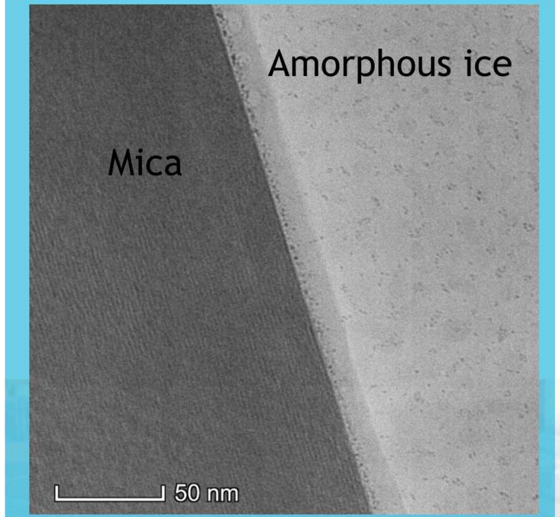
SAND2020-10535C

Molecular-Scale Studies of Surfactant Partitioning on Muscovite Surfaces



Jeffery A. Greathouse, Daniel M. Long, Guangping Xu, Hongkyu Yoon, and Katherine L. Jungjohann

Sandia National Laboratories
Albuquerque, New Mexico

jagreat@sandia.gov

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Surfactant-Mineral Interactions

Motivation

- Understand the behavior of complex fluids in the subsurface.
- Control the distribution of complex fluids by changing fluid chemistry, and to control rheological properties of complex fluids.

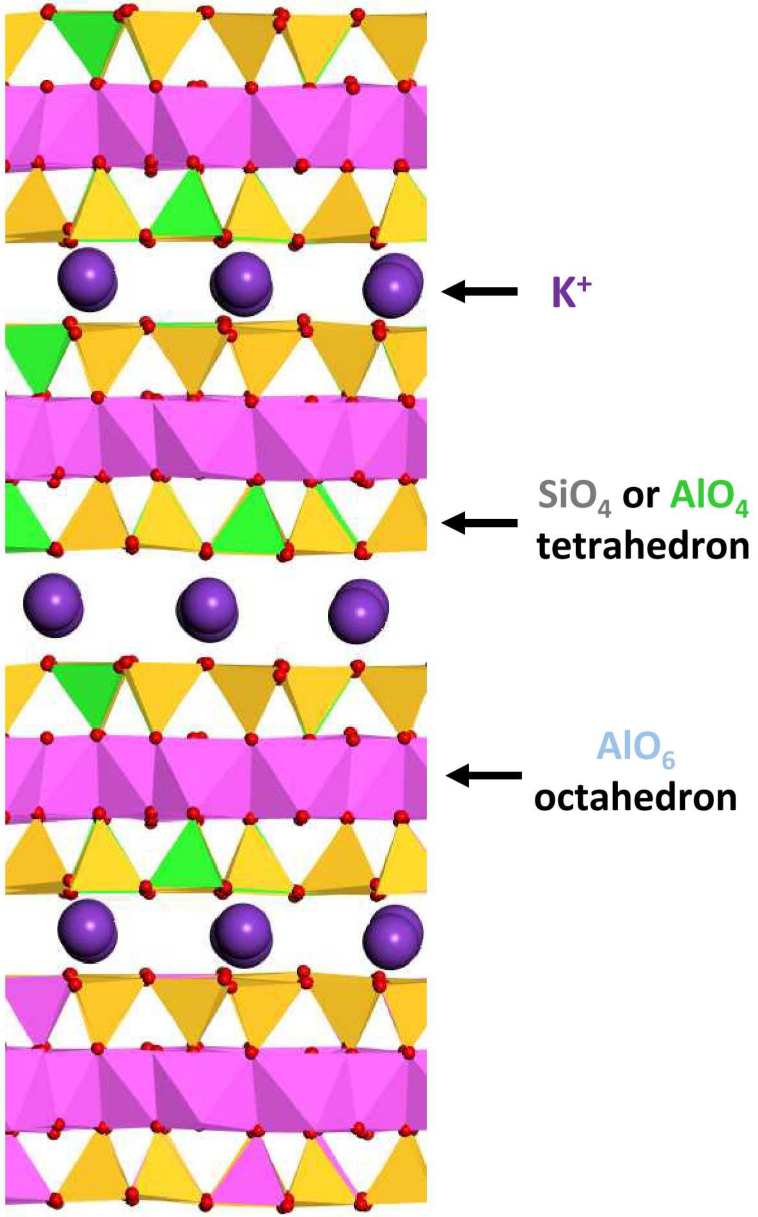
Relevance

Energy extraction, water treatment (produced water, energy generation)

Project goal

Quantify at the molecular scale the competing roles of fluid-fluid and fluid-surface interactions on fluid partitioning at a well-characterized mineral surface (**mica**).

mica
$K(Al,Si)_3Al_3O_{10}(OH)_2$

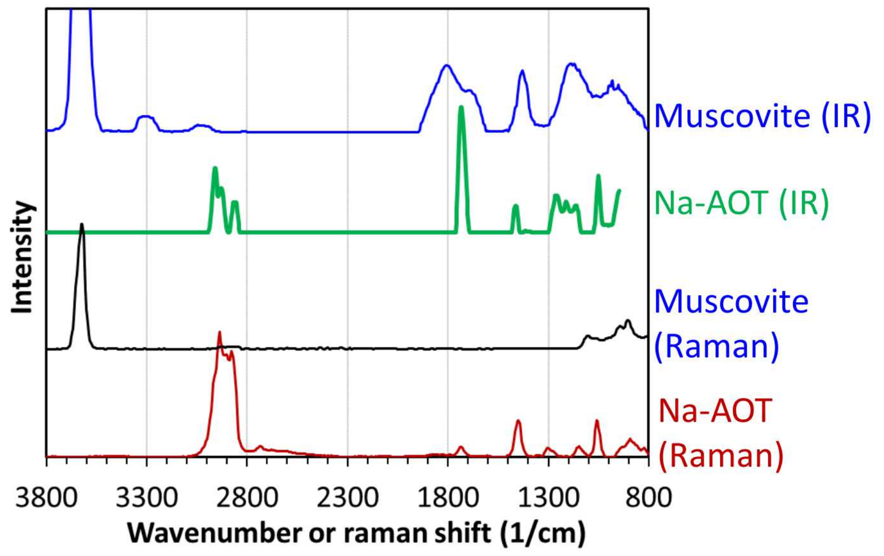


Research Plan

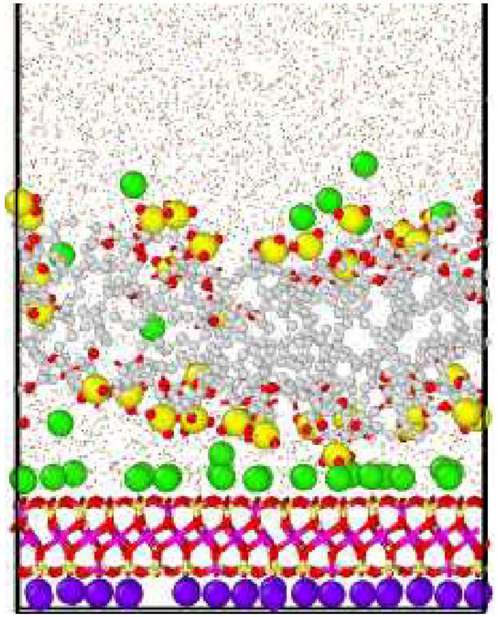
Experimental measurements + molecular modeling
→ Trends in wetting properties of complex fluids on mineral surfaces.

Complex fluid components: **water, aqueous cations**, nonpolar liquids, and **polar surfactant molecules**.

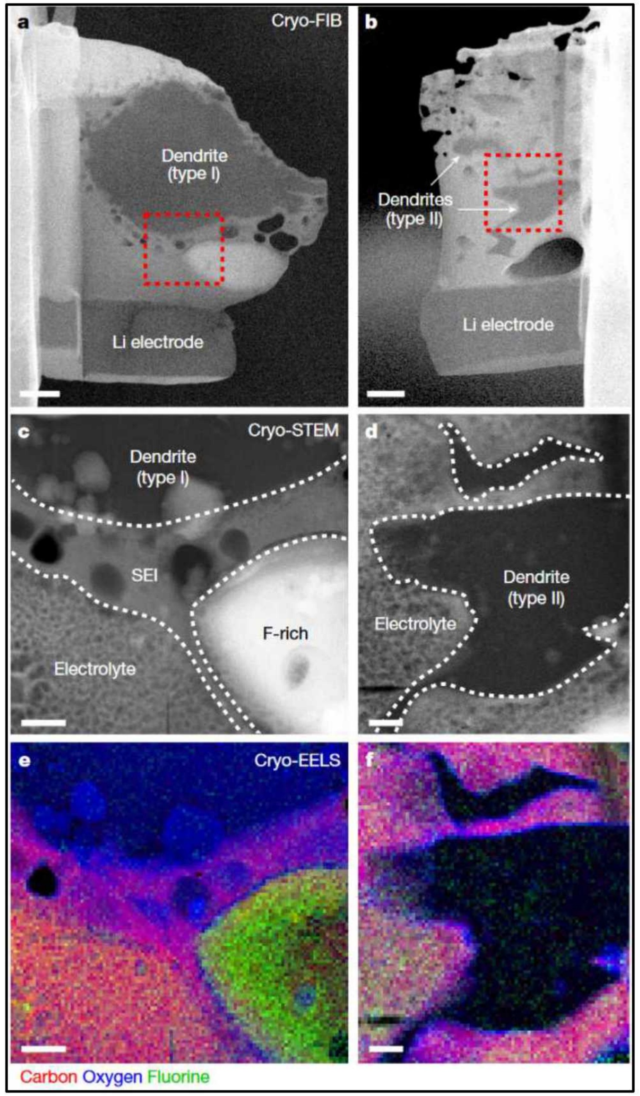
Determine how the adsorption properties change with cation composition.



