

Reactions of hydrogen vermiculite[☆]

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Single crystals of hydrogen vermiculite were synthesized at room temperature by ion-exchange from Na-vermiculite using 1 molar acetic acid for one week. The protonic transference number has been determined as unity in concentration cells. The protonic species in the interlayer region can undergo acid-base reactions as well as ion exchange reactions. Amines such as aniline and pyrrole can be readily intercalated and in the presence of oxidizing cations such as Cu^{2+} will undergo polymerization even in large single crystals.

1. Introduction

There has been much interest lately in structures with open crystal lattices that exhibit fast ionic conductivity and in which ion exchange and other reactions can take place. One class of these materials, prevalent in nature, are the layered aluminosilicates such as montmorillonite, vermiculite and mica. Their structures consist of negatively charged aluminosilicate sheets between which reside cations that are often hydrated. These compounds show rapid ion mobility when the ions between the aluminosilicate sheets are solvated; the sodium vermiculite compound is a pure cationic conductor with a cation transference number of unity [1]. The sodium ions in the single crystals of vermiculite may be exchanged for a variety of other cations but exchange can typically take several months to go to completion in aqueous solutions [2]. However, recently we found that the sodium could be completely replaced by hydrogen [3] in weak acids; this hydrogen can then be ion-exchanged within a week for a variety of ions. This enhanced reactivity makes possible the consideration of a variety of reactions not previously feasible in a reasonable time period. The range of re-

actions possible with layered silicates and zeolitic materials has been discussed by Barrer [4]. More recently in situ polymerization of amines has been accomplished in a number of layer materials [5,6], but not in single crystal sheet silicates. We therefore set out to determine the reactivity of this hydrogen form of vermiculite.

We chose to study single crystal silicates, because one can measure the bulk properties of such materials without contributions from the surface which might dominate in the case of fine powders. Vermiculite from Llano, Texas, was chosen because it is readily available in single crystal form with few impurities. It has the idealized formula $\text{M}^+(\text{Mg}_3)(\text{Si}_3\text{AlO}_{10})(\text{OH})_2 \cdot y\text{H}_2\text{O}$ where y can vary from 0 to above 5, and M is normally a monovalent or divalent cation. M can be ion-exchanged for other cations.

This letter describes some reactions of H-vermiculites, including ion exchange with metal cations, acid base reactions with organic amines, and in situ polymerization of amines. In addition, we have determined the cation transference number of hydrogen vermiculite.

2. Experimental

The vermiculite single crystals used here are from

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Llano, Texas and were obtained through the Clays Minerals Society. As discussed previously [3] these crystals were first immersed in aqueous sodium chloride solution at 60°C for two months to ensure complete exchange to the sodium form and then have the formula:



where y is a function of the water vapor pressure, and for this material varies from 0 to 4.6 [7]. The sodium crystals were then immersed in a 1 molar solution of acetic acid for about seven days, which converted them totally to the hydrogen form; no sodium ions were detectable. After this time a single phase was obtained with a basal spacing of 13.90 Å, as compared to the 14.89 Å of the starting sodium material. All X-ray measurements were made on a Scintag diffractometer using Cu K α radiation. Chemical analysis of the vermiculite so formed showed 1.5 milliequivalents of H⁺/g of H-vermiculite [3].

Cation transference measurements were done in a simple electrochemical cell in which the single crystal of H-vermiculite was glued into a glass tube using a silicone rubber cement as described previously [1]. This tube was then filled with a 0.001 M acetic acid solution and placed in another tube also containing acetic acid of varying concentration. The hydrogen activity in the acetic acid solutions was determined with a *pH* meter. Electrical contact to the solutions was made by Ag/AgCl electrodes.

Ion-exchange of the hydrogen in the vermiculite was carried out by immersing the single crystals of H-vermiculite in aqueous metal chloride solutions for about one week at 60°C. The degree of reaction was monitored by X-ray analysis and atomic absorption analysis. Reaction with organic amines was accomplished by immersion in the pure liquid amine at room temperature.

3. Results and discussion

H-vermiculite single crystals were successfully prepared from Na-vermiculite ($c = 14.89$ Å) under 1 M acetic acid. It was found necessary to have the Na-vermiculite in a pure form otherwise the reaction did not go to completion. The number of milliequivalents of H per gram of H-vermiculite is 1.5, slightly

less than that of the sodium starting material, 1.9. This is probably due to some of the hydrogen becoming bound to oxygen as hydroxide, thus lowering the number of counterions in the exchangeable layer. We have found that the hydrogen in the vermiculite ion exchanges much more rapidly with other cations than does the initial sodium vermiculite. We believe this is probably associated with the smaller charge density on the layers, 1.5 versus 1.9 meq. This permits the completion of ion exchange within about seven days even for crystals approaching 1 cm in length. We have successfully ion-exchanged copper and most of the rare-earth ions into the interlayer space in the crystal. The lattice repeat distances of a number of the lanthanide ion-exchanged compounds are given in table 1, and these clearly show a lanthanide contraction which corresponds to the change in the size of the lanthanide ion.

The concentration cell data are shown in fig. 1. The

Table 1

Lattice repeat distance for rare-earth intercalates.

