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ORGANOPHILIC BENTONITES BASED ON ARGENTINEAN AND BRAZILIAN BENTONITES. PART 1: INFLUENCE OF INTRINSIC PROPERTIES OF SODIUM BENTONITES ON THE FINAL PROPERTIES OF ORGANOPHILIC BENTONITES PREPARED BY SOLID-LIQUID AND SEMISOLID REACTIONS

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Abstract - This study describes the influence of the intrinsic properties of raw materials on the organophilization of bentonites from Argentinean raw sodium bentonites and Brazilian sodium activated bentonites. The organophilization was done with two methodologies: solid-liquid and semisolid reactions. Correlations between the properties of sodium and organophilic bentonites were established. The effectiveness of the treatments was verified by X-ray diffraction, swelling capacity in water and xylene and SEM to evaluate the morphology of the particles. The analysis was done before and after the modification process. The bentonites had organic cations intercalated, as shown by the increase of the basal spacings, and the organophilic character was confirmed because the bentonites showed xylene swelling capacity and particles with an expanded aspect in comparison to those of the sodium bentonites. Both methodologies were efficient to obtain organophilic clays. The organophilic bentonites obtained from raw sodium bentonites gave better results.

Keywords: Bentonite; Montmorillonite; Distearyl dimethylammonium chloride; Organoclays.

INTRODUCTION

Organoclays are hybrids that contain organic molecules intercalated between the layers of the clay mineral or adsorbed on its surfaces. These kinds of materials have been used in many applications, as adsorbents, rheological control agents, paints, grease, cosmetics, personal care products, oil well drilling fluids, etc. (Santos, 1989; Beall and Goss, 2004; Ramos Vianna *et al*., 2004; Xi *et al*., 2005; Araújo *et al*., 2005, Paiva *et al*., 2008). Nowadays, an important application of the organoclays is in the polymer nanocomposites area. Organoclays are essential materials for the development of polymer nanocomposites and are the most dominant commercial nanomaterial for this application, accounting for nearly 70% of the volume used among other materials (Markarian, 2005). The intercalation of alkylammonium cations in clay minerals such as smectites or even in bentonites is a

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common way to obtain organoclays. This process is driven by cation exchange of the cations located in the galleries of the clay mineral. Usually Na^+cations are substituted by organocations of the quaternary alkylammonium salt. This occurs because Na^+ is monovalent and the exchange is easier than with divalent or trivalent cations. According to Beall and Goss (2004), cation exchange has been used for five decades. The most common way to prepare organoclays based on bentonites and quaternary alkyl ammonium salts is through solid-liquid reactions, i.e., in aqueous dispersion. Basically, the procedure consists of dispersing the clay in water, followed by the addition of the organic salt. The dispersion is stirred, washed, filtered, dried, ground and sieved. Examples include the studies of Vaia *et al*. (1994), Moraru (2001), Park *et al*. (2002), Gorrasi *et al*. (2003), Zhu *et al*. (2005), etc. Although cation exchange in solid-liquid medium is commonly used, this methodology requires large quantities of water and generates aqueous residues, which is not friendly from the environmental aspect.

An alternative methodology is solid-solid reaction. In this case, the clay and the organic compound are mixed in the solid state without the use of a solvent. The intercalation of organic compounds by solid-solid reactions has the advantage of enabling the preparation of hybrids that are not easy to achieve in solution (Ogawa *et al*. 1989, 1990). The first solid-solid reaction of clay minerals and ammonium cations was reported by Ogawa *et al*. (1990). The results showed that the solid-solid reactions were efficient for exchanging the cations of the montmorillonite by the alkylammonium cations. According to Ogawa *et al*. (1992), acrylamide, n-alkylamine, and 2,2'-bipyridine are other organic compounds that were successfully intercalated through solid-solid reactions. Recently, Riaz and Ashraf (2011) reported the intercalation of polycarbazole in montmorillonite via reaction in the solid state using a mechano-chemical procedure.

Although it has advantages, there are few studies on the preparation of organoclays by solid-solid reactions. Further studies on the intercalation of compounds in clays are very important not only from the theoretical, but also from the practical point of view. Other examples of organic compound intercalation in clay minerals by solid-solid reactions have been discussed in a previous work, Paiva *et al*. (2008).

Besides the alternative methodologies of organoclay preparation, from the economical and practical standpoint, it is important to investigate the influence of sodium clay properties on the efficiency of the organophilization, but this aspect is little explored. The study of Chavarria *et al*. (2007) is the only that we can cite.

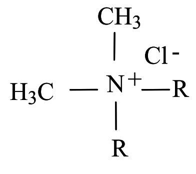
This paper aimed first at the study of the influence of the intrinsic properties of sodium bentonites on the final properties of the organophilic bentonites, and secondly, a comparison of two methodologies for the preparation of six organophilic bentonites from Argentina (raw sodium bentonites) and Brazil (activated sodium bentonites). The first methodology is the conventionally employed cation exchange in aqueous dispersion. The second one is an alternative proposal called semisolid reaction that consists of an adaptation of the solid-solid reactions.

