

A NUCLEAR MAGNETIC RESONANCE (NMR) AND FOURIER-TRANSFORM INFRARED (FTIR) STUDY OF GLYCINE SPECIATION ON A Cd-RICH MONTMORILLONITE

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Abstract—As a consequence of treatments with glycine solutions, glycine molecules enter the interlayer of both Ca- and Cd-rich montmorillonite. Measurements of d value suggest that at low glycine concentration (0.01 and 0.1 M glycine solutions) a “flat” arrangement of the glycine molecules occurs in the interlayer. In contrast, intercalation of more than one monolayer of glycine molecules occurs for the montmorillonite treated with a higher concentration of glycine (1 M glycine solution).

Interlayer complexation of glycine occurs only for the Cd-rich form of montmorillonite, whereas no complexation is observed for Ca-rich montmorillonite. Both nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) results suggest that the adsorbed glycine, which fully protonates in the interlayer of montmorillonite to give the GlyH_2^+ species, interacts with the interlayer Cd^{2+} to form the CdGly_x complex mainly through the carboxylate group. The interlayer cadmium, present as both Cd^{2+} and CdCl^+ , is complexed by the ligand glycine. In contrast, the cadmium adsorbed on the external surfaces of montmorillonite does not interact with the ligand. Complexation of CdCl^+ only occurs for large amounts of adsorption of glycine (e.g., for samples treated with 1 M glycine solution).

Key Words—Adsorption, Amino Acids, Cadmium, Glycine, Montmorillonite, Speciation.

INTRODUCTION

Among the inorganic constituents of soils, the clay minerals have the greatest adsorption capacity. The tetrahedral and/or octahedral sheets of the expandable clay minerals have negative charge which is balanced by exchangeable or charge-balancing cations. Organic and inorganic pollutants (e.g., large organic molecules such as atrazine and heavy metals such as Cd, Pb, and Hg) can easily exchange for innocuous elements, such as Ca or Na, from the interlayer of the expandable clay minerals. The intermolecular interactions of organic pollutants with clay-mineral surfaces are expected to be crucial in chemical/biological transformations, transportation, and retention of these contaminants (e.g., Inskeep and Baham, 1983; Siantar *et al.*, 1994; Singh *et al.*, 1996).

The interaction of heavy metals with sediments seems to be controlled by the nature and properties of the sediments, pH, and by ionic factors, including the presence of organic ligands (Stumm and Morgan, 1981; More and Ramamoorthy, 1984). Metal-organic complexes may be largely adsorbed on clay minerals if the organic ligands show affinity for the mineral surfaces. Conversely, speciation may hinder or prevent adsorption if the complexing ligands form strong complexes with metals and if these complexes do not adsorb on the mineral (Solomon and Forstner, 1984). The formation of metal-organic complexes in natural waters is strongly pH dependant (Stumm, 1992).

Glycine is an organic ligand commonly present in natural water systems and it may enhance the rate of

heavy metal adsorption by kaolinite and montmorillonite (Singh *et al.*, 1996). Barrie *et al.* (1993) and Gyani (1994) studied the complexation of cadmium with glycine. Glycine complexation, mainly occurring through oxygen and nitrogen donor groups ($-\text{COOH}$, $-\text{NH}_2$), may be used to reduce the toxicity of Cd by complexing it into a form that is innocuous (Croten *et al.*, 1992).

The object of this study was to investigate, under laboratory conditions, the intermolecular interaction of the organic molecule glycine with montmorillonite surfaces as well as the synergistic effect of the retention by the clay mineral of both the organic molecule and the highly toxic heavy metal cadmium. Data from solid-state nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR) spectroscopy, and X-ray diffraction is used to provide an understanding of the glycine speciation on montmorillonite.

EXPERIMENTAL

Clay preparation

The clay used is a naturally occurring Mg- and Ca-rich montmorillonite obtained from English China Clay, St. Austell, Cornwall (Westone L or WL). The measured cation-exchange capacity (CEC) is 77 meq/100 g (using a modified method based on Chapman, 1965). The sample has a low Fe content (0.8 wt. % Fe_2O_3) and thus there is no NMR line broadening or variation in chemical shift owing to ferromagnetic impurities, especially relating to Fe^{3+} (Bank *et al.*, 1989).

Clay purity was determined by X-ray diffraction (XRD) analysis (Siemens D5000, $\text{CuK}\alpha$ radiation,

