MONTMORILLONITE SURFACE AS A CATALYST FOR THE FORMATION OF SAT METAL TETRA (*P*-SULPHOPHENYL) PORPHYRINS

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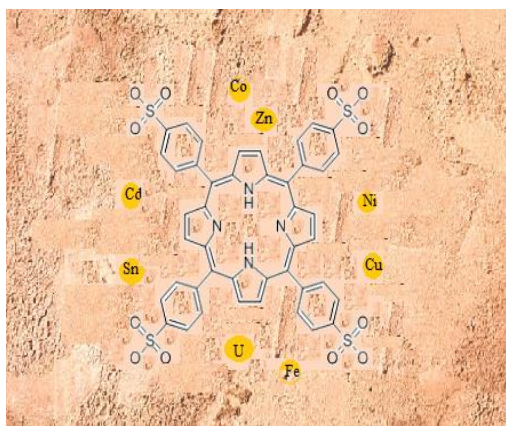[b]Centre for Phosphor and Display Materials, Wolfson Centre for Material Processing, Brunel University, Uxbridge, London, UB8 3PH, UK

Graphical abstract

Abstract

The adsorption of the water-soluble tetra(*p*-sulphophenyl)porphyrin (TPPS) compound on Fe(II), Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Sn(IV) and UO_2^{2+} metal ion-exchanged montmorillonite (MMT) facilitated the formation of the SAT metal-TPPS MMT complexes of these cations (where SAT indicates sitting atop, ie the metal is above the porphyrin plane and is bound to external ligands in this case the MMT surface). All the resulting powder samples have a brown-orange colour due to the presence of the metal-TPPS-MMT complexes of these cations. Heating the solid powder samples caused demetallation and changed the colour of the powder from brown-orange colour of the metal-TPPS-MMT complex to the green colour of the diacid porphyrin on the clay. When such samples were exposed to the open atmosphere where they could absorb water vapour, the brown-orange colour appeared again due to the remetallation. The cation remained in the vicinity of the TPPS molecule upon demetallation, which makes the metallation-demetallation process reversible. The TPPS has been found to be adsorbed only on the external surface, and can be intercalated using sodium ions in solution with the compound to open the clay lattice. The reactions were monitored using visible absorption spectra, diffuse reflectance spectra, Mössbauer spectroscopy and X-ray diffraction.

Keywords: Adsorption, montmorillonite, porphyrin, demetallation, metallation

1.0 INTRODUCTION

Porphyrins are tetrapyrrolic highly conjugated macrocycles [1]. Such compounds and their metallo complexes have been widely studied [2, 3]. They have been used as photo-catalysts as in the photooxygenation of alkenes [4], thermal catalysts [5, 6], electro-catalysts [7]. [177]Lu tetraphenyl porphyrin has been considered as a therapeutic agent [8]. An in vitro photodynamic therapy has been carried out on G361 cell lines by utilizing zinc-tetra(*p*-sulfophenyl)porphyrin (ZnTPPS) bound to cyclodextrin that induced single strand breaks of cellular DNA in the G361 melanoma cells [9]. Uv/Vis spectroscopy studies demonstrated that clay can induce aggregation of a tetra-cationic metalloporphyrin into a layer by layer self-assembled film. The resultant aggregates in the films are ultrathin [10]. The water soluble porphyrin (TPPS) is an anionic compound that has been used as a stain in order to analyze bacterial cells [11].

The interaction of porphyrins with clays has been widely studied since the late 1970's [12-16]. The presence of porphyrins is evidence for the biological source of petroleum. Porphyrins exist in both animals and plants tissue [15]. When porphyrins are adsorbed on clay saturated with metal cations in the exchange

sites, metalloporphyrin complexes form [16]. The ability to form these complexes is restricted to cations, which have a suitable size to fit into a porphyrin ring [17]. A study on the stability of metal-porphyrins on clays found that vanadyl and nickel complexes are the most stable. They found that Mg-porphyrin is unstable when it comes in contact with clay [18]. Metalloporphyrin ions were found to be intercalated in the montmorillonite interlayer perpendicularly, diagonal and horizontally [19]. The reaction of TPPS with metal ions is particularly interesting, since this compound is soluble in water. We have previously studied the reactions of Fe(III)TPPS and Fe(II)TPPS in water [20-22].

The aim of the studies presented in this work is to understand the mechanism of metal incorporation into the porphyrin ring in the presence of clays and the behaviour of these complexes on wet and dry clay surfaces.

2.0 METHODOLOGY

The MMT sample was obtained from Podmore and Sons LTD. All chemicals used in this work were of analytical grade obtained from Sigma-Aldrich. The electronic absorption spectra were recorded on Perkin-Elmer Lambda 5 Uv/Vis and Beckman DU-7 spectrophotometers. The spectra of the solid samples were collected as water suspensions. The Diffuse reflectance spectra of the solid samples were recorded on a Unicam SP. 700 spectrophotometer in the 30000-14000 cm^{-1} rang. The Mössbauer spectra were recorded on Canberra Multichannel Analyzer using ^{57}Co as a source. X-ray diffraction patterns were recorded on a Philips diffractometer using CuKa radiation. The tetra(*p*-sulphophenyl)porphyrin was prepared by some modification on the method described by other researchers [23].

