

Influence of Structural Features on Sorption of NOM-Analogue Organic Acids to Goethite

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A systematic study of the role of structural features of NOM-analogue organic acids in influencing mineral–organic acid interactions was performed. Goethite, a crystalline form of iron oxide important in geochemical systems, was employed as a model mineral. Sorption experiments with a series of small molecular weight, aromatic organic acids were performed to assess the effects of particular features of compound structure on sorption to goethite and to obtain insight into the kinds of surface reactions responsible for organic acid sorption. Important functional groups of the humic acid component of NOM were examined. Experiments were also performed with Aldrich humic acid to allow comparison between sorption behavior of simple organic acids and NOM and to determine suitable analogues for modeling NOM sorption. Sorption characteristics for most organic acids were typical for anionic sorbates, with high sorption at low pH and decreasing sorption as pH increased. Sorption of simple organic acids exhibited strong dependence on the number, type, and position of reactive functional groups, and compounds having particular structural features in common exhibited similar sorption behavior. The important structural characteristics governing sorption of simple aromatic organic acids appeared to be adjacent carboxylic groups, adjacent phenolic groups, phenolic groups in the ortho position relative to a carboxylic group, and overall acidity of the compound. Organic acid sorption also appeared to be influenced by hydrophobic interactions for some of the compounds. NOM sorption was best mimicked by 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid) and 2,3-dihydroxybenzoic acid. Compounds having a combination of the structural features present on these organic acids might better represent NOM sorption.

Introduction

Sorbed natural organic matter, particularly humic substances, can significantly alter the characteristics of mineral surfaces (1–5). Sorbed humic substances influence interactions between mineral surfaces and both organic and inorganic solutes in natural aquatic systems. For example, humic substances can profoundly influence trace metal sorption (6, 7).

While the sorption of NOM molecules on mineral surfaces has proven to be an important geochemical phenomenon,

the mechanisms by which it occurs are not well understood and our ability to model it is limited. Sorption of simple organic acids is thought to be governed by ligand-exchange mechanisms involving carboxylic/phenolic functional groups of the acids and the oxide surface sites. Data for sorption of several simple carboxylic and phenolic organic acids on oxides have been described successfully by invoking surface ligand-exchange reactions (8–13). Gu et al. (14) presented a range of evidence to suggest that ligand-exchange mechanisms between carboxylic/phenolic functional groups and the iron oxide surface are also the dominant mechanisms for NOM sorption. Understanding the surface reactions of acidic functional groups is essential to understanding the mechanisms controlling the sorption of simple and complex organic acids.

To advance understanding of mineral–NOM interactions in aquatic systems, we undertook to study in detail the sorption of smaller, well-characterized molecules containing the functional groups of humic acids over a wide range of experimental conditions. Research with simple organic acids has provided valuable insights into the behavior of NOM in systems containing mineral surfaces, but only a limited number of compounds has been studied. While simple organic acids do not approach the complexity of humic acids, their sorption properties can be remarkably similar to those of humates as demonstrated by Ali and Dzombak (12, 13).

We performed a systematic study of the role of structural features of NOM-analogue organic acids in influencing mineral–organic acid interactions. While others have studied aspects of the effect of organic acid structure on sorptive properties (11, 15), there has been little systematic work to elucidate the effect of the structure of organic acids on sorption. Sorption of a large group of simple organic acids, selected to examine a range of structural features, was studied in simple electrolyte media under different pH and total sorbate concentrations to assess the influence of structural features on sorption to goethite. These organic acids, shown in Figure 1, were selected because their relative sorption behaviors enabled evaluation of the effects of differences in particular structural features, including increasing number of carboxylic and phenolic group substituents on the benzene ring, differences of position of carboxylic and phenolic groups in isomeric substitution on the benzene ring with resulting effects on chelation properties, effects of aliphatic chains of increasing size as substituents on the benzene ring, and bridging potential to multiple surface iron sites. Sorption of double ring compounds was also studied to examine effects of greater hydrophobicity due to increasing number of rings.

Materials and Methods

Goethite. Goethite (α -FeOOH) was used as the model metal oxide in this study because of its abundance in nature, thermodynamic stability, and strong sorptive properties. Batches of goethite were prepared using the method developed by Atkinson et al. (16); the goethite crystalline structure was confirmed with X-ray diffraction. Properties of the goethite were measured in a previous study and are presented in Table 1 (13).

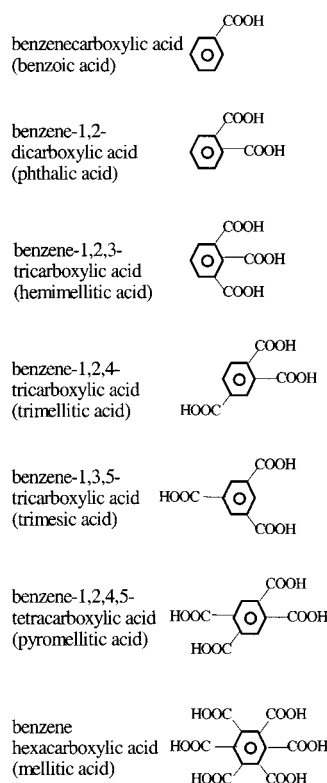
Simple Organic Acids. Sorption studies with several series of organic acids on goethite were conducted. All of the selected organic acids are available commercially (90–99.5% purity, Aldrich Chemical Co., Inc. and Sigma Chemical Co., Inc.), and the protonation constants for these organic acids are known or can be estimated.

Humic Acid. Sorption studies were also performed for Aldrich humic acid (Aldrich Chemical Co., Inc., St. Louis,

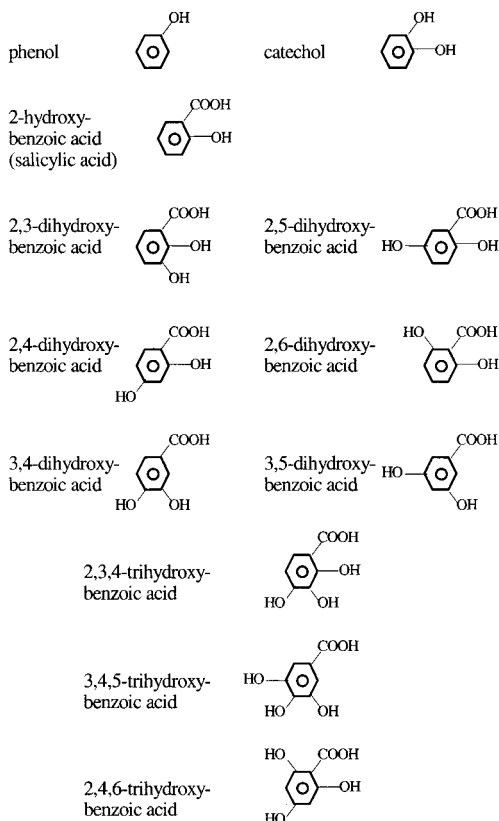
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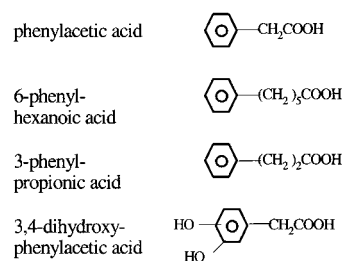
Effect of varying number and position of carboxylic groups:



