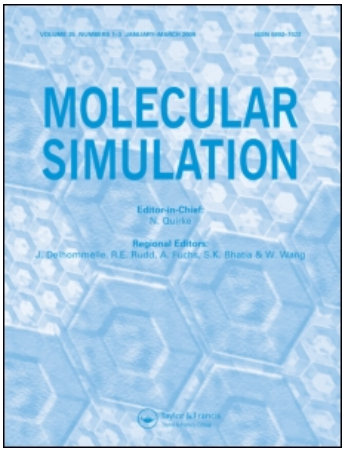

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Adsorption of Binary Mixtures in a Zeolite Micropore

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ADSORPTION OF BINARY MIXTURES IN A ZEOLITE MICROPORE

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We investigate the selective adsorption of xenon, argon, and methane in zeolite NaA by applying the grand canonical ensemble Monte Carlo simulation technique to an adsorbed binary mixture and to two reference systems: i) an adsorbed single component system and ii) a bulk mixture. We define and calculate selectivities and excess densities due to i) mixing and ii) adsorption in terms of differences between the binary adsorbed system and these reference systems. We observe that xenon selectively adsorbs in both xenon-argon and xenon-methane mixtures at low chemical potential (low pressure) due to its greater energetic interaction with the zeolite. However, a reversal in selectivity occurs at higher chemical potential in both of these mixtures. This is due in large part to the greater efficiency in which the smaller component "packs" in the pore as compared to the bulk. We show that the crossover in selectivity occurs at a lower chemical potential for a mixture where one component can occupy regions of the porespace inaccessible to the other. We suggest that this crossover in selectivity may be a general feature of microporous adsorption.

Keywords: Zeolite; binary mixture; adsorption; grand canonical; Monte Carlo

I. INTRODUCTION

Zeolites are a family of microporous aluminosilicates which have found widespread use as catalysts and separating agents. At the source of their utility is the presence of a crystalline network of monodisperse pores of

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molecular dimensions (typical pore sizes range from 10 to 50 Å). The small size of the pores provides i) a high surface to volume ratio, ii) an enhanced pore wall-adsorbate interaction due to appreciable curvature over molecular length scales, and iii) the possibility of entrapment, exclusion, and inhibition of certain species based on steric constraints. The monodisperse nature of the pore network ensures that each of these properties will be well defined for a given molecular species. The third property allows for the possibility of shape selective catalysis which results in the production of oftentimes thermodynamically disfavored products based on a preferred "fit" of certain reactants, intermediates, and/or products in the pore due to size and shape.

As a step towards understanding shape selective catalysis, we seek to better understand how and why zeolites selectively adsorb certain components in a mixture. We can think of selectivity as being due to either kinetic or thermodynamic factors. The former deals principally with molecular sieving and may be understood as the preferred adsorption based on the steric exclusion of certain species in a mixture. The latter occurs when several components can fit in the pore and in principle can be understood in terms of energetic and molecular packing effects. Interestingly, these are also the predominant effects behind liquid crystal phase behavior. It is the goal of this paper to investigate the equilibrium selectivity of mixtures of simple, spherical molecules in a model zeolite micropore.

Molecular computer simulation offers an attractive means to study adsorption in zeolitic materials. Experimental techniques, although crucial to a complete understanding, are by themselves unable to cover a wide parameter space or to provide molecular level information. Approximate theories (density functional, integral equation), on the other hand, suffer from the necessary approximations which become less appropriate in the widely varying potential field of a zeolite micropore. (However, very recently, density functional theory has been successfully applied to a zeolitic system [1] and the prospects for future success in this area appear promising.) In contrast, molecular simulation suffers from none of these pitfalls and is used extensively in the study of adsorption in zeolitic systems [2–19] with recent emphasis directed towards selectivity in multi-component systems [5,8,13,14].

In a recent work [14], we report grand canonical Monte Carlo simulations of the adsorption of xenon, argon, methane, and their binary mixtures in zeolite NaA and compare results to those predicted by an "ideal" isotherm model reference system. In this paper, we build on this previous work

by comparing simulations of adsorbed mixtures to two additional reference systems: i) simulated adsorbed single component systems and ii) simulated bulk mixtures. This allows us to calculate excess properties due to mixing and adsorption and the quantity known as the selectivity. We find two competing factors to be important in explaining selective adsorption: energetic effects and molecular packing effects. The former refers to the degree of energetic interaction between the adsorbate and the zeolite and is important at low loadings. The latter refers to the ability of the different components to pack efficiently in the pore, as compared to the bulk, and contributes to non-ideal mixing and a reversal of selectivity at higher pore loadings.