Preparation of Metal Exchanged MMT

The metal-MMT samples were prepared by shaking the clay sample on a magnetic stirrer with 1 M solution of the chloride salts of Fe(II), Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Sn(IV) ions for 24 hours in distilled water. Fe(II) MMT was prepared under nitrogen. The clay 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 in air overnight and then grinded. UO_2^{2+} MMT was prepared by dissolving 5 g of $UO_2(CH_3COO)_2.2H_2O$ in 100 ml of distilled water, then 1 g MMT was added. The suspension was stirred for 24 hours, then filtered and air dried.

TPPS Adsorption on Metal Exchanged MMT

In each experiment I gram of metal MMT was added to 75 ml of 10% TPPS in distilled water at PH 6. The mixtures were stirred at room temperature for 24 hours, after which the slurries were filtered, washed several times with the distilled water and air dried.

3.0 RESULTS AND DISCUSSION

TPPS Characterization

The tetra(*p*-sulphophenyl)porphyrin TPPS (Figure 1) exists as a free base above pH around 4 and as a diacid below this pH. The solution which is green at low pH turns to purple as the pH is raised. The visible absorption spectrum of the free base in water is characterized by a Soret band at 411 nm and four other bands (Q bands) at 515, 552, 580 and 633 nm. The spectrum of the diacid in water is characterized by a Soret band at 434 nm and two other bands (Q bands) at 595 and 644 nm [23] (Figure 2). The presence of two Q-bands points to an increased symmetry of the porphyrin core. In this case two additional protons are present.
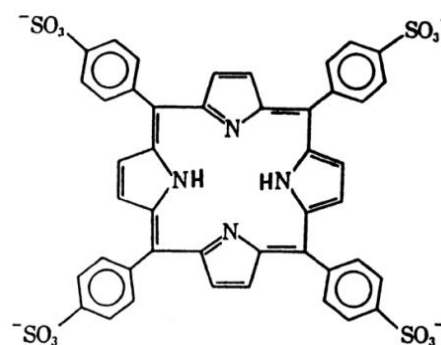

Figure 1 Structure of TPPS

Fe(II) and Fe(III) MMT

The adsorption of TPPS onto Fe(II) MMT was carried out under nitrogen. Less than 1 hour after the start of the reactions with both Fe(II) and Fe(III) MMT, the formation of some kind of Fe(II) and Fe(III) porphyrin complexes was evident from the visible spectra, however the reaction with Fe(II) was faster. The four bands of the free base TPPS in the 500-700 nm region were replaced by a band at 529 nm, with a shoulder at 500 nm in the case of the Fe(II) MMT and a band at 539, with a shoulder at 576 nm in the case of the Fe(III) MMT. The Soret band for both complexes appeared at 412 nm in a water solution (Figure 3). The slow formation of the Fe(III)TPPS complexes can be accelerated by heating the mixtures at 50° C. The positions of the Fe(II) and Fe(III) TPPS bands are slightly different from those reported for the same complexes in solution after refluxing [20-24]. We have previously studied the reactions of both Fe(III) and Fe(II) with TPPS in aqueous solution as a function of pH [20-22]. In the case of the Fe(III)TPPS two different species are found in solution. It was shown that at very low pH values less than 2.0 only five coordinate high spin Fe(II)TPPS molecules are present (Soret band at 392 nm and a further band at 528 nm) and above pH 4.0 only μ-oxo-oligomers which contain two high spin Fe(III)porphyrins

connected by a μ-oxo-bridge (Soret band 415 nm and a further band at 565 nm) are found [20, 21]. This agree with those reported by others [23] but are clearly different to those found in this work, see Figure 3 and Table 1.
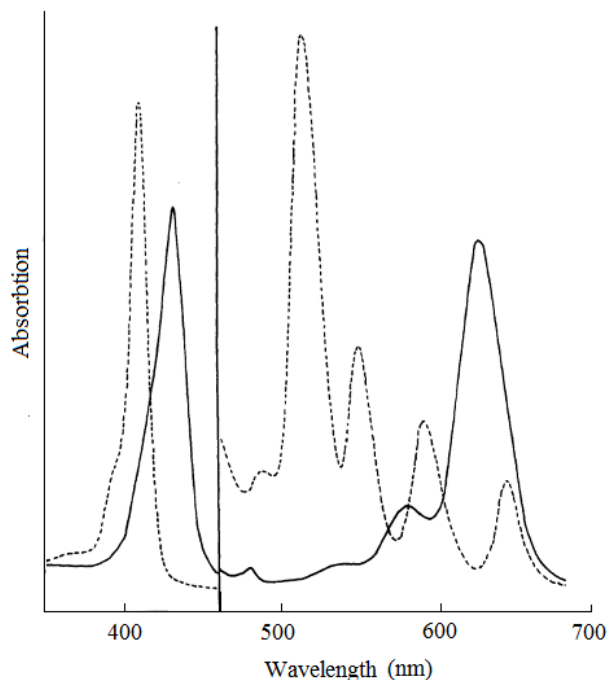

