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Adsorption of Quinoline to Kaolinite and Montmorillonite

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ABSTRACT

Adsorption of quinoline ($pK_a = 4.92$) and background electrolyte ($CaCl_2$) onto specimen kaolinite and montmorillonite were measured as a function of pH (3–7.5) and ionic strength (1–10 mM), and as a function of quinoline concentration (0.2–1.55 mM) at fixed pH values of maximum adsorption. Maximum sorption of quinoline occurred at pH 3.5–4.0 for kaolinite, and pH 3.0–5.0 for montmorillonite. At their respective pH values of maximum adsorption, the sorption capacity for quinoline was 100 times greater with montmorillonite than kaolinite on a mass basis. Selectivity coefficients, which were calculated from pH edge data, indicated selectivity for cationic quinoline (QH^+) over Ca^{2+} was greater with montmorillonite ($K_{exc} = 27$ at pH 4) compared to kaolinite ($K_{exc} = 1.6$ at pH 4), and K_{exc} was not affected by ionic strength for either clay. The results indicate the important role of charged siloxane sites in the adsorption of this N-heterocyclic contaminant.

Key words: quinoline; adsorption; kaolinite; montmorillonite; selectivity coefficients; heterocyclic aromatics

INTRODUCTION

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) are common residual contaminants at sites where coal was used to manufacture consumer gas in the early 20th century, and where creosote has been used to preserve wood. Because the composition of creosote in contaminated soils is approximately 85% PAHs and creosote contaminants are potentially toxic to humans (Thomsen *et al.*, 1999), knowledge of PAH–soil interactions are important. The sorption of neutral PAHs to soil has been modeled as an equilibrium partitioning process, where sorption capacity is proportional to the mass fraction of soil organic carbon (f_{OC}) and sorbate hydrophobicity (Means *et al.*, 1980; Dzombak and Luthy, 1984; Abdul *et al.*, 1987; Chiou, 1989). For ionizable PAHs, sorption to soil is not well correlated to f_{OC} but more strongly controlled by soil charge, solution pH, and sorbate ionization (Zachara *et al.*, 1986). Quinoline is a nitrogen-containing heterocyclic PAH whose weakly basic N het-

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*Corresponding author: Department of Civil and Environmental Engineering, The Pennsylvania State University, 212 Sackett Building, University Park, PA 16820; *Phone:* 814-863-0578; *Fax:* 814-863-7304; *E-mail:* bburgos@psu.edu eroatom ($pK_a = 4.92$) is protonated to cationic form under acidic conditions. Quinoline is one of the major contaminants of soil and groundwater in areas of creosote contamination (Bennet *et al.*, 1985). The sorption of quinoline to clay minerals (Helmy *et al.*, 1983; Ainsworth *et al.*, 1987; Zachara *et al.*, 1990; Chorover *et al.*, 1999), oxides (Helmy *et al.*, 1983), and whole soils (Zachara *et al.*, 1986, 1987; Thomsen *et al.*, 1999) has revealed two primary sorption mechanisms. At low pH values (ca. pH 4–5), the quinolinium cation (QH^+) is sorbed primarily via ion exchange. At higher pH values, the neutral quinoline species is sorbed less, but strongly, via hydrophobic interactions.

The fate and transport of the quinolinium ion and other cationic PAHs is thus affected by competition with background electrolytes for cation sorption sites. Although the sorption of quinoline to soils and soil minerals has been reported, few studies (Ainsworth *et al.*, 1987; Zachara *et al.*, 1990; Chorover *et al.*, 1999) have reported on conditional exchange coefficients (K_{exc}) for the selectivity of quinoline vs. major ions Na^+, Li^+, or Ca^{2+}. In addition, previous studies have shown discrepancies regarding quinoline adsorption isotherm shape and K_{exc}. For example, the adsorption isotherm of quinoline onto clay minerals has been shown to be intermediate between S- and H-type for Na- and Ca-saturated montmorillonite (Helmy *et al.*, 1983), S-type for Na-saturated mntmorillonite (Ainsworth *et al.*, 1987), and L-type for spent shale (Zhu *et al.*, 1995). Zachara *et al.* (1990) found K_{exc} for $Ca^{2+} \rightarrow QH^+$ exchange on montmorillonite increased as pH increased in 7.5 mM $Ca(ClO_4)_2$ solution, but K_{exc} was not affected by pH for $Na^+ \rightarrow QH^+$ exchange in 10 mM $NaClO_4$ solution. Chorover *et al.* (1999) found K_{exc} for $Li^+ \rightarrow QH^+$ exchange on kaolinite decreased as pH increased in 1 mM LiCl, but K_{exc} was not affected by pH in 10 mM LiCl solution.

Additional information on the selectivity of quinoline vs. inorganic cations with various soil minerals is needed to better predict the fate of this contaminant in mineral soils and aquifers. The objective of the present study was to evaluate the sorption behavior of quinoline onto kaolinite and montmorillonite over the pH range encountered in natural soils and water. These minerals were chosen to represent the range in surface chemical properties that exists among common secondary clays.

MATERIALS AND METHODS

All solutions were prepared using distilled water that was passed through a MilliQ UV-plus water purification system. All glassware and Teflon containers were acid washed in 10% HNO_3, copiously rinsed with MilliQ water, rinsed in a 50% MilliQ water–50% methanol solution, and rinsed again with MilliQ water prior to use.

