

INTERCALATION OF Al_{13} -POLYETHYLENEOXIDE COMPLEXES INTO MONTMORILLONITE CLAY

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Abstract—Novel promising modified clays adsorbents were synthesized by intercalating hydroxy-Al polymer associated with poly(ethyleneoxide) in the interlayer of montmorillonite. Two different PEOs of low molecular weight (600) and high molecular weight (100,000) were used. In both cases, the resulting materials are hydrolytically stable and display a slightly better crystallinity than the materials prepared in the absence of PEO. Thermal analysis and infrared spectroscopy indicate changes in the PEO molecular conformation after intercalation revealing interactions between the polycations and the organic molecules. The chain length of the polymer has a strong influence on the surface area of the pillared materials obtained after calcination at 500°C. The use of the high molecular weight polymer leads to products with a higher specific surface area (about 400 m²/g) whereas the lower molecular weight compound does not modify significantly the surface areas. This behavior can be explained by the different nature of the species intercalated in the interlayer. PEO(600) leads to isolated organometallic species whereas PEO(100,000) seems to lead to a network of complexed polycations linked by ethylene oxide units. In the case of the PEO(100,000), high amounts of polymer in the pillaring solution provoke a partial dissolution of the octahedral layer of the clay.

Key Words— Al_{13} , Intercalation, Microporous, Montmorillonite, Polyethyleneoxide.

INTRODUCTION

Metal oxide pillared clays were first synthesized by Vaughan and his coworkers in the late 1970's (Vaughan and Lussier 1980). These modified clays were prepared by exchanging the interlayer cations of smectite clays with bulky metal hydroxy polymeric cations. The most commonly used pillaring agent is the Keggin-like Al_{13} oligomer $[Al_{13}O_4(OH)_{24+x}(H_2O)_{12-x}]^{(7-x)+}$ (Johansson 1960, Bottero *et al* 1980). On calcination, the hydrated cations convert to fixed pillars leading to the generation of permanent microporosity in the interlayers (Poncelet and Schutz 1986, Tennakoon *et al* 1986, Lee *et al* 1989). Other complexes of zirconium (Figueras *et al* 1989), iron (Doff *et al* 1988) and other metals as well as mixed-metals complexes (Sterte and Shabtai 1987) have also been intercalated.

On the other hand, the intercalation of organic species into the interlayer of smectite clays has been thoroughly studied. The materials based on alkylammonium species are referred to as organo-clays and have interesting properties for the adsorption of micropollutants from aqueous solution (Boyd *et al* 1988, Wolfe *et al* 1985, Mortland *et al* 1986). More recently, some workers have tried to intercalate organometallic complexes (Fahey *et al* 1989, Michot and Pinnavaia 1992,

Michot *et al* 1993) in the interlayer space of montmorillonite in order to obtain thermally stable modified clays. The resulting materials have been tested for the adsorption of chlorinated phenols from solution (Michot and Pinnavaia 1991).

In the present study, such intercalated lamellar solids have been synthesized, with montmorillonite as the pristine lamellar silicate. The organic part of the intercalate was the PolyEthyleneOxide (PEO), $(CH_2-CH_2-O)_n$, where n is the number of ethylene oxide units (EOu) and the metallic part of the complex was the Keggin-like Al_{13} oligomer. The PEOs are known to be very good ligands as the oxygen atoms in EO units have a strong hydrogen bonding affinity that results in the formation of complexes (Bailey and Koleske 1990, Ananthapadmanabhan and Goddard 1987). Furthermore, the intercalation of PEO in montmorillonite clays has been recently performed by Ruiz-Hitzky and his collaborators to obtain materials with interesting ionic conduction properties (Ruiz-Hitzky and Aranda 1990, Aranda and Ruiz-Hitzky 1992).

These modified clays were characterized by different methods. The results reported here demonstrate that the cointercalation of PEO improves the hydrolytic stability of Al_{13} ions. In addition, in the alumina-pillared clay derivatives formed by calcining at 500°C, the intercalates exhibit higher specific surface areas than those observed for pillared derivatives prepared in the absence of PEO.

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EXPERIMENTAL

Host material

The clay used in this study was natural Wyoming sodium montmorillonite, purchased from the Source Clay Minerals Repository at the University of Missouri, Columbia MO. The idealized unit cell formula is: $(\text{Si}_{7.96}\text{Al}_{0.04})(\text{Al}_{3.12}\text{Mg}_{0.45}\text{Fe}^{\text{II}}_{0.16}\text{Fe}^{\text{III}}_{0.27})\text{O}_{20}(\text{OH})_4(\text{Na}^+)_{0.65}$ and the cation exchange capacity is 85 meq/100 g.

Prior to use the clay was purified and sodium-saturated. The procedure includes sedimentation for the removal of the $> 2 \mu\text{m}$ particle size fraction, treatment with acetic acid in sodium acetate at pH 5 at 80°C to dissolve the carbonates, three exchanges in 1.0 M NaCl and final washing in deionized water until the solution is chloride-free as judged by the silver nitrate test. The Na-montmorillonite is referred to as SW in this text.

Pillaring solution

The Al_{13} solution was prepared by adding dropwise a 0.45 M solution of sodium hydroxide to a 0.2 M solution of aluminum chloride in order to obtain a final hydrolysis ratio $\text{OH}^-/\text{Al}^{3+} = 2.25$. At this latter ratio, aluminum exists principally as Al_{13} units (80–95%), whereas larger oligomers form at higher hydrolysis ratios (Bottero *et al* 1987).

The poly(ethyleneoxide) compounds of two different average molecular weights 600 and 10^5 were supplied by Janssen Chimica. These two products were called PEO(600) and PEO(100,000), respectively.

