.05 g oven-dry soil separate kg^{-1} of solution. The reaction bottles were shaken at 298.0 ± 0.3 K for 24 h, then centrifuged at 19 745 RCF for 30 min and filtered as described above.

Organic Acid Experiments

A quantity of the stock soil separate suspension containing 0.40 ± 0.02 g solids was placed into a tared 250-mL polycarbonate centrifuge bottle and approximately 0.2 kg of acidified, 20 mol NaCl m^{-3} solution was added. The pH of the NaCl solution had been adjusted previously with HCl to provide a final pH value of 5.5 in the soil suspension. Aliquots containing 10 mol m^{-3} citric, tartaric, or formic acid (Baker, analyzed reagent-grade) in 20 mol NaCl m^{-3} at pH 5.5 were added to provide initial concentrations of added organic ligand ranging from 0 to 600 mmol m^{-3} . Orthophosphate-organic acid interactions at pH 7.0 were studied following an identical procedure except that 10 mol m^{-3} citric, tartaric, or formic acid in 20 mol NaCl m^{-3} at pH 7 was added to suspensions adjusted to pH 7. Duplicate samples were prepared for all experiments. The suspension density was 2.00 ± 0.05 g soil separate kg^{-1} for all samples.

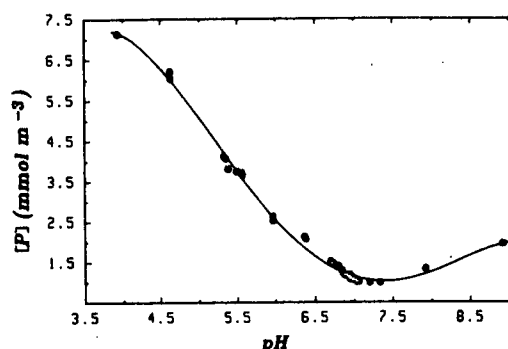


Fig. 2. Effect of pH on residual *o*-phosphate solubility for the Na-Altamont soil separate in a background of 20 mol NaCl m^{-3} . Vertical bars denote one standard deviation.

The reaction bottles were shaken at 298 K for 24 h, then centrifuged and filtered as described above.

Chemical Analysis

Solution concentrations of *o*-phosphate were determined by a molybdenum blue colorimetric procedure (Olsen and Sommers, 1982). Preliminary analysis indicated that the presence of 0 to 600 mmol m^{-3} citric, tartaric, or formic acid had no apparent effect on the colorimetric determination of *o*-phosphate. Thus the organic acids were not included in the colorimetric standards. Solution concentrations of Ca were measured with a Perkin-Elmer model 5000 atomic absorption spectrophotometer equipped with a background corrector using NO_2 -acetylene flame atomization. Solution concentrations of Al at pH 5.5 and 7.0 for the samples in NaCl background alone were determined by inductively-coupled plasma spectroscopy. All pH measurements were made with a Beckman model 71 pH meter equipped with an automatic temperature compensator and a glass/calomel electrode pair.

RESULTS AND DISCUSSION

Sorption isotherms for *o*-phosphate on the soil separate at pH 5.5 and 7.0 are plotted in Fig. 1, where the vertical lines indicate standard deviations for duplicate experiments. The shape of each isotherm is an L-curve, characteristic of *o*-phosphate sorption reactions (Sposito, 1984, Chap. 4). Unlike the isotherms for typical hydrous oxide adsorbents (Goldberg and Sposito, 1984), the isotherms for the Na-Altamont soil at lower *o*-phosphate concentrations show an increase in sorption with pH. At higher *o*-phosphate concentrations, the two sorption isotherms in Fig. 2 coalesce, but a distribution-coefficient plot of the data (Sposito, 1984, p. 119) indicated that neither isotherm was close to a sorption maximum, so no conclusion as to the effect of pH on the sorption maximum could be drawn.

Approximate ion-activity products (IAP) for hydroxyapatite, the least soluble Ca-phosphate expected to form under the conditions of the experiments, were calculated at each point on the isotherms with the pH values and total Ca and P concentrations measured in the supernatant solutions. The values estimated for $\log \text{IAP}$ always were four or more log units smaller than $\log K_{\text{so}}$ for hydroxyapatite (14.5; Lindsay, 1979, p. 165), indicating that the sorption process did not involve Ca-phosphate precipitation.

The solubility of residual *o*-phosphate in the Na-Altamont soil separate as influenced by pH in a 20

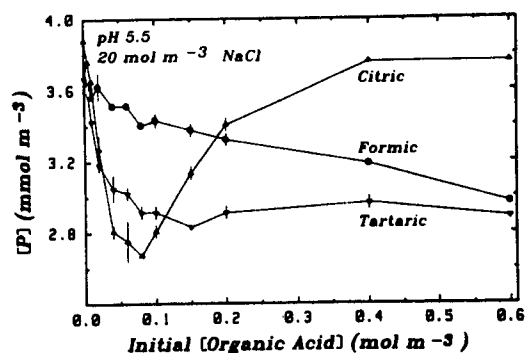


Fig. 3. Effect of organic acid addition at pH 5.5 on *o*-phosphate solubility for the Na-Altamont soil separate in a background of 20 mol NaCl m⁻³. Vertical bars denote one standard deviation.

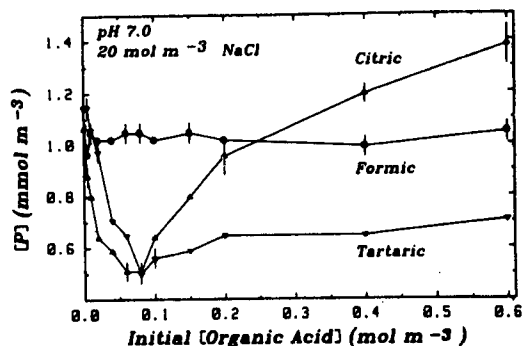


Fig. 4. Effect of organic acid addition at pH 7.0 on *o*-phosphate solubility for the Na-Altamont soil separate in a background of 20 mol NaCl m⁻³. Vertical bars denote one standard deviation.

mol NaCl m⁻³ background is depicted in Fig. 2. The data show clearly that a solubility minimum is achieved near pH 7.2, where the *o*-phosphate concentration in the aqueous solution phase was 25% of its value at pH 3.93 (7.1 mmol m⁻³). These results show a trend opposite to that expected for the solubility of an Al-phosphate under acidic conditions with the Al³⁺ activity controlled by dissolution of a clay mineral (Lindsay, 1979, Fig. 12.2), but they correspond very well with the solubility data for *o*-phosphate in the presence of exchangeable Al(III) on montmorillonite, reported in the classic study of Coleman et al. (1960), and with the general hypotheses advanced by White (1983) concerning pH effects on *o*-phosphate solubility in acidic soils containing exchangeable Al(III).

Evidently the hydrolysis of exchangeable Al(III) in the soil separate as pH increased provided additional reactant material for *o*-phosphate sorption processes, causing a decrease in solubility. That the sorption process did not involve the formation of a Ca-phosphate (except possibly above pH 8) was verified through a calculation of log IAP for hydroxyapatite as described above. The total Al concentration in the supernatant solution at pH 5.5 (10.3 ± 0.9 mmol m⁻³) and 7.0 (4.8 ± 0.6 mmol m⁻³) was used along with the corresponding pH value and *o*-phosphate concentration to estimate a log IAP corresponding to the solid, Al(OH)₂H₂PO₄(s). The results, log IAP = 28.9 (pH 5.5) and 31.8 (pH 7.0), are consistent at the lower pH value with the pK_a values for Al(OH)₂H₂PO₄(s) reported by Coleman et al. (1960) and a number of other investigators, as discussed above. Thus it may be inferred that the *o*-phosphate solubility data in Fig. 2 could represent as one mechanism the precipitation of Al(OH)₂H₂PO₄(s). The upper stability limit for this compound in soil is expected to be near pH 7 (Veith and Sposito, 1977). Above pH 7, the formation of other *o*-phosphates and/or of Al(OH)₃(s) is favored.

Figures 3 and 4 show the effect of citric, tartaric, and formic acid additions on the solubility of residual *o*-phosphate in the Na-Altamont soil separate initially at pH 5.5 or 7.0, respectively. In the case of citric acid, there is a sharp decline in *o*-phosphate solubility with increasing organic ligand concentration up to 80 mmol m⁻³, regardless of initial pH value, then a gradual increase in *o*-phosphate solubility until it approaches (pH 5.5) or slightly exceeds (pH 7.0) its value in the ab-

sence of organic ligand. These data are consistent with a mechanism in which the organic ligand at low concentration acts principally to increase the quantity of exchangeable Al(III) through displacement of hydroxyls from adsorbed Al-OH polymers by ligand exchange, thereby enhancing the potential for reaction with *o* phosphate, and at higher concentrations acts principally to decrease the quantity of exchangeable Al(III) in favor of soluble complexes that do not react with *o*-phosphate to reduce its solubility. Ultimately, complete displacement of exchangeable Al(III) by the organic ligand should occur at high ligand concentrations and *o*-phosphate solubility should increase even above its value in the absence of the ligand, parallel with the observations made by Earl et al. (1979).

The effect of tartaric or formic acid on residual *o*-phosphate solubility was less variable than that of citric acid. Tartaric acid produced the same sharp decline in solubility at low organic ligand concentrations as did citric acid, but the recovery of the solubility toward its initial value was slight as the organic acid concentration was increased. Formic acid was unable to produce a sharp decline in solubility at pH 5.5 and its total effect on *o*-phosphate solubility at pH 7 was almost negligible. These differences, given the ligand-exchange mechanism described above, can be correlated with the differences in log stability constants for 1:1 Al(III) complexes among the three organic acids: 7.4 (citric) > 6.0 (tartaric) > 2.0 (formic). Evidently, the stability of the Al(III)-tartaric acid complex is sufficient to cause hydroxyl displacement from adsorbed Al(III) but is not great enough to promote the complete displacement of exchangeable Al(III), whereas that of the Al(III)-formic acid complex is not sufficient even to mitigate strongly the hydrolysis of adsorbed Al(III).

Additional insight can be gained from Fig. 5, which shows the final pH values corresponding to the solubility data points in Fig. 3 and 4. For the experiments initiated at pH 5.5, the pH values as a function of the initial organic acid concentration are essentially the inverse of the *o*-phosphate solubility curves in Fig. 3. For example, the sharp decline in solubility is paralleled by a sharp rise in pH for the citric and tartaric acid experiments, and the slow decline in solubility produced by formic acid additions is mirrored by a slow rise in pH. The rising portions of all the pH curves

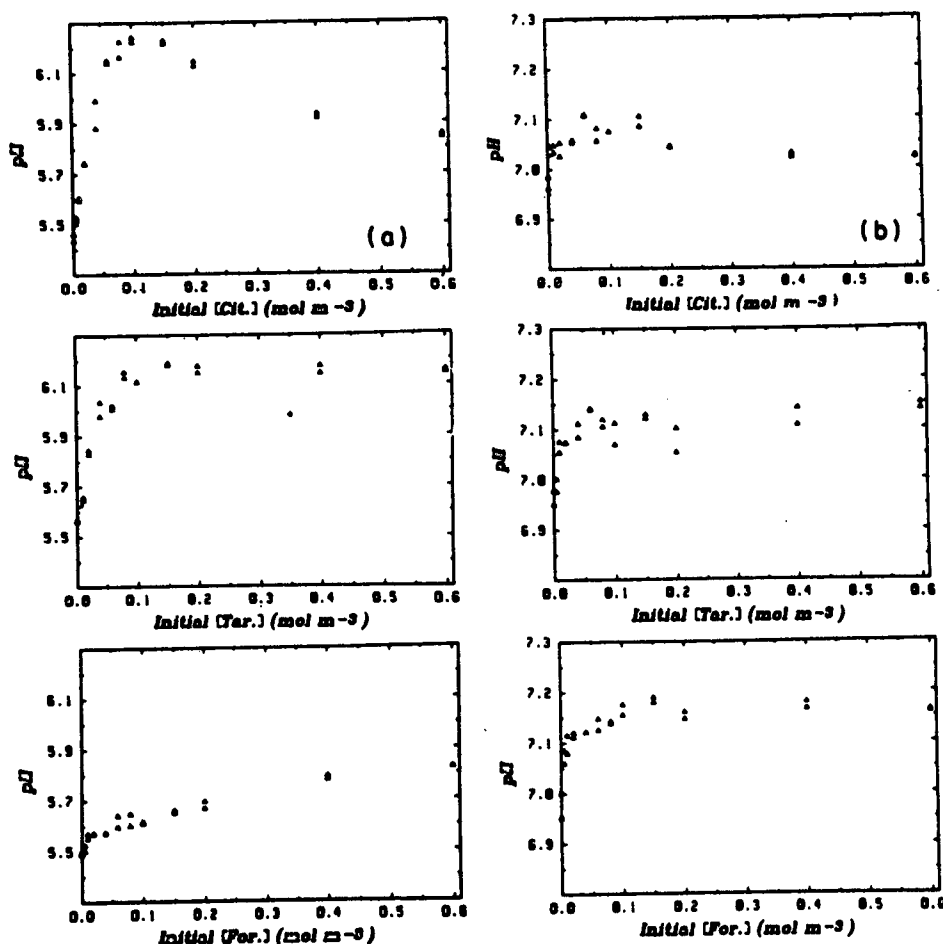


Fig. 5. Final pH_f values for the solubility experiments in Fig. 3 and 4: (a) initial pH_i = 5.5 (b) initial pH_i = 7.0.

are consistent with the replacement of hydroxyl groups bound to adsorbed Al(III) by organic ligands, a process which produces free OH⁻(aq) and renders the Al(III) exchangeable (Goh and Huang, 1984). It is possible that some of the newly-exchangeable Al(III) then can be displaced by Na⁺ from the background electrolyte to react with *o*-phosphate in solution to form either Al(OH)₂H₂PO₄(s), as proposed by Coleman et al. (1960), or possibly an Al-organic-phosphate solid (LeVesque and Schnitzer, 1967; Sinha, 1971a,b).

The possibility that Na⁺ in the 20 mol NaCl m⁻³ background can displace exchangeable Al(III) was supported indirectly in the present study by a comparative measurement of residual *o*-phosphate solubility in the absence of added electrolyte. At pH 5.0 the solubility in deionized water was 10.7 ± 0.1 mmol m⁻³ and it decreased to 6.8 ± 0.1 mmol m⁻³ at pH 6.2. These two values are much larger than the solubilities of 5.0 and 2.3 mmol m⁻³ measured at the same pH values in 20 mol NaCl m⁻³ (Fig. 2). Similar results were reported by Coleman et al. (1960) for Al-montmorillonite/*o*-phosphate suspensions and attributed to the displacement of exchangeable Al(III) by the metal cation of the background electrolyte. The same effect appeared in the model Al-resin/*o*-phosphate system studied by Robarge and Corey (1979, Fig. 2b). In the present experiments, the deionized water extracts ex-

hibited a pronounced yellow color relative to the NaCl extracts. Given that this color indicated an increased concentration of soluble organic matter, it is possible that some of the increase in *o*-phosphate solubility observed in the deionized water extracts resulted from soluble Al(III)-*o*-phosphate-organic matter complexes.

The falling portion of the pH curve in Fig. 5a for citric acid is consistent with the full complexation of exchangeable Al(III) and its removal to the aqueous solution phase as a 1:1 Al(III)-citrate complex. At pH 5.5 only two of the three titratable protons in a citric acid molecule are dissociated (Martell and Smith, 1932) and, therefore, full complexation of exchangeable Al(III) by the organic ligand would release one proton per complexed metal ion (Kwong and Huang, 1979), causing the initial pH value to drop. The soluble Al(III)-citrate complex formed is protected against both hydrolysis and *o*-phosphate reaction. At pH 7.0, soluble complex formation with exchangeable Al(III) is still possible, but no pH change should accompany it because all three titratable protons per citric acid molecule are dissociated. The plateau in the pH curve for citric acid in Fig. 5b is consistent with this mechanism.

The solubility-pH relationship in Fig. 2 can be represented mathematically by the overlapping regression equations:

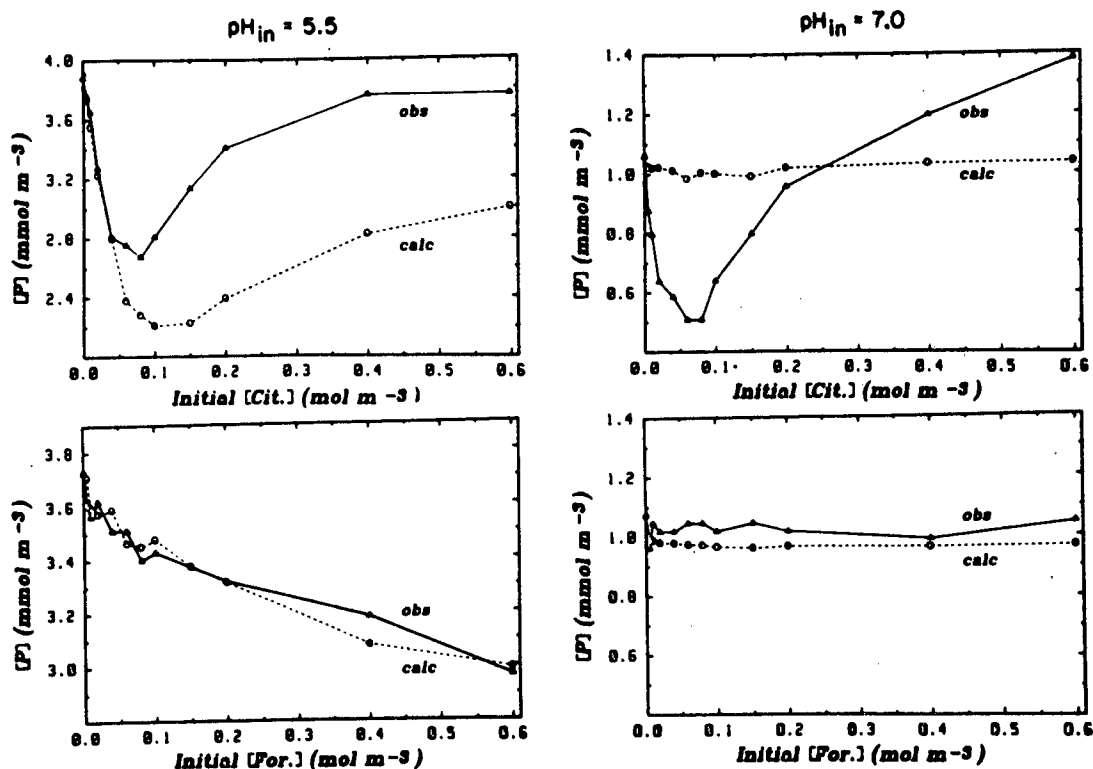


Fig. 6. Comparison of observed *o*-phosphate solubility in the presence of citric or formic acid and 20 mol NaCl m⁻³ with calculated values based on Eq. [1] and the pH_a values in Fig. 5.

$$[P] = -6.727 + 11.357 \text{ pH} - 2.658 (\text{pH})^2 + 0.171 (\text{pH})^3 \quad (r^2 = 0.99) \quad [1a]$$

for $3.93 \leq \text{pH} \leq 7.06$ and

$$[P] = 1358.548 - 670.14 \text{ pH} + 123.667 (\text{pH})^2 - 10.11 (\text{pH})^3 + 0.31 (\text{pH})^4 \quad (r^2 = 0.99) \quad [1b]$$

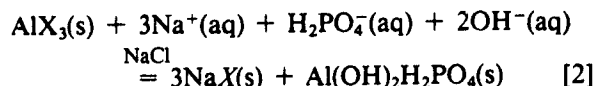
for $6.85 \leq \text{pH} \leq 8.94$, where $[P]$ is the *o*-phosphate concentration in mmol m⁻³. Given the inverse relationship between *o*-phosphate solubility and pH implied by Fig. 3 and 5, together with the pH effect shown in Fig. 2, it is reasonable to ask whether the solubility curves in Fig. 3 can be calculated with Eq. [1] and the pH values in Fig. 5. If this kind of calculation produces good estimates of *o*-phosphate solubility, it would suggest that the only role played by the organic acid is through the conversion of adsorbed, hydrolyzed Al(III) to exchangeable Al(III), which raises the pH value and shifts the solubility down the curve in Fig. 2.

Figure 6 compares *o*-phosphate solubilities calculated in this way to their measured values for citric and formic acid at initial pH 5.5 and 7.0. The results for tartaric acid (data not shown) were qualitatively the same as for citric acid, but the observed difference between the actual *o*-phosphate solubility and that predicted on the basis of the final pH alone was less pronounced for the former organic acid. On the other hand, *o*-phosphate solubility in the presence of formic acid was predicted reasonably well. The data obtained near pH 5.5 suggest that complexation of Al(III) by the organic acids competes with the conversion of ad-

sorbed Al(III) to an exchangeable form, thereby increasing *o*-phosphate solubility in the order: citric acid > tartaric acid > formic acid, with the latter exhibiting no significant effect. This result is consistent with the order of stability constants for 1:1 complexes of these acids with Al(III) (Martell and Smith, 1977; Kwong and Huang, 1979), as stated previously. It appears that formic acid acts primarily to convert adsorbed Al(III) to an exchangeable form and not to inhibit *o*-phosphate sorption through soluble Al(III) complex stability.

CONCLUSIONS

The effects of pH and organic acid addition on *o*-phosphate solubility in a montmorillonitic separate from Altamont clay loam are consistent with the results of previous model experiments on *o*-phosphate reactions with Al-montmorillonite. The effect of pH in the absence of added organic acids is consistent with the overall reaction scheme proposed by Coleman et al. (1960):



in a NaCl background, where X refers to 1 mol of montmorillonite surface charge. Equation [2] represents a mechanism in which Na⁺ displaces exchangeable Al(III) that subsequently reacts with *o*-phosphate to form a solid Al-phosphate. This mechanism differs fundamentally from the ligand-exchange adsorption mechanism characteristic of *o*-phosphate reactions

with hydrous oxides (Goldberg and Sposito, 1984). In particular, Eq. [2] requires the presence of exchangeable Al(III) and implies a decrease of *o*-phosphate solubility with increasing pH or increasing background electrolyte concentration.

The effects of added organic acid (at fixed pH) on *o*-phosphate solubility can be rationalized with two competing reactions. At lower organic acid concentrations, the principal reaction scheme is the exchange of OH for L (L = citrate, tartrate, or formate) in an adsorbed, polymerized hydroxy-Al(III) species, followed by a cation exchange reaction between an exchangeable Al-L complex and Na⁺ to promote the formation of an Al-phosphate. Since OH/Al molar ratios > 2 typically in adsorbed hydroxy-Al polymers (Veith and Sposito, 1979; Robarge and Corey, 1979), there is a net production of OH⁻(aq) that leads to the pH increases noted in Fig. 5. At high organic acid concentrations, the principal adsorbed Al(III) reaction with the ligand L is the formation of a soluble Al-organic complex and the production of H⁺(aq) if L is protonated. These two extremal reactions compete to provide the net *o*-phosphate solubility curves in Fig. 3 and 4. It is evident that both extremal reactions are favored by large stability constants for Al(III)-organic acid adducts and the differences between the curves in Fig. 3 and 4 reflect this kind of influence. The mechanisms proposed here do not provide a comprehensive description of the *o*-phosphate-organic acid interaction, but they suffice to account qualitatively for the behavior in Fig. 3 to 5.

ACKNOWLEDGMENTS

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Effects of Ionic Strength, Calcium, and Citrate on Orthophosphate Solubility in an Acidic, Montmorillonitic Soil¹

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ABSTRACT

A recent study by the authors of the effects of pH and organic acids on residual orthophosphate solubility in an acidic, montmorillonitic soil (Typic Chromoxererts) was extended to include variations of ionic strength (NaCl background) and Ca^{2+} concentration at fixed ionic strength. The objective of the experiments was to elucidate further the mechanism of orthophosphate solubility in a montmorillonitic soil containing exchangeable Al(III) and added citric acid. At ionic strengths between 20 and 100 mol m^{-3} (NaCl) and Ca^{2+} concentrations between 1 and 5 mol m^{-3} at 20 mol m^{-3} ionic strength (NaCl background), additions of citric acid at low concentrations (<0.1 mol m^{-3}) reduced orthophosphate solubility. The solubility then gradually returned to its value in the absence of added organic acid as the citric acid concentration was increased to 0.6 mol m^{-3} . The only significant effect of increasing the ionic strength or the Ca^{2+} concentration was to decrease orthophosphate solubility at any level of citric acid addition. Orthophosphate-citric acid in-

teractions in the soil were influenced only quantitatively, probably through the displacement of exchangeable Al(III) by Na^+ and/or Ca^{2+} , by increasing the concentration of these two metal cations in the soil solution.

