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# THERMAL BEHAVIOUR OF INTERCALATED 8-HYDROXYQUINOLINE (OXINE) IN MONTMORILLONITE CLAY

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## Abstract

The composite montmorillonite-8-hydroxyquinoline (Swy-1-8-HQ) was prepared by two different processes and studied by using thermogravimetric analysis (TG/DTG and DSC), as well as helpful techniques as fluorescence in the UV-visible region and X-ray diffraction. The composites developed fluorescent appearance, however with quantum poor efficiency and they exhibited distinct TG and DSC thermal behavior. The fluorescence data of spectra associated to the TG/DT curves allowed to suggest that the 8-HQ was present in the composites in two different circumstances: 1 – intercalated in the interlayer spaces (Swy-1-8-HQ2), rigidly associated to the substrate feasible as a monolayer with the aromatic rings parallel to the silica layer; and/or, 2 – adsorbed on the surface (Swy-1-8-HQ1), either as a bilayer formation or tilting of the molecules to the silicate layer sheet. All results confirmed above are in agreement with X-ray diffraction patterns, once the interlayer space increases when 8-HQ is incorporated. The experimental results confirm the formation of the composites in agreement with the method used in the preparation.

**Keywords:** DSC, montmorillonite, oxine, TG/DTG, X-ray diffraction

## Introduction

Ion exchange and adsorption properties of clay minerals have been investigated by several workers with different cations and also with charged large organic moieties [1–7]. The montmorillonite group of clays having the general formula

$$Al_4Si_8O_{20}(OH)_4\cdot nH_2O$$

shows cation exchange and can also take up extraneous molecules between the structural layers [8, 9]. Intercalation behavior of montmorillonite clay is of interest and many attempts have been made to introduce organic polar molecules in the interlayer spaces of these layered clay minerals [9–32]. Another important application of these interactions is the adsorption of organic dyes by clay minerals. This type of interac-

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tion has recently received increased attention in surface photochemistry [22–26]. Clay minerals serve as supporters for organic photochemical systems. They may organize the adsorbed molecules and thereby may direct energy transfer between molecules. A new approach for photostabilization of pesticides was reported in [25, 27]. The approach explores the unique surface properties of certain clays in order to build systems in which fast energy transfer process can take place. Thus, by the adsorption of the bioactive pesticide molecules on the surface of the clay along with a second adequately selected organic chromophore, which can efficiently deactivate the photoexcited pesticide molecules before their photodegradation starts [27, 28]. Recently, pharmaceutical–clay systems, as cinnamate/montmorillonite, and solar radiation shields/montmorillonite, have been studied [29, 30]. Pharmaceutical–clay systems, as solar radiation shields/montmorillonite, have an improved shielding ability *vs.* solar radiation in comparison with the pharmaceutical one by itself [30]. As above mentioned montmorillonite clay mineral shows remarkable ion exchange, intercalation and swelling properties. Then, it can act as a good host for large organic molecules, and is able to intercalate coordination compounds in the interlayer spaces of montmorillonite structure [31].

Although the process of intercalation and the structure of the intercalation complex have already been studied, e.g., by means of elemental analysis [31], infrared spectroscopy [27, 28, 31], and X-ray diffraction [31, 32], further detailed investigation will be necessary for a better understanding of the clay organic compound structure.

In spite of the fact that thermogravimetric analysis (TG-DTG and DTA) have long been used for the study of clay minerals, and that the application of these techniques for the investigation of intercalated montmorillonite is greatly employed, the studies concerning montmorillonite-8-hydroxyquinoline interactions are rather limited. In the present study the thermal behavior of montmorillonite intercalated with 8-hydroxyquinoline in the interlayer spaces of this layered clay mineral and adsorbed at the surface layer of the clay has been studied.

## Experimental

Preparation of both the intercalated and the surface layer adsorbed species.

The clay used was Na-montmorillonite Swy-1, from the Source Clays, University of Missouri, Columbia, MO, USA.

*1*) Intercalated 8-hydroxyquinoline (Swy-1-8-HQ2) was prepared in a way that a suspension of montmorillonite in methanol was stirred for 24 h at 25±1°C in presence of a solution of 8-hydroxyquinoline (Merck), in a proportion of 70 mass%. The solvent was thoroughly eliminated by passing a stream of $N_2$ gas into the suspension. The dried solid composite obtained was submitted to exhaustive extraction process with chloroform solvent to eliminate the 8-hydroxyquinoline which was not intercalated. Finally the solvent was removed by a $N_2$ stream gas, as in the methanol system, resuspended in methanol and dried as mentioned above. The product thus obtained was kept in a desiccator over $P_4O_{10}$, at constant mass, before analyses.