300 ml of a PEO solution was added to a 120 ml aliquot of the Al_{13} solution aged for two days. The pillaring solutions were prepared using different molar ratios PEO/ Al_{13} . These ratios are described in EO units per mole of Al_{13} . The different ratios used for the pillaring solution containing PEO of molar weight 10^5 are: 1, 2, 5, 10, 20, 50, 100, 200 and 500. The different ratios used for the pillaring solution containing PEO of molar weight 600 are: 1.3, 2.6, 4.4, 6.5, 13, 26, 65, 130, 200 and 500.

Intercalation

The intercalated clays were then synthesized by adding dropwise to the pillaring solution 200 ml of a 5.0 g/liter suspension of sodium-montmorillonite under vigorous stirring. The ratio of aluminum to clay was 15 millimole Al/meq of clay. After stirring during four hours, the suspensions were allowed to age overnight. The products were collected by centrifugation, washed until chloride free, and finally air dried on a glass plate.

For comparison purposes, two PEO intercalated products were synthesized by using a Al_{13} free pillaring solution containing 13 EO units per mole of Al_{13} and 500 EO units per mole of Al_{13} of PEO 600 and PEO 10^5 , respectively. These modified clays prepared with-

out Al_{13} in the pillaring solution were washed one time only.

The products were then calcined at 500°C during 12 hours. The heating rate was 1°C/min.

Characterization methods

X-ray diffraction patterns were obtained for oriented film samples using a diffractometer Jobin Yvon Sigma 2080 with $\text{CuK}_{\alpha 1}$ radiation.

Nitrogen adsorption experiments were carried out at 77 K using a classical step by step volumetric method. The samples were outgassed at 150°C overnight under a residual pressure of 10^{-2} Torr. Surface areas were obtained by using the Brunauer-Emmet-Teller (BET) equation. The t-plot method (De Boer *et al* 1966) was applied to determine the total micropore volume of the samples, as well as the nonmicroporous surface area.

Infrared spectra were obtained in the transmission mode on a Bruker IFS 88 Fourier transform IR spectrometer equipped with diffuse reflectance (Harrick Corporation).

An Uguine-Eyraud B70 balance (Setaram) with an universal TG-TD head was used for combined thermogravimetric and thermodifferential analysis. 135 mg of sample was heated in a platinum crucible from room temperature to 1030°C using a 2°C/minute heating rate. Temperature, sample weight and differential weight were recorded simultaneously on a PC computer.

Chemical analyses were performed on solid samples on the quantometer ARL 3100 coupled with a computer DIGITAL PDP 1105, by the analytical chemistry laboratory of the CRPG (Centre de Recherches Pétrographiques et Géochimiques, Vandoeuvre les Nancy, France).

RESULTS

X-ray diffraction studies

Table 1 shows the XRD d001 data of intercalated montmorillonite with different amounts of EO units in the pillaring solution. The d001 values are between 17 and 19 Å which suggests that intercalation of Al_{13} units has occurred in all cases. The peaks obtained are sharper than those obtained in the absence of PEO in the pillaring solution (Figure 1a) showing a better ordered structure. This effect is maximal for PEO/ Al_{13} ratios in solution higher than five. The structure remains stable after calcination at 500°C as the d-spacings remain above 15 Å which proves the presence of aluminum moieties in the interlayer space. The better order observed on the exchanged materials is conserved after calcination if we consider the half height widths (Figure 1b). Figure 2 demonstrates that the presence of PEO(100,000) improves the stability of the structure. When a sufficient amount of PEO is present in the pillaring solution ($> 5 \text{ EOu}/\text{Al}_{13}$, results not

Table 1. Interlayer distances determined by X-ray diffraction.

Samples intercalated with Al ₁₃ and PEO (600)										
EO units/Al ₁₃	1.3	2.6	4.4	6.6	13	26	65	130	200	500
d001 (Å)	16.8	18	18.7	18.7	18.6	17.3	18.4	18.2	18.4	18.6
Calcined samples	16.4	16.6	16.2	16.5	16.1	15.9	16.8	16.4	15.4	15.7
Samples intercalated with Al ₁₃ and PEO (100,000)										
EO units/Al ₁₃	0	1	2	5	10	20	50	100	200	500
d001 (Å)	18.8	17.8	17.6	18.6	19	19	19	18.8	18.7	18.7
Calcined samples	17.5	16	16.2	15.7	15.6	15.2	15.3	15.2	14.8	14.9

presented), the peak does not show a shift after aging as observed for samples prepared without PEO or with a very few EO units in the synthesis solution. Similar results were obtained in the case of samples synthesized in the presence of PEO(600).

These first results show that for all samples, with various amounts of PEO, the intercalation was performed. Several measurements after synthesis of the calcined or non calcined samples gave promising results as no change appears in the d001 spacings. These materials are stable before and after calcination.

Surface areas

Figure 3 and Table 2 show the variation of surface area with the ratio PEO(100,000)/Al₁₃ in the pillaring solution. When no PEO is present in the pillaring solution, the Al₁₃-montmorillonite exhibits a surface area

of 470 m²·g⁻¹ and a liquid microporous volume of 0.14 cm³·g⁻¹. For EO units/Al₁₃ < 200, the surface area decreases with increasing amounts of PEO(100,000) in the pillaring solution. However, the microporosity is still high as the microporous volumes lie between 0.09 and 0.13 cm³·g⁻¹. On the contrary, when no Al₁₃ is present in the pillaring solution, the surface area of the resulting material is very low (< 10 m²·g⁻¹). The organic species occupy the interlayer space and prevent the access of nitrogen molecules. The high microporous volumes obtained when Al₁₃ units are present in the pillaring solution confirm the X-ray data and show the presence of aluminum polycations in the interlayer space. As the decrease in surface area is due to a decrease in the amount of micropores (Figure 3a), it can be assigned to the presence of PEO units in the interlayer region. When the ratio EO units/Al₁₃ reaches 200 EOu/Al₁₃, the surface area decreases dramatically and the measurements for this sample and the following (500 EOu/Al₁₃) were very long. The adsorption equilibrium of nitrogen is normally reached 30 minutes after the introduction of nitrogen. In the cases of the samples 200 EOu/Al₁₃ and 500 EOu/Al₁₃

