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Monte Carlo Simulations of Adsorbed Solutions in Heterogeneous Porous Materials

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Abstract. We present results of a Monte Carlo simulation study of binary mixtures of ethane and methane in silica gel. The molecular model treats the adsorbent as a matrix of silica microspheres. The adsorption isotherms, adsorption selectivities and isosteric heats of adsorption have been determined for these systems. The results are compared with predictions from the ideal adsorbed solution (IAS) theory and with experiment. The heats of adsorption are accurately described by the IAS theory. The adsorption isotherms are accurately described by the IAS theory at low bulk pressure but the IAS theory overpredicts the density at high bulk pressure. This latter effect is opposite to that observed in bulk mixtures of this type where nonidealities generally lead to a density increase on mixing. The pressure dependence of the selectivity does not exhibit a maximum at low pressure. We discuss this effect in terms of the adsorbent microstructure.

Keywords: mixture adsorption, molecular simulation, silica gel, Monte Carlo simulation

1. Introduction

Over the last several years there has been significant interest in using molecular simulation and theory to understand the behavior of adsorbed solutions both on free surfaces (Monson, 1987; Finn and Monson, 1991; Kierlik et al., 1992) and in porous materials (Cracknell and Nicholson, 1995; Tan and Gubbins, 1992; Karavias and Myers, 1991a, 1991b, 1991c; Maddox and Rowlinson, 1993; Van Tassel et al., 1994; Monson, 1990). Much of this interest has come from a need to understand the molecular basis of adsorption separations. In particular, a thorough knowledge of the relationship between adsorbent microstructure and selective adsorption offers the prospect that adsorbent material design can be tailored to effect particular separations. Most of the work which has been done on this problem has focused on idealizations of pore structure (Cracknell and Nicholson, 1995, Tan and Gubbins, 1990, 1992) or on models of zeolites (Karavias and Myers, 1991a, 1991b, 1991c; Maddox and Rowlinson, 1993; Van Tassel et al., 1994). Less attention has been focused on heterogeneous disordered materials such as silica gels.

Molecular models have recently been developed which can describe the three dimensional energetic and structural heterogeneities present in real heterogeneous solids. These include models of silica gels (MacElroy and Raghavan, 1990; Kaminsky and Monson, 1991) and activated carbons (Segarra and Glandt, 1994). Kaminsky and Monson (1994) recently presented Monte Carlo simulation results for a model of argon-methane mixtures in silica gel. This work focused primarily on the low temperature behavior of the adsorption isotherms and selective adsorption. The present paper extends the scope of these studies in several important respects. We focus on a model of a methane-ethane mixture at ambient temperature where some experimental data are available for the adsorption isotherms. In addition to the calculation of adsorption isotherms and selectivity we have obtained the isosteric heat for each component in the mixture—the first such calculations for a molecular model of adsorption in a heterogeneous disordered porous material.

2. Molecular Model and Intermolecular Potentials

The adsorbent of interest is silica gel and is described by the composite sphere model developed by Kaminsky and Monson (1991) and we refer the reader to their paper for a more detailed account of the model. This model which is a simplification of an earlier model of MacElroy and Raghavan (1990) treats silica gel as an ensemble of spherical matrix particles in a predetermined arrangement and an analytic expression for the interaction between an adsorbate molecule and a matrix particle is obtained. We have

$$u^{\mathrm{cs}}(d) = \frac{16\pi\epsilon_{\mathrm{gs}}\rho_{\mathrm{s}}R^3}{3} \times \left[\frac{\left(d^6 + \frac{21}{5}d^4R^2 + 3d^2R^4 + \frac{1}{3}R^6\right)\sigma_{\mathrm{gs}}^{12}}{(d^2 - R^2)^9} - \frac{\sigma_{\mathrm{gs}}^6}{(d^2 - R^2)^3} \right] \quad (1)$$

where d is the distance from the center of the fluid molecule to the center of the matrix particle, ρ_{s} is the density of interaction sites in the matrix particles, R is the matrix particle radius. σ_{gs} and ϵ_{gs} are the collision diameter and well depth for the 12-6 potential between the fluid molecule and a matrix particle interaction center. The interaction parameters were those originally used in the work of Kaminsky and Monson (1991), apart from the adsorbate-adsorbent well depth for each species and the collision diameter for ethane. The parameter ϵ_{gs} was obtained so that the Henry's constant of that species coincides with that from experiment (Masukawa, 1967). σ_{gs} for ethane was obtained by applying the Lorentz-Berthelot combining rules as described by Kaminsky and Monson (1994). The adsorbent was represented by a 32 matrix particle configuration with the volume fraction of 0.386 (Kaminsky and Monson, 1991). The configuration of the matrix spheres was one from a Monte Carlo simulation of an equilibrium hard sphere fluid.

Both methane and ethane were modeled as spherical molecules interacting via Lennard-Jones 12-6 potentials. The adsorbate-adsorbate interaction parameters for each component were assumed to be those of the bulk fluids. These were chosen so that the bulk critical temperature and pressure matched the experimental values. The cross interaction parameters were obtained by applying the Lorentz-Berthelot combining rules. All the potential parameters used in this work are summarized in Table 1.

Table 1. Parameters for the adsorption of methane-ethane mixture.

