Chemisorption Role of Clay Surfaces in the Synthesis of Porphyrins from its Raw Materials via Room Temperature Reactions

J. H. Hassen[a,*] and J. Silver[b]

[a]Department of Pharmaceutical Chemistry, College of Pharmacy, University of Anbar, Ramadi, Iraq
[b]Wolfson Centre for Material Processing, Brunel University, London, UK

In the formation of porphyrin, at least one step is acid-catalyzed. Cation-exchanged clay was found to be able to provide the acidity needed in the formation of porphodimethine (an intermediate step in the route of porphyrin formation), from the reaction of pyrrole and aldehyde in water. Five different aldehydes were reacted with pyrrole in water in the presence of montmorillonite MMT and kaolinite KLT clays saturated with Fe(III), Cu(II), Cd(II), Co(II), Zn(II), Ni(II), and Na(I) cations. The initial appearance of a pink color, which indicates the beginning of the porphyrin formation, depends on the acidity of the cation in the exchanged sites of the clay, also on the cation exchange capacity of the clay. The intermediate compound was found to be formed in the montmorillonite interlayer in addition to the surface, and oxidized to porphyrin when desorbed from the clay surface by chloroform. In the presence of kaolinite, the intermediate compound formed only on the surface. The results were monitored using visible absorption spectra, diffuse reflectance spectra, and X-ray diffraction.

Keywords:
porphyrin, montmorillonite, kaolinite, pyrrole, aldehyde

Introduction

Adsorbents play a prominent role in chemistry, and various types of adsorbents are explored[1]. Activated charcoal has a major role in adsorption of pollutant materials[2], toxic substances, and drugs[3–6]. Likewise, clays have received great attention in adsorbing many organic matters[7] through chemical or physical processes. The adsorption of porphyrins on clays has received special attention due to the special importance of this pigment. The argument on the origin of the porphyrin pigments found in petroleum, and petroleum origin, has focused on the fact that their origin is plant or animal. These porphyrins came from precursor pigments present in the source material. They play an active role in the development of crude oil from its source, the biogenic material[8]. The role of the clay minerals in the degradation of chlorophyll to a homologous series of porphyrins, similar to that found in petroleum has been studied[9]. The generation of a series of porphyrins via the use of simulated geochemical conditions known to be important in the generation of petroleum has been conducted from single porphyrin[10]. The formation of porphyrins from simple molecules available in the environment in the presence of clay minerals is not clearly understood, and only a few studies appeared in the literature concern the subject[11–13]. The clay surface acidity has a great impact on achieving significant organic transformations[14]. The adsorption of porphyrins on clay minerals has been widely studied[15–17]. It was found that in the clay-porphyrin complexes formed by the reaction of synthetic clay and cationic porphyrins, the Soret bands of the compound were shifted to longer wavelengths compared to those in water, due to the parallel orientation of the molecule[18]. UV-Vis absorption study showed that porphyrins adsorption on nanoclay platelets resulted in the flattening of meso-groups substituted on the molecule[19]. An experiment concerning the adsorption of the zwitterionic porphyrin (tetrakis {4-(2-carboxyethyl)pyridinio}porphyrin (TPyCP)) showed that the compound is able to form a three-dimensional structure by electrostatic interactions on the clay surface between porphyrins[20]. It was found that when the compound 5,10-diphenyl-15,20-di(4-pyridyl)porphyrin adsorbed on saponite clay at pH 1, the Soret band slightly shifted to longer wavelength[21]. Researchers suggested that metalloporphyrin ions have the ability to be intercalated in the interlayer of MMT perpendicularly, diagonally and horizontally[22]. The results from XRD and absorp-

