

Comparison of Analysis Results and Modification of Na⁺-Montmorillonite with Ionic Liquids

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In this study, preliminary data are reported on the modification of sodium montmorillonite modified with imidazolium and pyridinium-based ionic liquids. Commercially available unmodified clay was treated under different conditions with aqueous solutions of three ionic liquids such as 1-butyl 3-methyl imidazolium tetrafluoroborate, 1-butyl 4-methyl pyridinium tetrafluoroborate and 1-methyl 3-octyl imidazolium tetrafluoroborate and the results were compared with ammonium dodecyl sulphate. The modified materials were characterized by FTIR, TGA, SEM and WXR analysis. The analysis results show an overall increase in interlamellar spacing as a result of sodium cation exchange with the cations of the ionic liquids and long chain quaternary ammonium salt. The thermal stabilities of the organoclays is higher than unmodified clay.

Keywords: Na⁺-Montmorillonite, Ionic liquids, Organoclays, Modification, Quaternary ammonium salt.

INTRODUCTION

Ionic liquids are gaining interest as a new reaction media for organic transformations. They can be used as solvents for a wide range of organic and inorganic reactions and their unique properties make them important candidates for the so-called "green chemistry"^{1,2}. Ionic liquids are substances with melting points below 100 °C composed solely by ions (so 'classical' high temperature molten salts are not included in this definition)³⁻⁵. Because of their insignificant vapour pressures, low melting points, good solvent characteristics for organic, inorganic and polymeric materials, adjustable polarity, selective catalytic effects, chemical and thermal stability, low viscosity, non-flammability and high ionic conductivity, high ion content, ionic liquids have generated significant interest for a wide range of industrial applications⁶⁻⁹. They have received extraordinary attention due to their potential commercial applications in electrochemistry, heavy metal ion extraction, phase transfer catalysis and polymerization, solubilization of materials and as substitutes for common volatile organic solvents including enzymatic reactions⁷⁻¹⁰.

Quaternary ammonium salts (QACs) are an economically advantageous class of industrial compounds. They have surface-active properties, possess anti-microbial activity and are known to be bioactive¹¹. The quaternary alkylammonium salts (QACs) are cationic surfactants¹². They are synthesized by completing alkylation of ammonia or amines¹³. For practical and industrial

uses, quaternary ammonium salts are preferred to primary alkylammonium ions because hydrolysis is absent and desorption of free alkylamine is strongly reduced. A further advantage is that the large amount of organic material (30-40 %) reduces the density of the dispersed particles¹⁴.

Many practical applications are based on the properties of dispersed bentonites¹⁵. Organo clay minerals (also called bentones) were initially used for their rheological properties, but their most recent application is as filler for a polymer, in order to modify its mechanical, thermal or barrier properties¹⁶⁻¹⁷. Cationic nanoclays are presently the focus of extensive R&D efforts are exemplified by smectites, a group of 2:1-layer minerals that includes the hydrated aluminum silicate, montmorillonite (Mt). Montmorillonite consists of thin platelets of less than 1 nm in thickness¹⁵⁻¹⁸.

Commercial organophilic montmorillonites used in polymer nanocomposites are usually prepared from the Na⁺-Mt form by ion exchange with long chain (C₁₆-C₁₈)¹⁹ alkylammonium-based ions. Ionic liquids containing long chain cations (mostly imidazolium based) have been recently evaluated as montmorillonite modifiers. Important incentives were the improvement of the thermal stability of the organoclays and the preparation of nanocomposites with enhanced flame retardant characteristics.

The purpose of this study is to compare the results of organoclays's analysis according to the difference between ionic liquid and quaternary ammonium salt.

EXPERIMENTAL

Chemicals of high purity were obtained from various commercial sources, which consisted of ammonium dodecyl sulphate (ADS) [CH₃(CH₂)₁₀CH₂OSO₃NH₄] (Aldrich) and ionic liquids (Fluka), silver nitrate (Merck), hydrochloric acid (Merck).