Effect of varying number and position of phenolic groups:



Effect of aliphatic chain length on benzene monocarboxylic acids:



Effect of ring size, varying functional groups and positions:

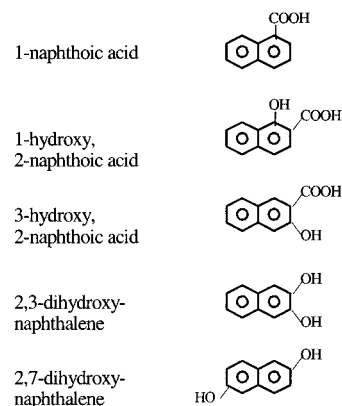


FIGURE 1. Series of organic acids studied to examine effects of structural features on sorption.

TABLE 1. Summary of Goethite Properties (13)

specific surface area (m^2/g)	79.4 ± 1
surface site density, N_s (sites/ nm^2)	1.4 (0.016 mol/mol Fe)
pH_{PZC}	8.0 ± 0.1
$\text{p}K_{\text{a}1}^{\text{int}}$	7.68
$\text{p}K_{\text{a}2}^{\text{int}}$	8.32

MO), which was used as received. This commercially available humic acid is isolated by extraction of brown coal in an aqueous solution of NaOH. The molecular weight of Aldrich humic acid ranges 2000–50000 g/mol. The acidity constants for the Aldrich humic acid used in this study were determined by potentiometric titration (17).

Single Solute Sorption Experiments. Several series of batch sorption experiments were conducted with each sorbate to examine a range of total sorbate concentrations (10^{-6} – 10^{-3} M) and pH conditions at an ionic strength of 0.01 M NaCl. A fixed amount of goethite, electrolyte solution, and sorbate spike along with varying amounts of HCl or NaOH were added to 30 mL polyethylene tubes to yield a range of pH values. Stock solutions were maintained CO_2 -free by purging with nitrogen. The reaction tubes were capped (after headspace was purged with N_2), placed on an end-over-end rotator, and agitated for 24 h, an amount of time demonstrated to be adequate for sorptive equilibrium to be established (12, 13, 18). After the equilibration period, the tubes were removed from the rotator and placed upright in a rack. After quiescent settling of suspension particles, the pH of the supernatant was measured with a microelectrode probe. The tubes were centrifuged for additional separation of fine particles from the supernatant, and a sample of the supernatant was withdrawn with a 5 mL plastic syringe. The sample was expressed through a $0.02 \mu\text{m}$ polycarbonate membrane filter attached to the syringe into a polyethylene

sample vial. The first 1 mL of filtrate was used to saturate the filter and was not collected for analysis. Replicate sorption experiments were performed for selected compounds and conditions.

Aqueous-phase concentrations of the organic acids were measured with UV–vis spectroscopy. For each organic acid, a dilute solution (0.02–0.05 mM) was analyzed across the UV–vis spectrum to determine an appropriate wavelength for analysis. HCl (10–25 μL , 0.1 N) was added to bring samples to the same pH value for measurement, because light absorption by organic acids can vary with protonation state and therefore pH. This simple analytical technique has proven to be robust as well as rapid in previous work with phthalic and chelidamic acid (12, 13, 18).

Four blank samples, each adjusted to a different pH value in the pH range of interest, were prepared and analyzed with each batch sorption experiment in order to assess losses from the system, which were not the result of sorption to goethite, over a range of pH values. Blank samples were prepared similar to the sorption samples except that goethite was not added to the blanks.

For initial experiments with each organic acid, the supernatants were analyzed for dissolved Fe by atomic absorption spectroscopy with graphite furnace combustion in order to determine if significant dissolution of the solid occurred in the presence of the organic acid.

Results and Discussion

Effects of concentration, number and position of carboxylic groups, number and position of phenolic groups, aliphatic chain length, and ring size were investigated experimentally. Selected data are presented; complete data for all conditions studied are provided in Evanko (19).

Reproducibility of the sorption experiment methods was demonstrated by the results from replicate sorption experi-

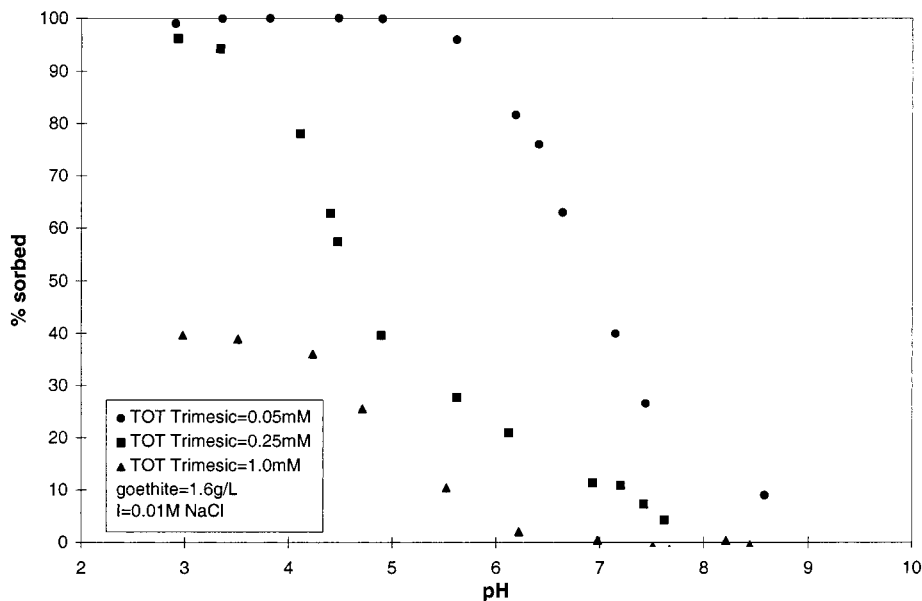


FIGURE 2. Fractional sorption of trimesic acid to goethite as a function of pH and total sorbate concentration.

ments which were consistent. Results from atomic absorption experiments indicated that dissolution of the goethite was not significant for the concentrations of organic acids studied in these experiments. The results from blank samples analyzed with each batch of sorption samples indicated that losses from the system were usually minimal (less than 5%). Results from sorption experiments were corrected for these losses by adjusting the total concentration of organic acid to account for the amount lost due to processes other than sorption, unless the losses accounted for more than 15% of the total mass added. The data associated with blanks having losses of greater than 15% were not used because these data were considered to be highly uncertain.

