ADSORPTION OF STEARIC ACID BY CHRYSOTILE[1]

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Abstract—Stearic acid adsorption by chrysotile asbestos in hexane was shown to occur by the formation of a Mg-stearate complex on the mineral surface. Infrared spectroscopy showed no evidence of physically adsorbed stearic acid over the range of concentration employed. Absorption bands at 1560 and 1410 cm^{-1} in the spectrum of the chrysotile-stearic acid complex correspond with band positions in the spectrum of a synthesized Mg-stearate complex. No evidence of the acid form, which produces a band at 1713 cm^{-1}, was present in the spectrum of the chrysotile complexes. At an equilibrium concentration of 0.8 mg stearic acid/ml, the mineral adsorbed 42 mg stearic acid/g. By heating the mineral in molten stearic acid, additional stearic acid beyond that observed by adsorption from solution was adsorbed in the carboxylate form. Calculations based on the molecular dimensions of stearic acid and the crystal structure of chrysotile indicate that the limiting factor in possible surface occupancy is the molecular size of stearic acid rather than the surface density of Mg–OH adsorption sites.

Key Words—Adsorption, Chrysotile, Infrared spectroscopy, Magnesium, Stearic acid.

INTRODUCTION

Interactions of asbestos minerals with biological materials have been noted for some time (e.g., Frohberg, 1974). In recent years, understanding of the chemical properties of the minerals has gained importance because of reactions with cell membranes and carcinogenic behavior. The mechanisms by which chrysotile interacts with biological tissues have not been completely elucidated, but they are thought to involve interactions of cell membranes with the fiber surface (Harington *et al.*, 1975) as well as various physical interactions (Stanton and Wrench, 1972). One such physiochemical interaction is the rupture of red blood cells (hemolysis). In the presence of chrysotile the hemolytic reaction appears to involve complexation of constituents of the cell membrane by the Mg-hydroxide surface (Harington *et al.*, 1975). The most convincing evidence of this reaction is its prevention by chelating compounds such as ethylenediaminetetraacetic acid (EDTA) and sodium-1-azo-2-hydroxy-3-(2,4-dimethylcarboxanalido) naphthalene-1-(2-hydroxybenzene-5-sulfonate) (Magon) which has a high affinity for Mg. There appears to be no correlation, however, between the carcinogenic effects of chrysotile and its hemolytic reactivity (Harington *et al.*, 1975).

Other reactions also may occur at the cell membrane-mineral interface. Adsorption of specific lipid components of the cell membrane by the mineral may also be responsible for the loss of integrity of the cell membrane. In the current theory, phosphoglycerides are thought to exist in a bilayer with their polar end projecting into the aqueous phase and their non-polar ends

forming the hydrophobic interior. The hydrophobic part is composed largely of long-chain, fatty-acid esters of glycerol (Morrison and Boyd, 1973). As a first step in studying adsorption of lipids by chrysotile, we chose to study the behavior of a structurally simple compound (stearic acid) whose fatty-acid chain is similar to those present in natural glycerides. The objective of the study was to determine whether the adsorption mechanism involved interaction with the alkyl chain of the stearic acid molecule or complexation through the carboxylic acid group.

MATERIALS AND METHODS

Chrysotile asbestos from Thetford Mines, Quebec, was obtained from Ward's Natural Science Establishment, Rochester, New York. The sample was comprised of fibers 8 to 10 mm long, which were separated from massive fragments and heated to 90°C in a Na-acetate solution (pH = 5.0) for 24 hr to remove carbonates. The mineral was then washed once in a pH 5.0 Na-acetate solution and comminuted for 30 min in a similar NaOAc solution in a blender. Magnetite impurities were removed by gentle stirring with a Teflon-coated magnetic stir bar. This process was repeated until no magnetite was observed on the stir bar. Air bubbles, which were entrapped in the net-like structure of the chrysotile suspension, were also removed by the stirring process. The suspension was then washed three times with 1 N NaCl by centrifugation and decantation.

