

Effect of Hydrocarbon Chain Length Surfactants on Particle Size of SWy-1 Montmorillonite Suspensions

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Abstract-- This paper reports the effect of the length of the alkyl chain of alkylammonium surfactants (C8, C10, C12, C14, C16, C18) on stability and particle size of the SWy-1 Mt suspensions. The particle size of these materials has been analyzed by DLS (Dynamic Light Scattering) and showed no significant change at low surfactant concentrations (~1.2% CEC). In this range of surfactant loadings (0.6 to 12% CEC), the zeta potential remains almost constant, suggesting an ion exchange mechanism. For C8 and C12 surfactants, the results using loading of 12% of CEC show increasing of the proportion of the smallest particles. Considering SWy-1 Mt suspension with C16 (12% CEC), the particle size decreases with the time. This can be attributed to adsorption of surfactant molecules on the external surface and the migration of these molecules to interlayer spaces promoting delamination effect. At higher concentrations of surfactants (95% CEC) zeta potential is close to the *pzc* (point of zero charge), so flocculation takes place. Comparing the delamination behaviour it is possible to observe that surfactants with larger chain lengths, such as C16, promote a more effective breaking of the layers.

Index Term-- surfactants, clay mineral, DLS, Zeta potential

1. INTRODUCTION

Clay minerals are materials that present scientific and technological interest, with wide applications in various areas, like ceramics, paper manufacture, sorption of environmental pollutants, ion-exchangers, etc [1,2].

Some important factors have to be taken into consideration for the application of the clay mineral, such as surface area, brightness, crystallinity, and particle size [3,4].

The widely used montmorillonite (Mt) belongs to the group of smectites, that are 2:1 layered silicates. These silicates are formed by two tetrahedral silica sheets and a central octahedral sheet of magnesia or alumina. The layers organize themselves in a parallel way to form stacks with regular interlayer spaces. These layers are negatively charged due to the isomorphous replacement of some cations by others of similar size but lower charge (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}). The negative charge is balanced by hydrated cations, that can be exchanged by others, placed in the interlayer spaces [5]. The number of the exchangeable cations that a mineral can adsorb determines its cation exchange

capacity (CEC), which ranges between 66 and 123 mequiv/100 g [6]. The presence of these hydrated cations renders the clay mineral surface hydrophilic in nature, making it an ineffective sorbent for organic compounds. Therefore, these clays mineral surface can be modified exchanging the interlayer cations by alkylammonium salts. The adsorption of the organic cations can significantly alter the properties of the mineral, increasing the compatibility with organic polymer matrices. A small quantity of these organomodified clay minerals can also be dispersed in a polymer matrix, at the nanometer scale, leading to a substantial increase of the polymer's physical properties [7,8,9].

Surfactants can be used as dispersing agent and main ingredient in cosmetics, creams, gels, etc. [10,11,12,13]. The adsorption of cationic surfactants onto clay minerals occurs by ion exchange and hydrophobic interaction mechanisms. The interactions between a surfactant and clay mineral depend on several factors such as, the clay mineral structure, potential and sign of the surface, porosity, ion exchange capacity, surface heterogeneity; type of surfactant, hydrocarbon chain length, for ionic surfactant, its polar group; and solution conditions (pH, temperature, polarity, dielectric constant, and ionic strength) [14].

Marras et al. [15] studied the modification of Mt with amphiphilic hexadecylammonium cations. They verified that the conformation of the hexadecylammonium cations inside the interlayer spaces of the clay mineral strongly depends on the amount of the inserted surfactant. Ersoy et al, in a study of the adsorption behaviour of quaternary ammonium cationic surfactants onto clinoptilolite, observed that hydrocarbon chain length of surfactant molecules has a significant effect on the ion exchange, as well as hydrophobic interaction mechanisms. The effectiveness of both ion exchange and hydrophobic interactions increases with increasing chain length [14]. Xu et al investigating cationic surfactant sorption onto vermiculitic subsoil proposed that hexadecyltrimethylammonium was initially adsorbed by cation exchange in the interlayer, causing extensive clay aggregation. As the loading increased, surfactant adsorbed to external surfaces of aggregates via both cation exchange and hydrophobic bonding [16].

