# Monte Carlo Simulation of Adsorption Using 2-D Models of Heterogeneous Solids

**V. F. Cabral, F. W. Tavares, and M. Castier**
Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil

*A new methodology proposed here correlates the adsorption of pure components and predicts the adsorption of binary and ternary mixtures in homogeneous and heterogeneous solids. This methodology uses the algorithm of molecular simulation in the grand canonical ensemble as an equation of state for the adsorbed phase. In all case studies presented, the simulations described the adsorption characteristics of systems. The results obtained for the adsorption of the binary mixtures of propane–$CO_2$ and propane–$H_2S$, which are strongly nonideal, were quite satisfactory, showing the potential of this technique for the description of real systems.*

## Introduction

The application of adsorption in several separation and purification processes has intensified the interest in the modeling of adsorption phenomenon, and many isotherm models are available in the literature. In particular, the interest in models based on the energy heterogeneity of the active sites is increasing. Two reasons can be pointed out: the energy nonhomogeneity of solids controls the adsorption phenomena, and the inadequacy of the models for homogeneous solids in predicting the behavior of adsorption phenomena on heterogeneous surfaces.

Most isotherm models do not use information about the solid structure. This type of information is available in the literature, but the models are not derived to use this type of information. In this context, a way of using this information is to utilize a molecular simulation technique as an equation of state for the correlation and prediction of adsorption phenomena in real systems. Therefore, the main motivation for using molecular simulation is that this technique turns the thermodynamic model more microscopic and, starting from information on the solid structure, it is possible to develop appropriate solid models for each type of real system. Another motivation is that the necessary computational effort is less prohibitive today, due to the progress in computer science and in hardware technology.

Even though the molecular simulation techniques were proposed in the 1950s, their applications to adsorption are more recent. The method commonly used to simulate this phenomenon is the Monte Carlo technique for a grand canonical ensemble, where the chemical potential ($\mu$), the number of sites ($M$), and the temperature ($T$) are specified.

Examples of the use of the Monte Carlo technique in adsorption are the work of Vlugt et al. (1999) and of Macedonia and Maginn (1999). A common feature of these publications is that they use detailed force fields for the solid and for the fluid. Even though very interesting results have been obtained from these simulations, their large computational effort still limits applications to engineering problems.

For this purpose, the use of less detailed models, which still capture the major aspects of adsorption phenomena, represents a feasible compromise. Several recent articles followed this approach. In these publications, the authors supposed that the adsorbent surface is represented by a two-dimensional square lattice of $M$ active sites. Ramirez-Pastor et al. (1995) studied the adsorption of dimers on heterogeneous surfaces, using experimental adsorption isotherms for $O_2$ and $N_2$ adsorbed on zeolites 5A and 10X to test the reliability of their simulation model. The parameters of the simulation model were adjusted to fit the experimental data. Nitta et al. (1997) used the Monte Carlo method to simulate the adsorption of dimers on heterogeneous solid surfaces represented by square lattices with two types of sites, each of them characterized by a different adsorption energy. The active sites were randomly distributed. Ramirez-Pastor et al. (2000) used Monte Carlo simulations to study the adsorption of noninteracting homonuclear linear k-mers on heterogeneous surfaces. The authors modeled the heterogeneous surface with two kinds of sites. These sites formed square patches distributed at random or in a chessboardlike ordered domain on a two-dimensional square lattice. Bulnes et al. (2001) studied the

---

Correspondence concerning this article should be addressed to F. W. Tavares.

adsorption of binary mixtures on solid heterogeneous substrates using the Monte Carlo simulation in the framework of the lattice gas model. A historical review of the application of computer simulation to adsorption phenomena, especially for two-dimensional systems, has been recently published elsewhere (Steele, 2002).

The present article provides a new and systematic methodology for applying the approach of these previous publications to real systems, with a small computational effort. For this purpose, the Monte Carlo technique of molecular simulation for a grand canonical ensemble ($\mu$, $M$, and $T$ specified) was used to correlate pure-component data and predict adsorption of binary and ternary mixtures. In this way, the molecular simulation acts as an equation of state for the adsorbed phase. In the simulations, a two-dimensional square lattice represents the adsorbent surface. The parameters of the simulation model are fitted using experimental data of pure components. This parameter-fitting procedure is analogous to that performed in the case of the usual equation of state for determining the PVT properties of a fluid.

Examples and reviews of the usage of normal equations of state to predict or correlate adsorption of the gas mixtures from single-gas adsorption isotherm data can be found in Martinze and Basmadjian (1996), Siperstein and Myers (2001), and Ustinov et al. (2002).

Experimental data of the adsorption of gaseous pure components and mixtures are used for evaluating this new methodology. The experimental data are divided in two adsorption systems:

*System 1.* Experimental data of $O_2$, $N_2$, CO, and their binary mixtures adsorbed on zeolite 10X, at 144, 172, 227 and 273 K (Danner and Wenzel, 1969).

*System 2.* Experimental data of propane, $H_2S$, $CO_2$, and their binary and ternary mixtures adsorbed on H-mordenite, in 303 K (Talu and Zwiebel, 1986).

The outline of the article is as follows: in the next section, we present the basis of the Monte Carlo technique for the grand canonical ensemble ($\mu$, $M$, and $T$ specified). Next, we present the strategy used for parameter fitting. We then present our predictions for adsorbed binary and ternary mixtures. Finally, in the last section, we present our conclusions.

## Molecular Simulation

In this work, the Monte Carlo technique is used to simulate the adsorption of chainlike molecules on homogeneous and heterogeneous surfaces. The lattice-gas model is used. In this way, each molecule segment occupies a specific site of the solid surface. Each of the sites is occupied by only one molecule segment.

The most important parameters in a lattice model with chainlike molecules are: (1) the total number of sites ($M$); (2) the number of neighboring sites each of them has, named coordination number ($Z$); (3) the adsorption energy between a molecule segment and a site of the solid ($\epsilon$); (4) the number of segments of each molecule ($m$); and (5) the interaction energy between two adsorbed segments in neighboring sites ($\omega$).

According to the Metropolis algorithm (Allen and Tildesley, 1987), the Monte Carlo method for a grand canonical ensemble ($T$, $M$, $\mu_1$, $\mu_2$, ..., $\mu_{nc}$ specified) consists of three basic movements: displacement, insertion, and removal of an adsorbed molecule. The transition probability from a configurational state, $m$, to a new state, $n$, is expressed by

$$P_{m\rightarrow n} = \min\left\{1, \frac{\rho_n}{\rho_m}\right\} \tag{1}$$

where $\rho_n/\rho_m$ is the ratio between the probability densities of the configurational states, $n$ and $m$. The movement is accepted if such probability $P_{m\rightarrow n}$ is larger than a number randomly generated between 0 and 1. The following subsections detail each movement.

