# INTERCALATION OF PORPHYRINS INTO Mg-Al HYDROTALCITE

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## Abstract

We present the structural and photophysical properties of Mg-Al hydrotalcite-like compounds intercalated with porphyrins. The anion exchange and rehydration methods were used for porphyrin intercalation into the host structure. The porphyrin anions have a tilted orientation with an angle of about 70° with respect to the hydroxide layers of hydrotalcite; the similar orientation was found also in the partially exchanged samples with a low porphyrin loading. Both intercalated and adsorbed porphyrin molecules preserved their photoactive monomeric form. The photophysical experiments proved that the porphyrin-doped materials have enough long lifetimes of the porphyrin triplet states to produce singlet oxygen, $^1O_2$, with high efficiency. Mg-Al hydrotalcite is an excellent host for imbedding of the photoactive compounds.

## Introduction

Hydrotalcite, magnesium-aluminum hydroxycarbonate, is a naturally occurring mineral of the chemical composition $Mg_6Al_2(OH)_{16}CO_3\ 4H_2O$. This mineral exhibits a layered crystal structure similar to that of brucite, $Mg(OH)_2$, where each $Mg^{2+}$ cation is octahedrally surrounded by six hydroxyl groups and the adjacent octahedra share edges to form infinite sheets. The sheets are stacked one on top of the other and are held together by hydrogen bonding. In hydroxide sheets of hydrotalcite, an $Mg^{2+}/Al^{3+}$ isomorphous substitution in the octahedral sites results in a net positive charge neutralized by interlayer anionic species. Hydrotalcite has been taken as a reference name for many isomorphous compounds of various chemical composition, which can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\ yH_2O]^{x-}$, where $M^{II}$ and $M^{III}$ are divalent and trivalent metal cations, $A^{n-}$ is n-valent anion and x varies usually between 0.20 and 0.35. These materials, known as hydrotalcite-like compounds, layered double hydroxides or anionic clays, offer a great variety of applications, e.g., in heterogeneous catalysis, polymer processing, adsorption and decontamination processes and pharmacy [1-4]. Hydrotalcite-like compounds represent also a host inorganic structure for preparation of hybrid materials with interesting physical and chemical properties.

Hydrotalcite-like compounds are characteristic by a weak bonding between interlayer anions and hydroxide sheets. Thus, anions can be exchanged under suitable conditions. Carbonate anions are the most preferred ones in this process and their replacement by anion exchange is very difficult. Therefore, the synthesis of hydrotalcite-like compounds containing specific interlayer anions requires carbonate- and $CO_2$-free conditions. The preparation of nitrate- or chloride-containing hydrotalcite-like compounds has been reported by Miyata [5]. Because interlayer $Cl^-$ or $NO_3^-$ anions can be easily exchanged, chloride and nitrate forms of hydrotalcite-like hosts are often used as precursors in anion exchange reactions.

An alternative procedure is rehydration of mixed oxides obtained by thermal decomposition of a hydrotalcite-like precursor containing volatile interlayer anions (e.g., $CO_3^{2-}$, $NO_3^-$). During heating of Mg-Al-$CO_3$ hydrotalcite, interlayer water is released at about 200 °C. At higher temperatures (350 – 450 °C) dehydroxylation of the hydroxide layers is accompanied by a loss of interlayer carbonate anions and the layered crystal structure collapses to periclase-type Mg-Al mixed oxide. Such mixed oxides prepared at moderate calcination temperatures ranging between 400 – 600 °C can be rehydrated in an aqueous solution. It results in the reconstruction of the layered hydrotalcite structure containing intercalated anions from the solution. This phenomenon is known as the "memory effect" and the rehydration procedure is often used for intercalation of various anions into the hydrotalcite-like hosts.

In the present study we report procedures for intercalation of porphyrins into the Mg-Al hydrotalcite host structure. Porphyrins and related macrocycles are well known as photosensitizers producing singlet oxygen ($^1O_2$), a short living and highly reactive form of molecular oxygen [6]. Singlet oxygen is involved in numerous oxidative processes and can cause a serious damage of biological systems. On the other hand, its oxidative potential can be utilized in chemical syntheses, photodynamic treatment of cancer and disinfection. The synthesis of layered double hydroxides intercalated with various porphyrin anions have been described [7-10], but no their photophysical properties and singlet oxygen production activity have been addressed so far. The sensitizer-doped inorganic host materials developed in this work are not only of utmost interest in terms of solid state photophysics, but also offer relevant applications as photo-disinfecting materials and effective sources of singlet oxygen.