Zeta potential data have been used for explaining the adsorption mechanisms of ionic surfactants [16,17,18,19], and in particular for examining the effect of chain length on surfactant adsorption at the mineral/water in interfaces [19,20].

DLS (Dynamic Light Scattering) was used in our previous work to determine variation of the particle size in Na⁺-SAz-1 and Na⁺-SWy-1 Mt suspensions as a function of sonication process [21].

The aim of this study was, therefore, to examine systematically the effect of chain length on the adsorption of cationic surfactants of homologue series onto SWy-1 clay mineral by correlating zeta potential curves with DLS data to determine the size of the particles in suspension. Changes in the particle sizes as a function of surfactant adsorption were analyzed using DLS (Dynamic Light Scattering).

2. METHODS

2.1. Materials

The montmorillonite clay Na⁺-SWy-1 (Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, Missouri) was used in this work. The clay was purified as described earlier [22]. CEC of SWy-1 clay mineral is 76.4 meq/100 g [23].

Stock suspensions were prepared by dispersing 0.07 g of clay mineral in a small amount (<25 mL) of Millipore water (Milli Q) and stirred for 10 h. Afterwards, the volume was adjusted to 25 mL. A second clay suspension with a concentration of 0.11 g.L⁻¹ was prepared from the former. The surfactants octyltrimethylammonium bromide (C8) (Fluka), decyltrimethylammonium bromide (C10) (Fluka), dodecyltrimethylammonium bromide (C12) (Fluka), tetradecyltrimethylammonium bromide (C14) (Fluka), hexadecyltrimethylammonium bromide (C16) (Sigma) and octadecyltrimethylammonium bromide (C18) (Fluka) were used in the experiments.

2.2. Zeta Potential Measurements

The zeta potential (ζ) of the SWy-1-surfactant suspensions were measured using an automated micro-electrophoresis instrument (Zeta Potential Analyser,

Brookhaven Instruments Corporation). At least 15 runs were conducted for each sample and mean values were recorded.

2.3. Dynamic Light Scattering

Scattering experiments were carried out on a BI200-SM light-scattering goniometer (Brookhaven Instr. Corp.) with a Nd-YAG laser ($\lambda = 532$ nm) light source. The signals were processed with a BI9000-AT correlator (Brookhaven Instr. Corp.). Decalin filtered through a 0.45- μ m membrane was used as refractive index matching fluid surrounding the sample cell. All measurements were performed at 25.0 °C and at a scattering angle of 90° [21Error! Bookmark not defined.].

3. RESULTS AND DISCUSSION

3.1. Electrophoretic Mobility

Fig. 1a and b illustrate electrophoretic mobility (Zeta potential) experimental results of SWy-1 Mt suspensions as a function of surfactants concentration after immediate and 24 hours of the addition of surfactant, respectively.

Fig. 1a and b show similar behaviour. Inspection of the Fig. 1b shows that the SWy-1-C18, SWy-1-C16 and SWy-1-C14 particles carry negative charge up to 1×10^{-5} mol L⁻¹ of surfactant. This negative charge arises from the isomorphous substitution of lattice-constituent metal ions by cations of lower charge. In the surfactant concentration range from 5×10^{-7} to 1×10^{-5} mol L⁻¹ zeta potential remains almost constant. The fact that increase in surfactant adsorption caused no change in electrophoretic mobility in this region (Fig. 1b) suggest that little adsorbed surfactant was distributed on the external surfaces of the aggregates at the equilibrium, electrophoretic mobility being sensitive only to the composition of the external surfaces [16].

