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► **To cite this version:**

J. Chaussidon, Raoul Calvet. Evolution of amine cations adsorbed on montmorillonite with dehydration of the mineral. The Journal of physical chemistry, 1965, 69, pp.2265-2268. hal-02730884

HAL Id: hal-02730884

<https://hal.inrae.fr/hal-02730884>

Submitted on 2 Jun 2020

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Evolution of Amine Cations Adsorbed on Montmorillonite with Dehydration of the Mineral

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(Received December 29, 1964)

Aliphatic and aromatic amine saturated montmorillonites are dehydrated by heating at temperatures up to 250°. Under these conditions the organic products undergo various transformations of which the first step is a break of the C-N link. An analysis of the reaction products shows that they consist of a mixture of hydrocarbons in the case of aliphatic amines and of phenols corresponding to the amines in the case of aromatic amines.

Introduction

The complexity of the dehydration mechanism of montmorillonite is well known. Fripiat, *et al.*,¹ have shown the impossibility of dehydrating thoroughly a montmorillonite without dehydroxylating the mineral. The residual water, probably chemisorbed on the clay surface around specific sites constituted by the exchangeable cations, may be expected to possess special properties. Among them, Mortland, *et al.*,² Chaussidon, *et al.*,³ and Calvet, *et al.*,⁴ have shown the occurrence of catalytic phenomena during dehydration, which appear as a proton transfer towards adsorbed ions or molecules. For instance, in the case of NH₃ sorption, the infrared spectrum exhibits a band due to NH₄⁺, and in the case of Co(NH₃)₆³⁺ the same result is obtained, moreover, with a rapid decomposition of the complex ion. Mortland, *et al.*,² have stressed the weak value of the dissociation heat of the residual water. Ducros, *et al.*,⁵⁻⁷ have observed the great mobility of the protons of adsorbed water by n.m.r.

As a consequence of these studies, the quoted authors were led to ascribe proton-transfer phenomena to a high degree of residual water dissociation. At this stage two questions arise. (1) Is it possible to show any reactivity of the OH⁻ anion resulting from water dissociation? (2) Is it possible to extend the previous results to other kinds of nitrogen compounds? In order to answer these questions, the evolution of adsorbed aliphatic and aromatic amines during dehydration of the clay has been studied.

Experimental

The clay used in this study was the fraction <2 μ of montmorillonite from Camp Berteau (Morocco) saturated with the following amine cations: aliphatic: methyl-, ethyl-, propyl-, butyl-, diethyl-, and triethylamine; aromatic: aniline, and *o*-, *m*- and *p*-toluidine. Clay samples were dehydrated by heating and studied by infrared spectroscopy. Reaction products were either trapped to -195° or extracted by benzene and studied by gas chromatography, thin layer chromatography, and visible spectroscopy of characteristic derivatives.

Results

A. *Aliphatic Amines.* (1) *Infrared Spectra.* When thermal treatment was applied, one observed a progressive weakening of bands due to amine cations and the development of two bands, one at 1430 cm.⁻¹ and the other at 3280 cm.⁻¹ characteristic of NH₄⁺ clay.

(1) J. J. Fripiat, J. Chaussidon, and R. Touillaux, *J. Phys. Chem.*, **64**, 1234 (1960).

(2) M. M. Mortland, J. J. Fripiat, J. Chaussidon, and J. Uytterhoeven, *ibid.*, **67**, 26 (1963).

(3) J. Chaussidon, R. Calvet, J. Helsen, and J. J. Fripiat, *Nature*, **196**, 161 (1962).

(4) R. Calvet, J. Chaussidon, P. Cloos, C. de Kimpe, J. J. Fripiat, M. C. Gastuche, J. Helsen, A. Jelli, A. Leonard, G. Poncelet, and J. Uytterhoeven, *Bull. Groupe Franc. Argiles*, **14**, 59 (1964).

(5) P. Ducros and M. Dupont, *Compt. rend.*, **254**, 1409 (1962).

(6) P. Ducros and M. Dupont, *Bull. Groupe Franc. Argiles*, **14**, 99 (1964).

(7) P. Ducros, *ibid.*, **14**, 143 (1964).