*2*) The composite containing the 8-hydroxyquinoline adsorbed on the surface (Swy-1-8-HQ1) was prepared as the intercalated one, except for the step of exhaustive extraction process with chloroform solvent. In this preparation the 8-hydroxyquinoline was present in a proportion of 30 mass%.

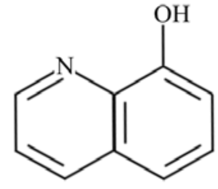
*3*) Concerning pure clay, the treatment was the same as described to Swy-1-8-HQ2.

### *X-ray diffraction*

The X-ray diffraction analyses were carried out on a Siemens D-5000, and the radiation used was $CuK_{\alpha}$=(1.54184 Å).

### *Fluorescence in UV-visible region*

The fluorescence spectrum of the 8-hydroxyquinoline in homogeneous medium as well as the spectrum of the composite in heterogeneous medium, both at room temperature, were measured by a Hitachi recording spectrofluorometer F 4500 type. The excitation was carried out with light of 240 and 280 nm of a high-pressure mercury-vapor lamp. Both fluorescence spectra were measured by a wavelength range of about 350–500 nm at 200 nm $min^{-1}$ and entrance/out slit 5/5. The spectra were not corrected for instrumental response.



8-hydroxyquinoline (8HQ)

### *Thermal analysis*

Simultaneous TG-DTG and DSC measurements of the intercalates and surface layer adsorbed composites were performed in a TC15 – Mettler system, using a TG-50 thermobalance and a DSC-25 modules, a TC-15 control unit, and a Star$^{e}$ software, in synthetic air atmosphere (flux 150 mL $min^{-1}$) at a heating rate of 5°C $min^{-1}$ and samples about 7 mg. An $\alpha$-$Al_2O_3$ crucible was used for the TG-DTG curves and an aluminum crucible with a perforated cover was used for the DSC curves.

## Results and discussion

The TG, DTG and DSC of the pure montmorillonite and montmorillonite-8-hydroxyquinoline composite containing 8-hydroxyquinoline (8-HQ) on the structural layers of the clay are shown in Figs 1 and 2a, respectively.

The TG curve of the montmorillonite, Fig. 1a, shows mass loss in two steps. The first step, observed between 30 to 70°C, is attributed to the loss of adsorbed solvent.

The anhydrous compound is stable up to 550°C and, above this temperature, up to 730°C, the mass loss of 4.20% is due to the dehydroxylation water.

The TG curve of the composite Swy-1-8-HQ1, Fig. 1b shows mass loss in two consecutive steps, although the DTG curve (Fig. 1c) suggests three steps. The mass loss in temperature ranging from 30 to 230°C observed in the TG curve is ascribed to the

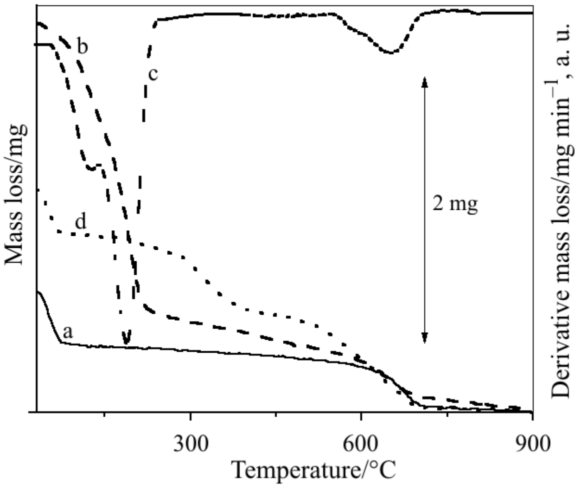


**Fig. 1** a – TG curves of pure montmorillonite, 7.04 mg; b – and c – TG and DTG curves of Swy-1-8-HQ1 composite, 6.87 mg (8-HQ adsorbed on Swy-1 surface), respectively; d – TG curve of Swy-1-8-HQ2 composite, 7.12 mg (8-HQ intercalated)