*Corresponding author: E-mail: ph.jasimhu@uoanbar.edu.iq

tion spectra showed that the intercalation of cationic porphyrin into clay interlayer was found to be parallel to the clay nanosheet[23]. Similar investigation on spectral behavior of *meso*-tetrakis(*N*-methylpyridinium-4-yl) porphyrin on montmorillonite showed that the change in spectra of such compound is due to flattening, protonation, and aggregation of the compound[24]. The absorption and emission spectra of some subporphyrin derivatives adsorbed on saponite clay exhibited strong shifts due to the molecule flattening on the clay sheet[25]. It was found that the parallel orientation of the porphyrin molecule was stabilized by the entropy term, while the tilted orientation was stabilized by enthalpy term[26]. When the iron(III)-tetrakis(*N*-methylpyridinium-4-yl)porphyrin complex was adsorbed on MMT, the resulting structure had catalytic properties for decolorization of Acid Orange 7[27]. Also, the intercalation of the complex μ-*meso*-tetra(4-pyridyl)porphyrinatecobalt(II) tetrakis[bis(bipyridine)(chlorido)ruthenium(II) into smectite interlayer yield a structure used to modify glassy carbon electrodes, in order to be used in the simultaneous determination of some organic compounds[28]. The aim of the present work was to investigate the formation of porphyrins in the presence of MMT and KLT clays saturated with various cations, and to study the effect of different substituents on the four meso-positions (from the corresponding aldehyde) on the properties of the clays.

Materials and methods

The clay samples were Wyoming MMT has the composition $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$, obtained from Podmore and Sons Ltd, and the KLT sample called Black Pool has the composition $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, was obtained from Ward's Natural Science Establishment. The chemicals used in this research were of analytical grade obtained from Sigma-Aldrich Company. The diffuse reflectance spectra of the solid samples were recorded on Unicam SP. 700 spectrophotometer in the 30000–14000 cm^{-1} range. The visible absorption spectra of the solutions were recorded on Perkin-Elmer Lambda 5 UV/Vis and Beckman DU-7 spectrophotometers. The X-ray diffraction patterns for the solid samples were recorded on a Philips diffractometer using CuKa radiation.

Reactions of pyrrole and aldehydes in the presence of cation-exchanged MMT and KLT clays

Five different aldehydes, known as l-naphthaldehyde, cinnamaldehyde, phenylacetaldehyde, salicylaldehyde, and 4-carboxy benzaldehyde were reacted separately with pyrrole in water in the presence of MMT and KLT clays saturated with the cations Fe(III), Cu(II), Cd(II), Co(II), Zn(II), Ni(II), and Na(I). In each separated experiment, 0.2 mL pyrrole was reacted with equimolar amounts of aldehyde in a flask containing 3 g of the exchanged clay in 100 mL distilled water. The reactions were allowed to proceed with stirring under air and at room temperature for 24 hours. After filtration and washing with distilled water, the purple slurries were air-dried.

Results and discussion

The initial point at which a change in the color of the slurries is observed, depends on the cation exchange capacity and on the metal cation present in the exchange site of the clay. The reactions of pyrrole and the aldehydes in the presence of Fe(III) MMT exhibited an immediate change in the color of the slurries from grey to pink. Whereas, in the presence of Fe(III) KLT, the change in the initial color took about 30 minutes longer. If the Cu(II), Cd(II), Co(II), Zn(II), Ni(II), and Na(I) ions were the exchangeable cations of MMT, the color change took longer than Fe(III) MMT, and varied from one ion to another depending on the acidity of the exchangeable cation. The exchanged KLT samples needed longer to exhibit a change in color. In the case of Na(I) KLT sample, the process needed a drop of acid to catalyze the reaction.

The reaction pathway of porphyrin formation involves the formation of porphyrinogen in the first stage. The porphyrinogen then oxidizes, through porphomethine and porphodimethine, to porphyrin as shown in Fig. 1. Porphyrins can also be reduced to phlorins, porphomethines or porphyrinogens. The process depends on the activity of the reducing agent[29].

