SORPTION OF 3-AMINO-1,2,4-TRIAZOLE AND Zn(II) ONTO MONTMORILLONITE

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Abstract—Acid-base titrations and attenuated total reflectance-infrared (ATR-IR) spectroscopy of solutions containing $Zn(NO_3)_2$ and the herbicide 3-amino-1,2,4-triazole suggested that soluble complexes ZnL^{2+} and $Zn(OH)L^+$ form, where L represents aminotriazole. Sorption experiments and modeling in systems containing K-saturated Wyoming (SWy-K) montmorillonite suggest that at low concentrations the aminotriazole sorbs primarily in cationic form via an ion-exchange mechanism. Sorption isotherms for aminotriazole are 's'-shaped, indicating a co-operative sorption mechanism as the concentration of the molecule increases. At higher concentrations, ATR-IR spectroscopy indicated the presence of cationic and neutral triazole molecules on the surface, while X-ray diffraction data suggest interaction with interlayer regions of the clay. When the concentration of the herbicide was high, initial sorption of aminotriazole cations modified the clay to make the partitioning of neutral molecules to the surface more favorable. Experiments conducted in the presence of Zn(II) indicated that below pH 7, Zn(II) and aminotriazole compete for sorption sites, while above pH 7 the presence of Zn(II) enhances the uptake of aminotriazole. The enhancement was attributed to the formation of an inner-sphere ternary surface complex at hydroxyl sites (SOH) on crystal edges, having the form $[(SOZn(OH)L)]^0$.

Key Words—Adsorption, Amitrole, ATR, FTIR, Intercalation, Surface Complexation.

INTRODUCTION

The behavior of pesticides and herbicides in soil and water systems is crucial to our understanding of the fate and action of these compounds in the environment. The transport, persistence and effectiveness of pesticides and herbicides in soils and water is controlled by a range of factors including sorption, biological and chemical degradation, leaching, removal by plants, leaching and volatilization (Ercegovich and Frear, 1964). In cases where herbicide is taken up by plant roots, interaction of the herbicide with soil particles will directly influence application regimes. For example, if a herbicide compound sorbs strongly to soil particles, then application rates may need to increase in order to achieve effective weed kill.

3-amino-1,2,4-triazole (aminotriazole), commonly known as amitrole, is an inexpensive herbicide that is widely used in agronomical business. Aminotriazole is a weak base, pK_a 4.41 (Lenarcik *et al.*, 1980), and is protonated and positively charged at lower pH. There have been a number of studies investigating the behavior of aminotriazole in soil systems. Sund (1956), for example, showed that the recovery of aminotriazole from soil depended on the soil type. Day *et al.* (1961) showed that leaching of aminotriazole from soils containing montmorillonite-like minerals was low, suggesting strong mineral-aminotriazole interaction. Russell *et al.* (1968) and Nearpass (1970) in separate

studies suggested that cation exchange of positively charged aminotriazole with negative exchange sites on clays was responsible for the strong retention of aminotriazole in soils. On the other hand, Morillo *et al.* (1991), using infrared (IR) and X-ray diffraction (XRD) data, proposed that aminotriazole was primarily adsorbed onto montmorillonite in neutral form. These investigators concluded that the extent of adsorption of aminotriazole to cation-saturated montmorillonite varied because of the polarizing power of the cation. For cations with low polarizing power, such as Na^+ and Li^+, aminotriazole was sorbed predominantly as the neutral non-polarized molecule. For cations with medium polarizing power, such as Zn^{2+} and Mg^{2+}, aminotriazole was adsorbed mostly as polarized neutral molecules.

In a study of the adsorption of Zn(II) onto montmorillonite (Ikhsan *et al.*, 2005), we found that in acid solution, Zn(II) is taken up at cation exchange sites both on the surface and interlayer regions of the clay. Above pH 7, Zn(II) forms surface complexes with hydroxyl sites on the mineral edges. Aminotriazole can form weak complexes with Zn(II) (Davarski *et al.*, 1997), and hence, the presence of aminotriazole may affect Zn(II) uptake. This study seeks to investigate the sorption of aminotriazole onto montmorillonite in the presence and absence of Zn(II) in an attempt to understand better the interactions of aminotriazole with montmorillonite particles.

MATERIALS AND METHODS

Montmorillonite

The clay sample used in this study was from The Clay Minerals Society Source Clays Repository: Na-mont-

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morillonite (Wyoming) SWy-2 from Crook County, Wyoming, USA. 250 g of the SWy-2 was stirred for 36 h in 2 L of 200 mM KNO$_3$ solution in water. The suspension was dialyzed against distilled water and the water replaced several times each day until the concentration of K$^+$ was <10^{-5} M (measured by atomic absorption spectrophotometry). Finally, the samples were freeze dried to produce the sample labeled SWy-K in this study. The surface area (BET, N$_2$ adsorption) and cation exchange capacity of the sample were 31.8 m^2 g^{-1} and 76.4 cmol kg^{-1}, respectively (see The Clay Minerals Society website: www.clays.org/sourceclays/sourceclays.html). We note that the surface area suggested by The Clay Minerals Society may not reflect the surface area available for sorption. In theory, the surface area of interlayer regions of the clay could exceed 800 m^2 g^{-1} (Van Olphen, 1977). However, for sorption experiments we have arbitrarily chosen to use a mass of montmorillonite (3.14 g L^{-1}) that gave a suspension concentration equivalent to a BET external surface area of 100 m^2 L^{-1}.

Reagents

Analytical reagent-grade chemicals were used throughout. The water was Milli-Q reagent grade (Millipore, Bedford, USA). The 3-amino-1,2,4-triazole was 99% (Sigma Aldrich).

X-ray diffraction

Suspensions of 2.82 g of montmorillonite in 300 mL of water, with and without added 0.03 M aminotriazole, were equilibrated for 24 h and the pH adjusted to 3.5, 6.0 or 10 with either 0.1 M KOH or HNO$_3$. Each suspension was centrifuged and the paste was then oven dried at 40ºC for 30 h. A small amount of a ground sample of the dried paste was mixed in isopropyl alcohol and placed onto ceramic discs and left for ~1 h until the isopropyl alcohol had evaporated leaving a dried sample that was analyzed with a Phillips PW 1710 X-ray diffractometer (CuKα radiation).

