

Intercalation Compounds between a Spanish Bentonite (Gador Montmorillonite) and Ethyl 2-Oxocyclopentanecarboxylate (EOCPC)

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Abstract. The process of retention of ethyl 2-oxocyclopentanecarboxylate (EOCPC) by samples of natural bentonite containing Gador montmorillonite has been studied. Firstly, the adsorbent and the adsorbate were studied by different techniques. Intercalation compounds between them were prepared by two different methods: imbibition at room temperature and reflux heating at 60 °C. The compounds obtained by both treatments were characterized structurally by X-ray diffraction (XRD), infrared spectroscopy (FT-IR), differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

Key words: Montmorillonite, ethyl 2-oxocyclopentanecarboxylate (EOCPC), interlayer compounds.

1. Introduction

Laminar silicates display the property of being able to form interlayer complexes through the interaction of organic molecules inside the interlayer spacing. The ease with which such compounds are formed depends, among other factors, on the nature of the silicate, on the exchange cations involved, on the molecular size of the adsorbate, and on the presence or absence in the latter of functional groups with unshared electrons able to form bonds through hydrogen bridges with suitable groups of the silicate or to become coordinated with the exchange cations of the silicate [1–6].

Bearing in mind that montmorillonite is a mineral with a large specific surface area and that, in view of its structural characteristics, it displays a weak electrostatic union between the layers of the silicate and the hydrated interlayer cations, polar ions readily penetrate into the interlayer space with the corresponding formation of an interlayer complex [7–10].

This type of research was begun by Giesecking [11] and Hendricks [12] in a study employing X-ray diffraction of interlayer complexes of montmorillonite with organic cations. Later, McEvan [13] and Bradley [14] prepared complexes of montmorillonite with neutral or polar molecules. In recent years these studies have acquired greater relevance owing to the use of other physical techniques such

as infrared and NMR spectroscopy; these have afforded better knowledge of the behaviour and properties of molecules adsorbed into the interlayer space. As a result of this, many papers have appeared addressing the formation of complexes with different organic compounds such as ketones, aldehydes, nitriles, amides, sulfoxides, etc. [15, 16]. Accordingly, we felt it of interest to attempt, in a preliminary study, to determine the possibility of the formation of interlayer complexes between montmorillonite and ethyl 2-oxocyclopentanecarboxylate (EOCPC). This molecule has a keto-enol equilibrium (Figure 1), and has been widely used in our Department to prepare coordination compounds both with transition and lanthanide cations [17–19]. It is liquid at room temperature and would be a model for the retention of both neutral and charged molecules, with C=O or C–OH groups, such as pesticides, drugs, etc.

2. Experimental

A montmorillonite from Gador (Almería, Spain), supplied by Minas de Gador S.A. was employed. EOCPC was supplied by Fluka and was of technical purity.

Elemental analysis of the silicate was carried out by plasma emission spectrometry using a Perking-Elmer emission spectrometer, model Plasma II. The sample was previously digested under pressure with a hydrofluoric-nitric acid mixture in a PTFE autoclave.

For the X-ray diffraction study, the Debye-Scherrer technique was employed using samples previously sieved through a 0.050 mm mesh, using a Siemens D-500 diffractometer and Cu K α radiation ($\lambda = 1.54050 \text{ \AA}$). This apparatus is equipped with a Ni filter and a graphite monochromator (efficiency for Cu K α radiation up to 90%) and a DACO-MP data station.

The IR absorption spectra, between 4000 and 400 cm^{-1} , were obtained using a Perkin-Elmer Model 1700 2B FT-IR spectrophotometer, by the KBr pellet technique. Pellets were obtained by mixing the sample and dried KBr (1 : 300 in weight approx.), and applying a pressure, under vacuum, of 8 tons cm^{-2} .

The $^1\text{H-NMR}$ spectrum of the adsorbate (EOCPC) was obtained on a Bruker WP 200 SY spectrometer (200 MHz) with 1,4-dioxane as internal reference. CCl_4 was used as solvent.

Thermal analyses were performed on Perkin-Elmer high temperature analyzers, models 1700 and TGS-2 for DTA and TGA, respectively, both equipped with a 3600 data station. In all cases the heating rate was 12 K min^{-1} and a 60 mL min^{-1} N_2 flow was used.

