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Sorption of Aminonaphthalene and Quinoline on Amorphous Silica

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■ The adsorption of quinoline and aminonaphthalene was investigated from aqueous solution on amorphous silica (SiO_2). Amorphous SiO_2 was not a strong adsorbent of these compounds and quinoline was adsorbed more strongly than aminonaphthalene. The adsorption of both compounds varied with pH. A maximum in adsorption occurred near their respective pK_a 's. Temperature effects were significant, suggesting enthalpy contributions in the range of H bonding. Both compounds appeared to adsorb via identical mechanisms that included H bonding and ion exchange. The greater basicity of quinoline combined with (1) the enhanced electron-donating properties of the heteroatom N and (2) the delocalized π -bonded ring system were proposed to account for its stronger adsorption. Aminonaphthalene showed greater exclusion from the internal region of porous SiO_2 , indicating that the compounds orient differently at the surface. The triple-layer adsorption model and three outer-sphere surface complexes were used to model the adsorption data. Good predictions of adsorption isotherms and the effects of ionic strength and electrolyte cation were obtained.

Introduction

Shallow, near-surface aquifers are often the recipients of contaminants because of their high permeability and linkage to the vadoze zone and soils (1, 2). Quartz and feldspars commonly dominate their mineralogy (3-7). Hydrophobic organic compounds are, in general, poorly retarded in these subsurface systems because the organic carbon content is low and sorption is minimal on silica, layer lattice silicate, or iron/aluminum oxide surfaces (3, 8). In contrast, hydrophobic ionizable organic compounds, including organic acids and bases, interact with specific surface sites on mineral surfaces, thereby retarding their migration (9, 10).

Organic bases containing nitrogen are common to coal and petroleum products, and their wastes and tars, as well as other industrial processes (11). These compounds ionize to organic cations and are strongly adsorbed by layer silicates that possess negative charge (12). Silica also represents a potential subsurface sorbent of organic bases because its surface contains weakly acidic silanol groups that ionize to negatively charged sites above pH 5 (13, 14). Silica behaves as an ion exchanger, forming both inner- and outer-sphere surface complexes with inorganic cations (13, 15-17).

Infrared spectroscopy has shown that hydrogen bonding, charge-transfer reactions, and electrostatic interactions control the sorption of organic bases (alkyl aliphatic amines and selected aromatic amines and pyridines) on silica from the vapor phase (18-22) and aprotic organic solvents (22-26). Little comparable information exists on the

sorption of aromatic amines and heterocyclic aromatic compounds on silica from aqueous solution, which could be used to assess the behavior of these compounds in groundwater in contact with silica-rich sediments.

The sorption of quinoline and aminonaphthalene on porous and nonporous amorphous silica was investigated in this paper. These compounds differ in their size, pK_a , and aqueous solubility. Sorption was measured over a range in sorbate concentration, pH, electrolyte concentration, electrolyte cation, and temperature to examine the surface reaction and establish the presence of specific types of surface complexes. A site-binding model was used to evaluate the consistency of specific surface reactions with the sorption data.

Experimental Procedures

Sorbates. 1-Aminonaphthalene and quinoline (99% purity, Aldrich Chemical Co.) were used without further purification for sorbate stock solutions. These stock solutions were spiked with ^{14}C -labeled aminonaphthalene or quinoline (Sigma Chemical Co.) that had been purified by high-pressure liquid chromatography (HPLC). The radiochemical purity of the ^{14}C -labeled compounds was >99% and their specific activity was approximately 10 mCi mmol $^{-1}$. Selected physicochemical properties of the sorbate molecules are summarized in Table I.

Porous and Amorphous SiO_2 . Microporous, amorphous, Merck silica gel [$\text{SiO}_2(\text{ap})$, Aldrich] was prepared by first washing in acid (0.1 M HCl) and then repeatedly (~ 10 times) in distilled/deionized water until chloride free. The $\text{SiO}_2(\text{ap})$ was then dried at 100 $^\circ\text{C}$. The microporous silica gel was reported by the supplier to have a surface area of 675 $\text{m}^2 \text{g}^{-1}$, a particle size of 212-500 μm , a pore size of 4.0 nm, and a pore volume of 0.68 $\text{cm}^3 \text{g}^{-1}$.

Nonmicroporous, amorphous SiO_2 [$\text{SiO}_2(\text{ac})$] was prepared by adding dry Aerosil 200 (Degussa, Inc.) to 0.01 M NaCl to yield a suspension with a 1:10 solids to solution ratio. The $\text{SiO}_2(\text{ac})$ had a surface area of 183 $\text{m}^2 \text{g}^{-1}$, a particle size of 0.012 μm , and no internal pore space.

General Experimental Procedures. Sorption experiments were conducted in an incubator-shaker controlled to within 0.5 $^\circ\text{C}$ of the desired temperature, which was usually 25 $^\circ\text{C}$. Preweighed 25-mL Corex centrifuge tubes, sealed with Teflon-lined silicon rubber septa, were used for all equilibrations. Sorption experiments were performed with a single sorbate concentration over a range in pH (sorption edges) and with variable sorbate concentration at a single pH (isotherms). Unless otherwise indicated, the electrolyte was 0.01 M NaCl and the titrants for controlling pH were 0.1 M NaOH and 0.1 M HCl. The sorbent concentration was 50 g of $\text{SiO}_2 \text{L}^{-1}$ (1:20 solids to solution ratio). The masses of dry $\text{SiO}_2(\text{ap})$ or $\text{SiO}_2(\text{ac})$ suspension, aminonaphthalene or quinoline stock, and

Table I. Physical Properties of Quinoline and Aminonaphthalene

compound	structure	K_a	dimens, ^a Å		solub, mg/L	K_{ow}	TSASA, ^b Å ²	TSA, ^b Å ²	TV, ^b Å ³	D , ^c D	σ^{+d}	
			X	Y								
quinoline		$10^{-4.93}$	8.5	7.2	6000	~110	301.75	141.70	121.16	2.20	NH	+0.071
aminonaphthalene		$10^{-3.93}$	8.7	8.0	1700	166	325.70	159.43	136.88	1.88	NH ₃	+0.571

