

## Molecular modeling of organically modified layered silicates

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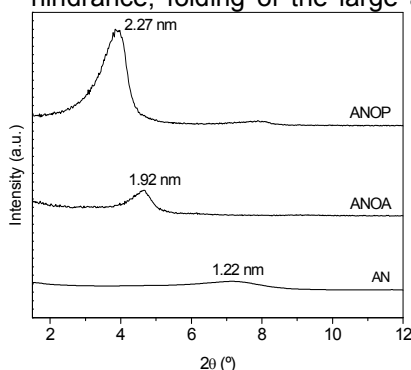
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**Abstract** – Understanding the interlayer swelling and molecular packing of the organic salts in organoclays is important for the formation and design of polymer nanocomposites. In this present work, conformational search studies based on the MMFF94 force field were performed to better understand the behavior of organic salts intercalated into layered silicates. A dense molecular packing and larger basal spacing is observed in organoclay containing butyl phosphonium salt. The molecular modeling results showed that the ionic group in the methyl ammonium salt can interact strongly with the clay surface since there is less steric hindrance, whereas the ionic head of the butyl phosphonium salt has a weaker interaction with the clay surface due to larger steric repulsions.

Organoclay represents a family of materials which have potential applications in a range of key areas, such as adsorbents for organic pollutants [1], rheological control agents [2], reinforcing fillers for plastics [3], and electric materials [4]. Based on the experimental techniques (for instance, X-ray diffraction and thermogravimetric analysis), several models have been proposed to understand the nature of intercalation process [5-8].

In our study, a sodium bentonite (AN) supplied by Bentonite União Nordeste-Campina Grande/Brazil was organically modified by ionic exchange reaction with methyl ammonium (ANOA) and butyl phosphonium (ANOP) salts. These salts were slowly added to aqueous bentonite dispersions (2% w/v), under vigorous stirring in amounts corresponding to 100% of the clay's theoretical ion exchange capacity (92 meq/100 g). Hereafter, the organoclays named ANOA e ANOP were characterized by (XRD) and thermogravimetric analysis (TG). Also, conformational search techniques using MMFF94 force field implemented in the SPARTAN 04 program were applied to these salts in order to yield information on their volume, steric hindrance, folding of the large alkyl chain (C<sub>16</sub>H<sub>33</sub>) and electrostatic potential maps. These results should provide some insights into the tendency of these organic salts for intercalation between galleries of the clay.



**Figure 1.** XRD diffractograms of natural clay and methyl ammonium (ANOA) and butyl phosphonium (ANOP) organoclays.

The d-spacing of the clays determined by XRD (Figure 1) show that the ANOP salt favors larger expansion of the clay galleries than the ANOA (2.27 nm vs. 1.92 nm). From the molecular modeling results, this observed behavior can be attributed to the larger steric effects due to the butyl groups in ANOP. Also, these butyl groups hinder the attractive interactions of the phosphonium cation with the clay surface. On the other hand, according to TG data, the ANOA salt is intercalated in larger amounts than the ANOP salt (98.8% vs. 41.0%), despite the smaller basal spacing. These results can be explained by two effects unveiled by the conformational study: *i*) the already mentioned smaller attractive interaction between the cation in ANOP with the clay surface; and *ii*) the fact that the ANOP salt has a larger degree of folding of the C<sub>16</sub> alkyl chain than ANOA (43% vs. 27%).

In conclusion, according to our results, ANOP yields a larger expansion of the clay galleries than ANOA. The reasons are related to the tendency of folding of the of the C<sub>16</sub> alkyl chain in ANOP, thus increasing its effective volume, and to the smaller attractive interactions of its cation group with the clay surface due to the shielding of the butyl groups. The latter effect is also responsible for the significantly small amounts of intercalated ANOP salt compared to the ANOA salt. In addition, since the ANOA salt has a smaller degree of folding of the C<sub>16</sub> alkyl chain than ANOP, it can promote larger intercalation of polymers than the ANOP salt.

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