Adsorption 2, 59–68 (1996)

Effect of Surface Active Sites on Adsorption of Associating Chain Molecules in Pores: A Monte Carlo Study

LOURDES F. VEGA
School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA; and
Departament d'Enginyeria Quìmica, Universitat Rovira i Virgili, 43006 Tarragona, Spain

ERICH A. MÜLLER
School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA; and
Departamento de Termodinámica y Fenómenos de Transferencia, Universidad Simón Bolívar,
Caracas 1080, Venezuela

LUIS F. RULL
Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, 41080 Sevilla, Spain

KEITH E. GUBBINS
School of Chemical Engineering, Cornell University, Ithaca, NY 14853, USA

Abstract. This work describes the adsorption behavior of associating and non-associating chains and their mixtures in pores with activated surfaces. The systems are studied using Gibbs ensemble Monte Carlo molecular simulations. Fluid molecules are modeled as freely jointed Lennard-Jones chains. Associating chains have, additionally, an associating square-well site placed in an end sphere. The pores are modeled as regular slit pores via an integrated Lennard-Jones potential (10-4-3); activation is achieved by placing specific association sites protruding from the surface. Two different solid-fluid interaction parameters are used, one of which corresponds roughly to alkanes on graphite, the other being a much weaker interaction. Adsorption isotherms are presented for several different cases: associating and non-associating chains confined within both neutral and activated walls. Mixtures of associating and non-associating chains are also considered. The effects of pore size, temperature and chain length are quantified. Selectivities obtained are in the range of those seen in adsorption experiments of alkane-alkanol mixtures.

Keywords:

1. Introduction

It is well known that the activation of porous materials, e.g. carbon, has a profound effect on adsorptivity. Unfortunately, our knowledge comes mainly from empirical observations, i.e., conclusions drawn from macroscopic measurements such as adsorption isotherms and isosteric heats. These observations are subject to a number of uncertainties, e.g., pore size distribution, poorly characterized surfaces and geometries, nature and structure of the heterogeneities, etc., so most conclusions are expressed in general qualitative terms. While it would be desirable to have a theory which could describe these effects, none can yet deal with the effect that heterogeneities on a molecular scale have on macroscopic properties. Molecular simulations are thus a valuable tool in understanding the microscopic processes of adsorption and the effect that well-defined heterogeneities have on macroscopic observable properties. In these simulations, analytic pair potentials are proposed which mimic the features thought to be important for the description of particular types of fluids and solids. The properties of heterogeneous systems can then be obtained unambiguously for well characterized (known pore geometries, site locations, energies, etc.) systems.

In this work we present a model of associating molecules which depart from simple molecules in two important ways: a) we consider flexible chain molecules of several lengths up to an aspect ratio (length/diameter) of 4, and b) molecular association is included in a simple but physically meaningful way by means of square well associating sites. The fluids are allowed to adsorb into graphite-like slit pores. The pores have structureless surfaces which may be doped (activated) by placing additional association sites on the walls. This model has enough flexibility to allow a systematic study of the main variables which we believe govern the adsorption of associated fluids in activated pores, while retaining enough simplicity to be computationally tractable.

We have studied this model using Gibbs ensemble Monte Carlo simulations to obtain the adsorption isotherms of pure associating and non-associating chains and selectivities of mixtures in slit-like pores. The effects of pore width, interaction energies, temperature, chain length, type and amount of heterogeneous sites on the surfaces are considered. Although our model is too crude to accurately represent any realistic fluid, it has most of the essential features of alkane/alkanol mixtures on activated carbons, and helps elucidate the molecular behavior of selective adsorption due to surface heterogeneities.

2. Model

We consider the equilibrium between a bulk and a confined phase of chains. Chain molecules are modeled as l freely-joined Lennard-Jones spheres, as shown in Fig. 1. The distance between bonded beads is fixed and equal to $\sigma_{\rm LJ}$. The potential of interaction between any two non-bonded spheres, belonging to the same chain or to different chains is given by the full Lennard-Jones potential

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

where $\varepsilon_{\rm LJ}$ and $\sigma_{\rm LJ}$ 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 the LJ characteristic length and energy parameters respectively, $\sigma_{\rm LJ}$ and $\varepsilon_{\rm LJ}$. Values chosen for these parameters will be given and discussed later.