## Experimental

### *Preparation of samples*

The tetrasodium salt of 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, TPPS, (Aldrich), Pd(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, PdTPPC, Zn(II)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (both Frontier Scientific Europe, Ltd., UK), $Mg(NO_3)_2$ $6H_2O$, $Al(NO_3)_3$ $9H_2O$, $MgCl_2$ $6H_2O$, $AlCl_3$ $6H_2O$, NaOH, and $Na_2CO_3$ (all Penta, Czech Republic) were used as purchased.

Synthesis of hydrotalcite hosts: The hydrotalcite hosts in the nitrate and chloride forms were prepared by coprecipitation according to Miyata [5]. Carbonate-free distilled water was used for dissolution of chemicals and the preparation was carried out under nitrogen to avoid any contamination of the product by carbonate anions. An aqueous solution (450 ml) of $Mg(NO_3)_2$ $6H_2O$ and $Al(NO_3)_3$ $9H_2O$ with Mg/Al molar ratio of 2 and total metal ion concentration of 1.0 mol $l^{-1}$ was added with a flow rate of 7.5 ml $min^{-1}$ into a 1000 ml reactor containing 200 ml of distilled water. A flow rate of simultaneously added 3M NaOH was controlled to maintain pH 10.0 ± 0.1. Coprecipitation was carried out under vigorous stirring at 75 °C. The resulting suspension was stirred for 1 h at 75 °C. The product was filtered off, washed several times with distilled water and dried at 60 °C. The obtained hydrotalcite was denoted as $Mg_4Al_2$-$NO_3$. The chloride form of hydrotalcite with Mg/Al molar ratio of 2, $Mg_4Al_2$-Cl, was prepared using $MgCl_2$ $6H_2O$ and $AlCl_3$ $6H_2O$ under the same conditions as described above. Similarly, carbonate hydrotalcite, $Mg_4Al_2$-$CO_3$, was prepared by coprecipitation of Mg and Al nitrates; an alkaline solution containing 3M NaOH and 0.5M $Na_2CO_3$ was used as a precipitation agent.

Anion exchange: The relevant hydrotalcite precursors were dispersed in a carbonate-free aqueous solution (400 ml) of corresponding porphyrin (0.001M, pH 9 adjusted by 3M NaOH). Porphyrins TPPS and ZnTPPC were intercalated into the $Mg_4Al_2$-$NO_3$ precursor, while PdTPPC into $Mg_4Al_2$-Cl one. After mixing the components, the suspension was sealed in a 500 ml glass bottle under nitrogen and stirred for 6 days at 30 °C. The intercalated products were filtered off, washed with carbonate-free distilled water and dried at 60 °C. The hydrotalcite host/porphyrin molar ratio was adjusted to achieve 10 and 100% loading with respect to the theoretical anion-exchange capacity (AEC). A 10% excess of porphyrin was used for the preparation of the samples with 100% loading. The obtained samples were denoted by acronyms describing the Mg/Al molar ratio in the hydroxide layers, intercalated porphyrin anion, its loading and the method used for intercalation (anion exchange, AE). For example, the $Mg_4Al_2$/TPPS(10)AE sample was obtained by anion exchange and 10 % of $NO_3^-$ in the $Mg_4Al_2$-$NO_3$ precursor was replaced by TPPS anions.

Rehydration procedure: Carbonate hydrotalcite $Mg_4Al_2$-$CO_3$ was heated 4 h at 450 °C in air and then cooled to room temperature. Obtained periclase-type Mg-Al mixed oxide was dispersed under nitrogen in 75 ml of a carbonate-free aqueous solution of corresponding porphyrin (0.001M, pH 9 adjusted by 3M NaOH) and placed in a 100 ml Teflon lined stainless steel bomb. The rehydration reaction was carried out under hydrothermal conditions at 120 °C and autogenous pressure for 20 h. The rehydrated products were filtered off, washed with carbonate-free distilled water and dried at 60 °C. The Mg-Al mixed oxide/porphyrin molar ratio was adjusted to achieve 10 and 100% loading with respect to the theoretical AEC. A 10% excess of porphyrin was used for the preparation of the samples with 100% loading. The obtained samples were labeled by R (e.g., $Mg_4Al_2$/TPPS(10)R).