Preparation of $CaCl_2$ saturated minerals

Georgia kaolinite (KGa-2) and Wyoming montmorillonite (SWy-2) were obtained from the Source Clay Minerals Repository (University of Missouri, Columbia, MO) and 100 g of each clay were added slowly to 1 L of MilliQ water while stirring. The clays were dispersed for size fractionation by adjusting suspension pH to 9.5 with dropwise addition of NaOH. The suspensions were size fractionated by centrifugation, and particles $>2\ \mu m$ were discarded. The suspensions were flocculated by addition of concentrated $CaCl_2$ and HCl to give a suspension concentration of 0.4 mol kg^{-1} $CaCl_2$ and pH 3. The suspension was shaken for 20 min and then centrifuged at $6{,}000 \times g$ and 25°C for 10 min. Supernatant solutions were discarded. The clay suspensions were resuspended in either 0.4 or 4.0 mM $CaCl_2$ and washed five more times to raise supernatant pH to 5.5. The clay suspensions were finally redispersed in 0.4 or 4.0 mM $CaCl_2$ and the solid concentration of each clay suspension was measured by oven drying triplicate samples at 180°C to constant mass, correcting for the contribution of $CaCl_2$. Specific surface area of each mineral was measured by $N_2(g)$ BET and ethylene glycol monoethyl ether (EGME) methods. Structural (permanent) charge was measured by the Cs adsorption method (Anderson and Sposito, 1991). Selected characterization data are presented in Table 1.

Cation exchange capacity

Adsorption of Ca^{2+} onto kaolinite and montmorillonite was measured as a function of pH at 6 to 8 duplicated pH values (pH 3–11) and two ionic strengths (0.4 or 4.0 mM $CaCl_2$) to determine cation exchange capacity (CEC). For each batch system, a known mineral mass equivalent to 200 $m^2\ kg^{-1}$ suspension based on total surface areas of 20 and 600 $m^2\ g^{-1}$ for kaolinite and montmorillonite, respectively (Table 1), was added to 50-mL PTFE centrifuge tubes of known mass. Variable proportions of 0.4 or 4.0 mM $CaCl_2$ and HCl, and 1.0 or 10.0 mM NaOH were added to each tube to obtain a range of final pH values. NaOH was required because $Ca(OH)_2$ was not a strong enough base at these concentrations, and would have led to unacceptable suspension dilutions. The maximum charge fraction of Na^+ in solution (i.e., $[Na^+]/2[Ca^{2+}]$) was 3.2% at the highest pH values tested. Centrifuge tubes were sealed with threaded PTFE caps, and suspensions were equilibrated at room temperature (20–23°C) by end-over-end rotation at seven revolutions per min for 24 h.

Following equilibration, suspensions were centrifuged

Table 1. Selected physical and chemical properties of adsorbents used in this study.

Adsorbent	*Specific surface area ($m^2\ g^{-1}$)* *N_2 BET*[a]	 *EGME*[b]	*Structural charge*[c] *($mmol_c\ kg^{-1}$)*	*CEC*[d] *pH 7, I = 10 mM ($mmol_c\ kg^{-1}$)*
Kaolinite	23.2	19.1 ± 0.8[e]	-13.4 ± 0.2[e]	43
Montmorillonite	37.0	600 ± 13	-627 ± 5	842

[a]BET is Brunauer-Emmett-Teller; [b]EGME is ethylene glycol monoethyl ether; [c]Structural charge resulting from isomorphic substitution in clay structure, measured using the Cs adsorption method (Anderson and Sposito, 1991); [d]From best fit to 10 mM ionic strength data shown in Fig. 1. Regression equations for CEC as a function of pH are presented in Table 2; [e]Data from Chorover et al. (1999).

at 27,000 × *g* and 25°C for 10 min. Supernatant solutions were aspirated into glass vials, and final pH was measured immediately using a combination glass electrode. The supernatant solutions were filtered (0.2 μm) and acidified to pH <2 by addition of conc. HNO_3 and stored at 2°C prior to analysis for Ca^{2+}. The mass of solution entrained in the mineral pellet was measured. Mineral pellets were then extracted with 20 g of 0.1 mol kg^{-1} NH_4NO_3 on a reciprocal shaker for 30 min, and this procedure was repeated three times. Extraction solutions for each pellet were combined into one container, and total mass was determined. The extraction solution was acidified and stored at 2°C prior to analysis for Ca^{2+}.

Adsorption edge experiments

Reagent grade quinoline (99%) was purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. Quinoline was dissolved in 0.4 or 4.0 mM $CaCl_2$ to produce stock solutions of 400 to 600 mg kg^{-1}. Adsorption of quinoline onto each mineral was measured as a function of pH at 11 to 16 duplicated pH values (pH 3–7.5) and two ionic strengths (0.4 or 4.0 mM $CaCl_2$). For each batch system, a known mineral mass equivalent to 200 $m^2\ kg^{-1}$ was added to 50-mL PTFE centrifuge tubes of known mass. Variable proportions of 0.4 or 4.0 mM $CaCl_2$ and HCl, and 1.0 or 10.0 mM NaOH were added to each tube to obtain a range of final pH values. Quinoline stock solution was added to give a total concentration of 0.23 mM in a total suspension mass of 41.0 g. Control experiments with no minerals were also performed, similar to the above, to account for any losses as sorption to PTFE tubes, volatilization, and transformation. The exact procedures used for the CEC experiments were followed except that quinoline was measured in the supernatant and NH_4NO_3 extraction solutions.

Adsorption isotherm experiments

Sorption of quinoline onto each mineral was measured as a function of quinoline concentration at 11 to 13 quinoline concentrations (0.02–1.55 mM) and two ionic strengths (0.4 or 4.0 mM $CaCl_2$) at their respective pH values of maximum adsorption (pH 3.4–3.7 for kaolinite, and pH 4.2–5.0 for montmorillonite). For each batch system, a known mineral mass equivalent to 200 $m^2\ kg^{-1}$ suspension was added to 50-mL PTFE centrifuge tubes of known mass, and the exact procedures as above were followed, except that NH_4NO_3 extractions were not performed. The final pH for all mineral suspensions was always within a ±0.20 pH unit of the target pH of maximum adsorption.

