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Preparation and Characterization of Intercalated Kaolinite with:Urea, Dimethyl formamide and an Alkylammonium SaltUsing Guest Displacement Reaction

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Abstract

In recent years, authors are interested largely to the cation exchange method for modifying kaolinite clay using intercalation reaction. The purpose of this study is to do a comparison between kaolinite intercalates per formed with DMF and urea using guest displacement method in which new guest species “alkylammonium salts” can be intercalated between the layers of kaolinite by displacing previous species “Urea” and “DMF”. Untreated and treated kaolinite samples were examined by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD spectra showed that the peak at 10.72Å increases in urea/kaolin complex, and the kaolinite/DMF complex was characterized by the same basal distance (d001), but the treatment with the ammonium salt caused the return to the initial state of the clay. Also, FTIR results confirmed the hydrogen bonding between urea and kaolin which showed the occurrence of a partial delamination during dry milling of kaolin with urea and kaolinite, but no new bands were detected in the kaolinite/DMF complex, also after the treatment with alkyl ammonium salt two new adjacent bands were observed in both cases characterizing the vibrations of symmetric and asymmetric valence of the C-H bonding. The displacement reaction is the most efficient way to expand the interlayer spacing of kaolinite.

1. Introduction

Clay minerals find almost innumerable applications, and the diversity of uses is still increasing. Swelling behavior, adsorption properties, colloidal and rheological phenomena can be optimized and adjusted to the intended uses. In addition, new uses are found and new types of materials are created. Clay minerals and clays are more and more involved in material science studies and are parent materials of organic–inorganic composites [1].

The nanocharges belong to the family of the phyllosilicates, which are characterized by the successive stacking of octahedral (O) and tetrahedral layers (T), giving consequently, various types of clays, of which primarily those of types T:O and T:O:T.

Kaolinite is the most abundant mineral of the family of clays of type T:O. It is an important industrial raw material having wide spread applications in the manufacture of paper, ceramics, inks and paints, as well as like an additive and reinforcement in the production of polymers [2,3]. By inserting polar organic molecules between his lamellar layers during chemical reactions in aqueous solutions, an increase in its interfoliar space was happened. This opened with kaolinite great prospects for its employment like reinforcement for the nanocomposites, but with the recourse to the method known as "guest displacement reaction" [4 - 6]

Kaolinite is 1:1 phyllosilicates, with the chemical composition: $2[Si_2Al_2O_5(OH)_4]$. It is a layered aluminosilicate in which each layer in the structure in reality consists of two sub layers. Since it is made up of two types of interlayer surfaces, One layer of the mineral consists of an alumina octahedral sheet $[Al_2\ (OH)\ 4]^{+2}$ and a silica tetrahedral sheet $[Si_2O_5]^{-2}$, kaolinite is remarkable by its non-Centro symmetric structure. This asymmetry creates large superposed dipoles in the lamellar structure and allows the formation of hydrogen bonds between consecutive layers, resulting in a large cohesive energy [2, 3, 7].

The ability to modify clay minerals by inserting an inorganic and/or organic guest species into the inter-lamellar region opens up a range of potential uses for these materials. The smectite group of minerals possesses exchangeable cations within their interlayers that facilitate the encapsulation of polar organic molecules. Kaolinite is devoid of this property as there are no exchangeable cations within its layers. However, the kaolinite interlayer region can react with a small group of organic and/or inorganic materials, a process called intercalation [8].

This work present the study of the intercalation of the kaolinite with different solvents urea and dimethylformamide (DMF), and an alkyl-ammonium salt using guest displacement reaction to increase the interfoliar space of clay and to elaborate polymer/kaolinite composites. The obtained complex kaolin/ urea and kaolin/DMF were characterized with infrared spectroscopy (FTIR) and X-ray diffraction.

2. Modification of kaolinite

2.1.Intercalation of kaolinite

Intercalation of kaolin minerals with inorganic and organic compounds has wide potential for scientific and industrial applications [9 -11]. The study on kaolinite intercalation began in the 1960's, and numerous publications are available on this subject. More than 300 kaolinite derivatives have been reported [6, 12]. In fact, the kaolin group of minerals had been classified as non-expandable until 1946, when halloysite organic complexes could be obtained from the hydrated form of halloysite by replacing the interlayer water with alcohols [5, 6]. The expansion of kaolinite by potassium acetate and other salts of low molecular weight organic acids were achieved in 1961 [6]. Kaolin minerals can thus be expanded by a number of apparently unrelated polar organic compounds and the expansion occurs under a variety of conditions. Organic compounds with relatively low dipole moments and varying molecular size were used to form inter lamellar kaolin complexes. [13[

Kaolinite has five surfaces: (a) the edge surfaces; (b and c) the two outer surfaces which may consist of one siloxane and one gibbsite-like surface or some modification of these surfaces; (d) the inner-surface hydroxyl surface; and (e) the inner-surface siloxane surface [14] (Figure.1).