Results indicated that losses (probably due to bio- or photodegradation) significantly affected a limited number of compounds at higher pH values (above pH 7 or pH 8). These compounds had adjacent phenolic groups as the common structural feature and included catechol, 3,4-dihydroxybenzoic acid, 2,3,4-trihydroxybenzoic acid, and 3,4,5-trihydroxybenzoic acid. Experimental data are not presented for these compounds in the affected pH range.

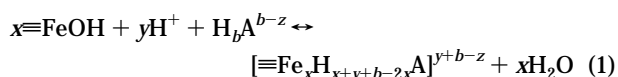
The correction of the sorption results could not account for possible redox transformations of the organic compounds on the goethite surface. However, such losses likely were not large as dissolution of goethite was not observed to be significant for the compounds studied. LaKind and Stone (20) found that dihydroxybenzenes and trihydroxybenzenes caused reductive dissolution of goethite at low pH (<4.5), but the 1–60 μM concentrations of Fe(II) released were much smaller than the organic acid concentrations as was the case here.

Effects of pH and Concentration. Results from the single solute sorption experiments were plotted as pH sorption edges, i.e., percent of total solute mass sorbed versus pH. For each sorbate, two or three pH edges, reflecting two or three different total sorbate concentrations, were obtained. Figure 2 shows pH sorption edges for trimesic acid at three different total sorbate concentrations. The pH sorption edges for trimesic acid, and for most of the organic acids studied, exhibited sorption behavior typical for anionic sorbents, with high sorption at low pH and decreasing sorption as pH increased.

Because the goethite surface exhibits a positive surface charge at low pH ($\text{pH}_{\text{PZC}} = 8.0 \pm 0.1$) and most organic acids contained at least one acidic carboxylic functional group

($\text{p}K_a$ values ranging from below 1.0 to 4.8), the observed organic acid adsorption was aided by electrostatic attraction. However, the electrostatic contribution to the free energy of ion adsorption is generally small (4, 13), and surface complexation modeling (SCM) can be used to fit sorption data successfully with ancillary consideration of electrostatic interactions.

Surface complex formation between acidic functional groups of the organic acid and surface hydroxyl groups on metal oxides plays an important role in organic acid sorption (8–13). Equation 1 provides a general description of organic acid surface complex formation on goethite:



This equation reflects the pH and surface site (solid concentration) dependence of organic acid sorption to goethite. At high pH, the surface is negatively charged, surface oxygen atoms are tightly bound and are less likely to exchange with acidic functional groups in solution. As pH decreases, neutral and positively charged surface sites are formed, the iron–oxygen bond is weakened due to decreased electron density of the bond, and the oxygens are exchanged as OH^- or OH_2 with functional groups of the organic acids. SCM has been performed to describe sorption of the organic acids studied here (21).

The fractional sorption of the organic acids at a particular pH decreased as total sorbate concentration increased. This phenomenon is due to progressive saturation of surface sites as total sorbate concentration increases and is often observed for inorganic and organic anion sorption.

Effects of Number and Position of Carboxylic Groups. Experiments were performed with simple aromatic organic acids with varying numbers of carboxylic groups: benzoic acid, phthalic acid, hemimellitic acid, trimellitic acid, trimesic acid, pyromellitic acid, and mellitic acid. The compounds are shown in Figure 1. Results of these experiments are presented for the lowest total sorbate concentration (0.05 mM) as pH sorption edges in Figure 3.

The presence of additional carboxylic groups enhanced the sorption of the organic acids shown in Figure 3. Sorption of benzoic acid was significantly lower than the other organic acids over the entire range of pH values investigated. Mellitic

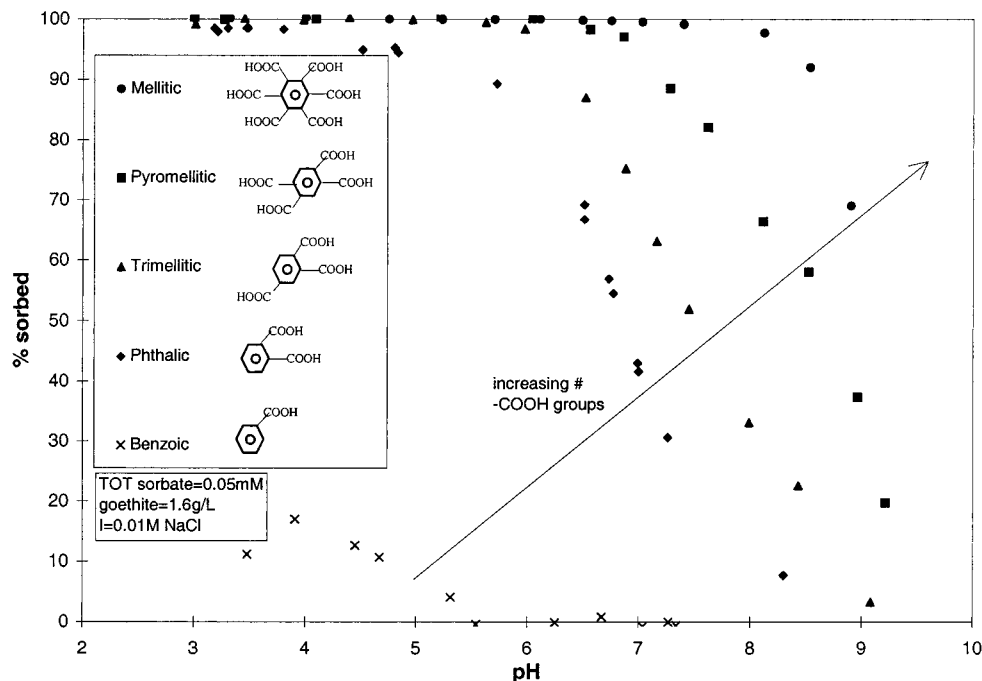


FIGURE 3. Fractional sorption of carboxylic acids to goethite as a function of pH and number of carboxylic functional groups.

acid sorbed most strongly, i.e., exhibited the highest percent sorbed, over the pH range investigated, as evidenced by the significant fraction that remained sorbed even at high pH values. Phthalic acid and trimellitic acid sorbed significantly onto the goethite, but the pH sorption edges for these acids were steeper and shifted to the left, indicating weaker sorption than for mellitic acid. The pH sorption edge for pyromellitic acid fell between trimellitic and mellitic acid. The fact that sorption increased and extended over a wider pH range as carboxyl groups were added suggests that additional surface complexes may form. These increases in sorption may also result from increases in the acidity of the carboxylic acids, although it is difficult to distinguish the two influences.