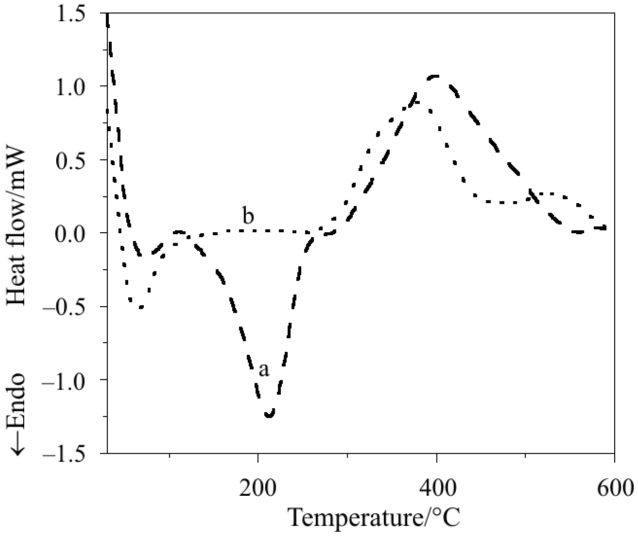


**Fig. 2** DSC curves of a – Swy-1-8-HQ1 composite, 4.08 mg (8-HQ adsorbed on Swy-1 surface) and b – Swy-1-8-HQ2, 4.02 mg (8-HQ intercalated)

loss of both adsorbed water and 8-HQ molecules. In this temperature range (30–230°C), the DTG shows two overlapping steps suggesting that the elimination of 8-HQ occurs through two different processes. At first, the elimination of the weakly adsorbed solvent occurs and of the 8-HQ molecules (8-HQ are present as a second monolayer, taking into account a bilayer system as it will be discussed further on), followed by the desorption of a monolayer of 8HQ molecules from the surface of the clay.

The second step of the TG curve, Fig. 1b at temperature ranging from 230 to 900°C, the mass loss begins in a slow process followed by a fast one. The slow mass loss that occurs up to about 620°C is attributed to the thermal decomposition of a residual 8-HQ strongly adsorbed on the structural layers. The fast process is attributed to the loss of the dehydroxylation water, in agreement with the TG curve of the pure montmorillonite.

The DSC curve, Fig. 2a shows endothermic and exothermic peaks. The endothermic peaks at 50 and 215°C are ascribed to the elimination of the weakly adsorbed solvent and of the 8-HQ molecules, as previously described. The presence of a single broad exothermic peak at 400°C, when compared with Fig. 2b, in the same temperature range (from 270 up to 600°C), is in agreement with the recent published model about the oxidation processes of organic–clay complexes in air atmosphere [33]. The exothermic peak (400°C) was attributed to the total oxidation of the residual 8-HQ molecules converted into water and $CO_2$, as expected for a high oxygen content atmosphere. These interpretations are still in agreement with the results of the TG and DTG curves.

The TG curve of the composite Swy-1-8-HQ2, Fig. 1d shows mass loss in three fast consecutive steps. The first mass loss which occurs at temperature ranging from 30 to 80°C, observed in the TG curve, is ascribed to the loss of adsorbed solvent. The second mass loss step, from 80 to 450°C, is attributed to the elimination of the solvent molecules which takes place simultaneously to the thermal decomposition of the 8-HQ intercalated into the structural layer of the clay. The last step, from 450 to 900°C, is attributed to two simultaneous processes: 1 – the oxidation of the charcoal, residue formed at the end of the second step under low oxygen content atmosphere; and 2 – the elimination of the dehydroxylation water from the structural layers of the clay.

The DSC curve, Fig. 2b shows endothermic and exothermic peaks. An endothermic peak at 50°C is ascribed to the elimination of the adsorbed solvent. The endothermic peak previously observed at 215°C is absent. The absence of this peak confirms the inclusion of the 8-HQ in such available spaces of layered clay. The two broad exothermic peaks at 350 and 550°C are attributed to the thermal decomposition of the 8-HQ intercalated between the structural layers. This decomposition can be seen in two steps, as pointed out in the specialized literature [33]. At first, hydrogen oxidation from the 8-HQ molecules occurs, under low oxygen content atmosphere, to form water and charcoal (or petroleum coke) as thermal degradation products and at the second step, at high temperatures, the charcoal is oxidized to $CO_2$. These interpretations are still in agreement with the results of the TG curve and are in accordance with the preparation method of this composite. Actually this composite was prepared so as to contain 8-HQ intercalated between the structural layers of the clay.