Species	σ_{gg} (nm)	σ_{gs} (nm)	ϵ_{gg}/k (K)	ϵ_{gs}/k (K)
Methane	0.39	0.33	154.8	349
Ethane	0.43	0.35	250	427

3. Monte Carlo Simulations

In our calculations we have set out to study adsorption at fixed temperature, bulk pressure and bulk composition. Since we use the grand canonical ensemble to study the adsorbed fluid we must determine the component chemical potentials or activities associated with these bulk conditions. If the bulk mixture behaves as a perfect gas then the chemical potentials are simply related to the pressure and composition. However, a significant part of our study focuses on a regime where gas imperfection is important. Moreover in addition to the chemical potentials, the partial molar enthalpies for the bulk mixture are required to determine the isosteric heats. Therefore we have chosen to use Monte Carlo simulations to study the bulk mixtures also. These simulations were carried out for fixed temperature, bulk pressure and bulk composition using the isothermal, isobaric ensemble (Allen and Tildesley, 1987). In these simulations 108 particles were used and each simulation was run typically for over 4×10^6 configurations, half of which were devoted to equilibration. Each configuration is an attempt of a translational move, a volume shift, and a species interchange move. The chemical potentials and partial molar enthalpies were determined by the test particle method (Shing, 1985; Sinzingre et al., 1987).

Having determined the component chemical potentials corresponding to a given set of bulk conditions (temperature, pressure and composition) the adsorption was studied using the grand canonical Monte Carlo simulation method (Allen and Tildesley, 1987). For a given bulk pressure, temperature and composition, the simulation was started with an empty matrix. Subsequent simulations at the same bulk pressure but different bulk composition were started from the configuration at the end of the previous simulation. For our adsorption studies, each simulation was run for 8×10^6 configurations, half of which was devoted to

equilibration. A configuration consists of an attempted creation or destruction (chosen with equal probability) of a molecule followed by an attempted translation of a molecule and an attempted interchange of the particle species of a molecule. The adsorbate-adsorbent interaction was truncated at $4.0\sigma_{gs}$ beyond the adsorbent surface. The adsorbate-adsorbate interaction was truncated at $2.5\sigma_{gg}$ for methane and $2.9\sigma_{gg}$ for ethane. To employ the IAS theory, similar simulations were performed for the pure components using the same matrix configuration and same truncations for each species as in the mixture simulations.

4. Ideal Adsorbed Solution Theory

A. *Thermodynamic Formulation*

Two recent papers (Cracknell and Nicholson, 1995; Vuong and Monson, 1996) have considered the thermodynamic formulation for molecular models of fluids confined in porous materials based on total properties rather than Gibbs adsorption excess properties. The first of these papers focuses on the slit pore geometry while the second applies to porous materials of any geometry whether ordered or disordered. We briefly review some features of the treatment presented in our previous work (Vuong and Monson, 1996). In this treatment the fundamental property relationship for a fluid mixture in an inert porous material is given by

$$d\underline{U}^{(a)} = Td\underline{S}^{(a)} + \phi d\underline{V}^{(a)} + \sum_i \mu_i^{(a)} dN_i^{(a)} \qquad (2)$$

where the underline refers to total (extensive) properties and the superscript (a) denotes properties of the adsorbed fluid. All the quantities in this expression have their usual meaning except for $\phi = \Omega^{(a)}/\underline{V}^{(a)}$ which is the grand potential density ($\phi = -P$ for a bulk fluid). The volume here includes volume occupied by the solids. In the treatment by Cracknell and Nicholson (1995) of adsorption in a slit pore they defined a quantity, Φ, which is the grand potential per unit surface area. For porous materials of nonplanar geometry the surface area is a poorly defined quantity and is not necessary for a thermodynamic treatment. However their treatment based on Φ is otherwise similar to that based on ϕ. The Gibbs adsorption isotherm in this formalism is written as

$$d\phi = -\sum_i \rho_i^{(a)} d\mu_i \qquad (3)$$

The natural definition of an ideal adsorbed solution for a mixture with n components is

$$\mu_i^{(a)}(T, \phi, x_1, \ldots, x_{n-1}) = \mu_i^{(a),0}(T, \phi) + RT \ln x_i \qquad (4)$$

where $\mu_i^{(a),0}(T, \phi)$ is the chemical potential of the pure adsorbate at the same T and ϕ as the mixture. It follows that the total density of the ideal adsorbed solution is given by

$$\rho^{(a)}(T, \phi, x_1, \ldots, x_{n-1}) = \left[\sum_i \frac{x_i}{\rho_i^0(T, \phi)} \right]^{-1} \qquad (5)$$

$\rho_i^0(T, \phi)$ is the density of pure adsorbate i at the same T and ϕ as the mixture. The calculation of adsorption equilibrium for a binary mixture using the IAS theory proceeds as follows. The equations of adsorption equilibrium are

$$\mu_1^{(b),0}(T, P) + RT \ln y_1 = \mu_1^{(a),0}(T, \phi) + RT \ln x_1 \qquad (6)$$

$$\mu_2^{(b),0}(T, P) + RT \ln(1 - y_1) = \mu_2^{(a),0}(T, \phi) + RT \ln(1 - x_1) \qquad (7)$$

where the superscript (b) denotes bulk properties, y_1 is the bulk mole fraction of component 1 and we have assumed ideal solution behavior in the bulk. The equality of grand potential densities for each pure component gives, via the Gibbs adsorption isotherm,

$$\int_{-\infty}^{\mu_1^{(a),0}(T,\phi)} \rho_1^{(a),0}(\mu)\, d\mu = \int_{-\infty}^{\mu_2^{(a),0}(T,\phi)} \rho_2^{(a),0}(\mu)\, d\mu \qquad (8)$$

