Towards Novel Separation Processes: Experimental Determination of the Composition of Liquid Condensate Confined in Nanopores

Hertanto Adidharma (team leader),[1] Morteza Dejam,[1] and Utkarsh Kapoor[2]

[1]*Department of Energy and Petroleum Engineering, University of Wyoming, Laramie, USA*

[2]*Department of Chemical and Biomedical Engineering, University of Wyoming, Laramie, USA*

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1. Description of research problem

Gas separation is a fundamental process underpinning the chemical and energy industries. It allows for the purification of raw materials, such as natural gas, or products of chemical reactions, separating valuable components for various applications. This is crucial for producing clean fuels, essential chemicals, and industrial gases. Furthermore, gas separation plays a vital role in environmental protection. It facilitates, for example, the capture of carbon dioxide from industrial emissions, a key technology in combating climate change.

Among gas separation techniques where gas selectivity is critical, two important techniques have been commercially implemented for decades, i.e., adsorption and membrane separations. All adsorption techniques and many membrane separations exploit porous media as the separating agents, by which gas components can be separated based on their different molecular interactions, diffusivities, or molecular sizes. When a high-purity gas is desired, the adsorption technique is usually preferable. A selective gas separation may be achieved using an adsorption process with a functionalized adsorbent that has a high affinity to one of the components in the gas mixture. However, this technology is known for its low throughput and capacity. Not to mention that its functionality usually degrades over time and it is harder and therefore consumes a lot more energy to desorb a gas from the modified adsorbent. Therefore, the challenges of finding new materials and methods that consume the least energy while maximizing separation efficiency remain.

In our recent fundamental investigation of the capillary condensation/evaporation of pure fluid in silica nanopores, we found that the heat of the phase transition of the confined fluid is lower than that of bulk,[1] and the mass transfer and capacity of the phase-transition-induced adsorption/desorption are much higher than those of the conventional adsorption/desorption process where no phase transition occurs in the pores. These findings are very attractive and can be exploited for gas separation, leading to lower energy consumption.

However, we should be able to experimentally investigate and determine the composition of the liquid condensate in nanopores first before a novel gas separation that has high selectivity, high capacity, high throughput, and low energy consumption can be developed. To date, the studies of the phase behavior of confined fluid mixtures are mostly done only using theoretical approaches, i.e., through rigorous computational approaches, including Grand Canonical Monte Carlo (GCMC) simulation[2] and density functional theory (DFT),[3] but for several aspects, including the composition of liquid condensate, no clear and consistent conclusion can be drawn. No efforts had been attempted to experimentally verify these results. It is our group at the University of Wyoming who pioneered experimental studies aiming at establishing the complete knowledge of confined fluid phase behavior.

[1] Yang, H.; Jayaatmaja, K.; Qiu, X.; Fan, M.; Dejam, M.; Tan, S.P.; Adidharma, H. Accurate Measurement of the Isothermal Heat of Capillary Condensation in Nanopores Using Differential Scanning Calorimetry and Adsorption/Desorption Experiments. *J. Phys. Chem. C*, 2023, 127, 21980−21988.

[2] Pitakbunkate, T.; Blasingame, T. A.; Moridis, G. J.; Balbuena, P. B. Phase behavior of methane-ethane Mixtures in nanopores. *Ind. Eng. Chem. Res*., 2017, 56, 11634-11643.

[3] Liu, J.; Wang, L.; Xi, S.; Asthagiri, D.; Chapman, W. G. Adsorption and phase behavior of pure/mixed alkanes in nanoslit graphite pores: An iSAFT application. *Langmuir*, 2017, 33, 11189-11202.

We developed, for the first time, a procedure using a high-pressure Calvet-type Differential Scanning Calorimeter (DSC) to accurately measure the phase transition conditions of confined pure fluids and fluid mixtures.[4] Also, for the first time, we have found that the behavior of a confined fluid mixture is similar to that of a confined pure fluid, and confined mixtures do not exhibit phase-coexistence regions as the bulk mixtures do.[5] However, we have not developed an experimental method that can determine the composition of the liquid condensate produced during capillary condensation.