The mechanism of the *meso*-tetrasubstituted porphyrin[30] involves pyrrole condensation with aldehyde to give carbinol I, which undergoes oxidation to aroylpyrrole II. Aroylpyrrole condensation with another molecule of pyrrole gives carbinol III, which then undergoes dehydration and reduction to dipyrromethane IV. Dipyrromethane condensation with a further molecule of aldehyde gives carbinol V. Carbinol V oxidation gives aryoldipyrromethane VI. The condensation of two molecules of this aroyldipyrromethane VI gives γ-dihydroxyporphyrinogen VII, which loses two molecules of water to produce porphodimethine intermediate VIII. The intermediate VIII rearrangement leads to chlorin IX or oxidation to porphyrin X.

In the formation of porphyrin, at least one step is acid catalyzed[31], and since cation exchanged clays are able to provide this acidic environment, previous researchers have utilized clays as catalysts in
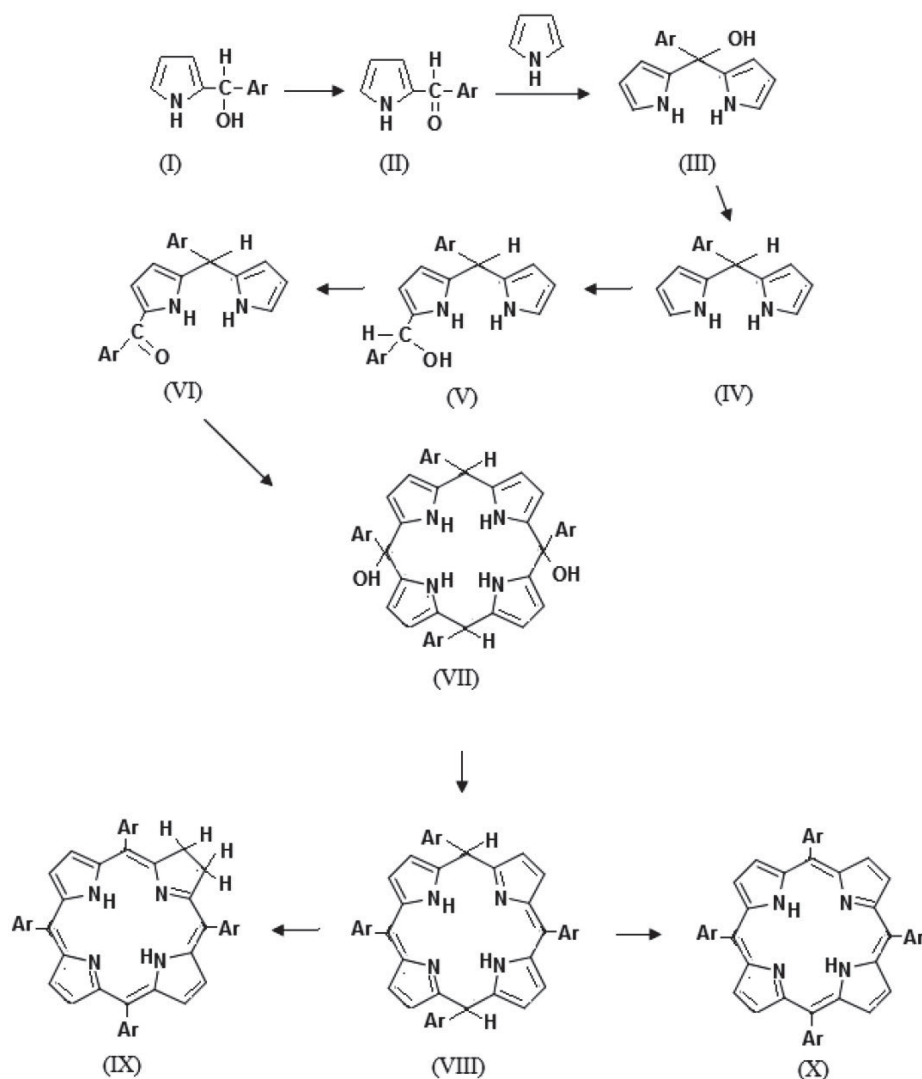
Fig. 1 – *Mechanism of porphyrin formation*

the formation of tetraphenylporphodimethine (TP-PDM) from the reaction of pyrrole and benzaldehyde in water[12]. The presence of a strongly acidic hydrated cation such as Fe(III)[32], in the exchange sites of the clay, initiates the reaction faster than that carried out in the presence of a weak acidic cation such as Na(I). The reaction in the presence of KLT is slower than that with MMT, even if Fe(III) is the exchangeable cation, presumably due to the low cation exchange capacity of KLT, which is about 10 meq 100 g^{-1} in comparison to that of MMT which is 70 meq 100 g^{-1} [33].