Given knowledge of the pure component adsorption isotherms and specifying T, P and y_1, Eqs. (6), (7) and (8) form a system of three equations in three unknowns: x_1, $\mu_1^{(a),0}$ and $\mu_2^{(a),0}$. Neglecting gas imperfection in the bulk allows the above three equations to be written as

$$Py_1 = P_1^0(T, \phi)x_1 \qquad (9)$$

$$P(1 - y_1) = P_2^0(T, \phi)(1 - x_1) \qquad (10)$$

$$\int_0^{P_1^0(T,\phi)} \frac{\rho_1^{(a),0}(P)}{P}\, dP = \int_0^{P_2^0(T,\phi)} \frac{\rho_2^{(a),0}(P)}{P}\, dP \qquad (11)$$

where $P_i^0(T, \phi)$ is the pressure of the bulk gas in equilibrium with the pure adsorbate i at the same T and ϕ as the mixture. This is the form of the IAS equations used in most applications except that here the adsorbate density is used rather than adsorption excess. Based on their work with the slit pore model Cracknell and Nicholson (1995) argue that, in applications of the IAS theory to molecular models of mixtures in pores, the total density should be used rather than the adsorption excess. We are in agreement with this view.

In order to calculate adsorbate density from experimental adsorption isotherms, which are obtained as the Gibbs adsorption excess, an estimate of the void volume must be made. On the other hand to calculate the Gibbs adsorption excess for a molecular model with a nonplanar pore geometry it is also necessary to estimate the void volume. A rigorous estimate of this quantity is not possible in either case. Of course, in adsorption from dilute gases the distinction between adsorption excess and total adsorption is insignificant. However these are not the conditions pertaining in the present work.

B. Isosteric Heat of Adsorption

When the adsorbed phase is assumed to be an ideal solution the internal energy is given by

$$\underline{U}^{(a)}(T, \phi, N_1, \ldots, N_n) = \sum_i N_i U_i^0(T, \phi) \tag{12}$$

The left hand side of this equation is the total (extensive) internal energy of the adsorbed phase. $U_i^0(T, \phi)$ is the internal energy per molecule of pure adsorbate i at the same T and ϕ as that of the mixture.

The isosteric heat of a component in a mixture is given by

$$q_{\mathrm{st},i} = \bar{H}_i^{(b)} - \left(\frac{\partial \underline{U}^{(a)}}{\partial N_i^{(a)}}\right)_{T,\underline{V}^{(a)},N_{j\neq i}} \tag{13}$$

where $\bar{H}_i^{(b)}$ is the partial molecular (or partial molar) enthalpy of component i in the bulk. For an adsorbed phase that behaves as an ideal solution we have,

$$\left(\frac{\partial \underline{U}^{(a)}}{\partial N_i^{(a)}}\right)_{T,\underline{V}^{(a)},N_{j\neq i}} = U_i^0 + \sum_j \rho_j \left(\frac{\partial U_j^0}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} \tag{14}$$

Using the chain rule we obtain

$$\left(\frac{\partial U_j^0}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} = \left(\frac{\partial U_j^0}{\partial \phi}\right)_T \left(\frac{\partial \phi}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} \tag{15}$$

Substituting Eq. (5) into Eq. (14) yields,

$$\left(\frac{\partial \underline{U}^{(a)}}{\partial N_i^{(a)}}\right)_{T,\underline{V}^{(a)},N_{j\neq i}} = U_i^0 + \rho \left(\frac{\partial \phi}{\partial \rho_i}\right)_{T,\rho_{j\neq i}} \times \sum_j x_j \left(\frac{\partial U_j^0}{\partial \phi}\right)_T \tag{16}$$

Using Eq. (5) we can write

$$\left(\frac{\partial \rho_i}{\partial \phi}\right)_{T,\rho_{j\neq i}} = \rho \rho_i^0 \sum_j \frac{x_j}{\rho_j^{0^2}} \left(\frac{\partial \rho_j^0}{\partial \phi}\right)_T \tag{17}$$

Substituting Eq. (17) into Eq. (16) gives

$$\left(\frac{\partial \underline{U}^{(a)}}{\partial N_i^{(a)}}\right)_{T,\underline{V}^{(a)},N_{j\neq i}} = U_i^0 + \frac{\sum_j x_j \left(\frac{\partial U_j^0}{\partial \rho_j^0}\right)_T \left(\frac{\partial \rho_j^0}{\partial \phi}\right)_T}{\rho_i^0 \sum_j \frac{x_j}{\rho_j^{0^2}} \left(\frac{\partial \rho_j^0}{\partial \phi}\right)_T} \tag{18}$$

Substituting Eq. (18) into Eq. (13) yields

$$q_{\mathrm{st},i} = \bar{H}_i^{(b)} - U_i^0 + \frac{\sum_j x_j \left(\frac{\partial U_j^0}{\partial \rho_j^0}\right)_T \left(\frac{\partial \rho_j^0}{\partial \phi}\right)_T}{\rho_i^0 \sum_j \frac{x_j}{\rho_j^{0^2}} \left(\frac{\partial \rho_j^0}{\partial \phi}\right)_T} \tag{19}$$

Equation (19) allows the component isosteric heats of adsorption to be calculated using the pure component properties (properties with superscript 0). Karavias and Myers (1991) have previously derived an expression corresponding to Eq. (19) in terms of adsorption excess and for the case where the bulk is a perfect gas mixture.

