Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 1, 227–234

PHYSICO-CHEMICAL STUDY OF SELECTED SURFACTANT–CLAY MINERAL SYSTEMS

C. del Hoyo[1], *C. Dorado*[2], *M. S. Rodríguez-Cruz*[2] *and M. J. Sánchez-Martín*[2]*

[1]Departamento de Química Inorgánica, Universidad de Salamanca, P. de la Merced s/n. 37008 Salamanca, Spain
[2]Instituto de Recursos Naturales y Agrobiología de Salamanca (IRNASA-CSIC), Apdo. 257, 37071 Salamanca, Spain

A physicochemical study of the systems formed by the clay minerals, montmorillonite and kaolinite (layered) and sepiolite (non-layered) and the surfactants Triton X-100 (TX100, non-ionic), dodecyl sodium sulfate (SDS, anionic) and trimethyloctadecylammonium bromide (ODTMA, cationic), with different chemical structure, was carried out by X-ray diffraction (XRD), infrared spectroscopy (FTIR) and thermogravimetric and differential thermal analysis (TG/DTA). TG/DTA results indicated an increase in the thermal stabilization of non-ionic (TX100) and cationic (ODTMA) surfactants adsorbed by all clay minerals in relation to pure compounds. This effect was greater in montmorillonite and sepiolite than in kaolinite owing to these minerals must allow the establishment of a stronger bond with the surfactants as indicated by XRD and FTIR results. Differences in decomposition of anionic surfactant SDS are not emphasized due to the low adsorbed amount of this surfactant by all systems. The results obtained indicate the interest of taking into account the structure of surfactant and the clay mineral type when preparing customized surfactant–clay mineral systems which contribute to establish more efficient soil and water remediation strategies based in the use of these systems.

Keywords: *clay minerals, infrared spectroscopy, surfactants, thermal analysis, X-ray diffraction*

Introduction

The extended use of toxic organic compounds in many industrial or agricultural activities and their frequent presence in soils and sediments represents an important environmental concern nowadays [1]. This involves the performance of numerous studies about the processes related with the behaviour of these compounds in soil, especially about adsorption–desorption and mobility processes [2]. Furthermore, in the last years, numerous studies about technologies related with the prevention of the contamination and the remediation of soil and water contaminated with these compounds have been carried out [3, 4].

Technologies preventing soil contamination are based on the use of natural or modified materials, which have a great capacity to adsorb organic compounds giving rise to its immobilization in the soil, decreasing therefore the water contamination [4]. Those technologies having as aim the remediation of contaminated soil and/or water are based on the extraction of organic contaminants with a mobile phase which increases its mobility controlled through an increment of the apparent solubility of the compound in water [5].

Surfactants are organic compounds with chemical properties which can be used in prevention and remediation technologies. Numerous studies have pointed out the interest of using cationic surfactants to modify clay minerals giving rise to efficient sorbent materials for non-ionic organic compounds [6–8]. Furthermore, anionic and non-ionic surfactants can increase the apparent solubility of contaminants in the system soil-water, adsorbing the contaminant in the inner part of the micelles or aggregates formed by surfactant molecules when the surfactant concentration is close or higher than the critical micelle concentration (*cmc*) [9–11]. However, although this type of surfactants can facilitate the transport of soluble contaminants, they can also be adsorbed by the soil matrix, especially by the clay minerals giving rise to a decrease in its mobility [12].

In relation to the use of surfactants for these aims, studies on adsorption of surfactants by soils and their components have been usually carried out [13–16]. However, studies on the surfactant–clay interaction mechanism involving thermal analysis or using X-ray diffraction and infrared spectroscopy have been more limited. In this sense, references in the literature indicate the systems made up by cationic surfactants [17–22] or non-ionic surfactants [23, 24] with the clay mineral montmorillonite like those more widely studied.

In this paper, a study of the systems formed by different clay minerals, montmorillonite (M), kaolinite (K) and sepiolite (S), and three surfactants with different chemical structure, Triton X-100 (non-ionic), dodecyl sodium sulfate (anionic) and trimethyloctadecylammonium bromide (cationic), was carried out by X-ray

---

* Author for correspondence: mjesussm@usal.es

1388–6150/$20.00
© 2008 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

diffraction (XRD), infrared spectroscopy (FTIR) and thermogravimetric and differential thermal analysis (TG/DTA). The aim was to know the interaction mechanisms between clay minerals and surfactants, the thermal stability of the adsorbed surfactants and the possible influence of the interaction between surfactant and clay mineral in this stability. The originality of this work lie in the following aspects: 1) The use of one layered non-expansible clay mineral (K) and another non-layered (S), besides the layered expansible clay mineral montmorillonite (M) as a model and 2) the use of three surfactants with very different structure and properties. Additionally, the results will complement those obtained in our previous paper [16] about the adsorption of these surfactants by clay minerals.

Experimental

Clay minerals (<1 mm) with different structures, representative of the different types of clays in soils, were used in the study: Tidinit montmorillonite (M) (Morocco), Cuenca kaolinite (K) (Spain) and Vallecas sepiolite (S) (Spain). The characteristics of these samples determined by the methods described elsewhere [16] are included in Table 1.