### *Particle displacement*

The adsorbed molecule that will be moved is chosen randomly. One end of the molecule is chosen at random to be the head, while the other is the tail. The head is moved to a new position on the lattice and all the other segments move one site along the chain and the tail position becomes vacant. If the site chosen as the new position of the head is occupied, the movement is immediately rejected. This type of motion is termed "reptation" movement (Allen and Tildesley, 1987). If the displacement is possible, the ratio between the probability densities of the new state ($n$) and old state ($m$) is calculated by the following expression (Allen and Tildesley, 1987)

$$\frac{\rho_n}{\rho_m} = \exp\left[-\frac{(U_n - U_m)}{kT}\right] \tag{2}$$

where $T$ is the temperature, $k$ is Boltzmann's constant, and $U_m$ is the configurational energy of the state $m$

$$U_m = -\sum_{i=1}^{nc}\sum_{j=1}^{ns} N_{ij}^{(m)}\epsilon_{ji} - \frac{1}{2}\sum_{i=1}^{nc}\sum_{k=1}^{nc} Nc_{ik}^{(m)}\omega_{ik} \tag{3}$$

In Eq. 3, $N_{ij}^{(m)}$ is the total number of adsorbed segments, $i$, in sites $j$; $\epsilon_{ji}$ is the adsorption energy between a segment $i$ and a site $j$; $Nc_{ik}^{(m)}$ is the number of contacts between adsorbed segments $i$ and $k$; and $\omega_{ik}$ is the interaction energy between adsorbed segments $i$ and $k$ in neighboring sites.

### *Particle insertion*

In order to add a molecule to the lattice, a position in the lattice is chosen to place the first segment of the molecule and, through another random number, a neighboring site is chosen for adding the second segment. If one of these sites is already occupied, the movement is rejected. To insert the third segment, only $(Z-1)$ neighboring sites are available. The procedure just described is repeated until the molecule is completely inserted. Next, the energy of this new configuration is computed, and the ratio between the probability densities of the new ($n$) and old ($m$) states (Allen and Tildesley, 1987) is calculated as follows

$$\frac{\rho_n}{\rho_m} = \frac{M}{N_i + 1}\exp\left[\frac{\mu_i}{kT} - \frac{(U_n - U_m)}{kT}\right] \tag{4}$$

where $N_i$ is the total number of molecules, $i$, adsorbed in the old state, and $\mu_i$ is the chemical potential of component $i$.

The movement is also accepted if a generated random number between zero and one is lower than the transition probability ($P_{m \to n}$) defined by Eq. 1.

### *Particle removal*

A randomly chosen adsorbed molecule is removed, the energy of this new configuration is calculated, and the ratio between probability densities of the new ($n$) and old ($m$) states (Allen and Tildesley, 1987) is computed as follows

$$\frac{\rho_n}{\rho_m} = \frac{N_i}{M} \exp\left[ -\frac{\mu_i}{kT} - \frac{(U_n - U_m)}{kT} \right] \tag{5}$$

The movement is accepted if a generated random number between zero and one is lower than the transition probability ($P_{m \to n}$) defined by Eq. 1.

## Relationship with Thermodynamics

The relationship connecting the fugacity, $\hat{f}_i$, and the chemical potential of the component $i$ in the gaseous phase is given by the classic equation

$$\mu_i = \mu_{0i} + kT \ln\left(\hat{f}_i\right) \tag{6}$$

where $\mu_{0i}$ is the reference-state chemical potential for the ideal gas under atmospheric pressure and at the temperature of the system. On the other hand, the Henry constant ($K_{bi}^*$) for adsorption on a homogeneous solid that only contains sites of a given type, $b$, is (Hill, 1960)

$$\frac{K_{bi}^*}{\zeta_i} = \exp\left( \frac{\mu_{0i}}{kT} \right) \exp\left( \frac{m_i \epsilon_{bi}}{kT} \right) = K_{bi} \tag{7}$$

where $m_i$ is the number of segments of adsorbed molecule $i$, and $\zeta_i$ represents a correction term for the partition function corresponding to the internal degrees of freedom (such as vibrational, electronic, rotational) of the adsorbed molecule $i$ compared to the same degrees of freedom in the condition of the ideal-gas reference state. For convenience, in the rest of this article, we will refer to the ratio $(K_{bi}^*/\zeta_i) = K_{bi}$ as the Henry constant. Therefore, from Eqs. 6 and 7, we obtain an expression for the chemical potential

$$\frac{\mu_i}{kT} = \ln\left(K_{bi} \hat{f}_i\right) - \frac{m_i \epsilon_{bi}}{kT} \tag{8}$$

## Solid Model

The solid heterogeneity is represented by the existence of two kinds of sites, characterized by the energies $\epsilon_a$ and $\epsilon_b$. The sites that performed a stronger connection (larger energy: $\epsilon_a$) are called active sites. The fraction of active sites is denoted by $\nu_a$. The solid lattice is modeled as a square matrix of dimension 100×100 ($M = 10{,}000$). For each fraction of active sites, several topologies can be generated, each of them characterized by a random distribution of square grains with a specific number of sites. To visualize this statement, Figure 1 shows four solid square-lattice samples with a fraction of 30% of active sites and clusters (grains) of sites with dimension $Dg = 1$, $Dg = 4$, $Dg = 8$, and $Dg = 12$. In order to minimize the effect of the solid size, periodic boundary conditions are considered both for distributing the grains of active sites on the solid and for moving a molecule in the lattice.

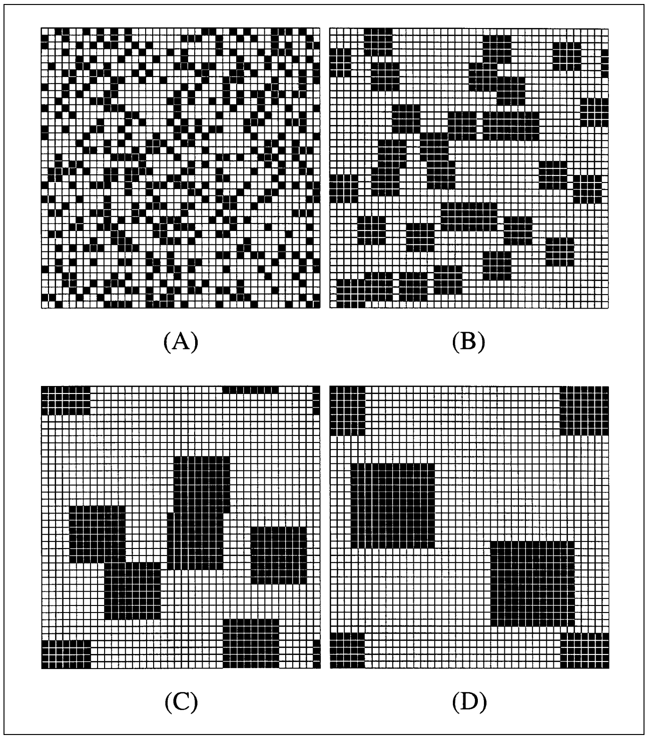

**Figure 1. Four 40×40 square-lattices with 30% of active sites, randomly distributed in grains with dimension (A) $Dg = 1$, (B) $Dg = 4$, (C) $Dg = 8$, and (D) $Dg = 12$.**

## Parameter Fitting

The parameters of the simulation model are the Henry's constant ($K_{bi}$); the amount adsorbed at infinite pressure ($N^\infty$); a parameter, $r_a$, that is related to the surface heterogeneity; and the interaction energy between two adsorbed segments in neighbor sites ($\omega/kT$).

Parameter $N^\infty$ was introduced because the results obtained in the simulations are in the form of a covering fraction. In this way, this parameter was created to relate the covering fraction ($\theta$) of the solid (obtained by molecular simulation) to the total amount adsorbed (obtained from experimental data). Therefore, the adsorbed amount of component $i$ ($N_i^{ads}$) is calculated through the following equation

$$N_i^{ads} = \theta N_i^\infty \tag{9}$$

The energetic heterogeneity of solids is characterized by an $r_a$ parameter. The equation of this parameter is given by

$$r_a = \exp\left[ \frac{(\epsilon_b - \epsilon_a)}{kT} \right] \tag{10}$$

Therefore, when the values of parameters $\epsilon_b$ and $r_a$ are defined, the adsorption energy between an active site and a molecule segment ($\epsilon_a$) is determined using Eq. 10. In the case of homogeneous solids, $\epsilon_b = \epsilon_a$ and the parameter $r_a$ is, therefore, equal to 1.