EXPERIMENTAL

Materials

Six commercial sodium bentonites from different suppliers were submitted to the organophilization process. The Argentinean sodium bentonites are natural, while the Brazilian ones are polycationic and were treated by the suppliers with Na_2CO_3 to transform them to the sodium form. The bentonites were used as received without any additional treatment, except for the sieving in 200 mesh. The bentonite properties and descriptions are presented in Table 1. The cation exchange capacity (CEC) was measured by the methylene blue method (the analyses were done in CCDM at USFCar according to method IT CPC – 136 revision: 05 of the respective laboratory); the semiquantitative analyses of sodium and calcium were performed by EDX analysis with a LEO equipment model LEOi. The analyses were carried out on 200 mesh previously sieved powder samples covered with a gold-palladium alloy.

The quaternary ammonium salt was distearyl dimethylammonium chloride, named Praepagen WB, from Clariant, whose structural formula is shown in Scheme 1. The R in the formula represents the alkyl radical which consists predominantly of chains of 18 carbons. Praepagen WB is a pasty solid, slightly yellow and with alcoholic odor. According to the supplier, the pasty consistency is due to a composition of 75.2% of active substance (quaternary ammonium salt), 5.4% water, 1.8 % free amine and 17.6% ethanol.



$$H_3C - \overset{\displaystyle CH_3}{\underset{\displaystyle R}{N^+}} - R \quad Cl^-$$

Scheme 1

Table 1: Characteristics of the bentonites.

Bentonite	Characteristic	Supplier	CEC meq/100 g bentonite	Na (%)	Ca (%)
Vulgel Argentinean	Sodium natural	Flow Chemical	81	4.37	0.82
TEC-09 Brazilian	Policationic – sodium activated	TECPOL/Ioto International	63	4.18	0.70
Reminas Brazilian	Policationic – sodium activated	J. Reminas Mineração Ltda.	43	4.74	1.28
Soleminas Dye-10 Brazilian	Policationic – sodium activated	Bentonisa	53	3.89	1.78
Bentogel Patag Argentinean	Sodium natural	Bentonisa	86	4.30	0.13
Brasgel PBS50 Brazilian	Policationic – sodium activated	Bentonit	65	4.21	- *

* Element not detected

Methods of Organophilic Bentonite Preparation

Intercalation of Organic Cations in Aqueous Dispersion (Solid-Liquid Medium)

Each sieved and dried bentonite sample was added to distilled water at 60 ºC to obtain an aqueous dispersion with 2% of bentonite. The dispersion was stirred for 30 minutes at 1600 rpm to destroy agglomerates. The distearyl dimethylammonium chloride was added at a ratio of 120 meq/100 g of bentonite, which corresponds to the concentration of 40.8% in mass. The organic salt was used in excess relative to the CEC of the clays to guarantee the cation exchange. The ratio of 120 meq/100 g of bentonite was adopted based on the study of Xi *et al*. (2004). They showed that the basal spacing of a modified montmorillonite with octadecyl trymethylammonium cations reached constancy for the addition of organic salt at a ratio of 1.5 times of the CEC of the clay. Considering the bentonites studied, the Bentogel Patag and Vulgel materials presented the largest CEC, 86 and 81 meq/100 g of bentonite, respectively. Therefore, 1.5 times of the CEC of these clays would be 129 and 121 meq/100 g of clay. The quantity of 120 meq/100 g was considered to be appropriate and the same for all bentonites in order to keep the concentration of the organic salt constant. After the addition of the distearyl dimethylammonium chloride, the stirring at 1600 rpm was continued for one hour and the temperature was maintained at 60 ºC in order to maintain the salt in a soluble state. The bentonite was filtered, washed with distilled water (ratio of 2 L of water/10 g of clay), dried at 60 ºC for 24 hours, ground and sieved again in a 200 mesh sieve to guarantee a particle size below 74 μm. The bentonites modified by this methodology were named with the respective name of the clay followed by O1 (referring to organophilic 1).

Intercalation of Organic Cations in Semisolid Medium

Each sieved and dried bentonite sample and distearyl dimethylammonium chloride were mixed in a mortar and pestle for three minutes to obtain a homogeneous mixture. The same ratio of the organic salt, 120 meq/100 g of bentonite was used. After this step, distilled water at 60 ºC in a mass equivalent to that of the bentonite was added and the sample was mixed again for five minutes in order to obtain a homogeneous mixture. The mixture was dried at 60 ºC for 24 hours, ground and passed through a 200 mesh sieve to guarantee the particle size control, as explained in the previous methodology. This method was named a semisolid reaction because distearyl dimethylammonium chloride, Praepagen WB, is pasty (containing water and alcohol) and some water was used to facilitate the mixture process. However, the preparation was not in solution, and the steps of filtering and washing were not employed. The bentonites modified by this methodology were named with the respective name of the clay followed by O2 (referring to organophilic 2).

Techniques of Characterization

The intercalation of the distearyl dimethylammonium chloride in the clay mineral layers was evaluated through the basal spacing obtained by X-ray diffraction. The analyses were carried out with a Shimadzu equipment, model XRD700, with a Cu λ =1.5406Å filament, a current of 30 mA and a voltage 40Kv, between $2\theta = 1.4^o$ to 10.0^o.

The organophilic character was evaluated by the swelling capacity of the bentonites in water and xylene. The test was performed in two steps. The first step was based on Foster's method, which is to slowly add 1 g of dried and sieved clay to 100 mL of a liquid and leave the system at rest for 24 hours. The swelling is measured in mL/g after the 24 h of rest (Santos, 1989). The second step was based on the procedure adopted by Díaz (1994). After resting for 24 h and after the first measurement was done, the samples were stirred with a glass rod for five minutes and left still for 24 hours more. Then, a new measurement was done.