The adsorption isotherms were obtained on a conventional volumetric adsorption apparatus, with a Baratron MKS model 220B pressure transducer, in the 0–1000 mbar range, after outgassing the samples at 110 $^\circ\text{C}$ for 3 hrs. 99.9992% N_2 from the Sociedad Castellana de Oxígeno (S.C.O.) was used. After obtaining the isotherms, the B.E.T. method was used for calculations.

Interlayer compounds were prepared using two different treatments: (1) Imbibition at room temperature and (2) Reflux heating at 60 °C. In the first method, the bentonite was submerged in a large excess of EOCPC, without stirring for 2, 3, 6 and 12 days. In the reflux heating method the adsorbent is submerged in a sufficient amount of the adsorbate, heating at 60 °C and maintaining it under reflux conditions for periods of 2, 4, 6 and 8 days. After this, the different samples were dried in an oven and kept in a desiccator with 50% wt. H₂SO₄ to avoid rehydration.

3. Results and Discussion

3.1. BENTONITE AND EOCPC

The X-ray diffractogram of a natural sample of bentonite shows that it is formed of montmorillonite, feldspar (~10%), quartz (~5%) and calcite (~5%). This natural bentonite sample, in spite of its impurities, was used in the formation of the intercalation compounds, because it would be more comparative when, for example, the interaction of a soil and a pesticide is investigated. However, a minor to 2 μm fraction, obtained by aqueous decantation, was also used for the characterization of montmorillonite.

The mineralogical formula of 2 μm montmorillonite, on the basis of 12 oxygen atoms, was found to be (Si_{3.71} Al_{0.29}) (Al_{1.43} Mg_{0.34} Fe_{0.12} Ti_{0.01} Mn_{0.01}) O₁₀ (OH)₂ (Ca_{0.08} Mg_{0.15} Na_{0.08} K_{0.06}). The cation exchange capacity (CEC) of this clay is 117 mEq 100 g⁻¹, principally Ca²⁺ and Mg²⁺, with lesser quantities of Na⁺ and K⁺, in agreement with its mineralogical formula.

The bentonite X-ray diffractograms gave a value for the basal spacing of montmorillonite of $d_{001} = 12.6 \text{ \AA}$. Peaks of quartz (3.33 Å), feldspar (3.17 Å) and calcite (3.01 Å) are also observed. Taking into account that the basal spacing of the completely dehydrated species is 9.6 Å, one can be said to be dealing with a one-layer interlayer compound of water.

The FT-IR spectrum of natural bentonite is given in Figure 4; Table I shows the assignment of the corresponding bands in the FT-IR spectrum of the starting bentonite.

DTA analyses of natural bentonite disclose the characteristic behaviour of montmorillonite: in the low temperature region there is an endothermic peak, centered at 140 °C and with a shoulder at 230 °C, due to the loss of adsorbed and hydration water and, in the high temperature region, another endothermic peak is observed. Additionally, an endothermic peak, due to the decomposition of calcite, appears at 650 °C. The overall weight loss is about 22%.

The N₂ adsorption isotherm of montmorillonite displays a sigmoidal shape, corresponding to type II of the BET classification; this is characteristic of non-microporous adsorbents. The specific surface area of natural bentonite was 27 m² g⁻¹.

TABLE I. Assignment of the IR absorption bands of natural bentonite and the intercalation compound obtained by the reflux heating method.

Assignment	Wavenumber (cm^{-1})		
	Bentonite	EOCPC	Interlayer compd.
ν (O—H)	3421	3463	3435
ν (C—H)	—	2980	—
δ (O—H)	1637	1659	1623
Calcite	1450	—	—
ν (C=O)	—	1757, 1727	1734
δ (Si—O—Al)	520	—	528
δ (Si—O—Mg)	467	—	472

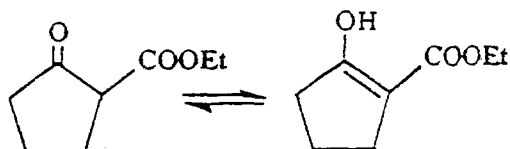


Fig. 1. Keto-enol equilibrium of the EOCPC molecule.

All these results are consistent with those found in the literature for other montmorillonites from different sources [16].

The $^1\text{H-NMR}$ spectra of EOCPC shows that the ketonic form is predominant in this compound, in a 76 : 24 ratio.

