# Effect of Adsorbate Size on Adsorption of Gas Mixtures on Homogeneous Adsorbents

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Adsorbate size differences play a critical role on the adsorption characteristics of pure gases and gas mixtures on homogeneous adsorbents. Thus, the analytical multisite Langmuir model (Honig, 1966; Nitta et al., 1984) should be preferred as a base model over the classical Langmuir model.

The adsorption equilibria for pure and mixed gases on homogeneous solids are most frequently described by the Langmuir model (Langmuir, 1918; Young and Crowell, 1962). It assumes that the adsorbed phase in the adsorbent (porous or nonporous) consists of a collection of adsorption sites of equal energies, and each adsorbate molecule occupies a single site. Mathematically, the model yields (Markham and Benton, 1931)

Pure Gas

$$n_i^o = \frac{m_i b_i P}{1 + b_i P}; \quad b_i P = \frac{\theta_i^o}{(1 - \theta_i^o)} \tag{1}$$

$$b_i = b_i^o \exp\left[\frac{q_i^o}{RT}\right]; \quad q_i^o = -RT^2 \cdot \left[\frac{d \ln b_i}{dT}\right] \tag{2}$$

Mixed Gas

$$n_i = \frac{m b_i P y_i}{1 + \Sigma b_i P y_i}; \quad b_i P y_i = \frac{\theta_i}{[1 - \Sigma \theta_i]} \tag{3}$$

$$q_i = q_i^o \tag{4}$$

For pure gas adsorption, $n_i^o$ in Eq. 1 is the specific amount (mol/g) of pure gas $i$ adsorbed at pressure $(P)$ and temperature $(T)$. $m_i$ is the temperature-independent monolayer (nonporous) or saturation (porous) capacity of the adsorbent for pure gas $i$. $b_i$ is the gas-solid interaction parameter for pure gas $i$ which is an exponential function of temperature given by Eq. 2. $b_i^o$ is the limiting value of $b_i$ at $T \rightarrow \infty$. $q_i^o$ is the isosteric heat of adsorption (cal/mol) of pure gas $i$ on the solid. $R$ is the gas constant. $q_i^o$ is independent of adsorbate loading $(n_i^o)$ indicating that the adsorbent is energetically homogeneous (Sircar, 1996).

For mixed gas adsorption, $n_i$ in Eq. 3 represents the specific amount (mol/g) of component $i$ adsorbed at pressure $(P)$, temperature $(T)$ and gas-phase mole fraction $(y_i)$. The isosteric heat of adsorption of component $i$ (cal/mol) in the mixture $(q_i)$ is independent of $n_i$ and it is equal to that for the pure gas $(q_i^o)$ as required by a homogeneous adsorbent.

Equations 1 and 3 also show the Langmuir model isotherms written in terms of fractional coverages for pure gas $[\theta_i^o = n_i^o/m_i]$ and mixed gas $[\theta_i = n_i/m]$. The parameter $m$ is described below.

It has been shown (Young and Crowell, 1962; Rao and Sircar, 1999) that a key requirement for the mixed gas Langmuir model to satisfy the differential and integral thermodynamic consistency tests between pure and binary gas adsorption isotherms is that the saturation and monolayer capacities of all pure adsorbates be equal $[m_i = m]$. In other words, the use of a mixed gas Langmuir model in a thermodynamically consistent manner must satisfy the condition that all adsorbates have equal sizes. This point is reflected by the form of Eq. 3.

It follows from Eq. 3 that the Langmurian selectivity of adsorption of component $i$ over component $j$ $[S_{ij} = (n_i y_j / n_j y_i)]$ is given by

$$S_{ij} = (b_i/b_j) = (b_i^o/b_j^o) \exp\left[(q_i^o - q_j^o)/RT\right] \tag{5}$$

Thus, $S_{ij}$ is independent of $P$ and $y_i$. It is a function of $T$ only.