The particle morphology was analyzed through scanning electronic microscopy, with a LEO equipment, model LEOi. The analyses were carried out with previously sieved 200 mesh powder samples covered with a gold-palladium alloy under a magnification of 12,000 times.

RESULTS AND DISCUSSION

Intercalation of Distearyl Dimethylammonium Cations

The XRD diagrams for the bentonite Vulgel sodium and the organophilic O1 and O2 are presented in Figure 1 as examples. Table 2 shows the values of basal spacing associated with the (001) reflection for all samples of bentonite. All bentonites showed similar XRD patterns, but with different basal spacings.

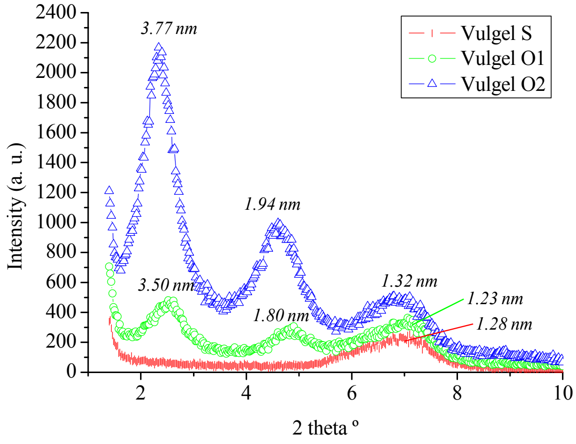


Figure 1: XRD patterns of sodium and modified Vulgel S, O1 and O2 bentonites.

The sodium bentonites showed (001) basal reflections in the regions of 6-7° (2θ) corresponding to basal spacing between 1.24 nm and 1.33 nm. These basal spacings are characteristic of the montmorillonite in hydrated form present in bentonites (Santos, 1989; Bergaya *et al.*, 2006). In anhydrous form, the basal spacing is about 1.0 nm (Santos, 1989). The intercalation of organic cations in clay mineral layers causes an increase in the basal spacing and is characterized by the dislocation of the diffraction reflections to lower angles on the XRD diagrams. The increase in the basal spacing varied from 2.22 nm to 2.54 nm, showing that the intercalation of the distearyl dimethylammonium cations between clay mineral layers occurred. The organophilic bentonites obtained by semisolid and solid – liquid methodologies showed similar XRD diagrams.

After the organophilization process by the two methods, all bentonites showed three diffraction reflections in the regions of 2° (2θ), 4° (2θ) and another between 6° - 7° (2θ) (data not shown). Previous studies (Barbosa *et al.*, 2006; Ferreira *et al.*, 2006) showed that bentonites modified with alkyl benzyl dimethylammonium, cetyl trimethylammonium and distearyl dimethylammonium chlorides presented three basal reflections only for bentonites modified with distearyl dimethylammonium chloride, the same quaternary ammonium salt used in the present study. This behavior can be attributed to the fact that this salt has two long alkyl chains with 18 carbons atoms in each one, while the other two organic salts have only one long alkyl chain.

The presence of more than one reflection in the region of the (001) basal reflection of organophilic bentonites is not well understood. The first hypothesis is that the distearyl dimethylammonium cation can acquire a highly ordered structure and the three diffraction reflections could be (001), (002) and (003) basal reflections, respectively. This possibility of the three basal reflections was also considered by Mandalia and Bergaya (2006). At small diffraction angles (θ is 20° or less), the various members of the *00l* series are equidistant, and identify different basal reflections that belong to the same clay mineral. Therefore, it can be proposed that, for the reflections of the planes (001), (002) and (003), the basal spacing can be calculated according to Equation (1) (Moore and Reynolds, 1997).

$$d = 1 \times d(001) = 2 \times d(002) = 3 \times d(003) \qquad (1)$$

Theoretically, the (002) and (003) basal reflections should be a half and one-third of the values of the (001) basal reflection, but the measured values are not exact. Our results fit this hypothesis very closely, in which the multiple reflections are approximately a half and one-third of the (001) basal reflection.

The second hypothesis is that the presence of the three basal reflections might be due to different levels of intercalation of the organic cation between the clay mineral layers. The two reflections at lower angles, in the regions of 2º and 5º (2θ), would then be due to different orientations of the organic cations, while the third reflection in the region 6º-7º (2θ), the region in which the (001) basal reflection of sodium bentonite occurs, would be due to a non-intercalated phase (Barbosa *et al.*, 2006; Zhou *et al.*, 2007). The reflections in the region of 2º (2θ), whose basal spacing varied from 3.8 nm to 3.47 nm, might be fractions with a paraffinic structure of the organic cations, characterized by a basal spacing above 2.2 nm. The basal reflections in the region of 4º (2θ), whose basal spacing varied from 1.95 to 1.79 nm, could be fractions with a bilayer structure, characterized by a basal spacing in the range of 1.75 nm. The lower basal spacings would then be fractions without intercalation or with only superficial coverage without expansion of the layers (Lagaly and Weiss, 1969).

