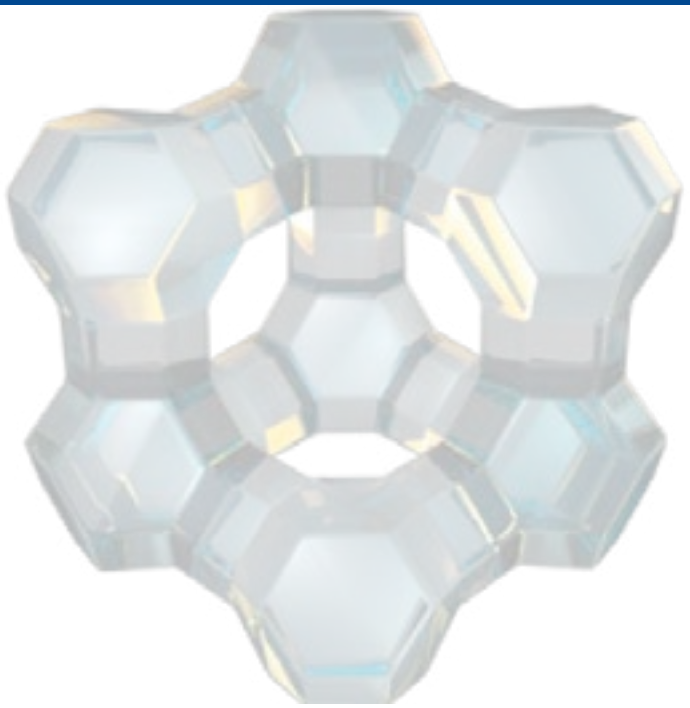
micromeritics®

INTRODUCTION TO IDEAL ADSORBED SOLUTION THEORY IN MICROACTIVE: PREDICTING MULTICOMPONENT ADSORPTION



Introduction

With the release of the MicroActive V6.0 and the 3Flex V6.0 software, multicomponent adsorption predictions using ideal adsorbed solution theory (IAST) have been added. IAST is a predictive technique developed by Myers and Prausnitz in 1965. It is used to predict mixed gas adsorption behavior from single component isotherms. This first release of IAST on V6.0 can be used to predict binary adsorption. IAST has proven to be in good agreement for a variety of binary systems, including methane/ethane mixtures in BPL carbon, Xe/Kr mixtures in zeolite NaA, and propane/propylene mixtures in HKUST-1 (Furmaniak, et. al., pccp, 2015).

IAST relies on several assumptions that are described in the original manuscript, which are listed below (Myers, Prausnitz, AIChE Journal, 1965).

- The surface of the adsorbent is heterogeneous. Homogeneous surfaces are likely to deviate from ideal behavior.
- The adsorbents are non-reactive and similar in size/shape to each other.
- Pure-component isotherms must be accurately measured at low surface coverage, because the integration for spreading pressure is sensitive to this portion of the pure-component isotherm.

IAST has been shown to accurately predict binary gas adsorption in many systems and is still commonly used today, almost 60 years after it was first developed, to anticipate multicomponent adsorption behavior. In this app note, pure component **CO_2, CH_4, and C_2H_6** adsorption isotherms on three microporous carbons were collected using the 3Flex. Those isotherms were then used to develop IAST predictions within MicroActive. Breakthrough curves were then collected for the binary components to compare to the IAST predictions This note will provide a framework for using the new IAST features in V6.0 software for MicroActive and the 3Flex.

Experimental

IAST calculations can be performed in MicroActive by selecting **Reports** then **Open Notebook**. If creating a new notebook, enter a name and press **Open**. The system will display a prompt that the chosen file name does not exist and ask whether to create that file. After proceeding with the file creation, the report selection screen will appear where **IAST Composition Reports** can be selected to open the IAST report template. On the IAST reporting window, up to two isotherms for IAST can be selected. The following isotherm models are also available: VTTE, Sips, Langmuir, Dual Site Langmuir, Toth, and Redlich Peterson. Choose the appropriate model, click Save, then press Preview to generate the report.

In this note, three microporous carbons were selected for demonstrating the new IAST features in MicroActive. The three carbons used in this study include: Carboxen 1018, Carboxen 1021, and Carbosieve S-III. The samples were each analyzed on the 3Flex for **CO_2, CH_4**, and **C_2H_6** adsorption. Prior to analysis, samples were activated on a SmartVac Prep by heating to 250 °C under vacuum for 10 hours. Following activation, the samples were analyzed for each gas.

Breakthrough analyses were conducted on the Micromeritics BTA. Samples were activated under nitrogen flow while heating to 250 °C overnight. Binary breakthrough measurements were conducted using a mixed gas feed consisting of 50:50 mixtures of **CO_2-CH_4, CO_2-C_2H_6**, and **CH_4-C2H6.** Nitrogen was used as a carrier gas and argon was used as a tracer gas to determine the start of the breakthrough experiment.

Results

Single Component Analysis using the 3Flex

The results of the single component isotherms for the three materials: Carboxen 1018, Carboxen 1021, and Carbosieve S-III are shown in Figures 1, 2, and 3 below.

The results for Carboxen 1018 are shown in Figure 1. Ethane showed strong affinity at low pressure, but less capacity than **CO_2** at 1000 mbar. At 1000 mbar, the adsorption capacity of **CO_2** was 55 cm^3 /g STP, while ethane reached a capacity of 40 cm^3/g STP. Methane was the weakest adsorbing species, reaching a capacity of 15 cm^3 /g STP.

