Stability of Fe(III) and Sn(IV) Metalloporphyrins Adsorbed on Cation-Exchanged Montmorillonite

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Abstract

The iron(III)tetraphenylporphyrin chloride Fe(III)TPPCl, iron(III)tetra-naphthylporphyrin Fe(III)TNPCl, μ-oxo-bis[tetraphenylporphyriniron(III)] [(Fe(III)TPP)$_2$O], μ-oxo-bis[tetranaphthylporphyriniron(III)] [(Fe(III)TNP)$_2$O], tin(IV)tetraphenylporphyrin chloride Sn(IV)TPPCl$_2$ and tin(IV)tetra-naphthylporphyrin Sn(IV)TNPCl$_2$ complexes were all found to be adsorbed onto the montmorillonite MMT clay without demetallation. The evidence from the visible absorption and diffuse reflectance spectra all showed that the species present on the montmorillonite are the metallated form. Also the evidence from Mossbauer spectroscopy confirm these findings. The only process that occurs is that the dimeric form of the iron complexes underwent transformation to the monomeric form. The clay-complex systems were characterized using visible absorption spectra, diffuse reflectance spectra, X-ray diffraction, Mossbauer spectra and Electron microscopy.

Keywords: Montmorillonite, Clay, Demetallation, Dimeric, Monomeric

Introduction

The interaction of clay with porphyrins has been of interest to researchers in the past and in recent years [1-3]. It was reported that porphyrins and other macrocycles of tetrapyrrole have many functional properties. When complexed with metals they can achieve and regulate vital processes such as light-harvesting, electron transfer and catalytic transformations [4]. The adsorption of the porphyrin compounds tetrakis(1-methylpyridinium-4-yl)porphyrin (*p*-TMPyP) and tetrakis(1-methylpyridinium-3-yl)porphyrin (*m*-TMPyP) on clay was studied. It was found that both *p*-TMPyP and *m*-TMPyP compound orientation on the clay monolyer is parallel and tilted with respect to the surface of the clay depending on the solution used [5]. The complexes of Cu(II) and Fe(III) water soluble porphyrins, tetrakis(*N*-methylpyridyl)porphyrin (TMPyP) and tetrakis(*N,N,N*-trimethylanilinium)porphyrin (TTAP) were intercalated in the Ca(II) montmorillonite interlayer. It was found that both Cu(II) and Fe(III) complexes do not demetalate upon adsorption. The free base porphyrin can metalate when adsorbed on Cu(II) exchanged clay forming stable metal complex [6]. The porphyrin compounds tetrakis(1-methylpyridinium-3-yl)porphyrin (*m*-TMPyP) and tetrakis(1-methylpyridinium-4-yl)porphyrin (*p*-TMPyP) were found to be the more suitable porphyrins to accomplish a quantitative energy transfer reactions [7]. The adsorption of 2 porphyrin compound on anionic clay was studied using photochemical energy transfer reaction. Moderate energy transfer reactions were observed. It was found that the adsorbed compounds are able to move on the surface but cannot move from the surface to the sheet [8]. The behavior of the complex formation between synthetic saponite clay and cationic porphyrin, was studied. It was found that the intermolecular distance average between the molecules of porphyrin on the clay surface can be controlled [9]. A series of porphyrin derivatives were used to investigate the mechanism of unfavorable quenching process of porphyrins on the surface of the clay as an ideal solid surface for the transfer of photochemical energy [10]. A study concern the reaction of photochemical electron-transfer that occurs after light harvesting from hydroquinone solution to the adsorbed porphyrin in the excited singlet on anionic clay state was examined [11]. By developing a new technique for sample preparation conditions, cationic porphyrin was successfully intercalated into the interlayer of transparent clay space [12]. Raman and Uv-visible spectroscopies technique were used to study the interaction between clays and the water soluble porphyrin 5,10,15,20-tetrakis(l-methyl-4-pyridyl)-21H,23H-porphine

TMPyP. A red shift of the soret band was observed for all clay-TMPyP systems [13]. A study concern the stability of metalloporphyrins on clay minerals in chloroformic medium revealed that vanadyl and nickel meso-tetraphenylporphyrin are stable toward demetallation, while magnesium porphyrin was particularly unstable [13]. The adsorption process of 2 meso-substituted porphyrins TPP and TPyP on cations exchanged clays showed that TPP is protonated during adsorption while TPyP behavior depends on the water content. Stable metallocomplexes like Sn(IV)TPP can be adsorbed without demetallation in the presence of enough water. Weak complexes like Fe(III)TPP are demetallated during adsorption [15]. A study using Uv/visible and luminescence spectroscopy concerns the adsorption of Sn(IV)TPyP meso-tetrapyridylporphyrin on sodium hectorite revealed that the complex demetallates to the dication TPyP on dehydration the clay. The process was found to be reversible [16]. The aim of the present study is to determine the stability of new metalloporphyrin species of Fe(III) and Tin(IV). The iron and tin porphyrins were chosen because they belong to different classes of metalloporphyrins and can be studied by Mossbauer spectroscopy due to the availability of those to isotopes.