An extension of the Langmuir pure gas adsorption model was proposed by Honig (1966) where the restriction of each adsorbate molecule occupying a single site is relaxed. Recently, this multisite Langmuir (MSL) model was extended by Nitta and coworkers (1984) for mixed gas adsorption on a homogeneous adsorbent where the adsorbate sizes can be different $(m_i \neq m_j)$. The mathematical form of this model yields

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Pure Gas

$$b_i P = \frac{\theta_i^o}{\left[1-\theta_i^o\right]^{a_i}} \tag{6}$$

Mixed Gas

$$b_i P y_i = \frac{\theta_i}{\left[1-\Sigma\theta_i\right]^{a_i}} \tag{7}$$

where $a_i$ ($>0$) is the number of adsorption sites (temperature-independent) occupied by each molecule of adsorbate $i$. The parameter $a_i$ is an indication of the size of the adsorbate molecule. The larger the value of $a_i$ is, the bigger the molecular size is. However, no exact relationship between $a_i$ and the molecular diameter can be established. $b_i$ is the gas-solid interaction parameter for pure adsorbate $i$. It can be shown from Eqs. 6 and 7 that (i) $b_i$ is again an exponential function of temperature given by Eq. 2, and (ii) the isosteric heat of adsorption of pure gas $i$ and that for the component $i$ in the gas mixture are equal ($q_i = q_i^o$) and they are independent of adsorbate loadings ($n_i^o$ or $n_i$) as required by a homogeneous adsorbent. $\theta_i^o$ or $\theta_i$, in this case, are equal to ($n_i^o/m_i$) and ($n_i/m_i$), respectively.

It has been shown (Rao and Sircar, 1999) that the MSL model satisfies the thermodynamic consistency tests if the constraint $[a_i m_i = \text{constant}]$ is obeyed. Thus, the MSL model can be used to describe pure and mixed gas adsorption equilibria for adsorbates of different sizes ($m_i \neq m_j$) on a homogeneous adsorbent under the above described constraint.

A very interesting behavior of the MSL model is that the selectivity of adsorption of component $i$ over component $j$ at a constant temperature is dependent on $P$ and $y_i$ (Sircar, 1995)

$$S_{ij} = \frac{a_j}{a_i}\cdot\frac{b_i}{b_j}\cdot(1-\theta)^{(a_i-a_j)} \tag{8}$$

where $\theta$ $[=\Sigma\theta_i]$ is the total fractional surface coverage for all adsorbates.

According to Eq. 8, the variation of the binary selectivity of adsorption of component 1 over component 2 ($S_{12}$) with respect to $P$ at constant $T$ and $y_i$ ($y_1 + y_2 = 1$) is given by

$$\left(\frac{\delta S_{12}}{\delta P}\right)_{y_1,T} = (a_2 - a_1)\frac{S_{12}}{P}\frac{\theta(1-\theta)}{\left[1+(a_1-1)\theta_1+(a_2-1)\theta_2\right]} \tag{9}$$

and the variation of $S_{12}$ with respect to $y_1$, at constant $P$ and $T$ is given by

$$\left(\frac{\delta S_{12}}{\delta y_1}\right)_{P,T} = \frac{(a_1-a_2)(a_2-S_{12}a_1)\theta_1(1-\theta)}{(a_1\cdot y_1)\left[1+(a_1-1)\theta_1+(a_2-1)\theta_2\right]} \tag{10}$$

The variation of $S_{12}$ with respect to $T$ at constant $\theta_i$ is given by

$$\left[\frac{\delta \ln S_{12}}{\delta T}\right]_{\theta_i} = -\frac{(q_1^o - q_2^o)}{RT^2} \tag{11}$$

Equation 9 shows that $S_{12}$ decreases with increasing pressure when $a_1 > a_2$, and the reverse is true when $a_2 > a_1$. $S_{12}$ is independent of $P$ if $a_1 = a_2$. Equation 10 shows that $S_{12}$ decreases with increasing $y_1$ when $a_1 > a_2$ and $S_{12} > 1$. For the case when $a_2 > a_1$, $S_{12}$ decreases with increasing $y_1$, if $S_{12} < a_2/a_1$, and $S_{12}$ increases with increasing $y_1$, if $S_{12} > a_2/a_1$. $S_{12}$ is not a function of $y_1$ if $a_1 = a_2$, or $S_{12} = (a_2/a_1)$. Equation 11 shows that $S_{12}$ decreases with increasing $T$ if $q_i^o > q_2^o$.

The MSL model reduces to the Langmuir model when $a_i = 1$ ($m_i = m_j = m$). The selectivity of adsorption ($S_{ij}^o$) at any temperature $T$ in the Henry's Law limit ($P \rightarrow 0$) by both models is given by (Sircar, 1995)

$$S_{ij}^o = K_i/K_j \tag{12}$$

where $K_i$ ($= m_i b_i$) is the Henry's Law constant for pure gas $i$ at temperature $T$ by the MSL model.