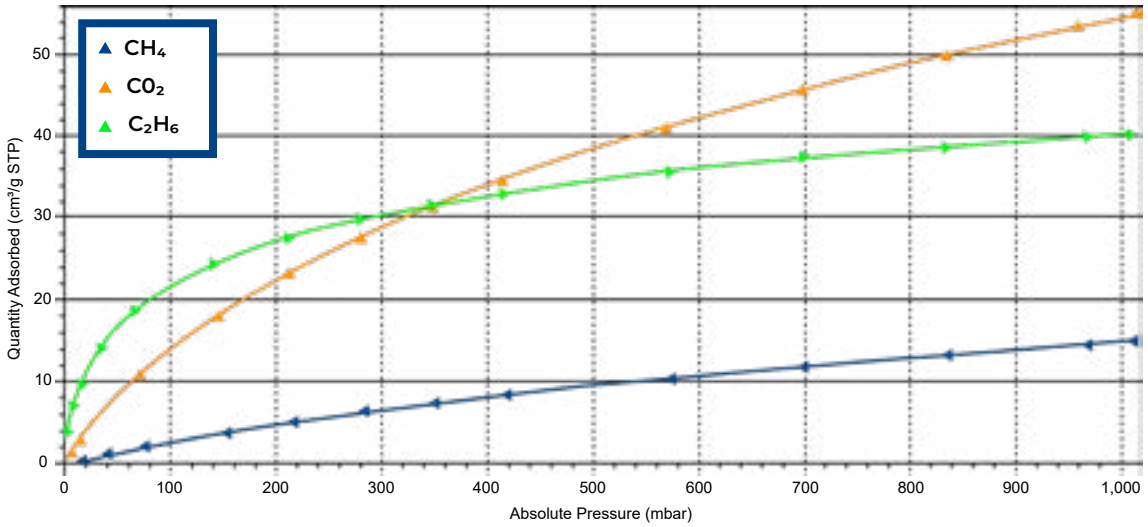


Figure 1. Single component isotherms of Carboxen 1018 for **CO_2** (orange), **CH_4** (blue), and **C_2H_6** (green)

Carboxen 1021 displayed a similar trend compared to Carboxen 1018; however, the adsorbed capacity at 1000 mbar was similar between ethane (58 cm³/g STP) and **CO_2** (55 cm³/g STP). Once again, methane adsorption was the lowest at 1000 mbar, reaching only 24 cm³/g STP.

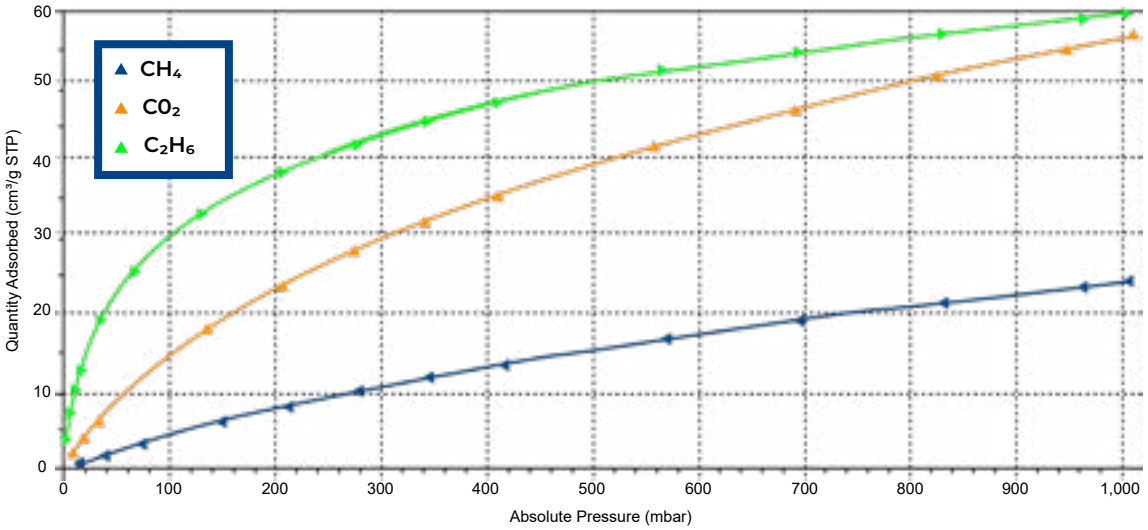


Figure 2. Single component isotherms of Carboxen 1021 for **CO_2** (orange), **CH_4** (blue), and **C_2H_6** (green)

Carbosieve S-III showed the strongest affinity for ethane, reaching an adsorbed capacity of 90 cm³/g STP at 1000 mbar. **CO_2** adsorbed the second most (74 cm³/g STP), followed by methane (33 cm³/g STP).

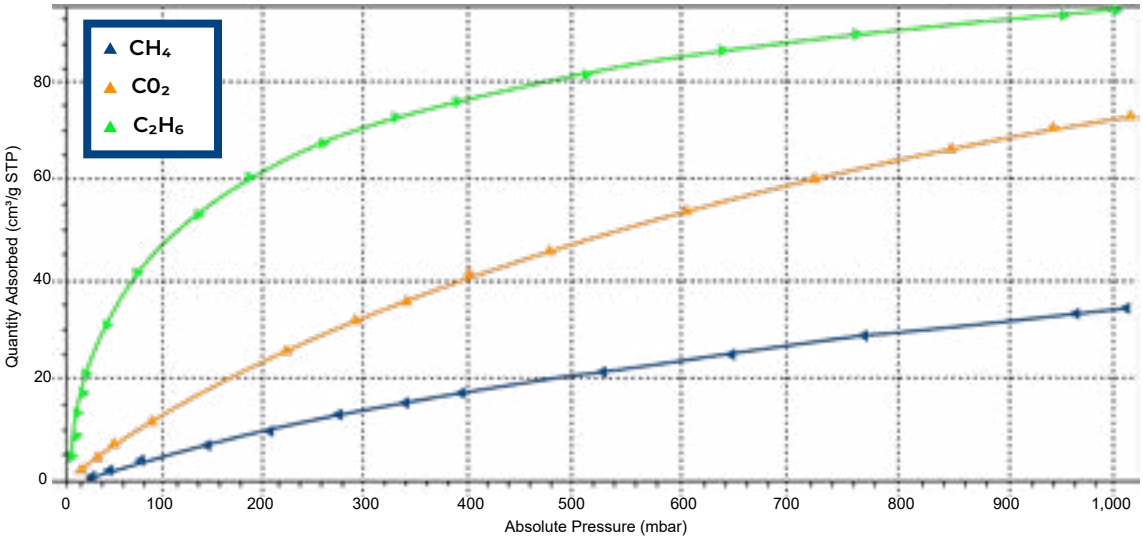
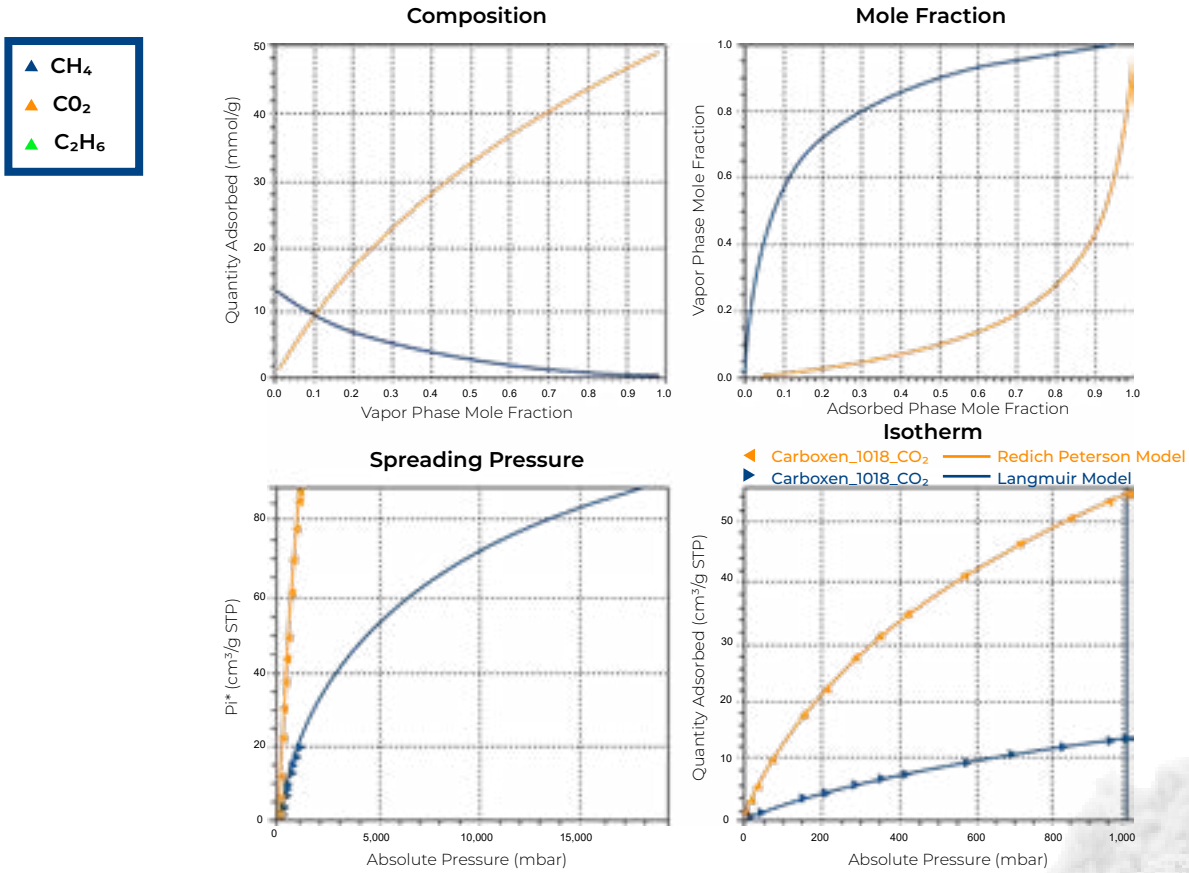