The pK_a values for these acids are presented in Table 2. The compounds having the lowest pK_{a1} are considered to be overall the most acidic. For compounds with multiple acidic functional groups (and, therefore, multiple pK_a s), however, the acidity of additional functional groups must be assessed for the entire pH range because more than one functional group can be involved in sorption and increased acidity of these additional functional groups can also influence sorption.

The acidity of organic acids has been observed to influence their sorption behavior. Ulrich et al. (15) and Kummert and Stumm (8) studied sorption of a number of aliphatic fatty acids with varying chain length onto alumina and found that the maximum extent of surface binding would occur close to the pK value of the fatty acids.

Work by Vasudevan and Stone (11) suggests that the types of substituents can have a significant effect on the sorptive properties of organic ligands by influencing acidity. In studying the sorption of aromatic amines onto metal oxides, they found that the presence of electron-withdrawing substituents lowered the basicity of the aromatic amine and phenolate donor groups and shifted the plateau of maximum sorption to more acidic pH values.

Edwards et al. (23) found that organic matter with very strong acid groups (groups ionized below pH 3.0) was sorbed to goethite preferentially to organic matter with weaker acid groups, suggesting that very strong acid groups are important for controlling NOM sorption to oxides. These findings are consistent with studies of simple organic acid sorption in

which polyprotic acids having at least one very strong acid group (salicylic, phthalic) sorbed strongly to oxide surfaces, whereas sorption of monoprotic acids without very strong acid groups (benzoic, acetic) was much weaker (24).

The influence of the position of carboxylic groups was studied for three different tricarboxylic acids: hemimellitic acid (three adjacent carboxylic groups), trimellitic acid (two adjacent groups), and trimesic acid (no adjacent groups). The compounds are shown in Figure 1. Results of sorption experiments with these compounds at a total concentration of 0.05 mM are shown in Figure 4.

Sorption of tricarboxylic acids varied somewhat with location of the carboxylic groups on the ring. Sorption of hemimellitic and trimellitic acid was similar, but the hemimellitic sorption edge extended to slightly higher pH before sorption started to decrease, indicating that sorption of hemimellitic was slightly stronger than trimellitic. The pH sorption edge for trimesic acid was shifted to the left of hemimellitic and trimellitic, indicating weaker sorption of trimesic acid.

Table 2 includes the pK_a s of the three tricarboxylic acids. On the basis of results of previous studies discussed above, one might expect increased acidity to influence the sorption of organic acids. However, correlation was not observed between acidity and sorption, and it is evident that differences in acidity cannot account for differences in sorption for these compounds.

The location of functional groups may influence sorption by governing the types of surface complexes that can form. Possible surface complex structures for mono- and dicarboxylic acids on goethite are shown in Figure 5, structures a-h. This figure demonstrates the influence of the number and position of functional groups on surface complex formation. Physical and thermodynamic factors will influence the likelihood that a particular structure will form. For example, structure c is less favorable than b or d since four-membered rings are not very stable (25). Structures e-h become possible when an additional carboxylic group is present in the ortho position.

As evident in Figure 4, the tricarboxylic acids with ortho carboxylic acid groups (hemimellitic and trimellitic) exhibited similar sorption behavior. However, sorption of trimesic acid, which has both carboxylic groups in the meta position, was

TABLE 2. pK_a Values for Organic Acids in 0.01 M NaCl^a

benzoic	phthalic	hemimellitic	trimellitic	trimesic	pyromellitic	mellitic	
4.12	2.87	2.79	2.39	2.84	1.52	0.61	
	5.23	4.49	3.87	4.12	2.95	1.35	
		6.95	5.28	4.92	4.65	3.95	
					5.89	4.74	
						5.88	
						6.97	
catechol	salicylic	2,3-DHBA	2,4-DHBA	2,5-DHBA	2,6-DHBA	3,4-DHBA	3,5-DHBA
9.34	2.88	2.41	3.23	2.96	1.43	4.46	4.08
13.24	13.56	10.30	8.84	10.46	13.03	9.08	9.90
		13.48	14.04	13.41	13.95	12.58	11.09
	2,3,4-THBA		2,4,6-THBA ^b			3,4,5-THBA	
	3.13		1.4			4.37	
	8.97		8.8			8.94	
	12.68		13.9			11.83	
	n/a		n/a			n/a	
phenylacetic		3-phenylpropionic		6-phenylhexanoic		3,4-dihydroxyphenylacetic	
4.28		4.60		4.85		4.25	
						9.74	
						14.08	
1-naphthoic		1-hydroxy-2-naphthoic ^c		3-hydroxy-2-naphthoic		2,3-dihydroxy naphthalene	2,7-dihydroxy naphthalene ^c
3.61		2.7		2.65		8.72	10.5
		12.8		12.72		12.74	13.4

^a pK_a values from Martell and Smith (22) were corrected for activity in 0.01 M NaCl. ^b pK_a values for 2,4,6-THBA were not available in the literature. These values were estimated using pK_a values for structurally similar compounds. ^c pK_a values for 1-hydroxy-2-naphthoic acid and 2,7-dihydroxynaphthalene were not available in the literature. These values were estimated using pK_a values for structurally similar compounds.

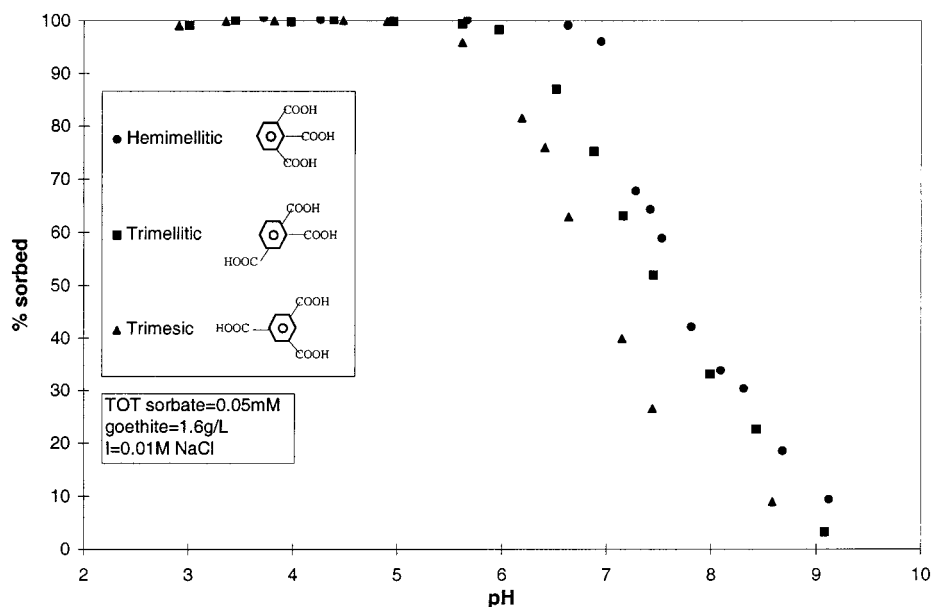


FIGURE 4. Fractional sorption of series of tricarboxylic acids to goethite as a function of pH and position of functional groups.

significantly lower than for both of these acids. It appears that structures e–h in Figure 5 play a significant role in sorption of tricarboxylic acids, and effectively enhance sorption over a wide range of pH values.

