

MONTE CARLO SIMULATION OF BINARY MIXTURES ADSORBED ON HETEROGENEOUS SURFACES

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Abstract – Most of the solids used in adsorption processes are heterogeneous and most isotherm models are not derived to use information about the solid structure and energy heterogeneity. A possible alternative is to use molecular simulation techniques, which turn the thermodynamic model more microscopic. Then, starting from information on the solid structure, it is possible to develop appropriate solid models for each type of real system. Therefore, the objective of this work is to use the grand canonical Monte Carlo technique of molecular simulation for correlating pure-component data and predicting adsorption of multicomponent mixtures. To decrease the computational effort, we use a simplified solid model that is represented by a two-dimensional square lattice. The solid heterogeneity is represented by a random distribution of different kinds of sites, characterized by distinct energy levels. The methodology developed by Cabral *et al.* (2003a) is used here to correlate pure components and for predicting binary mixtures of ethane, ethylene, isobutane, and carbon dioxide on zeolite 13X with good results.

Keywords – Monte Carlo Simulation, Adsorption, Heterogeneous Solids.

I. INTRODUCTION

Most solids existing in nature are inevitably heterogeneous, i.e., they have a distribution of pores with different shapes and sizes. The heterogeneity of an adsorbent is characterized by an energy distribution of active sites with distinct values for interactions between adsorbent and adsorbate. This energetic heterogeneity plays a major role in adsorption equilibrium, as in the selective adsorption of propane from a propane-carbon dioxide mixture on H-mordenite (Talu and Zwiebel, 1986). In this way, techniques or methodologies capable of taking this feature into account can be important for a better understanding of adsorption phenomena. Recently, adsorption of chain-like molecules on heterogeneous surface has been studied in the framework of the lattice gas model and molecular simulations (Nitta *et al.*, 1997; Ramirez-Pastor *et al.*, 1999, 2000; Borowko and Rzyzsko, 2001, 2003; Cabral *et al.*, 2003a, 2003b). In fact, the use of molecular simulation has increased because of progresses in computer science and in hardware technology. For example, Ramirez-Pastor *et al.* (2000) used Monte

Carlo simulations to study the adsorption of non-interacting homonuclear k-mer molecules on heterogeneous surfaces. These authors modeled the heterogeneous surface by using two kinds of sites. Sites were formed by square patches randomly distributed (or in a chessboard-like domain) on a two-dimensional square lattice. Grand canonical Monte Carlo simulations were used by Borowko and Rzyzsko (2003) to study the phase behavior of heteronuclear dimers adsorbed on heterogeneous surfaces. The dimers were composed of two types of segments. These authors considered a surface composed of alternating strips of non-interacting and attractive sites arranged on a square lattice. Rzyzsko and Borowko (2003) estimated the adsorption isotherms, phase diagrams and critical parameters. It is shown that surface heterogeneity markedly affects the adsorption and phase behavior of the films. The impact of surface topography on critical characteristics was also analyzed. Of special interest was the finding that these systems do not belong to the two-dimensional Ising class of universality. Cabral *et al.* (2003a) proposed a new methodology for correlating the adsorption of pure components and for predicting the adsorption of binary and ternary mixtures on homogeneous and heterogeneous solids. The methodology proposed by the authors uses the algorithm of molecular simulation in the grand canonical ensemble as an equation of state for the adsorbed phase. The results obtained for the adsorption of the binary mixtures of propane-CO₂ and propane-H₂S, which are strongly non-ideal, were quite satisfactory showing the potential of this technique for the description of real systems. A historical review of application of computer simulation to adsorption phenomena, especially for two-dimensional systems, has been published elsewhere (Steele, 2002).

In this paper, we use the methodology of Cabral *et al.* (2003a) to correlate the adsorption of pure components and for predicting the adsorption of binary mixtures of ethane, ethylene, isobutane and carbon dioxide on zeolite 13X (experimental data are taken from Hyun and Danner, 1982). Here, the simulations are performed on a two-dimensional square lattice in which the solid heterogeneity is represented by the existence of three kinds of sites, characterized by distinct adsorption energies. For a specific fraction of active sites, several topologies can be generated, each of them characterized by a random distribution of square grains of specific sizes.

