

Intercalation Compounds between Ethyl 2-oxocyclopentanecarboxylate and Saponite

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Abstract. The retention of ethyl 2-oxocyclopentanecarboxylate by a saponite has been studied. Intercalation compounds were prepared by two different methods: 1) in repose at room temperature and 2) heating at 60 °C under reflux. Contact times between 2 and 12 days were considered for each method. The intercalation compounds obtained were characterized by X-ray diffraction, infrared spectroscopy, chemical analyses and thermal analyses. This characterization indicates that the organic compound is retained both in the interlayer region and at the edge of the clay particles. The amount retained outside of the interlayer space is eliminated by careful washing with benzene and cyclohexane. The results obtained when using acid-activated saponite -obtained by treatment of the clay with dilute HCl solutions- in the intercalation experiments were similar to those obtained when using non-activated saponite.

Key words: ethyl 2-oxocyclopentanecarboxylate, saponite, interlayer compounds

1. Introduction

Organic molecules can intercalate into the interlayer region of layered silicates with expansion, if necessary, of this interlayer space. The intercalation process is conditioned by factors such as the size and the nature of the organic molecules and the nature of the clay. Mechanisms such as ion exchange, cation solvation, dipole-dipole interaction and hydrogen bonding are involved in the formation of the host-guest intercalation compounds [1,2].

Saponite is a magnesian trioctahedral smectite, which originates as a product of the hydrothermal alteration and weathering of basalts and ultramafic rocks. The negative layer charge of saponite is mainly due to the substitution of Si(IV) for Al(III) in its tetrahedral sheet. Mg(II) is the octahedral cation of this clay, a variable amount of other cations, especially Al(III) and Fe(II, III) partially replaces Mg(II) in natural samples [3].

Montmorillonite is the layered clay most widely used for preparing intercalation compounds. Many interlayer compounds between montmorillonite and different organic substances have been described in the literature. Saponite is much less

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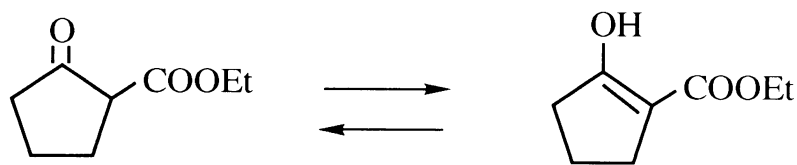


Figure 1. Ketoenolic equilibrium of ethyl 2-oxocyclopentanecarboxylate molecule.

common in Nature than montmorillonite and it has been less studied from all points of view, but in recent years interest in the study of its properties is increasing. For example, it has been found that saponite has an excellent pillaring ability; pillared saponites have been tested as catalysts and adsorbents [4–8].

The Yuncillos saponite deposit is situated in the Madrid Basin, which covers the provinces of Madrid and Toledo (centre of Spain), a zone very rich in Mg-silicates. Sepiolite is the most abundant clay in this basin, the Vallecas deposit being the most important sepiolite deposit in the world. Deposits of saponite and stevensite have recently been reported, although these minerals are much less common than sepiolite [9]. The Yuncillos deposit (province of Toledo) is one of the most important saponite deposits in this basin. The properties of the solids obtained by acid activation of this mineral [10] and the formation of intercalation compounds with nicotine [11] have recently been reported.

Ethyl 2-oxocyclopentanecarboxylate is a β -ketoester with a ketoenolic equilibrium (Figure 1). It has been widely used in coordination chemistry studies carried out in our Department, especially when forming Schiff base-type ligands by reaction with aminoacids; these ligands have been used for preparing coordination compounds with d-transition and lanthanide cations [12–14]. Ethyl 2-oxocyclopentanecarboxylate is liquid at room temperature (b.p. = 218 °C at 704 mm Hg) and would be a model for the retention of both neutral and charged molecules, with C=O or C—OH groups. Recently, we have reported the intercalation process between ethyl 2-oxocyclopentanecarboxylate and montmorillonite [15]. In the present paper, we report its interaction with saponite, with the aim of studying the influence of the properties of the clay on the intercalation process. Solids prepared by acid activation of saponite are also used in the intercalation experiments.