Figure 2 Visible absorption spectra of TPPS (——) diacid, (….......) free base

The fact that the spectrum found for the Fe(III)TPPS complex reported in this work is closer to but not the same as that of the μ-oxo-oligomers of Fe(III)TPPS is strong evidence that it is a new unreported complex that does not exist freely in aqueous solution. It is likely to be related to the μ-oxo-oligomers of Fe(III)TPPS but still bound in somewhat to the MMT surface. So this is evidence that the Fe(III)TPPS complexes remain closely associated with the clay surface through bonding that is strong enough to affect the observed absorbance spectrum.

The spectra of the Fe(II)TPPS MMT complex is not similar to those previously found in aqueous solution for different spin states [22]. This is evidence that the Fe(II)TPPS formed in this work does not become free in solution but is still bound in some way to the MMT surface.

Thus in the cases of the two iron TPPS complexes there is evidence that they are both associated with the surface of the MMT. The powdered samples retained a brown-orange colour after filtration. The brown-orange colour of the Fe(II)TPPS MMT sample is more stable than the Fe(III)TPPS MMT complex. Leaving the two samples exposed to the atmosphere, or by applying a mild heat, the colour is seen to change to green which is evidence of demetallation. Metallation takes place if the samples are dampened with water. The diffuse reflectance spectra of both brown-orange

samples supported the formation of the Fe(II) and Fe(III) TPPS MMT complexes. The diffuse reflectance spectrum found for the green samples is evidence of the presence of the diacid of TPPS. The position of the bands is similar to those of the visible spectra with a small shift. The reversibility of the re-metalation and demetallation reactions is further evidence for these new complexes to be bound to the MMT surfaces. This is further supported by the presence of shoulders on the Q bands of both the Fe(II) and Fe(III) TPPS complexes reported herein (see Figure 3 and Table 1); the shoulders are evidence that the Fe atoms are not in the porphyrin plane as that would have caused only two Q bands as then the complexes would have been more symmetrical.
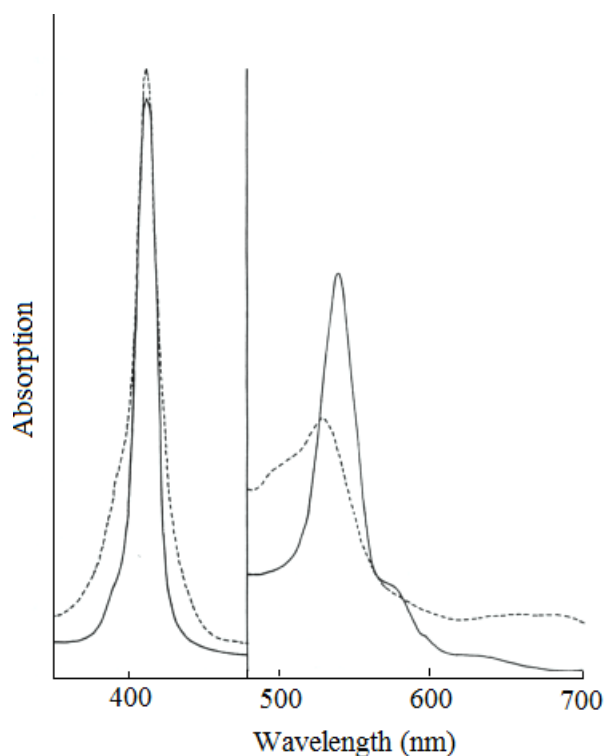

Figure 3 Visible absorption spectra of TPPS solution reacted with (——) Fe(III) MMT, (….......) Fe(II) MMT

