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TIN–CLAY COMPLEXES: A MÖSSBAUER STUDY

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Abstract—Divalent tin has been intercalated into montmorillonite by reacting partially hydrolyzed solutions of $SnCl_2$ under aerobic conditions at pH = 2.8 with aqueous dispersions of the smectite mineral. The precursor tin solution contains mainly the cationic trimeric ion $Sn_3(OH)_4^{2+}$, which is shown to take part in the exchange reactions with the surface cations of the mineral. Variable temperature Mössbauer spectroscopy was used in order to: 1) directly probe changes in the oxidation state and coordination environment of Sn^{2+} in the process of intercalation; 2) examine the nature of tin atoms on the external surfaces and in the interlayer space of the clay platelets; and 3) study the dynamics of motion of tin atoms on the clay surfaces.

The main conclusion from these studies is that about 75% of the Sn^{2+} ions undergo extensive oxidation to the +4 state with concomitant hydrolysis and condensation that lead to the precipitation of SnO_2 on the external surfaces of the clay. The rest of the Sn^{2+} ions are introduced into the lamellar zone, as evidenced by the detailed Mössbauer analysis of the dynamics of motion of tin atoms on the clay surfaces.

Key Words—Clay, Montmorillonite, Mössbauer, Intercalation.

INTRODUCTION

The aqueous chemistry of Sn^{2+} is complicated, because this ion is very sensitive to the combined action of hydrolytic, condensation and air oxidation reactions (Donaldson 1967; Abel 1973). The chemistry becomes even more complex when Sn^{2+} species take part in exchange reactions with the surface cations of smectite clays. The large surface area of the clays and their enhanced acidity could very well promote the reactions of hydrated Sn(II) ions, leading to polyoxo/hydroxo species that are likely to precipitate onto the clay surfaces. Such transformations on clay surfaces are well-documented in the chemistry of divalent iron–clay systems (Gerstl and Banin 1980; Helsen and Goodman 1983).

Recently, the interaction of Sn^{2+} with montmorillonite was reported by Breen et al. (1992). Their results indicate that, during intercalation, the majority of Sn^{2+} (>95%) was oxidized to some Sn^{4+} oxo/hydroxo form that precipitated on the montmorillonite surfaces. We have also addressed the problem of interaction of Sn^{2+} ions with montmorillonite, aiming at elucidating the chemistry occurring during the Sn^{2+} intercalation. Previous detailed studies of the hydrolysis of several Sn^{2+} salts in the absence of oxygen and in the pH range 2 to 4 have shown that the cationic trimeric ion $Sn_3(OH)_4^{2+}$ predominates in solution just before the basic Sn^{2+} salt starts to precipitate (Donaldson and Moser 1961; Donaldson 1967). In our studies, we have chosen to conduct the Sn^{2+} intercalation at pH approximately 2.5, anticipating to load the clay surfaces with trinuclear Sn^{2+} complex and, in this way, to prepare SnO pillars.

We have utilized variable-temperature Mössbauer spectroscopy in order to: 1) directly probe changes in the oxidation state and the coordination environment of Sn^{2+} in the process of intercalation; 2) examine the nature of tin atoms on the external surfaces and in the interlayer space of the clay platelets; and 3) study the dynamics of motion of tin atoms on the clay surfaces.

MATERIALS AND METHODS

Materials

The $SnCl_2{\cdot}2H_2O$ and other chemicals of reagent grade quality were obtained from commercial sources. The Na^+ montmorillonite was purchased from the Source Clay Minerals Repository (University of Missouri, Columbia, Missouri). The clay was sodium-saturated by reacting it overnight with an excess of 1 *N* NaCl, then washing the solid phase, received by centrifugation, several times with aqueous 1 *N* NaCl. The material was dispersed in water and the <2 μm clay fraction was collected and subjected to dialysis with frequent changes of water until the dialysate was free from chloride ions, as detected with a 4.2% $AgNO_3$ solution. The clay was dried at 50 °C and its cation exchange capacity (CEC) was found to be 85 meq/100 g of clay. This was measured by first converting the Na^+ montmorillonite to its $(CH_3)_4N^+$ form, then determining the C and N contents of the organoclay products by microanalysis.