II. MONTE CARLO SIMULATION

In this work, the Monte Carlo technique is used to simulate the adsorption of chainlike molecules on heterogeneous surfaces. Here, we present just a summary of the used methodology; Monte-Carlo-simulation details are reported elsewhere (Cabral *et al.*, 2003a).

The lattice gas model is used and, therefore, each molecular segment occupies one site of the solid surface. 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 to each of them, named coordination number (Z); (3) the adsorption energy between a molecular segment and a site of the solid (ϵ); (4) the number of segments of each molecule (m); and (5) the interaction energy between two adsorbed segments in neighboring sites (ω). The Monte Carlo method for a grand canonical ensemble (T , M , μ_1 , μ_2, \dots , μ_{nc} specified), consists of three basic movements (Allen and Tildesley, 1987; Frenkel and Smit, 2002): displacement, insertion, and removal of an adsorbed molecule. The transition probability from a configurational state o to a new state n is expressed by

$$P_{o \rightarrow n} = \min \left\{ 1, \frac{\rho_n}{\rho_o} \right\} \quad (1)$$

where ρ_n/ρ_o is the ratio between the probability densities of the configurational states n and o . The movement is accepted if such probability $\rho_{o \rightarrow n}$ is larger than a number randomly generated between 0 and 1. Next, the ratio between the probability densities of each kind of movement is presented.

A. Displacement Movement

The adsorbed molecule that will be moved is randomly chosen. One end of the molecule is chosen randomly to be the "head", while the other is the "tail". The head is moved to one of its neighbor sites, randomly chosen, all the other segments move one site along the chain, and the tail position becomes vacant. This type of motion is termed "reptation". If the site chosen is occupied, the movement is rejected. If the displacement is possible, the ratio between the probability densities of the new (n) and the old (o) states is given by:

$$\frac{\rho_n}{\rho_o} = \exp \left[-\frac{(U_n - U_o)}{kT} \right] \quad (2)$$

where T is the temperature, k is Boltzmann's constant, and U_o and U_n are the configurational energies of states o and n respectively.

B. Insertion Movement

A position is randomly chosen to place the first segment of the molecule and, also randomly, the others segments are sequentially added to neighboring sites. Next, the energy of this new configuration is computed and the

ratio between the probability densities of the new (n) and old (o) states is calculated by:

$$\frac{\rho_n}{\rho_o} = \frac{M}{N_i + 1} \exp \left[\frac{\mu_i}{kT} - \frac{(U_n - U_o)}{kT} \right] \quad (3)$$

where N_i is the total number of molecules of the component i adsorbed in the old state and μ_i is the chemical potential of such component.

C. Removal Movement

One molecule is randomly chosen and removed. Then, the energy of this new configuration is calculated and the ratio between probability densities of the new (n) and old (o) states is computed by:

$$\frac{\rho_n}{\rho_o} = \frac{N_i}{M} \exp \left[-\frac{\mu_i}{kT} - \frac{(U_n - U_o)}{kT} \right] \quad (4)$$

The configurational energy of the state o can be obtained by:

$$U_o = -\sum_{i=1}^{nc} \sum_{j=1}^{ns} N_{ij}^{(o)} \epsilon_{ji} - \frac{1}{2} \sum_{i=1}^{nc} \sum_{j=1}^{nc} N_{c_{ij}}^{(o)} \omega_{ij} \quad (5)$$

where $N_{ij}^{(o)}$ is the number of segments i adsorbed on sites j , ϵ_{ij} is the adsorption energy between them, $N_{c_{ij}}^{(o)}$ is the number of contacts between adsorbed segments i and j , ω_{ij} is the interaction energy between segments i and j adsorbed in neighboring sites, nc is the number of adsorbed components, and ns is the number of kinds of sites.

III. SOLID MODEL

In this work, the solid is modeled as a square lattice of dimension 100×100 ($M = 10,000$), and its heterogeneity is represented by the existence of three kinds of sites, characterized by energies ϵ_a , ϵ_b and ϵ_c . We choose c as a background site. For every fraction of active sites (v_a and v_b), several topologies can be generated, each one characterized by a random distribution of square grains of each kind of site over the solid matrix. Fig. 1 shows an example of a square lattice with $v_a = 0.15$ and $v_b = 0.10$ with the same grain dimension, equal to $D_g = 3 \times 3$. In order to minimize the effect of the solid size, periodic boundary conditions are considered in the lattice, for both the grains and the adsorbed molecules.