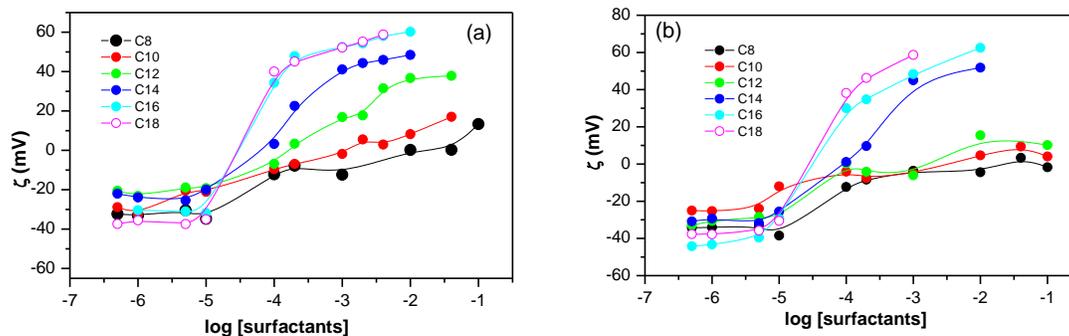


Fig. 1. Variation of zeta potential of SWy-1 clay mineral vs the surfactant concentration. The measurement was done (a) after immediate addition of surfactants and (b) after 24 hours of the addition.

As mentioned earlier, the most important two mechanisms responsible for cationic surfactant adsorption

onto clay minerals are ion exchange and hydrophobic interaction. In this way, this surfactant concentration range

(5×10^{-7} to 1×10^{-5} mol L⁻¹) should be dominated by ion exchange mechanism. The ion exchange mechanism occurs in an equivalent amount of cations in order to maintain total electroneutrality which requires the zeta potential to remain constant throughout the exchange process. The results obtained by Ersoy and Çelik [14] **Error! Bookmark not defined.** support this.

Zeta potential of SWy-1 clay mineral reaches its isoelectric point (iep) with increase of surfactant adsorption. The concentrations at the iep of SWy-1 clay mineral for C18, C16, C14, C12 and C10 are 2.7×10^{-5} , 3.2×10^{-5} , 9×10^{-5} , 1.6×10^{-3} and 3.2×10^{-3} mol L⁻¹, respectively. This can be due to the ability of the longer chain length to undergo better hydrophobic interactions. The surfactant adsorption in this region should be governed by hydrophobic interactions between the surfactant chains. The iep of SWy-1-C16, SWy-1-C14 and SWy-1-C12 systems obtained in this study are similar as that reported by Ersoy and Çelik in the study of the surfactants adsorption onto clinoptilolite [14].

The steep increase in electrophoretic mobility (Fig. 1b) with an increment of surfactant concentration (above 1×10^{-5} M of surfactant) implied a dramatic change in the composition of the external surfaces of the aggregates due to surfactant adsorption. The development of positive electrophoretic mobility in this region implied that at least some surfactant adsorbed via hydrophobic bonding was distributed on the external surfaces of aggregates. The positive charge, if sufficiently large in the interlayer, can dismantle the aggregates and increase the degree of clay dispersion [24].

At higher surfactant concentrations (above 1×10^{-4} mol L⁻¹), the surface sign of SWy-1 clay mineral is reversed from negative to positive and zeta potentials become +38, +30, +1, +0.3mV for C18, C16, C14 and C12, respectively. The very little change in electrophoretic mobility as surfactant loading increased, suggested the dismantlement of face-to-face association caused by surfactant adsorption via hydrophobic bonding in the interlayer [16].

For surfactant with shorter chain length (C10) the zeta potential inversion occurs above 1×10^{-2} mol L⁻¹ of surfactant, and for C8 the zeta potential remains negative in the range from 5×10^{-7} to 1×10^{-1} mol L⁻¹, suggesting that the hydrophobic interaction is not predominant for C8 due to the shorter length of chain.

The magnitude of the zeta potential values can be used to evaluate the stability of colloidal systems. Usually, stable suspensions show zeta potential values higher than +30mV or lower than -30mV [25].

3.2. Dynamic Light Scattering (DLS)

Particle size of SWy-1 clay mineral (0.11 g L^{-1}) was studied after addition of the surfactant with different chain sizes as a function of time. Changes in the particle sizes were analyzed using DLS (Dynamic Light Scattering). The particle size distribution of untreated SWy-1 clay mineral suspensions shows a bimodal distribution of diameters with maxima at 235 nm and 995 nm. Table I presents particles diameter of SWy-1 clay mineral suspensions in the presence of surfactants as a function of time.

Table I
Particles diameter of SWy-1 clay mineral suspensions in the presence of C8, C12 and C16.