In the presence of MMT or KLT saturated with various cations, the reaction between pyrrole and the five different aldehydes, under atmospheric oxygen, resulted in the formation of a porphyrin intermediate which absorbs near 500 nm. Other researchers[34] observed a similar band near 500 nm during the oxidation of the colorless uroporphyrinogen to uroporphyrin. They assigned porphomethine

and porphodimethine structures to this intermediate. In our research, porphodimethine structures were assigned to the compounds obtained during the reaction between pyrrole and the different aldehydes in the presence of MMT and KLT clays saturated with various cations. The aldehydes used are given in Table 1, along with the names of the intermediate compounds obtained, in which the four *meso*-positions α, β, γ, and δ carry the residue from the corresponding aryl aldehyde.

Table 1 – *Aldehydes used and the corresponding intermediate compounds formed*

Aldehyde	Intermediate compound
1- Naphthaldehyde	*meso*-tetranaphthylporphodimethine
Cinnamaldehyde	*meso*-tetracinnamylporphodimethine
Phenylacetaldehyde	*meso*- tetraphenylacetylporphodimethin
Salicylaldehyde	*meso*-tetrasalicylporphodimethine
4-Carboxybenzaldehyde	*meso*-tetracarboxyphenylporphodimethine

Visible absorption and diffuse reflectance spectra

The visible absorption spectra of all the clay samples suspended in water, self-supporting films and the diffuse reflectance spectra, showed a band near 500 nm indicating the formation of the porphodimethine, which is an intermediate compound on route to porphyrin. Fig. 2 shows the diffuse reflectance spectra of some of the powder samples. The visible absorption spectra of the powder suspensions in chloroform, in which the chloroform causes desorption of the compounds from the clay, showed the appearance of a small band near 415 nm. This band was assigned to porphyrin, which indicated rapid oxidation of some of the intermediate compounds to porphyrin after desorption. Fig. 3 shows the spectra of the suspensions in chloroform after less than 5 minutes.

The positions of the bands, assigned to the intermediate, and the band of the porphyrin (oxidized intermediate) after desorption in chloroform, are given in Table 2. From the spectra of the samples suspended in water, the self-supporting films, and the diffused reflectance spectra, which indicate the real environment of the compounds on the clay surface or the interlayer, it is clear that the intermediate compound in the adsorbed state is a cationic form of porphodimethine structure due to the similarity of the absorption spectra of this intermediate with that reported[35] during the formation of TPPH in acetic acid. This intermediate undergoes oxidation to porphyrin upon desorption from the clay.

Oxidation of the intermediate compounds of all the samples was completed when these solutions were left under air and at room temperature overnight (Fig. 4). Some of the visible absorption spectra of the samples showed bands near 450 nm together with the Soret band of the oxidized intermediate and the band near 500 nm. This band near 450 nm is assigned to diprotonated porphyrin. The acid catalyzed oxidation of porphyrinogen is assumed to be a free radical in nature, and the catalysis is a function of the protonation of pyrrolic nitrogen[36].