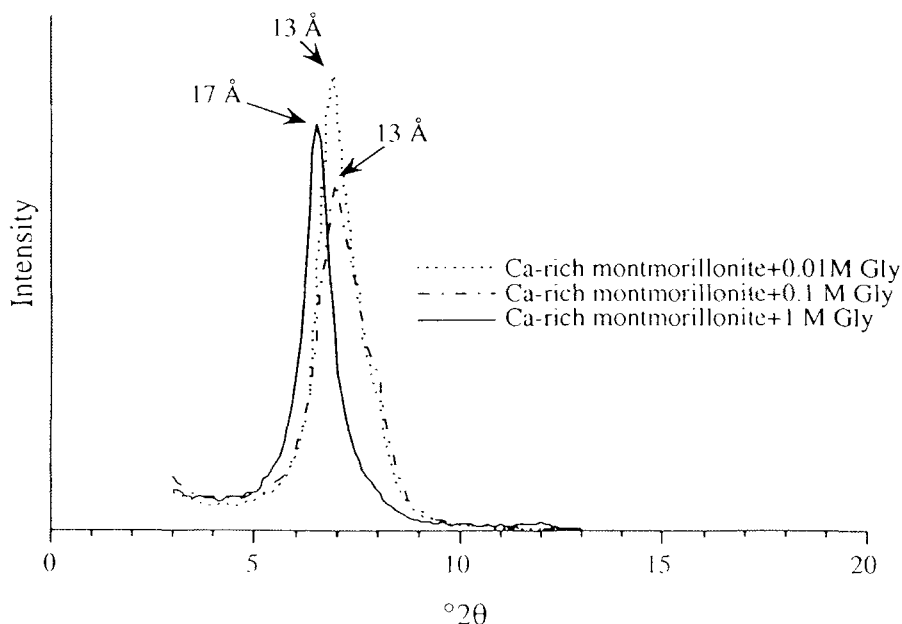


Figure 1. X-ray diffraction patterns of Ca-rich montmorillonite showing the changes of the $d(001)$ values as the sample is treated with 0.01, 0.1, and 1 M Gly solutions.

graphite secondary monochromator, sample spinner). The $d(001)$ of the untreated clay was $\sim 15.1 \pm 0.3$ Å. Brown and Brindley (1980) reported a similar spacing for a Ca-rich montmorillonite at 53% R.H. (relative humidity), corresponding to two layers of H_2O molecules in the interlayers.

To determine whether Ca or Mg is the interlayer cation in the WL montmorillonite, the Green-Kelly test (1953a) was used. This test differs from the Green-Kelly test (1953b) commonly used to distinguish between beidellite and montmorillonite, and there is no Li saturation. The sample is pre-heated to 430°C and treated with glycerol for several hours. At this temperature, a single-layer glycerol complex of $d(001) = 9.5$ Å occurs if the interlayer cation is Li or Mg, whereas a two-layer glycerol complex of $d(001) = 17.8$ Å is formed for interlayer cations of Na, Ca, Sr, La, K, or Ba. The observed d value for the WL montmorillonite after testing was 17.7 Å, implying that the interlayer cation was Ca.

The Westone L montmorillonite was first calcium exchanged (van Olphen, 1977) and ~ 0.5 g of this montmorillonite was treated, respectively, with 30 mL of 0.01, 0.1, and 1 M glycine solutions (1.6, 16, and 160× the CEC of the montmorillonite) at neutral pH and room temperature for 24 h. The Cd-exchanged form of Westone L (obtained treating 2 g of the Ca-exchanged montmorillonite with 50 mL of 1 M $CdCl_2$ solution) was also treated with 30 mL of 0.01, 0.1, and 1 M glycine solutions at neutral pH and room temperature for 24 h. In the recovered solutions, Cd was

detected by atomic absorption spectroscopy (AAS) using a Model 5100 Perkin-Elmer spectrometer.

Spectroscopic analyses

^{13}C and ^{113}Cd solid-state NMR spectra were recorded on a Bruker MSL-300 spectrometer using single pulse excitation (SPE), cross polarization (CP), magic angle spinning (MAS), and dipolar decoupling (DEC). The relevant experimental parameters are: spinning speeds 4–5 kHz; contact time 10–12 ms; proton decoupler power level 55 kHz; and recycle delays of 1 and 4 s. To minimize interferences from spinning side bands for some spectra, a total sideband suppression (TOSS) was used. The CP sequence incorporated a 90° proton flip-back pulse immediately after the acquisition period to reduce the recycle delay necessary between scans. All MAS and CP-MAS NMR spectra were recorded on samples equilibrated at room humidity and are referred to 0.1 M $Cd(ClO_4)_2$ solution (Nolle, 1978).

FTIR spectra were recorded on a Mattson Polaris instrument in the range of 400–4000 cm^{-1} using KBr discs (2 mg of sample to 200 mg of KBr) at 4 cm^{-1} resolution and 32 scans.

RESULTS

Powder XRD patterns for Ca- and Cd-exchanged montmorillonite treated with glycine solutions suggested that the glycine molecules enter the interlayers of montmorillonite: the $d(001)$ occurs at 15.26 Å (untreated Ca- and Cd-rich montmorillonite) and then oc-

