High-Pressure Gas Adsorption Selectivity Studies on Metal-Organic Frameworks

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ABSTRACT

The microporosity and high surface area of metal-organic frameworks make them excellent candidates to be used as mediums for gas storage applications. In many cases, it is required for the metal-organic framework of interest to have a high affinity and selectivity of a specific component in a mixture. Specifically, the selectivity of a gas in a high-pressure environment is of great significance because microporous solids such as metal-organic frameworks can adsorb and store greater volumes of gas at elevated pressures. For this reason, the adsorbate possesses a higher energy density when hydrogen, methane, or hydrocarbons are adsorbed at above ambient pressures. In this study, a high-pressure adsorption apparatus using a known mixture of carbon dioxide and methane gas measured the total uptake of the mixture onto the surface and into the pores of the metal-organic frameworks at pressures up to 2.5 MPa. The apparatus was equipped with a sampling valve connected to a mass spectrometer to determine the composition of the non-adsorbed gas, thus allowing for the uptake of each component to be calculated. The same experiments were conducted using pure carbon dioxide and pure methane as an experimental control. Additionally, the surface area, porosity, and total pore volume of the selected adsorbates were measured using traditional physisorption techniques to provide surface textural information.

OBJECTIVES

- Characterize each material using traditional gas adsorption techniques.
- Calculate adsorption selectivity of each material from pure component adsorption isotherms using ideal adsorbed solution theory (IAST).
- Generate an analysis method to generate known-composition gas mixtures, dose these mixtures onto materials of interest, and sample the non-adsorbed gas phase with a mass spectrometer to calculate the composition of the adsorbed phase.
- Compare experimental gas-mixture selectivity measurements with IAST calculations.

METHODS

MATERIALS

Two metal-organic frameworks of the same chemical makeup but synthesized by different companies were chosen for this study. The material used for this study was the copper-based MOF CuBTC. Sample A is CuBTC from BASF, also known as Basolite C300. Sample B is CuBTC from NuMat Technologies. For all high-pressure gas adsorption studies approximately 2g of material was used. Approximately 50 mg of material was used for surface characterization studies. The same samples were used for both pure component measurements and mixture analysis. Prior to all gas adsorption experiments the samples were heated to 100°C and evacuated below $7\text{x}10^{-7}$bar for at least 12 hours.

SURFACE CHARACTERIZATION

The surface properties of the selected materials were characterized with N_2 using a Micromeritics 3Flex Surface Characterization Analyzer (Fig. 1). The BET surface area was calculated using the Rouquerol transform for data selection and optimization. Total Pore Volume was calculated with a density conversion factor of 0.0015468.

Fig. 1: Micromeritics 3Flex

PURE COMPONENT ISOTHERMS

Fig. 2: HPVA II from Particulate Systems

CO_2 and CH_4 pure component isotherms were measured at 25°C, 15°C, and 5°C up to 5MPa (saturation pressure limiting) using the HPVA II from Particulate Systems (Fig. 2). A recirculating water bath was used to maintain a sample analysis temperature within +/- 0.1°C. All isotherms were modeled to calculate isosteric heats of adsorption with MicroActive software from Micromeritics. Ideal adsorbed solution theory (IAST), originally proposed by Myers and Prausnitz[1], was applied to the pure component isotherms at 25°C to calculate selectivity coefficients ($s_{1,2}$) defined as:

$$s_{1,2} = \frac{x_1 / y_1}{x_2 / y_2}$$

Where x_i is the mol fraction of component i in the adsorbed phase and y_i is the mol fraction of component i in the gas phase. If $s_{1,2} > 1$, the adsorbent favors component *1* over component *2*. For our data reporting, component *1* is CO_2 and component *2* is CH_4.

MIXTURE ANALYSIS

A isolated gas reservoir was added to the dosing manifold of the HPVA II to create binary CH_4/CO_2 mixtures of 50/50, 25/75, and 75/25 mol%. A ten minute period was allotted for gas mixing prior to sample dosing. Dosing pressures of 1MPa to 5MPa in steps of 1MPa were used to create 5-point mixture isotherms with a minimum gas equilibration period of 20 minutes. To sample the non-adsorbed gas phase, a 6-way valve with a 0.5 mL sampling loop (Fig. 3) was connected to the dosing manifold. After gas equilibration the main dosing valve was closed to prevent desorbing gas from compromising the subsequent mixture analysis.