In the presence of the clay, it was observed that the intermediate *meso*-tetraphenylporphodimethine (TPPDM) could be found under the same conditions in the absence of oxygen[37]. This led researchers to suggest that porphyrinogen oxidation also takes a free radical pathway. When a hydrogen atom is removed from the methylene bridge carbon, a resonance stabilized radical is generated. An oxidized dipyrromethane unit is then formed by protonation of pyrrolic nitrogen, followed by the loss of another hydrogen atom. This process is repeated a second time to give the intermediate compound. The clay acts as a stabilizer to the cationic interme-
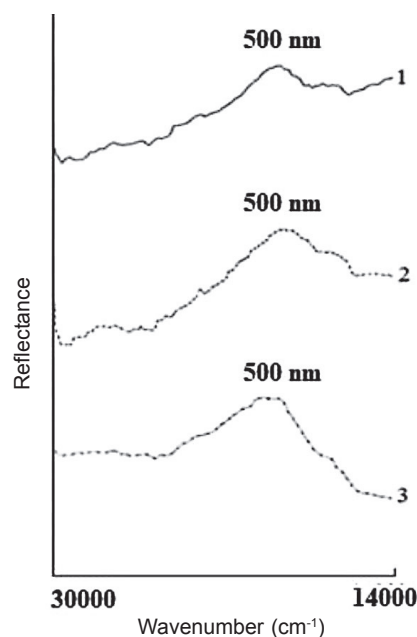

Fig. 2 – *Diffuse reflectance spectra of (1) Ni(II) MMT reacted with pyrrole and 4-carboxyrenzaldehyde, (2) Fe(III) MMT reacted with pyrrole and l-naphthaldehyde, (3) Fe(III) MMT reacted with pyrrole and cinnamaldehyde*
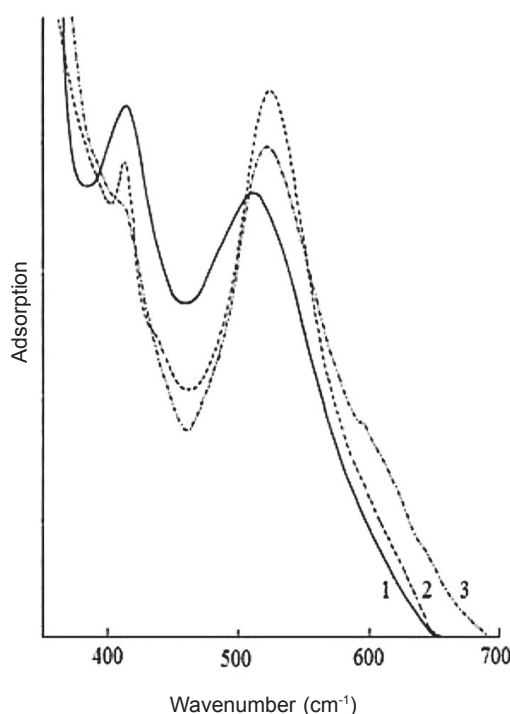

Fig. 3 – *Visible absorption spectra of (1) Fe(III) MMT reacted with pyrrole and 1-naphthaldehyde, (2) Zn(II) MMT reacted with pyrrole and salicylaldehyde, (3) Ni(II) MMT reacted with pyrrole and 4-carboxybenzaldehyde. The spectra were taken as suspensions in chloroform after less than 5 minutes.*

diate, as shown in the spectra of the suspensions in water, self-supporting film, and the diffuse reflectance spectra, which reveal the real environment of the compound on the clay.

Table 2 – *Position of the bands in nm in the visible absorption spectra of the intermediate compounds suspended in chloroform after less than 5 minutes*

M^{n+} MMT	1-Naphthaldehyde	Cinnamaldehyde	Phenylacetaldehyde	Salicylaldehyde	4-Carboxybenzaldehyde
Fe(III)	414, 512	415, 510	414, 510	417, 510	416, 510
Cu(II)	415, 509	417, 505	414, 512	414, 519	418, 513
Cd(II)	511	416, 512	416, 505	416, 513	420, 509
Zn(II)	418, 507	416, 506	415, 507	414, 526	416, 504
Co(II)	416, 511	415, 509	416, 508	418, 513	414, 523
Ni(II)	414, 504	420, 511	414, 512	418, 511	410, 526
Na(I)	418, 510	418, 507	418, 503	420, 508	416, 510

Table 3 – *Basal spacing of MMT samples reacted with pyrrole and different aldehydes*