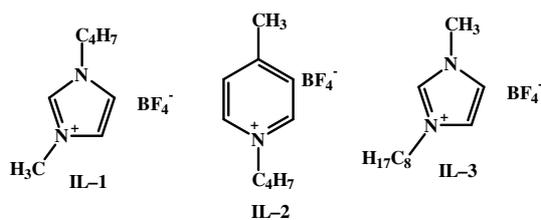
Montmorillonite, Na⁺-Mt, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Cloisite-Na⁺, CAS# 1318-93-0, Southern Clay Products Inc.) is a powder with typical particle size less than 2 μm. Specific gravity of Na⁺-Mt is between 2.8 and 2.9, pH value of a 10 % dispersion is 10 and its cation exchange capacity (CEC) as reported by the supplier is 92.6 meq /100 g clay. The physical and chemical properties of Na⁺-Mt are included in Table-1.

TABLE-1
PHYSICAL AND CHEMICAL PROPERTIES OF Na⁺-Mt

m.f.	(Na,Ca) _{0.33} (Al, Mg) ₂ Si ₄ O ₁₀ (OH) ₂ 6H ₂ O
Density (g/cm ³)	2.86
pH	8
Surface area (m ² /g)	750
CEC (meq/100 g)	92
Composition (%)	1.40 Na, 2.44 Ca, 9.99 Al, 8.88 Mg, 20.7 Si, 35.53 O, 0.37 H

The organoclay modified with ammonium dodecyl sulphate (ADS) was used for comparison with organoclays modified with ionic liquids.

Ionic liquids used for clay modification by ion exchange included: 1-butyl-3-methyl imidazolium tetrafluoroborate (IL-1), 1-butyl-4-methyl pyridinium tetrafluoroborate (IL-2) and 1-methyl-3-octyl imidazolium tetrafluoroborate (IL-3) is a liquid at room temperature. Their structures are shown below:



Chemical structures of the ionic liquids

Modification of clays: Cationic exchange of Na⁺-Mt (Mt) was carried out with 1-butyl-3-methyl imidazolium tetrafluoroborate (IL-1), 1-butyl-4-methyl pyridinium tetrafluoroborate (IL-2), 1-methyl-3-octyl imidazolium tetrafluoroborate (IL-3), ammonium dodecyl sulphate (ADS) and aqueous solutions at two different conditions (stirring at 80 °C for 2 h and stirring at 60 °C for 2 h) and at 1 and 2 concentrations of the clay based on CEC. After filtration, all modified clays were repeatedly (more than 15 times) washed with distilled water. For clays modified with IL-1, IL-2 and IL-3 washing was continued until no residual halogen anion was detected by adding 0.1 M silver nitrate solution in the filtrate. It is to be noted that filtration time for all treated clays was significantly shorter than that for the unmodified one. After 24 h at room

temperature, drying continued at 80 °C for 12 h under vacuum²⁰. Abbreviations used to describe the modified clays are given in Table-2.

TABLE-2
EXPERIMENTAL DESCRIPTION AND ABBREVIATIONS OF CLAYS MODIFIED

Clay	Modifiers	Ionic liquids	Exchange temp./time/CEC amount used (C/h/stoichiometry)
Mt	—	—	—
Mt-1	[C ₈ H ₁₅ BF ₄ N ₂]	IL-1	80 / 2 / 2 gr
Mt-2	[C ₈ H ₁₅ BF ₄ N ₂]	IL-1	60 / 2 / 2 gr
Mt-3	[C ₈ H ₁₅ BF ₄ N ₂]	IL-1	80 / 2 / 4 gr
Mt-4	[C ₈ H ₁₅ BF ₄ N ₂]	IL-1	60 / 2 / 4 gr
Mt-5	[C ₁₀ H ₁₆ BF ₄ N]	IL-2	80 / 2 / 2 gr
Mt-6	[C ₁₀ H ₁₆ BF ₄ N]	IL-2	60 / 2 / 2 gr
Mt-7	[C ₁₀ H ₁₆ BF ₄ N]	IL-2	80 / 2 / 4 gr
Mt-8	[C ₁₀ H ₁₆ BF ₄ N]	IL-2	60 / 2 / 4 gr
Mt-9	[C ₁₂ H ₂₃ BF ₄ N ₂]	IL-3	80 / 2 / 2 gr
Mt-10	[C ₁₂ H ₂₃ BF ₄ N ₂]	IL-3	60 / 2 / 2 gr
Mt-11	[C ₁₂ H ₂₃ BF ₄ N ₂]	IL-3	80 / 2 / 4 gr
Mt-12	[C ₁₂ H ₂₃ BF ₄ N ₂]	IL-3	60 / 2 / 4 gr
Mt-A	[C ₁₂ H ₂₅ OSO ₃ NH ₄]	ADS	60 / 2 / 2 gr

Mt = Montmorillonite

Infrared spectra were recorded as KBr pellets in the range 4000-400 cm⁻¹ on an ATI UNICAM systems 2000 Fourier transform spectrometer.