For fitting the parameters just described, the subroutine UMPOL of the ISML library was used. This subroutine minimizes a multivariable function using a direct search algorithm.

The objective function used for parameter fitting was the least-square function related to deviations in the adsorbed amount. The expression of this function is given by

$$\text{FOBJ} = \sum_{i=1}^{np} \left( N_{i_{ads}}^{\text{exp}} - N_{i_{ads}}^{\text{simul}} \right)^2 \tag{11}$$

where $np$ is the experimental number of points, and $N_{i_{ads}}^{\text{exp}}$ and $N_{i_{ads}}^{\text{simul}}$ are the adsorbed amount obtained from experimental data and calculated by molecular simulation, respectively.

In order to the reduce the computational time needed to fit the parameters, preliminary tests were performed for determining the minimum number of configurations necessary for calculating the average properties that would be obtained in the simulations. These tests indicated that $3 \cdot 10^4$ configurations were enough for the equilibration step and for the average properties calculation step. The standard deviation of the obtained average properties was around $10^{-3}$.

For the parameter fitting of each substance, approximately 700 evaluations of the objective function (Eq. 11) were necessary. One evaluation of the objective function demands several Monte Carlo simulations, each of them at the pressure of the corresponding experimental data point. Given that the experimental data sets typically contain 20 data points ($np$), about $20 \times 700 = 14{,}000$ Monte Carlo simulations were necessary for the parameter fitting. The fitting process was performed in a period of four to five hours in a PC with a Pentium II processor of 233 MHz and 64 Mb of memory. Next, we present the strategies employed for the parameter fitting.

### *System 1: $O_2$, $N_2$, and CO adsorbed on zeolite 10X*

The molecules of $O_2$, $N_2$, and CO were modeled as dimers. The solid heterogeneity was characterized by the existence of the random distribution of active sites with $Dg = 1$. The fraction of active sites ($\nu_a$) was assumed to be a ratio of the amount of $Ca^{++}$ cations to the amount of aluminum and silicon in the zeolite 10X. It is suggested in the literature (Nitta et al., 1984) that this value is equal to $\nu_a = 0.22$ for zeolite 10X. The choice of the parameter $Dg$ was based on the work of Nitta, but there is a difference in our approach. Nitta assumes independence among the grains. In the case of grains of dimension $Dg = 1$, our approach is less restrictive, because it allows, for example, that one segment of a dimer molecule adsorbs in an active site and the other in a nonactive site.

At each temperature, the fitting of the four parameters ($K_b$, $r_a$, $\omega/kT$, and $N^\infty$) for oxygen was made initially. As seen earlier, the three components had two segments. Therefore, the three components had the same value for the parameter $N^\infty$, that is, the amount adsorbed at the infinite pressure is the same for the three components. Next, the parameters $K_b$, $r_a$, and $\omega/kT$ were fitted for the molecules of $N_2$ and CO.

**Table 1. Parameters for System 1: Oxygen, Nitrogen, and Carbon Monoxide Adsorbed on Zeolite 10X at Temperatures of 144, 172, 227, 273 K**

| | | Parameters | | | |
|---|---|---|---|---|---|
| Substance | $T$ (K) | $K_b$ ($Pa^{-1}$) | $N^\infty$ (mol/kg) | $r_a$ | $\omega/kT$ |
| $O_2$ | 144 | $1.904 \times 10^{-1}$ | 7.2494 | $8.5606 \times 10^{-1}$ | $2.557 \times 10^{-1}$ |
| | 172 | $4.092 \times 10^{-2}$ | 6.5527 | 1.3967 | $1.715 \times 10^{-1}$ |
| | 227 | $7.077 \times 10^{-3}$ | 6.0000 | 0.999 | $3.899 \times 10^{-3}$ |
| | 273 | $1.868 \times 10^{-3}$ | 7.1129 | 1.1846 | $2.543 \times 10^{-2}$ |
| $N_2$ | 144 | 3.938 | 7.2494 | $6.9846 \times 10^{-1}$ | $-5.5783 \times 10^{-1}$ |
| | 172 | $7.966 \times 10^{-1}$ | 6.5527 | $2.2000 \times 10^{-1}$ | $-4.0774 \times 10^{-1}$ |
| | 227 | $3.258 \times 10^{-2}$ | 6.0000 | 1.000 | $-3.468 \times 10^{-1}$ |
| | 273 | $6.179 \times 10^{-3}$ | 7.1129 | 1.2112 | $-3.2479 \times 10^{1}$ |
| CO | 144 | $1.752 \times 10^{1}$ | 7.2494 | 1.8411 | $-6.3822 \times 10^{-1}$ |
| | 172 | 4.890 | 6.5527 | $3.2857 \times 10^{-1}$ | $-5.4263 \times 10^{-1}$ |
| | 227 | $2.223 \times 10^{-1}$ | 6.0000 | $1.067 \times 10^{-2}$ | $-2.277 \times 10^{-1}$ |
| | 273 | $1.076 \times 10^{-2}$ | 7.1129 | 5.689535 | $-2.3990$ |

Table 1 shows the parameter values fitted at each temperature. The Henry's constant has an Arrhenius-type temperature dependency. To verify this dependence, $\ln(K_b)$ was plotted as a function of inverse temperature. Figure 2 shows the linear fit with the parameters obtained on the fit. Figure 3 presents the results for the correlation of the pure components obtained by molecular simulation.

### *System 2: $H_2S$, $CO_2$, and propane adsorbed on H-mordenite*

In this system, the molecules of $CO_2$ and $H_2S$ were modeled with three segments. In this way, the amount adsorbed at infinite pressure had the same value for the molecules of $CO_2$ and $H_2S$. The number of segments of propane was empirically calculated using the following equation

$$m_{\text{propane}} = \text{round}\left[ m_{CO_2} \left( \frac{\sigma_{\text{propane}}}{\sigma_{CO_2}} \right)^{3/2} \right] \tag{12}$$

