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ON THE MECHANISM OF SPECIFIC PHOSPHATE ADSORPTION BY HYDROXYLATED MINERAL SURFACES: A REVIEW

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ABSTRACT

The mechanism of specific phosphate adsorption by hydroxylated mineral surfaces comprises two aspects: the phosphate-hydroxyl surface reaction and the configuration of the adsorbed phosphate ion. Evidence pointing to ligand exchange as the mechanism of the phosphate-surface hydroxyl reaction include kinetics of adsorption and desorption; hydroxyl ion release; infrared spectroscopy, and stereochemical calculations. Data pertaining to the coordination of adsorbed phosphate on hydroxylated mineral surfaces have not been conclusive overall. Isotopic exchange experiments and studies of desorption kinetics do not provide definitive information on surface coordination. Measurements of hydroxyl ion release and crystallographic calculations provide support for the existence of both monodentate and

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bidentate surface complexes of phosphate ions. Infrared spectroscopic investigations suggest a binuclear complex on dried, phosphated goethite. However, these studies cannot be extrapolated automatically to soil minerals, since the addition of water favors formation of a monodentate surface complex. Further research is needed to establish the configuration of adsorbed phosphate ions.

INTRODUCTION

The chemical mechanisms by which orthophosphate is adsorbed specifically by soils remain a topic of continued interest and controversy in soil science (Olsen and Khasawneh, 1980; White, 1981). In recent years, the direction of research on the soil chemistry of phosphate has shifted from studies of extraction techniques to investigations of a more fundamental kind pertaining to the mechanistic aspects of phosphate reactions with soil constituents (White, 1981). The objective of the present brief review is to assess the status of these more fundamental studies in respect to two critical issues: the nature of the strong reaction between orthophosphate and hydroxylated mineral surfaces and the molecular configuration of adsorbed phosphate on these surfaces.

The Ligand Exchange Mechanism

There is a broad concensus that orthophosphate is specifically adsorbed onto hydroxylated mineral surfaces by a ligand exchange mechanism (Beek and van Riemsdijk, 1977; Parfitt, 1978;

Mott, 1981; Hingston, 1981; Sposito, 1984). A generalized ligand exchange reaction for phosphate ions can be written as follows:

$$aSOH_{(s)} + H_bPO_4{}^{b-3}{}_{(aq)} + cH^+{}_{(aq)} \leftrightarrow S_aH_cPO_{4(s)} + bH_2O_{(l)} + (a-b)OH^-{}_{(aq)} \qquad [1]$$

where S refers to a metal ion in a hydroxylated mineral, OH to a reactive surface hydroxyl, and $b \leq 3$ is the degree of protonation of the phosphate ion. Surface complexes resulting from ligand exchange contain no water molecules between the surface Lewis acid site (S) and the adsorbed ion and, therefore, are referred to as inner-sphere. These complexes are quite stable, showing mainly covalent or ionic bonding character. Their formation provides a mechanism for what is referred to as specific adsorption (Sposito, 1984).

The conclusion that phosphate adsorbs through ligand exchange has been reached as a result of various kinds of experimental evidence, most of which are indirect. Studies of the adsorption envelope, a plot of maximum adsorption versus pH, have shown that phosphate behaves quite differently from ions which are not considered to be specifically adsorbed, such as chloride. In the absence of positive permanent charge, the adsorption of Cl^- becomes zero at pH values for which the surface takes on a negative charge (Mott, 1981). Phosphate adsorption, however, continues regardless of the sign of the surface charge, showing a steady decrease in maximum adsorption with increasing pH value.

Hingston et al. (1972) proposed that ligand exchange occurs when anions having a specific affinity for the metal atoms in a hydroxylated mineral enter the coordination layer of its surface and adsorb out of all proportion to their concentration or activity in aqueous solution. They showed that anions of incompletely dissociated acids, such as phosphate, are adsorbed beyond the neutralization of positive surface sites and even on a surface having a net negative charge. For this process they proposed the following mechanism. Protonated anions can be adsorbed onto a negatively charged surface after dissociation of their protons, which then react with surface hydroxyls to form water molecules that in turn can be readily replaced by the anions. The role of the protonated anion in this mechanism as a proton donor has since been disputed, however (Rajan et al., 1974; Hingston, 1981; White, 1981), because protonation-proton dissociation reactions of the hydroxylated mineral surface alone are adequate to explain the pH dependence of anion adsorption (Stumm et al., 1980).