Materials and methods

Fe(III)TPPCl, Fe(III)TNPCl, Sn(IV)TPPCl$_2$, Sn(IV)TNPCl$_2$, [(Fe(III)TPP)$_2$O] and [(Fe(III)TNP)$_2$O] complexes were prepared according to the methods described in the literature [17,18]. Wyoming montmorillonite, obtained from Podmore and Sons Ltd. All solvents were grade reagents and used without further purification. The visible absorption spectra were recorded on Perkin-Elmar Lambda 5 UV/vis and Beckman Du-7 spectrophotometer. The diffuse reflectance spectra were recorded on a Unicam SP 700 spectrophotometer. Mossbauer spectra were recorded on a Cannberra Multi Channel analyzer, using 25 mCi cobalt-57 in a rhodium matrix and 5 mCi tin-119 in a calcium stannate matrix, as sources. Transmission electron micrographs were recorded on a JEOL 200CX transmission electron microscope at 100 KV, using ultramicrotomic technique to prepare the sections, on a Sorvall Porter-Blum MT2 ultramicrotom.

The preparation of cation-exchanged MMT

The cation-exchanged MMT samples were prepared by shaking the MMT sample with 1 M solution of the chloride salts of different metals on a magnetic stirrer for 24 h in distilled water. The samples were then filtered and washed several times using distilled water until the AgNO$_3$ test for chloride ion was negative. The samples were then dried overnight in air and then crushed by mortar to a fine powder.

The adsorption reactions

500 mg of the metal cation-exchanged MMT were added to 100 mL of a chloroform solution of the porphyrin complex in different concentrations (10, 25 and 50 mgL^{-1}). The mixtures were stirred at room temperature for 24 h, and then filtered, washed several times with chloroform and air-dried.

## Results and discussion

Visible absorption spectra

The spectra of the porphyrins complexes were conducted by separating the clear chloroformic solution. Sn(IV) and Fe(III) complexes were classified as class I and class II respectively, among the 5 classes of metalloporphyrins according to their stability toward acids [19].

When the Fe(III)TNPCl and Fe(III)TPPCl monomer complexes (which have similar spectra) were adsorbed onto the MMT saturated with different metal cations, the complexes were found to be stable on the clay surface. The complexes have Soret band at 414 nm and Q bands at 512 nm. These bands appeared in the same position after the 24 h reaction with the MMT, which indicates that the 2 complexes are stable on the clay. No appearance for the free base or the diacid species. **Figure 1** illustrating the visible absorption spectrum of Fe(III)TNPCl in chloroform and the spectrum of the same complex suspension after separation from the Zn(II) MMT surface.

When the dimeric form of the 2 iron (III) porphyrin complexes adsorbed onto the MMT, the spectrum after 24 h of reaction is the same as that of the monomeric form of the complex (**Figure 2**). The results from the visible spectra reveal that when the dimeric form of the Fe(III) porphyrin complexes are adsorbed onto the MMT surface, the bridge between the 2 porphyrin molecules breaks down producing the monomeric form of the complex. The transformation process of the dimer to a monomer is time-dependent. After 1 h of reaction, the visible absorption spectrum of the suspensions of the dimer on MMT has an asymmetric Soret band indicating the presence of a mixture of the dimer and the monomer, the spectrum shows a trace of the band at 511 nm which is assigned to the monomer [18]. The appearance of

a trace of this band indicates the beginning of dimer transformation. The rest of the spectrum is that of the dimer. After 24 h reaction the transformation of the dimer to the monomer is completed.