Theoretical calculations that can be used to predict and also to confirm the results about intercalation of organic cations in clay minerals are based on the length of the main carbon chain of the compound and the basal spacing of the unmodified clay mineral. Equation (2) can be used to calculate the theoretical basal spacing of an organoclay (Ke and Stroeve, 2005).

$$d(001) = k(n-1) + d_c + d_m \qquad (2)$$

where:

n = number of carbon atoms in the surfactant chain
d_c = basal spacing of the unmodified clay mineral
d_m = the van der Waals radius of the terminal methyl group (0.4 nm)
k = constant = 0.126 (calculated from the increase, in length, for each C-C bond in the chain)

This equation assumes that the alkyl group of the organic cations adopts a totally extended molecular conformation or a *trans-trans* chain conformation normal to the clay surface.

Table 2 shows the theoretical and experimental basal spacing obtained for the organophilic bentonites modified by the two methods. Except for the organophilic bentonite Reminas O2, which showed the same basal spacing in both theoretical and experimental results, the other organophilic bentonites showed an experimental basal spacing slightly lower than the theoretical values. These results suggest that the chains of distearyl dimethylammonium chloride stayed inclined or even curved between the clay mineral layers, instead of being perpendicular to the surface as assumed by the theoretical model.

Table 2: Experimental and theoretical values of the basal spacing of sodium and modified bentonites.

Bentonite	*d(*001) nm experimental	*d(*001) nm theoretical
Vulgel S	1.28	-
Vulgel O1	3.50	3.82
Vulgel O2	3.71	3.82
TEC-09 S	1.31	-
TEC-09 O1	3.55	3.85
TEC-09 O2	3.80	3.85
Reminas S	1.33	-
Reminas O1	3.84	3.87
Reminas O2	3.87	3.87
Soleminas Dye-10 S	1.30	-
Soleminas Dye-10 O1	3.65	3.84
Soleminas Dye-10 O2	3.77	3.84
Bentogel Patag S	1.24	-
Bentogel Patag O1	3.53	3.78
Bentogel Patag O2	3.47	3.78
Brasgel PBS50 S	1.28	-
Brasgel PBS50 O1	3.74	3.82
Brasgel PBS50 O2	3.62	3.82

Considering the results, we suggest that the structures formed are of the paraffinic type. The results are similar for both methods of preparation of the organophilic bentonites, which shows that both techniques are efficient.

Evaluation of the Swelling Capacity in Water and Xylene

The swelling capacity in water and xylene was done by comparison of the volume of the dry bentonite, the swelling after the first step and the swelling after the second step. The scale proposed by Díaz (1994) was adopted to classify the swelling according to the values and symbols: no swelling equal or less than 4 mL/g (I0), low swelling of 5 to 8 mL/g (I↓), medium swelling of 9 to 15 mL/g (IM) and high swelling above 15 mL/g (I↑). Furthermore, to verify how many times the clay swelled in the solvent in comparison to the dry volumes of the clay, the swelling factor (SF) proposed by Burgentzlé *et al*. (2004) was used, as defined by the following Equation (3):

$$SF = \frac{V_S - V_D}{V_D} \tag{3}$$

where:

V_s = volume of the swollen clay
V_D = volume of the dry clay

The results of the swelling capacity in water of the sodium and modified bentonites are shown in Table 3. All sodium bentonites swelled in water. In the first step of the test, the highest swelling was observed for TEC-09 with 21 mL/g and SF=12, while the lowest value was for Reminas with 9 mL/g and SF=4. The swelling of clays in water occurs because of the capacity of the external and internal surfaces of the clay mineral layers to be hydrated. Sodium as exchangeable cation promotes layers of "oriented water". As the clay is immersed in water, it adsorbs several water layers between the clay mineral galleries, due to the hydrogen bonds and, consequently, the swelling occurs. The swelling occurs exclusively in the (001) planes, causing delamination of the layers, but the crystallographic integrity is kept during the expansion process (Santos, 1989; Moore and Reynolds, 1997; Wersin *et al*., 2004). The different levels of swelling can be related to the quantity of water molecules adsorbed between the clay minerals layers. A low swelling can be attributed to the fact that water molecules do not reach the more internal surfaces (Calvet and Prost, 1971).

During the second step of the test, two phases were observed: a sediment phase (which may contain larger particles and impurities) and a dispersed phase (containing smaller particles), whose values are also showed in Table 3. The classification of swelling and SF were not calculated because of the formation of the two phases.

The different observed phases can be related to the model of interaction of the clay particles. The interactions can be face-to-face, face-to-edge and edge-to-edge (Santos, 1989; Luckhan and Rossi, 1999; Burgentzlé *et al*., 2004). Dilute dispersions of sodium montmorillonite can flocculate face-to-edge or edge-to-edge, forming a gel structure. The sediment phase has a gel structure that is similar to a "house of cards" structure, in which the particles are kept together by face-to-edge interaction. The structure is fragile and can be destroyed by stirring and recovered when the system goes back to rest (Santos, 1989; Bergaya *et al*., 2006). This was the behavior of the sediment phase. The dispersed phase is a sol, where the edge-to-edge interaction is the most probable.

Table 3: Swelling capacity in water of sodium and modified bentonites.