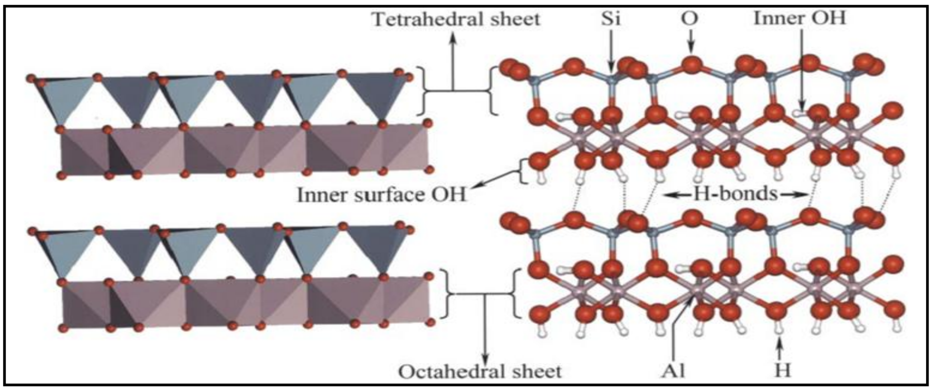

Figure 1: Structural models of kaolinite [11].

The interaction of molecules on the outer surfaces is fundamentally a process of adsorption [14]. Selective adsorption may also take place at the edge surfaces. Certain types of molecules may insert between the kaolinite layers and chemically react with the inner-surfaces. Such insertion of molecules between the layers causes the expansion of the kaolinite layers and this process is known as "intercalation reaction". Thus, the Intercalation is a chemical process of modifying kaolinite inner surfaces, resulting in significant changes in the kaolinite surface properties. For example, intercalation can cause significant disordering of the kaolinites, increased surface areas and provide surfaces, which are more readily available for chemical reactions [14 - 16]. Intercalation may take place through several mechanisms depending on the point of interaction of the inserting molecule and the kaolinite surface. This mechanism depends on the disruption of the hydrogen bonding between the kaolinite layers and the formation of new hydrogen bonds with the inserting molecule [15, 16]. These new bonds usually involve the inner surface hydroxyl groups (Ou OH) and changes are observed in the intensities of bands assigned to vibrations of these groups. This is observed for intercalated molecules such as potassium acetate, where hydrogen bonding occurs between the carboxylate group of the acetate anion and the inner surface hydroxyls of the gibbsite-like layer [15].

For the realization of the processes of intercalation of kaolinite successfully, it is necessary to break the hydrogen bonds between the lamellar layers and give a great cohesive energy to the kaolinite, making the processes of intercalation extremely difficult, and increase inter lamellar space by the insertion of organic molecules of strong polarities and small sizes which will react with the functional groups of kaolinite, in particular, hydroxyls of the octahedral layer and oxygen atoms of the tetrahedral layer [7]. The reason for this phenomenon is that there are hydrogen and molecular bonds that connect and there are no exchangeable ions between layers [12, 18].

As a consequence of the structure of kaolinite, only some limited organic molecules can intercalate the space between layers due to the hydrogen bonding between the layers, such as hydrazine, formamide, acetamide, alkyl amine, potassium acetate, cesium acetate, urea, dimethylsulfoxide, N-methylformamide, Dimethylformamide and so on [6,7,12, 13, 17], and among this large number of compounds that have been put in the interlayer of kaolin minerals, only a few of polar compounds can intercalate kaolinite directly [12,18]. The successful intercalation agents decrease the electrostatic attraction between the lamellar by causing an increase in the dielectric constant when the compounds penetrate between the layers. Intercalating compounds also have a certain hydrogen bonding capacity. Formamide, dimethyl- sulfoxide (DMSO), and N-methyl formamide (NMF) are known to directly intercalate, resulting in an increase of the interlayer spacing within the kaolinite. This increase depends on the size and arrangement of the guest species. Although not many compounds have the ability to intercalate, the number may be extended by the so-called "displacement method" [8].

2.2.Guest displacement reaction

In recent years, intercalation reactions of kaolinite have been extended by guest displacement method in which new guest species can be intercalated by displacing previous species [7, 19]. Guest displacement reaction is one of the various technics which were developed in order to facilitate the process of intercalation of the organic compounds between the lamellar layers of kaolinite. Displacement involves the replacement of a directly intercalated species (e.g., NMF or potassium acetate) by a second organic molecule. The use of a directly intercalating compound as an intermediate for the intercalation of other polar organic compounds opens up new areas for basic, strategic, and applied research [3,4,7, 8, 19], as it is illustrated in figure 2.

This method was considered the most effective and the most used to obtain nanocomposites polymer/kaolin, either by reaction of polymerization or direct intercalation of polymers to the melt in the inter-foliar space of kaolinite [3, 4, 7, 19, 20], it involves modifying the organo-philicity of kaolinite, synthesis of precursor/kaolinite, intercalation of monomer and polymerization of polymer kaolinite nanocomposites [7]. Various works were used this method for the intercalation of kaolinite, such as those of Olejnik et al. [13] which elaborate complexes of kaolinite/amides (formamide, N-methylformamide (NMF), dimethylformamide (DMF), acetamide, N-methylacetamide, dimethylacetamide and pyridine). Jia et al. [19] and Elbokl et al. [3]

were polymerized, respectively, the vinyl acetate and the styrene between the layers of kaolinite, by using the complex kaolinite/dimethyl sulfoxide (DMSO) as precursor.