The $Sn(IV)TNPCl_2$ and $Sn(IV)TPPCl_2$ complexes were also found to be stable on the MMT surface. **Figure 3** shows the visible absorption of $Sn(IV)TNPCl_2$ complex and the complex after reaction with Co(II) MMT and Zn(II) MMT in chloroform. The spectra are similar to those of the original complex, however, the intensities of the bands of the adsorbed species are slightly modified.
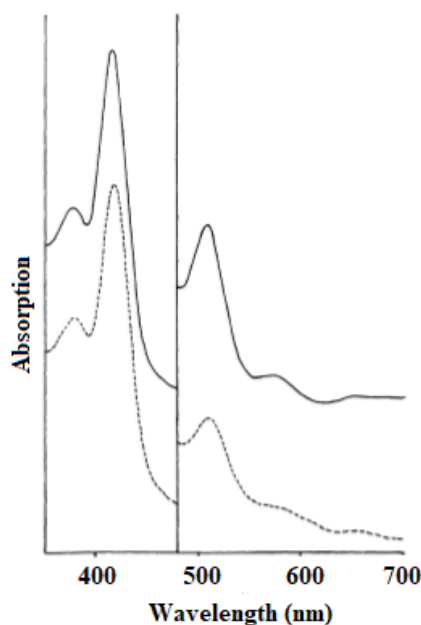
Figure 1 Electronic absorption spectra of (—) Fe(III)TNPCl, (----) the complex adsorbed on Zn(II) MMT.
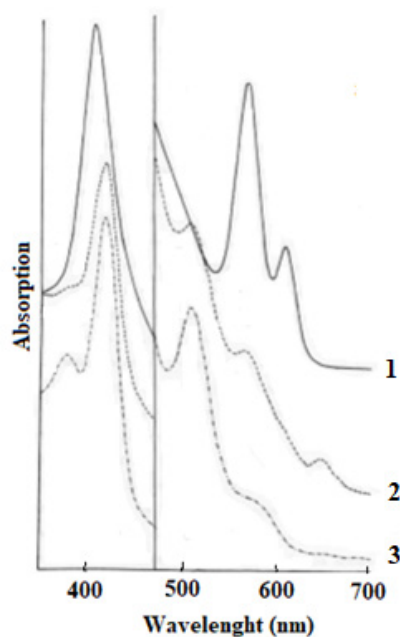

Figure 2 Electronic absorption spectra of (1) μ-oxo-dimeric Fe(III)TNP, the complex adsorbed on (2) Fe(III) MMT and (3) Sn(IV) MMT.
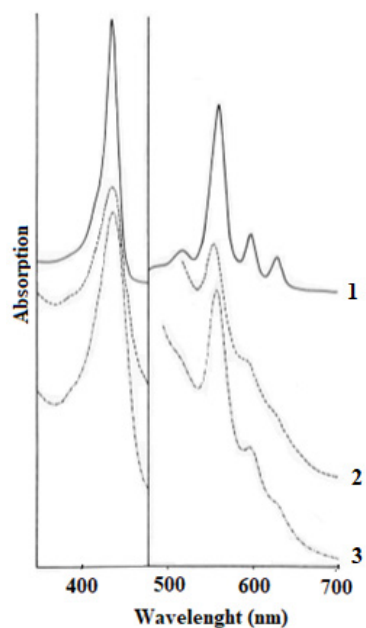
Figure 3 Electronic absorption spectra of (1) Sn(IV)TNPCl$_2$, the complex adsorbed on (2) Co(II) MMT and (3) Zn(II) MMT.

Diffuse reflectance spectra

The adsorbed complexes of both the Fe(III) and Sn(IV) were examined by diffuse reflectance spectra as a powder samples. The results are in agreement with the visible absorption spectra. **Figure 4** shows the diffuse reflectance spectra of μ-oxo-dimeric Fe(III)TPP and Fe(III)TPPC1 along with the diffuse reflectance spectra of the same complexes adsorbed on Sn(IV) MMT and Cd(II) MMT respectively. The transformation of dimer [(Fe(III)TPP)$_2$O] to the monomer form and the stability of Fe(III)TPPC1 are very obvious. **Figure 5** shows the diffuse reflectance spectra of Sn(IV)TNPCl$_2$ adsorbed on Fe(III) MMT and Zn(II) MMT.
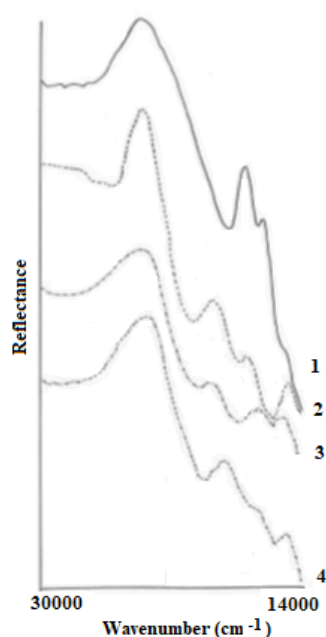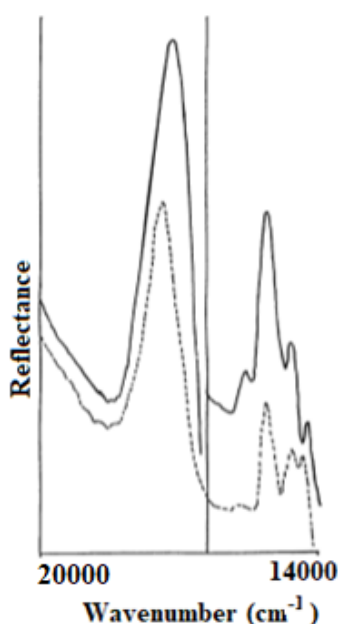