These findings differ from those of Tejedor-Tejedor et al. (26) who attributed the sorption of benzoate and phthalate on goethite primarily to the formation of a bidentate surface complex involving both oxygens of one carboxylic group and

one surface iron atom (bidentate chelate complex, Figure 5c). However, their findings were not consistent with the high maximum adsorption density observed for phthalate, and CIR-FTIR spectroscopy data were inconclusive. While bidentate-chelate surface structures may account for most of the binding to goethite, our results indicate that in cases where carboxylic groups are adjacent, additional complexes may be formed that involve more than one carboxylic group.

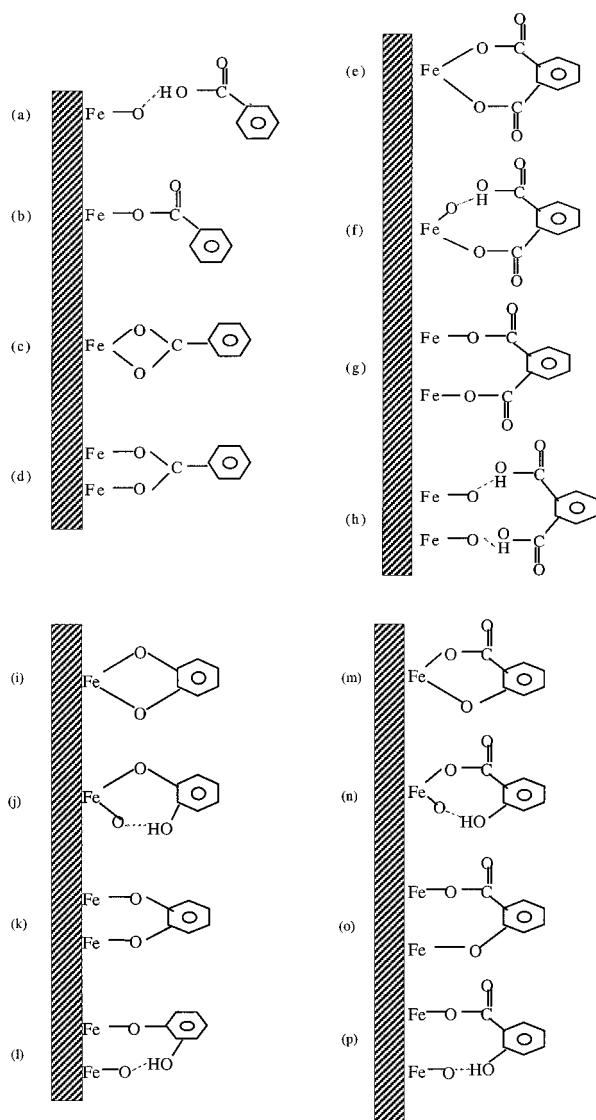


FIGURE 5. Possible structures for surface complexes of organic acids sorbed on goethite: (a–d) monocarboxylic acids; (e–h) dicarboxylic acids; (i–l) dihydroxybenzene/benzoic acids when phenolic groups are adjacent; and (m–p) dihydroxybenzoic acids with phenolic group in ortho position relative to the carboxylic group.

This hypothesis would explain the similar sorption behavior of the three different tricarboxylic acids, the increased sorption of hemimellitic and trimellitic over trimesic acid, and also the significantly higher sorption of phthalic acid over benzoic acid observed by Tejedor-Tejedor et al. (26).

Other studies have demonstrated the importance of the number and position of acidic functional groups in determining the sorption behavior of organic acids. Benoit et al. (27) provided evidence that enthalpies of sorption for a series of monodentate and bidentate organic ligands correspond to different ligand-exchange reactions and suggested that these reactions are influenced by the number of functional groups on the ligand. Davis (4) compared the sorption behavior of NOM with that observed for a number of simple organic acids having carboxylic and phenolic groups and concluded that compounds with carboxylic or phenolic groups in ortho or chelating positions are more reactive with iron and aluminum oxides than molecules with single groups or meta or para substitutions. In their study of sorption of simple organic acids to goethite, Ali and Dzombak (12, 13) found similarities in sorption characteristics of phthalic and

chelidamic acid, which suggested similar sorption mechanisms due to similarities in the position of functional groups. The data were described by invoking bidentate and monodentate surface complexes with goethite (13).

The importance of the position of carboxylic groups may also help to explain the trends observed in Figure 3. As carboxylic groups are added to the ring, the number of possible surface structures that may form between the surface iron atoms and the carboxylic acids increases. Surface complex structures involving more than two carboxylic groups seem unlikely, however, and the enhanced sorption with increasing number of carboxylic groups may also be due to changes in the acidity of the compounds as discussed previously.

Effects of Number and Position of Phenolic Groups.

Experiments were performed with simple aromatic organic acids with varying numbers of phenolic groups. Included in this series were compounds, shown in Figure 1, with phenolic functional groups: phenol and catechol, and compounds which contained one carboxylic group in addition to phenolic groups, including dihydroxybenzoic acids (DHBA) 2,3-DHBA, 2,4-DHBA, 2,5-DHBA, 2,6-DHBA, 3,4-DHBA, and 3,5-DHBA and trihydroxybenzoic acids (THBA), 2,3,4-THBA, 2,4,6-THBA, and 3,4,5-THBA.

Sorption of compounds in this series was relatively weak, compared to the previous series of compounds, at low pH (<6), and none of the phenolic compounds achieved 100% sorption over the range of pH values investigated. The pH sorption edges for the phenolic compounds were not as steep as for the carboxylic series, and significant sorption occurred over the entire range of pH values, including higher pH values where sorption decreased rapidly for the series of organic acids with carboxylic functional groups.