Concentration, mol L ⁻¹	Time, h	Particle Diameter, nm		
		C8	C12	C16
1×10^{-6} (1.2% CEC)	0	389, 1580	147, 631	191, 607, 1860
	3	337, 1360	170, 385,867	151, 639
	24	362, 1157	167, 652	166, 890
1×10^{-5} (12% CEC)	0	105, 858	247, 1128	1108
	3	358, 1087	344, 1326	603
	24	370, 1105	362, 2355	608

At lower C8, C12 and C16 concentrations (1×10^{-6} mol L⁻¹) there is practically no significant change in the particle size as function of time (Table 1). In fact, at small loadings (1.2% CEC), the adsorbed surfactant molecules do not significantly disturb the surface properties of the clay mineral.

For the C8 concentration at 1×10^{-5} mol L⁻¹ (12% CEC), the particle size distribution of SWy-1-C8 suspension shows the presence of two populations of particles with modal diameters centred at 185 and 858 nm at initial time. As can be seen in Fig. 2b, after 3 and 24 hours of the C8 addition the

distributions shift to 358, 1087 nm and 370, 1105 nm, respectively.

At initial time the ratio between the volumes corresponding to the large size particles and the smaller ones is about 92 (calculated by integration of the peaks in Fig. 2b). After 24h of surfactant addition this ratio falls to 5, confirming the conversion of the larger size particles in smaller ones.

The surfactant loading (12% CEC) suggest increasing of the proportion of the smallest particles. This can be attributed to adsorption of surfactant molecules on the external surface and the migration of these molecules to interlayer spaces promoting delamination effect.

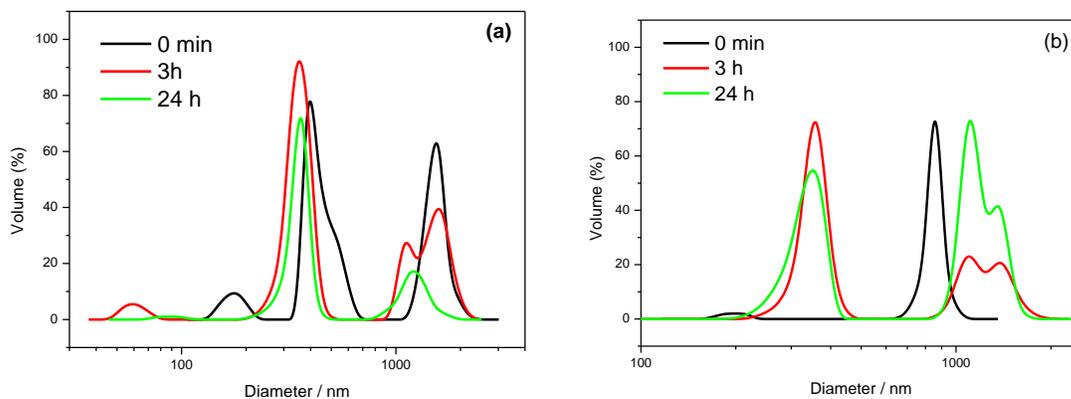


Fig. 2. Particle size distribution (DLS measurements) for SWy-1 clay mineral in the presence of (a) $1 \times 10^{-6} \text{ mol L}^{-1}$ C8 and (b) $1 \times 10^{-5} \text{ mol L}^{-1}$ as a function of time. presence of $1 \times 10^{-5} \text{ mol L}^{-1}$ C12 surfactant showed similar behaviour to that of SWy-1-C8.

It is possible to observe in Fig. 3b that the particle size distribution for SWy-1 clay mineral suspension in the