Figure 3. Single component isotherms of Carbosieve S-III for **CO_2** (orange), **CH_4** (blue), and **C_2H_6** (green)

IAST Binary Adsorption Predictions

From the isotherms, the composition, mole fraction, and spreading pressures can be determined. See Figures **4**, **5**, and **6** below.



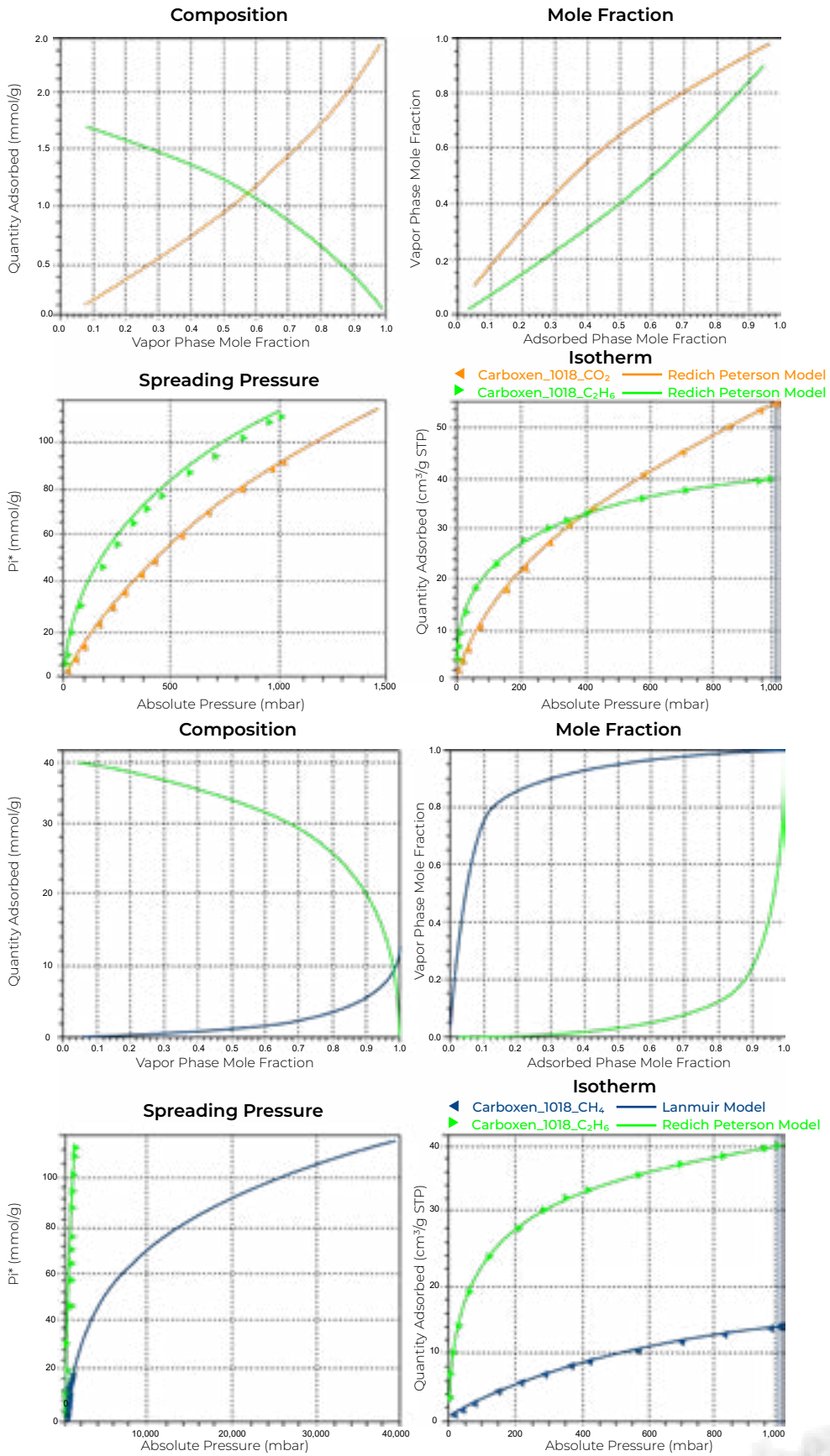
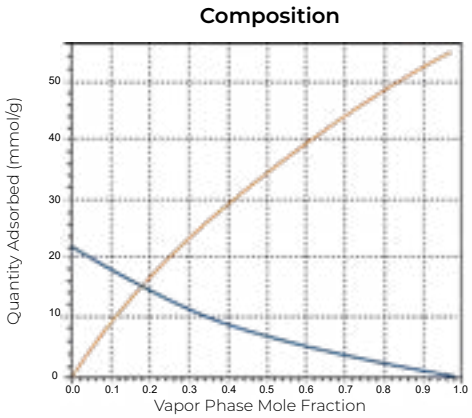
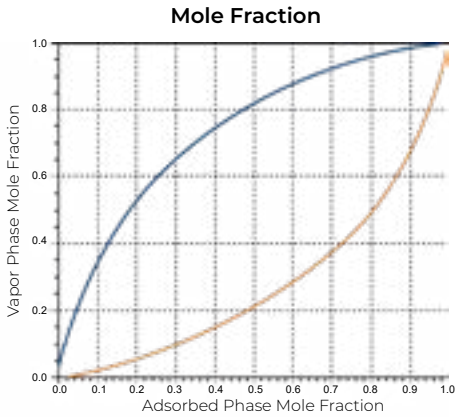
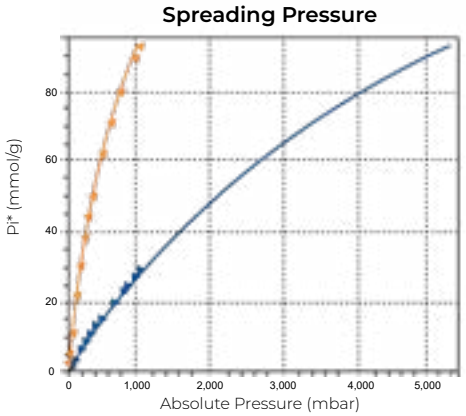