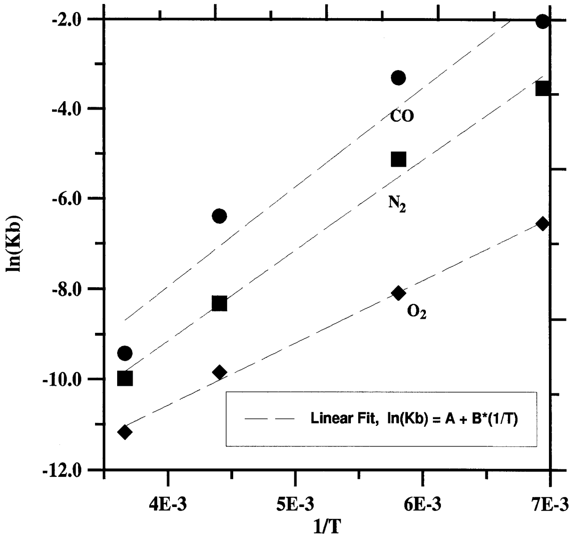

**Figure 2. Temperature dependence of the Henry constant ($K_b$).**

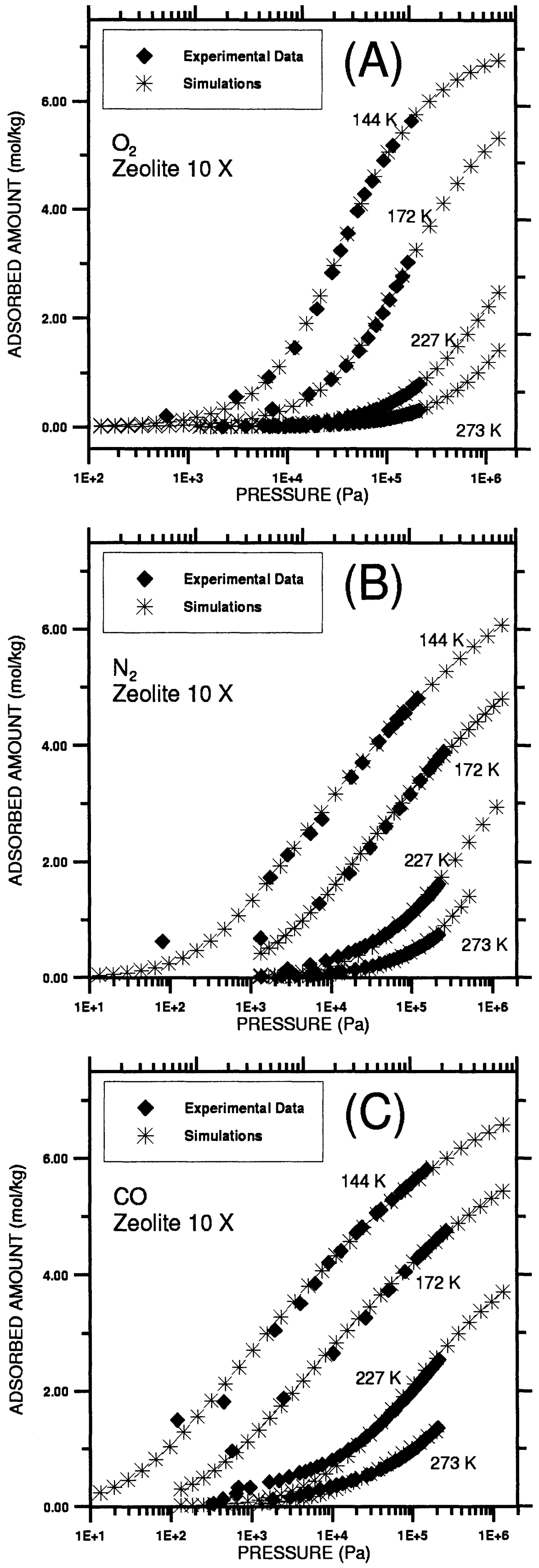

**Figure 3. Adsorption isotherms of (A) $O_2$, (B) $N_2$, and (C) CO on zeolite 10X.**

Equation 12 relates the number of segments of the molecules ($m_{\text{propane}}$ and $m_{CO_2}$) with their molecule diameters ($\sigma_{\text{propane}}$ and $\sigma_{CO_2}$). In this equation, "round" represents the round-off to the nearest integer. From doing this calculation, the value 4 was obtained for the number of propane-molecule segments. The amount of propane adsorbed at infinite pressure was calculated using the following equation

$$N^{\infty}_{\text{propane}} m_{\text{propane}} = N^{\infty}_{CO_2} m_{CO_2} = N^{\infty}_{H_2S} m_{H_2S} \qquad (13)$$

H-Mordenite is characterized by having two elliptic channels of different dimensions. The main channels have a maximum diameter of 7.0 Å and a minimum diameter of 6.5 Å. The secondary channels have diameters of 4.7 and 3.9 Å. The molecule diameters of $CO_2$, $H_2S$, and propane are 3.3, 3.6 and 4.3 Å, respectively. Therefore, the main channels are accessible to all of the molecules, but the secondary channels (65% in area) are accessible only to the molecules of the $CO_2$ and $H_2S$. For this reason, the surface was modeled by a random distribution of square grains of dimension $Dg = 4$ and a fraction of active sites $\nu_a = 0.35$. The Henry constant of propane in nonactive sites was set equal to $K_b = 1.0 \times 10^{-8}$ kPa$^{-1}$. This procedure requires that propane molecules adsorb exclusively on the active sites.

Initially, the four parameters of the $CO_2$ molecule ($K_b$, $\omega/kT$, $r_a$, and $N^{\infty}$) were fitted. Next, the three parameters ($K_b$, $\omega/kT$, and $r_a$) of the $H_2S$ molecule were fitted. The amount of $H_2S$ adsorbed at infinite pressure ($N^{\infty}_{H_2S}$) was determined by Eq. 13. Finally, the propane parameters $\omega/kT$ and $r_a$ were obtained by the fitting procedure. The parameter $K_b$ had been fixed previously, and the amount adsorbed at infinite pressure ($N^{\infty}_{\text{propane}}$) was also calculated by Eq. 13. Table 2 presents the values of parameters obtained in the fitting.

Figure 4 shows the results of isotherm diagrams of the three pure components.

## Binary Mixtures

The results of the predicted behavior of adsorbed binary mixtures are presented in two diagrams. The first diagram presents the mole fraction of component 1 in the gas phase ($y_1$) as a function of the mole fraction of component 1 in the adsorbed phase ($x_1$), and the second diagram presents the adsorbed amount vs. the mole fraction of component 1 in the adsorbed phase ($x_1$).

For each simulated point, $1 \cdot 10^6$ Monte Carlo steps were performed to allow the system to reach equilibrium. The average properties of the system were computed to each $10^5$ steps. This procedure was repeated 10 times, for different

**Table 2. Parameters for System 2: Propane, $H_2S$, and $CO_2$ Adsorbed on H-Mordenite at a Temperature of 303 K**

| T(K) Substance | Parameters |  |  |  |
|---|---|---|---|---|
|  | $K_b$ (Pa$^{-1}$) | $\omega/kT$ | $r_a$ | $N^{\infty}$ (mol/kg) |
| Propane | $1.0 \times 10^{-8}$ | −6.4975 | 69.4983 | 8.2612 |
| $CO_2$ | $1.7321 \times 10^{-2}$ | −4.9145 | $1.0677 \times 10^{-1}$ | 11.0149 |
| $H_2S$ | $1.6408 \times 10^{-1}$ | −4.6862 | $4.1198 \times 10^{-3}$ | 11.0149 |