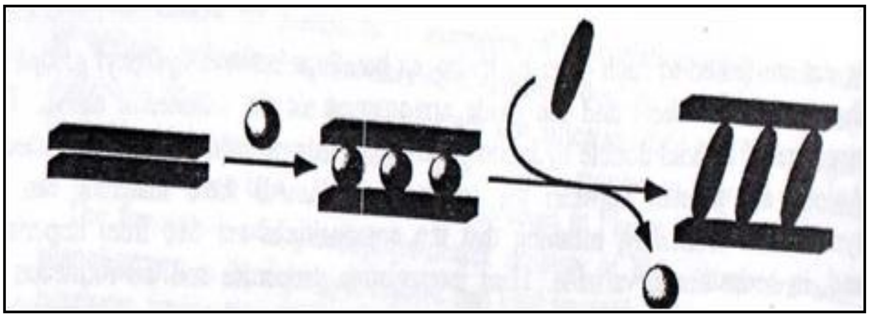

Figure 2: Method of Guest Displacement reaction [4].

Also, Itagaki et al. [20], were synthesized nanocomposites kaolinite/B-alanine by the reaction of in-situ polycondensation, by using as precursor the complex kaolinite/acetate of ammonium. In addition, Janec et al. [21] were elaborated hybrid systems containing kaolinite, by displacing the potassium acetate with the ethylene glycol and glycerol. However, various intermediates have been utilized such as DMSO/kaolinite, N-methylformamide (NMF)/kaolinite and methanol/ kaolinite [7, 19]. Other work used two composed organic for the intercalation of kaolinite. To prepare nanocomposites containing poly (methyl methacrylate (PMMA), Li et al. [18] were intercalated the DMSO initially. which allows to increase the basal space to 11.2Å, then the potassium acetate which allows to lead until 14.3Å

2.3. Intercalation of kaolinite by amides

The study of the intercalation of the organic substances in inter lamellar space of kaolinite was the object of various works by using various types of organic molecules [9, 10].

Consequently, the intercalation of kaolinite by amides such as: the formamide, N-methylformamide, the dimethylformamide, and acetamide were carried out by various authors [9, 22]. The majority of these compounds formed of the complexes inter lamellar with kaolinite and increased the basal distance (d001) from this one of 7.14Å to higher values. The characterization of the complexes obtained by the IR spectroscopy showed that new hydrogen bonding are established between hydroxyls of surface and the amide groups (>C=O) of the various organic compounds, thus giving place to new absorption bands [10]. According to Olejnik et al. [13], the spectra IR of the complexes kaolinite/formamide, kaolinite/NMF and kaolinite/DMF, showed the reduction in the intensity of the band of vibration situated at 3690 cm^{-1}, this reduction shows that the majority of the organic compounds are adsorbed on kaolinite by hydrogen bonds with inner surface hydroxyls. Whereas, the intensities of the bands with 3670 and 3650 cm^{-1} was varied from a complex with another, which indicates that these amides react differently with kaolinite [9].Also, the bands of vibration of Al-OH banding situated at 941 and 917 cm^{-1}, decrease the intensity in the complexes, which constitutes an indication of the occurrence of interaction between amides and the octahedral layer [9].

Thus, Olejnik et al [13] deduced that the intercalation of the DMF in kaolinite is very slow and weak bus they obtained an intercalation rate from only 0.5% at the end of 42 days and a small proportion of kaolinite which reached a basal space of 12.12Å. They as noted as the intercalation is affected neither by the addition of water nor by the heating. Weiss et al. [24] also noted a basal space of 12.10 Å, but without them not being able to highlight the formation of the complex. On the other hand, the various studies on the intercalation of kaolinite by N-methyl formamide noted that this last is intercalated quickly at the ambient temperature and causes the increase in basal space until 10.7Å at the end of three days [9, 13, 20, 23]. Also, various works which was released to elaborate kaolinite-formamide complex, noted that the intercalation of this compound results in the reduction of the intensities of the assigned bands with outer hydroxyl and that it is very favored by the increase in the temperature [9, 13, 17]. Thus, Olejnik et al. [13] as noted as this process is very sensitive to the addition of water because the rate of intercalation increases with the quantity of added water.