## Experimental Evidence

Three binary adsorption systems are presented from the published literature where the pure gas adsorption isotherms indicate that the adsorbents are energetically homogeneous in the range of the data (pure gas isosteric heats of adsorption are not functions of adsorbate loadings), yet the pressure dependence of adsorption selectivities at constant $T$ and $y_1$ exhibit three different characteristics. The pure gas isosteric heats of adsorption for these systems were estimated as functions of adsorbate loading from the adsorption isotherms at two temperatures using the following thermodynamic equation (Young and Crowell, 1962)

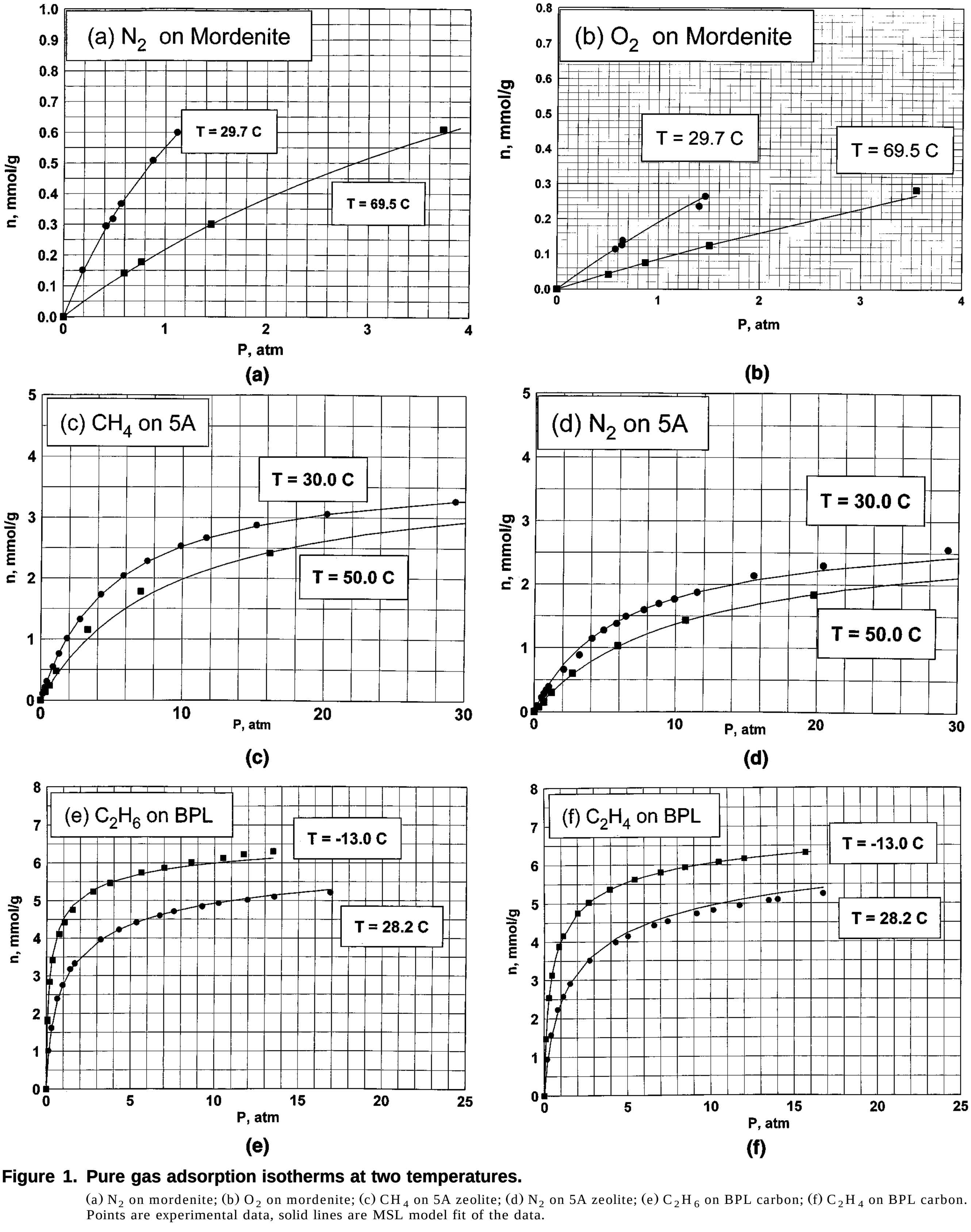
$$q_i^o = RT^2\left[\frac{\delta \ln P}{\delta T}\right]_{n_i^o} \tag{13}$$

Equations 2 and 4 are also derived by combining Eqs. 1, 3 and 13 with the assumption that the isosteric heats of adsorption are independent of $T$.