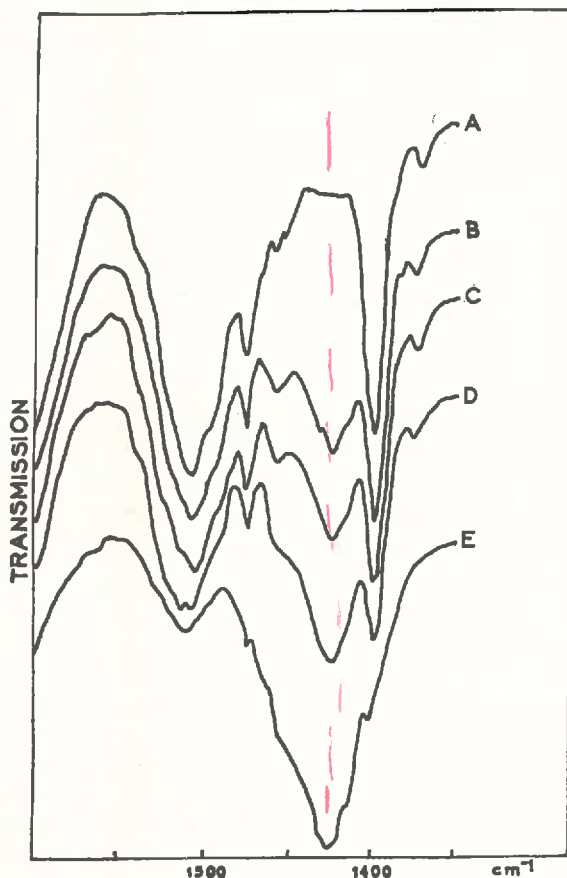


Figure 1. Infrared spectra of ethylamine clay. Samples heated at: A, 20°; B, 100°; C, 150°; D, 200°; E, 250°.

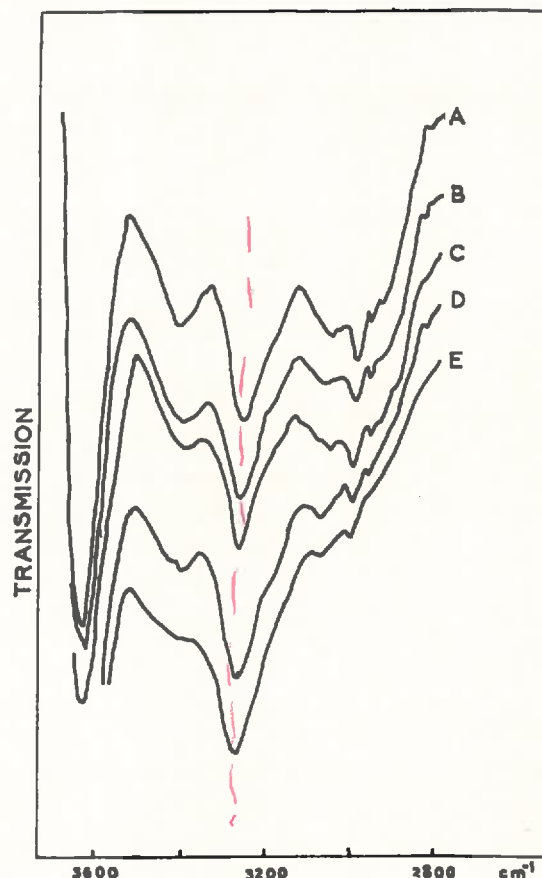


Figure 2. Infrared spectra of ethylamine clay. Samples heated at: A, 20°; B, 100°; C, 150°; D, 200°; E, 250°.

After heating at 250°, the evolution was achieved, and the spectrum corresponded to a mere NH_4^+ clay. Figures 1 and 2 show various intermediate states for ethylamine-saturated clay.

(2) *Gas Chromatography*. Reaction products are a mixture of saturated and ethylenic hydrocarbons. The qualitative composition of this mixture is practically the same whatever may be the nature of the adsorbed amine. The percentages of detected gas may change largely from one sample to another, especially for ethylene, propane, and propylene. Accurate determinations were possible up to 1,3-butadiene. C_6 hydrocarbons were detected but not analyzed.

B. Aromatic Amines. It was not possible to determine any gaseous product. Reaction products condensed in the cooled trap exhibited properties of phenolic compounds. These compounds were found also in the clay. They were analyzed by infrared spectroscopy and by chemical techniques as described previously.

(1) *Infrared Spectra*. For samples dried at room temperature no decomposition occurred. When the clays were heated at 150° for 6 hr., new bands developed. It is noteworthy that C-H out-of-plane vibrations were not modified throughout the heating process.

Figures 3-5 show spectral evolution of *o*-toluidine-saturated clay.

