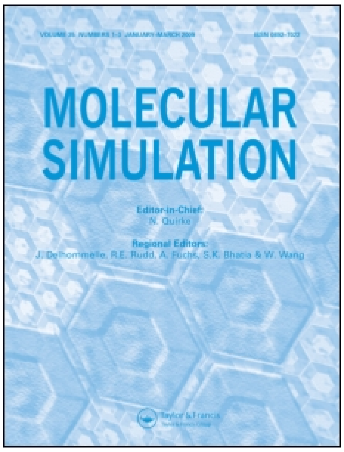

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Mixtures of Associating and Non-associating Chains on Activated Surfaces: A Monte Carlo Approach

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MIXTURES OF ASSOCIATING AND NON-ASSOCIATING CHAINS ON ACTIVATED SURFACES: A MONTE CARLO APPROACH

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The behavior of mixtures of associating and non-associating chains confined in pores with activated surfaces is studied by means of molecular simulation. The fluid molecules are modeled as a chain of four tangent Lennard-Jones spheres. Some of the chains have an additional associating square-well site placed in an end sphere. The activated surfaces of the slit pore are modeled via an integrated Lennard-Jones (10-4-3) potential with specific association sites protruding from the surface. We present Gibbs ensemble Monte Carlo simulation results for the partitioning of mixtures of chains in the bulk and confined phases for this particular model. The chain-wall association governs the adsorption behavior of the system. The preferential adsorption of associating chains is seen to strongly depend on temperature and pore width. Selectivities obtained are in the range of those seen in experiments of alkane-alkanol mixtures.

KEY WORDS: associating chains, mixtures, Gibbs ensemble Monte Carlo simulations, slit pores, activated surfaces, adsorption.

1. INTRODUCTION

The ability to separate mixtures of gases or liquids is fundamental to a large number of industrial processes. One method of performing such separations is to selectively adsorb one component of the mixture in a porous material. In the case of associating fluids an effective way of carrying out the process is to use activated surfaces in which associating molecules can bond to specific sites. It is known [1] that the major chemical forms in which heteroatoms are present in activated carbons are functional groups and heterocyclic compounds analogous to those in organic compounds. Some of these groups are exposed on the surface and have a major influence on the adsorption process.

We are interested in studying the influence of temperature, pore width and bulk density (or pressure) on the selectivity of associating chains versus non-associating chains on activated surfaces. Our goal is to obtain a fundamental understanding of how different variables affect the selectivity of a given component rather than to model a specific system. A longer range aim of our work is the understanding of the behavior of associating fluids in porous media for specific applications.

Unfortunately, direct experimental investigations are complicated by the difficulty of separating the effects of the different variables involved and/or because the materials are poorly characterized. Molecular simulation can provide valuable information on model systems since the effect of the different variables can be specifically separated in the study. While in principle a suitable theory can provide the same information, no accurate theories for the behavior of associating chains in confined media are yet available.

In a previous study [2] we have shown that the adsorption of associating molecules can be modified and enhanced by doping or activating the surfaces. We found that in the absence of association sites on the walls the adsorption behavior of associating chains is characterized by the medium range solid-fluid interactions. However, the presence of associating sites on the walls, even at very low concentrations, significantly enhances the adsorption of associating chains and radically modifies the pore filling structure of the fluid.

In this work we report Gibbs ensemble Monte Carlo simulation results for equimolar mixtures of associating and non-associating chains confined in slit-like pores with activated surfaces. The influence of temperature, pore width and pressure on the adsorption selectivity are presented and discussed here. As far as we are aware, this is the first simulation study in which mixtures of associating fluids confined in activated surfaces are considered.

2. MODEL

We consider the equilibrium between a bulk and a confined phase of an equimolar binary mixture of non-associating and associating chains. Our model molecules consist of a flexible chain of four tangently bonded *LJ* spheres, as shown in Figure 1. The distance between bonded beads is fixed and equal to σ_{LJ}. The potential of interaction between any two non-bonded spheres, belonging to the same chain or to different chains is given by:

$$\phi_{LJ} = 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right] \tag{1}$$

where ε_{LJ} and σ_{LJ} are the characteristic energy and size parameters of the *LJ* potential and r_{ij} is the center-to-center distance between any two *LJ* spheres *i* and *j* in the fluid. The total intermolecular potential will be the sum by pairs over all *i* and *j* spheres in the fluid. Reduced units are expressed in terms of σ_{LJ} and ε_{LJ}. The values used for these parameters will be given and discussed later.