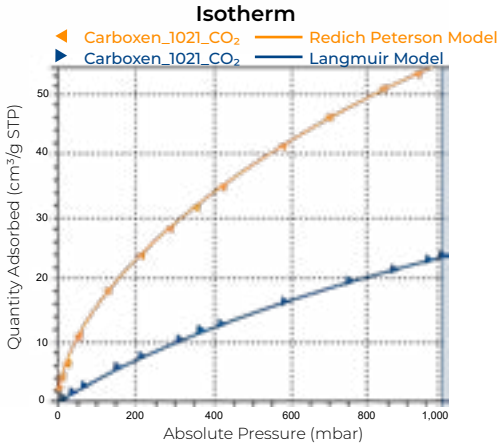
Figure 4. Composition, mole fraction, and spreading pressure for Carboxen 1018 (top) **CO_2-CH_4,** (middle) **CO_2-C_2H_6,** (bottom) **CH_4-C_2H_6**

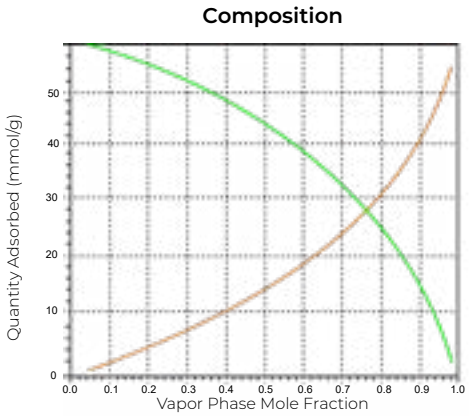
▲ CH_4
▲ CO_2
▲ C_2H_6

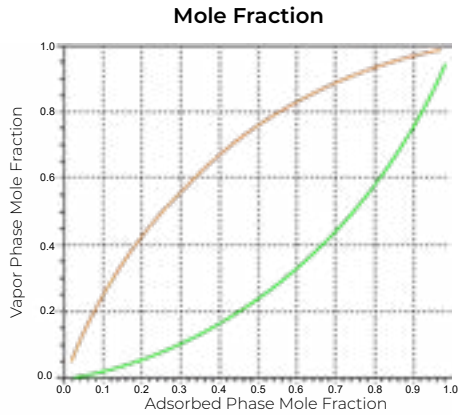

Composition
Quantity Adsorbed (mmol/g)
Vapor Phase Mole Fraction

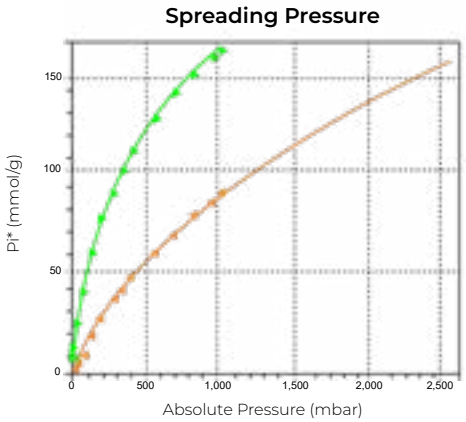

Mole Fraction
Vapor Phase Mole Fraction
Adsorbed Phase Mole Fraction

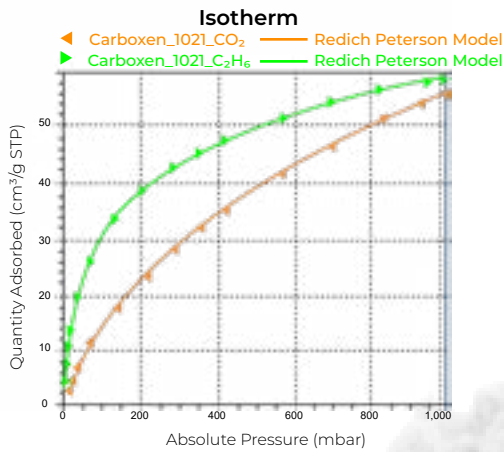

Spreading Pressure
Pi* (mmol/g)
Absolute Pressure (mbar)


Isotherm
Carboxen_1021_CO2
Redich Peterson Model
Carboxen_1021_CO2
Langmuir Model
Quantity Adsorbed (cm3/g STP)
Absolute Pressure (mbar)