II. SIMULATION METHOD AND SYSTEM

The simulation technique used in this work is the grand canonical Monte Carlo simulation method [20,21]. It may be used to measure the thermodynamic properties of any single- or multi-component fluid at fixed volume, temperature, chemical potential of each species, and external field. The appropriate free energy in this ensemble is defined as

$$\Omega = E - TS - \sum_{i=1}^{N_c} N_i \mu_i \tag{1}$$

where E is the energy, T is the temperature, S is the entropy, and N_i and μ_i are the number and chemical potential of the i'th species in a N_c component mixture.

In the course of the simulation, phase space is sampled by creating new states of the system and accepting them with a Boltzmann weight so as to achieve the desired distribution. New states are generated via random perturbations of the system; these typically take the form of random particle translations, random particle insertions, and random particle deletions. If molecular fluids were studied, random particle rotations would also be used. The frequency with which the various system perturbations are chosen must allow for the rate of exchange between any two system states to be equal at equilibrium (principle of detailed balance).

The adsorbent modeled in this work is zeolite NaA, a crystalline aluminosilicate with a unit cell composition of $Na_{12}Si_{12}Al_{12}O_{48}$. Adsorption occurs into the largest cavity of NaA, the α-cage, which is shaped roughly like a truncated cuboctahedron, makes up a single unit cell, has a diameter approximately equal to the lattice spacing of the crystal (12.263 Å),

and is connected to other α-cages in a cubic arrangement. The α-cage is shown in Figures 1 through 3. Framework and extraframework positions are available from X-ray diffraction studies [22]. Vibrational motion of the zeolite is known to occur and may indeed affect dynamic properties of adsorbates. As we seek only themodynamic properties in this work, we assume a rigid framework.

The adsorbates studied in this work are xenon, argon, and methane. We consider cases where they are i) adsorbed in zeolite NaA and ii) in a bulk phase. Bulk simulations take place in a cubic box of length $L = 30$ Å. The standard periodic boundary condition and minimum image convention are used [21]. Xenon, argon, and methane are treated as Lennard-Jones molecules with parameters given in Table I. No cut-off distance is imposed, but use of the minimum image convention implies that the longest distance of interaction is $\sqrt{3}L/2$. The Lorentz-Barthelot mixing rules are used to determine interaction parameters between unlike species. These are simply $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$ and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$. In addition to the standard insertion, deletion, and translation steps, we employ random particle identity change steps. These were found to increase the efficiency of the simulation.