Cu(II) and Co(II) MMT

The visible absorption spectra of the TPPS solution a few minutes after the addition of Cu(II) and Co (II) MMT indicated the formation of Cu(II) and Co(II) TPPS complexes. However, the formation of the Cu(II)TPPS complex appeared faster than that of the Co(II)TPPS complex. The formation of these complexes is confirmed by the change in the colour of the mixtures from purple to orange and by the change in the electronic spectra (Figure 4).
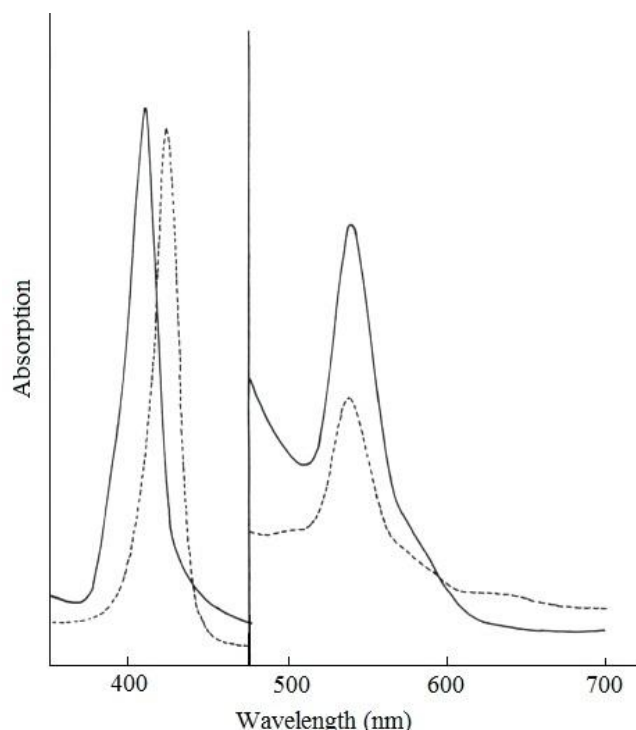
Figure 4 Visible absorption spectra of TPPS reacted with (——) Cu(II) MMT, (.......) Co(II) MMT

In the case of Cu(II) MMT, the Soret band appeared at 411 nm and the four bands of the free base in the 500-700 nm region were replaced by a Q band at 540 nm with a shoulder band at 590 nm. The reaction in the case of Co(II) MMT showed a Soret band at 422 nm and a Q band band at 536 nm with a shoulder around 590 nm with a further small Q band around 635 nm. Again the presence of these additional features in the Q band region indicates that neither the Cu(II) or the Co(II) are in the porphyrin plane centre.

The spectra of both Cu(II) and Co(II) TPPS complexes formed are not similar to those reported in the literature for the complexes formed in refluxed solution [25]. In fact Co(II)TPPS has been reported to have a Soret band at 416 nm and a Q band at 533 nm [26] whereas Cu(II)TPPS has a Soret band at 415 nm and Q bands at 538 nm and 573 nm [27]. The colour of the powder samples after filtration was brown-orange but they changed to green on drying. The appearance of the green colour indicates demetallation of the complex due to the increase of the MMT acidity. This is because removing the water from the clay causes the remaining water molecules around the exchangeable metal cation to become more polarized, which increases the acidity. However wetting the powder samples with water causes them to recover their brown-orange colour, which indicates re-metallation. The Cu(II)TPPS MMT complex turned to green after heating at 110° C for 10 minutes. Leaving the sample in an open atmosphere or wetting with any solvent, results in it recovering its brown-orange colour. The Co(II)TPPS MMT sample turned to green on drying in a dry atmosphere. The diffuse reflectance spectra of

both samples are similar to the absorption spectrum with a small shift of the band positions. Again the findings reported herein for the Cu(II) and Co(II) TPPS complexes are in keeping with these two complexes still being strongly associated with the surface of the MMT.

Ni(II), Zn(II) and Cd(II) MMT

The visible absorption spectra of the TPPS solution about 30 minutes after the addition of Ni(II), Zn(II) and Cd(II) MMT indicated the formation of metal TPPS MMT complexes. The positions of the absorption bands are similar but not the same as those reported in the literature for the metal TPPS complexes formed in refluxed solution [25-29]. In neutral aqueous solution Zn(II)TPPS has a Soret band at 421 nm and Q bands at 555 nm and 595 nm while Cd(II)TPPS has a Soret band at 428 nm and Q bands at 567 nm and 607 nm; [30-34] both these spectra are in fact significantly different to those we recorded from the reactions on MMT (see Table 1). The presence of shoulders on the Q bands of the Ni(II) and Cd(II) TPPS MMT complexes is again evidence that the metal atoms are not symmetrical in the porphyrin plane.

The diffuse reflectance spectra of the three samples indicated the formation of metal complexes. The Zn(II)TPPS MMT sample has a Soret band at 416 nm with a shoulder at 505 nm on the main Q band at 550 nm with a further shoulder on the other side at 595 nm (Figure 5). When this brown orange sample was heated at 110° C for 10 minutes under air it turned green. However, the spectrum of this green powder showed a blue shift in the Soret band of about 20 nm compared to the diacid of TPPS. This band appeared as an asymmetric broad band, indicating the presence of more than one species. The shoulder at 505 nm on the Q band disappeared, and a new Q band at 555 nm was present along with a second Q band at 609 nm. This latter Q band manifested a shoulder towards the red wavelengths. The change in colour to green on heating these samples also indicates demetallation. When this sample was examined again after exposure to the atmosphere for 15 minutes, the brown-orange colour had appeared again and it manifested a spectrum similar to that of the unheated sample. The Soret band was again in the original position at 416 nm. The shoulder and the other two bands also appeared in the same positions indicating remetallation of the Zn(II) complex.

