Analysis of Adsorption Selectivity in a One-Dimensional Model System

Julian Talbot
Dept. of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282

The adsorption selectivity, $S_{i,j} = (x_i/y_i)/(x_j/y_j)$, is examined in a 1-D model of a mixture of hard rods adsorbing on a linear substrate. The adsorbed components are characterized by their length, l_i, and equilibrium constant, k_i. We derive an expression for the bulk-phase pressure P_0, for which there is no separation of components i and j, $S_{i,j} = 1$, in terms of these parameters. The selectivity of the smaller component always increases with the bulk pressure, which results in a selectivity reversal if, as is usually the case, the larger component is more strongly adsorbed at low surface coverages. In a binary mixture, when $P < P_0$, the selectivity of the smaller component decreases with increasing bulk-phase mole fraction, y_1, while for $P > P_0$, the reverse is true. The effect of varying the molecular parameters on the selectivity is also studied.

Introduction

The separation of mixtures is frequently based on adsorption, a phenomenon that occurs whenever a bulk phase is exposed to an interface. Far from the interface, the thermodynamic state of the bulk is specified by a temperature T, pressure P, and a composition $\{y_i\}$, while the adsorbed phase has a specific density ρ (usually per unit area or per unit mass of the adsorbent) and a composition $\{x_i\}$. Separation processes exploit the preferential concentration of a desired component at the interface. To quantify this effect, one defines the *selectivity* (alternatively known as the *separation factor* or *partition coefficient*) of component i with respect to component j:

$$S_{i,j} = \frac{x_i}{y_i} \bigg/ \frac{x_j}{y_j}. \tag{1}$$

The selectivity is a key quantity in the design of separation processes, and hence it has been the focus of a number of recent molecular simulation studies of mixture adsorption (Maddox et al., 1996; Van Tassel et al., 1994, 1996). When $S_{i,j} < 1$, component i is depleted in the adsorbed phase compared with the bulk relative to component j, while $S_{i,j} > 1$ implies that component i is preferentially adsorbed compared with component j. The condition $S_{i,j} = 1$, which we will call the *isoselective point* (ISP), is of special interest since it defines the point of selectivity reversal, that is, the condition where no separation of components i and j occurs.

Depending on the application, it may also be of interest to consider the quantity

$$S_i = \frac{x_i}{y_i}, \tag{2}$$

which might be termed the *absolute selectivity* of component i, while $S_{i,j}$ would strictly be called the *relative selectivity*. One can easily show that the two are related as follows:

$$S_{i,j} = \frac{S_i}{S_j} = \frac{S_i y_j}{1 - S_i y_i} \quad \text{or} \quad S_i = \frac{S_{i,j}}{y_j + S_{i,j} y_i}, \tag{3}$$

and there is, of course, a constraint resulting from the dependence of the mole fractions, $\Sigma y_i S_i = 1$. Note that, although $S_{i,j}$ and S_i are, in general, different, in the case of a binary mixture both equal unity at the pressure of selectivity reversal, P_0, since both $S_{i,j} = 1$ and $S_i = 1$ imply $x_1 = y_1$.

For a given adsorption system, a knowledge of how the isoselective point, or more generally the selectivity itself, depends on the prevailing conditions of bulk pressure and composition, as well as the molecular properties of the components of the mixture, is invaluable in optimizing the separation of a desired component.

A selectivity reversal can occur in a model system that incorporates hard-core interactions between the adsorbed molecules and a constant adsorbate–adsorbent adsorption energy (Bakaev and Steele, 1997; Franses et al., 1995; Talbot, 1996). In a binary mixture, the larger component typically has a larger adsorption energy, and hence is preferentially adsorbed at low surface coverages. As the surface coverage increases, the smaller, sterically favored species progressively displaces the larger component. Although apparently simple, this model is not an unreasonable one for many adsorption systems since the adsorbate–adsorbate interactions are typically much smaller than the holding potential.

The study of one-dimensional systems is an extremely fecund area of statistical mechanics. Many of the properties of these systems can be determined exactly and analytically, and although they do not exhibit phase transitions, their behavior is otherwise qualitatively similar to their higher-dimensional counterparts. In recent years, one-dimensional models have been studied extensively in connection with adsorption processes (Monson, 1990; Chiang et al., 1996; Vanderlick et al., 1989; Davis, 1996). This approach is particularly germane to systems where the geometry of the adsorbent confines the adsorbed fluid in an effectively one-dimensional channel, for example, xenon adsorbed in mordenite. Also, when the pore structure is angular, the initial adsorption is restricted to a line of molecules along the edge (Bojan et al., 1996). In these cases, the predictions of the one-dimensional theories can be in *quantitative* agreement with experiment (Mitchell et al., 1994; Bojan and Steele, 1996).

The properties of one-dimensional fluid mixtures in the thermodynamic limit were first investigated systematically in the 1950s (Prigogine and LaFleur, 1954; Kikuchi, 1955; Longuet-Higgins, 1958). In this article, we derive *exact* expressions for the ISP in a model system of hard rods adsorbed on a linear substrate, and derive inequalities for the dependence of the selectivity on bulk pressure and composition, as well as the molecular-size ratio and equilibrium-constant ratio.