5. Results

A. Adsorption Isotherms and Selectivity

Figure 1 shows the comparison of the total adsorption isotherms ($\rho_1^{(a)} + \rho_2^{(a)}$) between predictions from the IAS theory and results from our molecular simulations. At low pressure, the predictions of IAS theory are very accurate. However, at the higher pressures, the

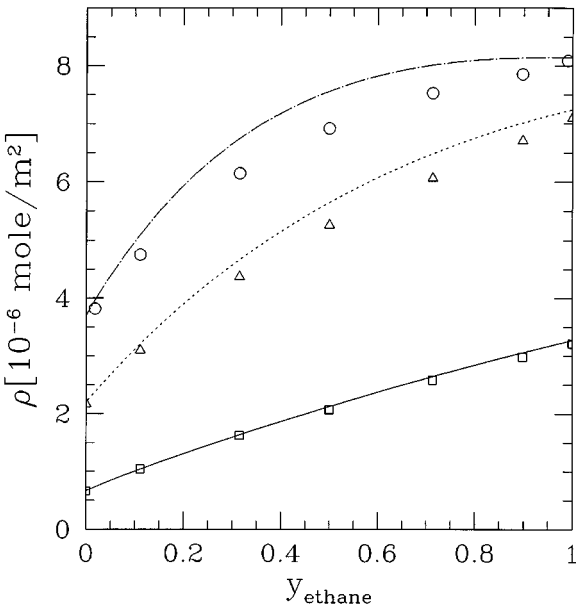

Figure 1. Total adsorption isotherms for methane-ethane mixtures in silica gel using the IAS theory and Monte Carlo simulation at $T = 298.15$ K. —, IAS theory at $P = 50$ psia; ---, IAS theory at $P = 200$ psia; —·—, IAS theory at $P = 400$ psia; □, Monte Carlo simulation at $P = 50$ psia; △, Monte Carlo simulation at $P = 200$ psia; ○, Monte Carlo simulation at $P = 400$ psia.

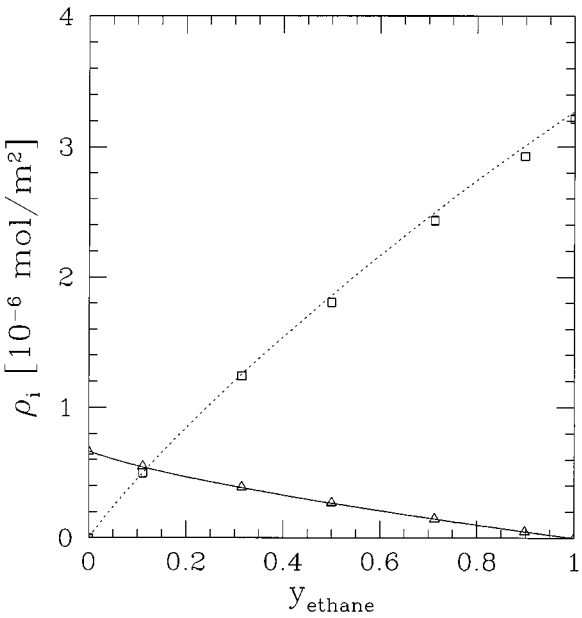

Figure 2. Component adsorption isotherms for methane-ethane mixtures in silica gel from IAS theory and Monte Carlo simulation at $T = 298.15$ K and $P = 50$ psia. —, methane adsorption via IAS theory; ---, ethane adsorption via IAS theory; △, methane adsorption from Monte Carlo simulation; □, ethane adsorption from Monte Carlo simulation.

IAS theory significantly overpredicts the total adsorption. We can think of this in terms of the simulations showing a decrease in density on isothermal mixing at constant grand potential density. This effect is different from what is normally observed in isothermal mixing at constant pressure for Lennard-Jones bulk liquid mixtures (Rowlinson and Swinton, 1982) which exhibit negative volumes of mixing. The most obvious explanation for this effect is that confinement inside the porous material decreases the ability of the component molecules in the mixture to pack efficiently. In terms of packing, one would expect that it is easier to pack particles of different sizes in the bulk than in the adsorbed phase where the matrix particles are present. One would also expect that the component with the larger size should experience more difficulty of packing in the adsorbed phase. Furthermore, the difficulty could be more pronounced as pressure increases due to the size exclusion effect at high pressure. These points can be illustrated by examining the contributions from each component to the total adsorption isotherms. Figures 2 and 3 show the component adsorption isotherms for two of the pressures studied. It is evident that the IAS results are more accurate for methane (the component with the smaller molecular size) than for ethane and it is the ethane contribution which causes the total adsorption to be overestimated. Figure 4 shows the results in terms of the *x*-*y* composition curves. Again we see that the IAS theory predictions are more accurate at the lower pressures.