When the sample was exposed to the open atmosphere, it adsorbed water vapour. This water vapour increases the water content of the samples, which helps in introducing the metal ions to the porphyrin ring. Again the presence of the additional features in the Q band region of the ZnTPPS MMT complex are evidence for the metal atoms not being in the centre of the porphyrin rings, and are evidence for additional bonding of the complexes to the MMT surface.
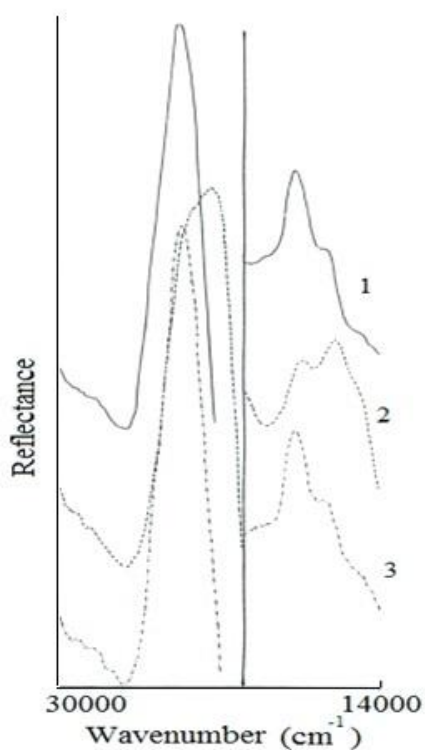
Figure 5 Diffuse reflectance spectra of TPPS adsorbed on Zn (II) MMT (1) unheated sample, (2) the sample heated at 110° C for 10 minutes, (3) the heated sample after exposing to air

The Ni(II) and Cd(II) samples needed less heating for demetallation. The exact nature of the species present when the Zn MMT TPPS complex was heated at 110° C for ten minutes is not known but it is likely that one is the diacid of TPPS and the other may be an intermediate form between the latter and the metallized form.

Sn(IV) and UO_2^{2+} MMT

The visible absorption spectra of the solutions resulting from the reaction of TPPS and the MMT samples saturated with Sn(IV) and UO_2^{2+} cations, after less than 1 hour reaction time indicated the formation of Sn(IV) and UO_2^{2+} TPPS complexes. The Sn cations originally present in the exchange sites of the MMT sample were both Sn(II) and Sn(IV), but the complex formed is Sn(IV) TPPS MMT, as verified by Mössbauer spectroscopy. The Mössbauer spectrum of the sample had an isomer shift of 0.13(1) mms^{-1} and quadrupole splitting of 0.62(1) mms^{-1}, which correspond to Sn(IV). The visible absorption spectrum of the Sn(IV) TPPS is similar to the spectrum of the complex formed in refluxed solution, [35, 36] though the spectrum reported in this work has a shoulder on one of the Q bands. The visible absorption spectrum of the complex formed in the presence of the UO_2^{2+} ion in the exchange sites of the MMT sample, is similar to those reported for the lanthanide and actinide tetraphenylporphyrin formed in refluxed solution [37] again except for the presence of a shoulder on one of the Q bands (Table 1).

The formation of both Sn(IV) and UO_2^{2+} TPPS complexes is very slow and the yield is very poor, but the reaction time can be reduced by heating the mixtures at 50° C. The diffuse reflectance spectra of both samples indicate the formation of metallocomplexes, but the observations of reversible reactions are indicative of complexes still chemically bound to the MMT surfaces. The additional features on the Q bands of the complexes are also evidence for this.

The Rates of the Metalloporphyrin Formation

The rates of the metalloporphyrin formation in the reactions of TPPS with the metal ion-exchanged MMT materials seems to follow the order of the rates of incorporation of the metal ions into porphyrins in aqueous solution, [38] that is: Cu(II) > Zn(II) > Co(II) > Fe(II) > Ni(II) > Cd(II), followed by Fe(III), Sn(IV) and UO_2^{2+} ions, where the formation of the metalloporphyrin was slower. This finding is very interesting as there is evidence outlined above for these complexes still being bound to the MMT surfaces.

The clay acts as a catalyst by introducing the metal ions to the porphyrin ring which is held in a preferred orientation for the incorporation of the metal ion compared to that in solution. It also appears that the resulting complex is closely bound to the MMT surfaces.

When the reaction between TPPS and the cations were carried out in the absence of the clay, the significant catalytic role of the clay became obvious. Cations like Fe(III) and UO_2^{2+} were not able to form complexes with TPPS in water as they are only soluble at acid pH's where the diacid of TPPS is favored (see references 20, 21 and 22). Solubility of TPPS in water plays a significant role in the metalloporphyrin formation process on the clay, since the water forms the hydrated coordination sphere around the metal cations and can also penetrate the clay. The metalloporphyrin complexes once formed desorb at the most only partially into solution, leaving behind their protons that are displaced from the porphyrin ring upon metalation on the clay, these presumably balance the charges in the clay when the metal ions leave.