3.2. INTERCALATION COMPOUNDS

Figure 2 shows the X-ray diffractograms corresponding to samples of natural bentonite treated with EOCPC at room temperature. The imbibition times correspond to period of 2, 3, 6 and 12 days. The results are shown in Table II, where it is seen that the d_{001} basal spacing of the bentonite increases with the imbibition time up to 6 days of treatment, after which it remains constant, with a value of approximately 14 Å.

X-ray diffractograms of the compounds obtained by the reflux heating method are shown in Figure 3 and the data relating to the basal spacing are shown in Table II. The basal spacing, d_{001} , of the natural bentonite is seen to increase with the time of treatment, reaching a value of 17.8 Å after 8 days, thereafter remaining constant. This shows that a stable composition has been attained under these circumstances. Peaks of quartz, feldspar and calcite also appear.

To determine the possible arrangement of the molecules in the interlayer space of natural montmorillonite, we considered the increase in basal spacing observed

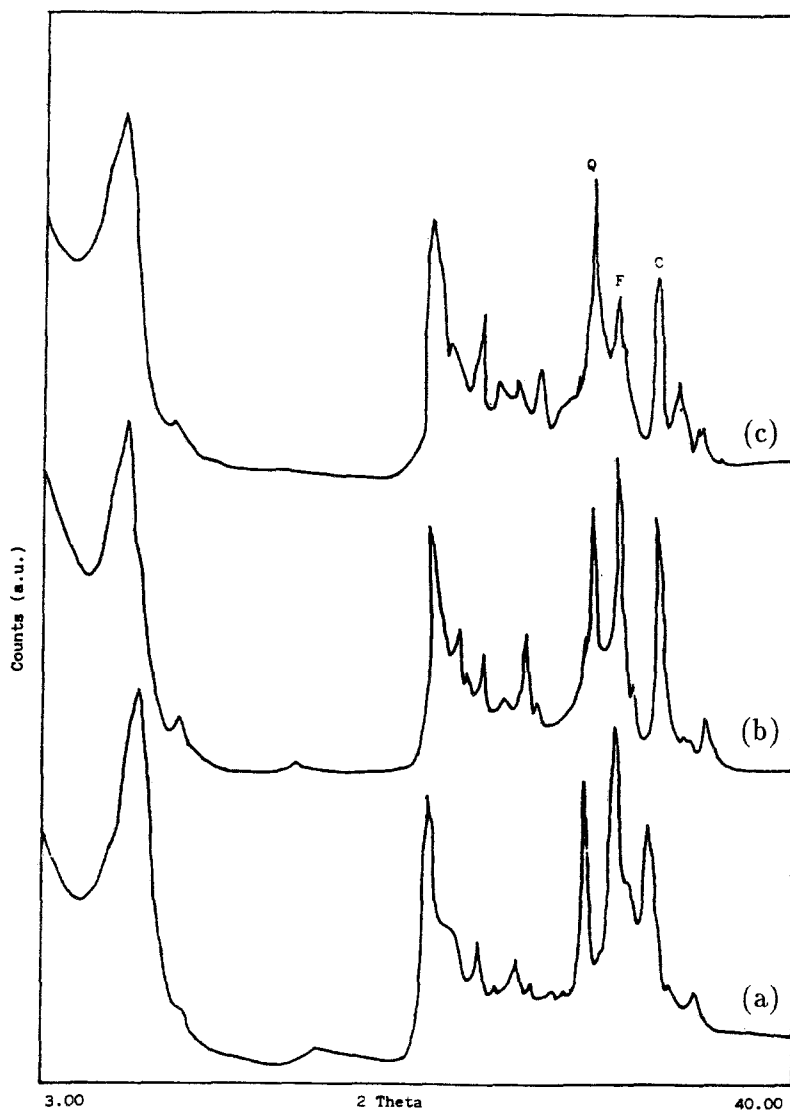


Fig. 2. X-ray diffractograms of natural bentonite treated with EOCPC at room temperature: (a) natural bentonite; (b) imbibition for 6 days and (c) imbibition for 12 days. (Q= quartz, F=feldspar and C=calcite peaks).

by XRD obtained upon the formation of intercalation complexes, together with the geometry of the EOCPC molecule. On comparing the basal spacings of samples obtained by the imbibition method – about 14.0 \AA – with that corresponding to the totally dehydrated montmorillonite, 9.6 \AA , an increase of 4.4 \AA is seen to have occurred in the basal spacing of the silicate. However, considering the basal spacings of samples obtained by the reflux method – about 17.8 \AA – an increase

TABLE II. Basal spacings of natural bentonite and intercalation compounds obtained by the imbibition and reflux heating methods.