In order to determine the adsorption mechanism for phosphate, Yates and Healy (1975) compared nitrate, sulfate, and phosphate adsorption on Cr(III) and Fe(III) oxides. In aqueous solution, these two metals form complexes of similar stability with the same ligands but at vastly different rates. Cr(III) ligand-substitution reactions have half-lives of the order of days, whereas Fe(III) reacts almost immediately. If phosphate adsorption on the oxides of these metals occurs by ligand exchange, then a large difference in reaction rates should be observed, with the lower rate shown by the oxide of Cr(III). This was indeed the case for phosphate adsorption by α-Cr_2O_3 and α-FeOOH, but not for nitrate adsorption, thus demonstrating indirectly that phosphate adsorption on goethite (α-FeOOH) occurred by a ligand exchange mechanism.

Mott (1981) states that, unlike non-specifically adsorbed ions, ligand-exchanged ions do not have adsorption and desorption isotherms that are identical kinetically. For ligand-exchanged ions, desorption at constant pH is a much slower process than adsorption. This kind of irreversibility has been shown to be the case for phosphate (Hingston et al., 1974; Kafkafi et al., 1967; Ryden et al., 1977).

Peinemann and Helmy (1977) studied the competition of the specifically adsorbing ligands aluminon and cupferron with phosphate on hydrous oxides of aluminum and iron. They found that the presence of these ligands reduced phosphate adsorption. It was suggested that all three ligands were competing for the same sites via the same mechanism, ligand exchange with hydroxyl groups.

Studies in which the moles of hydroxyl released per mole of phosphate adsorbed are measured are consistent with a ligand exchange mechanism (Breeuwsma and Lyklema, 1973; Rajan et al., 1974; Rajan, 1975; Rajan, 1976). However, often anion adsorption and hydroxyl release are not equivalent because ligand exchange always results in hydroxyl production, whereas the negative charging process accompanying ligand exchange may produce proton release (Hingston et al., 1972; Rajan et al., 1974; White, 1981). Thus only the net result of proton adsorption-desorption at the phosphated surface is reflected by the molar ratio of hydroxyl released per phosphate adsorbed (Beek and van Riemsdijk, 1977).

The only direct evidence for phosphate-OH exchange has come from infrared spectroscopic characterization of the mineral surface. Russell et al. (1974) and Parfitt et al. (1976) have deuterated the singly-coordinated surface hydroxyls of goethite and shown that the OD signal disappeared after phosphate saturation. The sample had been evacuated prior to study.

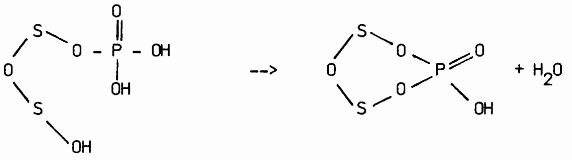
Stereochemical considerations also favor a ligand exchange mechanism for phosphate, since the area per phosphate anion and the area occupied by a hydroxyl surface group are of similar magnitude. Van Wazer (1958) gives the ionic radii of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ as 0.29 nm, which results in an area per adsorbed phosphate ion of approximately 0.26 nm^2. Crystallographic calculations give an area of 0.305 nm^2 per singly-coordinated surface hydroxyl on the reactive (100) face of goethite and an area of 0.246 nm^2 per OH on the reactive edge surfaces of gibbsite. Jurinak (1966), using water adsorption techniques, determined the area per hydroxyl ion on hematite to be 0.22 nm^2.

Configuration of the Surface Complex

Unlike the case for ligand exchange, controversy attends the problem of what stereochemical configuration a phosphate ion takes on when complexed by a surface Lewis acid site. As will become apparent, the difficulty of probing the structure of the phosphate surface complex in an aqueous environment that is similar to that in soils has precluded definitive conclusions.