Additional Index Words: aluminum-organic complexes, Al phosphates, exchangeable Al, phosphate precipitation.

Traina, S.J., G. Sposito, D. Hesterberg, and U. Kafkafi. 1986. Effects of ionic strength, calcium, and citrate on orthophosphate solubility in an acidic, montmorillonitic soil. *Soil Sci. Soc. Am. J.* 50:623-627.

EXTENDING THE CLASSIC investigation by Coleman et al. (1960) on orthophosphate (*o*-phosphate) reactions in a model Al-montmorillonite system, Traina et al. (1986) recently studied the effects of pH and organic acid addition on *o*-phosphate solubility in a suspension of Altamont clay loam (fine, montmorillonitic, thermic Typic Chromoxererts) in a 20 mol m^{-3} NaCl background. The principal results of their study were: (i) an observed decrease in residual *o*-phosphate solubility as the suspension pH value was increased from 4 to 7 with no organic acid present; (ii) a sharp

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decrease in *o*-phosphate solubility with additions of low concentrations ($<0.1 \text{ mol m}^{-3}$) of citric, tartaric, or formic acid at initial pH values of 5.5 and 7.0, and (iii) a gradual recovery of the *o*-phosphate solubility to its value in the absence of organic ligand as the concentration of citric acid was increased to 0.6 mol m^{-3} . These results were interpreted as consistent with a sorption mechanism involving the reaction of *o*-phosphate with hydrolyzed, exchangeable Al(III) to form $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4(\text{s})$, as first proposed explicitly by Coleman et al. (1960). The effect of pH and organic acids on this mechanism is principally to alter the quantity of *o*-phosphate-reactive Al(III) on the soil clay fraction. Increased pH also increases the extent of Al(III) hydrolysis and enhances the possibility of basic Al-phosphate formation. Organic ligand addition at low concentrations increases the amount of exchangeable (KCl-extractable) Al(III) that subsequently can react to form an Al-phosphate solid (Goh and Huang, 1984). As the concentration of organic ligand increases, and if the ligand forms strong complexes with Al(III), soluble Al-organic complexes compete with Al-phosphate formation to restore *o*-phosphate solubility (Traina et al., 1986).

Fundamental to the sorption mechanism proposed above is the accessibility of adsorbed Al(III) to reaction with dissolved *o*-phosphate. As shown by Traina et al. (1986), this accessibility was increased in the Altamont soil by increasing the quantity of exchangeable Al(III) through organic acid addition at low concentrations. The data of Coleman et al. (1960) suggest that, for Al-montmorillonite, the accessibility of Al(III) would also be enhanced by increasing the ionic strength of the background NaCl solution or by introducing metal cations that can displace exchangeable Al(III) more effectively than Na^+ . Traina et al. (1986) observed a much greater residual *o*-phosphate solubility in the Altamont soil suspension in the absence of added NaCl than when the NaCl concentration was 20 mol m^{-3} . Coleman et al. (1960) and Wild (1953) noted the effectiveness of added Ca^{2+} in reducing *o*-phosphate solubility in montmorillonite suspensions. All of these results are consistent with a mechanism whereby induced displacement of exchangeable Al(III) leads to the formation of additional basic Al-phosphate.

In this paper, the effects of varying ionic strength and of introducing Ca^{2+} on the solubility of residual *o*-phosphate in the Altamont soil will be examined both in the presence and in the absence of citric acid. The objective of this investigation is to provide additional insight as to the causative factors in *o*-phosphate solubility in acidic, montmorillonitic soil by way of extension of the experiments of Traina et al. (1986).

MATERIALS AND METHODS

Soil Separate

A sample of the 0- to 0.15-m depth of an unfertilized Altamont clay loam (fine, montmorillonitic, thermic Typic Chromoxererts) was used in this study. The pH value of the water-saturated soil paste (pH_{sp}) is 5.7 and the content of organic C is $29 \pm 1 \text{ g kg}^{-1}$ soil. Phosphate solubility experiments were conducted on a Na-saturated separate of this soil comprising the size fraction $<53 \mu\text{m}$. Details of the preparation of the soil separate are given by Fletcher et al.

(1984). The pH value of the filtered supernatant solution in a stock suspension of the separate (pH_s) was 7.2 ± 0.2 when measured on the freshly-prepared suspension and on the suspension aged 253, 341, or 452 d. The NaHCO_3 extractable phosphate in the separate was $3.0 \pm 0.1 \text{ mmol kg}^{-1}$ and the KCl extractable Al was $5.2 \pm 0.8 \text{ mmol kg}^{-1}$. Additional chemical properties of the Na-saturated soil separate have been reported by Traina et al. (1986).

The absence of Ca-phosphate from the Na-saturated separate was ascertained through calculation of an approximate ion activity product (IAP) for hydroxyapatite based on measured values of pH, total soluble Ca, and total soluble phosphate in the stock suspension after 253, 341, and 452 d of aging. The estimated log IAP was always 3.6 or more log units less than log $*K_{\text{so}}$ for hydroxyapatite (14.5; Lindsay, 1979, p. 165).

Solubility Experiments

Variation of Ionic Strength

A quantity of the stock soil separate suspension containing $0.40 \pm 0.02 \text{ g}$ solids was placed into a tared 250-mL polycarbonate reaction bottle and approximately 0.2 kg of either 30, 50, or 100 mol m^{-3} NaCl solution was added. The pH values of the NaCl solutions had been adjusted previously with HCl to produce an approximate final pH value of 5.5 in the soil suspension with less than a 0.4% change in the ionic strength. Aliquots containing 10 mol m^{-3} citric acid (Baker, analyzed reagent-grade) in 30, 50 or 100 mol m^{-3} NaCl at pH 5.5 were added to provide initial concentrations of citrate ligands ranging from 0 to 200 mmol m^{-3} . The suspension density was $2.00 \pm 0.05 \text{ g soil separate kg}^{-1}$ for all samples. Duplicate samples were prepared for each experiment. The reaction bottles were shaken at 298 K for 24 h, then centrifuged at 19 745 RCF (relative centrifugal force) for 30 min. A subsample of the supernatant solution was removed for pH measurement while the remainder of the solution was passed through a $0.2\text{-}\mu\text{m}$ Nucleopore polycarbonate filter membrane and saved for chemical analysis. Kinetics experiments (data not shown) indicated that no detectable changes in *o*-phosphate concentration in the supernatant solutions occurred after reaction times of 24 h, up to a maximum of 48 h. In other complementary experiments, it was found that addition of the citric acid/NaCl solutions (adjusted to pH 5.5) to the 20 mol m^{-3} NaCl background solution (also adjusted to pH 5.5) did not produce a shift in pH; thus no corrections of the pH measurements in the supernatant solutions after reaction were deemed necessary.

Variation of Ca^{2+} Concentration

Organic Acid Experiments—A quantity of the stock soil separate suspension containing $0.40 \pm 0.02 \text{ g}$ solids was placed into a tared 250-mL polycarbonate reaction bottle and approximately 0.2 kg of either acidified, 1 mol m^{-3} $\text{CaCl}_2/17 \text{ mol m}^{-3}$ NaCl solution or acidified, 5 mol m^{-3} $\text{CaCl}_2/5 \text{ mol m}^{-3}$ NaCl solution was added. The pH values of the electrolyte solutions had been adjusted previously with HCl to provide a final pH value of 5.5 in the soil suspension with less than a 0.4% change in ionic strength. Aliquots of 10 mol m^{-3} citric acid (Baker, analyzed reagent-grade) in either 1 mol m^{-3} $\text{CaCl}_2/17 \text{ mol m}^{-3}$ NaCl or 5 mol m^{-3} $\text{CaCl}_2/5 \text{ mol m}^{-3}$ NaCl, adjusted to pH 5.5, were added to produce initial concentrations of added citrate ligands ranging from 0 to 600 mmol m^{-3} . The suspension concentration was $2.00 \pm 0.05 \text{ g soil separate kg}^{-1}$ for all samples. Duplicate samples were prepared for each experiment. The reaction bottles were shaken at 298 K for 24 h, then centrifuged and filtered as described above.

Variable pH Experiments—A quantity of the stock soil separate suspension containing $0.40 \pm 0.02 \text{ g}$ solids was

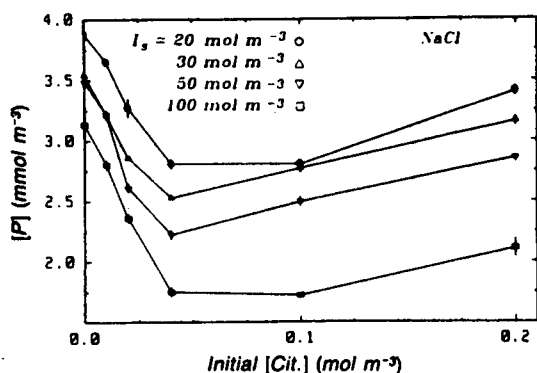


Fig. 1. Effect of ionic strength (I_s) and initial citrate concentration on residual *o*-phosphate solubility in NaCl (initial pH = 5.5). The data for $I_s = 20 \text{ mol m}^{-3}$ are from Traina et al. (1986).

placed into a tared 250-mL polycarbonate reaction bottle and approximately 0.2 kg of either 1 mol m^{-3} $\text{CaCl}_2/17 \text{ mol m}^{-3}$ NaCl solution or 5 mol m^{-3} $\text{CaCl}_2/5 \text{ mol m}^{-3}$ NaCl solution was added. The pH values of the electrolyte solutions had been adjusted with HCl or NaOH to produce final pH values between 3.5 and 7.5 in the soil separate suspensions with an ionic strength change of <4%. The suspension density was $2.00 \pm 0.05 \text{ g soil separate kg}^{-1}$. The reaction bottles were shaken at 298 K for 24 h, then centrifuged at 19 745 RCF for 30 min and filtered as described above.

Chemical Analysis

Solution concentrations of *o*-phosphate were determined by a molybdenum blue colorimetric procedure (Olsen and Sommers, 1982). Solution concentrations of Ca were measured with a Perkin-Elmer model 5000 atomic absorption spectrophotometer equipped with a background corrector. All pH measurements were made with a Beckman model 71 pH meter equipped with an automatic temperature compensator and glass/calomel electrode pair.

RESULTS AND DISCUSSION

The solubility of residual *o*-phosphate in the Na-Altamont soil separate suspended in NaCl, as influenced by both stoichiometric ionic strength (I_s) and citric acid concentration, is depicted in Fig. 1. (The vertical lines in the figure indicate 1 standard deviation for duplicate experiments). Figure 2 shows the effects of Ca^{2+} and citric acid concentration on *o*-phosphate solubility. The data in both figures for 20 mol m^{-3} NaCl are taken from Traina et al. (1986). Increases in I_s in a NaCl background and increases in Ca^{2+} concentration at a constant I_s of 20 mol m^{-3} generally caused a decrease in the solubility of *o*-phosphate at all levels of citric acid addition. These results are consistent in principle with trends in *o*-phosphate solubility reported for model Al-saturated exchange surfaces (Wild, 1953; Coleman et al., 1960; Robarge and Corey, 1979) and with the formation of an Al-phosphate solid subsequent to the release of exchangeable Al(III) to the aqueous solution phase. Inasmuch as increases in I_s and Ca^{2+} concentration should have promoted the displacement of exchangeable Al(III) from soil surfaces, these changes in *o*-phosphate solubility conform to the mechanism described by Traina et al. (1986) for the Altamont soil.

Approximate IAPs for hydroxyapatite were calcu-

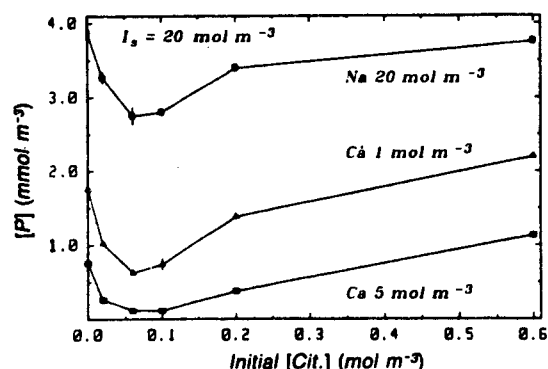
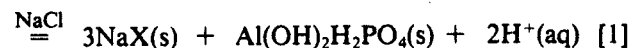
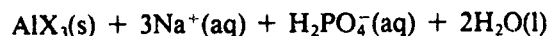


Fig. 2. Effect of initial Ca^{2+} and citrate concentration on residual *o*-phosphate solubility at a constant $I_s = 20 \text{ mol m}^{-3}$ (initial pH = 5.5). The data for 20 mol m^{-3} Na are from Traina et al. (1986).

lated for each point in Fig. 2 with measured pH values and values of total soluble Ca and P. Since the estimated log IAPs were always three or more log units less than $\log^* K_{so}$ for hydroxyapatite (14.5; Lindsay, 1979, p. 165), the marked decreases in *o*-phosphate solubility shown in Fig. 2 should not have resulted from basic Ca-phosphate precipitation. There is no systematic change in the overall shapes of the *o*-phosphate solubility curves in Fig. 1 and Fig. 2 caused by changes in the solution concentration of either Ca or Na. Thus, one may infer that increases in I_s or Ca^{2+} concentration had no qualitative influence on citric acid *o*-phosphate interactions in the Altamont soil.

The effect of citrate concentration on the pH value of the soil separate suspension for various ionic strengths and Ca^{2+} concentrations is illustrated in Fig. 3. As noted by Traina et al. (1986), the rising portions of the pH curves are consistent with the displacement of hydroxyl groups from adsorbed Al(III) by organic ligands, whereas at sufficiently large citrate concentrations, complexation of exchangeable Al(III) and its removal to the aqueous solution phase as a 1:1 Al(III)-citrate complex promotes the release of a proton from the citrate ligand and produces the falling portions of the pH curves. At a given concentration of added citrate, increases in I_s caused a decrease in the pH value of the Altamont soil-separate suspension (Fig. 3a). This behavior is in accord with the idealized scheme proposed by Coleman et al. (1960) for *o*-phosphate reaction with an Al-saturated montmorillonite in the presence of NaCl:



where X refers to 1 mol of montmorillonite surface charge. Direct displacement of protons from soil surfaces by Na^+ ions may also have contributed to some of the drop in pH.

Since Ca^{2+} should be more effective than Na^+ in displacing adsorbed protons and exchangeable Al(III) from soil surfaces, one could make the a priori hypothesis that the pH value of the soil separate suspension would decrease if the concentration of Ca were allowed to increase while I_s and the added citrate concentration were held constant. The data in Fig. 3b indicate that this does not occur. Instead, the pH value

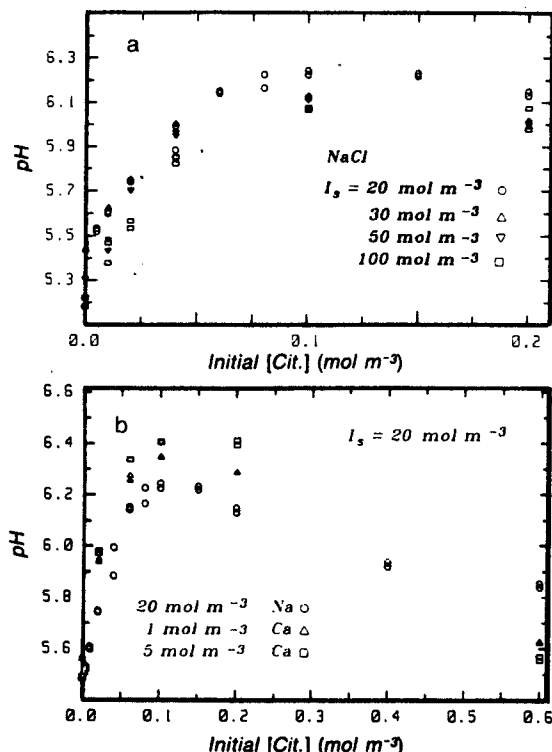


Fig. 3. Effect of (a) I_s and (b) Ca^{2+} concentration on the final pH value of the soil-separate suspension at varying concentrations of citrate. The data for 20 mol m^{-3} NaCl are from Traina et al. (1986).

of the soil separate suspension increased with increasing Ca concentration for citrate concentrations ranging from 20 to 200 mmol m^{-3} . This result may have been in part caused by the formation of soluble Ca-citrate complexes, which would inhibit by competition the complexation and concurrent deprotonation of soluble citrate by Al(III). It is also possible that the displacement by citrate of surface hydroxyl groups bound to Al(III) was enhanced in the presence of adsorbed Ca, since a decrease in the absolute magnitude of the negative charge present at soil surfaces and/or a decrease in the thickness of the diffuse double layer surrounding the soil particles should accompany Ca adsorption (Sposito, 1984). At a citrate concentration of 600 mmol m^{-3} , the suspension pH value decreased as the Ca concentration increased, indicating that sufficient citrate was present to allow complexation of exchangeable Al(III) and its removal to the aqueous solution phase, thereby masking hydroxyl release resulting from enhanced citrate adsorption.

The influence of Ca^{2+} concentration and pH in the absence of applied citrate and at constant I_s is shown in Fig. 4. The data indicate that, for $\text{pH} > 4.0$, increases in Ca^{2+} concentration decreased α -phosphate solubility. This result has been observed in Al-resin systems by Robarge and Corey (1979). Estimated values of log IAP for hydroxyapatite suggested that some precipitation of a Ca-phosphate may have occurred in the experiment at pH values in excess of 7.0. However, at $\text{pH} < 7.0$, the soil solutions were sufficiently undersaturated with respect to hydroxyapatite to pre-

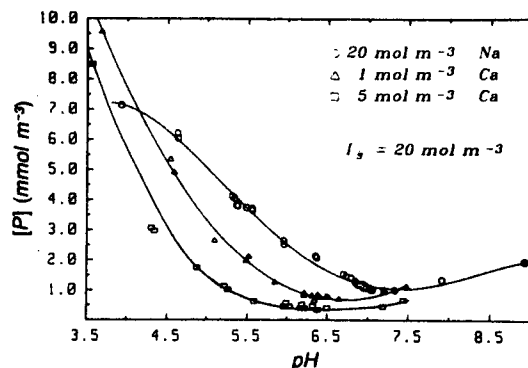
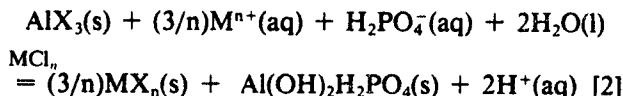


Fig. 4. Effect of pH and initial Ca^{2+} concentration on α -phosphate solubility in the absence of added citrate. The data for 20 mol m^{-3} NaCl are from Traina et al. (1986).

clude its precipitation. Apparently, the effect of Ca in the low-pH region was to displace exchangeable Al(III) and to enhance the formation of an Al-phosphate solid in a manner analogous to the reaction represented in Eq. [1]. Below pH 4, the solubility of α -phosphate was greater in the presence of Ca than in the presence of NaCl alone (Fig. 4). Model calculations of aqueous ion speciation with the computer program GEOCHEM (Sposito and Mattigod, 1980) indicated that under these acidic conditions, some Ca-phosphate solution complexes were present in sufficient concentration to increase the total α -phosphate solubility.

CONCLUSIONS

The effects of ionic strength and Ca^{2+} concentration on α -phosphate solubility in the Altamont soil separate are consistent with previous model experiments on α -phosphate reactions with Al-saturated montmorillonite (Coleman et al., 1960) and Al-saturated cation exchange resin (Robarge and Corey, 1979). A generalized form of Eq. [1], following Coleman et al. (1960), can be written to describe the influence of I_s and Ca^{2+} concentration on α -phosphate solubility in the Altamont soil separate at low concentrations of citric acid



where M^{n+} is a metal cation and MCl_n is its chloride salt.

Equation [2] suggests that there should be no direct effect of either I_s or Ca^{2+} concentration on citrate- α -phosphate interactions. This hypothesis was borne out in the present study by the observed lack of influence of either I_s or Ca^{2+} concentration on the shape of the α -phosphate-citrate solubility plots (Fig. 1 and 2). Apparently the primary role of I_s and Ca^{2+} was to control the initial concentration of soluble α -phosphate in the soil separate suspension. Thus the α -phosphate sorption mechanism proposed by Traina et al. (1986) is not altered by variations in I_s or Ca^{2+} concentration, but instead is affected quantitatively by changes induced in the amount of Al(III) available to react with α -phosphate in the absence of added organic ligands.

ACKNOWLEDGMENTS

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KINETIC STUDY OF CITRATE EFFECTS ON ORTHOPHOSPHATE
SOLUBILITY IN AN ACIDIC, MONTMORILLONITIC SOIL¹

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ABSTRACT

Previous studies by the authors of the effects of pH, organic acids, ionic strength and Ca on residual orthophosphate solubility in an acidic montmorillonitic soil (Typic Chromoxererts) were extended to include the variation of reaction time. The objective of the experiments was to determine the time dependence of the reactions and to elucidate further the mechanism of orthophosphate solubility in a montmorillonitic soil separate containing exchangeable Al (III) and citric acid, suspended in 20 mol NaCl m⁻³. In the absence of added organic acids, soluble orthophosphate and Al (III) activities were found to be at equilibrium with an amorphous hydroxy-Al-phosphate solid for $t \geq 24$ h. Initial citrate concentrations of 10, 100 and 400 mmol m⁻³ resulted in citrate sorption by the soil separate and an increase in soluble orthophosphate and Al (III) for $t \leq 1$ h. Citrate adsorption continued throughout the time course of the experiments. At $1 < t < 8$ h orthophosphate solubility was not affected by the initial citrate concentration. At $8 < t < 25$ h orthophosphate solubility decreased to constant levels consistent with previous equilibrium studies conducted by the authors. Soluble Al (III) decreased for $1 < t < 30$ h and then remained constant in the 10 and 100 mmol m⁻³ citrate treatments. The samples reacted with 400 mmol m⁻³ citrate exhibited a steady increase in soluble Al (III) for the same time period. The time dependent changes in aqueous orthophosphate and Al (III) were consistent with a previously proposed reaction describing organic ligand induced formation of an insoluble hydroxy-Al-phosphate. The time trends in the solution concentrations of Ca and Si were not affected by the addition of organic ligands nor were they related to the changes in soluble Al (III) or orthophosphate. Thus the former

1 elements did not directly take part in the citrate-Al-orthophosphate
2 interactions.

3
4 Additional Index Words: Al-organic complexes, Al phosphate, exchangeable Al,
5 phosphate precipitation

1 Traina et al. (1986a,b) recently have investigated the effect of citric acid
2 on the solubility of orthophosphate (o-phosphate) in a suspension containing
3 montmorillonitic soil in a NaCl background. They concluded that the principal
4 effect of the organic acid on o-phosphate solubility was a citrate-induced
5 displacement of adsorbed Al which then precipitated as an Al-phosphate,
6 $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$. Earlier research by Coleman et al. (1960) on a model
7 Al-montmorillonite system had established that hydrolyzed Al could be
8 exchanged by Na^+ in the presence of o-phosphate to precipitate as poorly
9 crystalline variscite. Subsequently Goh and Huang (1984, 1985) demonstrated
10 for the same type of model system that citric acid could render adsorbed
11 Al-hydroxy polymers exchangeable (KCl-extractable). These previous results
12 and their own data on the effect of citric acid on o-phosphate solubility under
13 varying conditions of pH, ionic strength, and aqueous solution composition led
14 Traina et al. (1986a,b) to the conclusion described above.