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

7.50 g of SWy-K were added to 50 mL of water and stirred overnight under nitrogen at 25ºC. The pH of the suspension was then adjusted to ~10 with KOH and a sufficient amount of the selected aminotriazole added to the suspension as a solid to give an initial concentration of 30 mM. After a further equilibration time of at least 3 h, a 5 mL sample of the suspension was taken and centrifuged at 7000 g for 10 min. The FTIR spectra of the empty cell, supernatant liquid and paste were taken separately as described below. The pH of the suspension was then adjusted down to a new value, the system was equilibrated for at least 3 h, a 5 mL sample taken and the process repeated.

A Bruker Equinox 55 FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector was used to collect the IR spectra. Samples were analyzed by use of a Docomp/ZnSe DurasamplIR 9-bounce ATR accessory (SensIR Technologies). For each sample, 500 scans were collected over the wavelength range from 700 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1} from the cell, supernatant liquid and paste. The instrument was continuously purged with N$_2$ at a flow rate of 3.5 L min^{-1}. Approximately 1 mm thickness of paste was applied uniformly to the ATR crystal before measurement of the paste spectrum. A PMMA lens with an o-ring gasket was pressed over each sample to prevent drying or CO$_2$ absorption during measurements. Supernatant liquid spectra were collected to check for possible contributions to the paste from aminotriazole remaining in solution. The spectra for the supernatant liquid were subtracted from the paste spectra to remove any contribution from ligands remaining in solution.

Spectra (500 scans) were also taken of montmorillonite suspensions at several pHs. These were subtracted from the spectrum of the AT/montmorillonite paste in order to obtain the spectrum of the adsorbed aminotriazole species. Care was taken to remove the spectral contribution due to interlayer water as completely as possible. The ATR-FTIR spectra of 10 mM solutions of aminotriazole with and without 10 mM Zn(II) were also collected at pH 3.5 and 8.0.

Adsorption experiments and potentiometric titrations

Titrations and sorption experiments were conducted in systems of montmorillonite alone, montmorillonite plus aminotriazole, and the ternary system montmorillonite plus aminotriazole plus Zn(II). Experiments were completed in triplicate and all of the results are presented in the Figures. The montmorillonite-Zn(II) system has been described in a previous paper (Ikhsan *et al.*, 2005). All experiments were conducted at a constant temperature of 25ºC in thermostated reaction vessels. Suspensions were purged continuously with oxygen-free humidified nitrogen to eliminate carbon dioxide. The background electrolyte was 10 mM KNO$_3$. The pH was measured with an Orion Ross Sure-Flow pH electrode which was calibrated with NBS buffers at pH 4.01 and 6.86. In all experiments the suspensions contained montmorillonite at a concentration of 3.14 g L^{-1}.

Acid-base titrations were conducted on montmorillonite suspensions with and without added 0.1 mM aminotriazole and/or Zn(II). Montmorillonite was equilibrated in water at its natural pH overnight before adding any aminotriazole or Zn(II) (if these were required). The pH of the system then was raised to ~10.0 by addition of 0.100 M KOH (Metrohm Dosimat 665), and the suspensions were back titrated with 0.100 M HNO$_3$ to pH ~4.0 using a computer-controlled titration system. Successive additions of HNO$_3$ were made only after the pH drift was <0.1 mV min^{-1}. Titrations typically took 2 days to complete. In addition, titrations of 10 mM solutions of aminotriazole solution, with and without 10 mM Zn(II), in

10 mM KNO$_3$ were also completed to determine the pK_a for aminotriazole and stability constants for aminotriazole-Zn(II) complexation.

Kinetic experiments were performed to determine the time required for the aminotriazole/montmorillonite system to equilibrate. Sufficient aminotriazole was added to an equilibrated montmorillonite suspension to give a total concentration of 0.1 mM, and the pH was fixed at 4.0 or 6.5. Samples were taken at intervals over a period of 4 days, centrifuged and the supernatant liquid analyzed for free aminotriazole concentration by use of HPLC (Shimadzu liquid chromatograph, with SPD-M10AVP Shimadzu diode array detector). Peak integration was carried out using LC-10 version 1.60 software. A 150 × 4.6 mm polar RP column with matching cartridges (Phenomenex, Australia) was used, with a mobile phase consisting of 3:2 (v/v) acetonitrile: water, with 0.01% NH$_4$OH. The wavelength used for detection was 210 nm.

Adsorption-edge experiments measured the effect of pH on the adsorption of aminotriazole at three initial aminotriazole concentrations: 0.05 mM, 0.1 mM and 1.0 mM. Montmorillonite suspensions were pre-equilibrated overnight at their natural pH, and then the pH was increased to 10 using KOH. After 30 min, an aliquot of selected aminotriazole was added to give the required initial concentration of aminotriazole. After a further 30 min of equilibration, a 4 mL sample was transferred into a 7 mL centrifuge tube, flushed with N$_2$ and capped. The pH of the stock solution was decreased in steps of ~0.5, and further 4 mL samples were taken after 30 min of equilibration. All the samples were then shaken for 2 days. The final pH of each sample was measured before it was centrifuged and the supernatant solution analyzed for aminotriazole by HPLC. Adsorption edges for aminotriazole were also measured in the presence of 0.1 mM Zn(II). The amount of Zn adsorbed in these ternary systems was also determined at each pH by measuring residual Zn(II) using flame atomic absorption spectroscopy (Varian SpectrAA 10) at 213.9 nm.