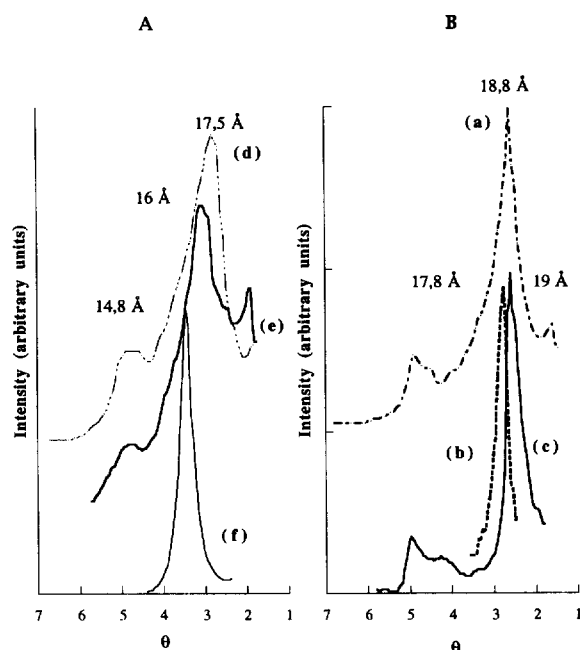


Figure 1. X-ray diffraction spectra; A: (a) SW + Al₁₃, (b) SW + Al₁₃ + PEO(100,000) 10 EOu/Al₁₃; B: after calcination at 500°C: (d) SW + Al₁₃ calcinated, (e) SW + Al₁₃ + PEO(100,000) 1 EOu/Al₁₃ calcinated, (f) SW + Al₁₃ + PEO(100,000) 500 EOu/Al₁₃ calcinated.

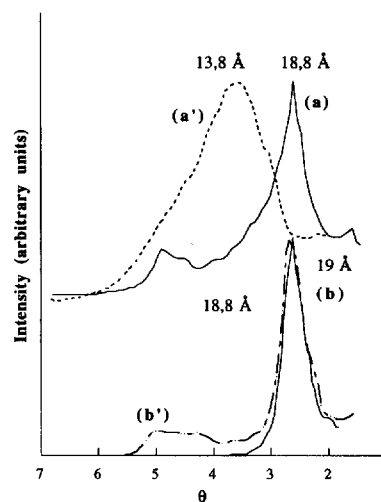


Figure 2. X-ray diffraction spectra; time stability: (a) SW + Al₁₃, (a') SW + Al₁₃ aged six months, (b) SW + Al₁₃ + PEO(100,000) 500 EOu/Al₁₃, (b') SW + Al₁₃ + PEO(100,000) 500 EOu/Al₁₃ aged six months.

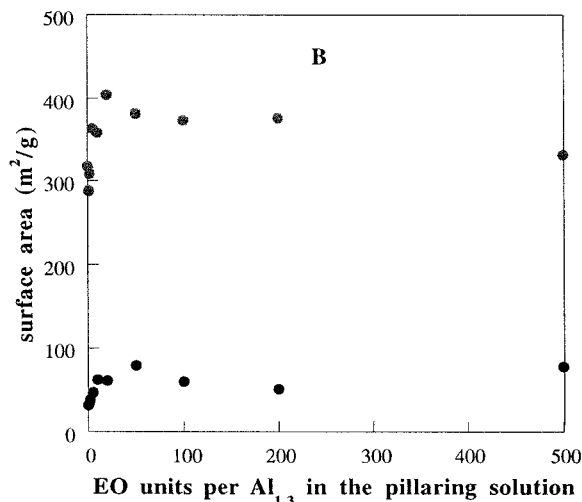
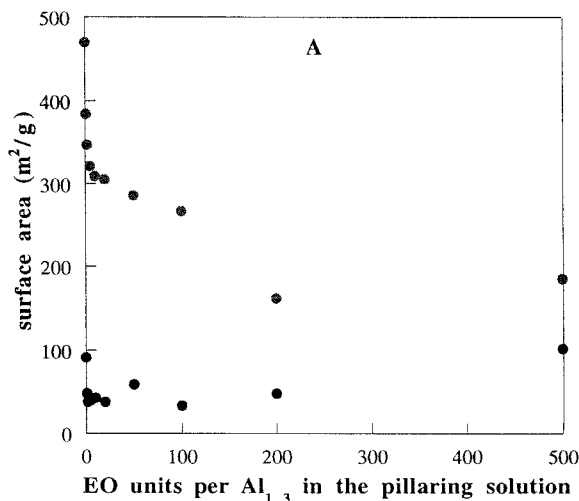


Figure 3. Effect of Polyethylene oxide on the BET surface area (●) and the non microporous surface area (■) A: SW + Al₁₃ + PEO(100,000) before calcination; B: after calcination at 500°C.

(PEO(100,000) and PEO (600)), it was necessary to wait up to five hours to reach the equilibrium.

The evolution of the surface area of calcined samples presents very clearly the effect of the presence of PEO(100,000) on the microporosity of the samples (Figure 3b). The total BET surface area increases with the number of EO units in the pillaring solution (Table 2) for ratio EO units/Al₁₃ ≤ 20. The surface area obtained for this particular ratio is equal to 400 m²·g⁻¹ (Table 2) and remains stable for higher ratios. This is related to an increase in the microporous volume of the samples.