2.4. Intercalation of kaolinite by urea

In the case of urea, interaction occurs through the NH_2 groups According to Frost et al. [15, 25], urea forms hydrogen bonds with the silica plane only, Also, The insertion of the urea molecules breaks the hydrogen bonds between the gibbsite like hydroxyls and the oxygen of the next adjacent siloxane surface with the subsequent formation of hydrogen bonds between the hydrogen of the urea and the oxygen of the siloxane layer [17]. Ledoux and White [26] proposed that urea forms hydrogen bonds on interacting with the silica plane and the inner surface hydroxyls via its NH_2 groups. Mako et al. [27] proposed a structural model comprising two types of urea bonding to the siloxane surface, involving the NH_2 groups and the oxygen atom of the silica layer. Letaif et al.[28] used the manual grinding followed by a mechanical one to the ambient temperature, which allowed the increase in the basal space of 7.15 to10.5Å. The FTIR characterization of the kaolinite intercalated according to this method revealed the disappearance of the bands situated at 3670 and 3650 cm^{-1} and the appearance of a new band at 3503 cm^{-1} characteristic of the interactions between NH_2 groups of urea and the tetrahedral layer of kaolinite .

The delamination by means of chemical exfoliation of kaolinite with urea entails two different processes. One of them is simple mixing of kaolinite with an aqueous solution of urea, and makes it possible to obtain a kaolinite/urea intercalate with a basal distance from 10.77Å. Valaskova et al. [29] could increase the basal distance of two types of kaolinite samples (with grosses and fine particles), until 10.78Å and rates of intercalation of 97% for the large particles and 93% for the fine particles. Frost et al.[16] too, could deduced the formation of two types of hydrogen bond: those of NH2 groups of urea and the oxygen atoms of the tetrahedral layer and those where intervene the groups carbonyls of urea and hydroxyls of the octahedral layer, by using the first procedure. The second procedure is dry grinding of kaolinite, to which were added variable amounts of urea, for different periods of time used a ball mill, a mechanical mortar, and a combination of both. It was concluded that the ball-milling of kaolinite-urea mixture alone is inefficient for urea intercalation. This process results in the increase the basal space to 10.8 Å [29].

2.5. Cation exchange with alkylammonium ions

One of the disadvantages of clays is their incompatibility with hydrophobic polymers, which often causes their agglomeration in the polymeric matrix. It is thus advisable to carry out a modification of this property to ensure a good dispersion of the clay [30].

The method most usually employed for the chemical modification of the phyllosilicates is the cation exchange [31]. Ion exchange with alkylammonium ions is a well-known method to make clay minerals and clays dispersible in organic solvents which become thus hydrophobic and to render them consequently compatible with hydrophobic materials, such as polymers, in compounding processes [30]. Exchanging the interlayer cations of natural and synthetic clay minerals by particular organic cations provides a simple method to prepare new types of organic-inorganic hybrid materials [1, 30-33].

Kaolinite particles are used for a long time as active fillers of polymers. However, only a few reactions are available to modify kaolinite. There is still interest in the reactions with silane coupling agents. In recent years, authors are interested largely to the cation exchange method for modifying this clay [1].

2. Experimental details

3.1.Materials

The raw kaolinite used in this study consisted of small diameter (≤45 µm) particles that had perfect crystallization and high purity and of a cation capacity of exchange with 15 meq/100g clay. Its chemical composition was determined by chemical analysis, as it is reported in Table1. The used kaolinite was modified with an alkyl ammonium is a hexadecyltrimethylammonium chloride abbreviated as (HDTMA), purchased from

Aldrich, and having the following chemical structure: $CH_3\,(CH_2)_{15}N\,(CH_3)_3Cl$.The DMF used in our study, is a Prolabo product. It is presented in the form of an incolor liquid, of low amino odor and empirical formula C_3H_7NO, and urea NH_2CONH_2 is a Prolabo Product .

Table1 Chemical composition (w t %) of the used kaolin

SiO_2	50.44
Al_2O_3	28.30
CaO	1.10
MgO	0.50
Fe_2O_3	2.29
Loi (loss on ignition)	10.01

3.2. Process of intercalation of kaolinite

3.2.1.Purification of kaolinite

30to 40 g of kaolin are put in suspension in one liter of distilled water. The suspension is put under magnetic agitation cold during 30 minutes. This operation is repeated six successive times in order to eliminate all the impurities. After each washing, the suspension is centrifuged during 10 minutes, then at the end, kaolinite is dried in a drying oven with 65°C during two days.

3.2.2. Preparation of kaolinite/DMF complex.

The intercalation of the kaolin with DMF was carried out according to the protocol suggested in work of Zhang et al. [7], which is explained as follows: 2 g of kaolin were mixed with 20 ml of DMF containing methanol 13%.The solution is put under magnetic agitation during 120 hours at 85C.Then, filtered, washed front suspension three times with ethanol until the complete elimination of the excess of DMF, then dried with 60C during 24 hours .

3.2.3. Preparation of Kaolinite/urea complex

The experimental method used for urea intercalation was performed according to procedure described by Letaief et al. [28]. It consists on a manual grinding in a mortar of a mixture of 5 g of kaolinite and 8 g of urea for a period of 2.5 hours, followed by a mechanical grinding for 15 minutes.

3.2.4.Treatment of intercalated kaolinite compounds with ammonium salt

For urea and DMF displacement from kaolinite, the resulting material was subjected to a reaction in a solution containing the ammonium salt at a temperature of 80°C for 24 hours. After that, the clay was filtered and dried then stored .