The excess salts were removed by dialysis against deionized water until a negative Cl$^-$ test (by AgNO$_3$) was obtained in the supernatant of the suspension. After washing twice with 95% ethanol, the mineral was dried at 110°C and stored under ambient conditions for future use. The N$_2$ specific surface was measured at 68.0 m^2/g using a Micromeritics Orr Surface Area Ana-

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lyzer and a BET plot of the adsorption isotherm. This surface area corresponds to that reported by Pundsack (1955). To determine the purity of the material used, the sample was examined by X-ray powder diffraction (XRD), thermal gravimetry (TGA), infrared spectroscopy (IR), and scanning electron microscopy. The XRD pattern showed peaks at 7.34, 4.46, 3.65, 2.57, 2.44, 1.82, 1.53, and 1.46 Å, indicating that serpentine minerals dominated the sample. Scanning electron micrographs showed only fibrous particles; platy or massive crystals were not observed as might be expected for lizardite and most antigorites. The IR spectrum, with band maxima at 3690, 3645, 1080, 1042, 958, and 600 cm^{-1}, was identical to that given by Brindley and Zussman (1959) for Transvaal silky fibers of chrysotile, ruling out a predominance of a fibrous variety of antigorite. Water loss from structural hydroxyls between 575° and 650°C, measured by TGA with a heating rate of 20°C/min was 12.7% compared to a theoretical value of 13.00% for $Mg_3Si_2O_5(OH)_4$. The only other weight loss occurred between room temperature and 125°C and presumably represents the loss of adsorbed water which also appeared in the IR spectrum. No weight loss occurred near 400°C, indicating the absence of brucite. Thus, the sample was predominantly chrysotile, although the presence of a small amount of fibrous antigorite is possible.

Adsorption isotherms of stearic acid (SA) on chrysotile were obtained by equilibrating (in duplicate) 5 mg of mineral with SA in hexane in the initial concentration range 0 to 250 mg SA/ml solution. Labelled SA (C^{14}) was purchased from the New England Nuclear Corporation and used as received. A total solution volume of 15 ml was placed into screw capped Teflon-lined glass tubes, and after 24 hr equilibration at 23°C, an aliquot of the supernatant solution was assayed for SA-C^{14} by scintillation counting. The concentrations of SA remaining in solution were calculated from a standard curve. Separate experiments showed that SA was not adsorbed by the tubes. The solubility of SA in hexane was measured at 10.22 mg SA/ml.

Water-vapor adsorption isotherms were obtained on the NaOAc-treated chrysotile and the SA-chrysotile complex which contained 40 mg SA/g chrysotile. The samples were equilibrated for seven days over saturated salt solutions at selected relative humidities. IR spectra of KBr pellets of selected samples were recorded on a Perkin-Elmer 567 IR spectrophotometer equipped with a transmittance-to-absorbance transducer for recording on a separate strip-chart recorder.

The Mg-salt of SA was prepared by reacting 0.2 mmole SA (56.8 g) with 0.1 mmole Mg(OCH$_3$)$_2$ (8.6 mg) in 95% ethanol. After the mixture was stirred at 80°C for 8 hr, the solids dissolved to form a clear solution. Upon cooling overnight, a white Mg-SA precipitate formed which was insoluble in 1 N HCl.
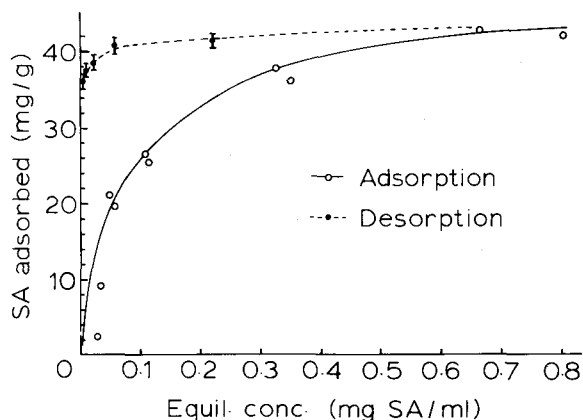

Figure 1. Adsorption and desorption isotherm of stearic acid by NaOAc-treated chrysotile in hexane. Bars signify standard deviation of duplicate samples.