We consider a mixture of both non-associating chains, consisting of four *LJ* spheres, and associating chains having four *LJ* spheres with an associating site on one end; this associating site allows for intermolecular association or association between a site on

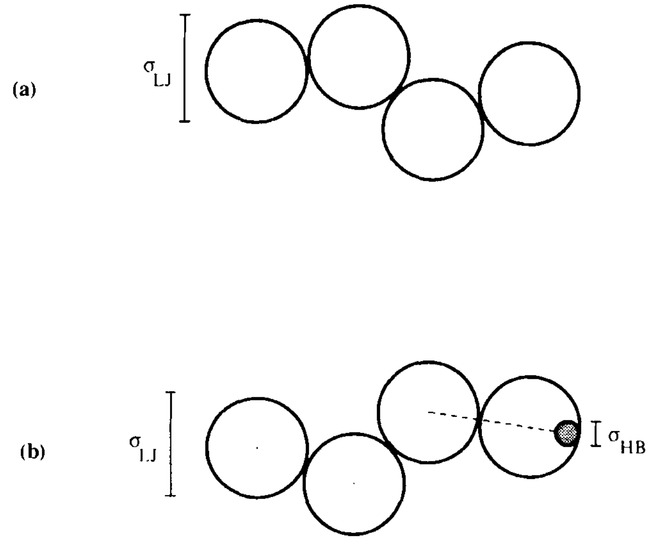

Figure 1 Two dimensional view of the molecules studied. a) Four freely jointed tangent *LJ* spheres. b) Four freely jointed tangent *LJ* spheres with a square-well site (shaded) on the end sphere. The exact position of the site is explained in the text.

a molecule and a site on a surface. The association between two different fluid molecules or between a fluid molecule and a site on the surface is mimicked by means of a spherical square-well site potential, ϕ_{HB},

$$\phi_{HB} = \begin{cases} -\varepsilon_{HB} & \text{if } r_{\alpha\beta} < \sigma_{HB} \\ 0 & \text{otherwise} \end{cases} \tag{2}$$

where ε_{HB} is the depth of the square-well, σ_{HB} is the diameter of the site and $r_{\alpha\beta}$ is the square-well site to square-well site distance. The depth of the square-well site ε_{HB}, was set equal to 30 times the characteristic *LJ* energy, ε_{LJ}. This value has been used previously [2] and is chosen as representative of a strong hydrogen bond [3]. A square-well site of diameter $\sigma_{HB} = 0.2\,\sigma_{LJ}$ is placed at a distance of $0.4\,\sigma_{LJ}$ from the center of the end sphere of each associating molecule, so as to be tangent to the *LJ* core. The exact position is determined by the direction of the vector joining the center of the end sphere and the center of its neighboring sphere, and in the position farthest from the center of the molecule, as shown in Figure 1. This placement forces two bonded molecules to have some degree of overlap of their respective *LJ* cores, as expected for real associating fluids.

The full intermolecular potential between two molecules in a bulk phase ϕ_{ff}, is the sum of two contributions, one that encompasses the principal effects of repulsion and dispersion between the spheres, ϕ_{LJ}; and another which takes into account the short range directional attraction peculiar to associating fluids, ϕ_{HB},

$$\phi_{ff} = \phi_{LJ} + \phi_{HB} \tag{3}$$

The confined phase consists of a single slit-like pore having two infinite parallel walls in the $x - y$ plane separated by a distance H in the z direction. Each of the two walls is taken to be a (100) plane of a FCC lattice. For the chain-wall interaction the full Lennard-Jones potential is used. The *LJ* potential between one sphere of the fluid and each of the molecules of the solid is integrated over the lateral solid structure. By summing over the planes of molecules in the surface the 10-4-3 potential is obtained [4]:

$$\phi_{\mathrm{wall}}(z) = 2\pi\rho_s\varepsilon_{sf}(\sigma_{sf})^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z+0.61\Delta)^3}\right] \tag{4}$$

where ρ_s is the solid density and Δ the separation between planes of molecules in the solid. The cross solid-fluid interaction parameters $(\sigma_{sf}, \varepsilon_{sf})$ are calculated from the Lorentz-Berthelot rules: $\sigma_{sf} = (\sigma_{ss} + \sigma_{LJ})/2$ and $\varepsilon_{sf} = (\varepsilon_{ss}\varepsilon_{LJ})^{1/2}$, where σ_{ss} and ε_{ss} are the size and energy parameters of the *LJ* spheres forming the walls. ρ_s, Δ and σ_{ss} have been chosen to model a graphite surface [4]: $\rho_s = 114\,\mathrm{nm}^{-3}$, $\Delta = 0.335\,\mathrm{nm}$ and $\sigma_{ss} = 0.340\,\mathrm{nm}$. The size parameter of the spheres of the fluid has been fixed to $\sigma_{LJ} = 0.3678\,\mathrm{nm}$, a value close to the size of the *LJ* methane [5]. Once the density of the walls is given, the parameter which mainly governs the effect on the attraction of the fluid molecules to the walls is the cross energy parameter, ε_{sf}. Since we are interested in improving the adsorption properties of weakly attractive walls, a relatively small value of the ε_{sf} parameter has been used, $\varepsilon_{sf}/\varepsilon_{LJ} = 0.0625$. For comparative purposes the $\varepsilon_{sf}/\varepsilon_{LJ}$ corresponding to a decane molecule confined in graphite plates is approximately 0.25 [5]. In our previous work [2] we showed that for such highly attractive walls, the adsorption is large for both associating and non-associating molecules. In this work we wish to study how to reverse the case of poor adsorption by the addition of heterogeneities on the pore surfaces (activation).

