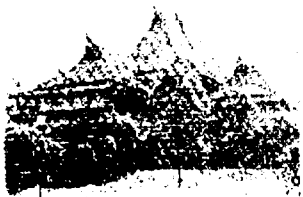*Faculty of Mathematics and Natural Sciences*
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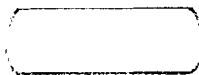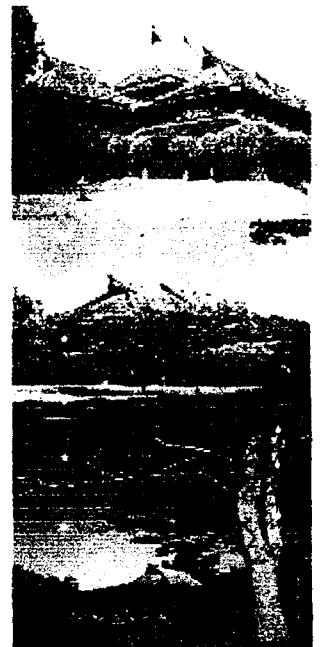
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Study of Reaction Mechanisms on the Adsorption of 9-Aminoacridine by Montmorillonite

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Abstract

Despite the adsorption of 9-aminoacridine (9-AA) to clay mineral montmorillonite has been investigated previously, the reaction mechanisms of the adsorption are still interesting to study. This research tries to describe the interaction between 9-AA and surface sites of montmorillonite by modeling experimental data using an extended constant capacitance surface complexation models (ECCMs).

Adsorption of 9-AA on K-saturated montmorillonite was measured at 30 °C with 5 mM KNO$_3$ as the background electrolyte. Three types of adsorption experiments; acid-base titrations, adsorption edges, and adsorption isotherms were carried out. Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD) measurements were also conducted to confirm ECCMs results.

ECCMs to the data of the adsorption experiments and FTIR data suggest that at low concentrations the 9-AA forms outer-sphere surface complexes with pH- dependently charged SOH sites on the edge of montmorillonite through hydrogen bonding, and with permanent- negatively charged sites (X$^-$) on the silica-like faces of the clay via cation exchange mechanisms. Adsorption isotherms are 'L' shaped at pH 4.0 and 's' shaped at pH 6.0. At pH 6.0, especially, the isotherms indicate a co-operative adsorption mechanism as the concentrations of the molecule increase because increasing the concentration of the dye might modify the clay to make binding of molecules with the surface more favorable. XRD data suggest that sorption occurs not only at external X$^-$ sites but also at those in the interlayer spaces.

I. Introduction

Montmorillonite crystals have two different regions which have been implicated in adsorption. 1), 2). The external regions (faces plus edges) carry both permanent negatively charged (X$^-$) sites and sites with pH-dependent charges SOH. The interlayer region has permanent negatively charged sites resulting from isomorphous substitution, which may be compensated by hydrated interlayer cations.

9-AA can sorb either to external active sites or in the interlayer space of montmorillonite as aminopyridines can. 3). Intercalation of cations or organic species into the interlayer space of 2:1 clay minerals like montmorillonite is known to change the basal spacing of the clays 4). Adsorption of organic molecules to montmorillonite can decrease, 5), increase, 4), or leave the basal spacing of the clay unchanged. 2). Thus determination of such changes by XRD can provide qualitative information on the type of the interaction between the organic molecule and montmorillonite.

The interaction of organic molecules and surface of clay minerals can also be identified by FTIR measurements. This research combines adsorption, FTIR spectroscopic, XRD and surface complexation modeling investigations to deduce the mode of interaction between 9-AA and montmorillonite.

II. Experimental Methods

All sorption experiments were conducted at a constant temperature of 30 °C in thermostated vessels. The background electrolyte was 5 mM KNO$_3$. In experiments with montmorillonite suspensions the surface area of the montmorillonite was 100 m^2 L^{-1}.

Acid-base titrations were conducted on montmorillonite suspensions without, and with, added 100 μM 9-AA. Montmorillonite was equilibrated in water at its natural pH for overnight and then, if necessary, 9-AA was added to give a final concentration of 100 μM 9-AA. The pH of the system then was raised to about 10.0 by addition of 0.100 M KOH, and the suspensions was titrated back with 0.100 M HNO$_3$ to about pH 4.0. Successive additions of HNO$_3$ were made only after the pH drift was less than 0.1 mV min^{-1} which is usually reached in 30 min.