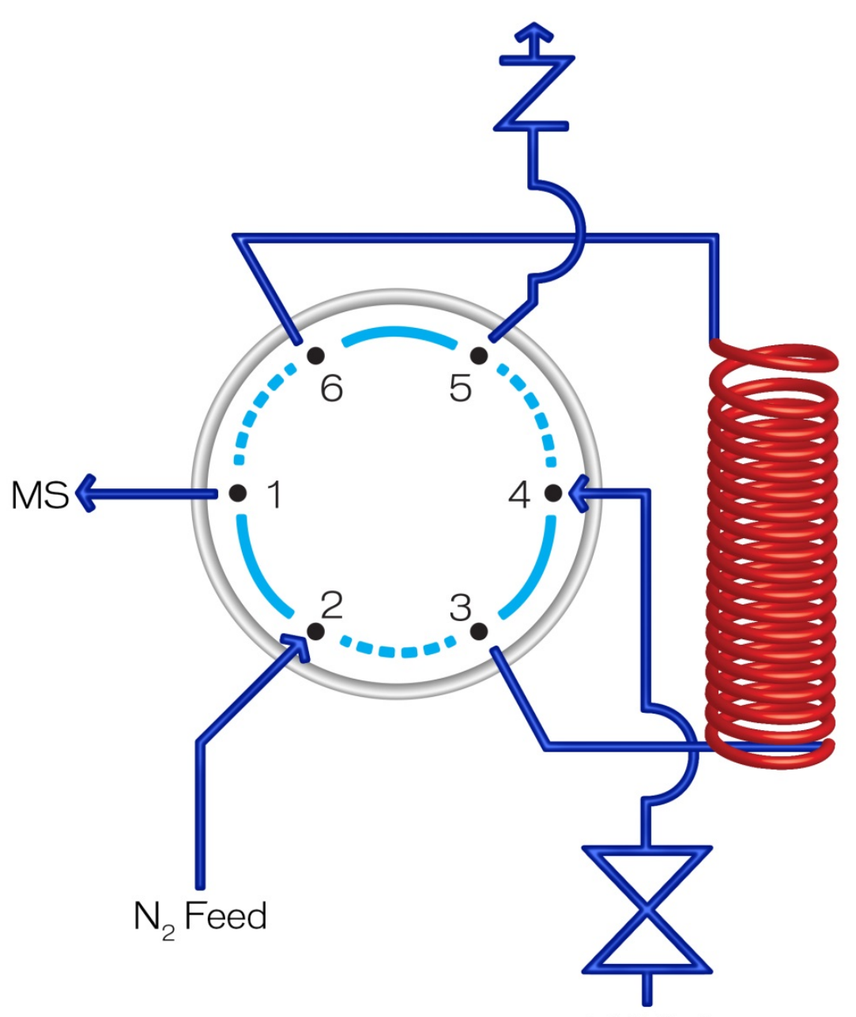

Fig. 3: 6-way Valve and Loop for Mixture Sampling

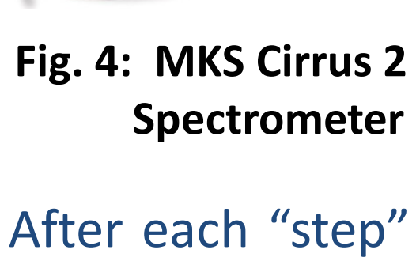

Fig. 4: MKS Cirrus 2 Mass Spectrometer

Next, a bellows valve connected to the 6-way valve in the ready (solid lines) position is opened. An in-line relief valve downstream of the loop relieves the high pressure to approximately 1.006 bar. When the 6-way valve is activated (dotted lines), a 50 mL/min N_2 feed sweeps the gas mixture to a MKS Cirrus 2 Mass Spectrometer (Fig. 4) for composition analysis.

After each "step" in the mixture isotherm process the sample pressure is relieved and the system is vacuumed down to $7\text{x}10^{-7}$ bar before moving forward with the next isotherm point in the analysis.