It is worthwhile to compare these results with some results for a mixture of argon and methane (Kaminsky and Monson, 1994b) obtained at very high pressures. Except at the very highest pressure considered, these results show an overestimation of the total density by the IAS consistent with that seen here. In all cases the adsorption of the larger component is overestimated by IAS. On the other hand the results at very high pressure show an underestimation of the adsorption of argon (the smaller component) by IAS indicating a mechanism whereby the smaller component can pack more efficiently than predicted by IAS. However, the pressure in this case is over ten times greater than the highest pressure considered in the present work.

Figure 5 compares the selectivities of the mixtures for a range of mole fractions in the bulk phase at the

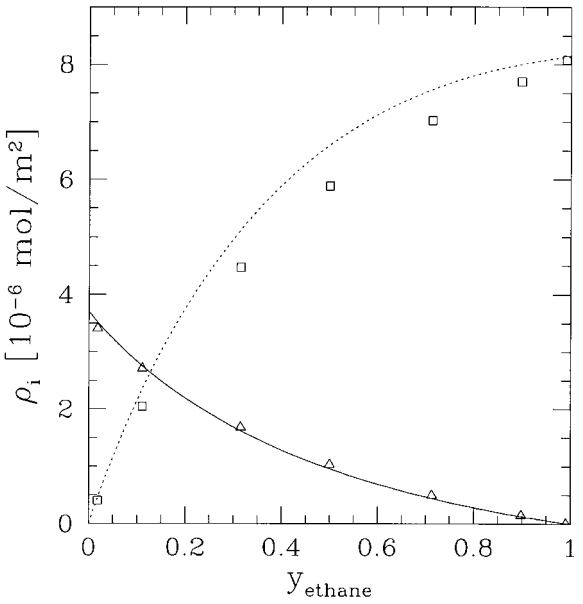

Figure 3. Component adsorption isotherms for methane-ethane mixtures in silica gel from IAS theory and Monte Carlo simulation at $T = 298.15$ K and $P = 400$ psia. —, methane adsorption via IAS theory; ---, ethane adsorption via IAS theory; △, methane adsorption from Monte Carlo simulation; □, ethane adsorption from Monte Carlo simulation.

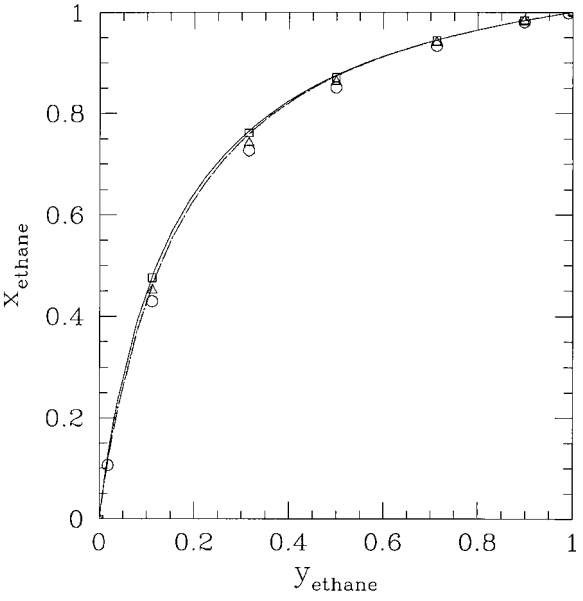

Figure 4. Comparison of x-y composition curves for methane-ethane mixtures in silica gel at $T = 298.15$ K and at various pressures between the IAS theory and Monte Carlo simulation. —, IAS theory at $P = 50$ psia; ---, IAS theory at $P = 200$ psia; ——, IAS theory at $P = 400$ psia; □, Monte Carlo simulation at $P = 50$ psia; △, Monte Carlo simulation at $P = 200$ psia; ○, Monte Carlo simulation at $P = 400$ psia.

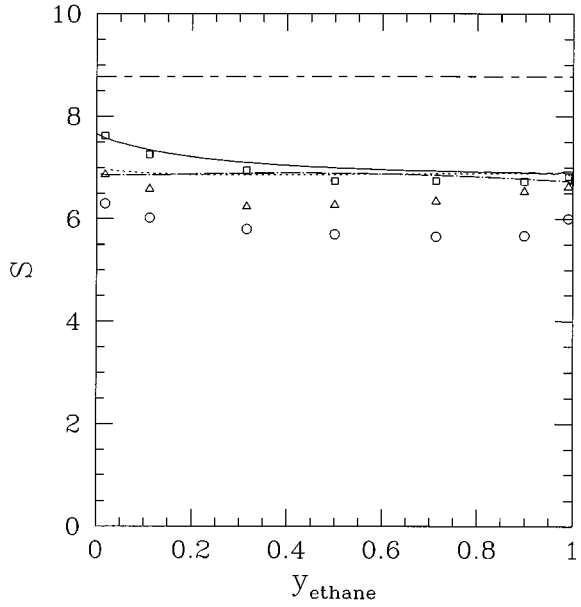

Figure 5. Selectivity for methane-ethane mixtures in silica gel using IAS theory and Monte Carlo simulation at $T = 298.15$ K. —, IAS theory at $P = 50$ psia; ---, IAS theory at $P = 200$ psia; ——, IAS theory at $P = 400$ psia; □, Monte Carlo simulation at $P = 50$ psia; △, Monte Carlo simulation at $P = 200$ psia; ○, Monte Carlo simulation at $P = 400$ psia; — – —, Henry's law prediction.

