Modeling the adsorption of mixed gases based on pure gas adsorption properties

N Tzabar, H J Holland, C H Vermeer, and H J M ter Brake

Energy, Materials and Systems, Faculty of Science and Technology, University of Twente, 7500 AE Enschede, The Netherlands

E-mail: nirtzabar8@gmail.com

Abstract. Sorption-based Joule-Thomson (JT) cryocoolers usually operate with pure gases. A sorption-based compressor has many benefits; however, it is limited by the pressure ratios it can provide. Using a mixed-refrigerant (MR) instead of a pure refrigerant in JT cryocoolers allows working at much lower pressure ratios. Therefore, it is attractive using MRs in sorption-based cryocoolers in order to reduce one of its main limitations. The adsorption of mixed gases is usually investigated under steady-state conditions, mainly for storage and separation processes. However, the process in a sorption compressor goes through various temperatures, pressures and adsorption concentrations; therefore, it differs from the common mixed gases adsorption applications. In order to simulate the sorption process in a compressor a numerical analysis for mixed gases is developed, based on pure gas adsorption characteristics. The pure gas adsorption properties have been measured for four gases (nitrogen, methane, ethane, and propane) with Norit-RB2 activated carbon. A single adsorption model is desired to describe the adsorption of all four gases. This model is further developed to a mixed-gas adsorption model. In future work more adsorbents will be tested using these four gases and the adsorption model will be verified against experimental results of mixed-gas adsorption measurements.

1. Introduction
Joule-Thomson (JT) cryocoolers that are driven by sorption compressors are free of vibrations and have potentially a long lifetime, thanks to the absence of moving parts. JT sorption cryocoolers that are reported in the literature operate with pure gases, where the working fluid is determined according to the desired cooling temperatures [1]. Cooling to temperatures around 80 K is usually obtained with nitrogen as the working fluid [2, 3], where cooling to higher temperatures is possible by using other working gases such as argon, methane, krypton, ethane, ethylene, xenon, and more.

A JT cryocooler that operates with a pure gas has an intrinsic low efficiency due to the irreversible heat transfer at its recuperative heat exchanger and the isenthalpic expansion at the restriction. This irreversibility can be dramatically decreased by using mixed gases as the working fluid. During the last two decades several groups have been investigating and developing JT cryocoolers that operate with gas mixtures, driven by mechanical compressors [4-12]. While most researches consider multi component mixtures, binary mixtures have been also investigated [13].

Recently, a study on sorption compressors for gas mixtures has been reported [14,15], investigating binary mixtures of nitrogen-methane and nitrogen-ethane on Chemviron activated carbon. The present study proceeds with binary mixtures of nitrogen with either methane, ethane, or propane on Norit RB-2 activated carbon. An enhanced modeling of the adsorption isotherms is further developed using the Sips model, also known as the Langmuir-Freundlich model. This paper presents a method to determine the adsorption of mixed gases out of pure gases adsorption characteristics. This method will be further incorporated in a sorption compressor simulation for driving JT cryocoolers.

2. Pure gas adsorption measurement procedure

We have measured the adsorption of pure nitrogen, methane, ethane, and propane on Norit-RB2 activated carbon, which is a steam activated extruded carbon with a packing density of 500 kg/m^3. The experimental setup is schematically described in Figure 1. The volumes of the sorption cell and the connecting tube are premeasured and the mass of the activated carbon in the cell is determined by weighing the sorption cell. A Bronkhorst M-12 mini-Coriolis flow controller is used to introduce a specific amount of gas into the sorption cell. A uniform temperature distribution in the cell is obtained by an electric heater around the cell. The temperature and pressure of the cell are measured once the equilibrium state is obtained.

The adsorption concentration, $C \left[\frac{\text{mg}_{\text{adsorbate}}}{\text{g}_{\text{adsorbent}}} \right]$, is calculated as follows:

$$C = \frac{1}{m_s} [\int \dot{m} dt - V_{void\;cell} \times \rho(p, T) - V_{tube} \times \rho(p, T_{amb})] \tag{1}$$

where $\dot{m}$ is the gas mass flow into the cell, m_s is the mass of the adsorbent (6.52 ± 0.02 g), $V_{void\;cell}$ is the void volume in the sorption cell (5.58 ± 0.17 cc), V_{tube} is the volume of the connecting tube (4.38 ± 0.1 cc), ρ is the density of the fluid, T_{amb} is the ambient temperature, and T, p are the measured temperature and pressure, respectively. The measurement were taken between 300 K and 400 K in steps of 20 K. Pictures of the sorption cell and of the adsorbent are presented in Figure 2.