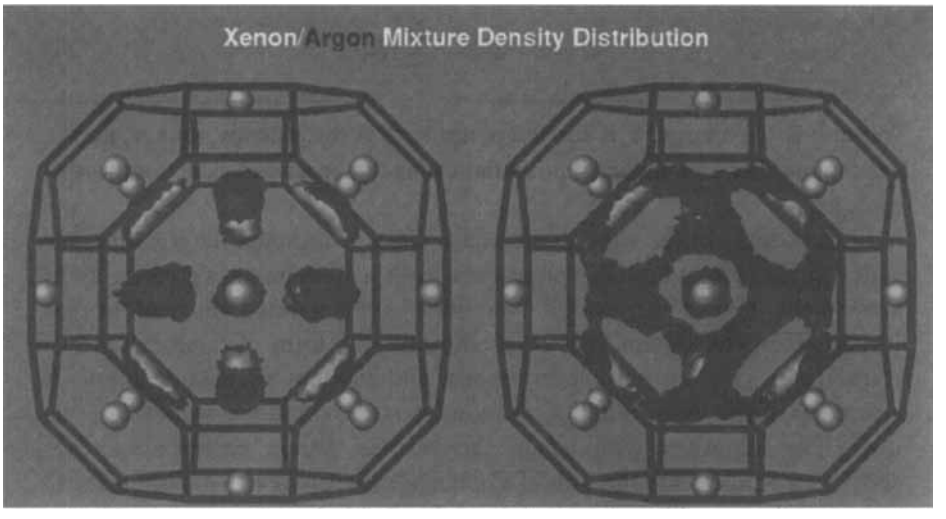

FIGURE 1 Xenon (white) and argon (purple) mixture isodensity surfaces in the zeolite NaA α-cage at $\mu = -15$ kJ/mol (left) and $\mu = 0$ (right). The surface corresponds, for a given component, to a density ten times that of its average density in the pore in this and subsequent color plates. The red bars represent the zeolite's silicon-aluminum-oxygen framework and the yellow spheres represent the its' extra-framework sodium ions in this and subsequent color plates. The length of the cage is 12.263 Å. Note that at high chemical potential, argon is able to occupy porespace inaccessible to xenon. (See Color Plate I).

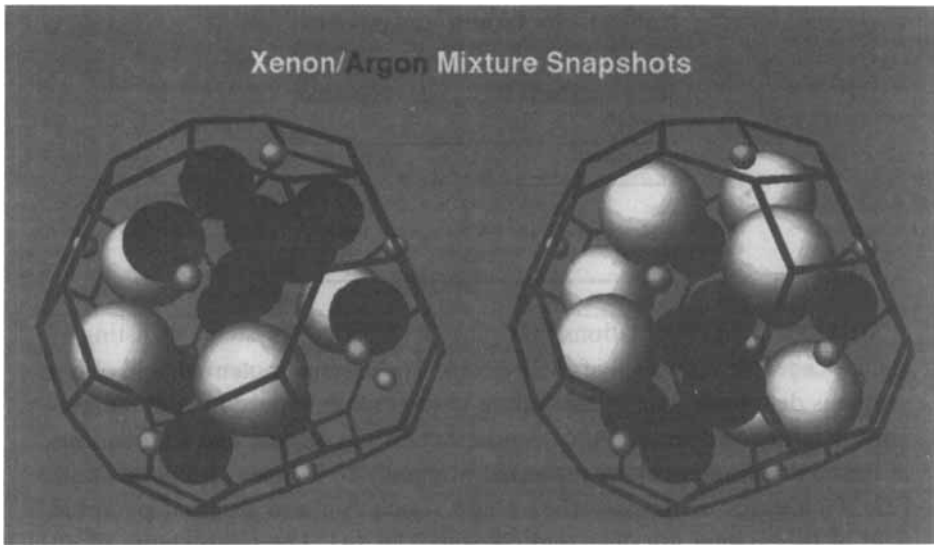

FIGURE 2 Snapshots of xenon (white) and argon (purple) atoms in the zeolite NaA α-cage at $\mu = -15$ kJ/mol (left) and $\mu = 0$ (right). (See Color Plate II).

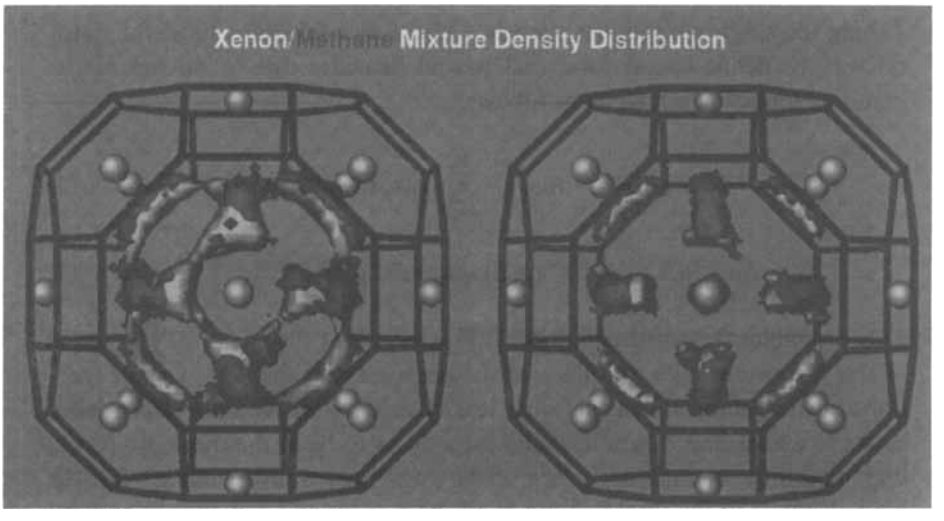

FIGURE 3 Xenon (white) and methane (blue) mixture isodensity surfaces in zeolite NaA α-cage at $\mu = -15$ kJ/mol (left) and $\mu = 0$ (right). Notice that xenon and methane occupy the same regions of the porespace at both chemical potentials. (See Color Plate III).