### *Characterization of the products*

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5005 diffractometer (Bruker AXS, Germany) with Cu $K\alpha$ radiation ($\lambda$ = 0.1542 nm, 40 kV, 30 mA, beam monochromator) in $2\theta$ range of 2 – 80°, step size 0.02° (10 s/point). The qualitative analysis was performed with a HighScore software package (PANalytical, The Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database. The Diffrac-Plus Topas software (Bruker AXS, Germany, version 2.1) in a combination with structural models based on the ICSD database was used for quantitative analysis of the XRD patterns.

The diffuse reflectance UV-vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer equipped with a Labsphere RSA-PE-20 integration sphere. Transient absorption measurements were performed by means of the diffuse reflectance accessory of a laser flash-photolysis system (LKII, Applied Photophysics) equipped with Xe lamp, arc pulser, monochromator and photomultiplier tube (PMT, R928, Hamamatsu). The 20-ns pulsed laser beam arising from an OPO (Rainbow, Quantel) pumped by Nd:YAG laser (Brilliant, Quantel) was used to excite the porphyrin-doped samples within the 420 – 550 nm range and a power density less than 20 mJ $cm^{-2}$. Time-dependent near-infrared luminescence of singlet oxygen at 1270 nm was monitored in a Ge detector (Edinburgh Instruments, Ltd.) or by a home made detector unit (interference filter, amplifier, Ge diode Judson J16-8SP-R05M-HS) upon laser excitation of the solids.

## Results and discussion

The powder XRD patterns of hydrotalcite-like compounds intercalated with TPPS are demonstrated in Fig. 1. The $Mg_4Al_2$/TPPS(100)AE sample exhibited a marked shift of the basal (003) diffraction line to lower diffraction angles, which confirmed intercalation of bulky porphyrin anions into the interlayer space. The $d_{003}$ value of 8.77 Å corresponding to the $Mg_4Al_2$-$NO_3$ precursor increased to about 22 Å (Table 1). Taking into account the thickness of the hydroxide sheet (~ 4.8 Å), the interplanar distance corresponds to about 17 Å. This value indicates that the planar porphyrin units can be oriented perpendicularly towards the hydroxide layers with four peripheral sulfo-groups interacting *via* the hydroxyl groups with the positively charged sites of the brucite-like sheets [7]. Based on the analysis of the TPPS solution before and after anion exchange, the TPPS loading reached about 80 % of AEC. The TPPS-intercalated phase with $d_{003}$ of about 22 Å was also confirmed in the $Mg_4Al_2$/TPPS(10)AE sample (Table 1). It means that TPPS anions are oriented similarly to the $Mg_4Al_2$/TPPS(100)AE sample regardless of the low porphyrin loading.

**Table 1.** The porphyrin loading of the intercalated hydrotalcite samples and the evaluated $d_{003}$ values.

| Sample | Porphyrin loading (% AEC) | $d_{003}$ (Å) |
|---|---|---|
| $Mg_4Al_2$-$NO_3$ | - | 8.77 |
| $Mg_4Al_2$-OH | - | 7.63 |
| $Mg_4Al_2$/TPPS(100)AE | 80 | 22.5 |
| $Mg_4Al_2$/TPPS(100)R | 70 | 21.4 |
| $Mg_4Al_2$/PdTPPC(100)AE | not determined | 23.3 |
| $Mg_4Al_2$/PdTPPC(100)R | 72 | 22.4 |
| $Mg_4Al_2$/ZnTPPC(100)R | 70 | 22.4 |
| $Mg_4Al_2$-$CO_3$ | - | 7.64 |

According to the molecular modeling results [11], the plane of guest porphyrin anions is tilted with an angle of about 70° with respect to the hydroxide layers. The porphyrin units are parallel and shifted to each other with a shift approximately a half of the anion diameter. The tilted orientation of porphyrin anions can be explained by the presence of interlayer water as the water molecules predominantly fill the space between the hydroxide layers and porphyrin molecules due to a rather hydrophobic character of the porphyrin ring. The molecular modeling of the hydrotalcite structure with a low porphyrin content in the interlayer space showed similar orientation of porphyrin anions.