Table 1 shows the *c* lattice parameters ($d_{001}$) for a monoclinic cell of montmorillonite, obtained for pure montmorillonite and for the prepared composites, through X-ray diffraction technique (Fig. 3 shows the X-ray powder diffraction patterns of Swy-1, Swy-1-8-HQ1 and Swy-1-8-HQ2).

**Table 1** Interlayer distance values ($d_{001}$/Å) determinate for pure clay and its 8-hydroxyquinolines composites

| Compound | *d* | $\Delta d^*$ |
|---|---|---|
| Pure montmorillonite (Swy-1) | 12.59 | – |
| Montmorillonite–8-hydroxyquinoline intercalated (Swy-1-8-HQ2) | 13.82 | 1.23 |
| Montmorillonite–8-hydroxyquinoline adsorbed (Swy-1-8-HQ1) | 16.64 | 4.15 |

$^*\Delta d=(d_{001}$ composite – $d_{001}$ pure Swy-1)

A significant change in *c* value is reported with a change in the interlayer content because of the inclusion of different molecules or cations in such available spaces of layered clays [20, 27, 28]. In the present study, the $d_{001}$ spacing of montmorillonite clay is also observed to be significantly changed after treatment with 8-hydroxyquinoline. The observed $d_{001}$ spacing for Swy-1-8-HQ2 and Swy-1-8-HQ1 are 13.82 and 16.64 Å, respectively. This shows that the interlayer spaces are increased by 1.23 and 4.15 Å when compared with pure montmorillonite (Table 1). These increases in the interlayer space are expected with the mass increase of 8-HQ incorporated by the clay, leading to changes in the clay structural characteristics.

Figure 4 shows the fluorescence emission spectrum, normalized, obtained in the UV-visible region (350 to 500 nm) for the suspensions prepared with the composites containing 8-hydroxyquinoline (curve a: Swy-1-8-HQ2, $\lambda_{\text{excitation}}=280$ nm and $d_{001}=13.82$ Å; curve b: Swy-1-8-HQ1, $\lambda_{\text{excitation}}=240$ nm and $d_{001}=16.64$ Å). The emission fluorescence spectrum observed from the curve a and b presents a large emission band in the region from 350 to 500 nm, however with low quantum efficiency. This emission is of a small intensity, but easily verified when the solid samples are illuminated and observed by naked eye. The intercalated 8-HQ shows vibrational unfolding spectrum, curve b. The observed vibrational unfolding was ascribed to an increase in the molecular coplanarity of 8-HQ, suggesting that the molecules were in the interlayer space, rigidly associated to the substrate feasible as a monolayer with the aromatic rings parallel to the silica layer. This drawing was in accordance with the results obtained from the TG and DSC curves (Figs 1 and 2) and with the X-ray diffraction data (Table 1).

On the other hand, the absence of the vibrational unfolding observed to Swy-1-8-HQ1 composite suggests that the great majority of 8-HQ molecules were outside the interlayer space. However, as observed from the TG and DSC curves, molecules inside the interlayer spaces are likely to be present. These molecules outside were present as a bilayer formation or tilting of the molecule relative to the silicate layer. This can be established because their $d_{001}$ value is between $15<d_{001}=16.64<20$ Å values. The intermediate values are expected by dimmer formation and/or inclined packing of molecules ($d_{001}$<15 Å) and molecules oriented perpendicularly to the lamella plane ($d_{001}$>20 Å), respectively. However, when molecules are exactly perpendicular to the clay surface a basal spacing of more than 20 Å would be expected.

Figure 3 shows X-ray powder diffraction patterns obtained to pure montmorillonite and to the respective composites. This figure reveals some important aspects, which confirm the clay structural modifications that appear when 8-hydroxyquinoline is incorporated. Such aspects are: 1 – the disappearance of the line present at 3.12 Å, for the pure clay; 2 – the interlayer space line ($d_{001}$) displacement to higher values when compared to pure clay, with mass increase due to 8-hydroxyquinoline incorporation; 3 – the appearance of a broad band signal for $15° < 2\theta < 35°$ interval, and its intensification as 8-hydroxyquinoline molecules are incorporated, suggesting a decrease in the composite crystallinity degree.

