Nanopore Confinement of C-H-O Mixed-Volatile Fluids Relevant to Subsurface Energy Systems

Final report

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Companion project with Ohio State University (D.R. Cole, PI)

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PERSONNEL

DOE BES Geosciences funds have been used exclusively to fund graduate students. The funds are sufficient to support 1 student, but because of financial contributions from the Deep Carbon Observatory, and because of contributions from University College London as part of the start-up package to Prof. Striolo, funds have been used to partially support two students. This strategy helps synergism between the two students, and secures faster progress.

The two students involved in this project are Ms. Anh Phan, who is expected to complete her Ph.D. at the end of 2015, and Ms. Thu Le, who is in her 3rd year of graduate studies and is expected to graduate at the beginning of 2017.

PROGRAM SCOPE

The goal of this project is to employ molecular dynamics approaches to understand the structure and dynamics of fluids containing hydrocarbons, water, and oxygenated compounds confined within narrow pores that could be found in sub-surface formations. The theoretical results are compared systematically to experimental data obtained by our collaborator David Cole of the Ohio State University, and his team.
The distinctive feature of our project is the inclusion of both organic and aqueous fluids. Immediate practical applications can be found in the design of environmentally benign fracturing fluids for hydrodynamic stimulation of shale formations.

Striolo's group contribution, based on atomistic simulations, will characterize fluids confined within alumina, carbon-based, and silica pores of various widths and geometries. The results will be comparable to neutron scattering, NMR, and high-resolution X-ray reflectivity data. We will also determine the physical driving forces responsible for the phenomena observed, which might extend the applicability of our results to many other situations of practical interest (e.g., separation of water-ethanol mixtures, sweetening of natural gas, understanding of the fundamental mechanisms that take place during gas extraction from shale plays).

RESEARCH ACTIVITIES

FY 2012 HIGHLIGHTS

Our first publication was highlighted in the cover of the Journal of Physical Chemistry C. In this publication we quantified how three metal oxide surfaces determine structure and dynamics of liquid water. This publication was the conclusion of our prior collaborations with David Cole and his collaborators at ORNL, and it sets the stage for the research conducted exclusively under the current grant.

FY 2013 HIGHLIGHTS

At the end of 2012 we concluded our modeling analysis regarding the behavior of another hydrogen-binding fluid (ethanol) adsorbed an aluminum oxide surfaces. We quantified hydrogen bonding networks, structure, orientation of interfacial molecules, and mobility. The results are in strikingly good agreement with sum frequency vibrational spectroscopy experimental data available in the literature. The results have been published in the journal J. Phys. Chem. B in 2013.

As highlighted in the Program Scope, above, we are interested in mixed fluid systems. Our third publication, by Cole et al., 2013, has compiled our initial experimental and modeling efforts towards understanding mixed fluids under confinement. In our review article, published in the Reviews in Mineralogy and Geochemistry, we have summarized the state of the art. This helped us focusing our efforts towards topics of interest to the geochemistry community.

FY 2014 HIGHLIGHTS

We focused on the equilibrium and transport behavior of water-ethanol mixtures near a slit-shaped pore carved out of alumina, considered a proxy for many minerals. The pore was of width ~ 1nm. The results showed that water preferentially adsorbs on the protonated surface, while a few ethanol molecules can enter the pore but they stay near the pore center. As a consequence of this preferential partition, we estimated that adsorption can help separating water-ethanol mixtures (a process important for the dehydration of ethanol produced during fermentation processes), and in particular it can help 'breaking' the azeotrope: when a liquid mixture of composition comparable to the azeotrope is exposed to the porous material, preferential water adsorption leads to resultant mixture compositions that can be separated with simple distillations. In addition, the diffusion of water within the pore has been found about 1 order of magnitude faster than that of ethanol. The combination of preferential water adsorption and faster diffusion suggests that membranes can be manufactured for the economical dehydration of ethanol without energy-intensive distillation procedures. The paper has been published in Langmuir in 2014.

We considered mixtures of water and methane confined within narrow pores carved out of silica, considered a proxy for cristobalite and other rocks. The pores were slit-shaped and of width ~ 1nm. The results suggested that the solubility of methane in water within the confined space can be up to 1 order of magnitude larger than that in the bulk. The results show that the structure of confined water, template by the solid surface, is responsible for this enhanced

methane solubility. The structure of water molecules surrounding one methane molecule is reminiscent of that of hydrates. These results have been published in J. Phys. Chem. C.

To establish a connection with the experimental data obtained by Cole and coworkers, we simulated the adsorption of propane in slit-shaped silica pores. The results, in qualitative agreement with the experiments, show a maximum in the density of the confined fluid that occurs at conditions approaching the gas-to-liquid transition of the bulk fluid. These results have been published in Chemical Engineering Science.

We also conducted a number of equilibrium simulations for systems composed by (a) octane and CO2, and (b) butane and CO2 confined within slit-shaped silica pores, a proxy of several minerals. We considered pores of varying widths, systems of varying composition and density, and different temperatures. The results, in general, suggest that CO2 preferentially adsorbs on the silica surfaces. This promotes the dislocation of the hydrocarbons and effectively reduces the activation energy of hydrocarbon diffusion. While it was expected that CO2 molecules adsorb on the pore surface because of the possibility of forming hydrogen bonds with the surface OH groups, the effect on the diffusion coefficient was not foreseen. The results are being compiled in two manuscripts that will soon be submitted for publication.

