Pure and Binary Adsorption of Methane and Nitrogen by Silicalite

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Methane is the most important non-CO_2 greenhouse gas (GHG) responsible for global warming with more than 10 % of total GHG emissions. The greenhouse warming potential (GWP) of this gas is much higher than carbon dioxide. Therefore, any reduction in methane emissions is really important in atmosphere reconstruction. Nitrogen is needed to be removed from landfill gas to obtain low grade natural gas as a renewable source of energy from garbage, but the separation is really difficult. Adsorption was considered as a possibility for this separation, and silicalite was studied as the adsorbent. The adsorption behavior of methane and nitrogen with this adsorbent was studied by concentration pulse chromatography and constant volume techniques. Ideal separation factors were obtained from the experimental pure adsorption isotherms by using the temperature independent Toth isotherm model. Mixture adsorption isotherms for the binary system of methane and nitrogen at (40, 70, and 100) °C at 1 bar total pressure were determined experimentally. Corresponding $x-y$ diagrams and separation factors were obtained from these data. The thermodynamic consistency tests between pure and binary gas adsorption systems were also carried out. The separation factors obtained with silicalite for the separation applications of methane and nitrogen gases in this work are much better than those obtained for other systems in the literature.

Introduction

Methane is the most important non-CO_2 GHG responsible for global warming with more than 10 % of total GHG emissions. Despite the small amounts of methane released to the atmosphere, the greenhouse warming potential (GWP) of this gas is much higher than that of carbon dioxide, so any reduction in methane emissions is very important in short- and medium-term atmosphere reconstruction.[1,2] Nitrogen is needed to be removed from landfill gas and low grade natural gas for getting a new resource of energy, but the separation is really difficult. Some papers have been reported on CH_4-N_2 adsorption separation.[3−8] Sheikh et al.[3] studied the adsorption isotherms on a new high specific area activated carbon Maxsorb with volumetric and chromatographic methods for this separation. Cavenati et al.[4] obtained the kinetic separation factor on Carbon Molecular Sieve CMS 3K for this separation. Jayaramana et al.[5] studied the selectivity of this system on clinoptilolites. Their results were not satisfactory, and further improvements in separation were needed before real applications could be considered. Warmuzinski and Sodzawiczny[6] did PSA computer simulations on the effect of adsorption pressure for this separation. Dong et al.[7] worked on PSA with activated carbon, zeolite 13X, and carbon molecular sieves for separating a mixture of carbon dioxide, methane, and nitrogen. Harlick and Tezel[8−10] studied the binary adsorption isotherms of methane and nitrogen by the HT−CPM (Harlick and Tezel−concentration pulse method) for ZSM-5 with SiO_2/Al_2O_3 ratios of 30 and 280.

In this study, the adsorption separation of CH_4 and N_2 gases was considered with silicalite as the adsorbent. Silicalite is one of the most important synthetic zeolites. It is widely used as a selective adsorbent. Its distinctive features include high thermal and hydrothermal stability, hydrophobic and organophilic adsorptive properties, and an intermediate (ten-ring) pore size which leads to molecular sieve size selectivity. Its extremely low aluminum content (the SiO_2/Al_2O_3 ratio is in the thousands) is responsible for its hydrophobic nature.[11]

In this study, pure component adsorption isotherms of CH_4 and N_2 were determined with silicalite using a constant volume technique. This method involves measuring the pressure change in a known volume of gas subjected to an adsorbent sample. As the gas is adsorbed and allowed to come to equilibrium, the measured decrease in the system pressure yields the amount of gas adsorbed under the given conditions. This method has been used extensively to determine adsorption isotherms.[12−14] Ideal separation factors were determined from the pure component isotherms obtained.

The binary mixture adsorption behavior of CH_4 and N_2 with silicalite was determined by using the chromatographic technique at (40, 70, and 100) °C at 1 bar total pressure. This dynamic method of analysis can be employed in several ways: tracer gas, step change, and pulse chromatography. The use of concentration pulse chromatography for adsorbent screening is very attractive since it is relatively inexpensive to set up and easy to employ. A method using the slope of the isotherms proposed in the literature for determining the binary isotherms from concentration pulse chromatographic data has been given and shown capable of interpreting even highly selective binary systems.[10,13−20]

From these experimental binary isotherms obtained, corresponding phase diagrams and separation factors were determined for this binary system. The thermodynamic consistency tests between pure and binary gas adsorption systems are also discussed.

Theory and Experimental Section

There are many models used for adsorption isotherms of pure gas systems. The simplest and still the most useful pure gas isotherm is the Langmuir isotherm

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$$\theta = \frac{q}{q_m} = \frac{BP}{1 + BP} \tag{1}$$

where B is the affinity constant; θ is the fractional coverage; q is the amount adsorbed; q_m is the saturation adsorption capacity or maximum amount adsorbed; and P is the pressure.[21,22]