Adsorption edge experiments measured the effect of pH on the adsorption 100 μM 9-AA on montmorillonite. Montmorillonite suspensions were pre-equilibrated overnight at their natural pH, and then the pH increased to 10 using KOH. After 30 min an aliquot of 9-AA was added giving a total concentration of 100 μM. After a further 30 min a 7 mL sample was transferred into a centrifuge tube, and capped. The pH of the stock solution was decreased in steps, and further 7 mL samples taken after 30 min equilibration at each pH. All the samples were then shaken for 2 d and centrifuged. The supernatant solution were then analyzed for free 9-AA.

Adsorption isotherms describing the effect of 9-AA concentration on adsorption were conducted at pH 4.0 and 6.0. The 9-AA concentration was increased in steps from 1 μM to 500 μM by addition of a stock solution whose pH had been adjusted to pH 4.0 or 6.0. After each addition the system was equilibrated for 2 h, with the pH maintained by addition of KOH or HNO₃, before a 7 mL sample was transferred to a centrifuge tube, and capped. All the samples were then shaken for 2 d, and the pH remeasured before they were centrifuged, and the supernatant solution analyzed for 9-AA.

III. Results and Discussions

A. Results

FTIR spectra

Infrared spectra indicates the availability of –NH functional groups on the surface as shown by specific absorption of heterocyclic rings at wavenumbers of about 1590 and 1640 cm⁻¹. The absorption of secondary amine at 3286.5 cm⁻¹, C=N in 1479 – 1502.4 cm⁻¹, and C-N stretching at 1371.3 cm⁻¹ are also obvious evidences of sorbed 9-AA on the surface of montmorillonite, but the adsorption does not shift absorption bands of SiO in wavenumbers of 453, 794, and 1022 cm⁻¹.

XRD Diffractogram

The c-axis spacing for montmorillonite in the absence of 9-AA was 13.23 Å, and changed into 15.07 Å in the presence of 0.01 M 9-AA (graphs are not shown).

Adsorption experiments and modeling

The surface complexation model was developed to determine reaction mechanisms by considering spectroscopic data and by fitting adsorption edges, adsorption isotherms and titration data using a computer software GRFIT. 6). The model parameters for the adsorption

reactions are given in Table 1. The fit of the model to the adsorption and titration data is shown in each of the Figures. Fig. 1 gives the titration data for solution of 0.01 M 9-AA and for suspensions containing 100 m² L⁻¹ montmorillo-nite without and with 0.1 mM 9-AA.

Adsorption edges describing the effect of pH on the uptake of 9-AA by montmorillonite is shown by the data in Fig. 2. Adsorption of 9-AA with initial concentration smaller than 0.1 mM was strong in low pH values (below 6.5). As the pH increased the amount of adsorbed 9-AA decreased. Fig. 2 also show that when the total concentration of 9-AA increased the uptake of 9-AA increased dramatically in high pH, but did not change in low pH values.

Adsorption isotherms at pH 4.0 and 6.0 are shown in Fig. 3. At pH 4.0 the amount of adsorbed 9-AA is high until a plateau is reached. On the other hand, at pH 6.0 the isotherm data show non-Langmuirian behavior indicating greater amounts of the 9-AA adsorbed as the total 9-AA concentration was increased.

Table 1. Surface complexation model parameters for adsorption of 9-AA by montmorillonite

