ONE-STEP SYNTHESIS OF ALKYLTRIMETHYLAMMONIUM-INTERCALATED MAGADIITE

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Abstract—Cetyltrimethylammonium- and tetradecyltrimethylammonium-intercalated magadiites were prepared by direct syntheses, starting from sodium metasilicate (Na_2O/SiO_2 = 1.0) and nitric acid. Total substitution of sodium by cetyltrimethylammonium or tetradecyltrimethylammonium cations was not achieved in the range of surfactant:silicon molar ratios used in this study. When a phosphoniun-based surfactant replaces the ammonium surfactants in the same procedure, the result of the synthesis is a mixture of quartz and unmodified surfactant. If dodecylammonium bromide is used, an MCM-41 molecular sieve is obtained. The substitution of the silicon source by tetramethylammonium silicate or of nitric acid by hydrochloric, hydrofluoric, or acetic acids also yields MCM-41 molecular sieves, indicating that the formation of magadiite is greatly dependent on the presence of sodium cations and nitrate anions.

Key Words—Alkylammomium-Intercalated Magadiite, Intercalation, Magadiite, Organo-Magadiite.

INTRODUCTION

Magadiite is a naturally occurring crystalline silicate (Beneke and Lagaly, 1977, 1983; Eugster, 1967; Fletcher and Bibby, 1987; Iler, 1964), although it can also be synthesized (Schwieger *et al.*, 1988, 1991). Magadiite is a member of a family of silicic acids comprising also makatite [the only member whose structure is known (Annehed *et al.*, 1982)], kanemite, octosilicate, and kenyaite. The general formula is $Na_2O\cdot(4{-}22)SiO_2\cdot(5{-}10)H_2O$. Generally, the structure of these materials is comprised of silicate layers separated by hydrated sodium cations. Each of these materials is characterized by a basal spacing varying from 0.9 to 2.0 nm and a specific silicate-layer thickness (Almond *et al.*, 1997).

These materials display ion-exchange properties; the exchanged or intercalated forms have found many applications. Surfactant-intercalated kanemite is used in the synthesis of mesoporous molecular sieves (Inagaki *et al.*, 1993), and surfactant-intercalated magadiite is used for the preparation of elastomeric polymer-layered silicate nanocomposites (Wang *et al.*, 1996; Wang and Pinnavaia, 1998) that show improved tensile properties owing to the reinforcement effect of the silicate nanolayers. Magadiite with isomorphous substitution of aluminum may be used to prepare pentasil zeolites (Borbély *et al.*, 1997) as well as ferrierite (Borbély *et al.*, 1998). Interestingly, it is obtained as a by-product in the synthesis of high-silica zeolites (Araya and Lowe, 1985; Van der Gaag *et al.*, 1985). The interlayer galleries in magadiite can also be modified by organosilylation, which creates organically-modified surfaces. These materials find uses in chromatographic stationary phases (Wirth *et al.*, 1997).

Although organic compounds have not been reported as templates for magadiite formation, other clay materials are known to be prepared by a templated-synthesis process. Carrado *et al.* (1991, 1996) showed that hectorite may be obtained by synthesis with porphyrins and metalloporphyrins and water-soluble polyvinyl alcohols. Direct-synthesis techniques were also employed to prepare layered magnesium silicate materials modified by alcoxysilanes (Burkett *et al.*, 1997).

In this work, we show that cetyltrimethylammonium- and tetradecyltrimethylammonium-intercalated magadiite can be prepared directly in a one-step synthesis, a procedure that takes three days. Upon extraction of the organic counterpart, the alkyltrimethylammonium-intercalated magadiite converts to pure H and Na-rich magadiite.