15 The solubility experiments of Traina et al. (1986a,b) pertained to a
16 suspension equilibrated for 24 h. Preliminary studies indicated that little or no
17 change in o-phosphate solubility occurred for reaction times between 24 and
18 48 h (Traina et al., 1986b), but data were not taken for reaction times less than
19 24 h. In this paper, the kinetics of o-phosphate-citrate interactions in the
20 montmorillonitic soil studied by Traina et al. (1986a,b) are reported for reaction
21 times between 1 and 50 h. The objectives of the investigation were to provide
22 insight as to the time scales over which citric acid acts to produce
23 exchangeable Al and induce the precipitation of o-phosphate, as well as to test
24 the internal consistency of this concept with kinetics data.

25
26
27

MATERIALS AND METHODS

Soil Separate

A sample of the 0 to 0.15-m depth of an uncultivated Altamont clay loam (fine, montmorillonitic, thermic, Typic Chromoxererts) was used in this study. The pH value of the water-saturated soil paste (pH_{sp}) is 5.7 and the content of organic carbon is $29 \pm 1 \text{ g kg}^{-1}$ soil (Traina et al., 1986a). Residual o-phosphate solubility experiments were conducted on a Na-saturated separate of this soil comprising the size fraction $< 53 \mu\text{m}$. Details of the preparation of the soil separate are given by Fletcher et al. (1984) and its chemical properties have been described by Traina et al. (1986a,b). Those relevant to the present study are the content of NaHCO_3 -extractable phosphate ($3.0 \pm 0.1 \text{ mmol kg}^{-1}$), the content of KCl-extractable Al ($5.2 \pm 0.8 \text{ mmol kg}^{-1}$), the supernatant solution pH value ($\text{pH}_e = 7.2 \pm 0.2$), and the significant undersaturation with respect to Ca-phosphate solid phases.

Solubility Kinetics Experiments

A quantity of the stock soil separate suspension containing $0.40 \pm 0.02 \text{ g}$ solids was placed into a tared 250-mL polypropylene reaction bottle and approximately 0.2 kg of 20 mol m^{-3} NaCl was added. The pH value of the NaCl solution had been adjusted previously with HCl to result in a soil suspension pH value near 5.5, in the absence of added organic ligands, after 24 h equilibration. Aliquots of 10 mol m^{-3} citric acid (2-hydroxypropane-1, 2, 3-tricarboxylic acid) (Baker, analyzed reagent-grade) in 20 mol m^{-3} NaCl, adjusted to pH 5.5, were added to produce initial concentrations 0, 10, 100, or 400 mmol m^{-3} citrate ligands. In one experiment, formic acid (methanoic acid) was added to give an initial concentration of 200 mmol m^{-3} formate ligands. The suspension

1 density was 2.00 ± 0.05 g soil separate kg^{-1} for all samples. Duplicate samples
2 were prepared for each reaction time to be investigated. The reaction bottles
3 were shaken gently at 298 K for periods of 1 to 50 h, then each sample was
4 divided and added uniformly into eight 40-mL polypropylene centrifuge tubes.
5 Transfer to the 40-mL tubes allowed the subsamples to be centrifuged at
6 19,745 RCF for a period of 5 min. The supernatant solutions of these
7 subsamples then were combined in a 250-mL Pyrex beaker. A subsample of the
8 remixed supernatant solution was removed for immediate pH measurement,
9 while the remainder of the solution was passed through a 0.2- μm Nucleopore
10 polycarbonate membrane filter and retained for chemical analysis. In all cases,
11 less than 2 min was required for sample filtration. The total elapsed time for
12 each experiment was considered to be the time period from organic acid
13 addition to and including filtration of the supernatant solutions. In all cases,
14 the total elapsed time required for the separation of solid from the aqueous
15 phase was <10 min.

17 Chemical Analysis

18 Solution concentrations of o-phosphate were determined by a
19 molybdenum-blue colorimetric procedure (Olsen and Sommers, 1982). Soluble
20 Al, Ca, and Si were determined by inductively-coupled plasma emission
21 spectroscopy. Measurements of pH were made with a Beckman model 71 pH
22 meter equipped with an automatic temperature compensator and glass/calomel
23 electrode pair.

24 The concentration of citrate ligands in the extracted solutions was
25 inferred from a measurement of total dissolved organic carbon (TOC) with a
26 Dohrman-Xertex DC-80 total carbon analyzer. A correction was made for the
27

1 TOC concentration in the supernatant solutions in the absence of added citrate.
2 Identical final citrate concentrations were measured in solutions extracted
3 from the soil suspension after reaction both in the presence and absence of
4 $2 \text{ kg m}^{-3} \text{ NaN}_3$ (a microbicide). Thus the calculation of citrate concentrations
5 from TOC values was not affected by microbial activity.

6 7 RESULTS

8 The time dependence of citrate sorption by the Altamont soil is shown in
9 Fig 1. (Sorption was calculated as the blank-corrected loss of organic C from
10 solution divided by the molar C content of citrate, divided by the mass of soil in
11 the suspension.) At an initial concentration of 10 mmol m^{-3} , citrate sorption
12 exhibited a sigmoid time dependence during the first few hours, then attained a
13 plateau which persisted from 4 to 47 h. At higher initial citrate concentrations,
14 both the early plateau near 5 h and a second plateau near 25 h are apparent in
15 the sorption time dependence. The amounts sorbed at each plateau were not
16 proportionate to the initial concentrations of citrate (e.g., 5 mmol kg^{-1} at
17 10 mmol m^{-3} initial concentration versus 30 mmol kg^{-1} at 400 mmol m^{-3} for
18 the early plateau) and the 25-hour plateaux appear to be superimposed on an
19 overall continuous increase of sorption with time.

20 The time dependence of soluble α -phosphate (P_T), Al (Al_T), Si (Si_T), and
21 Ca (Ca_T) are shown in Fig. 2 to 5. When citrate was not present, P_T increased
22 by about 30% over a 25-hour period to a value consistent with the "equilibrium"
23 solubility reported by Traina et al. (1986a, Fig. 2). Under the same condition,
24 Al_T hovered around a very low value (about 0.5 mmol m^{-3}), Si_T increased
25 gradually by about 20%, and Ca_T fluctuated around $35\text{--}40 \text{ mmol m}^{-3}$. The
26 solution data were used to speciate Al and P with the computer program
27

1 GEOCHEM (Sposito, 1985) in order to calculate the log ion activity product
2 (IAP) for the poorly crystalline solid phase, $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$. The results, log
3 $\text{IAP} = 30.5$ at 24, 30, and 40 h, were consistent with a trend toward equilibrium
4 with this solid phase, for which $\log K_{\text{SO}}$ lies between 27 and 31 (Sposito, 1981,
5 Chap. 2; Traina et al., 1986a).

6 In the presence of citrate, P_T increased sharply for $t < 7$ h, then
7 decreased to an "equilibrium" value consistent with the solubility data reported
8 by Traina et al. (1986a, Fig. 3) at $t = 25$ h. In the presence of 200 mmol m^{-3}
9 formate, P_T showed a small, short-time increase, then decreased gradually
10 (Fig. 2). The value of P_T at 25 h was consistent with the "equilibrium" value
11 reported by Traina et al. (1986a, Fig. 3).

12 In the presence of citrate, Al_T showed a decrease with time at 10 and
13 100 mmol m^{-3} initial citrate concentration, but increased with time at 400 mol
14 m^{-3} initial concentration (Fig. 3). The initial values of Al_T increased as the
15 citrate concentration was increased. The value of Al_T in the presence of
16 200 mmol m^{-3} formate (data not shown) was not significantly different from
17 that found in the absence of added organic acid. The time trend of Si_T in the
18 presence of citrate was similar to that in the absence of organic ligand (Fig. 4),
19 but the absolute value of Si_T was decreased below that in the absence of
20 organic ligand when the initial citrate concentration was 10 or 100 mmol m^{-3} .
21 At 400 mmol m^{-3} initial citrate concentration, Si_T exceeded the values
22 observed in the citrate-free suspension. The time trend of Ca_T also was similar
23 in both the presence and absence of citrate (Fig. 5), but 100 mol m^{-3} citrate
24 caused an overall decrease in Ca_T whereas Ca_T was increased at 10 and
25 400 mmol m^{-3} citrate.

1 The time dependence of pH is shown in Fig. 6. In all cases pH increased
2 with time and the addition of organic ligands resulted in overall higher pH
3 values. The pH increased more at 100 mmol m⁻³ citrate and 200 mmol m⁻³
4 formate than at 400 mmol m⁻³ citrate. The data at 25 h are consistent with
5 the "equilibrium" pH values reported by Traina et al. (1986a, Fig. 5).

6 7 DISCUSSION

8 The kinetics data in Fig. 1 to 6 represent the net effect of concurrent
9 reactions in a complex assembly of soil minerals, organic matter, and adsorbed
10 species. No rationalization of these data in terms of simple mechanistic models
11 can claim to be either unique or complete, but a discussion of the data based on
12 the inferences made by Traina et al. (1986a,b) and general concepts of surface
13 reactions in soils (Sposito, 1984) should have heuristic value.

14 The solubility and pH data in the absence of organic ligands are consistent
15 with the relatively rapid adjustment of exchangeable H⁺, Ca²⁺, and Al (III) to
16 an acidic solution and the slower release of o-phosphate and silica from
17 solid-phase and/or adsorbed chemical forms. The pH increase observed would
18 be the net result of protonation of surfaces and/or soluble anions. As
19 mentioned above, the o-phosphate solubility data for t > 20 h are consistent
20 with the presence of Al(OH)₂H₂PO₄.

21 For t < 1 h, it is evident from Fig. 2 to 6 that, at an initial citrate
22 concentration of 10 mmol m⁻³, a rapid loss of Al, Ca, and o-phosphate from
23 solid phases occurs after attack by the organic ligand. The cations are likely in
24 the form of organic complexes (confirmed by speciation calculations with
25 GEOCHEM and the sigmoid sorption curve in Fig. 1). The o-phosphate may
26 have been solubilized by ligand exchange with citrate, which is a bivalent anion
27

1 at pH < 6 (Martell and Smith, 1977). The concentration of P solubilized at
2 $t < 1$ h was 0.46 ± 0.03 mmol m⁻³ greater than the concentration in the absence
3 of citrate, regardless of the initial citrate level. The concentration of Al
4 solubilized was much in excess of P_T, which suggests that weathering of
5 Al-bearing solid phases occurred. This weathering would expose fresh surfaces
6 for the adsorption of solutes. Adsorption of silica by these surfaces could have
7 produced the reduction in Si_T observed (Fig. 4) as the initial citrate
8 concentration was increased from 0 to 10 mmol m⁻³. Silica, o-phosphate,
9 citrate, and chloride ligands all would be in competition for surface sites
10 exposed by Al dissolution. The net result of surface and soluble cation
11 reactions with these ligands was an overall reduction in Si_T, possibly because
12 the initial form of Si was aqueous and its ability to solubilize Al is minimal.
13 Increases in the initial citrate concentration above 10 mmol m⁻³ resulted in
14 increased Al_T and Si_T, with a decrease in Ca_T (at 100 mmol m⁻³), and no
15 change in P_T. The effect on Si_T at higher citrate concentrations can be
16 attributed to competition with citrate for exposed adsorption sites. The effect
17 on Ca_T may be the net outcome of adsorption by sorbed citrate (Fig. 1) in
18 competition with soluble Ca-citrate complexes, with the latter predominating
19 as the citrate concentration increases.

20 For $1 < t < 8$ h, citrate is sorbed. Coprecipitation with Al and Ca is
21 consistent with the data in Fig. 3 and 5, and displacement of adsorbed Si is not
22 absolutely ruled out by the data in Fig. 4. The displacement of o-phosphate by
23 citrate also appears consistent with the data in Fig 2. However, the increase in
24 P_T for $t > 1$ h is most likely simple dissolution following the kinetics in the
25 absence of organic ligand. The differential o-phosphate dissolution for
26 $1 < t < 8$ h is shown in Fig. 7, where

$$P_T(\text{net}) = P_{\text{cit}}(t) - [P_{\text{cit}}(t=1) - P_O(t=1)] \quad (t \geq 1) \quad [1]$$

where $P_{\text{cit}}(t)$ is P_T in the presence of citrate at time $t \geq 1$ h and $P_O(t)$ is P_T in the absence of citrate at time $t \geq 1$ h. The data in Fig. 7 indicate that, for $1 < t < 8$ h, the α -phosphate dissolution rate was not affected by the presence of citrate. Thus the sorption of citrate by the soil separate in this time period was not on an α -phosphate-bearing surface, and had no additional net effect on P_T . Continued sorption of citrate on other Al-bearing solids is both possible and likely, particularly with Al-hydroxy materials on montmorillonite in the Altamont soil.

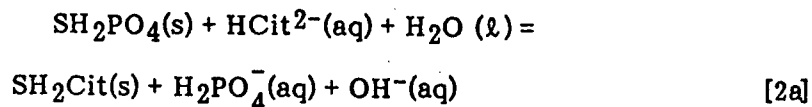
For $8 < t < 30$ h, the precipitous decline in P_T and Al_T observed in the presence of citrate at initial concentrations of 10 and 100 mmol m^{-3} (Fig. 2 and 3) is consistent with the mechanism proposed by Traina et al. (1986a,b), whereby citrate complexation of adsorbed Al renders it exchangeable to the aqueous phase and hence accessible to precipitation by α -phosphate. The coprecipitation of Al, P, and citrate at high citrate concentrations could be the cause of the second sorption plateau in Fig. 1 and the decline/flattening of the Al_T curves in Fig. 3. Complicating the picture are the sorption of citrate that does not result in exchangeable Al and the formation of soluble Al-citrate complexes, apparent especially at the 400 mmol m^{-3} initial citrate concentration. The indifference of the Ca_T and Si_T data to the developments in Fig. 1 to 3 supports the concept that the essential reaction is among Al, citrate, and α -phosphate. A similar indifference was observed in kinetics data for Fe_T and Mn_T (data not shown). Traina et al. (1986a) showed that formate was much less effective than citrate at inducing α -phosphate precipitation,

evidently because of its lesser ability to displace OH and render adsorbed hydroxy-Al exchangeable. The data in Fig. 2 and 6 indicate that formate at 200 mol m⁻³ could not solubilize o-phosphate for t < 1 h, but was able to reduce P_T gradually through attack on Al-hydroxy material. Its effectiveness fell between those of citrate at 10 and 100 mmol m⁻³. The equality of Al_T in the samples reacted with 200 mmol m⁻³ formate and those not treated with organic acids indicates that the rate of Al-phosphate interactions must have been equal to or exceeded the rate of OH displacement by formate.

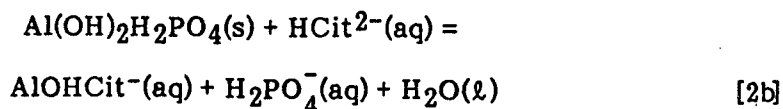
CONCLUSIONS

The kinetics data developed in the present study can be interpreted in respect to o-phosphate solubility with the following hypothetical sequence of reactions:

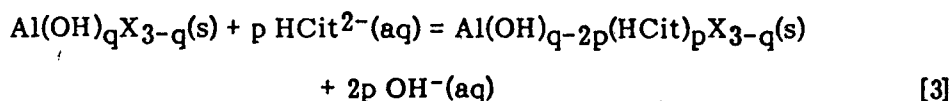
(1) For reaction times less than 1 h, citrate acts to solubilize adsorbed and structural Al by complexation, thus exposing fresh mineral surfaces for solute adsorption. Solubilization of adsorbed o-phosphate by citrate also occurs and may be described by the reaction:



where S represents 1 mol of positive surface charge, and the surface and solution species of o-phosphate at pH 5 are as given by Goldberg and Sposito (1984) and Lindsay (1979) respectively. Dissolution of an o-phosphate solid would follow a similar reaction:

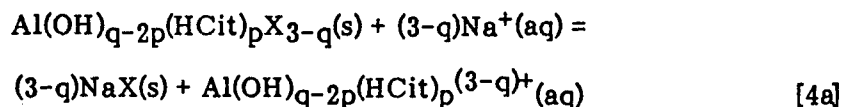


(2) For reaction times between 1 and 8 h, citrate is sorbed on mineral surfaces, among which are those bearing Al-hydroxy material. A general reaction scheme for the Al-hydroxy-citrate interaction via ligand exchange is:

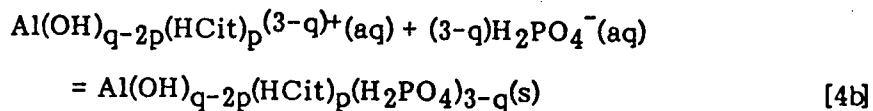


where $q \approx 2.5-2.7$ (Goh and Huang, 1984) and X refers to an amount of adsorbent bearing 1 mol of negative surface charge. This reaction will immobilize citrate and increase pH. The proton in the citrate reactant could be replaced by AlOH^{2+} or Ca^{2+} to give a reaction that would immobilize Al and Ca also. Alternatively, these cations could be complexed by sorbed citrate.

(3) For reaction times between 8 and 30 h, Al rendered exchangeable by complexation with citrate according to Eq. [3] is displaced and then precipitates with α -phosphate. Data reported by Veith (1977) indicate that $\text{Al(OH)}_q^{(3-q)+}$ adsorbed on montmorillonite becomes exchangeable if $q < 2.5$. Given that stable interlayer Al-hydroxy polymers require $2.5 < q < 2.7$ (Goh and Huang, 1984), it follows that citrate sorption as in Eq. [3] would render the complexed Al exchangeable. In a NaCl ionic background, the exchange reaction can be expressed:



1 where $q-2p < 2.5$. This reaction is followed by the precipitation of an
 2 Al-phosphate:



7 where allowance for coprecipitation of citrate and o-phosphate has been made.
 8 In the presence of excess citrate, both Al products in Eq. [4] will be found, but
 9 the soluble Al-citrate complex will come to dominate (with $q = 3p$) as the
 10 citrate concentration increases, thus inhibiting the precipitation reaction
 11 (Traina et al., 1986a).

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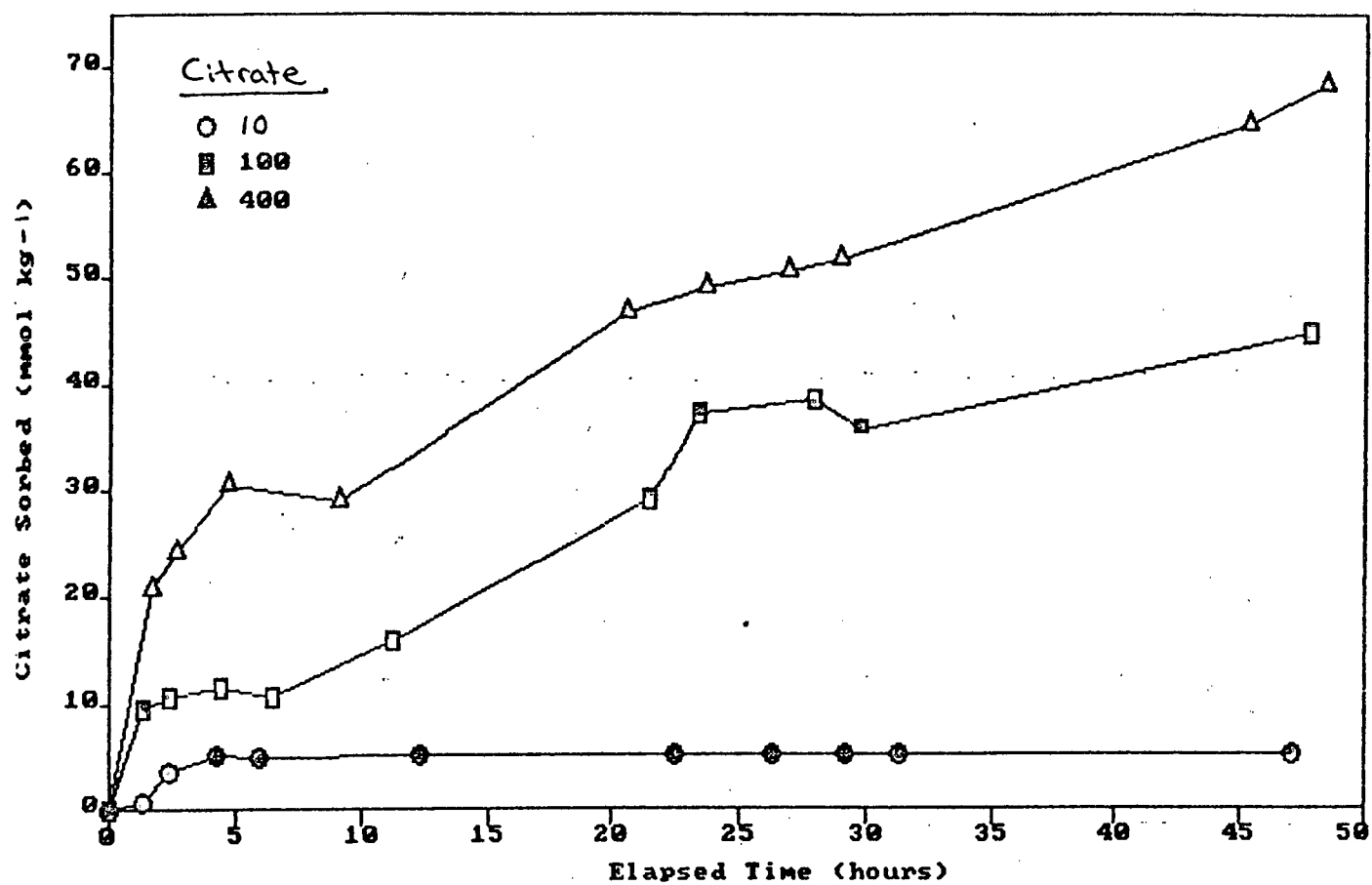
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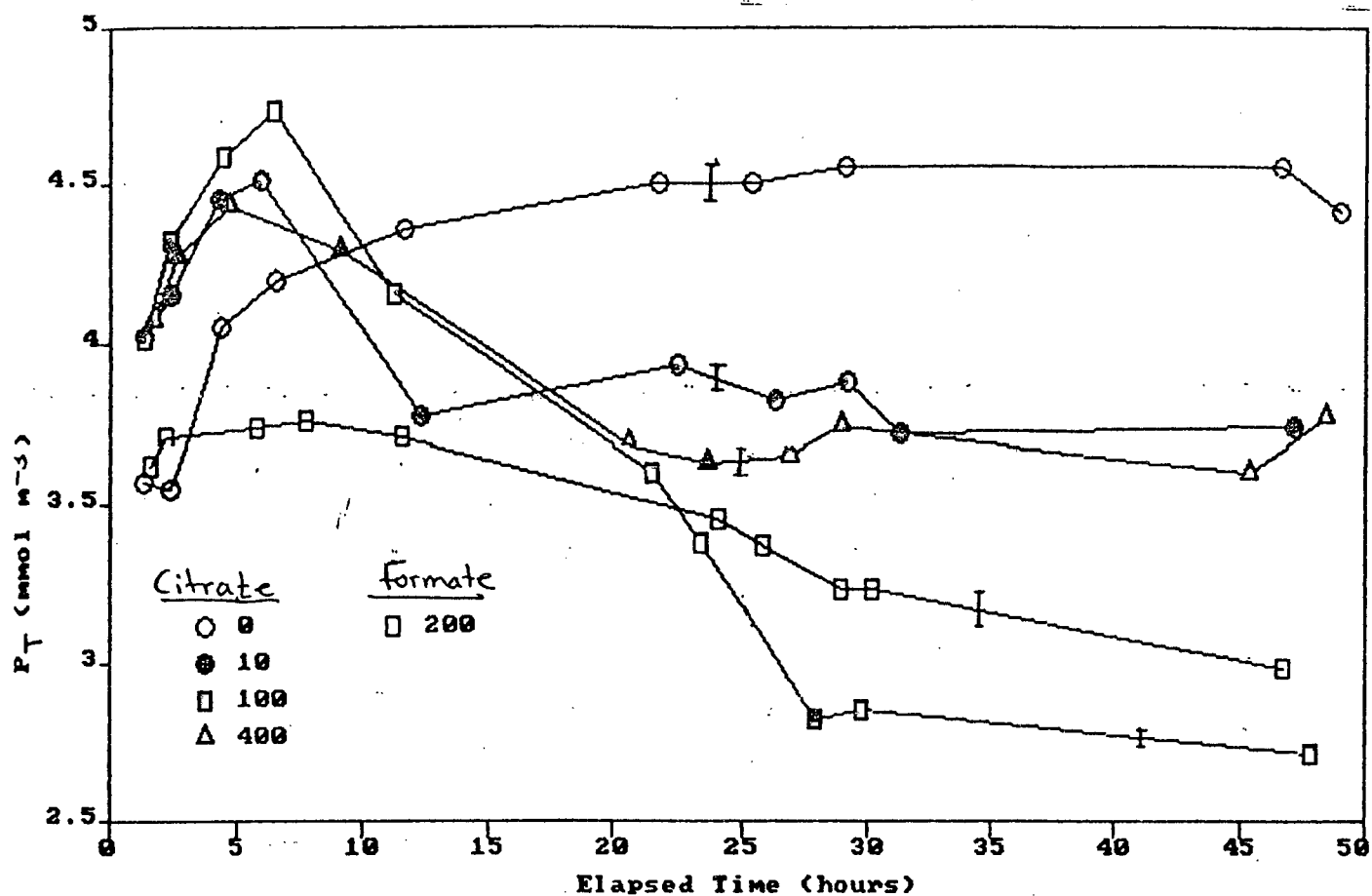
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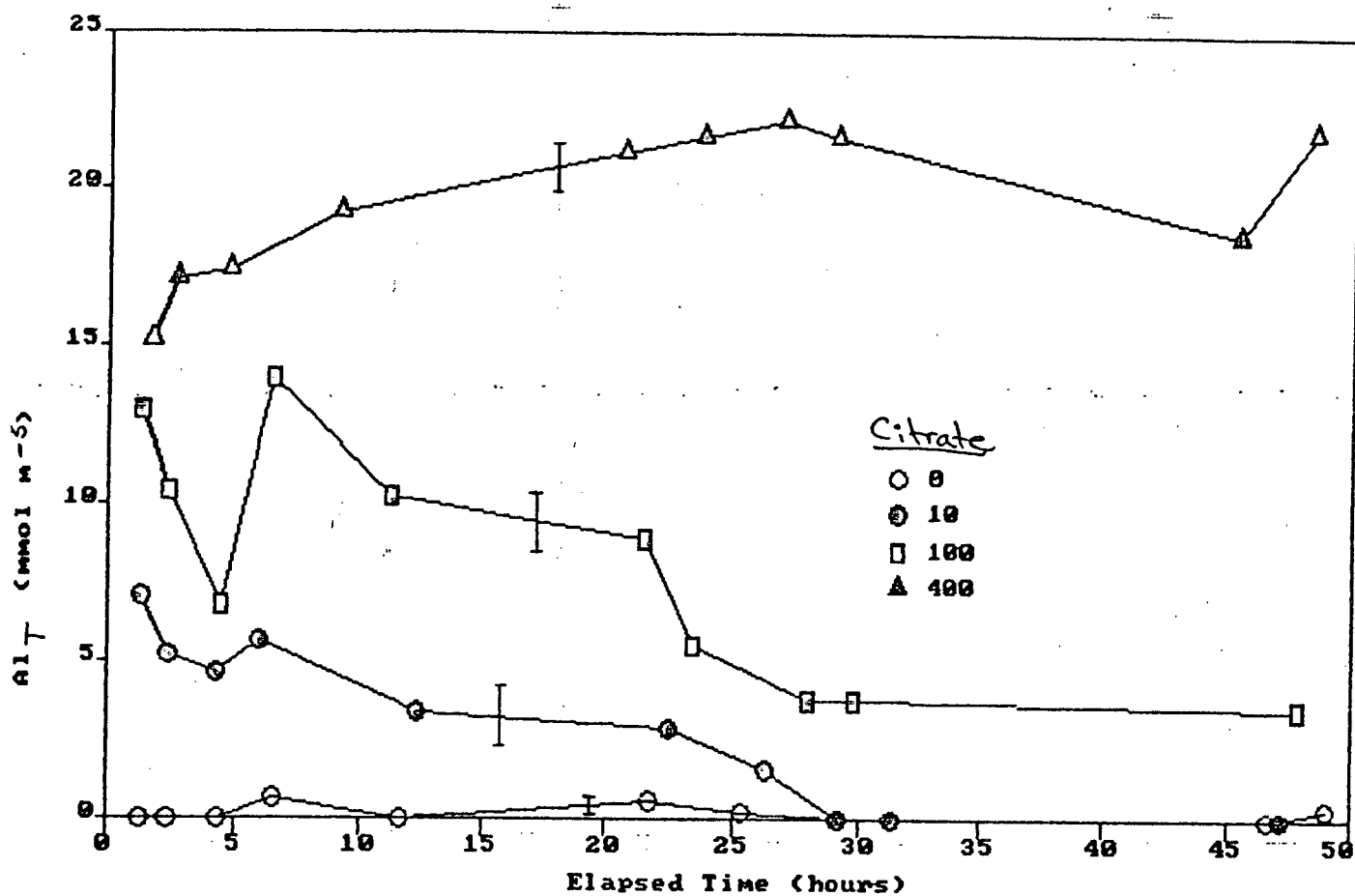
1 7. Differential o-phosphate dissolution by citrate for a Na-Altamont soil
2 separate, calculated with Eq. [1], for $1 \leq t < 7$ h. Citrate concentrations
3 are in millimoles per cubic meter.
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1. Time dependent sorption of citrate by a Na-Altamont soil separate in a background of 20 mol m⁻³ NaCl.