### *Nitrogen (1) + Oxygen (2) on Na-Mordenite (Kumar and Sircar, 1986)*

Figures 1a and 1b show the pure gas adsorption isotherms of, respectively, $N_2$ and $O_2$ on Na-Mordenite at 29.7 and 69.5°C. The pure gas isosteric heats of adsorption of $N_2$ and $O_2$, calculated by Eq. 13, were essentially constants in the range of these data [$q_1^o = 6.25$; $q_2^o = 4.53$ kcal/mol]. Table 1 reports the binary gas adsorption isotherms of $N_2 + O_2$ mixture on the mordenite at 30°C at a pressure of 1.0 atmosphere. It may be seen that $N_2$ is selectively adsorbed over $O_2$ on the mordenite ($S_{12} > 1$), and $S_{12}$ is not a function of gas composition for this system.

The pure gas adsorption isotherms for this system can be described very well by the Langmuir model as shown by the



(a) (b)

(c) (d)

(e) (f)

**Figure 1. Pure gas adsorption isotherms at two temperatures.**

(a) $N_2$ on mordenite; (b) $O_2$ on mordenite; (c) $CH_4$ on 5A zeolite; (d) $N_2$ on 5A zeolite; (e) $C_2H_6$ on BPL carbon; (f) $C_2H_4$ on BPL carbon. Points are experimental data, solid lines are MSL model fit of the data.

**Table 1. Binary Gas Adsorption of $N_2$ (1) + $O_2$ (2) on Na-Mordenite at 30°C**

| | | Experimental | | | MSL Model | | | |
|---|---|---|---|---|---|---|---|---|
| $P$ | $y_1$ | $n_1$ | $n_2$ | $S_{12}$ | $n_1$ | % Error | $n_2$ | % Error |
| (atm) | | (mmol/g) | (mmol/g) | | (mmol/g) | | (mmol/g) | |
| 1.0 | 0.086 | 0.0647 | 0.1720 | 4.00 | 0.0610 | −6.0% | 0.1676 | −2.6% |
| 1.0 | 0.200 | 0.1430 | 0.1430 | 4.00 | 0.1374 | −4.0% | 0.1415 | −1.1% |
| 1.0 | 0.480 | 0.3230 | 0.0902 | 3.88 | 0.3036 | −6.4% | 0.0846 | −6.6% |
| 1.0 | 0.790 | 0.4940 | 0.0333 | 3.95 | 0.4590 | −7.6% | 0.0314 | −5.7% |
| | | | | | | avg. ±6.0% | | ±4.0% |

solid lines of Figures 1a and 1b . The same values of $m$ were used to fit the data for both gases. The other Langmuir parameters will be given in Table 4. The binary adsorption isotherms calculated by the mixed gas Langmuir model and the parameters of Table 4 will be compared with the experimental data in Table 1. They show that the model describes the data fairly well. Thus, the constancy of selectivity of adsorption of $N_2$ over $O_2$ on Na-mordenite is caused by adsorption of two adsorbates of equal sizes on a homogeneous adsorbent.

### *Methane (1) + Nitrogen (2) on 5A Zeolite (Sievers and Mersmann, 1993)*

Figures 1c and 1d show the pure gas adsorption isotherms of, respectively, $CH_4$ and $N_2$ on 5A zeolite at 30.0 and 50.0°C. The isosteric heats of adsorption of these pure gases are also practically constant ($q_1^o = 5.76$, $q_2^o = 5.70$ kcal/mol) in the range of the data. Table 2 reports the binary adsorption isotherms for this system at 30°C for $y_1$ values of $\sim 0.201$ and 0.594. $CH_4$ is selectively adsorbed over $N_2$ and $S_{12}$ ($>1$) increases with increasing $P$ at constant $T$ and $y_1$.