RESULTS

SURFACE CHARACTERIZATION

	BET SA (m^2/g)	TPV (cm^3/g)	p/p^o
Sample A	1680	0.6859	0.9478
Sample B	2340	1.0034	0.9619

Table 1: BET Surface Area and Total Pore Volume of Samples A & B

PURE COMPONENT ISOTHERMS

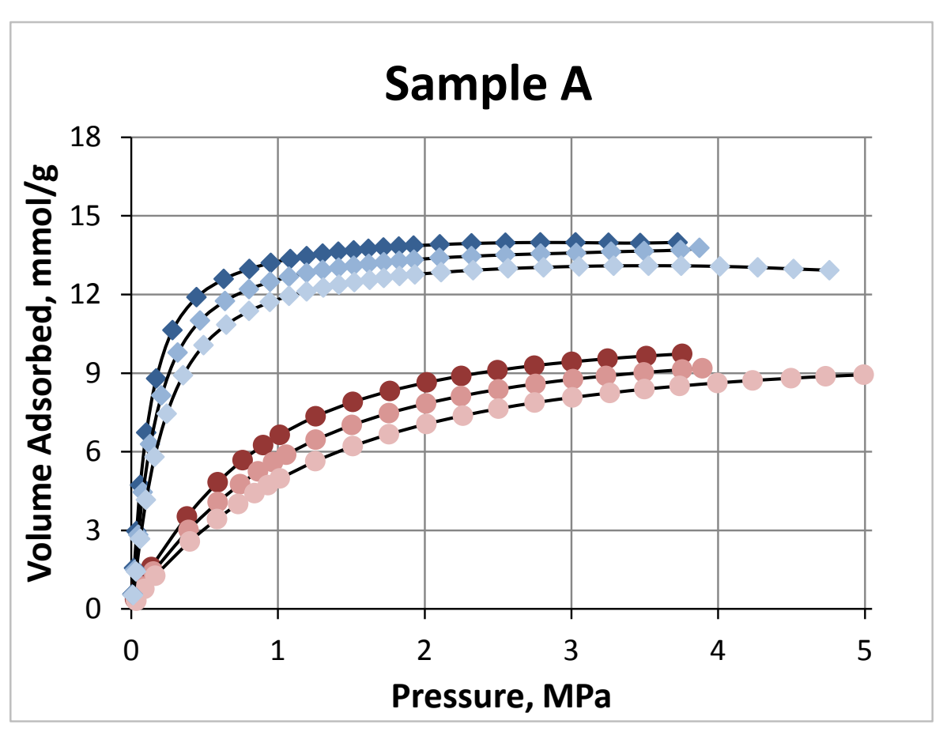

Fig. 5: Sample A Pure Component Isotherms

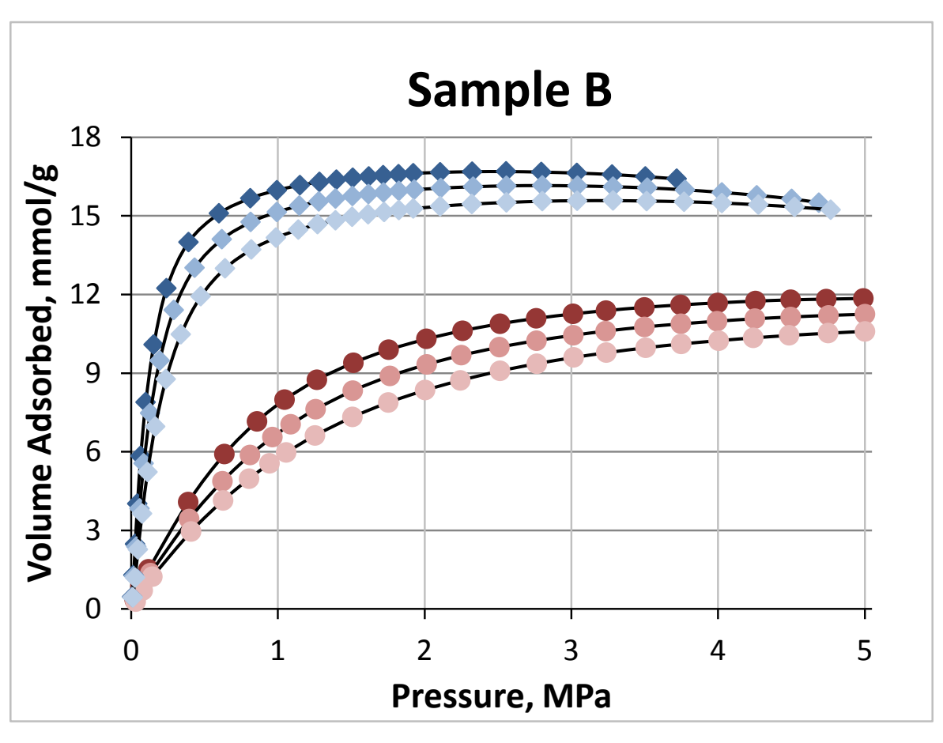

Fig. 6: Sample B Pure Component Isotherms

	Sample A		Sample B	
	CH_4	CO_2	CH_4	CO_2
5°C	1.604	8.583	1.518	12.206
15°C	1.225	5.717	1.181	8.002
25°C	0.953	3.913	0.934	5.397