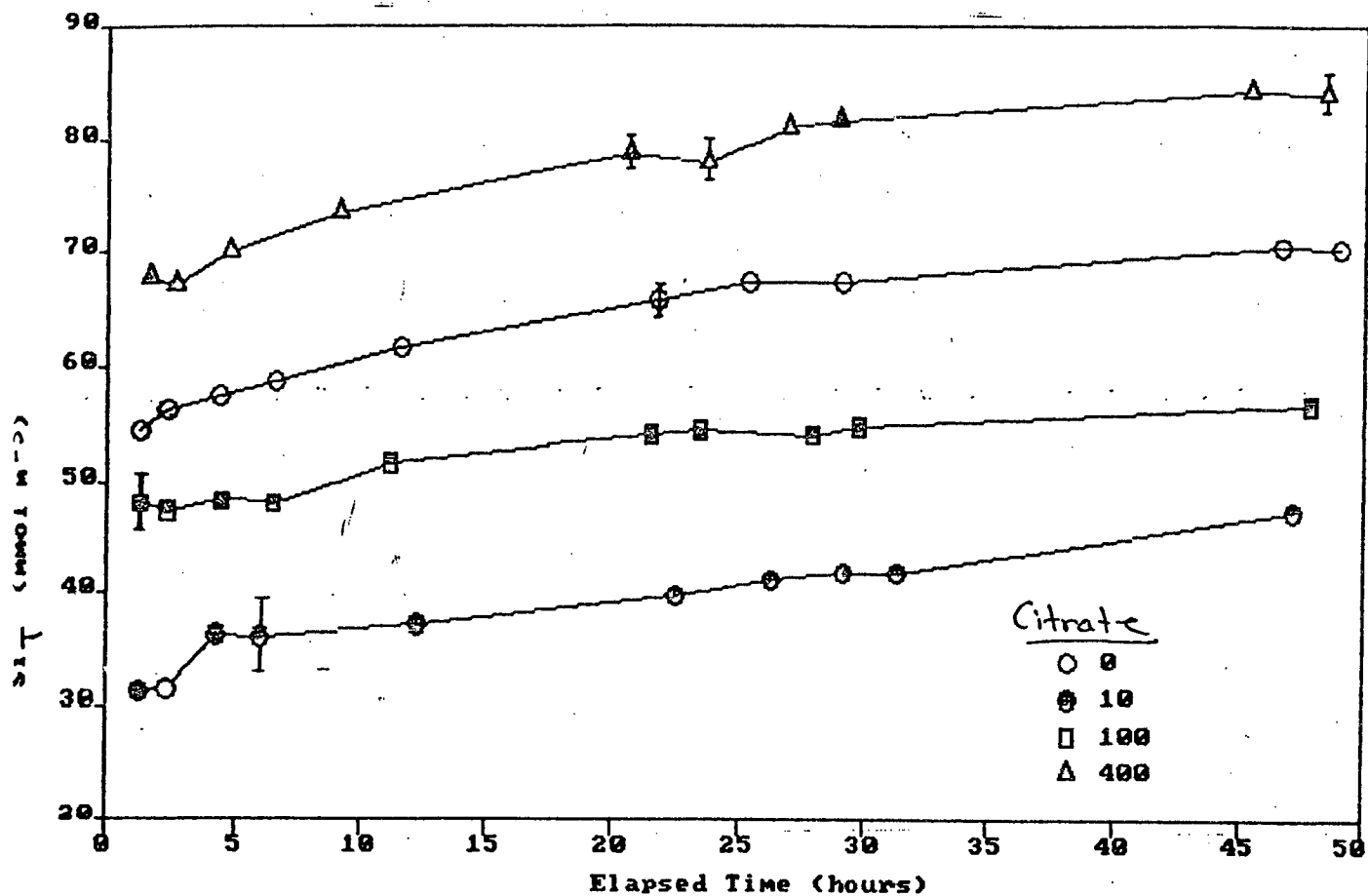


2. Effect of reaction time and organic acid concentration (in $mmol\ m^{-3}$) on residual o-phosphate solubility for a Na-Altamont soil separate in a background of $20\ mol\ m^{-3}$ NaCl. Vertical bars denote one standard deviation.

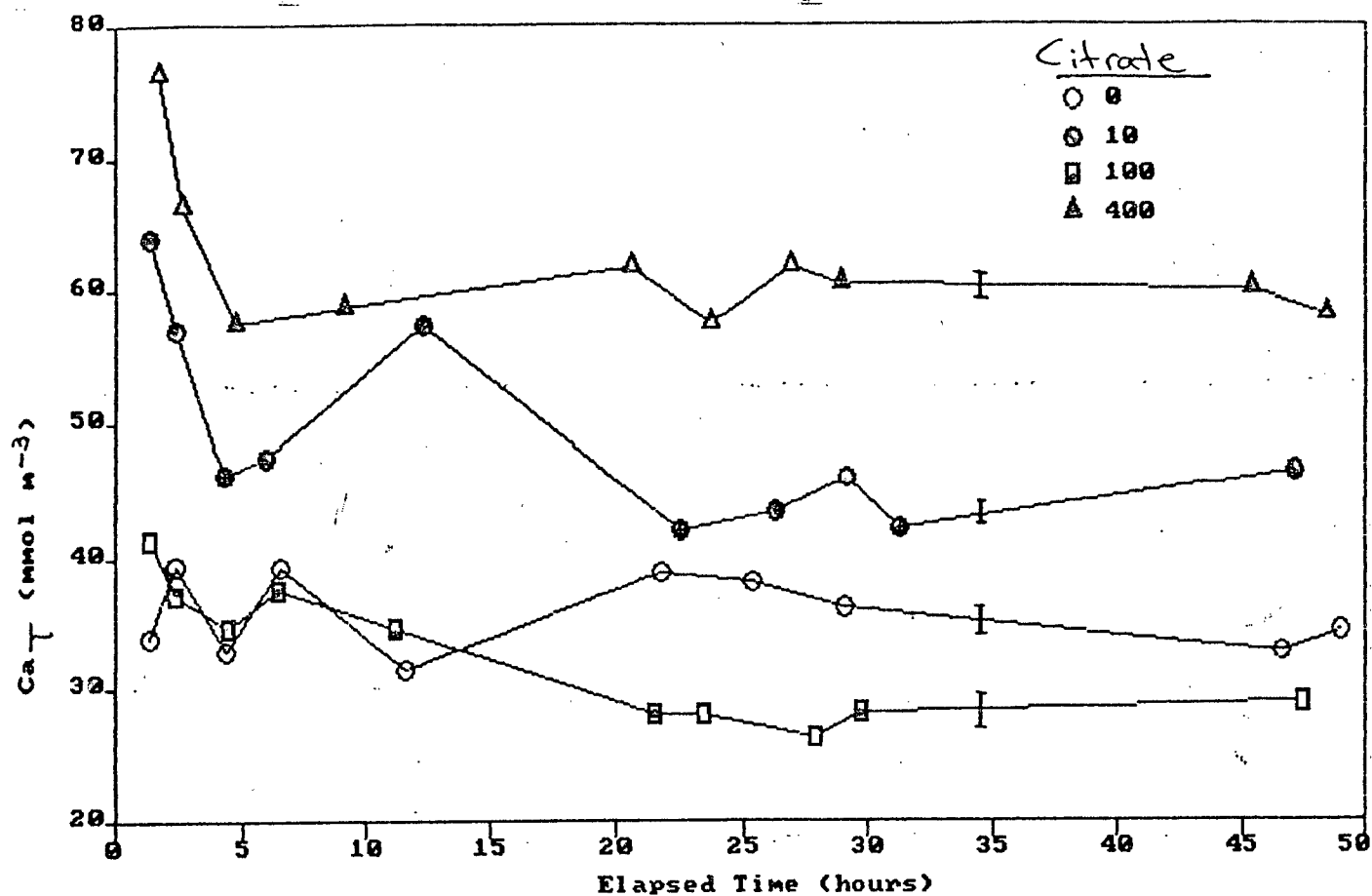


3. Effect of reaction time and citrate concentration (in mmol m^{-3}) on Al (III) solubility for a Na-Altamont soil separate in a background of 20 mol m^{-3} NaCl. Vertical bars denote one standard deviation.

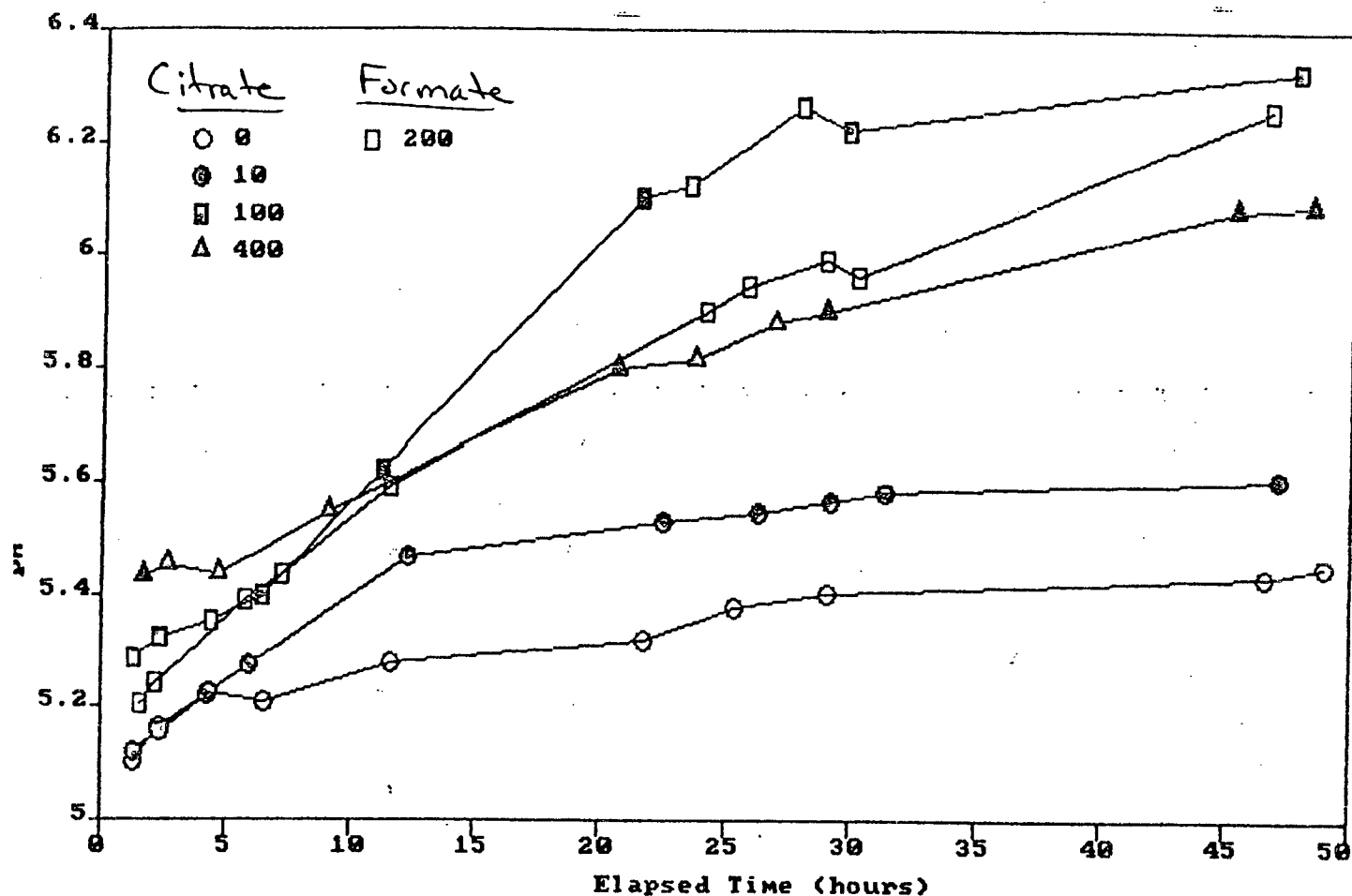
Fig 4)



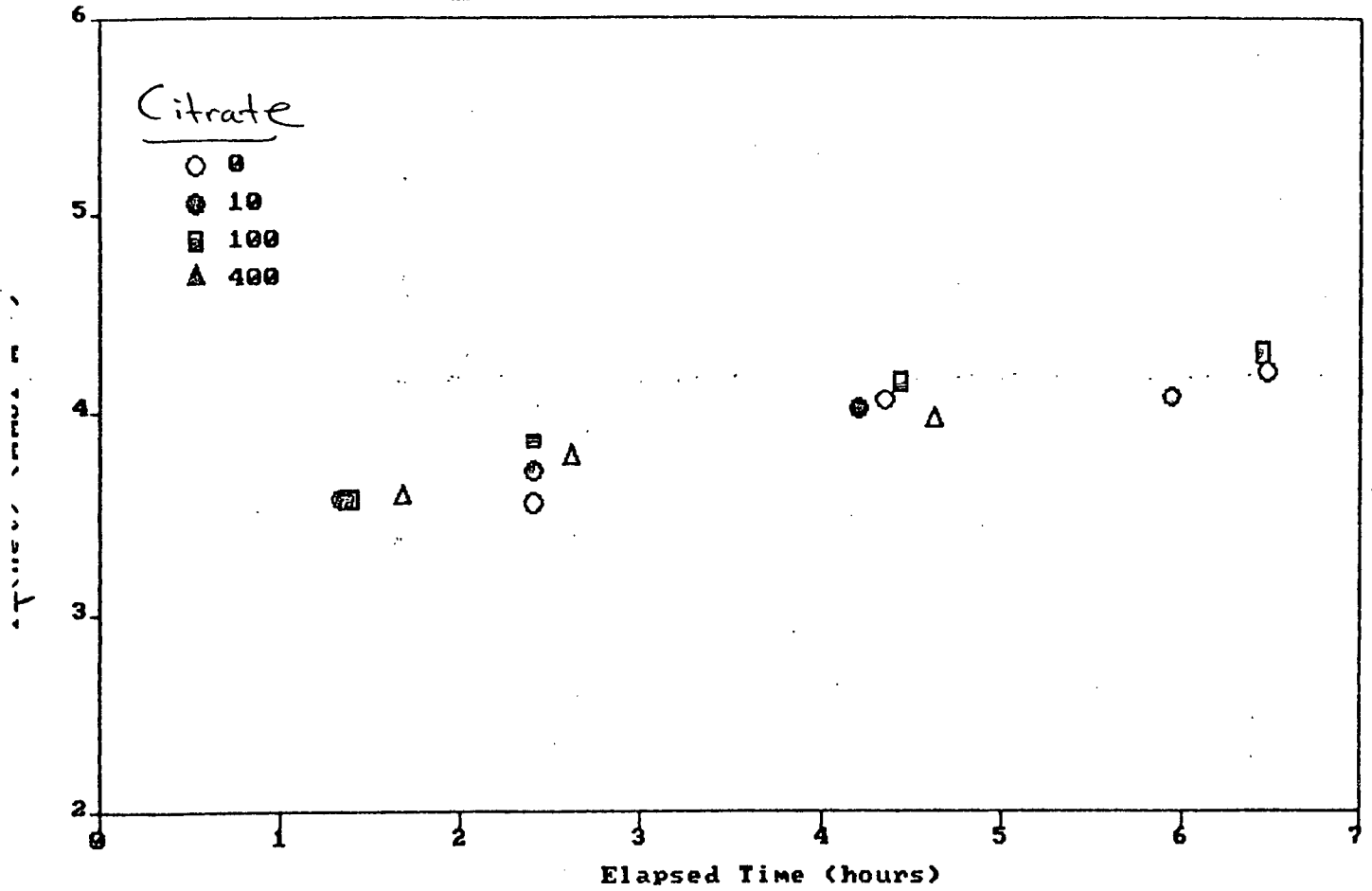
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6. Effect of reaction time and organic acid concentration (in mmol m^{-3}) on the final solution pH values for a Na-Altamont soil separate in a background of 20 mol m^{-3} NaCl. Symbol size exceeds one standard deviation for all samples.



7. Differential o-phosphate dissolution by citrate for a Na-Altamont soil separate, calculated with Eq. [1], for $1 \leq t < 7$ h. Citrate concentrations are in millimoles per cubic meter.

Competitive Adsorption of P by Ca-and K- Saturated
Kaolinite and Montmorillonite: I. Effect of Equilibration
Time, Ionic Strength, P Concentration and pH.¹

B. Bar-Yosef², U. Kafkafi³, Rivka Rosenberg², G.Sposito⁴

Abstract

The objective of this work was to study effects of total P concentration, pH, ionic strength and equilibration time on P partitioning between solid and solution phases of Ca-and K-kaolinite and montmorillonite suspensions as model systems of soils containing these minerals.

Phosphorus concentration in the solution phase (Cp) stabilised within 24 to 48 hours after introducing P to the system. Increased electrolyte concentration, which elevated the EC from 0.2 to 5.0 dS/m, decreased Cp. Further increase to about 40 dS/m had a negligible effect on Cp. It is postulated that since reduced electrolyte concentration increases the extent of the diffuse double layer of clay platelets' faces, the accessibility of P to adsorption sites on clays' edges is reduced due to enhanced overlapping of edge and face electrical fields. This mechanism is supported by data showing that P adsorption by Ca-clay exceeded that by K- clay.

P solution concentration as a function of pH was minimal in the studied clays around pH 6. In the investigated pH range (5 to 9), P partitioning was controlled by adsorption, which could be described by a competitive modified Langmuir model. The model

accounts for effects of Cp and pH on adsorption, and considers retention of individual P species by the adsorbent.

Key Words: Specific adsorption, Langmuir

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Introduction

The mechanisms controlling P adsorption by metal oxides have been intensively studied during the last two decades. Models describing quantitatively P retention as a function of (i) P solution concentration; (ii) pH and (iii) ionic strength (I) have been developed for such systems. The models include electrical and chemical components, accounting for surface charging and covalent ion-surface atoms bonding. The models assume either a multi-capacitance (Bowden et al, 1980) or a single capacitance (SC) configuration (Goldberg and Sposito, 1984a). The SC model, which has more simplifying assumptions but fewer parameters, was used to describe P adsorption by noncalcareous soils as well (Goldberg and Sposito, 1984b).

Phosphate adsorption on clay minerals has been the subject of intensive study too (Coleman et al, 1960; Muljadi et al, 1967; Kafkafi et al, 1968; Pissarides et al, 1968). However, no quantitative adsorption model accounting for effects of P solution concentration, pH and I on P retention has been suggested for them. The reason is that unlike the uniform metal-oxide surface, clay minerals are characterized by a face surface of constant negative charge, and an edge surface of variable charge on which specific adsorption occurs (Muljadi et al, 1967). The possible overlapping of the face and edge electric fields (Secor and Radke, 1985), and the edge-to-face card structure characteristic of montmorillonite and kaolinite prohibit application of the above mentioned adsorption models to clay systems. Simpler, semi-empirical approaches which were used to describe P sorption by clay minerals were the Langmuir equation (Muljadi et al, 1967; Pissarides et al, 1968), and the formation of amorphous solid phase Al-phosphate (Coleman et al, 1960;

Traina et al, 1986). These models were limited to specific pH and ionic strength values.