During rehydration of the calcined $Mg_4Al_2$-$CO_3$ precursor, the hydroxide form ($Mg_4Al_2$-OH) with the basal spacing $d_{003}$ of 7.63 Å was formed. The intercalated phase with $d_{003}$ of 21.4 Å together with the admixture of the $Mg_4Al_2$-OH phase were found in the samples rehydrated in porphyrin-containing solutions (Fig. 1). The $d_{003}$ value of the intercalated phase was close to that of the samples prepared by anion exchange. Evidently, during the rehydration process hydroxide anions in the interlayer space are substituted by the porphyrin molecules.

A series of the $Mg_4Al_2$-$CO_3$ samples with adsorbed porphyrins was prepared in order to compare photophysical properties of intercalated and adsorbed porphyrins. The samples were prepared under the same hydrothermal conditions as the rehydrated ones using the $Mg_4Al_2$-$CO_3$ precursor in a porphyrin-containing solution. The hydrotalcite/porphyrin molar ratio was adjusted to achieve a 10 % loading with respect to the theoretical AEC. The obtained products exhibited no shift in $d_{003}$ basal spacing, i.e. no porphyrin intercalation took place (Fig. 2). These samples were denoted as “ads”.

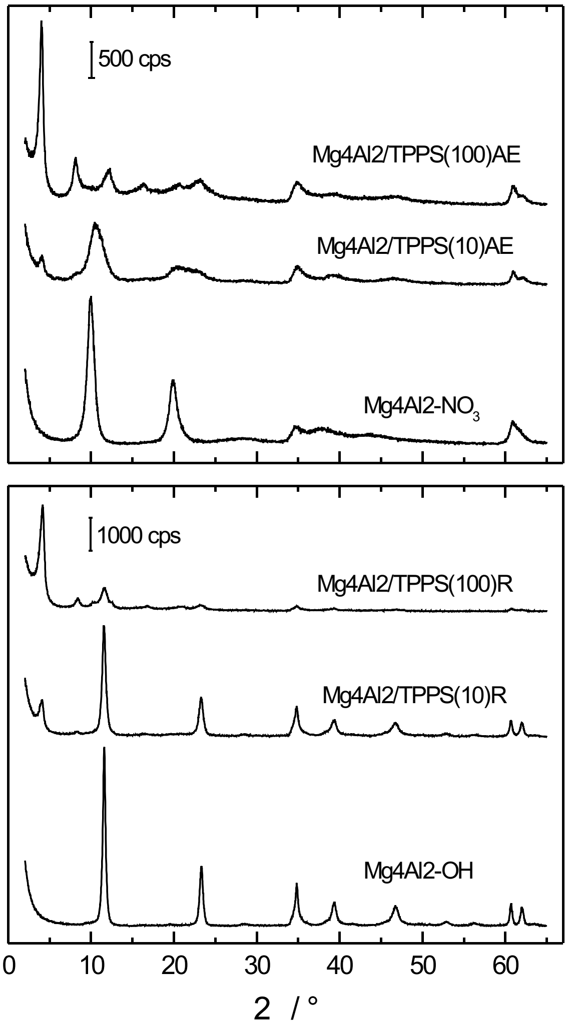

**Figure 1.** Powder XRD patterns of Mg-Al hydrotalcite intercalated with TPPS by the anion exchange (AE) and rehydration (R) methods: $Mg_4Al_2$-$NO_3$ – starting material for anion exchange, $Mg_4Al_2$-OH – product obtained by rehydration in distilled water, $Mg_4Al_2$/TPPS(100) and $Mg_4Al_2$/TPPS(10) – products obtained under concentration conditions for 100% and 10% porphyrin loading with respect to the theoretical AEC.

Diffuse reflectance UV-vis spectroscopy showed that neither intercalated nor adsorbed porphyrin molecules aggregate when bound to the hydrotalcite hosts, but predominantly preserve the photoactive monomeric form. Since the kinetic parameters of the sensitizer triplet states predetermine the $^1O_2$ formation, the triplet state dynamics within solid hydrotalcite samples was studied by means of time-resolved diffuse reflectance [12]. We observed that the triplet states of intercalated and adsorbed porphyrins are quenched by oxygen. In air atmosphere the lifetimes of the triplet states were in the microsecond range. Our attention was focused on the porphyrin samples with 10 % loading with respect to the theoretical AEC since the samples with lower concentration of intercalated porphyrins (2% AEC) yielded small spectroscopy signals and those with