Theory

The isothermal–isobaric partition function for a mixture of hard rods adsorbed on a line with periodic boundary conditions is

$$\Delta(N,\beta\Pi,\beta)=\exp(-\beta G)$$
$$=\frac{1}{L_0}\frac{N!}{(\beta\Pi)^{N+1}}e^{-\beta\Pi l_N}\prod_i\frac{e^{\beta N_i\epsilon_i}}{N_i!\Lambda_i^{3N_i}}q_i^{N_i} \quad (4)$$

where Π is the (one-dimensional) spreading pressure; Λ_i is the thermal wavelength, $\beta=1/k_BT$; where k_B is Boltzmann's constant; T is the absolute temperature; l_i and $-\epsilon_i$ are the length and adsorption energy of species i; and $l_N=\Sigma N_il_i$ is the total length occupied by the $N=N_1+N_2+\cdots$ rods. The configurational partition function of a single adsorbed molecule of species i is denoted by q_i and has dimensions of length squared. Finally, the factor L_0 represents an (unimportant) reference length that renders the expression dimensionless. The chemical potential of the ith adsorbed species is

$$\beta\mu_i=\ln\left(\frac{\beta\Pi\Lambda_i^3}{q_i}\right)-\beta\epsilon_i+\beta\Pi l_i+\ln x_i, \quad (5)$$

which, incidentally, implies that the adsorbed mixture is ideal (Bakaev and Steele, 1997). We now assume that an equilibrium exists between the adsorbed phase and an ideal bulk phase in which the chemical potential of component i is $\beta\mu_i=\beta\mu_i^0+\ln(P_i/P_i^0)$. The equilibrium condition, or equality of the chemical potential of each species, gives

$$k_iP_i=\beta\Pi x_i\exp(\beta\Pi l_i), \quad (6)$$

where

$$k_i=\frac{e^{\beta\epsilon_i\epsilon^{\beta\mu_i^0}}}{\Lambda_i^3}\frac{q_i}{P_i^0} \quad (7)$$

is the Henry's law constant of component i. At low spreading pressures, Eq. 6 reduces to $k_iP_i=\beta\Pi x_i$, so the selectivity is determined solely by the $\{k_i\}$: $S_{i,j}=k_i/k_j$.

At higher coverages, the interaction among the adsorbed molecules becomes significant and one requires the equation of state of the adsorbed fluid. This may be obtained from the relation $L=\partial G/\partial\Pi$:

$$\frac{1}{\rho}=\frac{1}{\beta\Pi}+\sum x_il_i. \quad (8)$$

This exact equation has an obvious physical interpretation: at low spreading pressures, it approaches the ideal gas equation, while in the limit of infinite spreading pressure, the adsorbed molecules form a close-packed array with no void space. Although the isobaric–isothermal partition function for a mixture of rods on a line does not appear to have been given previously, the thermodynamic properties of this system are known and have been presented by several authors including Davis (1996) and Bakaev and Steele (1997).

To find the spreading pressure for a given bulk pressure and composition we eliminate the $\{x_i\}$ from Eq. 6:

$$\frac{1}{P}=\frac{1}{\beta\Pi}\sum k_iy_ie^{-\beta\Pi l_i}. \quad (9)$$

This equation can be solved numerically to find $\beta\Pi$, and then the mole fractions of the adsorbed components can be found from

$$x_i=\frac{k_iy_ie^{-\beta\Pi l_i}}{\sum k_jy_je^{-\beta\Pi l_j}}. \quad (10)$$

Finally, the adsorbed density is computed from Eq. 8.

From the definition, Eq. 1, we easily show that the selectivity of component i with respect to component j is

$$S_{i,j}=\frac{k_i}{k_j}e^{\beta\Pi(l_j-l_i)}. \quad (11)$$

When the size of the components is equal, the selectivity $S_{i,j} = k_i/k_j$ is a constant, independent of bulk pressure or composition. This is the behavior of the multicomponent Langmuir equations. In the remainder we consider the more interesting case when there is a size difference.

Effect of bulk pressure and composition

For definiteness, we assume that component j is the larger of the two species. We first consider the effect of varying bulk pressure on the selectivity

$$\left(\frac{\partial S_{i,j}}{\partial P}\right)_{l_k,k_k,y_k} = \left(\frac{\partial S_{i,j}}{\partial \Pi}\right)_{l_k,k_k,y_k}\left(\frac{\partial \Pi}{\partial P}\right)_{l_k,k_k,y_k}$$
$$= (l_j - l_i) S_{i,j} \frac{\sum y_n k_n e^{-\beta \Pi l_n}}{1 + P \sum y_n k_n l_n e^{-\beta \Pi l_n}} \quad (12)$$

and is clearly always positive, that is, the selectivity of the smaller component always increases with increasing bulk pressure. This behavior is illustrated in Figure 1.

It follows from this result that if the larger component has the larger Henry's law constant—$k_j/k_i > 1$—selectivity reversal is possible and occurs at a spreading pressure

$$\beta \Pi_0 = \frac{\ln(k_j/k_i)}{l_j - l_i}, \quad (13)$$

which, from Eq. 9, corresponds to a bulk phase pressure of

$$\frac{1}{P_0} = \frac{l_j - l_i}{\ln(k_j/k_i)} \sum_n y_n k_n \left(\frac{k_i}{k_j}\right)^{l_n/(l_j - l_i)} \quad (14)$$