Composition
Quantity Adsorbed (mmol/g)
Vapor Phase Mole Fraction


Mole Fraction
Vapor Phase Mole Fraction
Adsorbed Phase Mole Fraction


Spreading Pressure
Pi* (mmol/g)
Absolute Pressure (mbar)


Isotherm
Carboxen_1021_CO2
Redich Peterson Model
Carboxen_1021_C2H6
Redich Peterson Model
Quantity Adsorbed (cm3/g STP)
Absolute Pressure (mbar)

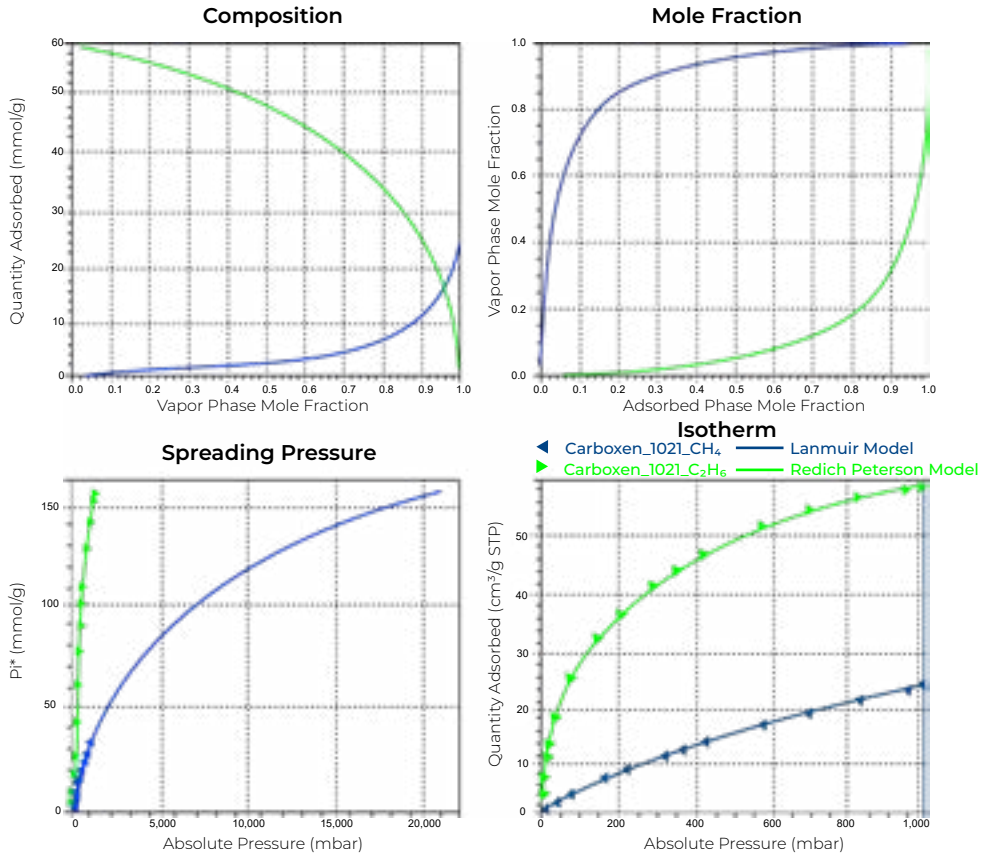
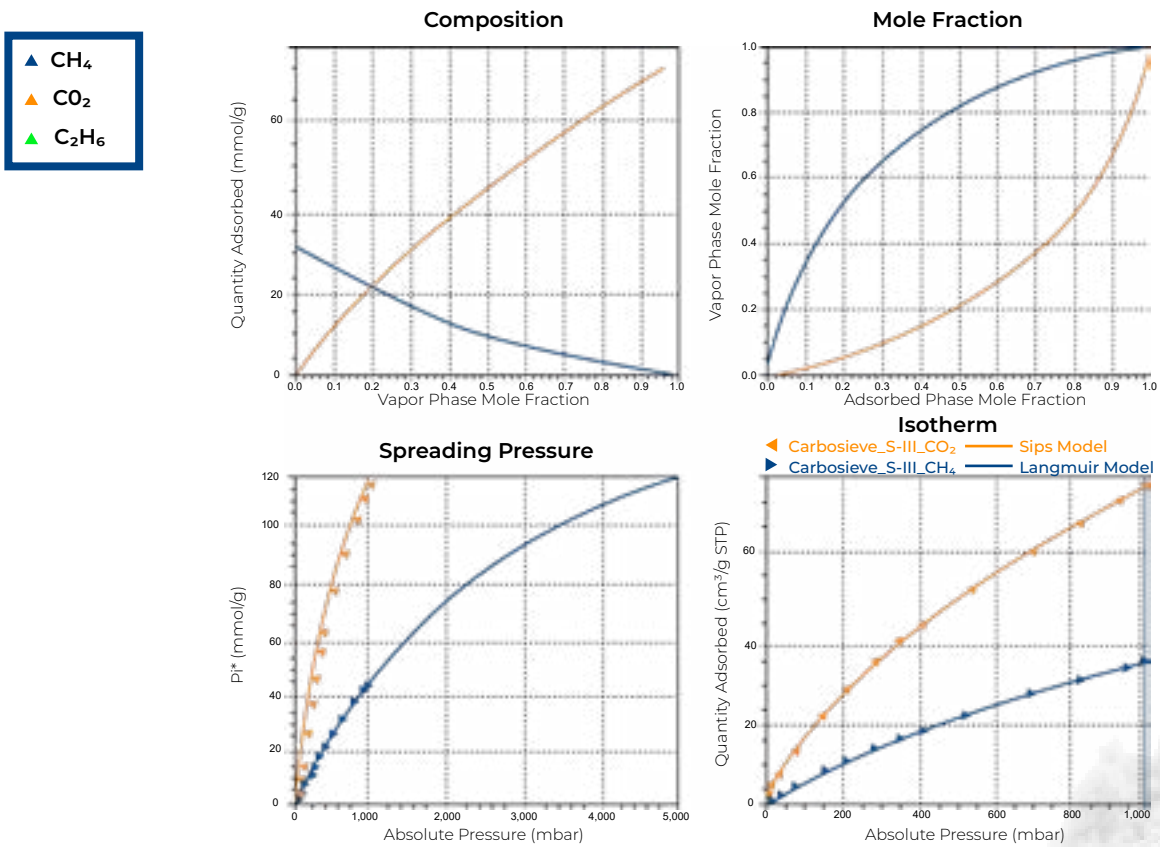