The objectives of the present work were to (i) add comprehensive information on P adsorption by montmorillonite and kaolinite suspensions as determined by adsorbed cations, ionic strength, reaction time, pH and total P concentration in the system; and (ii) test the suitability of a pH-dependent competitive adsorption model to describe P retention by the two clays under a wide range of P solution concentrations and pH values. Such a model successfully described B (Keren et al, 1981) and Se (Bar-Yosef and Meek, 1987) adsorption by montmorillonite and kaolinite, and Zn sorption by soils (Bar-Yosef, 1979). The further elucidation of P behaviour in the presence of clay minerals predominant in soils could help in improving P management under field conditions, especially in the rhizosphere, where pH and total P are rapidly changing, and under saline conditions.

Materials and Methods

Wyoming montmorillonite and Peerless kaolinite were brought to monoinic form by a procedure described by Keren and Shainberg (1975). The clay suspensions were shaken at a temperature of 297°K. The clays were centrifuged and in the supernatant the electrical conductivity (EC), pH and concentration of P, K and Ca were determined. Each treatment was duplicated. Specific experiments were:

a. The adsorption isotherm of P by Ca- and K-montmorillonite and kaolinite at constant pH and ionic strength.

To a 200 mL polypropylene bottle, 1.5 g of clay was introduced and 95 mL KCl at the appropriate pH and ionic strength were added. Microvolumes of HCl or KOH were added to adjust the pH to 5 or 8 respectively. The suspensions were shaken for 24 hours, and the pH was corrected again. After additional 24 hours, 50 mL of KH_2PO_4 in the appropriate electrolyte concentration and pH were added to the suspension. After the first 1 and 6 hours the pH was corrected. The suspension was shaken horizontally for a week and samples were withdrawn for analysis after 5, 24, 48, 72 and 168 hours.

b. The effect of pH on P partitioning between solid and liquid phases at constant ionic strength and quantity of P in the system.

The clays examined were K- or Ca-montmorillonite and Ca-kaolinite. The clay:solution ratio was the same as in experiment a. The pH values ranged between 4.5 and 9.5. The rest of the procedures were identical to those in experiment a.

c. Ionic strength effect on P concentration of the equilibrium solution of clay suspensions at a constant amount of P.

The studied clays were Ca- and K-kaolinite and montmorillonite. The ionic strength, I , was estimated by the empirical equation $I = 0.013 \times \text{EC}$ (Griffin and Jurinak, 1973), which was widely used in the literature (e.g. Lindsay, 1979). EC is given in dS/m and I is in mM. The measurements ranged between 0.2 to 40 dS/m. P concentration was measured after 48 hours of equilibration. The electrolyte was in all cases KCl to avoid P-Ca precipitation.

d. Computations.

The adsorption model (Bar-Yosef, 1979; Keren et al, 1981; Bar-Yosef and Meek, 1987) is given in eq [1]:

$$A = T * K_j * M_j / [1 + K_i * M_i] \quad [1]$$

Here A is total P adsorption (mol/g), K (indexed i or j) is related to the affinity of a given ionic species to the surface, M is activity in solution, j is an index of the n P species which are assumed to be adsorbed ($H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} , $CaPO_4^-$) and i is an index of the n P species plus other than P competing ions (in this case OH^- ; m=5). The parameter T is the maximum adsorption sites (mol/g). Bar-Yosef and Meek (1987) introduced an empirical correction factor T, to account for expected pH effects on the surface charge:

$$T = T_o * EXP[G * (RPH/pH - 1)] \quad [2]$$

Here T_o is T at a reference pH (RPH) and G is a dimensionless parameter specific to each adsorbent. When $G=0$, T is independent of pH and equals to T_o . To minimize the number of parameters in the model, RPH was denoted a fixed value of 6. The rationale for selecting this value was its agreement within 0.2 pH units with the pH at the inflection point of both clays' titration curve, obtained in a preliminary experiment. Sensitivity analysis showed that when RPH was varied by ± 1 pH unit, the best fit values of G and T_o were changed by ± 20 to 25%, and the performance of the model was still acceptable.

The activity of the adsorbing ions was calculated from the measured total P and Ca concentrations (spectrophotometric and atomic absorption, respectively), EC and pH. Routine equilibrium

equations relating the above P species and CaHPO_4^0 (assumed to be non-adsorbing) were used for the speciation. Reaction constants were taken from Lindsay (1979).

P adsorption was corrected for anion exclusion according to de Haan (1966).

The procedure NLIN in the SAS library was used to estimate the coefficients in eqs.[1] and [2] and their standard errors from experimental data.

The presented adsorption isotherms are expressed in terms of concentration rather than activity to enable comparison with experimental data.

Results

Adsorption kinetics

The effect of time on the concentration of P left in solution (C_p) in contact with montmorillonite and kaolinite clays is presented in Fig.1. Kaolinite shows a nearly linear reduction in P concentration with time between 1 and 7 days of equilibration. The change between 2 and 4 days is small, indicating that the 48 hours of equilibration used in most of the measurements of this work represents a relatively stable condition.

With montmorillonite, the most stable concentration also was found between 2 and 4 days of equilibration. The major changes in the P concentration in solution occur within 1 day.

The effect of ionic strength on P adsorption

Increasing the ionic strength (I) increased P retention by the surface in all studied clays. The main effect occurred between 0.2 and 5 dS/m. In kaolinite, increasing I was more effective the higher the initial pH. Elevated I decreased the pH of the kaolinite slurry. This could be the effect of exchanging adsorbed protons by the added cation, or an increase in the specific adsorption of OH^- by the surface. When the initial pH was 5.1, increase of salt concentration did not have any effect on pH or P adsorption by Ca- kaolinite. This pH is therefor the point of zero salt effect of kaolinite (Sposito, 1984). It is not too far from 4.7, which is the point of zero charge of kaolinite (Parks, 1965; Sposito; 1984).

In Ca- montmorillonite (Fig.2), an abrupt decrease of C_p was observed at relatively low I (2 dS/m); the effect of I on K- montmorillonite was more gradual.

Effect of clay type and adsorbed cation on P adsorption.

Phosphate adsorption on kaolinite as a function of C_p is presented in Fig. 3. The ionic strength was kept constant at 0.02M. In both mono- cationic clays the adsorption at pH 5.2 was higher by about 50% or more than in the pH range of 8.0, in agreement with Traina et al (1986) on soil separates. The points are the experimental results and the lines were drawn according to eqs. [1] and [2] and the coefficients in Table 1. The apparent good agreement between measured and calculated lines was obtained despite the great standard errors of the best fit coefficients (Table 1) and the fact that most of them were not significantly different than zero (T- test, $P=0.10$). When running the model under the assumption of $G=0$, the best fitted parameters were different, but their standard errors and the standard error of

the model estimate were considerably greater than in the current case.

P adsorption by Ca and K-montmorillonite in the pH range of 5.5-5.9 and 8.2-8.3 are presented in Fig.4. As with kaolinite, increase in pH decreased P adsorption. Ca-montmorillonite adsorbed at a given P solution concentration and pH about 10% more P than the K-clay.

The estimated maximum P adsorption by montmorillonite at the RPH (T_o) was 7- 8 $\mu\text{mol/g}$, and that on kaolinite about 6 $\mu\text{mol/g}$; The exchangeable cation had no effect on T_o , but strongly affected G. In the case of Ca and K, G was about 1 and 3, respectively, in both clays. No consistent trend was observed in the numerical values of the K_i in the studied clay systems (Table 1.).

Effects of pH on P solution concentration.

Changes in Ca and P concentrations in the solution of K or Ca-montmorillonite as a function of pH are presented in Fig. 5. In the absence of clay, the expected total P concentration in the solution would have been 38.7 μM . As can be seen in Fig. 5a, a minimum of P concentration in the solution was found in the pH range of 5.5 to 6.5 in both K and Ca clays. The simultaneous determination of Ca in the solution (Fig. 5b) revealed that above pH 7 the Ca concentration in the solution decreased from 1.25 mM at pH 6.5 to 0.75 mM at pH 9.2. The fact that Ca concentration decreased and that of P increased suggests that precipitation of Ca phosphate is unlikely. Indeed, except 2 cases at $\text{pH} > 9$, all the data points of Fig.5a were undersaturated with respect to octacalcium phosphate. Similar dependency on pH was found in systems that contained lower total P per g clay, like 2.2 or 1.5

umol/g, which for the sake of brevity were not included in this report.

The solid lines in Fig. 5a were calculated based on eqs. [1] and [2] and the parameters given in Table 1. The agreement between experimental and calculated results is unsatisfactory, especially at the extreme pHs.

The effect of pH on Cp in Ca-kaolinite suspension (Fig. 6) was similar to that in montmorillonite, with a minimum around pH 6. In this system the agreement between experimental and computed results was better, and the simulated curve predicted the observed minimum in concentration at the appropriate pH.

Discussion

The major effects of ionic strength (I) and exchangeable cation on P retention by the studied clays are in accord with earlier reports (Pissarides et al, 1968), namely, that elevated I and exchangeable Ca rather than K decrease P concentration in the solution phase (Cp). From qualitative electrostatic considerations (Bowden et al, 1980), increased I is expected to decrease Cp only at pH values below the zero point of charge (ZPC) of the clay's edges, which is less than 5 (Park et al, 1965). Since in our case I increased Cp at pHs appreciably higher than the ZPC, it is postulated that the effect stems from the influence of I on the extent of the diffuse double layer (DDL) of clay faces. Increased I restricts the extent of the DDL and consequently reduces the masking of P adsorption sites on clay edges by the negative electric field of clay faces. This mechanism also explains the fact that higher P adsorption was obtained under given conditions when Ca rather than K was the

exchangeable cation. A similar effect of I and exchangeable cation on anion adsorption by the same clays was obtained in the case of B (Keren and Oconner, 1982).

Negative adsorption may significantly affect C_p in montmorillonite suspensions at an electrolyte concentration < 3 mM ($EC \sim 0.2$ dS/m) (de Haan et al, 1968). The effects of I on C_p shown in Fig.7 cannot be attributed therefor to anion exclusion. The effect of I on activity coefficients should induce a diminished adsorption with elevated I. This is contrary to the obtained results. The current adsorption model considers effects of I on anion exclusion and activity coefficients, but it still could not simulate the experimental results of C_p vs. I. This is due to the fact that the effect of I on the accessibility of P to adsorption sites on the clay edges was not taken into account.

The ionic strength could not be maintained constant in all experimental points because of pH adjustments and different levels of P added. The range in EC in the various adsorption experiments reported herein is given by the parallel dotted lines in Fig.2 (2 to 5 dS/m). Variation in I within this range could induce considerable variability in C_p which is not taken into account by the adsorption model. This may partly explain the poor agreement, in some cases, between experimental and computed results, especially where the studied variable was pH.

The effect of pH on P adsorption reported herein agrees with earlier reports by de Haan (1966), Muljadi et al (1966) and Murrman and Peech (1969). The role of pH stems from (i) its effect on the relative fraction of the various P species, which differ in their affinity to the adsorbent; (ii) the variations in clay edges charge density with pH; (iii) the competition between OH^- and P on common adsorption sites. Those factors are included in eqs. [1] and [2]. When factor (ii) was disregarded, the

predictability of the model was appreciably reduced. The fact that in all studied cases the adsorption coefficient of OH was not significantly different than 0, while G, which describes the change in surface charge due to pH gave more significant results (Table 1), indicates that mechanism (ii) is more important in determining P adsorption than mechanism (iii). The effect of pH on edge-to-face flocculation, which may affect P accessibility to adsorption sites is not taken into account in the reported model.

The parameter G was greater in K-clays than in Ca-clays (Table 1). This may be related to the effect of exchangeable cation on the extent of the diffuse double layer.

The performance of the adsorption model is not satisfactory. It can be judged from the fact that most of its parameters did not pass a T-test at the 0.10 probability level (Table 1), and the inconsistency between the K_i values of the various clays. However, a better adsorption model to predict P retention by montmorillonite and kaolinite under varying pH conditions has not been published yet. The model should be considered as an empirical one with the advantage of being differentiable with respect to both P solution concentration and pH, which make it applicable to P transport equations in complex media like the rhizosphere.

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Table 4. Regression parameters for the P-adsorption model (eq. [1], [2]). (RPH=6.0 in all cases).

| | To | G | log K (1/mole) | | | | | SEE ⁺⁺ |
|--------------------|---------|-------|---|--------------------------------|-------------------------------|--------------------------------|------|-------------------|
| | umole/g | | H ₂ PO ₄ ⁻ | HPO ₄ ²⁻ | PO ₄ ³⁻ | CaPO ₄ ⁻ | OH | umol/g |
| Ca-montmorillonite | | | | | | | | |
| Parameter | 7.0 | 1.00 | 0 | 7.02 | 0 | 9.07 | 9.88 | 0.26 |
| SE | 1.8 | 1.01 | | 6.59 | | 8.68 | | |
| Signif.* | ** | | | * | | | | |
| K-montmorillonite | | | | | | | | |
| Parameter | 8.0 | 3.80 | 2.75 | 5.63 | 9.83 | 9.72 | 8.69 | 0.40 |
| SE [†] | 4.9 | 2.10 | | 5.61 | | | | |
| Signif. | | | | | | | | |
| Ca-kaolinite | | | | | | | | |
| Parameter | 6.0 | 10.85 | 4.97 | 7.36 | 0 | 9.06 | 8.26 | |
| SE | 0.3 | 10.32 | 5.54 | 7.59 | | | 8.46 | |
| Signif. | ** | | | | | | | |
| K-kaolinite | | | | | | | | |
| Parameter | 5.7 | 2.50 | 5.00 | 0 | 9.04 | 8.70 | 0 | 1.20 |
| SE | 1.0 | 0.91 | 6.41 | | | 10.0 | | |

*Significance by T-test. **p<0.05; *p<0.10. Where significance is not given, the estimate is not statistically different than 0 at p=0.10.

[†]SE is standard error. When not provided, it was too big to be provided by the NLIN program.

⁺⁺SEE is the standard error of the model estimate.

Figure Legends

Fig. 1. P concentration in the solution of Ca-montmorillonite (Ca-Mt) suspension as a function of time at 3 pH values and of Ca-kaolinite (Ca-Kl) at pH 7.5. Suspension density 1%. Electrical conductivity 2.0 dS/m. Numbers near data points are pHs.

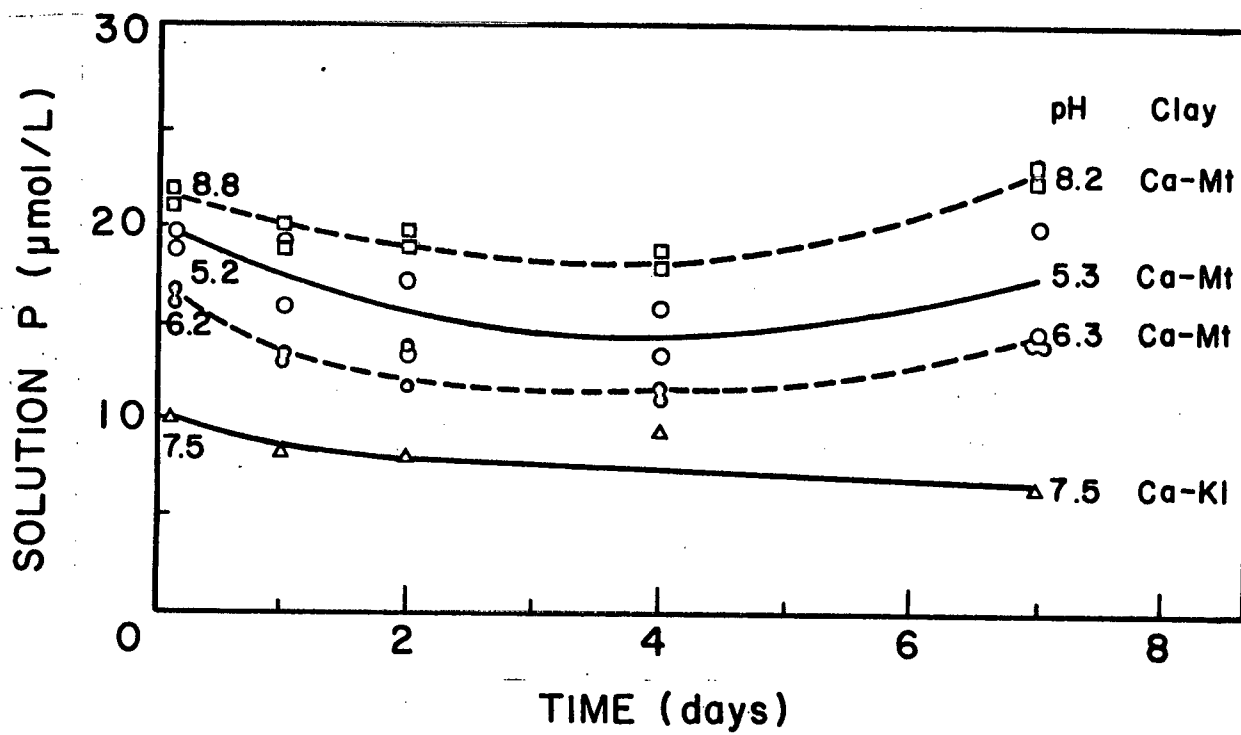
Fig. 2. Effect of increasing KCl concentration (expressed as electrical conductivity) on the concentration of P left in solution at a constant amount of P in the clay systems. Numbers in brackets are "equilibrium" pH. Parallel lines on abscissa are explained in text.

Fig. 3. Adsorption isotherms of P at two pH levels by K and Ca kaolinite at 0.02 M KCl. Suspension density 1%. The lines were calculated according to eqs. [1] and [2] using the parameters in Table 1.

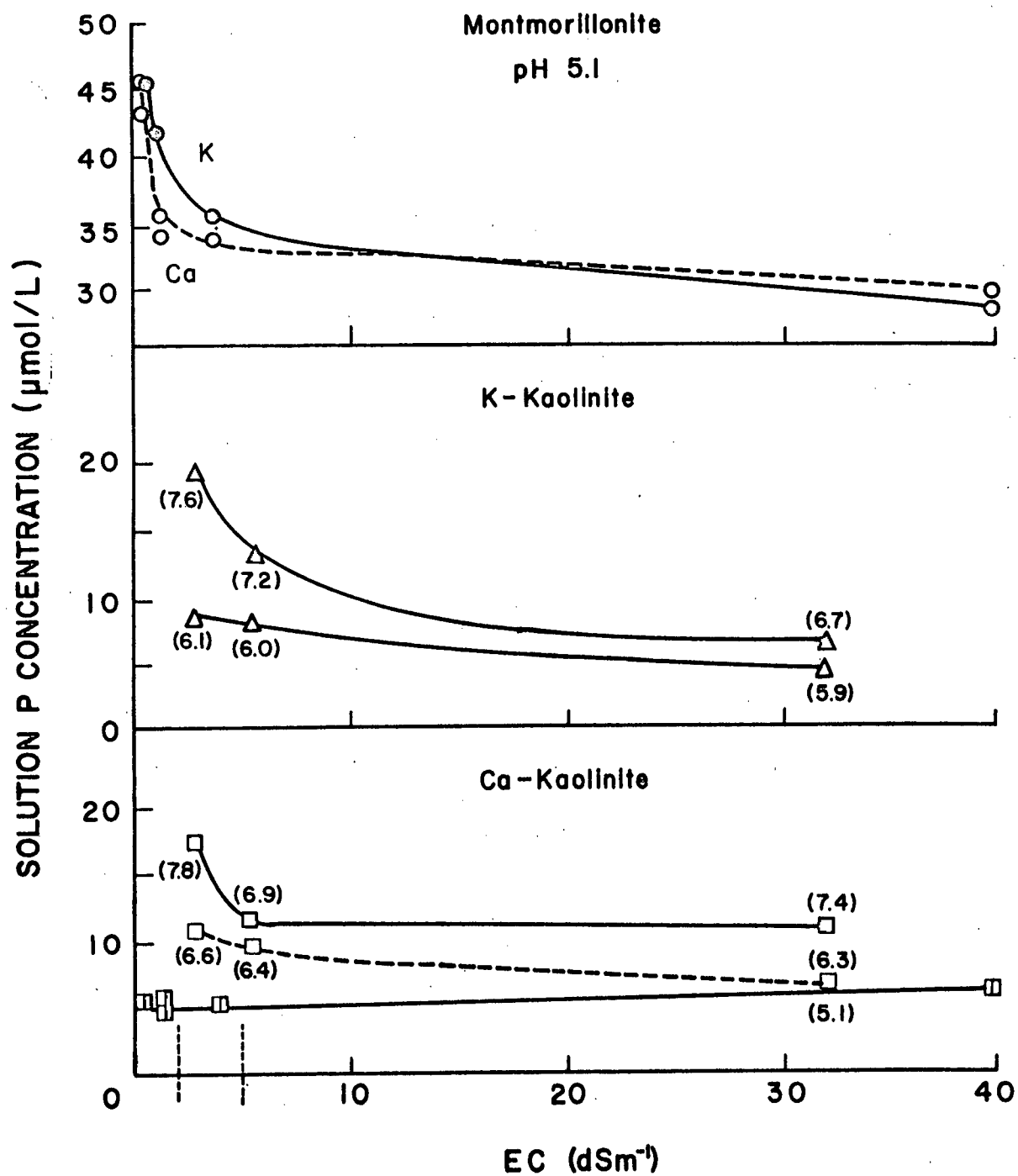
Fig. 4. Adsorption isotherm of P at two pH levels by K- and Ca-montmorillonite at 0.03 M KCl. Suspension density 1%.

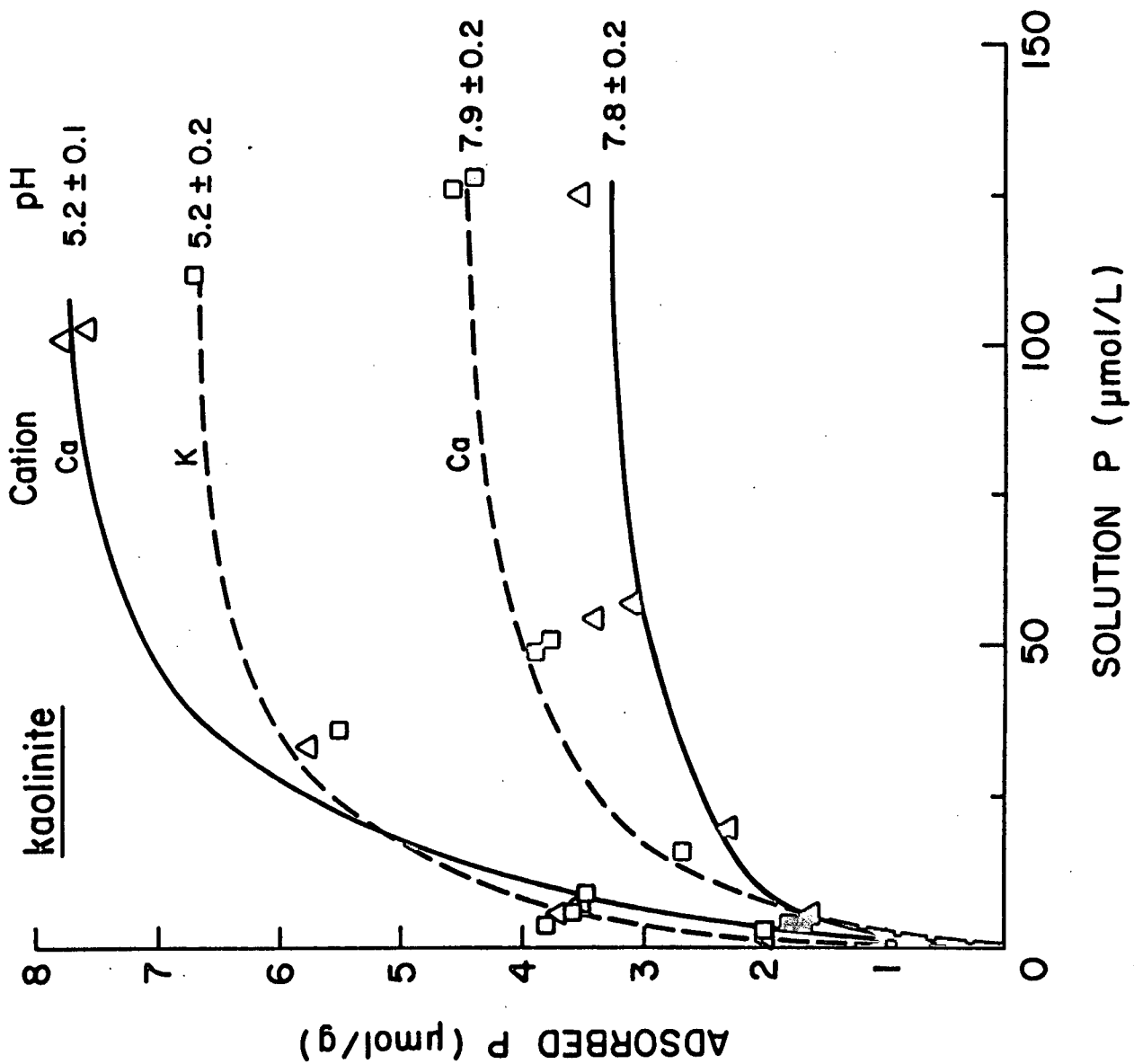
Fig. 5. Experimental and computed solution P concentration in K and Ca montmorillonite (Mont.) suspensions, and experimental Ca concentration in the solution of Ca-montmorillonite as a function of pH. Calculation according to eqs [1] and [2] and parameters in Table 1. The total P quantity in the system (Q_p) was 3.87 $\mu\text{mole/g}$. Electrolyte concentration 0.01 M KCl. Suspension density 1%.