2. Experimental

Natural and acid activated saponite from Yuncillos (Toledo, Central Spain), kindly supplied by TOLSA (Madrid, Spain), were employed as host materials. The raw sample was very pure and only small amounts of quartz and traces of sepiolite were observed as impurities. The $<2 \mu\text{m}$ fraction, obtained after careful aqueous decantation of raw saponite, and acid activated solids were used for retention experiments. The acid activated solids were prepared by treatment of 5 g of the

raw clay with 150 mL of 0.62 wt.% HCl, at room temperature for 6 and 24 hours. The solids were then washed with distilled water until free of chloride anions and air-dried at 50 °C.

Ethyl 2-oxocyclopentanecarboxylate was supplied by Sigma (reference 16,809–2). It was used as supplied, without further purification.

The intercalated compounds were prepared by two different methods: 1) in repose at room temperature and 2) with reflux heating at 60 °C. In the first method, 1.5 g of saponite were immersed in 5.0 mL of ethyl 2-oxocyclopentanecarboxylate in sealed bottles and kept at room temperature for periods of between 2 and 12 days. In the reflux heating method, 1.5 g of saponite were immersed in 5.0 mL of ethyl 2-oxocyclopentanecarboxylate and maintained at 60 °C under reflux conditions and with continuous stirring for periods of between 2 and 12 days. After treatment, the different samples were filtered and dried at 50 °C.

Elemental analyses of the natural and acid activated clays were carried out by plasma emission spectrometry using a Perkin-Elmer emission spectrometer, model Plasma II. The samples were previously digested with a hydrofluoric-nitric acid mixture, under pressure in a PTFE autoclave. The carbon and hydrogen content in the intercalated samples was measured by using a Perkin-Elmer CHN 2400 analyzer.

For the X-ray diffraction study, a Siemens D-500 diffractometer with filtered Cu K_{α} radiation was employed, working at 40 kV and 30 mA (1200W). This apparatus is equipped with a DACO-MP data station and uses Diffract-AT software.

The IR spectra were obtained using a Perkin-Elmer M1700 2B FT-IR spectrophotometer, in the region between 4000 and 350 cm^{-1} and using the KBr pellet technique. Pellets were obtained by mixing the sample and dried KBr (1 : 300 in weight aprox.), and applying a pressure, under vacuum, of 8 tons/ cm^2 . The spectrum of ethyl 2-oxocyclopentanecarboxylate was obtained from a drop of this compound deposited between two pellets of KBr.

Thermal analyses were performed on Perkin-Elmer analyzers, models 1700 and TGS-2 for Differential Thermal Analyses (DTA) and Thermogravimetric Analyses (TGA), respectively, both equipped with a 3600 data station. In all cases the heating rate was 10°/min and a 60 cm^3/min air flow was used.

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

Specific surface area and porosity analyses of natural and acid activated saponite were determined from the corresponding nitrogen adsorption-desorption isotherms at 77K, obtained from a Micromeritics ASAP 2010 analyzer, after outgassing the samples at 110 °C for 8 hours.

3. Results and Discussion

3.1. NATURAL AND ACID ACTIVATED SAPONITE

Saponite from the Yuncillos deposit (Province of Toledo, Spain) was employed as raw material for the present study. This saponite is very pure and only small amounts of quartz and sepiolite are observed as impurities. The $<2 \mu\text{m}$ fraction was used for retention experiments. Some of the data about this $<2 \mu\text{m}$ fraction are [10]:

Chemical composition: SiO_2 : 49.45; Al_2O_3 : 4.72; Fe_2O_3 : 1.29; MgO : 24.34; TiO_2 : 0.20; MnO : 0.03; CaO : 0.78; Na_2O : 0.07; K_2O : 0.44; H_2O : 18.31%.

Structural formula: $[\text{Si}_{3.71} \text{Al}_{0.29}] \text{O}_{10} (\text{OH})_2 [\text{Al}_{0.13} \text{Mg}_{2.58} \text{Fe}_{0.07} \text{Ti}_{0.009} \text{Mn}_{0.02}] [\text{Ca}_{0.062} \text{Mg}_{0.12} \text{Na}_{0.010} \text{K}_{0.042}]$.

Cation exchange capacity (CEC): 115 mEq/100 g.

BET surface area: $165 \text{ m}^2/\text{g}$.