Vibrational spectroscopy



Simulation

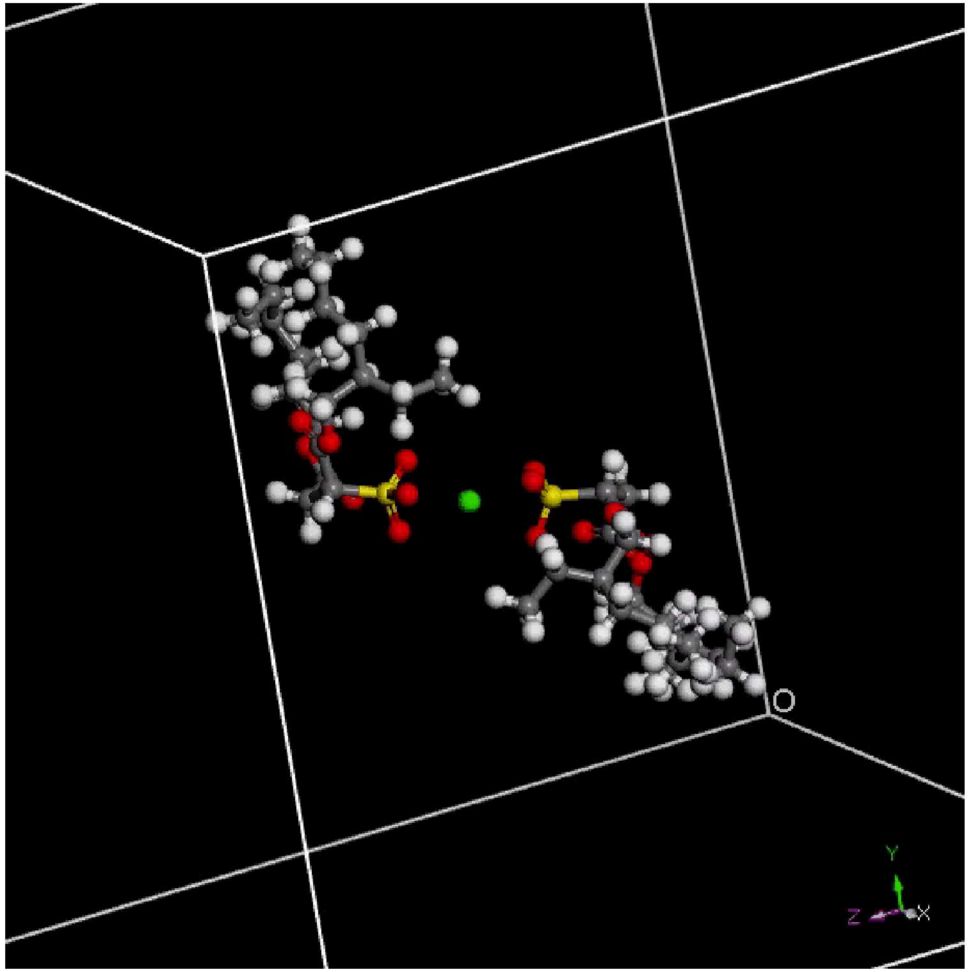


Cryo electron microscopy

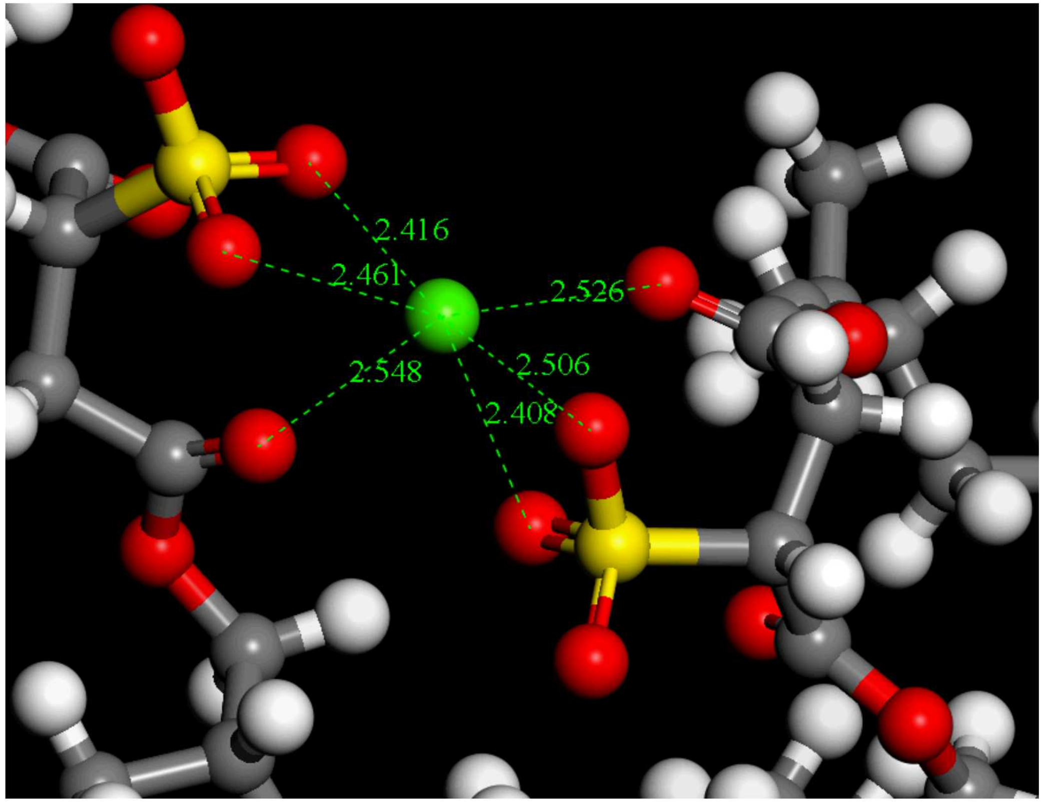
Zachman et al., *Nature* **2018**

AOT Surfactant

- Dioctyl calcium sulfosuccinate (Aerosol-OT, AOT)
- Anionic surfactant used in experimental and modeling studies
- Neutron data suggests bilayer formation on mica.



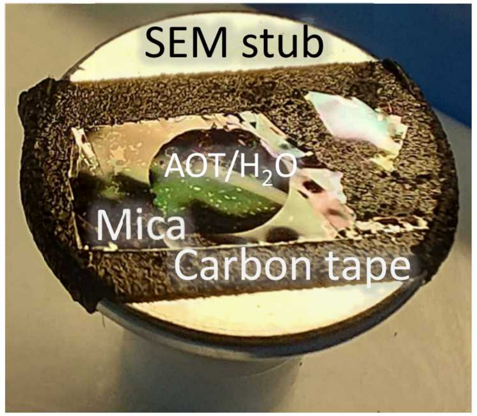
- 2 AOT monomers bridged by Ca^{2+}.
- Formation of polar and nonpolar regions.



- Bidentate coordination with each sulfate.
- Coordination with carbonyl oxygens.