IV. PARAMETER FITTING

The parameters of the model for a pure adsorbed component are the Henry constant of the adsorption in the background sites (K_{ci}); the amount adsorbed at infinite pressure (N_i^{∞}); parameters r_{ai} and r_{bi} , related to the surface heterogeneity; and the interaction energy between two segments adsorbed in neighbor sites (ω_{ij}/kT).

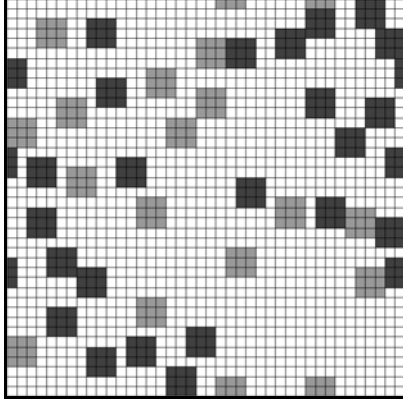


Figure 1. Illustrative diagram of a 40x40 square lattice with $\nu_a = 0.15$ (dark grey) and $\nu_b = 0.10$ (light grey) randomly distributed in grains with dimension $Dg = 3 \times 3$.

Parameter N_i^∞ is introduced to relate the covering fraction (θ) obtained from molecular simulations to the total amount adsorbed obtained from experimental data. Parameters r_{ai} and r_{bi} are related to the energetic heterogeneity of the solid. Parameters N_i^∞ , r_{ai} , and r_{bi} are given by:

$$N_i^{\text{ads}} = \theta N_i^\infty \quad (6)$$

$$r_{ai} = \exp\left[\frac{(\varepsilon_{ai} - \varepsilon_{ci})}{kT}\right]; \quad r_{bi} = \exp\left[\frac{(\varepsilon_{bi} - \varepsilon_{ci})}{kT}\right] \quad (7) \text{ and } (8)$$

Therefore, with the obtained parameters ε_{ci} , r_{ai} and r_{bi} (as explained later), the adsorption energies (ε_{ai} and ε_{bi}) between a site and a adsorbed molecule segment is determined using Eqs. (7) and (8). For fitting the parameters above described, the subroutine UMPOL of the ISML library is used. This subroutine minimizes a multivariable function using a direct search algorithm. The objective function used for parameter fitting is the least-square function related to deviations in the adsorbed amount:

$$\text{FOBJ} = \sum_{j=1}^{\text{np}} (N_j^{\text{exp}} - N_j^{\text{simul}})^2 \quad (9)$$

where, np is the number of points simulated and N_j^{exp} and N_j^{simul} are the adsorbed amount obtained from experiments and simulations, respectively. Next, we present the strategies used to fit these parameters.

A. Adsorption of Pure Ethane, Ethylene, Isobutane, and CO₂ on zeolite 13 X

The size of each molecule on the two-dimensional structure is actually arbitrary. In order to give a linear shape for carbon dioxide, we assume $m_{\text{CO}_2} = 2$. Because the molecular volumes of ethane and ethylene are roughly the same as that of CO₂, we use $m_{\text{ethane}} = 2$

and $m_{\text{ethylene}} = 2$. Using a similar argument, isobutane volume ratio is modeled with 3 segments, i.e., $m_{\text{isobutane}} = 3$. The faujasite structure (zeolite 13X) has large cavities, of about 12 Å in diameter (supercage), connected by windows about 8 Å wide. According to Hyun and Danner (1982), faujasite's unit cell is cubic with size of around 25 Å. We consider three kinds of sites. The sites of type "a" represent the area for adsorption available in the supercage of a zeolite 13X, whose fraction (ν_a) is

$$\nu_a = \left(\frac{V_{\text{supercage}}}{V_{\text{unit cell}}}\right)^{\frac{2}{3}} \cong 0.15 \quad (10)$$