X-ray diffraction measurements

X-ray diffraction of oriented samples was used to monitor changes in montmorillonite interlayer spacing that accompanied increased loading of quinoline. A dry mass equivalent of 8.35 mg of clay was reacted with 250 mL of quinoline-containing 0.4 mM $CaCl_2$ solution (as above) for 24 h in polypropylene bottles. Suspensions were filtered (0.45 μm) via vacuum flask, and filtrate was collected for the analysis of quinoline and pH after reaction. The filter retentate (clay) was then washed with 100 mL of 90% ethanol that was adjusted to the same pH as the filtrate solution using HCl. Clay samples were carefully removed from the filter paper and completely dispersed in 5 mL of Milli-Q water. Two milliliters of the clay suspension were then deposited onto a 26 × 46-mm clean glass slide. X-ray diffraction data were collected with CuKα radiation (35 kV and 30 mA) on a Scintag Pad X diffractometer (θ–2θ/liquid N_2 cooled solid state detector), using a step size of 0.020°, a counting time of 0.5 s per step, and a scanning range from 4 to 10° 2θ. Each sample was scanned five times, and the average d (001) spacing was calculated.

Analytical procedures

Quinoline concentrations in the supernatant and NH_4NO_3 extraction solutions were measured with a high-performance liquid chromatograph (HPLC, Waters 2690, Milford, MA) equipped with a 150 × 4.6 mm reverse-phase column (Pinnacle ODS, Restek, Bellefonte, PA) and a photodiode array detector (PDA, Waters 996). The mobile phase consisted of 30% (v/v) acetonitrile in 50 mM triethylamine–phosphate buffer at pH 3.5. Quinoline was quantified by integrating the 4.10 min peak at 315 nm. Concentrations of Ca^{2+} in the supernatant and NH_4NO_3 extraction solutions were measured by atomic absorption spectrometry (Shimadzu AA-6601F, Columbia, MD).

The surface excess of Ca^{2+} was calculated from the concentrations and solution masses measured:

$$q_{Ca} = N_{Ca,NH4NO3} - M_{ent} * m_{Ca} \qquad (1)$$

where q_{Ca} is the surface excess of Ca (mol kg^{-1} solid), $N_{Ca,NH4NO3}$ is the number of mol per unit clay mass of Ca extracted with NH_4NO_3, M_{ent} is the mass of entrained solution per unit clay mass, and m_{Ca} is the molinity of Ca^{2+} (mol kg^{-1} solution) in the supernatant solution. The quantity of quinoline sorbed (Γ_Q, mol kg^{-1} solid) was calculated on the basis of loss from solution and accounted for any loss (found to be negligible based on mineral-free controls) to the reaction vessel:

$$\Gamma_Q = (m_{Q,0} - m_{Q,eq}) * M_w \qquad (2)$$

where $m_{Q,0}$ and $m_{Q,eq}$ are, respectively, the molinities of quinoline (mol kg^{-1} solution) in the supernatant solution of a mineral-free blank and the experimental suspension following 24-h equilibration time, and M_w is the gravimetric water content of the suspension (kg solution kg^{-1} solid).

RESULTS AND DISCUSSION

Adsorbent cation exchange capacities

Figure 1 shows the effect of pH and ionic strength on the CEC of kaolinite and montmorillonite as measured by Ca^{2+} adsorption. Lines shown in Fig. 1 represent best-fit polynomial regressions and the corresponding equations are presented in Table 2. These regression equations are later used to calculate Ca^{2+} adsorption to determine K_{exc} for $Ca^{2+} \rightarrow QH^+$. The CEC values measured for kaolinite and montmorillonite and their pH dependence (Fig. 1, Tables 1 and 2) are comparable to values reported in the literature (Schroth and Sposito, 1997; Kraepiel *et al.*, 1998). Chorover *et al.* (1999) found that kaolinite CEC increased from 4 to 37 $mmol_c\ kg^{-1}$ as pH was increased from 3 to 9.5 in 10 mM LiCl solution. Zachara *et al.* (1990) reported that CEC values for Ca-saturated montmorillonite (SWy-1) ranged from 980–1,020 $mmol_c\ kg^{-1}$ between pH 4–8 in 7.5 mM $Ca(ClO_4)_2$ solution. Structural charge, which was measured independently by the Cs adsorption method (Anderson and Sposito, 1991), contributes 13.4 and 627 $mmol_c\ kg^{-1}$ to the CEC of the kaolinite and montmorillonite, respectively (Table 1). Increased CEC at higher pH (Fig. 1), therefore, reflects Ca^{2+} adsorption to negatively charged aluminol and silanol sites that become progressively dissociated with increasing pH. Figure 1 also shows that at constant pH, CEC increases with ionic strength, a result that is consistent with prior surface titrations of kaolinite (Schindler *et al.*, 1987) and montmorillonite (Wanner *et al.*, 1994).

Quinoline adsorption edges

Figure 2 shows the effects of pH and ionic strength on the adsorption of quinoline to kaolinite and montmorillonite. Overlain on these plots is a dotted line that represents α, the ionized (protonated) fraction of quinoline (QH^+) in solution, which ranges from ca. 1.0 at pH 2 to