The surfactants used were: a non-ionic surfactant, 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (TX100), an anionic surfactant, dodecyl sodium sulphate (SDS), and a cationic surfactant, trimethyloctadecylammonium bromide (ODTMA), supplied by Sigma-Aldrich (St. Louis, MO). The three surfactants were used as received.

Surfactant–clay systems were obtained by treatment of the different clay minerals with surfactant solutions of concentration of 6000 μg mL^{-1} for TX100 and SDS, and 2000 μg mL^{-1} for ODTMA, according to the method indicated in a previous paper by the same authors [16]. The prepared samples were slightly washed to avoid the excess of organic compound coming from solutions and its precipitation on the clay mineral surface, dried at room temperature and grounded. The fraction <1 mm was selected by sieving, and kept in a controlled humidity atmosphere for later use.

Natural clay minerals and these samples treated with the surfactants were studied by the XRD technique using CuK$_\alpha$ radiation on a PW1710 Philips Analytical diffractometer controlled by a X'Pert Quantify software (EA Almelo, The Netherlands) operating at 50 kV and 40 mA between 3 and 30° at a step size of 0.04° 2θ at 2.5 s step^{-1}. FTIR spectra of the same samples were registered in a Midac M Series FTIR spectrometer (Midac Corporation, California, USA). All the FTIR spectra were measured in the 4000–600 cm^{-1} range by the co-addition of 64 scans with a resolution of 4 cm^{-1}. Spectral manipulation was performed using the GRAMS/32-AI software package (ThermoGalactic, Wobum USA).

Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) of different samples (approximately 10 mg) were performed in ceramic pans using a TA Thermogravimetric Analyzer (TA Instruments, New Castle, USA), model SDT Q600 operating at 20°C min^{-1} heating rate from 40 to 800°C in a flowing air atmosphere of 100 mL min^{-1}. Derivative thermogravimetric curves (DTG) were also obtained by using the data analysis software of the instrument.

Results and discussion

XRD study

Table 1 shows the d$_{001}$ basal spacing values of XRD patterns corresponding to the clay minerals treated with the surfactants studied and Fig. 1 includes those XRD patterns obtained for the surfactant-montmorillonite system. The amounts of surfactant adsorbed by each clay mineral are also included in Table 1. The adsorbed amounts of cationic surfactant ODTMA represent 2.5, 2 and 8 times the cation exchange capacity (CEC) of montmorillonite, kaolinite and sepiolite, respectively. A modification of d_{001} spacing is observed for montmorillonite treated with TX100 and ODTMA, while spacings for kaolinite and sepiolite are not modified. The d_{001} spacing of montmorillonite increase 0.82 or 1.15 nm in relation to the 0.96 nm value of dehydrated montmorillonite after the treatment with TX100 or ODTMA. Expansion of montmorillonite treated with TX100 must correspond to

Table 1 Characteristics of natural clay minerals, amounts of surfactants adsorbed (Cs) by clay minerals and X-ray diffraction spacing of different surfactant-clay mineral systems studied

Clay mineral	CEC/ cmol g^{-1}	Specific surface/ m^2 g^{-1}	Natural d_{001}/ nm	+TX100		+ODTMA		+SDS	
				Cs/mg g^{-1}	d$_{001}$/nm	*Cs*/mg g^{-1}	d_{001}/nm	*Cs*/mg g^{-1}	d_{001}/nm
Montmorillonite	82.0	750	1.46	415	1.78	758.0	2.11	11.4	1.46
Sepiolite	5.0	189	1.23	267	1.23	128.0	1.23	28.7	1.23
Kaolinite	6.1	12	0.71	134	0.71	40.8	0.71	22.9	0.71

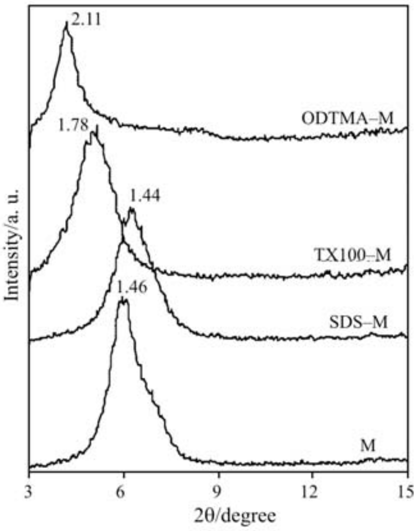

Fig. 1 X-ray diffraction patterns for the studied surfactant–montmorillonite systems

the intercalation of two layers of surfactant with a parallel arrangement to the silicate layers according to that proposed for other non-ionic ethoxylate surfactants [23, 24]. In the case of ODTMA, the spacing increment must correspond to a pseudotrimolecular arrangement with a parallel disposition to the silicate layers or a paraffin-type monomolecular arrangement as indicated by other authors [18, 25]. This cationic surfactant could be also adsorbed in the structural zeolite-like channels of fibrous silicate sepiolite, being its size similar to the trimethylammonium group of ODTMA [26].