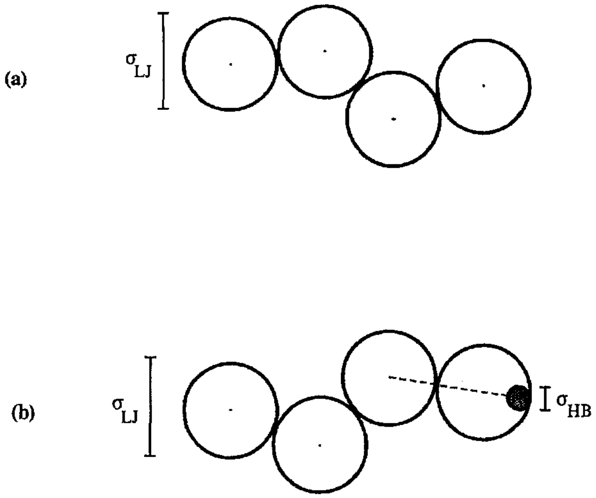

Figure 1. Two dimensional view of the molecules studied. a) Four freely jointed tangent LJ spheres. b) Four freely jointed tangent LJ spheres with a square-well site (shaded) on the end sphere. The exact position of the site is explained in the text.

We consider both non-associating chains and homomorphic chains with an associating site on one end; this associating site allows for either chain-chain association or association between a site on a molecule and a site on the 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, $\phi_{\rm HB}$,

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

where $\varepsilon_{\rm HB}$ is the depth of the square-well, $\sigma_{\rm HB}$ 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, $\varepsilon_{\rm HB}$, was set equal to 30 times the characteristic LJ energy, $\varepsilon_{\rm LJ}$. This value has been used by us previously (Müller et al., 1994) and is chosen as representative of a strong hydrogen bond (Israelachvili, 1992). A square well site of diameter $\sigma_{\rm HB} = 0.2\,\sigma_{\rm LJ}$ is placed at a distance of $0.4\sigma_{\rm LJ}$ from the center of the end sphere of each associating molecule, so as to be tangent to the LJ

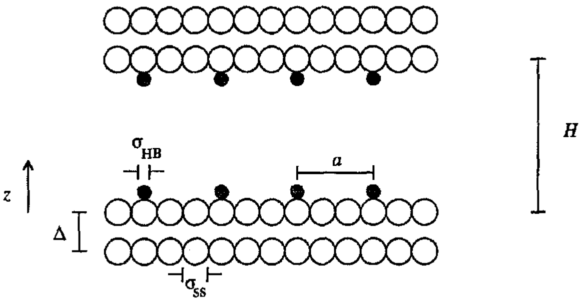

Figure 2. Lateral view of the pore geometry. Open circles represent the LJ atoms forming the walls of the pore, shaded circles represent the square-well sites. Other parameters are detailed in the text.

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 Fig 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},

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

We have modeled the confined phase as a single slit-like pore having two infinite parallel walls in the x-y plane separated by a distance H in the z direction, as shown in Fig. 2. H is defined as the distance separating the planes, on each side of the pore, through the centers of the LJ atoms forming the surface of the walls. Each of the two walls is taken to have the structure of the basal plane of graphite. For the chain-wall interaction the full Lennard-Jones potential is used. The LJ potential between one sphere of the fluid molecule 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 (Steele, 1974):

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

where ρ_{ss} is the solid density and Δ the separation between planes of molecules in the solid. The crossed solid-fluid interaction parameters (σ_{sf}, ε_{sf}) are calculated according to the Lorentz-Berthelot rules: $\sigma_{\text{sf}} = (\sigma_{\text{ss}} + \sigma_{\text{LJ}})/2$, $\varepsilon_{\text{sf}} = (\varepsilon_{\text{ss}} \cdot \varepsilon_{\text{LJ}})^{1/2}$, where the subscript ss refers to the solid while LJ refers to the fluid parameters. ρ_{ss}, Δ and σ_{ss} have been chosen to model a graphite surface (Steele, 1974): $\rho_{\text{ss}} = 114\ \text{nm}^{-3}$, $\Delta = 0.335$ nm, and $\sigma_{\text{ss}} = 0.340$ nm. σ_{LJ} has been chosen to be 0.3678 nm, a value close to the size of the LJ methane (Tee et al., 1966). Once the density of the walls is fixed, the parameter which mainly governs the attraction of the fluid molecules by the walls is the crossed energy parameter, ε_{sf}. We have chosen this to be a variable parameter in order to study the influence of the medium range solid-fluid interaction on the adsorption behavior of the system. For the case of pure fluids (either associating or non-associating chains) two different values of $\varepsilon_{\text{sf}}/\varepsilon_{\text{LJ}}$ have been considered, 0.25 and 0.0625. For comparative purposes, the $\varepsilon_{\text{sf}}/\varepsilon_{\text{LJ}}$ corresponding to a decane molecule confined in graphite plates is approximately 0.25 (Tee et al., 1966), one of the cases considered in this work. For mixtures, only the value $\varepsilon_{\text{sf}}/\varepsilon_{\text{LJ}} = 0.0625$ has been considered.