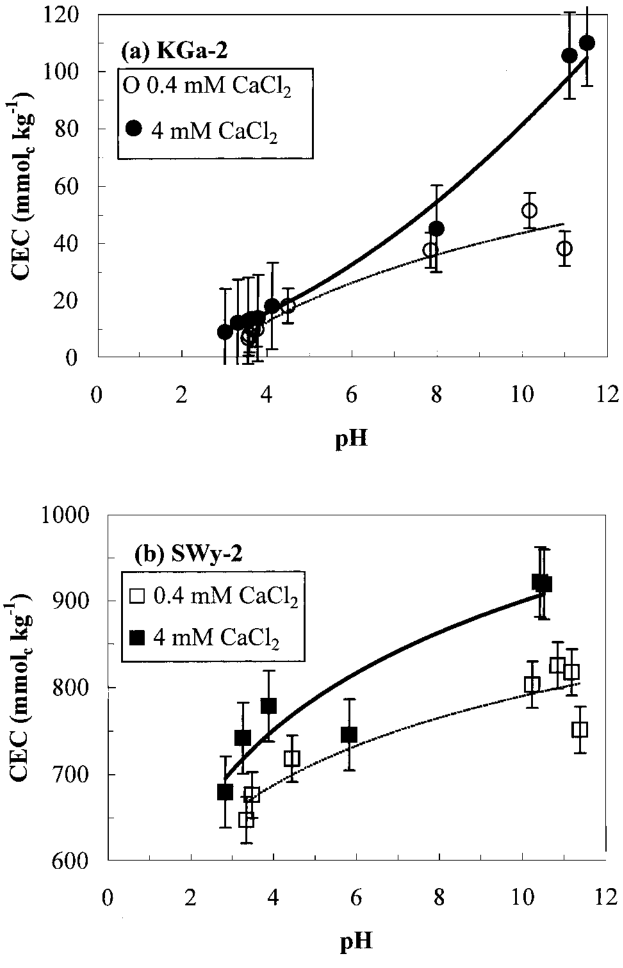

Figure 1. Cation exchange capacity of (a) kaolinite (KGa-2) and (b) montmorillonite (SWy-2) as a function of pH in 0.4 and 4 mM $CaCl_2$ solutions. Error bars represent one standard deviation.

Table 2. Cation exchange capacity regression equations for kaolinite and montmorillonite shown in Fig. 1.

Clay	*$CaCl_2$ solution*	*Equation*	r^2	*Eq. #*
KGa-2	0.4 mM	CEC = 34 ln (pH) − 35	0.93	(3)
	4.0 mM	CEC = 1.3 $pH^{1.8}$	0.99	(4)
SWy-2	0.4 mM	CEC = 111 ln (pH) + 533	0.84	(5)
	4.0 mM	CEC = 162 ln (pH) + 527	0.86	(6)

All CEC equations are in units of $mmol_c\ kg^{-1}$.

near zero at pH 8 (the scale for α is not shown on the y axes). The value of α is given by $[QH^+]/[Q]_T$, where $[QH^+]$ and $[Q]_T$ represent concentrations of the quinolinium cation and total quinoline, respectively. The ionized fraction was calculated from the measured final pH and reported acid dissociation constant for quinoline ($pK_a = 4.92$). Activity coefficients for H^+ and QH^+ were determined from the Davies equation, and the neutral species (Q) was assigned an activity coefficient of unity (Stumm and Morgan, 1996). Sorbed values reported in all figures refer to total sorbed quinoline, not the ionized fraction.

The sorption of quinoline to kaolinite was strongly pH dependent: sorption increased from the lowest pH values tested to a maximum ($\Gamma_{Q,\max}$) at pH 3.7 for the low ionic strength and pH 3.4 for the high ionic strength (Fig. 2a). Decreases in sorption above these pH values tended to parallel the α line. Similar pH-dependent trends for quinoline sorption to kaolinite (Chorover *et al.*, 1999), montmorillonite (Ainsworth *et al.*, 1987), and subsurface sediments (Zachara *et al.*, 1986) have been reported and highlight the greater sorption of QH^+ vs. neutral quinoline. At the lowest pH values, competition with H^+ and/or dissolved Al^{3+} for surface sites likely caused the decreased sorption of QH^+. As the ionic strength increased, the sorption of quinoline to kaolinite decreased at nearly all pH values. Chorover *et al.* (1999) also reported a decrease in quinoline sorption to kaolinite with increasing ionic strength of LiCl solution; $\Gamma_{Q,\max}$ values were 7.2 and 4.0 mmol kg^{-1}, respectively at 1.0 and 10 mM ionic strength. In the current study, $\Gamma_{Q,\max}$ values of 4.9 and 2.9 mmol kg^{-1}, respectively, in 0.4 and 4 mM $CaCl_2$ solution demonstrate that Ca^{2+} competes more effectively than Li^+ for quinoline sorption sites. This valence effect has also been reported for Na- vs. Ca-saturated montmorillonite (Zachara *et al.*, 1990).

Figure 3a shows the fraction of kaolinite-sorbed quinoline that was not desorbed during three successive 30-min extractions in 0.1 mol kg^{-1} NH_4NO_3 solution (i.e., the "nonextractable" fraction) corresponding to the adsorption edge of Fig. 2a. For kaolinite, the nonextractable fraction increased with pH, and was essentially independent of ionic strength. These results suggest that while the extent of quinoline sorption to kaolinite decreased with increasing pH, sorption reversibility was reduced. These trends are in agreement with Chorover *et al.* (1999); however, the nonextractable fraction of quinoline was greater in $CaCl_2$ solution (0.77–0.98) compared to LiCl solution (0.4–0.9). These results suggest that quinoline was sorbed more strongly in the presence of Ca^{2+} vs. Li^+. More effective competition of Ca^{2+} (relative to Li^+) for surface sites may "restrict" quinoline to higher affinity sorption sites.