3. Pure gas adsorption results and analysis

The measured adsorption results of the pure gases were fitted to the adsorption model of Sips [16]:

$$\frac{C}{C_0} = \frac{(ap)^{\frac{1}{n}}}{1 + (ap)^{\frac{1}{n}}} \tag{2}$$

Where p is the pressure in bar, C_0 is the saturated adsorption concentration [mg/g], a is the adsorption affinity [1/bar], and n is a dimensionless parameter that qualitatively characterizes the heterogeneity of the adsorbate-adsorbent system.
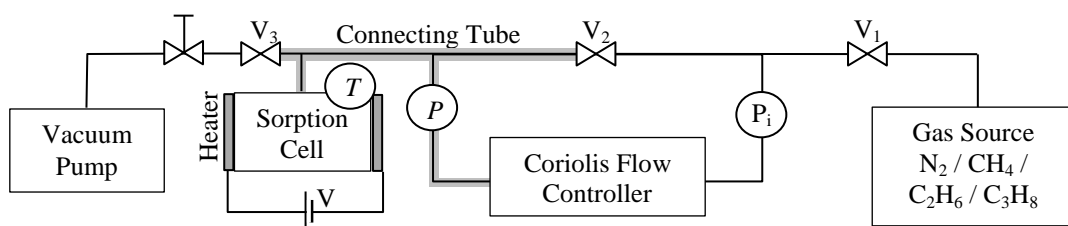

Figure 1: Schematic of the experimental setup for measuring the adsorption isotherms. The connecting tube, which is at room temperature, is indicated by the thick line.
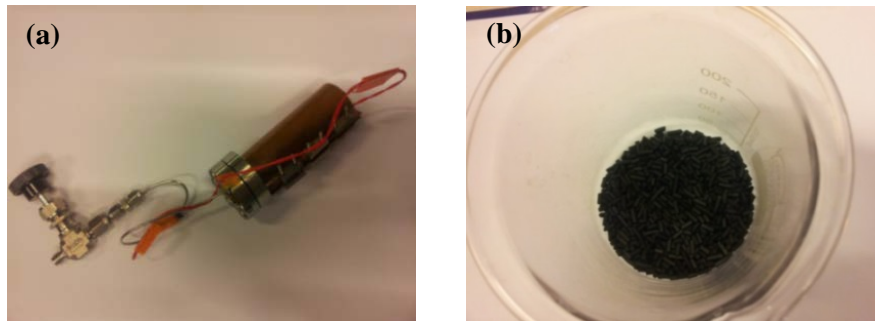
Figure 2: Pictures of the experimental setup. (a) the sorption cell wrapped with the electrical heater and a copper envelope, (b) the adsorbent (Norit-RB2).

In order to obtain the three parameters directly out of the experimental results, Eq. (2) is linearized as:

$$ln\left(\frac{C}{C_0-C}\right) = \frac{1}{n}ln(p) + ln\left(a^{\frac{1}{n}}\right)$$ (3)

Obviously, a direct determination of three parameters by a linearized model is impossible; therefore, C_0 is first iteratively found to obtain a linear relation between $ln(p)$ and $ln(C/(C_0-C))$, then n is determined by the slope and a by the intersect point. This procedure is made for every adsorption isotherm and the parameters are temperature dependent. All parameters are listed in table 1.

The saturated adsorption concentration, C_0, is decreasing with increasing temperature as expected, due to the fact that at higher temperatures the amount of adsorbed gas is usually less than at lower temperatures. The value of the adsorption affinity, a, for nitrogen, methane, and ethane also decreases with increasing temperature, as expected. However, in the case of propane the adsorption affinity increases with increasing temperature. This may be explained by the relatively high value of the n parameter that indicates high heterogeneity of propane adsorption on Norit-RB2. For propane, n decreases dramatically with increasing temperature, relative to the other gases. The different trends of the propane adsorption parameters indicate different adsorption characteristics, probably reflected in the adsorption heterogeneity.