Intercalation

For the ion exchange reaction, 0.45 g of $SnCl_2{\cdot}2H_2O$ (a quantity that corresponds to 5 times the CEC of 1 g Na^+ montmorillonite, on the basis that Sn^{2+} is the dominant species in solution) were added to 50 mL of 0.1 *M* $NaNO_3$, and the pH of the resulting solution was adjusted to 2.5 by the dropwise addition of 0.2 *N* NaOH. The solution became a little cloudy and it was

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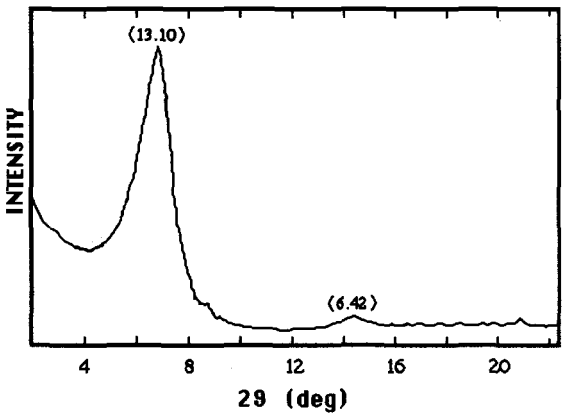


Figure 1. X-ray diffraction pattern of air-dried sample.

then filtered to a stirred dispersion of 1 g of Na^+ montmorillonite in 50 mL of water. Flocculation took place immediately. After the mixture was stirred for 2 h, the supernatant liquid was discarded and the centrifuged solid washed twice with 50 mL of distilled water and air-dried on a glass plate at room temperature. Oriented films of the tin–montmorillonite complexes were obtained by spreading a water dispersion of the material on glass plates that were air-dried at room temperature.

Physical Methods

A Siemens D500 X-ray diffractometer with Cu$K\alpha$ radiation was used for determining the $d(001)$ spacing in the intercalated clay structures. The ^{119}Sn Mössbauer spectra of powder samples were obtained in the temperature range 20–300 K, using a constant acceleration spectrometer and a 10-mCi calcium stannate source kept at room temperature. Spectrometer calibration was effected using a metallic iron foil. Isomer shifts are reported relative to $CaSnO_3$, assuming that they are the same as the $BaSnO_3$ shifts.

RESULTS AND DISCUSSION

Aqueous solutions of Sn(II) chloride in 0.1 *M* $NaNO_3$, which were hydrolyzed previously to pH 2.7, reacted readily with a sodium montmorillonite suspension, affording a gray-white tin–clay complex. The X-ray diffraction (XRD) patterns from several air-dried samples showed interplanar spacings centered between 1.25 and 1.30 nm (Figure 1).

The small spacing implies a monolayer coverage of the lamellar space that could result from the intercalation of an intermediate product formed during the hydrolysis of the divalent tin. Previous studies have shown that the trimer $Sn_3(OH)_4^{2+}$ with the ring structure below is the predominant species when Sn(II) salts undergo hydrolysis under controlled conditions (Donaldson and Moser 1961; Donaldson 1967). This ring structure contains 1 layer of oxygen atoms, and

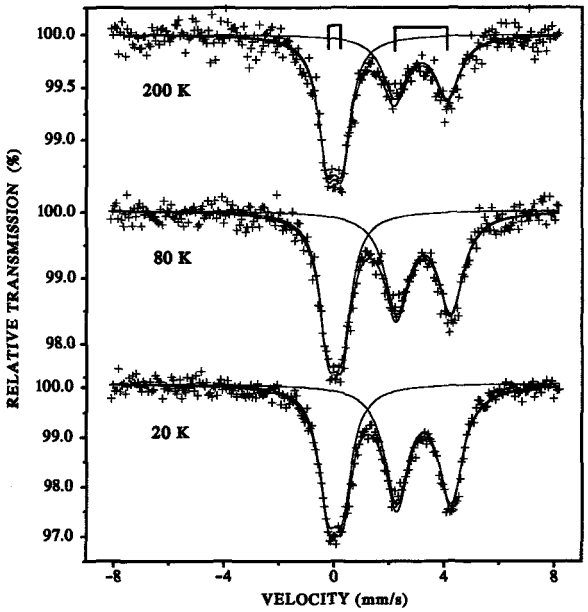
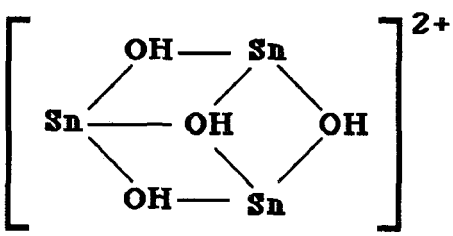


Figure 2. Mössbauer spectra of a tin–clay complex as taken at 200, 80 and 20 K. Crosses denote experimental data. The result of the least-squares fit is drawn by solid lines. The bar diagram on the top indicates the position of the lines for tetravalent and divalent tin.

therefore could account for the observed small $d(001)$ spacing. More information about the nature of the intercalated Sn(II) species was obtained from the Mössbauer spectra.



