

1 Self-assembling of tetradecylammonium chain on
2 swelling high charge micas (Na-Mica-3 and Na-
3 Mica-2): Effect of alkylammonium concentration
4 and mica layer charge

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17

18 ABSTRACT. A family of tetradecylammonium micas is synthesized using synthetic swelling
19 micas with high layer charge ($\text{Na}_n\text{Si}_{8-n}\text{Al}_n\text{Mg}_6\text{F}_4\text{O}_{20}\cdot\text{XH}_2\text{O}$, where $n= 2$ and 3) exchanged with
20 tetradecylammonium cations. The molecular arrangement of the surfactant is elucidated on the
21 basis of XRD patterns and DTA. The ordering conformation of the surfactant molecules into the
22 interlayer space of micas is investigated by IR/FT, ^{13}C , ^{27}Al and ^{29}Si MAS NMR. The structural
23 arrangement of the tetradecylammonium cation in the interlayer space of high-charge micas is
24 more sensitive to the effect of the mica layer charge at high concentration. The surfactant
25 arrangement is found to follow the bilayer-paraffin model for all values of layer charge and
26 surfactant concentration. However, at initial concentration below the mica CEC a lateral
27 monolayer is also observed. The amount of ordered conformation *all-trans* is directly
28 proportional of the layer charge and surfactant concentration.

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31 INTRODUCTION

32 The term organoclays (OC) denotes a family of hydrophobic materials, obtained by modifying
33 clays and clay minerals with various organic compounds through intercalation processes and
34 surface grafting.^{1,2,3,4,5} Organoclays have important practical applications, notably as adsorbents
35 of organic pollutants^{6,7,8,9} and as components in the formation of clay polymer
36 nanocomposites^{2,10,11,12}. A large volume of literature has been accumulated over the past two
37 decades on various aspects of OC research, including i) synthesis and characterization^{4,13,14}; ii)
38 surface properties and stability^{4,13,14}; iii) production of clay-based nanocomposites^{10,11,12,15}; and
39 iv) synthesis of novel materials using the OC as precursors^{16,17}.

40 A more recent development that has attracted much interest is the organo-functionalization of a
41 new family of swelling high-charged micas.^{18,19,20} Those synthetic micas have a charge density
42 similar to brittle micas but with a higher swelling capacity, higher crystallinity and controllable
43 composition.^{21,22,23} In this way, those synthetic micas overcome some limitations of the natural
44 clay minerals to be used as host materials.

45 Dodecylammonium and octadecylammonium have been successfully intercalated in the
46 interlayer space of a whole family of synthetic high-charge mica. In all case, a paraffin-type
47 bilayer structure was observed with a tilt angle between 51° and 65°.^{19,20} However, the structural
48 arrange of alkylammonium in the interlayer space for the lowest chain length (12 vs 18 carbon
49 atoms) was more sensitive to the mica charge because the adsorbed amount of alkylammonium
50 was slightly less than the cation exchange capacity of mica. In the case of the highest chain
51 length (18 vs 12 carbon atoms), alkylammonium was adsorbed by: exchange reaction and on the
52 surface by hydrophobic interaction.²⁰

53 Many studies have been performed to analyze the effect of alkyl chain length,^{24,25,26,27} the
54 species of cationic surfactant^{28,29}, and its-concentration^{30,31,32} on the d-spacing and the alkyl chain
55 arrangements on organoclays. Among them, the most important factor was found to be the
56 surfactant concentration. Lagaly³³ reported that the surfactant package on clay minerals changes
57 from a lateral monolayer to a lateral bilayer, and, finally to a pseudotrimolecular layer or a
58 paraffin-type monolayer depending on the nature of surfactant and layered silicate. Later on, also
59 the d-spacing was found to increase with the increment on the surfactant concentration, allowing
60 the alkyl chains to adopt a paraffin-type bilayer with a tilting angle of 35° at a surfactant
61 concentration higher than its exchange capacity (CEC).³⁴ Moreover, this alkyl chain arrangement
62 but with a larger tilting angle (60°) has also been reported in KNiAsO₄.³⁵ However, the effect of
63 surfactant concentration on the hydrophobicity, d-spacing and alkyl chain arrangement of
64 modified swelling high-charged micas has not been analyzed yet.

65 Thus, the aim of this work is to evaluate the arrangement and interlayer properties of different
66 swelling high charge micas, Na-Mica-*n* (*n* is the layer charge; *n*=2 and 3), as a function of
67 alkylammonium concentration and mica layer charge. Based on our previous work,²⁰
68 tetradecylammonium has been chosen, it has an carbon chain length between the 12 and 18 as
69 previously analyzed, to satisfy the 0.5-10 CEC of the micas.