RESULTS AND DISCUSSION

Adsorption of stearic acid and water

The adsorption of SA onto chrysotile from hexane solution showed typical Langmuir-type behavior (Figure 1). The adsorption process was not reversible, and the desorption curve indicated that SA was chemically bonded in some way to the mineral surface. Mechanisms responsible for SA adsorption by chrysotile include (1) reaction of the Mg-hydroxide sheet with the carboxylic acid group of SA to form a Mg-carboxylate salt; (2) hydrogen bonding of SA through the carboxylic acid group (similar to the mechanism described by Yariv *et al.*, 1966); or (3) hydrophobic-type interactions between the mineral and the long hydrocarbon chain of SA (Theng, 1979). The latter mechanism would be favored by entropic forces whenever a solvent is used in which SA is only sparingly soluble (or attracts SA weakly, such as water), but would not be expected to predominate in a solvent system which is more lipophilic than water, such as hexane. The adsorption isotherm shown in Figure 1 is consistent with attachment of the carboxylic acid moiety to the external Mg-hydroxide surface exposed to the solution.

The proportion of surface covered (θ) by SA can be estimated by considering the molecular dimensions of SA. Chain axes of SA molecules bonded to the chrysotile can orient at angles between 0° and 90° with respect to the plane of the surface, assuming that all carbon-carbon bonds in the hydrocarbon chain are in the *trans*-configuration. Values of θ at 42 mg stearic acid/g chrysotile were calculated to be 0.26 and 1.77 for 90° and 0° orientations, respectively, using the nitrogen surface area of chrysotile (68 m^2/g) and molecular dimensions of $c = 24.4$ Å, $b = 3.6$ Å, and $a = 5.55$ Å for stearic acid (Müller, 1927). The angular orientation of the hydrocarbon chains should increase from 0° to nearly 90° as the amount of adsorbed stearic acid increases.
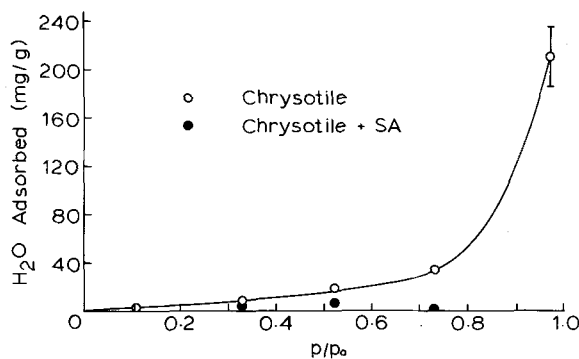
Figure 2. Adsorption isotherms of water by NaOAc-treated chrysotile and the chrysotile-stearic acid complex.

Table 1. Band assignments of infrared spectra of stearic acid, chrysotile, and the stearic acid-chrysotile complex.

Wave number (cm^{-1})	Assignment	Reference
1713	ν(C=O)	Hadzi and Sheppard (1953)
1620	δ(H–O–H) from H_2O	Russell and Farmer (1964)
1560	ν(C=O) (asymmetric) from carboxylate	Nakamoto (1978)
1464	ν(C–O) from acid and ν(C–O) (symmetric) from carboxylate	Hadzi and Sheppard (1953)
1410	δ(C–O) from carboxylate	Nakamoto (1978)
1400	δ(O–H) from acid	Hadzi and Sheppard (1953)

For $\theta = 1$, a maximum of 23.7 mg SA/g would be adsorbed at 0° orientation and 160.6 mg SA/g at 90° orientation. Stearic acid in the interlayer space of smectite forms complexes one molecule thick in which the chain axes are inclined at an angle of 60° to the silicate surface (Brindley and Moll, 1965). Here, van der Waals forces are strong enough for the stearic acid molecules to orient in a close-packed manner. Similar orientations were found on TiO_2 surfaces (Doroszkowski and Lambourne, 1978) and metals (Menter and Tabor, 1951).

In the present study, not all surface hydroxyls were apparently involved in bonding the stearic acid to the surface. Assuming that one SA molecule associates with one surface hydroxyl or Mg^{2+} ion, the average area occupied by each surface hydroxyl is one sixth of the unit-cell area; with $a = 5.34$ Å and $b = 9.25$ Å (Deer et al., 1967), the average area is 8.23 Å^2. Comparing this area with the minimum area required for an SA molecule perpendicular to the surface (19.98 Å^2) shows that the limit of occupancy is determined by the dimensions of the SA molecule. The maximum level of SA adsorption was evidently not attained in the present study. These results do not distinguish between SA molecules adsorbed in "patches" or randomly distributed over the surface.