Cryo-EM Workflow For Mica/AOT System

1 Sample Setup



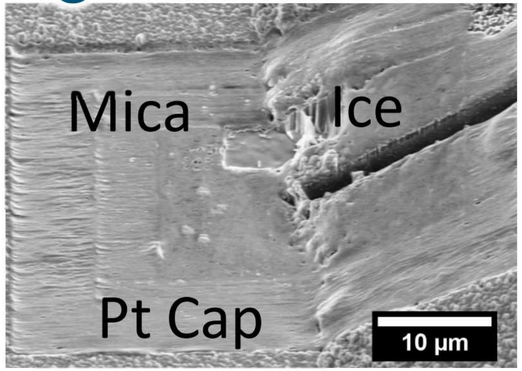
2 Vitrification

3 Load, Coat, Transfer (Leica)

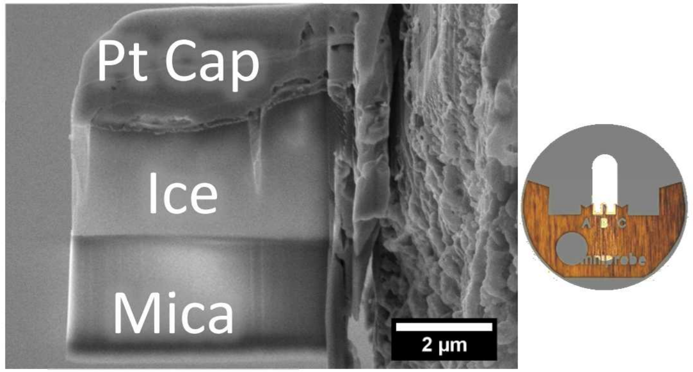
4 Scios FIB/SEM

5 Identify Region on Interest

6 Pt deposition, FIB Milling



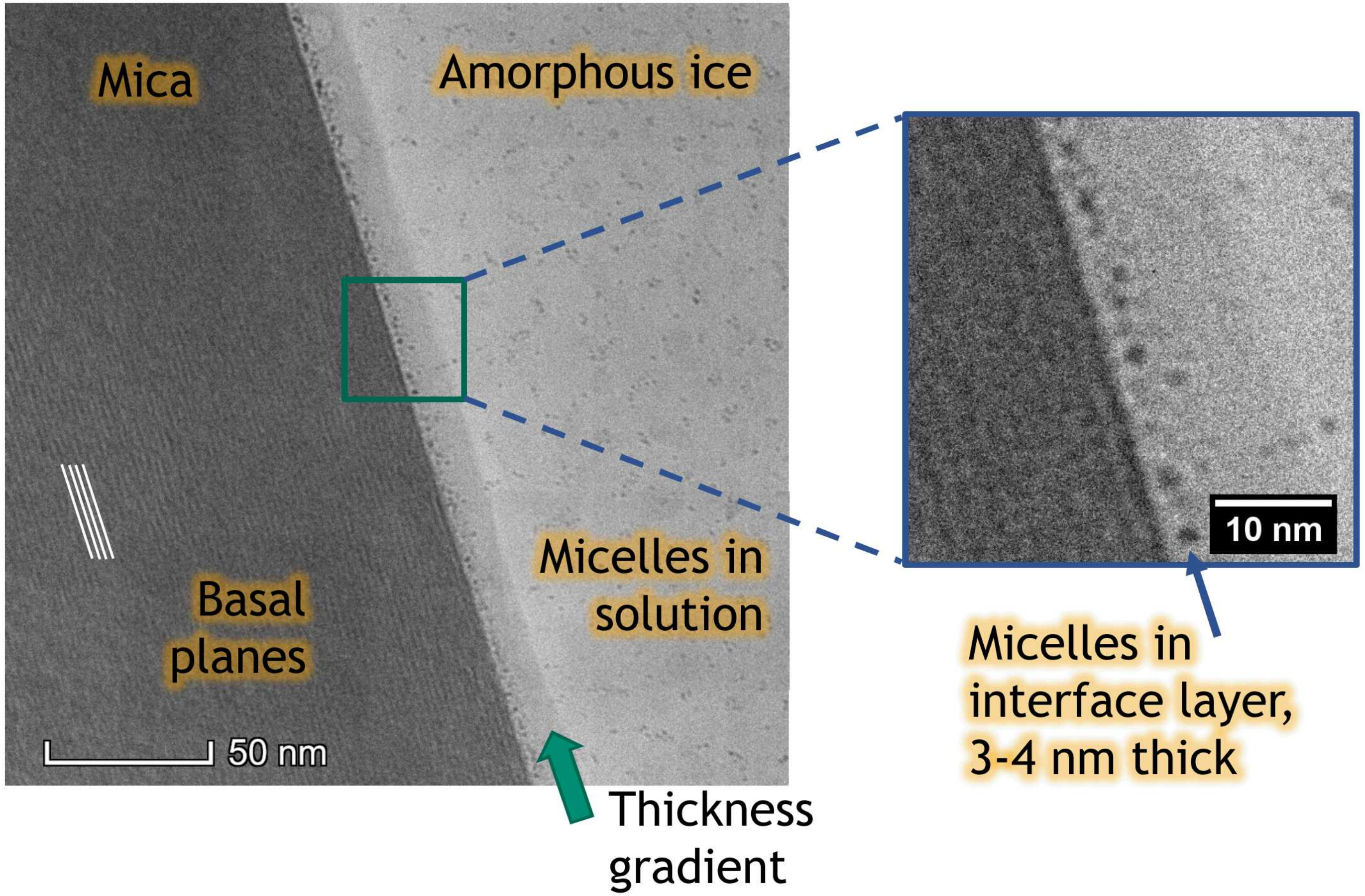
7 Liftout, Thinning and Transfer



8 Talos L120C Cryo-TEM

Cryo-EM Results

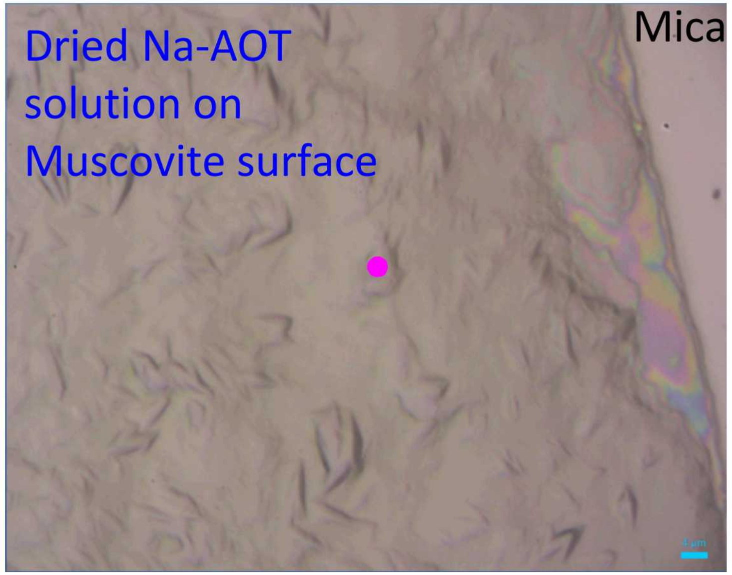
2.3 mM Na-AOT on mica (CMC is 2.5 mM)
Imaging – Talos 120 kV



- Organized interfacial layer, AOT micelles ~2 nm diameter
- Thin ice layer between mica and micelles
- Surface damage caused the micelles in the amorphous-ice bulk to cluster
- Interfacial micelle formation predicted at low surface concentration.

Depth Profile of Raman Spectra on Muscovite Surface

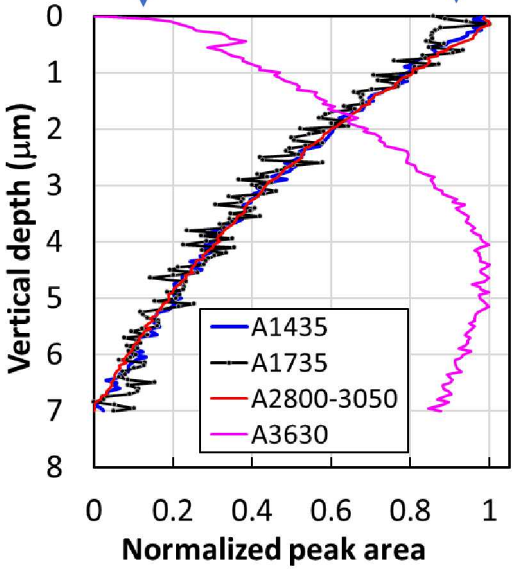
Raman confocal microscope can measure Raman spectra across AOT-mica interface by vertical profiling



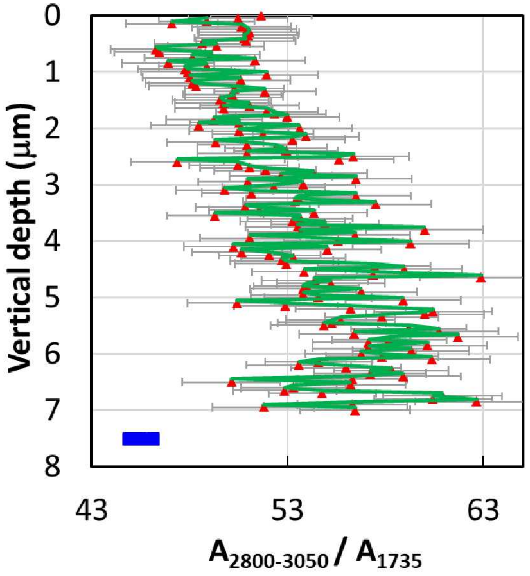
As depth increases (closer to the mica surface):

- Slight increases in tail/head ratios
- Constant tail/tail ratio
- AOT head and tail re-orientation at the interface