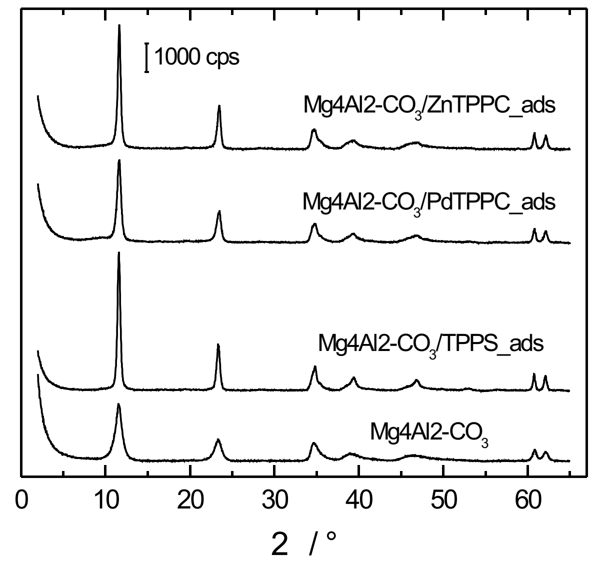

**Figure 2.** Powder XRD patterns of $Mg_4Al_2$-$CO_3$ samples with adsorbed porphyrins.

the highest loading reached (up to 80 % AEC) were optically too dense.

To assess the efficiency of the $^1O_2$ generation we measured its photoluminescence at $_{\mathrm{em}}$ = 1270 nm upon pulsed laser excitation [12]. Emission at this wavelength arises from relaxation of $^1O_2$ back to the triplet ground state. Fig. 3 shows the time dependence of the $^1O_2$ luminescence intensity produced by the samples with intercalated ($Mg_4Al_2$/TPPS(10)AE), and adsorbed porphyrin molecules ($Mg_4Al_2$-$CO_3$/TPPS_ads) in the presence of oxygen. It is evident that the $^1O_2$ signals obtained for the solids containing intercalated TPPS are significantly larger than for those with TPPS adsorbed at the hydrotalcite surface. The most effective producers of $^1O_2$ were the hydrotalcite samples with intercalated or adsorbed PdTPPC molecules. We ascribe it to the higher yield of the triplet state formation of Pd(II)-containing porphyrins. Having proved the ability of the solid samples with intercalated photosensitizers to act as singlet oxygen sources, a contingent application will depend on the lifetime of $^1O_2$ since the longer the lifetime the more powerful its oxidative performance. Therefore, we analyzed the factors determining the singlet oxygen lifetime. The $^1O_2$ lifetimes were derived by a bi- or monoexponential fitting of the singlet oxygen decay curves and varied between 12 and 30 s. The largest lifetimes were obtained with the $Mg_4Al_2$/PdTPPC(10)AE and $Mg_4Al_2$-$CO_3$/PdTPPC_ads samples while excitation of the $Mg_4Al_2$/PdTPPC(10)R sample produced $^1O_2$ with the lifetime of 12 to 15 s. The details of photophysical measurements are discussed elsewhere [12].

## Conclusions

The structural and photophysical properties of the hydrotalcite hosts doped with porphyrin sensitizers were examined. A marked shift of the $d_{003}$ basal spacing indicated a successful intercalation of the bulky porphyrin anions into the hydrotalcite interlayers. Based on $d_{003}$ values and molecular modeling results, the porphyrin anions have a tilted orientation with an angle of about 70° with respect to the hydroxide layers; the similar orientation was found also in the partially exchanged samples with a low porphyrin loading. The photophysical experiments carried out under defined conditions proved that the porphyrin-doped materials exhibit enough long lifetimes of the porphyrin triplet states to produce $^1O_2$ with high efficiency. The properties of the photoexcited triplet states do not seem to be critically altered by the surrounding matrix with respect to their behavior in solution. The lifetime of these triplet states decreases in the presence of oxygen as a result of energy transfer to $O_2$ molecules and generation of $^1O_2$. This process is found to be very effective in case of the PdTPPC-doped samples. Mg-Al hydrotalcite appears to be excellent host for imbedding photoactive compounds. On account of the long lifetime of $^1O_2$ produced by this hybrid material, we conclude that the singlet oxygen molecules generated in the interior of the hydrotalcite matrix can diffuse out of the solid and react with an outer substrate. We envisage hydrotalcite-like compounds with the intercalated PdTPPC molecules as efficient, easy-to-use sources of singlet oxygen.