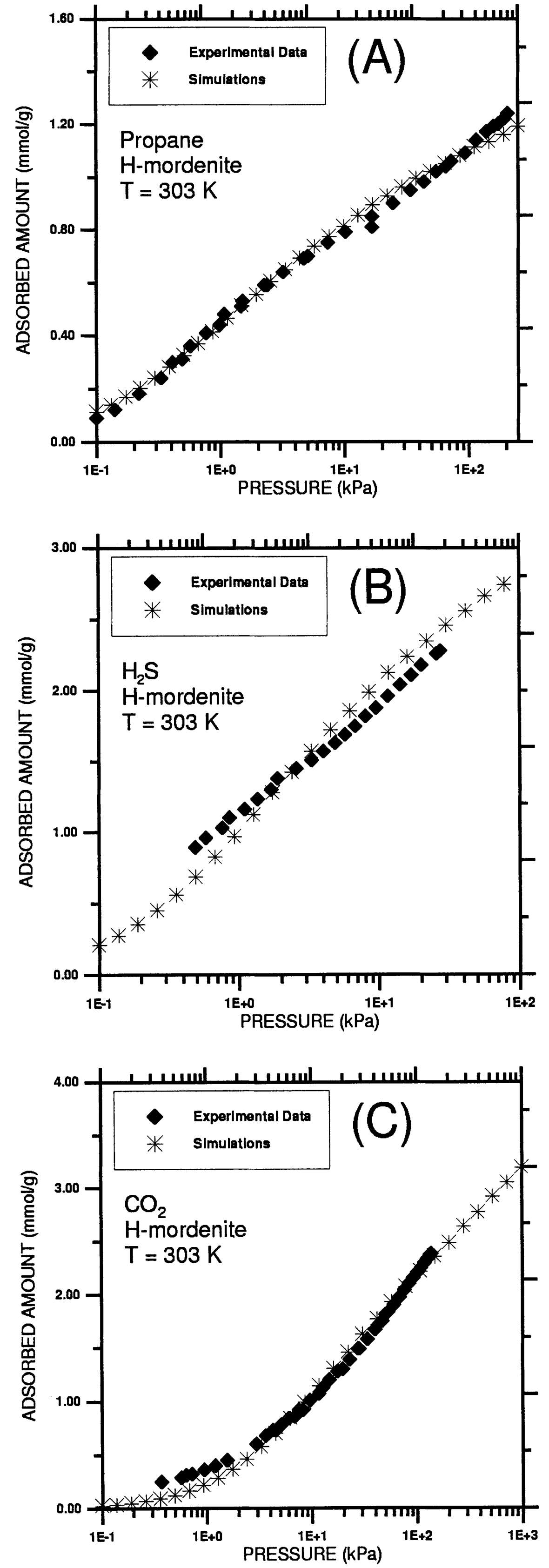

**Figure 4. Adsorption isotherms of (A) propane, (B) $H_2S$, and (C) $CO_2$ on H-mordenite.**

randomly generated solids with the same fraction of active sites and the same dimension ($Dg = 1$ for zeolite 10X, and $Dg = 4$ for H-mordenite). The global average and the standard deviation of the properties, in each point, were calculated using the 100 average values obtained.

The proposed simulation model needs combining and mixing rules, in the same fashion as an equation of state applied to the determination of the PVT properties of a gas mixture. The following mixing rule was used to determine the amount of mixture adsorbed at infinite pressure ($N_{\text{mix}}^{\infty}$)

$$\frac{1}{N_{\text{mix}}^{\infty}} = \sum_{i=1}^{nc} \frac{x_i}{N_i^{\infty}} \tag{14}$$

where $N_i^{\infty}$ is the amount of component $i$ adsorbed at infinite pressure and $x_i$ is the mole fraction of component $i$ in the adsorbed phase. Equation 14 is obtained using the following reasoning: at infinite pressure, the excess area is equal to zero and the area occupied by each pure component is equal to the area occupied by the mixture in the infinite pressure. In this way

$$A_{\text{mix}}^{\infty} = A_i^{\infty} = A_{i+1}^{\infty} = \ldots = A_{nc}^{\infty} \tag{15}$$

and

$$\frac{A_{\text{mix}}^{\infty}}{N_{\text{mix}}^{\infty}} = A_{\text{mix}}^{\infty} \sum_{i=1}^{nc} \frac{x_i}{N_i^{\infty}} \tag{16}$$

The following combining rule, suggested by Romanielo (1991), was used to calculate the cross-contact energy ($\omega_{ki}/kT$)

$$\frac{\omega_{ki}}{kT} = \frac{(m_k m_i)^{1/2}}{kT} \left( \frac{\omega_{kk} + \omega_{ii}}{m_k + m_i} \right) \tag{17}$$

### *Binary mixtures of $O_2$, $N_2$, and CO adsorbed on zeolite 10X*

Danner and Wenzel (1969) and Nolan et al. (1981) studied the binary mixtures of $O_2$–$N_2$, $O_2$–CO, and $N_2$–CO adsorbed on zeolite 10X at 101.32 kPa and temperatures of 144, 172, 227 and 273 K. The three binary mixtures present similar characteristics. All mixtures exhibit nearly ideal behavior.

*Mixture $O_2(1)$–$N_2(2)$ at a Pressure of 101.32 kPa.* The mixture $O_2(1)$–$N_2(2)$, at temperatures of 144, 172, 227 and 273 K, presents a selective adsorption of $N_2$ with respect to $O_2$, which is more pronounced in the region of high oxygen concentration in the gaseous phase. The diagrams of phase equilibrium of this mixture are similar at all of the temperatures, except 144 K. In this condition, in contrast with the behavior of the system at the other temperatures, the total adsorbed amount increases with the increase in the oxygen concentration of, as shown in Figure 5b. The simulations provide satisfactory predictions for the $O_2$–$N_2$ mixture, as can be observed in Figure 5.

*Mixture $O_2(1)$–$CO(2)$ at a Pressure of 101.32 kPa.* The $O_2(1)$–$CO(2)$ mixture adsorbed on zeolite 10X at temperatures of 144, 172, 227 and 273 K is characterized by an adsorption of CO much larger than that of $O_2$. In all of the