The activated surface is obtained by placing associating sites in a regular square array of periodicity a [2]. The site density of the wall is equal to $1/a^2$ sites per unit area; in this work a relatively high density of sites, $\sigma_{LJ}^2/a^2 = 0.25$, is considered. The associating sites have the same characteristic size and well depth ($\varepsilon_{HB} = 30\varepsilon_{LJ}$, $\sigma_{HB} = 0.5\sigma_{LJ}$) as the ones placed on the molecules. Sites are placed with their centers at a distance $z = 0.5\sigma_{LJ}$ from the wall into the pore, i.e. exposed to the surface, as observed in experimental situations [1] and in contrast to the associating molecules of the fluid in which the site is embedded into the *LJ* core. The influence of these placements on the adsorption behavior will be discussed later. In summary, the total solid-fluid interaction potential is then given by:

$$\phi_{sf} = \phi_{\mathrm{wall}} + \phi_{HB} \tag{5}$$

Since equation (5) is the potential exerted by one wall, for a given slit pore width H, the external potential ϕ_{ext} experienced by any *LJ* sphere in the fluid at z is calculated as the superposition of ϕ_{sf} for the two walls:

$$\phi_{\mathrm{ext}}(z) = \phi_{sf}(z) + \phi_{sf}(H - z). \tag{6}$$

where the pore width H is defined as the distance separating the planes, on each side of the pore, through the centers of the LJ forming the surface of the walls.

3. SIMULATION DETAILS

As in our previous work [2] we have used an extension of the Gibbs methodology applied to inhomogeneous fluids, as presented by Panagiotopoulos [6]. One of the simulation boxes represents the confined phase and the other one represents the bulk. In this case only displacement of molecules and transfer of molecules between phases are necessary in order to achieve equilibrium. Volume changes are not necessary, since mechanical equilibrium is automatically enforced. The advantage of using GEMC versus a more traditional Grand canonical Monte Carlo simulation is that in our case we obtain the equilibrium properties of the two phases in a single simulation.

Molecules were placed in random positions at the beginning of the simulation. Volumes for the bulk and pore regions were assigned and kept constant. A total of 100 molecules (400 spheres) were placed in each phase, with a 50–50 distribution (half of them associating, half of them non-associating chains). The system evolves through Monte Carlo cycles, consisting of 100 attempts of reptation moves within each phase, followed by 100 attempts to transfer molecules between phases. The insertion of chains was performed bead-by-bead, adding the associating site to the molecule only if it has been successfully inserted. In cases where an overlap was detected the move was immediately rejected. The acceptance rate was about 30% and 4% for the displacement and transfer moves, respectively.

Standard periodic boundary conditions [7] and minimum image conventions were applied in all Cartesian directions for the bulk fluid and in the x and y directions in the pore. The periodic length was adjusted to achieve the desired density. In the bulk phase the potential cutoff was set to half the box size and long range corrections [7] were applied. No long range corrections were applied to the confined fluid, due to the computational difficulties associated with it. However, care was taken so that the minimum pore length ($L_{x,y}$) was at least $10\sigma_{LJ}$. The maximum error in energy resulting in from the neglect of long range corrections is less than 0.1% in this case.

Simulations needed to be very long in order to ensure that equilibrium was reached. The system was allowed to equilibrate for a minimum of 25000 cycles (7.5×10^6 configurations), and averages were taken over a minimum of 30000 cycles after equilibration (9×10^6 configurations). Longer runs were necessary for the lower temperatures considered. Figure 2 shows an example of a typical run, where the number of molecules in the confined phase is plotted versus the number of Monte Carlo cycles. Fluctuations in the number of associating molecules are greater than those of the non-associating molecules, due to the formation and destruction of bonds along the simulation.

Three different reduced temperatures have been considered $T^* = kT/\varepsilon_{LJ} = 4.5$, 3.5, and 3.0. A previous study [8] has shown that the bulk critical temperature of the associating chains is close to $T^* = 3.0$. In order to study the influence of the pore size on the adsorption selectivity, two different pore widths are also considered: $H^* = H/\sigma_{LJ} = 15$ and 7. In all cases a selectivity curve is calculated as a function of the bulk density.