The pure gas data of Figures 1c and 1d can be described very well (solid lines) by the MSL model using the parameters given in Table 4. The constraint ($a_1 m_1 = a_2 m_2$) is obeyed in fitting these data. It may be seen that $a_2 > a_1$ for this system even though component 1 is more selectively adsorbed over component 2. Thus, Eq. 9 can explain the observed behavior of $S_{12}$ as a function of $P$ at constant $T$ and $y_i$ for this system.

A comparison between the experimental binary isotherm data for this system and those calculated by using the MSL model and the parameters of Table 4 will show that the model indeed describes the binary data very well (Table 2).

### *Ethane (1) + Ethylene (2) on BPL Activated Carbon (Reich et al., 1980)*

Figures 1e and 1f show the pure gas adsorption isotherms of, respectively, $C_2H_6$ and $C_2H_4$ on BPL activated carbon at −13.0 and 28.3°C. The carbon behaves like a homogeneous adsorbent for these gases. The isosteric heats of pure gas adsorption are nearly constant [$q_1^o = 6.78$, $q_2^o = 5.30$ kcal/mol] in the range of these data.

Table 3 reports the binary adsorption isotherm data for this system at 28.3°C for $y_1$ values of 0.472 and 0.682. It may be seen that, in this case, $C_2H_6$ is more selectively adsorbed than $C_2H_4$ and $S_{12}$ decreases with increasing $P$ at constant $T$ and $y_1$.

The pure gas isotherms for this system can also be described very well by the MSL model (solid lines in Figures 1e and 1f). Table 4 reports the pure gas model parameters. The constraint [$a_1 m_1 = a_2 m_2$] is obeyed. In this case, $a_1$ is larger than $a_2$ even though $S_{12} > 1$. Consequently, Eq. 9 correctly describes the variation of $S_{12}$ with $P$ for this system.

The calculated binary isotherms for this system using the MSL model and the parameters of Table 4 compare fairly well with the experimental data (Table 3).

The above described binary adsorption data and their interpretation using the MSL model clearly show that the adsorbate size differences play an important role in determining the adsorption characteristics of gas mixtures. The three distinctly different behaviors of experimental adsorption selectivities as functions of gas pressures at constant $T$ and $y_1$, replotted in Figure 2, prove the point. The selectivities in Figure 2 are normalized with respect to the Henry's Law region selectivities ($S_{12}^o$) for the systems. The MSL model (Eq. 9) predicts that the selectivity increases or decreases with increasing $P$ and then it becomes constant [$(\delta S_{12}/\delta P)_{T, y_1} \rightarrow 0$

**Table 2. Binary Gas Adsorption of $CH_4$ (1) + $N_2$ (2) on 5A Zeolite at 30°C**

| | | Experimental | | | MSL Model | | | |
|---|---|---|---|---|---|---|---|---|
| $P$ | $y_1$ | $n_1$ | $n_2$ | $S_{12}$ | $n_1$ | % Error | $n_2$ | % Error |
| (atm) | | (mmol/g) | (mmol/g) | | (mmol/g) | | (mmol/g) | |
| 1.0 | 0.207 | 0.123 | 0.312 | 1.510 | 0.132 | +7.0% | 0.327 | +4.6% |
| 6.0 | 0.197 | 0.450 | 1.077 | 1.703 | 0.466 | +3.5% | 1.100 | +2.1% |
| 29.7 | 0.199 | 0.880 | 1.852 | 1.913 | 0.916 | +4.1% | 1.739 | −6.1% |
| | | | | | | avg. ±5.0% | | avg. ±4.3% |
| 1.0 | 0.588 | 0.371 | 0.157 | 1.655 | 0.371 | 0.0% | 0.167 | +6.6% |
| 6.0 | 0.594 | 1.345 | 0.483 | 1.903 | 1.314 | −2.3% | 0.512 | +6.0% |
| 29.7 | 0.600 | 2.406 | 0.694 | 2.311 | 2.316 | −3.7% | 0.701 | +0.9% |
| | | | | | | avg. ±2.0% | | avg. ±4.5% |