Three observations may be made from Figures 3-5: (a) the aromatic structure is maintained as well as the type of substitution; (b) bands at 1430 and 3280 cm^{-1} due to NH_4^+ clay appear in the spectra; (c) similar compounds are formed whatever may be the initial amine. They can be characterized by two bands in the 1200-1400- cm^{-1} region and one band in the 3380-3390- cm^{-1} region.

This last point needs some discussion. The high frequency band may be due either to an OH group or an NH group (stretching mode). In the clay samples investigated nitrogen can only be engaged in the forms NH_3^+ or NH_4^+ , and it has been recognized that

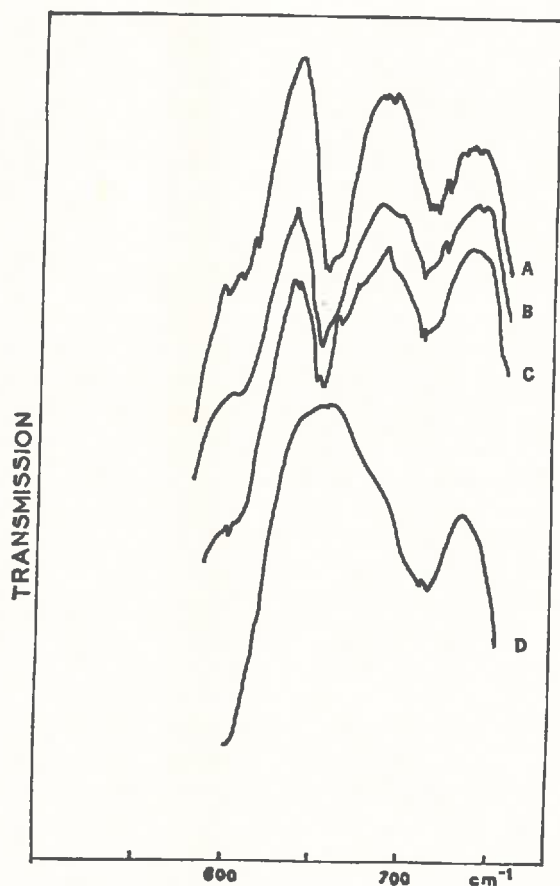


Figure 3. Infrared spectra of *o*-toluidine clay. Samples heated at: A, 20°; B, 100° (for 4 hr.); C, 100° (for 7 hr.); D, 250° (for 2 hr.).

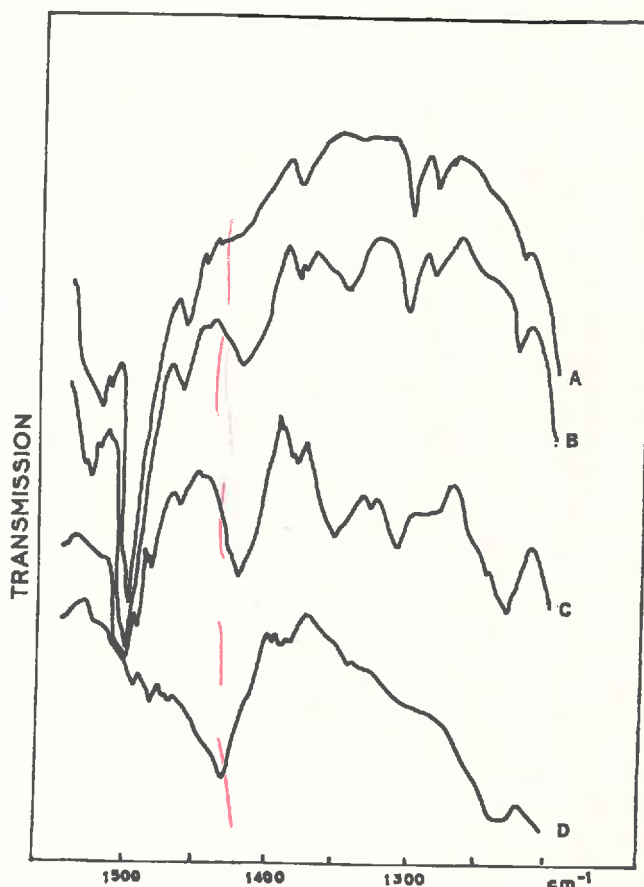


Figure 4. Infrared spectra of *o*-toluidine clay. Samples heated at: A, 20°; B, 100° (for 4 hr.); C, 100° (for 7 hr.); D, 250° (for 2 hr.).

the upper frequency for these groups on the clay is 3300 cm^{-1} . This leads one to assume that the 3380 cm^{-1} band is due to OH groups, the low frequency of which implies evident H bonding. The two bands in the $1200\text{--}1400\text{ cm}^{-1}$ region are more difficult to interpret. It may be observed that compounds such as phenol or *o*-, *m*-, and *p*-cresols exhibit the same bands which are attributed to a complex C-OH deformation.