The conditions employed in the acid treatments of saponite are very mild, using dilute HCl solutions and room temperature. In spite of this, and because of the easy attack of saponite with HCl, the treatments produce important structural alterations in the clay. The acid treatments result in removal of the exchange cations, substituted by H^+ , and of variable amounts of the octahedral cations, especially Mg(II). About 46 and 53% of the total of the octahedral cations have been removed in the two acid activated solids considered. The surface area of the solids thus obtained is higher than that of the raw clay, reaching values of 288 and $309 \text{ m}^2/\text{g}$ for the solids treated with 0.62% HCl for 6 and 24 hours, respectively.

3.2. INTERLAYER COMPOUNDS

As indicated, intercalation compounds between ethyl 2-oxocyclopentane-carboxylate and saponite were prepared after repose and after reflux heating for periods of between 2 and 12 days. The interlayer compounds are pale red to pale brown in colour, while raw saponite is pale yellow in colour. The colour of the interlayer compounds may be due to the coordination bonds between the adsorbate and the Fe(III) octahedral cations of the clay; it should be taken into account that the iron content of the clay is moderately high, 1.29% expressed as Fe_2O_3 .

The interlayer compounds have basal spacings between 18.1 and 18.9 \AA (15.1 \AA in the raw saponite). These spacings were similar when the repose and the reflux heating methods were used for the preparation of the interlayer compounds and when natural and acid activated saponite were used as host materials (Figure 2, Table I). The 001 reflection peaks are narrower and more intense in intercalated solids than in natural and acid activated saponite, as shown by the lower values of their f.w.h.m. indexes. The minimum basal spacing of natural saponite, corresponding to the totally dehydrated clay, is 9.8 \AA . Thus, the molecules of ethyl

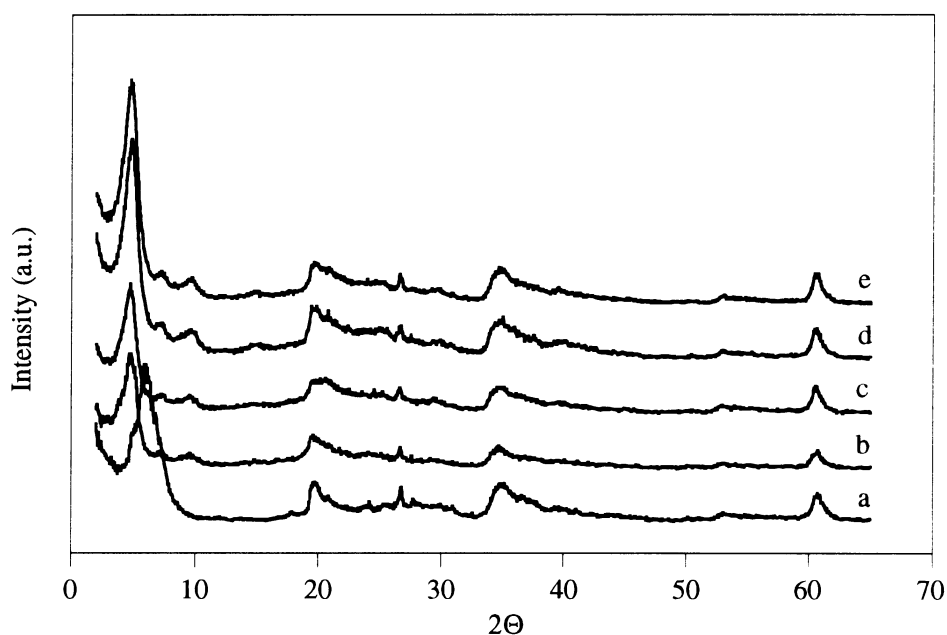


Figure 2. X-ray diffractograms of natural saponite (a) and intercalation compounds obtained after repose for 2 (b), 5 (c), 8 (d) and 12 (e) days.

2-oxocyclopentanecarboxylate occupy a thickness of 8.3–9.1 Å in the interlayer space of the clay. The minimum thickness of the organic molecule, parallel to the C₅ ring, has been calculated to be 4.4 Å, considering the ketonic form of the molecule, predominant (76%) according to the ¹H-NMR data [15]. Thus, the intercalation compounds are formed, in all cases, by a bilayer coverage of the adsorbate molecules in the interlayer space of the clay. α -Type complexes, with the C₅ rings situated coplanarly to the saponite layers, may be formed. The differences observed in the basal spacings of the interlayer compounds may be due to the different packing of the organic molecules on the surface of the clay.