Montmorillonite, kaolinite and sepiolite treated with the anionic surfactant SDS do not modify their basal spacings, indicating that the adsorption of this surfactant does not take place in the interlayer space of these minerals.

FTIR study

Figure 2 shows the FTIR spectra of surfactants (Fig. 2a) and of the montmorillonite natural and treated with the different surfactants (Fig. 2b), and Table 2 includes the wavenumbers (cm^{-1}) of characteristic absorption bands for surfactants, and for the surfactant–clay systems studied. Subtraction technique of clay mineral spectra from surfactant–clay mineral spectra was used to evaluate modifications on the absorption bands of surfactant after adsorption.

FTIR spectra of natural clay minerals display bands in the regions 3700–3600 cm^{-1} (structural OH vibrations), 3500–3200 and 1663–1636 cm^{-1} (adsorbed water OH stretching and bending vibrations) and 1040–600 cm^{-1} (linkage vibrations), and those of free surfactants display bands in the regions 3500–3000 and around 1600 cm^{-1} (OH stretching and bending vibrations for TX100 and for environmental water molecules), 3000–2800 and 1500–1300 cm^{-1} (CH stretching and bending vibrations for different surfactants and CO and OH bending vibrations for TX100).

FTIR spectra of the surfactant-clay mineral systems indicate the presence of absorption bands corresponding to adsorbed surfactant. Bands corresponding to the adsorbed water indicate that not all the water has been replaced by surfactant molecules. However, changes in wavenumbers of these bands are observed and they could indicate partial displacement of water molecules by adsorbed surfactant. Moreover, wavenumber shifts of some adsorbed surfactant bands compared to those registered in the spectrum of the free compound (Table 2) indicate that some type of interaction has been settled down between organic molecules and the clay minerals surface.

In the spectra of TX100-silicate systems a displacement of the absorption band corresponding to

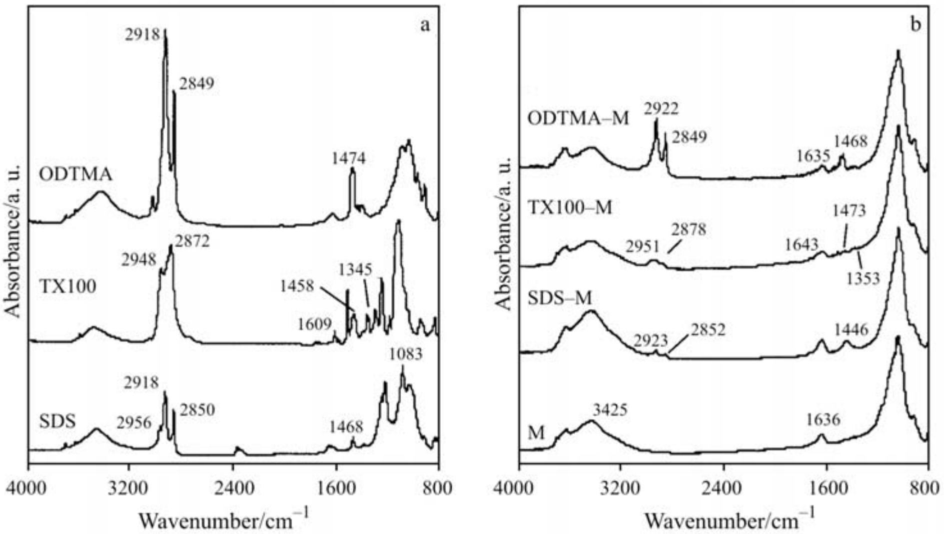

Fig. 2 a – Infrared spectra of pure surfactants and b – montmorillonite natural and treated with the different surfactants studied

Table 2 Wavenumbers (cm^{-1}) of characteristic absorption bands of the FTIR spectra for the natural clay minerals, surfactants and surfactant–clay mineral systems

Sample	ν_{OH}	$\nu_{OH}H_2O$	$\delta_{OH}H_2O$	$\nu_{as(CH)}$	$\nu_{s(CH)}$	δ_{CH}	$\nu_{C–O}$
Natural clay minerals							
Montmorillonite	3622	3425	1636	–	–	–	–
Kaolinite	3695, 3620	3432	1630	–	–	–	–
Sepiolite	3620, 3564	3404, 3260	1662	–	–	–	–
TX100–clay mineral systems							
TX100	–	3474	1609	2948	2872	1458	1345
TX100–M	3626	3414	1643, 1615	2951, 2923	2878	1473, 1457	1353
TX100–K	3695, 3619	3435	1637	2960, 2924	2856	1457	–
TX100–S	3566	3408, 3260	1652, 1609	2953, 2926	2883	1474, 1457	1354
ODTMA–clay mineral systems							
ODTMA	–	–	–	2918	2849	1474	–
ODTMA–M	3627	3420	1635	2922	2849	1468	–
ODTMA–K	3693, 3619	3440	1625	2918	2849	1471	–
ODTMA–S	3565	3415, 3252	1663, 1622	2926	2853	1468	–
SDS–clay mineral systems							
SDS	–	–	–	2956, 2918	2850	1468	–
SDS–M	3620	3439	1636	2958, 2923	2852	1446	–
SDS–K	3694, 3619	3445	1630	2962, 2923	2853	–	–
SDS–S	3564	3414	1660	2962, 2926	2855	1462	