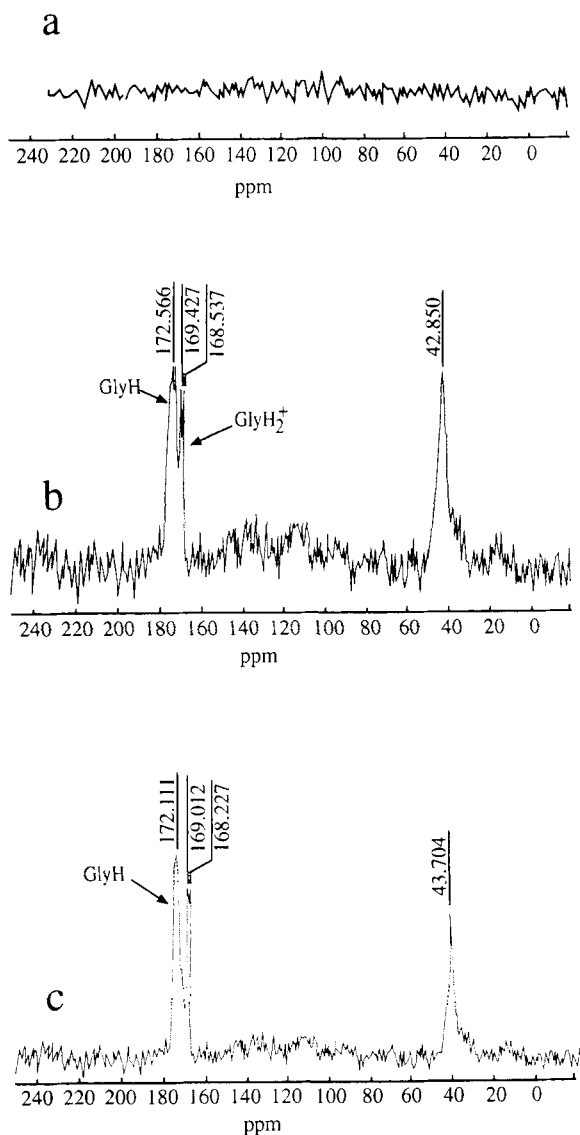


Figure 2. ^{13}C CP-MAS NMR spectra of Ca-rich montmorillonite treated with a) 0.01, b) 0.1, and c) 1 M Gly solutions.

curs at 13.35 \AA after the sample is treated with 0.01 and 0.1 M glycine solutions. For both Ca- and Cd-rich montmorillonite treated with 1 M glycine solution, the most concentrated solution, the $d(001)$ is 17 \AA (Figure 1).

The sample treated with 0.01 M glycine solution shows no ^{13}C CP-MAS NMR signal (Figure 2a), whereas samples treated with 0.1 and 1 M glycine solutions show two ^{13}C CP-MAS signals (Figure 2b and 2c) occurring at 172 and 168–169 ppm.

^{13}C CP-MAS and ^{113}Cd CP-MAS NMR spectra were recorded for the Cd-rich montmorillonite treated with glycine solutions (Figures 3 and 4; Tables 1 and 2). The Cd-rich sample treated with 0.01 M solution shows a ^{13}C CP-MAS NMR signal (Figure 3a) and the

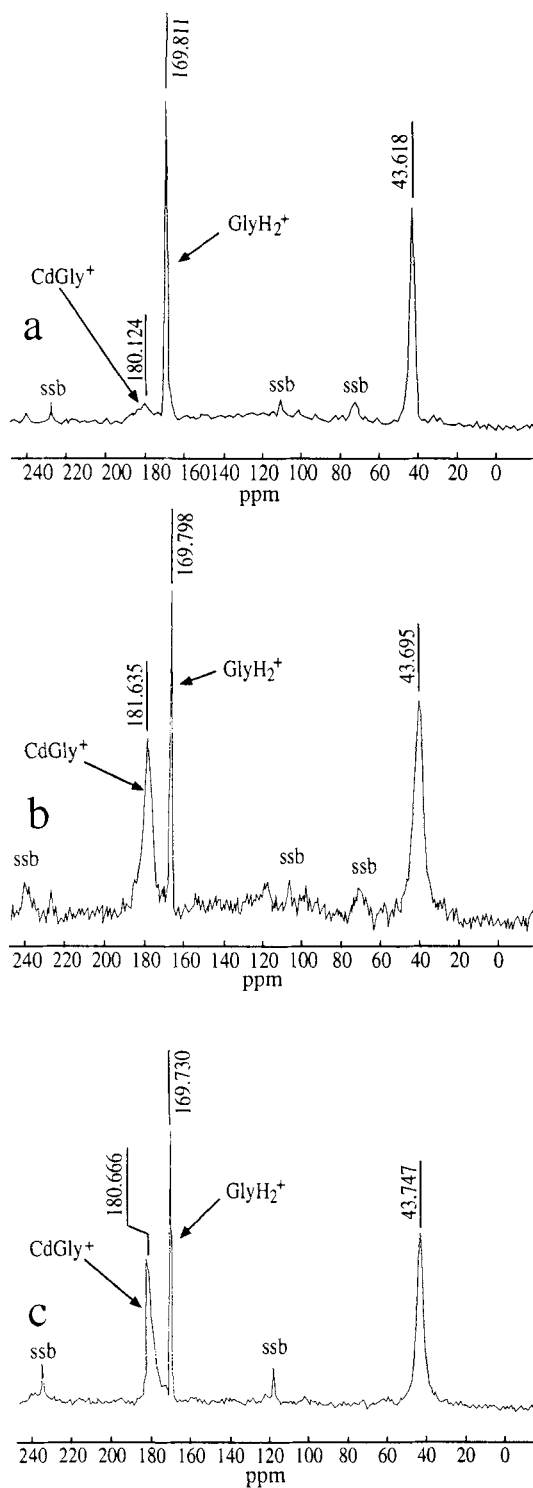


Figure 3. ^{13}C CP-MAS NMR spectra of Cd-rich montmorillonite treated with a) 0.01, b) 0.1, and c) 1 M Gly solutions; ssb indicates spinning side bands.