Bentonite	**VD mL/g**	**S1 mL/g**	**SF**	**S2 mL/g**	**SF**
Vulgel S	1.5	15 (IM)	9	5 *(SP)* 95 *(DP)*	-
Vulgel O1	2.1	~ 2 (I0)	-	~ 2 (I0)	-
Vulgel O2	1.9	~ 2 (I0)	-	~ 2 (I0)	-
TEC-09 S	1.6	21 (I↑)	12	7 *(SP)* 95 *(DP)*	-
TEC-09 O1	1.8	~ 2 (I0)	-	~ 2 (I0)	-
TEC-09 O2	1.9	~ 2 (I0)	-	~ 2 (I0)	-
Reminas S	1.7	9 (IM)	4	6 *(SP)* 95*(DP)*	-
Reminas O1	1.6	~ 2 (I0)	-	~ 2 (I0)	-
Reminas O2	1.6	~ 4 (I0)	~1.5	~ 4 (I0)	1.5
Soleminas Dye-10 S	1.6	13 (IM)	7	10 *(SP)* 93 *(DP)*	-
Soleminas Dye-10 O1	1.9	~ 2 (I0)	-	~ 2 (I0)	-
Soleminas Dye-10 O2	1,9	~ 5 (I↓)	~1.6	~ 4 (I0)	1
Bentogel Patag S	1.6	18 (I↑)	10	5 *(SP)* 95 *(DP)*	-
Bentogel Patag O1	2.3	~ 2 (I0)	-	~ 2 (I0)	-
Bentogel Patag O2	2.1	~ 2 (I0)	-	~ 3 (I0)	~ 0.5
Brasgel PBS50 S	1.6	15 (IM)	8	5 *(SP)* 95 *(DP)*	-
Brasgel PBS50 O1	1.9	~ 2 (I0)	-	~ 2 (I0)	-
Brasgel PBS50 O2	2.0	~ 5 (I↓)	~1.5	~ 5 (I↓)	~1.5

(SP) = sedimented phase; (DP) = disperse phase
VD = volume of 1g of dry bentonites (measured in a tube of 10 mL with 0.1 mL scale)
S1 = swelling (mL/g) after standing 24 h without stirring
SF = swelling factor
S2 = swelling (mL/g) after stirring + standing 24 h

While sodium bentonites swelled in water, the bentonites modified in aqueous dispersion did not show swelling in water. Concerning the bentonites modified in semisolid medium small swelling in water was observed for the Reminas O2, the Soleminas Dye-10 O2, the Bentogel Patag O2 and the Brasgel PBS50 O2 bentonites. In the first step of the test, the swelling varied from 4 mL/g and SF=1.5 (no swelling) for the Reminas O2 to 5 mL/g and SF=1.6 for the Soleminas Dye-10 (low swelling). In the second step of the test, the swelling varied from 3 mL/g and SF=0.5 for the Bentogel Patag O2 (no swelling) to 5 mL/g and SF=1.5 for the Brasgel PBS50 O2 (low swelling). The small swelling for these bentonites was associated with the fact that some particles stayed dispersed in the water, which suggests that small fractions of the bentonites remained in the sodium form or were only partially covered with distearyl dimethylammonium cations. In spite of this, the observed swellings were much inferior to the ones observed for the sodium bentonites and this behavior indicates that the organophilic fraction is predominant.

The results of swelling capacity of the sodium and modified bentonites in xylene are shown in Table 4. During the test in xylene, no sodium bentonite showed swelling in either of the two steps of the test.

The volumes were approximately 2 mL/g, the same as the dry bentonites. As expected, the absence of swelling is due the organophobic character of the bentonites that does not permit interaction with the organic solvent. On the other hand, all bentonites modified by the two methodologies showed swelling in xylene. For the organophilic bentonites in contact with the organic solvent, the swelling occurred due to the diffusion of the molecules of the solvent between the clay mineral layers. This process is favored by the balance between the nature of xylene, a compound of low polarity, and the alkyl chains of the organic salt that decrease the polarity of the clays. The decrease in the polarity of the clays is one requirement for making them more compatible with non-polar polymers for the preparation of nanocomposites. The volume increase after mechanical stirring occurs because the shear destroys the agglomerates of clay, breaking the van der Waals interactions. Consequently, it improves the layers' surface wetting and, as the slow settling of bentonite occurs, the face-to-face interactions between particles change to edge-to-edge interactions (Jones, 1983). Furthermore, some alkyl chains of the organic salt that are parallel to the surface of the layers of the clay mineral may come in contact with the solvent (Jones, 1983).

The swelling results show that the bentonites submitted to both modification methodologies acquired organophilic character and complement the X-ray diffraction results.

Table 4: Swelling capacity in xylene of sodium and modified bentonites.