where $V_{\text{supercage}}$ is the volume occupied by the supercage in the structure of the zeolite 13X and $V_{\text{unit cell}}$ is the volume of the unit cell. The ratio in Eq. (10) is raised to an empiric factor of 2/3 trying to consider a dimensional change from three- to two-dimensional structure. The fraction of sites of type "b" is calculated based on the adsorption experimentally observed for CO₂. This molecule adsorbs, at infinite pressure, more than ethane and ethylene at the same temperature. To be consistent with the constraint $m_{\text{CO}_2} = m_{\text{ethane}} = m_{\text{ethylene}}$, carbon dioxide should access a part of the solid that is inaccessible for ethane and ethylene. This area is assumed to be equal to 30% of the total area available for adsorption, i.e., $\nu_b = 0.3$. In order to impose that this fraction of the solid will be inaccessible for ethane, ethylene, and isobutane, the parameter r_{bi} is set equal to 10^{-30} for these components. For CO₂, r_{bi} is set equal to unity, i.e., this type of site acts as a background site for CO₂. The sites of types "a" and "b" are grouped in square grains of dimension $Dg = 3$. For ethane, parameters K_{ci} , ω_{ij}/kT , r_{ai} and N_i^∞ are fitted at each temperature. Next, the amounts adsorbed at infinite pressure (N_i^∞) of all molecules are calculated using the segment-balance equation (Eq.(11)), which imposes that all pure components occupy all the adsorbent surface at infinite pressure.

$$\begin{aligned} N_{\text{ethane}}^\infty m_{\text{ethane}} &= N_{\text{ethylene}}^\infty m_{\text{ethylene}} = \\ N_{\text{CO}_2}^\infty m_{\text{CO}_2} &= N_{\text{isobutane}}^\infty m_{\text{isobutane}} \end{aligned} \quad (11)$$

Then, for CO₂, ethylene, and isobutane, three parameters are fitted (K_{ci} , ω_{ij}/kT , r_{ai}) at each temperature (Table 1).

Fig. 2 shows a comparison of adsorption isotherms obtained from simulations with those from experiments for ethane and isobutane on zeolite 13X at several temperatures. The good results presented in this figure for ethane and isobutane confirm the high correlation performance of the procedure proposed here. Similar results are obtained for ethylene and carbon dioxide, not shown here for the sake of conciseness.

Table 1. Parameters for ethane, ethylene, isobutane and carbon dioxide adsorbed on zeolite 13 X.

Molecule	Parameters					
	T (K)	K_{ci} (Pa ⁻¹)	N_i^∞ (kmol/kg)	r_a	r_b	ω/kT
Ethane	273	0.02460	4.5019	2.1283	10 ⁻³⁰	0.3918
	298	0.01364	4.6917	1.5619	10 ⁻³⁰	0.1863
	323	0.00503	4.5770	1.5543	10 ⁻³⁰	0.2660
Isobutane	298	4.4382	3.1280	0.7456	10 ⁻³⁰	-0.1740
	323	3.1022	3.0513	0.3979	10 ⁻³⁰	-0.3002
	373	0.1600	3.0214	0.7012	10 ⁻³⁰	-0.1516
Ethylene	298	0.1516	4.6917	2.1826	10 ⁻³⁰	0.07071
	323	0.04571	4.5770	1.8749	10 ⁻³⁰	0.01626
	373	0.00538	4.5321	3.0918	10 ⁻³⁰	0.07277
CO ₂	298	0.1033	4.6917	1.7215	1.0	-0.08175
	323	0.03036	4.5770	2.0498	1.0	-0.03829

V. PREDICTIVE ADSORPTION CALCULATIONS: BINARY MIXTURES

Results of predictive calculations of binary adsorption of several mixtures are analyzed and presented in two types of diagrams. The first diagram presents the mole fraction of component 1 in the gas phase (Y_1) as a function of its mole fraction in the adsorbed phase (X_1), and the second diagram presents the adsorbed amount versus the mole fraction of component 1 in the adsorbed phase (X_1).