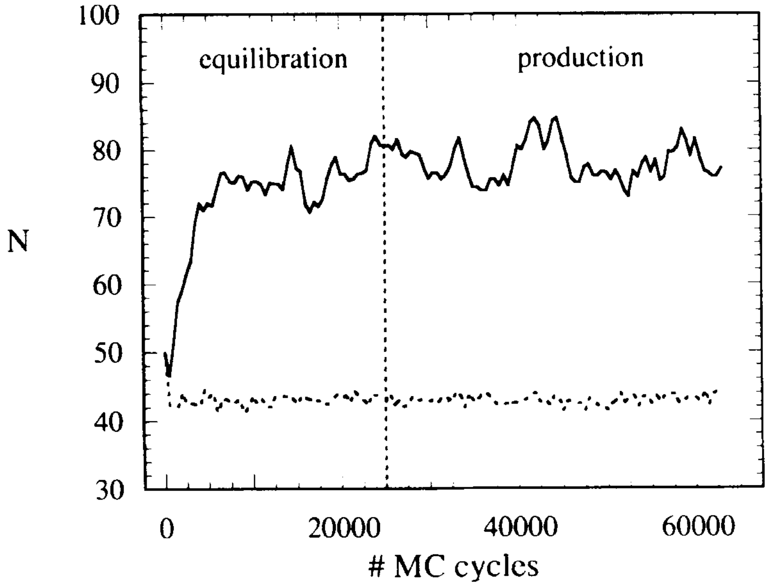

Figure 2 Number of associating (full line) and non-associating chains (dashed line) in the pore versus number of Monte Carlo cycles. Vertical dashed line indicates the division between the equilibrium and the production stages of the run. The system is studied under conditions of reduced temperature $T^* = 3.5$, reduced pore width $H^* = 7$ and reduced bulk density $\rho^*_{\text{bulk}} = 0.0167$.

We have defined the selectivity of component 2 (associating chain) versus component 1 (non-associating chain) as the ratio of mole fractions in the pore divided by the ratio of the mole fractions in the bulk, namely:

$$S_2 = \frac{(x_2/x_1)_{\text{pore}}}{(x_2/x_1)_{\text{bulk}}} \tag{7}$$

where x_2 is the mole fraction of associating molecules and x_1 refers to the mole fraction of non-associating molecules, i.e. $(x_i)_{\text{pore}} = (N_i/N)_{\text{pore}}$ where N_i refers to the number of molecules of component i and N to the total number of molecules. Selectivity curves are plotted versus the sphere bulk density of the system (total number of LJ spheres divided by the bulk volume).

4. RESULTS AND DISCUSSION

The equilibrium between a bulk and a confined phase of mixtures of associating and non-associating chains is studied via Gibbs ensemble Monte Carlo simulations. The system is studied under three different reduced temperatures ($T^* = 3.0$, 3.5 and 4.5) and two reduced pore widths ($H^* = 7$ and 15). Results concerning the adsorption selectivity under these conditions are presented and discussed here. The selectivity is greater than 1 in all cases considered. We have also studied the competition between self-association in the fluid and grafting to the walls.

We will first discuss the influence of pore width and temperature on the adsorption selectivity. The competition between self-association and association with the walls will be addressed later.

4.1 *Influence of Pore Size on Adsorption Selectivity*

In the case where molecules have different sizes and energies of interaction the pore size has been proved to strongly influence the selectivity of one of the components, especially in the infinite dilute regime [9]. At very small pore widths, the larger component is excluded from the pore by steric hindrance, and therefore the selectivity of the smallest component is greatly enhanced; at intermediate pore sizes both components can enter the pore, and the selectivity will be greater for the molecules with the strongest solid-fluid attraction; at very large pore sizes the attraction of the walls decreases for both components, the fluid inside the pore behaves as a bulk fluid and the separation is ineffective.

In the cases considered here, all molecules have the same size, so differential adsorption (selectivity) will be directly related to the characteristics of the fluid-wall interactions. In Figure 3 GEMC results for selectivity isotherms for reduced pore widths $H^* = 15$ and 7 at a reduced temperature $T^* = 3.5$ are shown. It can be seen that the selectivity is higher for the smallest pore considered here ($H^* = 7$) and it decreases as the pore size increases. The selectivity decreases when the bulk density is increased. Once the first associating molecules are able to graft to the surfaces they "shield" the strong attraction exerted by the activated surfaces. The selectivity is greater than 1 in all the cases considered.