Since our objective is to see how activated surfaces affect the adsorption behavior, we have modified the original 10-4-3 walls by placing associating sites in a regular square array of periodicity a as shown in Fig. 2. The site density of the wall is equal to $1/a^2$ sites per unit area; in this work three densities of sites, $\sigma_{\text{LJ}}^2/a^2 = 0$, 0.0625 and 0.25 are considered. The associating sites have the same characteristic size and well depth ($\varepsilon_{\text{HB}} = 30\varepsilon_{\text{LJ}}$, $\sigma_{\text{HB}} = 0.2\sigma_{\text{LJ}}$) as the ones placed on the molecules. Their position is different however; sites are placed with their centers at a distance $z = 0.5\sigma_{\text{ss}}$ from the wall (identified as the plane through atomic centers in the first layer) into the pore, i.e., exposed to the surface, as observed in experimental situations (Bandosz et al., 1993). This is in contrast to the associating molecules of the fluid in which the site is embedded into the LJ core.

In summary, the total solid-fluid interaction potential is then given by:

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

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:

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

3. Simulations

We have used an extension of the Gibbs methodology applied to inhomogeneous fluids, as presented by Panagiotopoulos (1987). In this method one of the simulation boxes represents the confined phase while the other represents the bulk, and there is no physical contact between them. When considering a bulk phase in equilibrium with a confined phase mechanical equilibrium is automatically enforced, and only thermal ($T_{pore} = T_{bulk}$) and diffusive ($\mu_{pore} = \mu_{bulk}$) equilibria are required to ensure thermodynamic equilibria. T represents the temperature, μ the chemical potential and the subscripts *pore* and *bulk* refer to the fluid inside the pore and in the bulk phase respectively.

The Gibbs ensemble Monte Carlo technique achieves thermal equilibrium within each phase through displacement of molecules in each box. Equality of chemical potentials is obtained by transferring molecules between boxes. The advantage of using GEMC versus a more traditional Grand Canonical Monte Carlo simulation is that in our case we obtain simultaneously the properties of both phases in equilibrium. As an example, in a traditional GCMC simulation the chemical potential, temperature and volume of the confined phase are fixed. If one wishes to obtain the properties of the bulk phase in equilibrium, they must be obtained by other means, e.g., another simulation or an equation of state at a given temperature and chemical potential. For the range of densities, chain length and hydrogen bonding energy, ε_{HB}, used in this study we have previously shown (Vega et al., 1995) that the method can be applied in its original form. While the absolute value of the hydrogen bonding energy is high, it is the ratio ε_{HB}/kT (which in this case is less than or equal to 10), which is of relevance to determine if a non-biased MC technique should be used. More sophisticated sampling techniques, such as the configurational bias Monte Carlo (see, for example, de Pablo et al., 1992; Mooij et al., 1992) are required for longer chains and/or higher densities and/or higher association energies.

At the beginning of the simulation, molecules were placed in random positions. Volumes for the bulk and pore regions were assigned and kept constant. A total of N molecules were placed in each phase, where $N = 400$, 200 and 100 for molecules of chain length $l = 1, 2$ and 4 respectively; thus the "initial" sphere density is the same for all cases (l is the number of spheres which make up a molecule). For mixture calculations, 100 molecules of $l = 4$ were placed in each phase in random positions, 50 of them being non-associating chains and 50 of them associating chains. In all cases, 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. For mixtures, the molecules are randomly selected for the displacement or transfer steps according to their type (associating or non-associating) with an equal probability. The insertion of chains was performed bead-by-bead. 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. While the division of the simulation in cycles rather than in random moves (either reptation or transfer at each simulation step) is inherently irreversible, microscopic reversibility is ensured on the average by the very large number of configurations sampled.

Simulations needed to be very long in order to ensure that equilibrium was reached. The systems were 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 equation (9×10^6 configurations). Longer runs were necessary for the denser states and those with the strongest association effects and/or lowest temperatures.

Periodic boundary conditions (Allen and Tildesley, 1987) and minimum image conventions were applied in all cartesian directions for the bulk 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 (Allen and Tildesley, 1987) 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 $10\sigma_{LJ}$ (i.e., all molecular interactions up to at least a distance of $5\sigma_{LJ}$ in the x and y direction are explicitly taken into account). This practice ensures that long range corrections can be neglected.

The simulations yield the number of molecules in each of the equilibrated phases, pore and bulk. Since the volumes of each phase are fixed, the results are more easily interpreted in terms of the number of densities of phases. Adsorption isotherms are plotted as the density in the bulk versus the density in the pore; selectivities are shown versus the density in the bulk.

All densities considered in this work correspond to sphere densities (as opposed to molecular densities). The reason for this becomes apparent when comparing results for molecules of different lengths. The densities are calculated using the ratio of the average number of molecules in a phase divided by the phase volume. In the case of the pore, this volume is ill-defined, and we take it to be $H \cdot L_x \cdot L_y$.