Figure 4 Diffuse reflectance spectra of (1) μ-oxo-dimeric Fe(III)TPP, (2) Fe(III)TPPC1, (3) μ-oxo-dimeric adsorbed on Sn(IV) MMT, (4) Fe(III)TPPCl adsorbed on Cd(II) MMT.

The clay acidity is known to be no more than 0.8 of a pH unit [20-22], it is less than that of the known acids, and so it seems reasonable to postulate that this acidity is not enough to cause demetallation of the complexes. Sn(IV) metalloporphyrin complexes are not completely demetallate, even in 100 % H_2SO_4. On the other hand, Bergaya and Damme [14] have suggested that other factors apart from acidity, such as steric constraints on the molecules, effect the stability of metalloporphyrins on clay. They have come to a conclusion that the order of complexes stability on the clay is different to that in solution. They found that complexes such as Zn(II)TPP remain stable on the clay surface, although it can be completely demetallated in a weakly acidic media while complex like Cu(II)TPP, which is known to be stable in solution, is extensively demetallated when adsorbed onto the clay.

The concentration of the metalloporphyrin molecules on the clay surface could affect the stability of the complex. Clay surfaces with low complex concentrations may cause demetallation by applying more forces on the molecules. An experiment was conducted to adsorb the Fe(III) and Sn(IV) metalloporphyrin complexes from a of very low concentrations chloroform solution. The powdered samples after drying showed diffused mixed spectra of the metallated and demetallated species with poor resolution.

The diffuse reflectance spectra confirm that the species present on the clay surface are the metallated forms. The demetallation may occur to such a small extent that it cannot be detected because of the dominant metallated form.


Figure 5 Diffuse reflectance spectra of Sn(IV)TNPCl$_2$ adsorbed on (——) Fe(III) montmorillonite and (-----) Zn(II) montmorillonite.
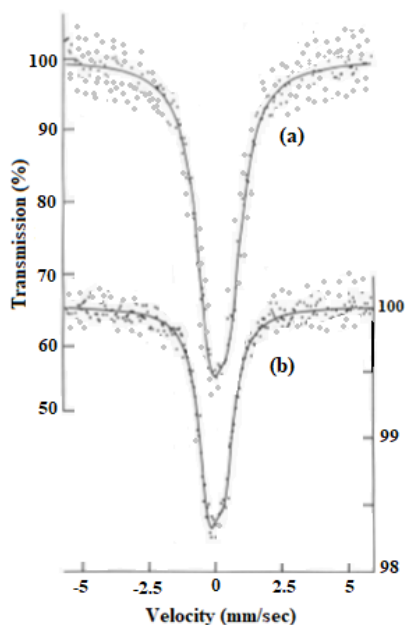
Mossbauer spectra

The species present on MMT surface, after adsorption of Fe(III) and Sn(IV) tetraphenylporphyrin complexes were examined by Mossbauer spectroscopy. **Figure 6** shows the Mossbauer spectrum of the μ-oxo-bis[tetraphenylporphyriniron(III)] complex, which is a symmetric doublet with parameters similar to those reported [23]. The spectrum of the complex adsorbed onto the Cu(II) MMT (which was collected from several experiments by extracting the remaining complex on the MMT surface) is also shown. The spectrum clearly shows an asymmetric doublet, which indicates the formation of a monomer Fe(III)porphyrin complex. The Mossbauer parameters of the complex after adsorption is slightly different to those of the unreacted complex.