**Table 3. Binary Gas Adsorption of Ethane (1) + Ethylene (2) on BPL Carbon at 28.3°C**

| | | Experimental | | | MSL Model | | | |
|---|---|---|---|---|---|---|---|---|
| $P$ | $y_1$ | $n_1$ | $n_2$ | $S_{12}$ | $n_1$ | % Error | $n_2$ | % Error |
| (atm) | | (mmol/g) | (mmol/g) | | (mmol/g) | | (mmol/g) | |
| 1.422 | 0.682 | 2.489 | 0.777 | 1.494 | 2.335 | −6.2% | 0.717 | −7.8% |
| 3.415 | 0.682 | 3.047 | 1.023 | 1.389 | 3.000 | −1.6% | 0.962 | −6.0% |
| 6.836 | 0.682 | 3.631 | 1.235 | 1.371 | 3.458 | −4.7% | 1.151 | −6.8% |
| 13.497 | 0.682 | 4.076 | 1.526 | 1.245 | 3.822 | −6.2% | 1.327 | −13.1% |
| | | | | | | avg. ±4.7% | | avg. ±8.4% |
| 2.149 | 0.472 | 2.009 | 1.585 | 1.418 | 1.967 | −2.1% | 1.471 | −7.2% |
| 5.421 | 0.472 | 2.533 | 2.051 | 1.382 | 2.456 | −3.1% | 1.927 | −6.1% |
| 11.180 | 0.472 | 2.862 | 2.512 | 1.275 | 2.763 | −3.4% | 2.259 | −10.1% |
| | | | | | | avg. ±2.9% | | avg. ±7.8% |

**Table 4. MSL Model Parameters**

| | $m_i$ (mmol/g) | $a_i$ | $b_i^o$ (atm$^{-1}$) | $q_i^o$ (kcal/mol) |
|---|---|---|---|---|
| Mordenite | | | | |
| $N_2$ | 1.650 | 1.0 | $1.56 \times 10^{-5}$ | 6.25 |
| $O_2$ | 1.650 | 1.0 | $6.98 \times 10^{-5}$ | 4.53 |
| 5A Zeolite | | | | |
| $CH_4$ | 3.887 | 1.038 | $1.36 \times 10^{-5}$ | 5.76 |
| $N_2$ | 3.188 | 1.226 | $1.22 \times 10^{-5}$ | 5.70 |
| BPL Carbon | | | | |
| $C_2H_6$ | 7.316 | 2.693 | $1.66 \times 10^{-5}$ | 6.78 |
| $C_2H_4$ | 7.850 | 2.510 | $11.01 \times 10^{-5}$ | 5.30 |

as $P \to \infty$] at larger values of $P$ when $a_1 \neq a_2$. The data of Figure 2 depict that behavior.

It should be mentioned here that for most adsorption systems, $S_{12}$ ($>1$) is either found to be independent of $P$ ($a_1 = a_2$ case) or it decreases with increasing $P$ ($a_1 > a_2$ case). The case of $S_{12}$ increasing with increasing $P$ is rare ($a_2 > a_1$ case). Thus, the data for $CH_4 + N_2$ adsorption on 5A zeolite are critical proof of the effect of adsorbate size difference on adsorption isotherms.

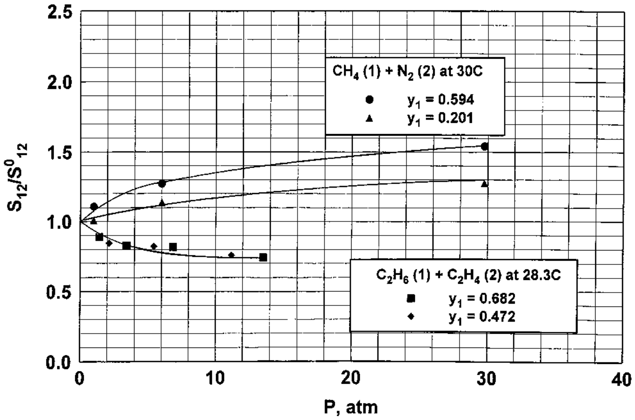


**Figure 2. Selectivity of adsorption of binary gas mixtures as functions of total gas pressure at constant temperature and mole fractions.**

It is recommended that the MSL model be treated as a base model to describe the effects of adsorbate size on the adsorption of multicomponent gas mixtures on an energetically homogenous adsorbent as long as the thermodynamic constraint ($a_i m_i =$ constant) is obeyed. The MSL model presented here does not include the effects of lateral interactions in the adsorbed phase. A recent publication by Martinez and Basmadjian (1996) extends the MSL model to account for lateral interactions. The criteria for thermodynamic consistency of that extended model has also been established (Rao and Sircar, 1999). It shows that the model is not consistent when the lateral interactions between the molecules of the components of the gas mixture are considered.

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