4. Results and Discussion

The results presented in this section are divided in two groups. First, we consider the case of pure fluids (either associating or non-associating) with chain length fixed to $l = 4$ and investigate the influence of different parameters on the adsorption behavior. The results are presented in the form of adsorption isotherms, e.g., the density of the fluid inside the pore as a function of the equilibrium bulk density. Second, we have studied mixtures of associating and non-associating chains in activated pores. The influence of temperature and pore width on the selectivity is presented for chains of four tangent LJ spheres. In addition to the 4-mers, dimers and monomers are also considered in order to study the effect of chain length on the selective adsorption.

4.1. *Pure Fluids: Adsorption Isotherm of Associating and Non-Associating Chains in Slit-Like Pores*

We present Gibbs ensemble Monte Carlo simulation results showing the influence of different parameters on the adsorption isotherm of associating and non-associating chains. The systems are studied under conditions of reduced pore width $H^* = H/\sigma_{LJ} = 10$ and reduced temperature $T^* = kT/\varepsilon_{LJ} = 3.5$. The critical temperature of the bulk phase for the associating fluid is close to $T^* = 3.0$. The influence of the solid-fluid medium range interaction is investigated by considering two solid-fluid interaction parameters, a value close to decane on graphite, $\varepsilon^* = \varepsilon_{sf}/\varepsilon_{LJ} = 0.25$ and a weaker wall with $\varepsilon^* = 0.0625$. This last value was chosen to see how activation affects the adsorption behavior of weakly attractive walls; examples of such "weak walls" that have been studied experimentally include krypton on sodium and sodium oxide, and water on graphite.

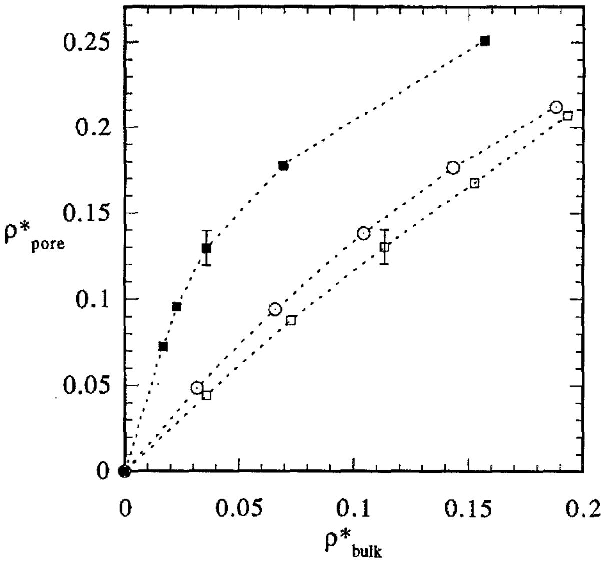

Figure 3. Adsorption isotherms for chains of $l = 4$ adsorbed in a pore of $H^* = 10$, $\varepsilon^* = 0.25$ (strongly attractive wall), $T^* = 3.5$. Open circles are for non-associating chains on neutral walls (no associating sites on the walls), open squares are for associating chains on neutral walls. Solid squares show the effect of placing associating sites on the walls with a surface density of sites $\sigma_{LJ}^2/a^2 = 0.25$. Dashed lines join the points and are a guide to the eye. Typical error bars are shown.

Four adsorption isotherms are calculated for each system, corresponding to the following conditions: 1) a case in which there is no association in the fluid, either fluid-fluid or fluid-wall, i.e., non-associating chains with neutral walls, 2) a case with association within the fluid but with no association with the walls, i.e., associating chains and neutral walls, 3) a case with an associating fluid and a relatively sparse concentration of associating sites on the walls, corresponding to a surface density of $\sigma_{LJ}^2/a^2 = 0.0625$, i.e., associating chains with activated surfaces, and 4) as in (3) but with a relatively large concentration of associating sites, $\sigma_{LJ}^2/a^2 = 0.25$.

Figure 3 shows adsorption isotherms expressed as the density in the bulk versus the density in the pore, for attractive walls (reduced solid-fluid interaction parameter $\varepsilon^* = 0.25$). Results obtained for cases (2) and (3) are very close, so for clarity case (3) is omitted in the figure. Since the pore is relatively wide compared to the chain length and radius of gyration of the molecules there is little competition between entropic and enthalpic effects, especially at low densities, i.e., chains can have essentially the same conformation as they would have in the bulk phase. However, there is an energetic benefit of being adsorbed, due to the attraction of the walls, resulting in a positive adsorption in all the systems considered. The adsorption is greater for lower densities; above a density of $\rho^*_{\mathrm{bulk}} = \rho\sigma^3_{\mathrm{LJ}} = 0.3$ the isotherms flatten out and the trend reverts, presumably because of the difficulty in packing of the molecules inside the pore despite the energetic benefit of being close to the walls.