Figure 3 shows the adsorption isotherms for nitrogen (a), methane (b), ethane (c), and propane (d), where the experimental results are in symbols and the Sips model results are in solid lines. Nitrogen and methane show a "type I" BET (Brunauer, Emmett, and Teller) isotherm [17] while ethane shows a "type II" BET isotherm that is common in the case of physical multilayer adsorption. This type of isotherm can not be described by the Sips model. Therefore, only the experimental results at low pressures are used to determine the Sips parameters. One should notice that the Sips model agrees with the experimental results. Propane shows a unique behavior where it has a large increase in adsorption at low pressures and then the increase of the adsorption concentration with pressure is more moderate.

4. Modified Sips model

In order to have a single model expression covering all relevant temperatures, the above Sips model was modified. The parameters a and n in the Sips model were assumed to linearly depend on temperature, whereas C_0 was assumed to have an exponential dependence:

$$\frac{C}{C_A T + C_B} = \frac{[a_A exp(a_B T)p]^{\frac{1}{n_A T + n_B}}}{1+[a_A exp(a_B T)p]^{\frac{1}{n_A T + n_B}}}$$ (4)

Table 1: Sips parameters, Eq. 2.

T	Nitrogen			Methane			Ethane			Propane		
	C_0	a	n	C_0	a	n	C_0	a	n	C_0	a	n
[K]	[mg/g]	[1/bar]		[mg/g]	[1/bar]		[mg/g]	[1/bar]		[mg/g]	[1/bar]	
300	84	0.0372	1.259	55	0.1323	1.372	109	1.2278	2.060	550	0.0041	6.333
320	83	0.0289	1.155	51	0.0919	1.303	100	0.6869	1.795	435	0.0403	4.713
340	78	0.0235	1.142	49	0.0625	1.273	97	0.3861	1.709	310	0.3406	3.080
360	78	0.0159	1.177	47	0.0442	1.286	99	0.2187	1.648	274	0.3846	2.422
380	75	0.0125	1.191	45	0.0316	1.262	99	0.1190	1.582	250	0.3497	2.065
400	75	0.0093	1.120	41	0.0272	1.173	99	0.0820	1.475	220	0.3774	1.623

Here C_A, C_B, a_A, a_B, n_A, and n_B are fitting parameters that are listed in table 2. Again, the pressure p is expressed in bar. The parameters of nitrogen, methane, and ethane maintain a certain logic that complies with the fact that they all have similar adsorption characteristics (for ethane, up to the pressures where a dramatic increase in adsorption concentration occurs). On the other hand, propane doesn't fit well with the formula in Eq. 4 and has totally different values for the parameters in Eq. 4. Figure 4 shows the adsorption isotherms for nitrogen (a), methane (b), ethane (c), and propane (d), where the experimental results are in symbols and the modified Sips model results are in dashed lines.

A deviation parameter, *Dev*, is defined to evaluate the agreement between the experimental and calculated isotherm results:

$$Dev = \frac{1}{N} \sum_{i=1}^{N} \frac{|C_{calculated} - C_{measured}|}{C_{measured}} \tag{5}$$

where N is the number of measured points at a given temperature. Table 3 summarizes all the *Dev* values for nitrogen, methane, ethane, and propane adsorption on Norit-RB2. The Sips model shows deviations which are less than 2 % (in most cases about 1 % only); however, methane has a minor exception at 300 K and nitrogen has a more severe exception, about 10 %, at 300 K. The modified Sips model shows slightly higher deviations for most of the case; however, it has better performance at the two exception points of nitrogen and methane, a fact that suggests that these deviations are probably inaccuracies in measurements that are damped by the smoothness of the modified Sips model. Furthermore, note that the Sips model has been modified not to get a better fit but to have a closed model expression for all relevant temperatures.

Table 2: Modified Sips parameters, Eq. 4.

Gas	C_A	C_B	a_A	a_B	n_A	n_B
Nitrogen	-0.0986	113.33	2.6126	-0.014	-0.0008	1.4507
Methane	-0.1286	93	16.976	-0.016	-0.0016	1.8317
Ethane	-0.0729	126	4760.8	-0.028	-0.0052	3.5252
Propane	-3.2014	1460.3	5.00E-08	0.0417	-0.0459	19.448

Table 3: Deviation functions, *Dev*, of the Sips model and the modified Sips model calculated by Eq. 5.