EXPERIMENTAL METHODS

The samples were prepared by dissolving an appropriate amount of sodium metasilicate (Vetec, Rio de Janeiro, Brazil; 25.9 wt. % SiO_2, 26.6 wt. % Na_2O, 47.3 wt. % H_2O, Na_2O/SiO_2 = 1.0) in distilled water to produce a 1.5 mol L^{-1} silica solution. A 33 wt. % suspension of aqueous cetyltrimethylammonium bromide (CTABr, Alfa Æsar, Wardhill, Massachusetts, USA) solution, aged for at least 12 h at room temperature, was added to the silicate solution to give a reaction mixture of composition: $Na_2O\cdot SiO_2\cdot xCTA_2O\cdot 100H_2O$, where x was adjusted to yield CTA/Si molar ratios of 0.5, 1.0, and 2.0. After a 30-min stirring period at room temperature, concentrated nitric acid (Merck, Rio de Janeiro, Brazil; 63 wt. %, density of 1.40 g mL^{-1}) was added under vigorous stirring until the pH was lowered from ~13.5 to 10.8–10.9. At pH ~11.0, the suspension became extremely viscous and required mechanical stirring. This suspension was aged and stirred for 4 h at 347–349 K. Then, the suspension was placed in a Teflon-lined autoclave and heated at 423 K for 66 h. The white product in solution was still a very viscous suspension. Approximately

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Table 1. Elemental analysis for intercalated magadiites.

[1]Surf/Si (gel)	% SiO_2	% Surf	% Na	Surf/Si (solid)	Unit cell	$d(001)$/nm
0.5	65.11	18.50	1.16	0.06	$H_{0.53}Na_{0.57}CTA_{0.90}Si_{14}O_{29}$	3.4
1.0	65.66	21.77	1.60	0.07	$H_{0.07}Na_{0.95}CTA_{0.98}Si_{14}O_{29}$	3.1
2.0	60.47	32.90	[3]b.d.	0.12	$H_{0.32}CTA_{1.68}Si_{14}O_{29}$	3.1
[2]1.0	82.90	3.93	3.32	0.01	$H_{0.58}Na_{1.28}TDTMA_{0.14}Si_{14}O_{29}$	4.2

[1] Surf = surfactant cations.
[2] Sample prepared with tetradecyltrimethylammonium cations, TDTMA.
[3] Below detection.

five times more distilled water was added and the solution sonicated until the solid separated from the mother liquor. The solid was filtered and washed until no foam was produced. This white powder was placed in a dessicator above a saturated $CaCl_2$ aqueous solution. The organic portion was extracted with a Soxhlet apparatus, with a 50:50 ethanol:heptane solution (Whitehurst, 1992), to which HCl (Merck, Rio de Janeiro, Brazil; 35 wt. %) was added to yield a 0.15 mol L^{-1} solution. The alkyltrimethylammonium-intercalated magadiite was transfered to a folded filter paper and placed in the Soxhlet extractor. A ratio of 500 mL of solution per gram of solid was used in the extraction procedures. This solid was washed for 45 h at 80°C. One sample of tetradecyltrimethylammonium bromide (Aldrich, Milwaukee, Wisconsin, USA), cetyltri-n-butylphosphonium bromide (Alfa Æsar, Wardhill, Massachusetts, USA) and dodecylammonium bromide (prepared in the laboratory by the neutralization of dodecylamine with hydrobromic acid) was prepared, using the procedure given above with a surfactant/Si molar ratio of 1.0. A pure magadiite sample was also prepared by the above procedure without the addition of a surfactant.