^a Dimensions estimated from internuclear angles and distances calculated according to the INDO/S approximation (54). X is horizontal distance; Y is vertical distance. ^b Total solvent accessible surface area, total van der Waals surface area, and total volume, respectively, as defined by and calculated according to Pearlman (55, 56). ^c Dipole moment (debyes) for B calculated according to the INDO/S approximation (54). ^d Formal charge on BH⁺ cation centers (Mulliken) calculated according to the INDO/S approximation (54).

titrant plus electrolyte were measured to enable strict mass accounting. Replicate tubes were used at each pH value or sorbate concentration. Following overnight equilibration of the SiO₂ suspension with the organic sorbate (approximately 10 000 cpm initial activity), the tubes were centrifuged: 10 min at 5000 rcf for SiO₂(ap) and 1 h at 5000 rcf for SiO₂(ac). Two aliquots for liquid scintillation counting were removed from each tube to tared vials. The mass of the analytical aliquots were recorded, and final pH was measured in the remaining equilibrium solution.

Sorption Kinetics and Compound Stability. One gram of SiO₂(ap) was equilibrated with 18 mL of 0.01 M NaCl overnight in each of a group of Corex tubes. After the pH of the suspensions was adjusted to pH 4 or 6, 1 mL of aminonaphthalene stock and sufficient electrolyte to bring the total volume to 20 mL were added to each tube. The suspensions were then equilibrated for periods of time ranging from 0.5 h to 1 week. The percent removal of both compounds reached steady state rapidly, within 0.5 h (data not shown). These steady-state concentrations remained stable for over 48 h, and direct analysis by HPLC indicated that no conversion of the compounds had occurred.

Sorption Edge Experiments. The sorption of quinoline and aminonaphthalene over a range in pH was investigated by using a jacketed-water cooled/heated reaction flask attached to a titrator fitted with a Ross combination electrode. The experiment was begun by maintaining a SiO₂(ap or ac)/NaCl(aq) suspension at pH 8 overnight at the appropriate temperature (10, 25, or 40 °C). The sorbate stock solution was then added. The suspension was held at pH 8 for 30 min and two 10-mL aliquots of the suspension were transferred to Corex tubes. The pH of the suspension was adjusted to pH 7.5 and maintained for 30 min before another pair of 10-mL aliquots were removed. This procedure was continued by reducing the pH in 0.5-unit increments to pH 2.5. The sealed tubes were then removed to a gas-tight chamber in the incubator-shaker. The chamber was flushed with N₂ and the suspensions were equilibrated overnight. Centrifugation, ¹⁴C analyses, and final pH measurements were conducted as described above.

Sorption Isotherms. Isotherm experiments with SiO₂(ap or ac) were conducted using the titrator with pH = pK_a of the sorbates (BH⁺ = B) and at pH = pK_a + 3 (B ≫ BH⁺). Once the desired pH of a SiO₂ suspension had been stabilized, aliquots (10 mL) of the suspension were transferred to preweighed centrifuge tubes. After weighing to determine the mass of suspension in each tube, 0.5-mL aliquots of the appropriate organic solute stock solution were added to replicates tubes to yield a sorbate concentration range of 1.0×10^{-8} – 1.0×10^{-4} M. The tubes were then equilibrated overnight, centrifuged, and sampled as described above for the sorption edge experiments. Iso-

Table II. Reactions and Associated Equilibrium Constants Used in Modeling Sorption of the Organic Compounds to Silica

reactions	constants
H ⁺ + OH ⁻ = H ₂ O	14.00
B + H ⁺ = BH ⁺	pK _a of compd
SiOH + H ⁺ = SiOH ₂ ⁺	-0.95 ^a
SiOH = SiO ⁻ + H ⁺	-6.8 ^a
SiOH + Na ⁺ = SiO ⁻ -Na ⁺ + H ⁺	-7.0 ^a
SiOH + Ca ²⁺ = SiO ⁻ -Ca ²⁺ + H ⁺	-7.32 ^b

^a From Riese (32) for α-SiO₂. ^b This study.

therms were measured on SiO₂(ap) at 25 °C in 0.01 M NaCl, 1.0 M NaCl, and 0.005 M CaCl₂, and on SiO₂(ac) at 10, 25, and 40 °C in 0.01 M NaCl.

Sorption Modeling. a. SiO₂(ac). Data from the sorption edge experiments were used with the program FITEQL (27, 28) to fit sorption constants for hypothesized sorption reactions. The triple-layer model (TLM) (28, 29) was used. We note that alternative approaches requiring less parameterization exist to the TLM to describe the ionization behavior of SiO₂ (30). The TLM was used because (1) the organic sorbate surface complexes were thought to be outer sphere and (2) the model contains different adsorption planes that could be used to simulate H-bonded and electrostatic surface complexes. The solution speciation and acidity/electrolyte constants that were used in the TLM modeling are given in Table II. The site density, outer layer capacitance, and inner layer capacitance used for both SiO₂(ac) and SiO₂(ap) were 5.0 sites nm⁻² (31), 0.20 F m⁻², and 1.25 F m⁻², respectively. The TLM surface acidity and electrolyte constants for SiO₂ were taken from Riese (32) for α-SiO₂ in NaNO₃ electrolyte. These values were similar to TLM constants reported by Davis (33) for SiO₂ derived from the data of Abendroth (13). Previous studies (34) showed that the results of the FITEQL modeling are not affected significantly by variations in the inner and outer layer capacitances; therefore, these values were fixed for all the analyses presented in this paper. Several different combinations of surface complexes were evaluated to determine the best set of reactions that fit the data from the sorption edge experiments. These reactions and their equilibrium constants were used to model the sorption isotherms for SiO₂(ac).