Adsorption isotherms describing the effect of aminotriazole concentration on adsorption were conducted at pH 5.0. The aminotriazole concentration was increased in steps from 1 µM to 500 µM by addition of a stock solution which had been adjusted to pH 5.0. After each addition, the system was equilibrated for 2 h with the pH maintained by KOH or HNO$_3$ addition before a 4 mL sample was transferred to a centrifuge tube. The tube was flushed with N$_2$, stoppered and shaken for 2 days. Then the pH was measured, the tube was centrifuged, and the supernatant solution analyzed for aminotriazole. The amount of KOH or HNO$_3$ added enabled determination of the proton stoichiometry for the sorption system (*i.e.* the number of protons adsorbed or released per aminotriazole molecule adsorbed). Aminotriazole was also measured at pH 5.0 in the presence of 0.1 mM Zn(II).

Adsorption isotherms for Zn(II) were measured at pH 5.0 in the presence of aminotriazole. The concentrations of Zn(II) in solutions ranged from 0 to ~0.1 mM. Aliquots of a Zn(II) stock solution at pH 5.0 were added to a pre-equilibrated suspension containing 0.1 mM or 1.0 mM aminotriazole at pH 5.0. The experiments were conducted in the same way as described above for the aminotriazole isotherms. The concentrations of Zn(II) in the filtrate from the equilibrated samples were measured using flame atomic absorption spectroscopy. Solution aminotriazole concentrations were also measured.

Surface complexation modeling

The results of all potentiometric titration and sorption experiments were modeled with an extended constant capacitance surface complexation model (ECCM) using the computer program GRFIT (Ludwig, 1987). In our modeling, we have assumed two different populations of surface reactive sites. SOH sites represent amphoteric aluminol and silanol groups on the mineral edges. Proton exchange at these sites is modeled with the following reactions:

$$SOH + H^+ \rightleftharpoons SOH_2^+$$
$$SOH \rightleftharpoons SO^- + H^+$$
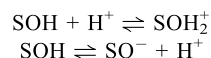
For simplicity, we make no distinction between surface aluminol and silanol hydroxyl groups, so the constants obtained represent an average contribution of these sites. The model for surface acidity includes the additional reactions:

$$(X^- - H^+) + K^+ \rightleftharpoons (X^- - K^+) + H^+$$
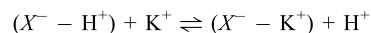
and for systems involving Ca

$$2(X^- - H^+) + Ca^{2+} \rightleftharpoons (X_2^{2-} - Ca^{2+}) + 2H^+$$
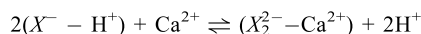
These reactions account for the permanent-charge exchange sites present on the surface and interlayer regions because of isomorphous substitution. In these reactions, X^- represents an exchange site while H$^+$, K$^+$ and Ca^{2+} are ions from the electrolyte solution. The constants for all surface reactions were obtained by optimizing the fits to titration and sorption data. Protonation reactions at the mineral surface were modeled using titration data (Ikhsan *et al.*, 2005). Constants for sorption reactions involving aminotriazole and Zn(II) were obtained by simultaneously optimizing fits to titration, sorption edge and isotherm data.

RESULTS

ATR-FTIR

Figure 1a shows the ATR-FTIR spectra of aminotriazole solutions at pH 3.5 (where the aminotriazolium cation is the dominant species), and pH 8.0 (where the dominant species is the neutral aminotriazole molecule). There are clear differences between the protonated and

deprotonated spectra of the triazole solution species. The most obvious features are the presence of a strong band at 1700 cm^{-1} in the pH 3.5 spectrum that is clearly absent from the spectrum at pH 8.0, and the lack of strong absorbance bands below 1700 cm^{-1} in the pH 3.5 spectrum compared with the spectrum at pH 8.0.

Figure 1b shows spectra for solutions of 1 mM aminotriazole in the presence of 2 mM Zn(II) at pH 6.0 and pH 8.5. These two pH values were selected to provide solution conditions that favored the formation of the ZnL (pH 6.0) and ZnOHL (pH 8.5) solution complexes. There are two significant features in the spectra of the complexes. First, comparison of Figures 1a and 1b reveal that the spectra of the AT-Zn(II) complexes are different from the spectrum of the aminotriazole at the same pH. This is reflected by the significant shifting in bands near 1200 and 1275 cm^{-1} in the spectra for the complexes (Figure 1b) compared to the solution aminotriazole (Figure 1a). Second, the spectra for the complexes at pH 6.0 and 8.5 are different: most notable is the presence of a band at 1115 cm^{-1} in the spectrum of the complex at pH 8.5 that is not observed at the lower pH, and a

change in the relative intensities of the peaks around 1600 and 1250 cm^{-1}.

Shown in Figure 2 are spectra of aminotriazole sorbed to montmorillonite at pH 4.0 and 7.0, encompassing the pH range over which aminotriazole sorbs strongly to the clay surface. The spectrum of sorbed aminotriazole at pH 4.0 is very similar to the solution spectrum of the protonated aminotriazole (bands at 1700 and 1580 cm^{-1}). It is worth noting, however, that the broad feature in the sorbed spectrum around 1650 cm^{-1} is probably inter-lamellar water, which is difficult to remove by subtraction. The spectrum at pH 7.0 also shows the strong band around 1700 cm^{-1} characteristic of the protonated aminotriazole, but some features of the deprotonated aminotriazole molecule in the region below 1700 cm^{-1} are also evident. Most prominent are the bands at 1630, 1555 and 1490 cm^{-1}.