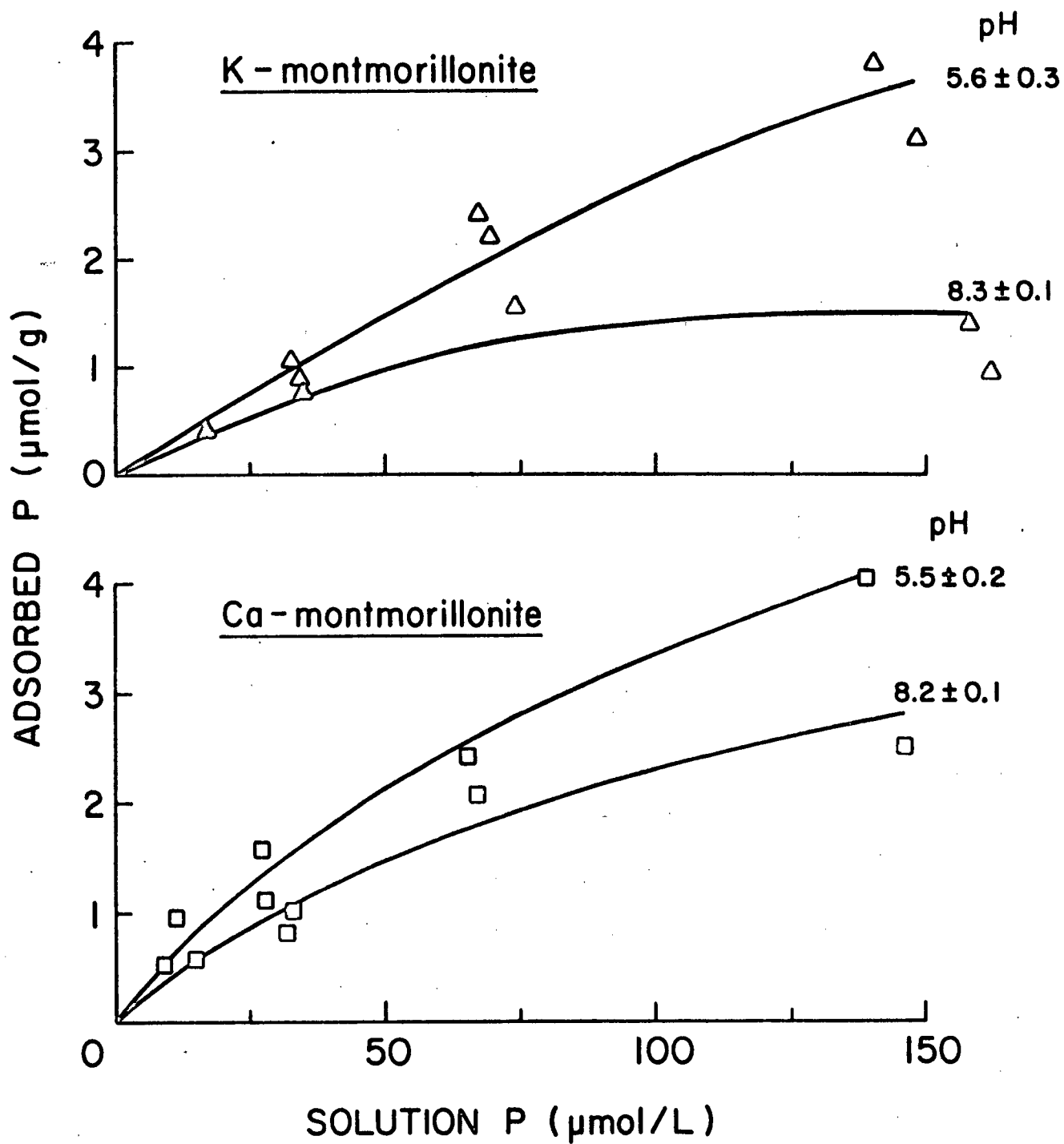
Fig. 6. Experimental solution P and Ca concentrations in Ca kaolinite suspensions as a function of pH. Solid line was calculated according to Eqs. [1] and [2] and parameters in Table 1. Electrolyte concentration 0.025 M KCl. Suspension density 1%.

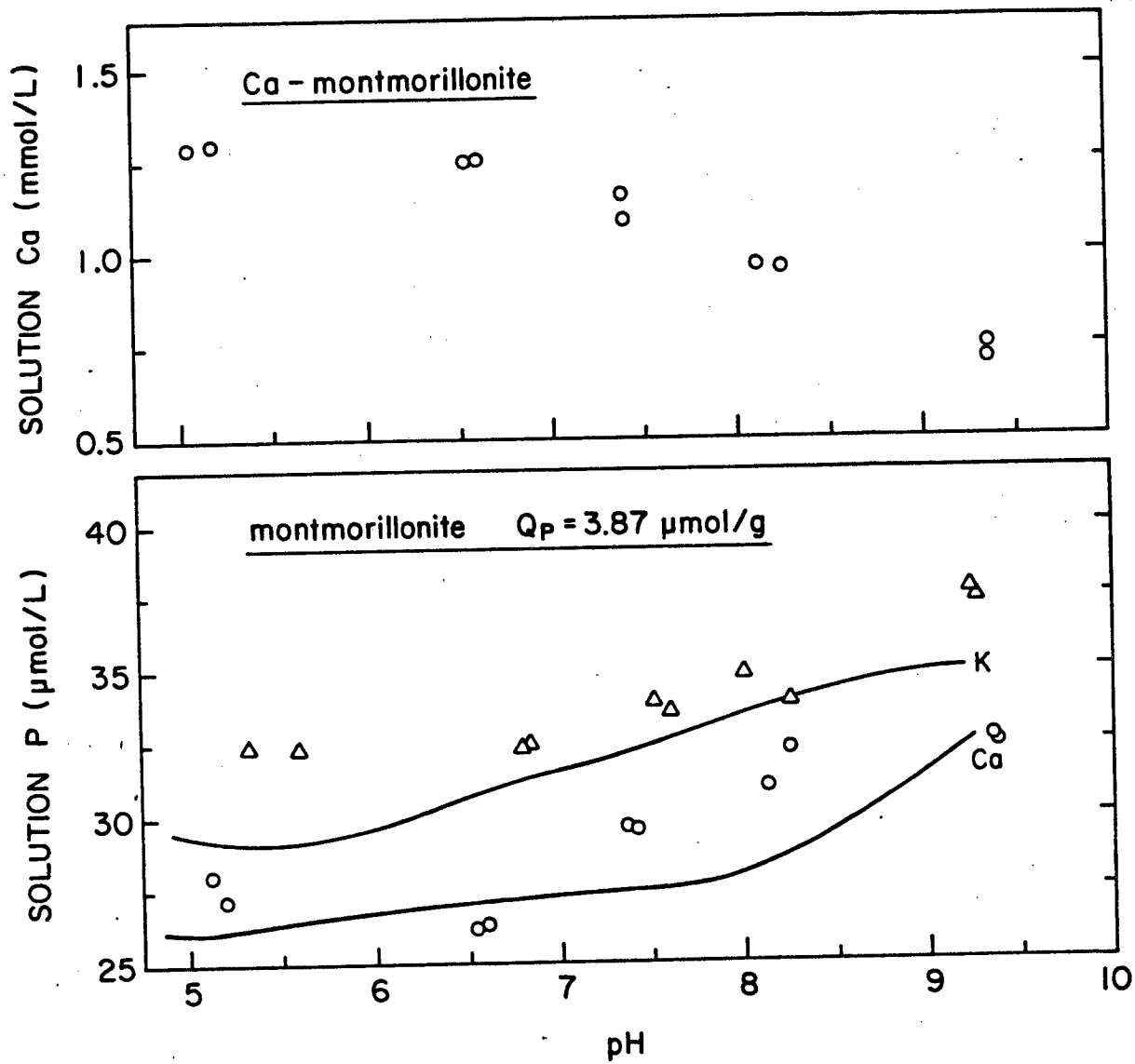


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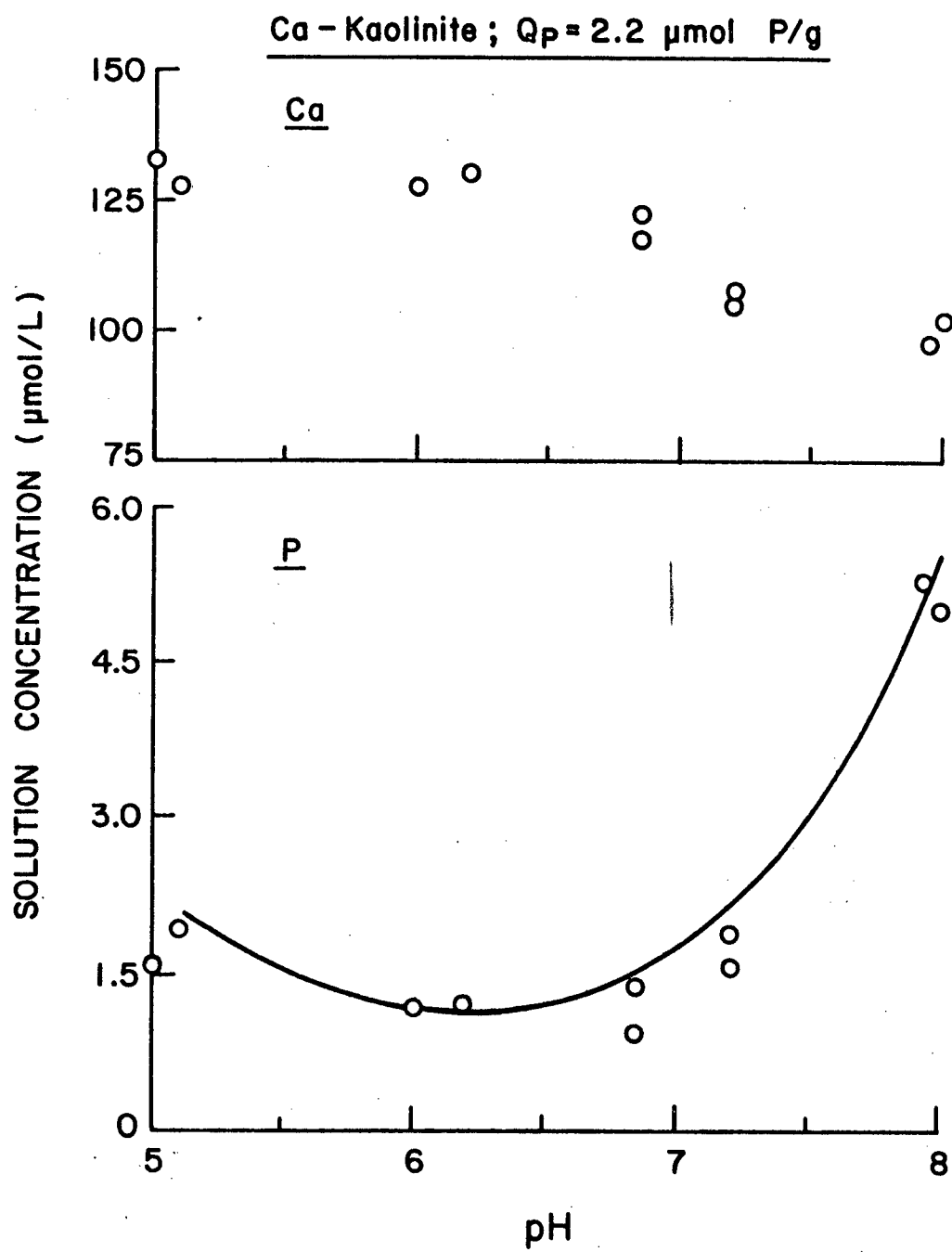








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Competitive Adsorption of P by Ca- and K- Saturated Kaolinite and
Montmorillonite: II. Organic Anion Competition¹

U. Kafkafi², B. Bar-Yosef³, Rivka Rosenberg³ and G. Sposito⁴

Abstract

Phosphate adsorption and desorption from clay surfaces has been studied extensively. In the soil, living roots excrete various organic compounds. The present work was aimed to study the competition between organic anions and the phosphate anion on kaolinite and montmorillonite sorption sites. The organic anions studied were: bicarbonate, citrate, acetate, phenylalanine and α -amino isobutyric acid, all of them are being excreted by plant roots. Organic agents concentration and pH were varied at a constant amount of P in the clay-solution system.

Citrate and Bicarbonate reduced and the amino acids increased P adsorption to the clays. The unifying principle that explains these findings is that P adsorption on a clay depends on the extent of the depression of the negative potential of the clay platelets. Sodium bicarbonate and citrate anions at pH >8 are competing with P and reduce its adsorption to active Al sites on the clay. The increased P adsorption in the presence of amino acids is suggested to stem from the fact that H-bonding of the amino groups cause a decrease in inter-lamellar spacing, and produces quasi-crystals. The quasi-crystals reduces the spillover of negative charge from the surface to the edges and allowed closer approach of the phosphate ion to the Al site.

Additional Index Words: Citrate, Bicarbonate, oxalate, α -amino isobutyric acid, pH.

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Introduction

In the first article of the present work (Bar Yosef et al., 1986) the competition of OH^- with P in a pure mineral surrounding was studied. The present work was devoted to study the effect of different organic acids, reported to be excreted from roots, on the adsorption and desorption of P from K and Ca saturated clays.

Roots excretion of carboxylic and organic acids were reported (Riviere, 1960; Smith, 1969; Hale and Moore, 1979). The idea that citric acid is excreted from roots led Dayer (1894) to suggest citric acid to estimate plant available P in the soil, and the phosphate industry still uses the citrate soluble phosphate to identify soluble P in their products.

A detailed review of the physico-chemical reactions of P in soils was published (Olsen & Khasawneh, 1980).

Olsen et al. (1954) suggested to use NaHCO_3 and Morgan (1941) has used sodium acetate to estimate available P in the soil. In these compounds the carboxylic group is the active one in desorbing P from the soil. The degree of dissociation of this group depends on whether the acid or the salt are used. There is one carboxyl group in NaHCO_3 and 3 in citric acid. The ability of the citrate ion to form complexes with iron and aluminum and by that prevents phosphate from the adsorption site (Struthers & Sieling, 1950) is known for a long time. Recently it was shown (Inoue and Huang, 1985) that complexing Al by citrate prevented the crystal growth (precipitation reaction) of aluminum silicate.

Since the amino acids phenylalanine and butyric acid were also reported to be excreted by roots (Riviere, 1960), they were also included in the present study. These compounds contain in addition to the carboxyl negatively charged group a positively charged amino group in alfa-position. Behaving as a zwitterion, the amine compounds are long known to be strongly adsorbed to clay surfaces (Grim, 1953).

The purpose of this work was to study the effect of these carboxylic compounds on the competition with phosphate on the adsorption sites of montmorillonite and kaolinite. Understanding the mechanism of the competition could lead to better understanding of P extraction by roots from soil surfaces.

Materials and Methods

Phosphate adsorption in absence and presence of organic compounds

a) Simultaneous additions of P and organic compound. Oxalic acid (OX), Phenylalanine (PA) and α -amino-2-methyl propanoic acid (α -amino isobutyric acid) (BA) were added simultaneously with 4 levels of

KH_2PO_4 (22, 45, 90, 180 μM) to the clay suspensions at a molar ratio of 1:1.

After 72 h of equilibration the phosphate concentration was determined and compared to that found at the same time with KCl suspensions. The pH and ionic strength were kept constant.

b) Desorption of previously adsorbed P by organic compound. This procedure was taken with the intention to simulate the possible extraction of P by potential root exudates.

A constant amount of P was added to a clay slurry at a 1:100 clay to solution ratio and after 48 hours the competing organic anion was added for an additional 48 h and the phosphate concentration was determined in the clear supernatant solution. The organic compounds used were: citric acid, sodium bicarbonate, ammonium acetate, PA and BA.

Results and Discussion

Phosphate adsorption in the presence of organic anions.

The organic compound selected to simulate potential root excretion and the pK values of their acids and log K of potential ligand complexes that may occur in solution are specified in Table 1.

Oxalic acid (OA), phenylalanine (PA), and α -amino iso butyric acid (BA) were each mixed in solution with phosphate at equal molar concentrations. After 72 hours the clay was separated and the concentration of P in the solution was determined. The ratio between P concentration in the solution with OA to that of P in the presence of Cl^- is presented in Table 2.

In Ca-montmorillonite the oxalate masked some of the sites (9-19%) available for phosphate adsorption, thus leaving more P in the solution as compared to that found in the presence of Cl at pH of

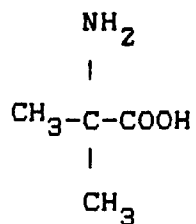
5.7-5.8. When the pH was increased to 7.9-8.0, where the $C_2O_4^{2-}$ ion of the oxalic acid is predominant (pK_2 4.3) no competing effect could be found except in the very low P concentration. In the case of Ca-kaolinite the masking effect of the oxalate ion is observed at the pH range of 5.3 - 5.5, where substantial fraction of the oxalate is present as $C_2O_3OH^-$, and much less at the higher pH range. Increasing the phosphate concentration decreased the blocking effect of the oxalate on phosphate adsorption. These observations suggest that the binding to the site needs not only the negative charge but also the presence of OH on the adsorbing molecule.

The effect of increasing organic agent concentration at a constant quantity of P in a Ca-kaolinite suspension is presented in Fig. 1. In this case P and the organic agent were added simultaneously. Citric acid and $NaHCO_3$ reduce the adsorption of phosphate with the same effect up to about 5 mmol m^{-3} and further increase in agent concentration did not produce further change in the amount of phosphate in the solution. Ammonium acetate and phenylalanine increased the amount of adsorbed P.

In Fig. 2 the organic acid was added after P had reacted with the surface. The relative effect of the organic compounds remained the same as in Fig. 1. The effect could not be explained by ionic strength since at 5 mM initial concentration almost the same ionic strength was observed and the affinity of P to the surface increases in the presence of α -amino isobutyric acid, phenylalanine and ammonium acetate but decreases with $NaHCO_3$ and citric acid. Increasing the phosphate 10 times more than that in Fig. 1 resulted (Fig. 3) in the same order of the effect of the organic compounds on the decrease or increase of phosphate adsorption to the surface. The same effect of organic agent is also found in montmorillonite (Fig. 4). The unifying principle that could be traced in this work and in the previous paper (Bar-Yosef et al, 1987) is that the increase in P adsorption is

obtained when the electrical field forces of the clay faces are depressed.

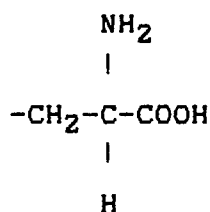
Neutralization of the edge surface charge is achieved by specific adsorption. -amino isobutyric acid and phenylalanine have both amino and carboxylic groups:



-amino

isobutyric acid

pK 7.69



phenylalanine

pK 2.4; 9.5

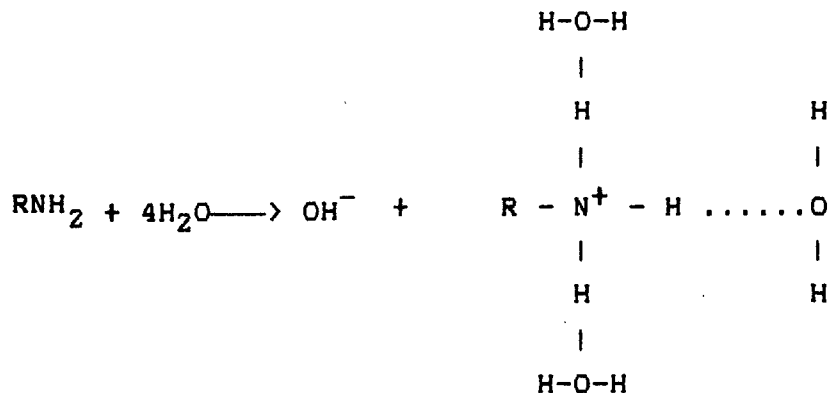


ammonium acetate

pK 4.8

The amine group is known to develop strong hydrogen bonding.

Huheey (1987) suggested the following bond of the amine group with water:



If the amine is entering between two adjacent clay platelets, quasi crystals may be formed with the amine adsorbing to the face surface through hydrogen bonding to the oxygens of the silica layer (Grim, 1953). According to Jordan (1949) the small amino isobutyric acid molecule with only 2 carbons on the amine chain would have caused the clay to collapse to 1.36 nm basal spacing between the plates. The carbon skeleton of the amines is situated parallel to the clay plane;

therefore, the phenylalanine molecule with the attached methyl and 6 carbon ring to the side will also cause the clay to collapse to the same spacing. Besides neutralizing the charge the main effect of the adsorbed amines is to produce large quasi crystals.

There is little doubt that Al is the only species in pure clay that can bind the o-phosphate (Coleman et al., 1960) especially in a K-saturated clay. The effectiveness of added Ca^{2+} on reducing o-phosphate concentrations in equilibrium solutions with montmorillonite was noted by Coleman et al. (1960), Wild (1953) and by Ravikovitch (1934), and recently by Traina et al. (1986). Early studies of Ravikovitch (1934) assumed a Ca-phosphate bond. This explanation might hold at very high pH values where the solubility of Ca-phosphate is very low (Lindsay, 1979). At pH values below 7, Ca-phosphate precipitation is ruled out, and the only agent left to react with phosphate is the Al (III) on the clay. The position of that Al (III) on the clay is still an open question. Traina et al. (1986b) have suggested the mechanism by which adding cation to an acidic montmorillonite induced displacement of exchangeable Al (III) that leads to the formation of additional solid phase basic Al-phosphate. This mechanism cannot explain why the montmorillonite clay at pH 6 or 7 will adsorb more P than a clay at pH 4 that has much more exchangeable Al (Traina et al., 1986; Bar-Yosef et al., 1987()). It is possible that the common phenomena observed of increased P adsorption by increasing ionic strength, Ca^{2+} and pH of maximum adsorption between 6-7, all leads to the direction of reducing the electric charge on the clay surface. It is suggested here that as a result of nullifying the surface charge, stacking of tactoid platelets create a much larger area of edges in which the Al (III) can react with the negative phosphate ion. In other words, the negative electric force lines around a single platelet can prevent the approach of the H_2PO_4^- ion in the suspension (Secor & Radke, 1985). Increasing the platelet stacking and reducing the charge, as is the case in increasing ionic

strength and around pH the PZC, specific adsorption into the IHP, as was shown in the case of adsorbing amino carboxylic acids (Fig. 1-4), more edge Al becomes available to Al-P interaction. This condition is similar to the case of kaolinite edge surfaces as was shown by Muljadi et al. (1964) and Kafkafi et al. (1967). The effect of platelet stacking on phosphate adsorption was also suggested by Pissarides et al. (1968).