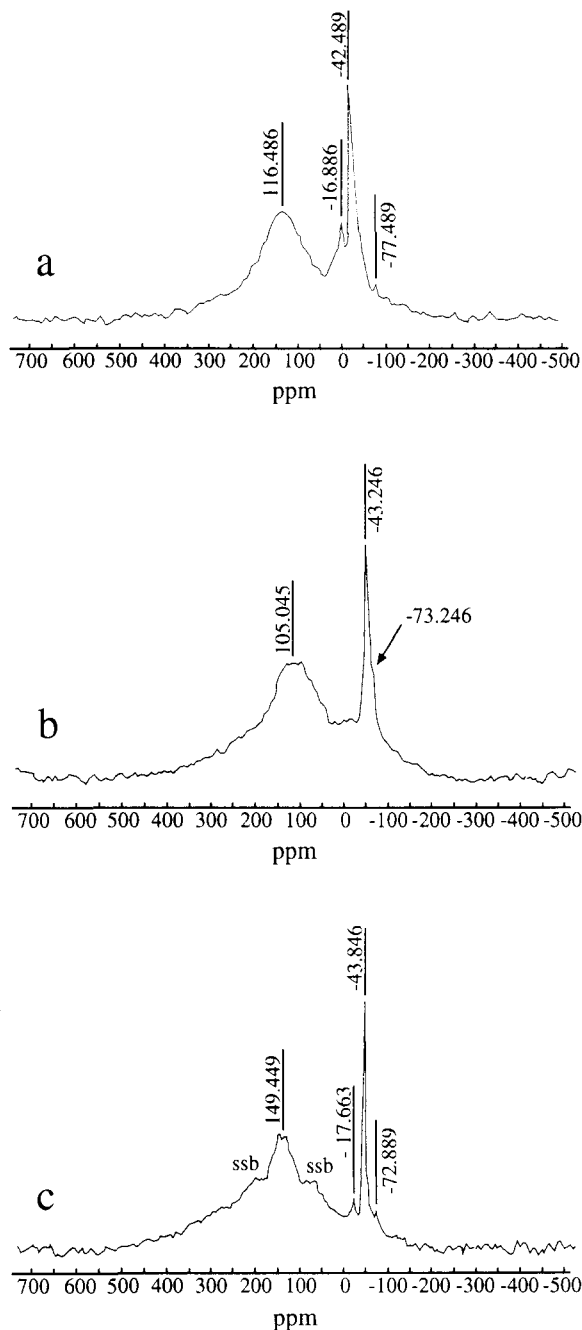


Figure 4. ^{113}Cd MAS NMR spectra of Cd-rich montmorillonite treated with a) 0.01, b) 0.1, and c) 1 M Gly solutions; ssb indicates spinning side bands.

^{13}C CP-MAS spectra of the sample treated with 0.01, 0.1, and 1 M glycine solutions exhibit a peak at ~ 181 ppm (Figure 3), which is not observed in the ^{13}C CP-MAS of the glycine-treated Ca-rich montmorillonite. ^{113}Cd MAS NMR spectra show three different peaks occurring, respectively, at ~ 116 , ~ -16 , and ~ -43 ppm (Figure 4). As more glycine is adsorbed on the

Cd-exchanged montmorillonite, changes in the intensities of the peak occurring at ~ -16 ppm are observed. In contrast, the ~ -43 -ppm peak intensities remain the same. Further, in the spectrum of Figure 4c a relevant shift of the resonance line occurring at ~ 116 ppm, which shifts to 150 ppm, can be observed.

For the FTIR spectra, the frequency of the band relative to the carboxylate functional group of glycine changes as the amount of glycine in the solutions used to treat the Cd-rich montmorillonite increases (Figure 5). The C=O asymmetrical stretching band occurring at a frequency of 1520 cm^{-1} for uncomplexed glycine in aqueous solution (Gyani, 1994, and references therein) occurs at progressively higher frequencies (1591 cm^{-1}) as the concentration of glycine increases. Changes are also observed in the C-O symmetric stretching band, but not for the $-\text{NH}_3^+$ band, which occurs at 1629 cm^{-1} as in uncomplexed glycine in aqueous solution (Gyani, 1994, and references therein). The symmetric C-O stretch at $\sim 1330\text{ cm}^{-1}$ is absent for the Cd-rich montmorillonite treated with 0.01 and 0.1 M glycine solutions but occurs in the IR spectrum of the sample treated with 1 M glycine solution. No relevant changes are observed for the IR band relative to both the carboxylate functional group and the amine group in the Ca-rich montmorillonite treated with 0.01, 0.1, and 1 M glycine solutions.