When studying the intercalation of montmorillonite with ethyl 2-oxocyclopentanecarboxylate [15], the formation of bilayer compounds was observed only when using the reflux conditions, while in the case of saponite the bilayer coverage is also obtained when repose conditions are used. Thus, the formation of intercalated compounds seems to be easier when using saponite than when using montmorillonite.

The FT-IR spectra of all the intercalated compounds are very similar. As an example, the spectrum of the solid prepared by the reflux treatment for 5 days, compared with the spectra of saponite and of ethyl 2-oxocyclopentanecarboxylate, are given in Figure 3. A summary of the assignment of the different bands is given in Table II. The bands of the clay are most intense in the spectra of the interlayer compounds and only some small bands of the adsorbate are clearly observed. In

Table I. Basal spacings of saponite and of the intercalation compounds with ethyl 2-oxocyclopentanecarboxylate

Sample	Basal spacing (Å)	f.w.h.m. (2 θ degrees)
Raw saponite	15.1	1.616
Repose 2 days	18.5	1.055
Repose 5 days	18.9	1.026
Repose 8 days	18.1	1.044
Repose 12 days	18.2	1.129
R. heating 2 days	18.5	1.059
R. heating 5 days	18.9	1.075
R. heating 12 days	18.9	1.094
HCl 0.62% – 6 hours	14.6	1.282
HCl 0.62% – 6 hours, Rep. 5 days	17.8	1.196
HCl 0.62% – 24 hours	15.1	1.250
HCl 0.62% – 24 hours, Rep. 5 days	18.5	1.064
Repose 5 days washed with benzene	17.8	1.221
Repose 5 days washed with cyclohexane	18.1	1.122
Reflux 5 days washed with benzene	18.5	1.093
Reflux 5 days washed with cyclohexane	18.9	1.146
HCl 0.62% – 24h, Rep. 5 days washed with benzene	14.8	1.224
HCl 0.62% – 24h, Rep. 5 days washed with cyclohexane	15.1	1.741

Rep. = Repose method; R. heating=Reflux heating method.

the region of higher wavenumbers, bands corresponding to OH and CH bonds are observed. The Mg_3OH vibration mode appears in the interlayer compounds at 3682 cm^{-1} . In the natural clay, this mode is observed only as a small shoulder at the same wavenumber. The increase in intensity of this peak may be due to the exclusion of the water molecules of the clay during the intercalation process, preventing H-bonding of the $\text{Mg}_3\text{O-H}$ hydroxyl, and suggests the interaction of the adsorbate with the OH groups of the clay. This effect has been previously observed during the interaction of organic compounds in sepiolite, attapulgite and saponite [2, 11, 16].

The O—H bond appears in the interlayer compounds at 3420 cm^{-1} , very close to its wavenumber in the spectrum of natural saponite (3426 cm^{-1}), while in ethyl 2-oxocyclopentanecarboxylate it appears at 3463 cm^{-1} . The O—H bond is only present in the enolic form of this compound; its $^1\text{H-NMR}$ spectrum indicates that this isomer is present in 24% abundance.

The C—H vibration band appears in the interlayer compounds at about 2980 cm^{-1} , at the same wavenumber as in the organic compound. The same behaviour is observed for the bands at about 1450 , 1400 , 1370 , 1265 and 1180 cm^{-1} , which have no variation from the organic compound to the intercalated solids.