In the case of a binary mixture this takes the particularly simple form

$$P_0^* = \frac{\kappa^{1/(\lambda-1)} \ln \kappa}{\lambda - 1}, \quad (15)$$

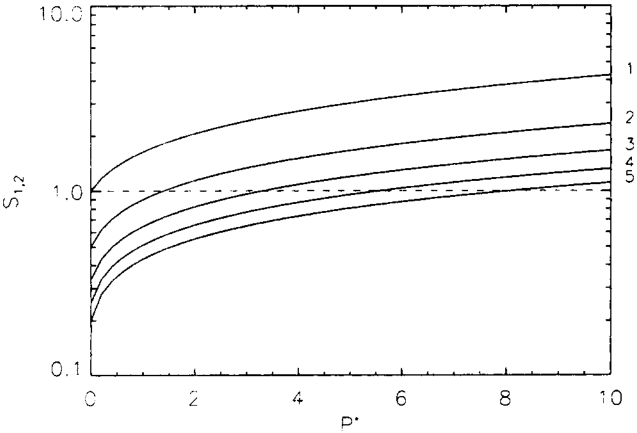

Figure 1. Selectivity of component 1 as a function of the reduced pressure for different values of the equilibrium constant ratio, κ.

In all cases, $\lambda = 2$ and $y_1 = 0.5$.

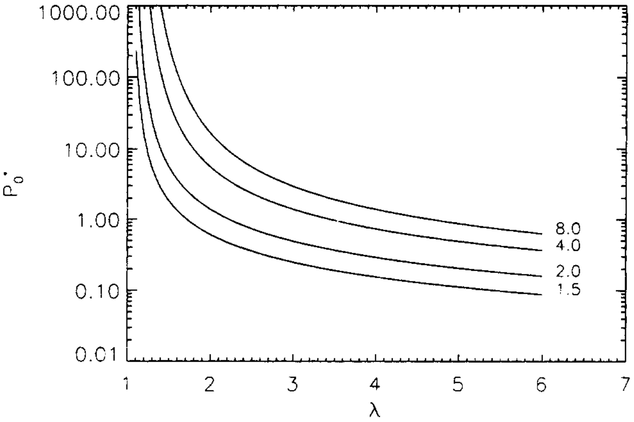

Figure 2. Effect of size ratio on the pressure at which $S_{1,2} = 1$; the curves are for different values of the equilibrium constant ratio, κ.

where $\kappa = k_2/k_1$, $\lambda = l_2/l_1$, and $P^* = Pl_1k_1$. Thus, the pressure of the ISP increases with increasing equilibrium constant ratio, κ, and decreases with increasing size ratio, λ. Some examples of this dependence are shown in Figure 2. The pressure of the ISP is extremely sensitive to λ at small values of this quantity. An implication of this result for separations is that if the molecular sizes of the two components are almost equal, a very high pressure will be required for significant separation based on the size difference. Another important property of the model is that, for a binary mixture, P_0^* does not depend on the bulk-phase composition. Thus, selectivity reversal cannot be achieved by varying the bulk composition at fixed pressure.

Table 1 shows the predicted pressures of selectivity reversal for various binary mixtures of light gases adsorbing in zeolite 5A. Henry's law constants were calculated at 300 K using the data provided by Ruthven (1984), and the molecular dimensions were taken as the Lennard Jones σ parameter estimated from the second virial coefficient (Reed and Gubbins, 1973). We should immediately point out that there is considerable uncertainty in the estimated P_0^*. For example, with the CH_4 and CO_2 mixture just a 1% increase in λ results in a three orders of magnitude reduction in P_0^*. The data do, however, serve to illustrate the wide variation in the

Table 1. Adsorption Parameters for Various Light Gases Adsorbed in Zeolite 5A*

1	2	λ	κ	P_0^*
N_2	CH_4	1.09	0.093	—
N_2	CO_2	1.20	160	5.4×10^{12}
N_2	C_2H_6	1.41	1.2	0.63
N_2	nC_4H_{10}	1.94	560	5.8×10^3
CH_4	CO_2	1.10	1,800	8.5×10^{33}
CH_4	C_2H_6	1.30	13	4.0×10^4
CH_4	nC_4H_{10}	1.78	6,000	7.4×10^5
CO_2	C_2H_6	1.18	0.007	—
CO_2	nC_4H_{10}	1.62	3.4	14
C_2H_6	nC_4H_{10}	1.37	470	2.7×10^8

*The Henry's law constant ratios, $\kappa = k_2/k_1$, at 300 K were computed from the data supplied by Ruthven (1984), and the molecular size ratios, $\lambda = l_2/l_1$, were estimated from the Lennard-Jones σ parameters (Reed and Gubbins, 1973). The reduced pressures at selectivity reversal were computed with Eq. 15.

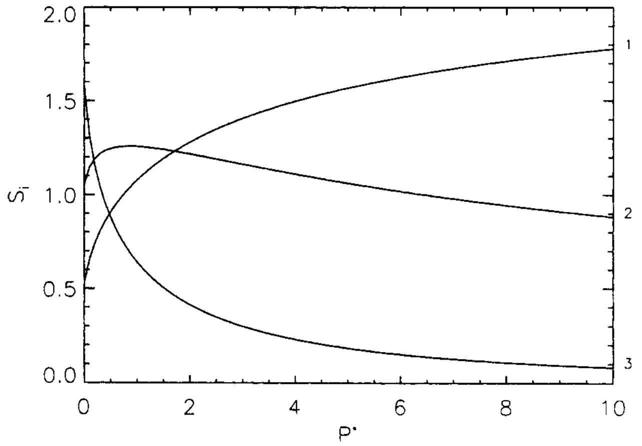

Figure 3. Absolute selectivity, $S_i = x_i/y_i$ of each component in a ternary hard-rod mixture.