The samples were analysed by powder X-ray diffraction in the form of hand-pressed wafers, in a Shimadzu XD3A powder diffractometer at 20 mA and 30 kV. Cu$K\alpha$ radiation was used at a scanning rate of 2 °2θ/min. For the infrared-spectroscopic study, samples were mixed with KBr at a concentration of ~1 wt. %, and analyzed in a Bomem M-8 spectrometer, with an accumulation of 16 scans at a resolution of 4 cm^{-1}. For ^{29}Si-magic angle spinning nuclear magnetic resonance (MAS-NMR), samples were packed into zirconia rotors and spun at 4 kHz in a Bruker AC300 P spectrometer, at a frequency of 59.6 MHz, decoupled from protons, with 200-s delay time, and 0.1-s acquisition time. Chemical shifts were referenced to tetramethylsilane (TMS). For thermogravimetry, samples were loaded into alumina pans and heated at a rate of 20 K min^{-1}, in an atmosphere of 100 mL min^{-1} argon, from room temperature to 1273 K in a Hi-Res TGA 2950 (TA Instruments). For scanning-electron microscopy, samples were suspended in acetone (approximately one part of solid sample in 30–40 parts of ac-

etone) and sonicated for at least 15 min. One drop of this suspension was placed in a sample holder, the acetone was allowed to evaporate, and the sample coated with carbon. Secondary-electron images were obtained in a Jeol, model JSM T-300 microscope with 20 kV accelerating voltage.

Samples were analyzed for sodium content by atomic absorption spectrometry (AAS). Typically, 500 mg of each sample was heated at 800°C for 6 h and dissolved with 3 mL of HF (Merck; 47 wt. %), 3 mL of HNO_3 (Merck; 65 wt. %), and 3 drops of $HClO_4$ (Merck; 70 wt. %) in Teflon containers, using a sand bath at 150°C. After dissolution and complete drying of the sample, it was dissolved in deionized water in 100-mL volumetric flasks and subsequently diluted to 0.5 mg L^{-1}. These solutions were analyzed at 589 nm in a Perkin Elmer 5100 Spectrometer operating with an air/acetylene flame. The content of surfactant in each sample was determined by thermogravimetric analysis. The silica content was determined by the mass of the residue in the thermogram by considering the mass of sodium. The results of the sodium analysis by AAS, as well as those of sodium and organic analyses, are given in Table 1.

RESULTS AND DISCUSSION

Note in Table 1 that an increase in CTA/Si molar ratio in the synthesis causes an increased substitution of Na^+ by CTA^+, but no sample shows a complete substitution by CTA^+ ions. When the ratio of CTA/Si in the gel is 1.0, further increases in CTA concentration do not occur in the solid.

Figure 1 shows the powder X-ray diffractograms of samples after the aging period and after hydrothermal crystallization. The patterns (Figure 1, traces b, c, and d) are similar to the hexagonal mesoporous molecular sieves of Beck et al. (1992), whereas the diffractogram in Figure 1 (trace e) appears to be of non-organized silica-surfactant rods (Chen et al., 1995). Figure 1 (trace a) is the product of the aged sample where no CTABr was added.