(2) *Chemical Analysis*. All the methods showed that the reaction product was constituted by the phenol corresponding to the adsorbed amine, that is, phenol for aniline and *o*-, *m*-, and *p*-cresol for *o*-, *m*-, and *p*-toluidine.

In the case of high temperature experiments (for instance, heating at 250° for 24 hr.) the formation of condensed products cannot be precluded.

Discussion

According to the results presented by Mortland, *et al.*,² Chaussidon, *et al.*,³ and Calvet, *et al.*,⁴ it has been

recognized that protons due to a highly dissociated state of residual water can react with physically adsorbed NH_3 or $\text{Co}(\text{NH}_3)_6^{3+}$ balancing the clay exchange capacity, to give NH_4^+ ions.

Experiments reported in this paper allow us to ascribe to these protons the same properties toward adsorbed aliphatic or aromatic amines. This was proved by the steady transformation of amine cation into NH_4^+ which under experimental conditions exhibited two bands at 1430 and 3280 cm^{-1} . Moreover, X-ray diffraction data indicated a collapse of the clay during thermal treatment. For the samples dried at room temperature a rational basal spacing of 13.8 \AA was observed under a vacuum; under the same conditions, heated samples showed a smaller spacing which was no more rational. This indicated a mixed-layer system, one of the components being the 10-\AA NH_4^+ clay.

In addition to these results it is possible to give an interpretation of the role played by OH^- ions. Let

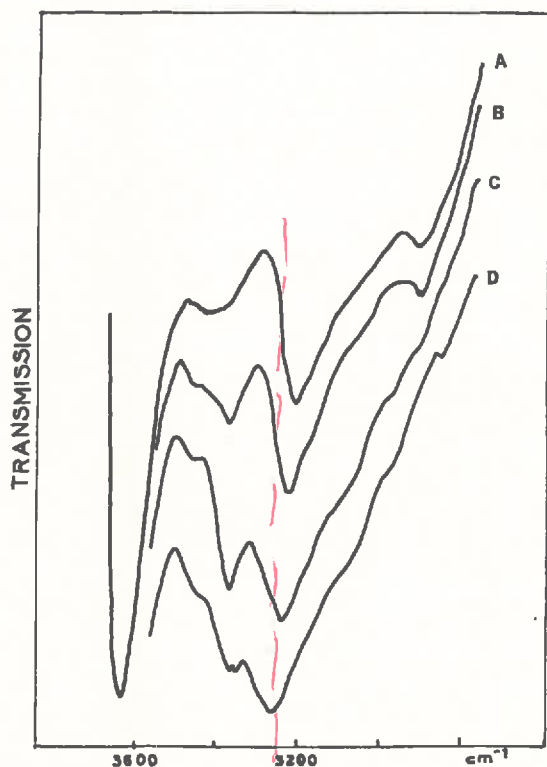


Figure 5. Infrared spectra of *o*-toluidine clay. Samples heated at A, 20°; B, 100° (for 4 hr.); C, 100° (for 7 hr.); D, 250° (for 2 hr.).

$]-\text{ANH}_3^+$ represent an adsorbed amine. One can write schematically



AOH is either an alcohol or a phenol.

It was not possible to detect any alcohol when dehydrating a clay saturated with an aliphatic amine. This is not surprising because it is well known that clay is a very efficient dehydration catalyst for alcohols, leading to hydrocarbons through complex cracking and reforming reactions. It was only possible to check the formation of hydrocarbons, which agrees implicitly with the proposed scheme.

It is difficult to correlate quantitative data with the nature of the amine because a simultaneous break of the C-N link and of C-C links is possible.

With aromatic amines the AOH compound must be phenolic. It may be expected in this case that a part of this reaction product will still be detectable after heating, this being due to the higher stability of this kind of product. Once again, experimental facts agree with the hypothesis. Chemical analyses show that phenolic compounds corresponding to adsorbed amines are formed. This is also observed by infrared spectroscopy and probably means that, in the transformations encountered in the investigated systems, only the C-N link is broken, without any visible alteration of the aromatic ring.

Such reactions may explain some special features of the evolution of fresh organic matter in the soil and represent in part a possible explanation for the genesis of oil and natural gas.