70

71 **EXPERIMENTAL DETAILS**

72 **a. Materials.** Na-Mica-*n* (*n*=2 and 3) were synthesized using the NaCl-melt method following
73 a similar procedure to that described by Alba et al.²³ Their structural formulae are Na_{*n*}[Si₈₋
74 _{*n*}Al_{*n*}]Mg₆O₂₀F₄·*z*H₂O, where *n* represent the charge per unit cell (*n*=2 and 3) and *z* is the number
75 of water molecules. The starting materials employed were SiO₂ (Sigma; CAS no. 112945-52-5,

76 99.8% purity), Al(OH)₃ (Riedel-de Haën; CAS no. 21645-51-2, 99% purity), MgF₂ (Aldrich;
77 CAS no. 20831-0, 98% purity), and NaCl (Panreac; CAS no. 131659, 99.5% purity).
78 Stoichiometric proportions of reactants were weighed and mixed in an agate mortar. The molar
79 ratio between the reactants were (8-*n*)SiO₂:(*n*/2)Al₂O₃:6MgF₂:(2*n*)NaCl. It was added twice the
80 amount of NaCl to ensure the complete charge balance with Na⁺ cation into the interlayer
81 space.³⁶ The optimal amount of mixture reaction for grinding was up to 2 g per batch during 30
82 min for ensuring the homogeneity of the mixture in an agate mortar. The heat treatments were
83 carried out in a closed Pt crucibles at 900 °C during 15 h using a heating rate of 10 °C·min⁻¹. The
84 product was washed with distilled water and the solid was separated by filtration, dried at room
85 temperature and then ground in the agate mortar.

86 **b. Preparation of tetradecylammonium micas.** The organomicas were prepared by a cation-
87 exchange reaction between the micas and variable concentration of tetradecylammonium salt to
88 satisfy the 0.5, 1, 2, 3 or 10 times the cation exchange capacity (CEC) of Na-Mica-*n*. Thus, the
89 primary amine was dissolved in an equivalent amount of HCl (0.1 M) and the resulting mixture
90 stirred for 3 h at 80 °C. The tetradecylammonium dispersion was then mixed with 0.6 g of Na-
91 Mica-*n* and stirred for 3 h at 80 °C. After adding hot deionized water, the mixture was stirred for
92 30 min at 50 °C and then the dispersion was centrifuged at 10,000 r.p.m. for 20 minutes. The
93 product was dissolved in a hot ethanol-water mixture (1:1) and stirred for 1 h at 50 °C and then
94 centrifuged.¹³ The precipitate was dried at room temperature. The sample will be named as C₁₄-
95 Mica-*n*-*m*; where *n* is the interlayer charge 2 or 3 and *m* is the initial concentration of the
96 tetradecylammonium salt (*m*=0, 0.5, 1, 2, 3 and 10 CEC). The samples C₁₄-Mica-*n*-0
97 corresponds to the as-synthesized sample Na-Mica-*n*.

98 **c. Techniques.** Simultaneous TG/DTA measurements were performed at the Departamento de
99 Cristalografía, Mineralogía y Química Agrícola (University of Seville, Spain) using a NETZSCH
100 (STA 409 PC/PG) instrument which is equipped with a Pt/Pt-Rh thermocouple for direct
101 measurement of the temperature at the sample/reference crucible from room temperature up to
102 900 °C (heating rate: 10 °C·min⁻¹) in an atmosphere of N₂. Approximately 150 mg of sample
103 was used and the DTA reference was pure aluminum oxide.

104 X-ray diffraction (XRD) patterns were obtained at the CITIUS X-ray laboratory (University of
105 Seville, Spain) on a Bruker D8 Advance instrument equipped with a Cu K_α radiation source
106 operating at 40 kV and 40 mA. Diffractograms were obtained in the 2θ range of 1–70° with a
107 step size of 0.05° and a step time of 3.0 s.

108 FTIR spectra were recorded in the range 4000–300 cm⁻¹ by the Spectroscopy Service of the
109 ICMS (CSIC-US, Seville, Spain), as KBr pellets, using a Nicolet spectrometer (model 510P)
110 with a nominal resolution of 4 cm⁻¹.

111 Single-pulse (SP) MAS-NMR experiments were recorded on the samples where the
112 tetradecylammonium concentration were the lowest and the highest because they should exhibit
113 appreciable differences at short-range order, C₁₄-Mica-n-m (n=2 and 3; m=0.5 and 10 CEC), the
114 C₁₄-Mica-n-2 was also measured for comparison with previous works^{19,20}. The measurements
115 were carried out on the Spectroscopy Service of the ICMS (CSIC-US, Seville, Spain) using a
116 Bruker DRX400 spectrometer equipped with a multinuclear probe. Powdered samples were
117 packed into 4-mm zirconia rotors and spun at 10 kHz. ²⁷Al MAS NMR spectra were acquired at
118 a frequency of 104.26 MHz, using a pulse width of 0.92 μs (π/2 pulse length = 9.2 μs) and a
119 delay time of 0.1 s. ²³Na MAS NMR spectra were recorded at 105.84 MHz with pulse widths of
120 2.0 μs (π/2 pulse length=12.0 μs) and a delay time of 0.1 s. ²⁹Si MAS NMR spectra were