DISCUSSION

In aqueous solution, glycine speciation is pH dependent: glycine (Gly) exists predominantly in its zwitterionic form ($\text{H}_3\text{N}^+-\text{CH}_2-\text{COO}^-$; hereafter GlyH) between pH 4–8.5. However, in acidic solutions (pH ~ 4.0), glycine becomes fully protonated ($\text{H}_3\text{N}^+-\text{CH}_2-\text{COOH}$; hereafter GlyH $_2^+$) whereas at pH > 8.5 the GlyH species deprotonates to form the free ligand Gly $^-$ ($\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$). In the presence of Cd, speciation is affected and cadmium complexes with glycine above pH 6.0 to form CdGly $^+$ and subsequently, the more complex species CdGly $_2$ (Figure 6). Complexation may also occur even at low pH (pH ~ 2).

As indicated by changes in d value, the glycine molecules enter the interlayer of the montmorillonite (Figure 1). The $d(001)$ of a Ca-rich montmorillonite equilibrated at room humidity is $\sim 15.3\text{ \AA} \pm 0.3$ (Brown and Brindley, 1989) whereas a $d(001)$ of $\sim 13\text{ \AA}$ was observed for a “flat” arrangement of a monolayer of n -alkylammonium (n -dodecyl-ammonium) in the interlayer of montmorillonite (Lagaly and Weiss, 1969). The $d(001)$ of 13 \AA observed for the Ca-montmorillonite treated with both 0.01 and 0.1 M glycine solutions suggests a flat arrangement of glycine molecules in the interlayer at low glycine concentration. In contrast, the higher $d(001)$ observed for the montmorillonite treated with the 1 M glycine solution (17 \AA) suggests that the concentration of intercalated glycine is higher than that in the Ca-rich montmorillonite treat-

Table 1. ^{13}C chemical shifts.

	Carboxylate peak ppm	α -carbon ppm
Zwitterionic form of glycine in solution (GlyH) ¹	173	44
Fully protonated glycine in solution (GlyH ₂ ⁺) ¹	169	44
Cd-glycinate complex ¹	178	44
Ca-montmorillonite treated with 0.01 M Gly solution	no signal	no signal
Ca-montmorillonite treated with 0.1 M Gly solution	172; 169–168	43
Ca-montmorillonite treated with 1 M Gly solution	172; 169–168	44
Cd-montmorillonite treated with 0.01 M Gly solution	180; 169	43
Cd-montmorillonite treated with 0.1 M Gly solution	182; 169	43
Cd-montmorillonite treated with 1 M Gly solution	180; 169	43

¹ Gyani (1994).

ed with 0.01 and 0.1 M glycine solutions, and may be interpreted as intercalation of more than one monolayer of glycine molecules (Lagaly and Weiss, 1969).

At the pH used for the treatments (pH 7), the glycine species present in solution is the zwitterionic form GlyH, as indicated by the speciation diagram (Figure 6). However, as the ^{13}C CP-MAS NMR spectra of Cd-rich montmorillonite treated with glycine solutions indicate (Figure 2), once the GlyH molecules are in the interlayer of the montmorillonite they become fully protonated. The GlyH and GlyH₂⁺ species are both present in Ca-rich montmorillonite. This result is suggested by the presence of both the carboxylate-carbon peak at 169 ppm, attributed to fully protonated glycine in aqueous solution and indicative of ligand protonation (Gyani, 1994), and of the carboxylate-carbon peak at 172 ppm, which is typical of the zwitterionic form of glycine. The protonation of the glycine molecules in the interlayer is related to the higher acidity of the interlayer H₂O compared to the bulk water in montmorillonite (Sposito, 1989). Various techniques, such as conductivity measurements (Fripiat *et al.*, 1965), NMR (Ducros and Dupont, 1962; Hetch *et al.*, 1966), and adsorption of inorganic and organic bases (Mortland *et al.*, 1963; Mortland, 1970) indicated that the degree of dissociation of adsorbed H₂O on montmorillonite is seven orders of magnitude greater than that of bulk water. Assuming that the only source of H⁺ ions in the interlayer of Ca-rich montmorillonite is the adsorbed H₂O, interlayer pH is estimated to be ~3.5. In this acidic condition, according to Figure 6, glycine molecules will become fully protonated. The ratio between the two species GlyH₂⁺/GlyH is estimated at 1:10 for a pH of 3.5 on the basis that the