Time of treatment	Basal spacing
Nat. bentonite	12.60 Å
Imb. 2 days	13.46 Å
Imb. 3 days	13.84 Å
Imb. 6 days	13.93 Å
Imb. 12 days	13.98 Å
R. heat. 2 days	14.10 Å
R. heat. 4 days	17.43 Å
R. heat. 6 days	17.74 Å
R. heat. 8 days	17.80 Å

of 8.2 Å is deduced. This suggests that one-layer intercalation compounds are obtained when using the first method, but two-layer compounds are obtained when reflux conditions are used.

In an attempt to ascertain that one-layer and two-layer compounds had indeed been obtained, the most probable geometry of the adsorbate molecule, corresponding to its minimum potential energy and deduced from the interatomic distances, the van der Waals radii and the bonding angles of the molecule in its ketone form – which is predominant according to the $^1\text{H-NMR}$ data – was drawn. Taking into account the geometry of the adsorbate, and considering that it is almost flat and has a height of 4.4 Å, it can be said that in the imbibition treatment a one-layer intercalation compound of molecules of EOCPC is formed in the interlayer region of the silicate (Figure 5a). By contrast, when two molecules of EOCPC are considered, these can be situated as indicated in Figure 5b, with a height of 8.2 Å, which is exactly that observed in the compounds obtained by the reflux method. As is well known, montmorillonite, like all smectites, can undergo a swelling in its structure in the direction of the 'c' axis owing to the adsorption of organic compounds in its interlayer space. This behaviour has been observed in other intercalation compounds of similar structure prepared by the authors, obtaining one-layer and two-layer organophosphorus derivatives for different conditions of preparation [20–22].

The FT-IR spectra of natural montmorillonite, EOCPC and the intercalation compound are given in Figure 4, and the assignment of the peaks in Table I. The IR spectra of the intercalated compounds are a mixture of that corresponding to natural bentonite and that of EOCPC. Between 4000 and 3000 cm^{-1} , the peaks corresponding to OH and CH bonds from montmorillonite and EOCPC appear