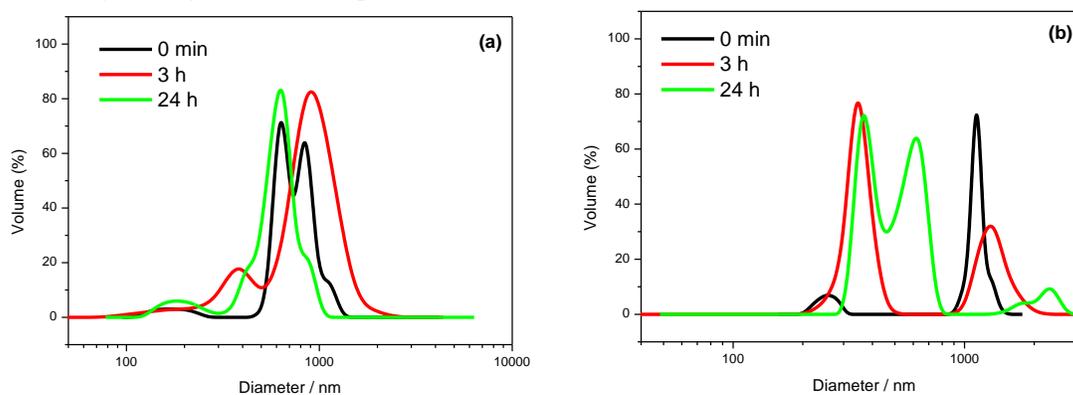
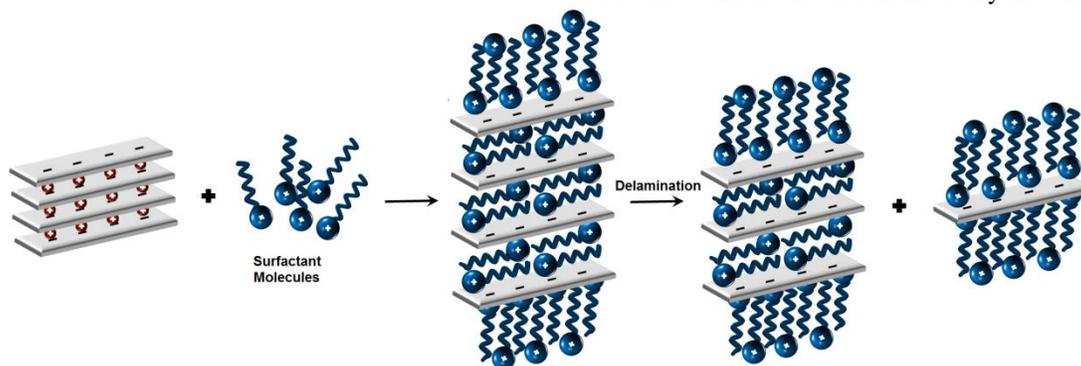


Fig. 3. Particle size distribution (DLS measurements) for SWy-1 in the presence of (a) $1 \times 10^{-6} \text{ mol L}^{-1}$ C12 and (b) $1 \times 10^{-5} \text{ mol L}^{-1}$ as a function of time.

Considering SWy-1 clay mineral suspension with $1 \times 10^{-5} \text{ mol L}^{-1}$ C16 the modal distribution of diameters appears at 1108 nm (Fig 4b). The particle size decreases with the time and maximum of this population shifts to 608 nm.

After 24 hours of surfactant addition, suspensions containing C8 show that the majority population have particles size (1105 nm) larger than SWy-1 clay mineral with C16 (608 nm). Therefore, surfactants with larger chain lengths, such as C16, promote a more effective breaking of the layers.

The behaviour of clay delamination with C8, C12 and C16 surfactants is shown schematically in Scheme 1.



Scheme 1. Schematic representation of breaking of the layers with Surfactants addition in SWy-1 clay mineral suspension.

These results agree with zeta potential measurements (Fig. 1B) for surfactants with longer chains, such as C16. In concentration range from 1×10^{-5} to $1 \times 10^{-4} \text{ mol L}^{-1}$ of C16 occurs the transition of the surface sign of SWy-1 clay mineral from negative to positive.

The development of positive electrophoretic mobility in this region implied that at least some surfactant adsorbed via hydrophobic bonding was distributed on the external surfaces of tactoid. The positive charge, if sufficiently large in the interlayer, can dismantle the tactoid and increase the degree of

clay mineral dispersion [Error! Bookmark not defined.].