4. Measurements

4.1. X-ray diffraction (XRD)

XRD was used to study the modified and unmodified kaolin using XPERT diffractometer equipped with Cu-kα radiation (λ=0.154nm) at room temperature. The scans were taken in a 2 range from 4 to 30°, with 0.02° step size and the counting time of one scan 5 s .

4.2.Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopic analysis (FTIR) was employed to get insight into interactions between kaolinite, urea and ammonium salts modifier, it was undertaken using a Shimadzu FTIR 8400S spectrometer. FTIR spectra were obtained between 500 and 4000cm^{-1}. The samples of treated and untreated kaolinite were prepared at KBr pellets (ca. 3% by mass in KBr).

5. Results and discussion

5.1. XRD analysis

The XRD was used to observe intercalation process into kaolinite. Significant segments of XRD patterns described process of intercalation (DMF, DMF/HDTMA) and, (urea, urea/HDTMA), are presented in Figure.3 and Figure.4, respectively. Figure 3 showed clearly that the peak (001), characteristic of basal space, kept the same position (2θ) that neat kaolin (curve a). And showed that there was no variation in the values of the basal distances from the various samples (7, 17 Å). This carries out us to conclude that the intercalation of the DMF in the interfoliar space of the kaolin did not occur, or that the DMF/kaolin complex was formed but its instability generated by the fast desintercalation of solvent caused the return to initial basal space. The same results were observed for the kaolinite modified by an alkylammonium salt. Although that we did not succeed in intercalating the DMF, thus the alkylammonium cannot be inserted while using the DMF/kaolin complex as precursor, we cannot thus expect to obtain kaolin exchanged by the HDTMA.

Figure 4 showed a decrease in intensity of d001 basal diffraction of kaolinite with maxima at d=0.717nm (curve a), is evident after the intercalation with urea. The new peak with maxima at d=1.072 nm is connected with formation of kaolinite-urea complex (curve b). Figure.4 (curve c), depicting the XRD pattern of the kaolinite treated with the alkylammonium salt in aqueous solution, shows that the treatment does not produce any detectable structural changes on the interlayer spacing of the clay .

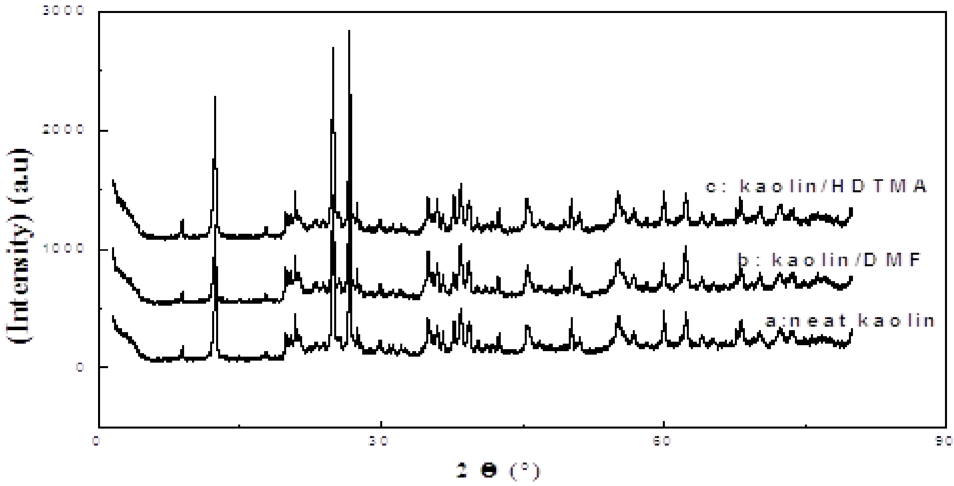

Figure 3: X-ray diffraction curves of neat kaolinite and kaolin/DMF and kaolin/HDTMA mixtures.

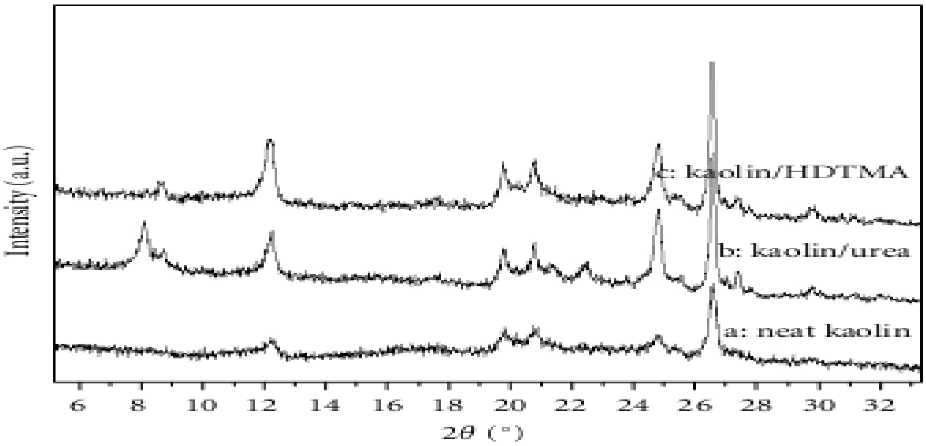

Figure4: X-ray diffraction curves of neat kaolinite and kaolin/urea and kaolin/HDTMA mixtures.