An interesting feature observed in these simulations is the reduced adsorption of associating chains versus non-associating chains when confined in neutral walls (cf. Fig. 3). When there is intermolecular association, fluid molecules associated with other fluid molecules behave as non-associating chains composed of eight spheres. These effective 8-mers will have a weaker adsorption than corresponding 4-mers, due to entropic effects, and will need to distort their shapes to get inside the pore.

An enhanced adsorption is observed in cases with association sites on the walls. In this case molecules are able to graft to the walls, and the energetic benefit is improved with respect to the neutral walls. This enhancement is more pronounced at low densities, where the relatively empty pore allows the molecules to assume an orientation compatible with the association on the wall.

Figure 4 shows adsorption isotherms corresponding to the same systems but considering a weakly attractive wall ($\varepsilon^* = 0.0625$). The systems are studied under conditions of reduced temperature $T^* = 3.5$ and reduced pore width $H^* = 10$, as in Fig. 3. The adsorption behavior of these systems is different from those of Fig. 3; the isotherms, with the exception of the one corresponding to a high density of sites on the walls, show in general a higher density in the bulk than in the confined phase, indicating that chains prefer to stay outside the pore. There is little enthalpic benefit to adsorption in this case, and the entropy loss the chains will experience by entering the pore is uncompensated. This is enhanced at high densities, when the chains must distort their shapes to get inside the pore. On the other hand, the activation of the surfaces greatly enhances the adsorption of the associating chains and a positive adsorption is observed in this case.

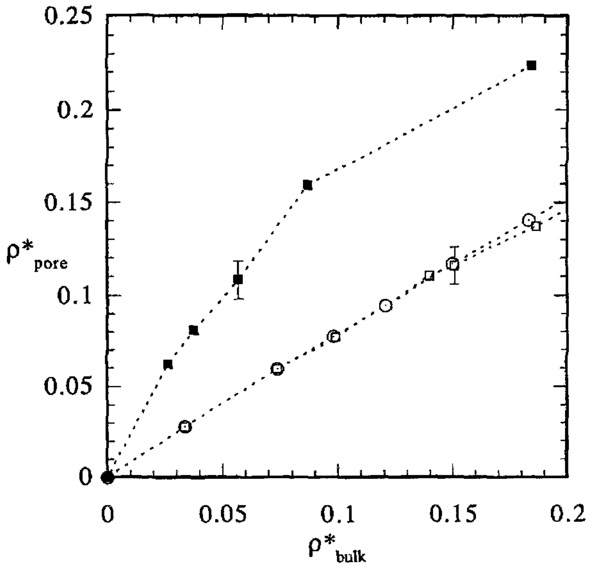

Figure 4. Adsorption isotherms for chains of $l = 4$ adsorbed in a pore of $H^* = 10$, $\varepsilon^* = 0.0625$ (weakly attractive wall), $T^* = 3.5$. Symbols as in Fig. 3.

4.2. *Mixtures: Selectivity of Associating Chain Mixtures in Activated Surfaces*

In the previous section we showed how activation enhances the adsorption of associating fluids. This selective adsorption can be built into the design of separation processes. In this section the equilibrium between a bulk and a confined phase of mixtures of associating and non-associating molecules has been studied. Walls have fixed parameters in this case: a relatively high density of activated sites, $\sigma^2_{\mathrm{LJ}}/a^2 = 0.25$ and a weak solid-fluid interaction parameter $\varepsilon^* = 0.0625$. The overall bulk-pore system has a fixed number of molecules, with equal numbers of associating and non-associating chains. During adsorption the two species distribute themselves between the bulk and pore phases. Our interest here is to reverse the case of poor adsorption by activating the surfaces. We first consider the case of chains composed of four tangent LJ spheres. The influence of temperature and pore size on the selective adsorption of one of the components (associating versus non-associating chains) has been investigated by considering three reduced temperatures, $T^* = 4.5$, 3.5 and 3.0, and two pore widths, $H^* = 7$ and 15.

Figure 5 shows a snapshot of the confined phase in equilibrium with the bulk phase, Fig. 6, as obtained by GEMC simulations for a particular case. Grey spheres represent the centers of the LJ cores of the associating molecules, while non-associating molecules are shown in white. Associating sites on the walls and on the molecules are represented by the smaller (and lighter) grey spheres. Spheres are shown with a volume smaller than their corresponding core volume for visualization