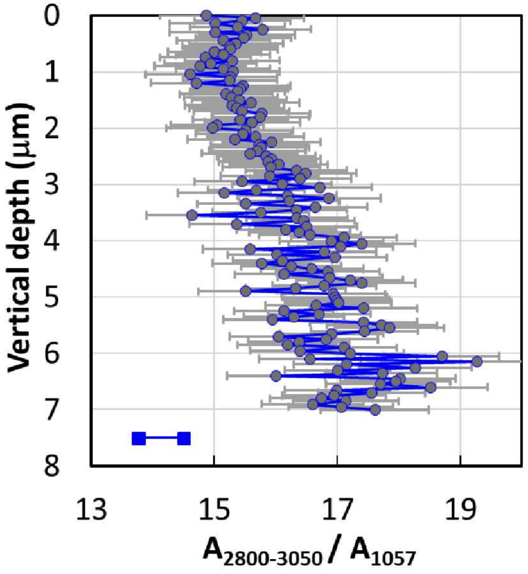
Mica signal AOT signal



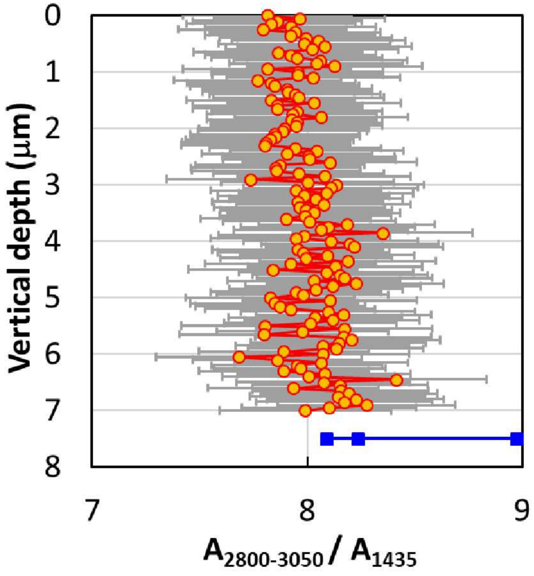
Step size: 50 nm



tail/head



tail/head



tail/tail

Mica-AOT interface

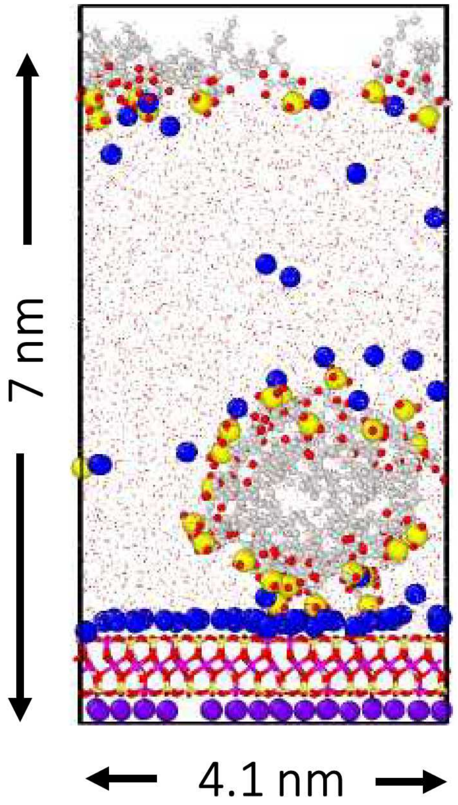
Pure AOT powder

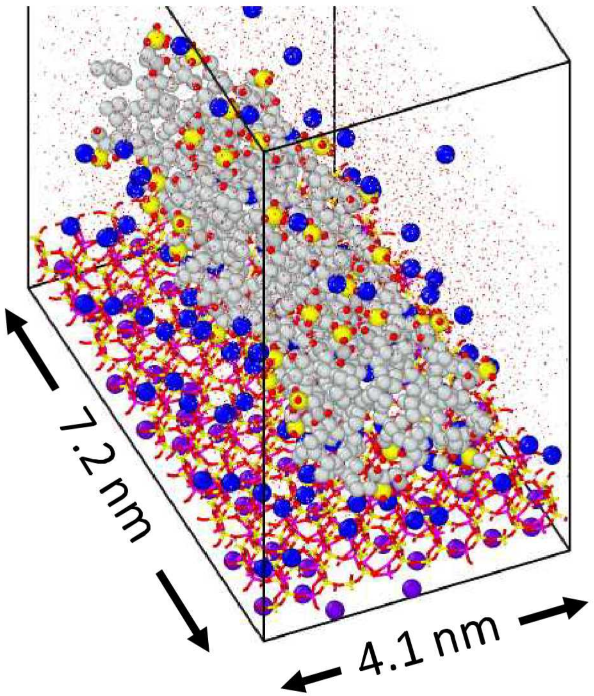
MD Simulation of AOT Interfacial Structure

Details

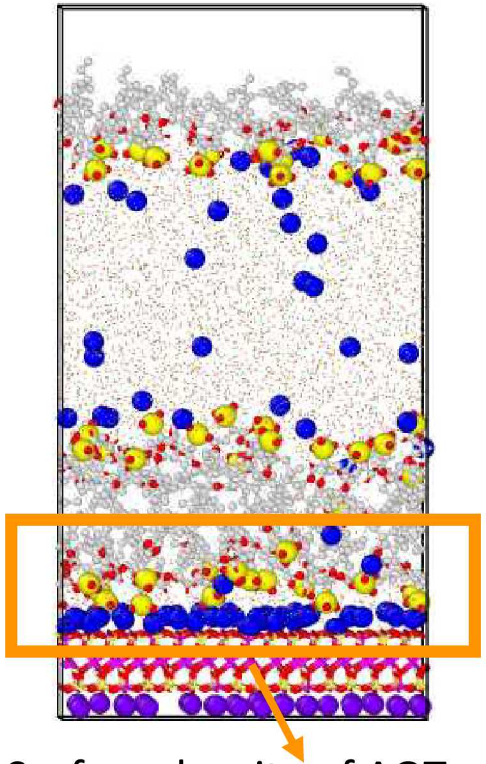
- LAMMPS, ClayFF + OPLS force fields, 110 ns
- 2D periodicity (vacuum-fluid interface)

32 Na-AOT
1 AOT per binding site
Adsorbed micelle (cylinder)



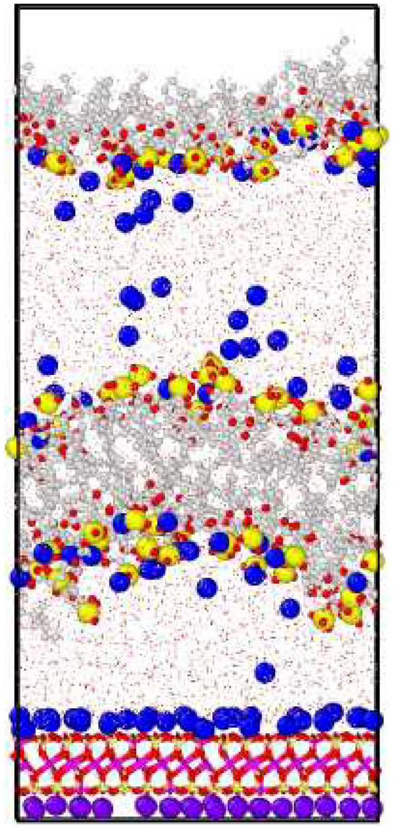


48 Na-AOT
1.5 AOT per binding site
Adsorbed bilayer



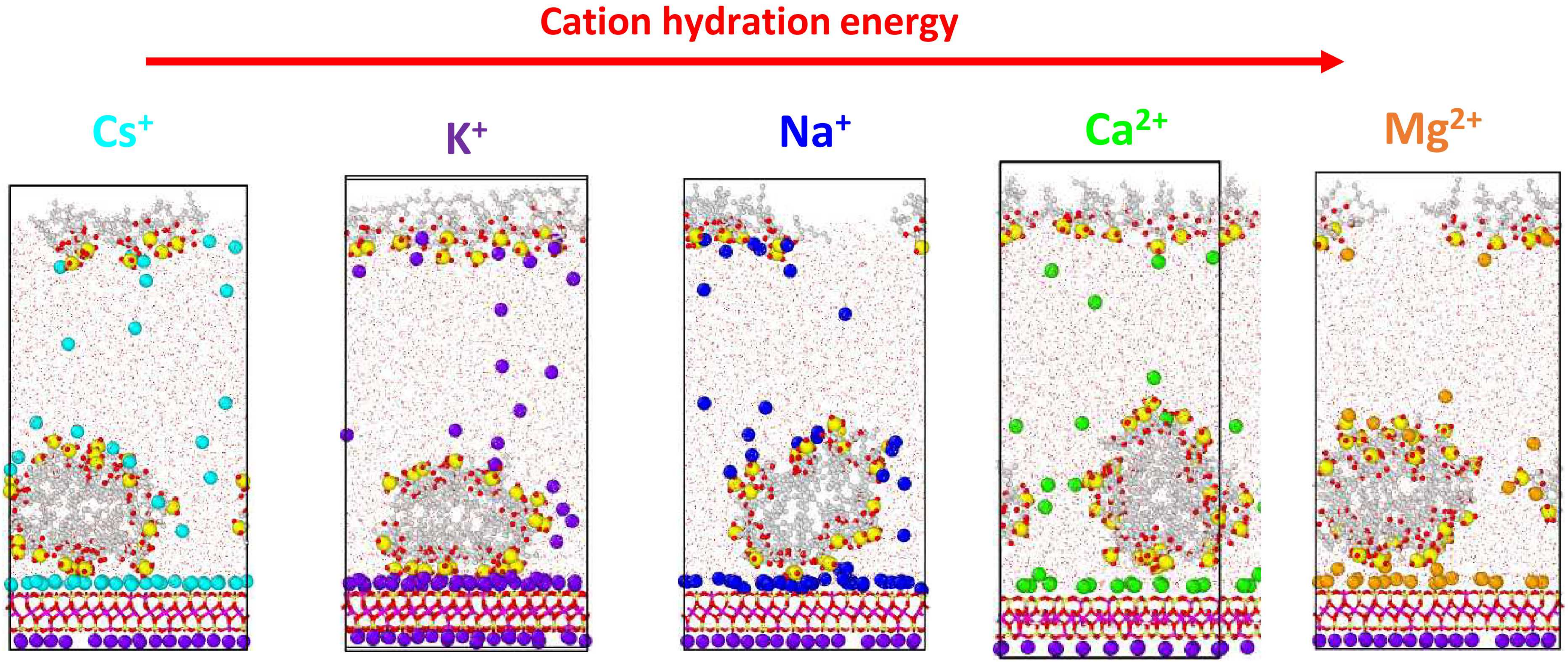
Surface density of AOT
0.9 AOT/nm^2 (Mg^{2+})
1.3 AOT/nm^2 (K^+)

64 Na-AOT
2 AOT per binding site
Desorbed bilayer



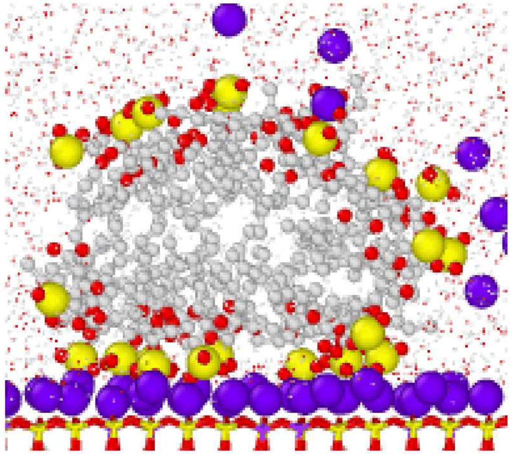
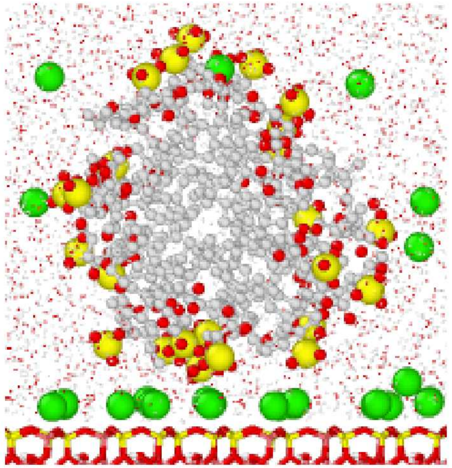
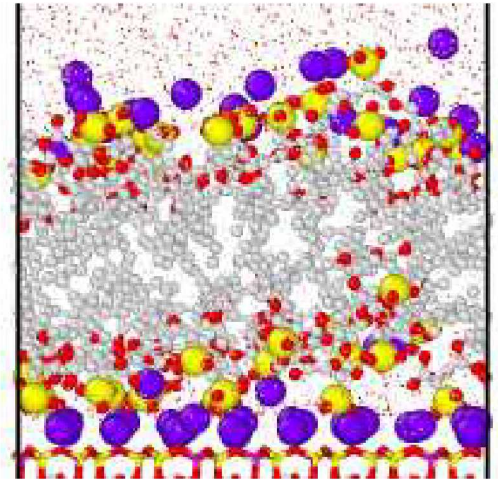
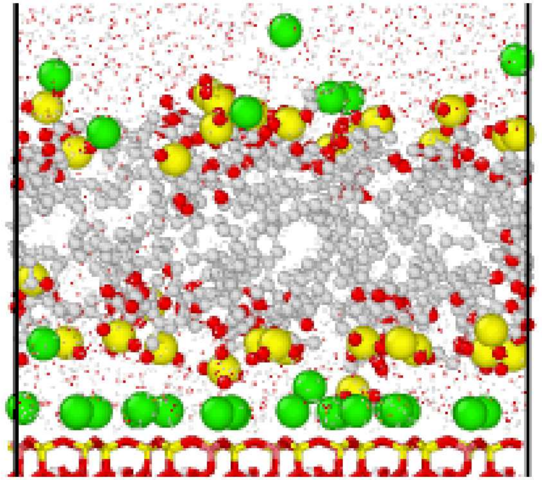
Mica surface charge
2.2 e/nm^2