We also investigated systems composed of water and methane confined within slit-shaped pores carved out of montmorillonite. This mineral was chosen because it is similar to illite, a clay often found in the shale formations in the Marcellus region. We conducted non-equilibrium molecular dynamics simulations to understand whether the Darcy's law can be applied to describe the two-phase fluid flow in these narrow pores. We found that the Darcy's law can describe, qualitatively, the transport of water. However, when applied to describe the transport of methane, the Darcy's law can in some cases fail. This occurs when the structure of the confined fluid changes upon the application of varying driving forces, or when the pressure applied perpendicular to the pore surfaces changes. The manuscript summarizing these results has recently been submitted for publication.

CONFERENCE PRESENTATIONS

Our results have been disseminated to several conferences, listed here. The presenter is highlighted with the symbol *.

A. Phan,* A. Striolo, and D.R. Cole, *Liquid Ethanol Simulated on Crystalline Alpha Alumina*, **AIChE Annual Meeting**, Pittsburgh, PA, October 28th – November 2nd, **2012**.

A. Striolo,* A. Phan, and D.R. Cole, *Ethanol-Water Mixtures Simulated on α-Alumina*, **ACS 245th National Meeting**, New Orleans, LA, April 7th-12th, **2013**.

Y. Hu, D. Devegowda,* A. Striolo, T.A. Ho, A. Phan, F. Civan, and R. Sigal, *A Pore Scale Study Describing the Dynamics of Slickwater Distribution in Shale Gas Formations Following Hydraulic Fracturing*, paper SPE 164552, **SPE Unconventional Gas Conference**, The Woodlands, TX, April 9th-12th, **2013**.

A. Phan,* D.R. Cole, and A. Striolo, *Preferential Adsorption from Liquid Ethanol-Water Mixtures in Alumina Pores*, **AIChE Annual Meeting**, San Francisco, CA, November 3rd – November 8th, **2013**.

T. Le,* A. Phan, D.R. Cole, and A. Striolo, *CO_2-Propane Mixtures in Silica Pores: Relation between Structure and Dynamics*, **AIChE Annual Meeting**, San Francisco, CA, November 3rd – November 8th, **2013**.

A. Phan* and A. Striolo, *Aqueous Methane in Slit-Shaped Silica Nanopores: High Solubility and Traces of Hydrates*, **ChemEngDayUK 2014 Conference**, Manchester, UK, April 7th-8th, **2014**.

A. Phan, T.A. Ho, and A. Striolo,* *Aqueous Systems Under Confinement: From Preferential Adsorption and Exotic Structures to Their Relevance in the Energy Landscape*, **ChemEngDayUK 2014 Conference**, Manchester, UK, April 7th-8th, **2014**.

A. Striolo,* *Aqueous Systems Under Confinement: Preferential Adsorption and Exotic Structures*, **9th Liblice Conference on the Statistical Mechanics of Liquids**, Sec, Czech Republic, June 16th-20th, **2014**.

A. Phan,* D.R. Cole, and A. Striolo, *Aqueous Methane in Slit-Shaped Silica Nanopores: High Solubility and Traces of Hydrates*, **AIChE Annual Meeting**, Atlanta, GA, November 16th-21st, **2014**.

T. Le,* D.R. Cole, and A. Striolo, *Structure-Transport relationship for Confined Fluids: The Example of CO_2 and n-Butane in Silica Pores*, **AIChE Annual Meeting**, Atlanta, GA, November 16th-21st, **2014**.

PUBLICATIONS

A. Phan, T.A. Ho, D.R. Cole, A. Striolo, *Molecular Structure and Dynamics in Thin Water Films at Metal Oxide Surfaces: Magnesium, Aluminum, and Silicon Oxide Surfaces*, **Journal of Physical Chemistry C** 116 (**2012**) 15962-15973. Also featured in the *cover art* of **J. Phys. Chem. C**, volume 116, issue # 30, August 2nd, **2012**.

A. Phan, D.R. Cole. A. Striolo, *Liquid Ethanol Simulated on Crystalline Alpha Alumina*, **J. Phys. Chem. B** 117 (**2013**) 3829-3840.

D.R. Cole, Ok Salim, A. Phan, G. Rother, A. Striolo, L. Vlcek, *Carbon-Bearing Fluids at Nanoscale Interfaces*, **Procedia Earth and Planetary Science** 7 (**2013**) 175-178.

D.R. Cole, A. Striolo, A. Phan, *Hydrocarbon Behavior at Nanoscale Interfaces*, in 'Carbon in the Earth', Reviews in Mineralogy and Geochemistry, R.M. Hazen, R.J. Hemley, A. Jones, and J. Barross Editors, **2013**.

A. Phan, D.R. Cole, A. Striolo, *Aqueous Methane in Slit-Shaped Silica Nanopores: High Solubility and Traces of Hydrates*, **J. Phys. Chem. C** 118 (**2014**) 4860-4868.

A. Phan, D.R. Cole, A. Striolo, *Preferential Adsorption from Liquid Water-Ethanol Mixtures in Alumina Pores*, **Langmuir** 30 (**2014**) 8066-8077.

A. Striolo, *Understanding Interfacial Water and Its Role on Various Practical Applications Using Molecular Simulations*, **MRS Bulletin** 39 (**2014**) 1062-1068. *Invited article*.

T. Le, D.R. Cole, A. Striolo, *Propane Simulated in Silica Pores: Adsorption Isotherms, Molecular Structure, and Mobility*, **Chem. Eng. Sci.** 121 (**2015**) 292-299.