b. SiO₂(ap). The sorption reactions and constants fitted for quinoline and aminonaphthalene on SiO₂(ac) were used to model the sorption edge and isotherm data on SiO₂(ap). Because the surface area of the SiO₂(ap) accessible to the two compounds was not known, the total number of sites was used in FITEQL as a fitting parameter. The active surface area was calculated from the total number of sites fitted by the model using the site density

Figure 1. Calculated fractional distribution of surface sites on SiO_2 using the TLM and constants in Tables I and II. Electrolyte composition was 0.01 M NaCl.

and solid to solution concentration. The sorption isotherm data were modeled as described for the $\text{SiO}_2(\text{ac})$, using the average estimated surface area for the $\text{SiO}_2(\text{ap})$ and the sorption reactions and constants for quinoline and aminonaphthalene on $\text{SiO}_2(\text{ac})$.

c. Calcium Sorption on $\text{SiO}_2(\text{ac})$. Sorption constants for calcium on $\text{SiO}_2(\text{ac})$ were determined to model quinoline and aminonaphthalene sorption on $\text{SiO}_2(\text{ap})$ in 0.005 M CaCl_2 electrolyte. The sorption constants were fitted from Ca^{2+} fractional sorption data over the pH range 4.5–8.5. The initial Ca^{2+} concentration was 1.0×10^{-4} M, the electrolyte was 0.01 M NaCl, and the $\text{SiO}_2(\text{ac})$ was at 50 g L^{-1} . The pH of 50% sorption was 7.2 (not shown). The fitted sorption reaction was

The Ca^{2+} constant was used along with the estimated surface area of $\text{SiO}_2(\text{ap})$ and the other surface complexation constants on $\text{SiO}_2(\text{ac})$ to model the quinoline and aminonaphthalene isotherms on $\text{SiO}_2(\text{ap})$ in 0.005 M CaCl_2 .

Calculation of Surface Charge on $\text{SiO}_2(\text{ac})$. The calculated fraction of surface sites on $\text{SiO}_2(\text{ac})$ that are negatively charged over the conditions used in the sorption experiments is shown in Figure 1. The extent of surface ionization and complex formation with Na was calculated with TLM by use of the silica properties mentioned previously and the constants in Table II. Neutral sites dominate the surface over the pH range and the fraction of ionized sites reaches a maximum of approximately 3% ($\log F \approx -1.5$) at pH 8.5.

Results and Discussion

Sorption at 25 °C. a. Sorption Edges. Both quinoline and aminonaphthalene were sorbed on silica (Figures 2 and 3). Sorption varied with pH in an identical way for both compounds, with a maximum in sorption noted at a pH near the compound pK_a . Increased ionization of SiOH to SiO^- groups above the pK_{SiO^-} had no apparent effect on the sorption of either compound. Quinoline was sorbed more strongly than aminonaphthalene over the entire pH range by a factor of approximately 2.

The sorption of quinoline and aminonaphthalene on SiO_2 differed from that of inorganic cations. Inorganic cations display an abrupt pH edge where sorption increases rapidly from near 0 to 100% (see, for example, ref 13). This rapid increase in cation sorption is due to the development of negative charge on SiO_2 (Figure 1) and the

Figure 2. Fractional sorption of quinoline on $\text{SiO}_2(\text{ac})$ and $\text{SiO}_2(\text{ap})$ as a function of pH. Electrolyte composition was 0.01 M NaCl.

Figure 3. Fractional sorption of aminonaphthalene on $\text{SiO}_2(\text{ac})$ and $\text{SiO}_2(\text{ap})$ as a function of pH. Electrolyte composition was 0.01 M NaCl.

hydrolysis of the sorbing ion. The pH of maximum sorption for quinoline and aminonaphthalene occurred when the silica surface carried little negative charge, which suggested binding of the organic molecule or organic cation to neutral sites.

The two organic compounds displayed concentration-dependent sorption on both types of silica. Fractional sorption at a given pH decreased with an increase in the initial concentration of the compound from 10^{-6} to 10^{-5} M (Figures 2 and 3). Both compounds exhibited greater affinity on a mass basis for $\text{SiO}_2(\text{ap})$ (Figures 2 and 3), which has a 3-fold greater surface area. The increase in sorption of $\text{SiO}_2(\text{ap})$ over $\text{SiO}_2(\text{ac})$, however, was less than proportional to its increase in surface area, implying that the internal pore space was only partly available. The increase in quinoline sorption on $\text{SiO}_2(\text{ap})$ over $\text{SiO}_2(\text{ac})$ (≈ 20 –30%) was far greater than that observed for aminonaphthalene ($\approx 5\%$).

b. Sorption Isotherms. Both compounds produced curvilinear isotherms when plotted on an arithmetic scale that were mostly linearized on a log–log basis (Figure 4). The log–log isotherms showed slight curvature above $\log C_e \approx -5.5$, possibly signifying the onset of surface saturation. As in the pH edge experiments, more quinoline was sorbed than aminonaphthalene. The log–log isotherms for both compounds exhibited similar slope, and the quinoline isotherms were displaced 0.75 log unit to a higher sorption density (Figure 4).