Cation Dependence on Interfacial Structure



Equilibrium structures with 32 AOT after ~100 ns of MD simulation

Surfactant Structure – Layer Thickness

	K^+	Ca^{2+}
Micelle	2.3 nm 	3.0 nm 
Bilayer	2.2 nm 	2.3 nm 

Ideal thickness of a single AOT chain 1.8 nm
Bilayer thickness from neutron reflectometry 2.2 nm

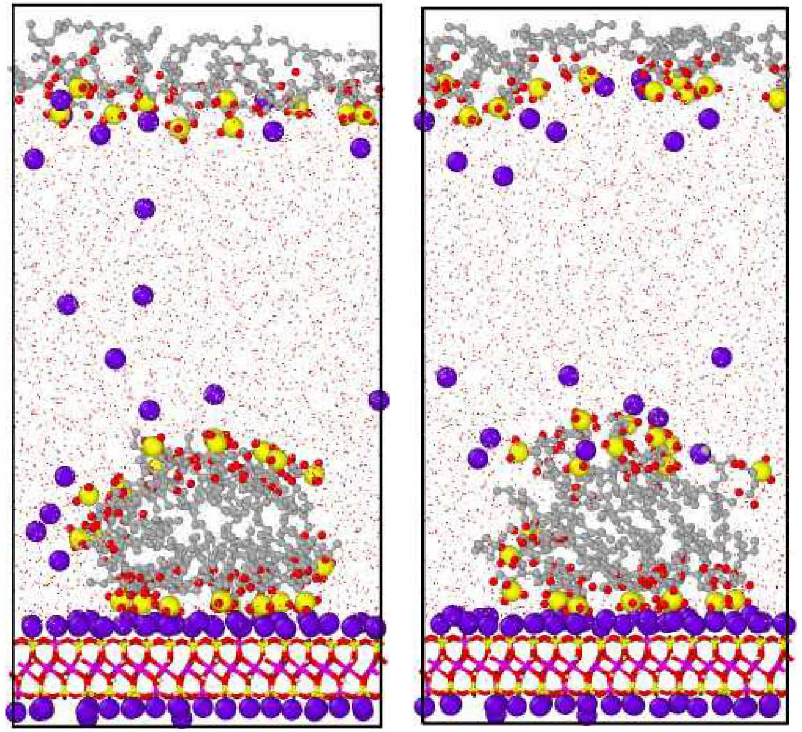
Allen et al., *Langmuir* **2017**

Effect of Heating (300 K → 350 K)

Heating causes transition from micelle to bilayer structure
Facilitated by additional sulfate-cation binding at the surface

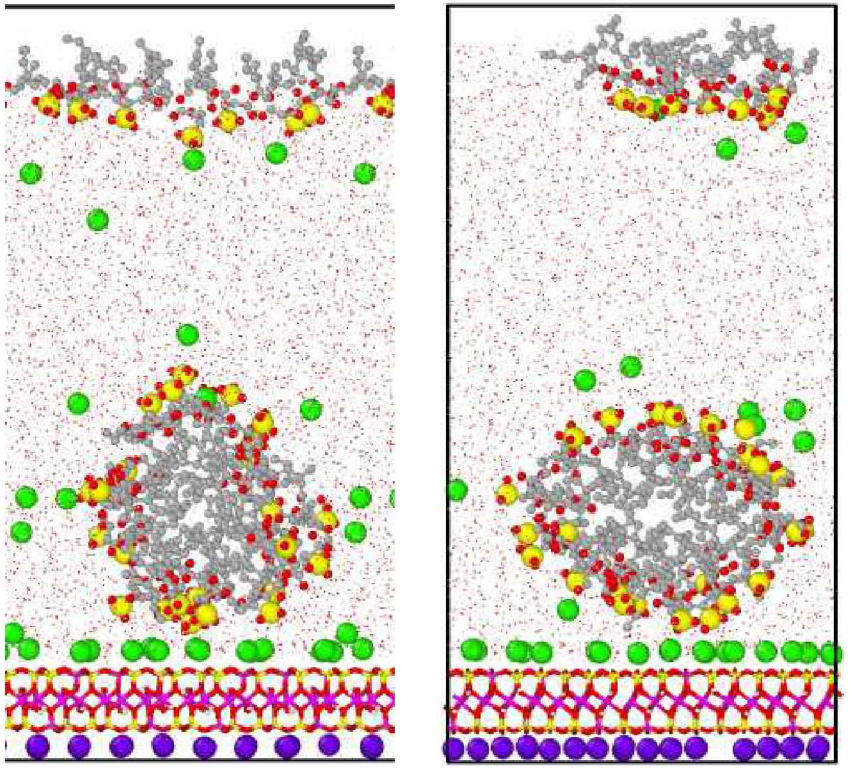
K^+

300 K   350 K



Ca^{2+}

300 K   350 K

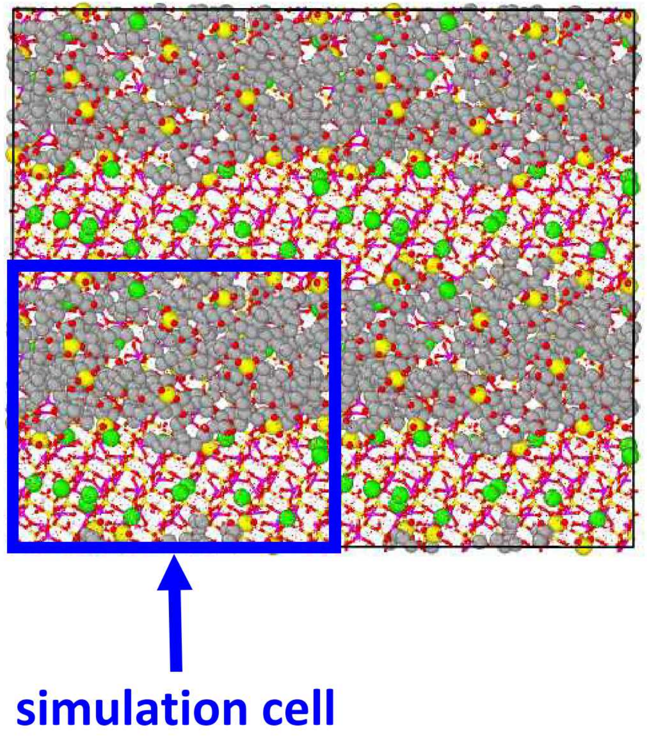


x →   y →

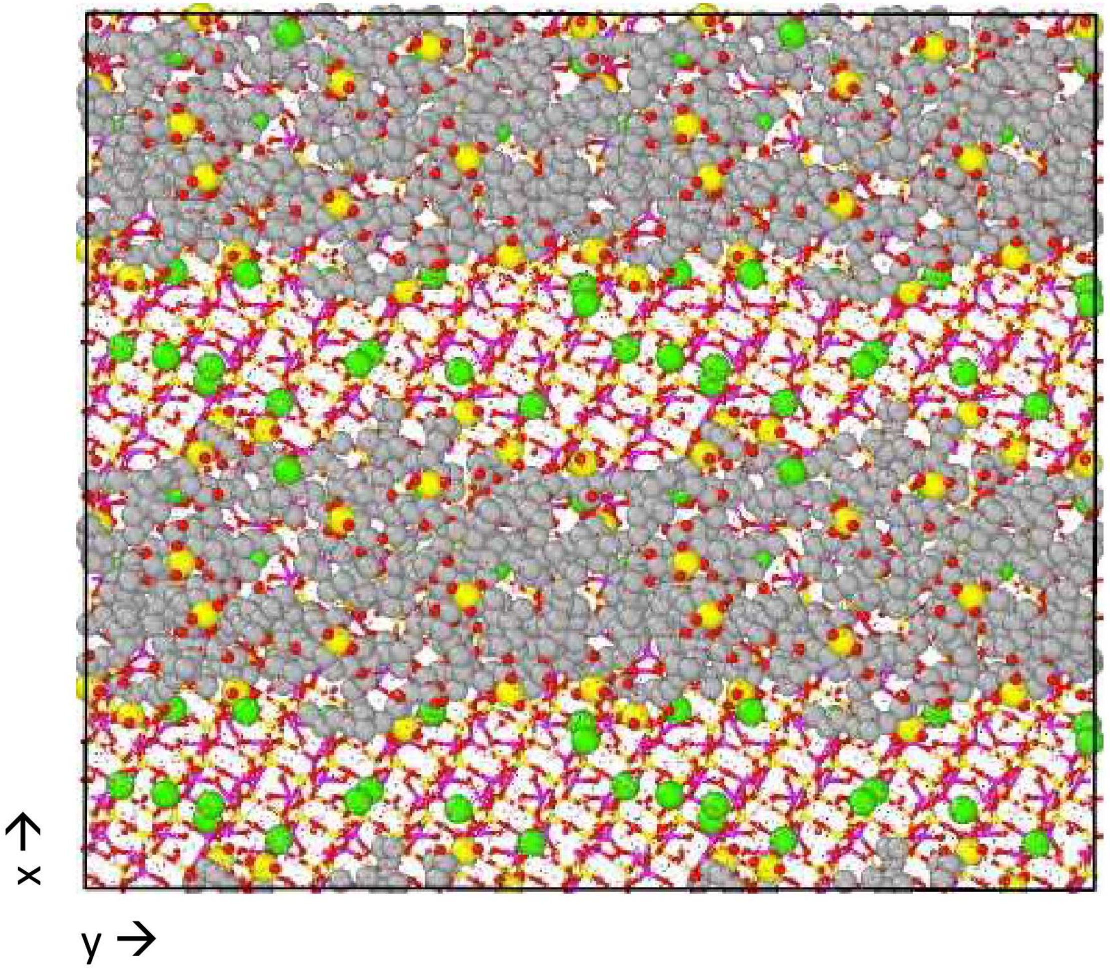
Note shift in Ca micelle from y-parallel to x-parallel!