Catechol and phenol were the only compounds in this series that did not contain a carboxylic functional group. These compounds were therefore much more basic than the carboxylic acids (Table 2), and were present mostly as neutral species at pH values within the range investigated. Phenol did not sorb to goethite significantly over the range of pH values investigated. Catechol sorption differs from sorption of organic acids containing a carboxylic functional group, with sorption increasing as pH increases (19). Catechol forms strong surface complexes with surface iron atoms at high pH. The association of protons with phenolic oxygens as pH decreases weakens the Fe-catechol bonds, resulting in decreased sorption. The presence of these phenolic groups and the fact that they enhance sorption at high pH explains the higher sorption observed for this series of compounds at high pH as compared with the carboxylic acid series.

Results of experiments with the entire series of organic acids are presented for the lowest total sorbate concentration (0.05 mM) in Figure 6. This figure shows that sorption of organic acids with a single phenolic group (phenol) was negligible. The addition of a second functional group in the ortho position, whether it was a phenolic group (catechol) or carboxylic group (salicylic acid), increased sorption to goethite significantly, but the effect of functional group addition depended on the type of functional group added. Sorption to goethite increased with increasing pH for catechol but decreased with increasing pH for salicylic acid. The addition of a phenolic and/or carboxylic group in the meta position relative to the phenolic group (as with 3,5-DHBA) increased sorption significantly, but not as much as additions in the ortho position.

These results indicate that the position of the phenolic functional groups influences sorption more than the number of groups. For example, sorption of salicylic acid (1-OH), 2,4-dihydroxybenzoic acid (2-OH), and 2,4,6-trihydroxybenzoic acid (3-OH) were similar, whereas 2,3-DHBA (2-OH)

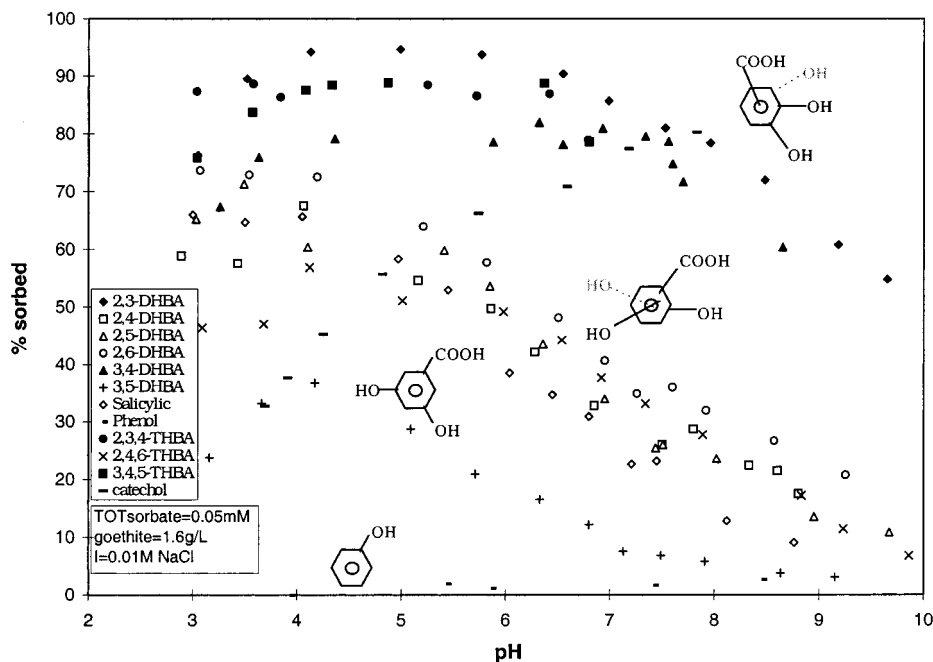


FIGURE 6. Fractional sorption of organic acids to goethite as a function of pH, number and position of phenolic groups.

and 2,4-DHBA (2-OH) exhibited significantly different sorption behavior.

Phenolic compounds exhibiting similar sorption behavior appear to fall into two groups. The first group is represented by solid symbols on Figure 6 and includes 2,3-DHBA, 3,4-DHBA, 2,3,4-THBA, and 3,4,5-THBA. Sorption of these compounds increased slightly with increasing pH, reached a maximum of 80–90% at neutral pH (5–7), and then decreased slightly as pH increased, but remained high over a wide range of pH values. This group of compounds comprises di- and trihydroxybenzoic acids that contain at least two adjacent phenolic groups on the benzene ring. The position of the carboxyl group relative to the adjacent phenolic groups did not have a significant influence on sorption, but the presence of the carboxyl group was important for sorption at low pH, since otherwise sorption would resemble that of catechol. Also, the presence of a third phenolic group had little effect on sorption. Possible surface structures formed by surface complexation involving adjacent phenolic groups of these organic acids are shown in Figure 5, structures i–l. Binding may also occur through the single carboxylic group (Figure 5, structures a–d), which probably accounts for the high sorption observed at lower pH values.

The second group of phenolic compounds is represented by open symbols and includes salicylic acid, 2,4-DHBA, 2,5-DHBA, 2,6-DHBA, and 2,4,6-THBA. Sorption of these compounds reached a maximum of 60–70% sorbed at low pH (between 3 and 4), and decreased with increasing pH. This group of compounds comprises mono-, di-, and trihydroxybenzoic acids with one adjacent carboxylic and phenolic group (i.e., a phenolic group in the ortho position relative to the carboxylic group) being their common structural feature. Also, for the compounds with two or more phenolic groups, none of the phenolic groups are adjacent to one another. Figure 5, structures m–p, represents surface complexes formed between surface iron atoms and the adjacent carboxylic and phenolic functional groups that likely account for this sorption behavior.

Yost et al. (28) used CIR-FTIR spectroscopy to study the sorption of salicylate to goethite. They proposed a surface chelate structure involving binding of the phenolic oxygen and one carboxylic oxygen with one surface iron atom, similar

to Figure 5m in which the organic ligand forms two bonds with the same surface iron atom. Yost et al. hypothesized that goethite contains relatively few surface iron atoms with two exchangeable OH ligands. The limited number of such sites may explain the lower sorption we observed for salicylic acid relative to other organic acids. Yost et al. also found that other benzoate compounds with phenolic groups in the ortho position formed the same type of surface complex on goethite, which explains the similar sorption behavior observed here for compounds with adjacent carboxylic and phenolic functional groups.

Biber and Stumm (29) studied salicylate sorption to goethite and concluded that the surface structure proposed by Yost et al. (28) was most consistent with their data. They proposed an alternate surface complex structure for salicylate sorption to alumina involving binding of one carbonyl oxygen and hydrogen bonding between surface oxygens and phenolic functional groups (similar to Figure 5n). These types of surface structures would be possible for salicylic sorption to goethite, but FTIR evidence indicates that the phenolic oxygen binds to the surface iron atom.