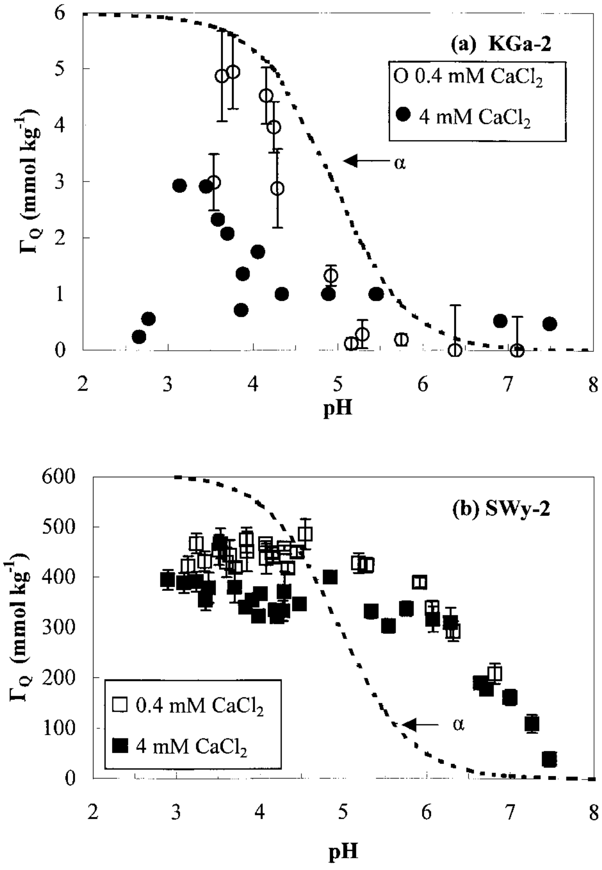

Figure 2. Quinoline adsorption onto (a) kaolinite (KGa-2) and (b) montmorillonite (SWy-2) as a function of pH in 0.4 and 4 mM $CaCl_2$ solutions. The dotted line represents the ionized fraction in solution ($[QH^+]/[Q]_T$). Total quinoline concentration = 0.23 mM. Error bars represent one standard deviation.

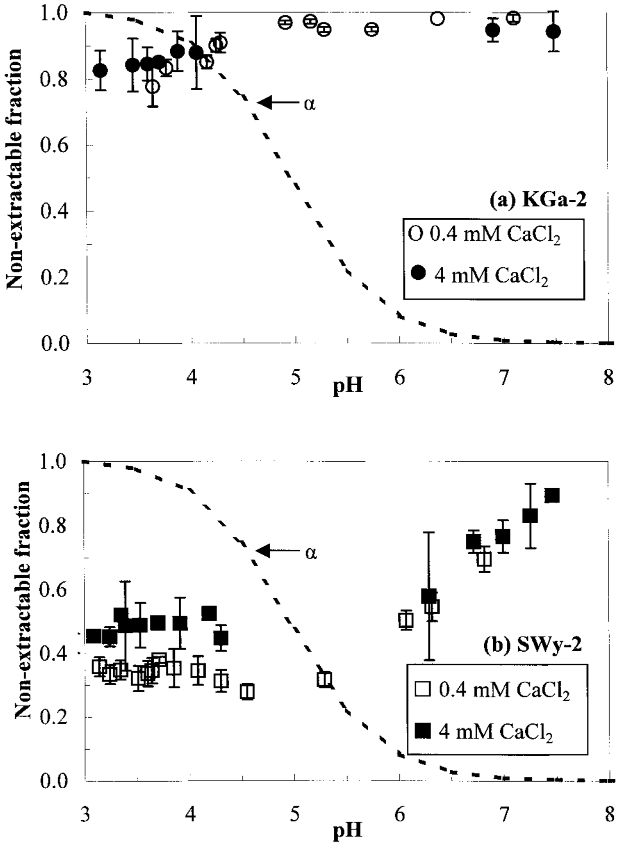

Figure 3. The fraction of sorbed quinoline that was retained by the clays following three sequential extractions in unbuffered 0.1 M NH_4NO_3 solution following equilibration in 0.4 and 4 mM $CaCl_2$ at the pH shown: (a) kaolinite (KGa-2) and (b) montmorillonite (SWy-2). The dotted line represents the ionized fraction in solution ($[QH^+]/[Q]_T$). Error bars represent one standard deviation.

The sorption of quinoline to montmorillonite was two orders of magnitude greater than for kaolinite, but also strongly pH dependent (Fig. 2). Sorption was nearly constant at a maximum value from pH 2.9–4.8, and then decreased in parallel to the α line at pH $> pK_a$ (Fig. 2b). These results are in agreement with other studies on the sorption of quinoline to montmorillonite (Helmy *et al.*, 1983; Ainsworth *et al.*, 1987; Zachara *et al.*, 1990). Persistence of quinoline sorption at pH $> pK_a$ may be attributed to the high surface charge density of montmorillonite, resulting predominantly from isomorphic substitutions, coupled with enhanced protonation of quinoline in the acidic, near-surface environment and a strong preference for QH^+ over Ca^{2+} (Zachara *et al.*, 1986; McBride, 1994). Bailey *et al.* (1968) suggested that the "apparent surface acidity" at the mineral–water interface of negatively charged clay minerals may be 2–4 pH units lower than the bulk solution. Because montmorillonite has a much greater structural charge than kaolinite, its surface acidity should be greater. Quinoline sorption was generally greater at the lower ionic strength, although the effect of ionic strength was less significant with montmorillonite compared to kaolinite.

A large mass of montmorillonite-sorbed quinoline was nonextractable, but the fraction was lower than observed for kaolinite (Fig. 3). The nonextractable fraction increased with pH at pH $> pK_a$, and the trend was independent of ionic strength. At pH $< pK_a$, $NH_4{}^+$ exchange of QH^+ was $<100\%$ effective, and a larger fraction was retained after reaction at the higher ionic strength. As in the case for kaolinite, these results suggest that quinoline is increasingly restricted to higher affinity surface with increasing ionic strength (and thus greater sorptive competition with Ca^{2+}). Desorption from high-affinity sites is less favorable energetically.