TABLE I The Lennard-Jones parameters for the potential energy of interaction among the adsorbates. Parameters were taken from Ref. [32]. k_B is the Boltzmann constant

adsorbate	σ/Å	$(\varepsilon/k_B)/K$
Xe	4.10	221
CH_4	3.82	148
Ar	3.40	120

Adsorbed phase simulations take place in a periodic system consisting of eight α-cages (or unit cells) of zeolite NaA. The external potential field of the zeolite is determined via a summation of dispersion, repulsion, and polarization interactions between the adsorbates and the oxygen and sodium ions of the zeolite framework as suggested originally by Kiselev and co-workers [23,24]. Details of the adsorbed phase simulation and external potential field of this system are discussed elsewhere [6, 14]. The temperature of all simulations presented here is 300 K.

III. EXCESS PROPERTIES

Taking the single component adsorbed phase as a reference state, the natural way to define excess total and partial densities due to mixing in the grand canonical ensemble is as follows:

$$\Delta\rho^{\text{mix}}(\mu,T) = \rho^{\text{ads mix}}(\mu,T) - \sum_{i=1}^{N_c} x_i(\mu,T)\ \rho^{\text{ads 1-comp}}(\mu_i,T) \tag{2}$$

$$\Delta\rho_i^{\text{mix}}(\mu,T) = \rho_i^{\text{ads mix}}(\mu,T) - x_i(\mu,T)\ \rho^{\text{ads 1-comp}}(\mu_i,T) \tag{3}$$

This resembles the usual definition [25] except that the chemical potentials of the N_c species take the place of the pressure and the $N_c - 1$ mole fractions as the "natural" variables in this ensemble. No volume dependence exists as we assume V is sufficiently large so as to be in the thermodynamic limit and that the microstructure of the adsorbent is independent of V. (In NaA, V refers to the total volume of all the α-cages and can change only by discrete amounts as the α-cages themselves have fixed volume.)

In addition to non-idealities brought about by mixing, the process of adsorption itself may bring about unexpected mixture equilibria. To determine the effect of the adsorbent on the mixture, we consider the bulk phase

of the mixture to be the reference state and define excess total and partial densities due to adsorption as

$$\Delta\rho^{\text{ads}}(\mu,T) = \rho^{\text{ads mix}}(\mu,T) - \rho^{\text{blk mix}}(\mu,T) \tag{4}$$

$$\Delta\rho_i^{\text{ads}}(\mu,T) = \rho_i^{\text{ads mix}}(\mu,T) - \rho_i^{\text{blk mix}}(\mu,T) \tag{5}$$

We can think of these excess properties as arising from various contributions of the potential energy function. Eqs. 2 and 3 account for the contribution of the intermolecular potential between unlike species and Eqs. 4 and 5 account for the contribution of the external potential between the adsorbates and the adsorbent. Figure 4 provides a pictorial representation of this.

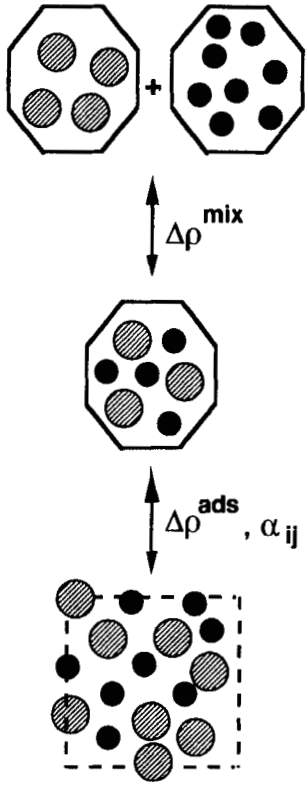

FIGURE 4 Schematic showing the relationship between the adsorbed mixture and the two reference systems considered here. The excess density due to mixing comes from differences between the adsorbed mixture and the adsorbed single component reference system and the selectivity and the excess density due to adsorption come from differences between the adsorbed mixture and a bulk mixture reference system.