A three-parameter isotherm that is an empirical and popular one used and satisfies both low and high pressure ranges is the Toth isotherm[22]

$$\theta = \frac{q}{q_m} = \frac{BP}{[1 + (BP)^n]^{\frac{1}{n}}} \tag{2}$$

The temperature dependence of the equilibrium parameters is required to extrapolate or interpolate the adsorption equilibrium data to other temperatures and to calculate the isosteric heat of adsorption. The temperature dependence of the Toth equation for the affinity constants B is given by

$$B = B_0 e^{\frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)} \tag{3}$$

where B_0 is the adsorption affinity constant at reference temperature T_0; Q is the isosteric heat of adsorption; and R is the gas constant. The saturation capacity of the Toth equation either can be taken as constant or it can take the following temperature dependence

$$q_m = q_{m0} e^{\chi\left(1 - \frac{T}{T_0}\right)} \tag{4}$$

where q_{m0} is the saturation capacity (maximum amount adsorbed) at the reference temperature T_0 and χ is a constant parameter. The exponent n of the Toth equation may take the following form as a function of temperature

$$n = n_0 + \alpha\left(1 - \frac{T_0}{T}\right) \tag{5}$$

where n_0 is the parameter n at the reference temperature T_0 and α is a constant parameter.[20] Substituting eqs 3 to 5 into eq 2 gives a six-parameter Toth isotherm with temperature dependence. The six parameters (B_0, Q, q_{m0}, χ, n_0, α) can be determined by nonlinear regression by using all the isotherm data obtained at several temperatures.

Models for mixed-gas adsorption are crucial to the design of adsorptive gas separation processes. They should be capable of predicting the equilibrium amount adsorbed from pure gas isotherms. Because of the scarcity of experimental data, however, none of the theories or models have been extensively tested.

The simplest theory for a binary system is the extended Langmuir model[23]

$$\theta_A = \frac{q_A}{q_{mA}} = \frac{B_A P_A}{1 + B_A P_A + B_B P_B} \tag{6}$$

where subscripts A and B refer to gases A and B, respectively.

For the determination of binary isotherms, the concentration pulse chromatographic technique was used. In this technique, a pulse of the sample gas is injected into the mixed carrier gas stream and passes through the column packed with the adsorbent. The response of the column to the injection of the adsorbate at the inlet of the column is measured as concentration vs time at the exit of the column. From this response peak, a mean retention time of the sample, μ, defined as the first moment of the chromatogram, is determined experimentally.[16] Dimensionless Henry's Law constant, K, can be calculated from the corrected first moment of the response peak as follows[10,24−26]

$$\mu = \frac{\int_0^\infty c(t - \mu_D)\,dt}{\int_0^\infty c\,dt} = \frac{L}{v}\left[1 + \frac{(1 - \varepsilon)K}{\varepsilon}\right] \tag{7}$$

where t is the time; c is the adsorbate concentration measured at the outlet of the column; L is the column length; ε is the bed porosity; v is the interstitial fluid velocity; K is the dimensionless Henry's Law adsorption equilibrium constant; and μ_D is the dead time of the system.

The dimensionless Henry's Law constants, K, can be converted to a dimensional form, K_p, as follows[24−26]

$$K_p = \frac{K}{RT\rho_P} \tag{8}$$

where T is the absolute temperature; ρ_p is the density of the pellets of the adsorbent excluding the pores; and K_p is the dimensional Henry's Law adsorption equilibrium constant.

The K_p value is related to the slopes of the isotherms of the components in the carrier gas mixture. For a binary mixture, the relationship is given as follows[16]

$$K_p = (1 - y_1)\frac{dq_1}{dP_1} + y_1\frac{dq_2}{dP_2} \tag{9}$$

where dq_1/dP_1 and dq_2/dP_2 are the slopes of the binary adsorption isotherms for components 1 and 2, respectively.

This method allows for the experimental evaluation of the binary mixture isotherms when K_p values are determined for different concentrations of the carrier gas which is composed of the two components of the binary system.[16]

For binary isotherms, both components in the mixed carrier gas are adsorbed, and the experimental K_p data represent the combined contribution of both components to the isotherms. The interpretation of the binary K_p data has been treated by several methods in the literature,[10,13,15,20,27,28] and their details are available in the Supporting Information. It has been shown in these references in the literature that the concentration pulse chromatographic method works very well as long as a good fit to the K_p vs concentration in the gas phase (y_1) can be obtained. Results obtained by this method have been compared to those obtained by other methods, and agreements were shown to be very good. The MVV−CPM (Modified Van der Vlist and Van der Meijden concentration pulse method) were used in this work, since experimental data were well represented by this method, as will be discussed in the Results and Discussion section of this paper.

For binary gas adsorption equilibrium, there are only a few published data.[29] However, designing models and optimizing processes require accurate binary adsorption equilibrium data. Because of that, the thermodynamic consistency of experimental binary gas adsorption data and the predictive or correlative models should be checked before they are used for process design purposes.[30]

Sircar et al. studied the thermodynamics of pure and binary gas adsorption systems using the Gibbsian surface excess (GSE) model.[31−33] The model can be differentiated or integrated using different thermodynamic paths to generate various thermodynamic consistency tests. The integral test gives the relationship between both pure gas adsorption isotherms and binary gas adsorption isotherms as follows[30]

$$\left(-\int_0^P \frac{q_2^0}{P}dP\right) - \left(-\int_0^P \frac{q_1^0}{P}dP\right) = \int_0^1 \frac{q_1(1 - y_1) - q_2 y_1}{y_1(1 - y_1)}dy_1 \tag{10}$$

where $q^0{}_1$ and $q^0{}_2$ are the amount adsorbed of components 1 and 2, respectively, in the pure gas systems; P is both the

Table 1. Details of the Gases Used

gases	grade	purity	supplier
CH_4	ultrahigh purity 3.7	99.97 %	Praxair Inc., Ottawa
N_2	ultrahigh purity 5.0	99.999 %	Praxair Inc., Ottawa
He	ultrahigh purity 5.0	99.999 %	Praxair Inc., Ottawa

pressure of pure gas systems and the total pressure of the binary system; q_1 and q_2 are the amounts adsorbed of components 1 and 2, respectively, in the binary system; and y_1 is the mole fraction of component 1 in the binary system. These integrals are calculated from experimental pure and binary adsorption data, and the validity of eq 10 is checked for thermodynamic consistency. The two terms on the left side are the potentials of adsorption at P and T for pure gases 2 and 1, respectively, and they can be evaluated at any given values of P and T from the pure gas adsorption isotherms of the components of the binary gas mixture. The quantity on the right side can be evaluated at any given values of P and T using the binary gas adsorption isotherm at constant P and T.