If this theory is correct, clay particles condensation due to decreasing solution-to-clay ratio should have a similar effect on P adsorption. To test this hypothesis, equal amounts of P (6.45 $\mu\text{mol/g}$) and clay were shaken in different volumes of solution. Concentrating the slurry from 1000 mL/g clay to 100 mL/g clay increased the solution P simply by the dilution factor (Fig. 5). Further concentration of the slurry to 10 mL/g deviate from the expected concentration and a sharp reduction in solution P is observed. This reduction has not occurred in Ca concentration in the solution phase (Fig.5).

Condensing the slurry to 10 mL/g had much greater effect on P adsorption than either ionic strength or pH in the range of the PZC. Further condensation to 1.5 mL/g of clay posed severe problems of solution separates. It is suggested here that stacking of montmorillonite platelets reduces the negative electrostatic repulsion lines from the edges and by that allowing phosphate approach and interact with $\text{Al}^+(\text{OH})$ or $\text{Al}^0(\text{H}_2\text{O})$ groups located in the platelets edges (Hingston et al. 1968).

The findings in the work suggest that in the field, phosphate is bound more strongly than could be envisaged from dilute extractions. The early works of Burd and Martin (1923) that displaced the soil solution and did not dilute it, should be reconsidered when the reactions of hydroxy anions in soils are studied.

Acknowledgment

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Table 1: Organic compounds used in the current study, their log stability constant with Ca and pK values of their acids at 0.01 M ionic strength[†].

| -anino isobutyric [#] | L-Phenyl- alanine | Oxalic acid | Ammonium acetate | Citric acid | Sodium carbonate | |
|-----------------------------------|----------------------|----------------|---------------------|----------------|---------------------|--------|
| $C_4H_9NO_2$ | $C_9H_{11}NO_2$ | $C_2H_2O_4$ | CH_3COONH_4 | $C_6H_8O_7$ | $NaHCO_3$ | Ligand |
| ----- log K ----- | | | | | | |
| | | 2.64 | | 4.25 | 3.15 | CaL |
| | | | | 8.71 | 1.0 | CaHL |
| | | 3.15 | | 7.75 | | CaL2 |
| ----- pK ----- | | | | | | |
| 7.69 ^{††} | 2.4;9.5 | 1.3;4.3 | 4.8 | 3.1;4.8 6.4 | 6.4;10.3 | H-L |

[†] Data taken from Martel and Calvin (1953) and from Lindsay (1979)

[#] amiono 2 methyl prupanoic acid

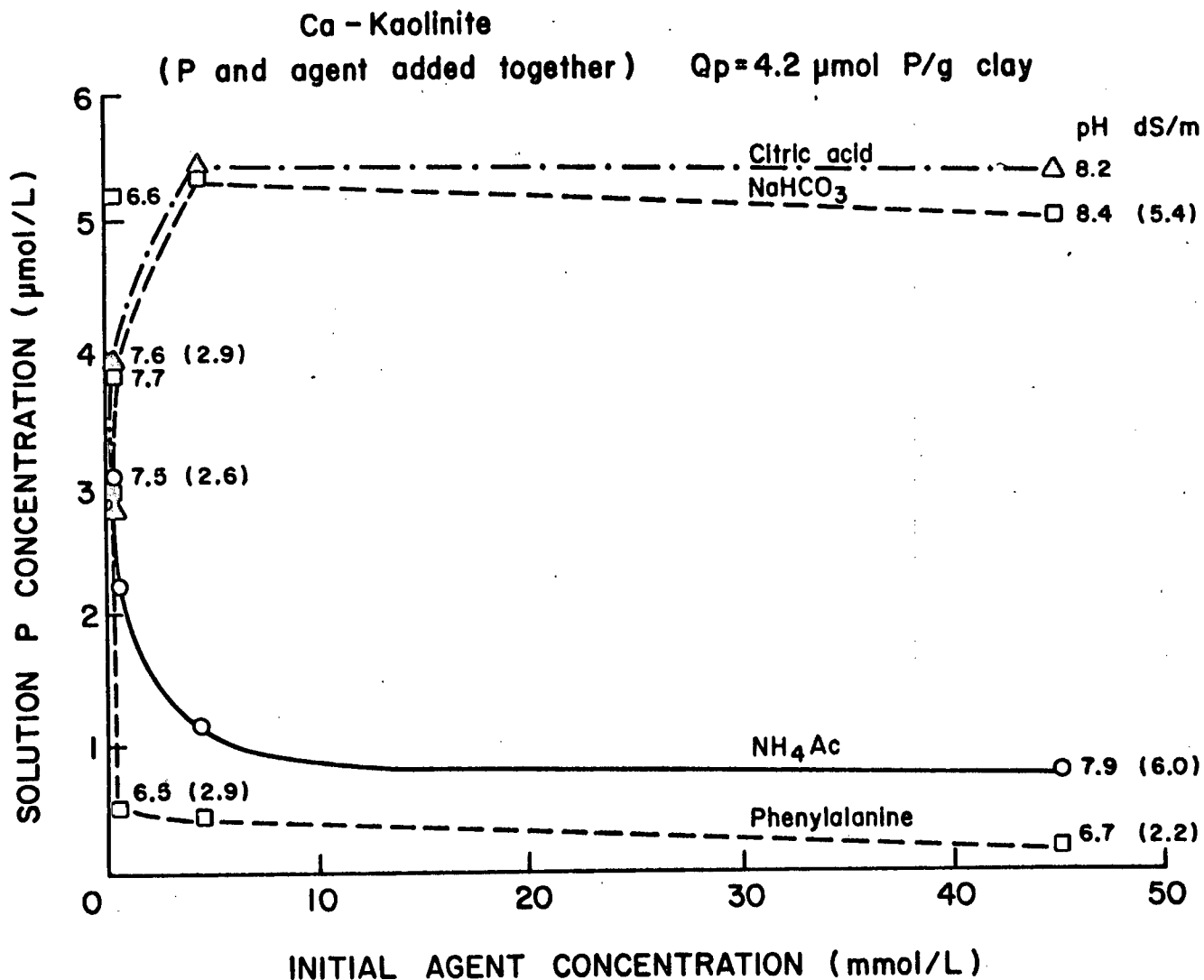
^{††} I = 0.1 M

Table 2: The phosphate concentration in the presence of oxalate (P_{ox}) divided by that in the presence of chloride (P_{Cl}) in Ca-montmorillonite and Ca-kaolinite at two pH ranges. Phosphate and oxalate were added simultaneously at equal molar ratios. Ionic strength was 0.025 mmol/L and equilibration time 72 h.

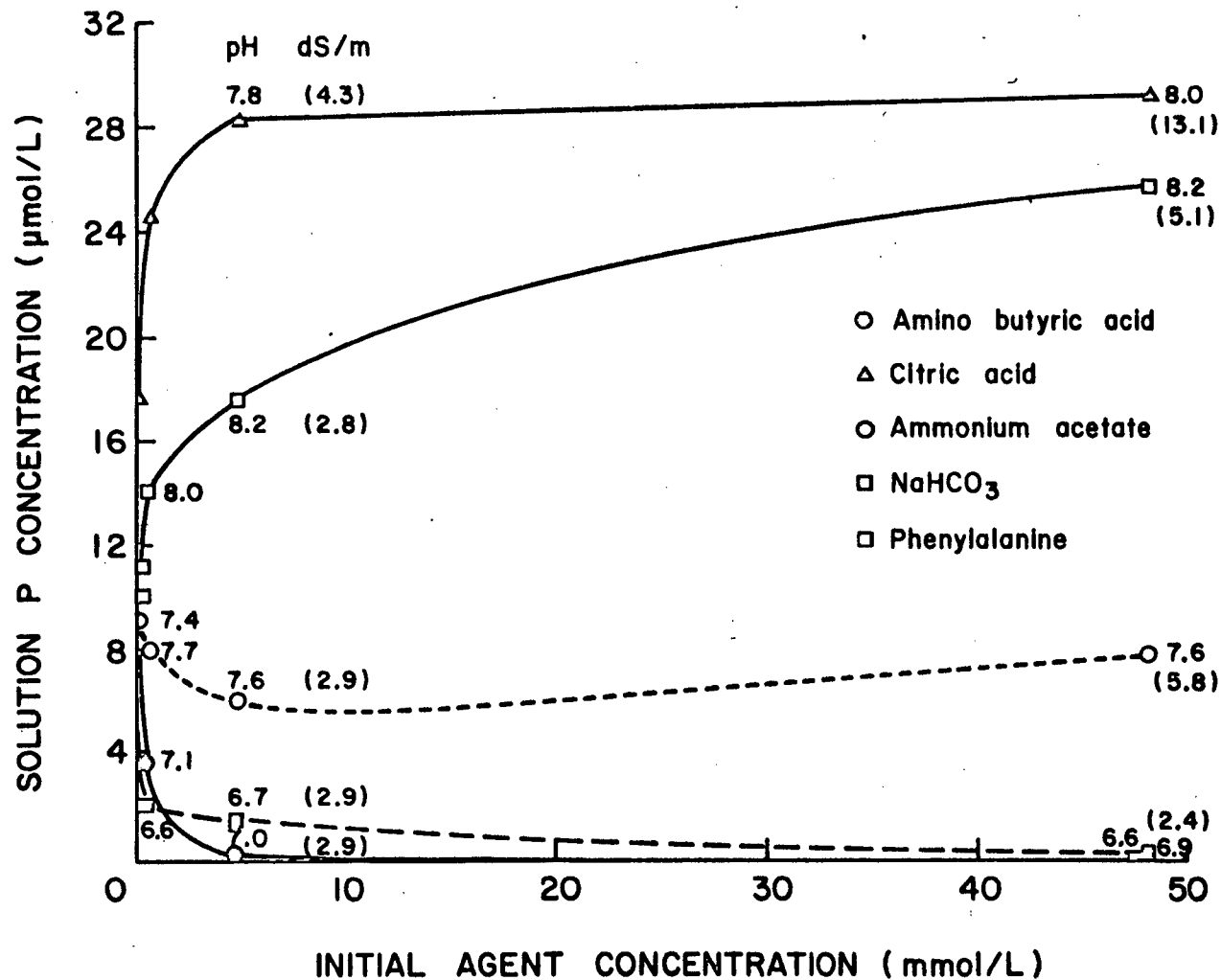
| Cp initial (μm) | P_{ox}/P_{Cl} | | | |
|---------------------------|-----------------|---------------|---------------|---------------|
| | Ca Mont. | | Ca Kaol. | |
| | pH 5.7-5.8 | pH 7.9-8.0 | pH 5.3-5.5 | pH 7.0-7.9 |
| 22 | 1.16 | 1.93 | - | - |
| 45 | 1.19 | 0.97 | 2.0 | 1.33 |
| 90 | 1.09 | 1.02 | 1.83 | 1.08 |
| 180 | 1.10 | 1.09 | 1.22 | 1.10 |

Figure Legends

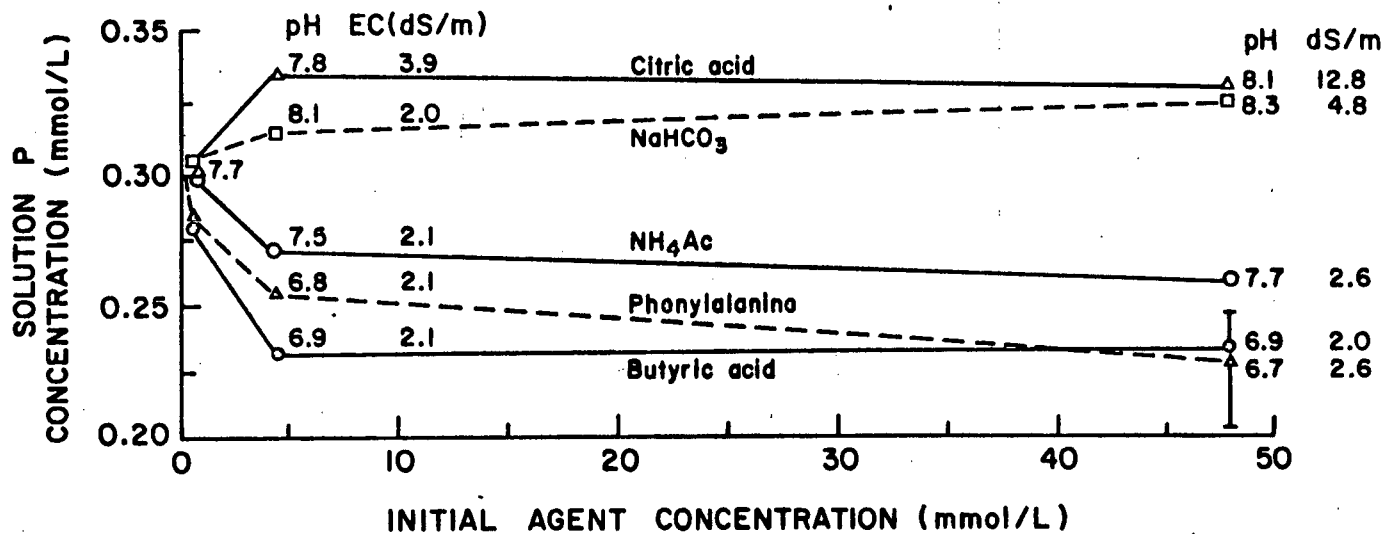
- Fig. 1: Effect of increasing concentration of organic compounds simulating root excretions on the concentration of P in the solution at constant total P quantity ($Q_P=4.2$ $\mu\text{mol/g}$). pH values are presented near the points. The EC (dS/m) is given in parenthesis. The P and organic agent were added together.
- Fig. 2: Effect of organic agent concentration on desorption of previously adsorbed phosphate on Ca kaolinite clay. (Comments see Fig. 1). $Q_P= 3.83$ $\mu\text{mol/g}$.
- Fig. 3: Effect of organic agent concentration on desorption of previously adsorbed P (comments see Fig. 1). $Q_P= 41.1$ $\mu\text{mol/g}$).
- Fig. 4: Effect of organic agent concentration on desorption of previously adsorbed phosphate on Ca-montmorillonite.
- Fig. 5: Effect of clay slurry density on P and Ca concentrations in the equilibrium solution of Ca montmorillonite. Numbers above arrows give Q_P .

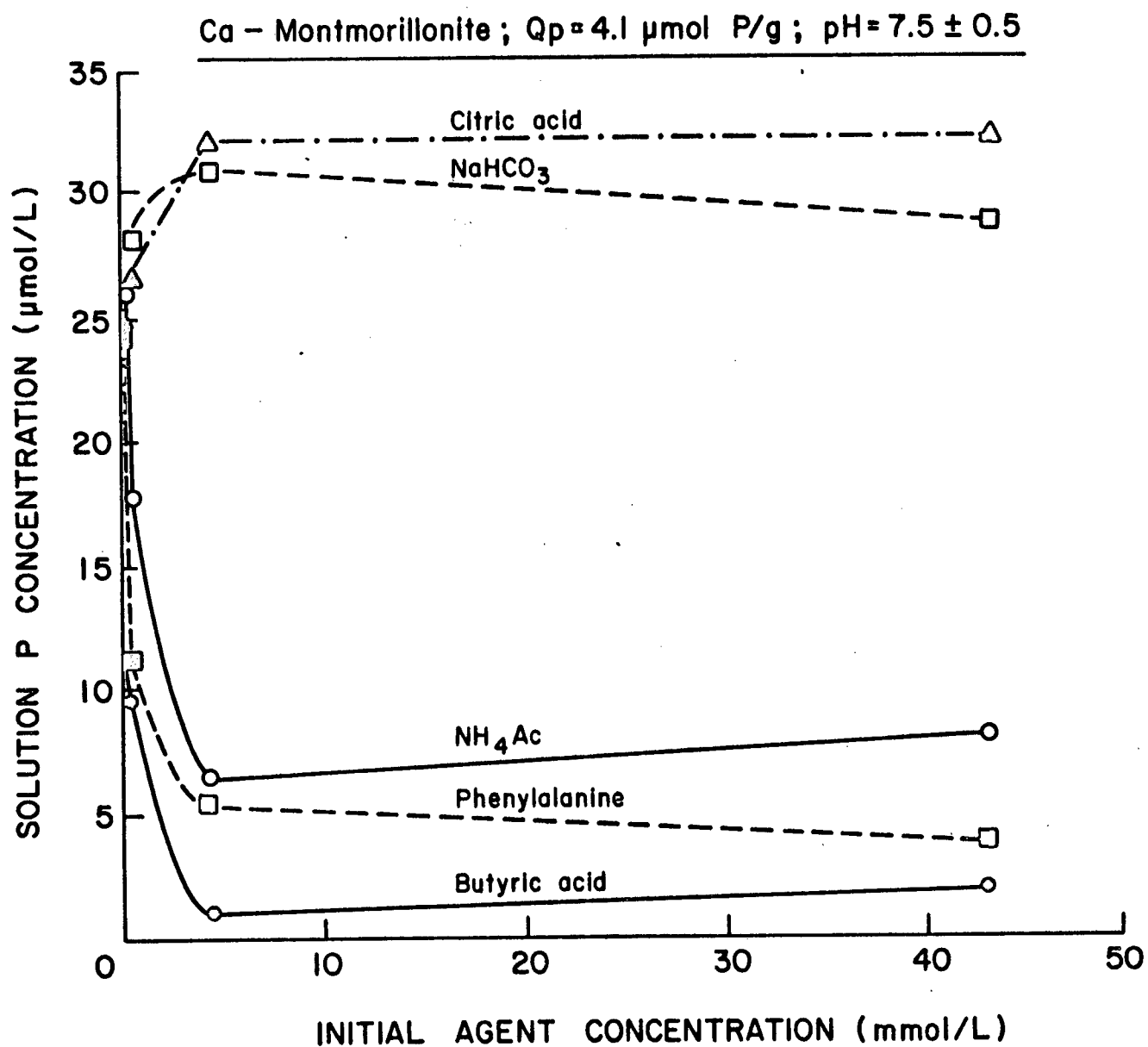


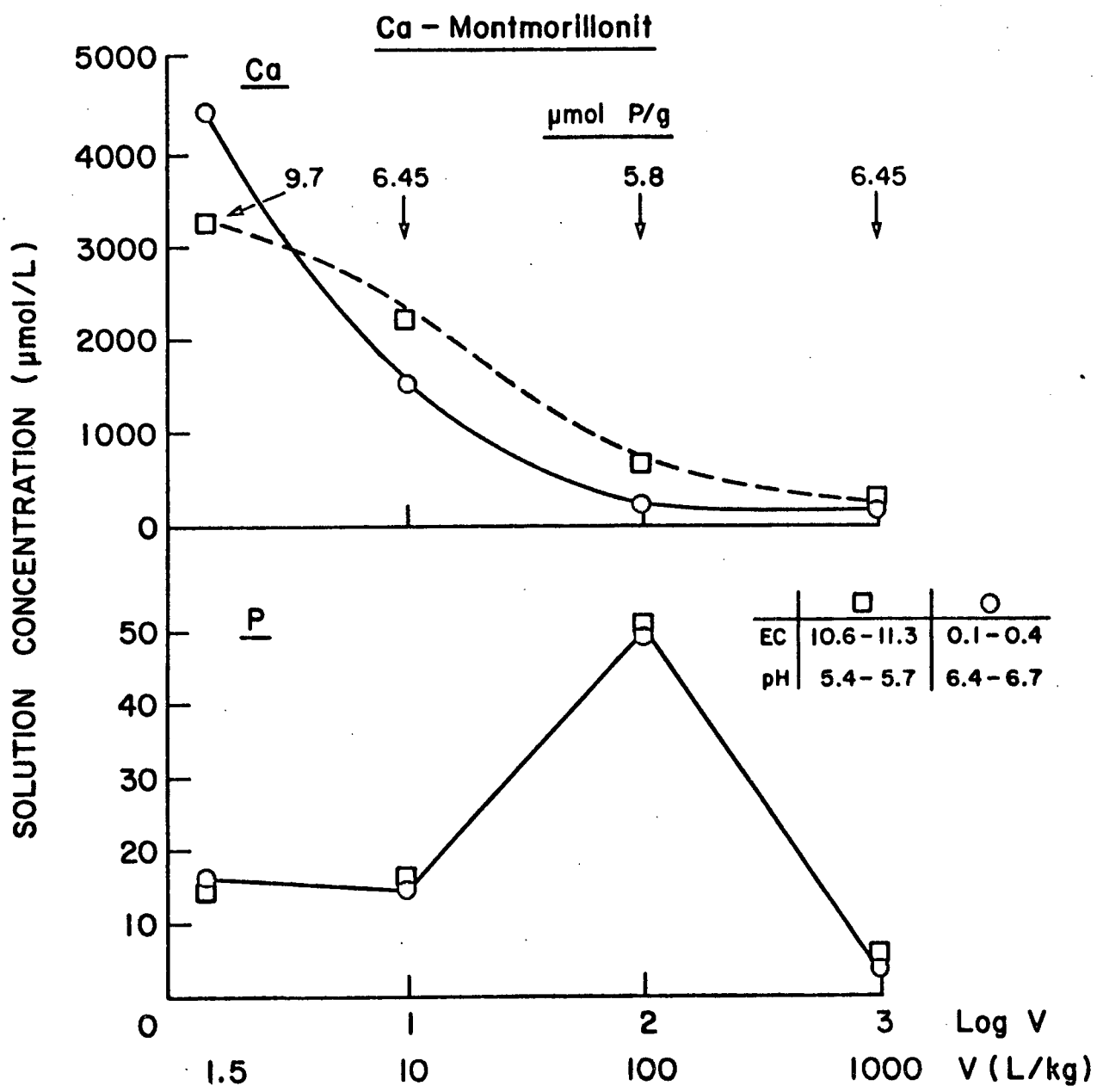
Ca - Kalinite $Q_p = 3.83 \mu\text{mol P/g clay}$



Ca - Kaolinite 41.1 $\mu\text{mol P/g clay}$







On Distinguishing Adsorption From
Surface Precipitation

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Measurements of the chemical composition of an aqueous solution phase are interpreted commonly to provide experimental evidence for either adsorption or surface precipitation mechanisms in sorption processes. The conceptual aspects of these measurements vis-à-vis their usefulness in distinguishing adsorption from precipitation phenomena are reviewed critically. It is concluded that the inherently macroscopic, indirect nature of the data produced by such measurements limit their applicability to determine sorption mechanisms in a fundamental way. Surface spectroscopy (optical or magnetic resonance), although not a fully developed experimental technique for aqueous colloidal systems, appears to offer the best hope for a truly molecular-level probe of the interfacial region that can discriminate among the structures that arise there from diverse chemical conditions.

The loss of a chemical species from an aqueous solution phase to a contiguous solid phase may be termed a sorption process. Among the mechanisms by which sorption processes occur, the three principal ones are: precipitation, the growth of a solid phase exhibiting a primitive molecular unit (a complex) that repeats itself in three dimensions; adsorption, an accumulation of matter at the interface between an aqueous solution phase and a solid adsorbent without the development of a three-dimensional molecular arrangement; and absorption, the diffusion of an aqueous chemical species into a solid phase (1,2). A precipitation mechanism may be initiated by either homogeneous or heterogeneous nucleation, may involve the formation of a solid mixture either by inclusion or by coprecipitation, or may take place on the surface of a pre-existent solid phase (surface precipitation). Regardless of these variations, the essential characteristic of precipitation is the development of a solid phase whose molecular ordering is intrinsically three-dimensional (2). An adsorption [strictly speaking, positive adsorption (1)] mechanism, on the other hand, involves only two-dimensional molecular arrangements

on a surface. This latter restriction does not preclude mixed adsorbates ["two-dimensional solid solutions" (2)], but it does eliminate solid phases whose structure is inherently three-dimensional, even if they form on surfaces and are hindered in their growth for stereochemical reasons [e.g., interlayer metal hydroxides on 2:1 layer type aluminosilicates (1)]. From this point of view, "multilayer adsorption" must refer to a succession of adsorbate layers, each of whose molecular ordering can be influenced only by the layer on which it forms and not by any other previously adsorbed layers. In the same vein, "absorption" must refer to the penetration of a chemical species into a solid phase beyond the nanometer depth from its periphery that operationally defines the interfacial region.