Thus, this decrease in crystallinity degree of the composite associated to the results obtained from fluorescence and from thermal analysis technique confirms the clay structural modification, revealing an increasing organophilic character of the montmorillonite substrate as 8-hydroxyquinoline molecules are intercalated.

## Conclusions

The curves TG/DTG and DSC, the results from UV-visible fluorescence spectra and XRD data allowed to confirm 8-HQ intercalated in the composites interlayer region to Swy-1-8-HQ1 and Swy-1-8-HQ2; however, as stated before in this study, Swy-1-8-HQ1 can be found in much greater amount in external sites of the clay sheet. These results are in agreement with the methodologies employed to prepare it.

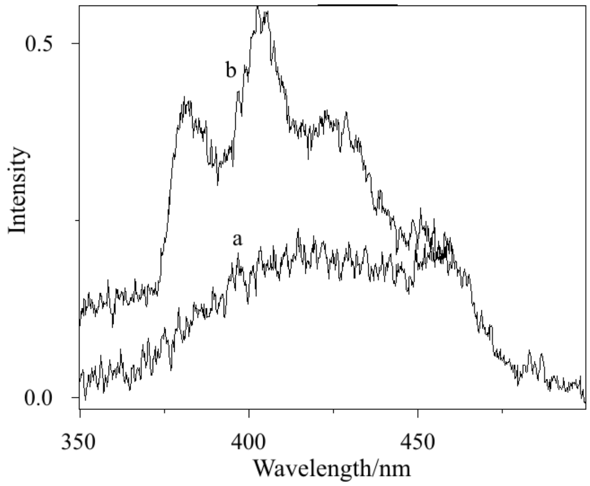


**Fig. 3** XRD patterns of a – Swy-1 pure, b – Swy-1-8-HQ1 composite (8-HQ adsorbed on Swy-1 surface), c – Swy-1-8-HQ2 composite (8-HQ intercalated)

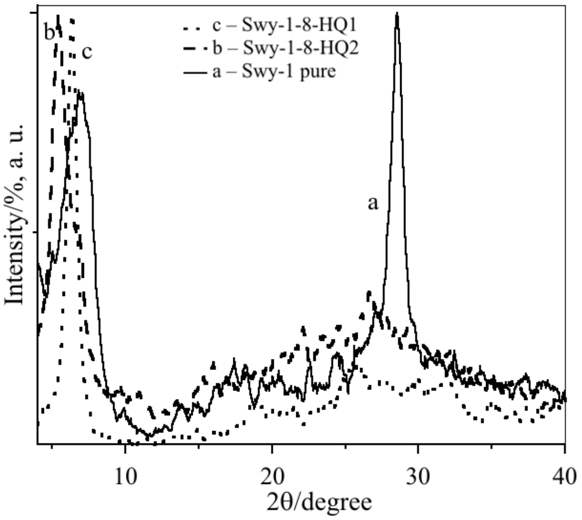


**Fig. 4** Fluorescence spectra of aqueous suspension (0.05 g $L^{-1}$) of a – Swy-1-8-HQ1 composite (8-HQ adsorbed on Swy-1 surface), $\lambda_{excitation}$=280 nm, $d_{001}$=13.82, and b – Swy-1-8-HQ2 (8-HQ intercalated), $\lambda_{excitation}$=240 nm and $d_{001}$=16.64 Å

The 8-HQ molecules adsorption geometry could be also suggested from the UV-visible fluorescence spectrum and from X-rays data, in accordance with TG/DTG and DSC curves: 1 – for Swy-1-8-HQ2 composite, the 8-HQ molecules appear intercalated in the interlayer space, and rigidly associated to the substratum feasible as a monolayer with the aromatic rings parallel to the silica layer; 2 – for the composite Swy-1-8-HQ1 the 8-HQ molecules are outside the interlayer space, present as a bilayer formation or tilting of the molecule relative to the silicate layer, however still containing molecules inside the interlayer spaces as shown by the TG and DSC curves.

The intercalation of the 8-HQ molecules inside the interlayer space and on the clay surface, acquiring different geometric orientations, plane or inclined, leads to important structural modifications which, in turn, brings about an increase in the organophilic character of montmorillonite clay.

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