Thermogravimetric analysis was obtained by using a TGA 50 Shimadzu (thermal gravimetric analyzer). The heating rate was 10 °C/min in all cases in the temperature range 0-950 °C in nitrogen atmosphere.

The samples were characterized by X-ray diffraction (XRD) for the crystal structure, average particle size and the concentration of impurity compounds present. Rigaku Rad B-Dmax II powder X-ray diffractometer was used for X-ray diffraction patterns of these samples. The 2θ values were taken from 20° to 110° with a step size of 0.04° using CuK_α radiation (λ value of 2.2897 Å). The dried samples were dusted onto plates with low background. A small quantity of 30 (± 2) mg spread over 5 cm² area used to minimize error in peak location and also the broadening of peaks is reduced due to thickness of the sample. This data illustrate the crystal structure of the particles and also provides the inter-planar space, d.

Morphology of the organoclays was examined by a JEOL JSM 5600 LV scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

FT-IR spectra of unmodified Mt, clays modified Mt-2, Mt-6, Mt-10 and Mt-A were compared. The clay's CEC concentration with IL-1 (Mt-2), IL-2 (Mt-6), IL-3 (Mt-10), ADS (Mt-A). All compositions were prepared at 60 °C/2 h/2 gr conditions. All spectra of the modified clays contain characteristic peaks of the respective modifier, an indication of their presence. In the spectrum of montmorillonite, the silicon-oxygen and aluminum-oxygen bonds are respectively observed at 1044 cm⁻¹ and 620 cm⁻¹ and the magnesium-oxygen is assigned to a band between 470 and 530 cm⁻¹. The strong peak at 1650 cm⁻¹ and the broad band at 3440 cm⁻¹ have been

assigned to the bending and stretching modes of absorbed water. Sharp peaks around 3600 cm^{-1} are assigned to the hydroxyl group.

The spectrum of Mt-2 shows peaks for the imidazolium functional group in the range between 1650 and 1000 cm^{-1} ; for example, the peaks in the range of 1600 - 1320 cm^{-1} are due to C-C and C-N vibrations; the conjugated strong peaks around 1570 and 1630 cm^{-1} are due to C-N-C or C-C bonds²⁰.

In the FT-IR spectrum of Mt-6, the spectrum of IL-2 (pyridinium based) shows peaks at 1460 , 1490 , 1580 and 1650 cm^{-1} assigned to C-C and C-N stretching vibrations in pyridinium.

In the FT-IR spectrum of Mt-10, a longer hydrocarbon chain in IL-3 gives significantly strong peaks in the ranges of 3100 - 2800 cm^{-1} and 1640 - 1465 cm^{-1} . These peaks occur at 1470 cm^{-1} , 1570 cm^{-1} and in the range of 2860 - 3060 cm^{-1} , indicating the presence of IL-3 in the modified Mt-10.

In the FTIR spectrum for Mt modified with ammonium dodecyl sulphate (quaternary ammonium salt), Mt-A shows peaks at 2900 - 2800 cm^{-1} was caused by the stretching of ammonium dodecyl sulphate (aliphatic C-H stretching vibration)^{3,21}.

XRD analyses: Fig. 1 shows typical XRD for the clay and organoclays. The d001 reflection has sharp intense peak at $2\theta = 9.079$, 6.620 , 6.660 , 6.320 , 8.00 for Mt, Mt-2, Mt-6, Mt-10 and Mt-A, respectively. The d001 spacing was calculated and listed in Table-3 from peak positions using Bragg's law $d = \lambda/2 \sin \theta$. It is clear that the d-spacing for Mt (9.08 \AA) increased to (13.97 , 13.26 \AA) since the small inorganic Na^+ cation is exchanged by onium group through an ion exchange process. Fig. 1. presents series of XRD corresponding to clays.