The compound 3,5-DHBA did not exhibit sorption behavior similar to either of the previously identified groups of compounds. Sorption of 3,5-DHBA was relatively weak and closely resembled that of benzoic acid (19). As noted previously, addition of phenolic or carboxyl groups in the meta position increases sorption relative to phenol, but not as much as groups added in the ortho position. Tejedor-Tejedor et al. (26) studied sorption of *p*-hydroxybenzoate to goethite using CIR-FTIR and found that it complexed with the surface through binding of both oxygen atoms of the carboxylic group, while the phenolic group was not involved in surface binding. The spacing of the phenolic groups in 3,5-DHBA thus is likely to explain their limited contribution.

Effects of Aliphatic Chain Length. Experiments were performed with a series of simple monocarboxylic acids containing aliphatic chains of varying length in order to study the influence of aliphatic chain length on sorption to goethite: phenylacetic acid, 3-phenylpropionic acid, and 6-phenylhexanoic acid. 3,4-Dihydroxyphenylacetic acid was also included in this series in order to investigate the influence of aliphatic groups on sorption when phenolic groups are also present. The compounds are shown in Figure 1. pK_a

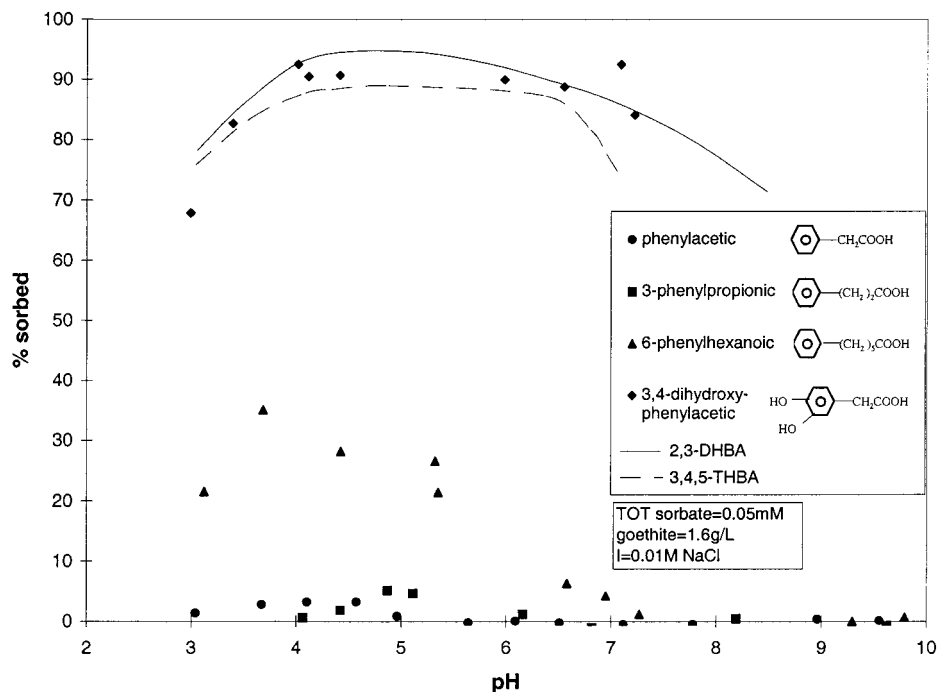


FIGURE 7. Fractional sorption of organic acids with chain-substituents to goethite as a function of pH and aliphatic chain length. Data for 2,3-DHBA (—) and 3,4,5-THBA (---) are represented as curves for comparison.

values for these compounds are presented in Table 2.

Results of these experiments are presented in Figure 7, where it may be seen that the influence of aliphatic chains on sorption to goethite depends on the length of the chain. Sorption of compounds containing shorter aliphatic chains, such as phenylacetic acid (CH_2) and 3-phenylpropionic acid (CH_2)₂, was negligible. Sorption of 6-phenylhexanoic acid, the compound with the longest aliphatic chain (CH_2)₅, was significantly higher. This increased sorption may be due to interactions between hydrophobic parts of the molecule.

The effect of hydrophobic interactions on sorption to solid surfaces has been observed in experiments with surfactant molecules. Wakamatsu and Fuerstenau (30) found that increasing the hydrocarbon chain length of alkyl sulfonates enhanced adsorption to alumina significantly and resulted in high sorption densities for the larger molecules relative to the smaller molecules.

Compounds such as long-chain fatty acids have been observed to sorb onto oxides at least partially by surface complex formation (8, 15). Ulrich et al. (15) determined that a free-energy contribution due to the hydrophobic effect becomes important for molecules with a hydrocarbon chain containing eight or more carbons. This hydrophobic contribution may cause some carboxylic acids to adsorb more than one layer on the oxide surface due to hemimicelle formation, and surface coverage may therefore be increased (31).

6-Phenylhexanoic acid (6-PHA) may sorb in a similar manner, complexing to the goethite surface through the carboxylic group. Hydrophobic interactions through association of the longer hydrocarbon chains would explain the relatively high sorption of this compound. Sorption data for 6-PHA at three different total sorbate concentrations (21) indicated that sorption increased slightly as total sorbate concentration increased, which could also be explained by hydrophobic interactions.

Sorption of 3,4-dihydroxyphenylacetic acid is also shown in Figure 7. Sorption of 3,4-DHPAA is much higher than the other compounds in this series and extends over a larger range of pH values. 3,4-DHPAA sorption most closely resembles sorption of di- and trihydroxybenzoic acids with

adjacent phenolic groups, such as 2,3-DHBA and 3,4,5-THBA (the solid and dashed lines, respectively, in Figure 7). The presence of the short aliphatic chain appears to have a negligible effect on sorption when other important structural features are present.

Effects of Ring Size. Figure 8 shows the results for experiments performed with a series of organic acids comprising double ring compounds: 1-naphthoic acid, 1-hydroxy-2-naphthoic acid, 3-hydroxy-2-naphthoic acid, 2,3-dihydroxynaphthalene, and 2,7-dihydroxynaphthalene. The compounds are shown in Figure 1. pK_a values for these compounds are given in Table 2.

As evident in Figure 8, double ring structures did not appear to have a systematic effect on sorption to goethite. Rather, sorption of these organic acids resembled sorption of smaller molecular weight organic acids with similar functional groups. For example, sorption of 1-naphthoic acid was similar to sorption of benzoic acid, although 1-naphthoic acid sorption was a bit higher, perhaps due to increased hydrophobic interactions for the double ring compound.