XRD

Diffraction patterns for montmorillonite with various loadings of aminotriazole prepared at pH 4.5 are given in Figure 3. The significant feature is the shift in the peak
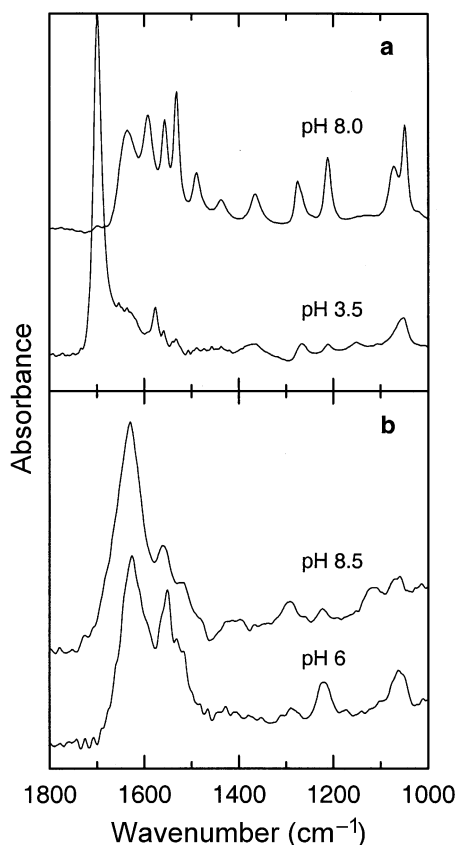

Figure 1. (a) ATR-FTIR spectra for 30 mM solutions of aminotriazole (pK_a = 4.41) at pH 3.5 and pH 8.0. (b) ATR-FTIR spectra for 1 mM solutions of aminotriazole plus 2 mM Zn(II) at pH 6.0 and pH 8.5. Spectra of the aminotriazole have been subtracted to give spectra for the complexes.
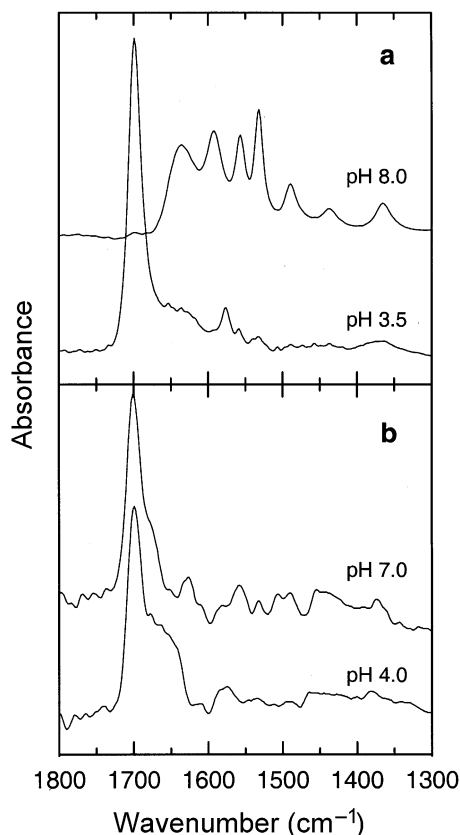

Figure 2. (a) ATR-FTIR spectra for 30 mM solutions of aminotriazole at pH 3.5 and pH 8.0. (b) ATR-FTIR spectra for aminotriazole sorbed onto montmorillonite at pH 4.0 and 7.0. The spectrum of the supernatant liquid and montmorillonite substrate have been subtracted from the adsorbed spectrum in each case.

that corresponds to the *c*-axis spacing (~6°2θ) as the aminotriazole loading is increased. The *c*-axis spacing for SWy-K-montmorillonite in the absence of aminotriazole was 14.5±0.2 Å (six replicates), and did not change in the presence of 0.2 mM aminotriazole. However, at higher loadings of aminotriazole (0.4−0.8 mM), a spacing decrease of 1.5±0.4 Å was observed. When the suspension concentration of aminotriazole was increased to 1.1 mM, the *c*-axis spacing increased to 14.6±0.2 Å.

Sorption experiments and modeling

The sorption of aminotriazole from a 0.1 mM solution onto montmorillonite occurs in two kinetic stages (results not shown): a rapid initial stage where ~25% of the aminotriazole from the initial 0.1 mM solution sorbed rapidly within 2−3 min, and a slower stage, where a further 10% sorbed over a period of ~6 h. There was no further sorption, even when experiments were allowed to continue for several days.

The surface complexation model for the montmorillonite-Zn(II), montmorillonite-aminotriazole, and the ternary systems was developed from consideration of the spectroscopic data and by fitting the sorption edge, sorption isotherm and titration data. The model parameters, including pK_a and stability constants for AT-Zn(II) complexes, are given in Tables 1 and 2. The fit of the model to the sorption and titration data is shown in each of the Figures. Figure 4 gives the titration data for suspensions containing 100 m^2 L^{-1} montmorillonite, 0.1 mM aminotriazole with and without 0.1 mM

Zn(II), and of suspensions containing 3.14 g L^{-1} montmorillonite, 1.0 mM aminotriazole with and without 0.1 mM Zn(II).

Sorption edges for aminotriazole and Zn(II) onto montmorillonite were measured in binary and ternary systems (Figures 5 and 6). The effect of pH on the uptake of aminotriazole by montmorillonite is shown by the data in Figure 5. Sorption was strongest below pH 7.0, with a sorption maximum at ~pH 4.0. As the pH increased, the amount of sorbed aminotriazole decreased, with negligible sorption above pH 7.0. The data in Figure 5 also show that the uptake of aminotriazole increased as the total concentration of aminotriazole increased. In the ternary systems, the presence of 0.1 mM Zn(II) had little effect on aminotriazole uptake below 7.0. At high pH, however, there was significant enhancement of aminotriazole sorption. Figure 6 shows that the presence of aminotriazole suppressed the adsorption of Zn(II) below pH 7.0, with the suppression most noticeable when the aminotriazole concentration was 1 mM. The presence of aminotriazole had little impact on Zn(II) uptake above pH 7.0.