"Kinetic irreversibility"

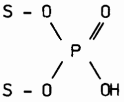
Hingston et al. (1974) studied the desorption of specifically adsorbed anions and showed phosphate adsorption to be "kinetically irreversible" to some degree. "Irreversible" adsorption was defined by the criterion that anion desorbability becomes negligible while anion adsorption is not, desorbability being estimated from a comparison of expected and actual net adsorption following two washings with NaCl at constant ionic strength. Desorption of phosphate by washing at constant pH value and ionic strength produced a net gain of positive charge on the surface of goethite and gibbsite. Thus it appeared that hydroxyl ions had been desorbed instead of the specifically adsorbed anions. Hingston et al. (1974) suggested that, as desorption occurs, some of the remaining adsorbed phosphate hydrolyzes, converting from a reversibly-adsorbed, monodentate form to a bidentate form which is "irreversibly" adsorbed (see also White, 1981). This mono- to bidentate shift had been postulated previously by Kafkafi et al. (1967) to explain "kinetic irreversibility" in phosphate adsorption by kaolinite:



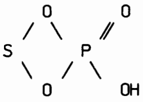
[2]

Hydroxyl ion release

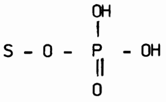
Hydroxyl ion release during phosphate adsorption by a sample of hydrous alumina containing bayerite ($Al(OH)_3$) and pseudoboehmite ($AlOOH$) of low crystallinity was studied by Rajan et al. (1974). They assumed a monodentate surface phosphate species and used curves depicting changes in the molar ratio of hydroxyl released to phosphate adsorbed to distinguish phosphate-reactive sites. They suggested that three types of reactive sites are involved in phosphate adsorption. At low phosphate concentrations, adsorption occurs by displacing aquo groups from Lewis acid sites, $Al\text{-}H_2O$. At higher concentrations, hydroxyl groups (Al-OH) are displaced and, at very high concentrations binuclear hydroxyl bridges (Al-OH-Al) are broken and new adsorption sites are created. Rajan (1975) determined the molar ratio of hydroxyl ions released to phosphate ions adsorbed, finding it to be larger than unity. Given this result, he proposed that phosphate ions react with hydrous alumina to form both monodentate and binuclear complexes. Three phosphate surface complexes are possible:



Binuclear



Bidentate



Monodentate

Isotopic exchange experiments

Atkinson et al. (1972) studied the rate of isotopic exchange between ^{32}P-labelled orthophosphate solutions and Fe(III) phosphate surface complexes on goethite. They asserted that the rate constants found, 1.7 to 46 x 10^{-5} s^{-1}, were extremely low for a transition metal complex. Papers by Stranks (1960) and Stranks and Wilkins (1957), which were used by Atkinson et al. (1972) to reach this conclusion, give values of the time required for the free ion concentration to reach half its initial value ($t_{1/2}$) ranging from 20 seconds to 64 hours for Fe(III) solution complexes. The expression $t_{1/2} = 0.693/k$ indicates that the half-lives for phosphate exchange on goethite determined by Atkinson et al. (1972) ranged from 25 minutes to 11 hours. Kyle et al. (1975) studied the kinetics of isotopic exchange for phosphate adsorbed by gibbsite. They also compared their data to reaction rates for transition metal complexes taken from Stranks (1960) and Stranks and Wilkins (1957) to assert that the exchange rates on gibbsite were low. The rate constants they measured ranged from 2.56 x 10^{-2} s^{-1} to undetectably small. The rate constant of 2.56 x 10^{-2} s^{-1} converts to a half-life of 27 s. Lincoln and Stranks (1968) studied the isotopic exchange of the phosphate ligand in phosphato complexes of cobalt(III). The half-lives for these reactions ranged from minutes to hours. Thus it appears that the isotopic exchange rates of adsorbed phosphate on goethite and on gibbsite are in good agreement with those expected typically for complexes of trivalent metal ions and in fact are not unusually low.

Atkinson et al. (1972) explained what they considered to be the small magnitude of their rate constants for isotopic exchange of phosphate surface complexes on goethite by postulating a binuclear bridging structure (Fe-O-P-O-Fe) and some spin-pairing in the Fe-O-P bonds. Kyle et al. (1975) also used a binuclear bridging complex to explain what they saw as the inertness of phosphated gibbsite. However, since it is evident that, on the basis of rate constants, these surface complexes need not be classified as unusually inert, the binuclear structure need not be invoked.

