

## IDENTIFICATION OF TETRAMETHYLAMMONIUM ION IN METHYLATED $\text{NH}_4$ -BENTONITE

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**Abstract**—Treating  $\text{NH}_4$ -bentonite with diazomethane results in methylation of adsorbed ammonium with the formation of the tetramethylammonium ion. This ion, which can be completely removed through ion exchange, is distinguished in the IR spectrum by a strong band at  $1480\text{ cm}^{-1}$  due to  $\text{CH}_3$  group bending vibrations. X-ray diffractograms, CEC, and surface area of the clay are not modified by treatment with diazomethane.

**Key Words**—Bentonite, Diazomethane, Exchange, Montmorillonite, Tetramethylammonium.

### INTRODUCTION

The possibility of forming chemical bonds between clay minerals and organic compounds is a much discussed question (Berger, 1941; Martin-Vivaldi et al., 1956; Fripiat et al., 1954; Deuel et al., 1957; Brown et al., 1952; Greenland and Russel, 1955).

Researches on methylating a montmorillonite saturated with different ions have shown the influence of the adsorbed ion on the reactivity of the mineral (Gessa et al., 1976, 1977).

A different behavior has been observed on methylated  $\text{NH}_4$ -clay; in fact, preliminary tests revealed that methylation modifies considerably the  $\text{NH}_4$ -clay IR spectrum and in particular that, in some way, the  $\text{NH}_4^+$  ion reacts with diazomethane.

The object of this work is to establish how  $\text{NH}_4$ -clay behaves under methylation and to clarify the transformation that the  $\text{NH}_4^+$  ion undergoes after diazomethane treatment.

### MATERIALS AND METHODS

Uri bentonite (Sardinia) was used and fractions selected not exceeding  $2\ \mu\text{m}$ .  $\text{NH}_4$ -clay was prepared by treating the clay with 1 N  $\text{NH}_4\text{Cl}$  solution; excess salt was eliminated by washing with water and dialysis.

The  $\text{NH}_4$ -clay methylation was carried out using 180 ml of diazomethane per g of clay as shown in an earlier report (Gessa and Franco, 1974).

Methylated and nonmethylated samples were  $\text{Mg}^{2+}$  saturated, dispersed in  $\text{H}_2\text{O}$  and dried on a glass slide for X-ray analyses, using a Philips diffractometer with  $\text{CuK}_\alpha$  radiation. X-ray diffractograms also were made of the glycolated samples. Potentiometric titrations were carried out with a Radiometer apparatus, employing 0.05 N NaOH as titrating agent.

The CEC determination was made in centrifuge tubes using 1 N  $\text{CaCl}_2$  solution; the adsorbed  $\text{Ca}^{2+}$  ions were determined by means of atomic absorption spectrophotometry using a Beckman apparatus. IR spectra were

produced using a Perkin-Elmer apparatus with KBr discs each containing 0.5% of sample. The surface area was ascertained following the method adopted by Bowler and Goertzen (1959).

### RESULTS AND DISCUSSION

The  $<2\ \mu\text{m}$ -fraction consists of montmorillonite ( $>95\%$ ) and illite ( $<5\%$ ) (Pietracaprina, Novelli and Rinaldi, 1969, 1972). Table 1 shows in meq the NaOH consumed during the potentiometric titrations made in 1 N NaCl solution, the CEC determined with neutral  $\text{CaCl}_2$  solution and the surface area values.

It can be seen that methylation does not modify the permanent and pH-dependent charge of the clay. Surface area values determined with ethylene-glycol are not different when measured before and after the diazomethane treatment.

Potentiometric titration curves of  $\text{Al}^{3+}$ -saturated samples (by treatment with  $\text{AlCl}_3$ ), methylated and nonmethylated, have the same behavior, showing the same buffer range of exchangeable  $\text{Al}^{3+}$  (pH range = 4.2-4.9) and the same "third buffer range" (pH range = 5.5-7.5) as widely discussed in the literature (Harward and Coleman, 1954; Schwertmann and Jackson, 1963, 1964; Sawhney and Frink, 1966; Eschens and Solinas, 1968; Gessa, 1973).

These results show that clay surfaces have not been affected by methylation; this is confirmed by the X-ray diffractograms which are not different after diazomethane treatment.

Figure 1 shows the IR spectrum of  $\text{NH}_4$ -bentonite (a). It will be noticed that the field between 4000 and  $1300\text{ cm}^{-1}$  contains, besides the characteristic bands of OH stretching ( $3630\text{ cm}^{-1}$ ) and  $\text{H}_2\text{O}$  stretching and bending ( $3450, 1630\text{ cm}^{-1}$ ), a broad band at about  $3150\text{ cm}^{-1}$  and a sharper band at  $1400\text{ cm}^{-1}$ , both characteristic of the  $\text{NH}_4^+$  ion. In fact in the case of this ion with Td symmetry, one expects four different vibrations and only the symmetrical stretching  $\gamma_3(\text{F}_2)$  and the asymmetrical bending  $\gamma_4(\text{F}_2)$  are IR active, falling respectively at  $3145$  and  $1400\text{ cm}^{-1}$  (Nakamoto, 1970). The methylated  $\text{NH}_4$ -clay spectrum (Figure 1b) shows a quite strong band at  $1480\text{ cm}^{-1}$ , in addition to the char-