Water adsorption isotherms are shown in Figure 2 for NaOAc-treated chrysotile and the SA-chrysotile complex. The amounts of water adsorbed by NaOAc-treated chrysotile are similar to that adsorbed by kaolinite (Johansen and Dunning, 1959). The data of Figure 2 show that the surface of the chrysotile was made more hydrophobic upon adsorption of SA. Behavior of this nature was expected because of the well-known hydrophobicity of the alkyl chain of SA.

Infrared spectroscopy

IR spectra of the SA-chrysotile complex showed that virtually all of the SA reacted and bonded to the surface through the carboxylate ligand. Table 1 summarizes the band assignments of the spectra. The absence of a 1713 cm^{-1} band (indicative of the acid form, Figure 3B) in the spectra of the SA-chrysotile complex (Figure 3C) and the close correspondence of the bands at 1560 and 1464 cm^{-1} with those of the spectra of Mg-stearate (Figure 3A) show that the complex resulted from reaction involving surface Mg–OH.

The positions and separation of the ν(C=O) and the ν(C–O) bands indicate that the molecule is coordinated through both oxygen ligands in the carboxylate group. Nakamoto (1978) found ν(C=O) bands at 1507 and 1526 cm^{-1} for the bidentate structures of a series of transition metal-acetate complexes. The separations between ν(C–O) and ν(C=O) bands were probably more indicative of the structure than the actual ν(C=O) position. That separation for unidentate complexes ranged from 315 to 228 cm^{-1}; for bridging complexes it was 140–169 cm^{-1}; and for bidentate structures, it was 42–77 cm^{-1}. The spectra of stearic acid complexed with chrysotile (Figure 3C) shows a separation of 96 cm^{-1} which corresponds most nearly to the values listed above for bidentate structures. However, a bidentate structure is difficult to envision on the Mg-hydroxide surface, because only one hydroxyl is replaced during the reaction. Likewise, a bridging complex in which the carboxylate connects two Mg^{2+} ions would not be expected for the chrysotile complex. It is also unlikely that the carboxylate salt formed by the reaction of SA with magnesium hydroxide which might have been released by mineral dissolution. The structure of the adsorbed SA may be similar to that shown in Figure 4. Here one oxygen of the carboxylate satisfies a coordination position of Mg, and the other oxygen is hydrogen-bonded to the proton of an adjacent hydroxyl group or to adsorbed water on the surface of the mineral complex, depending on the hydration level.