The Absorption Spectra-Transformation from the Free Base TPPS to the Metallo Form

The initial formation of the metalloporphyrin MMT complexes of the Fe(II), Fe(III), Cu(II), Co(II) ions was almost instantaneous and cannot be followed spectrophotometrically easily, while the formation of the metalloporphyrin MMT complexes of the Ni(II), Zn(II), Cd(II), Sn(IV) and UO_2^{2+} cations, which have similar final spectra, were slower and the change in the spectra from the free base TPPS to the metallo form took more than 25 minutes to occur. However, the formation of the Sn(IV)TPPS and UO_2^{2+} TPPS could not easily be followed because of the poor yields and incomplete conversion.

The reaction of the Zn(II) MMT and TPPS was followed spectrophotometrically by observing the change in the Q bands in the 500-700 nm region (Figure 6). The four bands of the free base TPPS undergo transformation to those of the Zn(II)TPPS MMT complex within 25 minutes. The speed of this reaction opened the opportunity of further studies on the complex as explained in the following section.

Table 1 The visible absorption spectra of the TPPS compound and the spectra of the metal-TPPS complexes resulting from the reaction of the TPPS compound and the cation-exchanged MMT

Complexes	Bands positions (nm)
TPPS free base	411, 515, 552, 580, 633
TPPS diacid	434, 595, 644
Fe(II) TPPS	412, 510 (shoulder), 529
Fe(III) TPPS	412, 539, 576 (shoulder)
Cu(II) TPPS	411, 540, 590 (shoulder)
Co(II) TPPS	422, 536, 590 (shoulder), 635
Ni(II) TPPS	420, 518 (shoulder), 555, 595
Zn(II) TPPS	418, 517 (shoulder), 556, 592
Cd(II) TPPS	414, 520 (shoulder), 561, 606
Sn(IV) TPPS	420, 518 (shoulder), 555, 592
UO_2^{2+} TPPS	418, 514 (shoulder), 555, 592

Stability of the Cu(II)TPPS and Zn(II)TPPS off the Clay

The stabilities of the Cu(II)TPPS and Zn(II)TPPS MMT complexes formed in these experiments and adsorbed onto the clay surface have been examined off the clay, after they have been collected and separated from the clay mixtures. This was carried out by filtering the solutions containing the Cu(II)TPPS and Zn(II)TPPS MMT complexes. The resulting solutions showed the same spectra as before filtration, and the complexes must have therefore been present as nanoparticles in the filtrates. The Cu(II)TPPS MMT, was found to be stable towards reducing the pH of the solution, whilst the Zn(II)TPPS MMT demetallated on reducing the pH of a solution. Figure 7 shows the change in the visible absorption spectra in the Soret band region for the complex at pH 2.9. This process was found to be time dependent. Each spectrum was taken 2 minutes after the previous one. The Soret band at 419 nm started to decrease in intensity, and a new band at 434 nm corresponding to the diacid TPPS started to appear. The isosbectic point visible around 430 nm is evidence that only two species are present during the experiment the starting species and the final species.
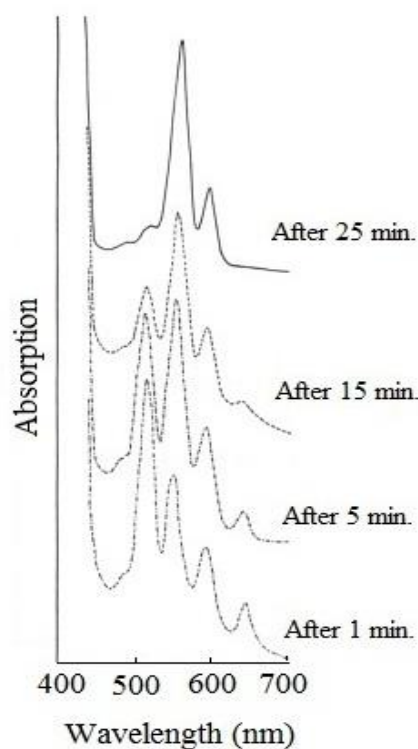

Figure 6 Typical visible absorption spectra of Zn(II)TPPS formation from the reaction of Zn(II) MMT and TPPS. Time of reaction is indicated
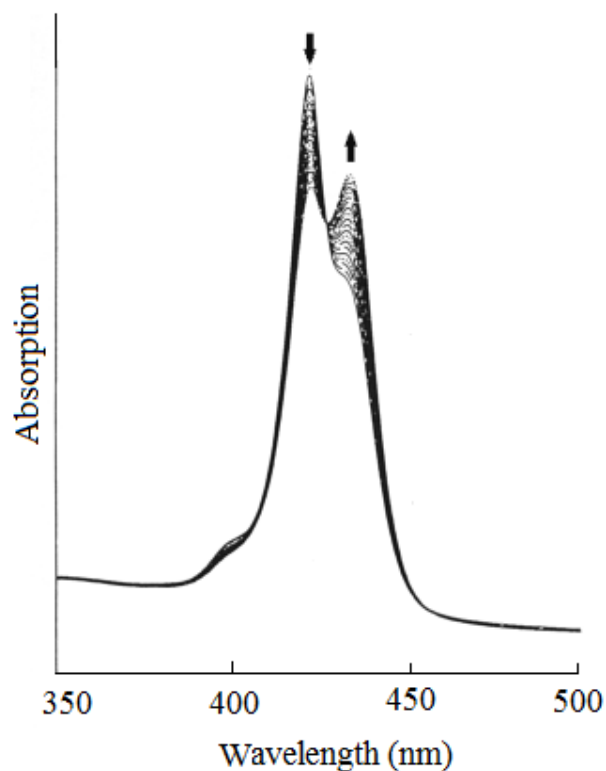