The hydrothermal crystallization of these precursors produces CTA-intercalated magadiites for each of the CTA/Si molar ratios used (Figure 1, traces g, h, and j), as indicated by the occurrence of a peak at 3.0–4.2
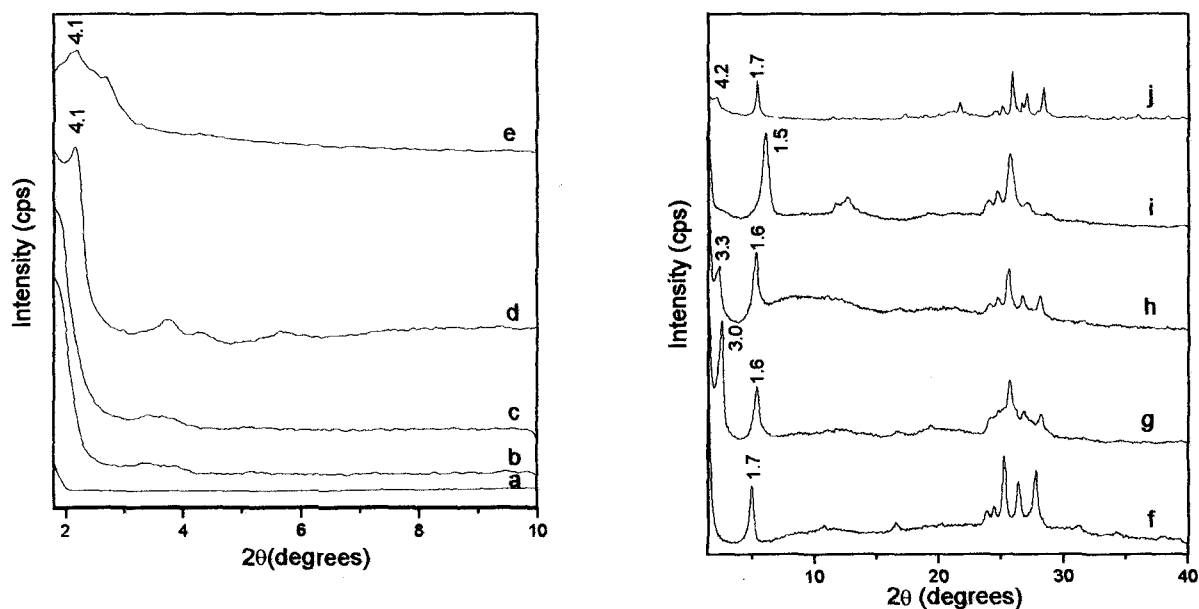
Figure 1. Powder X-ray diffractograms of precursor samples, (a) Na^+-rich magadiite after aging, (b) MCM-41 from a starting ratio of CTA/Si = 1.0, (c) MCM-41 prepared with CTA/Si = 2.0, (d) MCM-41 prepared with CTA/Si = 0.5, (e) non-organized silica-surfactant rods prepared with tetradecyltrimethylammonium bromide in a surfactant:Si molar ratio of 1.0. Samples after hydrothermal treatment (f) Na^+-rich magadiite, (g) CTA/Si = 1.0, (h) CTA/Si = 0.5, (i) sample from (h) after the extraction of the organic molecules, (j) sample prepared with tetradecyltrimethylammonium bromide.

nm owing to the interlayer spacing created by the surfactant molecules. The success of the extraction procedure was evaluated by infrared spectra, where no bands assignable to organics were observed and by thermal analysis, where the peak corresponding to CTA^+ cations was no longer present. The diffractogram of the extracted sample, Figure 1 (trace i), compares well with pure magadiite in Figure 1 (trace f). The relative intensities of peaks below 0.356 nm (above 25 °2θ) are different in the intercalated and organics-extracted magadiite from the magadiite prepared in the absence of surfactant molecules. The peak at ~0.343 nm (~25.9 °2θ) is more intense in these samples than in magadiite. This result is probably related to the exchange of Na^+ ions by H^+. In H-rich magadiite, only one peak is observed in powder X-ray diffraction patterns, at ~0.342 nm (~26 °2θ) (Kosuge and Tsunashima, 1996). This peak (~0.343 nm) is more evident in samples where the organic molecules have been extracted (Figure 1, trace i) because an acid solution is used that probably promotes exchange of CTA^+ and/or Na^+ by H^+.

The interlayer spacing observed for these samples also indicates that the samples are at least partially acidic. Table 1 shows that the CTA-intercalated magadiites show a *d* value of 3.4–3.1-nm, whereas the tetradecyltrimethylammonium-intercalated magadiite shows a 4.2-nm basal spacing. The *d* value in H-rich magadiite is smaller than Na-rich magadiite (Yanagisawa *et al.,* 1988). Thus, if some sodium ions were

exchanged by protons, the spacing will be smaller than expected. Also, different relative configurations of the hydrophobic tails of the surfactant may account for the larger *d* value in the sample prepared with tetradecyltrimethylammonium bromide. Note that the sodium cations were not completely exchanged by H^+, probably because of the steric hindrance of the larger CTA^+ cations.

