

INFRARED STUDY OF ATTAPULGITE* AND HCl TREATED ATTAPULGITE

EFRAIM MENDELOVICI

Instituto de Investigación Química, Facultad de Farmacia, Universidad de los Andes, Mérida, Venezuela

(Received 21 September 1972)

Abstract—Infrared absorption spectra show important changes in the positions and form of the absorption bands of a film of attapulgite after it has been pumped out. An attempt to differentiate among some of the multiple frequencies due to OH groups is based on the information obtained from dehydration and deuteration experiments. The 1198 cm^{-1} shoulder, characteristic of attapulgite, is assigned to a Si-O vibration. When attapulgite is refluxed with 5N HCl for 5 hr the octahedral layer is dissolved. The acid attack causes the disappearance of the Si-O-Si absorption bands from attapulgite giving rise to a characteristic vibration at 1090 cm^{-1} , as well as another absorption at 960 cm^{-1} . The latter indicates the presence of silanol groups.

INTRODUCTION

THE i.r. spectra of attapulgite have been reported by Gonzalez Garcia *et al.* (1956) and by Otsuka *et al.* (1968). Also, infrared studies of heated attapulgite have been published (Ovcharenko, 1966; Hayashi *et al.*, 1969; Taracevich, 1970).

The object of this work is to present additional information on the behavior of attapulgite when evacuated. Moreover, some interpretations regarding the frequencies of the OH groups are based on isotopic exchange experiments.

Another aspect of this work deals with the modification of attapulgite upon HCl attack. I.R. spectra of HCl treated attapulgite have not been previously reported.

EXPERIMENTAL

Materials

The material examined in this study was the 43 Georgia attapulgite as supplied by Ward's Natural Science Establishment. The cation exchange capacity is given as 30 mequiv per 100g. This material was suspended in water and the fraction finer than $2\mu\text{m}$ siphoned off. A portion of this fraction was saturated with Ca^{2+} by washing three times with a 1N solution of the chloride and centrifuging. Excess salt was removed by washing with distilled water until a AgNO_3 test for chloride was negative. Unless otherwise indicated the term "attapulgite" employed henceforth will refer to the above prepared sample.

*Part of this work has been done at the Soil Sciences Department, Michigan State University, East Lansing, U.S.A.

Dehydration

Thin self supporting films ($2\text{--}3\text{ mg/cm}^2$) were prepared by drying an aqueous suspension of attapulgite of suitable concentration in aluminum foil dishes. The suspensions had been dispersed for 3 min by ultrasonic vibration.

For the dehydration and deuteration experiment, the resulting films were mounted in an evacuable brass cell fitted with NaCl windows. The vacuum inside the cell, after pumping for 30 min was about 25×10^{-3} mm Hg. The cell could be heated to 100°C and the temperature measured by calibrated thermistors.

Deuteration

Isotopic exchange of hydrogen with deuterium was carried out at 20°C (room temperature) and at 100°C . In the latter case the procedure was as follows: admission of H_2O -free D_2O in contact with the film; evacuation of the cell; and repetition of this process 6 to 7 times during 1 hr, while maintaining the cell at 100°C .

Infrared spectra ($4000\text{--}600\text{ cm}^{-1}$) were recorded on a Beckman i.r.-7, double beam spectrophotometer fitted with NaCl prism and gratings. The films were always oriented normal to the incident beam.

HCl treatment

1.00g of Georgia attapulgite was ground to colloidal size and transferred to a 250 ml round bottomed flask. Then 70 cm^3 of hydrochloric acid (32 per cent) was added, followed by 70 cm^3 distilled water. Two such mixtures were refluxed for 5 and 9 hr. After each period, the solid was

separated and washed until free of Cl^- and then dried in an oven.

For the i.r. study, 1 per cent transparent discs of the dry sample were prepared using potassium bromide of spectroscopic grade. An evacuable die was used for the preparation of the discs.

The i.r. spectra of these discs were recorded using a Perkin-Elmer 621, double beam spectrophotometer.