Figure 7 Visible absorption spectra in the 350-500 nm region of Zn(II)TPPS losing Zn(II) at pH 2.9, over a total time of 40 minutes. Each successive spectrum was taken 2 minutes after the preceding one

The reaction was also followed in the 500-700 nm region, at pH 2.9 (Figure 8). Again an isosbestic point is present around 590 nm is evidence that only two species are involved. The intensity of the shoulder at 517 nm and the band at 556 nm started to decrease, concomitantly the band at 592 nm started to increase in intensity. Also the band at 644 nm corresponding to the diacid TPPS appeared and started to increase in intensity. This behaviour in both the Soret band and the 500-700 nm regions indicates that the complex demetallates around pH 3.

The process of demetallation at the start of the reaction is represented by the straight line in Figure 9, in which the absorbance A of the band at 644 nm is plotted against the time t. The reaction then slowed down. The rate constant of the reaction has been calculated by plotting:

$$\ln A\text{-}A_\infty \ / \ A_0\text{-}A_\infty$$

against the time t, [39] where A, A_∞ and A_0 are the absorbance at t = t, t = ∞ and t = 0 respectively (Figure 10). The straight line indicates a first order rate equation showing that one species is being replaced by another. There is only a slight deviation from at the end of the experiment.

The rate equation can be expressed as:

$$\ln A\text{-}A_\infty \ / \ A_0\text{-}A_\infty = - kt$$
$$\text{Slope} = -0.6 \ / \ 9.6 = -0.0625 \ \text{min}^{-1} = -K$$
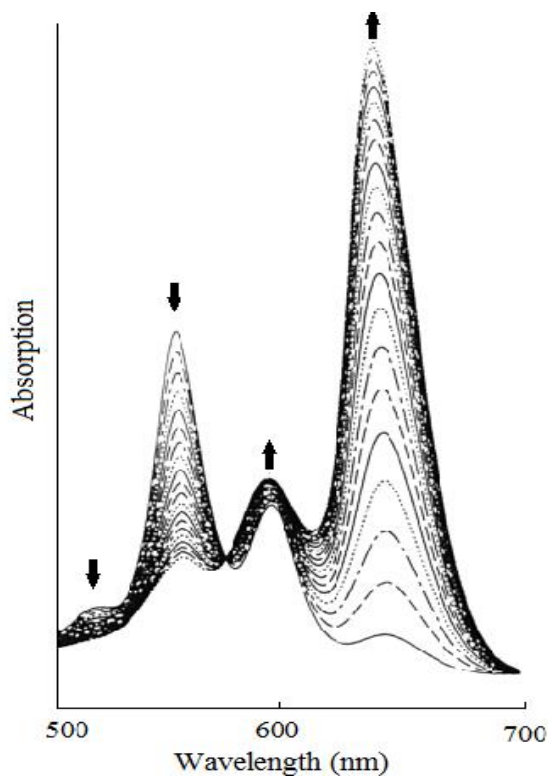$$K = 0.0625 \ \text{min}^-$$

Figure 8 Visible absorption spectra in the 500-700 nm region of Zn(II)TPPS losing Zn (II) at pH 2.6, over a total tine of 40 minutes. Each successive spectrum was taken 2 minutes after the preceding one