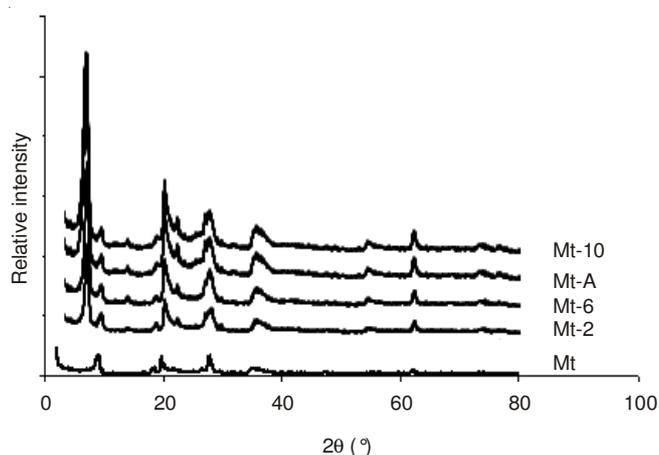


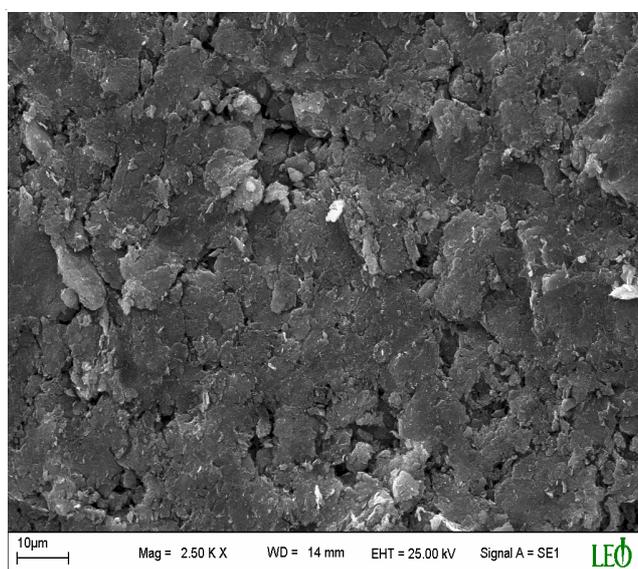
Fig. 1. XRD patterns of clay (Mt) and organoclays (Mt-2, Mt-6, Mt-A, Mt-10)

TABLE-3
X-RAY DIFFRACTION AND THERMAL
ANALYSIS DATA FOR THE SAMPLES

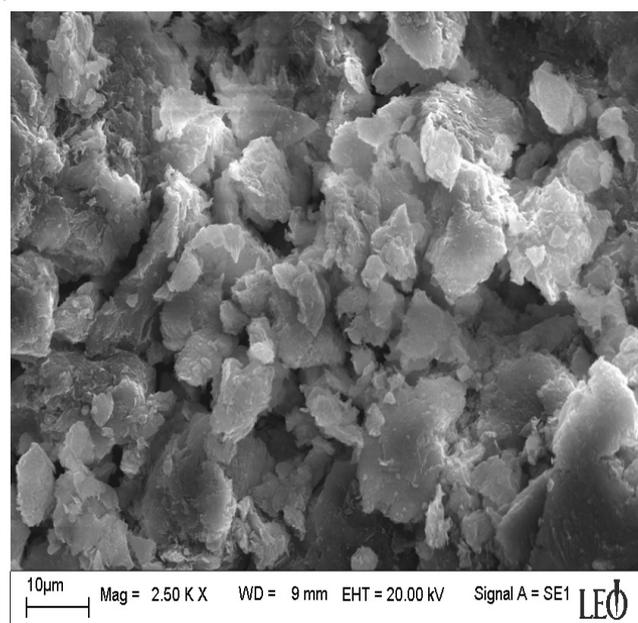
Sample	X-ray data	
	2θ	d-spacing
Mt	9.079	0.973
Mt-2	6.620	1.334
Mt-6	6.660	1.326
Mt-10	6.320	1.397
Mt-A	8.000	1.298

This confirmed that the organoclay is intercalated between the layers. Increase in d-spacing vs. the washed unmodified montmorillonite follows the order Mt-10 > Mt-6 > Mt-2 > Mt-A. The higher extent of intercalation corresponding to the largest interlayer distance of 1.397 nm in Mt-10 (compare with 0.973 nm for Mt) is obtained with IL-3, which has a relatively bulkier cation than the other two ionic liquids. Results are comparable with those reported in for dimethyl imidazolium ionic liquids with variable alkyl chain length. As anticipated, the d-spacing of organoclay (Mt-10) was found to be significantly higher (13.97 nm) than Mt-A.