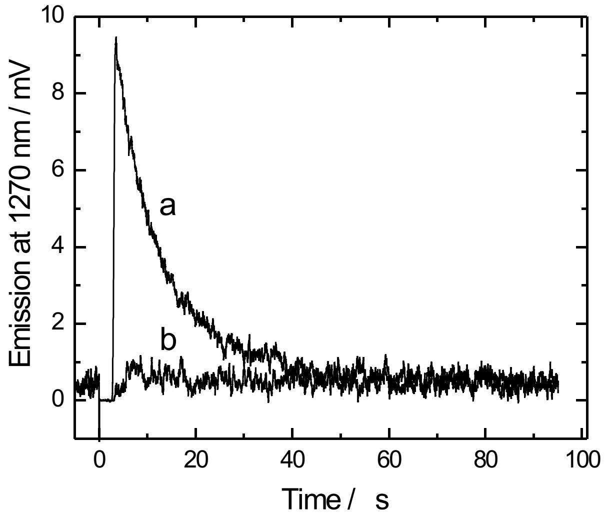

**Figure 3.** Qualitative comparison of the singlet oxygen productivity of the TPPS-containing samples Mg4Al2/TPPS(10)AE (a) and Mg4Al2-$CO_3$/TPPS_ads (b). The solid samples were evacuated before saturation with $O_2$ and Ar and excited at 425 nm using ~ 1 mJ/pulse.

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# ADSORPTION OF THE CATIONIC SURFACTANTS ON MONTMORILLONITE

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## Abstract

Adsorption of cetyltrimethylammonium (CTA) and cetylpyridinium (CP) on Na-rich montmorillonite (MMT) was studied. For this purpose, the adsorption isotherms of CTA and CP along with desorption curves of metal cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) were constructed. The adsorption of CP is well described by the Langmuir isotherm. In the case of CTA, the best fitting Langmuir- Freundlich model with the power constant $r<1$ was found. It can be explained by the CTA higher degree of intercalation into the MMT interlayer space. Infrared, X-ray diffraction patterns, specific surface area, porosity, and moisture adsorption measurements of montmorillonite also revealed that both the surfactants were adsorbed in a monolayer arrangements but CP in a higher amount than CTA.

The results of molecular modelling showed that interaction energies between CTA and the external MMT surface have lower energy values than in the case of CP. This supports an idea that CTA keeps more strongly near the MMT layer and also restrict interaction of another CTA cations with the layer. This finding agrees with the experimental determination of higher amount of CP bound to the MMT face.

## Introduction

Phyllosilicates are layered silicates in which the $SiO_4$ tetrahedra are linked together in infinite two-dimensional sheets and are condensed with the layers of $AlO_6$ or MgO octahedra in the ratio 2:1 or 1:1. The negatively charged layers attract positive cations (e.g., $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) which hold the layers together. Their large cation exchange capacities enable them to adsorb heavy metals and to be modified with quaternary salts [1] including cationic surfactants [2]. One of the exceptional properties of such prepared organo-phyllosilicates is their ability to sorb hydrophobic organic contaminants, such as chlorinated phenols [3,4], perchlorethylene, naphtalene and phenanthrene [5-7], aniline [8] or phenol [9] etc. The retention of inorganic oxyanions, such as chromate, nitrate, and arsenate, on organo-kaolinite [10] and organo-clinoptilolite [11] have been studied, as well.

The aim of this work was to understand the cationic surfactants (CSs) sorption on phyllosilicates in order to prepare efficient and selective organo-phyllosilicate adsorbents. For this study Na-rich montmorillonite was used along with the typical cationic surfactants, such as cetyltrimethylammonium and cetylpyridinium.

## Materials and methods

### *Adsorption procedure*

$Na^+$-rich montmorillonite type Wyoming $(Al_{2.90}Mg_{0.59}Fe^{3+}_{0.49}Ti_{0.01})_{3.99}$ $(Si_{7.92}Al_{0.08})_{8.0}$ $O_{20}(OH)_4$ with a cation exchanged capacity (CEC) about 0.9 meq/g was used as the host structure for the absorption of CTA and CP. The cationic surfactants were dissolved in a mixture of water and ethanol (50:50, v/v), a portion of MMT was added and this suspension was shaken vigorously for 2 hours. The suspension was centrifuged for 20 minutes and a supernatant was analysed by a capillary isotachophoresis and the atomic absorption spectrometry. The organo-montmorillonite samples intended for spectral and surface anal-