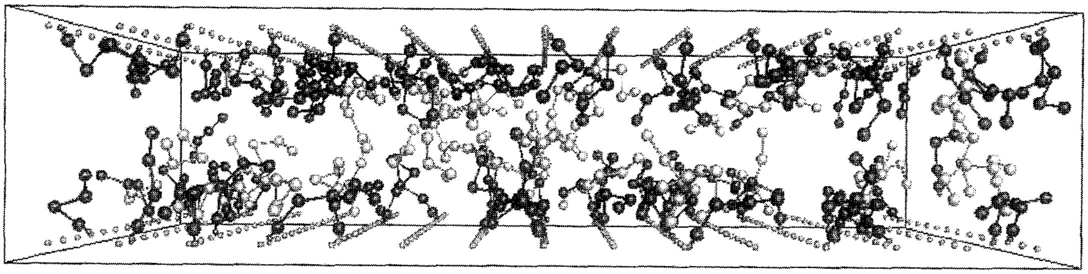

Figure 5. Snapshot of a configuration of a mixture of associating and non-associating chains of 4 spheres inside a pore of $H^* = 7$, at $T^* = 3.0$. The LJ cores corresponding to the associating chains are represented by the dark grey spheres. Non-associating molecules are represented by the white spheres, corresponding to their LJ cores. Associating sites on the walls and on the associating molecules are shown as smaller black spheres. Spheres are shown with a volume much smaller than their actual core volume to help visualize the structure of the molecules. Pore walls are on the top and bottom of the box.

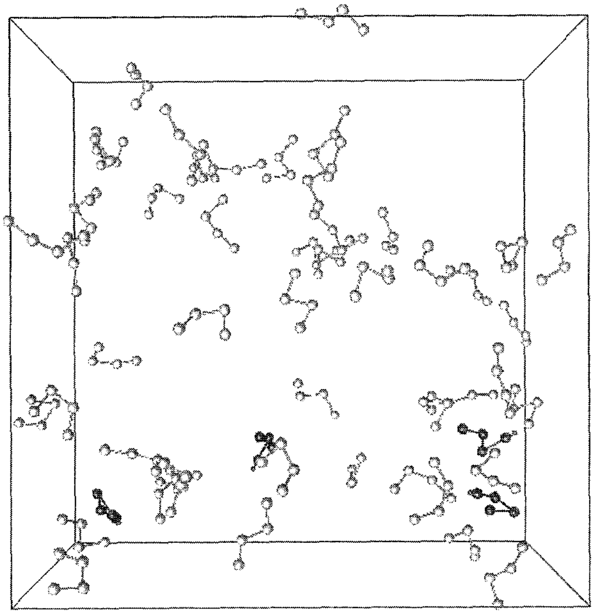

Figure 6. Snapshot of a configuration of the bulk phase (bulk density $\rho^*_{\text{bulk}} = 0.012$ in equilibrium with the confined phase shown in Fig. 5. Symbols as in Fig. 5.

purposes. It is interesting to notice that although the simulation began with the same number of associating and non-associating chains in each phase, once equilibrium is reached most of the associating chains are inside the pore while non-associating chains are in the bulk phase, leading to an effective separation of associating chains due to the activation of the walls. 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) and the strongly favorable bonding of the end sphere of an associating molecule onto the wall forces them to graft to the surfaces. Most of the non-associating molecules are located in the middle of the pore, while associating chains are close to or grafted to the surfaces. In the bulk phase most of the molecules are non-associating chains and only few associating chains can be found. Since the pore walls are weakly attractive to the non-associating molecules, the driving force for their adsorption is small.

The microscopic behavior of the system is reflected in macroscopic properties such as selectivity isotherms. The selectivity of component 2 (associating chain) versus component 1 (non-associating chain) is defined as the ratio of the mole fractions in the pore divided by the ratio of the mole fractions in the bulk, namely:

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

where $x_i = (N_i/N)$, $i = 1, 2$. Selectivity curves are plotted versus the sphere bulk density of the system (total number of LJ spheres divided by the bulk volume).

Since all molecules have the same size, differential adsorption (selectivity) depends only on the characteristics of the fluid-wall interactions. Results obtained from the simulations are presented in Fig. 7, where the selectivity isotherms for the system at a reduced temperature $T^* = 3.5$ and pore widths $H^* = 15$ and 7, and also for $T^* = 3.0$, $H^* = 7$, are plotted versus the bulk density. The selectivity is enhanced in the smallest pore considered: the proximity of the walls increases the effective attraction of the molecules and associating chains have a greater probability of grafting to the walls, as opposed to the wider pore where the fluid presents a bulk-like behavior. The selectivity decreases

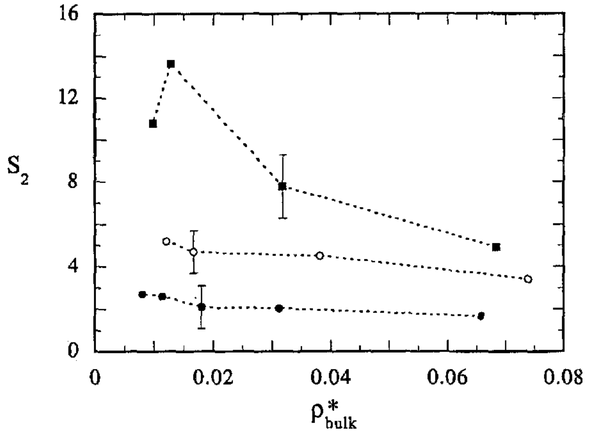

Figure 7. Selectivity isotherms as a function of reduced bulk density. Open circles are for $T^* = 3.5$ and $H^* = 7$. Solid circles show a wider pore, $T^* = 3.5$ and $H^* = 15$. Solid squares show a lower temperature, $T^* = 3.0$ and $H^* = 7$. Dashed lines join the points and are a guide to the eye. Typical error bars are shown.