Table 2: Henry's Coefficients

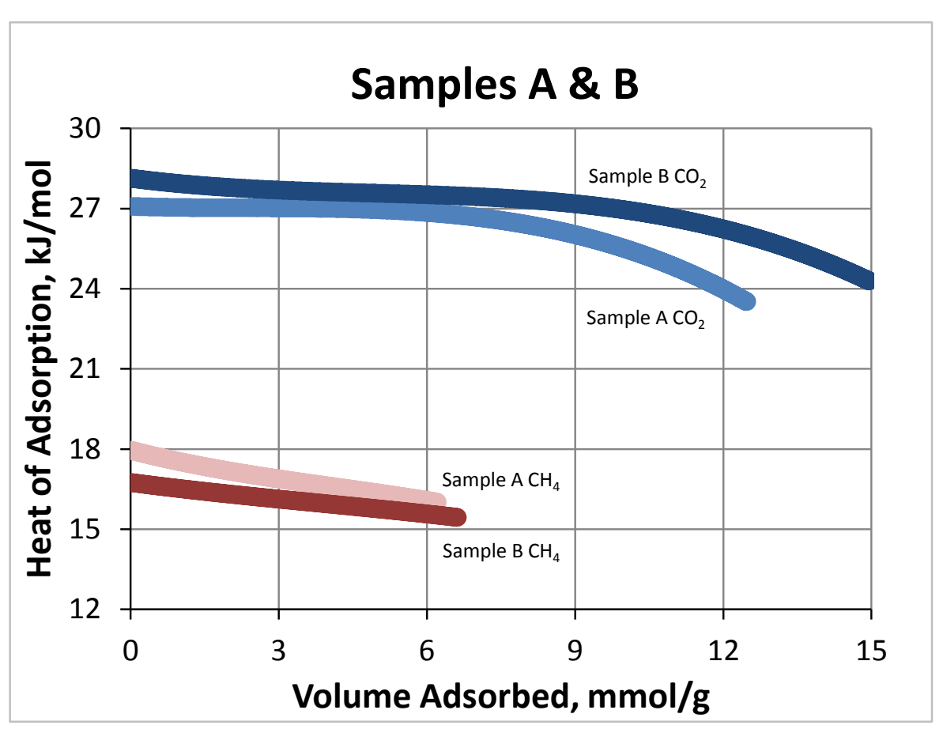

Fig. 7: Isosteric Heats of Adsorption

Figures 5 & 6 show pure component isotherms for Samples A & B. CO_2 isotherms are represented by blue/diamond markers and CH_4 isotherms are represented by red/circle markers. Temperatures of 5°C, 15°C, and 25°C are shown, where uptake increases as temperature decreases. Table 2 shows Henry's coefficients calculated over the linear portion of each isotherm at low pressure. Figure 7 shows the isosteric heats of adsorption calculated from the pure component isotherms where blue lines represent CO_2 and red lines represent CH_4. Lighter lines represent Sample A and darker lines represent Sample B.