Infrared spectra are given in Figure 2. The bands corresponding to internal and external vibrations of SiO_4 tetrahedra (Flanigen *et al.,* 1976) are coincident within the 4-cm^{-1} resolution for CTA-intercalated magadiite (Figure 2, trace a), tetradecyltrimethylammonium-intercalated magadiite (Figure 2, trace b), and pure magadiite (Figure 2, trace c). The major differences observed are the better resolution of CTA-intercalated magadiite and the bands corresponding to the different surfactant molecules in the range of 850–960 cm^{-1} and at ~720 cm^{-1}.

The three bands in the "quartz" gap (~620, 580, and 540 cm^{-1}) are present in all samples and correspond to double-ring vibrations (Flanigen *et al.,* 1976) which are characteristic of magadiite among the other silicic acids of this family (Kosuge and Tsunashima, 1996).

Figure 3 shows the ^{29}Si-MAS NMR spectra of magadiite (Figure 3, trace a) and CTA-intercalated magadiite (Figure 3, trace b). Magadiite has three peaks corresponding to Q^4 at −112.9, −110.3, and −109.3 ppm in relation to TMS. Q^3 groups occur at −98.6
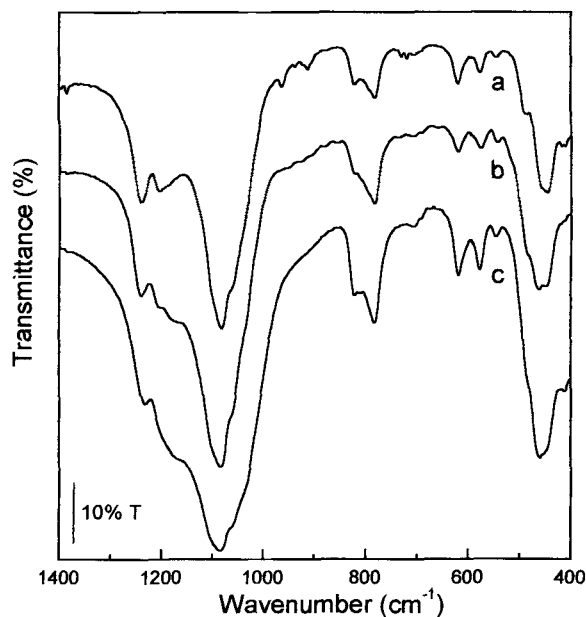
Figure 2.   Fourier-transform infrared spectra of (a) CTA-rich magadiite, (b) $C_{14}H_{29}^+$-rich magadiite, and (c) Na^+-rich magadiite.

Figure 3. ^{29}Si-MAS NMR of (a) Na^+-rich magadiite and (b) $C_{16}H_{33}^+$-rich magadiite.

ppm. The intercalated material shows one peak corresponding to Q^4 at -111.2 ppm and another at -99.9 ppm with a shoulder at -102.0 ppm, which is assigned to Q^3 (Engelhardt and Michel, 1987). These assignments are in agreement with those for dodecyltrimethylammonium-intercalated magadiite (Yanagisawa *et al.*, 1988; Ogawa *et al.*, 1998). The shoulder (Q^3) after intercalation may be related to different cations in the interlayer. The lack of side peaks of Q^4 may be related to a homogeneous distribution of angles in the silicate layer because of the presence of the organic cation (Engelhardt and Michel, 1987).