The use of the obtained kaolinite/urea complex failed in the intercalation of the ammonium salt in the interlayer gallery of the clay. So, it is clear now that the ammonium salt molecules interacted with the kaolinite hydroxyls groups involved at the surface of the clay particles and not with those situated in the interlayer space.

5.2. *Infrared analysis (FTIR)*

The infrared spectrum of kaolinite and particularly its OH stretching region are very sensitive to interlayer modifications [6]**.** The hydroxyl deformation modes of kaolinite are important in the spectroscopic analysis of intercalated kaolinite. Kaolin clay minerals contain two types of hydroxyl groups (i) the outer hydroxyl groups, or so-called inner surface hydroxyls and (ii) the inner hydroxyl groups. These hydroxyl groups were designated Ou OH and In OH, respectively. The Ou OH groups are situated in an outer, unshared plane, whereas the In OH groups are located in the plane shared with the apical oxygen atoms of the tetrahedral sheet [15-17].

In the case of neat kaolinite and as it is reported in Figure.5, four distinct bands are observed in the infrared spectrum of kaolinite at 3697, 3668, 3653 and 3620 cm^{-1} [6, 9, 16]. The three higher frequency bands are assigned to OH stretching modes of the three inner surface hydroxyl groups (Ou OH) [16, 5, 9], and they are influenced very strongly by inter lamellar modifications [6]. The band at 3620 cm^{-1} is assigned to the stretching mode of an inner hydroxyl group (In OH), which are in the plane common to both the tetrahedral and octahedral sheets and this band at 3620cm^{-1} which is typical of the stretching of the internal OH groups in the kaolinite structure, Their movement is restricted as a result of chemical bonding between the silica and alumina sheets. Usually, this internal hydroxyl group is not significantly affected by inter lamellar modifications, and do not participate to the establishment of hydrogen bonds with the inserted molecules[6, 9, 15, 16].

The absorption bands situated at 3452 and 1635 cm^{-1} are respectively assigned to the vibrations of the O-H and H-O-H bonding of the water adsorbed on kaolinite [9, 21]. In addition, the bands at 1114, 1030 and 1006 cm^{-1} are attributed to the vibration of the bands Si-O and Si-O-Si, whereas the Al-OH bond vibrations are visibly characterized by the bands appearing at the wave numbers 937, 912, 795, and 756 cm^{-1}[9,12, 13, 34].According to Zhang et al.[7], the bands situated at 466, 430 and 536 cm^{-1} are assigned to (Si – O – Al) bonding, whereas the band situated at 696 cm^{-1} is assigned to the vibration of (O –Al – OH) bonding.

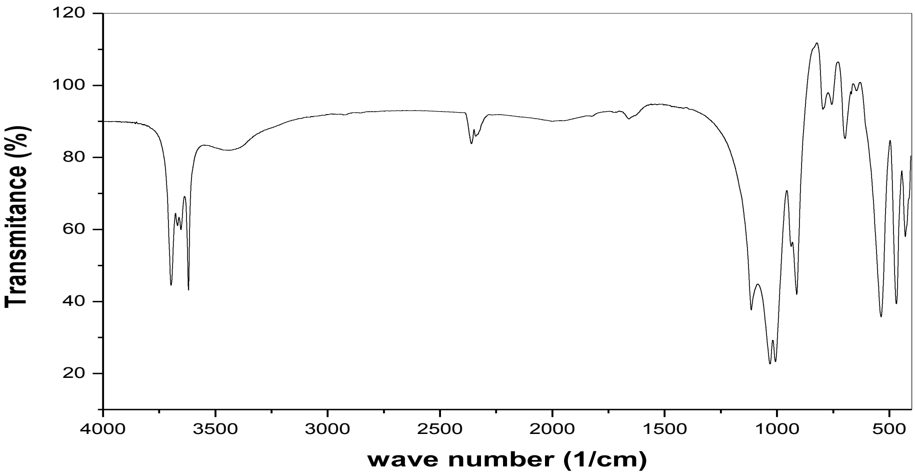

Figure5: FTIR spectra of neat kaolinite.

The FTIR spectrum of the kaolinite/DMF complex (Figure.6)show similar positions of the hydroxyl vibrations like untreated kaolinite, and the band intensities ratio are slightly less than of the neat kaolinite. Also there is no detectable appearance of new bands after the insertion of DMF into the clay. Nevertheless, the intercalated DMF must hydrogen-bond to some of the kaolinite hydroxyls explains the appearance of the new band at 3625 cm^{-1} in the spectrum of the kaolin/DMF complex [9].These results show that the hydrogen bonding is not very strong; this is probably the reason that the intercalated DMF is able to be removed easily from the complex.

