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Interaction of C10, C11 and C18 fatty acids with calcite surface as revealed by IR spectroscopy, X-ray diffraction and atomic force microscopy

Belkacem Benaissa *, Mustapha Bouhenguel and Ahcene Bouchemma

Laboratory of Applied Chemistry and Materials Technology, Faculty of Exact Sciences, Natural Sciences and Life, Sciences of Material Department, Larbi Ben M'hidi University, Oum El Bouaghi 04000 Algeria

* Corresponding author at: Laboratory of Applied Chemistry and Materials Technology, Faculty of Exact Sciences, Natural Sciences and Life, Sciences of Material Department, Larbi Ben M'hidi University, Oum El Bouaghi 04000 Algeria.
Tel.: +213.32442029. Fax: +213.32442029. E-mail address: sofyas2013@gmail.com (B. Benaissa).

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ABSTRACT

The adsorption of C_{10}, C_{11} and C_{18} fatty acids from aqueous solution is a phenomenon of major importance in flotation, geochemistry and oceanography. There is an approach that allows identifying the origin of the formation of aggregates of condensed molecules and the filling mechanism of the adsorbed layer. The different homogeneous domains of the surface are filled by decreasing energetic order. The size of different homogeneous domains controls the size of the lamellar aggregates to one layer and two layers for high concentration. Fatty acid adsorption was investigated at the calcite surface by infrared spectroscopy, atomic force microscopy and X-ray diffraction studies. The adsorption process was studied for different fatty acids in acid medium created by phosphoric acid at pH = 4.8-5.0.

1. Introduction

Adsorption of surfactants on minerals is an important process in flotation. The interactions leading to adsorption include chemical bonding, electrostatic interaction, desolvation of surfactant's polar group and the mineral surface species *etc*. Water chemistry plays an important role in the adsorption process by affecting the surfactant-solution equilibrium, the mineral-solution equilibrium and the mechanism of interactions between the surfactants and the mineral particles [1-3]. Understand the surfactants adsorption mechanisms, it is necessary to have knowledge about the physical chemistry of the adsorbate in aqueous solution, the nature of the surface phase of the solid and consequences of its hydratation. For this aim, the use of adsorbed phase's characterization methods is preferred. Calcite is one of the most important mineral processed by flotation; studied in interaction with organic acids in seawater *etc*.

The fatty acids are considered weak acids. In solution, they ionize weakly according to the following reaction:

$$R\text{-}COOH \leftrightharpoons RCOO^- + H^+ \tag{1}$$
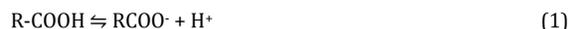
In their pure state, they are found practically in solid state. Fatty acids are insoluble in water. The neutralization of fatty acids is carried out using sodium hydroxide giving the salts called soaps.

$$R\text{-}COOH + MOH \rightarrow RCOOM + H_2O \tag{2}$$
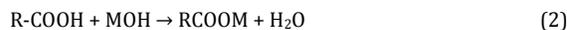
These soaps are readily soluble in water and easily hydrolysable:

$$R\text{-}COO^- + H_2O \leftrightharpoons RCOOH + OH^- \tag{3}$$
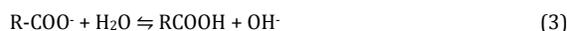
The introduction of the latter in water decreases the surface energy. In this case, the molecules of fatty acids are strongly adsorbed on mineral surfaces in comparison to the carboxylate anion. The hydrolysis reaction condition a low surface energy of soap solutions. The pH increase toggles, the reaction from the right to the left, and the surface energy increases. In aqueous solution, the saponified fatty acids tend to give rise to micelles. Concentrations for which there is occurrence of micelles depend on the length of the hydrocarbon chain. The micelles appear easily when the hydrocarbon chain is long.

Table 1. Characterization of used fatty acids.

Fatty acids	Molar mass (g/mol)	Supplier and purity	Structural formula
Oleic acid	282.46	Merck > 99	$CH_3(CH_2)_6CH_2CH=CH(CH_2)_7COOH$
10-Undecenoic acid	184.28	Aldrich ≥ 98%	$CH_2=CH(CH_2)_8COOH$
9-Decenoic acid	170.25	Aldrich ≥ 90%	$CH_2=CH(CH_2)_7COOH$

The adsorption of the carboxylic acids on the mineral surface is determined by the properties of its polar group (carboxyl group) capable of undergoing hydrolysis. This type of compounds can react with the metal cations of the lattice of the mineral where adsorption occurs and the appearance of a hard soluble hydrophobic surface. The action of carboxylic acids towards the mineral surfaces depends on their length and unsaturation of the hydrocarbon chain. The fixing of the carboxylic acids on the surfaces of non-sulfide minerals such as carbonates is estimated by the nature and structure of the surfaces and the conditions of use of fatty acids. Upon interaction of carboxylic acids with minerals, it appears a hard soluble hydrophobic film. It is experimentally demonstrated in our research that the carboxylic acids are fixed on the surfaces of non-sulfide minerals in molecular and ionic form (IR spectroscopy).