the OH bending vibration of adsorbed water is observed, especially in the TX100–M system. These modifications and those observed in the bands corresponding to the CO bending vibrations (1345 cm^{-1}) of the surfactant towards higher wavenumbers could indicate a possible ion-dipole interaction between the surfactant and the silicate through the OH group of TX100 and the water coordinated to the exchangeable cations of clay minerals. Changes in the absorption bands corresponding to CH_2-stretching and bending modes of hydrocarbon chain groups of TX100 (2948 and 2872 cm^{-1}) are also observed towards higher wavenumbers (Table 2). These displacements can be related to a reorganization of the organic compound molecules when an interaction with the adsorbent is established. The observed effects take place, in general, in all systems but they are more emphasized for TX100 adsorbed by montmorillonite and sepiolite. These minerals are those that present the highest amount of adsorbed surfactant (Table 1) and, in addition, the adsorption of TX100 in the interlayer space of montmorillonite, as indicated by XRD, must possibly allow the establishment of a stronger bond with the surfactant.

The FTIR spectra of the ODTMA–clay mineral systems present modifications in the CH stretching (2918 and 2849 cm^{-1}) and bending modes (1474 cm^{-1}) of adsorbed ODTMA compared to the pure ODTMA. Some authors [27] have indicated that the CH_2-stretching vibration of amine chains is very sensitive to the conformational ordering of the chains. Xi *et al.* [18, 19] studied modification of montmorillonite by different alkyl ammonium surfactants by FTIR spectroscopy and they found asymmetric stretching frequencies (ν_{as}) of CH_2 groups in all organoclays higher than that in pure surfactants reflecting some disordered conformations in the surfactant adsorbed in these systems in relation to pure compound. The displacement of CH wavenumbers in ODTMA–M is lesser than that in ODTMA–S involving a more ordered arrangement of the surfactant molecules when the adsorption takes place in the interlayer space [28]. Changes in the CH bending vibration of ODTMA adsorbed in montmorillonite and sepiolite towards higher wavenumbers are also ascribed to the locking of the methyl groups into the siloxane layer [19] and a hydrophobic bonding or Van der Waals forces between the hydrocarbon chains of surfactants and the hydrophobic siloxane surface of clay minerals can be established.

A displacement of the CH stretching and bending vibrations is also observed in the FTIR spectra of SDS–clay mineral systems towards higher wavenumbers, and a modification in the stretching mode Al–OH of silicate network (1083 cm^{-1}) is observed in the FTIR spectrum of SDS-kaolinite towards higher wavenumbers (1112 cm^{-1}). This shift could correspond to an interaction between the surfactant and the charged octahedral layer of the kaolinite as it has been indicated by Sastry *et al.* [29] in the interaction of dodecyl and sodium benzenesulphonate with this clay mineral. This interaction could support the higher amount of this surfactant adsorbed by kaolinite (Table 1).

The bands corresponding to alkyl groups of surfactant are always observed by the FTIR analysis in all systems studied indicating its presence although the amount adsorbed is low in some systems (i.e. kaolinite).

Thermal analysis (TG/DTA)

Figures 3 and 4 show TG/DTA curves of free surfactants and those corresponding to different surfactant–clay mineral systems. For the free surfactants TG curves present mass losses in the temperature intervals: 200–376°C (TX100), 175–575°C (ODTMA) and 128–437°C (SDS), which corresponds to the loss of the 100, 96 and 75% of the organic compound, respectively. These mass losses are related to exothermic peaks (↑) at 311°C (TX100) and also to endothermic (↓) and exothermic effects at temperatures of 207, 264, 331 and 487°C (ODTMA) and of 201, 241, 267 and 422°C (SDS) due to combustion of these compounds. Endothermic effects are seen after initial combustion of ODTMA and SDS possibly as a result of the flowing air within the furnace has not enough oxygen to give rise to a total combustion [17]. DTA diagrams display another endothermic effect to lower temperature originated by the melting or transition phase of organic compounds that does not give rise to mass losses.

Results from the TG (mass losses, %) and DTA analysis (minimum/maximum temperatures corresponding to mass losses, °C) of surfactant–clay mineral systems studied are included in Table 3. For natural clay minerals a mass loss is observed in the 50–200°C region caused by their dehydration and another one in the range 450–700°C corresponding to their dehydroxylation [30–32]. The dehydration stage is associated with two endothermic effects; one around 90°C, related to the hygroscopic water loss and another one, in the 120–200°C zone, caused by the adsorbed water elimination. The fibrous silicate, sepiolite, present mass losses much more elevated than the laminar silicates in this zone due to the hygroscopic and zeolitic water losses, the last one adsorbed in the structural zeolite-like channels [33, 34].