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

$$\frac{1}{N_{mix}^\infty} = \sum_{i=1}^{nc} \frac{X_i}{N_i^\infty} \tag{12}$$

where N_i^∞ is the amount of component i adsorbed at infinite pressure and X_i is the mole fraction of component i in the adsorbed phase. Eq. (12) is obtained considering that 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 at infinite pressure. The following combining rule is used to calculate the cross-contact energy (Romanielo, 1991).

$$\frac{\omega_{ij}}{kT} = \frac{(m_i m_j)^{1/2}}{kT} \left(\frac{\omega_{ii} + \omega_{jj}}{m_i + m_j} \right) \tag{13}$$

For each simulated point, 1×10^6 Monte Carlo steps are calculated to allow the system to reach equilibrium. Each thermodynamic property is computed after 10^5 Monte Carlo steps. This procedure is repeated 10 times, for different randomly generated solids with the same fraction of a and b sites and the same dimension ($Dg = 3$). Then, average thermodynamic properties are computed.

Figs. 3 and 4 show a comparison of MC simulations and experimental data of isobutane(1)-ethylene(2) binary mixture at 137.8 kPa and temperatures of 298, 323, 373K. The methodology predicts the trends observed experimentally. For example, at low isobutane concentrations, isobutane adsorbs preferentially, especially at high temperature. At low temperature, there is an inversion in selectivity, and ethylene adsorbs preferentially at high isobutane concentration. The simulation procedure predicts not only the azeotropic behavior but also its disappearance at high temperature. The total amount absorbed is also reasonably well predicted by the simulations at all temperatures. This complex behavior presented by the isobutane-ethylene mixture is difficult to describe using a classical isotherm model, especially with a predictive strategy.

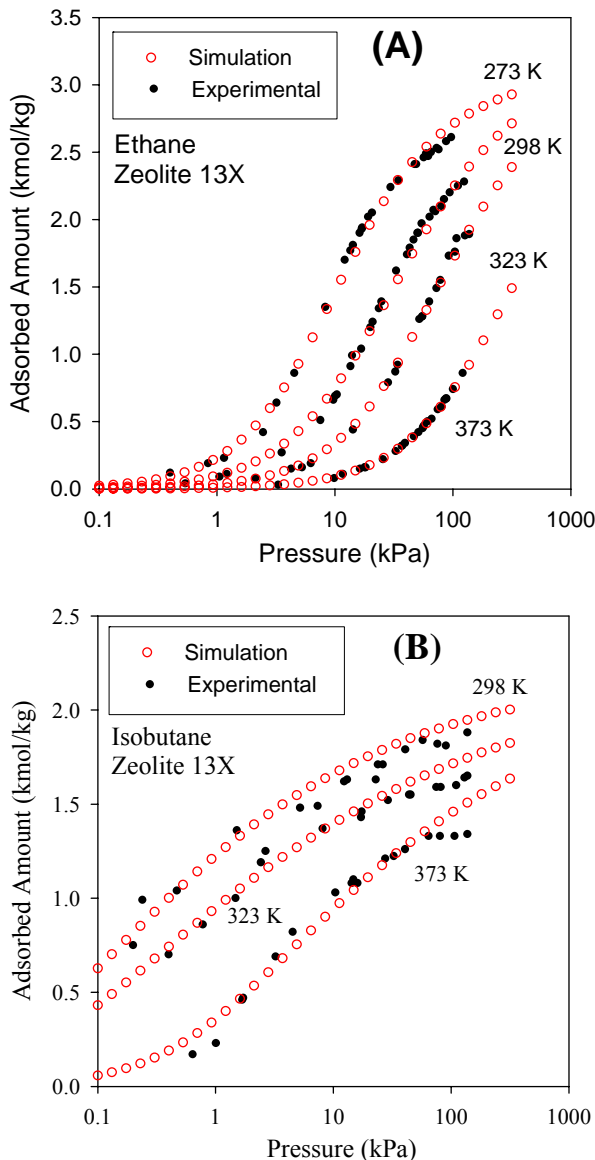


Figure 2. Adsorption isotherms for ethane (A) and for isobutane (B) on zeolite 13X at several temperatures.