$k_2/k_1 = 2$, $k_3/k_1 = 3$; $l_2/l_1 = 2$, $l_3/l_1 = 4$; $y_1 = 0.4$, $y_2 = 0.3$ as a function of the reduced bulk pressure, $P^* = Pk_1l_1$.

pressure of selectivity reversal. Moreover, the qualitative predictions, for example, that methane displaces ethane at a lower pressure than n-butane, are likely to be more, though not completely, reliable.

Converting the reduced pressure to a real pressure introduces further uncertainty and the assumption of a strictly one-dimensional fluid is clearly not valid in the case of zeolite 5A. Nevertheless, for the CO_2/nC_4H_{10} mixture using k_{CO_2} (300 K) = 6.8 molecules/cage/torr and taking the length of one cage as 12.3 Å (Ruthven, 1984), we estimate $P_0^* = 10$ torr, indicating that carbon dioxide easily displaces the large n-butane. The P_0 for other mixtures are many orders of magnitude larger and, due to the large uncertainties involved, are not presented.

We now return to the theoretical development and address mixtures with more than two components. As an example, Figures 3 and 4 show the absolute selectivity and density for each component in a ternary mixture. At low pressures the component with the largest k_i, in this case component 3, has the largest S_i. While this decreases monotonically with increasing P, the selectivity of the smallest component (1) increases monotonically. Component 2, however, displays a maximum selectivity at an intermediate pressure. In the low-to-intermediate-pressure regime molecules of species 2 displace the larger component 3, only to be ultimately dislodged themselves by the smaller component 3.

We next wish to understand the effect of bulk-phase composition on the selectivity. In a multicomponent mixture there is no unique way to vary the composition, so we restrict our examination to a two-component mixture where there is no ambiguity.

$$\left(\frac{\partial S_{1,2}}{\partial y_i}\right)_{P,l_i,k_i} = \left(\frac{\partial S_{1,2}}{\partial \Pi}\right)_{P,l_j,k_j}\left(\frac{\partial \Pi}{\partial y_1}\right)_{P,l_i,k_j}$$

$$= (l_2 - l_1)S_{1,2}\cdot\frac{P(k_1e^{-\beta\Pi l_1} - k_2e^{-\beta\Pi l_2})}{1 + Pk_1l_1y_1e^{-\beta\Pi l_1} + Pk_2l_2y_2e^{-\beta\Pi l_2}}, \quad (16)$$

which is zero when $\Pi = \Pi_0$. Thus, the selectivity is independent of the bulk-phase mole fraction at the point of selectivity reversal. If $\Pi > \Pi_0$, $(\partial\Pi/\partial y_1) > 0$, so at high bulk-phase pressures, that is, when $P > P_0$, $S_{1,2}$ increases with y_1, while at low bulk-phase pressures, $P < P_0$, $S_{1,2}$ decreases with y_1. At high bulk pressures the selectivity is quite sensitive to bulk composition, while in the latter case, it is a very weak function of composition. Some examples are shown in Figure 5.

Finally, in this section, we consider the effect of varying the partial pressure of component.

$$\left(\frac{\partial\beta\Pi}{\partial P_j}\right)_{P_{k\neq j},k_k,l_k} = \frac{k_je^{-\beta\Pi l_j}}{1 + P\sum y_nk_nl_ne^{-\beta\Pi l_n}} \quad (17)$$

and the effect on the selectivity is

$$\left(\frac{\partial S_{i,j}}{\partial P_k}\right)_{P_{l\neq k},k_l,l_l} = S_{i,j}(l_j - l_i)\left(\frac{\partial\beta\Pi}{\partial P_k}\right)_{P_{l\neq k},k_l,l_l}, \quad (18)$$

which is always positive, even when $k = j$.

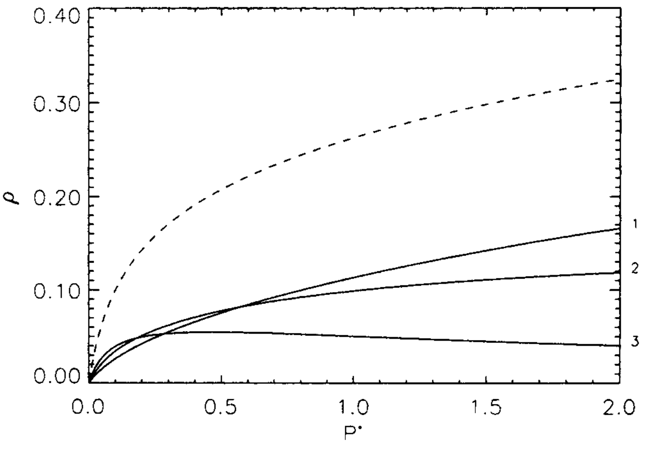

Figure 4. Same as Figure 3, except the adsorbed densities of each component and the total adsorbed density are shown.