SEM images: The surfaces of Mt and Mt modified samples was observed by using a Jeol JSM-5610 scanning electron microscopy after gold coating to determine the dispersibility of organoclay. SEM examination of the surfaces samples occurred fractures. Fig. 2(a). shows a micrograph of the fracture surface at 2.50 magnifications.



(I)



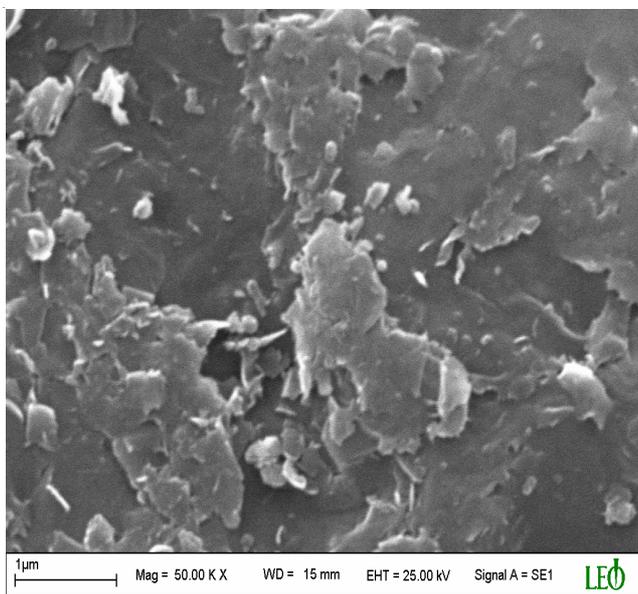
(II)

Fig. 2(a). SEM images of samples, (I) Mt, (II) Mt-A

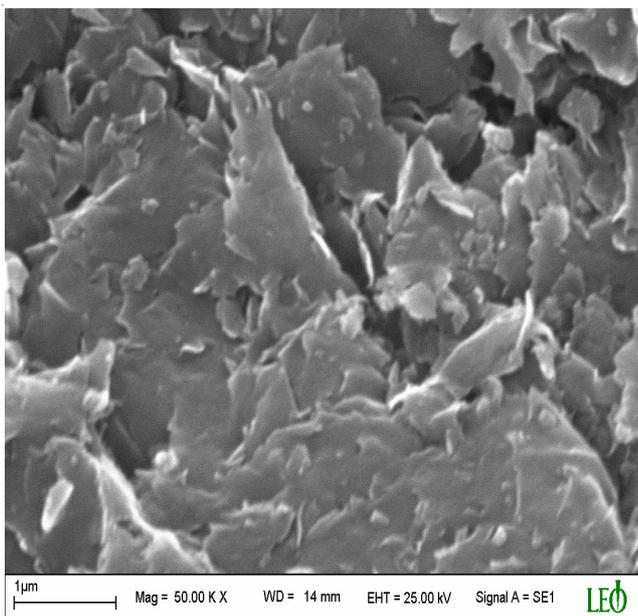
Fig. 2(a) shows SEM images of Mt (unmodified clay) and Mt -A (modified clay). Fig. 2(b) shows Mt, Mt-2, Mt-6 and Mt-10 clays. Fig. 2(b). shows a micrograph of the fracture surface at 50.00 magnifications.

The stress and strain at the breaks at surface of clays increase depending on the state of clay dispersion, concentration and modifiers. The energy values showed a correlation with the stress and strain at break. These properties may show an increase or a decrease due to restrictions in the mobility of clays during stretching. Hence, for Mt-10, the increase in the values for the mechanical properties can be attributed to the good dispersion and exfoliation of the ionic liquids observed by XRD and consequent interactions between the clay and the IL-3.