Counterion	Lattice repeat (Å)
lanthanum	15.171(28)
neodymium	15.051(16)
samarium	14.982(8)
gadolinium	14.937(15)
dysprosium	14.888(19)
erbium	14.859(18)

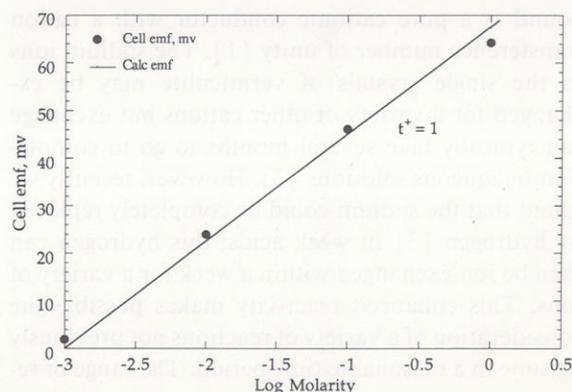


Fig. 1. EMF of acetic acid concentration cell with hydrogen vermiculite as electrolyte and using Ag/AgCl electrodes; 0.001 M acetic acid was used as the reference solution.

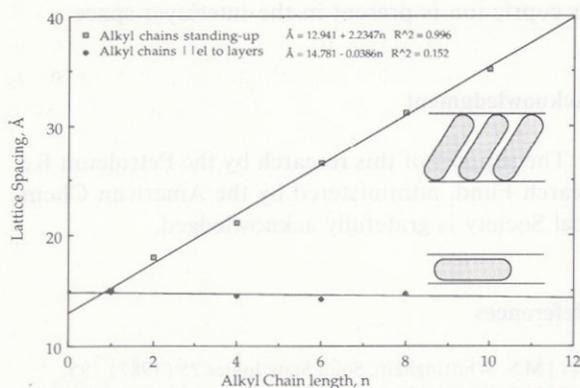


Fig. 2. Lattice expansion of amine intercalated vermiculite as a function of the length of the alkyl chain.

observed EMF values are within experimental error the same as those calculated from the hydrogen activity difference measured by the *pH* meter using the equation (1):

$$E = (2t^+) (RT/F) \ln(a_1/a_2)$$

for the cell Ag/AgCl/0.001 M acetic acid/H vermiculite/?M acetic acid/AgCl/Ag. Thus, hydrogen vermiculite is a pure cationic conductor just as previously determined for sodium vermiculite [1].

The hydrogen vermiculite readily reacts with straight chain alkylamines with an expansion of the crystalline lattice perpendicular to the basal planes as shown in fig. 2. This figure clearly shows the pres-

ence of two phases. These may be associated with two configurations of the alkyl chains. In the one with the smaller repeat distance, $c \approx 14.78 \text{ \AA}$, where the expansion is independent of the number of alkyl groups the alkyl chain must be lying flat in the interlayer region essentially parallel to the silicate layers. In the other the observed expansion is directly proportional to the number of carbon atoms in the chain and the alkyl chains must be standing up. The change of expansion of 2.2 \AA per carbon is consistent with previous reports [8] of amine in layered compounds where the chains are optimally nested at an angle just around 60° to the silicate layers.

If we first partially ion-exchange an oxidizing cation, such as Cu^{2+} , into the lattice then we can cause the in situ polymerization of certain amines such as aniline and pyrrole as reported earlier for polycrystalline silicates [6]. The X-ray pattern of an aligned single crystal of the polyaniline vermiculite complex is shown in fig. 3. Clearly the polymerization of the molecules within the layer has not changed the crystallinity of the host material. The repeat distance of this black compound is 14.4 \AA , not too different from the clear non-colored aniline vermiculite, 14.5 \AA . The latter compound is an insulator, whereas the former is a semiconductor with a conductivity dependent on the degree of oxidation. The maximum conductivity we have obtained to date is 0.005 S/cm , and a complete systematic study will be published elsewhere [9]. This relatively low conductivity is prob-

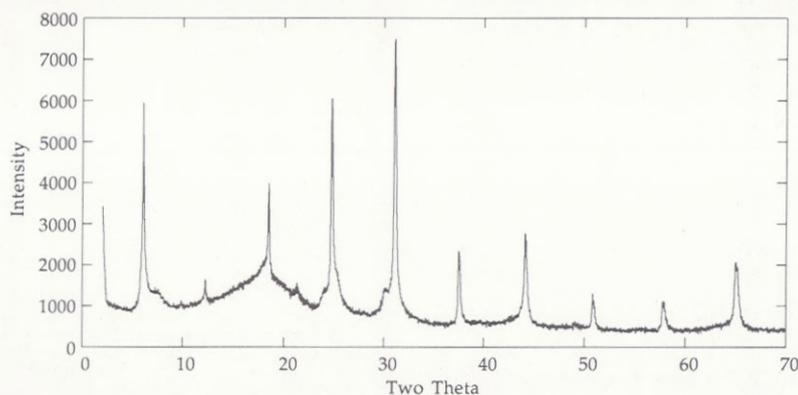


Fig. 3. X-ray powder diffractogram of polyaniline vermiculite showing its single crystal nature; the diffraction lines are associated with the 001 reflections from the basal planes. Cu K α radiation was used.

ably due to the polymers being limited and variable in size, as suggested by Raman studies on these crystals [10].

Pyrrrole reacts with the partially exchanged copper vermiculite in much the same way as aniline. In this case the monomer samples are a silverish color and the polymer samples again a black color. The conductivity of the polymer in this case appears to be significantly higher, approaching 1 S/cm similar to the 1.5 S/cm reported for polypyrrole in FeOCl [5] which after treatment with a magnesium perchlorate solution increases still further.

4. Conclusions

A hydrogen form of vermiculite has been synthesized by ion exchange. It shows pure cationic conductivity, and shows behavior typical of a solid acid and ion exchanger. Thus, the protons react with bases such as sodium hydroxide and organic amines both alkyl and aromatic with an associated expansion of the lattice perpendicular to the basal planes. Amines such as aniline and pyrrole are readily polymerized in situ between the silicate layers if an oxidant such

as cupric ion is present in the interlayer space.

Acknowledgment

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