Olejnik et al.[9, 13] showed that after intercalation of amides such as the DMF, the latter will be bound by a hydrogen bonds which is established with C=O amide groups and inner surface hydroxyls of kaolinite, which entrain a disturbance in the region characteristic of these hydroxyls. Also, bands of vibration of the bonds Si-O, Si -O- Si and Al-O-H are not affected and kept the same positions and the same intensities. However, we can conclude according to these results, that there is no assertion on the intercalation of the DMF in kaolinite.

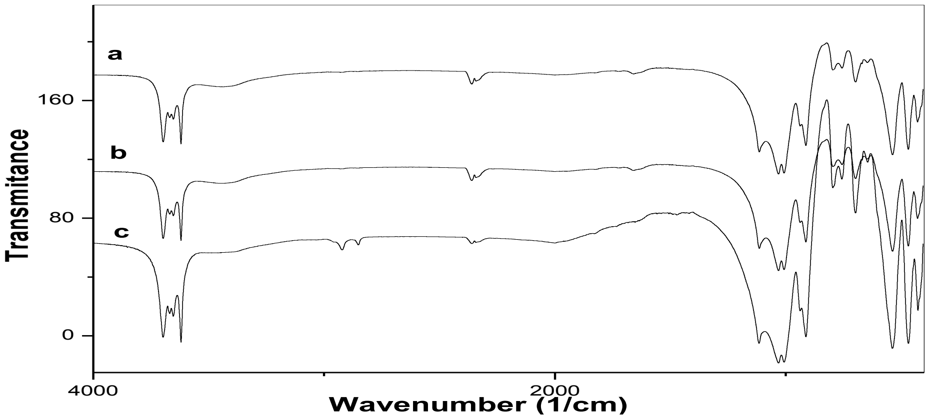

Figure 6: FTIR spectra of: (a) neat kaolinite, (b) kaolin/DMF, and (d) kaolin/DMF/HDTMA.

These deductions confirm our results of x-ray diffractions, which can be attributed either to the easy desintercalation of the DMF, or to the difficulty of its insertion because it's large size and the structure of its molecules may impede intercalation. And this is further substantiated by the fact that DMF with the lowest basicity (0.78) intercalates very slowly forming a complex, and the intercalated DMF is readily lost on exposure to air, compared with DMSO with a lower basicity (1.05) intercalates readily [13]. Also, S. Olejnik et al. [13] and Weiss et al. [24], showed that the intercalation of DMF into kaolinite is very slow and only a very small proportion of the kaolinite expands to 12.12Å and 12.00Å for their complex respectively.

Concerning the kaolinite exchanged with an alkylammonium salt,(figure.6 (curve c)),we observed the same intensities and positions of the absorption bands concerning the four hydroxyls characteristic of kaolinite and the bonds Si-O, Si-O-Si, Si-O-Al and Al-O-H. However, two new adjacent bands are observed at 2922 and 2850 cm^{-1} assigned to the symmetric and asymmetric vibrations of the (C–H) bonding which are attributed to the alkyl chain of ammonium salt. From the XRD results, the interfoliar distance of kaolinite does not change after the treatment by the DMF and the alkylammonium salt, so the appearance of these two bands can be explained only by their interaction with hydroxyls of edge surfaces of kaolinite. As kaolinite does not contain a C-H bonding, so these bands can be attributed only to the alkyl chain of ammonium salt. Since of x-rays diffraction results showed that the inter foliar distance from kaolinite did not change after the treatment by the DMF and the alkylammonium salt, the appearance of these two bands can be explained only by the interaction of this last with hydroxyls of edge surfaces of kaolinite.

The FTIR spectra of, neat kaolinite, urea, kaolin /urea and kaolin/ HDTMA, is shown in figure.7. The FTIR spectrum of urea, (Figure.7 (curve b)), has bands, between 3600 and 3300 cm^{-1} assigned to symmetric and asymmetric stretching vibrations of the N-H, at 1603, 1630 and 1683cm^{-1} assigned to the C=O vibrations, and the band at 1468 cm^{-1} attributed at C-N stretching vibration.

The FTIR spectra of kaolinite/urea intercalate is presented in Figure.7 (curve c). It is noted the apparition of only two bands at 3697 and 3620 cm^{-1} assigned to the kaolinite hydroxyls and disappearance of the hydroxyl groups bands observed for the untreated kaolinite at 3668 and 3653 cm^{-1}, and appearance of two new bands at about 3498 and 3404 cm^{-1}indicated that urea disrupted the interlayer hydrogen bonding between the kaolinite layers**,** these resultsare the same found by Letaif et al.[28]when they observed the disappearance of the bands at 3670 and 3650 cm^{-1} and the appearance of a new band to 3503 cm $^{-1}$ which are attributed to the formation of hydrogen bond between the NH_2 groups and the oxygen of the basal tetrahedral sheet.The band at 3404 cm^{-1} is due to the symmetric and asymmetric vibrational modes of the urea NH groups interacting with the siloxane surface.