Figure 4 shows the morphology of these samples. Magadiite prepared in the absence of organics (Figure 4a) is more dense and suffered less disaggregation during the syntheses. In contrast, the tetradecyltrimethylammonium-intercalated magadiite (Figure 4b) is more disaggregated and more exfoliated than magadiite. This result also supports the partial replacement of Na^+ ions by H^+ since this procedure is known to cause exfoliation (Kosuge and Tsunashima, 1996). Unexchanged-magadiite aggregates, with a morphology similar to samples prepared by other methods (Kosuge and Tsunashima, 1996; Crone *et al.*, 1995), are also larger than alkyltrimethylammonium-intercalated magadiite: aggregates from 3.8 to 16.9 μm in size were found. Aggregates of alkyltrimethylammonium-intercalated magadiites are more homogeneous and smaller, varying from 4.2 to 8.4 μm for $C_{16}H_{33}^+$-rich magadiite, and ~10.3 μm for the $C_{14}H_{29}^+$-rich magadiite. No additional phases are observed, showing that the samples
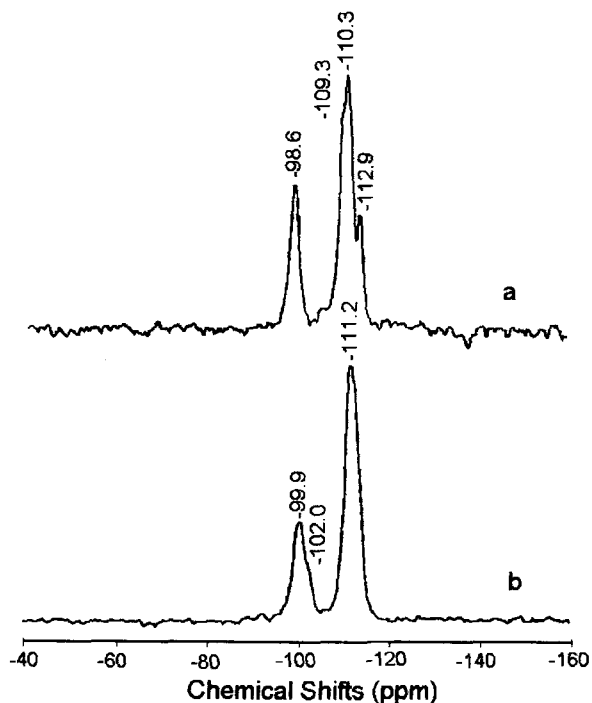
are pure and that no other silicic acid is contaminating magadiite.

When tetramethylammonium silicate with TMA/Si = 1.0 replaces sodium silicate, magadiite is not obtained. Instead, the precursors transform to more organized MCM-41 (molecular sieve) structures. Also, when acetic, hydrochloric, or hydrofluoric acids are used, only MCM-41 mesophases are obtained. This result is probably related to the presence of silicon in the precursor as a cubic octamer, Q_8^3, which is preferentially bound by the CTA^+ supramolecular arrangement (Firouzi *et al.*, 1997; Pastore *et al.*, 1999). This anion behaves as a chelate ligand, therefore bringing additional stability to the organic-inorganic composite. This does not occur for sodium silicate since the form of silicon differs from Q_8^3 (Engelhardt and Michel, 1987): the most polymerized silicon species in this solution is Q_6^3, the prismatic hexamer. Although Q_6^3 can also behave as a polydentate ligand, the fit between the charged head-group of the surfactant molecules and one of the triangular faces of Q_6^3 may be less satisfactory than for the cubic octamer.