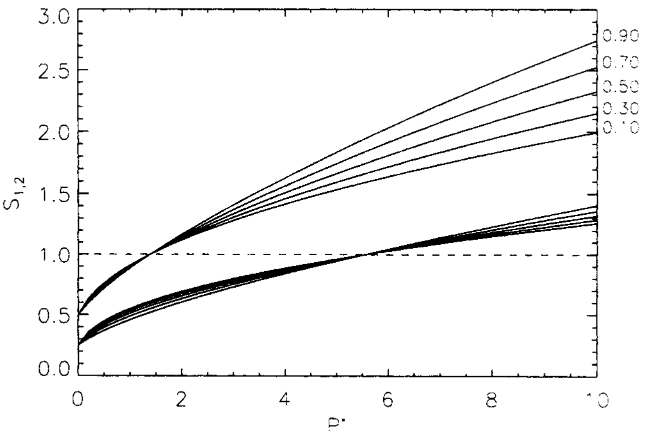

Figure 5. Selectivity of component 1 as a function of the reduced bulk pressure, P^*.

The number labeling each curve is the mole fraction of component 1. Upper group of curves: $\kappa = 2$; lower: $\kappa = 4$. The dashed line is the condition of no separation.

Effect of varying molecular parameters

We next consider the effect of varying the molecular parameters on the adsorption selectivity. There is no unique way to vary these parameters, but we consider three possibilities: varying length ratio at constant equilibrium constant ratio, vice versa, and by assuming that the adsorption energy is proportional to the length of the particle.

The effect of varying the length of component k on the spreading pressure is given by

$$\left(\frac{\partial \beta \Pi}{\partial l_k}\right)_{l_{n \neq k}, k_n, y_n, P} = -\frac{\beta \Pi P y_k k_k e^{-\beta \Pi l_k}}{1 + P \sum y_n k_n l_n e^{-\beta \Pi l_n}}, \quad (19)$$

and the effect on the selectivity is

$$\left(\frac{\partial S_{i,j}}{\partial l_k}\right)_{l_{n \neq k}, k_n, y_n, P} = S_{i,j}\left[\beta \Pi(\delta_{jk} - \delta_{ik}) + (l_j - l_i)\left(\frac{\partial \beta \Pi}{\partial l_k}\right)_{l_{n \neq k}, k_n, y_n, P}\right], \quad (20)$$

where $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$. The selectivity decreases if $k \neq i$, $k \neq j$, or if $k = i$. The derivative is positive, however, if $k = j$. For a binary mixture, $(\partial S_{1,2}/\partial \lambda)_{y_1, \kappa, P} > 0$ is a realization of the latter case, and an example is presented in Figure 6.

The effect of varying the equilibrium constant of component l is

$$\left(\frac{\partial \beta \Pi}{\partial k_l}\right)_{k_{n \neq l}, l_n, y_n, P} = \frac{P y_l e^{-\beta \Pi l_l}}{1 + P \sum y_n k_n e^{-\beta \Pi l_n}}, \quad (21)$$

and the effect on the selectivity is

$$\left(\frac{\partial S_{i,j}}{\partial k_l}\right)_{l_{n \neq l}, k_n, y_n, P} = S_{i,j}\left[\frac{\delta_{il}}{k_i} - \frac{\delta_{jl}}{k_j} + (l_j - l_i)\left(\frac{\partial \beta \Pi}{\partial k_l}\right)_{k_{n \neq k}, l_n, y_n, P} e^{\beta \Pi (l_j - l_i)}\right]. \quad (22)$$

Again, there are three cases. If $l \neq i$, $l \neq j$, or $l = i$, then this derivative is positive, while if $l = j$, the selectivity decreases with increasing k_j.

We now consider the more realistic case where the length and Henry's law constant vary simultaneously. The general expression for the effect of varying the length of component k on the selectivity of i with respect to j is

$$\left(\frac{\partial S_{i,j}}{\partial l_k}\right)_{l_{n \neq k}, y_n, P} = S_{i,j}\left[\frac{1}{k_i}\frac{\partial k_i}{\partial l_k} - \frac{1}{k_j}\frac{\partial k_j}{\partial l_k} + \beta \Pi(\delta_{jk} - \delta_{ik}) + (l_j - l_i)\left(\frac{\partial \beta \Pi}{\partial l_k}\right)_{y_n, P}\right]. \quad (23)$$

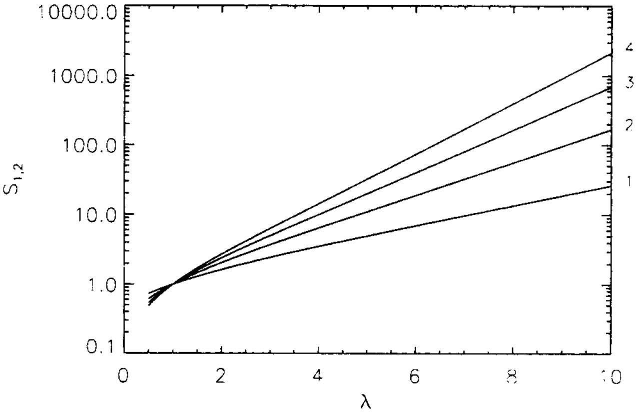

Figure 6. Selectivity as a function of the length ratio: $\kappa = 2$ and $y_1 = 0.5$.

The number labeling each curve is the bulk pressure, P^*.