Infrared spectroscopy studies

Atkinson et al. (1974) used infrared (IR) spectroscopy to study dried samples of phosphated goethite. Because no hydrogen-bonded OH bands were observed they asserted that phosphate was adsorbed as discrete phosphate anion tetrahedra and not as the protonated forms, $H_2PO_4^-$ or HPO_4^{2-}. If OH bands had been present, they would have been found in the 2300-3000 cm^{-1} region, in contrast with the goethite bands which occur at 3160, 1780, 1650, 900, and 805 cm^{-1}. They concluded also that phosphate was adsorbed as a binuclear bridging complex. The possibility of a monodentate surface complex was ruled out, even though their spectra showed a peak at 1000 cm^{-1}, since they expected this complex to absorb in the 900-1000 cm^{-1} region. This conclusion was reached by comparison of their data with the spectra reported by Lincoln and Stranks (1968) for $Co(NH_3)_5PO_4$ and $Co(NH_2CH_2CH_2NH_2)PO_4$ and by Kumamoto (1965) for $K_2CH_3OPO_3$ and $Li(CH_3O)_2PO_2$. These researchers had found that the monodentate phosphate complex (belonging to the C_{3v} point group) gives IR bands at distinctly lower wavenumbers than does the bidentate phosphate complex (belonging to the C_{2v} point group). However, Chapman and Thirlwell (1964), in their study of the C_{3v} complex HPO_4^{2-} and the C_{2v} complex $H_2PO_4^-$ in aqueous solution, found that the former complex gave IR bands at 988 and 1076 cm^{-1} and the latter complex at 947, 1072, and 1150 cm^{-1}. Russell et al. (1975) also studied dried phosphated goethite and found that the P-O stretching frequencies were displaced on deuteration. They concluded that these displacements could only result from an adsorbed, protonated phosphate group.

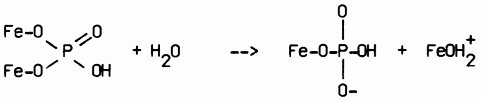
When Parfitt et al. (1976) studied dried phosphated goethite, with IR spectroscopy, they found that, after deuterating the phosphate-reactive A-type OH, groups, the A-OD signal was lost after the adsorption of 200 µmol g^{-1} phosphate. The A-type OH are protonated surface oxygen atoms singly-coordinated to Fe(III) atoms. They are present on the (100) plane. Parfitt et al. (1976) calculated a charge density of 400 µmol g^{-1} of A-type OH on the (100) face and concluded with their adsorption data that phosphate formed a binuclear surface complex. (The unit cell dimensions of goethite are: $\underline{a}$ = 0.465 nm, $\underline{b}$ = 1.002 nm and $\underline{c}$ = 0.304 nm (Schwertmann and Taylor, 1977). On the (100) plane, the A-type hydroxyls occur once per unit cell and, therefore, each OH group occupies 0.305 nm^2 in the (100) plane. Since the (100) plane makes up about 80% of the goethite surface, the conversion of this area figure to µmol g^{-1} proceeds as follows:

$$\frac{\text{OH}^-\text{ions}}{0.305\ \text{nm}^2} \times \frac{\text{mol}}{6.02\times10^{23}\ \text{OH}^-\text{ions}} \times \frac{10^{18}\ \text{nm}^2}{\text{m}^2} \times \frac{10^{6}\ \mu\text{mol}}{\text{mol}} \times 0.8 \times \frac{90\ \text{m}^2}{\text{g}}$$

$$= 392\ \frac{\mu\text{mol}}{\text{g}}.)$$

Parfitt et al. (1976) excluded the monodentate surface species, FeOPO(OH)$_2$ and FeOPO$_2$(OH)$^-$, on the grounds that the former complex required two bands at 900 cm^{-1}, and the latter complex two bands at 1100 cm^{-1}, which were not observed.