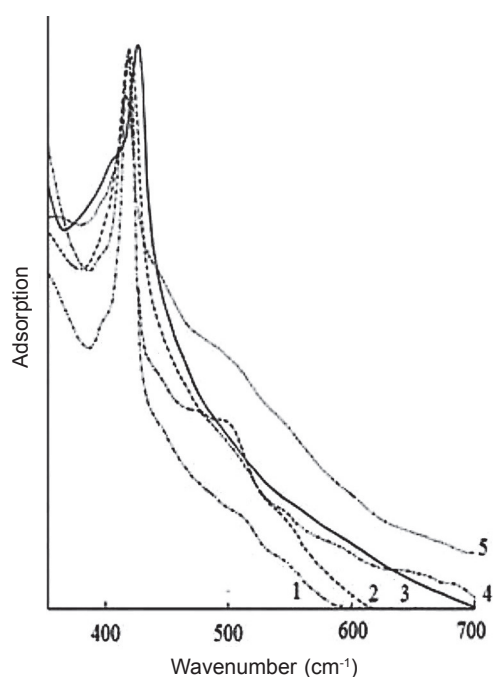| Samples	The Basal spacing in Å			
	Air dried	120 °C	375 °C	EG
MMT	13	12.6	9.6	17
Fe(III) MMT + pyrrole + phenylacetaldehyde	16.2	18.4	15.8	18.8
Ni(II) MMT + pyrrole + 4-carboxybenzaldehyde	16.1	16.1	14.3	17.7
Fe(III) MMT + pyrrole + 1-naphthaldehyde	18.4	18.1	16.4	19.6

Fig. 4 – *Visible absorption spectra of (1) Cd(II) MMT reacted with pyrrole and cinnamaldehyde, (2) Zn(II) MMT reacted with pyrrole and salicylaldehyde, (3) Ni(II) MMT reacted with pyrrole and phenylacetaldehyde, (4) Fe(III) MMT reacted with pyrrole and l-naphthaldehyde, (5) Co(Il) MMT reacted with pyrrole and 4-carooxybenzaldehyde. The spectra were taken as suspensions in chloroform after 24 hours.*

X-ray powder diffraction

The X-ray diffraction patterns of the powdered samples of MMT saturated with different cations, which were used in the synthesis of the porphodimethines showed a basal spacing of 15.8 Å for Fe(III) MMT reacted with pyrrole and phenylacetaldehyde, 14.3 Å for Ni(II) MMT reacted with pyrrole, and 4-carboxybenzaldehyde and 16.4 Å for Fe(III) MMT reacted with pyrrole and 1-naphthaldehyde, after drying at 375 °C. MMT gives a basal spacing of 9.6 Å, when no molecules are between the unit layers. The 14.3 Å basal spacing of the Ni(II) MMT sample indicates an interlayer separation of 4.7 Å, which is the approximate thickness of the porphyrin molecule[38]. This reveals that the porphyrin molecule lies parallel to the MMT layers, though it does not give proof of the relative position of the phenyl rings. The Fe(III) MMT sample reacted with pyrrole and l-naphthaldehyde showed an interlayer separation of 6.8 Å, which indicated that the naphthalene ring lies almost perpendicular to MMT layers. The air-dried Fe(III) MMT sample, reacted with pyrrole and phenylacetaldehyde, showed two peaks corresponding to a different basal spacing, also a diffuse diffraction with asymmetrical peaks was obtained, which indicated a different interstratification of the layers by porphyrin. On heating, or after ethylene glycol (EG) treatment, the sample showed a uniform peak. That is because the treatment with EG opens all the layers to 17 Å and heat treatment closes all the layers down uniformly. The basal spacing of the sample, after different treatments, are listed in Table 3.