Intercalation of the Metal-TPPS Formed

X-ray powder diffraction studies showed that the TPPS compound is only externally adsorbed onto the clay surface, even after 24 hours of reaction, which is unexpected. In order to facilitate the intercalation process, the clay lattice was opened by dispersing 1 g of the sample in a solution of NaCl, as the sodium ions are able to open the interlayer to about 20 Å in solution. The mixture was stirred for 1 hour and then a TPPS solution was added. The slurry was left stirring for 24 hours, then filtered, washed and air dried. The X-ray diffraction pattern of the sample gave a basal spacing of 14.2 Å, which indicates an interlayer separation of 4.6 Å which is the approximate thickness of the porphyrin molecule [40]. Heating the sample at 120° C causes the interlayer space to be reduced to 4.2 Å. This reduction could indicate a change in orientation of the porphyrin relative to the clay structure (or part of the porphyrin molecule such as the phenyl rings becoming more into the porphyrin plane) or more likely it is due to the removal of water molecules that were loosely interacting with the TPPS molecules in the clay.
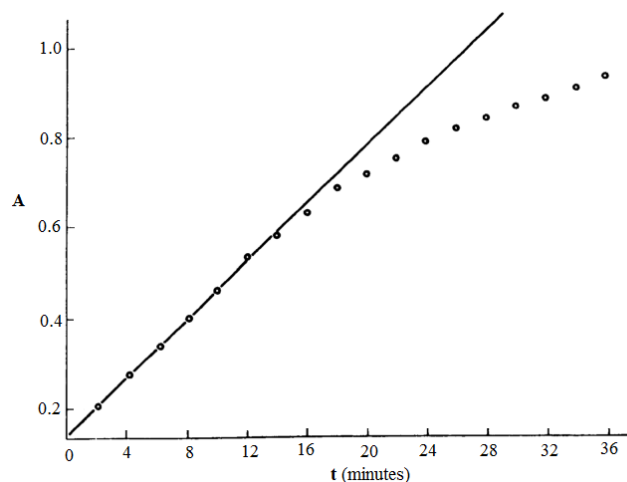

Figure 9 Plot of the absorbance against time for the 644 nm band in Figure 8 of the demetallation of Zn(II)TPPS
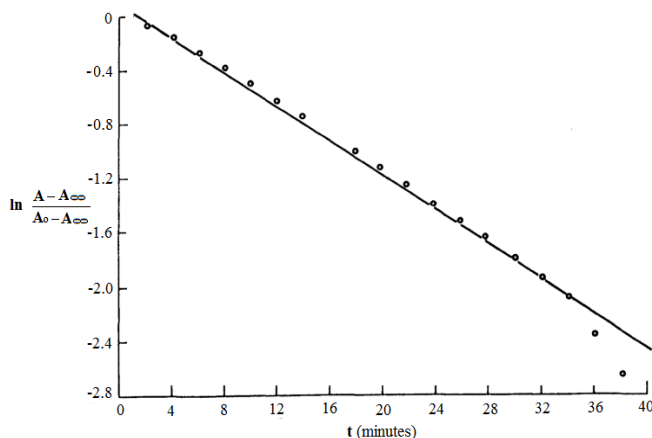

Figure 10 The relationship between ln A-A_∞ /A_0-A_∞ and the time for the 644 nm band

Structure of the Metal-TPPS-MMT Complexes

The fact that the spectra of all the complexes presented herein manifest evidence of none symmetrical environments rather than having the metals at the centre of the porphyrin planes would be in keeping with the complexes being described as sitting atop complexes (SAT complexes) where the metals are still partially bonded to the MMT. Thus, when the metallisation reactions take place we envisage the porphyrin to have already bound to the clay surface through the protons of the diacid species. The metal atoms then displace some of the protons binding in part to some of the central 4 pyrolic-nitrogen atoms in the porphyrin ring. The ring concomitantly moves slightly away from the MMT surface so the phenyl rings can rotate out of the porphyrin plane causing the colour change from green to orange brown. The metal atom still is bound to the clay via probably bridging water or OH⁻ molecules. When the pH is made acidic the process reverses and the metal returns to the clay and the porphyrin return to the clay surface as the diacid which binds to the clay via either the central protons or possible also by the SO_3^- groups on the phenyl rings which must have rotated into or much closer to the porphyrin plane extending the conjugation and causing the green colour of the diacid.

Structures of the kind we have outlined above for the metal TPPS MMT complexes reported herein are thought to be similar to the metallo porphyrin SAT complexes reported in the literature [40-48].

4.0 CONCLUSION

Metallocomplexes of the TPPS with Fe(II), Fe(III), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Sn(IV) and UO_2^{2+} cation are formed during the adsorption of the free base on the metal exchanged MMT with these cations. The incorporation of the metal ion on/into/with the porphyrin ring follow the order: Cu(II) > Zn(II) > Co(II) > Fe(II) > Ni(II) > Cd(II) > Fe(III) > Sn(IV) > UO_2^{2+}. The colour of the powdered sample was brown-orange due to the formation of the metal SAT complexes of these cations. The metallation-demetallation process of some samples can be easily observed by heating the powdered samples. The colour of the powder change from brown-orange, (which indicates the presence the metallo SAT complexes) to green, (which is the colour of the diacid of TPPS). When the green powders were exposed to the open atmosphere they absorb water vapour, the brown-orange colour appeared again due to the remetallation. The cations remain in the vicinity of the porphyrin upon demetallation which makes the metallation-demetallation process reversible. The TPPS has been found to be adsorbed only on the external surface, of the clay but can be intercalated using sodium ions in solution with the TPPS to open the MMT lattice.

It has been shown herein that the clay acts as a catalyst in the chemistry taking place on the surface of the MMT with the cations and TPPS, and the complexes formed are not those that would form in the absence of the MMT.

Finally as the clay particles can be very small (nanometer size) the metal SAT TPPS MMT complexes can float in solution.

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