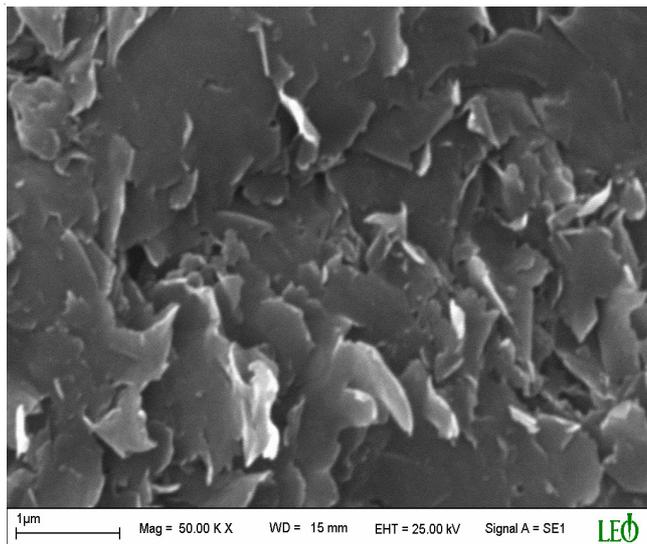
Thermogravimetric analysis: Table-4 shows TGA data for unmodified clay and for modified clays, respectively. Thermal stability of the organoclays is ranked as Mt-10 > Mt-A > Mt-6



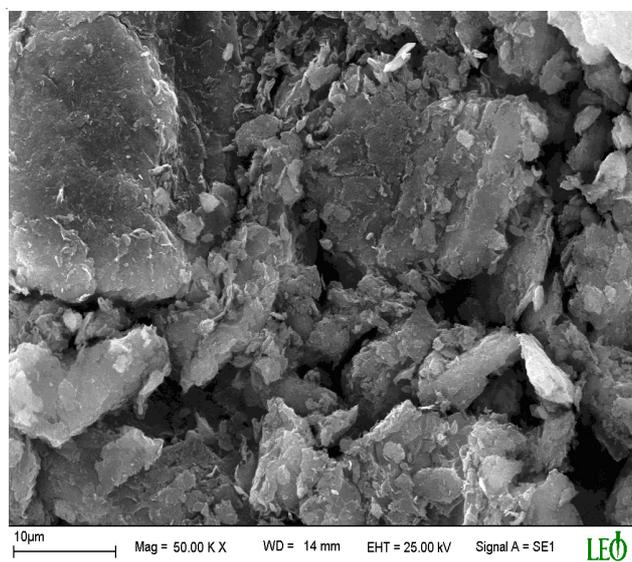
(I)



(II)



(III)



(IV)

Fig. 2(b). SEM images of samples, (I) Mt, (II) Mt-2, (III) Mt-6, (IV) Mt-10

TABLE-4
TGA RESULTS OF FREE AND
MODIFIED MONTMORILLONITE

Sample	Modi-fiers	Initial temp. (°C)	Initial weigh (mg)	End temp. (°C)	Remaining amount (mg)	Weight loss (%)
Mt	–	15.7	13.34	949.6	12.298	7.81
Mt-2	IL-1	16.2	13.23	949.4	11.199	15.35
Mt-6	IL-2	24.6	12.22	949.1	10.327	15.49
Mt-10	IL-3	24.9	13.77	949.2	11.413	17.12
Mt-A	ADS	25.6	11.57	949.5	9.680	16.34

> Mt-2 >. The results are in general agreement with those of Awad *et al.*²² where thermal stability of trialkyl imidazolium decreases as the length of the alkyl group attached to the nitrogen increases (in present case IL-3 > IL-2, IL-1). The high thermal stability of modified with IL is probably due to a large extent to the presence of the higher stability of the BF₄ anion *vs.* The presence of the pyridinium cation that has been reported, to have lower thermal stability than imidazolium cations²³.

It is noted that the overall weight losses are lower for Mt-A (modifier: ADS) than Mt-10 (modifier: IL-3). Table-4 also contain data for the unmodified Mt and Mt-A that is modified with large amounts of thermally unstable tallow based quaternary ammonium salts. The thermal stability of the Mt-A is lower than thermal stability of the Mt-10.

Conclusion

Organoclays obtained by modifying with organic cations were synthesized and characterized. The intercalation of four modifier in montmorillonite through exchange with interlamellar sodium ions was confirmed by comparing with the results of untreated montmorillonites and modified clays with organic cations by the following results: The highest thermal stability was obtained with modified clay using ionic liquid (higher than Mt-A). The highest extent of intercalation was obtained with IL-3.

A reasonable correlation was obtained between the above methods in determining the amounts of cations present in the modified clays and efficiency of intercalation. All clays modified with ionic liquids showed power alternative to quaternary ammonium salts in modification by comparison with Mt-A.

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