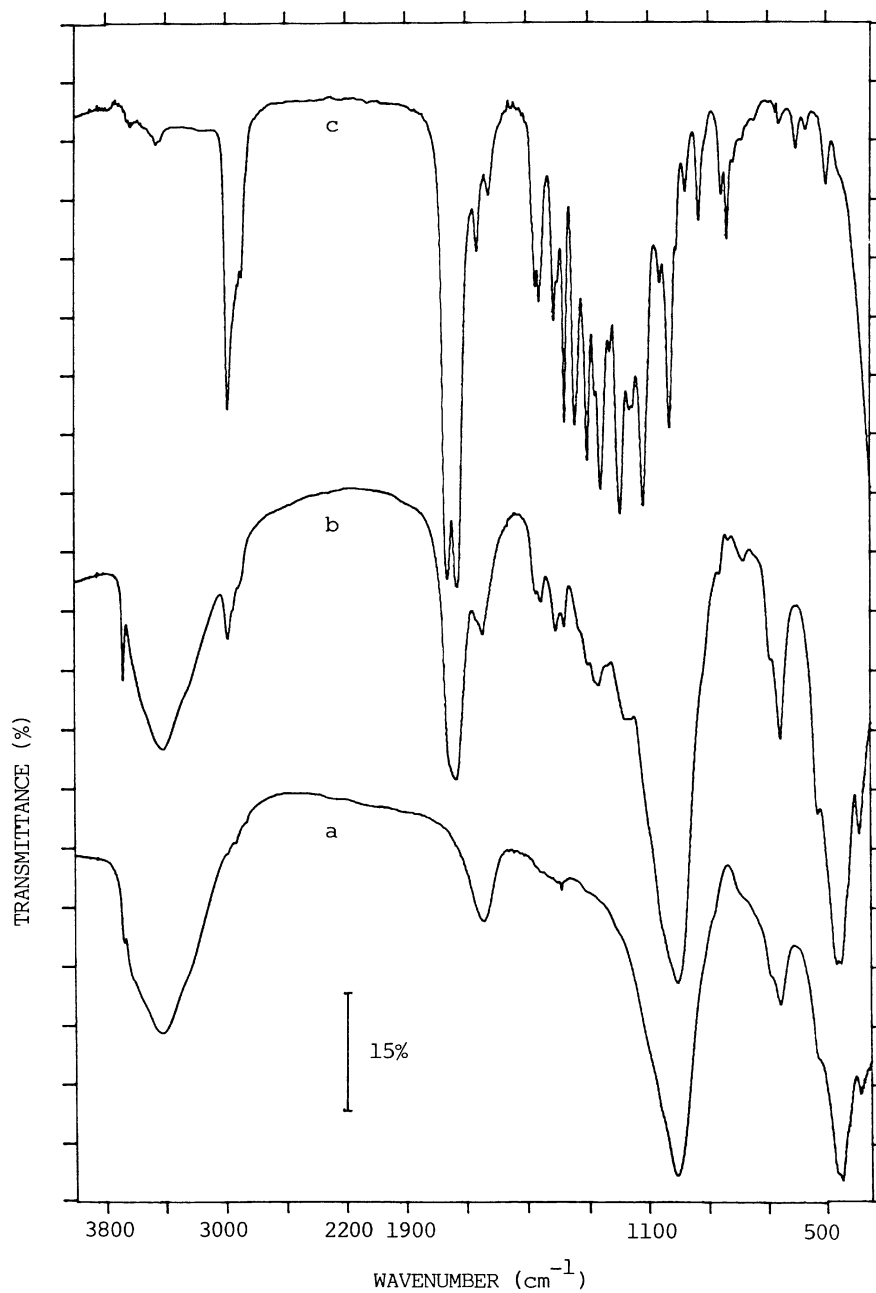


Figure 3. FT-IR spectra of natural saponite (a), ethyl 2-oxocyclopentanecarboxylate (c) and the intercalation compound obtained after reflux heating for 5 days (b).

Table II. Assignment of the FT-IR absorption bands of saponite and of the intercalation compounds with ethyl 2-oxocyclopentanecarboxylate

Assignment	Wavenumber (cm ⁻¹)		
	Saponite	EOCPC	Interlayer compd.*
ν (O—H)	3678(sh), 3426	3463	3683, 3418
ν (C—H)	—	2980	2983
C=O	—	1757, 1727	1728, 1752(sh)
δ (H ₂ O)	1637	—	1639
Si—O—Si	1011	—	1006
Si—O—Al	530 (sh)	—	530
Si—O—Si	—	—	466
Si—O—Mg	448	—	449

* Similar in all the interlayer compounds. Data on the solid obtained after 5 days under reflux heating are given as example.