The details of the volumetric system used, concentration pulse chromatography unit, adsorbent, and numerical methods are given in our earlier paper.[34] The sample gases used in the experiments are listed in Table 1.

It should be noted that the values of adsorption capacity obtained from experiments in this work were corrected assuming that the binder used for making the pellets has negligible adsorption capacity before they were compared with the literature data which were mostly obtained with silicalite crystals, without binder.

Results and Discussions

Pure component adsorption equilibrium isotherm data and corresponding Toth isotherm models for CH_4 and N_2 with silicalite pellets had been obtained at three different temperatures for pressures up to 5 atm in our previous work and are given in Figure 1.[35,36] In this figure, experimental data are given as data points, and Toth isotherm models are shown as curves and compared to other data available in the literature. For this comparison, all the experimental amounts of adsorbed values obtained in this work were corrected with respect to the binder assuming that it has negligible adsorption capacity. Literature data are mostly obtained with silicalite crystals, without binder. Although it is not possible to find isotherm comparisons at exactly the same temperature as the ones presented here, qualitative comparisons can be obtained since adsorption capacity increases as temperature decreases. As can be seen from Figure 1, the experimental data match very well with data from the literature for methane with much higher adsorption capacity for it compared to nitrogen. Our values are a little higher than those in the literature for nitrogen. This difference can be due to different suppliers of the adsorbent.

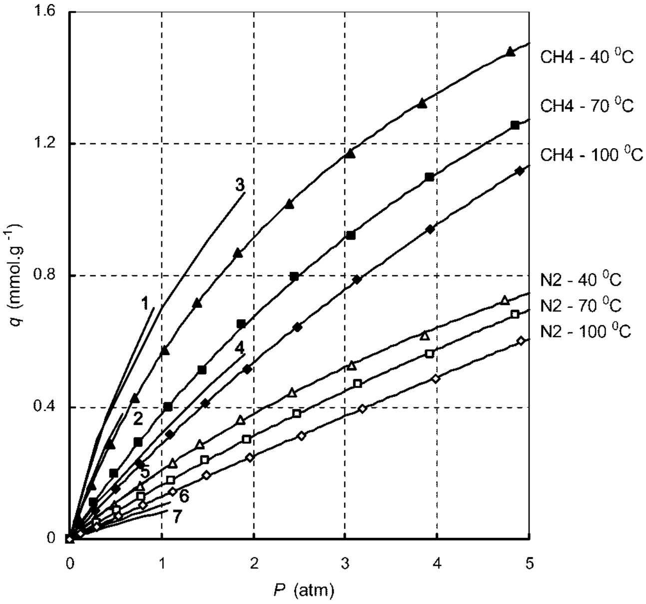

Figure 1. Pure adsorption isotherms for CH_4 and N_2 with silicalite. The points are experimental data, and the curves are the Toth isotherm model fits. The numbered curves indicate comparisons with the literature: **1**, CH_4, 23 °C;[37] **2**, CH_4, 25 °C;[38] **3**, CH_4, 31 °C;[39] **4**, CH_4, 81 °C;[39] **5**, N_2, 23 °C;[37] **6**, N_2, 61 °C;[37] **7**, N_2, 72 °C.[37]

For useful descriptions of adsorption equilibrium data at various temperatures, the temperature-dependent form of the Toth equation was used. From the curve regressions of the experimental data with the temperature-dependent Toth model, the relevant parameters for estimation are obtained for the purpose of extension of these data to other temperatures and pressures.

For an economic separation process, an adsorbent should have high selectivity and capacity. For comparing selectivity, it is convenient to define an ideal adsorption separation factor

$$\alpha_{A/B} = \frac{x_A/x_B}{y_A/y_B} \tag{11}$$

where x_A, x_B, y_A, and y_B are the mole fractions of components A and B in the adsorbed and fluid phases at equilibrium, respectively. For linear isotherms under low pressures, the separation factor is given simply by the ratio of the amounts adsorbed for pure components

$$\alpha_{i,A/B} = \frac{q_A}{q_B} \tag{12}$$

where q_A and q_B are the amounts adsorbed of components A and B. These ideal equilibrium separation factors obtained from pure component isotherms are shown as a function of pressure and temperature in Figure 2 using temperature-dependent Toth isotherm fits. According to the results, both pressure and temperature are very important for the separation. In general, separation factors increase with decreasing pressure and/or temperature. It is difficult to separate the system at high temperature and/or high pressure. Pressure influences the separation factors more at low temperatures than at high temperatures; however, temperature influences the separation factors more at low pressures than at high pressures.