Moist samples of phosphated goethite as might occur in soils were studied for the first time by Parfitt and Atkinson (1976). They found that drying shifted the P-O bands from 1080 and 1040 cm^{-1} to 1192 and 1000 cm^{-1}, respectively. Since these bands returned immediately upon rewetting, they decided that surface rearrangement to a monodentate complex was unlikely and postulated instead that an ionized, binuclear complex, (FeO)$_2$POO$^-$Na$^+$, existed in the wet sample. However, the addition of water to a bidentate complex will drive the equilibrium to the monodentate complex, the reverse of the reaction in Eq. [2]:



[3]

Lincoln and Stranks (1968) in their study of Co-phosphate complexes (already used as a model system by Atkinson et al., 1974) found that equilibrium between monodentate and bidentate coordination was established within a few minutes. It appears, therefore, that rearrangement of a bidentate phosphate surface complex to the monodentate form upon wetting is favored and should not be ruled out as an explanation for the band shifts observed by Parfitt and Atkinson (1976).

Parfitt et al. (1975) also studied the infrared spectra of phosphate adsorbed by hematite, lepidocrocite, β-ferric hydroxide and amorphous ferric hydroxide gel. As had previously been the case for goethite, the majority of the bands observed were only weak shoulders. Nevertheless, Parfitt et al. (1975) asserted that phosphate was present on all these minerals as a binuclear bridging surface complex.

In summary, (see Table 1) all of the phosphate bands encountered in these studies fit into the following ranges of wavenumbers: One band at 980-1020 cm^{-1}, another at 1040-1100 cm^{-1}, and a third at 1100-1200 cm^{-1}. These wavenumber ranges are similar to those in the data of Chapman and Thirlwell (1964) for orthophosphates in solution and to those in the data of Lehr et al. (1967) for the iron phosphate minerals, strengite and metastrengite (both $FePO_4 \cdot 2H_2O$). The minerals have a three-dimensional structure in which PO_4^{3-} tetrahedra in tetradentate coordination link isolated Fe-centered oxygen octahedra. Each Fe(III) octahedron has two water ligands associated with it, whereas one P atom and one Fe atom are associated with each phosphate oxygen (Moore, 1966). Thus, infrared spectroscopic data by themselves would seem insufficient to identify uniquely the coordination of adsorbed phosphate.

TABLE 1

Infrared adsorption bands of phosphated minerals and systems used for comparison

Sample	Band positions (cm^{-1})	Source
goethite$^+$	1780,1650,900,805	Atkinson et al. (1974)
phosphated goethite$^+$	1000,1100,1190	
phosphated goethite$^+$	990,1040,1130 990,1045,1100	Parfitt et al. (1975)
phosphated β-ferric hydroxide$^+$	990,1100	
phosphated lepidocrocite$^+$	1115	
phosphated hematite$^+$	1020,1070,1100	
phosphated hydroxide gel$^+$	1010,1075	
phosphated goethite suspensions		
pH = 3.6	1000,1115	Parfitt and Atkinson (1976)
pH = 5.1	1000,1100	
pH = 8.1	1042,1086	
pH = 9.7	1040,1070	
phosphated goethite$^+$		
pH = 3.6	996,1192	
pH = 5.1	986,1000,1192	
pH = 8.1	1000,1192	
pH = 9.7	986,1000,1192	
strengite ($FePO_4 \cdot 2H_2O$)	550,575,600,750 994,1012,1040, 1617,3200,3370	Lehr et al. (1967)
metastrengite ($FePO_4 \cdot 2H_2O$)	461,547,573,608, 752,992,1007,1044, 1104,1610,3110,3358	
PO_4^{3-}	1004	Chapman and Thirlwell (1964)
HPO_4^{2-}	862,988,1076,1230	
$H_2PO_4^-$	878,947,1072,1150, 1230	
H_3PO_4	885,1007,1070,1165	
HPO_4^{2-}	840,960,1055,1080, 1120	Kumamoto (1965)
$H_2PO_4^-$	890,1090,1290	

$^+$ evacuated sample

Crystallographic calculations

Atkinson et al. (1972) studied the relationship between the amount of phosphate adsorption and the surface area of goethite. They found it to be linear, with a slope corresponding to a packing area of one phosphate ion per 0.66 nm^2. This packing area was compared to the area of 0.305 nm^2 per A-type OH group on the (100) face of the mineral and it was concluded that adsorbed phosphate formed a binuclear surface complex. The A-type hydroxyls on the (100) face are separated by a distance of 0.304 nm. This correlates well with the 0.285-0.320 nm distance between two oxygens of the phosphate tetrahedron reported by Van Wazer (1958), making a binuclear complex feasible.