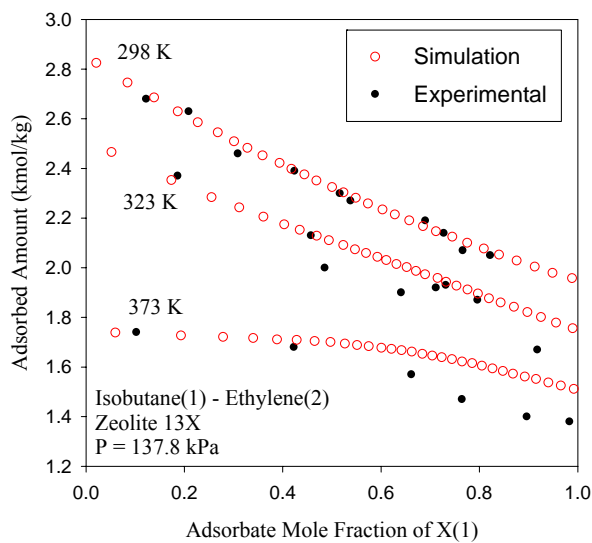


Figure 3. Total amount adsorbed for isobutane(1)–ethylene(2) on zeolite 13X at 137.8 kPa and temperatures of 298, 323, 373 K.

Figs. 5 and 6 show a similar comparison, MC simulations versus experiments, for isobutane(1)-ethane(2) binary mixture at 137.8 kPa and temperatures of 298 and 323 K. In this case, isobutane adsorbs preferentially in the entire concentration range, and at both temperatures. The proposed methodology predicts very well this adsorption selectivity. The total absorbed amount is also reasonably well predicted by the simulations at both temperatures. We have also compared the MC simulations with experimental data for ethylene-carbon dioxide mixtures. For the sake of conciseness, and because we observed very similar performance, we do not present these results.

VI. CONCLUSIONS

In this work, the methodology proposed by Cabral *et al.* (2003a) for correlating the adsorption of pure components and for predicting the adsorption of binary mixtures in homogeneous and heterogeneous solids is tested for different mixtures. This methodology used the Monte Carlo algorithm of molecular simulation for a grand canonical ensemble as an equation of state of the adsorbed phase. Results presented here confirm the potentiality of the proposed method. The predictive calculations describe the behavior of all studied systems, even for the isobutane-ethylene mixture that shows a complex phase diagram.