$Ca^{2+} \rightarrow QH^+$ exchange

In the acid pH range, adsorption of QH^+ predominates and a conditional selectivity coefficient, K_{exc}, for

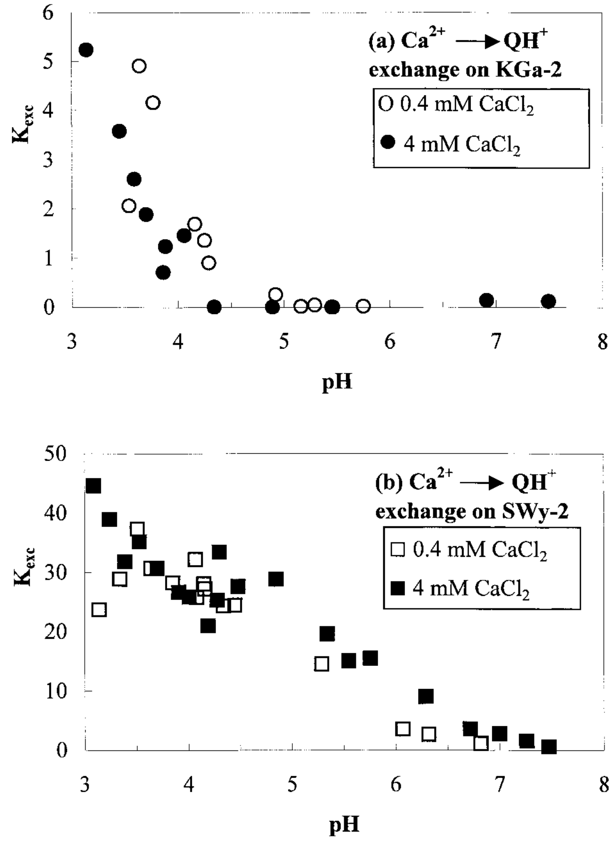

Figure 4. Conditional selectivity coefficients for $Ca^{2+} \rightarrow QH^+$ exchange as a function of pH in 0.4 and 4 mM $CaCl_2$ solutions: (a) kaolinite (KGa-2), and (b) montmorillonite (SWy-2).

$Ca^{2+} \rightarrow QH^+$ exchange may be calculated for the exchange reaction:

$$Ca_{0.5}X(s) + QH^+(aq) \rightarrow QHX(s) + 0.5Ca^{2+}(aq) \quad (7)$$

where X represents 1 mol of cation exchanger charge. The value of K_{exc} was determined from:

$$K_{exc} = \{[QHX](\gamma_{Ca2+} m_{Ca2+})^{0.5}\} / \{[Ca_{0.5}X](\gamma_{QH+} m_{QH+})\} \quad (8)$$

where the surface concentration of QH^+ ([QHX]) was assumed to equal Γ_{QH+} (= $\alpha\Gamma_Q$), and the surface concentration of Ca^{2+} was assumed to equal:

$$[Ca_{0.5}X(s)] = CEC - \Gamma_{QH+} \quad (9)$$

where CEC was calculated for specific pH values using the appropriate regression equation [Equations (3)–(6)] in Table 2. Solution phase activity coefficients were calculated with the Davies equation.

Calculated values of K_{exc} for kaolinite and motmorillonite showed a clear pH dependence at both ionic strengths (Fig. 4). Kaolinite selectivity for QH^+ decreased from 5 to 0 with increasing pH from 3.2 to 5 (Fig. 4a). Chorover *et al.* (1999) found K_{exc} for $Li^+ \rightarrow QH^+$ exchange on kaolinite decreased from 120 to 50 with increasing pH from 3.5 to 6 in 1 mM LiCl solution. They observed less pH dependency in 10 mM LiCl solution where K_{exc} ranged from 80 to 120. Based on comparison with the results presented in the current study (where ionic strengths are identical to those of Chorover *et al.* 1999), Ca^{2+} clearly competes more effectively than Li^+ with QH^+ for kaolinite surface sites. Zachara *et al.* (1986) showed that quinoline sorption to an acidic subsurface sediment was reduced in 10 mM $CaCl_2$ solution compared to MilliQ water; however, no electrolyte effect was observed for a neutral subsurface sediment. All of these studies suggest that background cations will compete with QH^+ for mineral surface sites under acidic conditions.

At a given pH, montmorillonite exhibits greater selectivity for QH^+ than does kaolinite; K_{exc} decreased from 36 to 2 with increasing pH from 3.5 to 7 independent of ionic strength (Fig. 4b). Ainsworth *et al.* (1987) found conditional K_{exc} for $Na^+ \rightarrow QH^+$ exchange on montmorillonite (SWy-1) varied from 350 to 1,200 as the mol fraction of sorbed QH^+ ([QHX]/[QHX + NaX]) was decreased from 0.05 to 0.02 at pH 5 in 10 mM $NaClO_4$ solution. In the current study, the mol fraction of sorbed QH^+ ([QHX]/[QHX + $Ca_{0.5}X$]) decreased from 0.53 to 0.086 in 4 mM $CaCl_2$ solution as pH was increased from 3 to 7.5, and a relatively greater variation in K_{exc} was observed. In contrast, Zachara *et al.* (1990) found conditional K_{exc} for $Ca^+ \rightarrow QH^+$ exchange on montmorillonite (SWy-1) increased from 10^4 to 10^5 with increasing pH from 5 to 7.5 in 7.5 mM $Ca(ClO_4)_2$ solution. These much higher K_{exc} values compared to the current study are likely the result of different experimental procedures. For example, Zachara *et al.* (1990) used quinoline/montmorillonite ratios of 0.3 to 10 mmol kg^{-1} clay for pH edge experiments, while a constant ratio of 690 mmol quinoline kg^{-1} montmorillonite was used in the current