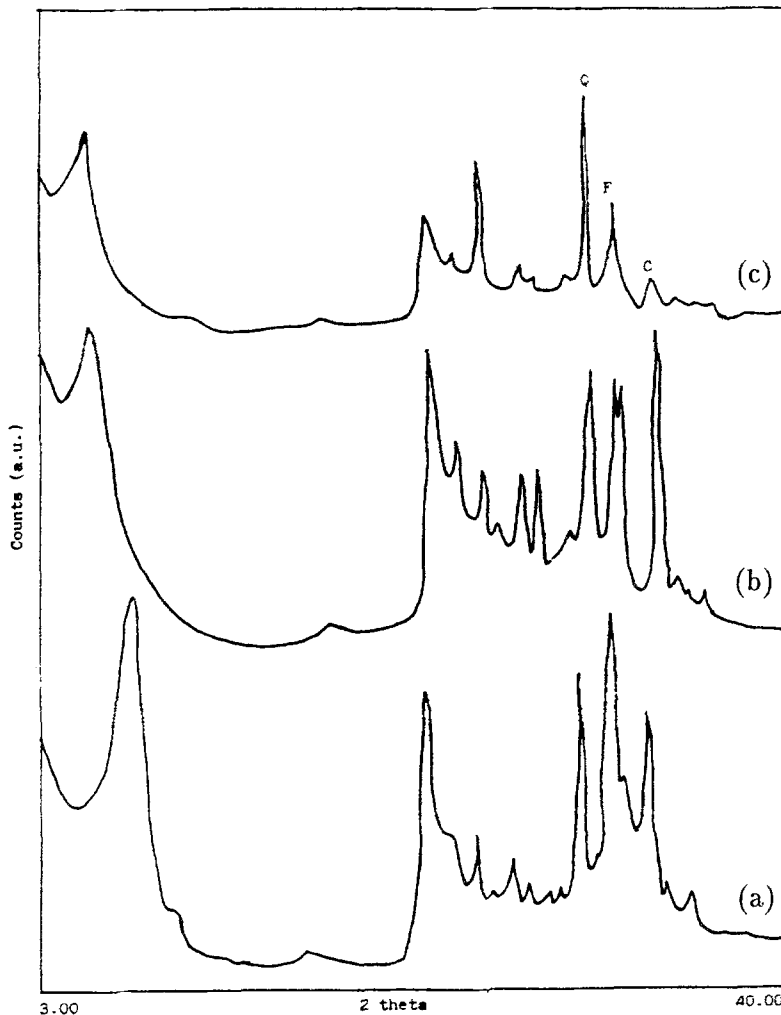


Fig. 3. X-ray diffractograms of (a) natural bentonite and treated with EOCPC under reflux conditions for (b) 6 days and (c) 8 days. (Q=quartz, F=feldspar and C=calcite peaks).

in the intercalation compound. The C=O vibration wavenumber, which in free EOCPC appears as two peaks at 1757 and 1727 cm^{-1} due to the ester and ketone groups respectively, appears in the interlayer compound as single peak situated at 1734 cm^{-1} , demonstrating the interaction of this group with the exchange cations in the interlayer spacing which, due to the positive charge of the cation, affords a lower electronic density between the C=O bond and hence a decrease in the stretching vibration of that bond. The characteristic peaks of EOCPC below 1600 cm^{-1} are almost totally encompassed in the large bands characteristic of the silicate and situated between $1400\text{--}800$ and $800\text{--}300\text{ cm}^{-1}$, respectively.

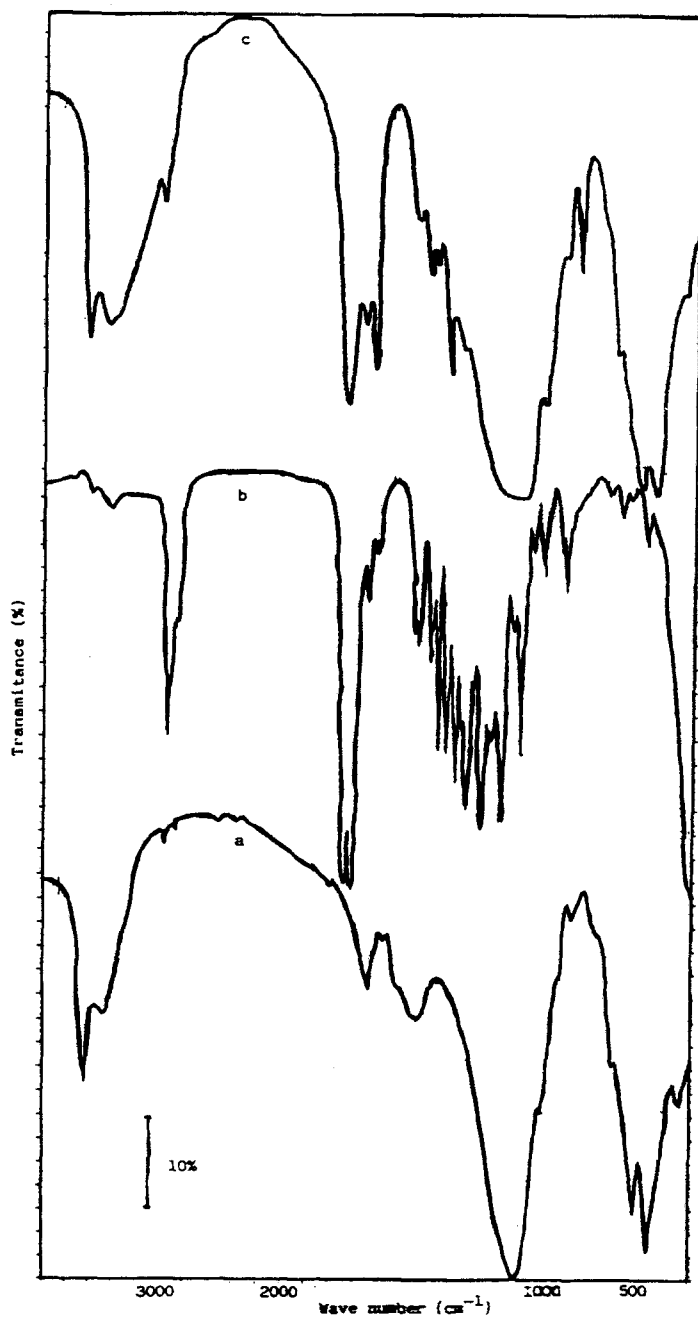


Fig. 4. IR absorption spectra of (a) natural bentonite, (b) EOCPC and (c) bentonite treated with EOCPC under reflux conditions.