Another useful property for comparing adsorbed versus bulk mixtures is the selectivity of component i over component j which is defined as

$$\alpha_{ij} = \frac{x_i y_j}{x_j y_i} \tag{6}$$

where x_i and y_i are the mole fraction of species i in the adsorbed and bulk phases, respectively. This is a measure of the propensity of one component in a bulk mixture to adsorb preferentially over another. A value greater than unity indicates a preference of component i over component j.

IV. RESULTS

Figures 5a-b show xenon-argon and xenon-methane mixture and single component adsorption isotherms plotted as density of the adsorbed phase versus chemical potential. By considering an equi-chemical potential ordinate, we observe differences in mixture equilibria that are due to physical differences between the components. The volume per unit cell (or per α-cage) of NaA is 1.844 nm^3 and includes regions of the zeolite unreachable by the adsorbates. At low chemical potential, we observe that xenon adsorbs preferentially to the virtual exclusion of the competing species. At higher chemical potential, the smaller component is observed to enter the pore. In the case of argon, some of the xenon is displaced and argon becomes the dominant species. In the case of methane, xenon is not displaced but some methane is able to enter the porespace. This feature is discussed further below.

Differences between the mixture and single component isotherms may be determined by calculating the excess density due to mixing from Eqs. 2 and 3. These are plotted in Figure 6. We note that at low chemical potential, both mixtures are nearly ideal (excess densities are near zero). At high chemical potential, the mixing may become non-ideal. In the xenon-argon mixture, the excess xenon and argon becomes positive and negative, respectively. The total excess density of mixing is positive at intermediate chemical potential, reflecting a more efficient packing of the mixture, and negative at high chemical potential, reflecting a more efficient packing of the single components. The xenon-methane mixture is seen to behave in a much more ideal manner: non-idealities occur only at high chemical potential.

To further understand these observations, it is instructive to consider the structure of the adsorbed phase. Figure 1 shows the xenon-argon mixture

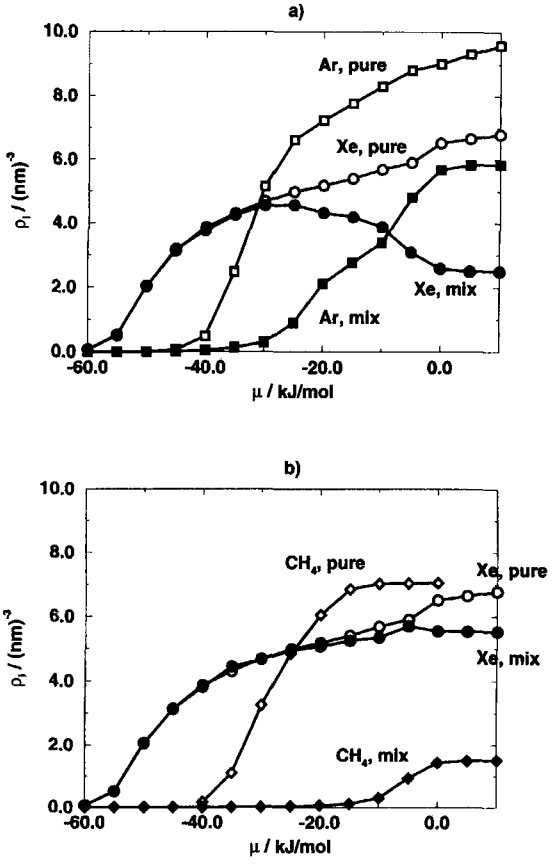

FIGURE 5 Single component (pure) and mixture a) xenon-argon and b) xenon-methane isotherms plotted as density of the adsorbed phase versus chemical potential. An equi-chemical potential ordinate is considered for the mixure in this and subsequent figures. Note that while xenon is favored at low chemical potential, argon (but not methane) may displace xenon at high chemical potential.