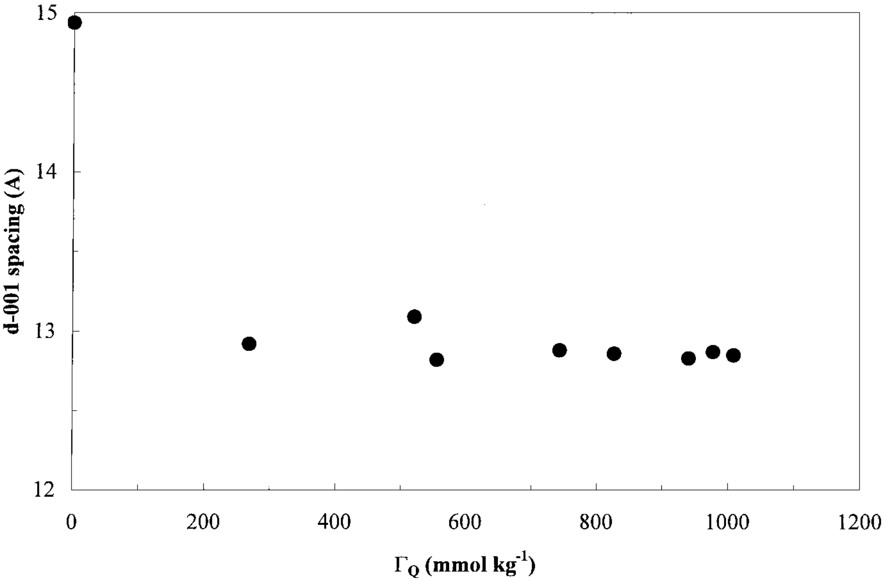

Figure 5. Interlayer (d-001) spacing of montmorillonite (SWy-2) as a function of quinoline loading in 0.4 mM $CaCl_2$ solution. X-ray diffraction data were collected with CuKα radiation (35 kV and 30 mA), each sample was scanned five times, and the standard deviations were smaller than the symbols.

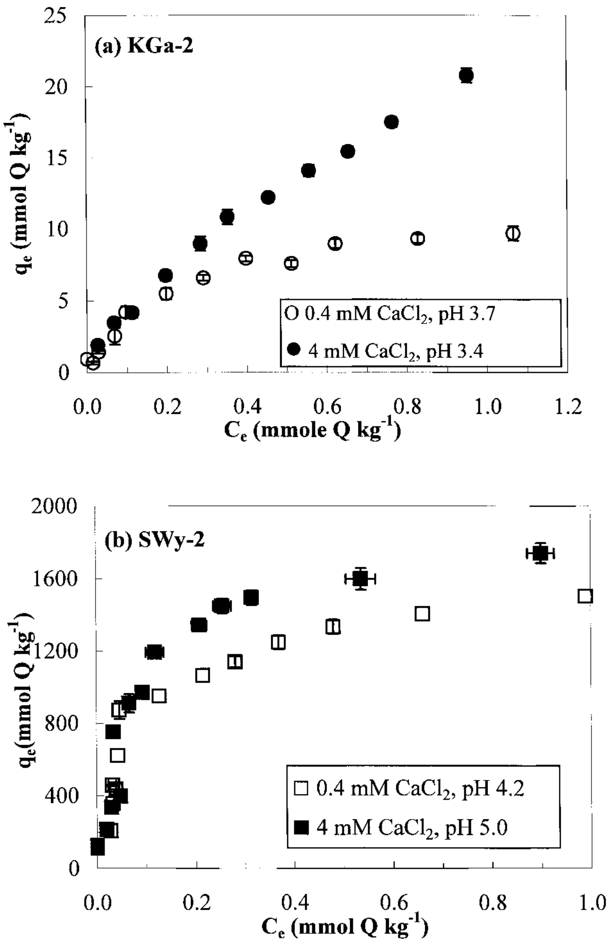

Figure 6. Adsorption isotherms of quinoline to (a) kaolinite (KGa-2) and (b) montmorillonite (SWy-2) in 0.4 and 4 mM $CaCl_2$ solutions. Error bars represent one standard deviation.

study. At higher sorbate-to-sorbent ratios a corresponding lesser amount of quinoline sorption (on % basis) and higher quinoline molinities would be expected.

The higher K_{exc} for montmorillonite than for kaolinite strongly suggests that the high-affinity quinoline sites in both cases are the ditrigonal siloxane cavities rather than negatively charged surface hydroxyl groups. Accessible charged siloxane sites are about 50 times more prevalent in montmorillonite (as reflected by the structural charge densities reported in Table 1) and are high affinity sorption sites for this N heterocyclic compound. Ukrainczyk and Smith (1996) used ^{15}N-NMR spectroscopy to show that the heterocyclic N of pyridine can key into the ditrigonal hole of montmorillonite, forming an H-bond to the proton of structural OH. This kind of H-bonding interaction may also explain the nonextractable fraction that occurs at higher pH.

To confirm that adsorption of quinoline occurred at the smectite basal plane, we measured interlayer (d-001) spacing as a function of quinoline loading. The results, summarized in Fig. 5, indicate a significant decrease in d-spacing as quinoline is sorbed to the montmorillonite surface. The d-spacing for Ca-saturated montmorillonite (i.e., zero adsorbed quinoline) is 14.94 Å, consistent with interlayer adsorption of the hydrated Ca^{2+} cation (Brindley and Brown, 1980). Increased surface loading of quinoline (Γ_Q), even below surface saturation, results in contraction of the interlayer space to 12.82 Å, indicating expulsion of hydrated calcium ions (Fig. 5). The size of a single 2:1 smectite layer itself is ca. 10 Å, and the vertical size of the quinoline ring (either the N-heterocycle or the benzene ring) is ca. 2.5 Å, similar in size to the thickness of a water molecule (2.8 Å). Therefore, these data are consistent with innersphere complexation of the N-heterocycle at siloxane sites, an observation that may also explain the low reversibility of this sorption reaction.

Quinoline adsorption isotherms

Figure 6 shows quinoline adsorption isotherms collected at the pH of maximum adsorption for each ionic strength with kaolinite and montmorillonite. For kaolinite, both the Langmuir and Freundlich isotherm equations fit the data well (Table 3) and the isotherms are L-type (Sposito, 1989). At low final quinoline concentrations ($C_e < 0.12$ mmol kg^{-1}), quinoline sorption was independent of ionic

Table 3. Fitting parameters for Freundlich and Langmuir isotherms describing quinoline adsorption to clay minerals.