Translation of Ca-AOT Micelle During Heating

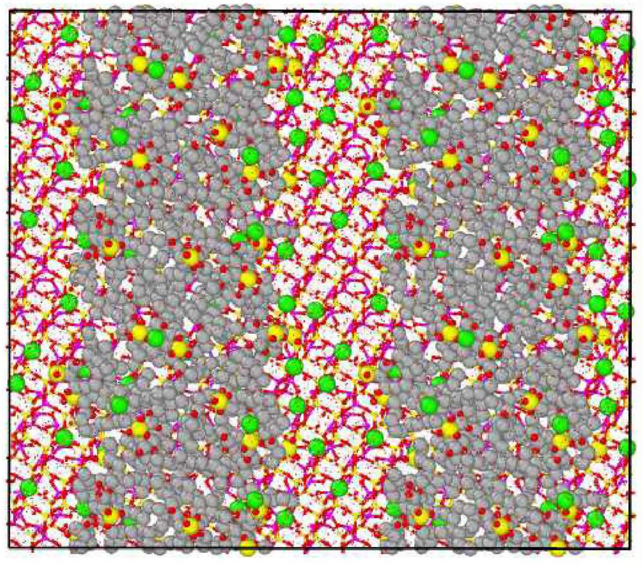
300 K



Heating



350 K



Summary

- Raman depth profiling and cryo-EM confirm the adsorption of an anionic surfactant (AOT) on mica.
- AOT adsorption is confirmed by MD simulations:
  - AOT binds to the negatively-charged mica surface via cation bridging.
  - Surfactant thickness is consistent with a bilayer (or micelle).
  - Cation hydration properties affect anionic surfactant binding at the mica surface (cation/water bridging).
  - AOT bilayers form at the mica surface at surface concentration of ~ 1 AOT/nm^2.
- The combination of nano-scale characterization (spectroscopy, cryo-EM) and MD simulation provides molecular-level insight to understand complex fluid behavior in the subsurface.

Funding

Sandia Laboratory Directed Research and Development (LDRD) Program

LDRD

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

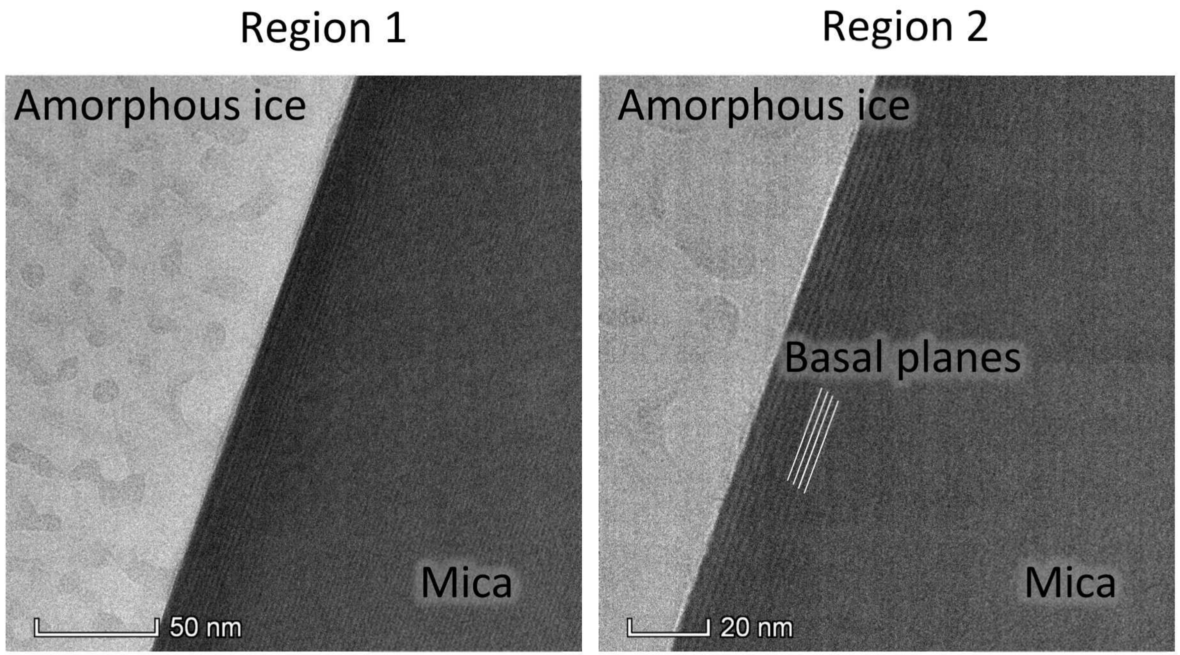
People

Katherine Jungjohann
Daniel Long
Guangping Xu
Hongkyu Yoon

Additional slides

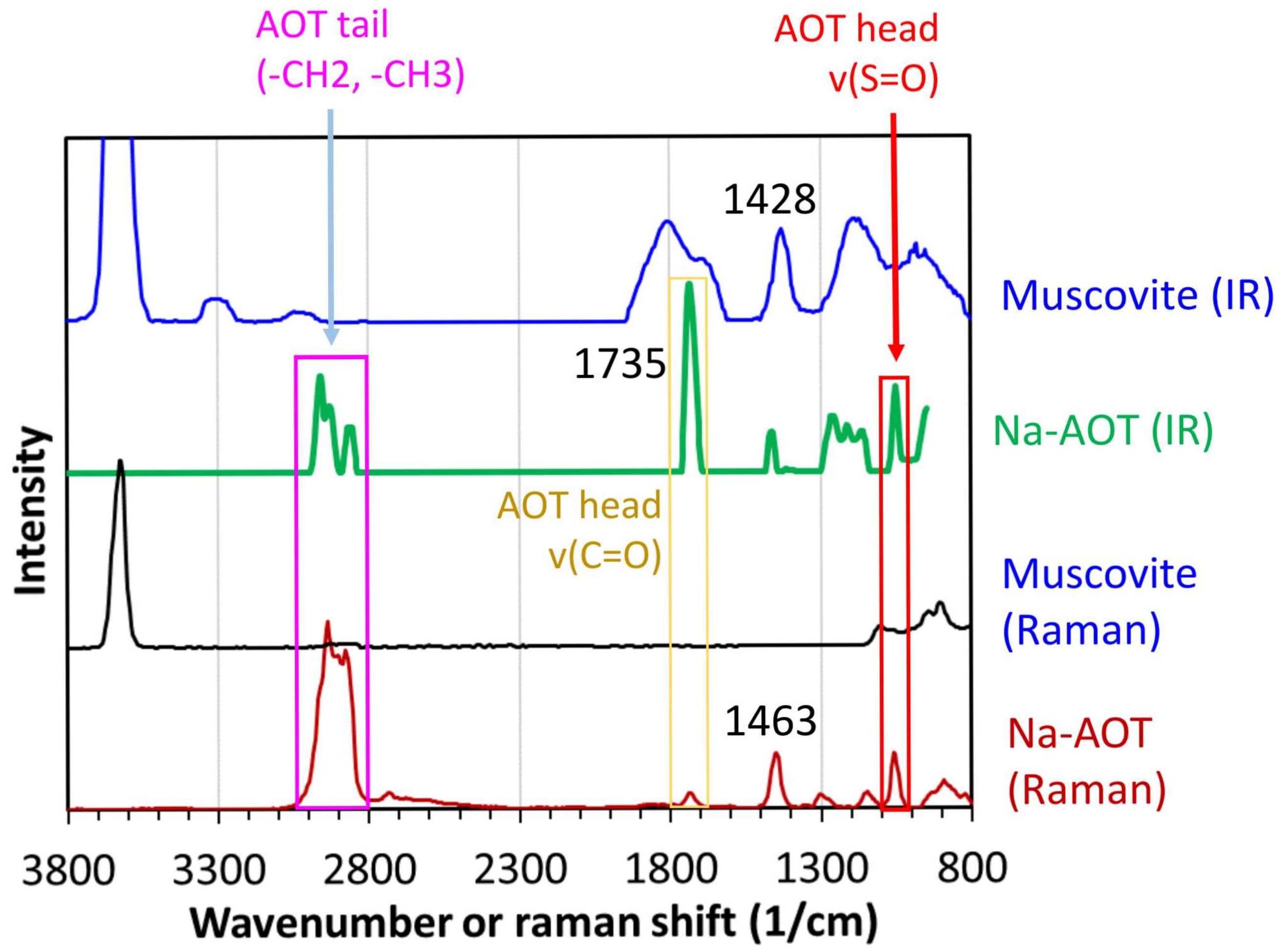
Cryo-TEM Results

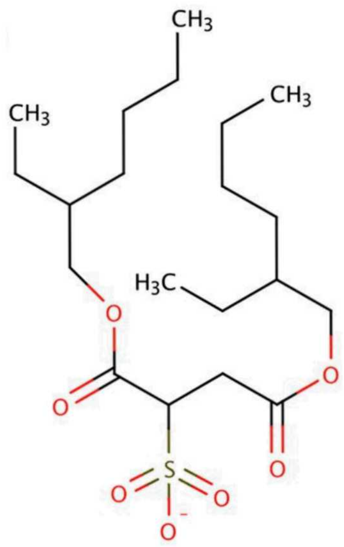
Control Sample – Deionized H_2O on Mica
Imaging – Talos 120 kV