RESULTS AND DISCUSSION

Dehydration

The spectra shown in Fig. 1 reflect the changes in the absorption bands of a film of attapulgite resulting from evacuation at ambient beam temperature. Thus, the vibrations at 915 and 1198 cm^{-1} virtually disappear as a new absorption at 930 cm^{-1} becomes evident. The large and dissymmetric band at $1655\text{--}1660\text{ cm}^{-1}$ becomes sharp and symmetrical about a maximum at 1625 cm^{-1} (Figs. 1 and 2). Simultaneously the 3330 , 3400 , 3555 and 3595 cm^{-1} absorption bands are removed, the last two being shifted to 3520 and 3570 cm^{-1} respectively. The intensity of the 3625 cm^{-1} band is increased. The spectra in Fig. 2, which cover the stretching and deformation regions of the OH vibrations, show also the partial and complete rehydration of a film of attapulgite due to evacuation and heating at 50 and 100°C . It can be easily seen that total rehydration, brought about by leaving the film in contact with atmospheric moisture during the night at 20°C (ambient temperature), completely regenerated the original absorptions of attapulgite (Fig. 2 d).

Without evacuation, the same results are not obtained. That is, when attapulgite was only heated, the absorption bands did not show any major modi-

fication until the temperature reached 400°C . Similar results have been reported by Hayashi *et al.* (1969).

Deuteration

Exchange with D_2O at 100°C has reduced by 80 per cent the intensities of the 1625 and 3525 cm^{-1} absorption bands, shifting them to 1217 and 2595 cm^{-1} respectively (Fig. 3). The intensity of the

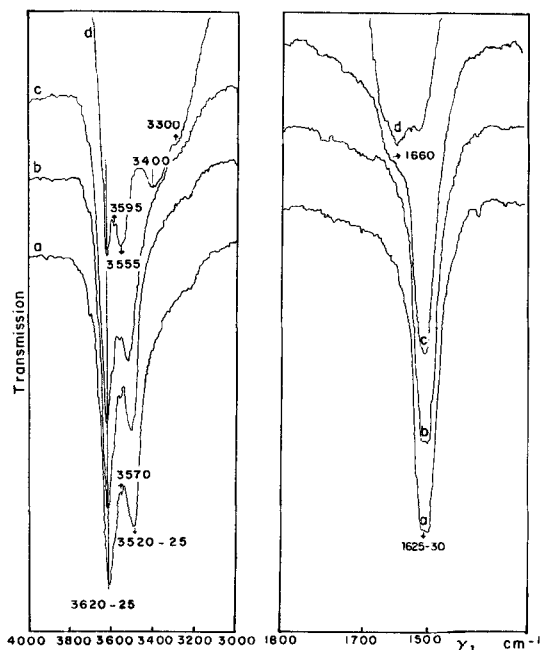


Fig. 2. I.R. spectra of attapulgite films after: (a) evacuation at 50°C , (b) evacuation at 100°C , (c) partial rehydration at room temperature, (d) total rehydration at room (ambient) temperature.

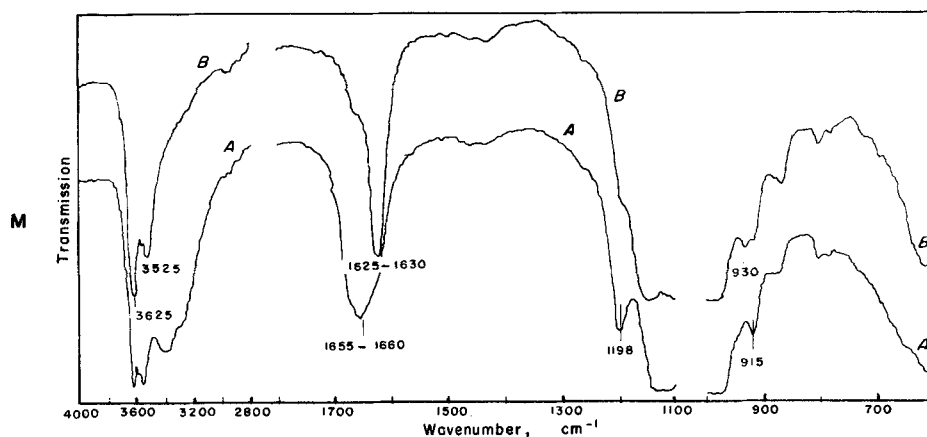


Fig. 1. I.R. spectra ($4000\text{--}600\text{ cm}^{-1}$) of: (a) attapulgite at ambient beam temperature; (b) after evacuation at ambient beam temperature for 30 min.