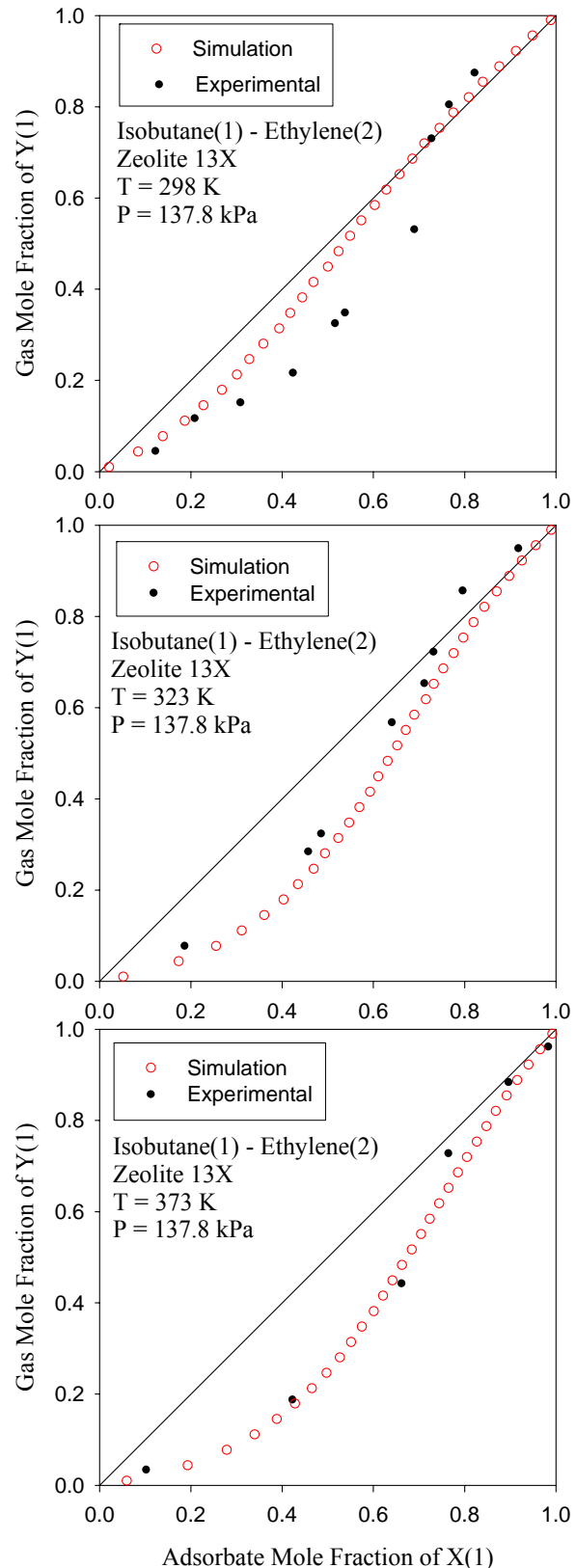


Figure 4. Phase-equilibrium diagrams for isobutane(1)–ethylene(2) on zeolite 13X at 137.8 kPa and temperatures of 298, 323, 373 K.

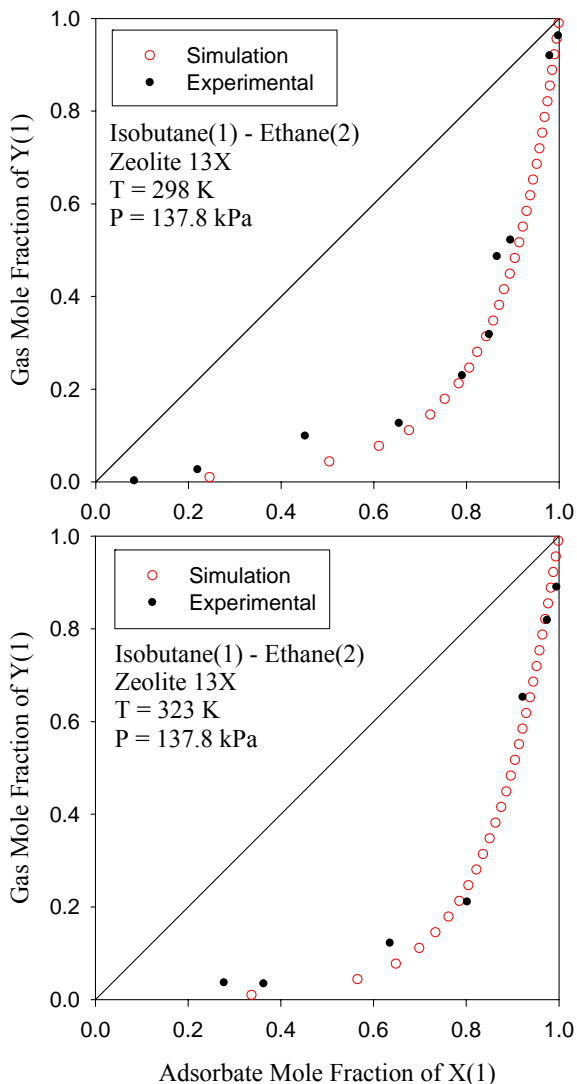


Figure 5. Phase-equilibrium diagrams for the mixture isobutane(1)–ethane(2) on zeolite 13X at 137.8 kPa and the temperatures 298, 323 K.

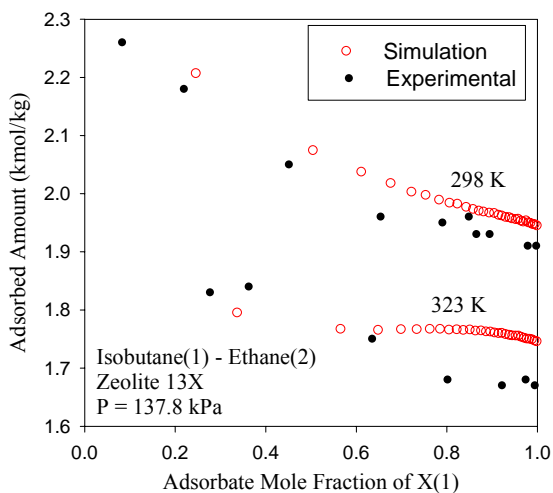


Figure 6. Total amount adsorbed for the mixture isobutane(1)–ethane(2) on zeolite 13X at 137.8 kPa and the temperatures 298, 323 K.

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