In agreement with Figures 2 and 3, variation in pH had a small effect on the isotherms (Figure 4). Sorption was lower at the higher pH, by a factor of 0.4 log unit for quinoline and 0.2 log unit for aminonaphthalene. For each

Table III. Isotherm Parameters for Quinoline Sorption on SiO₂(ap) and SiO₂(ac)

solid	pH	electrolyte	temp, °C	Langmuir-Freundlich parameters ^a				
				log <i>K</i> , L mol ⁻¹	<i>M</i> , mol g ⁻¹	<i>N</i>	<i>R</i> ²	RMS
SiO ₂ (ap)	5.0	0.01 M NaCl	25	4.58	3.27 × 10 ⁻⁶	0.934	0.999	0.040
SiO ₂ (ap)	5.0	1.00 M NaCl	25	4.42	3.60 × 10 ⁻⁶	0.946	0.999	0.029
SiO ₂ (ap)	5.0	0.01 M CaCl ₂	25	4.73	3.03 × 10 ⁻⁶	0.932	0.998	0.050
SiO ₂ (ap)	8.0	0.01 M NaCl	25	4.45	2.56 × 10 ⁻⁶	0.944	0.999	0.041
SiO ₂ (ap)	8.0	0.01 M CaCl ₂	25	4.52	2.17 × 10 ⁻⁶	0.942	0.998	0.048
SiO ₂ (ac)	5.0	0.01 M NaCl	25	4.76	1.70 × 10 ⁻⁶	0.922	0.999	0.045
SiO ₂ (ac)	5.0	0.01 M NaCl	25	4.67	1.61 × 10 ⁻⁶	0.973	0.999	0.029
SiO ₂ (ac)	5.0	0.01 M NaCl	25	4.58	2.48 × 10 ⁻⁶	0.916	0.999	0.039
SiO ₂ (ac)	5.0	0.01 M NaCl	10	4.76	1.77 × 10 ⁻⁶	1.000	0.999	0.036
SiO ₂ (ac)	5.0	0.01 M NaCl	40	4.41	1.48 × 10 ⁻⁶	0.942	0.999	0.043

^aThe Langmuir-Freundlich equation is $S = (KC^N)M/[1 + KC^N]$ where *S* is the sorbed concentration, *C* is the aqueous equilibrium sorbate concentration, *K* is the binding constant, *M* is the adsorption maximum, and *N* is an empirical parameter reflecting surface heterogeneity.

Table IV. Isotherm Parameters for Aminoanthracene Sorption on SiO₂(ap) and SiO₂(ac)

solid	pH	electrolyte	temp, °C	Langmuir-Freundlich parameters ^a				
				log <i>K</i> , L mol ⁻¹	<i>M</i> , mol g ⁻¹	<i>N</i>	<i>R</i> ²	RMS
SiO ₂ (ap)	4.0	0.01 M NaCl	25	3.70	1.06 × 10 ⁻⁶	0.962	0.999	0.026
SiO ₂ (ap)	4.0	1.00 M NaCl	25	4.01	7.64 × 10 ⁻⁷	0.968	0.999	0.030
SiO ₂ (ap)	4.0	0.01 M CaCl ₂	25	3.93	8.94 × 10 ⁻⁷	0.986	0.999	0.031
SiO ₂ (ap)	7.0	0.01 M NaCl	25	3.67	8.46 × 10 ⁻⁷	0.986	0.999	0.024
SiO ₂ (ap)	7.0	0.01 M CaCl ₂	25	3.99	4.28 × 10 ⁻⁷	1.02	0.999	0.037
SiO ₂ (ac)	4.0	0.01 M NaCl	25	4.51	4.47 × 10 ⁻⁷	0.852	0.982	0.156
SiO ₂ (ac)	4.0	0.01 M NaCl	25	3.92	1.15 × 10 ⁻⁶	0.887	0.999	0.031
SiO ₂ (ac)	4.0	0.01 M NaCl	10	3.98	1.11 × 10 ⁻⁶	0.929	0.999	0.012
SiO ₂ (ac)	4.0	0.01 M NaCl	40	4.21	4.26 × 10 ⁻⁷	0.882	0.999	0.029

^aParameters as defined in Table III.

compound the log-log isotherms at the two pH values were parallel, which suggested that the degree of pH dependency observed for the sorption of 10⁻⁶ and 10⁻⁵ M concentrations in Figures 2 and 3 occurred over the entire sorbate concentration range spanned by the isotherms (10⁻⁸–10⁻⁴ M).

The electrolyte composition and ionic strength had minor effects on compound sorption. At comparable ionic strength (*I* ≈ 0.01), sorption was slightly higher in Ca²⁺ electrolyte (0.005 M CaCl₂) than in Na⁺ electrolyte (0.01 M NaCl) (Figure 4). At equal ionization fractions, (pH 5 and 4 for quinoline and aminoanthracene, respectively), an increase in ionic strength from *I* = 0.01 to *I* = 1.0 caused a slight increase in quinoline sorption and a small decrease in aminoanthracene sorption. The lack of ionic strength and cation effects suggested that the surface complexes either were strong and inner sphere (35) or were dominated by interaction with neutral sites where competition with the electrolyte cations was minimal.

The log-log isotherms could be described with Freundlich, multisite Langmuir, and Langmuir-Freundlich (L-F) isotherm equations (36). The Langmuir-Freundlich equation exhibited the lowest root mean square (RMS) deviation (RMS, shown only for the L-F equation in Tables III and IV). Unlike the Freundlich equation, which yields a linear log-log transform, the L-F equation with its additional adjustable parameter (an adsorption maximum *M*) was able to simulate the curvature in the log-log isotherms of Figure 4 at high surface coverage. Analyses of the individual replicate isotherms for both compounds on SiO₂(ac) at 25 °C (Tables III and IV) show the extent of variability in the isotherm parameters.

The sorption maxima (*M*; Table III and IV) for quinoline on both SiO₂ sorbents [(2.4–5.7) × 10⁻⁶ mol g⁻¹, extrapolated from the Langmuir-Freundlich equation] exceeded that of aminoanthracene [(0.7–1.6) × 10⁻⁶ mol g⁻¹]

Figure 4. Sorption isotherms of quinoline and aminoanthracene on SiO₂(ap) at different pH levels, ionic strength, and electrolyte composition.

by factors of 2–4 (Tables III and IV). The sorption maxima for both compounds on SiO₂(ap) were not proportionally larger than their maxima on SiO₂(ac). The sorption maxima for quinoline on SiO₂(ap) in 0.01 M NaCl (3.96 × 10⁻⁶ mol g⁻¹ at pH 5 and 2.75 × 10⁻⁶ mol g⁻¹ at pH 8) were well below (1) the total concentration of SiOH sites and (2) the computed concentrations of SiO⁻ sites at pH 5 (2.45 × 10⁻⁵ mol g⁻¹), and the [SiO⁻]_T and SiO⁻ site concentrations (2.56 × 10⁻⁴ and 1.17 × 10⁻⁴ mol g⁻¹, respectively) at pH 8. On SiO₂(ac), where the total surface area was readily accessible to the compounds, the extrapolated maximum for quinoline at pH 5 in 0.01 M NaCl (2.48 × 10⁻⁶ mol g⁻¹) was below the total concentration of SiOH sites but was close to the computed concentration of SiO⁻ sites (6.63 × 10⁻⁶ mol g⁻¹).