- Sample successfully thinned to electron transparency, difficult given large difference in material density and milling rates
- Sample prepared with mica/H_2O interface normal to incident beam
  - Mechanical exfoliation of mica yields atomically flat surface
  - Preparation allows for easy visibility of the interface
- Features in ice layer due to surface damage, difficult to avoid

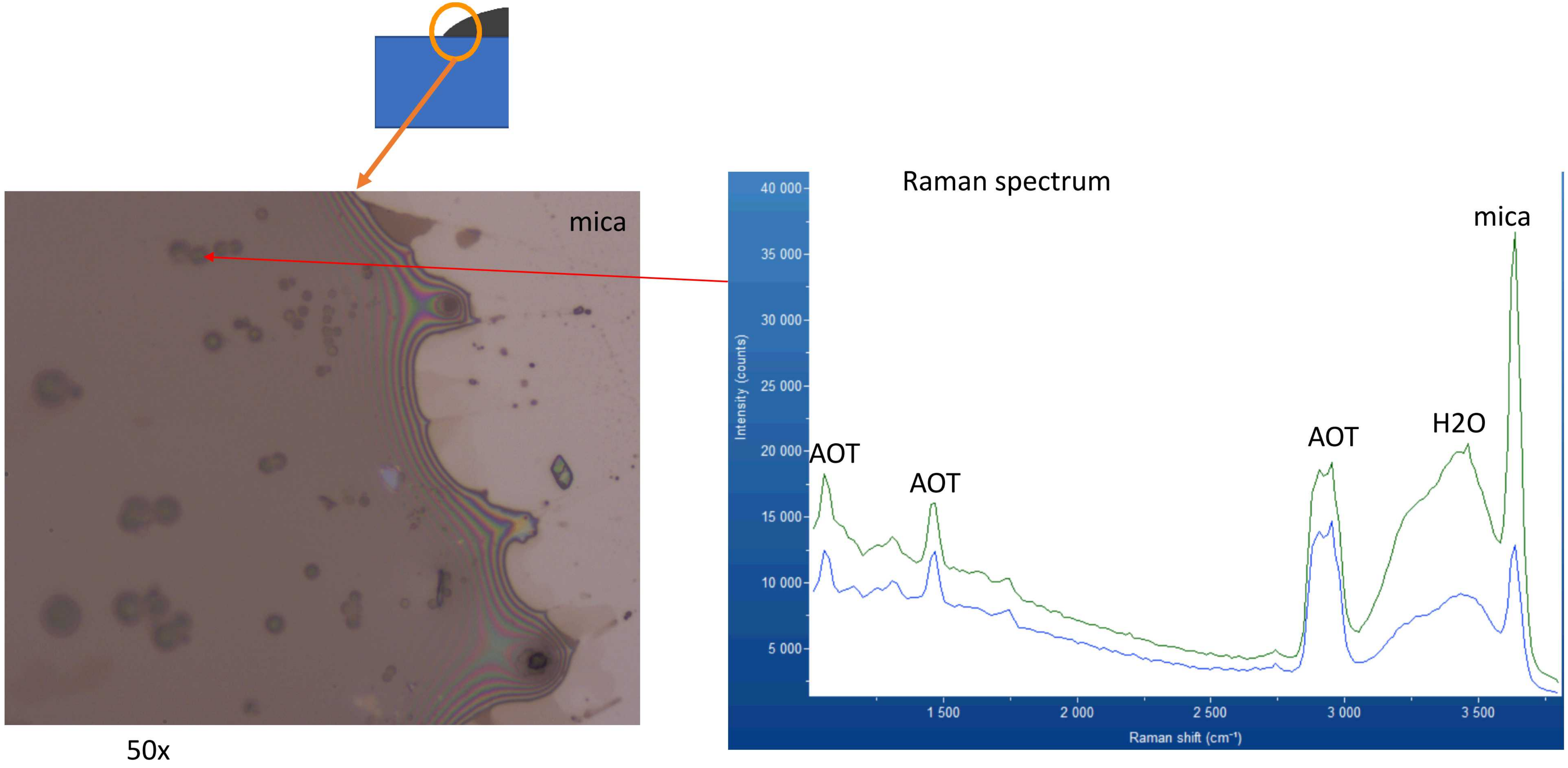
Raman and Infrared Spectra for Muscovite and AOT



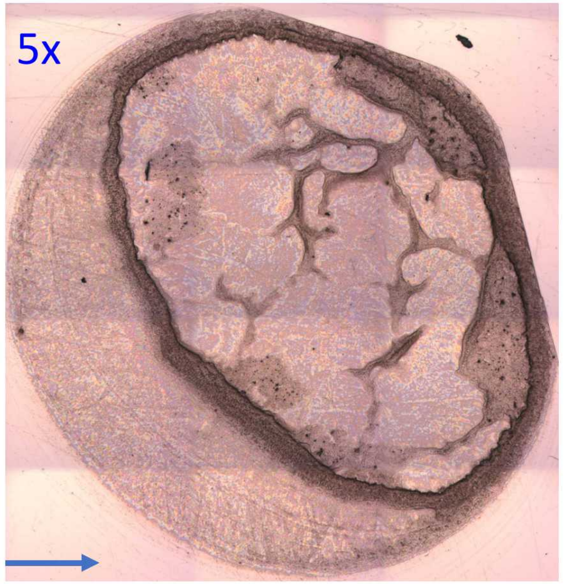


wavenumber (cm^{-1})	mode
3630	OH vibration (mica)
2800 – 3050	CH_2, CH_3 stretching vibration (AOT tail)
1735	C=O stretching vibration (AOT head)
1463	CH_2, CH_3 bending vibration (AOT tail)
1057	S=O stretching vibration (AOT head)

Raman Microscope

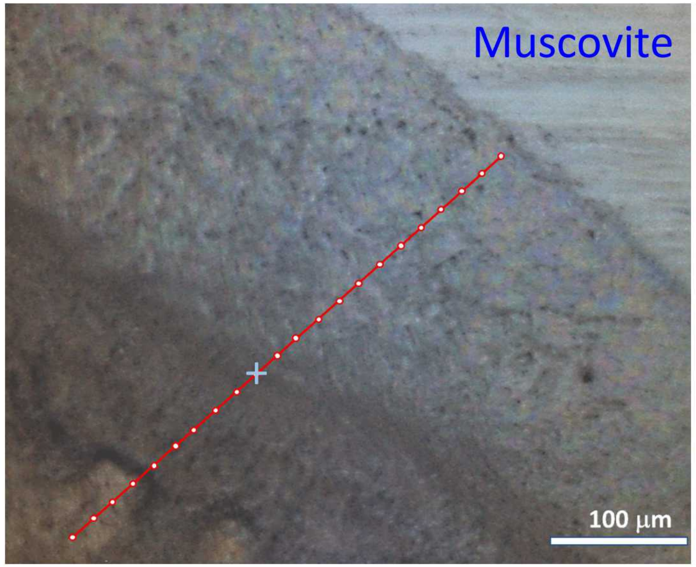


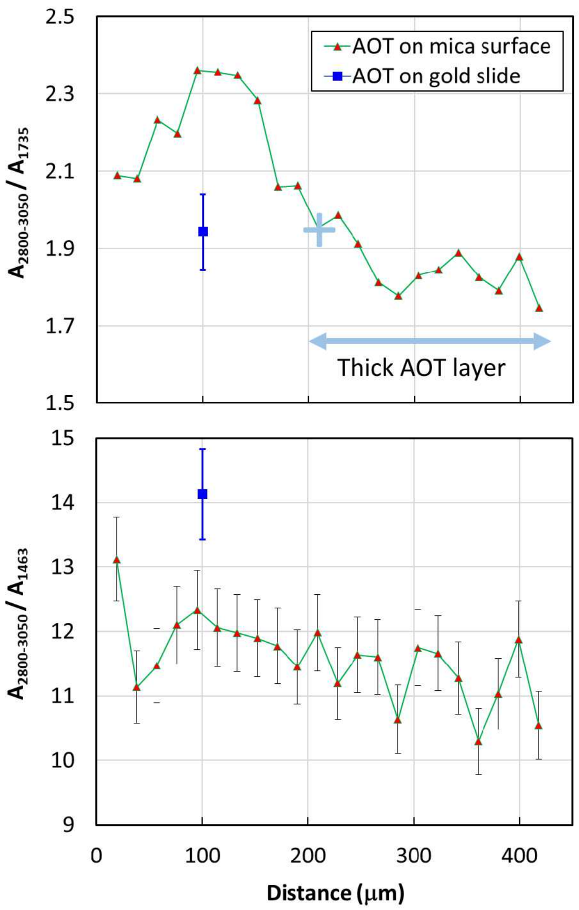
Cross-section Profile of IR Spectra on Muscovite Surface