Table 1. Influence of chain length on the selective adsorption of associating chains. $H^* = 7, T^* = 3.5, \varepsilon^* = 0.0625$ and $\sigma^2_{\rm LJ}/a^2 = 0.25$.

L	$\rho^*_{\rm bulk}$	S_2
4	0.048	5.197
2	0.040	11.8869
1	0.054	2.950
4	0.068	4.670
2	0.056	9.932
1	0.074	2.621
4	0.152	4.527
2	0.142	4.632
1	0.170	1.948
4	0.296	3.420
2	0.297	2.237
1	0.300	1.591

when the bulk density (or pressure) is increased; at low densities the walls are relatively empty and associating molecules can easily bond to them. At higher densities both types of molecules are forced into the pores. At such densities, the adsorption sites, which are the main cause of selective adsorption, will be screened by the first layers of adsorbing molecules. The selectivity increases with decreasing temperature, as expected. The effect is even greater for low bulk densities. Since for associating fluids the association strength is related to the temperature by $\exp(\varepsilon_{\rm HB}/kT)$, an increase in temperature produces a decrease of the relative importance of association.

We have also investigated the influence of chain length on the selective adsorption of associating fluids. It is well known that the behavior of confined chains differs from that of simple fluids. In simple fluids only enthalpic effects are relevant and the adsorption will be governed by the solid-fluid and fluid-fluid interaction solely. On the other hand, chains may need to distort their shape to get inside the pore, losing some entropy, and hence the adsorption will be the result of a competition between entropic (connectivity) and enthalpic effects. We have considered three different chain lengths: 4-mers, dimers and monomers. In all these cases an equimolar mixture of associating and non-associating chains has been considered under reduced temperature $T^* = 3.5$ and reduced pore width $H^* = 7$. Walls were characterized by $\varepsilon^* = 0.0625$ and a density of activated sites, $\sigma^2_{\rm LJ}/a^2$, equal to 0.25.

Results obtained from these simulations are shown in Table 1 for several different bulk fluid densities. The selectivity is seen to depend on chain length. In these simulations, the number of activated sites on the walls is a fixed quantity, while the total number of associating sites on the fluid molecules depends on chain length: for chains of length $l = 4$, there is one associating site per each 4 LJ spheres, while for chains of length $l = 1$ each molecule is a sphere and carries an association site. Thus for a given LJ sphere density, the fluid of 4-mers will have four times less fluid associating sites available than the 1-mer. Thus, for a given density of LJ spheres in the fluid, the choice of l affects the number of molecules which can be attached to the walls.

At higher densities, the number of associating sites on the wall is small compared to the number of associating molecules, the wall sites effectively saturate and the overall selectivities decrease. At a given density, once a monolayer is formed on any wall, the driving force for the selectivity is lost, since in our model, the activated sites are of a short range. The rest of the pore volume available (the volume left after formation of the monolayers) will be neutral with respect to the association character of the adsorbing molecules (see Fig. 4).

At the lowest densities, the pore is only sparsely filled. Then there are more associating sites available on the wall than associating sites present in the fluid molecules. Selectivities are enhanced by almost an order of magnitude, since now the activation sites can effectively separate the mixture. At these densities, the differences in selectivities can be ascribed exclusively to the effects of chain length. Longer chains (e.g., 4-mers) need to distort their shapes to get inside the pore, with a consequent loss of entropy which is not fully compensated by the energetic benefit of adsorption. Such entropic effects are much reduced in the case of dimers, so that their adsorption is governed largely by the energy of adsorption. Monomers are similar in this sense, but the adsorption of a single monomer molecule is accomplished by a much smaller decrease of energy of the system than a two-center molecule. It is thus observed that $l = 2$ is the optimum chain length for selective adsorption at the temperature, pore width and density of activated sites on the walls considered in this work, except at the highest bulk fluid density.

These general trends should hold for other pore widths and chain lengths, as long as the ratio of pore width to chain length is kept fixed. This relationship is the dominant factor (for the same type of walls) in the competition between entropic and enthalpic effects.

5. Conclusions

We have observed that the presence of associating sites on the walls greatly affects the adsorption properties. In particular, the adsorption of associating chains can be enhanced by doping or activating surfaces, especially in cases where the walls would be weakly attractive otherwise. Our results are in conformity with experiments (e.g., Bandosz et al., 1993) which show that the chemical heterogeneity of the walls modifies the adsorption behavior of the fluids. This is of special interest for separation processes, where the selectivity of a component can be enhanced by activating the surfaces.