The samples prepared with PEO(600) do not exhibit the same behavior (Table 2). The decrease of the BET

Table 2. BET surface areas measured from nitrogen adsorption isotherms (outgassing conditions 150°C, residual pressure 10⁻³ torrs).

SW + Al ₁₃ + PEO (600)			SW + Al ₁₃ + PEO (100,000)		
EO units/ Al ₁₃	BET surface (m ² /g)	BET surface (m ² /g) calcined samples	EO units/Al ₁₃	BET surface (m ² /g)	BET surface (m ² /g) calcined samples
0	469	317	0	469	317
2,6	333	369	1	384	288
6,6	326	276	2	347	308
13	324	289	5	321	363
40	329	290	10	309	358
200	230	350	20	305	404
500	247	321	50	286	381
			100	267	373
			200	162	376
			500	185	331

surface area is smaller and there is a weak effect on the surface area of the calcined sample.

Thermal analysis

Figure 4 presents the TGA curves obtained with the different samples. For clarity reasons, only the most representative samples are presented. The curve (a) corresponding to the Na-montmorillonite SW exhibits a first decrease due to the loss of the hydration water and a second one towards 600°C due to the loss of the hydroxyl groups. The intercalation of Al₁₃ and of the species Al₁₃ + PEO increases the weight loss compared to a pristine clay sample. It can also be observed that the second plateau disappears with the presence of the intercalates. By derivation of the TGA data, it is possible to distinguish different temperature ranges cor-

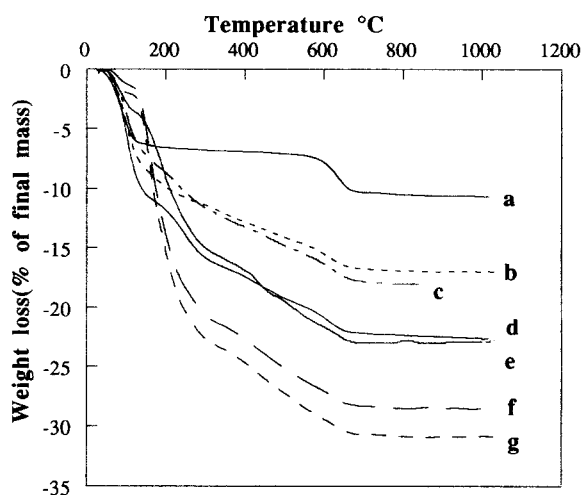


Figure 4. TGA curves: a: SW; b: SW + Al₁₃; c: SW + Al₁₃ + PEO(100,000) 1 EOu/Al₁₃; d: SW + Al₁₃ + PEO(100,000) 2 EOu/Al₁₃; e: SW + Al₁₃ + PEO(100,000) 5 EOu/Al₁₃; f: SW + Al₁₃ + PEO(100,000) 50 EOu/Al₁₃; g: SW + Al₁₃ + PEO(100,000) 100 EOu/Al₁₃.

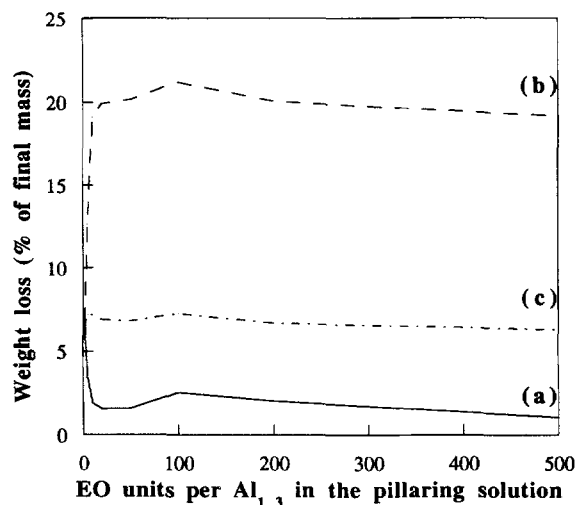


Figure 5. % Weight loss/final mass of the different samples in three distinct temperature ranges; (a): first range 30 to 110°C elimination of remaining water; (b): second range from 110 to 340°C loss of the PEO; (c): third range from 340 to 700°C dehydroxylation.

responding to different reaction steps. A first range from 30° to 110°C is assigned to the elimination of physisorbed water. A second range from 110° to 340°C is assigned to the loss of organic species by combustion. The last range from 340° to 700°C is assigned mainly to the dehydroxylation of the polycations. Figure 5 presents the weight loss corresponding to these three temperature ranges. As the amount of intercalated PEO(100,000) increases, the weight loss corresponding to the elimination of remaining water decreases suggesting that PEO replaces a part of the physisorbed water. The weight loss assigned to the combustion of PEO increases linearly up to the sample 20 EOu/ Al_{13} . For the last samples, the curve reaches a plateau. The weight loss due to the dehydroxylation has the same shape, it suggests a more complete dehydroxylation of the pillars as soon as the ratio of the solution ≥ 20 EOu/ Al_{13} .