density distributions in the NaA α-cage. At intermediate chemical potential, both species compete for positions near the 4-membered rings and as xenon is favored energetically, it adsorbs preferentially. At higher chemical potential, argon is able to occupy additional pore space not accessible to xenon. Simulation snap shots (Fig. 2) also provide evidence of argon being able to sample more of the pore space than xenon. This represents a clear packing advantage; it's presence results in non-ideal mixing and is responsible for the displacement of xenon seen in Figure 5. In contrast, Figure 3

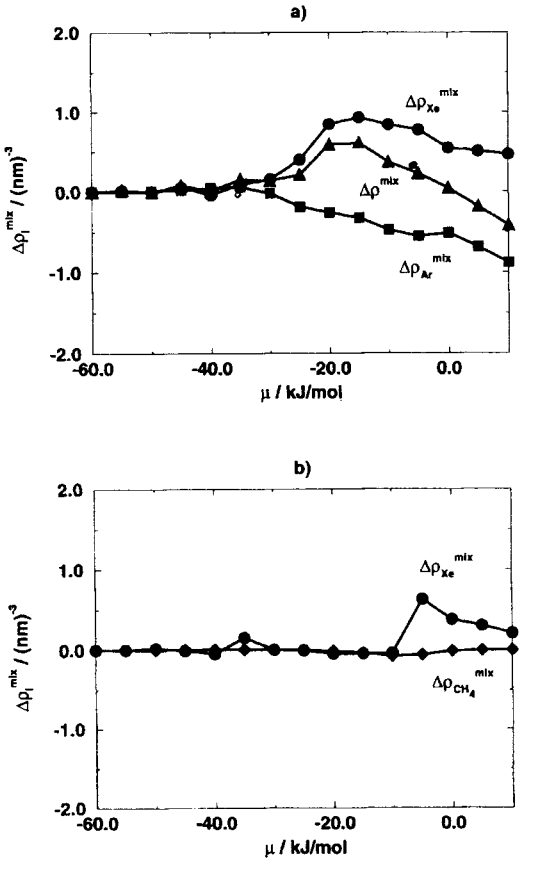

FIGURE 6 The excess density of mixing as defined in Eqs. 2–3 for a) xenon-argon and b) xenon-methane mixtures. Note that the mixing is much more ideal in the xenon-methane system.

shows that xenon and methane compete for the same positions in the pore. The mixing is much more ideal, no appreciable packing advantage is apparent, and we observe no displacement to occur.

We now turn our attention to the explicit effect of the adsorbent on the mixture and examine selective adsorption. The appropriate reference system is a bulk mixture at the same temperature and chemical potentials. Figures 7a-b show the partial densities of adsorbed and bulk xenon-argon and xenon-methane mixtures. Interestingly, the bulk phases exhibit qualitatively similar behavior: xenon favored at low chemical potential in both mixtures and argon (but not methane) being able to displace xenon. The total density

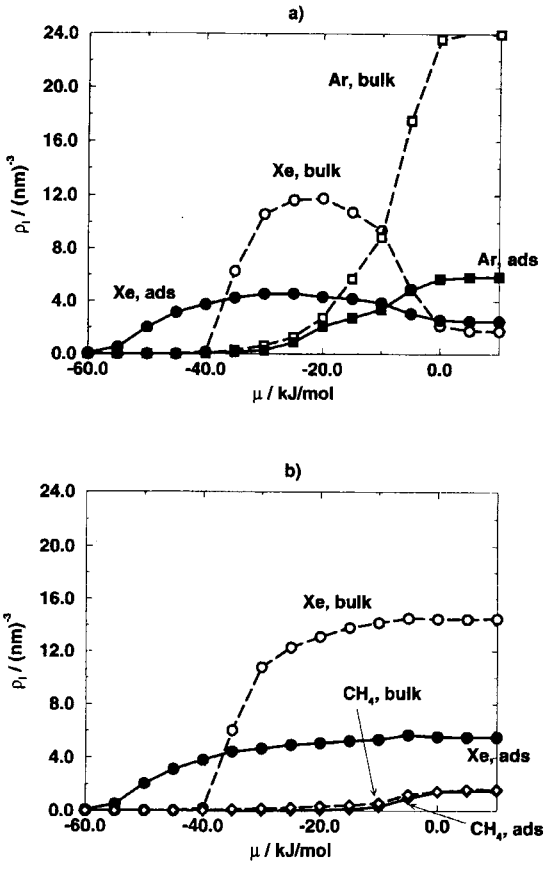

FIGURE 7 Adsorbed and bulk phase a) xenon-argon and b) xenon-methane mixture isotherms plotted as density of the adsorbed phase versus chemical potential. Note that the behavior of the adsorbed and bulk mixtures are qualitatively similar.

of the bulk fluid can be greater than the adsorbed one; this reflects the presence of unavailable space in the zeolite.