Temperature Effects. Temperature affected the sorption of both quinoline and aminoanthracene on

Figure 5. Effect of temperature on the fractional sorption of quinoline on $\text{SiO}_2(\text{ac})$ over a range in pH. Electrolyte composition was 0.01 M.

Figure 6. Effect of temperature on quinoline and aminonaphthalene sorption on $\text{SiO}_2(\text{ac})$. pH was near their pK_a values. Solid lines show Langmuir-Freundlich isotherm fits to the data.

$\text{SiO}_2(\text{ac})$, indicating enthalpy contributions to the free energy of sorption. A reduction in temperature to 10 °C increased sorption, while an increase in temperature to 40 °C decreased sorption (shown in Figure 5 for quinoline only). The effects of temperature were uniform over the pH range, indicating that enthalpy contributions were independent of the aqueous speciation of the compounds. Enthalpy was important even above the pK_a when the neutral compound was the predominant solution species. A slight enhancement in the sorption maxima was observed at 10 °C. In contrast to these findings, entropy dominated the free energy of exchange of alkyl ammonium ions on sodium montmorillonite (37) and the free energy of sorption of hydrophobic organic compounds on mineral surfaces (38).

Isotherms for both compounds on $\text{SiO}_2(\text{ac})$ varied with temperature (Figure 6). As observed in Figure 5, sorption was highest at 10 °C. Temperature effects were greater for quinoline, and the isotherms for each compound were parallel at the different temperatures (Figure 6, Tables III and IV). The extrapolated L-F isotherm parameters show a reduction in K (L-F binding constant) with increasing temperature, and a relatively constant sorption maximum.

The isosteric heat of sorption (ΔH_T) was calculated as a function of sorption density (Γ) by use of the Clausius-Clapeyron equation (38):

$$\Delta H_T = R \ln (C_2/C_1) / (1/T_2 - 1/T_1) \quad (2)$$

where R is the gas constant, C_2 is the equilibrium concentration of the solute at temperature T_2 at the specified Γ , and C_1 is the equilibrium solute concentration at T_1 at

Table V. Isosteric Heat of Sorption of Quinoline and Aminonaphthalene on $\text{SiO}_2(\text{ac})$

sorpntn dens, log mol g ⁻¹	ΔH , kJ mol ⁻¹	
	10–25 °C	25–40 °C
Quinoline		
–6.00	–35.3	–60.2
–7.00	–25.0	–46.0
–8.00	–21.6	–41.8
–9.00	–18.5	–37.8
–10.0	–15.5	–33.8
–11.0	–12.5	–29.9
Aminonaphthalene		
–6.40	–20.3	–39.5
–7.00	–17.1	–39.5
–8.00	–11.7	–29.2
–9.00	–6.44	–27.7
–10.0	–1.15	–26.9
–11.0	0.99	–26.2

the same Γ . The isosteric heat of sorption is a macroscopic measurement incorporating the effects of solute-surface, solute-solvent, and solvent-surface interactions and changes that accompany sorption (39).

The isosteric heat of sorption was exothermic and varied with both surface coverage and temperature interval (Table V). The isosteric heat of sorption for nonionic organic compounds on dehydrated mineral surfaces (38) and phenoxyacetic acid anions on hydrated mineral surfaces (40) decreased with surface coverage. Surface site heterogeneity was proposed to cause these trends. In direct contrast, ΔH_T for both quinoline and aminonaphthalene increased with sorption density on $\text{SiO}_2(\text{ac})$. Lateral interaction between sorbate molecules on the silica surface may cause this trend in enthalpy (39). McCloskey and Bayer (41) also observed an increase in ΔH_T with surface loading for fluridone sorption on smectitic soil. Quinoline exhibited a higher ΔH_T (–12.5 to –60.2 kJ mol⁻¹) than did aminonaphthalene (0.99 to –39.5 kJ mol⁻¹). These enthalpies span the ranges reported for van der Waals and hydrogen bonding of –20 to –60 kJ mol⁻¹ (39, 42). Our values were lower than those observed for butylamine sorption on silica from *n*-hexane (–190 kJ mol⁻¹) where specific complexation with ionized sites was the proposed mechanism (24).

Sorption Modeling. a. Sorption Edges. The sorption data in Figures 2 and 3 could only be reproduced with FITEQL/TLM (Figure 7) using the three following surface reactions:

These surface species were required for both quinoline and aminonaphthalene; they are hypothesized species that lead to agreement between model calculations and the experimental data. All combinations of only two surface species lead to poor agreement with the experimental data. Sorption constants for the quinoline surface species varied between replicate experiments by as much as 30% (Table VI). The constants also showed some variation at different sorbate concentrations (Table VI), with the greatest difference observed for the SiO^-BH^+ complex.

The $\text{SiOH}\text{--}\text{B}$ and SiO^-BH^+ surface species represent outer-sphere hydrogen-bonded and ion-exchange complexes, respectively. While these two complexes exhibit the same reaction stoichiometry (eq. 3 and 4), they are viewed as distinct species within the TLM with H^+ residing

Figure 7. TLM modeling of aminonaphthalene and quinoline sorption on $\text{SiO}_2(\text{ac})$ in 0.01 M NaCl. The solid line is the summation of all the species.