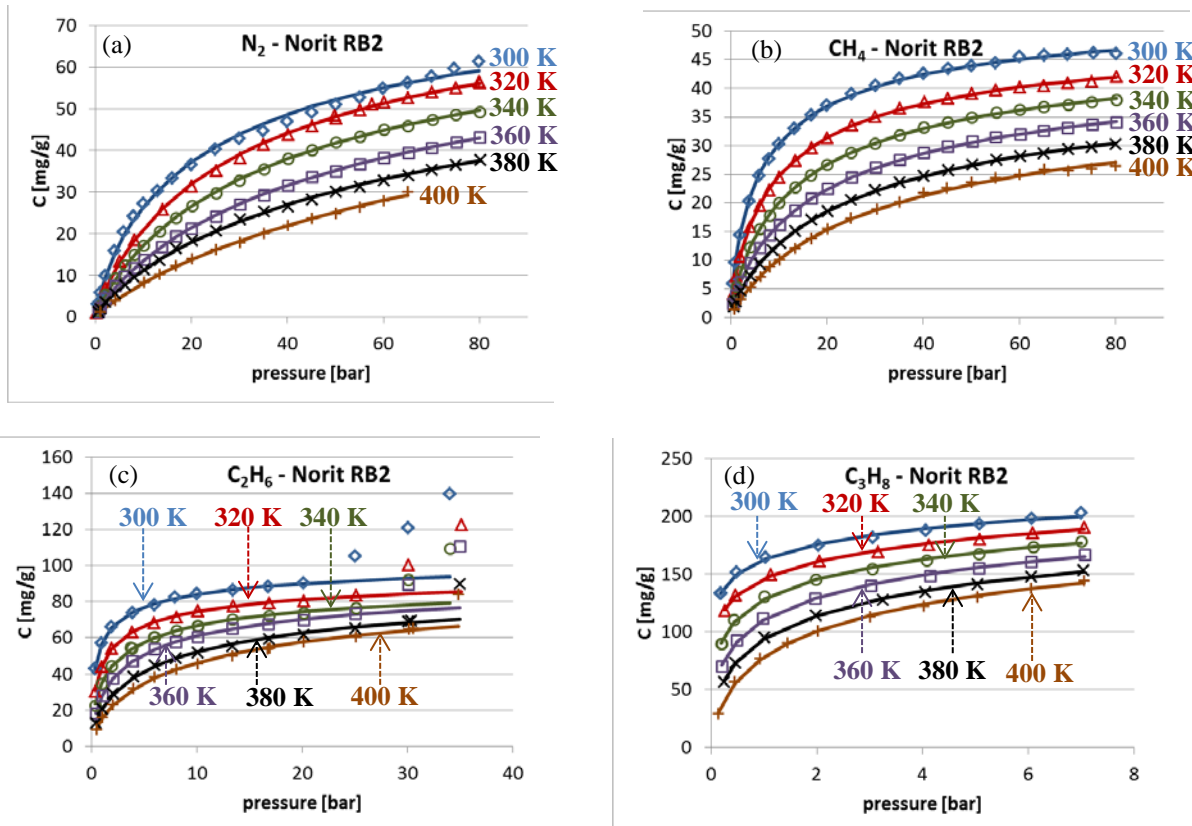| T	Nitrogen		Methane		Ethane		Propane	
(K)	Sips	Modified Sips	Sips	Modified Sips	Sips	Modified Sips	Sips	Modified Sips
300	0.0999	0.0353	0.0242	0.0086	0.0183	0.0693	0.0058	0.0172
320	0.0104	0.0255	0.0061	0.0501	0.0059	0.0069	0.0065	0.0280
340	0.0134	0.0209	0.0039	0.0697	0.0061	0.0180	0.0093	0.0353
360	0.0167	0.0311	0.0099	0.0663	0.0055	0.0186	0.0101	0.0371
380	0.0156	0.0363	0.0109	0.0634	0.0144	0.0258	0.0086	0.0103
400	0.0126	0.0260	0.0171	0.0405	0.0146	0.1125	0.0140	0.1067

Figure 3: Nitrogen (a), methane (b), ethane (c), and propane (d) adsorption on Norit-RB2. experimental results in symbols and Sips model results in solid lines.