The carboxylate form of the adsorbed acid was the only species detected over the entire IR range investigated. Spectra of complexes formed at adsorption
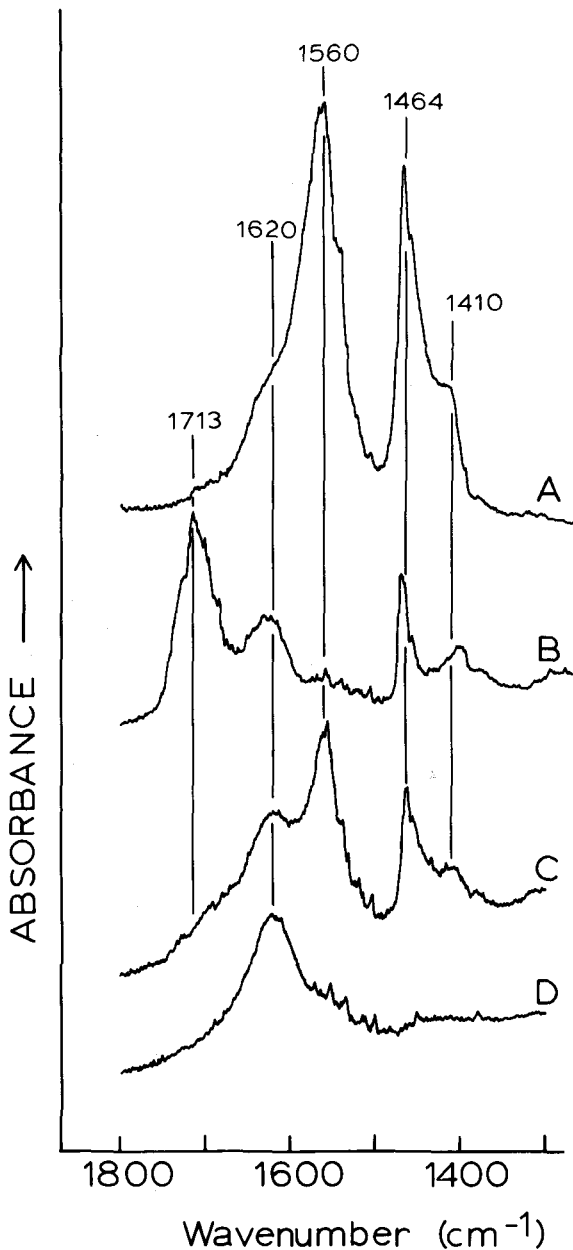
Figure 3. Infrared spectra of (A) Mg-stearate, (B) stearic acid, (C) NaOAc-treated chrysotile with adsorbed stearic acid, and (D) NaOAc-treated chrysotile. All spectra were recorded on samples prepared in KBr. Spectra (A) and (B) were recorded from 0.3 mg sample in 300 mg KBr. Spectra (C) and (D) were recorded from 3.0 mg sample in 300 mg KBr.
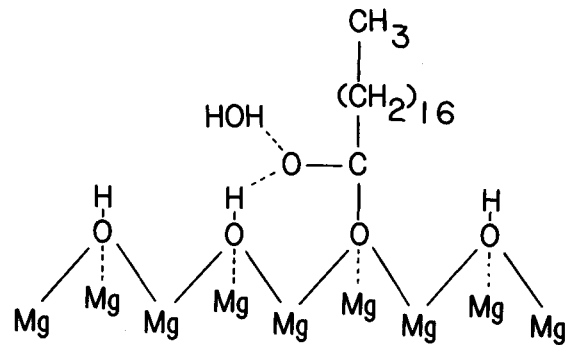

Figure 4. Diagram of the carboxylate form of stearic acid attached to the Mg-hydroxide surface of chrysotile.

heated in SA (100 mg chrysotile and 500 mg SA) at 110°C for 16 hr. Excess SA in the acid form was removed by repeated washings with hexane. IR spectra of the complex showed more carboxylate intense bands at 1560, 1464, and 1410 cm^{-1} than the spectra of complexes prepared by adsorption from hexane. Thus, the mineral surface was not completely covered by stearic acid in the complexes prepared by adsorption because of the low concentrations used. Similarly, the IR spectra showed an absence of the acid form on the complexes prepared by adsorption. From these data, it can be concluded that surface coverage was less than one monolayer, although the amount required for monolayer coverage was not measured.

The alkaline behavior of chrysotile in aqueous suspension is well known (Pundsack and Reimschussel, 1956), and the adsorption reaction described above is in agreement with this property. From HCl-titration data, Pundsack and Reimschussel (1956) estimated that approximately 7% of the total number of hydroxyl groups in the mineral are on the surface of individual fibrils. Because of the basic nature of the chrysotile surface, bonding of suitable organic ligands can be accomplished by simple acid-base reactions (e.g., carboxylic acids) in a manner similar to that found for organosilane-reacted asbestos (Sample *et al.*, 1980). The carboxylate complex appears to be stable in hexane because of the low solubility of the ionic carboxylate form. Formation of this complex resulted in the irreversibility of the SA adsorption-desorption process.

CONCLUSIONS

The lipophilic environment imposed upon the surface of the mineral by SA would likely favor the adsorption of other nonpolar compounds and influence the mobility of small polar molecules associated with the hydrocarbon layer. Acid-base reactions in biological systems containing organic acids may disrupt the bilayer cell membranes as Harington *et al.* (1975) suggested. The SA-chrysotile complex may be useful as an adsorbent

levels of 2.5, 9.2, 21.0, 29.3, and 42.6 mg SA/g chrysotile showed no change in the positions of the bands at 1560, 1464, and 1410 cm^{-1} (as in Figure 3), although the intensities of these bands increased in proportion to the amount of SA adsorbed. To saturate all stearic acid adsorption sites completely, a sample of chrysotile was

material for nonpolar compounds from aqueous solution. The strict geometric arrangement of basic Mg-hydroxide sites on the surface of chrysotile may be useful as a template for surface attachment of metal catalyst ligands.