Carboxylic acids are active towards mineral surfaces containing in their crystalline structure the alkaline earth metals such as calcium, magnesium, strontium and barium. The strength of fixing of the carboxylic acids on mineral depends on the nature and surface condition of the minerals and concentration of their solutions. Minerals containing in the mesh alkaline earth, carboxylic acids bind a sufficiently rigid manner and their water desorption is difficult, as shown in the experimental part. The state of carboxylic acids and soaps is generally determined by the pH value. The amount of carboxylic acid in the molecular form and the ionic form depending on the pH of the solution is determined using the equation:

$$R\text{-}COO^- + H^+ \leftrightharpoons RCOOH \qquad (4)$$

From this equation, it is established that the carboxylic acids in basic medium increases the amount of oleate ions in the case of oleic acid from where their adsorption in basic medium. The acid medium promotes dissolution of the mineral surfaces carbonates and creates a new free surface with the appearance of M^{2+} metal cations such as Ca^{2+} and Mg^{2+}. These free surfaces react instantly with the carboxylic acids. In our study, we considered the adsorption of oleic acid, 10-undecenoic and 9-decenoic in a weakly acid medium created by the phosphoric acid.

2. Experimental

2.1. Materials

The studied material is a calcite collected from a mineralogy laboratory located in Research Center of Ferphos in Djebel Onk in Algeria. Calcite is a carbonate mineral ($CaCO_3$) with trigonal-rhombohedral crystal system. It is colorless and white with occasional gray, yellow and green shades. Calcite is the main constituent of limestone, marble and shells of marine species [1]. Fatty acids used: Oleic acid was supplied from Merck; 9-decenoic acid and 10-undecenoic acid were supplied from Sigma-Aldrich (USA). The characteristics of fatty acids were presented in Table 1. IR spectra of these fatty acids are presented in Figure 1.

2.2. Methods

2.2.1. FT-IR Spectroscopy
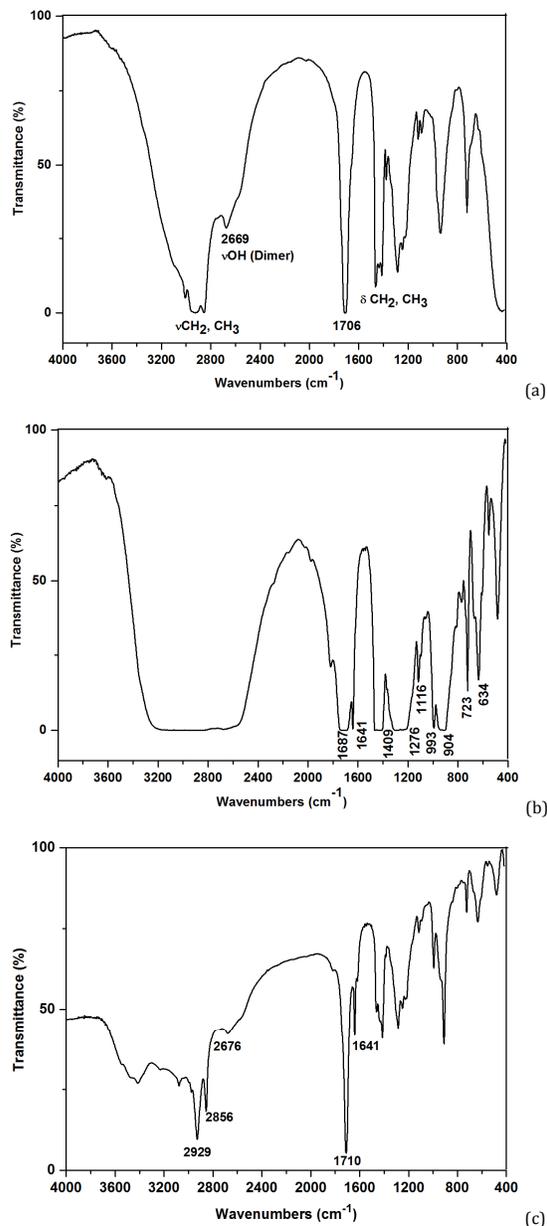
Figure 1. IR spectra of oleic acid (a), 10-undecenoic acid (b) and 9-decenoic acid (c)