Figure 5. Composition, mole fraction, and spreading pressure for Carboxen 1021 (top) **CO_2-CH_4**, (middle) **CO_2-C_2H_6**, (bottom) **CH_4-C_2H_6**



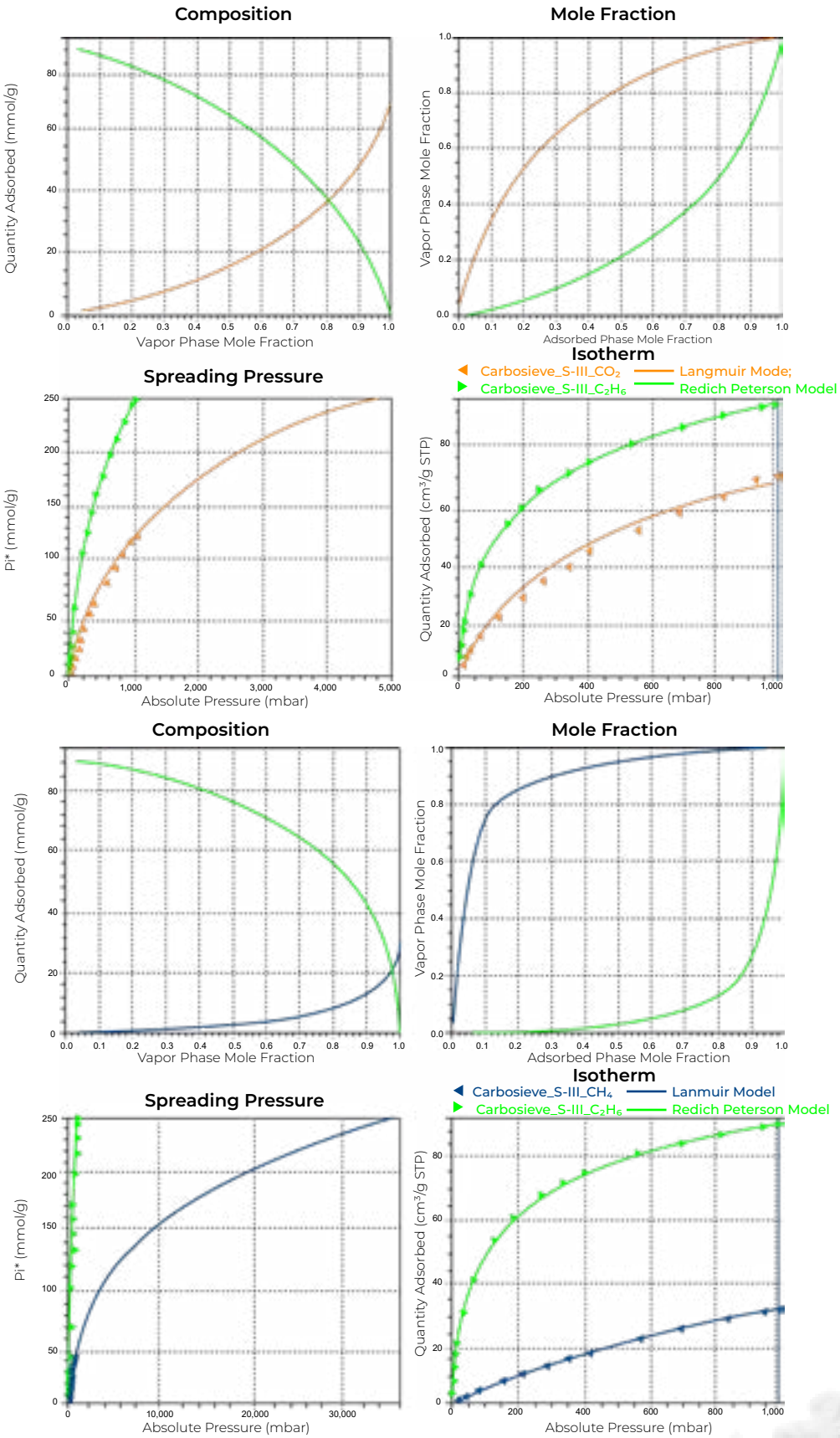


Figure 6. Composition, mole fraction, and spreading pressure for Carbosieve S-III (top) **CO_2-CH_4**, (middle) **CO_2-C_2H_6**, (bottom) **CH_4-C2H6**

From the IAST compositional data, the selectivity for a dual gas system can be calculated. The selectivity for multicomponent systems of **CO_2**, **CH_4**, and **C_2H_6** are shown in Table 1 below. Across the three materials, a similar trend was observed. Carbon dioxide was selective over methane, and ethane was selective over both methane and carbon dioxide.

Table 1. IAST predicted selectivity from single component isotherms

Material	Gases	Selectivity
Carbosieve S-III	CO_2/CH_4	4.50
	CO_2/C_2H_6	0.19
	C_2H_6/CH_4	31.38
Carboxen 1018	CO_2/CH_4	12.08
	CO_2/C_2H_6	0.60
	C_2H_6/CH_4	34.82
Carboxen 1021	CO_2/CH_4	5.07
	CO_2/C_2H_6	0.32
	C_2H_6/CH_4	21.86

Breakthrough Adsorption Multicomponent Analysis

Following IAST selectivity predictions, breakthrough experiments were conducted using equimolar flows of **CO_2**, **CH_4**, and **C_2H_6** in binary mixtures. Experiments were conducted in nitrogen carrier gas and were activated overnight in nitrogen prior to the experiments at a temperature of 250 °c. After activation, the sample column was allowed to cool before breakthrough experiments. In breakthrough experiments, the flow consisted of 10 sccm **N_2**, 5 sccm of each of the adsorbing gases, and 1 sccm of argon, which was used as a tracer gas. The results of the breakthrough curves for Carboxen 1018, Carboxen 1021, and Carbosieve S-III are shown in Figures 7 – 9, respectively.