MIXTURE ANALYSIS

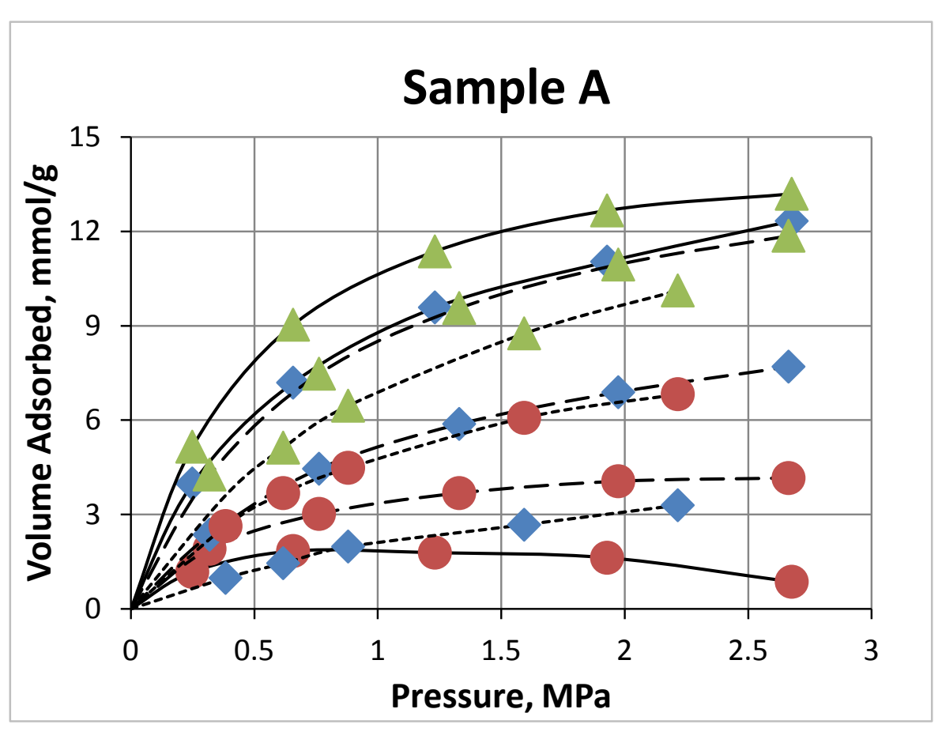

Fig. 8: Sample A Multi-Component Isotherms

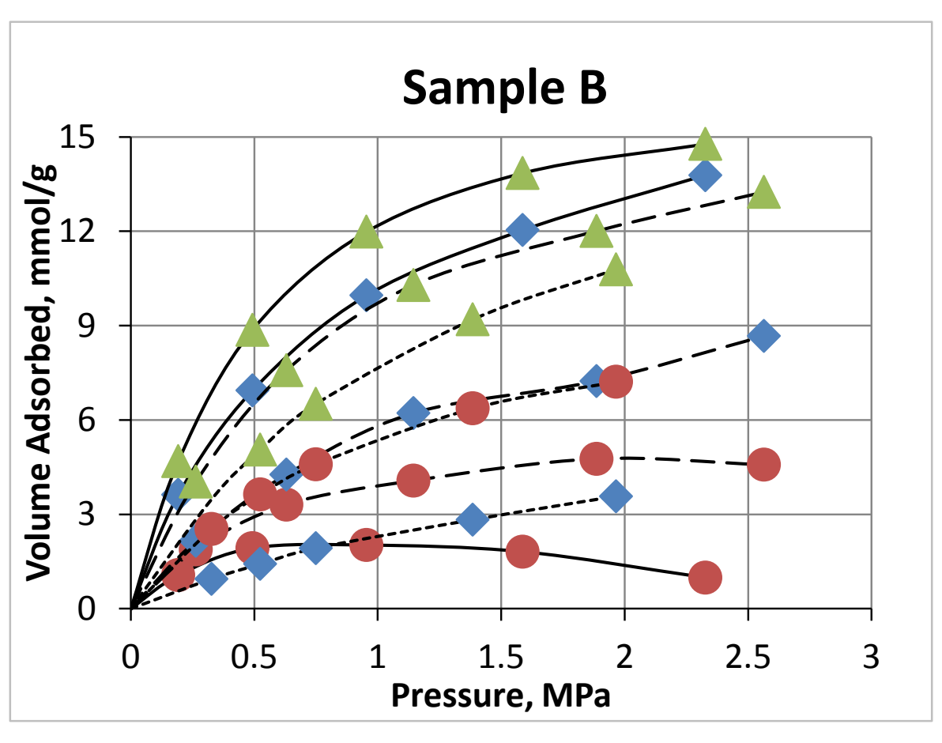

Fig. 9: Sample B Multi-Component Isotherms

In Figures 8 & 9 green/triangle markers indicate total adsorption, blue/diamond markers indicate CO_2 adsorption, and red/circle markers indicate CH_4 adsorption. Solid lines represent CH_4/CO_2 dosing mixtures of 25/75 mol%, long dashes represent CH_4/CO_2 dosing mixtures of 50/50 mol%, and short dashes represent CH_4/CO_2 dosing mixtures of 75/25 mol%.