Comparison with NOM. Sorption of Aldrich humic acid was investigated to allow comparison between sorption of simple organic acids and sorption of more complex NOM molecules. Results of experiments at three different total sorbate concentrations are presented in Figure 9. Humic acid exhibited sorption behavior typical of anions that sorb via ligand-exchange mechanisms, with high sorption at low pH and decreasing sorption as pH increased. The percent sorbed at a given pH decreased as total sorbate concentration increased for the lower two total sorbate concentrations (0.05 and 0.25 mM). The pH sorption edge for the highest total sorbate concentration (1.0 mM) was slightly lower than that for the intermediate total sorbate concentration (0.25 mM). This behavior indicates that surface site saturation was not limiting humic acid sorption at higher total sorbate concentrations and that hydrophobic interactions may influence humic acid sorption to goethite. Humic acids have significant aliphatic and aromatic character, which could easily account for such hydrophobic interactions (32). Results very similar to those presented in Figure 9 were obtained in comparable

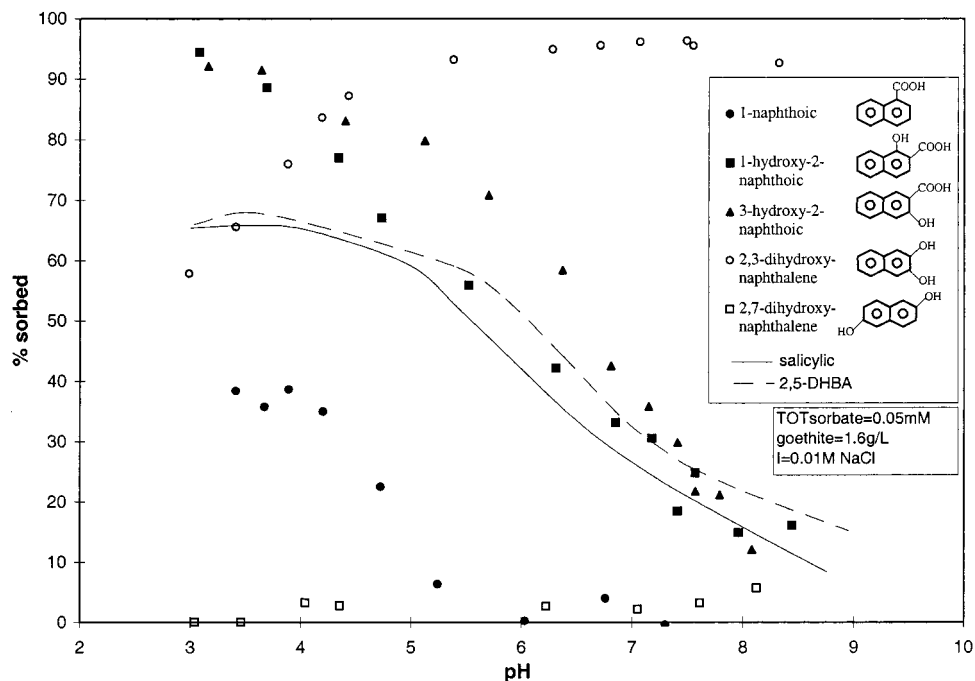


FIGURE 8. Fractional sorption of organic acids containing double ring structures to goethite as a function of pH. Data for salicylic acid (—) and 2,5-DHBA (- -) are represented as curves for comparison.

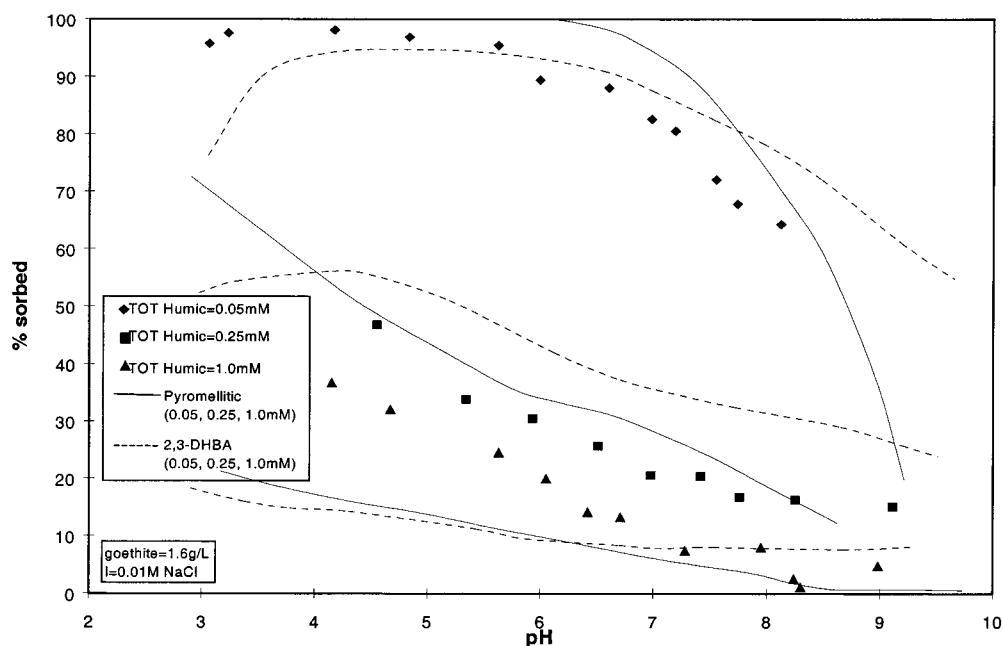


FIGURE 9. Fractional sorption of Aldrich humic acid to goethite as a function of pH and total sorbate concentration. Data for pyromellitic acid (—) and 2,3-DHBA (- -) at the corresponding total sorbate concentrations are represented as curves for comparison.

experiments with Suwanee River fulvic acid (33).

Day et al. (34) observed slight increases in sorption density with increasing equilibrium NOM concentration for three different types of NOM on goethite. They also found that larger, more hydrophobic NOM fractions had higher affinities for goethite than lower molecular weight hydrophilic fractions. One explanation they offered for this behavior was that a small degree of multilayer sorption occurred involving the more hydrophobic molecules, which increased the amount of NOM that could sorb to the surface relative to the hydrophilic compounds that reached maximum sorption upon saturation of surface sites.

Figure 9 also shows pH sorption edges for pyromellitic acid and 2,3-DHBA. Of the compounds studied, the shape

of these pH sorption edges and the extent of sorption of these compounds at different total sorbate concentrations most closely resembled the sorption behavior of Aldrich humic acid. These two compounds also mimicked most closely comparable sorption data obtained for Suwanee River fulvic acid (33). Humic and fulvic acid sorption thus may be best represented by compounds having structural features common to both of these simple organic acids, i.e., adjacent phenolic groups, adjacent carboxylic groups, and highly acidic carboxylic acid groups ($pK_a \leq 1.5$).

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