Magadiite is only observed in the presence of nitrate anions and not in the presence of fluoride, acetate, or chloride. This result may be explained by the lower specificity constants, $K^X_{ex,Br}$, for these anions (Barriet *et al.*, 1980; Morgan *et al.*, 1994; Sepulveda and Cortés, 1985). This constant is approximated by the equilibrium constant for the following reaction:
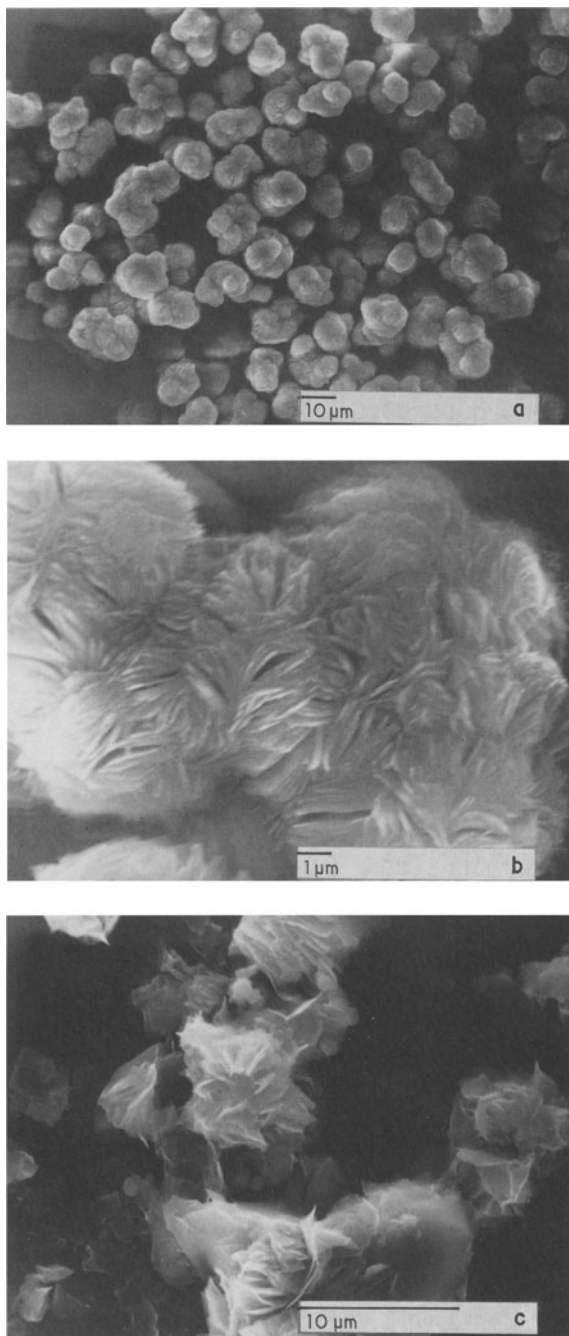
Figure 4.   Scanning-electron micrographs of Na⁺-rich magadiite (a,b) and $C_{14}H_{29}^+$-rich magadiite (c).

X^-	$^1K^X_{ex,Br}$
F^-	0.044
$^2OAc^-$	0.098
Cl^-	0.20
NO_3^-	1.3

[1] Barriet *et al.*, 1980; Morgan *et al.*, 1994; Sepulveda and Cortés 1985.
[2] OAc^- = acetate.

the silicon source is sodium silicate and favors silicate when tetramethylammonium silicate is used. Therefore, different silicon-based phases are obtained depending upon the nature of the species that populate the organic-inorganic interface.

Cetyltri-n-butylphosphonium bromide was also used in this synthesis study but the reaction results, either after aging or after hydrothermal treatment, were a mixture of quartz and the crystalline, unmodified surfactant in the lamellar mesophase. In contrast, when dodecylammonium bromide was used, MCM-41 was obtained as the precursor and as the product after hydrothermal synthesis.

This result also supports the importance of the adjustment of the polar head of the surfactant and the silicon source in determining the obtained phase. The tri-n-butylphosphonium surfactant comprises a softer polar head than with trimethylammonium and thus, is not bound either by silicate or nitrate; a mixture of quartz and the unmodified surfactant is obtained. Magadiite is not observed probably because sodium cations are associated with the nitrate. By the same reasoning, the harder nonsubstituted ammonium polar head of the dodecylammonium bromide is strongly bound by the silicate, and the nitrate anions cannot displace them. Thus, MCM-41 is obtained.

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$$CTABr + X^- \rightleftarrows CTAX + Br^- \qquad (1)$$

where X = acetate, chloride, fluoride, and nitrate. Table 2 is a tabulation of $K^X_{ex,Br}$ values.

Note that nitrate is the anion with the most effective bonding to CTA^+. The competition established between bromide, nitrate, and silicate anions for the CTA^+ supramolecular arrangement favors nitrate when

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