pressures studied. The selectivity or separation factor, S is defined as (Ruthven, 1984)

$$S = \frac{x_1/y_1}{x_2/y_2} \tag{20}$$

where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk phase. In this equation, ethane is denoted by component 1 and methane is denoted by component 2. In the limit of low pressure, we have

$$\rho_i^{(a)} = K_{H,i}\rho_i^{(b)} \tag{21}$$

where $K_{H,i}$ is the Henry's constant of species i, $\rho_i^{(a)}$ and $\rho_i^{(b)}$ are the density of species i in the adsorbed and bulk phase respectively. Substituting Eq. (21) into Eq. (20) yields the selectivity in the Henry's law limit, S_H

$$S_H = \frac{K_{H,1}}{K_{H,2}} \tag{22}$$

The Henry's law relects only the relative strengths of the adsorbate-solid interactions in determining selective adsorption. At higher pressures the adsorbate-adsorbate interactions are also important which could

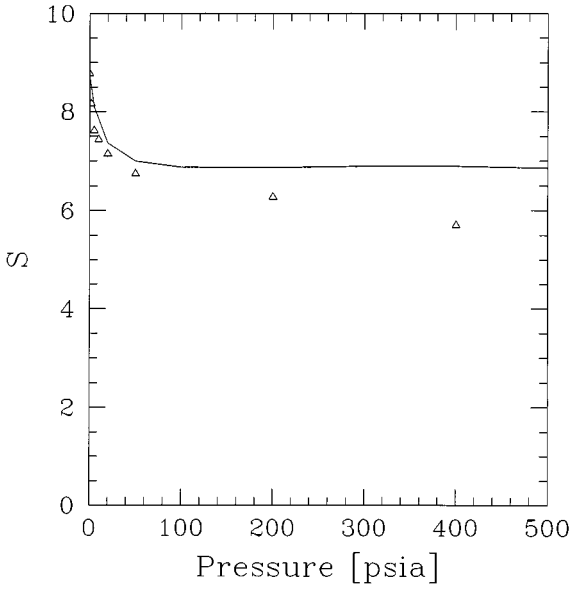

Figure 6. Pressure dependence of selectivity for methane-ethane mixtures in silica gel using IAS theory and Monte Carlo simulation at $T = 298.15$ K and bulk mole fraction of 0.5. —, IAS theory; △, Monte Carlo simulation.

give rise to the pressure and composition dependence of the selectivity.

It is evident from Fig. 5 that the agreement between the IAS theory and the molecular models is very good at the lower pressure. However, at higher pressures the theory predicts that the selectivity is almost independent of the bulk phase composition while the molecular simulation results show a more significant dependence on the bulk phase composition. Figure 6 compares the selectivity as a function of bulk pressure for a single bulk composition between prediction from the IAS theory and results from molecular simulations. Both the Monte Carlo and IAS results show a similar trend with increasing pressure with the selectivity decreasing relative to its value in the Henry's law limit. A similar behavior has been observed in experiments on methane-ethane mixtures adsorbed in activated carbon (Gusev et al., 1996). A primary effect in this selectivity decrease is the energetic heterogeneity of the adsorbent. The regions of the void space with the strongest adsorbate-adsorbent interactions have the highest selectivity for ethane. As the pressure is increased these regions become filled and only regions of lower selectivity are available. This effect is further enhanced by the effects of the size difference between the components which favor the adsorption of the smaller component. It is interesting to note that contrary to observations made in studies of molecular models of adsorption on free surfaces (Knight and Monson, 1987) and single pores (Tan and Gubbins, 1992; Cracknell and Nicholson, 1995), there is no maximum in the selectivity-pressure curve in Fig. 6. This maximum occurs because of an additional contribution to the selectivity from adsorbate-adsorbate interactions which are generally stronger for the component which has the stronger adsorbate-adsorbent interactions. At higher pressures this is counteracted by the effect of size differences. While the contribution to the selectivity from attractive adsorbate-adsorbate interactions is presumably present in the systems studied here it is being masked by the effect of energetic heterogeneity in the adsorbent described above.

B. Isosteric Heats of Adsorption

We have determined the component isosteric heats of adsorption from the methane-ethane mixtures in silica gel at ambient temperature and at pressures of 50, 200, and 400 psia using both Monte Carlo simulations and the IAS theory. The results from the theory were obtained based on the assumption that the adsorbed phase and the bulk phase both behave like an ideal solution, so that the partial molar enthalpy in Eq. (19) is replaced by the bulk enthalpy of pure i, $H_i^{(b)}$. For the molecular simulation results, the component heats were calculated via Eq. (13) where the number derivative of the internal energy of each species was calculated directly from the simulation via the fluctuation method (Nicholson and Parsonage, 1982; Karavias and Myers, 1991a).

Figure 7 shows the component isosteric heats of adsorption for the highest pressure studied. It is evident that the predictions from the IAS theory agree quite well with those from the molecular models. The scatter in the Monte Carlo simulation results is a reflection of the fluctuation method which has intrinsically large uncertainties as illustrated in our previous work on the pure component adsorption (Vuong and Monson, 1996). The numerical differentiation method provided more accurate results for pure components but we have not been able to extend this to mixtures (Vuong and Monson, 1996; Vuong, 1998).