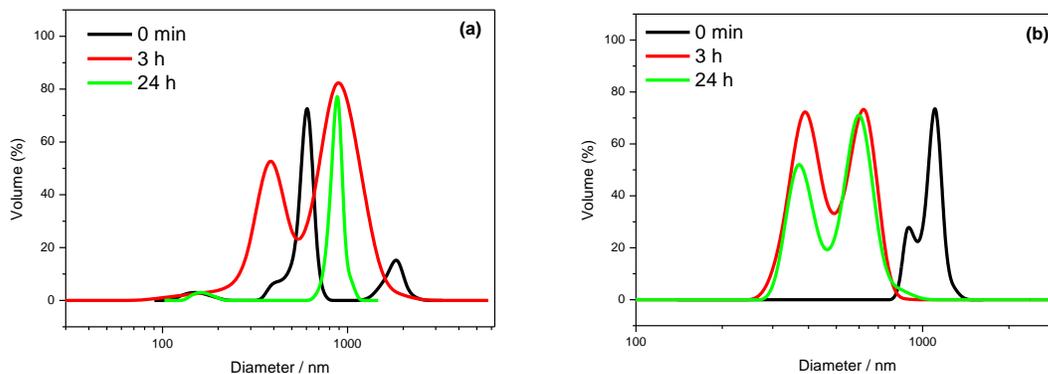


Fig. 4. Particle size distribution (DLS measurements) for Swy-1 clay mineral in the presence of C16 (a) 1×10^{-6} mol L⁻¹ and (b) 1×10^{-5} mol L⁻¹ as a function of time.

Particle size was not determined at higher surfactants concentration (8×10^{-5} mol L⁻¹). In this concentration, where zeta potential is close to pzc (point of zero charge) the flocculation takes place.

4. CONCLUSIONS

Particle size analysis by DLS of clays treated with surfactants C8 and C12 showed that at lower concentrations of them (1×10^{-6} mol L⁻¹) there is practically no significant change in the particle size. In the surfactant concentration range from 5×10^{-7} to 1×10^{-5} mol L⁻¹ zeta potential remains almost constant suggesting ion exchange mechanism. At small loadings (1.2% CEC), the adsorbed surfactant molecules do not significantly disturb the surface properties of the clay.

For C8 and C12 surfactants, the results using loading of 12% of CEC show increasing of the proportion of the smallest particles. Considering SWy-1 clay mineral suspension with C16 (12% CEC), the particle size decreases with the time. This can be attributed to adsorption of surfactant molecules on the external surface and the migration of these molecules to interlayer spaces promoting delamination effect.

At higher concentrations of surfactants (95% CEC) zeta potential is close to the pzc (point of zero charge), so flocculation takes place. Comparing the delamination behaviour it is possible to observe that surfactants with larger chain lengths, such as C16, promote a more effective breaking of the layers.

The hydrocarbon chain length of surfactant molecules is found to have a significant effect on the interaction mechanisms. The effectiveness of both ion exchange and hydrophobic interaction increases with increasing chain length.