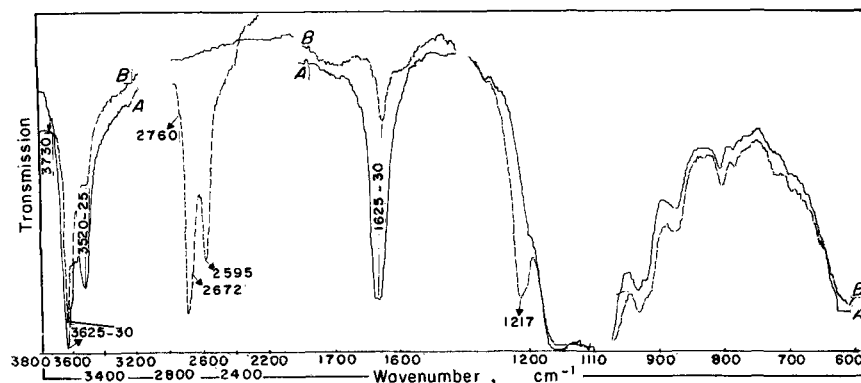


Fig. 3. I.R. spectra of attapulgite after: (a) evacuation at 100°C, (b) deuteration at 100°C.

3625 cm^{-1} band is only slightly diminished; its corresponding deuteroyxl appears at 2705 cm^{-1} . The weak peak at 3730 cm^{-1} on the evacuated attapulgite (Fig. 3a) is also affected by deuteration; its counterpart may be observed at 2760 cm^{-1} . The isotopic ratios of frequencies OH:OD for the 1625, 3525, 3625 and 3730 cm^{-1} vibrations are 1.34, 1.35, 1.34 and 1.35 respectively.

Rehydration of the above deuterated films, by leaving them in contact with atmospheric water for 3 hr, leads to the reappearance of the original frequencies of attapulgite, including that at 3730 cm^{-1} .

Physically sorbed water was removed from attapulgite by evacuation and heating, as is shown by the disappearance of the 3400 cm^{-1} frequency (Figs. 1 and 2). This frequency can be ascribed to the vibrational stretching modes of associated water molecules.

The disappearance of the 3400 cm^{-1} frequency is matched by the shift of the 3555 cm^{-1} band to 3525 cm^{-1} . At the same time the H-O-H deformation band at 1660 cm^{-1} is shifted to a lower frequency at 1625 cm^{-1} . This result suggests that energetically different hydrogen bondings may be involved. The fact that the bands at 3525 and 1625 cm^{-1} are affected by deuteration in a parallel manner (Fig. 3) indicates that they could arise from the same source.

From the continued presence of the 3625 cm^{-1} absorption after the disappearance of the 3555 and 3400 cm^{-1} bands upon dehydration, it seems that the species responsible for this vibration are different from those associated with the other absorption bands observed in the 3000–4000 cm^{-1} region. From the deuteration results we can conclude that the OH which produces the band at 3625 cm^{-1} must be located in inaccessible positions in attapulgite minerals.

The absorption at 3625 cm^{-1} in the H_2O system

of Mg-saponite has been interpreted by Farmer and Russell (1971) as corresponding to bonds to uncharged surface oxygens. Frequencies below 3625 cm^{-1} are assigned to hydrogen bonding to the oxygen of an Si-O-Si linkage, and the lower frequency components to water-water bonds and to H-bonding to the oxygen of an Al-O-Si linkage.

According to Farmer and Russell (1971), when saponite and other trioctahedral layer silicates are evacuated, the chains of water molecules are shortened. This shortening would lead to a trihydrate configuration, which might be responsible for a reduction in the effective symmetry in the silicate lattice and be the cause of perturbation of the Si-O vibrations. A similar interpretation would explain the disappearance upon evacuation of the 1198 cm^{-1} band (assigned to a stretching Si-O vibration) in attapulgite (Fig. 1). Since the frequency at 1198 cm^{-1} has not been reported for any other clay silicate it appears to be characteristic of attapulgite.

Absorption bands at 1200 cm^{-1} arising from silicon-oxygen bonds, have been mentioned by Fripiat *et al.* (1963) in silica gel prepared from ethyl orthosilicate and by Benesi and Jones (1959) in amorphous forms of silica.

The shoulder marked at 3730 cm^{-1} in attapulgite (Fig. 3a) could be due to the presence of silica impurity as has been shown for example in rutile by Jones and Hockey (1971). On the other hand, absorption bands at 3740 cm^{-1} have been mentioned by Angell and Schaffer (1965) in zeolites and by Cannings (1968) in sepiolite and ascribed in both cases to Si-OH vibrations.