Clay mineral	*$CaCl_2$ solution*	*Freundlich*[a]			*Langmuir*[b]		
		K_F	n	r^2	K_L	*b*	r^2
KGa-2	0.4 mM	12.2	0.61	0.94	5.76	11.1	0.97
	4.0 mM	21.7	0.73	0.99	2.23	27.0	0.67
SWy-2	0.4 mM	1840	0.42	0.75	9.23	1860	0.98
	4.0 mM	2544	0.48	0.79	12.5	2000	0.98

[a] $\Gamma_Q = K_F\, C_e{}^n$; [b] $\Gamma_Q = (\text{b}\, K_L\, C_e)(1 + K_L\, C_e)^{-1}$; where (units) are: Γ_Q (mmol kg^{-1} clay), C_e (mmol kg^{-1} solution), K_F ({mmol kg^{-1} clay}{mmol kg^{-1} solution}$^{-n}$), *n* (dimensionless), K_L (kg solution mmol^{-1}), b (mmol kg^{-1} clay).

strength. At higher quinoline concentrations, greater quinoline sorption occurred at pH 3.4 in 4 mM $CaCl_2$ solution compared to pH 3.7 in 0.4 mM $CaCl_2$ solution (Fig. 6a). It was expected that greater quinoline sorption would occur at the lower ionic strength because of less competition with Ca^{2+} and less Al^{3+} dissolution/readsorption (Wieland and Stumm, 1992; Furrer *et al.*, 1993).

The results with the kaolinite adsorption isotherm experiments contrast with the adsorption edge experiments where quinoline sorption increased with decreased ionic strength (Fig. 2a, $C_e > 0.11$ mmol kg^{-1} for all results). These contrasting results suggest that the different pH values tested (i.e., pH 3.7 ± 0.20 vs. 3.4 ± 0.20) exerted a greater effect than ionic strength (i.e., 1 vs. 10 mM, respectively). Another explanation, one that is highly speculative, is that high quinoline concentrations may enhance sorption via intermolecular associations (i.e., with increasing quinoline concentration attractive quinoline–quinoline interactions may be enhanced on the surface, especially if the positive charges are shielded by association with the surface). Intermolecular attraction at the surface may thereby be enhanced by increasing ionic strength in a manner that is analogous to the salting out effect.

The sorption of quinoline to montmorillonite was better fit with the Langmuir vs. the Freundlich isotherm equation (Table 3) and the isotherms are S-type (Sposito, 1989). At low final quinoline concentrations ($C_e <$ 0.08 mmol kg^{-1}), quinoline sorption was independent of ionic strength. At higher quinoline concentrations, behavior similar to that of kaolinite was observed: greater quinoline sorption occurred at higher (4 mM $CaCl_2$, pH 5.0) compared to lower (0.4 mM $CaCl_2$, pH 4.2) ionic strength (Fig. 6b). At pH 5.0 in 4 mM $CaCl_2$, the estimated CEC is 788 mmol$_c$ kg^{-1} and at pH 4.2 in 0.4 mM $CaCl_2$ solution, the estimated CEC is 692 mmol$_c$ kg^{-1} (Table 3). Thus, while the Ca^{2+} concentration increased by 7.2 mEq kg^{-1} between the high and low ionic strength experimental conditions, the CEC correspondingly increased by 96 mEq kg^{-1} between pH 5 and 4.2. Therefore, greater quinoline sorption to montmorillonite at the higher ionic strength could be explained by a reduction in cation competition at the different pH values tested.

CONCLUSIONS

Adsorption of quinoline to kaolinite and montmorillonite is dominantly via cation exchange reactions involving the quinolinium cation ($pK_a = 4.92$) on both siloxane and hydroxyl sites. Interaction with hydroxylated sites on kaolinite is evidenced from the sharp decrease in adsorption that occurs at pH < 3.6. At this pH, aqueous proton concentration is approximately equal to total initial quinoline concentration, and H^+ competes effectively with the quinolinium cation for surface sites. Adsorption to montmorillonite is not affected by H^+ concentration at $pH < pK_a$ acid range because of the greater prevalence of permanent-charged siloxane sites that exhibit low proton affinity. However, increased Ca^{2+} concentration diminishes sorption to both clays at constant pH via ion competition at low quinoline concentrations.

On a mass basis, montmorillonite adsorbs approximately 100 times more quinoline than kaolinite does under identical conditions. Although this is partly due to the 30-fold higher specific surface area of smectite, quinoline clearly exhibits a higher affinity for siloxane sites, as indicated by higher selectivity coefficients for $Ca^{2+} \rightarrow QH^+$ exchange on montmorillonite relative to kaolinite. A decrease in adsorption to both clay minerals occurs at pH values near the pK_a for quinoline, reflecting the fact that the neutral species has a lower tendency to partition out of solution. For kaolinite, a sharp decrease in sorption occurs with increasing pH at $pH < pK_a$ (pH 3.4 to 3.7, depending on ionic strength), whereas for montmorillonite the sharp decrease occurs at $pH > pK_a$ (pH 5.0 to 6.0). Extension of this "plateau" for $\Gamma_{Q,\max}$ to $pH > pK_a$ likely reflects the surface acidity of montmorillonite, which increases the ionized fraction (α) near the surface, relative to the bulk solution. With increasing pH, despite diminished adsorption overall, a smaller fraction of that quinoline that does sorb at $pH > pK_a$ is extractable with $NH_4{}^+$, and this indicates strong binding interactions. These high-affinity interactions were observed for both clays, and may reflect H-bonding between the heterocyclic N atom and the proton of structural OH within the ditrigonal siloxane cavity. These data suggest that the quinolinium cation will be much less mobile than the neutral form of quinoline in subsurface environments. However, the presence of calcium, which is common in alkaline groundwater, will increase quinoline mobility.

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