In Figures 4 and 5 we show two snapshots of the system under the same temperature ($T^* = 3.5$) and similar bulk density, at two different pore widths; the effect of the pore

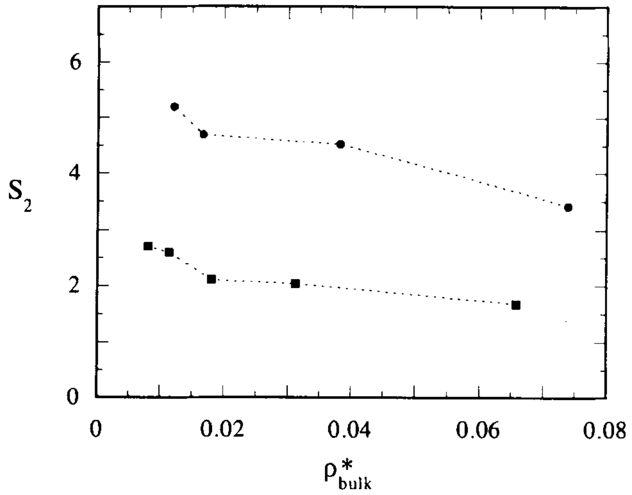

Figure 3 Selectivity isotherm versus reduced bulk density for two different pore widths at $T^* = 3.5$. Circles represent $H^* = 7$ and squares $H^* = 15$. Dashed lines join the points, and are a guide to the eye.

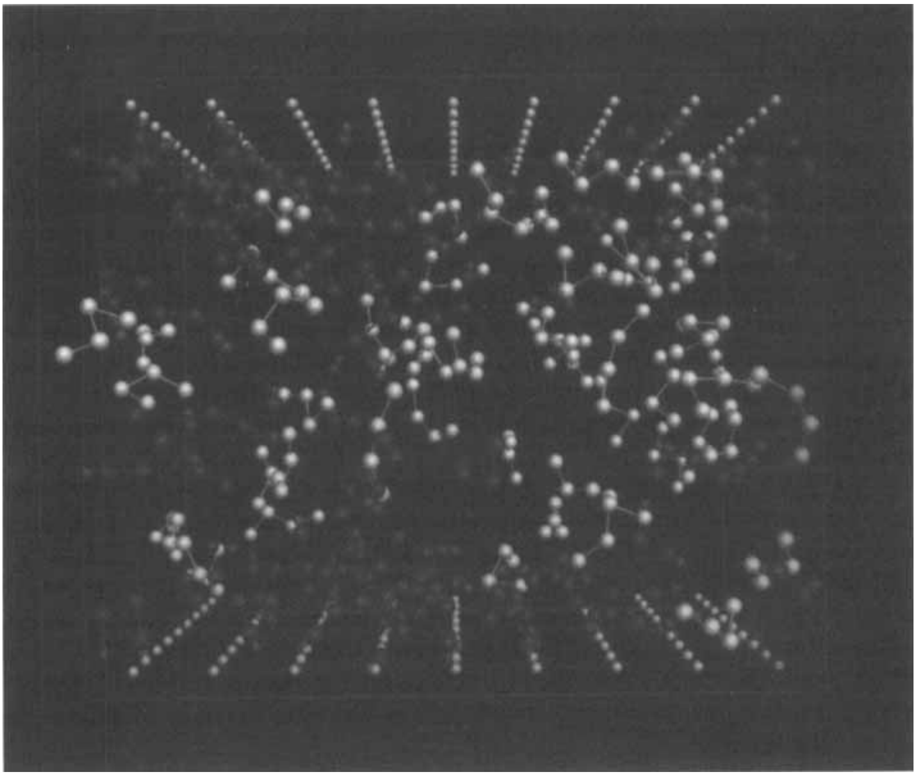

Figure 4 Snapshot of a configuration inside a pore of $H^* = 15$, $V^* = 4860$, $T^* = 3.5$ and bulk density $\rho^*_{\text{bulk}} = 0.0181$. Associating chains are represented by the red spheres, correspond to the *LJ* cores and green spheres, corresponding to the associating sites. Non-associating molecules are represented by the white spheres, corresponding to the *LJ* cores. Sites on the walls are represented by yellow spheres. Spheres are shown with a volume much smaller than their corresponding core volume to help visualize the structure of the molecules. Pore walls are on the top and bottom of the box. See Color Plate I.

width on the selective adsorption is clearly seen. In the case of the wider pore, $H^* = 15$ (Figure 4), many of the molecules are in the middle of the pore, and only those associating chains close to the walls are able to bond to the surfaces. This is mainly due to the fact that the walls are weakly attractive to the fluid ($\varepsilon_{sf} = 0.0625\varepsilon_{LJ}$). Only associating chains very close to the walls are able to feel the short range, highly directional, attraction of the active sites on the surfaces. The competition between the tendency of the individual *LJ* spheres forming a chain to place themselves in the middle of the pore (which happens when neutral chains are confined between weakly attractive walls [2]) and the strongly favorable bonding of the end sphere of an associating molecule onto the wall encourages them to graft in a direction perpendicular to the surfaces. Some fluid molecules are associated among themselves in the middle of the pore.