Table VI. Sorption Constants for Quinoline and Aminonaphthalene on $\text{SiO}_2(\text{ac})$

concn, M	log K sorption constants for surface species		
	SiO^-BH^+	SiOH-B	SiOH-BH^+
quinoline			
10^{-6}	0.890 ± 0.12	0.650 ± 0.08	5.68 ± 0.14
10^{-5}	0.576 ± 0.19	0.669 ± 0.14	5.58 ± 0.17
aminonaphthalene			
10^{-6}	0.306	0.034	4.25
10^{-5}	0.229	-0.476	4.06

in the 0 plane for the SiOH-B complex and within the β plane for SiO^-BH^+ . The existence of these separate species is supported by infrared (43) and sorption studies (44, 45). The SiOH-BH^+ complex may be viewed as an analogue of SiOH_2^+ that is stabilized by electron sharing with Si-bound oxygen, which exhibits a negative dipole moment. A similar complex was postulated to form for quaternary ammonium cations (46) and water (47) on SiO_2 .

After the effects of surface and solution ionization reactions were removed, SiO^-BH^+ was the most stable calculated surface complex, followed by SiOH-BH^+ (Table VII). The strength of the SiO^-BH^+ complex exceeded that of both SiO^-Na^+ and $\text{SiO}^-\text{Ca}^{2+}$, indicating stabilization of the organic surface complex by hydrophobic forces or surface H bonding to the π electron cloud. The model calculations in Figure 7, however, suggested that sorption of the ionized and molecular species to neutral SiOH groups contributed more to the total adsorption than the ion-exchange complex (SiO^-BH^+). The SiOH-BH^+ and SiOH-B complexes dominated total sorption because of the large excess of SiOH sites compared to SiO^- sites (Figure 1) and because $[\text{BH}^+]_{\text{aq}}$ was small when $[\text{SiO}^-]_{\text{T}}$ was large.

The constants in Table VI for $\text{SiO}_2(\text{ac})$ were used along with the sorption edge data for $\text{SiO}_2(\text{ap})$ in Figures 2 and 3 in FITEQL to estimate a surface area for $\text{SiO}_2(\text{ap})$ that was accessible to the two compounds. Less than 50% of the

Table VII. Intrinsic Strength of Quinoline and Aminonaphthalene Surface Complexes

reaction	log K
Quinoline (10^{-6} M)	
$\text{SiO}^- + \text{QH}^+ = \text{SiO}^-\text{QH}^+$	2.76
$\text{SiOH} + \text{QH}^+ = \text{SiOH-QH}^+$	0.75
$\text{SiOH} + \text{Q} = \text{SiOH-Q}$	0.65
Aminonaphthalene (10^{-6} M)	
$\text{SiO}^- + \text{AH}^+ = \text{SiO}^-\text{AH}^+$	2.18
$\text{SiOH} + \text{AH}^+ = \text{SiOH-AH}^+$	0.32
$\text{SiOH} + \text{A} = \text{SiOH-A}$	0.034
Na^+	
$\text{SiO}^- + \text{Na}^+ = \text{SiO}^-\text{Na}^+$	-0.2
Ca^{2+} (10^{-4} M)	
$\text{SiO}^- - \text{Ca}^{2+} = \text{SiO}^-\text{Ca}^{2+}$	-0.5

total surface area on $\text{SiO}_2(\text{ap})$ ($258.2 \text{ m}^2 \text{ g}^{-1}$) was calculated to be available to aminonaphthalene. In contrast, the entire surface area of $\text{SiO}_2(\text{ap})$ was calculated to be accessible to quinoline. Size considerations alone cannot fully account for the apparent inaccessibility of the internal pore space of $\text{SiO}_2(\text{ap})$ to aminonaphthalene, because the average 4.0-nm pore size is at least 4 times larger than the long dimension of the compounds (Table I). A range in pore diameter about the 4.0-nm average is expected (48), and aminonaphthalene sorption in the smaller diameter pore regions may be sterically inhibited because of its larger molecular volume (Table I) and the bulky amine group. Specifically, the amine group may be physically unable to interact with hydrated SiOH sites in the narrow pore areas. For alkylamines, Van Cauwelaert et al. (20) suggested that steric factors influence sorption on SiO_2 , while Rochester and Yong (43) saw no evidence of such effects. Steric interactions appeared to have little influence on the sorption of substituted pyridines on SiO_2 from CCl_4 (23).

b. Sorption Isotherms. The constants in Tables I and VI (for 10^{-6} M sorbate concentrations) and the active surface area estimated for $\text{SiO}_2(\text{ap})$ were used to simulate the sorption isotherms in Figure 4 and the 25°C isotherms in Figure 6. The calculated isotherms exhibited similar slopes and good agreement with the experimental data (shown for selected isotherms in Figure 8). Because the isotherms were nonlinear, the use of a single set of sorption constants yields a slight underprediction of sorption at low C_e and an overprediction at high C_e (Figure 8). The inflection or pivot point to this over- or underprediction was the approximate sorbate concentration at which the constants were fit. The difference between the measured and predicted fractional sorption at initial sorbate concentrations of 5.0×10^{-7} and 1×10^{-5} M ranged from +30.0% to -3.4% (Table VIII). The agreement was usually within 10% for $\text{SiO}_2(\text{ap})$, and higher for $\text{SiO}_2(\text{ac})$. The close agreement for $\text{SiO}_2(\text{ap})$ suggested that the effective surface area of the sorbent for each compound was independent of surface coverage. Thus, the increased diffusional gradient created at higher aminonaphthalene concentrations did not increase access to the internal pore space of $\text{SiO}_2(\text{ap})$.