The FT-IR spectra of calcite, fatty acids and adsorption spectra of calcite treated with oleic acid; 10-undecenoic acid and 9-decenoic acid were recorded for band assignments. For solid materials, the KBr disc method was used; for liquid materials, the KBr-film method was used. Infrared spectra were recorded by using the Jasco Fourier transform infrared spectrometer resolution 4 cm⁻¹ in the range of 400-4000 cm⁻¹. The pure calcite powders were packed with 25 mL phosphoric acid solution pH = 5 and 25 mL of fatty acids solution of 500 mg/L concentration and 80 °C temperature.
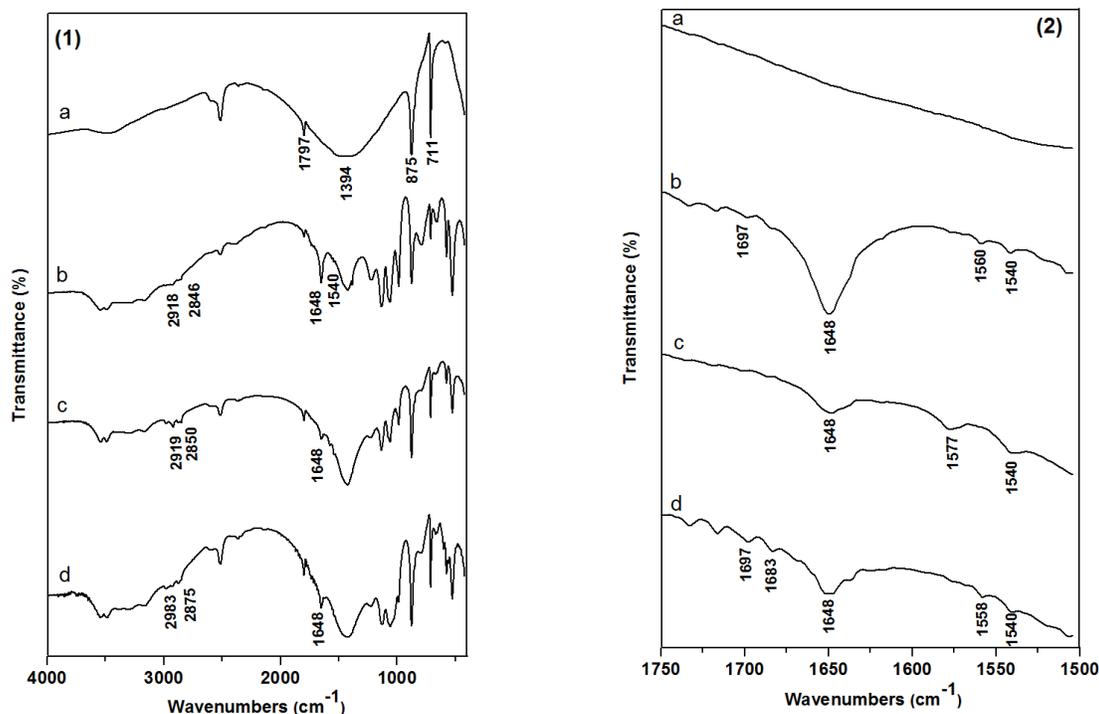
Figure 2. IR Spectra of calcite powder before (a) and after C_{18} (b), C_{11} (c) and C_{10} (d) adsorption in ranges 4000-400 cm^{-1} (1) and 1750-1500 cm^{-1} (2).

While being stirred with a magnetic stirrer for 5 minutes. The suspension was then let stand for 15 minutes and then filtered with a filter paper, and the solids were dried in the open air overnight at room temperature. The samples were prepared by dispersing the dried powder, followed by pressing with a hydraulic press to form transparent pellets.