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REFERENCES

- [1] L. Fowden, R.M. Barrer, P.B. Tinker, Clay Minerals: Their structure, Behaviour and Use, The Royal Society, London, 1984.
- [2] C.S.F. Gomes, in: C.S.F. Gomes (Ed.), Argilas: Aplicações na Indústria, 2002.
- [3] H.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: a general overview, Appl. Clay Sci. 17 (2000) 207-221.
- [4] F. Franco, L.A. Pérez-Maqueda, J.L. Pérez-Rodríguez, The effect of ultrasound on the particle size and structural disorder of a well-ordered kaolinite, J. Colloid Interface Sci. 274 (2004) 107-117.
- [5] [1] M.F. Brigatti, E. Galan, B.K.G. Theng, Structure and Mineralogy of Clay Minerals. In: F. Bergaya, B.K.G. Theng, G. Lagaly, Handbook of Clay Science, Elsevier Ltd. 1, (2006) 19-86.
- [6] D. Borden, R.F. Giese, Baseline studies of the clay minerals society source clays: cation exchange capacity measurements by the ammonia-electrode method, Clays Clay Miner. 49 (2001) 444-445.
- [7] S.I. Marras, I. Zuburtikudis, C. Panayiotou, Nanostructure vs. microstructure: Morphological and thermomechanical characterization of poly(l-lactic acid)/layered silicate hybrids, Eur. Polym. J. 43 (2007) 2191-2206.
- [8] S.R. Valandro, P.C. Lombardo, A.L. Poli, M.A. Horn Jr, M.G. Neumann, C.C.S. Cavalheiro, Thermal Properties of Poly (methyl methacrylate)/ organomodified montmorillonite nanocomposites obtained by *in situ* photopolymerization, Mater. Res. *In press*
- [9] S.R. Valandro, A.L. Poli, M.G. Neumann, C.C. Schmitt, Organomontmorillonite/poly(methyl methacrylate) nanocomposites prepared by *in situ* photopolymerization. Effect of the organoclay on the photooxidative degradation, Appl. Clay Sci. *In press*
- [10] H.A. Patel, R.S. Somani, H.C. Bajaj, R.V. Jasra, Nanoclays for polymer nanocomposites, paints, inks, greases and cosmetics formulations, drug delivery vehicle and waste water treatment Bull. Mater. Sci. 29 (2006) 133-143.
- [11] B.J. Brownawell, H. Chen, J.M. Collier, J.C. Westall, Adsorption of organic cations to natural materials, Environ. Sci. Technol. 24 (1990) 1234-1241.
- [12] Z. Li, S. J. Roy, Y. Zou, R. S. Bowman, [Long-Term Chemical and Biological Stability of Surfactant-Modified Zeolite](#), Environ. Sci. Technol. 32 (1998) 2628-2632.
- [13] M.O. Adebajo, R.L. Frost, J.T. Klopogge, O. Carmody, S. Kokot, Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties, J. Porous Mater. 10 (2003) 159-170.
- [14] B. Ersoy, M.S. Çelik, Effect of hydrocarbon chain length on the adsorption of cationic surfactants onto clinoptilolite, Clays Clay Miner. 51 (2003) 172-180.
- [15] S.I. Marras, A. Tsimliaraki, I. Zuburtikudis, C. Panayiotou, Thermal and colloidal behavior of amine-treated clays: The role of

- amphiphilic organic cation concentration, *J. Colloid Interface Sci.* 315 (2007) 520-527.
- [16] S. Xu, S.A. Boyd, Cationic Surfactant Adsorption by Swelling and Nonswelling Layer Silicates, *Langmuir* 11 (1995) 2508-2514.
- [17] P. Somasudaran, D.W. Fuerstenau, Mechanism of Alkyl Sulfonate Adsorption at the Alumina-Water Interface, *J. Phys. Chem.* 70 (1966) 90-96.
- [18] Y. Yamaguchi, H. Hoffmann, Interaction between saponite and cationic, zwitterionic and nonionic surfactants, *Colloids and Surf. A* 121 (1997) 67-80.
- [19] P. Somasudaran, T.W. Healy, D.W. Fuerstenau, Surfactant Adsorption at the Solid-Liquid Interface-Dependence of Mechanism on Chain Length, *J. Phys. Chem.* 68 (1964) 3562-3566.
- [20] J.R. Hunter, *Zeta Potential in Colloid Science, Principles and Applications*, Academic Press, San Diego, 1981.
- [21] A. L. Poli, T. Batista, C.C. Schmitt, F. Gessner, M.G. Neumann, Effect of sonication on the particle size of montmorillonite clays, *J. Colloid Interface Sci.* 325 (2008) 386-390.
- [22] F. Gessner, C.C. Schmitt, M.G. Neumann, Time-Dependent Spectrophotometric Study of the Interaction of Basic Dyes with Clays. I. Methylene Blue and Neutral Red on Montmorillonite and Hectorite, *Langmuir* 10 (1994) 3749-3753.
- [23] H. van Olphen, J.J. Fripiat, *Handbook for Minerals and other non-Metallic Minerals*, Pergamon, Oxford, 1979.
- [24] Xu, S.A. Boyd, Alternative model for cationic surfactant adsorption by layer silicates, *Environ. Sci. Technol.* 29 (1995) 3022-3028.
- [25] S. Tunç, D. Osman, B. Kanci, Rheological measurements of Na-bentonite and sepiolite particles in the presence of tetradecylmethylammonium bromide, sodium tetradecyl sulfonate and Brik 30 surfactants, *Colloid Surf. A* 398 (2012) 37-47.