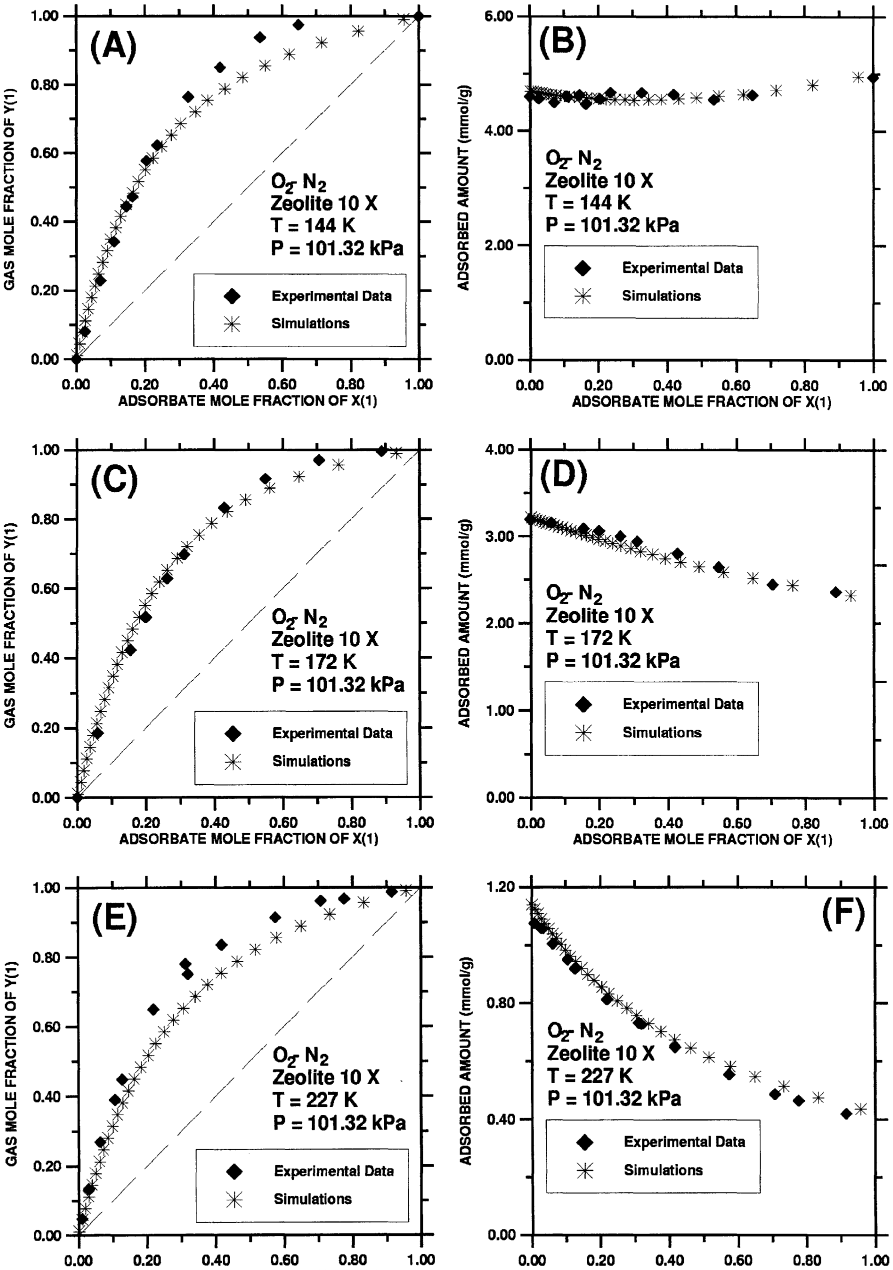

**Figure 5. (A, C, E) Phase-equilibrium diagrams and (B, D, F) of total adsorbed amount for the mixture $O_2$(1)–$N_2$(2) on zeolite 10X at 101.32 kPa and the temperatures of 144, 172, 227 K.**

analyzed conditions, the total amount adsorbed decreases with the increase in the mole fraction of oxygen.

All of the simulations predict the behavior of the $O_2$(1)–CO(2) mixture at the temperatures studied (Figure 6). The best results are obtained at the temperatures of 227 and 273 K, where there is an almost quantitative prediction of the experimental data.

*Mixture $N_2$(1)–CO(2) at a Pressure of 101.32 kPa.* The binary $N_2$(1)–CO(2) mixture adsorbed on zeolite 10X presents the same characteristics as the previous mixture ($O_2$(1)–CO(2)), that is, nitrogen adsorbs less than CO, and the total amount adsorbed decreases with the increase in the composition of $N_2$, at all the four analyzed temperatures.

Again, the simulations represent the experimental behavior well (Figure 7). The largest deviations are found at the temperature of 227 K. However, the simulations continued to predict the phase-equilibrium diagrams qualitatively and the total adsorbed amount.

### *Binary mixtures of $H_2S$, $CO_2$, and propane adsorbed on H-mordenite*

Talu and Zwiebel (1986) obtained experimental data for the adsorption on H-mordenite of the binary gaseous mixtures of $CO_2$(1)–$H_2S$(2), propane(1)–$CO_2$(2), and propane(1)–$H_2S$(2) at 303 K adsorbed.

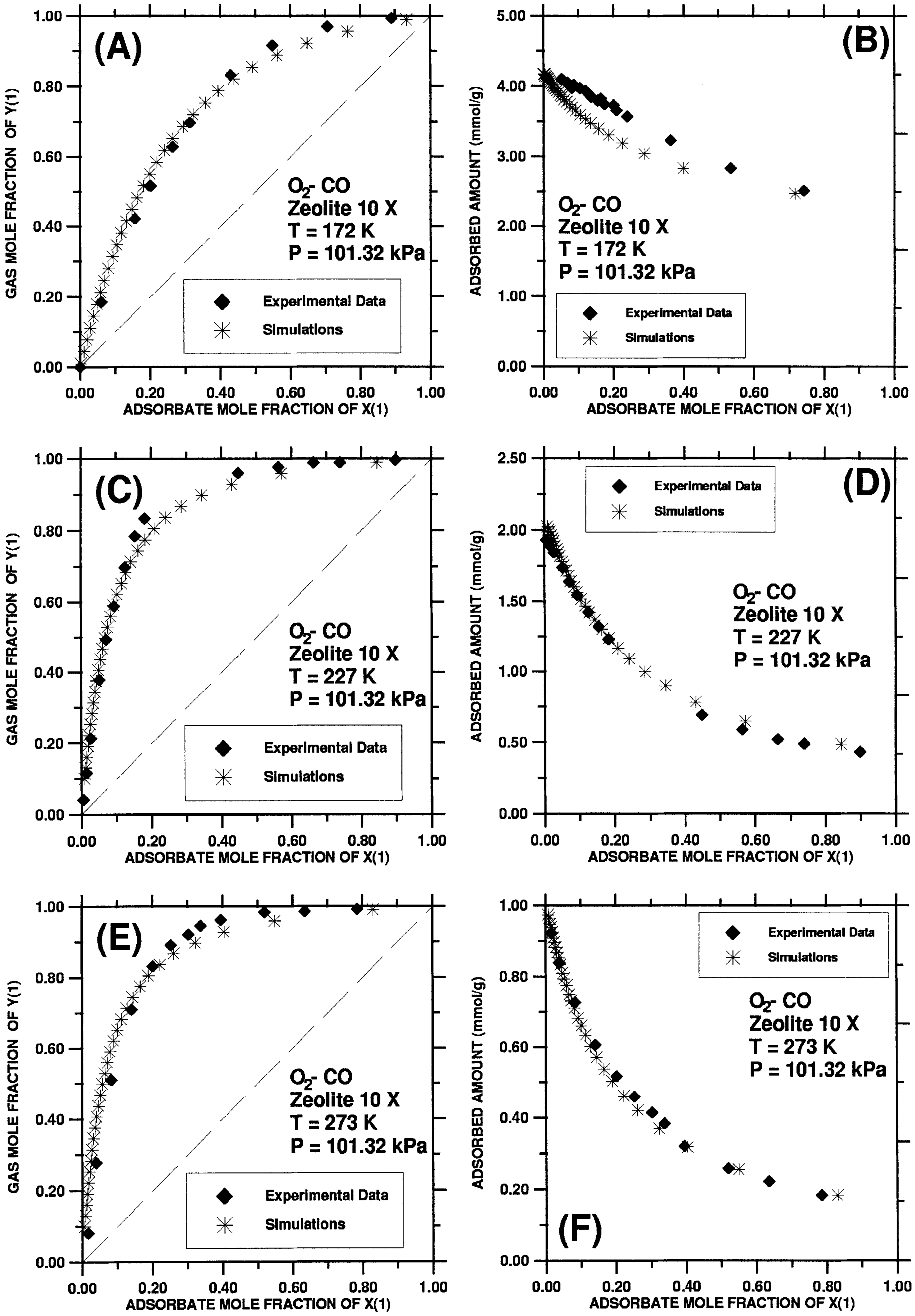

Figure 6. (A, C, E) Phase-equilibrium diagrams and (B, D, F) of total adsorbed amount for the mixture $O_2$(1)–CO(2) on zeolite 10X at 101.32 kPa and the temperatures of 172, 227, 273 K.

*Mixture $CO_2(1)-H_2S(2)$ at a Pressure of 15.5 kPa.* The $CO_2(1)-H_2S(2)$ mixture adsorbed on H-mordenite presents typical behavior of the ideal mixture in the adsorbed phase, where the $CO_2$ adsorbs less than the $H_2S$ and the total adsorbed amount decreases with the increase in the $CO_2$ composition.