2.2.2. Atomic force microscopy (AFM) and X-ray diffraction

Atomic force microscopy, often abbreviated as AFM, is one of the elected techniques for fine surface and geometrical characterization. The AFM was introduced in 1986 by G. Binnig, CF Quate and C. Gerber [2]. The basic operating principles of AFM have been described in detail many times in the literature [4-6]. The atomic force microscope AFM is a tool for analyzing the relief at the atomic scale. This type of microscopy is essentially based on the analysis of an object point by point by means of a scan through a local probe, similar to a pointed tip. The adsorption of fatty acids (C_{10}, C_{11} and C_{18}) on calcite surface could be visualized using contact mode of atomic force microscopy. The contact mode AFM can be utilized to visualize the topography of surfaces adsorbed with surfactant molecules. It is the simplest and most basic imaging mode available. The AFM is used type APE Research A100-AFM. The DRX characterization was performed using Bruker diffractometer type AXS-8D operating at 45 kV and 40 mA with CuKα radiation (1.5406 Å).

3. Results and discussion

In James J. Zullig and John W. Morse paper [7] a short chain fatty acid (C_4 to C_{12}) did not adsorb on carbonates surfaces. Fatty acids with chain lengths greater than twelve carbon atoms adsorbed strongly and irreversibly, with adsorption increasing with alkyl chain length. The pH was adjusted to 8. However in our previous study, adsorption of fatty acids was performed at pH = 4.8-5.0 [8].

To study the adsorption of oleic acid, 10-undecenoic acid and 9-decenoic acid (C_{18}, C_{11} and C_{10}) on the surface of calcite particle, FT-IR was recorded and the spectra of samples of these fatty acids are shown in Figure 1. The FT-IR spectra of the calcite before and after fatty acids adsorption were recorded in the range from 400 to 4000 cm^{-1} and 0.5 g of calcite was equilibrated with 25 mL of the studies reagents solutions (fatty acids) at concentration of 500 mg/L and at a pH of 4.8-5.0, after conditioning the calcite was washed two times with double distilled water. According, the infrared bands a 711, 875 and 1394 cm^{-1} were attributed to carbonate anion [9,10].

The corresponding peaks of P-O due of phosphoric acid used to adjust pH are presented in Figure 2 (1). The peaks at 599, 575 and 526 cm^{-1} are due to P-O bending. P-O asymmetrical stretching is shown at 1032 and 1130 cm^{-1}. The peaks for P-O band before and after fatty acids adsorption are shown without any significant shift. The additional bands at 2981 and 2874 cm^{-1} are attributed to fundamental stretching vibration. The adsorption at 2929 cm^{-1} and 2856 cm^{-1}, assigned as asymmetrical and symmetrical C-H stretching vibrations the alkyl group, confirm the presence of studied fatty acids molecules at the calcite surface [11-16] and the carboxylate anion COO$^-$ bands at 1576-1540 and 1648 cm^{-1}, which indicates the existence of C_{18}, C_{11}, C_{10} on the surface of calcite particles (Figure 2 (2)).