| Sites Concentration	
SOH / mmol m⁻²	0.0069
X⁻ / mmol m⁻²	0.0112
Inner capacitance (F m⁻²)	3
Outer capacitance (F m⁻²)	7
Equilibrium constants, log₁₀ K, for site protonation and deprotonation reactions	
1) $SOH + H^+ \rightleftharpoons SOH_2^+$	2.400
2) $SOH \rightleftharpoons SO^- + H^+$	-6.640
3) $[X^- - K^+]^0 + H^+ \rightleftharpoons [X^- - H^+]^0 + K^+$	6.558
Equilibrium constants, log₁₀ K, for 9-AA (L) protonation and deprotonation reactions	
4) $L + H^+ \rightleftharpoons LH^+$	2.382
5) $L + OH^- \rightleftharpoons L(OH)^-$	-9.271
Equilibrium constants, log₁₀ K, for surface complex formation	
6) $[X^- - K^+]^0 + 3L + 2H^+ \rightleftharpoons [(XLH)^0 - (LH.L)^-]^- + K^+$	19.637
7) $SOH + 2L + 2H^+ \rightleftharpoons [(SOH)^0 - (LH^+)_2]^{2-}]^{2-}$	21.373
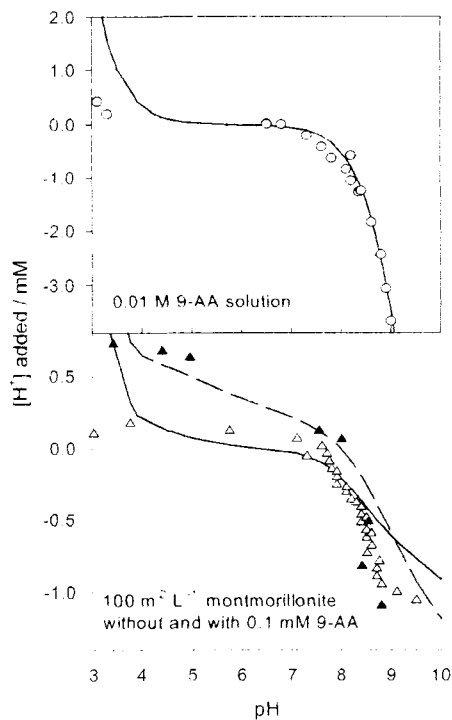
Fig. 1. Acid-base titrations of singly and binary systems. The symbols are experimental data: ( ) 9-AA solution only. (▲) montmorillonite suspension only. and (△) montmorillonite with 9-AA. The lines are calculated by ECCMs with parameters from Table 1.

B. Discussion

General Observation

The greater basal spacing of montmorillonite due to the adsorption of 0.01-M 9-AA shows the importance of cation exchange sites (X sites) in interlayer regions of montmorillonite for adsorption of 9-AA. A previous investigation on adsorption of 2-aminopyridine by montmorillonite proposed that basal spacing of montmorillonite that adsorbed 2-aminoprydine increased dramatically because the molecules are arranged with the plane of the ring approximately perpendicular to the silicate layer. However, the adsorption was reported primarily onto external sites (SOH on the edges of crystals) based on rapid adsorption and desorption rate. Significant role of external SOH sites for the adsorption was also shown by infrared spectra from which adsorbed –NH functional groups identified on the surface, but the adsorption does not shift the bands of adsorbed species meaning that the interaction involves outer-sphere complex formation because the interaction involves weak chemical bond. Strong chemical interactions with surfaces have been associated with significant

shifts and changes in the spectra of the sorbing species. 8). Therefore, it was not surprising that adsorbed 9-AA can desorb from the surface of montmorillonite rapidly. 9).
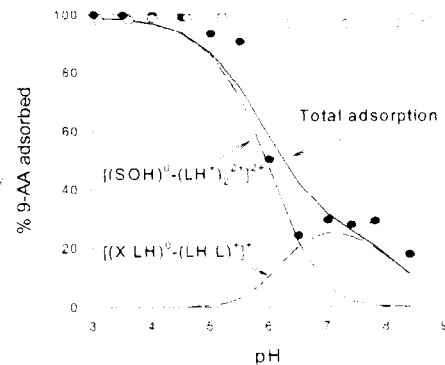

Fig. 2. The effect of pH on the adsorption of (●) 0.1 mM and ( ) 1 mM 9-AA by montmorillonite. The lines are calculated using ECCMs with parameters listed in Table 1.
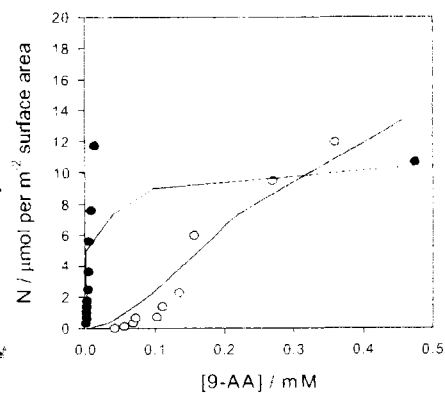

Fig. 3. The effect of 9-AA concentration on the adsorption of 9-AA by montmorillonite at (●) pH 4. and ( ) pH 6.0. The lines are the best fit calculated by ECCMs with parameters given in Table 1.