HCl treatment

The i.r. spectra of acid-treated Georgia attapulgite (Fig. 4) show that as the absorption band at 915 cm^{-1} is removed, characteristic vibrations appear at 800 and 955–60 cm^{-1} . The latter band

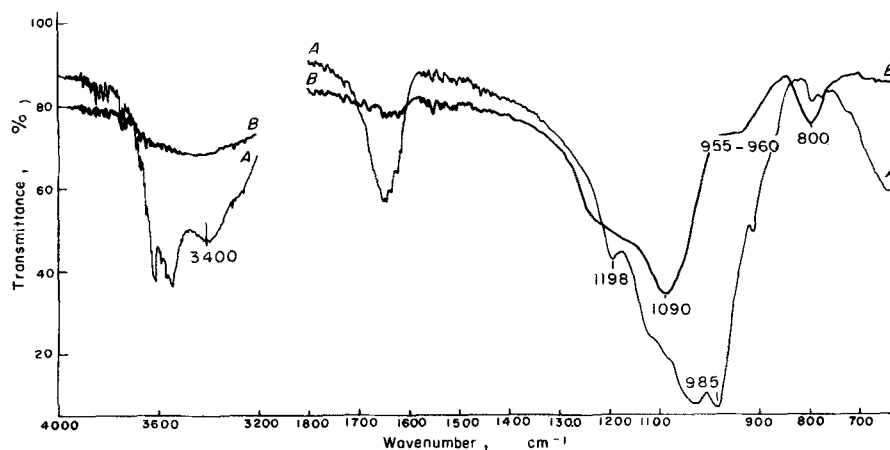


Fig. 4. I.R. spectra of discs of: (a) Georgia attapulgite, (b) after 5 or 9 hr boiling with HCl 5N.

has been attributed to the Si-O-H angle deformation vibration (Fripiat *et al.*, 1963).

Absorptions at 800 and 970 cm^{-1} have also been reported by Gastuche (1963) in HCl treated biotite and at 960 cm^{-1} by Fripiat and Mendelovici (1968) in HCl treated chrysotile. Thus, the 960 cm^{-1} vibration in HCl treated attapulgite must arise from silanol groups. Moreover the large band at 1660 cm^{-1} in attapulgite is considerably reduced upon the HCl treatment, whereas the OH stretching vibrations are replaced by a very broad band covering the OH stretching region.

After 5 hr of acid attack the dissolution of the attapulgite octahedral layer is inferred from the development observed in the absorption bands due to Si-O vibrations. Thus, the absorptions at 985, 1030 and at 1198 cm^{-1} are converted into one characteristic band at 1090 cm^{-1} (Fig. 4). Similar results have been observed in HCl modified chrysotile by Fripiat and Mendelovici (1968).

Studying the HCl modification of attapulgite both by X-ray and DTA, Nathan (1968) also concluded that strong acid attack dissolves completely the octahedral layer of this silicate.

Acknowledgements—The author wishes to express his gratitude to Professor M. M. Mortland of Michigan State University for his guidance, to Dr. Myles Keogh from the Natural Products Division of this Institute for helping in the preparation of the manuscript, and to Dr. W. Hertl for spectra recorded on the 621 Perkin-Elmer Spectrophotometer.

REFERENCES

Angell, C. L. and Schaffer, P. C. (1965) Infrared spectroscopic investigations of zeolite and adsorbed molecules: *J. Phys. Chem.* **69**, 3463–3470.

Résumé—Les spectres d'absorption infrarouge montrent des modifications importantes dans la position et la forme des bandes d'absorption d'un film d'attapulgite, après que ce dernier ait été mis sous vide par pompage. On essaie de faire une différenciation entre les multiples fréquences dues aux

Benesi, H. A. and Jones, A. C. (1959) An infrared study of the water-silica gel system: *J. Phys. Chem.* **63**, 179–182.

Cannings, F. R. (1968) An infrared study of hydroxyl groups on sepiolite: *J. Phys. Chem.* **72**, 1072–1074.

Farmer, V. C. and Russell, J. D. (1971) Interlayer complexes in layer silicates: *Trans. Faraday Soc.* **67**, 2737–2749.