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. The effect of chain length on selectivity is a compromise between loss of entropy upon adsorption and the energy benefit of adsorbing a multi-center molecule. Except at the higher bulk fluid densities, the selectivity is found to be a maximum for chains of two mers; for this length the reduction in energy is large, while the entropy loss is small, due to adsorption.

Our model is too crude to represent any realistic fluid accurately, and 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. However, we note that selectivities obtained are of the same order of magnitude as those observed experimentally for alkane-alkanol mixtures on activated carbons (Valenzuela and Myers, 1989).

Nomenclature

a	x, y distance between associating sites on the surface	nm
H	pore width,	nm
$H^* = H/\sigma_{\mathrm{LJ}}$	reduced pore width	
k	Boltzmann's constant	J/K
l	number of Lennard Jones spheres in a molecule	
$L_{x,y}$	pore length in the x and y directions	nm
N	number of molecules	
r_{ij}	center to center distance between any two LJ spheres in the fluid	
$r_{\alpha\beta}$	center to center distance between two associating sites	
S_2	selectivity of component 2 versus component 1	
T	temperature	K
$T^* = kT/\varepsilon_{\mathrm{LJ}}$	reduced temperature	
x	mole fraction	
Δ	separation between planes of molecules in the solid	nm
ε	energy parameter	J
$\varepsilon^* = \varepsilon_{\mathrm{sf}}/\varepsilon_{\mathrm{LJ}}$	energy parameter characterizing the attraction of the wall	
ϕ	potential of interaction	J
ϕ_{ext}	external potential experienced by the fluid molecules due to the walls	J
ϕ_{wall}	potential exerted by a wall on a LJ sphere situated at a distance z from it	J
μ	chemical potential	J
ρ	number density	nm^{-3}
$\rho^* = \rho\sigma_{\mathrm{LJ}}^3$	reduced sphere number density	
σ	size parameter, diameter of core	nm

$\sigma_{\mathrm{LJ}}^2/a^2$	density of activated sites on the walls

Subscripts

1	non associating molecules
2	associating molecule
bulk	bulk
ff	fluid-fluid
HB	association
LJ	Lennard-Jones fluid
pore	pore
sf	solid-fluid
ss	solid-solid

Acknowledgment

We are grateful to the Department of Energy (grant no. DE-FG02-88ER13974) for financial support of this research. The international collaboration is supported through a NATO grant (no. CRG.931517). Additional support was given by the DGICYT (project PB91-0602) and by the Junta de Andalucía. We acknowledge the use of the supercomputer facilities at the Cornell Theory Center (IBM SP2), the Pittsburgh Supercomputing Center (Cray C90), and the Centro Informático y Científico de Andalucía where some of the simulations were performed. The computations were supported by a NSF Metacenter Supercomputing grant (no. MCA93S011P).

References

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

Bandosz, T.J., J. Jagiello, and J.A. Schwarz, "Effect of Surface Chemical Groups on Energetic Heterogeneity of Activated Carbons," *Langmuir*, **9**, 2518 (1993).

de Pablo, J.J., M. Laso, and S.W. Suter, "Estimation of the chemical potential of chain molecules by simulation," *J. Chem. Phys.*, **96**, 6157 (1992).

Israelachvili, J., *Intermolecular & Surface Forces*, 2nd ed., p. 125, Academic Press, 1992.

Mooij, G.C.A.M., D. Frenkel, and B. Smit, "Direct Simulation of Phase Equilibria of Chain Molecules," *J. Condens. Matter*, **3**, 3053 (1992).

Müller, E.A., L.F. Vega, and K.E. Gubbins, "Theory and Simulation of Associating Fluids: Lennard-Jones Chains with Association Sites," *Mol. Phys.*, **83**, 1209 (1994).

Panagiotopoulos, A.Z., "Adsorption and Capillary Condensation of Fluids in Cylindrical Pores by Monte Carlo Simulation in the Gibbs Ensemble," *Mol. Phys.*, **62**, 791 (1987).

Steele, W.A., *The Interaction of Gases with Solid Surfaces*, p. 56, Pergamon, Oxford, 1974.

Tee, L.S., S. Gotoh, and W.E. Stewart, "Molecular Parameters for Normal Fluids," *Ind. Eng. Chem. Fundam.*, **5**, 356 (1966).

Valenzuela, D.P. and A.L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice Hall, 1989.

Vega, L.F., E.A., Müller, L.F. Rull, and K.E. Gubbins, "Mixtures of Associating and Non-Associating Chains on Activated Surfaces: A Monte Carlo Approach," *Mol. Simulation*, **15**, 141 (1995).