In general, it is difficult to separate CH_4/N_2 as the separation factor is smaller than 3 for the conditions studied in this work. For this separation, the operating conditions need to be controlled at low temperatures and pressures.

After the regeneration of the silicalite adsorbent, the binary isotherms were determined for this adsorbent by increasing the CH_4 mole fraction in CH_4-N_2 carrier gas from 0 % up to 100 %. Very small amounts of samples of CH_4 and N_2 were injected after attaining equilibrium for each concentration change in the compositions of the carrier gas. Equilibrium of the mixture with the adsorbent was confirmed by noting the end of the baseline drift for the GC as equilibrium was approached. The results of the series of runs of the binary study are shown with MVV−CPM with error bars in Figure 3 as K_p vs the mole fraction of CH_4 in the carrier gas, where all the end-points of the binary isotherms were combined with the fit to the Toth isotherms of pure gases by the volumetric method.

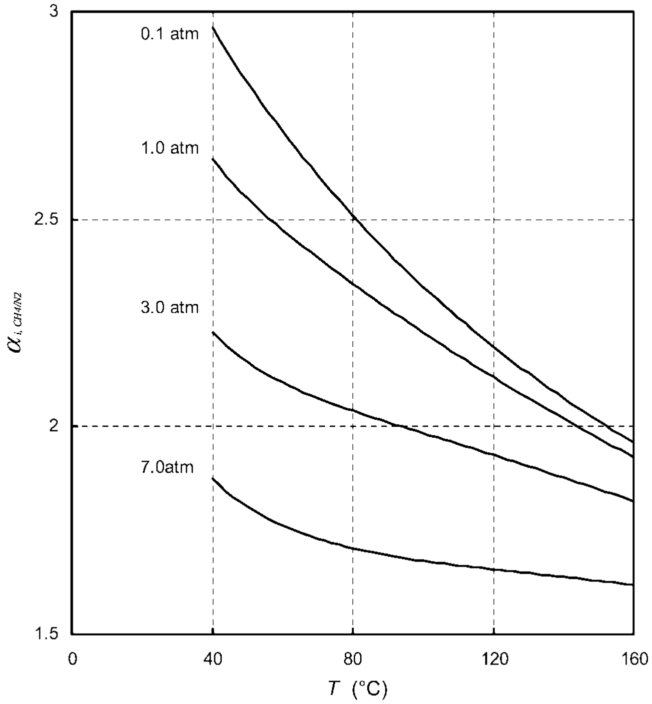

Figure 2. Ideal separation factors for CH_4/N_2 on silicalite from pure component data.

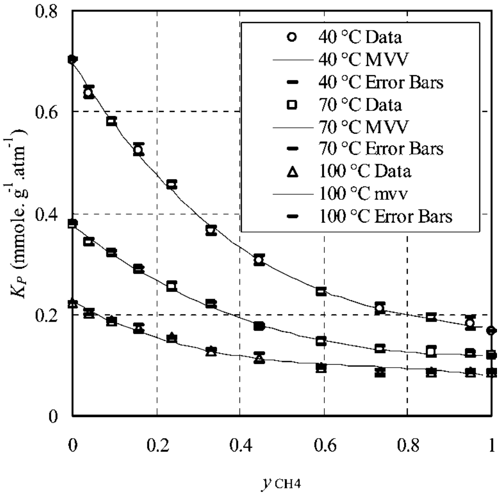

Figure 3. Regressions for CH_4/N_2, binary K_p with silicalite by MVV−CPM at different carrier gas compositions at 1 bar total pressure.

For the calculation of the binary isotherms, K_p vs y_{CH4} data were fitted by using three different methods: MVV−CPM (Modified Van der Vlist and Van der Meijden concentration pulse method), HT−CPM (Harlick and Tezel concentration pulse method), and MTT−CPM (modified Triebe and Tezel concentration pulse method).[10,13,15,20,27] It was observed that all these methods matched the experimental data very well since there is a rather small difference in the adsorption capacities of the two components in the binary systems. Among them, the MVV−CPM is the simplest polynomial one although it cannot be used for systems with a big difference in the adsorption capacities of the two components in the binary systems.[13,35] Therefore, the MVV−CPM was used to describe these systems for our further study in this paper. The parameters for MVV−CPM are listed in Table 2.

The experimental binary isotherms for CH_4-N_2 with silicalite were obtained at three temperatures at 1 bar total pressure and are given in Figures 4 to 6. When y_{CH4} increases, the CH_4 adsorption capacity, q_{CH4}, increases and the N_2 adsorption capacity, q_{N2}, decreases as expected. At 40 °C, the total adsorbed capacity, q_{total}, increases with y_{CH4} as the increase of q_{CH4} is larger than the decrease of q_{N2}. At (70 or 100) °C, q_{total} has a

Table 2. Parameters of MVV−CPM for CH_4-N_2 with Silicalite

CPM methods	parameters	units	40 °C	70 °C	100 °C
MVV−CPM	B_0	mmol·g^{-1}	0.6972	0.3740	0.2251
	B_1	mmol·g^{-1}	−1.2183	−0.8601	−0.7692
	B_2	mmol·g^{-1}	1.4179	1.3033	1.3420
	C_0	mmol·g^{-1}	0.5892	0.6029	0.5320
	C_1	mmol·g^{-1}	−1.4487	−1.6731	−1.5148
	C_2	mmol·g^{-1}	1.0318	1.1905	1.0617