The TG/DTA curves of surfactant-silicate systems present thermal effects in the clay dehydration and dehydroxylation region of the clays (Table 3) and thermal effects corresponding to the oxidation of the organic material. The oxidation reaction is exother-

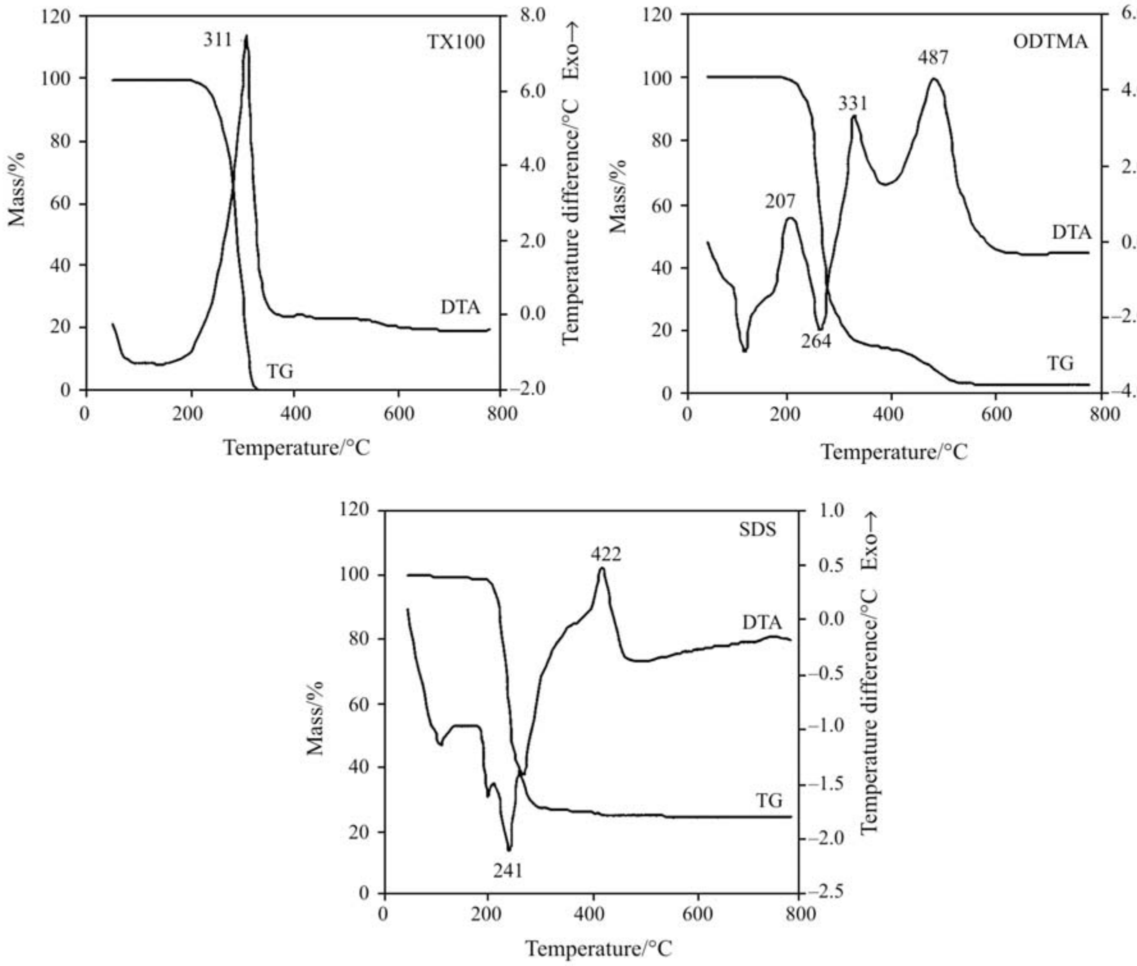

Fig. 3 TG and DTA curves of pure surfactants studied

Table 3 Results from the TG (mass losses (%)) and DTA analysis (minimum/maximum temperatures corresponding to mass losses/°C) of natural clay minerals and surfactant–clay mineral systems studied

Clay mineral	Natural		+TX100		+ODTMA		+SDS	
	Mass loss/%	*T*/°C	Mass loss/%	*T*/°C	Mass loss/%	*T*/°C	Mass loss/%	*T*/°C
Montmorillonite	2.31	90.6	2.0	138	0.6	74.8	2.83	87.9
	0.64	165	–	244	30.9	235	2.43	202, 398
	2.99	682	16.4	327	8.20	394	5.18	688
			5.1	415	7.02	582		
			4.9	661	3.77	690		
Kaolinite	0.1	93.5	0.3	82	0.15	81.4	0.06	83
	11.1	525	–	201	4.75	350	0.90	343
			1.35	375	10.7	523	11.4	520
			11.5	521				
Sepiolite	3.87	94.4	1.50	86.2	2.48	93	3.41	90
	3.04	296	–	218	3.17	359	4.27	305
	2.83	538	21	385	12.5	404, 480	2.42	517
					5.38	749		