Bentonite	VD mL/g	S1 mL/g	SF	S2 mL/g	SF
Vulgel S	1.5	~ 2 (I0)	-	~ 2 (I0)	-
Vulgel O1	2.1	14 (IM)	6	43 (I↑)	19
Vulgel O2	1.9	12 (IM)	5	41(I↑)	21
TEC-09 S	1.6	~ 2 (I0)	-	~ 2 (I0)	-
TEC-09 O1	1.8	10 (IM)	5	19 (I↑)	10
TEC-09 O2	1.9	9 (IM)	4	15 (IM)	7
Reminas S	1.7	~ 2 (I0)	-	~ 2 (I0)	-
Reminas O1	1.6	8 (I↓)	4	14 (IM)	8
Reminas O2	1.6	7 (I↓)	3	7 (I↓)	3
Soleminas Dye-10 S	1.6	~ 2 (I0)	-	~ 2 (I0)	-
Soleminas Dye-10 O1	1.9	8 (I↓)	3	12 (IM)	5
Soleminas Dye-10 O2	1.9	8 (I↓)	3	11 (IM)	5
Bentogel Patag S	1.6	~ 2 (I0)	-	~ 2 (I0)	-
Bentogel Patag O1	2.3	14 (IM)	5	46 (I↑)	19
Bentogel Patag O2	2.1	12 (IM)	5	41 (I↑)	19
Brasgel PBS50 S	1.6	~ 2 (I0)	-	~ 2 (I0)	-
Brasgel PBS50 O1	1.9	10 (IM)	4	13 (IM)	6
Brasgel PBS50 O2	2.0	7 (I↓)	3	13 (IM)	6

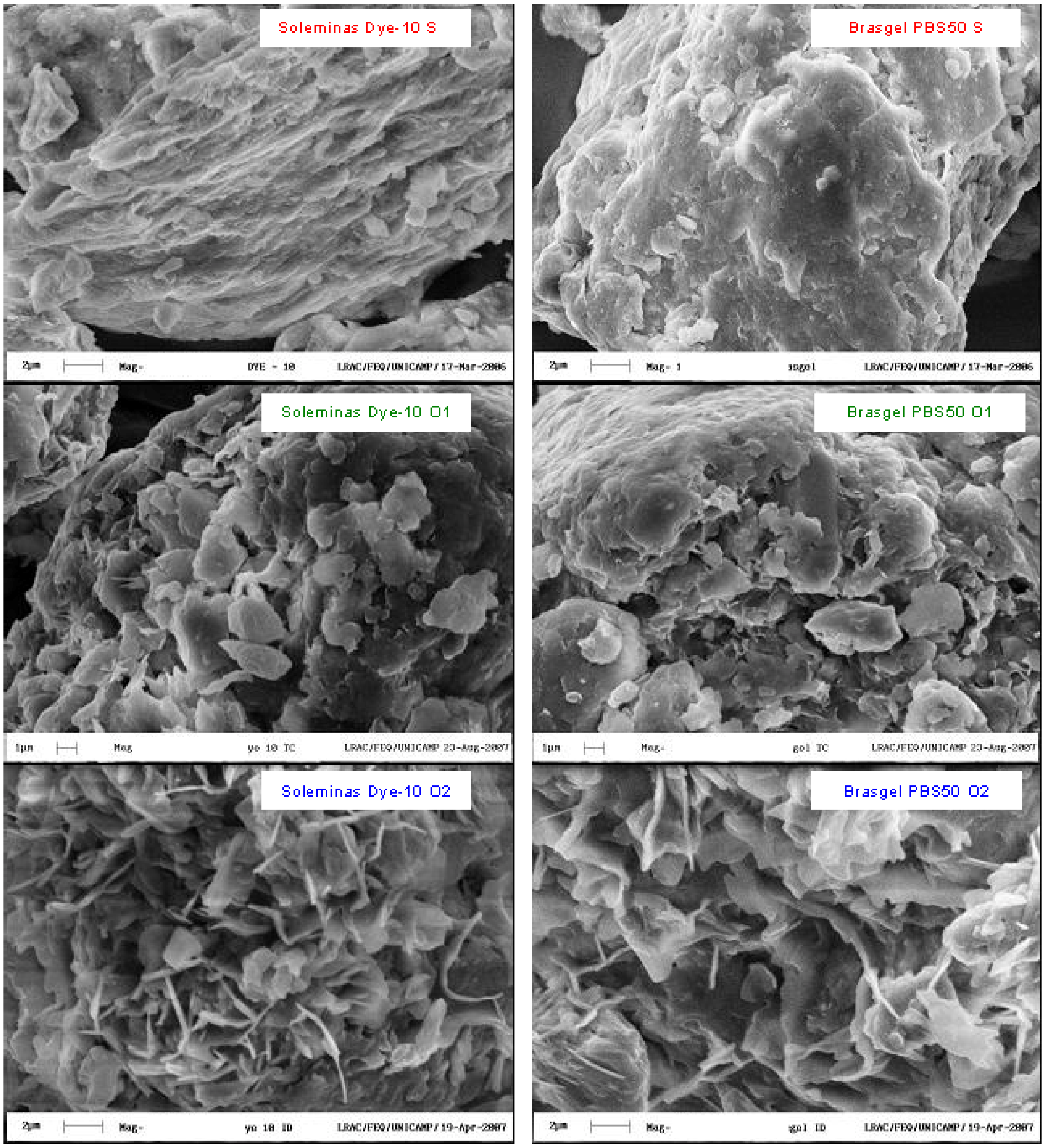
VD = volume of 1g of dry bentonites
S1 = swelling (mL/g) after standing 24 h without stirring
SF = swelling factor
S2 = swelling (mL/g) after stirring + standing 24 h

Evaluation of the Particle Morphology by Scanning Electronic Microscopy

Figures 2a and 2b show micrographs of sodium bentonites and organophilic bentonites as examples of the particle morphology. The particles of sodium bentonites are agglomerated and compact. This can be due to face-to-face and face-to-edge interactions (García López *et al*., 2005).