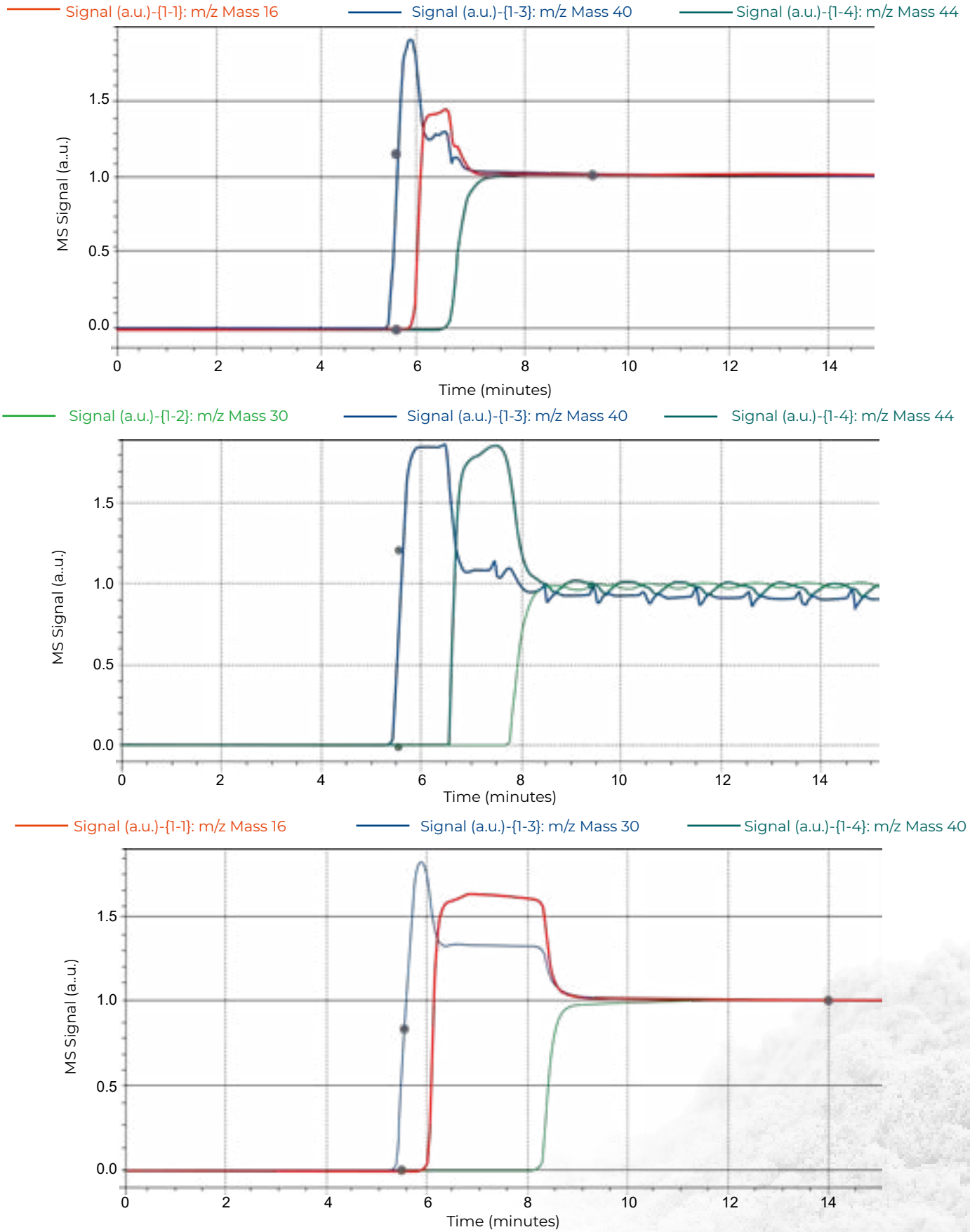


Figure 7. Breakthrough results for Carboxen 1018. (Top) **CO_2/CH_4**. (Middle) **$CO_2/C2H_6$**. (Bottom) **CH_4/C_2H_6**.

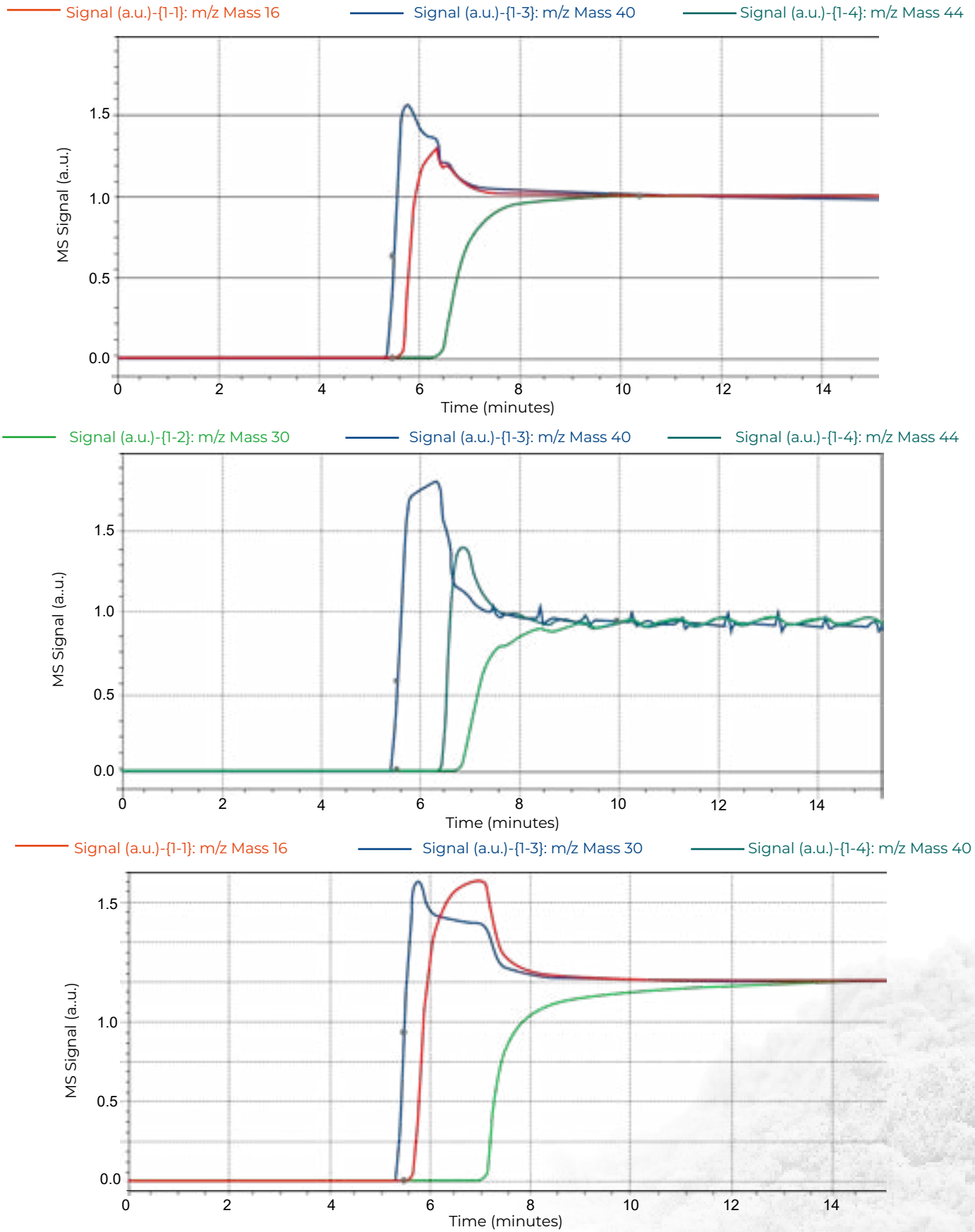


Figure 8. Breakthrough results for Carboxen 1021. (Top) **CO_2/CH_4**. (Middle) **CO_2/C_2H_6**. (Bottom) **CH_4/C_2H_6**.