121 acquired at a frequency of 79.49 MHz, using a pulse width of 2.7 μs ($\pi/2$ pulse length = 7.1 μs)
122 and a delay time of 3 s. ^{13}C MAS NMR spectra were recorded at 104.26 MHz with proton
123 decoupling, a pulse width of 2.5 μs ($\pi/2$ pulse length = 7.5 μs) and a delay time of 2 s. The
124 chemical shift values are reported in ppm with respect to 0.1 M AlCl_3 solution for ^{27}Al , 0.5 M
125 NaCl solution for ^{23}Na and tetramethylsilane for ^{29}Si and ^{13}C .

126

127 **RESULTS AND DISCUSSIONS**

128 **a. Adsorption in the interlayer space of organomicas: Hydrophobicity and stability.** To
129 investigate the structure and properties of the tetradecylammonium molecules adsorbed onto Na-
130 Mica-n, the adsorbed amount of the organic cations are monitored by TG.^{37,38,39} Table 1 shows
131 the content of water and surfactant obtained from the analysis of the TG curves, where the
132 amount of interlayer water is determined from the weight loss in the temperature range of 25–
133 170 $^\circ\text{C}$ and the amount of the adsorbed tetradecylammonium molecules is determined from the
134 weight loss between 170 and 900 $^\circ\text{C}$.⁴⁰

135 The amount of adsorbed tetradecylammonium is higher in C_{14} -Mica-3 than in C_{14} -Mica-2,
136 thus, the main adsorption may occur by cation exchange, and this adsorption is proportional to
137 the initial concentration of alkylammonium. In C_{14} -Mica-n-m ($m < 2$), tetradecylammonium is
138 adsorbed in less amount than their CEC (ca. 0.60 CEC for $m=0.5$ and ca. 0.95 CEC for $m=1$). At
139 $m \geq 2$ the alkylammonium cations adsorption exceeds the mica exchange capacity and this excess
140 is stabilized by van der Waals interactions between alkyl chains.^{41,42,43,44} This excess is only
141 slightly higher than the CEC for C_{14} -Mica-3-m, for $m=2$ and 3, but is five time higher than CEC
142 for $m=10$. The alkylammonium concentration necessary to satisfy the layer charge is higher for

143 C₁₄-Mica-3 and, thus, the packing density is higher and the van der Waals interactions between
144 alkyl chains are favored.

145 DTG analysis (Figure 1) suggests two distinct states for the intercalated surfactant molecules:
146 (i) the first one is associated to the thermal decomposition of intercalated alkylammonium, with
147 stronger interaction, and, thus, requires a higher temperature (442 °C) to decompose^{45,46}, and, (ii)
148 the second one is due to the presence of ion-pair alkylammonium ions,²⁰ with weaker interaction,
149 whose decomposition temperature is slightly lower (ca. 350 °C). For m=0.5 only the
150 decomposition at the higher temperature is observed and agrees with the adsorption of surfactant
151 of ca. 60 % of their CEC (Table 1). As the initial concentration of alkylammonium increases the
152 decomposition at lower temperature is more relevant and becoming the dominant process for
153 C₁₄-Mica-3-10.

154 Mica surface properties can be altered from hydrophilic to organophilic by the exchange of the
155 hydrated Na⁺ interlayer cation by an organic one,⁴⁷ and consequently causing a drastic
156 diminishing of the water content. Thus, whereas the water content on Na-Mica-n-0 is found to be
157 between 3.17 and 3.63 molecules per unit cell; it decreases on C₁₄-Mica-n-m due to the
158 replacement of Na⁺ for the organic cations favoring the hydrophobic character of the interlayer
159 space (Table 1). For m≤1, a gradual decrease of interlayer water with alkylammonium
160 concentration is observed, being in concordance with an increasing in the exchange of inorganic
161 cations by the organic ones. However, for m≥2, the amount of water slightly increases with
162 alkylammonium concentration due to that is adsorbed not only by cation exchange reaction but
163 also by ionic pair which could adsorb some water molecules in the hydrophilic head of the
164 cationic surfactant.

165 The hydrophilic character of the interlayer space after the adsorption of different
166 concentrations of tetradecylammonium can be explained from the analysis of the ^{23}Na MAS
167 NMR spectra (Figure 2). The ^{23}Na MAS NMR spectra of $\text{C}_{14}\text{-Mica-n-0}$ (Na-Mica-n) is
168 characterized by two signals one at 3.7 ppm due to sodalite⁴⁸, and other at -10.1 ppm due to fully
169 hydrated exchangeable sodium^{49,50}. When the initial concentration of the alkylammonium
170 increases the signal of interlayer sodium decreases, this effect is more evident as the layer charge
171 increases. It corroborates the increasing hydrophobic character of the interlayer space and that
172 the slightly increasing of water content observed for $m \geq 2$ (see Table 1) is due to water associated
173 at ionic pair tetradecylammonium. The interlayer sodium is completely replaced in $\text{C}_{14}\text{-Mica-3-}$
174 10 in good agreement with the extremely high content of adsorbed tetradecylammonium (Table
175 1).