5. Mixed gases adsorption model

While introducing a gas mixture to an adsorbent, the composition of the adsorbed phase depends on the temperature, pressure, and the composition of the vapor phase. The Sips model for the adsorption of pure gases is extended to gas mixtures as follows:

$$\frac{C_i}{C_{0,i}} = \frac{(a_i p_i)^{\frac{1}{n_i}}}{1+\sum_{j=1}^{N}(a_j p_j)^{\frac{1}{n_j}}} = \frac{(a_i y_i p)^{\frac{1}{n_i}}}{1+\sum_{j=1}^{N}(a_j y_j p)^{\frac{1}{n_j}}} \tag{5}$$

where C_i is the adsorption concentration of component i, in mg of component i per g of adsorbent, C_0, a, and n with the subscript i or j are the pure adsorption Sips model parameters of the pure substances i and j, respectively. The parameters p_i and p_j are the partial pressures of components i and j in the vapor phase, and y_i and y_j are the molar fractions in the vapor phase, respectively. in the vapor phase. N is the number of components in the mixture. Note that in Eq. (5) the parameters a, n and C_0 can be constants or temperature dependent, as discussed above. The composition of the adsorbed phase is determined by:

$$x_i = \frac{C_i/M_i}{\sum_{j=1}^{N} C_j/M_j} \tag{6}$$

Here x_i is the molar concentration of component i in the adsorbed phase, M_i and M_j are the molar masses of components i and j, respectively.
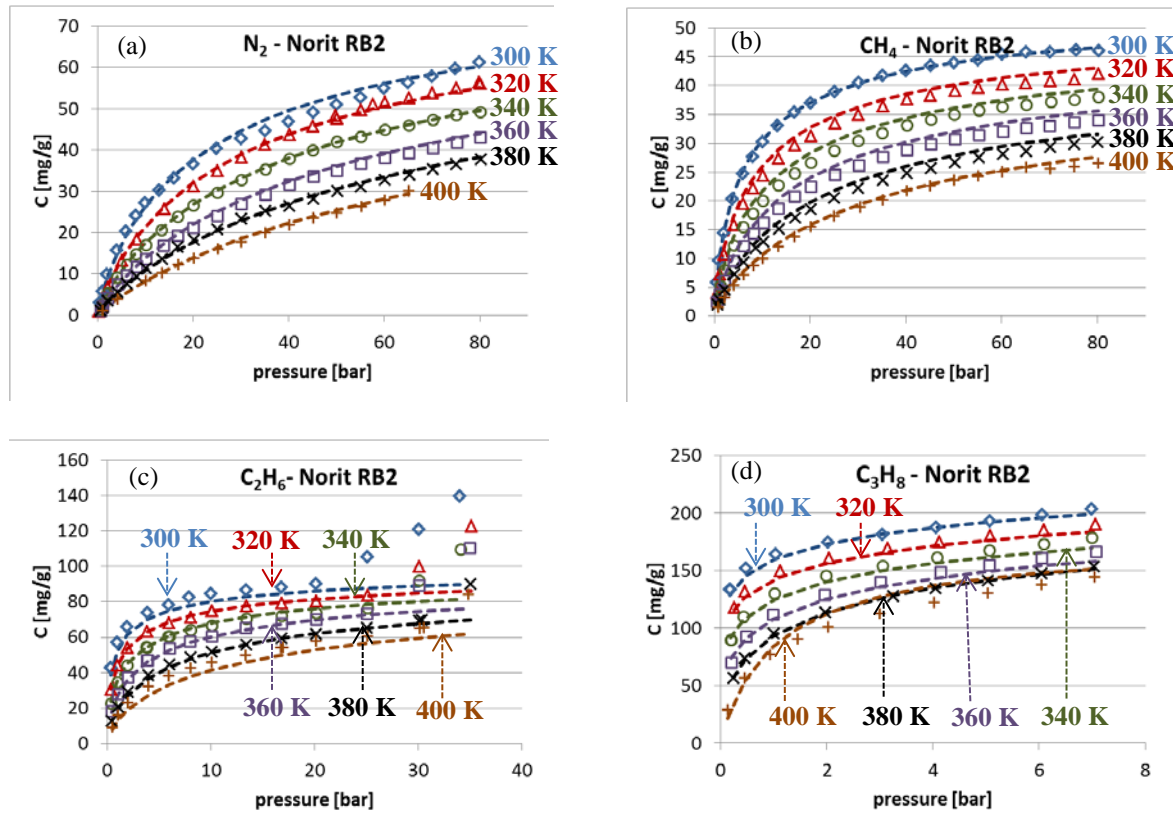
Figure 4: Nitrogen (a), methane (b), ethane (c), and propane (d) adsorption on Norit-RB2. experimental results in symbols and modified Sips model results (temperature-dependent parameters) in dashed lines.