Adsorption isotherms for aminotriazole at pH 5.0 in the absence and presence of 0.1 mM Zn(II) are shown in Figure 7. The most obvious feature of the isotherm data is the non-Langmuirian behavior, evident at higher total aminotriazole concentrations, where greater amounts of the aminotriazole sorbed as the total aminotriazole concentration was increased. The Zn(II) isotherm plots at pH 5.0 (Figure 8) show that Zn(II) uptake was suppressed in the presence of aminotriazole.
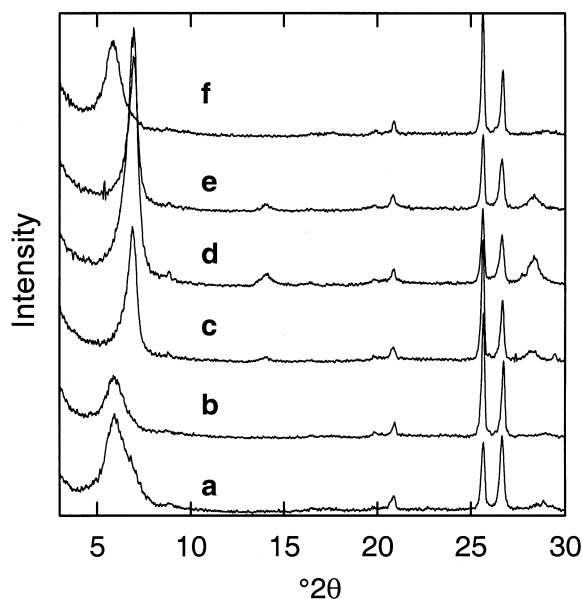

Figure 3. The effect of aminotriazole concentration on the basal spacing of montmorillonite measured by XRD (CuKα) at various aminotriazole concentrations: (a) 0 mM aminotriazole, (b) 0.2 mM, (c) 0.4 mM, (d) 0.6 mM, (e) 0.8 mM, and (f) 1.1 mM.
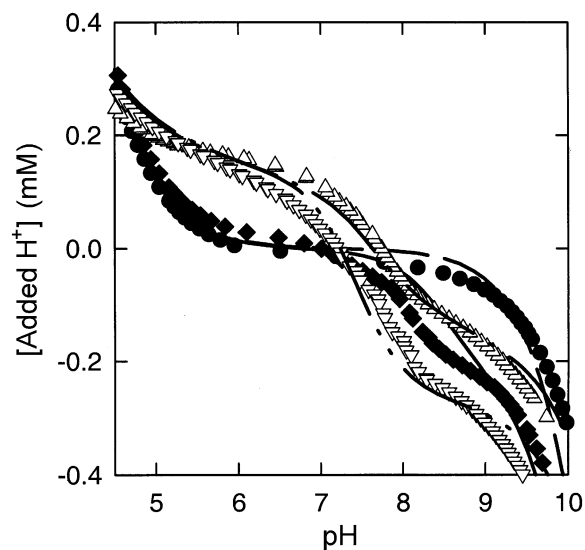

Figure 4. Acid-base titration data (symbols) and model fits (lines) of solutions containing: 1 mM aminotriazole (●) (——), 1 mM aminotriazole and 0.1 mM Zn(II) (◆) (− − −), and of systems for binary and ternary components containing: 0.1 mM aminotriazole in 3.14 g L^{-1} montmorillonite suspension either without (△) (— · —) or with 0.1 mM Zn(II) (▽) (— · · —). Model parameters are given in Tables 1 and 2.

Table 1. Single-component system parameters for adsorption of Zn(II) and 3-aminotriazole onto montmorillonite.

Total concentration of sites[a], SOH (mM), X^- (mM)	0.17, 1.25
Specific capacitance, C_{inner} (F m^{-2}), C_{outer} (F m^{-2})	7, 3
Solution concentration of Ca^{2+} (mM)	1.0
Constants for surface protonation-deprotonation[a]	$\log_{10} K$
$SOH + H^+ \rightleftharpoons SOH_2^+$	5.0
$SOH \rightleftharpoons SO^- + H^+$	-7.2
$(X^- - K^+) + H^+ \rightleftharpoons (X^- - H^+) + K^+$	2.2
$2(X^- - K^+) + Ca^{2+} \rightleftharpoons (X_2^{2-} - Ca^{2+}) + 2 K^+$	4.1
$SOH + Ca^{2+} \rightleftharpoons (SOCa)^+ + H^+$	-6.9
Constants for hydrolysis of Zn(II)[b]	
$Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+$	-8.96
$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$	-16.9
$Zn^{2+} + 3H_2O \rightleftharpoons Zn(OH)_3^- + 3H^+$	-28.4
Constants for dissociation of aminotriazole	
$L + H^+ \rightleftharpoons LH^+$	4.1
	(4.41)[c] (4.23)[d] (4.24)[e]
$L \rightleftharpoons L(OH)^- + H^+$	-10.4
	(-10.51)[c]

[a] Ikhsan *et al.* (2005)
[b] Baes and Mesmer (1976)
[c] Lenarcik *et al.* (1980), glass electrode, 0.5 M KNO$_3$, 25ºC
[d] Davarski *et al.* (1997), glass electrode, 0.1 M KNO$_3$, 25ºC
[e] Barszcz *et al.* (1989), glass electrode, 0.5 M KNO$_3$, 25ºC

DISCUSSION

pK$_a$ and complexation with Zn(II)

The physical constants (pK$_a$ and stability constants for aminotriazole-Zn(II) complexes) determined from titrations of 1 mM solutions of aminotriazole and aminotriazole plus 1 mM Zn(II) are similar to those reported in previous studies (Lenarcik *et al.*, 1980, Davarski *et al.*, 1997, Barszcz and Lenarcik, 1989). For systems containing aminotriazole and Zn(II), our modeling suggests that solution complexation between the two species is weak, the most significant complex having the stoichiometry Zn*L* (where *L* represents aminotriazole). Davarski *et al.* (1997) reported other complexes with stoichiometry Zn*L*$_2$ and Zn*L*$_3$, but we did not find that these were significant in the concentration ranges of metal and ligand used in our study. We have, however, included a complex of the form ZnOH*L*, which significantly improved the fit to the titrations in the pH region 7−10. The presence of such a complex is also supported by the ATR spectroscopy because the spectra of the AT-Zn(II) complexes at pH 6.0 and 8.5 are clearly different (Figure 1b). While it is possible that the spectral differences could be accounted for by the

Table 2. Binary- and ternary-component system constants for adsorption of Zn(II) and 3-aminotriazole onto montmorillonite.