A drop of Na-AOT on tilted muscovite slide and dried

Dried Na-AOT solution



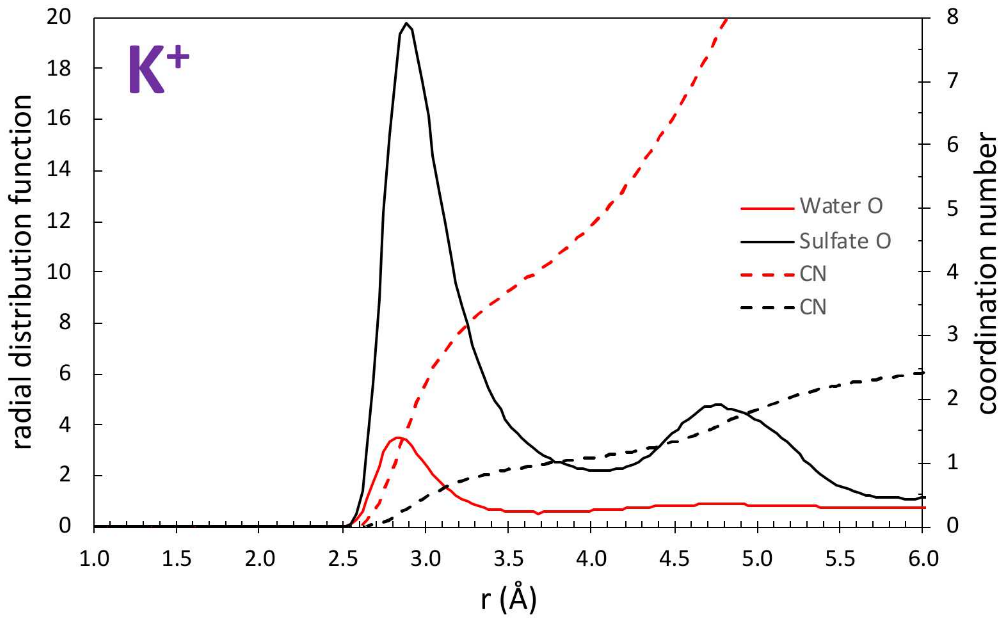


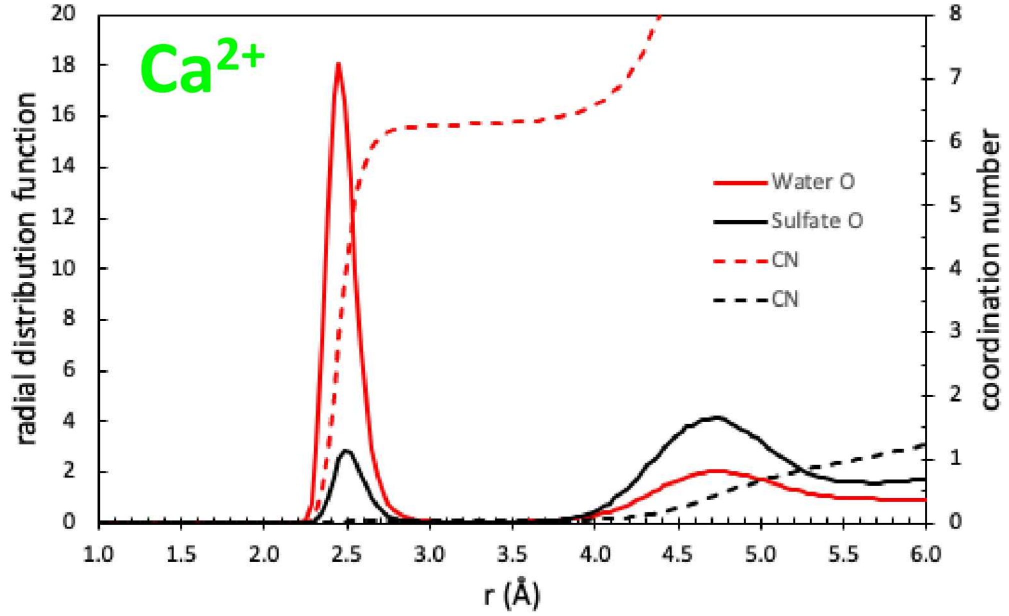
The ratios of AOT tail/head intensities on mica surface, which should be ~1.9 for AOT, change in cross-section.

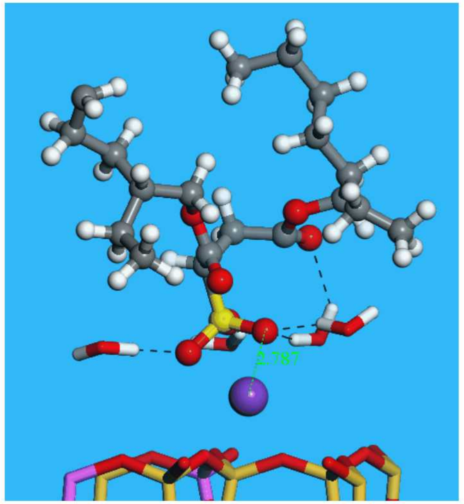
- Tail/head ratios are higher than 1.9 on thin AOT layer, and close to *pure AOT* on thick AOT layer
- Tail/tail ratios are constant, lower than *pure AOT* due to the interference of mica peak at 1428 cm^{-1}

Surfactant Binding Mechanisms

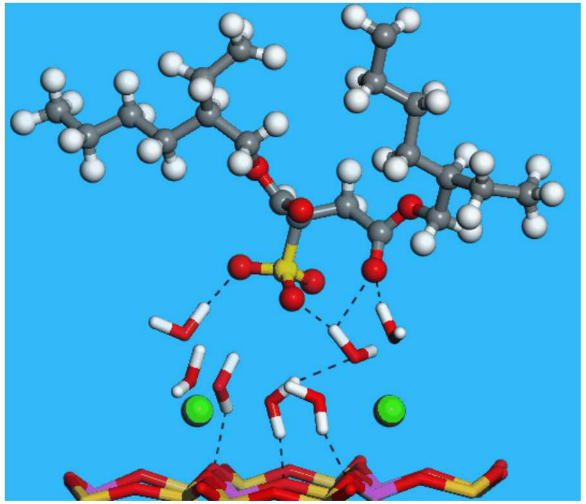
Cation-oxygen distances from radial distribution functions (RDFs)





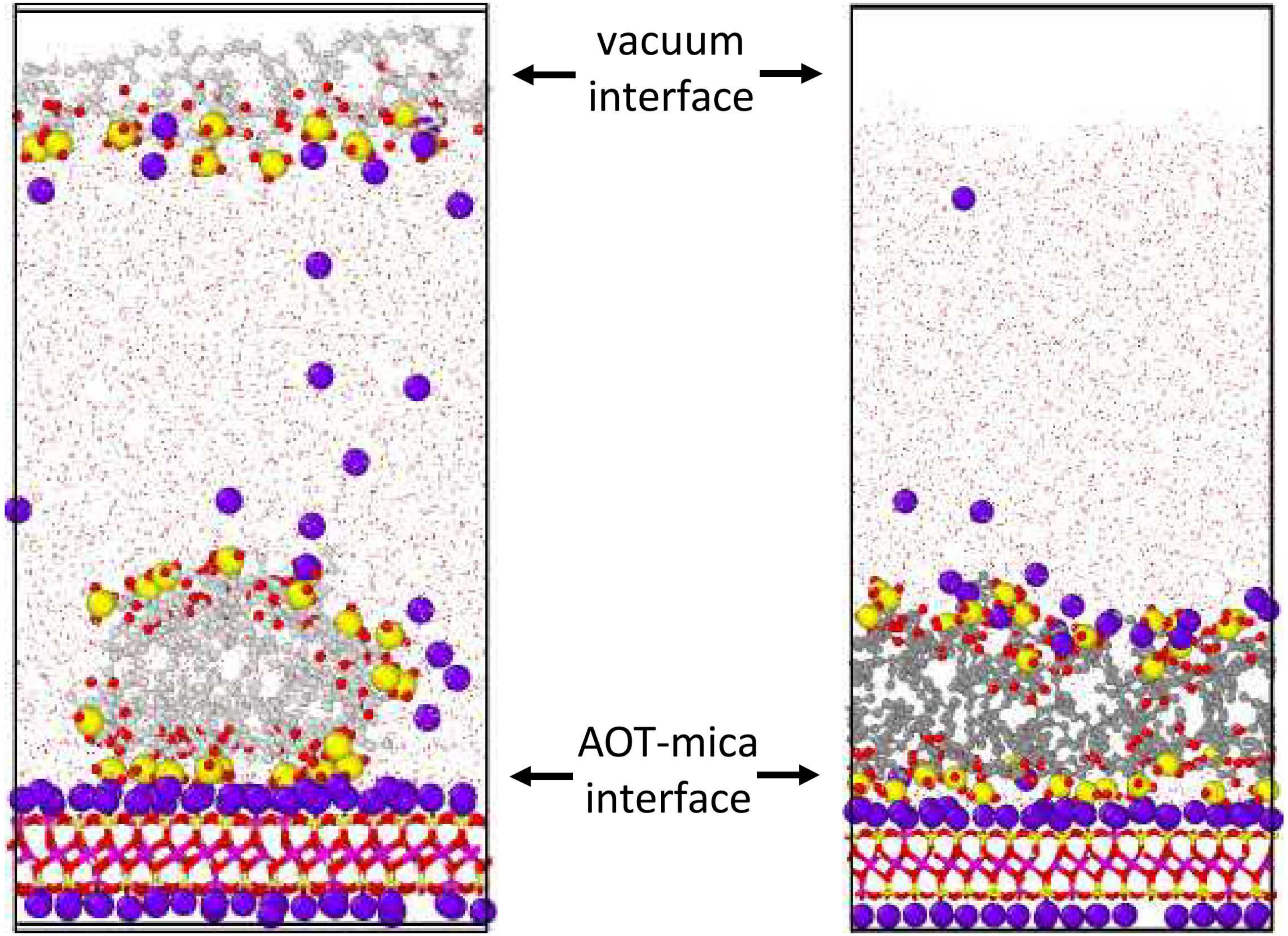


- Weakly hydrating cations (K^+) bind sulfate O atoms directly (inner-sphere coordination).
- Strongly hydrating cations (Ca^{2+}) retain water hydration shells, which in turn form H-bonds with sulfate O atoms (outer-sphere coordination).



Micelle vs Bilayer

32 K-AOT (1 AOT per binding site)



Initial
Configuration

Random fluid

Adsorbed bilayer

Initial fluid configuration affects surfactant structure but not surfactant-surface structure