Role of hydration energy on near-surface H_2O and ion molecular-scale dynamics: Comparing Na- and Ca-hectorites with NMR spectroscopy

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Solid-state NMR spectroscopy is uniquely equipped to study behavior at interfaces and in confinement within complex geochemical systems. The primary advantage of this technique is that it can simultaneously provide information on the molecular-scale structure and dynamic behavior over a broad range of rate scales difficult to probe via other methods (kHz to MHz) and on a site-specific basis. In this work, we share recent results from our ongoing variable temperature NMR studies of phyllosilicate/H_2O interfaces [1-4] by focusing on the influence that metal charge and hydration energy have on H_2O and metal ion structure and dynamics in the interlayer of Na- and Ca-hectorites between -120°C and 50°C. We find that near-surface ^2H_2O in 2-layer hydrates of Na- and Ca-hectorites are well modeled by simultaneous C2/C3 reorientation of a slightly compressed or extended hydration shell (with respect to an ideal octahedral hydration shell) at a rate in excess of 200 kHz between -50°C and 40°C [1]. Though our model and ^2H VT NMR show the hydration shell compression/extension varies slightly over the temperature range in each type of hectorite, the Ca^{2+} hydration shell geometry deviates less from the ideal case at all temperatures, consistent with the higher hydration energy of Ca^{2+} vs. Na^+. Associated ^2H T_1 relaxation experiments at several temperatures shows nearly identical reductions in T_1 with respect to temperature, though the ^2H nuclei in Ca-hectorite relax more quickly at all temperatures, suggesting a higher intensity of motion in the power spectrum at 45.6 MHz and that the power spectrum intensity increases with decreasing temperature for Na- and Ca-hectorite. With respect to the associated metal dynamics, both Na^+ and Ca^{2+} in 2-layer hectorite hydrates are dominated by rapid diffusion in 2 or 3 dimensions, though comparison of the ^{23}Na and ^{43}Ca VT NMR shows that Ca^{2+} experiences very rapid diffusion at much lower temperatures than Na^+ (-120°C vs. -20°C, respectively). These results are consistent with our recently published general principle that rapid diffusion becomes the dominant mode of metal cation motion for near-surface water and ions in smectites at lower temperatures as the metal hydration energy increases if the ionic radii are similar [1].

[1] Bowers et al. (2011) *Journal of Physical Chemistry C* **115**, 23395-23407. [2] Bowers et al. (2008) *Journal of Physical Chemistry C* **112**, 6430-6438. [3] Weiss et al. (1990) *Geochimica et Cosmochimica Acta* **54**, 1655-1669. [4] Bowers et al. (2012) in preparation.

Characterization of naphthenic acids in oil sands tailings ponds by two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOF-MS)

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Naphthenic acids are a complex mixture of aliphatic and polyalicyclic organic acids found naturally in hydrocarbon deposits. Oilsand ore is refined using the Clark hot water extraction procedure; naphthenic acids are extracted and end up in the process water. These waters are sent to large tailing ponds where particulate materials settle out slowly. Naphthenic acids are of environmental concern due to their toxicities in various mammals and fish; these concerns have lead to a zero discharge policy for oil sands tailings.[1] Naphthenic acids are known to be utilized by plants.[2] We have proposed that these compounds may be utilized by soil bacteria in the tailings ponds which may serve as a source for the generation of H_2S.

In this study, we are using two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOF-MS) to provide profiles of complex mixtures of naphthenic acids (see Figure 1). Using this method it is possible to resolve over 8000 components in this sample. We hypothesize that the profiles of naphthenic acids will be altered by bacterial biodegradation and that these changes will be detectable using GCxGC. The extraordinary peak capacity and resolving power of two-dimensional gas chromatography makes it a suitable tool for the comparison of profiles of naphthenic acid mixtures.

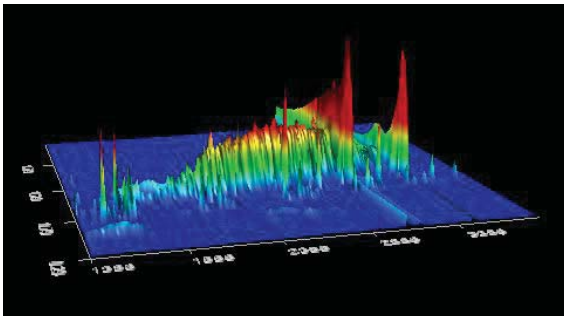

Figure 1: Two-dimensional total ion chromatogram (TIC) plot of naphthenic acids in oil sand process water sample (sample provided by Syncrude).

[1] Hao, C.; Headley, J.; Peru, K.; Frank, R.; Yang, P.; Solomon, K. (2005) *Journal of Chromatography A* **1067**, 277-284.
[2] Headley, J. V.; Armstrong, S. A.; Han, X.; Martin, J. W.; Mapolelo, M. M.; Smith, D. F.; Rogers, R. P.; Marshall, A. G (2009) *Rapid Communications in Mass Spectrometry* **4**, 515-522.