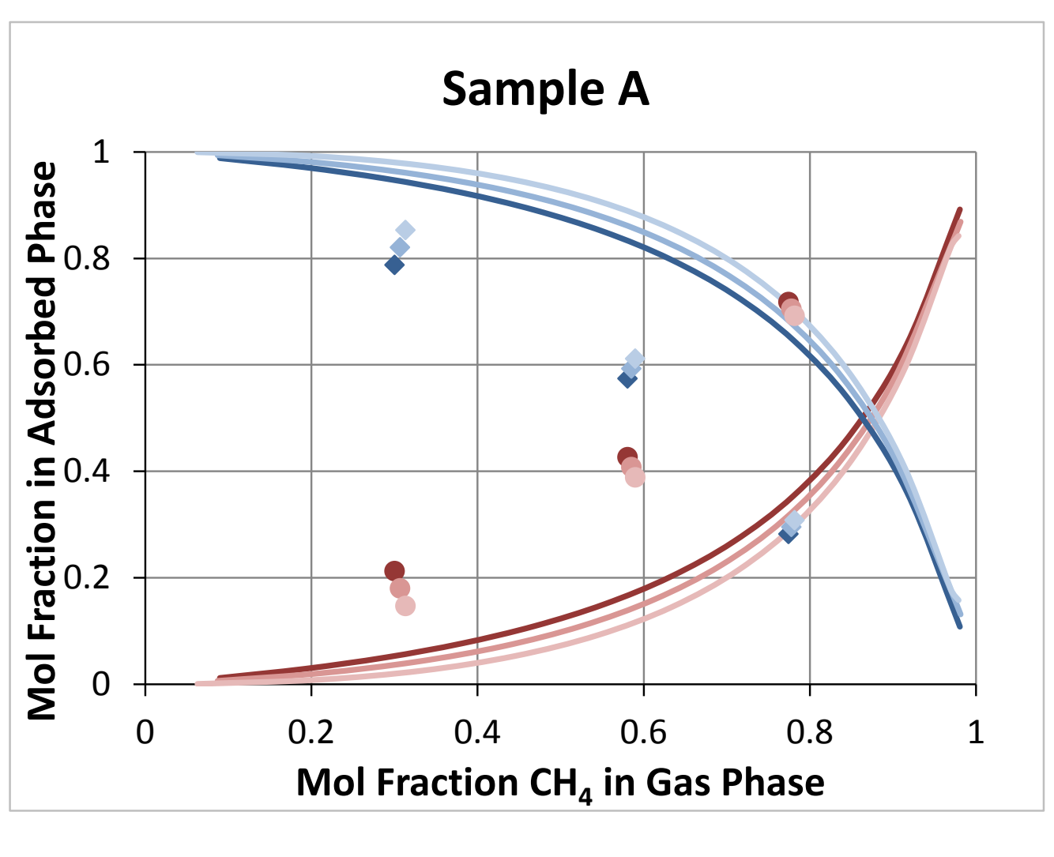

Fig. 10: Equilibrium Gas and Adsorbed-Phase Composition of CH_4/CO_2 Mixtures

Pressure	Amount CH_4 in Gas Phase		
	30%	58.5%	77.5%
	IAST		
0.5MPa	7.67	6.91	6.49
1.0MPa	11.42	8.56	7.40
1.5MPa	22.78	11.08	8.49
	Experimental Values		
0.5MPa	1.59	1.86	1.35
1.0MPa	1.86	2.05	1.47
1.5MPa	1.35	2.26	1.59

Table 3: Selectivity Coefficients of CO_2/CH_4 on Sample A

Pressure	Amount CH_4 in Gas Phase		
	33%	57.5%	79%
	IAST		
0.5MPa	7.27	6.82	6.48
1.0MPa	9.34	7.98	7.11
1.5MPa	12.93	9.52	7.82
	Experimental Values		
0.5MPa	1.82	1.68	1.42
1.0MPa	2.49	1.88	1.60
1.5MPa	3.56	2.11	1.81