176 **b. Tetradecylammonium package on organomicas.** The analysis of the $00l$ reflections of the
177 XRD patterns (Figure 3) can be shed a light on the long-range structural order of the
178 organomicas. The basal spacing of Na-Mica-n is 1.20 nm, which corresponds to Na^+ in the
179 interlayer space surrounded by one water pseudomonolayer.²³ The exchange reaction between
180 Na^+ and the tetradecylammonium cation causes an increase in the basal spacing (d_{00l}). An unique
181 and well-ordered sequence of the $00l$ reflections is only observed for the $\text{C}_{14}\text{-Mica-3-10}$, and that
182 corresponds to a basal spacing of 4.02 nm, an interlayer gallery height of 3.08 nm (Table 2),
183 compatible with paraffinic bilayer -type structures.^{51,52,53} Paul et al.⁵⁴ observed that the surfactant
184 molecules adopt an arrangement that allow them to pack efficiently; therefore, the maximum
185 concentration of adsorbed tetradecylammonium in $\text{C}_{14}\text{-Mica-3-10}$ could favor a high and ordered
186 packing which is reflected in a well-ordered sequence of the $00l$ reflections. However, in the
187 other $\text{C}_{14}\text{-Mica-n-m}$, at least two $00l$ reflections sequences are observed. The splitting of the $00l$

188 reflections cannot be explained by inhomogeneity of the charge distribution, which is not
189 expected as the starting material is the same for all the micas, and in C₁₄-Mica-3-10, a unique *00l*
190 sequence is observed.

191 In C₁₄-Mica-n-0.5, the most intense *00l* reflection corresponds to a basal spacing of 2.48 nm
192 (for n=2) and 3.50 nm (for n=3), which could be compatible with a paraffin conformation but a
193 small *00l* reflection due to a basal spacing of 1.43 and 1.34 nm (for n=2 and 3, respectively) is
194 also observed and is compatible with a monolayer conformation (Table 2).⁵⁵ Hydrocarbon chains
195 lying flatly on the surface would make the clay hydrophobic even at low surface coverage and it
196 can explain the decreases in the interlayer space water content although only the 60 % of CEC
197 was satisfied in C₁₄-Mica-2-0.5.

198 The arrangement of a lateral monolayer of the alkyl chains evolves to a paraffin-type bilayer in
199 the interlayer of micas with the increase in surfactant concentration.³³ The reason is that the
200 interlayer alkylammonium molecules cannot form parallel layer arrangements in the interlayer
201 space of the mica when the interlayer cation density is higher than 1.94.²⁰

202 The d-spacing of the main *00l* reflection increases with the increase surfactant concentration
203 and the layer charge, as previously reported in montmorillonites.⁵⁶ Mainly,
204 the alkyl chains take the arrangement of a paraffin-type bilayer with a tilting angle ranging
205 between 24° and 59° (Table 2).

206 IR/FT spectroscopy is used to support the evidence of compaction of the surface film on the
207 clay minerals. The IR/FT absorption bands at 1450–1480 cm⁻¹ (Figure 4) can be ascribed to the
208 methylene scissoring mode. They have been found to be sensitive to the interchain interactions
209 and consequently, can be used as a probe of the packing arrangements in alkyl chain
210 assemblies.^{57,58} When the methylene groups are found in an all parallel arrangement, a triclinic

211 subcell, a sharp and narrow singlet at 1472 cm^{-1} is observed.⁵⁸ However, when they are displayed
212 in a hexagonal phase, the band position moves up to 1468 cm^{-1} and when they conform an
213 orthorhombic subcell, the bands change to a doublet at 1462 and 1473 cm^{-1} .⁵⁸ With the exception
214 of C₁₄-Mica-3-10, in all the samples (Figure 4) the band is a singlet located at $1468 \pm 1\text{ cm}^{-1}$,
215 reflecting that the surfactant surface is arranged in a hexagonal phase.⁵⁹ For C₁₄-Mica-3-10,
216 where the interlayer Na⁺ is completely replaced by tetradecylammonium, a doublet at 1462 and
217 1475 cm^{-1} is observed indicating an orthorhombic cell with intermolecular interaction between
218 the two adjacent hydrocarbon chains.⁵⁷ Those interactions are favored by the high adsorption of
219 tetradecylammonium, ca. 500 % of its CEC (Table 1).