The particles of the organophilic bentonites are less compact than those of the sodium bentonites and reveal the expansion of the layers due to the intercalation of the distearyl dimethylammonium cations. The micrographs do not permit us to conclude whether the expansion of the layers is uniform in the whole mass of the modified clay, but, together with the other techniques, is a good indication that the clay was modified.

The expanded aspect of the particles of the organophilic bentonites is a strong indication that they can be dispersed with some exfoliation or intercalation in polymeric matrices to produce nanocomposites.



(a) (b)

Figure 2: Micrographs of sodium and organophilic bentonites (a) Soleminas Dye-10 S, O1 and O2; (b) Brasgel PBS50 S, O1 and O2.

Property Correlations

The six studied sodium and organophilic bentonites showed variable results concerning the properties evaluated. This can be attributed to their origin from different regions and the intrinsic properties due to their natural formation. The treatment also has an important influence.

In this section, the influence of the basic properties of the sodium bentonites on the final properties of the organophilic bentonites and values for the correlation coefficient, r, are presented.

Figure 3 shows the correlation between the CEC and the swelling capacity in water of sodium bentonites. As expected, the results showed a tendency of higher swelling capacities in water for clays with a higher CEC. The Reminas S bentonite showed the lowest CEC and the lowest swelling capacity in water, while the Bentogel Patag S showed the highest CEC but the second highest swelling capacity in water. A complete expansion of the clay layers in water stops when the CEC is below 60 meq/100 g of clay (Brindley and Ertem, 1971), which corroborates the results for Reminas S and Soleminas Dye-10 S. This behavior suggests that there are fewer sites available for hydration in clays with a low CEC, resulting in lower swelling.

The content of calcium and the swelling capacity in water also show some correlation, as shown in Figure 4. The two bentonites with a higher calcium content, Reminas S and Soleminas Dye-10 S, showed the lowest swelling capacities in water.

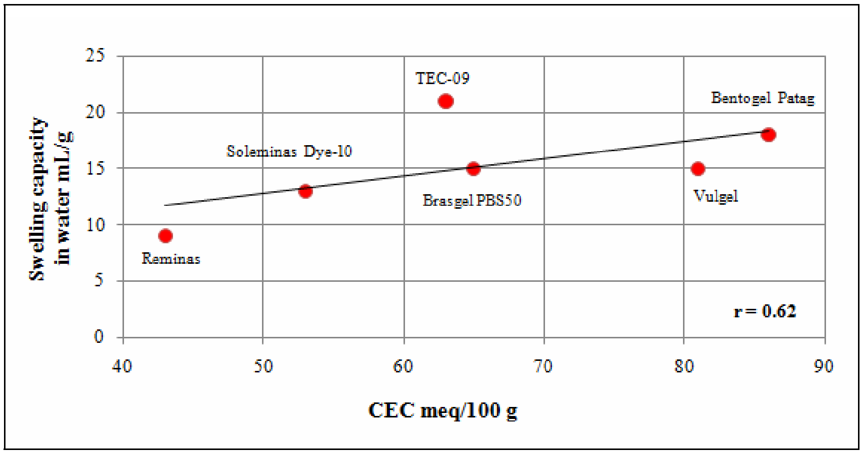


Figure 3: Swelling capacity in water versus cation exchange capacity of the sodium bentonites.

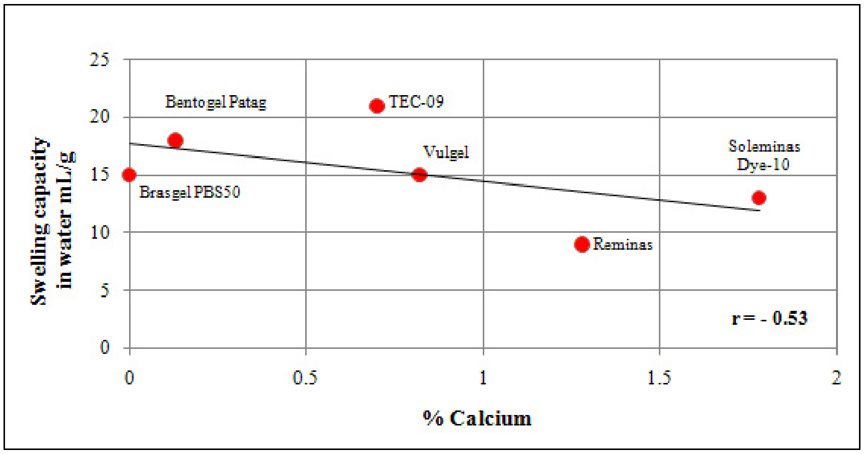


Figure 4: Swelling capacity in water versus content of calcium of the sodium bentonites.

Although the highest content of calcium does not correspond to the lowest swelling and vice versa, there is a tendency that the presence of calcium reduces the swelling of clays in water. According to Bergaya *et al*. (2006), calcium ions hold the silicate layer together, especially in large quantities, forming small aggregates. Caballero and Cisneros (2011), in a recent study, pointed out that the calcium has a higher polarizing power than sodium. In calcium bentonites, the adsorbed water occupies the interlayer spaces, while in sodium bentonites the adsorbed water fills the interlayer, condenses capillarily in the micropores and can also be adsorbed on the in external surfaces of the particles. For this reason, sodium bentonites can swell freely until they form a gel or a suspension of the individual layers.