For a more specific expression we must specify the dependence of k_i on l_i. A physically plausible choice is to assume that the adsorption energy of a molecule is proportional to its length, $\epsilon_i = \alpha l_i$, as might be the case for a homologous series of compounds. If we also assume that q_i results from harmonic motion in the two directions perpendicular to the line then, to a good approximation, $q_2/q_1 = \epsilon_1/\epsilon_2$ (Bakaev and Steele, 1997). Finally, taking the bulk species as ideal monatomic gases for which $\exp(\beta \mu_i^0) = P_i^0 \Lambda_i^3 \beta$, we have

$$\frac{\partial k_i}{\partial l_i} = (\beta \alpha - l_i^{-1}) k_i \quad (24)$$

with this choice, the effect on the spreading pressure is

$$\left(\frac{\partial \beta \Pi}{\partial l_k}\right)_{y_n, P} = \frac{P y_k k_k e^{-\beta \Pi l_k}}{1 + P \sum k_i y_i l_i e^{-\beta \Pi l_i}}(\beta \alpha - l_k^{-1} - \beta \Pi). \quad (25)$$

Substituting this in Eq. 23 yields

$$\left(\frac{\partial S_{i,j}}{\partial l_k}\right)_{l_{n \neq k}, y_n, P} = S_{i,j}(\beta \alpha - l_k^{-1} - \beta \Pi) \times \left[\delta_{ik} - \delta_{jk} + \frac{(l_j - l_i) k_k P y_k e^{-\beta \Pi l_k}}{1 + P \sum k_i y_i l_i e^{-\beta \Pi l_i}}\right]. \quad (26)$$

If $k = i$ or $k \neq i$, $k \neq j$, then $\partial S_{i,j}/\partial l_k > 0$ at low $\beta \Pi$ with a crossover at $\beta \Pi = \beta \alpha - l_k^{-1}$. If $k = j$, then $\partial S_{i,j}/\partial l_k < 0$ at low pressure with a change in sign at the same value of $\beta \Pi$ as in the other two cases.

Some numerical examples are presented in Figure 7 for the two-component case where

$$\kappa = \frac{1}{\lambda} e^{\beta \alpha (\lambda - 1)}. \quad (27)$$

At low total pressures the selectivity of component 1 decreases with increasing length ratio, but at sufficiently high

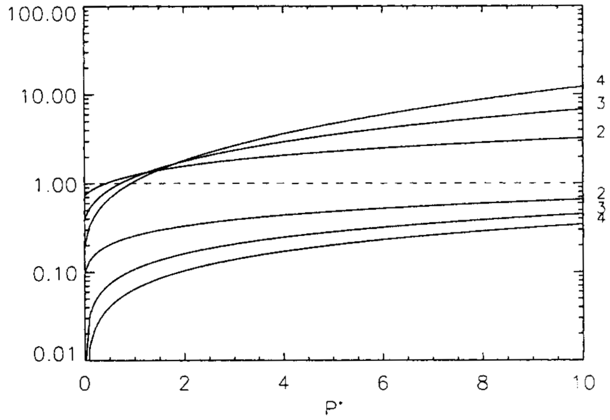

Figure 7. Selectivity as a function of bulk pressure for various mixtures when κ depends on λ (number labeling each curve) according to Eq. 27.

The upper set of three curves is for $\beta\alpha = 1$, while the lower group has $\beta\alpha = 3$.

pressures, the reverse is true. A large length ratio strongly favors the larger species at low surface coverages but, at sufficiently high pressure, the increase in binding strength of the larger particle is more than offset by its steric disadvantage and the smaller species prevails. Increasing the parameter $\beta\alpha$ at constant pressure, as expected, decreases the selectivity of component 1.

We also examine in this case the total and partial coverages and densities of the adsorbed fluid. The former are obtained from

$$\theta_1 = \rho_1^*, \qquad \theta_2 = \lambda \rho_2^*. \tag{28}$$

The total and partial coverages of component 1 are monotonically increasing functions of the bulk pressure, while the coverage of the larger component exhibits a maximum. The position and height of the maximum decreases and increases, respectively, with increasing length ratio. At low pressures, the total coverage increases with increasing λ, while the reverse is true at high pressures. The behavior of the adsorbed densities are qualitatively similar, except that the total density increases with increasing λ at high pressures.

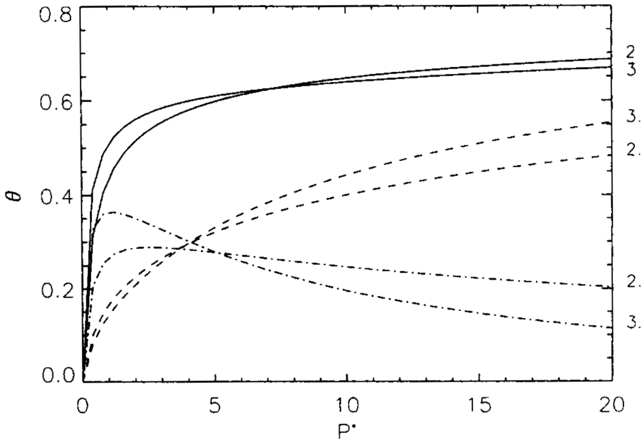

Figure 8. Total and partial coverages of the adsorbed species as a function of the bulk pressure, P^*.

The number labeling each curve is the length ratio, λ. The equilibrium constant ratio, κ, is computed from Eq. 27, with $\beta\alpha = 1$. The bulk-phase mole fraction, y_1, is 0.5. Solid lines: total coverage; dashed lines: coverage of the smaller component, θ_1; dashed-dot lines: coverage of the larger component, θ_2. Note the maximum in θ_2.