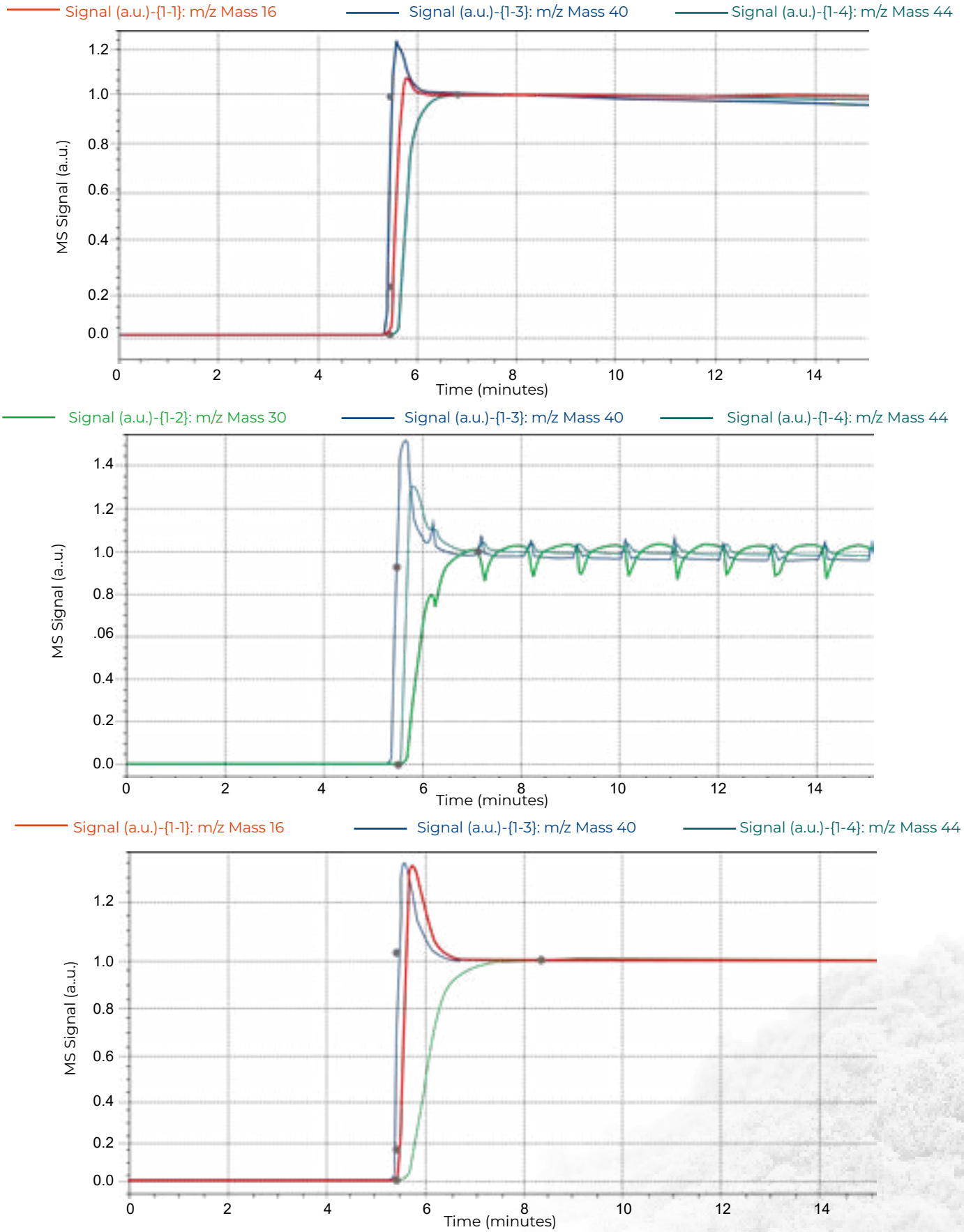


Figure 9. Breakthrough results for Carbosieve S-III. (Top) **CO2/CH4**. (Middle) **CO2/C2H6**. (Bottom) **CH4/C2H6**.

From the breakthrough curves, the three samples were selective towards carbon dioxide over methane. Additionally, all samples were selective to ethane over both methane and carbon dioxide, which matches the predictions from IAST. Furthermore, the breakthrough curves were sharp such that mass transfer limitations were not observed, and all gas species can readily adsorb into the pore space of the materials. Lastly, no pressure drop was observed in all breakthrough experiments.

Comparing the IAST predictions to the breakthrough results, the IAST selectivity for **C_2H_6/CH_4** was greater by a factor of two compared to the measured breakthrough results. The **C_2H_6/CO_2** selectivity measured by IAST was less than what was observed in breakthrough measurements. The **CO_2/CH_4** selectivity from IAST was in good agreement with breakthrough results. The selectivity of the three binary mixtures for the three microporous carbons are shown in **Table 2**.

Table 2. Calculated breakthrough selectivity from multicomponent analysis

Material	Gases	Selectivity
Carbosieve S-III	CO_2/CH_4	9.90
	CO_2/C_2H_6	0.003
	C_2H_6/CH_4	4.01
Carboxen 1018	CO_2/CH_4	13.65
	CO_2/C_2H_6	0.025
	C_2H_6/CH_4	4.25
Carboxen 1021	CO_2/CH_4	20.76
	CO_2/C_2H_6	0.363
	C_2H_6/CH_4	4.68

Conclusions

MicroActive and the 3Flex software can be used to predict multicomponent gas adsorption in dual gas systems using the newly added IAST functionality. This note provided a simple example on how to use the new functionality as well as a test case using microporous carbon samples.

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