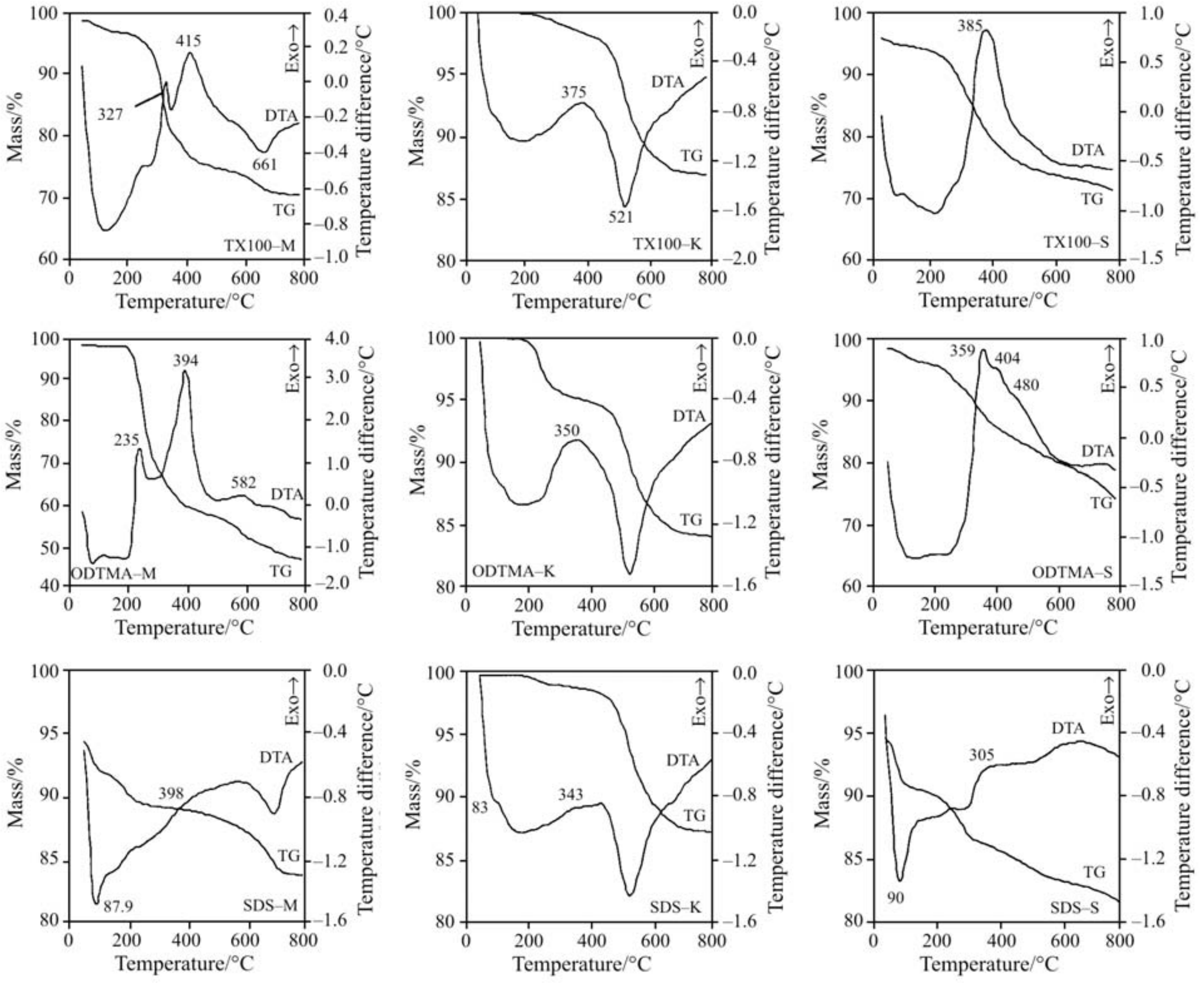

Fig. 4 TG and DTA curves of different surfactant–clay mineral systems studied

mic (↑) and occurs during the gradual heating of the sample. It can take place in two steps, in the range 200–500°C, oxidation of organic hydrogen and formation of water and charcoal, and in the range 400–750°C, oxidation of charcoal and formation of CO_2. The exothermic peak temperatures and the total oxidation of the charcoal depend on the mineral, the organic compound and the types of bonding between the charcoal and the clay mineral [31].

The decomposition of TX100 adsorbed by clay minerals begins after two endothermic effects. One of them corresponds to a mass loss due to the dehydration of the system and another one due to the melting of non- or weakly adsorbed surfactant molecules to temperatures <250°C (Fig. 4). The first mass loss is smaller than that in the untreated clays since some of the water molecules are replaced by the adsorbed organic molecules. Next, the organic matter begins to release in agreement with TG curves, originating one or several exothermic peaks, as indicated in DTA curves, caused by the combustion of the organic compound in the presence of air. The decomposition of the TX100 molecule, with a chain of 9.5 ethoxylate groups and one OH function, must imply ruptures of bonds C–OH of the ethoxylate part, and C–C of the alkyl part, previously to its combustion. It is noted that the oxidation temperatures registered in all TX100–silicate systems are more elevated than for the pure TX100. This could indicate a greater stabilization of the organic compound in adsorbed state due to the interaction between adsorbent and surfactant in a greater or lesser extension.