The ideal-like behavior of this mixture was predicted by the simulations, as can be seen in Figure 8.

*Mixture Propane(1)$-CO_2(2)$ at a Pressure of 40.93 kPa.* This mixture presents a strong nonideality effect characterized by the occurrence of a maximum in the curve of the total amount adsorbed vs. the mole fraction of component 1×(1) and also by the inversion of selectivity exhibited in the phase diagram. The simulations (Figure 9) predict this azeotropy and the maximum in the curve of the total adsorbed amount. The largest deviations are found in this last diagram. In this study, the results are all predictive, that is, without the use of binary interaction parameters. Should these be used, the calculations would lose their predictive character, but better results might be obtained.

*Mixture Propane(1)$-H_2S(2)$ at a Pressure of 8.13 kPa.* As in the previous case, this mixture also presents a strong non-

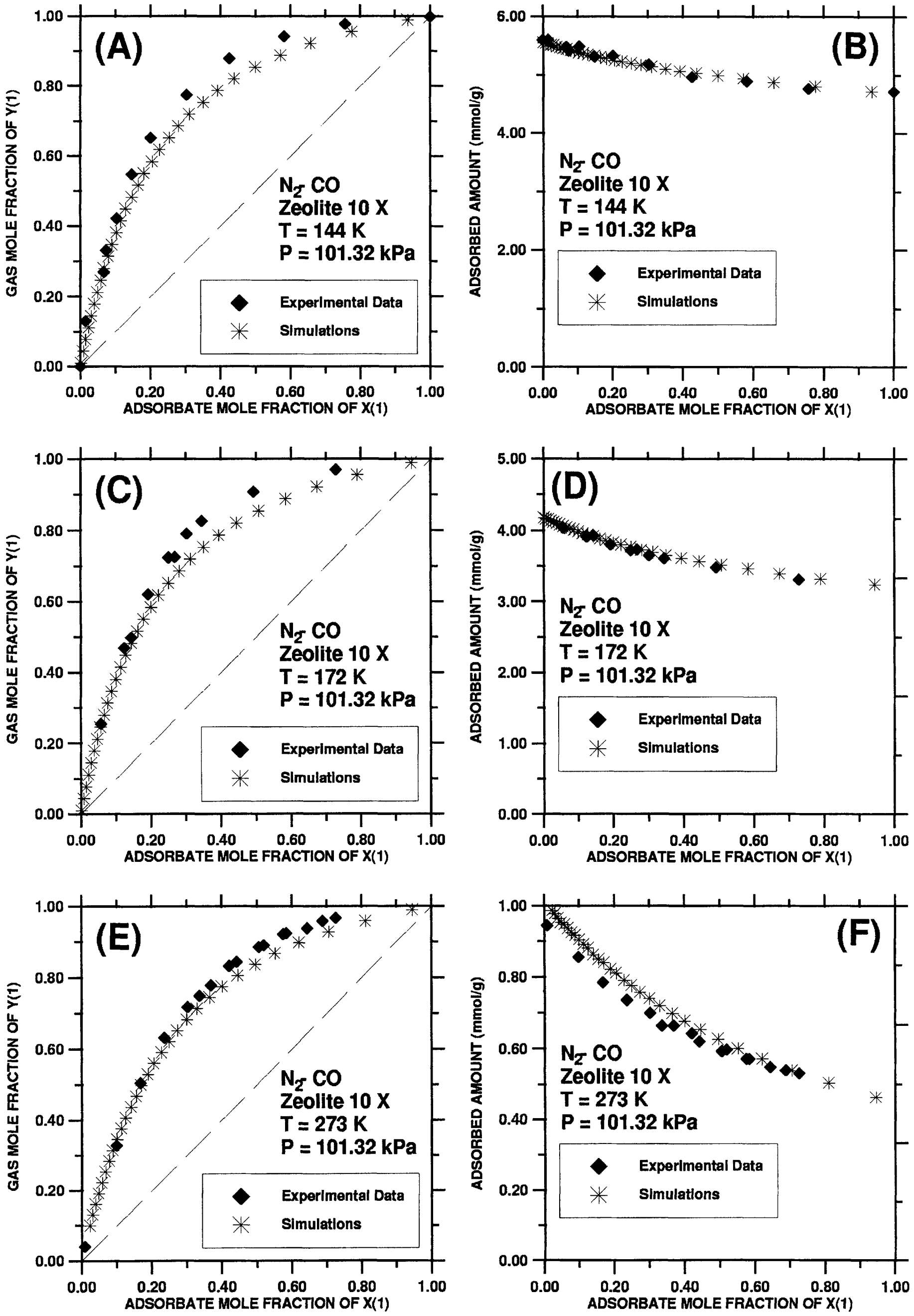

Figure 7. (A, C, E) Phase-equilibrium diagrams and (B, D, F) of total adsorbed amount for the mixture $N_2$(1)–CO(2) on zeolite 10X at 101.32 kPa and the temperatures of 144, 172, 273 K.

ideality effect with the same characteristics as the previous mixture. Again, the simulations (Figure 10) predict the behavior of the mixture. The largest deviations are found in the prediction of the total adsorbed amount, which is overpredicted.

## Ternary Mixture

The results of the predicted behavior of adsorbed ternary mixtures of propane–$H_2S$–$CO_2$ at 13.35 kPa and 303 K are presented in Figure 11. This figure contains a comparison between the experimental and calculated mole fraction of each component adsorbed in H-mordenite for different vapor compositions. The simulations are in good agreement with the experimental data.

## Conclusions

In this work, a new methodology was proposed for correlating the adsorption of pure components and for predicting the adsorption of binary mixtures in homogeneous and heterogeneous solids. This methodology used the Monte Carlo

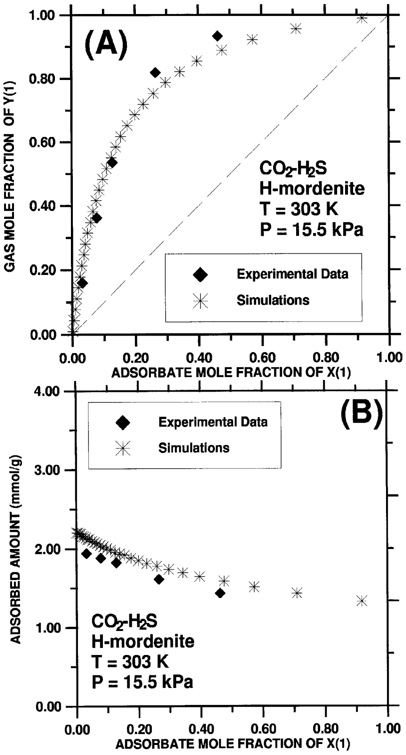

Figure 8. (A) Phase-equilibrium diagrams and (B) of total adsorbed amount for the mixture $CO_2$(1) $H_2S$(2) on H-mordenite at 15.5 kPa and 303 K.