The spectra were recorded for the extracted solution, as the presence of high spin Fe(III) in the MMT structure would interfere with the high spin Fe(III) of the complex. The Mossbauer parameters of the monomer Fe(III)TPPCl are also similar to those reported in the literature [24]. When this complex is adsorbed on the Zn(II) MMT, no change in the parameter was observed.

The Mossbauer spectrum of the Sn(IV)TPPCl$_2$ is shown in **Figure 7**. The parameters are similar to those previously reported [25]. The spectrum of the complex adsorbed on the Zn(II) MMT is slightly effected by the presence of the MMT. The Mossbauer parameters are presented in **Table1**.
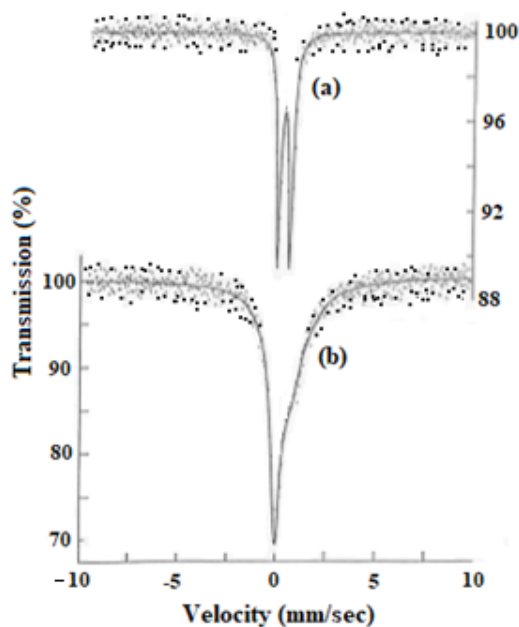
Figure 6 Mossbauer spectra at 77 °K of (a) μ-oxo-bis[tetraphenylporphyrin-iroo(III) (b) complex a after recovering from Cu(II) MMT.

Figure 7 [119]Sn Mossbauer spectra of 77 °K of (a) Sn(IV)TPPC1$_2$ f (b) Sn(IV)TPPC1$_2$ adsorbed on Zn(II) MMT.

Table 1 The ^{57}Fe and ^{119}Sn Mossbauer parameter at 77 °K for the porphyrin complexes adsorbed on MMT.

Complex	δ mms^{-1}	Δ mms^{-1}	Γmms^{-1}
[(Fe(III)TPP)$_2$O]	0.41 (1)	0.65 (1)	0.14 (1)
Fe(III)TPPCl	0.40 (1)	0.48 (1)	0.15 (1)
[(Fe(III)TPP)$_2$O] adsorbed on Cu(II) MMT	0.39 (2)	0.45 (1)	0.13 (1)
Fe(III)TPPCl adsorbed on Zn(II) MMT	0.38 (2)	0.52 (2)	0.15 (3)
Sn(IV)TPPCl$_2$	0.13 (1)	0.62 (1)	0.71(1)
Sn(IV)TPPCl$_2$ adsorbed on Zn(II) MMT	0.11 (2)	0.60 (2)	0.68 (3)

Electron microscopy

Like other clays, MMT clays have morphological characteristics which can be used to identify it. Using the high resolution mode, the MMT appeared under the electron microscope as fibers. **Figure 8** represents transmission electron micrograph of MMT sample. The appearance of the lattice stripes that correspond to the basal planes of montmorillonite [26] is clear. **Figure 9** shows the transmission electron micrograph of the Sn(IV)TPPCl$_2$ complex adsorbed onto the MMT. The appearance of the complex on the MMT surface is very clear from the micrograph.

Figure 8 Transmission electron micrograph of MMT sample.

Figure 9 Transmission electron micrograph of Sn(IV)TPPCl$_2$ adsorbed on montmorillonite surface. The appearance of the complex is indicated by the arrows.

Conclusions

The porphyrin complexes Fe(III)TPPCl, Fe(III)TNPCl, [(Fe(III)TPP)$_2$O], [(Fe(III)TNP)$_2$O], Sn(IV)TPPCl$_2$ and Sn(IV)TNPCl$_2$ were all found to be adsorbed onto the MMT without demetallation. All the evidence from the visible absorption and diffuse reflectance spectra showed that the species present on the MMT are the metallated form. In addition, the evidence from Mossbauer spectroscopy confirm these findings. The only process that occurs is that the dimeric form of the iron complexes underwent a transformation to the monomeric form. The acidity of the clay surface is not enough to cause demetallation of the complexes. The results from the Electron microscope indicate the presence of the compounds on the clay surface.

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