Fripiat, J. J., Leonard, A. and Barake, N. (1963) Relation entre la structure et texture des gels de silice: *Bull. Soc. Chim.* **1**, 122–140.

Fripiat, J. J. and Mendelovici, E. (1968) Dérivés organiques des silicates—I. Le dérivé méthylé du chrysotile: *Bull. Soc. Chim.* **2**, 483–492.

Gastuche, M. C. (1963) Kinetics and dissolution of biotite—I. Interfacial rate process followed by optical measurement of the white silica rim: *Proc. 1963 Int. Clay Conf.*, Stockholm **1**, 67–75.

Gonzalez Garcia, S., Beutelspacher, H. and Flaig, W. (1956) Espectroscopia infrarroja de arcillas y minerales estructuralmente análogos: *An. Real Soc. Esp. Fis. Quim.* **52B**, 369.

Hayashi, H., Otsuka, R. and Imai, N. (1969) Infrared study of sepiolite and palygorskite on heating: *Amer. Mineral.* **53**, 1613–1624.

Jones, P. and Hockey, J. A. (1971) Infra-red studies of rutile surfaces—I: *Trans. Faraday Soc.* **67**, 2669–2678.

Nathan, Y. (1968) Dissolution of palygorskite by hydrochloric acid: *Israel J. Chem.* **6**, 275–283.

Otsuka, R., Hayashi, H. and Shimoda, S. (1968) Infrared absorption spectra of sepiolite and palygorskite: *Mem. Sch. Sci. Eng., Waseda Univ.* **32**, 13–24.

Ovcharenko, F. D. (1966) The regulation of colloidal chemical properties of clay minerals. *Proc. 1966 Int. Clay Conf.*, Jerusalem, **1**, 299–310.

Taracevich, Yu. I. (1970) Spectral study of the thermal dehydration of palygorskite: *Dokl. Akad. Nauk. Ukr. SSSR* **32**, 938–942; quoted in *Chem. Ab.* **74**, 34203M (1971).

groupes OH, en se fondant sur les informations obtenues lors d'expériences de déshydratation et de deutération. L'épaulement à 1198 cm^{-1} caractéristique de l'attapulgite est attribué à une vibration Si–O. Lorsque l'attapulgite est traitée à reflux par HCl 5 N pendant 5 heures, la couche octaédrique est dissoute. L'attaque acide entraîne la disparition des bandes d'absorption Si–O–Si de l'attapulgite, et donne naissance à une vibration caractéristique à 1090 cm^{-1} , ainsi qu'à une autre absorption à 960 cm^{-1} . Cette dernière indique la présence de groupes silanol.

Kurzreferat—Nach Evakuierung eines Attapulgit-Filmes zeigen die Infrarot-Absorptionsspektren wichtige Veränderungen in Lage und Form der Absorptionsbanden. Aufgrund der Informationen, die aus Dehydratisierungs- und Deuterierungsversuchen erhalten wurden, wird der Versuch unternommen, zwischen einigen der vielfachen durch OH-Gruppen hervorgerufenen Frequenzen zu unterscheiden. Die für Attapulgit charakteristische 1198 cm^{-1} Schulter wird einer SiO-Schwingung zugeordnet. Bei 5stündiger Behandlung von Attapulgit mit 5 n-HCl unter Rückfluß wird die Oktaederschicht aufgelöst. Der Säureangriff bewirkt das Verschwinden der Si–O–Si-Absorptionsbanden des Attapulgit und läßt eine charakteristische Schwingung bei 1090 cm^{-1} , sowie eine weitere Absorption bei 960 cm^{-1} entstehen. Letztere zeigt das Vorliegen von Silanol-Gruppen an.

Резюме — Инфракрасные спектры поглощения показывают важные изменения в положениях и в форме полос спектра поглощения пленки аттапульгита, после выкачки. Попытка дифференцирования между многими частотами вследствие присутствия групп OH основано на информации полученной опытами дегидратации и дейтерирования. «Плечо» 1198 см^{-1} , характерное для аттапульгита, относят за счет вибраций Si–O. Если нагревать аттапульгит с 5N HCl в течение 5 часов, то растворяется октаэдральный слой. Агрессивное действие кислоты причиняет исчезновение из аттапульгита полос спектра поглощения Si–O–Si, что ведет к характерной вибрации при 1090 см^{-1} , также как и к добавочному поглощению при 960 см^{-1} . Последнее указывает на присутствие групп силанола.