A central problem in the chemistry of natural water systems is the establishment of experimental methods with which to distinguish adsorption from surface precipitation (1-3). Corey (2) has written a comprehensive review of this problem which should be read as an introduction to the present essay, particularly for his set of six conclusions that set out general conditions likely to result in adsorption or precipitation. The discussion to follow is not a comprehensive review, but instead focuses on three popular approaches to the adsorption/surface precipitation dichotomy. The emphasis here is on the conceptual relationship of each approach to the defining statements made above: To what extent is an approach capable of distinguishing adsorption from surface precipitation?

Solubility Methods

Adsorption isotherms. The quantity of a chemical species i adsorbed per unit mass of a solid material contacting an aqueous solution phase is calculated with the equation (1):

$$q_i^{(w)} = n_i - M_w m_i \quad (1)$$

where n_i is the total number of moles of species i in the suspension per kilogram of solid, M_w is the mass of water per unit mass of solid, and m_i is the molality of the adsorptive i in the aqueous solution phase. In batch experiments M_w is the inverse of the suspension density, whereas in column experiments M_w is the gravimetric water content. Equation 1 represents the surface excess of species i assigned to an interface where there is no net accumulation of water (1); hence, the superscript w on the left side of the equation.

Adsorption phenomena frequently are studied by measuring solely the change in concentration of a species i in the aqueous solution phase. Simple mass-balance considerations (1) show that Equation 1 can be rewritten in a form compatible with this methodology:

$$q_i^{(w)} = \Delta m_i M_{Tw} \quad (2)$$

where $\Delta m_i = m_i^0 - m_i$ and m_i^0 is the molality of species i in M_{Tw} kilograms of water in the aqueous solution phase prior to its being

brought into contact with 1 kg of solid material. Equation 2 provides a basis for calculating $q_i^{(w)}$ as a loss of mass from aqueous solution. The critical assumption underlying its equivalence to Equation 1 is that the species i (e.g., $H_2PO_4^-$ or Cd^{2+}) preserves its chemical identity after it accumulates on the adsorbent. This assumption seldom is checked experimentally by chemical species analysis of the solid material after reaction. Often even the aqueous solution phase is not speciated and i refers, for example, to $Cd(II)$ instead of $Cd^{2+}(aq)$, with a concomitant lack of specificity in what is actually being adsorbed. When $q_i^{(w)}$ and m_i refer to total concentrations instead of species concentrations, the task of distinguishing adsorption from surface precipitation becomes correspondingly more difficult.

A graph of $q_i^{(w)}$ against m_i , or an equivalent concentration variable, at fixed temperature and pressure is an adsorption isotherm. Data of this kind typically have been fitted numerically to special cases of the equation (3):

$$q_i^{(w)} = \sum_{m=1}^n \frac{b_m K_m^{\beta} c_i^{\beta}}{[1 + B_m c_i^{\delta}]^{\gamma_m}} \quad (3)$$

where c_i is the concentration of an adsorptive i in the aqueous solution phase (e.g., the molality) and b_m , K_m , B_m , β_m , δ_m , and γ_m ($m = 1, \dots, n$) are adjustable parameters. Equation 3 represents an adsorption isotherm equation. Popular special cases of this expression include (3,4) the Langmuir equation ($\beta_m = \delta_m = \gamma_m = 1$, $B_m = K_m$; $n = 1$ or 2), the van Bemmelen-Freundlich equation ($B_m = 0$, $0 < \beta_m < 1$; $n = 1$), and the Tóth equation ($\beta_m = 1$, $B_m = K_m^{\delta_m}$, $\gamma_m = 1/\delta_m$; $n = 1$). In general, the larger is the number of adjustable parameters in an adsorption isotherm equation, the better its fit to experimental data is likely to be.

The provenance of expressions like that in Equation 3 has never been shown to be uniquely an adsorption mechanism. On the contrary, it is possible to derive special cases of Equation 3, such as the classical Langmuir equation

$$q_i^{(w)} = \frac{b K c_i}{1 + K c_i} \quad (4)$$

on the basis of sorption mechanisms for cations and anions involving only precipitation reactions (1,5). The situation for the "two-surface" Langmuir equation, a four-parameter version of Equation 3,

$$q_i^{(w)} = \frac{b_1 K_1 c_i}{1 + K_1 c_i} + \frac{b_2 K_2 c_i}{1 + K_2 c_i} \quad (5)$$

is yet more ambiguous. On strictly mathematical grounds (6), it has been shown that Equation 5 can be fit to any set of sorption data for

which a plot of $q_i^{(w)}/c_i$ (the distribution coefficient) against $q_i^{(w)}$ is convex toward the x -axis and has finite (extrapolated) y - and x -intercepts. This result is independent of the mechanism of the sorption process. Unfortunately, many sorption data — indeed, most — meet the mathematical criteria required in order to apply Equation 5. These kinds of difficulties make evident the point that adsorption isotherm equations should be regarded simply as curve-fitting devices without a priori chemical significance, but with predictive capability under limited conditions. The mechanistic implication of this conclusion can be formalized in the following rule (1):

The adherence of experimental sorption data to an adsorption isotherm equation provides no evidence as to the actual mechanism of a sorption process.

The scope of this general rule extends to adsorption isotherms which turn convex to the concentration axis at higher adsorptive concentrations (7) and to adsorption "edges" or "envelopes" observed in plots of $q_i^{(w)}$ against pH at fixed total adsorptive i concentration (1). Adsorption isotherms that show a "monolayer knee" at lower concentrations followed by an upward turn at higher concentrations of adsorptive can be modeled by retaining two or more terms in Equation 3 and choosing the adjustable parameters judiciously (e.g., a Langmuir first term and a van Bemmelen-Freundlich second term (7)). This possibility does not imply that adsorption alone governs the process described by isotherms that grow continually with the adsorptive concentration, any more than fitting the data by an adsorption-surface precipitation model (7) would imply that surface precipitation was indeed the controlling process at higher concentrations. The same conclusion applies to the modeling of adsorption "edges" or "envelopes". That an adsorption "edge" for a metal reacting with a hydrous oxide exhibits its sharp rise at lower pH values than it does when the adsorbent is absent can mean either that an adsorption process has occurred or that surface precipitation of the metal as a hydrous oxide has been induced by the presence of the adsorbent. No direct evidence favoring one interpretation or the other can be provided by these data alone. Similarly, the enhancement of metal sorption sometimes observed when a strongly sorbing anion has been reacted previously with a hydrous oxide adsorbent may be modeled either as a metal-anion surface precipitate effect (8) or a metal-anion surface complex effect (9). Sorption data themselves do not provide for a choice of model, unless the ion-activity product for a proposed surface precipitate exceeds the corresponding solubility product constant.

Ion-Activity Products. As in the determination of the amount sorbed through Equation 2, the characterization of surface precipitates often utilizes measurements made solely on the aqueous solution phase. Solubility studies limited in this way run a risk of being ambiguous as to mechanism because of the lack of direct information about the solid phase (10). In respect to the aqueous solution phase, ambiguity can be minimized if equilibrium is approached both from supersaturation and from undersaturation; if the equilibration time is varied

systematically; if the aqueous solution phase is monitored through two or more concentration (or activity) variables susceptible to quantitation with high precision, and if the stoichiometry of the assumed precipitation-dissolution reaction is verified experimentally (10).

Once the composition of the aqueous solution phase has been determined, the activity of an electrolyte having the same chemical formula as the assumed precipitate can be calculated (11,12). This calculation may utilize either mean ionic activity coefficients and total concentrations of the ions in the electrolyte, or single-ion activity coefficients and free-species concentrations of the ions in the electrolyte (11). If the latter approach is used, the computed electrolyte activity is termed an ion-activity product (12). Regardless of which approach is adopted, the calculated electrolyte activity is compared to the solubility product constant of the assumed precipitate as a test for the existence of the solid phase. If the calculated ion-activity product is smaller than the candidate solubility product constant, the corresponding solid phase is concluded not to have formed in the time period of the solubility measurements. This judgment must be tempered, of course, in light of the precision with which both electrolyte activities and solubility product constants can be determined (12).

The difficulty here is that the ion-activity product includes not only the Gibbs energy change in a solid dissolution process but also the activity of the solid itself. Consider, as a simple example, the dissolution of $\text{CdCO}_3(\text{s})$, for which the ion-activity product (IAP) is (12):

$$\text{IAP} = [\text{Cd}^{2+}][\text{CO}_3^{2-}] = K_{\text{so}}[\text{CdCO}_3(\text{s})] \quad (6)$$

where $K_{\text{so}} = 10^{-11}$ at 298 K (10) and [] represents a thermodynamic activity. If $\text{Cd}(\text{II})$ has coprecipitated with another metal (e.g., $\text{Ca}(\text{II})$) to form a solid solution, then $[\text{CdCO}_3] < 1$ and $\text{IAP} < K_{\text{so}}$. Thus a homogeneous, mixed surface precipitate typically can be expected to produce low IAP values and, if the chemical element of interest is in the mixture only in trace amounts, the discrepancy between IAP and K_{so} easily can be an order of magnitude (1,10). A low IAP value of this kind then might be interpreted to mean that surface precipitation had not occurred, and that adsorption had occurred, because undersaturation existed in the aqueous solution phase. The error of such a conclusion, in the absence of a direct examination of the solid phase, is apparent from Equation 6: Only precipitates whose activity equals or exceeds 1.0 have been eliminated. The inference to be drawn from this discussion can be formalized conservatively in the rule (1):

The experimental observation that an ion-activity product is smaller than a corresponding solubility product constant by an order of magnitude or less provides no evidence as to the general mechanism of a sorption process.

In systems where surface precipitation has been verified on the basis of a direct examination of the solid phase, it sometimes is true that, because of epitaxial or other stereochemical constraints, the activity of even an aged precipitate is larger than 1.0, relative to a standard state in which the solid phase is macrocrystalline and free of inclusions (12). The larger solid-phase activity leads to an IAP larger than K_{so} (cf. Equation 6). A typical example of this effect is in the precipitation of aluminum hydrous oxides onto the interlayer siloxane surfaces of 2:1 layer type aluminosilicates during weathering. When an aluminum hydroxy-solid precipitates onto the interlayer surface of smectite or vermiculite, $IAP = [Al^{3+}][OH^-]^3 \approx 10^{-32}$, whereas for macrocrystalline gibbsite, $K_{so} = 10^{-34}$ (13). The fact that $IAP > K_{so}$ implies a lower degree of crystallinity or crystalline size exists in the surface precipitate.

Kinetics Methods

Electrokinetic behavior. A shearing stress applied to or induced in an aqueous solution phase contacting a charged adsorbent produces a response at the solid-liquid interface known as an electrokinetic phenomenon (1,14). The principal electrokinetic phenomena of relevance to sorption experiments are: electrophoresis, the response of a charged adsorbent to an applied, constant electric field; electro-osmosis, the response of an electrolyte solution near a stationary, charged adsorbent to an applied electric field, and the streaming potential, the response of an electrolyte solution near a stationary, charged adsorbent to an applied, uniform pressure gradient. For all three phenomena, experimental data can be summarized in calculations of the zeta potential ζ , the inner electrostatic potential near the adsorbent surface at the plane of shear induced by an applied electric field or produced by an applied pressure gradient (1,14).

The significance of ζ for distinguishing adsorption from surface precipitation has been brought into clear focus by James and Healy (15). They pointed out that ζ often decreases to a minimum value, followed by a rise to a maximum value then decline toward negative values, as the pH is increased in an aqueous suspension containing a hydrous oxide adsorbent and a hydrolyzable metal cation adsorptive. This behavior can be interpreted as the result of a gradual accumulation of hydrolytic species of the metal on the surface of the adsorbent (producing a net increase in surface charge and an increase in ζ with increasing pH) which culminates in the formation of a hydroxy-polymer coating of the metal on the adsorbent (producing ultimately a net decrease in both ζ and the surface charge, which gradually reflects that of the coating, not the adsorbent). This interpretation applies to any bivalent, trivalent, or tetravalent metal cation that hydrolyzes to some extent above pH 6 in aqueous solution (16). The magnitude of the concentration of hydrolytic metal species in solution is not relevant, even if the concentration is very small, since aqueous solutions are effectively open systems with respect to these species. If an adsorbent exhibits a high enough affinity for a hydrolytic species, it can be adsorbed at once and be replaced in the aqueous solution phase through hydrolysis of a

solvated species until the availability of the latter has been exhausted. The concentration of the hydrolytic species may remain quite small, but its adsorption is determined by the affinity of the adsorbent for it and the total metal concentration in aqueous solution.

If a surface precipitate of metal hydroxy-polymer has formed on an adsorbent, the ζ -pH relationship for the coated adsorbent should resemble closely that observed for particles consisting purely of the hydroxy-polymer or the hydrous oxide of the metal (15). This kind of evidence for Co(II), La(III), and Th(IV) precipitation on silica colloids was cited by James and Healy (15). It should be noted, however, that the increase in ζ toward a maximum value often occurs at pH values well below that required thermodynamically to induce bulk-solution homogeneous precipitation of a metal hydrous oxide (15,16). If surface precipitation is in the incipient stage under these conditions, it must be a nucleation phenomenon. James and Healy (15) argue that the microscopic electric field at the surface of a charged adsorbent is sufficiently strong to lower the vicinal water activity and induce precipitation at pH values below that required for bulk-solution precipitation of a metal hydrous oxide.

Both Schindler (17) and Fuerstenau et al. (18) have called attention to the point that the surface precipitation concept need not be invoked to explain the ζ -pH relationship described above. If only solvated metal cations adsorb in inner-sphere surface complexes, their adsorption will be enhanced by decreasing the adsorbent charge through increasing the pH and they will concomitantly increase ζ by bringing positive charge to the solid-liquid interface. At high pH values, the metal cations will begin to hydrolyze significantly in aqueous solution and these hydrolytic species can form at the expense of adsorbed species, with the result that ζ decreases as the metal cations desorb to hydrolyze. The qualitative form of the ζ -pH relationship produced by this mechanism resembles experimental observations for the bivalent metal cation-silica system closely (17). The implication of this fact is that an observed ζ -pH relationship does not provide an unambiguous method of distinguishing adsorption from surface precipitation.

Reaction kinetics. The time-development of sorption processes often has been studied in connection with models of adsorption despite the well-known injunction that kinetics data, like thermodynamic data, cannot be used to infer molecular mechanisms (19). Experience with both cationic and anionic adsorptives has shown that sorption reactions typically are rapid initially, operating on time scales of minutes or hours, then diminish in rate gradually, on time scales of days or weeks (16,20-25). This decline in rate usually is not interpreted to be homogeneous: The rapid stage of sorption kinetics is described by one rate law (e.g., the Elovich equation), whereas the slow stage is described by another (e.g., an expression of first order in the adsorptive concentration). There is, however, no profound significance to be attached to this observation, since a consensus does not exist as to which rate laws should be used to model either fast or slow sorption processes (16,21,22,24). If a sorption process is initiated from a state of supersaturation with respect to one or more possible solid phases involving an adsorptive, or if the adsorbents present are

either poorly crystallized or well hydrated, it is likely that multiple sorption mechanisms will operate right from the beginning (1,2). The time-development of the sorption process then should reflect this multiplicity and defy any simple interpretation in terms of an adsorption mechanism.

When the kinetics of a sorption process do appear to separate according to very small and very large time scales, the almost universal inference made is that pure adsorption is reflected by the rapid kinetics (16,21,22,26). The slow kinetics are interpreted either in terms of surface precipitation (20) or diffusion of the adsorbate into the adsorbent (16,24). With respect to metal cation sorption, "rapid kinetics" refers to time scales of minutes (16,26), whereas for anion sorption it refers to time scales up to hours (1,21). The interpretation of these time scales as characteristic of adsorption rests almost entirely on the premise that surface phenomena involve little in the way of molecular rearrangement and steric hindrance effects (16,21).

An illustration of the reaction kinetics approach to distinguishing adsorption from surface precipitation is provided by the sorption of o-phosphate by calcite (27-30). The loss of o-phosphate from aqueous solution in the presence of calcite is pronounced on a time scale of tens of minutes and is enhanced by increasing temperature or pH (27-29). Thereafter, on a time scale of hours or days, the o-phosphate solubility decreases gradually, then drops sharply again (27,28). This behavior is interpreted mechanistically as adsorption of o-phosphate at selective sites on calcite followed by the nucleation of a calcium phosphate solid on the surface (27,29,30). The gradual decline in o-phosphate solubility, which persists longer the smaller is the initial o-phosphate concentration (28), represents the period of rearrangement of adsorbed o-phosphate clusters into calcium phosphate nuclei (27,29). Epitaxial, three-dimensional growth of calcium phosphate crystals then follows. Scanning electron micrographs of calcite taken during the rearrangement period (30) show hemispherical growths of o-phosphate (identified by microprobe analysis) at edge sites and dislocations on the crystal surface. Griffin and Jurinak (29) found the adsorption kinetics to be second-order, whereas the rearrangement kinetics were first-order. Similar results for the slower kinetics of o-phosphate sorption by metal hydrous oxides and soils have been reported (20,21), but no consensus exists (23,25,31). The principal criterion, however, is not homogeneity of the rate law, but a clear separation of the kinetics according to time scale (1).

Surface Spectroscopy

Solubility and kinetics methods for distinguishing adsorption from surface precipitation have the common features of being essentially macroscopic in nature and of not utilizing a direct examination of sorbed material. The essential difference between an adsorbate and a surface precipitate lies with molecular structure, however, and it is inevitable that methodologies not equipped to explore that structure directly will produce ambiguous results requiring ad hoc assumptions in order to interpret them. The principal technique for

investigating molecular structure is spectroscopy (32,33). Surface spectroscopy, both optical and magnetic, offers the best opportunity at present to elucidate the structures of chemical species at the solid-liquid interface.

Surface spectroscopic techniques must be separated carefully into those which require dehydration for sample presentation and those which do not. Among the former are electron microscopy and microprobe analysis, X-ray photoelectron spectroscopy, and infrared spectroscopy. These methods have been applied fruitfully to show the existence of either inner-sphere surface complexes or surface precipitates on minerals found in soils and sediments (13b,30,31-37), but the applicability of the results to natural systems is not without some ambiguity because of the dessication pretreatment involved. If independent experimental evidence for inner-sphere complexation or surface precipitation exists, these methods provide a powerful means of corroboration.

X-ray diffraction, Raman spectroscopy, and magnetic resonance spectroscopy (nuclear and electron), on the other hand, do not require dehydration of the sample. X-ray diffraction is a method of long standing for the detection of surface precipitates that is usually — but need not be — applied to dried materials (30,38-41). Raman spectroscopy (42) and nuclear magnetic resonance spectroscopy (32,33) have not often been used to distinguish surface species in aqueous systems comprising natural colloids, but their potential for this kind of investigation remains significant (33,37). Perhaps the most useful technique has been electron spin resonance spectroscopy (32,43), particularly the applications of it made by McBride and his coworkers (44-48). Although limited intrinsically (32) to only three metals of major interest in natural colloidal systems — Fe(III), Mn(II), and Cu(II) — this method has been uniquely successful in providing a general understanding of the conditions under which adsorption or surface precipitation is likely to occur.

A prototypical example of electron spin resonance (ESR) spectroscopy applied to surface speciation on a layer silicate is Cu(II) sorption by hectorite (44b). The ESR spectrum of a Cu-hectorite suspension shows a gradual decrease in the intensity of the line characteristic of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ species as pH increases, consistent with the gradual appearance of hydrolytic species of Cu(II) which do not produce an ESR signal. At pH < 5.2, the fraction of Cu(II) in hydrolytic species on the hectorite surface is much larger than in aqueous solution, indicating a high affinity of the surface for these species. Air-dried Cu-hectorite presents ESR spectra assignable to Cu(II) bound in inner-sphere surface complexes in the hectorite interlayers, by contrast with the diffuse-ion swarm or outer-sphere surface complex Cu(II) inferred from the suspension spectra. As pH increases, this adsorbed Cu(II) converts gradually to hydrolytic species. Kinetics data taken with the ESR spectra in suspension were consistent with the formation of surface precipitates at pH > 6. A similar study of Cu(II) sorption by microcrystalline gibbsite (47) produced spectral evidence for inner-sphere surface complexes of Cu^{2+} predominating below pH 5 and Cu-hydroxy species — eventually $\text{Cu}(\text{OH})_2(\text{s})$ — predominating above pH 5. For both hectorite and gibbsite, the $\text{IAP} = [\text{Cu}^{2+}][\text{OH}^-]^2$ for the surface hydroxy species was

smaller than the solubility product constant of macrocrystalline $\text{Cu}(\text{OH})_2(\text{s})$.

Concluding Remarks

Solubility and kinetics methods for distinguishing adsorption from surface precipitation suffer from the fundamental weakness of being macroscopic approaches that do not involve a direct examination of the solid phase. Information about the composition of an aqueous solution phase is not sufficient to permit a clear inference of a sorption mechanism because the aqueous solution phase does not determine uniquely the nature of its contiguous solid phases, even at equilibrium (49). Perhaps more important is the fact that adsorption and surface precipitation are essentially molecular concepts on which strictly macroscopic approaches can provide no unambiguous data (12, 21). Molecular concepts can be studied only by molecular methods. It is for this reason that spectroscopy offers the only experimental method for characterizing the interfacial region that is not automatically destined to run into basic conceptual difficulties. This is not to say that difficulties of a technical nature will not arise (40-48), nor that the conceptual difficulty of differing time scales among spectroscopic techniques will cause no problems (50). Nonetheless, it is to be hoped that future investigations of sorption reactions will focus more on probing the molecular structure of the mineral/water interface than on attempting simply to divine what the structure may be.

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Description of cooperation

Three phases of cooperation were observed during this study.

- 1) Project preparation. The project was developed and prepared during the period of a sabbatical leave of the principal investigator in U.C. Riverside. Careful planning and sharing of efforts were decided. The Israeli group concentrated on pure clays. The American group concentrated on reactions on clay separates from soil.
- 2) Exchange of ideas and reviewing each other's results during the actual period of work, which resulted in joint publications, that was strengthened by a meeting at Oxford in summer 1984 of the two leaders of this project.
- 3) Final interpretation of the results of the two groups was done during the summer of 1986, during the visit of the principal investigator in Riverside. The unifying principles of phosphate adsorption on clays were formulated in this meeting.

Evaluation of the research achievements

The work followed exactly the outlines specified in the project.

Studies of P adsorption at constant pH values, ionic strength and constant amount of P in the system led us to define the PZCe of Kaolinite at 5.1 and Montmorillonite at 6.9.

The use of carboxylate with and without amino groups at various supporting electrolyte ionic strength has clarified the adsorption model of phosphate on montmorillonitic clays and confined it to the edges of the quasi-crystals of the montmorillonite. It was postulated that increasing the size of the quasi crystal in the c-axis due to increase in the ionic strength or hydrogen bonding of amino groups exposes more active Al^{3+} ions on the clay edges by reducing the spillover of the permanent negative force lines. Phosphate can come in contact with these active Al^{3+} ions since it is not repelled from the quasi crystal side, while it is repelled from a single plate of clay in dilute salt solution.

Chemical compounds that can contribute OH^- to the surface, increase the pH above the pK of the surface or complex Al^{3+} ions, are capable of releasing P from its binding sites on the clay.

It is concluded that root excretions of carbonate or citrate ions can desorb P from clay surfaces while excretion of Amino acids will increase the phosphate binding to montmorillonitic clays. The phosphate desorb from swelling clays at low ionic strength and at high solution to clay ratios. The measurements of water soluble P in the soil should be measured at actual columns of soils at the same density as found in the field.

List of Publications

- 1) Traina, S.J., G. Sposito, D. Hesterberg and U. Kafkafi, 1986.
Effect of pH and Organic Acids on Orthophosphate Solubility in an Acidic Montmorillonitic Soil. Soil Sci Soc. Amer. J. 50, 45-52.
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