The bands observed for urea at 1683 and 1630 cm^{-1} are little shifted to 1670 and 1627 cm^{-1} And those appeared at 1603 cm^{-1} is disappeared in the urea-intercalates, which are attributed to urea amine groups hydrogen bonded with the oxygen atom to the siloxane layer. The relative intensities of the two bands are almost the same. The band at 1468 cm^{-1} attributed at C-N stretching vibration in urea kept the same position but it is reduced in intensity. Mako et al. [27] noticed that the stretching vibration of urea C=O groups, detected at 1673 cm^{-1}, is shifted to a higher wavenumber in kaolinite/urea intercalate. The new band that they observed at 1683 cm^{-1} is due to the free C=O vibration since the conjugation between the C=O and NH_2 groups no longer occurs and new hydrogen bonds are formed between the NH2 groups and oxygen atoms of the siloxane layer. In addition,Frost et al.[16]werededuced the formation of two types of hydrogen bonds: those of NH_2 groups of urea and the oxygen atoms of the tetrahedral layer and those where intervene the groups carbonyls of urea and hydroxyls of the octahedral layer.

Changes in the Al-OH vibrational modes of kaolinite also occurred. The Al-OH vibration in our kaolinite is observed as the bands at 912, 937, 795 and 756 cm^{-1}. For the urea intercalate bands at 937 cm^{-1} and 795 cm^{-1} are disappeared. And those at 912 and 756 cm^{-1} are lightly shifted. The shift in these bands was attributed to the loss of hydrogen 1006 cm^{-1} characteristic Si-O-Si bonds, these changes were attributed to the formation of hydrogen bonds between the Si-O tetrahedral and the N-H of the urea.

After treatment with the alkylammonium salt, the spectra reported in (Figure.7 (curve d)) reveals no characteristic peaks of urea molecules bonded. The disappearance of this characteristic absorption indicates the complete displacement of the urea molecules from the interlamellar space of kaolinite during the treatment with the ammonium salt.In addition, the FTIR spectra points out the presence of two new weak bands at approximately 2925 and 2859 cm^{-1} attributed, respectively, to the symmetric and a symmetric stretching vibrations of the -CH_3 groups contained in the alkyl chains of the ammonium salt. These bands confirm the occurrence of interactions between the ammonium molecules and the kaolinite groups.

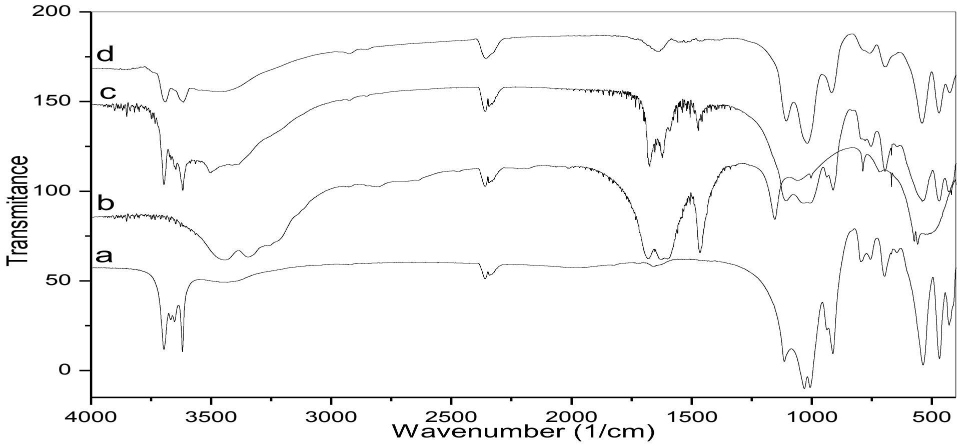

Figure7: FTIR spectra of: (a) neat kaolinite, (b) urea, (c) kaolin/urea, and (d) kaolin/HDTM.

6.Conclusions

The preparation and characterization of intercalated kaolinite is important for industries such as those using nanocomposites, but the number of compounds that can be intercalated into these clay minerals is rather limited.

Samples of kaolinite were intercalated with dimethylformamide (DMF) and urea to form complexes kaolin/DMF and kaolin/urea as precursors for the intercalation of an alkylammonium salt into the interlamellar space of kaolinite using guest displacement reaction.

In the case of clay samples intercalates by the DMF, the infrared spectroscopy results revels no new bands were detected in the kaolinite/DMF complex. On the other hand Infrared analysis results of kaolinite/urea complex, showed the occurrence of a partial delamination during dry milling of kaolin with urea. And after the treatment with alkylammonium salt two new adjacent bands were observed in both cases, and characterizing the vibrations of symmetric and asymmetric valence of the C-H bonding. as soon as the X-rays diffraction showed that both the kaolinite/DMF and kaolinite-urea were characterized by the same basal distance (d_{001}) and that the 001 reflection of the clay was not affected by the treatment, and the appearance of new bands after treatment with alkylammonium salt can be explained only by the interaction of this last with hydroxyls of edge surfaces of kaolinite, which states that the interactions concerned essentially the superficial groups of kaolinite via an adsorption process.

The results show that the most successful intercalation agent for used kaolinite was urea compared to the DMF. The preparation and characterization of intercalated kaolinite showed that the displacement reaction is the most efficient way to expand the interlayer spacing of kaolinite.

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