6. Comparison with Experiment

We have made a comparison between the results obtained by the molecular simulations and those from

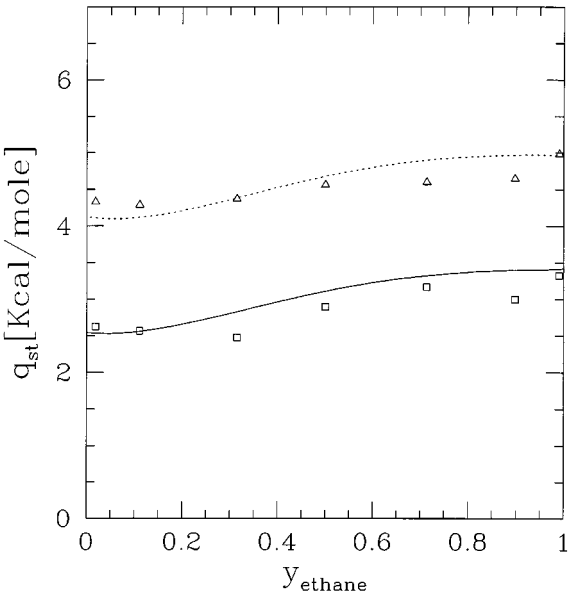

Figure 7. Comparison of the component isosteric heats of adsorption for methane-ethane mixtures in silica gel at $T = 298.15$ K and $P = 400$ psia between the IAS theory and Monte Carlo simulation. —, q_{st} of methane via IAS theory; □, q_{st} of methane from Monte Carlo simulation; ---, q_{st} of ethane via IAS theory; △, q_{st} of ethane from Monte Carlo simulation.

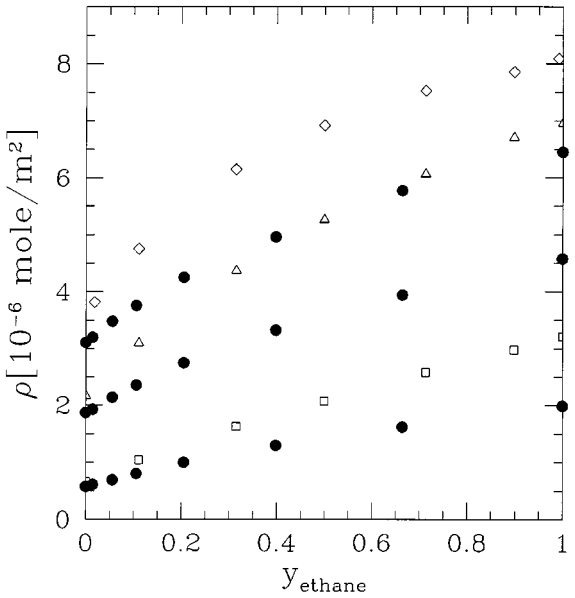

Figure 8. Total adsorption isotherms for methane-ethane mixtures in silica gel at $T = 298.15$ K and at various pressures between Monte Carlo simulation and experiment. □, Monte Carlo simulation at $P = 50$ psia; △, Monte Carlo simulation at $P = 200$ psia; ◊, Monte Carlo simulation at 400 psia; ● (from bottom to top), experiment at $P = 50$, 200, and 400 psia.

experimental data (Masukawa, 1967) for the adsorption of methane-ethane mixtures in silica gel at $T = 298.15$ K and $P = 50$ psia, 200 psia, and 400 psia in terms of total and component adsorption isotherms and selectivities. Figure 8 shows the comparison of total adsorption. The total adsorption isotherms from all the pressures were overestimated by the molecular models used. This can be understood more clearly by decomposing the total adsorption into the component adsorption isotherms. Figure 9 shows the corresponding component adsorption isotherm at the highest pressure studied. It is evident from the figure that the molecular models employed have slight overpredictions for the methane adsorption isotherms. However, the ethane adsorption isotherms from the molecular models are higher than those shown by experiment. Therefore, the overprediction of the total adsorption isotherm was primarily due to the discrepances in the adsorption of the ethane component in the mixtures. The discrepancies in the ethane adsorption could be due to the molecular model used for silica gel. As shown in our previous work, where a more realistic model of the adsorbent was used to study the adsorption of methane in silica gel (Vuong and Monson, 1996) and

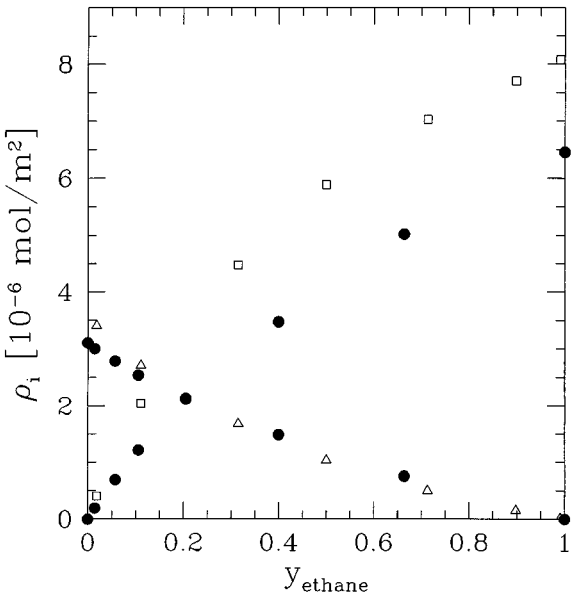

Figure 9. Component adsorption isotherms for methane-ethane mixtures in silica gel at $T = 298.15$ K and $P = 400$ psia between Monte Carlo simulations and experiment. △, methane adsorption from Monte Carlo simulation; □, ethane adsorption from Monte Carlo simulation; ●, experiment.