On the other hand, the fact that the concentration of 0.01 M 9-AA can increase the basal spacing of 1.84 Å is evidence that significant amount of 9-AA are intercalated when their initial total concentrations are high.

Surface Complexation Model to Study Adsorption Process

ECCMs was firstly done to titration data of singky and biary systems. The model fit very well to experimental data as represented by the

lines in Fig. 1 whose parameters are listed in Table 1. The parameters are then used as fixed parameters for modeling adsorption edges and isotherms data which also produced very well fit (Figs. 2 and 3).
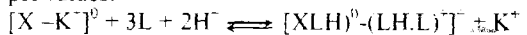
The uptake of 0.1 mM 9-AA by montmorillonite was strongly pH dependant, and strongest below the pK_a of 9-AA, suggesting that it is the 9-AA cation that adsorbs. The model suggest the adsorption at low pH follows reaction:
$$SOH + 2L + 2H^- \rightleftharpoons [(SOH)^0-(LH^-)_2^{2-}]^{2-}$$

The reaction suggests that 9-AA cation forms outer-sphere complex with external SOH sites on the edges of montmorillonite through hydrogen interactions. Fig. 2 shows the fraction of 9-AA adsorbed from total concentrations 0.1 mM and 1 mM are about 97%. Increasing concentration of 9-AA requires more surface sites to adsorb, that will result in decreasing the fraction of 9-AA that is able to adsorb. In fact, the fraction of 9-AA does not decrease indicating formation of 9-AA clusters in solution before interacting the surface. Isotherms data at pH 4.0 also support the assumption with very high adsorptive capacity of surface sites. Further evidence for this mechanism comes from very rapid kinetic sorption reported previously. 9).

The speciation drawn in Fig. 2 shows that $[(SOH)^0-(LH^-)_2^{2-}]^{2-}$ complex exist predominantly at low pH and responsible for most total adsorption of 9-AA.

Model also assumes an ion exchange interaction with negative sites on the clay at high pH values:
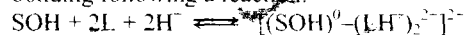$$[X^--K^-]^0 + 3L + 2H^- \rightleftharpoons [XLH)^0-(LH.L)^-]^- + K^+$$
In the above reaction we have written the exchanged ion as K^- because the clay was potassium saturated. Cation exchange sites on montmorillonite exist in silica sheets present on outer faces of the clay and in interlayer regions. XRD data indicate interaction of 9-AA also in the interlayer regions of the clay, as there is a significant increase in the basal spacing in the loadings of 0.01 M 9-AA. Fig 2 shows that $[XLH)^0-(LH.L)^-]^-$ complex exist at high pH. This species becomes more important at higher 9-AA concentrations.

The most interesting aspect of our investigation was the increased uptake of 9-AA at high pH as the total concentration increased. This is clearly demonstrated by the upward curvature of the 9-AA adsorption isotherms at pH 6.0 (Fig. 3). There is a number of possible explanations for this behavior. Firstly, the number of accessible sorption sites may increase as the 9-AA concentration increases. Alternatively, there

maybe a co-operative sorption mechanism, whereby the initial sorption of 9-AA increases the probability of further 9-AA uptake. Another possibility is the formation of aggregates or clusters of 9-AA 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 stoichiometry does support the hypothesis that 9-AA sorbs in clusters or layers at higher concentration.

IV. Conclusion

9-AA adsorbs montmorillonite by forming an outer sphere complexes with pH-dependently charged sites through hydrogen bonding following a reaction:
$$SOH + 2L + 2H^- \rightleftharpoons [(SOH)^0-(LH^-)_2^{2-}]^{2-}$$
and with permanent negatively charged sites both on faces and interlayer regions via cation exchange reaction:
$$[X^--K^-]^0 + 3L + 2H^- \rightleftharpoons [XLH)^0-(LH.L)^-]^- + K^-$$
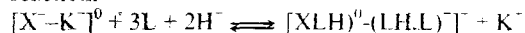
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