The behavior of swelling capacity of the bentonites studied is in accord with the well known aspects already investigated by many authors, as reported in Bergaya *et al*. (2006).

Figure 5 shows that there is a tendency for an initially higher basal spacing of sodium bentonites, which generates a final higher basal spacing in organophilic bentonites.

The correlation between the CEC and the swelling capacity in xylene is shown in Figure 6. The four bentonites that showed higher swelling capacities in xylene, Vulgel O1, Vulgel O2, Bentogel Patag O1 and Bentogel Patag O2, were derived from the two sodium bentonites with higher CEC, which are the raw sodium bentonites. On the other hand, the Reminas O1 and Reminas O2 bentonites showed lower swelling capacities in xylene and were derived from the sodium bentonite with the lowest CEC.

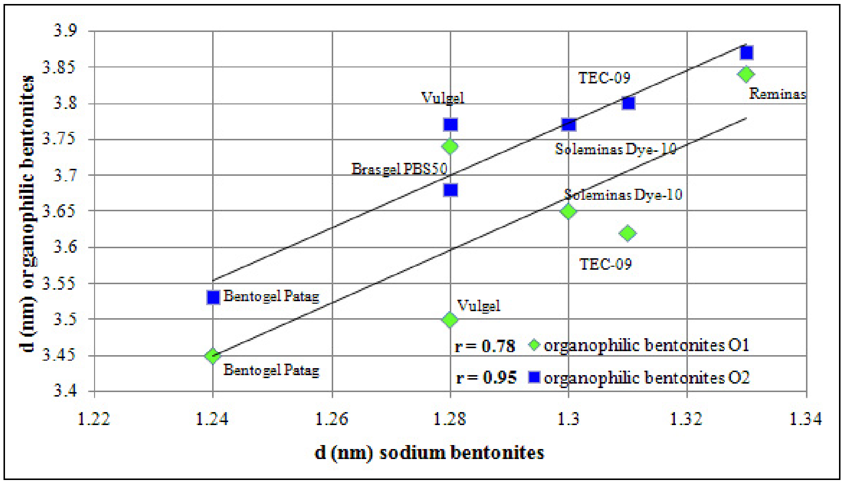


Figure 5: Organophilic bentonite basal spacing (d (nm)) versus sodium bentonites basal spacing (d (nm)).

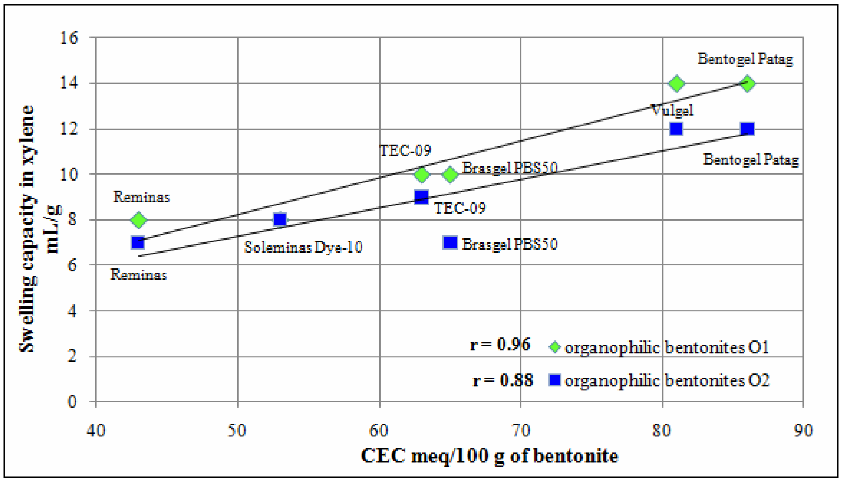


Figure 6: CEC of sodium bentonites versus swelling capacity in xylene of organophilic bentonites.

The results show that, although the organic cations were intercalated in all bentonites, the CEC had an influence on the organophilic behavior. One hypothesis is that a high CEC can promote a better distribution of the intercalated organic cations between the clay mineral layers, resulting in a better swelling.

Based on the correlations evaluated, it was observed that, to obtain organophilic bentonites with the quaternary ammonium salt distearyl dimethylammonium chloride, properties of the sodium bentonites such as the cation exchange capacity, the swelling capacity in water and the basal spacing must be considered.

CONCLUSION

The bentonites modified by two methodologies, cation exchange in an aqueous dispersion andintercalation in a semisolid medium, presented intercalated organic cations and acquired organophilic characteristics. The proposed methodology of intercalation in a semisolid medium was very efficient and provided organophilic bentonites with properties similar to the conventional methodology and can thus be considered an alternative methodology to obtain organophilic clays. Furthermore, the semisolid method is faster and easier to process, does not require large quantities of water and does not generate effluent water. Thus, it constitutes an economically and environmental friendly alternative.

Intrinsic properties like the cation exchange capacity, the swelling capacity in water and the basal spacing must be considered in the organophilic modification of sodium bentonites.

The evaluation of the potential of sodium bentonites of Brazilian and Argentinean origin for producing organophilic bentonites showed that there exist several clays in the region that can be used as alternatives to the commercial organophilic clays available.

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