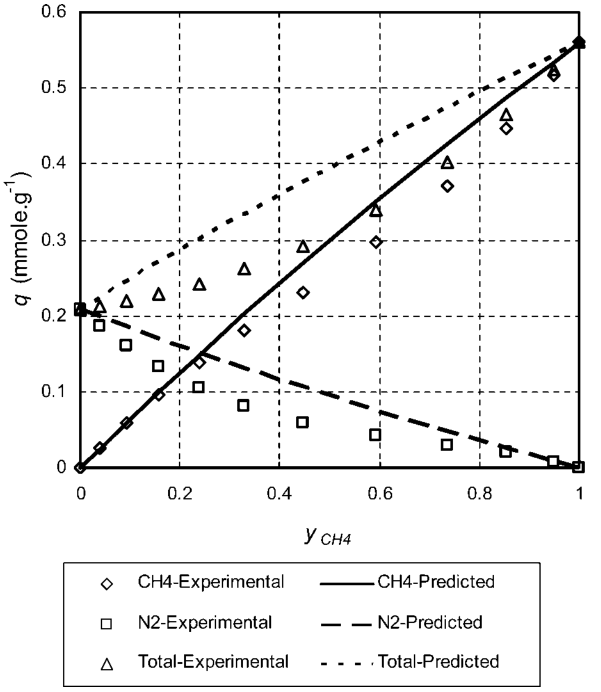

Figure 4. CH_4/N_2 binary isotherms with silicalite at 40 °C and at 1 bar total pressure: experimental by MVV−CPM and predicted by the statistical model.

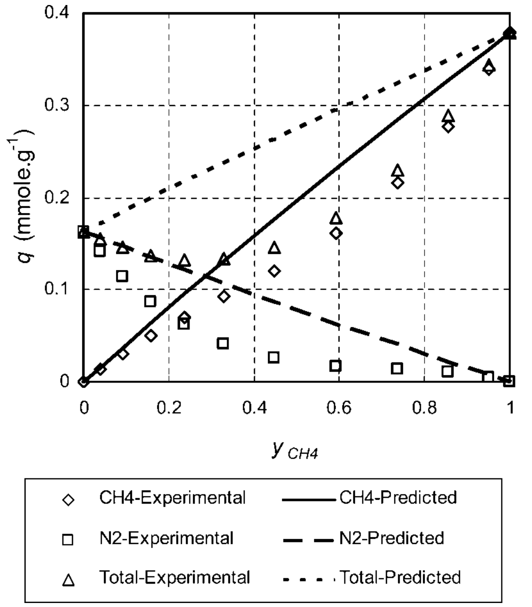

Figure 5. CH_4/N_2 binary isotherms with silicalite at 70 °C and at 1 bar total pressure: experimental by MVV−CPM and predicted by the statistical model.

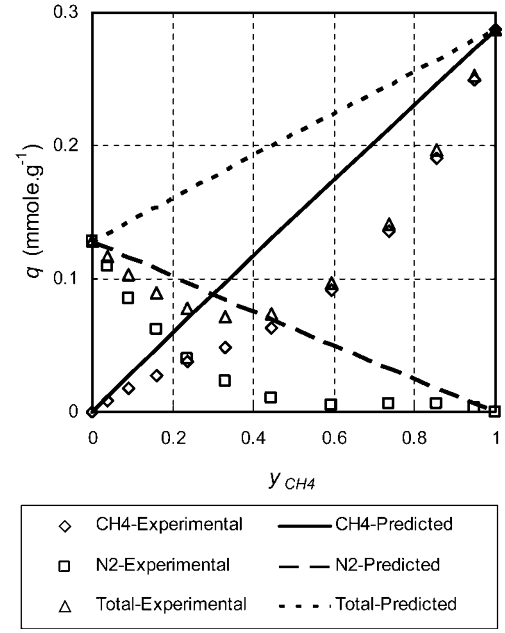

Figure 6. CH_4/N_2 binary isotherms with silicalite at 100 °C and at 1 bar total pressure: experimental by MVV−CPM and predicted by the statistical model.

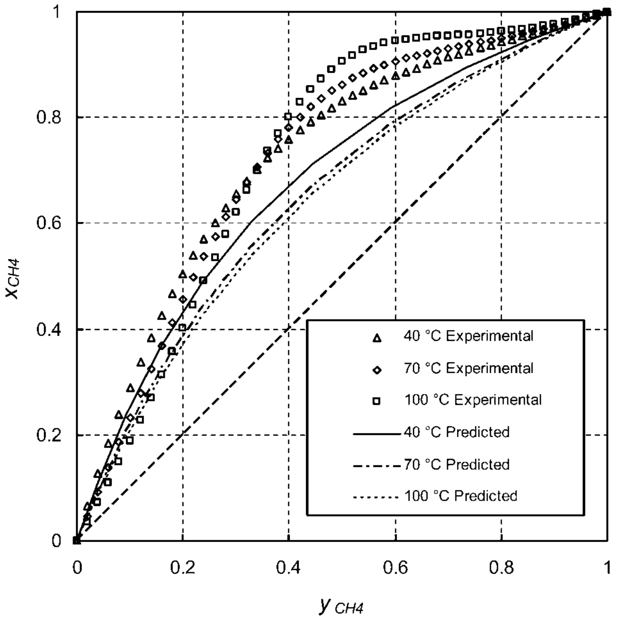

Figure 7. $x-y$ diagrams for the CH_4/N_2 binary system with silicalite at 1 bar total pressure: experimental and predicted by the statistical model.