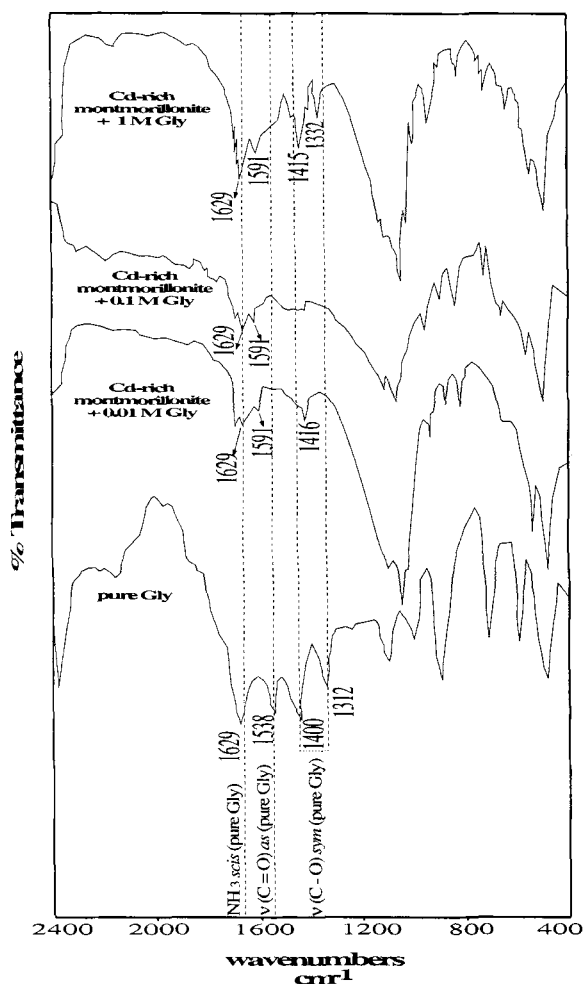


Figure 5. FTIR spectra of Cd-rich montmorillonite treated with 0.01, 0.1, and 1 M Gly solutions. NH₃ sciss (*scis*) frequencies (cm⁻¹): 1629 pure Gly, 1629 for Cd-rich montmorillonite + 0.01 M Gly, + 0.1 M Gly, + 1 M Gly. ν(C=O) asymmetrical (*as*) frequencies (cm⁻¹): 1538 pure Gly, 1591 for Cd-rich montmorillonite + 0.01 M Gly, + 0.1 M Gly, + 1 M Gly. ν(C-O) symmetrical (*sym*) frequencies (cm⁻¹): 1400 and 1312 pure Gly, 1415 and 1332 for Cd-rich montmorillonite + 0.01 M Gly, 1416 and 1312 for Cd-rich montmorillonite + 1 M Gly.

Table 2. ^{113}Cd chemical shifts.

	σ_{iso} (no Gly) ¹ ppm	σ_{iso} (0.01 M Gly) ppm	σ_{iso} (0.1 M Gly) ppm	σ_{iso} (1 M Gly) ppm
Surface Cd ²⁺	116	116	105	149
Interlayer Cd ²⁺	-12	-16	no peak	-17
Interlayer CdCl ⁻	-41	42	43	43

¹ Di Leo and O'Brien (1999).

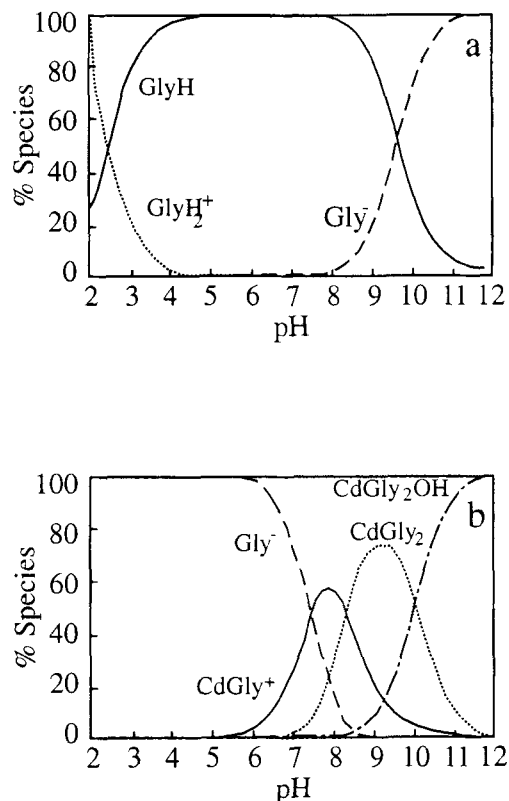


Figure 6. Speciation diagrams for (a) glycine and (b) Cd-glycine [no $[\text{Cd}(\text{Gly})_3]^-$] (from Gyani, 1994).

dissociation constant for the glycine protonation reaction in aqueous solution is equal to 2.44 (Gyani, 1994). Thus, the expected amount of the GlyH_2^- species in the interlayer of Ca-rich montmorillonite is $\sim 10\%$ of the total glycine adsorbed, with the remaining present as uncomplexed ligand in its zwitterionic form (GlyH). This is consistent with the measurements of the relative areas (normalized per number of scans) of the peaks at 172 and 169 ppm in the spectra of Figure 2, indicating a $\text{GlyH}_2^-/\text{GlyH}$ ratio of 1:10.