In their study of phosphate adsorption onto gibbsite, Parfitt et al. (1977) found the (001) face, the face of mineral cleavage, to be unreactive. This result was established by the fact that the IR absorption band for hydroxyls on the (001) face was unchanged after oxalate saturation. Crystallographic calculations give approximately 60 µmol g^{-1} of edge-face hydroxyls. Hydroxyl release at maximum oxalate adsorption was 45 µmol g^{-1}, with an additional 25 µmol g^{-1} resulting from the adjustment for positive charge on gibbsite at pH = 6, to give 70 µmol g^{-1}. These values agree reasonably well with each other, leading Parfitt et al. (1977) to conclude that anion adsorption on gibbsite occurs only on the edge faces. These faces contain pairs of one OH and one OH_2 group coordinated to the same aluminum ion. The separation between these two groups is about 0.28

nm, since the oxygen radius is 0.14 nm. The distance between oxygens of successive layers is 0.29 nm. Both of these distances agree well with the O-O separation in the phosphate tetrahedron (Van Wazer, 1958), so that a binuclear complex again is possible.

van Riemsdijk and Lyklema (1980) calculated the area of the edge faces of gibbsite using shadowed electron micrographs. With this information the area exhibiting singly-coordinated OH(H) groups and the maximum adsorption density of phosphate per total area were calculated. van Riemsdijk and Lyklema (1980) found that the phosphate adsorption maximum was about twice the density of singly-coordinated groups calculated from crystal structure parameters and concluded that adsorption occurs via mono and/or bidentate ligand exchange reactions.

Jurinak (1966) found that the surface hydroxyl density doubled after phosphate adsorption onto hematite. This result was explained by the exchange of one $H_2PO_4^-$ ion for each OH^- ion, forming a monodentate surface complex of the type $Fe\text{-}O\text{-}PO(OH)_2$.

Conclusions

From a number of different types of experimental studies and a lack of contradictory evidence, a ligand exchange mechanism for phosphate adsorption by hydroxylated minerals can be established, despite the fact that most lines of evidence are indirect. However, studies of isotopic exchange on phosphated soil minerals and infrared spectroscopic studies of phosphated mineral surfaces are inconclusive in establishing the coordination of adsorbed phosphate. Infrared spectra taken on samples dried under vacuum cannot be extrapolated automatically to aqueous solution conditions. For example, Parfitt and Russell (1977) have shown that even NO_3^- and Cl^- ions are adsorbed specifically on an evacuated goethite sample. In aqueous systems, these ions are adsorbed solely by electrostatic interaction, not specifically. Thus, while it is reasonable that a binuclear, bridging surface complex is formed on dry phosphated minerals, this may have no direct application to minerals in soils since the presence of water would favor the formation of a monodentate surface complex, as in Eq. [3]. Indeed, Jurinak (1966) found only a monodentate phosphate surface complex to form on hematite in the presence of water.

Additional research is needed to establish the configuration of adsorbed phosphate ions. In order to allow meaningful extrapolation to soil mineral systems, further studies should be carried out on aqueous samples. Extension of the water adsorption techniques developed by Jurinak (1966) to aluminum oxides and to additional iron oxide minerals should prove fruitful. The requirement of a moist sample restricts the choice of spectroscopic technique. Raman spectroscopy has been used by Alvarez et al. (1976) in a preliminary study of phosphate adsorption on gibbsite. They found evidence for specific interactions of phosphate ions with surface hydroxyl groups. High resolution ^{31}P nuclear magnetic resonance (NMR) has been used to distinguish among Al-phosphate minerals and to show that phosphate in an acid soil was not simply $AlPO_4$ (Williams et al., 1981). Both Raman spectroscopy and ^{31}P NMR can be applied to aqueous systems and, therefore, they represent potential sources of direct spectroscopic evidence which may aid in establishing the predominant configurations of specifically adsorbed phosphate ions on hydroxylated mineral surfaces in soils.

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