The microscopic behavior of the system changes drastically when the pore size is reduced from 15 to 7 σ_{LJ}, as seen in Figure 5. Due to the proximity of the walls the

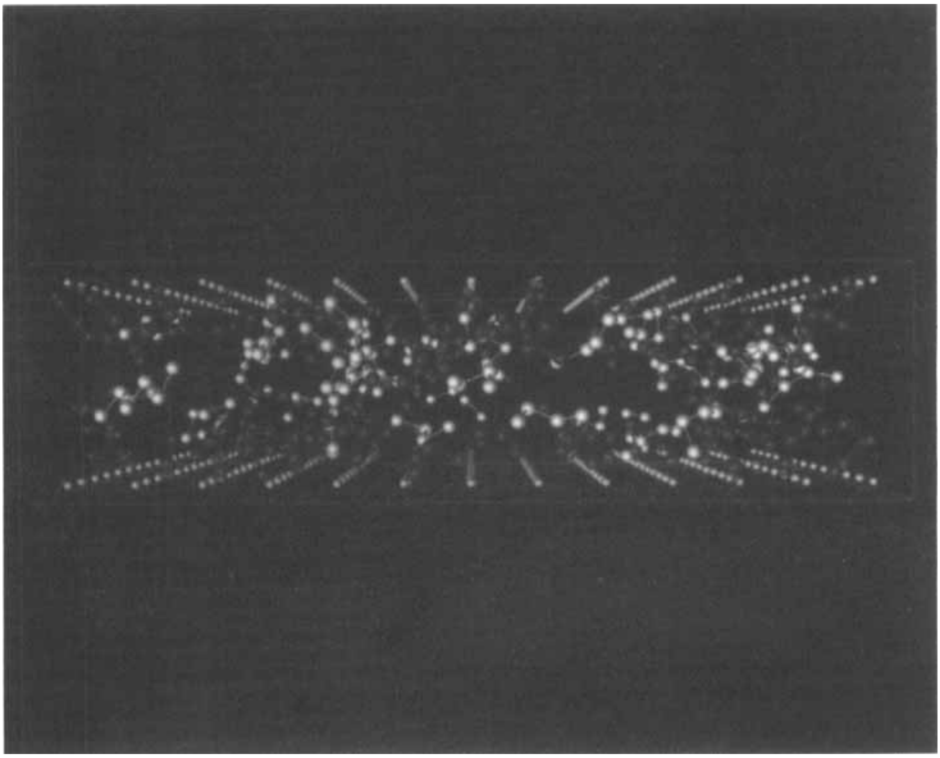

Figure 5 Snapshot of a configuration inside a pore of $H^* = 7$, $V^* = 4732$, at $T^* = 3.5$ and bulk density $\rho^*_{\text{bulk}} = 0.0167$. Symbols as in Figure 4. See Color Plate II.

effective attraction is increased and associating molecules have an increased probability of grafting onto the walls. The net effect is an enhancement of the selectivity.

4.2 *Influence of Temperature on Adsorption Selectivity*

To investigate the influence of temperature on the preferential adsorption of associating chains we have chosen the smallest pore in our study ($H^* = 7$), where the selectivity is greater.

In Figure 6 we show three selectivity isotherms as a function of the bulk density. The selectivity decreases with increasing temperature, as expected. The effect is even greater for low bulk densities. There is a drastic change between $T^* = 3.0$ and the other two reduced temperatures, $T^* = 3.5$ and 4.5: for the lower densities the selectivity is an order of magnitude greater $T^* = 3.0$ than at $T^* = 4.5$, while for high temperatures values are close to unity. For associating fluids, the associating strength is related to $\exp(\varepsilon_{HB}/kT)$, hence an increase in temperature produces a marked decrease in the relative importance of association. Figure 6 shows that temperaturue can play an important role in enhancing the selectivity of associating fluids.

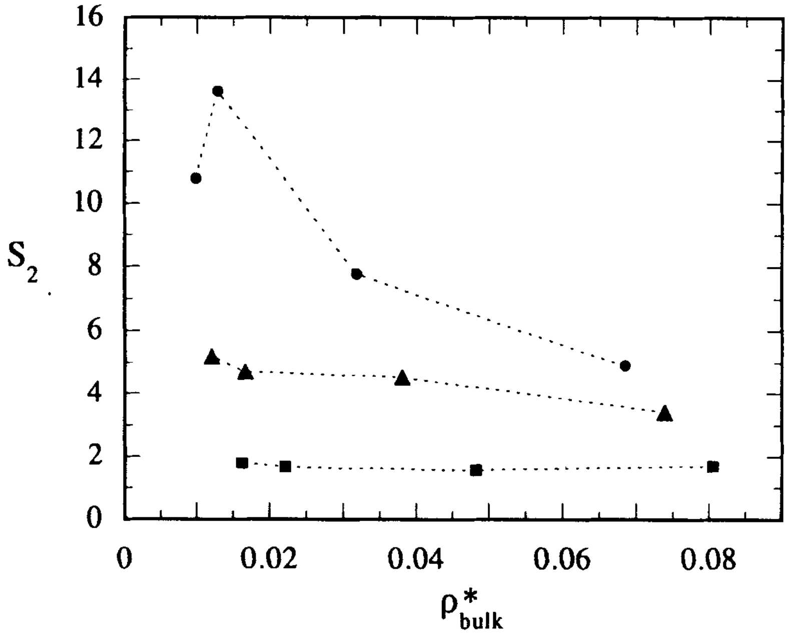

Figure 6 Selectivity isotherms versus reduced bulk density at $H^* = 7$. Circles represent $T^* = 3.0$, triangles $T^* = 3.5$ and squares $T^* = 4.5$. Dashed lines join the points as a guide to the eye.