The model calculations correctly predicted the direction and magnitude of the shift in the isotherms, relative to those in 0.01 M NaCl at pH 5 for quinoline and pH 4 for aminonaphthalene, that occurred in the presence of increased ionic strength (1.0 M NaCl, predictions not shown) and Ca^{2+} (0.005 M CaCl_2 ; Figure 8b). The small effect of ionic strength and Ca^{2+} on compound sorption (Figure 4, Figure 8b) was consistent with the calculated dominance

Figure 8. TLM predictions of selected isotherms for $\text{SiO}_2(\text{ap})$ in Figure 4. Solid and dashed lines represent model calculations.

Table VIII. Percent Difference between Experimental and Predicted Sorption Isotherms^a

conditions	% diff ^b	% diff ^c
Quinoline on $\text{SiO}_2(\text{ac})$		
0.01 M NaCl, pH 5	30.0	15.3
Quinoline on $\text{SiO}_2(\text{ap})$		
0.01 M NaCl, pH 5	0.97	-3.4
0.01 M NaCl, pH 8	9.0	3.4
1.0 M NaCl, pH 5	-0.09	-8.4
0.005 M CaCl_2 , pH 5	4.7	1.0
0.005 M CaCl_2 , pH 8	11.8	6.2
Aminonaphthalene on $\text{SiO}_2(\text{ac})$		
0.01 M NaCl, pH 4	12.1	7.2
0.01 M NaCl, pH 7	19.4	2.66
Aminonaphthalene on $\text{SiO}_2(\text{ap})$		
0.01 M NaCl, pH 4	0.1	-3.71
0.01 M NaCl, pH 7	4.0	-2.60
1.0 M NaCl, pH 4	9.3	2.1
0.005 M CaCl_2 , pH 4	3.8	2.9
0.005 M CaCl_2 , pH 7	3.8	4.6

^a Constants for 10^{-6} M initial sorbate concentrations in Table VI were used. ^b (Measured % adsorbed) - (predicted % adsorbed) at an initial concentration of 5.0×10^{-7} M. ^c (Measured % adsorbed) - (predicted % adsorbed) at an initial concentration of 1.0×10^{-5} M.

of surface complexes on neutral SiOH sites. Increased Na^+ concentrations and Ca^{2+} will decrease free SiO^- , which would reduce aminonaphthalene and quinoline sorption if they were binding primarily to SiO^- sites. The predicted three species surface speciation model (Figure 7) was, therefore, consistent with the pH, concentration, and ionic strength influences on quinoline and aminonaphthalene sorption (Figure 8).

Reasons for Selectivity Differences. The shift ($\Delta\nu_{\text{OH}}$) in the infrared O-H stretching band of the free SiOH hydroxyls (3750 cm^{-1}) that accompanies adsorption from the gas phase or organic solvents (e.g., CCl_4) has been repeatedly used as a measure of sorbate binding strength on SiO_2 . The shift has been correlated with the enthalpy of sorption, ΔH_{ads} (49, 50) and the extent of H bonding and charge transfer. Combined with spectral data on the sorbate, $\Delta\nu_{\text{OH}}$ has been used to determine the extent of covalency, charge transfer, and ionicity of the surface complexes (18, 21-23, 25, 43, 51). For organic N bases, $\Delta\nu_{\text{OH}}$ and, therefore, ΔH_{ads} have been shown to increase with increasing basicity of the sorbate (20, 23, 43). Griffiths et al. (23) demonstrated that $\Delta\nu_{\text{OH}}$ increases with electron donor substituent groups that promote stronger interaction with the hydroxyl groups (20, 43).

Consistent with the above observations, aniline ($\text{pK}_a = 4.93$) is observed to have a lower $\Delta\nu_{\text{OH}}$ (ΔH_{ads}) in CCl_4 (51) than pyridine ($\text{pK}_a = 5.52$) (23). Resonance structures withdraw electron density from N to the ring, making aniline a weaker base than pyridine (52). While $\Delta\nu_{\text{OH}}$ data are not available for quinoline and aminonaphthalene, their isosteric heats of sorption and sorption behavior in water agree with these observations. Aminonaphthalene is a weaker base, has a lower pK_a (Table I), and, therefore, forms weaker bonds with acidic SiOH groups than quinoline.

Physical properties of the two compounds related to the electronic configuration of the ring are also consistent with their sorption. Water interacts strongly with the SiO_2 surface (47, 48), and H_2O as a lone-pair adsorbate competes with the aromatic amine and heteroatom N compounds for H-bonding SiOH sites on SiO_2 . Quinoline is a better competitor with H_2O than aminonaphthalene because it forms stronger H bonds. The stronger H-bonding character of quinoline is manifested in its higher dipole moment and aqueous solubility (Table I). As a cation, QH^+ may be more strongly bound than AH^+ to SiO^- sites because positive charge is delocalized throughout the aromatic ring structure of QH^+ . Delocalization of charge to H atoms around the periphery of the ring system leads to a lower formal charge on the NH atom centers of the quinolinium ion as compared to the NH_3 atom centers of the aminonaphthalene cation (Table I). Delocalization allows for a larger interaction electrostatic area of overlap integral with the surface (53).

Significance to Field Attenuation. Retardation factors were calculated to determine whether SiO_2 surfaces can attenuate quinoline and aminonaphthalene migration in the subsurface. With the data in Figures 2 and 3 for 10^{-6} M initial concentrations at maximum sorption on $\text{SiO}_2(\text{ac})$, distribution coefficients (K_d 's in L m^{-2}) of 1.34×10^{-4} and 2.73×10^{-5} were calculated for quinoline and aminonaphthalene, respectively. If, for example, a subsurface material is assumed to have a SiO_2 surface area of $10 \text{ m}^2 \text{ g}^{-1}$, then K_d 's (mL g^{-1}) of approximately 1.34 and 0.273 for quinoline and aminonaphthalene could be anticipated. The further assumption of a bulk density of 1.5 g cm^{-3} and porosity of 0.5 yields retardation factors (R_f , ref 51) of 4.02 and 1.82 for quinoline and aminonaphthalene, respectively. The subsurface migration rates of these two solutes would, therefore, be approximately 25% (quinoline) and 55% (aminonaphthalene) of the linear velocity of the groundwater.