The DTA curves on Figure 6 show the effect of intercalation on the configuration of PEO(100,000). The curve (Figure 6c) concerning the pure PEO(100,000) exhibits an exothermic peak centered at 190°C. The sample called SW + PEO (Figure 6d) which is prepared with PEO(100,000) exhibits two peaks at 180°C and 284°C, respectively. The pattern of this DTA curve is similar to that obtained by Aranda and Ruiz-Hitzky (Aranda and Ruiz-Hitzky 1992) under a nitrogen flow. They assigned the shift in combustion temperature to crown-ether like associations between the PEO and the interlayer cation of the clay. Therefore, the first peak can be due to PEO molecules physically sorbed on the external surface of the clay particles whereas the second one corresponds to intercalated PEO molecules com-

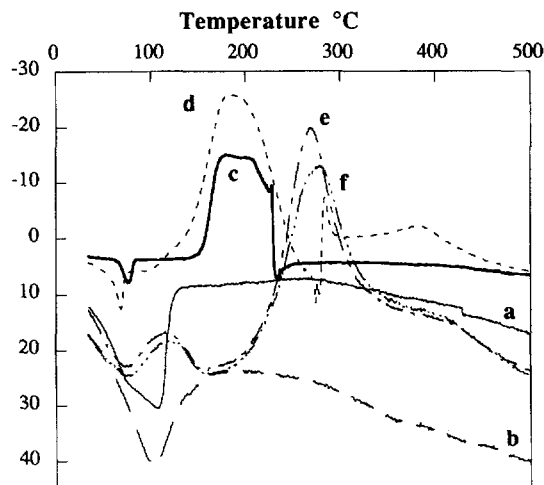


Figure 6. TDA curves: a: SW; b: SW + Al_{13} ; c: PEO(100,000); d: SW + PEO(100,000); e: SW + Al_{13} + PEO(100,000) 100 EOu/ Al_{13} ; f: SW + Al_{13} + PEO(100,000) 200 EOu/ Al_{13} .

plexing sodium cations. When PEO(100,000) is intercalated together with Al_{13} units, the combustion DTA peak is located between 270° and 290°C which proves that PEO is engaged in associations with the aluminum polycations. The peak is broader than in the case of the sample SW + PEO which suggests different interaction modes between the PEO molecules and the Al_{13} units. For PEO/ Al_{13} ratio in the pillaring solution ≤ 20 (Figure 6e and 6f), the temperature of this peak shifts from 270° to 290°C. For higher ratios it remains at the same temperature.

IR spectroscopy

The infrared spectra on Figure 7 illustrate the PEO bands and the marked changes in their wavenumbers and shape. These observations should be interpreted as revealing a different configuration of the organic species intercalated in the silicate layers (Ruiz-Hitzky and Aranda 1990, Aranda and Ruiz-Hitzky 1992).

The stretching vibration bands $\nu_s(\text{CH}_2)$ are present as a very broad and strong band centered at 2869 cm^{-1} and 2887 cm^{-1} for PEO(100,000) and PEO(600), respectively. As soon as a low amount of PEO(100,000) is cointercalated (sample SW + Al_{13} + PEO(100,000), 2 EOu/ Al_{13}) three bands of similar intensity at 2948, 2907 and 2885 cm^{-1} , can be observed. When the amount of EO units increases in the pillaring solution, the spectra of the corresponding samples present a shift of these bands and changes in their relative intensities. The band centered at 2885 cm^{-1} increases in intensity and is shifted to $2872 \pm 1 \text{ cm}^{-1}$ with increasing amount of EO units. The 1500–800 cm^{-1} region exhibits shifts of the wagging (1342 \rightarrow 1350), twisting (1280 \rightarrow 1306) and rocking (1099 \rightarrow 1110) vibration modes of the CH_2 . The slow disappearance of the twisting vibration

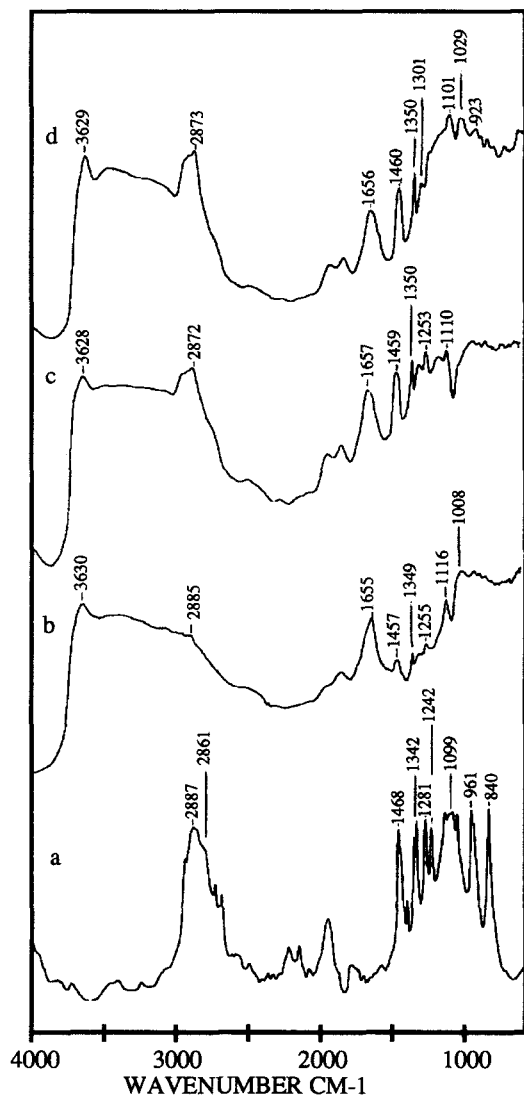


Figure 7. IR spectra: a: pure PEO(100,000); b: SW + Al₁₃ + PEO(100,000) 2 EOu/Al₁₃; c: SW + Al₁₃ + PEO(100,000) 50 EOu/Al₁₃; d: SW + Al₁₃ + PEO(100,000) 500 EOu/Al₁₃.

band at 1250 cm⁻¹ can also be noticed. These changes are similar to those observed on IR spectra of montmorillonite modified with crown-ethers (Casal *et al* 1984). They confirm the formation of associations with polycations that change the hydrodynamic conformation of the expanded random coil to a considerably more anisotropic conformation (Bailey and Koleske 1990). No new bands appear on IR spectra of samples intercalated with PEO(100,000), there is no indication of any breaking of the organic molecule.