XRD patterns of calcite powder before and after C_{18}, C_{11} and C_{10} adsorption are only crystalline phases in all samples [17]. The XRD patterns of calcite before and after acting with C_{18}, C_{11} and C_{10} are shown in Figure 3. Figure 3 shows the XRD patterns of oleic acid, 10-undecenoic acid and 9-decenoic acid. Only the strong peak and the weak peak around 11.50 and 20.96 degrees associated with calcite are observed in all the patterns, and are in good agreement with the reference patterns (Number PDF JCPDS 11-0802, 37-1811 oleic acid and α-oleic acid and 24-0027 for calcite in ASTM files) concerning the oleic acid and calcite.
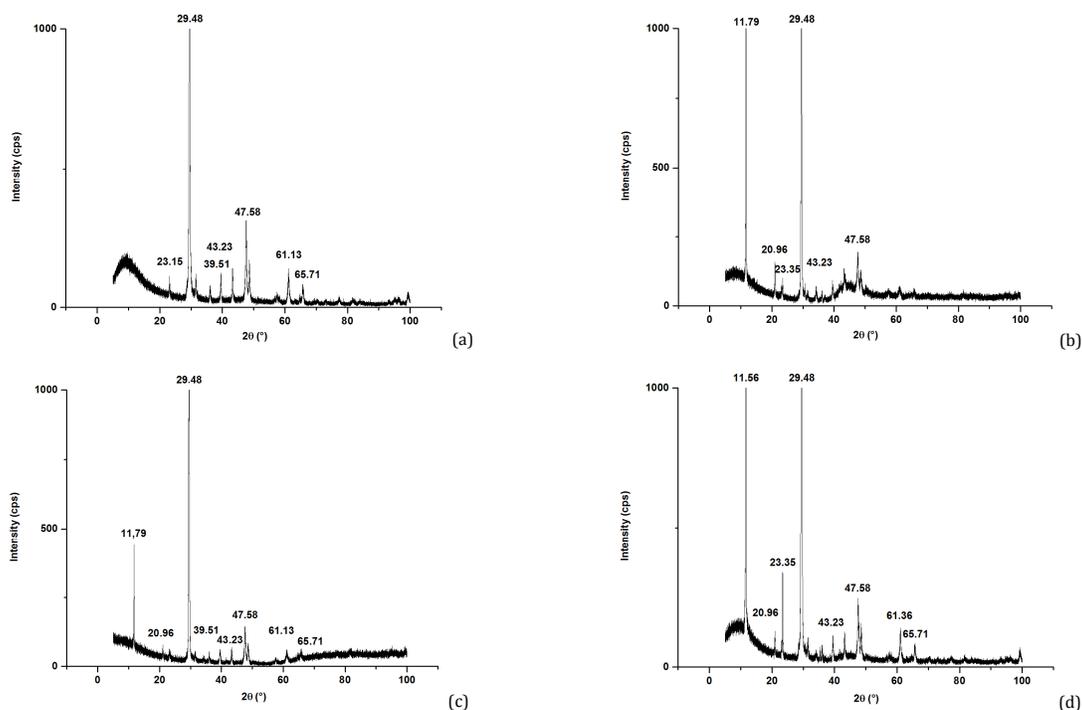
Figure 3. XRD patterns of calcite before (a) and after C_{18} (b), C_{11} (c) and C_{10} (d) adsorption.
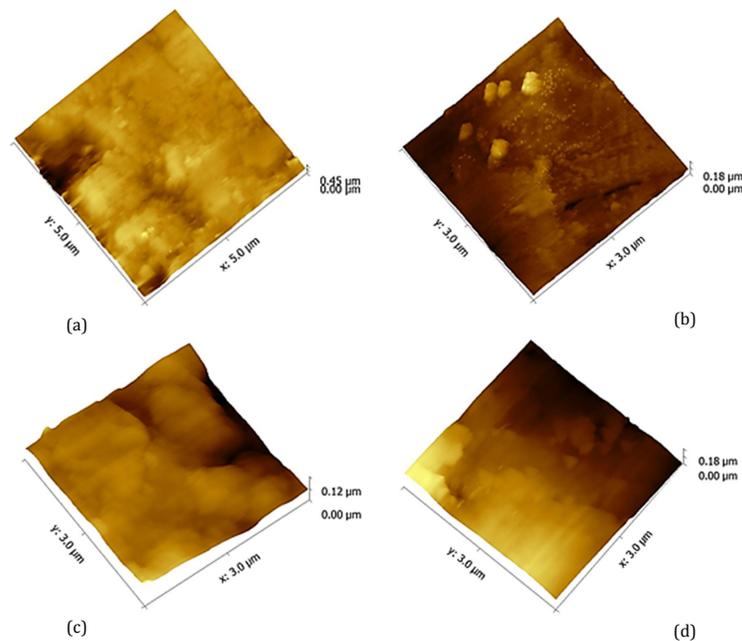
Figure 4. Micro-topography in three dimensional of calcite before and after adsorption of studies fatty acids.

The AFM images were obtained for calcite before and after adsorption of C_{18}, C_{11} and C_{10} fatty acids at concentration 500 mg/L. The surface was selected and the corresponding images were recorded. The analysis of images was carried by the use of Gywddion Software.

Figure 4 shows the micro-topography in three dimensional of calcite before and after adsorption of studies fatty acids. The AFM images denote the uneven surfaces. The image in Figure 4 (a) displays a homogeneous surface showing clearly that three (Figure 4 (b), (c), (d)) were heterogeneous. The use of AFM was possible to identify that studies fatty acids precipitates on the crystal of calcite surface in the form of agglomerates [18].

4. Conclusion

The use of IR spectroscopy, AFM and XRD for study of adsorption are of great importance. AFM images demonstrate that calcite after exposing to studies fatty acids is very rough

compared to calcite before exposing to fatty acids. The roughness and morphology at the scale 3 micrometer for samples exposed to pH = 5 solutions or when treated with C10, C11 and C18 fatty acids, even though at microscopic scale, differences in morphological aspects are observed. The applications and advantages of IR spectroscopy and XRD in the study of mineral surface and reagent interaction are useful. Some results of fatty acids adsorption on calcite are presented in the paper.

Acknowledgement

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