The selectivity curve corresponding to $T^* = 3.0$ in Figure 6 presents a maximum. Lower densities (larger pore surfaces and more associating sites) will not further enhance adsorption since all molecules are already grafted to the walls. On the other hand, at higher densities molecules must compete for the associating sites and selectivity again decreases.

A typical equilibrated configuration at the highest temperature can be seen in Figure 7, where we show a snapshot of the system at the same pore width and volume as in Figure 5, but at a different temperature, $T^* = 4.5$. Due to the high temperature considered, few associating molecules are bonded to the walls. For such high temperatures the activation of the walls becomes unimportant and molecules show a bulk-like behavior inside the pore. The equilibrium density in the pore is smaller than for the lower temperature case, although both simulations began with the same initial conditions (volumes, number of molecules in each phase, etc.) confirming that the selectivity of associating molecules is improved when the temperature is lowered.

In summary, it has been seen that the selectivity of associating molecules versus non-associating molecules confined in pores with activated surfaces is enhanced when both the pore width and the temperature are reduced. In the next section we discuss the effect that the choice of the associating sites and their location has in the adsorption behavior of the system.

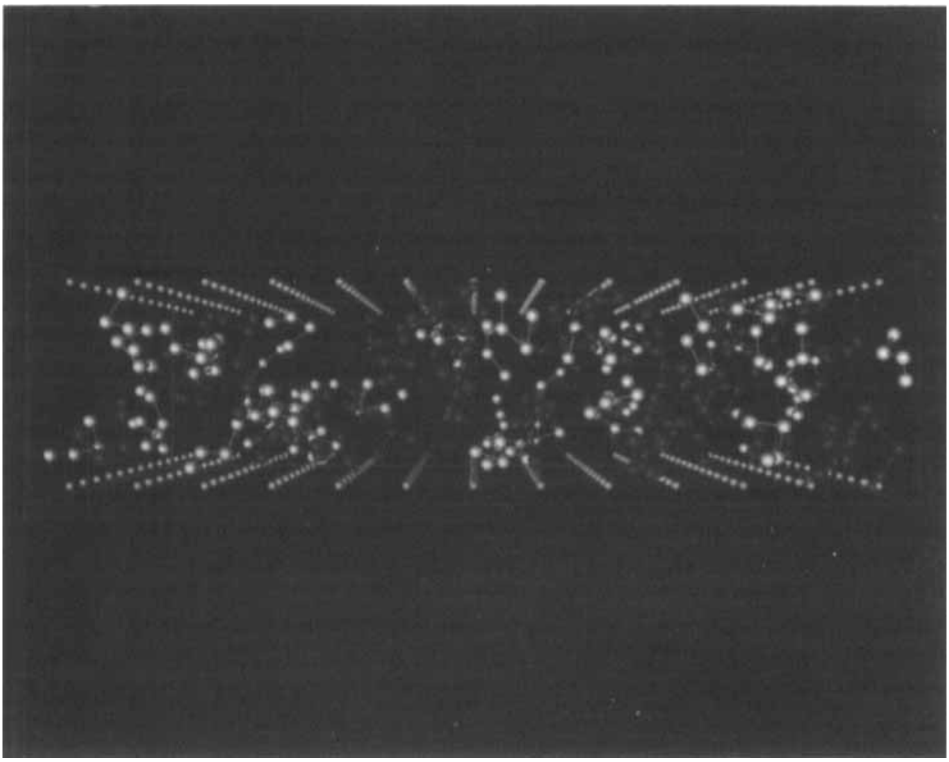

Figure 7 Snapshot of a configuration inside a pore of $H^* = 7$, $V^* = 4732$, at $T^* = 4.5$ and bulk density $\rho^*_{\text{bulk}} = 0.0221$. Symbols as in Figure 4. See Colour Plate III.

4.3 *Self-Association versus Grafting to the Walls*

When studying associating fluids confined in activated surfaces it is of interest to investigate the competition between self-association in the fluid and association with the walls. There are several factors governing this behavior: temperature, pore width, strength of the different sites, density of sites on the walls and position of the associating sites in the molecules and on the surfaces.

