## Supporting information

# Phase transitions and chain dynamics of surfactants intercalated into the galleries of the naturally occurring clay mineral, magadiite

Boris B. Kharkov,[a,b] Robert W. Corkery,[a,c] Sergey V. Dvinskikh[a,b*]

[a]*Royal Institute of Technology KTH, Department of Chemistry, Teknikringen 36, SE-10044 Stockholm, Sweden*

[b]*St. Petersburg State University, Laboratory of Biomolecular NMR and Institute of Physics, St. Petersburg, 199034 Russia*

[c]*Australian National University, Research School of Physical Sciences, Canberra ACT 0200 Australia*

**Corresponding author. E-mail: sergeid@kth.se. Phone: +46 8 790 8824. Fax +46 8 790 8207*

## S1. Pulse sequences for SLF spectroscopy under MAS

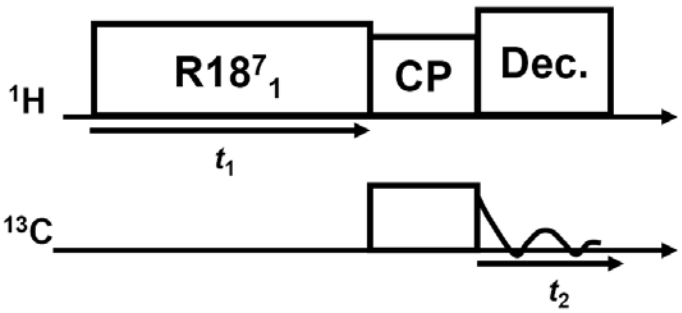


**Figure S1a.** Proton Detected/encoded Local Field spectroscopy with R-type recoupling (R-PDLF).[1] Proton magnetization evolves during the time period $t_1$ under the effect of the heteronuclear recoupling sequence R18$^7_1$.[2] This magnetization, modulated by the $^1$H–$^{13}$C dipolar interaction, is transferred via cross polarization (CP) to the $^{13}$C spins for detection during $t_2$ in the presence of the heteronuclear proton decoupling.

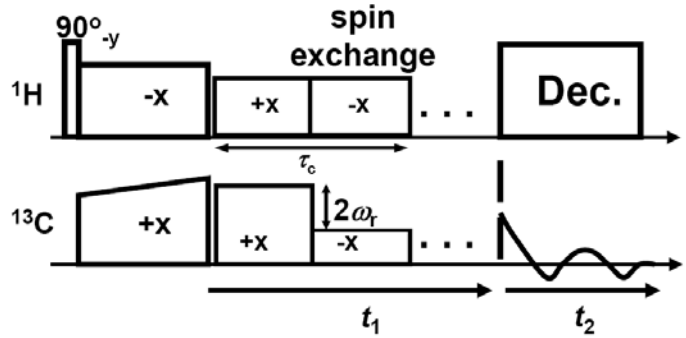


**Figure S1b.** Amplitude- and Phase-Modulated Cross-Polarization (APM-CP).[3,4] After the CP signal enhancement, the dipolar evolution period is initiated by inverting the phase of the $^1$H spin-lock field. The CP fields during $t_1$ period are phase- and amplitude-modulated to achieve the $^1$H-$^{13}$C heteronuclear dipolar recoupling. Finally, the $^{13}$C signal is detected in the presence of the heteronuclear $^1$H decoupling.