Nonideal bulk phase

Selectivity reversal is predicted to occur at very high pressures for some of the mixtures examined where the assumption of ideal gas behavior for the bulk phase may be questionable. The theory may be easily extended to treat such cases by introducing the fugacity coefficient, $\phi_i(P,T,\{y_i\})$, of each component in the bulk phase (recall that the hard-rod adsorbed phase is always ideal). Thus, for example, Eq. 6 becomes

$$k_i P_i \phi_i = \beta \Pi x_i \exp(\beta \Pi l_i), \tag{29}$$

the more general expression for the selectivity is

$$S_{i,j} = \frac{k_i \phi_i}{k_j \phi_j} e^{\beta \Pi (l_j - l_i)}, \tag{30}$$

and the pressure at selectivity reversal for a binary mixture is

$$P_0 k_1 \phi_1(P_0) l_1 = (\lambda - 1)^{-1} \ln\left(\kappa \frac{\phi_2(P_0)}{\phi_1(P_0)}\right)\left(\kappa \frac{\phi_2(P_0)}{\phi_1(P_0)}\right)^{1/(\lambda - 1)} \tag{31}$$

If the dependence of ϕ_i on P is known, this equation can be solved numerically for P_0. Unlike the ideal case, the pressure at selectivity reversal *does* depend on the bulk-phase composition.

As an illustration of the effect of bulk-phase nonideality we consider an equimolar mixture of methane and ethane. Figure 9 shows the fugacity coefficients for this mixture, computed from the van der Waals equation, for pressures up to 200 atm, and significant deviations from ideality are evident at high pressures. The adsorbed densities of the mixture, with adsorption parameters taken from Table 1, were calculated numerically and the results are given in Figure 10. Although the total density is barely modified, the partial densities of methane and ethane are increased and decreased, respectively, which results in a considerable enhancement of the methane selectivity compared with the ideal case.

Summary and Discussion

The key results of this article concerning the effect of bulk pressure and composition on the selectivity in the case of a binary mixture can be presented succinctly as follows:

Point of isoselectivity (ISP)

$$S_{1,2} = 1, \qquad P^* = P_0^*, \tag{32}$$

where

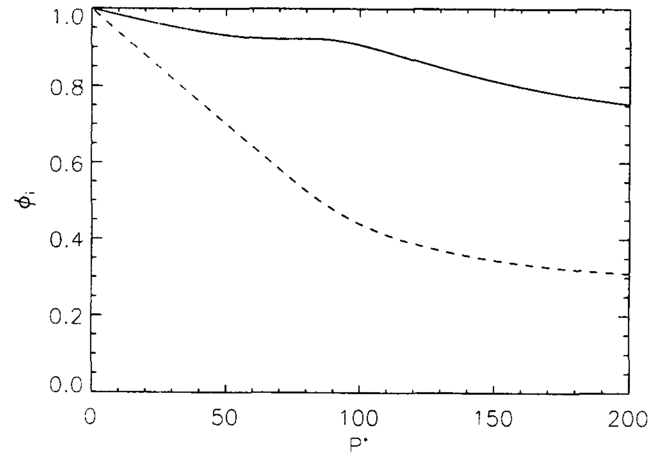

Figure 9. Fugacity coefficients in an equimolar mixture of methane (solid line) and ethane (dashed line) at 300 K computed from the van der Waals equation of state.

The van der Waals constants were taken from the *CRC Handbook* (1991), and standard mixing rules with a zero binary interaction parameter were used. The reduced pressure, P^*, is numerically equal to the pressure in atmospheres.

$$P_0^* = \frac{\kappa^{1/(\lambda-1)} \ln \kappa}{\lambda - 1}. \tag{33}$$

Effect of bulk pressure ($\lambda > 1$)

$$\left(\frac{\partial S_{1,2}}{\partial P^*}\right)_{\kappa,\lambda,y_1} > 0. \tag{34}$$

Effect of bulk composition

$$\left(\frac{\partial S_{1,2}}{\partial y_1}\right)_{\kappa,\lambda,P^*} \begin{array}{ll} < 0, & P^* < P_0^* \\ = 0, & P^* = P_0^* \\ > 0, & P^* > P_0^*. \end{array} \tag{35}$$

In terms of engineering practice, Eq. 33 could, in the absence of detailed experimental or simulation results or a more sophisticated theory, provide a first estimate for the pressure of selectivity reversal from a knowledge of only the size and Henry's law constant ratios.

The properties of the one-dimensional system are in qualitative agreement with those of the two-dimensional system of a binary mixture of disks adsorbing on a planar surface, as computed from scaled particle theory (SPT) (Talbot, 1997). Thus, this model predicts that the selectivity of the smaller species always increases with bulk pressure, and a selectivity reversal occurs if the larger species is preferentially adsorbed at low surface coverages. The selectivity of the smaller component increases with bulk-phase mole fraction at high pressures, while the reverse is true at low pressures. Unlike the one-dimensional system, however, the pressure at which the selectivity is independent of the bulk-phase mole fraction, P_1, is not equal to the pressure of selectivity reversal, P_0.