minimum when y_{CH4} is in the range between 0.2 and 0.4. At the beginning, when y_{CH4} is small, the increase of q_{CH4} is less than the decrease of q_{N2}, so q_{total} decreases. Then, after the minimum of q_{total}, the increase of q_{CH4} is larger than the decrease of q_{N2}, so q_{total} increases. Additionally, at the minimum, the drop of q_{total} is smaller at 70 °C than at 100 °C. Therefore, it is noted that the drop of q_{total} decreases with decreasing temperature, and there is a temperature between (40 and 70) °C below which no minimum in q_{total} is observed. Besides, q_{CH4}, q_{N2}, and q_{total} increase with decreasing temperature since adsorption is exothermic. Temperature is a very important factor for the separation of this system.

Previously, Harlick and Tezel[8] determined the experimental binary isotherms of CH_4-N_2 for ZSM-5-280 adsorbent at 40 °C under the same conditions as the present work. Silicalite and ZSM-5 have the same structure. However, their ZSM-5 adsorbent had a different SiO_2/Al_2O_3 ratio indicated by the last number in the code of the adsorbent: 280. In the present study, silicalite adsorbent has a SiO_2/Al_2O_3 ratio in the thousands. Harlick and Tezel quoted: "The CH_4-N_2 binary system exhibited slight competitive adsorption behavior at low CH_4 mole fraction in the feed". This behavior can be seen in Figures 4 to 6 in the present study, as well. The slopes of the binary isotherms are rather high when y_{CH4} is very low, and then the slopes decrease with increasing y_{CH4} for mole fractions of CH_4 less than 0.4. This suggests that the two adsorbates are attempting to occupy the same active adsorption site at low CH_4 concentrations.

To predict the adsorption behavior of the binary system from pure gas systems to compare with the experimental ones, six models were tried: extended Langmuir, extended dualsite Langmuir, ideal adsorbed solution theory, statistical model, Flory−Huggins of vacancy solution theory, and extended Sips. All these models gave similar results. That is why only statistical model predictions are shown in Figures 4 to 6. However, they have considerable differences with the experimentally determined binary system. None of the six models can describe the real binary system accurately. They can be used only for rough estimation for the binary system when there are no binary experimental data. In Figures 4 to 6, experimental binary isotherms are compared with their counterparts predicted by the statistical model isotherms, which gave results similar to other predicted models. As can be seen from these comparisons, they overpredict the isotherms compared to the real ones at all the temperatures studied.

The phase diagrams at different temperatures were determined from the experimental binary isotherms and are shown in Figure 7, together with comparison with the predictions from the statistical model isotherms. The selectivity decreases with increasing temperature when y_{CH4} is small, while it increases with increasing temperature when y_{CH4} is high. Within the temperature range studied, separation can be performed since the curves are far away from the 45° line. Realistic experimental data gave better separation than the statistical model predicted under comparable conditions. For comparison with others, we searched the literature. However, no other binary phase diagrams were found for the separation of methane and nitrogen.

The equilibrium separation factors are calculated from eq 11 by using experimental values of x and y at three temperatures and are plotted as a function of CH_4 composition in the gas phase in Figure 8. The equilibrium separation factor has a maximum in the range of y_{CH4} between 0.5 and 0.6, where selectivity is good, and this maximum value increases with temperature. In the range of conditions considered in this study, the highest equilibrium separation factor obtained is 11.6 at 100 °C and $y_{CH4} = 0.58$.

When the experimental binary separation factors are compared to the ones predicted from the pure component data by using the partial pressures for the mixture, it was observed that the experimental separation factors from actual binary behavior are much better, as can be seen from Figure 8. When the compositions approach pure systems (mole fractions 0 or 1), predicted separation factors are close to actual ones. At that time, predicted separation factors can be used to do rough estimations if experimental binary data do not exist.

For landfill gas applications, y_{CH4} is around 0.8. Around that composition range, selectivity increases with increasing temperature and with decreasing y_{CH4}, and the equilibrium separation factor is in the range between 4 and 6, giving good

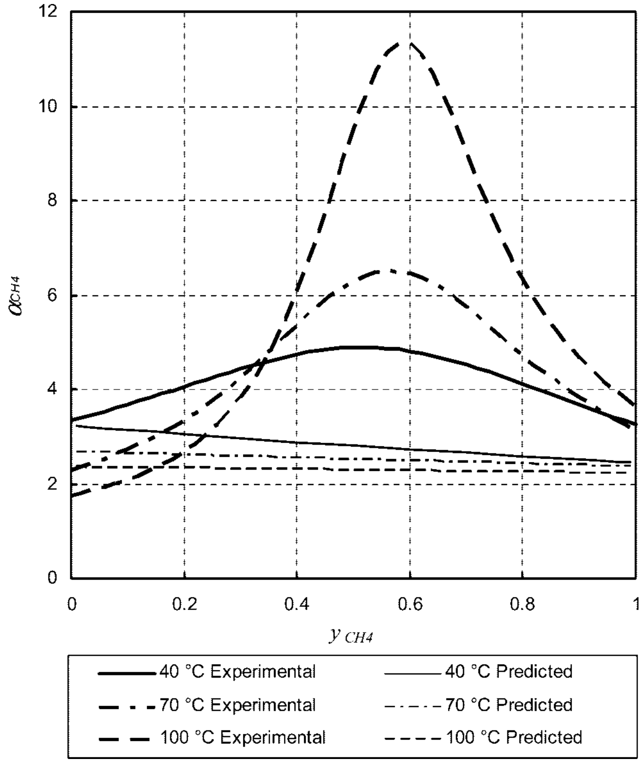

Figure 8. Comparison of equilibrium separation factors for the CH_4/N_2 binary system. Thicker lines: experimental by MVV−CPM. Thinner lines: predicted from pure component systems.