Loss of TX100 adsorbed by montmorillonite takes place in two steps at temperatures of 327 and 415°C (Fig. 4) possibly due to the presence of surfactant adsorbed on the surface and in the interlayer space of this mineral [16] or to decomposition of different units of TX100 adsorbed in the interlayer space of montmorillonite. Breen *et al.* [35] showed that only the ethoxylated chain remains at temperatures >400°C. Surfactant oxidation adsorbed in TX100-K and TX100-S systems only occurs in a step at temperatures of 375 and 385°C, respectively, suggesting a lesser interaction of surfactant molecules with the surface of these minerals.

The DTA curves of ODTMA–clay mineral systems (Fig. 4) show at first an endothermic peak due to loss of adsorbed water or water around the exchangeable cations. The amount water in these systems decreases in relation to the natural clays as indicated by TG results (Table 3), because the replacement of exchangeable cations by the cationic surfactant increases the hydrophobic character of the surface. After, the organic compound begins to be released (~200°C), DTA curves show several exothermic peaks due to combustion of surfactant. Four mass loss steps (235, 394, 582 and 690°C) are observed in the ODTMA–M system for the total disappearance of the surfactant (Table 3), being the decomposition temperature of the adsorbed ODTMA increased when compared with that of the pure surfactant. It is considered that the arrangement of ODTMA in the interlayer space of more than one molecular layer can give rise to the stabilization of some product originated in the surfactant decomposition and its later oxidation to more elevated temperature. Total disappearance does not take place until a temperature of 600–700°C is reached indicating the oxidation of residual organic carbonaceous matter [31].

The combustion of ODTMA adsorbed by kaolinite and sepiolite begins at higher temperatures (350 and 359°C, respectively) than that observed in the pure surfactant and in the ODTMA–M system. It would therefore appear that the thermal stability of ODTMA decrease as the amount of adsorbed surfactant increases (Table 1), as it has been also indicated by some authors [21, 36]. It is observed one or four mass loss steps, respectively, for the decomposition of ODTMA adsorbed by kaolinite and sepiolite. The adsorption of surfactant in the structural channels of this silicate could permit the stabilization of some decomposition products until temperatures >700°C. It must be noted that the endothermic peak corresponding the dehydroxylation of clay minerals between 500–600°C is not observed in ODTMA–M and ODTMA–S systems because of the overlapping by the four exothermic oxidation steps of residual organic carbonaceous matter.

TG/DTA curves (Fig. 4) corresponding to the studied SDS–clay mineral systems indicate low presence of the surfactant in agreement to the low adsorbed amount of SDS by clay minerals (Table 2). Only it is appreciated a little change in the temperature of water loss in relation to the natural clay minerals, this fact could be due to the replacement of some of the water by organic molecules [31].

Conclusions

The XRD study of surfactant-clay mineral systems has showed the adsorption of non-ionic and cationic surfactants (TX100 and ODTMA) in the interlayer space of montmorillonite. The adsorption of these surfactants by kaolinite and sepiolite and the adsorption of anionic surfactant SDS by all systems did not modify the X-ray diagrams, indicating its adsorption on the surface of these minerals and/or in the structural channels of sepiolite. FTIR spectra of surfactant–clay mineral systems showed absorption bands that indicate the presence of surfactant adsorbed by clay minerals. Wavenumber modifications of the clay mineral OH vibration modes were observed for the non-ionic surfactant TX100, especially when adsorbed by montmorillonite. They indicated interaction of surfactant with the silicate through the functional groups of organic compound and the water coordinated to the exchangeable cations of clay minerals by ion-dipole or hydrogen bonding. On the other hand, modifications in

CH stretching wavenumbers of three surfactants were also observed in all systems indicating a re-arrangement of the adsorbed surfactant molecules and hydrophobic bonding or Van der Waals forces between the hydrocarbon chains of surfactants and the hydrophobic siloxane surface of clay minerals. Concerning the TG/DTA study, the results indicated an increase in the stabilization of non-ionic (TX100) and cationic (ODTMA) surfactants adsorbed by all clay minerals studied in relation to pure compounds. This effect is greater in montmorillonite and sepiolite than in kaolinite systems owing to these minerals must allow the establishment of a stronger bond with the surfactants as indicated by XRD and FTIR results. Differences in decomposition of anionic surfactant SDS are not emphasized due to the low adsorbed amount of this surfactant by all systems. The results obtained indicate the interest of taking into account the structure of surfactant and the clay mineral type when preparing customized surfactant–clay mineral systems to be used in environmental applications related with the remediation of soils and water contaminated by toxic organic pollutants.

Acknowledgements

This work was funded in Spain by the 'Ministerio de Ciencia y Tecnología' and the 'Junta de Castilla y León' as part of Projects REN2000-0884/TECNO and CSI15-03, respectively. The authors thank L. F. Lorenzo, J. M. Ordax and A. González-Núñez for technical assistance.