Constants for solution complex formation	$\log_{10}$ K
$Zn^{2+} + L \rightleftharpoons (ZnL)^{2+}$	2.0
	(2.14)[a]
$Zn^{2+} + L \rightleftharpoons Zn(OH)L^+ + H^+$	-5.6
Constants for Zn(II) adsorption[b]	
$2(X^- - K^+) + Zn^{2+} \rightleftharpoons (X_2^{2-} - Zn^{2+}) + 2K^+$	4.3
$SOH + Zn^{2+} + H_2O \rightleftharpoons SOZnOH + 2H^+$	-10.3
Constants for 3-aminotriazole adsorption	
$[(X^- - K^+)]^0 + L + H^+ \rightleftharpoons [(X^- - LH^+)]^0 + K^+$	6.0
$3[(X^- - K^+)]^0 + 3L + 2H^+ \rightleftharpoons [(X^-)_3 - (LH^+)_2.L]^- + 3 K^+$	22.5
Constants for ternary complex formation	
$SOH + L + Zn^{2+} + H_2O \rightleftharpoons [(SOZn(OH)L)]^0 + 2H^+$	-7.4

[a] Davarski *et al.* (1997), glass electrode, 0.1 M KNO$_3$, 25ºC
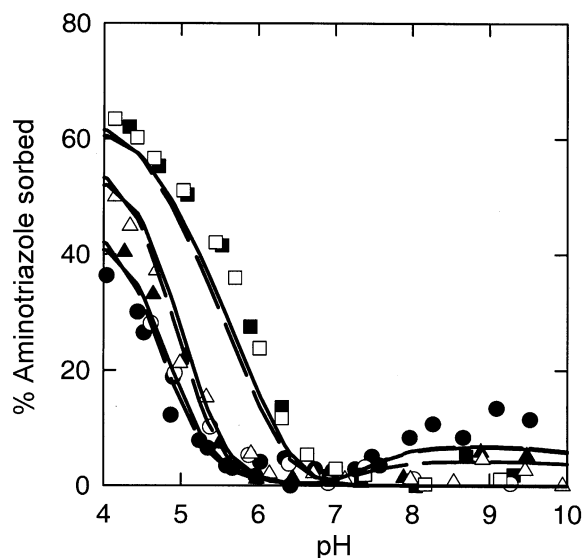[b] Ikhsan *et al.* (2005)

Figure 5. The sorption of various concentrations of aminotriazole onto 3.14 g L^{-1} montmorillonite as a function of pH in the absence (open symbols) and presence (closed symbols) of 0.1 mM Zn(II): 0.05 mM (circles), 0.1 mM (triangles), 1 mM (squares). The best fits from ECCM for the adsorption of aminotriazole in the absence of 0.1 mM Zn are represented by solid lines, and those in the presence of 0.1 mM Zn(II) by dashed lines.

Figure 7. Sorption isotherms for aminotriazole onto 3.14 g L^{-1} montmorillonite at pH 5.0 in the absence (closed symbols) and in the presence (open symbols) of 0.1 mM Zn(II). The lines are the best fits calculated by the ECCM the parameters of which are given in Tables 1 and 2. (− −) system without 0.1 mM Zn(II), and (− − −) with 0.1 mM Zn(II). The lines (· · · · ·) and (− · −) represent the species $[(X^--LH^+)]^0$ and $[(X^-)_3 \text{-}(LH^+)_2.L]^-$ respectively.

formation of ZnL_2 or ZnL_3 complexes, we think it unlikely because speciation calculations, based on literature stability constants, suggest that the concentrations of those species would be very low under the conditions used for our spectroscopic measurements.
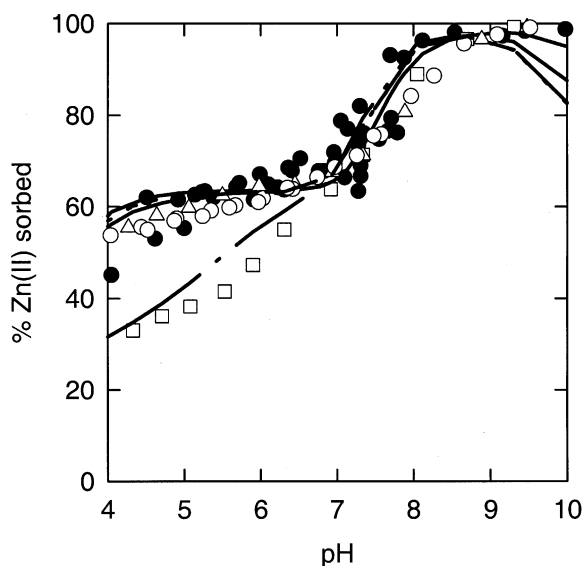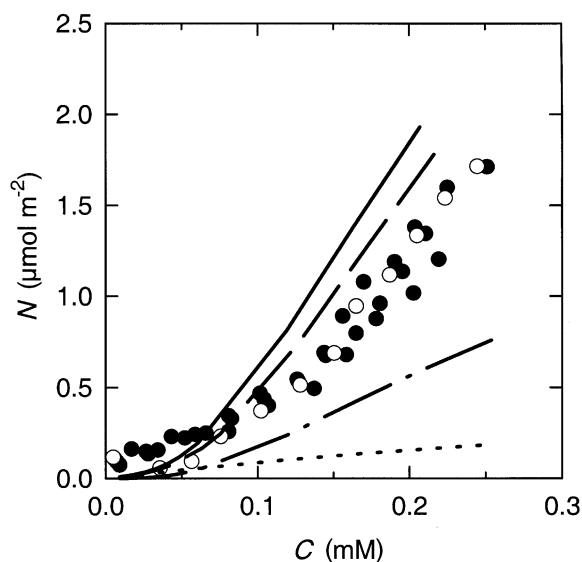

Figure 6. The effect of various concentrations of aminotriazole on the sorption of 0.1 mM Zn(II) onto 3.14 g L^{-1} montmorillonite as a function of pH: (●) 0 mM, (○) 0.05 mM, (△) 0.1 mM, (□) 1.0 mM. Lines are best fit from ECCM with parameters shown in Tables 1 and 2.