2. Short-term objectives and work plan

It is the purpose of this proposed work to develop an experimental procedure for determining the composition of liquid condensate in nanopores. For the record, the development of such an experimental method will also be the first in the world. In this proposed work, we will use one binary mixture, such as CH_4/C_3H_8 or CO_2/N_2. For the nanoporous medium, we will use a well-defined silica porous medium, such as MCM-41 or SBA-15.

The conditions of capillary condensation of the gas mixture will be measured first by implementing the isochoric procedure we recently developed using the high-pressure Calvet-type DSC available in our lab. To develop a procedure for determining the composition of liquid condensate in nanopores, we need to analyze the total and component isotherms from adsorption/desorption experiments, which can only be derived from a careful analysis of mass balance under dynamic mode. We will run such experiments using the Dynamic Gas Sorption Intelligent Gravimetric Analyzer (IGA-003), by which such challenging experiments can be performed. The composition of gas exiting IGA-003 will be determined using a gas analyzer or a Dynamic Sampling Mass Spectrometer. Hertanto Adidharma and Morteza Dejam will manage these experimental works.

To further provide a better picture of the underlying physics, explain the factors mass transfer, sorption properties, and selectivity depend on, and determine the composition of liquid condensate in nanopores, we will also use molecular simulations. We will perform Monte Carlo simulations using CASSANDRA package to simulate isotherms for the sorbate–nanoporous material. Additionally, starting with the equilibrated configuration (molecule coordinates) obtained from the Monte Carlo simulations, we will also do molecular dynamics simulations using GROMACS package and determine how the degree of confinement and fluid-fluid and fluid-wall interactions govern the configuration and dynamics, at a given composition. It is possible that standard force field models do not capture the molecular interactions realistically. If so, using our experimental results, we will make necessary modifications to refine the nonbonded interactions. Utkarsh Kapoor will manage this simulation work.

The overall goal is to be able to make predictions as to how the composition of liquid condensate depends on confinement effects and therefore design or select nanopores properly for specific applications, which will be very important for our follow-up proposals.

3. Long-term benefits

The seed results will open the door to collaborative proposals among departments within our college and beyond addressing vast gas separation applications that are still challenging nowadays, such as natural gas purification, carbon dioxide capture, volatile organic compounds removal, etc.

4. List of funding sources and programs that could fund the proposed research

The obtained seed results will strongly help capture external grants from several agencies, including National Science Foundation, Department of Energy, and Environmental Protection Agency.

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[4] Qiu, X., Tan, S.P., Dejam, M., Adidharma, H. Simple and accurate isochoric differential scanning calorimetry measurements: phase transitions for pure fluids and mixtures in nanopores. *Phys. Chem. Chem. Phys.*, 2019, 21, 224-231.

[5] Qiu, X.; Tan, S.P.; Dejam, M.; Adidharma, H. Binary fluid mixtures confined in nanoporous media: Experimental evidence of no phase coexistence. *Chem. Eng. J.*, 2021, 405, 127021.

Budget and budget justification

The following table summarizes the required items (personnel, supplies and materials, and budget for this project. The budget for PhD student 1 is to partially cover the student's stipend in the Department of Energy and Petroleum Engineering during the one-year funding period; PhD student 1 will be working on the experimental works. The budget for PhD student 2 is to partially cover the student's stipend in the Department of Chemical and Biomedical Engineering during summer; PhD student 2 will be working on the simulation work. In addition, the budget for supplies and materials (O-rings, pipe fittings, liquid N_2, gases, adsorbents, etc.) is $ 8,000.

Item	**Budget**
Personnel	
Stipend of PhD student 1	$ 12,000
Stipend of PhD student 2	$ 5,000
Supplies and Materials	
O-rings, pipe fittings, liquid N_2, gases, adsorbents, etc.	$ 8,000
Total	$ 25,000