220 The CH₂ stretching bands are generally the strongest bands and the frequency of these ν_{as} and
221 ν_{s} bands are sensitive to the *gauche/trans* conformer ratio of the hydrocarbon chains. A shift
222 from low frequencies characteristic of highly ordered, *all-trans* conformations, to higher
223 frequencies and increased width is accompanied as the number of *gauche* conformers (the
224 "disorder" of the chain) increases.⁵⁹ Independently of the initial tetradecylammonium
225 concentration, those bands are centered at $2919 \pm 1\text{ cm}^{-1}$ and $2849 \pm 1\text{ cm}^{-1}$, for ν_{as} and ν_{s}
226 vibrational modes respectively, (Figure S1) which denotes a high proportion of *all-trans*
227 arrangement.⁶⁰

228 Substantial information of the tetradecylammonium structure can be obtained from the ¹³C
229 MAS NMR analysis (Figure S2). In general, the spectra are similar to those previously reported
230 for C_x-Mica-n (n=2, 3 or 4; and x=12 or 18).^{19,20} As previously reported,^{19,20} the spectra show a
231 set of narrowed signals (marked with asterisk in Figure S2) that is likely corresponds to
232 tetradecylammonium with a different package in good agreement with the various *00l*
233 reflections families observed by XRD. It is also remarkable a narrow and intense peak at ca. 15

234 ppm from the terminal peak in C₁₄-Mica-3-10 where tetradecylammonium was adsorbed in an
235 amount over the 500 % of CEC. Among the signals, the resonances at 30-33 ppm, internal
236 methylene (Figure 5), are important to be analyzed since information on the chain configuration
237 can be obtained.⁶¹ That signal is the convolution of two peaks at ca. 30 ppm (mixed *gauche* and
238 *trans*, disordered configuration) and at ca. 33 ppm (all-*trans*, ordered configuration).^{62,63} When
239 the interlayer tetradecylammonium concentration increases, the proportion of disordered
240 configuration diminishes as the alkyl chain freedom decreases. These data are consistent with
241 results reported in the literature, where He et al.⁶⁴ observed that the all-*trans* conformer is
242 favored at high amine concentration. The high proportion of C₁₄-Mica-3-0.5 in disordered
243 configuration may be explained by its high available volume per tetradecylammonium cations
244 (0.66 nm³/mol in C₁₄-Mica-3-0.5 compared to 0.10 nm³/mol in C₁₄-Mica-3-10).

245 **c. Analysis of organomicas framework.** The short-range framework structural order of the
246 organomicas is analyzed by ²⁹Si and ²⁷Al MAS NMR.

247 The ²⁹Si MAS NMR spectra (Figure 6) is characterized by a set of bands in the range between
248 $\delta = -70$ to -95 ppm, consistent with the existence of four Q³(*q*Al) ($0 \leq q \leq 3$) environments.⁶⁵
249 While the spectra of C₁₄-Mica-n-0 is consistent with those previously reported for these micas,¹⁹
250 the Q³(3Al) signals of C₁₄-Mica-n-m ($m \geq 0.5$) are shifted up to ca. 2.1 and 2.5 ppm, for n= 2 and
251 3 respectively, towards lower frequencies. A similar shift has already been observed in the ²⁹Si
252 frequencies of high charge swelling silicates, and was attributed to the formation of inner sphere
253 complexes between the interlayer cations and the basal oxygen of the silicate tetrahedral layer.⁶⁶
254 In the same manner, and according to the high tilt angle observed by XRD (Table 2), the ²⁹Si
255 signal shifts in C₁₄-Mica-n is caused by the inclusion of the NH₃⁺ into the pseudohexagonal hole
256 of the silicate framework. The above results reinforce the proposed bi-layer structure with alkyl

257 chains in an all-*trans* configuration, and that the polar part of the surfactant is close to the basal
258 oxygen plane.

259 All the ^{29}Si MAS NMR spectra of $\text{C}_{14}\text{-Mica-n-m}$ ($m \geq 0.5$) show similar relative peak intensities
260 in comparison with $\text{C}_{14}\text{-Mica-n-0}$. The ^{27}Al MAS NMR spectra of $\text{C}_{14}\text{-Mica-n-0}$ (Figure S3) are
261 characterized by a signal at ca. 60 ppm typical of tetrahedral aluminum. No additional signals
262 due to a different Al coordination number after tetradecylammonium adsorption is observed.
263 Therefore, the exchange process does not alter the Si and Al distribution.

264

265 **CONCLUSIONS**

266 Tetradecylammonium has been intercalated in the interlayer space of synthetic swelling high-
267 charge micas. Both the interlayer charge of mica and the initial concentration of
268 tetradecylammonium determine the adsorbed amount and, therefore, the arrangement of the
269 organic cations in the interlayer space.

270 The effect of the mica layer charge is more evident at high concentration. The molecular
271 arrangement of the surfactant is found to follow the bilayer-paraffin model for all values of layer
272 charge and surfactant concentration. However, at initial concentration below the mica CEC, a
273 lateral monolayer is also observed.