Aminotriazole sorption

The uptake of aminotriazole by montmorillonite was strongly pH dependent, and strongest below the pK_a of aminotriazole. This suggests that it is the aminotriazolium cation that sorbs, probably via a cation-exchange process with negative-charge sites on the clay. Further evidence for this mechanism comes from the sorption results for the ternary monmorillonite-AT-Zn(II) systems. It has been suggested previously by a number of workers (Stadler and Schindler, 1993; Undabeytia *et al.*, 1996; Bradbury *et al.*, 1999; Barbier *et al.*, 2000; Ikhsan *et al.*, 2005) that cation exchange is the dominant mechanism responsible for the uptake of metal ions, including Zn(II), at low pH on montmorillonite. In this study, the Zn(II) isotherms at pH 5.0 (Figure 8) show that Zn(II) uptake is suppressed by the presence of higher concentrations of aminotriazole. This suggests that there is competition between aminotriazole and Zn(II) for exchange sites. The ATR spectroscopy of these systems at low pH also indicates that the sorbed aminotriazole is in cationic form. Further, the sorbed and solution spectra at the same pH are virtually identical − the lack of band shifting or broadening in the sorbed spectrum suggests a weak electrostatic interaction with the surface. Strong chemical interactions with surfaces have been associated with significant shifts and changes in the spectra of the sorbing species (*e.g.* Boily *et al.*, 2000; Johnson *et al.*, 2004).

Based on the spectroscopic and sorption data, our model assumes an ion-exchange interaction with negative sites on the clay:

$$(X^- - K^+) + LH^+ \rightleftharpoons (X^- - LH^+) + K^+$$
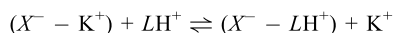
In the above reaction, we have written the exchanged ion as K^+ because the clay was K-saturated, but the exchange may involve H^+ at low pH, or Ca^{2+}, which was also found to be present in the suspensions. In assuming an exchange reaction, our model provided a good fit to the titration and sorption data in the binary and ternary systems.

This model for the uptake of aminotriazole by montmorillonite does not entirely agree with the assessment by Morillo *et al.* (1991) who suggested that in a Zn-montmorillonite system, aminotriazole sorbed as a polarized neutral molecule. This argument was based largely on IR spectroscopy of dried clay samples before and after sorption of aminotriazole. We think that our sorption data, particularly the fact that the sorption edge corresponds to the pH region where aminotriazole is cationic, and the ATR spectroscopy (using wet samples) are more indicative of a sorption mechanism that involves aminotriazole cations. Morillo *et al.* (1991) did note, however, that in the presence of ions of greater polarizing power (*e.g.* Fe^{3+}) aminotriazole was sorbed in cationic form. It is also worth noting that, although we suggest that cation exchange is the dominant mechanism, there was some evidence in the ATR spectroscopy that neutral aminotriazole was sorbed when the surface loading was high. Russell *et al.* (1968), using IR spectroscopy, also studied aminotriazole uptake by montmorillonite and concluded that sorbed aminotria-
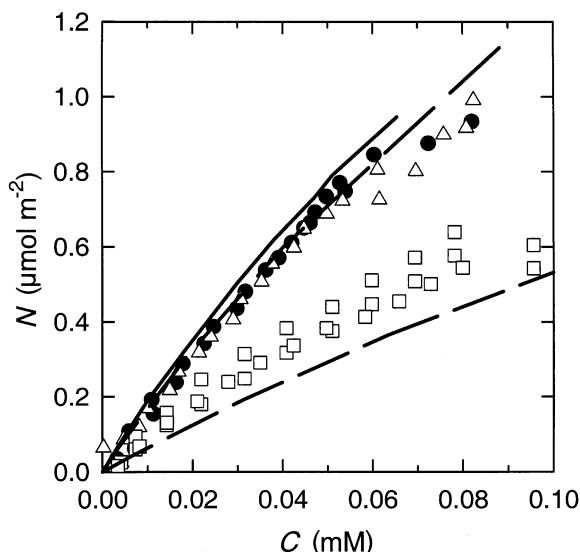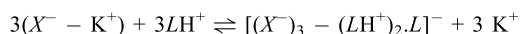
zole was protonated. Nearpass (1970), on the basis of sorption data, and particularly the sensitivity of aminotriazole uptake to salt concentration, also suggested a cation-exchange mechanism.

Cation-exchange sites on montmorillonite exist because of isomorphic substitution in silica sheets present on outer faces of the clay and in interlayer regions. Intercalation mechanisms are often characterized by slow kinetics and basal-spacing changes (*e.g.* Morillo *et al.*, 1991; Rytwo *et al.*, 1996; Akyüz *et al.*, 1999; Akyüz *et al.*, 2001; Gemeay *et al.*, 2002; Van Emmerik *et al.*, 2003). At lower aminotriazole concentrations, it is probable that aminotriazole sorbs predominantly to external exchange sites, as indicated by rapid sorption kinetics, and the fact that no measurable alteration of the basal spacing was observed. At higher aminotriazole loadings, however, our XRD data indicate interaction of aminotriazole in the interlayer regions of the clay as there is a significant reduction in the basal spacing at aminotriazole concentrations between 0.6 and 0.8 mM. Morillo *et al.* (1991) also observed a reduction in the basal spacing of montmorillonite after aminotriazole was sorbed. These workers suggested that the reason for the decrease was the loss of hydrating water molecules in the interlayer regions of the clay and the expulsion of solvated metal cations. The fact that we have observed an alteration in the basal spacing is strong evidence that aminotriazole interacts with interlayer regions of the clay.