References

1 D. L. Wise and D. J. Trancolo, Remediation of Hazardous Waste Contaminated Soils, Marcel Dekker, New York 1994.
2 B. L. Shawhney and K. Brown, Reactions and Movement of Organic Chemicals in Soils, Soil Sci. Soc. Am. Inc., Madison, USA 1989.
3 J. A. Smith and S. E. Burns, Physicochemical Groundwater Remediation, Kluwer Academic, New York 2001.
4 K. L. Roehl, T. Meggyes, F. G. Simon and D. I. Stewart, Long-Term Performance of Permeable Reactive Barriers, Elsevier, Amsterdam 2005.
5 D. A. Sabatini, R. C. Knox and J. H. Harwell, Surfactant-Enhanced Subsurface Remediation, American Chemical Society, Washington 1995.
6 L. Groisman, C. Rav-Acha, Z. Gerstl and U. Mingelgrin, Appl. Clay Sci., 24 (2004) 159.
7 M. Cruz-Guzmán, R. Celis, M. C. Hermosín, W. C. Koskinen and J. Cornejo, J. Agric. Food Chem., 53 (2005) 7502.
8 M. J. Sánchez-Martín, M. S. Rodríguez-Cruz, M. S. Andrades and M. Sánchez-Camazano, Appl. Clay Sci., 31 (2006) 216.
9 D. Di Cesare and J. A. Smith, Rev. Environ. Contam. Toxicol., 134 (1994) 1.
10 S. Deshpande, L. Wesson, D. Wade, D. A. Sabatini and J. H. Harwell, Water Res., 34 (2000) 1030.
11 M. Sánchez-Camazano, M. S. Rodríguez-Cruz and M. J. Sánchez-Martín, Environ. Sci. Technol., 37 (2003) 2758.
12 M. S. Rodríguez-Cruz, M. J. Sanchez-Martin and M. Sanchez-Camazano, J. Environ. Qual., 33 (2004) 920.
13 Z. Ou, A. Yediler, Y. He, A. Kettrup and T. Sun, Chemosphere, 32 (1996) 827.
14 L. Zhu, K. Yang, B. Lou and B. Yuan, Water Res., 37 (2003) 4792.
15 M. S. Rodríguez-Cruz, M. J. Sanchez-Martin and M. Sanchez-Camazano, Chemosphere, 61 (2005) 56.
16 M. J. Sánchez-Martín, M. C. Dorado, C. del Hoyo and M. S. Rodríguez-Cruz, J. Hazard. Mater., 150 (2008) 115.
17 M. M. G. Ramos Vianna, J. Dweck, V. F. J. Kozievitch, F. R. Valenzuela-Diaz and P. M. Buchler, J. Therm Anal. Cal., 82 (2005) 595.
18 Y. Xi, R. L. Frost and H. He, J. Colloid Interface Sci., 305 (2007) 150.
19 Y. Xi, Z. Ding, H. He and R. Frost, Spectrochim. Acta, Part A, 61 (2005) 515.
20 Y. Xi, W. Martens, H. He and R.L. Frost, J. Therm. Anal. Cal., 81 (2005) 91.
21 H. He, Z. Ding, J. Zhu, P. Yuan, Y. Xi, D. Yang and R. L. Frost, Clays Clay Miner., 53 (2005) 387.
22 A. Tabak, B. Afsin, S. F. Aygun and E. Koksal, J. Therm. Anal. Cal., 87 (2007) 375.
23 Y. Deng, J. B. Dixon and G. N. White, Clays Clay Miner., 51 (2003) 150.
24 L. S. Sonon and M. L. Thompson, Clays Clay Miner., 51 (2005) 45.
25 W. F. Jaynes and S. A. Boyd, Soil Sci. Soc. Am. J., 55 (1991) 43.
26 Z. Li, C. Willms and K. Kniola, Clays Clay Miner., 51 (2003) 445.
27 Y. Li and H. Isihida, Langmuir, 19 (2003) 2479.
28 Z. Li and L. Gallus, Appl Clay Sci., 35 (2007) 250.
29 N. V. Sastry, J. M. Séquaris and M. J. Schwuger, J. Colloid Interface Sci., 171 (1995) 224.
30 R. C. Mackenzie, Differential Thermal Analysis, Academic Press, London 1970.
31 S. Yariv, Appl. Clay Sci., 24 (2004) 225.
32 M. Önal and Y. Sarikaya, J. Therm. Anal. Cal., 90 (2007) 167.
33 R. L. Frost and Z. Ding, Thermochim. Acta, 397 (2003) 119.
34 N. Yener, M. Önal, G. Üstünsik and Y. Sarikaya, J. Therm. Anal. Cal., 88 (2007) 813.
35 C. Breen, G. Thompson and M. Webb, J. Mater. Chem., 9 (1999) 3159.
36 C. B. Hedley, G. Yuan and B. K. G. Theng, Appl. Clay Sci., 35 (2007) 180.

Received: December 20, 2007
Accepted: March 18, 2008
OnlineFirst: August 15, 2008

DOI: 10.1007/s10973-007-8934-6