## S2. Carbon-13 MAS spectra in CTA/Magadiite

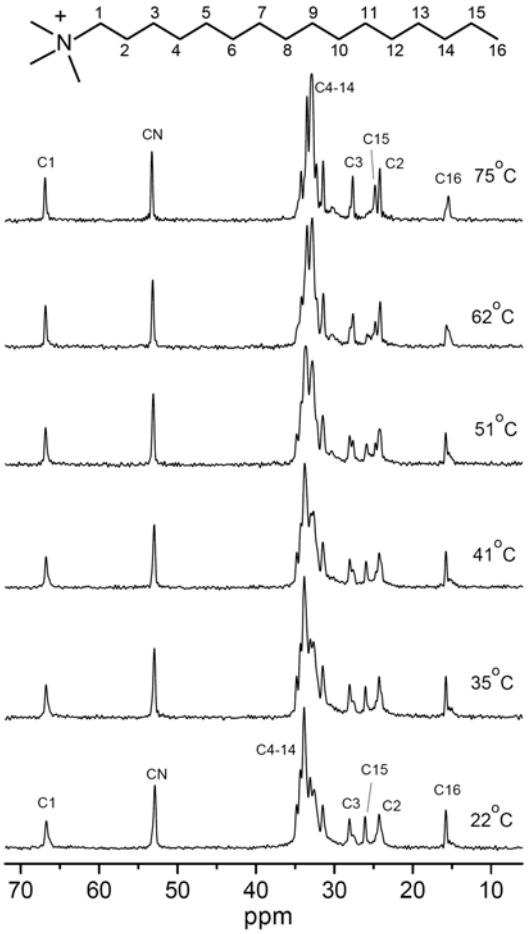


**Figure S2a**. $^{13}$C MAS NMR proton decoupled spectra of CTA/magadiite composite recorded at indicated temperatures.

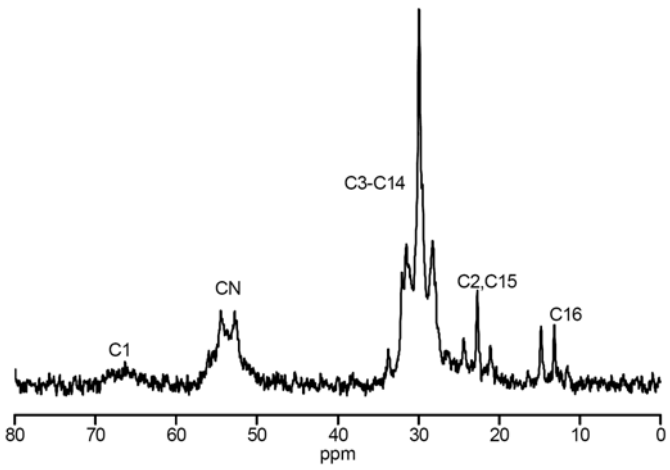


**Figure S2b**. $^{13}$C MAS NMR spectrum of CTA/magadiite at 110 °C recorded without proton decoupling. *J*-coupled multiplets are resolved.

J-resolved multiplets indirectly indicate the presence of translational dynamics. Low limit of the diffusion coefficient can be estimated from the Einstein-Smoluchowski relationship $D=\langle R^2\rangle/2\tau\sim10^{-14}\mathrm{m}^2/\mathrm{s}$, with $\tau=1/(2\pi D_{\mathrm{HH}})$, $D_{\mathrm{HH}}\sim10$ kHz, $\langle R^2\rangle^{1/2}\sim10^{-9}$ m.