ACKNOWLEDGMENT

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Резюме—Показано, что адсорбция стеариновой кислоты хризотиловым азбестом в гексане осуществляется путем образования комплекса Mg-стеарата на минеральной поверхности. Инфракрасная спектроскопия не показала никаких следов физической адсорбции стеариновой кислоты в применяемом диапазоне концентрации. Абсорбционные полосы при 1560 см$^{-1}$ и 1410 см$^{-1}$ в спектре комплекса хризотилостеариновой кислоты соответствовали положениям полос в спектре синтетического комплекса Mg-стеарата. Присутствия кислотной формы, которая характеризуется полосой при 1713 см$^{-1}$, не наблюдалось в спектре хризотиловых комплексов. При концентрации равновесия 0,8 мг стеариновой кислоты/мл, минерал адсорбировал 42 мг стеариновой кислоты/г. Дополнительная к наблюдаемой адсорбцией из раствора стеариновая кислота адсорбировалась в форме карбоксило путем нагрева минерала в плавленной стеариновой кислоте. Расчеты, полученные на основе молекулярных размеров стеариновой кислоты и кристаллической структуры хризотила, показывают, что размер молекул стеариновой кислоты является более ограничивающим фактором в возможном заполнении поверхности, чем поверхностная плотность адсорбционных мест Mg–OH. [E.C.]

Resümee—Es zeigte sich, daß die Adsorption von Stearinsäure durch Chrysotilasbest in Hexan durch die Bildung von Mg-Stearatkomplexen auf der Mineraloberfläche erfolgt. Infrarotspektroskopische Messungen zeigten im gesamten untersuchten Konzentrationsbereich keine physikalisch adsorbierte Stearingsäure. Die Adsorptionsbanden bei 1560 cm^{-1} und 1410 cm^{-1} im Spektrum des Chrysotil-Stearinsäurekomplexes stimmen gut mit der Lage der Banden im Spektrum eines synthetischen Mg-Stearatkomplexes überein. Die Säureform, die eine Bande bei 1730 cm^{-1} verursacht, wurde im Spektrum des Chrysotilkomplexes nicht gefunden. Bei einer Gleichgewichtskonzentration von 0,8 mg Stearinsäure/ml adsorbierte das Mineral 42 mg Stearinsäure/g. Wenn das Mineral in geschmolzener Stearinsäure erhitzt wird, wird mehr Stearinsäure als Karboxylat adsorbiert. Berechnungen aufgrund der Molekülgröße der Stearinsäure und der Kristallstruktur des Chrysotil deuten darauf hin, daß als der bestimmende Faktor für die mögliche Oberflächenbesetzung eher die Molekülgröße der Stearinsäure anzusehen ist als die Dichte der Mg–OH-Adsorptionsstellen auf der Oberfläche. [U.W.]

Résumé—On a montré que l'adsorption d'acide stéarique par l'asbeste chrysotile dans l'hexane se produisait par la formation d'un complexe stéarate-Mg sur la surface du minéral. La spectroscopie infrarouge n'a montré aucune évidence d'acide stéarique absorbée physiquement sur l'étendue de concentrations employées. Des bandes d'adsorption à 1560 cm^{-1} et 1410 cm^{-1} dans le spectre du complexe chrysotile-acide stéarique correspondaient aux positions de bandes dans le spectre d'un complexe stéarate-Mg synthétisé. Aucune évidence de la forme acide, qui produit une bande à 1713 cm^{-1} n'était présente dans le spectre des complexes chrysotile. A une concentration d'équilibre de 0,8 mg d'acide stéarique/ml, le minéral a adsorbé 42 mg d'acide stéarique/g. Une quantité d'acide stéarique supplémentaire au-delà de celle observée par l'adsorption à partir d'une solution a été adsorbée dans la forme carboxylate par échauffement du minéral dans l'acide stéarique fondu. Des calculs basés sur les dimensions moléculaires de l'acide stéarique et la structure cristalline de la chrysotile indiquent que le facteur limitant dans l'occupation de surface possible est la taille moléculaire de l'acide stéarique plutôt que la densité de surface des sites d'adsorption Mg–OH. [D.J.]