The bands corresponding to ester and ketone groups appear in the ethyl 2-oxocyclopentanecarboxylate spectrum at 1757 and 1727 cm⁻¹, the ketone group only being present in the ketonic isomer, which constitutes, according to the ¹H-NMR spectrum, 76% of the total of molecules. In the interlayer compounds, a single band appears at 1728–1730 cm⁻¹, with a small shoulder at 1752 cm⁻¹. This variation proves the interaction of the ester and ketone groups of the adsorbate with the interlayer cations of the clay. This interaction was observed, even with higher intensity, when studying the intercalation of ethyl 2-oxocyclopentanecarboxylate in montmorillonite [15].

The bands situated at lower wavenumber, due to the vibration of the clay groups, do not undergo important changes from the clay to the interlayer compounds. The very intense Si—O—Si vibration shifts from 1011 to 1006 cm⁻¹, masking the bands of the adsorbate in this region; the band at 658 cm⁻¹, due to Si—O—Si bonds, does not change. The intensity of the Si—O—Al mode, which appears in the natural clay as a small shoulder at 530 cm⁻¹, is enhanced in the interlayer compounds and the band at 448 cm⁻¹ appears in the interlayer compounds as two bands at 466 and 449 cm⁻¹, assigned to Si—O—Si and Si—O—Mg modes, respectively.

The IR spectra of the acid activated saponite are similar to those of natural saponite, with bands of free silica at 795 and 465 cm⁻¹. The spectra of the solids obtained after intercalation of acid activated saponite are very similar to those obtained by intercalation of natural saponite, showing the bands indicated before.

TG and DTA analyses were employed to study the thermal decomposition of the interlayer compounds. Natural saponite shows the thermal behaviour usually described for this clay, with a weight loss from 30 to 200 °C, due to the loss of adsorbed water, a very gentle slope from 200 to 800 °C and, in excess of this temperature, the loss of constitution hydroxyl groups, these losses totalling up to

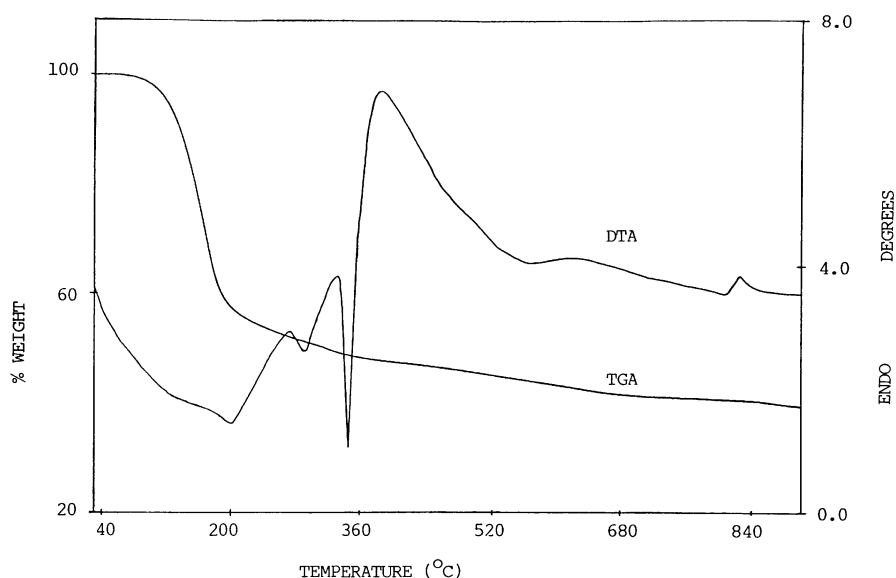


Figure 4. TGA and DTA curves of the intercalation compound obtained after repose for 8 days.

18% of the weight of the clay. In the DTA curve, the corresponding endothermic effects due to the loss of water molecules and hydroxyl groups are observed, giving a final exothermic effect at 840 °C due to the final phase change from saponite to enstatite [17].

The thermogravimetric analyses of the intercalated compounds show a very intense weight loss from 60 to 400 °C, due to the desorption of the adsorbate. At higher temperature, a gentle loss is observed, attributed to the loss of remaining adsorbate and of hydroxyl groups (Figure 4).