## S3. 2D HETCOR $^{13}C$-$^{1}H$ spectrum in CTA/magadiite

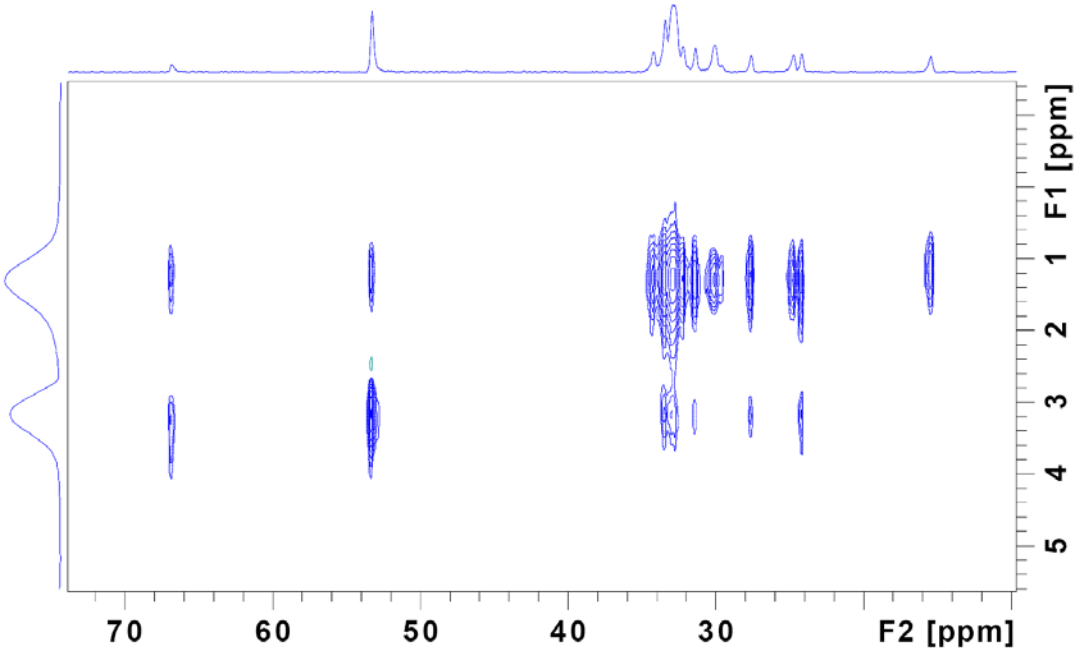


**Figure S3**. 2D heteronuclear correlation (HETCOR[5]) $^{13}C$-$^{1}H$ spectrum of CTA/magadiite composite in phase II at 75 °C.

Cross-peak C1/C2 in HETCOR spectrum aids to resolve an ambiguity of the C2 and C15 assignments.

## S4. $^{29}Si$ MAS spectra in magadiite and CTA/Magadiite

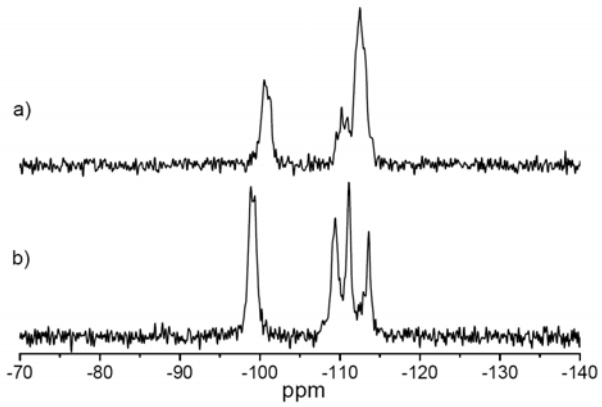


**Figure S4**. Silicon-29 MAS NMR spectra of (a) CTA/magadiite composite and (b) unmodified natural magadiite. Spinning speed 8 kHz, relaxation delay 960 s, number of scans 32, room temperature.

Silicon-29 MAS NMR spectrum of untreated magadiite exhibits two partly-resolved $Q^3$ and three well-resolved $Q^4$ sites in excellent agreement with previous studies.[6]

## References

(1) Dvinskikh, S. V.; Zimmermann, H.; Maliniak, A.; Sandström, D. Measurements of Motionally Averaged Heteronuclear Dipolar Couplings in MAS NMR using R-type Recoupling, *J. Magn. Reson.* **2004**, *168*, 194-201.
(2) Zhao, X.; Edén, M.; Levitt, M. H. Recoupling of heteronuclear dipolar interactions in solid-state NMR using symmetry-based pulse sequences, *Chem. Phys. Lett.* **2001**, *342*, 353-361.
(3) Dvinskikh, S. V.; Castro, V.; Sandström, D. Probing Segmental Order in Lipid Bilayers at Variable Hydration Levels by Amplitude- and Phase-Modulated Cross-Polarization NMR, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3255-3257.
(4) Dvinskikh, S. V.; Chizhik, V. I. Cross-Polarization with Radio-Frequency Field Phase and Amplitude Modulation under Magic-Angle Spinning Conditions, *J. Exp. Theor. Phys.* **2006**, *102*, 91-101.
(5) vanRossum, B. J.; Forster, H.; deGroot, H. J. M. High-field and high-speed CP-MAS C-13 NMR heteronuclear dipolar-correlation spectroscopy of solids with frequency-switched Lee-Goldburg homonuclear decoupling, *J. Magn. Reson.* **1997**, *124*, 516-519.
(6) Almond, G. G.; Harris, R. K.; Graham, P. A Study of the Layered Alkali-Metal Silicate, Magadiite, by One-Dimensional and 2-Dimensional H-1 and Si-29 NMR-Spectroscopy, *J. Chem. Soc., Chem. Commun.* **1994**, 851-852.