The IR spectra of calcined samples reveal the loss of the organic matter after thermal treatment as the peaks corresponding to PEO have disappeared. A shoulder at 3742 cm⁻¹ appears as soon as the amount

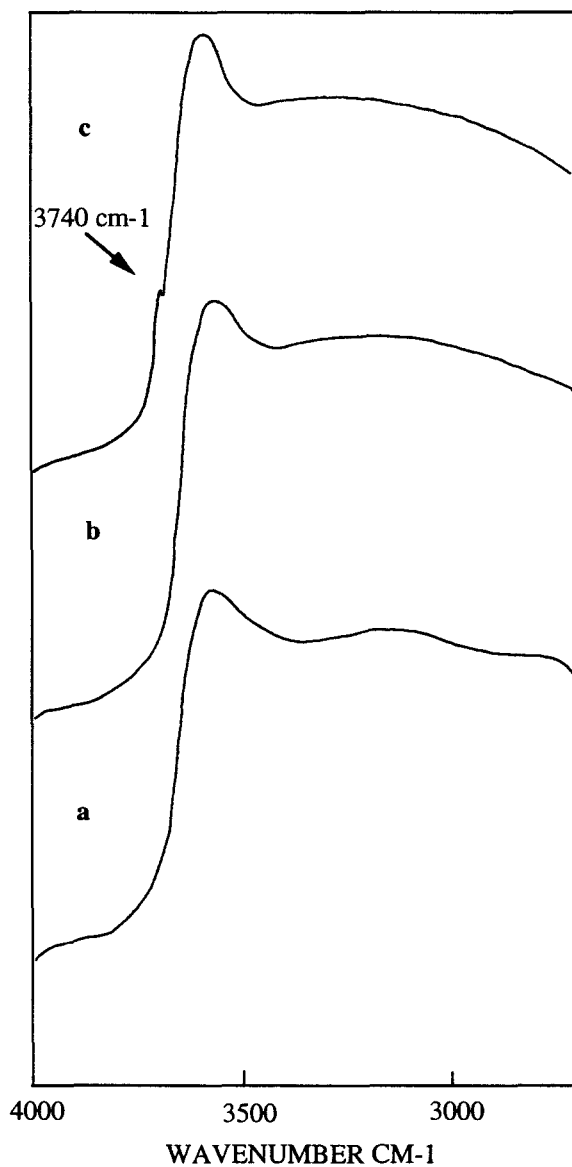


Figure 8. IR spectra in the 4000–2700 cm⁻¹ region. Calcined samples, a: SW + Al₁₃ + PEO(100,000) 2 EOu/Al₁₃; b: SW + Al₁₃ + PEO(100,000) 50 EOu/Al₁₃; c: SW + Al₁₃ + PEO(100,000) 500 EOu/Al₁₃.

of PEO of the pillaring solution reaches 100 EOu/Al₁₃ (Figure 8, spectrum c). This shoulder reveals the presence of free silanol groups (Chevalier *et al* 1994).

Chemical analysis

Chemical analysis results (Table 3) reveal that the intercalation process in the presence of PEO(100,000) is rather complex. A nearly complete ion exchange has occurred for all the samples, synthesized with PEO(600) or with PEO(100,000). Indeed, the remaining sodium content is always very low. The content in aluminum

Table 3. Chemical analyses of the different samples.

Sample	% SiO ₂	% Al ₂ O ₃	% MgO	% Fe ₂ O ₃	% Na ₂ O	% PEO
SW	59.77	19.66	2.28	4.21	2.56	0
SW + Al ₁₃	48.6	25.63	1.91	3.6	0.01	0
PEO (100,000)						
1 EOu/Al ₁₃	47.33	24.02	1.92	3.51	0.06	3.1
2 EOu/Al ₁₃	47.84	24.29	1.92	3.5	0.04	5.7
5 EOu/Al ₁₃	45.56	22.64	1.81	3.3	0.03	13.7
10 EOu/Al ₁₃	42.96	20.68	1.69	3.08	0.03	21.6
20 EOu/Al ₁₃	42.6	20.63	1.66	3.04	0.03	22
50 EOu/Al ₁₃	43.39	20.31	1.66	3.04	0.01	22
100 EOu/Al ₁₃	43.82	19.78	1.57	2.94	0.03	22
200 EOu/Al ₁₃	45.88	18.29	1.46	2.74	0.03	22
500 EOu/Al ₁₃	50.19	16.07	1.27	2.38	0.01	22
PEO (600)						
1.3 EOu/Al ₁₃	49.1	23.88	1.93	3.54	0.03	6.8
2.6 EOu/Al ₁₃	49.16	24.03	1.94	3.56	0.04	12.1
4 EOu/Al ₁₃	47.41	23.93	1.92	3.51	0.03	13.2
6.5 EOu/Al ₁₃	47.65	23.67	1.97	3.55	0.03	14.5
13 EOu/Al ₁₃	47.98	22.53	1.84	3.34	0.05	17.8
26 EOu/Al ₁₃	48.11	22.41	1.85	3.36	0.05	17.8
40 EOu/Al ₁₃	47.62	22.07	1.81	3.26	0.07	19.8
65 EOu/Al ₁₃	46.28	22.25	1.82	3.31	0.03	21.5
130 EOu/Al ₁₃	49.2	20.99	1.71	3.23	0.1	20.9
200 EOu/Al ₁₃	43.97	23.77	1.83	3.43	0.01	20.9
500 EOu/Al ₁₃	42.84	23.04	1.78	3.3	0.01	20.9

increases showing the presence of aluminum moieties in the intercalated clay. However, for the samples SW + Al₁₃ + PEO(100,000), the MgO, Fe₂O₃, Al₂O₃ contents start decreasing as soon as the ratio EO units/Al₁₃ is equal to 2. Comparing the MgO and Fe₂O₃ contents with those of the sample SW + Al₁₃, the loss percents per unit cell of the two cations can be determined. The corresponding results are presented in Figure 9. It clearly appears that these two octahedral cations are released together in solution when PEO(100,000) and Al₁₃ are both present in the pillaring solution. The loss reaches 40% for the highest EO content. The pH of the solution (4.4) and the high complexing character of the organic species are the essential factors of this reaction.