Figure 8a shows that the excess density of xenon due to adsorption in the xenon-argon mixture is positive at low chemical potential (reflecting its strong adsorption) and negative at higher chemical potential (reflecting the greater volume available in the bulk compared to the zeolite). The fact that at the highest chemical potential, the excess density due to adsorption returns to zero indicates a second domain of preferential adsorption of xenon (see below). The excess density of argon and the excess total density due to adsorption are always non-positive and are seen to decrease steadily

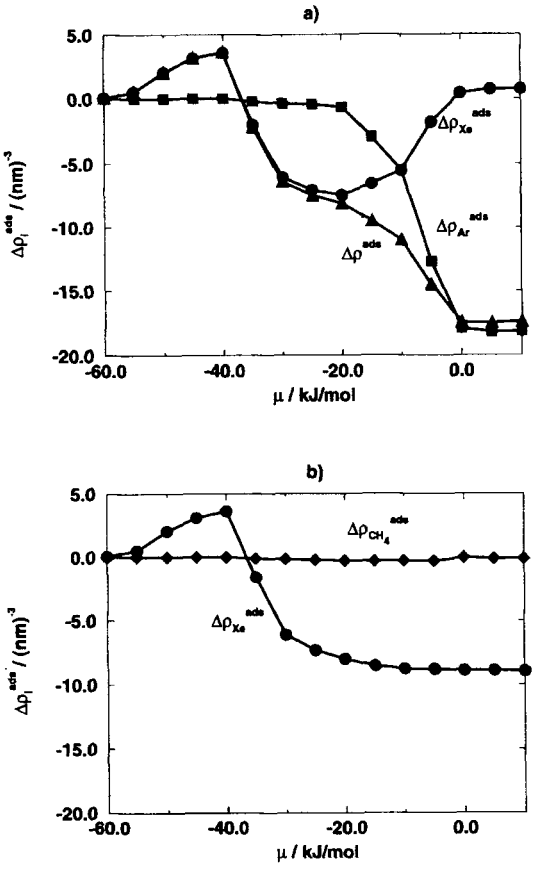

FIGURE 8 The excess density of adsorption as defined in Eqs. 4–5 for a) xenon-argon and b) xenon-methane mixtures.

with chemical potential, this again being due to the presence of inaccessible volume in the zeolite.

In the xenon-methane mixture (Fig. 8b), the excess density of xenon due to adsorption again goes from positive to negative with increasing chemical potential, but does not begin to increase at the highest chemical potentials. This is mainly due to the lack of displacement by methane of xenon in the bulk. Interestingly, the excess density of methane due to adsorption remains near zero.

The selectivity calculated via Eq. 6 is shown in Figure 9. Xenon is seen to adsorb selectively in both mixtures at low chemical potential due to its greater energetic attraction to the zeolite as compared to argon or methane. The selectivity decreases with chemical potential and eventually a reversal

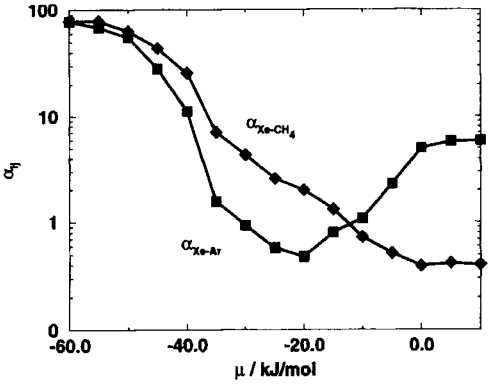

FIGURE 9 The selectivity as defined in Eq. 6 for xenon-argon and xenon-methane mixtures plotted versus chemical potential. Note that in both systems, the selectivity shifts from xenon to argon or methane upon going from low to high chemical potential.

occurs so that either argon or methane is selectively adsorbed. This reversal in selectivity, discussed further below, occurs at a lower chemical potential in the xenon-argon mixture. This reflects the greater packing advantage of argon (compared to methane). Finally, we note that in the xenon-argon mixture, the selectivity reaches a minimum and at very high chemical potential, xenon again is selectively adsorbed. This shows that the preferential packing arrangement of the xenon-argon mixture becomes a disadvantage at high chemical potential, that is, argon actually packs more efficiently in the bulk.