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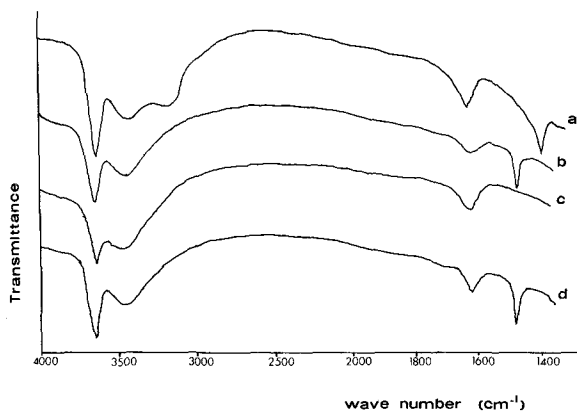


Fig. 1. Infrared spectra on KBr samples: (a)  $\text{NH}_4$ -clay; (b)  $\text{NH}_4$ -clay methylated; (c)  $\text{NH}_4$ -clay methylated and washed with  $\text{MgCl}_2$  solution and water;  $[\text{N}(\text{CH}_3)_4]^+$ -clay.

acteristic clay bands. The  $\text{NH}_4^+$  ion bands at 3150 and 1400  $\text{cm}^{-1}$  have completely disappeared.

The IR spectrum of  $\text{HN}_4$ -clay methylated and washed with  $\text{MgCl}_2$  and  $\text{H}_2\text{O}$  is shown in Figure 1c.

It differs from Figure 1b spectrum in the loss of the band at 1480  $\text{cm}^{-1}$ . The disappearance of the  $\text{NH}_4^+$  ion and the presence of the band at 1480  $\text{cm}^{-1}$  of the methylated compound indicate that methylation of  $\text{NH}_4^+$  takes place with the formation of a compound which is removed through ion exchange.

The methylation of the  $\text{NH}_4^+$  ion is possible in acid media which prevents hydrolysis of the ammonium ion (Eistert et al., 1968); it cannot be excluded in the case of  $\text{NH}_4$ -bentonite which registers a pH index of 5.62 in aqueous suspension (0.2 g of clay in 30 ml of  $\text{H}_2\text{O}$ ).

Partial methylation of the  $\text{NH}_4^+$  ion with the formation of  $[\text{NH}_3(\text{CH}_3)]^+$ ,  $[\text{NH}_2(\text{CH}_3)_2]^+$ ,  $[\text{NH}(\text{CH}_3)_3]^+$  is inadmissible after examining the IR spectra of these ions in other works (Ebsworth and Sheppard, 1959). They all reveal  $-\text{CH}_3$  group stretching bands between

3000 and 2800  $\text{cm}^{-1}$ , which are more intense than the  $-\text{CH}_3$  bendings appearing between 1400 and 1500  $\text{cm}^{-1}$ . Therefore, the most probable hypothesis is the formation of the  $[\text{N}(\text{CH}_3)_4]^+$  ion, which shows its most intense band that relative to the  $\delta(\text{CH}_3)$  asymmetric vibration (Ebsworth and Sheppard, 1959). Other weaker bands of this ion are not distinguishable in the spectrum of methylated  $\text{NH}_4$ -bentonite (Figure 1b); this may be due to the fact that the adsorbed amount of it is rather small.

In order to verify this hypothesis the Mg-clay was treated with a normal  $[\text{N}(\text{CH}_3)_4]^+\text{Cl}^-$  solution and washed with  $\text{H}_2\text{O}$ ; its IR spectrum (Figure 1d) is exactly like that of methylated  $\text{NH}_4$ -bentonite spectrum (Figure 1b).

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Table 1. NaOH consumed in potentiometric-titration.

| SAMPLE  | meq/g clay |        | CEC with $\text{CaCl}_2$<br>meq/g clay | SURFACE AREA<br>$\text{m}^2/\text{g}$ clay |
|---|------------|--------|--|--|
|   | 5.5 pH     | 8.5 pH |  |  |
| Al-clay   | 0.60       | 0.66   | - - -                                  | - - -                                      |
| Al-clay (prepared after methylation of $\text{NH}_4$ -clay) | 0.60       | 0.66   | - - -                                  | - - -                                      |
| Ca-clay   | - - -      | - - -  | 0.62                                   | 620  |
| Ca-clay (prepared after methylation of $\text{NH}_4$ -clay) | - - -      | - - -  | 0.61                                   | 624  |

NaOH consumed during titration at two pH levels, CEC determined with  $\text{CaCl}_2$  and surface areas values.

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Резюме- Обработка бентонита, содержащего  $\text{NH}_4$ , диазометаном определяет метилизацию адсорбированного аммония с образованием иона тетраметиламмония. Этот ион, который может быть полностью удален путем ионного обмена, определяется в инфракрасном спектре интенсивной полосой на  $1480 \text{ см}^{-1}$  благодаря искривляющим колебаниям группы  $\text{CH}_3$ .

Дифрактограммы рентгеновских лучей, катионная обменная способность и площадь поверхности глины не изменились в результате обработки ее диазометаном.