To underscore the complexing capacity of the PEO, synthesis were carried out in the absence of Al₁₃ in the pillaring solution. Table 4 presents the chemical analyses of SW + PEO which is synthesized without any polycations and with an excess of PEO in the pillaring solution, and, of SW + PEO pH 4, which is prepared with a similar solution which pH was adjusted to 4. Indeed, for these two samples Al, Mg and Fe were released in solution. The results of these experiments were compared to three other samples, SW + Al₁₃ + PEO, SW + Al₁₃ and SW pH 4. The latter was prepared with a suspension of montmorillonite at pH 4. The loss in octahedral cations reaches 30% for the samples SW + PEO, SW + PEO pH 4, and SW + Al₁₃ + PEO.

DISCUSSION

Determination of the number of Al₁₃ units intercalated

Chemical analysis and X-ray results lead to the assumption that the whole octahedral layer is not affected by this partial dissolution and that the reaction occurs at the periphery of the elementary clay platelets. The system is then formed of two different zones: a peripheral zone where only silica is present and a central zone where the initial structure of the clay is conserved. In this central zone, cointercalated Al₁₃ and PEO(100,000) molecules are present. The presence of silicium rich zones is confirmed by the IR data which show the presence of silanol groups. Such silanol groups are observed in the case of acid leached clays (Chevalier *et al* 1994). The perennity of the central zone is supported by the X-ray, surface area and IR data. Indeed, the d-spacing does not change for high amounts of EO units in the pillaring solution; the surface area remains high and the DTA and IR data reveals EO units engaged in associations with cations.

According to the proposed hypothesis and to the results presented in Table 4, the loss in octahedral Al can be deduced from the Mg and Fe data presented in Figure 9. It is then possible to determine the number

Table 4. Chemical analyses results of samples SW, SW pH4, SW + Al₁₃, SW + PEO, SW + PEO pH4, SW + Al₁₃ + PEO.

	Si	Al	Mg	Fe	Na
SW weight %	59.77	19.66	2.28	4.21	2.6
% loss of cations		0	0	0	0
SW pH4 weight %	52.71	18.31	2.31	4.04	2.56
% loss of cations		0	0	0	
SW + A weight %	51.29	25.7	2.17	3.84	0.03
% loss of cations		0	0	0	
SW + PEO weight %	67.83	15.9	1.89	3.12	2.08
% loss of cations		23	25	27	
SW + PEO pH4 weight %	68.36	16.01	1.87	3.41	2.07
Number of atoms by unit cell		12	22	16	
SW + A + PEO weight %	58.74	20.95	1.57	2.96	0.03
Number of atoms by unit cell			33	33	

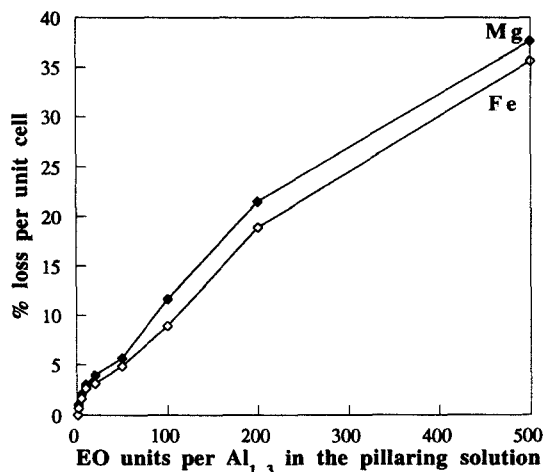


Figure 9. Loss in octahedral cations as a function of the ratio PEO(100,000)/Al₁₃ in solution.

of Al₁₃ polycations actually intercalated. The result of this calculation is plotted in Figure 10 as a function of the PEO/Al₁₃ ratio in the pillaring solution. The number of intercalated Al₁₃ per unit cell is almost constant around 0.13 when pillaring has been carried out in the presence of PEO. It is slightly lower than that obtained in the absence of PEO. This could reveal a slightly higher charge per Al₁₃ suggesting that PEO surrounding the polycation protects it from hydrolysis. The average charge per intercalated Al₁₃ is then around 5⁺. Its general formula can then be written as [Al₁₃O₄(OH)₂₆-(H₂O)₁₀]⁵⁺. Assuming that the interaction between PEOs and Al₁₃ occurs through hydrogen bonding between the OH groups of the polycations and the oxygen atom of the EO unit, the association ratio should be equal to 26.

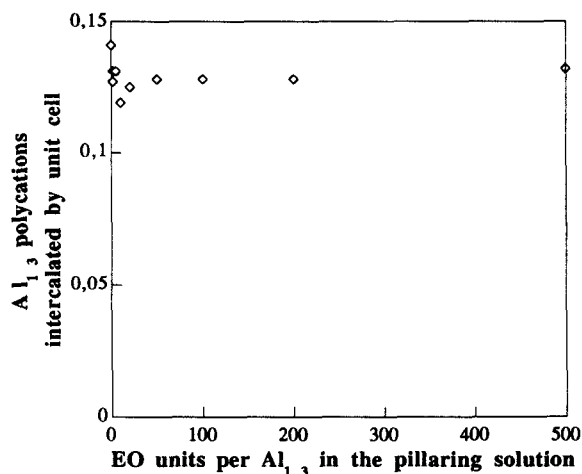


Figure 10. Moles of polycations intercalated by unit cell as a function of the ratio PEO(100,000)/Al₁₃ in solution.