Table 4: Selectivity Coefficients of CO_2/CH_4 on Sample B

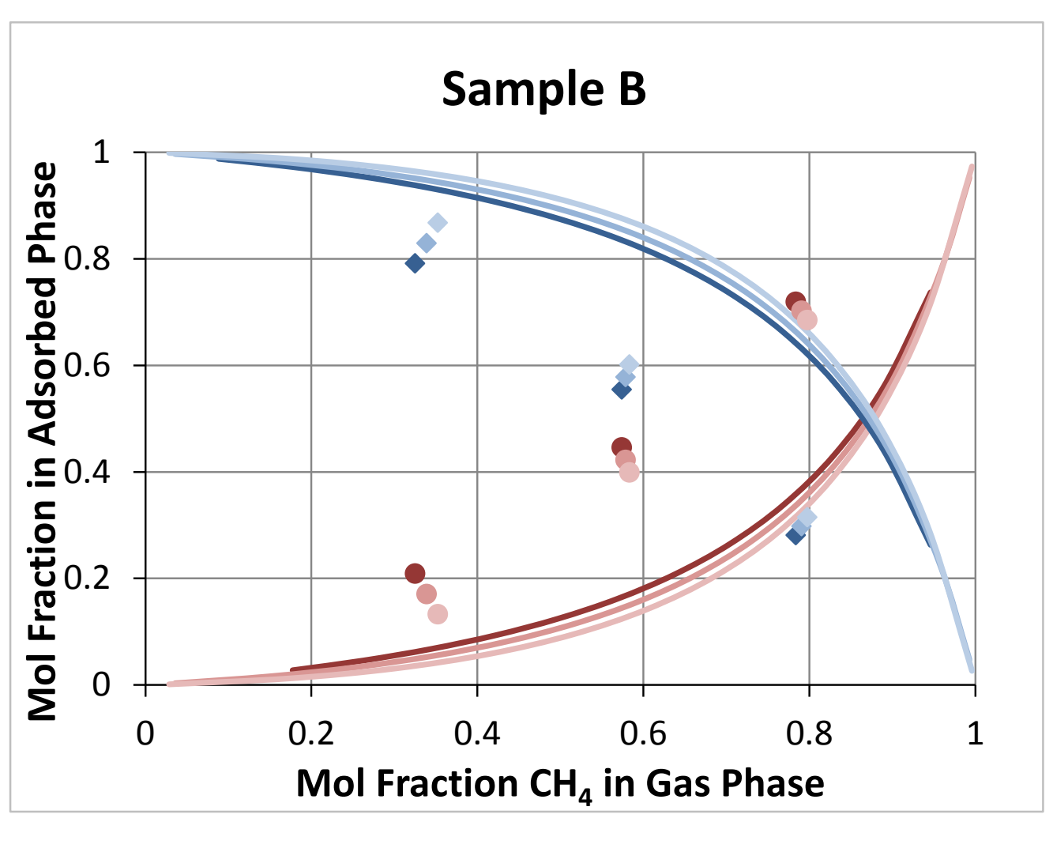

Fig. 11: Equilibrium Gas and Adsorbed-Phase Composition of CH_4/CO_2 Mixtures

Figures 10 & 11 show the mol fraction of each component in the adsorbed phase as a function of the mol fraction of CH_4 in the gas phase. Solid lines represent IAST predictions and single points are taken from experimental data. Blue represents adsorbed CO_2 and red represents adsorbed CH_4. Three separate pressures are represented where the darkest shade is 0.5MPa, the middle shade is 1.0MPa and the lightest shade is 1.5MPa. Selectivity coefficients were calculated for IAST and experimental data as a function of both pressure and gas composition, displayed in Tables 3 & 4.

CONCLUSIONS

- Sample B adsorbed more total gas during the pure component analyses and mixture analyses than Sample A. The higher BET surface area and total pore volume of Sample B support this information.
- Experimental mixture data indicates that both samples are more selective of CO_2 over CH_4. However, both samples do not have as high of a selectivity for CO_2 over CH_4 as predicted by IAST calculations and literature[2].
- Experimental mixture data follows the same selectivity trend as IAST predictions where selectivity increases as a function of pressure.

ACKNOWLEDGEMENTS

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1. Myers, A. L., and J. M. Prausnitz. "Thermodynamics of Mixed-gas Adsorption." *AIChE Journal* 11.1 (1965): 121-27.
2. Hamon, L., Jolimaître, E., and Pirngruber, G. D. "CO_2 and CH_4 Separation by Adsorption Using Cu-BTC Metal-Organic Framework." *Ind. Eng. Chem. Res.* 49.16 (2010): 7497-7503.

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