selectivity. Sheikh et al.[3] studied the adsorption isotherms on a new high specific area active carbon Maxsorb and obtained 3 for the equilibrium separation factor with volumetric and chromatographic methods at 300 K up to a pressure of 550 kPa, predicted from pure systems for methane and nitrogen. Cavenati et al.[4] obtained 1.9 for the kinetic separation factor on carbon molecular sieve CMS 3K under 250 kPa at 308 K and $y_{CH4} = 0.57$ for this separation. Harlick and Tezel[8] studied the binary system of CH_4/N_2 with ZSM-5-280 as the adsorbent at 40 °C and 1 bar total pressure by HT−CPM. On the basis of their data, when separation factor was calculated at $y_{CH4} = 0.8$, a value of 2.9 was obtained, which is lower than the values obtained with silicalite in this work. It is interesting to note that although the individual amounts adsorbed for both of the adsorbates were higher for ZSM-5-280 the separation factors were lower. Silicalite and ZSM-5 have the same crystalline structure. Harlick and Tezel's ZSM-5 adsorbent had the SiO_2/Al_2O_3 ratio indicated by the last number in the code of the adsorbent: 280. In the present study, silicalite adsorbent has a SiO_2/Al_2O_3 ratio in the thousands. Since the only difference between the adsorbent studied in this work and Harlick and Tezel's adsorbent was the SiO_2/Al_2O_3 ratio, it was concluded that a higher ratio gives better selectivity for this system.

The integral thermodynamic consistency test between pure and binary equilibrium adsorption data was carried out according to eq 10, and results are shown in Table 3. For the binary systems, the integrands of the right-hand side in eq 10 as functions of y_1 are plotted, and the area under these curves between $y_1 = 0$ and $y_1 = 1$ is calculated. For pure systems, the integrands of the left side as functions of P can be plotted, and the areas under these curves between $P = 0$ and $P = 1$ bar are listed in Table 3. It should be pointed out that the ranges of pressure of the pure systems are the same as the ranges of the partial pressures of the two components since the total pressure of the binary system is kept at 1 bar.

Table 3. Integral Thermodynamic Consistency Test between Pure and Binary Methane (1) + Nitrogen (2) Equilibrium Adsorption Data on Silicalite Using Equation 20

temperature' °C		40	70	100
RHS: $\int_0^1 \{[q_1(1 - y_1) - q_2 y_1]/[y_1(1-y_1)]\}dy_1$	$mmol\cdot g^{-1}$	0.4170	0.2283	0.1404
1st term in LHS: $\int_0^1 (q_1^0/P)dP$	$mmol\cdot g^{-1}$	0.6456	0.4036	0.3138
2nd term in LHS: $\int_0^1 (q_2^0/P)dP$	$mmol\cdot g^{-1}$	0.2200	0.1671	0.1298
LHS: $\int_0^1 (q_1^0/P)dP - \int_0^1 (q_2^0/P)dP$	$mmol\cdot g^{-1}$	0.4256	0.2365	0.1841
$\vert(LHS - RHS)/RHS\vert\cdot 100$	%	2.07	3.65	31.15

In Table 3, it can be seen that the integral thermodynamic consistency test is obeyed fairly well by the binary CH_4-N_2 adsorption data on silicalite at (40 and 70) °C, and gets worse at 100 °C. Therefore, the binary CH_4-N_2 adsorption data on silicalite at low temperature satisfy the integral thermodynamic consistency test fairly well. This consistency becomes worse as temperature increases. In addition, the results of the integral thermodynamic consistency test matches the results of predicting the adsorption behavior of the binary system from pure gas systems in Figures 4 to 6 very well. At low temperature, the thermodynamic consistency is good, so the difference of predicting the adsorption behavior of the binary system from pure gas systems is small; at high temperature, the thermodynamic consistency is not satisfied, so the difference of predicting the adsorption behavior of the binary system from pure gas systems is big or it is impossible to predict the adsorption behavior of the binary system from pure gas systems accurately. Thus, it is recommended that one key requirement for predicting the adsorption behavior of the binary system from pure gas systems is that they satisfy the integral thermodynamic consistency tests between pure and binary gas adsorption equilibria. Moreover, these data sets can be used to prove the validity of predictive or correlative binary equilibrium models.

On the basis of the results obtained in this study, silicalite is an excellent adsorbent for the separation of methane and nitrogen. The separation factors are much better than the ones obtained in the literature for real industrial applications. When y_{CH4} is about 0.8, the separation factors (4−6) are rather high for real industrial applications so that the separation of the CH_4/N_2 binary system will be possible with silicalite as the adsorbent in the (40 to 100) °C temperature range. When y_{CH4} is about 0.58, the separation factors go up to a maximum. In particular, the maximum separation factor is 11.6 at 100 °C and $y_{CH4} = 0.58$. This separation factor may be increased further when temperature is increased and/or total pressure is changed.