Figure 5 shows the nitrogen molar fraction of the adsorbed phase at 300 K as a function of pressure and with the nitrogen molar fraction of the vapour phase as a parameter. These are presented for nitrogen-methane (a), nitrogen-ethane (b), and nitrogen-propane (c) mixtures. The results show that a nitrogen-methane mixture may cover a wide range of adsorbed phase compositions, whereas nitrogen-ethane and nitrogen-propane cover a relatively small range of nitrogen adsorbed phase compositions. These results can be explained by the definition of adsorption selectivity:

$$S_{i,j} = \frac{x_i/y_i}{x_j/y_j} \tag{7}$$

where $S_{i,j}$ is the adsorption selectivity between component i and component j. Incorporating the Sips model to Eq. 7 yields:

$$S_{i,j} = \frac{C_{0i} M_j y_j \left(a_i y_i p\right)^{\frac{1}{n_i}}}{C_{0j} M_i y_i \left(a_j y_j p\right)^{\frac{1}{n_j}}} \tag{8}$$
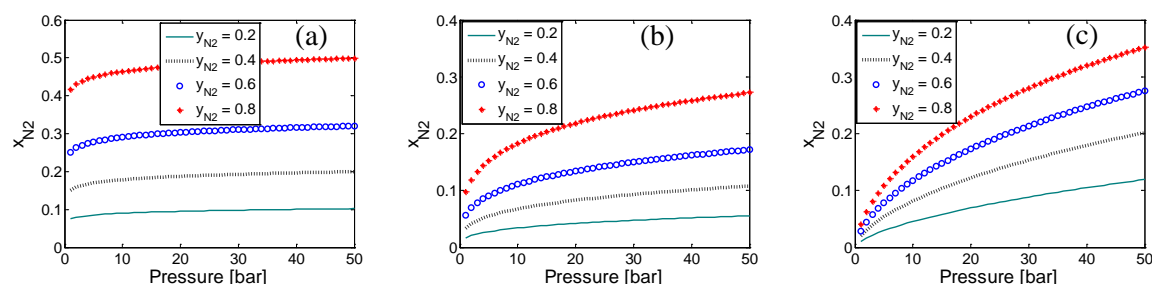
Figure 5: Calculated nitrogen molar fraction in the adsorbed phase at 300 K for different compositions of the vapor phase of: (a) nitrogen-methane, (b) nitrogen-ethane, and (c) nitrogen-propane.

Ethane's and propane's C_0, a, and molecular weights are larger than those of nitrogen; therefore, ethane and propane are clearly adsorbed more intensely relative to nitrogen, as shown in Figure 5 (b) and (c), respectively. The fact that ethane and propane also have higher n parameters than nitrogen does not change the final results. On the other hand, methane and nitrogen have similar adsorption isotherms, where methane's isotherms are characterized with lower saturated adsorption concentration, C_0, and a higher adsorption affinity parameter a. The n parameter of methane is slightly higher than that of nitrogen, whereas the molecular weight of methane is lower. Figure 5 (a) shows that the nitrogen concentration in the adsorbed phase is lower relative to its concentration in the vapor phase, proving that the selectivity of methane is higher than that of nitrogen.

6. Conclusions

Adsorption isotherms were measured for nitrogen, methane, ethane, and propane on Norit-RB2 activated carbon. The Sips adsorption model is used to describe the adsorption isotherms, and a linearization method is used to determine the parameters out of the experimental results, where C_0, which is the most convenient parameter to predict, is iteratively determined to obtain a linear relation between $ln(C/(C_0-C))$ and $ln(p)$. The parameters of nitrogen, methane, and ethane show logical and consistent dependence on temperature, whereas propane's parameters indicate different adsorption characteristics that apparently do not obey the same temperature dependency like the other gases. A modified Sips model that incorporates the temperature dependence is suggested.

The adsorption model is further developed for the adsorption of gas mixtures. The adsorption selectivity is discussed and the results of nitrogen-methane, nitrogen-ethane, and nitrogen-propane are presented. The characteristics of ethane and propane already suggest that these two gases have higher selectivity relative to nitrogen, as proved by the detailed calculation results. However, the selectivity of methane and nitrogen is less intuitive and more difficult to be predicted. The results show that methane selectivity is slightly higher relative to nitrogen; therefore, the adsorbed phase has higher methane concentration than the vapor phase.

Future work will include more pure gas adsorption measurements with additional adsorbents and some experimental measurements of mixture adsorption to verify the analytical model.

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