Conclusions

Quinoline was more strongly sorbed than aminonaphthalene under all experimental conditions. The heterocycle nitrogen promoted a stronger interaction with

the silica surface than did nitrogen within the aromatic amine group. The two compounds adsorbed to silica via a similar mechanism, as shown by their parallel isotherms and the similar effects that both temperature and pH had on sorption. Surface complexes involving the neutral compound (B) and/or neutral sites (SiOH) were found to be important as evidenced by the insensitivity of sorption to ionic strength and electrolyte cation. Only aminonaphthalene was excluded from the internal space of porous silica, which indicated that the two compounds oriented differently at the surface and that steric factors were potentially important.

A three-complex surface model provided good descriptions of compound sorption on porous and nonporous silica at different pHs and sorbate concentrations. The model correctly predicted the small effects of ionic strength and electrolyte cation on N aromatic compound sorption. The surface complexes represented electrostatically bound and H-bonded sorbate molecules on the surface and were consistent with the calculated isosteric sorption enthalpies. The greater stability of the quinoline surface complexes, as compared with aminonaphthalene, was consistent with the greater basicity of quinoline and its ability to delocalize charge through its ring structure.

Sorption to silica, such as quartz sand grains in groundwater, can retard quinoline and, to a lesser extent, aminonaphthalene migration. Silica surface areas in excess of $2 \text{ m}^2 \text{ g}^{-1}$ in the saturated zone are required before sorption effects are observed or become significant.

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Registry No. SiO₂, 7631-86-9; quinoline, 91-22-5; aminonaphthalene, 25168-10-9.

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Dissolution Kinetics of Minerals in the Presence of Sorbing and Complexing Ligands

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■ This study investigated and modeled the important reactions controlling oxide dissolution in a system containing strongly complexing and strongly sorbing ligands. Polyphosphate and ferrihydrite were the model ligand and oxide studied, respectively. The dissolution of ferrihydrite in these systems is via a process called ligand-promoted dissolution, which is controlled by a surface reaction and is initiated by sorption of tripolyphosphates. Fe and tripolyphosphate leave the surface as one entity. If empty surface sites are available, Fe-tripolyphosphate complexes that are released to solution can quickly readsorb to the surface, forming a species different from the precursor to the dissolution reaction. The strong adsorption of complexes counteracts the iron dissolution reaction and leads to nonlinear net dissolution kinetics. An adsorption/dissolution kinetic model is developed that successfully simulates the experimental observations here as well as previous work reported in the literature for systems where adsorption of free ligands and complexes is much weaker.

Introduction

The surfaces of iron and aluminum oxides (and hydroxides) are capable of coordinating with (i.e., adsorbing) dissolved anions via ligand-exchange reactions (1-3). Several studies have shown that the solubility and the rate of dissolution of sparingly soluble oxides can be significantly increased by certain sorbing anions and organic substances (4-7). The increased rate of dissolution has been attributed to surface processes initiated by the sorbed species (8-10). Although the dissolution rate of these oxides may at times be limited by solid- or liquid-phase transport processes (11-16), Stumm and co-workers (16, 17) concluded that in most cases the rate of dissolution of slightly soluble oxides is controlled by the rate of surface chemical reactions.

Some dissolution processes include reduction of the structural metal ion; in such cases dissolution involves the adsorption of reductants, precursor complex formation, electron transfer, release of oxidized adsorbate (anionic ligand or organic substance), and the release of reduced structural metal ion (10, 18). The reaction steps for non-reductive dissolution can be represented as follows (6):

- (1) adsorption of ligand

- (2) formation of precursor complex

- (3) detachment of metal ion and generation of new site

Once ligands adsorb to the surface, they may begin to polarize, weaken, and finally break the metal-oxygen bonds, causing the release of metal into solution. The overall process is referred to as "ligand-promoted dissolution" (6). In the absence of anionic ligands and under acidic conditions, surface hydroxyl groups are protonated. These protonated surface OH groups can also initiate the dissolution process in a way analogous to that caused by sorbed ligands. This is called "proton-promoted dissolution" (6).

Stumm and co-workers (6, 7) combined the surface complexation model of adsorption with the concepts of ligand-promoted dissolution to develop an overall model of the dissolution process. Specifically, the ligand-promoted dissolution rate of an oxide is presumed to be directly related to the concentration of "precursor complexes" on the surface: $R_L = k[\text{Me-O-}-\text{MeL}]$, where R_L , k , and $[\text{Me-O-}-\text{MeL}]$ denote the ligand-promoted dissolution rate, a first-order rate constant, and the concentration of precursor complex, respectively. They suggested that in general the concentration of precursor complexes (which are not amenable to direct experimental analysis) will be proportional to the concentration of adsorbed ligands (which is easily measured). In such cases, $R_L = K_L C_L^s$, where K_L and C_L^s denote the ligand-promoted dissolution rate constant and the sorbed ligand concentration. If sorption of the ligand is fairly weak, C_L^s will be small and a large number of surface sites will be vacant, even when the soluble ligand concentration is large. Under these conditions, C_L^s attains a pseudo steady state, and a constant dissolution rate can be established and maintained in a system for a fairly long period of time.

Despite the undeniable importance of linear ligand-promoted dissolution kinetics ($R_L = K_L C_L^s$) in many systems, a number of studies have shown that under certain conditions the rate of dissolution decreases as dissolution proceeds and that the relationship between the dissolution rate and the adsorbed ligand concentration can be nonlinear (4, 5, 9, 19). These observations have been attributed to a decrease in oxide surface area, heterogeneity of the surface, and the adsorption of released metal ions (18).

The majority of the studies described above were conducted with weakly sorbing ligands. The controlling reactions might be quite different in systems with strongly sorbing ligands. The current study investigated the applicability of available models in systems of strongly