V. DISCUSSION

Our simulation study of adsorbed and bulk binary mixtures demonstrates the existence of two related phenomena. The first is a reversal in selectivity which indicates a change from one preferentially adsorbed species to another (according to Eq. 7). The second is a crossover in the binary isotherm. It is tempting to conclude from the presence of a crossover in the xenon-argon adsorption isotherm and lack thereof in the xenon-methane one that a reversal in selectivity is occurring in the former and not in the latter. However, selectivity depends equally on the bulk system whose behavior is shown here to be qualitatively similar. Is selective adsorption occurring? If so, are we truly seeing a reversal in selectivity in the xenon-argon mixture? Figure 9 indicates that the adsorption is indeed selective and that actually *two* reversals are occurring with first xenon, then argon, then xenon again

being selectively adsorbed in going from low to high chemical potential. Figure 9 further shows that we are also seeing a reversal in selectivity in the xenon-methane mixture, even though no crossover exists in the isotherm for that system.

The existence of the crossover in the xenon-argon bulk and adsorption isotherms may be explained by considering the grand potential free energy defined in Eq. 1. In the limit of low chemical potential, a very low density minimizes Ω. The composition is then dictated by the infinite dilution energy and entropy; both of these favor xenon [14]. At a high chemical potential, a high density minimizes Ω. The composition is dictated by packing effects (i.e. how many molecules may be placed in a given volume) along with energetic and entropic effects. Argon, differing sufficiently in size from xenon, will be favored at high chemical potentials due to packing effects. Hence, one observes crossovers in both adsorbed and bulk systems. In contrast, the size ratio is closer to unity in the xenon-methane mixture, methane enjoys less of a packing advantage, and no crossover is observed. It must be remembered that although an isotherm crossover depends only on the components energy, entropy, and packing ability in a single phase, the selectivity depends on differences in these quantities between adsorbed and bulk phases.

In addition to selectivities, we define and present excess properties due to mixing and adsorption. Although well defined, the information they give must be carefully interpreted. For example, the excess partial density due to mixing (Eq. 3, Fig. 6) is seen to be positive (negative) for the component which is disfavored (favored) in the xenon-argon mixture. This seemingly paradoxical result is due to the higher plateau of the argon single component isotherm, which itself is related to the packing advantage that causes the displacement of xenon and the rapid decrease in selectivity with chemical potential. Another example is that the excess partial density due to adsorption (Eq. 5, Fig. 8) may be negative even when the component in question is the one selectively adsorbed ($\alpha_{ij} > 1$). This is mainly due to the inaccessible volume of the zeolite. In contrast, the total excess density due to mixing has a direct interpretation: it represents the efficiency of pore filling in the mixture as compared to the single component systems.

Based on the mixtures studied here, we postulate that a reversal in selectivity may be a general feature associated with microporous materials such as zeolites. A larger, more polarizable component in a mixture will adsorb preferentially at low pressure for energetic reasons, and a smaller component will adsorb preferentially at high pressure due to a combination of

packing, energetic, and entropic effects. We further suggest that the greater the difference in size between the components, the lower the pressure at which the crossover will occur. Monson has noted a decrease in selectivity of the larger species with increased pressure in one-dimensional mixtures which is more pronounced for large size differences [26]. This finding is in qualitative agreement with the trends observed here.

Recent work has demonstrated that reversals in selectivity can also be achieved simply by changing the size of a geometrically shaped pore [27–31]. This finding offers the promise of flexible control over separations by choosing from amongst various adsorbents. Based on the present work, we add that the *same* adsorbent can be used to selectively adsorb either component in a binary mixture. This potentially allows for even further flexibility in gas-phase separations using zeolites.

Acknowledgements

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