^{13}C CP-MAS NMR spectroscopy suggests that complexation of the adsorbed ligand glycine with the interlayer cation occurs only for the Cd-rich montmorillonite. The occurrence of a resonance line at ~ 181 ppm in the ^{13}C CP-MAS NMR (Figure 3), probably arising from a Cd-glycine complex (Barrie *et al.*, 1993), is clear evidence for this complexation. The presence of a small peak at -74 ppm (average value) in the ^{13}C CP-MAS NMR spectra (Figure 4) is further evidence for the complexation of the interlayer cation by the glycine ligand. A similar resonance was observed for a CdGly^- complex in solution (Bain Ackerman and Ackerman, 1980). Adsorption of glycine using a solution of 0.01 M only occurs for the Cd-rich montmorillonite (Figure 2 and 3). Glycine has two functional groups capable of complexing with cadmi-

um, *i.e.*, the amino and the carboxylate groups. The absence of any change in the chemical shift of the amine-group peak, which occurs at nearly the same resonance frequency in both the ^{13}C CP-MAS NMR spectra of Ca- and Cd-rich montmorillonite (*cf.*, Figures 2 and 3; Tables 1 and 2) suggests that complexation mainly occurs through the carboxylate group. The IR data also show a relevant shift in the asymmetric C=O stretching frequencies (Figures 5). Liquid IR spectra recorded for glycine solutions in the presence of cadmium chloride showed a shift in the asymmetric C=O stretching frequencies from 1538 cm^{-1} (pure glycine solution) to $\sim 1590\text{ cm}^{-1}$ (glycine in presence of CdCl_2) (Gyani, 1994, and references therein). The lack of the symmetric C-O stretch at $\sim 1330\text{ cm}^{-1}$ in the Cd-rich montmorillonite treated with both 0.01 and 0.1 M glycine solutions indicates that Cd is bound to only one oxygen atom of glycine at the concentration condition achieved in the interlayer. On the other hand, the occurrence of the symmetric C-O stretch as additional glycine is adsorbed on Cd-rich montmorillonite (sample treated with 1 M glycine solution) also indicates that Cd is bound to both oxygen atoms of glycine.

Cd-Glycine interaction on montmorillonite

Previous studies on adsorption of Cd on montmorillonite suggest a two-site model for sorption of Cd^{2+} on montmorillonite; Cd^{2+} is localized in the montmorillonite in two different sites, *i.e.*, in the interlayer as hydrated Cd^{2+} and on the external surfaces. Cadmium is also adsorbed as CdCl^+ in the interlayer (Di Leo and O'Brien, 1999).

By comparing the ^{113}Cd MAS-NMR spectra of Cd-exchanged montmorillonite with increasing amounts of adsorbed glycine (Figure 7) it can be concluded that glycine interacts selectively with Cd^{2+} and CdCl^+ , and these interactions depend on the type of adsorption site that cadmium species occupy. From Figure 7 it is evident that the relative intensity of the interlayer Cd^{2+} peak, *i.e.*, the peak occurring at ~ -16 ppm, decreases as glycine concentration in solutions increases. In contrast, no changes of peak intensity are observed for the resonance relative to external Cd^{2+} (*i.e.*, the ~ -43 -ppm peak; *cf.* Figure 7a, 7b, and 7c). The reduced intensity of the ~ -16 -ppm peak suggests that some interlayer Cd^{2+} is lost during glycine treatments. Increased amounts of cadmium were detected in the solutions recovered after glycine treatments. The spectral differences observed in Figure 7 suggest that interlayer Cd^{2+} is ion-exchanged by glycine molecules. This phenomenon is more evident as more glycine molecules enter the montmorillonite interlayer (Figure 7c). However, the relevant loss of interlayer Cd^{2+} , as suggested by the strong reduction in intensity of the interlayer Cd^{2+} peak in the ^{113}Cd CP-MAS NMR spectrum of Figure 7c, is explained if the cadmium/glycine ratio in