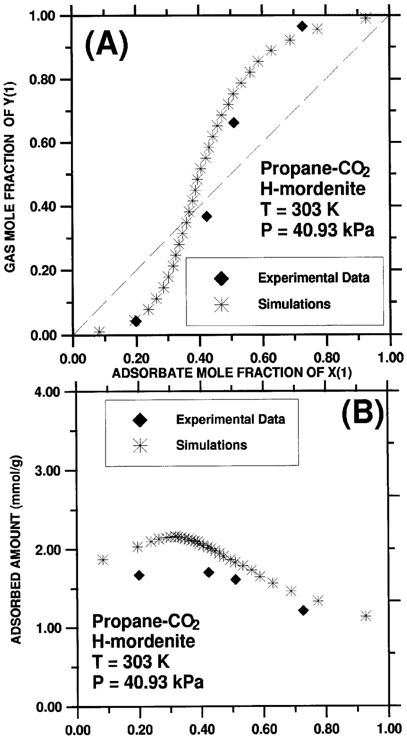

Figure 9. (A) Phase-equilibrium diagrams and (B) of total adsorbed amount for the mixture propane(1)–$CO_2$(2) on H-mordenite at 40.93 kPa and 303 K.

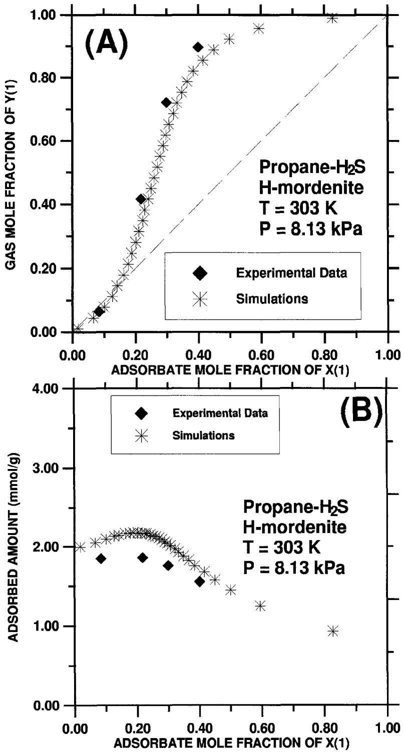

Figure 10. (A) Phase-equilibrium diagrams and (B) of total adsorbed amount for the mixture propane(1)–$H_2S$(2) on H-mordenite at 8.13 kPa and 303 K.

algorithm of molecular simulation for a grand canonical ensemble as an equation of state of the adsorbed phase.

In the case of pure components, the simulations correlated the studied systems very well. The parameter-fitting procedure was affected, probably by the absence of experimental data in certain pressure ranges. For example, in the adsorption of $H_2S$ on H-mordenite (Figure 4b), the lack of experi-

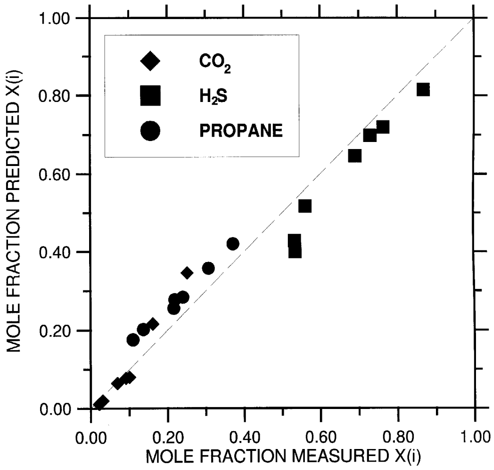

Figure 11. Ternary mixtures on H-mordenite, data of Talu and Zwiebel (1986); predicted mole fractions are obtained by simulations.

mental data in both the low and higher pressure ranges decreases confidence in the estimated values of the Henry constant and of the amount adsorbed at infinite pressure.

In the case of the adsorption of multicomponent mixtures, the simulations predict the behavior of all systems studied. The knowledge of microscopic information about the solid structure facilitates an understanding of the nonideal behavior presented by the binary mixtures of $H_2S$–propane and $CO_2$–propane. This type of information was one of the factors that allowed the quite reasonable results for adsorption in those systems to obtained. Although a large amount of information of this type exists in the literature, models that use this information are still scarce. Therefore, this technique makes the thermodynamic model more microscopic and provides parameters with a clearer physical meaning.

## Acknowledgments

This work was supported by CNPq, FAPERJ, and by PRONEX (Grant No. 124/96) (Brazilian Federal Government).

## Literature Cited

Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford Univ. Press, Oxford (1987).

Bulnes, F., A. J. Ramirez-Pastor, and V. D. Pereyra, "Study of Adsorption of Binary Mixtures on Disordered Substrates," *J. Mol. Catal. A: Chem.*, **167**, 129 (2001).

Danner, R. P., and L. A. Wenzel, "Adsorption of Carbon Monoxide-Nitrogen, Carbon Monoxide-Oxygen, and Oxygen-Nitrogen Mixtures on Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

Hill, T. L., *An Introduction to Statistical Thermodynamics*, Addison-Wesley, London (1960).

Macedonia, M. D., and E. J. Maginn, "Pure and Binary Component Sorption Equilibria of Light Hydrocarbons in the Zeolite Silicalite from Grand Canonical Monte Carlo Simulations," *Fluid Phase Equilib.*, **160**, 19 (1999).

Martinez, G. M., and D. Basmadjian, "Towards a General Gas Adsorption Isotherm," *Chem. Eng. Sci.*, **51**, 1043 (1996).

Nitta, T., M. Kuro-Oka, and T. Katayama, "An Adsorption Isotherm of Multi-Site Occupancy Model for Heterogeneous Surface," *J. Chem. Eng. Jpn.*, **17**, 45 (1984).

Nitta, T., H. Kiriyama, and T. Shigeta, "Monte Carlo Simulation Study for Adsorption of Dimers on Random Heterogeneous Surfaces," *Langmuir*, **13**, 903 (1997).

Nolan, J. T., T. W. Mckeehan, and R. P. Danner, "Equilibrium Adsorption of Oxygen, Nitrogen, Carbon Monoxide, and Their Binary Mixtures on Molecular Sieve Type 10X," *J. Chem. Eng. Data*, **26**, 112 (1981).

Ramirez-Pastor, A. J., M. S. Nazzaro, J. L. Riccardo, and G. Zgrablich, "Dimer Physisorption on Heterogeneous Substrates," *Surf. Sci.*, **341**, 249 (1995).

Ramirez-Pastor, A. J., V. D. Pereyra, and J. L. Riccardo, "Adsorption of Linear k-mers on Heterogeneous Surfaces with Simple Topographies," *Langmuir*, **16**, 682 (2000).

Romanielo, L. R., *Adsorção de Gases Multicomponentes*, MSc Thesis, PEQ/COPPE, Univ. Federal do Rio de Janeiro, Rio de Janeiro, Brazil (1991).

Siperstein, F. R., and A. L. Myers, "Mixed Gas-Adsorption," *AIChE J.*, **47**, 1141 (2001).

Steele, W., "Computer Simulations of Physical Adsorption: A Historical Review," *Surf. Appl. Sci.*, **7820**, 1 (2002).

Talu, O., and I. Zwiebel, "Multicomponent Adsorption Equilibria of Nonideal Mixtures," *AIChE J.*, **32**, 1263 (1986).

Ustinov, E. A., D. D. Do, A. Herbst, R. Staudt, and P. Harting, "Modeling of Gas Adsorption Equilibrium Over a Wide Range of Pressure: A Thermodynamic Approach Based on Equation of State," *J. Colloid Interface Sci.*, **250**, 49 (2002).

Vlugt, T. J. H., B. Smit, and R. Krishna, "Molecular Simulation of Adsorption Isotherms for Linear and Branched Alkanes and their Mixtures in Silicalite," *J. Phys. Chem. B*, **103**, 1102 (1999).

*Manuscript received Dec. 27, 2001, and revision received Aug. 27, 2002.*