As mentioned in Section 2, we have considered in our model sites which are protruding from the walls, while associating sites on the molecules are embedded inside the *LJ* sphere. Both cases (walls and chains) correspond to the actual experimental observations. It should be noticed that even though the associating sites on the walls have the same parameters as the associating sites on the molecules, the intermolecular association is not equivalent [2]. The fact that the sites are embedded inside the *LJ* core forces two bonded molecules to have some degree of overlap of their respective *LJ* cores, which is energetically unfavorable due to the strong repulsive forces of the *LJ* cores. On the contrary, molecules can easily bond to the surfaces under the same conditions, since their cores do not need to overlap in this case.

Under these circumstances, association to the walls occurs more readily than fluid–fluid association, especially at high temperatures where there is little association in the fluid.

To further investigate this phenomenon we have run two parallel sets of simulations. In the first set associating molecules in the fluid are able to associate with themselves and with the walls, the energy and size parameters of the sites are the same for both fluid-wall and fluid-fluid interactions ($\varepsilon\varepsilon_{HB} = 30\varepsilon_{LJ}$, $\sigma_{HB} = 0.2\sigma_{LJ}$), and sites are placed as explained previously. In the second set the associating chains of the mixture are able to bond to the surfaces but not to themselves (no intermolecular bonding); the other parameters are the same as in the first set. An example of such a physical situation is a system having charged chain molecules, where the walls have sites with opposite charge to those of the fluid molecules. Such a situation occurs in the preparation of some nanocomposites [10]. The rest of the parameters are kept the same: temperature, pore width, density, number of molecules, etc. Comparative results from these simulations are presented in Figure 8, where the selectivity curves for $T^* = 3.5$ are plotted as a function of the bulk density. It can be seen that the adsorption behavior for the model used here is dominated by the grafting to the walls, especially for high temperatures.

We have performed two additional studies for a particular point ($T^* = 3.5$, $H^* = 7$, $V^*_{\text{pore}} = 4372$) to see how relevant the position of the sites on the molecules is. In these simulations, the square-well site was placed at a distance of a) 0.45 and b) $0.5\sigma_{LJ}$ from the center of the sphere. While for the original position ($0.4\sigma_{LJ}$) the selectivity obtained was 4.70, values of 5.12 and 5.77 were obtained for cases a) and b) respectively. By

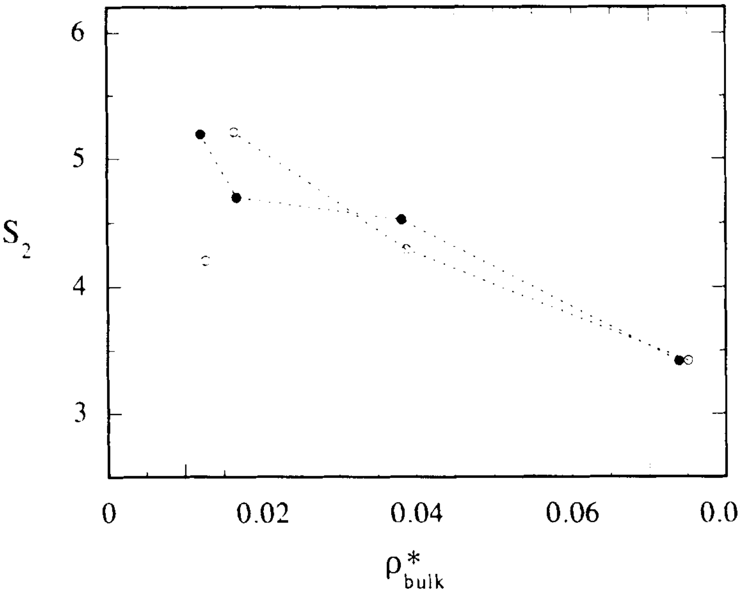

Figure 8 Selectivity isotherms versus reduced bulk density at $H^* = 7$ and $T^* = 3.5$. Full symbols correspond to the fluid able to associate to the walls and to other molecules, open symbols correspond to the fluid able to bond only to the walls. See text for details.

protruding the sites from the center of the repulsive *LJ* core, association is enhanced. The general trends are otherwise unchanged.

5. CONCLUSIONS

In this work the behavior of equimolar mixtures of associating and non-associating chains confined in activated surfaces has been studied by Gibbs ensemble Monte Carlo simulations. The influence of pore size and temperature on the selectivity of the associating chains has been investigated by considering three pore sizes as well as three reduced temperatures. We have also considered several bulk densities for each pore size and temperature.

Our results show that the preferential adsorption of associating chains decreases with increasing temperature and pore width, especially at low bulk densities. We have also seen that for the model used in this work the selective adsorption of the associating components is dominated by its grafting to the walls. The fact that the surfaces are activated plays the essential role in the adsorption behavior of these systems.

Our model is too crude to represent any realistic fluid, but at this point we are more interested in understanding the influence of different variables on the preferential selectivity of associating chains rather than in any specific system. Nevertheless, we note that the selectivities obtained are of the same order of magnitude as those observed experimentally for alkane-alkanol mixtures on activated carbons [11].

Acknowledgment

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