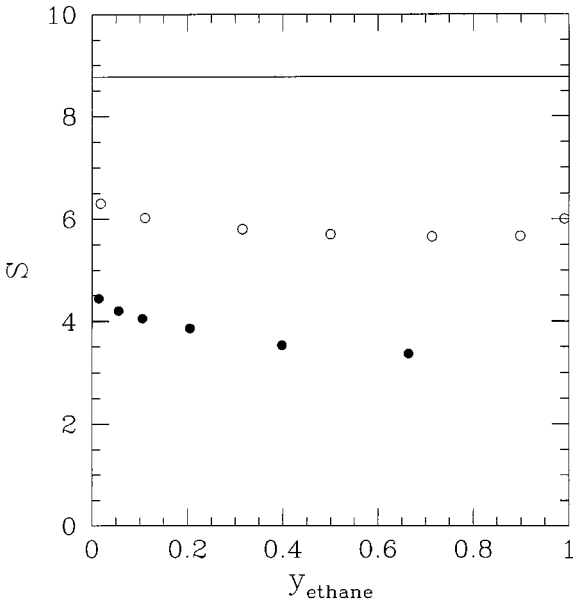

Figure 10. Selectivity from Monte Carlo simulation and from experiment for methane-ethane mixtures in silica gel at $T = 298.15$ K and $P = 400$ psia. ○, Monte Carlo simulation; ●, experiment; —, Henry's law predictions.

the adsorption of ethane in silica gel (Vuong, 1998), surface roughness has an important influence on the adsorption isotherms. Therefore, this could be a possible cause for the discrepancies in the ethane adsorption. Figure 10 shows the comparisons of the selectivities (as defined by Eq. (20)) from the molecular models and those from the experiment for the highest pressure studied. The selectivities from the Henry's law limit is also included. Since the Henry's constants from the models coincide with those from experiment, the Henry's law prediction of the selectivity is the same as that from experiment. Outside of the Henry's law region, the molecular models overpredict the selectivity, but the trends are similar in the two cases. The primary contribution to the overestimation of the selectivity by the molecular model is an overestimation of the ethane adsorption. There are as yet no experimental data for the heats of adsorption data for these mixtures.

7. Summary and Conclusions

In this paper we have described a Monte Carlo simulation study of the adsorption of mixtures of ethane and methane in a silica gel focusing on selective adsorption and the heats of adsorption. A comparison of the simulation results with the IAS theory and with experiment was made.

Nonidealities in the system appear primarily in the adsorption isotherms at higher pressure where the IAS overpredicts the density relative to that seen in the Monte Carlo simulations. We have interpreted this in terms of the influence of size differences on packing of molecules in confined geometries. Both the IAS theory and the Monte Carlo results for the model indicate that at low pressures the selectivity decreases sharply with increasing pressure at low pressures. This is interpreted in terms of the energetic heterogeneity in the disordered material. This effect masks the enhancement in the selectivity due to adsorbate-adsorbate interactions seen in studies of mixture adsorption on homogeneous free surfaces (Knight and Monson, 1987) and in single pores (Tan and Gubbins, 1992; Cracknell and Nicholson, 1995). The Monte Carlo results for the isosteric heats were accurately described by the IAS theory.

Our comparison with experiment indicates that this molecular model overestimates the adsorbate density. The disagreement with experiment arises primarily from the overpredictions of the ethane adsorption. We do not think that the kind of modifications we have made to the model of the adsorbent in our recent work (Vuong and Monson, 1996; 1997) are likely to account for this entirely. At least part of the discrepancy may arise from the close proximity to the critical temperature of ethane and our ability to model the thermodynamic properties of ethane in this region both in the bulk and in the porous material.

Nomenclature

ϵ_{gg}/k	Adsorbate-adsorbate well depth, K
ϵ_{gs}/k	Adsorbate-adsorbent well depth, K
$\mu_i^{(a)}$	Chemical potential of i in the adsorbed phase
$\mu_i^{(b)}$	Chemical potential of i in the bulk phase
ϕ	Grand potential density, psia
ρ_i	Density of i, mole
σ_{gg}	Adsorbate-adsorbate collision diameter, nm
σ_{gs}	Adsorbate-adsorbent collision diameter, nm
$\bar{H}_i$	Partial molar enthalpy, kcal/mole
$K_{H,i}$	Henry's constant of i
N_i	Number of particle of i
P	Bulk pressure, psia
P_i^0	Pressure of pure i at the same temperature and pressure as the mixture, psia
q_{st}	Isosteric heat of, kcal/mole

R Gas constant
S Selectivity
S_K Selectivity in the Henry's law limit
T Temperature, K
U Internal energy, kcal/mole
y_i Mole fractions in the bulk phase
x_i Mole fractions in the adsorbed phase

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