274 The alkyl chain of the tetradecylammonium adopts a configuration that is a mixture between
275 ordered (all-*trans*) and disordered (mixed *gauche-trans*); the amount of the disordered
276 arrangement being higher in $\text{C}_{14}\text{-Mica-n-0.5}$ where the CEC of the mica is not satisfied.

277 For a high adsorbed tetradecylammonium, $\text{C}_{14}\text{-Mica-3-10}$, a unique family of *00l* plane and a
278 change from hexagonal phase to orthorhombic cell is observed.

279

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282 **Author Contributions**

283 The manuscript was written through contributions of all authors. All authors have given approval
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Table 1. Water and tetradecylammonium contents of the C₁₄-Mica-n-m (n=2 and 3)

n	m	25°-170° C			170°-900° C	
		%	mol H ₂ O/ mol mica ^[b]	% ^[a]	mol C ₁₄ / mol mica ^[b]	%CEC
2	0	6.6	3.17	0.9	-	--
	0.5	2.2	1.30	24.7	1.20	60.0
	1	0.1	0.07	34.7	1.90	95.0
	2	0.3	0.21	39.4	2.30	114.8
	3	0.4	0.28	40.2	2.36	118.2
	10	0.3	0.23	44.9	2.83	141.6
3	0	7.3	3.63	1.2	-	--
	0.5	3.5	2.40	34.1	1.90	63.4
	1	0.0	0.00	44.3	2.84	94.7
	2	0.3	0.26	51.2	3.65	121.7
	3	0.3	0.25	50.7	3.59	119.5
	10	0.7	1.46	87.1	15.18	506.1

^[a] % weight loss of the dry samples

^[b] It has been calculated taking into account the unit cell formulae (C₁₄)_mNa_{n-m}(Si_{8-n}Al_n)Mg₆O₂₀F₄; n=2 or 3

Table 2. Geometrical and Package Parameters of the C₁₄-Mica-n-m (n=2 and 3)

m	C ₁₄ -Mica-2					C ₁₄ -Mica-3				
	0.5	1	2	3	10	0.5	1	2	3	10
d ₀₀₁ (nm)	3.51 ⁱ 2.48 ^{ii*} 1.43 ⁱⁱⁱ	4.08 ⁱ 2.65 ^{ii*}	4.19 ⁱ 3.06 ^{ii*}	4.06 ⁱ 3.14 ^{ii*}	4.18 ^{i*} 3.63 ^{ii*} 3.13 ⁱⁱⁱ 2.40 ^{iv}	3.50 ^{i*} 2.56 ⁱⁱ 1.34 ⁱⁱⁱ	4.05 ^{i*} 2.99 ⁱⁱ 2.66 ⁱⁱⁱ	4.18 ^{i*} 3.06 ⁱⁱ	4.05 ^{i*} 3.49 ⁱⁱ 3.01 ⁱⁱⁱ	4.02
h ^[a] (nm)	2.57 1.54* 0.49	3.14 1.71*	3.25 2.12*	3.12 2.20*	3.24* 2.69* 2.19 1.46	2.56* 1.62 0.40	3.11* 2.05 1.72	3.24* 2.12	3.11* 2.55 2.07	3.08
V ^[b] (nm ³)	1.27 0.76* 0.24	1.55 0.84*	1.61 1.05*	1.54 1.09*	1.60* 1.33* 1.08 0.72	1.26* 0.80 0.20	1.54* 1.01 0.85	1.60* 1.05	1.54* 1.26 1.02	1.52
α ^[c] (°)	42.70 23.97* --	55.94 26.82*	59.04 34.01*	55.41 35.48*	58.75* 45.22* 35.30 22.66	42.49* 25.31 --	55.14* 32.74 26.99	58.75* 34.01	55.14* 42.29 33.10	54.36

^[i-iv] from the [00l]^{i-iv} planes of Figure 3

* from the most intense 00l reflection

^[a] h=d₀₀₁-0.94 and it is the high of interlayer gallery

^[b] V=h·a·b (a=0.534 nm, b=0.925 nm) and it is the interlayer volume

^[c] h=2·[(n_c-1)·0.126+0.131]·sinα; where α is the tilt angle of the alkylchain and n_c is the number of carbon atoms in the alkyl chain (n_c=14)

FIGURE CAPTIONS

Figure 1. DTG curves of the C₁₄-Mica-n-m (n=2 or 3 and m=0.5, 1, 2, 3 and 10 CEC) in the tetradecylammonium decomposition temperature range.

Figure 2. ²³Na MAS NMR spectra of the C₁₄-Mica-n-m (n=2 or 3 and m=0, 0.5, 1, 2, 3 and 10 CEC).

Figure 3. XRD patterns of the C₁₄-Mica-n-m (n=2 or 3 and m=0, 0.5, 1, 2, 3 and 10 CEC).