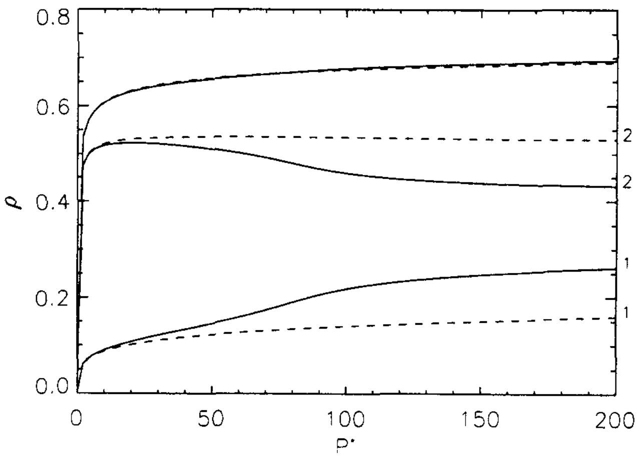

Figure 10. Adsorbed densities of methane (1) and ethane (2) as a function of reduced pressure at 300 K.

The adsorption parameters, taken from Table 1, are for the adsorption of this mixture in zeolite 5A. The dashed lines are predictions assuming ideal bulk-phase behavior.

The theory considered here applies to molecules adsorbing on a homogeneous substrate and in the thermodynamic limit. Various elaborations of the model should yield interesting results, but it is unlikely that in these cases that simple analytical expressions would be available. Possible variations include the addition of attractive interactions between the adsorbed molecules, finite-size systems, fluids adsorbing on a heterogeneous substrate, or any combination of these. Monson (1990), for example, has studied the adsorption selectivity of the inhomogeneous square-well fluid mixtures. Kofke and Post (1993) studied systems in which the adsorbed molecules, while constrained to a fixed-order, have some freedom to move off axis. Lebowitz et al. (1987) investigated one-dimensional fluids where the molecular centers are constrained to a line, but the molecules have a continuous orientation with respect to this line. These two models could be extended to the case of mixtures.

Acknowledgment

The author thanks Petroleum Research Fund of the American Chemical Society (no. 27899-AC9) for partial support of this work.

Literature Cited

Bakaev, V. A., and W. A. Steele, "Hard Rods on a Line as a Model for Adsorption of Gas Mixtures on Homogeneous and Heterogeneous Surfaces," *Langmuir*, **13**, 1054 (1997).

Bojan, M. J., E. Cheung, M. W. Cole, and W. A. Steele, "Topologies of Capillary Condensation," *Adsorption*, **2**, 53 (1996).

Bojan, M. J., and W. A. Steele, "Theoretical Analysis of Computer Simulations of Sorption in a Cylindrical Micropore," *Mol. Simul.*, **17**, 303 (1996).

Chiang, A. S. T., C. K. Lee, and F. Y. Wu, "Theory of Adsorbed Solutions: Analysis of One-dimensional Systems," *AIChE J.*, **42**, 2155 (1996).

Davis, H. T., *Statistical Mechanics of Phases, Interfaces and Thin Films*, VCH Publishers, New York (1996).

Franses, E. I., F. A. Siddiqui, D. J. Ahn, C.-H. Chang, and N.-W. L. Wang, "Thermodynamically Consistent Equilibrium Adsorption Isotherms for Mixtures of Different-Size Molecules," *Langmuir*, **11**, 3177 (1995).

Kikuchi, R., "Theory of One-Dimensional Fluid Binary Mixtures," *J. Chem. Phys.*, **23**, 2327 (1955).

Kofke, D. A., and A. J. Post, "Hard Particles in Narrow Pores. Transfer Matrix Solution and the Periodic Narrow Box," *J. Chem. Phys.*, **98**, 4853 (1993).

Lebowitz, J. L., J. K. Percus, and J. Talbot, "On the Orientational Properties of Some One-Dimensional Model Systems," *J. Stat. Phys.*, **49**, 1221 (1987).

Longuet-Higgins, H. C., "One-Dimensional Multicomponent Mixtures," *Mol. Phys.*, **1**, 83 (1958).

Maddox, M. W., S. L. Sowers, and K. E. Gubbins, "Molecular Simulation of Binary Mixture Adsorption in Buckytubes and MCM-41," *Adsorption*, **2**, 23 (1996).

Mitchell, M. C., A. V. McCormick, and H. T. Davis, "Predicting Adsorption in One-dimensional Zeolite Pores with the Exact Theory of One-Dimensional Hard Rods," *Mol. Phys.*, **83**, 429 (1994).

Monson, P. A., "The Properties of Inhomogeneous Square Well Mixtures in One Dimension," *Mol. Phys.*, **70**, 401 (1990).

Priogine, I., and S. LaFleur, "Sur la Méchanique Statistique des Mélanges," *Bull. Acad. R. Belg. Cl. Sci.*, **40**, 484 (1954).

Reed, T. M., and K. E. Gubbins, *Applied Statistical Mechanics*, Butterworth-Heinemann, Boston (1973).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley-Interscience, New York (1984).

Talbot, J., "Molecular Thermodynamics of Binary Mixture Adsorption: A Scaled Particle Theory Approach," *J. Chem. Phys.*, **106**, 4696 (1997).

Vanderlik, T. K., L. E. Scriven, and H. T. Davis, "The Statistical Mechanics of Inhomogeneous Hard Rod Mixtures," *J. Chem. Phys.*, **90**, 2422 (1989).

Van Tassel, P. R., H. T. Davis, and A. V. McCormick, "Adsorption Simulations of Small Molecules and Their Mixtures in a Zeolite Micropore," *Langmuir*, **10**, 1257 (1994).

Van Tassel, P. R., H. T. Davis, and A. V. McCormick, "Adsorption of Binary Mixtures in a Zeolite Micropore," *Mol. Simulation*, **17**, 239 (1996).

Manuscript received Feb. 7, 1997, and revision received June 9, 1997.