The simple cation-exchange model outlined above accurately described aminotriazole uptake when the total aminotriazole concentration was low (<0.1 mM). Perhaps the most interesting aspect of our investigation, however, was the increased uptake of aminotriazole as the total concentration increased — a feature that has not been reported previously. This is clearly demonstrated by the upward curvature of the aminotriazole sorption isotherms at pH 5.0 (Figure 7). There is a number of possible explanations for this behavior. Firstly, the number of accessible sorption sites may increase as the aminotriazole concentration increases. Alternatively, there maybe a co-operative sorption mechanism, whereby the initial sorption of aminotriazole increases the probability of further triazole uptake. Another possibility is the formation of aggregates or clusters of aminotriazole molecules in solution or at the surface. When modeling this system, we found that the sorption data could not be explained by simply allowing for more sorption sites in the model. The best model fit to the sorption edges (at the three aminotriazole concentrations) and the isotherm data was obtained with a reaction that had the following stoichiometry:

Figure 8. Sorption isotherms for Zn(II) onto 3.14 g L^{-1} montmorillonite at a pH of 5.0 in the presence of various concentrations of aminotriazole: 0 mM (closed circles), 0.1 mM (open triangles), and 1 mM (open squares). The solid line represents the best fit calculated using the ECCM with the parameters in Tables 1 and 2 for the sorption with 0 mM aminotriazole, and dashed lines with 0.1 mM and 1 mM aminotriazole.

$$3(X^- - K^+) + 3LH^+ \rightleftharpoons [(X^-)_3 - (LH^+)_2.L]^- + 3 \; K^+$$

In the model, the $[(X^-)_3 - (LH^+)_2.L]^-$ consists of two protonated triazole molecules and one neutral molecule occupying two exchange sites. The speciation drawn in

Figure 7 shows that this species only becomes important at higher aminotriazole concentrations (>0.1 mM). We do not suggest that this is a definitive sorption mechanism, but the stoichiometry does support the hypothesis that aminotriazole sorbs in clusters or layers at higher concentration. The ATR spectroscopy (Figure 2) at high surface loading is consistent with a species of this type − the spectra show evidence that protonated and deprotonated aminotriazole coexist at the surface. The XRD data are also interesting at high triazole loading: an increase in basal spacing at 1.1 mM aminotriazole over that at 0.8 mM is suggestive of an increased occupation of the interlayer regions of the clay. Again, this observation is consistent with the formation of clusters or layers of sorbed molecules. Ainsworth *et al.* (1987) found that the sorption of neutral organic species increased as the surface coverage of organic cations increased. It was thought that sorbed organic cations modified the surface hydrophobicity of the clay to make sorption of neutral species more favorable. A similar mechanism was proposed by Angove *et al.* (2002) in a study where the presence of organic species at goethite and kaolinite surfaces were found to increase the uptake of anthracene. In a study of the sorption of nitrogen-containing heterocyclic compounds onto montmorillonite, Zachara *et al.* (1990) found that the neutral compounds were present on the surface only at high surface loading, indicating that surface modification of the clay played a role in the uptake of the neutral compounds. In our study, it is possible that the increased aminotriazole uptake at high surface loadings results from the initial sorption of cations which neutralize surface charge and provide a surface onto which neutral molecules can more favorably partition.

Sorption in the AT-Zn(II) ternary system

The sorption data, particularly the Zn(II) isotherm data (Figure 8), indicate that aminotriazole suppresses the uptake of Zn(II) by montmorillonite. This suppression might simply be the result of competition for exchange sites between cationic aminotriazole molecules and Zn^{2+}. Undabeytia *et al.* (1996), for example, concluded that competition from chlordimeform generally resulted in the suppression of Zn(II) and Cd(II) uptake by montmorillonite. Nearpass (1969) also noted that Na^+ and Ca^{2+} ions competed with aminotraizole for sorption sites, with Ca^{2+} competing more strongly. Another possibility is the formation of non-adsorbing AT-Zn(II) complexes. Wu *et al.* (2003) found that the Pb(II) uptake by montmorillonite was diminished as the concentration of EDTA and citric acids increased, and concluded that the presence of non-sorbing metal complexes was responsible for the reduction. Model calculations in our study suggest that the extent of complexation is insufficient to account for the suppression observed, suggesting that competition for exchange sites is the most likely explanation.

The more interesting feature of the sorption data obtained from the ternary systems is the enhancement of aminotriazole uptake in the presence of Zn(II) above pH 7 (Figure 5). Enhancement occurs across the pH region where, in binary systems, Zn(II) sorbs strongly to the clay but aminotriazole does not sorb at all. This points to a mechanism that involves sorption of aminotriazole onto the surface via a metal bridge. To model the Zn(II) sorption data in the presence of aminotriazole, we have used a complex with the following stoichiometry:

$$SOH + L + Zn^{2+} \rightleftharpoons [(SOZn(OH)L)]^0 + 2H^+$$
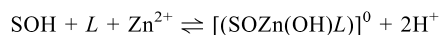
The model fitted the sorption data better when the ternary complex was modeled as an inner-sphere complex, [SOZn(OH)L], rather than as an outer-sphere species $[(SO^-)\text{-}(Zn(OH)L)^+]^0$, though our model cannot distinguish between the complexes [SOZnOHL] (L in the inner sphere) or [SOZnOH-L] (L in the outer sphere). We also tested models that allowed for sorption of $Zn(OH)L^+$ onto X^- exchange sites, but these could not fully account for the enhancement above pH 7. The form of the ternary complex is reasonable given that at higher pH, Zn(II) sorbs at variable charge (SOH sites) as an inner-sphere complex [SOZnOH] (Ikhsan *et al.*, 2005). The enhanced uptake of aminotriazole above pH 7 also corresponds to the pH region over which the $Zn(OH)L^+$ solution species forms, so it is perhaps not surprising that a surface species exists that has a similar stoichiometry to the solution species in the same pH range. However, given the abundance of permanent charge sites on the clay, the interaction of the ternary complex with X^- sites cannot be completely ruled out.

CONCLUSIONS

At low concentrations (<0.1 mM), 3-amino triazole sorbs onto montmorillonite predominantly as a cation. As the total concentration of aminotriazole increases, triazole appears to sorb in layers or clusters, with both cationic and neutral aminotriazole species present at the surface. Below pH 7, in ternary systems, Zn(II) and aminotriazole compete for cation-exchange sites on the clay; above pH 7, the formation of a ternary surface complex accounts for the observed enhancement of aminotriazole uptake when Zn(II) is present.

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