DTA analyses of the intercalated compounds show a wide endothermic effect between room temperature and about 240 °C, which may be due to the desorption of the molecules of the adsorbate retained out of the interlayer space. A second endothermic effect is centered at 295 °C, probably due to the boiling point of the adsorbate (the boiling point of the free molecule is 218 °C at 704 mm Hg). Subsequently, a very narrow endothermic effect appears at 345 °C, and immediately a very wide exothermic effect is observed (Figure 4). The endothermic effect is probably due to the evaporation of the molecules of ethyl 2-oxocyclopentanecarboxylate retained in the interlayer space, the exothermic effect being due to the subsequent combustion of these molecules.

Thermogravimetric analyses were used to calculate the amount of adsorbate retained in the different intercalation compounds. The weight losses in the curves of the intercalated compounds reach values between 37 and 58% of the weight of the solids, these amounts varying irregularly from one sample to another. These

differences also indicate that a variable amount of the adsorbate is retained out of the interlayer space, at the edges of the clay particles. The high amount of the adsorbate retained may be related to the high surface area of the raw saponite, $165 \text{ m}^2/\text{g}$, higher than that usually found for layered clays because of the very small particle size of this sample.

In order to remove the molecules of the adsorbate retained out of the interlayer space, in the edges of the clay particles, the intercalated solids were carefully washed with benzene and cyclohexane, non-polar solvents in which ethyl 2-oxocyclopentanecarboxylate is soluble. The solids from the intercalation of natural saponite have, after washing, basal spacings between 17.8 and 18.9 Å, thus proving the maintenance of the adsorbate molecules in the interlayer space of the clay. In the intercalated solids from the acid activated saponite, after washing with benzene and cyclohexane, the basal spacing decreases to 14.8–15.1 Å, indicating an almost total dissolution of the adsorbate. This difference in behaviour between the solids from the intercalation of natural and acid-activated saponite may be due to the higher accessibility of the acid treated solids because of the removal of impurities and of exchangeable and octahedral cations.

The thermal analyses of the solids washed with benzene and cyclohexane show weight losses which depend on the methods of preparation of the intercalated solids. When the samples prepared by the repose method were considered, the weight losses varied between 30–35%; when the samples prepared by the reflux method were studied, the weight losses increased to 40–45% and for the acid activated solids values of 20–25% were obtained. Selected washed samples were submitted to CHN analyses to obtain their actual adsorbate content. The results obtained are given in Table III. It can be observed that the adsorbate is more easily removed by benzene than by cyclohexane, while the samples from intercalation by the reflux heating method contain a higher amount of adsorbate than those from the repose method. The amount of adsorbate retained by the samples from the acid activated saponite suggest that these solids present a monolayer stacking of adsorbate molecules between their layers. The CHN analyses allows calculation of the amount of adsorbate retained in the interlayer space of the clay, giving values of between 225–510 mg of ethyl 2-oxocyclopentanecarboxylate per gram of natural saponite and of between 120–260 mg of ethyl 2-oxocyclopentanecarboxylate per gram of acid activated saponite. The fact that these values correspond to benzene and cyclohexane washed samples should be taken into account. Before this washing, the amount retained is similar for both natural and acid activated saponite. In the acid activated solids, ethyl 2-oxocyclopentanecarboxylate may be retained by the free silica produced during the acid activation, and is easily removed by the washing of the solids.

Table III. Ethyl 2-oxocyclopentanecarboxylate content in the intercalated solids after washing with benzene and cyclohexane

Sample	Adsorbate content (%)
Repose 5 days washed with benzene	21.4
Reflux 5 days washed with benzene	30.2
Reflux 5 days washed with cyclohexane	38.4
HCl 0.62%-24h, Rep. 5 days washed with benzene	12.6
HCl 0.62%-24h, Rep. 5 days washed with cyclohexane	26.3

4. Conclusions

Intercalated compounds were prepared by treatment of natural and acid activated saponite with ethyl 2-oxocyclopentanecarboxylate, in repose at room temperature or with heating at 60 °C. Times of contact between 2 and 12 days were used. Solids with basal spacings of 18–19 Å, with a bilayer packing of the adsorbate molecules, were obtained.

The adsorbate content in the intercalated solids reaches values of up of 58% in weight, being retained both in the interlayer space and at the edge of the clay particles. The adsorbate is desorbed between room temperature and 400 °C. The molecules of the adsorbate retained out of the interlayer space were removed by washing with benzene and cyclohexane. The analyses of the washed solids showed that the amount of adsorbate retained in the interlayer region was between 120–510 mg/g of saponite.

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