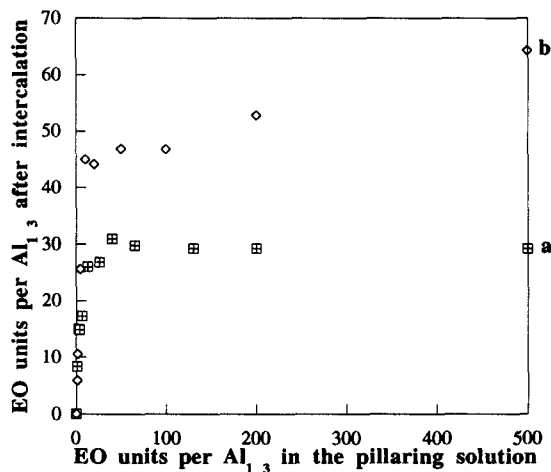


Figure 11. Complexation rate PEO/Al₁₃ as a function of the ratio PEO(100,000)/Al₁₃ in solution, (a): PEO(600); (b): PEO(100,000).

Nature of the intercalated species

The ratios EOu/Al₁₃ in the clay, calculated taking into account the partial dissolution of the octahedral layer, are plotted in Figure 11 as a function of the PEO/Al₁₃ ratio in the pillaring solution. For both PEOs two different domains can be distinguished on this plot. In the first domain, for EOu/Al₁₃ in the pillaring solution ≤ 20, the ratio in the clay increases strongly up to 40 for PEO(100,000) and up to 30 for PEO(600). In this region, the ratio PEO/Al₁₃ in the clay is much higher than that introduced in solution. This reveals a preferred intercalation of PEO-associated Al₁₃ with regard to isolated Al₁₃. Indeed, in this domain, more than 80% of the PEO present in solution is intercalated in the clay layer. In the second domain, for EOu/Al₁₃ in the pillaring solution > 20, the ratio in the clay increases slowly to reach 65 for PEO(100,000) and remains constant for PEO(600).

The ratio of 30 obtained in the case of PEO(600) is very close to the expected value of 26. Furthermore, as the average EO units per molecule of PEO(600) is around 13, every Al₁₃ unit is associated with two PEO molecules showing the presence in the interlayer of isolated organometallic species. The behavior of PEO(100,000) which is formed of an average of 2270 EO units is more complex. The higher association ratio (40 to 65) compared to the PEO(600) suggests that one PEO(100,000) molecule is associated with several Al₁₃ units and links these polycations. This is confirmed by infrared spectra that do not indicate any breaking of the molecule. The ratio of 40 obtained at the beginning of the plateau in Figure 11 would then correspond to a structure in which Al₁₃ would be associated with around 30 EO units and linked together by an average of 10 EO units. This could impose a more regular repartition of the pillars in the interlayer region. The

distance between PEO- Al_{13} units could be controlled by electrostatic repulsions. However, a simulation of the random disposition of excess Al_{13} in a polymer chain with a minimal distance between the cations of 30 EO units, yields an average ratio of 40 EO units per Al_{13} . Then the actual influence of electrostatic repulsions is difficult to assess.

At the beginning of the plateau in Figure 11 most of the PEO in solution (>80%) is present in the intercalated material. For higher PEO contents in the solution, the fraction of intercalated PEO decreases sharply. In the case of PEO(600), the ratio $\text{EOu}/\text{Al}_{13}$ remains constant in the solid but it still increases in the case of PEO(100,000). In this latter case, this range of PEO concentration in solution also corresponds to a strong increase in the dissolution of the octahedral layer. The maximal value of 65 $\text{EOu}/\text{Al}_{13}$ in the solid is much lower than the value in the pillaring solution (500). The reason for this partition between the solid and the solution is not clearly understood at the moment.

The chain length of the polymer used in the pillaring solution has a strong influence on the nature of the intercalated species. For a low molecular weight polymer such as PEO(600), initial sodium ions are exchanged by isolated organometallic complexes. For high molecular weight polymers such as PEO(100,000), the interlayer region of the intercalated material is filled with a network of complexed units linked together by EO units. The different evolution of the surface areas of intercalated and pillared materials can then be explained. The presence of PEO(600) in the pillaring solution has very little influence on the BET surface area of the calcined samples which are comparable to those obtained for calcined samples prepared in the absence of PEO. On the other hand, the presence of PEO(100,000) in the pillaring solution increases the BET surface area of the calcined samples which becomes 30% higher than for classical pillared Wyoming montmorillonites. This is likely to result from a more regular pillar distribution due to EO units linking the polycations together.

CONCLUSIONS

The Al-pillaring of smectite in the presence of PEO appears as a promising synthesis procedure as it confers an increased stability and a higher microporosity to the resulting pillared clay. High molecular weight PEOs appear to be more effective in improving the properties of pillared materials than lower molecular weight species. High PEO contents in the pillaring solution provoke a partial dissolution of the clay octahedral layer without important modifications of the interlayer structure.

As far as the synthesis method is concerned, the PEO content in the pillaring solution can be controlled in order to obtain products with improved properties

without an important dissolution rate. Such materials will be tested for the adsorption of heavy metals such as copper, mercury, cadmium and nickel. Indeed, the strong affinity of PEOs for metal ions (Sakai *et al* 1986, 1993; Takahashi *et al* 1973) could be utilized to design clay-based recyclable adsorbents.

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