The Mössbauer spectra from a tin–clay complex at 3 different temperatures are shown in Figure 2, while pertinent data are collected in Table 1. The spectra consist of 3 lines: an intense broad absorption near zero velocity and a doublet at positive velocities with intensity varying considerably with temperature. The hyperfine parameters of the more intense line near zero velocity are consistent with those of Sn^{4+} in the form of hydroxide or $SnO_2{\cdot}2H_2O$, IS = 0.00 mm s^{-1}, QS = 0.50 mm s^{-1} (Collins et al. 1979). The values of isomer shift and quadrupole splitting of the high-velocity doublet indicate the presence of divalent tin that probably exists in some oxo/hydroxo form. The presence of simple hydrated Sn^{2+} ions in the clay interlayer space is excluded on the basis of the Mössbauer results obtained from a frozen solution of $SnCl_2{\cdot}2H_2O$ in 0.1 *M* HCl, where Sn^{2+} predominates (Figure 3). The observed values of isomer shift and quadrupole splitting

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Table 1. Mössbauer hyperfine parameters of the tin complex at various temperatures.

Temperature (K)	δ† (mm/s)	ΔE_q† (mm/s)	Area‡ (%)	δ† (mm/s)	ΔE_q† (mm/s)	Area‡ (%)
20	3.24	1.98	59	0.03	0.53	41
40	3.23	1.97	57	0.01	0.52	43
80	3.22	1.97	55	0.02	0.52	45
120	3.25	1.96	52	0.02	0.54	48
160	3.19	1.99	47	0.02	0.52	53
200	3.19	1.97	44	0.02	0.53	56
210	3.17	1.96	43	0.02	0.54	57
220	3.14	2.00	47	0.01	0.52	53
230	3.13	1.96	42	0.03	0.53	58
240	3.11	1.98	44	0.01	0.52	56
250	3.12	2.00	43	0.02	0.52	57

† The estimated error is ±2 on the last significant figure.
‡ The estimated error is ±5 on the last significant figure.

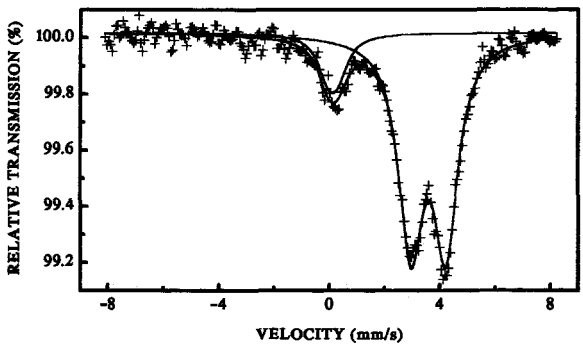


Figure 3. Mössbauer spectrum of frozen solution of $SnCl_2 \cdot 2H_2O$ in 0.1 *M* HCl at 80 K. Crosses denote experimental data. The result of the least-squares fit is drawn by solid lines.

from the frozen Sn^{2+} solution are quite different from those of the intercalated tin species (Table 1). On the other hand, the spectrum of the intercalated tin and the corresponding Mössbauer parameters are very similar to those reported in the literature for the trimer $Sn_3(OH)_4^{2+}$ (Davies and Donaldson 1968). These findings offer evidence that the precursor solution comprises mainly the $Sn_3(OH)_4^{2+}$ species and that the same structural unit is also present in the interlayer zone after the ion exchange reaction. Another conclusion from the Mössbauer spectra is that, during intercalation under the described conditions, approximately 75% of the Sn^{2+} ions undergo extensive oxidation to the +4 state with concomitant hydrolysis and condensation that lead to the precipitation of stannic hydroxide.

Turning to the Mössbauer spectra at different temperatures, it is clear that the spectral areas show a temperature dependence that is particularly marked for the quadrupole split spectra of the divalent tin. In a Mössbauer experiment, such temperature-dependent line intensities originate from the variation of the recoil free fraction, $f(T)$, of the absorbed or emitted γ-rays with temperature. In the high-temperature limit $T > \Theta_D/2$, where Θ_D is the Debye temperature of the solid, the factor $f(T)$ is linearly related to the spectral area of the absorption line(s), A, and is given by:

$$f(T) = \exp(-6E_R T/k\Theta_D^2) \approx A(T) \qquad [1]$$

where E_R is the recoil energy of the absorbing γ-rays and k the Boltzmann constant. The key point is that the values of E_R characterize the rigidity with which the Mössbauer atom is bound to the lattice; large values of E_R, corresponding to small $f(T)$, indicate less tightly held atoms in the lattice than do smaller values. In accord with these arguments, plots of $-\ln A$ vs. T are expected to be linear with a slope α ($-d\ln A/dT$) indicating the extent of vibrational freedom of the Mössbauer atom in the solid: i.e., more tightly bound ions will have smaller α values than less tightly bound ions. Reported α values for several organotin compounds support this conclusion. For instance, the α value for polymeric Ph_3SnOH is 1.10×10^{-2} K^{-1}, whereas the corresponding value for the less tightly bound tin atom in the dimer $(Ph_3Sn)_2O$ is 1.56×10^{-2} K^{-1} (Molloy and Quill 1985). Inorganic structures are expected to show even smaller α values; and indeed, for SnO it is 0.23×10^{-2} K^{-1} (Harrison et al. 1977; Collins et al. 1979) and for SnO_2, 0.59×10^{-2} K^{-1}. Accordingly, α values are expected to be very useful for extracting information regarding the nature of species associated with clay surfaces. Intercalated cations or other complex structures are expected to show smaller α values because the rigid interlayer zone will restrict the respective vibrational motion. Conversely, physically absorbed surface species will be more free to move, and therefore will display large α values.

Figure 4 shows plots of $\ln A$ vs. T in which each area is normalized by the area at 20 K. First, we note that within the error of measurements we obtain good linear responses for both divalent and tetravalent tin

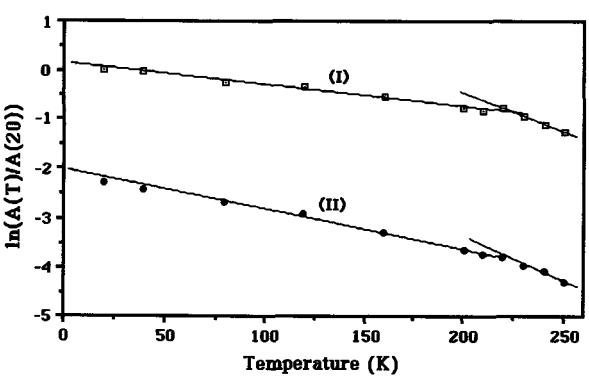


Figure 4. Temperature dependence of the normalized Mössbauer spectral area [$A(T)/A(20)$]. Line I corresponds to divalent tin species and line II to tetravalent. Straight lines are least-squares fits to the experimental points.

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species. Each plot gives 2 straight lines with different slopes, and the lines cross each other at approximately 220 K. The origin of the 2 lines will be discussed below. Line I, showing the larger variation of the peak intensities with temperature, corresponds to divalent tin species: while line II, with smaller α values, to $SnO_2 \cdot 2H_2O$. Line I yields α values of 0.78×10^{-2} K^{-1} from 20 to 220 K and 0.38×10^{-2} K^{-1} from 220 to 250 K, whereas line II gives α values of 0.43×10^{-2} K^{-1} from 20 to 220 K and 0.60×10^{-2} K^{-1} from 220 to 250 K. We consider that the smaller α values from line I arise from the insertion of divalent species between the clay layers. In this instance, the rigidity of the clay structure inhibits the motion of the divalent tin atoms sandwiched between the clay layers and, as a consequence, we anticipate small α values. Alternatively, the larger α values extracted from line II indicate that the tetravalent tin species were precipitated on the external clay surfaces.

Other noticeable features of the Mössbauer spectra are the near absence of divalent absorption as well as the diminished tetravalent absorption at room temperature. Similar behavior has been reported for Fe(II)-exchanged montmorillonite (Diamant et al. 1982) and montmorillonite intercalated with dimethyltin(IV) complexes (Simopoulos et al. 1988). It was also discussed by Breen et al. (1992) in their study of the Sn(II)-clay interactions. The lack of, or diminished, absorption in the room-temperature Mössbauer spectra from cations residing on clay surfaces has been attributed to water molecules associated with the clay surfaces. Apparently, the vibrational freedom of a Mössbauer atom is enhanced in an environment of loose water molecules at the clay surfaces and, therefore, its recoil-free fraction and the corresponding absorption are depressed. Accordingly, the melting of the clay water occurring around 220 K will greatly affect the intensity of a Mössbauer line. The small discontinuity in the $-\ln A$ vs. T plots observed at about 220 K might arise from the melting of the clay water, whereupon the tin species become less tightly bound to the clay surfaces, and, as a result, the corresponding slopes become larger. More drastic changes in the recoil-free fraction at approximately 230 K have been observed in the intercalation of dimethyltin(IV) cationic complexes in montmorillonite (Simopoulos et al 1988). In the present study, it is possible that the small change in $-\ln(A(T))$ vs. T plot arises from the approximations in deriving Equation [1], i.e., ignoring anharmonic effects and intramolecular vibrations.

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