On treatment with EG, the original MMT sample swelled to 17 Å, while the sample containing the intermediate showed a higher basal spacing, as shown in Table 3. The X-ray diffraction patterns of the KLT samples, which also showed the formation
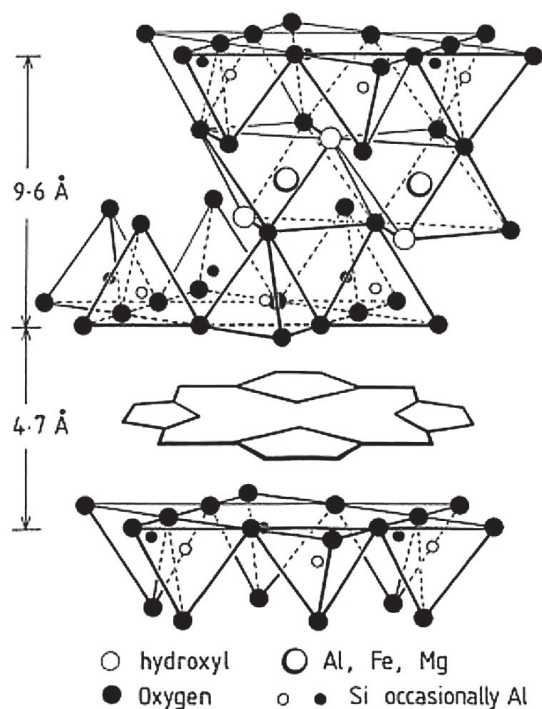
Fig. 5 – *Schematic presentation of the orientation of the porphyrin molecule in MMT interlayer*
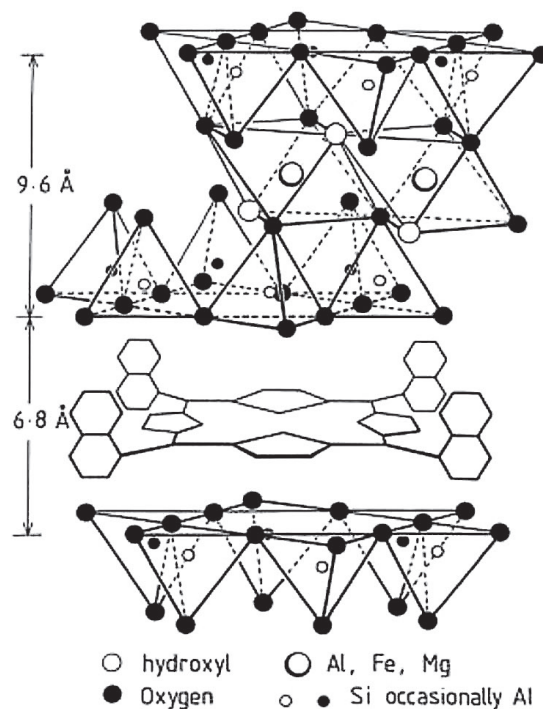

Fig. 6 – *Schematic presentation of the orientation of the naphthalene groups in the MMT interlayer*

of the intermediate, indicated no change in the basal spacing. This suggests that only the KLT surface catalyzes the formation of porphyrin. Thus, the process is slower than that of MMT, in which both the interlayer and the surface catalyze the porphyrin formation, as the compound is able to enter into the interlayer, and also it is in contact with the surface. Fig. 5 shows a schematic presentation of the orientation of the porphyrin molecule in the MMT interlayer. Fig. 6 shows how the naphthalene ring lies perpendicular to the layers when pyrrole reacts with 1-naphthaldehyde in the presence of cation-exchanged clay.

Conclusions

Cation-exchanged clays are able to provide the acidity needed in the porphyrin formation from the reaction of pyrrole and aldehyde in water. The initial appearance of a pink color, which indicates the initial point of porphyrin formation, depends on the acidity of the cation in the exchange sites, also on the cation exchange capacity of the clay. The compound formed is a porphodimethine, which is an intermediate step in the route of porphyrin formation. This compound is oxidized to porphyrin when desorbed from the clay surface by chloroform. A free radical acid-catalyzed mechanism was proposed for the formation of the intermediate. This intermediate compound formed in the interlayer of MMT in addition to the surface, while in the presence of KLT it formed on the surface only.

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