Conclusions

1. Among concentration pulse chromatographic methods, the MVV−CPM is good for determining binary adsorption isotherms of CH_4-N_2 on silicalite.

2. q_{CH4}, q_{N2}, and q_{total} increase with decreasing temperatures, so temperature is a very important factor for the separation of this system, as expected.

3. The six predicted models cannot describe the real CH_4/N_2 binary system accurately with silicalite, and they can be used only at low temperature or for rough estimation when the binary data are not available.

4. The selectivity has a maximum in the range of y_{CH4} between 0.5 and 0.6 for the CH_4-N_2 binary system on silicalite. At the maximum, the selectivity increases with increasing temperature, and it is good at 100 °C.

5. For the composition range of landfill gas, the selectivity increases with increasing temperature and with decreasing y_{CH4}.

6. The CH_4-N_2 binary adsorption data on silicalite at low temperature satisfy the integral thermodynamic consistency test fairly well. The thermodynamic consistency decreases as temperature increases.

7. For real landfill gas applications, the separation factors are good with silicalite. When y_{CH4} is about 0.8, the separation factors are in the range of 4 to 6 for temperatures between (40 and 100) °C.

8. In the range of our study, the highest equilibrium separation factor is 11.6 at 100 °C and $y_{CH4} = 0.58$.

Supporting Information Available:

Concentration pulse chromatographic technique and the MVV−CPM method. This material is available free of charge via the Internet at http://pubs.acs.org.

Nomenclature

B = adsorption affinity constant, usually atm^{-1} (units depending on models)
B_0 = adsorption affinity constant at some reference temperature, atm^{-1}
B_1 = adsorption affinity constant in Site 1, atm^{-1}
B_2 = adsorption affinity constant in Site 2, atm^{-1}
B_A = adsorption affinity constant in Site A, atm^{-1}
B_B = adsorption affinity constant in Site B, atm^{-1}
C = parameter, dimensionless
K = Henry′s law constant, dimensionless
K_P = dimensional Henry′s law constant, mmol·g^{-1}·atm^{-1}
k = Freundlich adsorption coefficient, mmol·g^{-1}·atm$^{-1/n}$
n = adsorption exponents or number of actives sites, dimensionless
n_0 = adsorption exponents at some reference temperature, dimensionless
P = (total) pressure, atm
Q = isosteric heat, J·mol^{-1}
P_1 = pressure of component 1, atm
P_2 = pressure of component 2, atm
P_A = pressure of component A, atm
P_B = pressure of component B, atm
q = amount adsorbed, mmol·g^{-1}
q_A = amount adsorbed of component A, mmol·g^{-1}
q_B = amount adsorbed of component B, mmol·g^{-1}
q_1 = amount adsorbed of component 1, mmol·g^{-1}
q_2 = amount adsorbed of component 2, mmol·g^{-1}
$q^{0}{}_{1}$ = amount adsorbed of component 1 in pure system, mmol·g^{-1}
$q^{0}{}_{2}$ = amount adsorbed of component 2 in pure system, mmol·g^{-1}
q_m = adsorption saturation capacity or maximum amount adsorbed, mmol·g^{-1}
q_{mA} = adsorption saturation capacity or maximum amount adsorbed of component A, mmol·g^{-1}
q_{m0} = adsorption saturation capacity or maximum amount adsorbed at some reference temperature, mmol·g^{-1}
q_{m1} = adsorption saturation capacity or maximum amount adsorbed in site 1, mmol·g^{-1}
q_{m2} = adsorption saturation capacity or maximum amount adsorbed in site 2, mmol·g^{-1}
R = gas constant, 8.314 J·K^{-1}·mol^{-1}
T = temperature, K
T_0 = reference temperature, K
x = mole fraction in adsorbed phase at equilibrium, dimensionless
x_A = mole fraction of component A in adsorbed phase at equilibrium, dimensionless
x_B = mole fraction of component B in adsorbed phase at equilibrium, dimensionless
y = mole fraction in fluid phase at equilibrium, dimensionless
y_A = mole fraction of component A in the fluid phase at equilibrium, dimensionless
y_B = mole fraction of component B in fluid phase at equilibrium, dimensionless
y_1 = mole fraction of component 1 in fluid phase at equilibrium, dimensionless

Greek Letters

α = adsorption constant, adsorption separation factor, dimensionless
$\alpha_{A/B}$ = adsorption separation factor (the ratio of component A over component B), dimensionless
$\alpha_{i,A/B}$ = ideal adsorption separation factor (the ratio of component A over component B), dimensionless
ε = bed porosity, dimensionless
θ = fraction of monolayer coverage, dimensionless
θ_A = fraction of monolayer coverage of component A, dimensionless
μ = (corrected) mean retention time, the first moment of the response peak, s
χ = constant parameter, dimensionless

Abbreviations

CPM = concentration pulse method
GC = gas chromatograph
GHG = greenhouse gases
GSE = Gibbsian surface excess
GWP = greenhouse warming potential
LFG = landfill gas
MVV−CPM = modified Van der Vlist and Van der Meijden concentration pulse method
HT−CPM = Harlick and Tezel concentration pulse method
MTT−CPM = Modified Triebe and Tezel concentration pulse method
PSA = pressure swing adsorption
rms = root-mean-square
SSR = sum of the square residuals
TCD = thermal conductivity detector
TSA = temperature swing adsorption
VST = vacancy solution theory

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