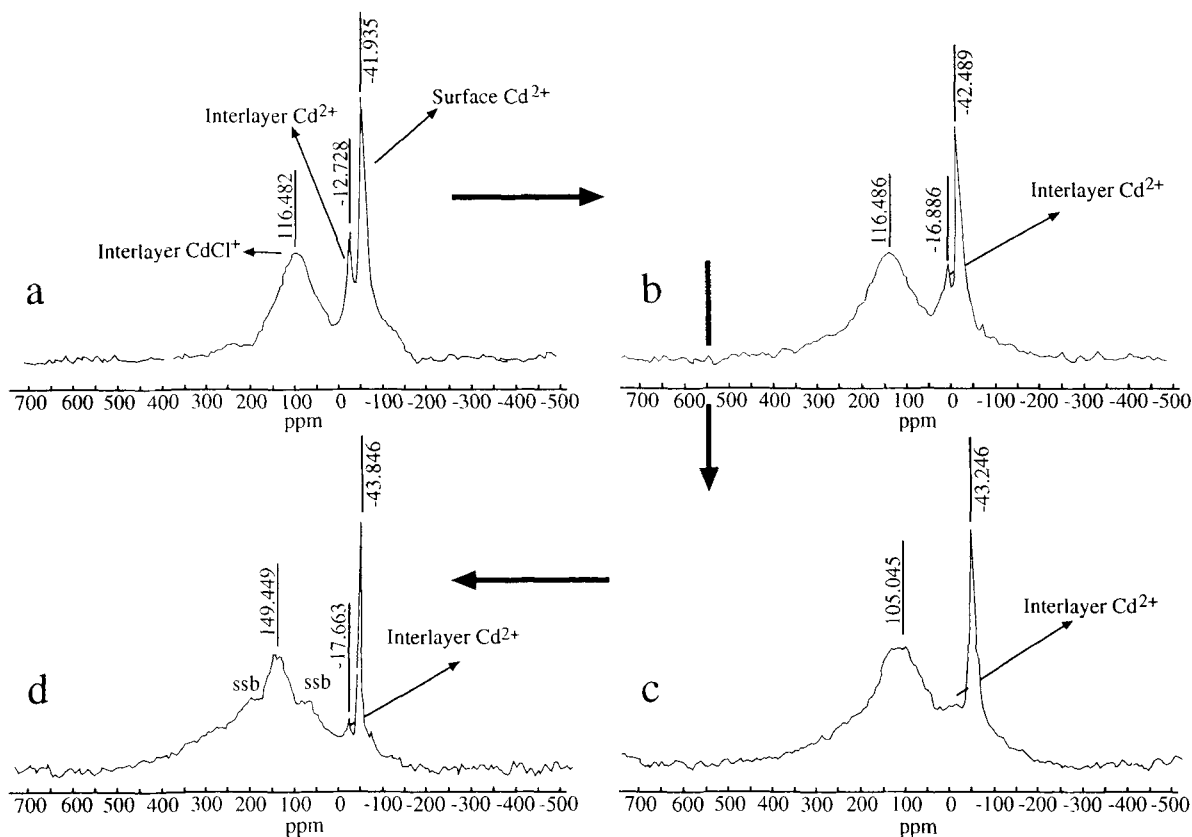


Figure 7. Scheme indicating changes in the ^{113}Cd MAS NMR spectra of Cd-rich montmorillonite treated with b) 0.01, c) 0.1, and d) 1 M Gly solutions. The spectrum relative to Cd-rich montmorillonite not treated with glycine (a) is from Di Leo and O'Brien (1999). All spectra have comparable signal areas.

the interlayer of Cd-rich montmorillonite after treatment with 0.1 M glycine solution is favorable for the formation of the neutral complex CdGly_2 , as suggested by Gyani (1994). This neutral complex is easily removed from the interlayer. In contrast, the lack of any change in the ~ -43 ppm-peak intensities strongly suggests that no complexation occurs for Cd^{2+} adsorbed on the external surfaces. It is likely that the formation of inner-sphere Cd complexes with the external surfaces of montmorillonite (Di Leo and O'Brien, 1999) reduces the tendency of the Cd^{2+} adsorbed on these sites to form coordination complexes with glycine molecules. Treatments with glycine solutions may therefore be considered less "aggressive" for the surface Cd^{2+} than for the interlayer Cd^{2+} .

The lack of chloride ions in the solutions collected after glycine treatments and a constant 116-ppm peak intensity in the NMR MAS spectra (Figure 7) clearly indicate that the loss of Cd is only caused by release of free Cd and that no CdCl^- ions are removed from the montmorillonite interlayer by glycine treatments. However, treatment with more concentrated glycine solutions (1 M) affects the CdCl^+ species; note the relevant shift of the resonance line relative to the in-

terlayer CdCl^+ , which shifts from ~ 116 to 150 ppm. The interaction of CdCl^+ species with glycine in aqueous solutions causes the ^{113}Cd resonance line to occur at positive values (Rivera and Ellis, 1992). The observed shift of the peak relative to the interlayer CdCl^+ toward positive resonance frequencies, as observed in the ^{113}Cd MAS NMR spectrum of Cd-rich montmorillonite treated with 1 M glycine solution (Figure 7), is therefore related to complexation of CdCl^+ species by glycine molecules. The large adsorption of glycine in the interlayer of the Cd-rich montmorillonite treated with 1 M glycine solution with respect to the Cd-rich samples treated with 0.01 and 0.1 M glycine solutions is the main cause of CdCl^+ complexation.

CONCLUSIONS

The speciation of the ligand glycine on montmorillonite is affected by the type of interlayer cation. In Ca-rich montmorillonite, the adsorbed glycine undergoes only protonation; whereas in the Cd-rich montmorillonite, the adsorbed ligand complexes with the interlayer cation. Such complexation mainly occurs through the carboxylate group, as suggested by both NMR and IR data, and it occurs at low pH (pH ~ 3)

in contrast to the conclusions of Gyani (1994) where metal-ligand complexes such as CdGly^- and CdGly_2 were observed only above pH of 6.0.

Only the interlayer cadmium, present both as Cd^{2+} and CdCl^+ , is complexed by the ligand glycine. Cd^{2+} is ion-exchanged by glycine molecules and also complexes with glycine at low and high adsorption of glycine, whereas CdCl^+ only complexes when a large amount of ligand is adsorbed on the montmorillonite (sample treated with 1 M glycine solution). The surface cadmium, *i.e.*, the cadmium adsorbed on the external surfaces of montmorillonite, does not interact with glycine. The formation of inner-sphere complexes with the external montmorillonite surfaces (Di Leo and O'Brien, 1999) reduces the tendency of the surface Cd^{2+} to form coordination complexes with glycine molecules.

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