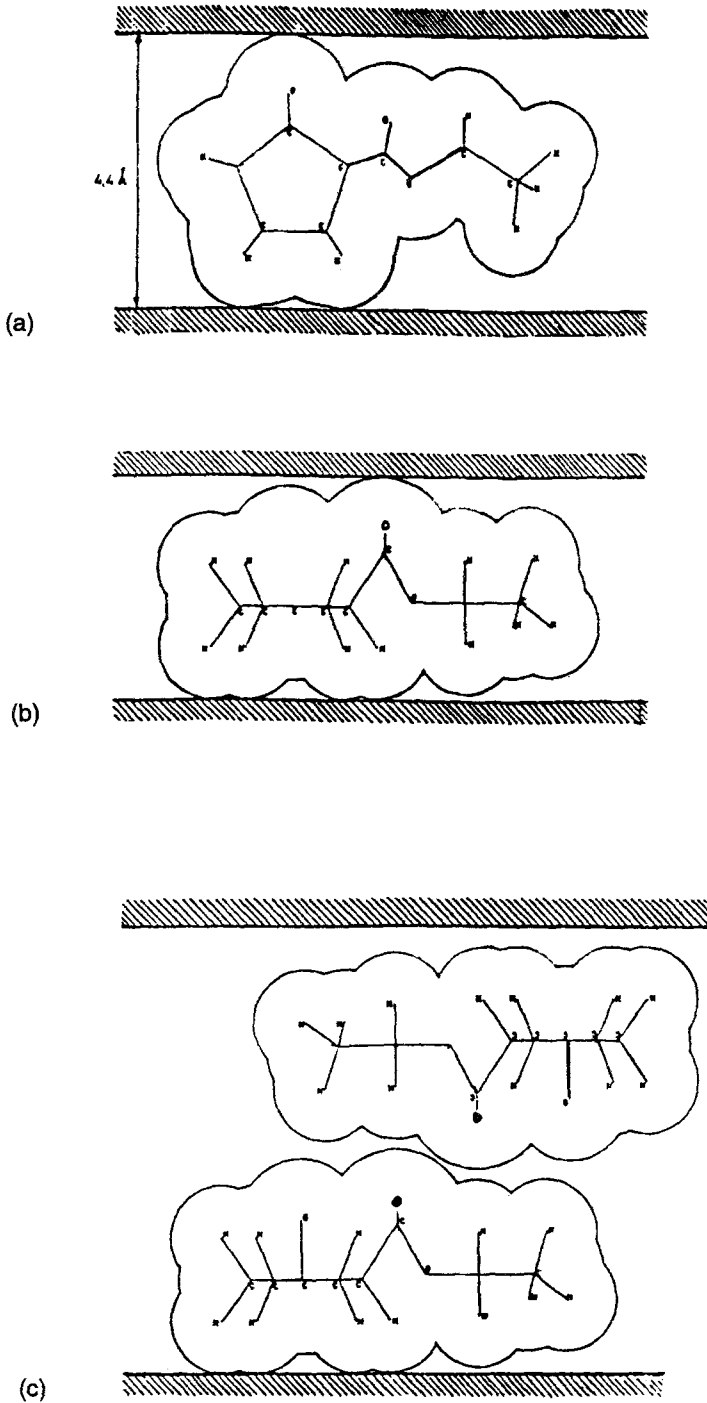


Fig. 5. Arrangement of EOCPC molecules in the interlayer space of montmorillonite: (a) and (b) one-layer compound, (c) two-layer compound; in (a) viewed from the *a* or *b* axes of montmorillonite; in (b) and (c) viewed from the *c* axis of montmorillonite.