Figure 4. The methylene scissoring vibrational region of the IR/FT spectra of the C₁₄-Mica-n-m (n=2 or 3 and m=0.5, 1, 2, 3 and 10 CEC).

Figure 5. Internal methylene groups region of the ¹³C MAS NMR raw spectra (left) and deconvoluted spectra (right) of the C₁₄-Mica-n-m (n=2 or 3 and m=0.5, 2 and 10 CEC). The light grey area corresponds to the *trans* configuration contribution (I_t) and the dashed light grey area corresponds to the *trans-gauche* configuration contribution (I_{t-g}).

Figure 6. ²⁹Si MAS NMR spectra of the C₁₄-Mica-n-m (n=2 or 3 and m=0, 0.5, 2 and 10 CEC). Dashed line indicates the Q³(qAl) environments.

Figure 1

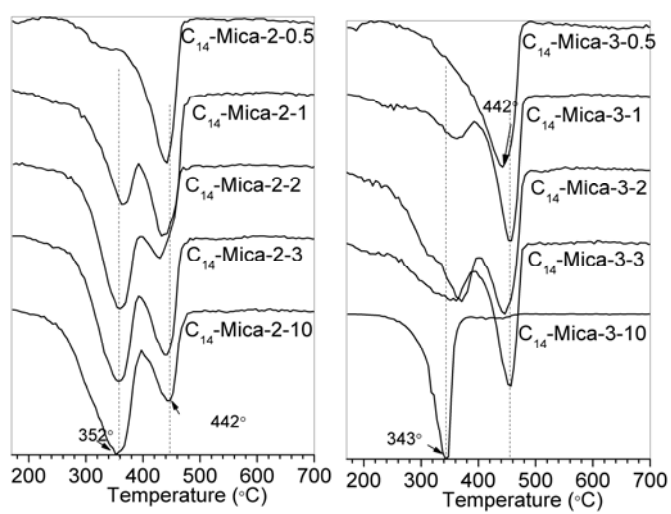


Figure 2

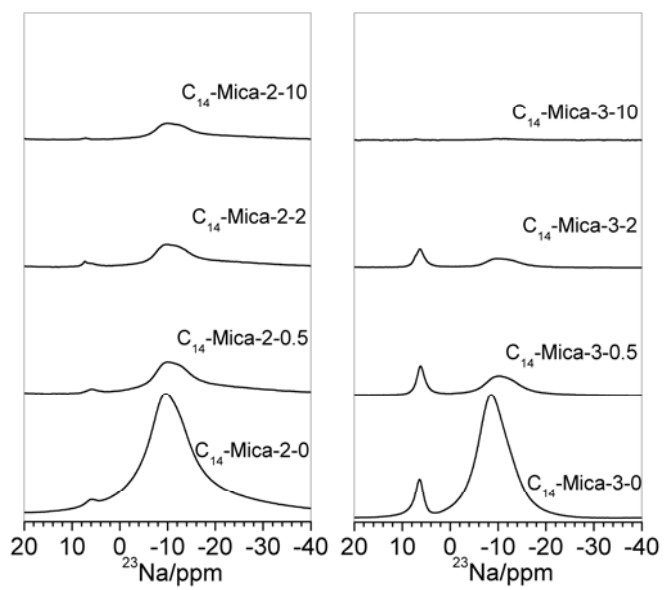


Figure 3

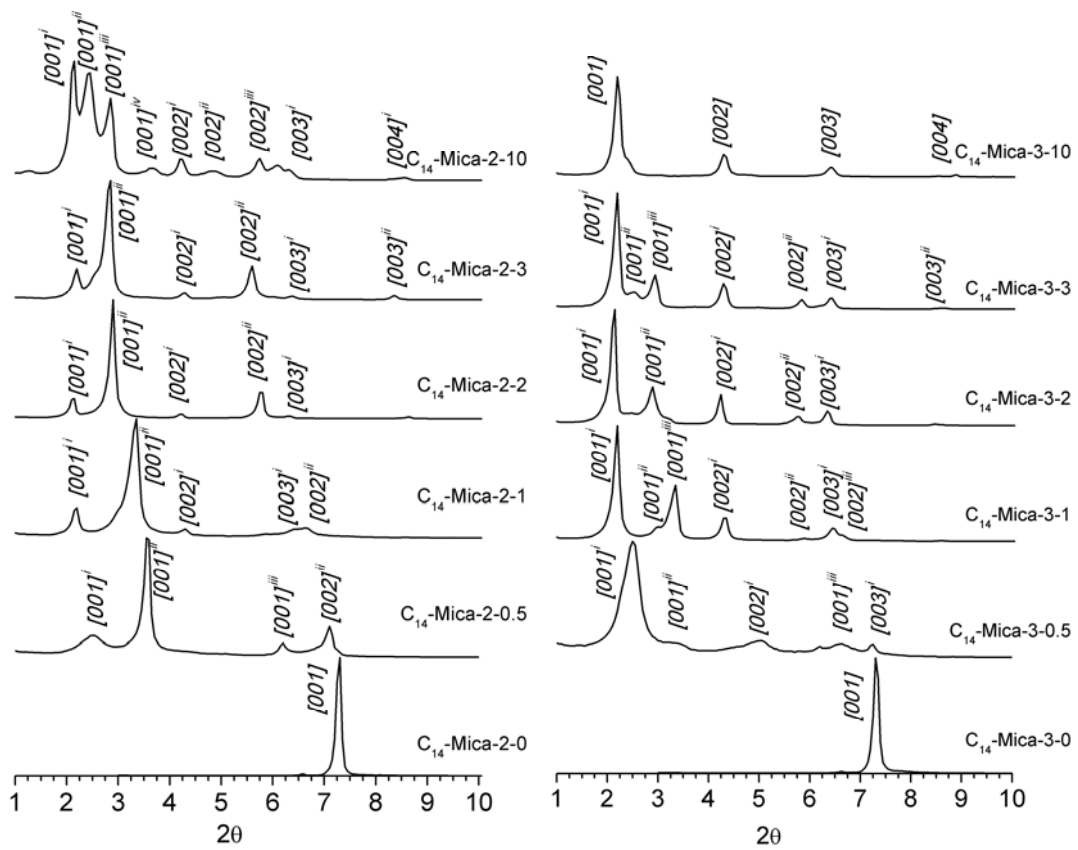


Figure 4

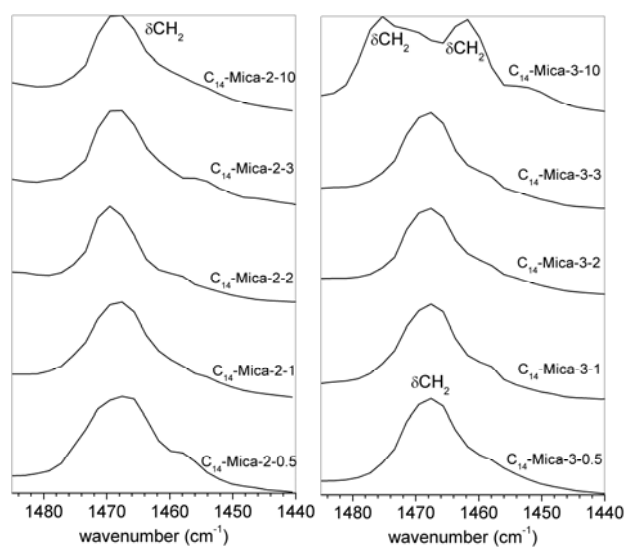


Figure 5

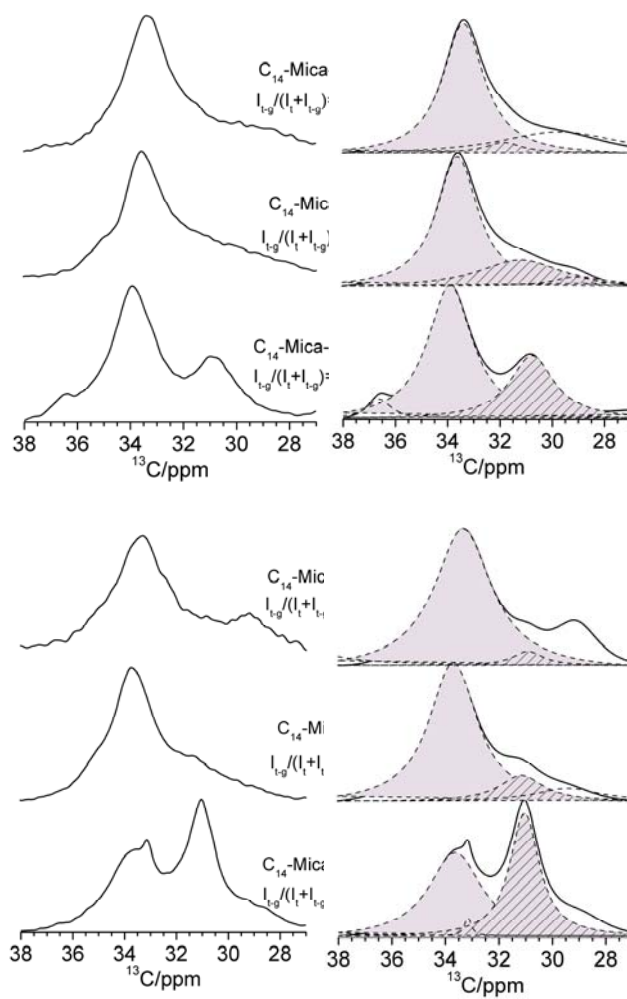


Figure 6