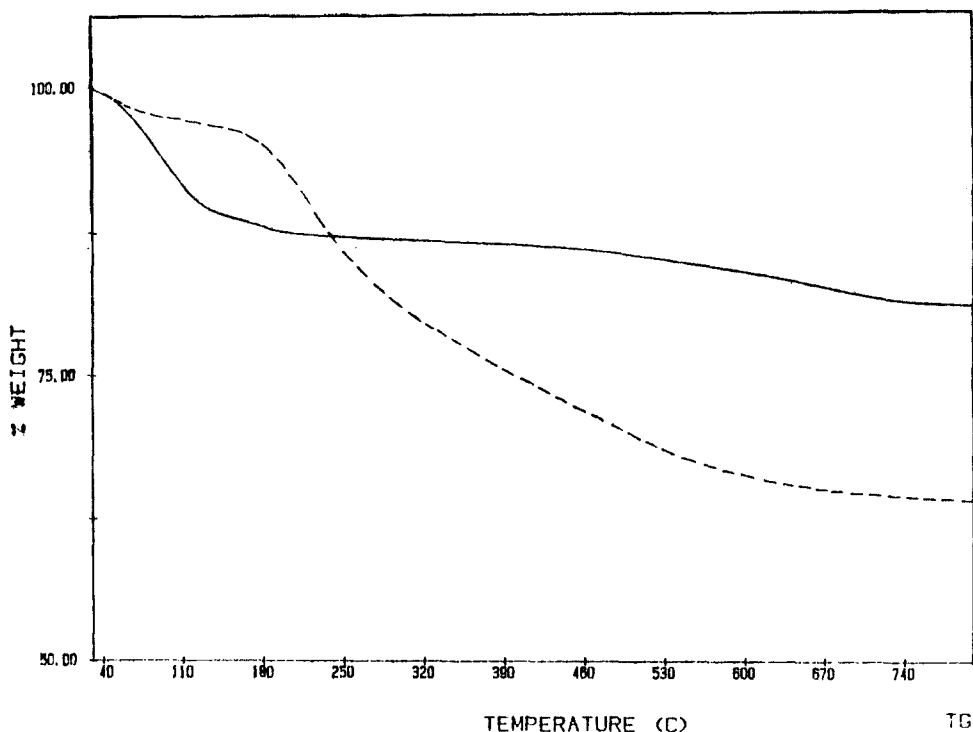


Fig. 6. TGA diagrams of natural bentonite (full line) and the interlayer compound obtained under reflux conditions (dotted line).

In order to determine the thermal stability of the intercalation compounds formed, the thermal behaviour of these compounds was studied in an atmosphere of nitrogen. As can be seen in Figure 6, the process corresponding, in natural bentonite, to the loss of the hydration water of the cations and water less energetically bound, between 30 and 150 °C, has almost disappeared, a quantity of water representing about 2% of its weight remaining in the sample. This is corroborated by the almost complete disappearance of the peak corresponding to this process in the DTA curve. This shows that the molecules of EOCPC penetrate into the interlayer space of the montmorillonite displacing the corresponding molecules of water formerly present in that interlayer, although a few of these molecules do remain in the solid. The loss of EOCPC from the interlayer compounds begins at 150 °C and ends at approximately 550 °C, the total weight loss being 40% of the initial mass.

The different weight losses in the TG curves of natural bentonite (22%, due to the elimination of water and a small quantity of calcite) and of the intercalation compounds (40%, due to the elimination of EOCPC and a small amount of water and calcite) permit one to calculate the amount of EOCPC retained by a given amount of bentonite. In the intercalation compounds obtained by the reflux method,

where this amount is larger, the result obtained was 520 mg of EOCPC g⁻¹ of bentonite.

4. Conclusions

From the study carried out, it can be concluded that treatment of bentonite with EOCPC leads to the formation of one-layer and two-layer intercalation compounds, depending on the method used in the preparation: imbibition at room temperature or reflux heating, respectively.

The incorporation of the organic molecule into the interlayer space of the clay leads to an almost complete elimination of the adsorbed water and a swelling of the clay structure.

The C=O group of EOCPC, by coordination with octahedral cations in the clay, was seen to participate in the clay-organic compound interaction. When using the reflux heating method, the maximum amount of EOCPC retained by the solid was found to be 520 mg/g.

The formation of intercalation compounds between montmorillonite and a model ketoenolic organic molecule has been demonstrated.

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