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The temperature dependence of single-file separation mechanisms in one-dimensional nanoporous materials

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Abstract

The mobility of fluids adsorbed in nanoporous materials with one-dimensional porous networks can be exploited to effect kinetic separations of small hydrocarbons. These nanopores provide an environment in which fluids, with similar bulk diffusivities, exhibit drastically different mobilities in the adsorbed phase. The basis of this difference in mobilities is linked to the two different modes of motion within the nanopore: ordinary uni-directional diffusion and single-file motion. This transport phenomenon has no bulk analog; it is a novel characteristic of fluids confined in nanoscale channels. The transition between these two fundamentally different modes of motion is a sensitive function of pore size, adsorbate size, density of the adsorbed phase, and the temperature. In this work, we investigate the temperature dependence of the transition from ordinary diffusion to single-file motion and apply it to a model separation system. Using molecular dynamics simulations of methane and ethane in the one-dimensional molecular sieve, $AlPO_4$-5, this work demonstrates, first, that temperature can be used to control whether a pure component undergoes ordinary or single-file motion. Second, we examine the temperature dependence of the diffusivities of components in a binary adsorbed mixture. Third, we demonstrate that the operating temperature places limitations on whether the separation of a mixture can be successfully obtained using this technique. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Temperature dependence; One-dimensional; Nanopores

1. Introduction

1.1. $AlPO_4$-5

There exists a class of zeolites and molecular sieves that contain a porous network of roughly cylindrical channels, which are arranged parallel to each other and, in the perfect crystal, never intersect. $AlPO_4$-5 is a molecular sieve with this one-dimensional pore structure. There is, of course, a radial dimension to the channel but, in terms of transport properties, there will only be a long-time non-zero mean square displacement of the adsorbate in the axial direction. $AlPO_4$-5 contains roughly cylindrical pores created by a ring of 12 oxygen, 6 phosphorus, and 6 aluminum atoms. These rings have a nominal diameter of 7.3 Å, although the cross-sectional area varies with position along the channel axis, depending on whether one is at a ring or between rings [1]. Fig. 1 shows a schematic of the $AlPO_4$-5 crystal structure. The crystal structure has been determined experimentally by X-ray diffraction [2].

1.2. Uni-directional and single-file motion of single component fluids

When a single-component fluid is adsorbed in a one-dimensional porous network, two modes of motion are possible. The first mode of motion is ordinary, uni-directional diffusion, as predicted by Einstein's relation, where the mean square displacement is proportional to the time of observation, t, in the long-time limit. The proportionality constant is twice the coefficient of diffusion, D, which has units of length squared per unit time [3]

$$\lim_{t\to\infty} \langle [z(\tau = t) - z(\tau = 0)]^2 \rangle = 2Dt \quad (1)$$

One physical assumption built into the diffusion equation, which yields this result, is that the individual atoms or molecules result is that the individual atoms or molecules that make up the diffusing species be allowed to pass each other. If the channel is so small as to prohibit passing of the adsorbate molecules then the motion can no longer be described as ordinary diffusion. Instead, a single-file motion is predicted by the one-dimensional hard-rod (1DHR) theory [4]. In 1DHR theory, each molecule undergoes a constrained random walk. Molecules are unable to exchange positions

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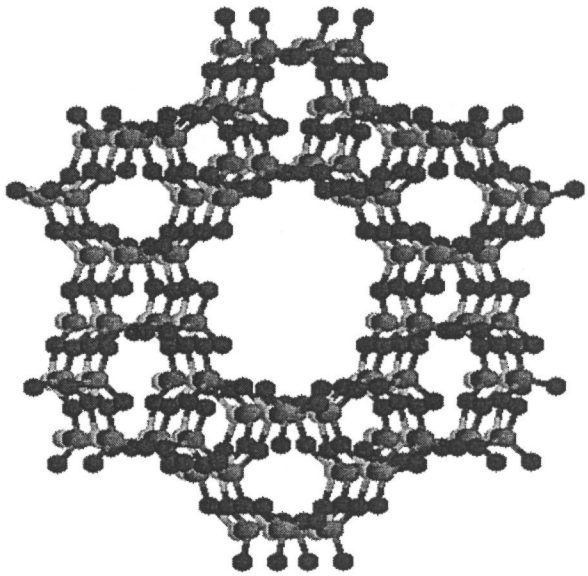

Fig. 1. Schematic of the molecular sieve $AlPO_4$-5.

within the channel and, thus, the ordered sequence of molecules is maintained. The entire chain of adsorbates then undergoes a second random walk. It is this individual random walk within a collective random walk that gives rise to a mean-square displacement, proportional not to the observation time but to the square root of the observation time. 1DHR expresses this relation in a form obviously analogous to Einstein's relation:

$$\lim_{t\to\infty} \langle [z(\tau = t) - z(\tau = 0)]^2 \rangle = 2\alpha t^{0.5} \tag{2}$$

The proportionality constant between the mean-square displacement and the square root of the observation time is twice the single-file mobility factor, α. The single-file mobility factor has units of length squared per time raised to the power of one-half—to be contrasted with that of a diffusion coefficient. In this system, a diffusion coefficient is not defined. The single-file mobility factor has an analytical form which yields the dependence on the adsorbate one-dimensional number density, N, the adsorbate size, σ, and, the temperature, T, via an infinite dilution diffusivity, D_{id}:

$$\alpha = \frac{(1 - N\sigma)}{N} \left(\frac{D_{id}(\sigma, T)}{\pi} \right)^{0.5} \tag{3}$$

A recent work has demonstrated that the difference between the ordinary uni-directional diffusion and single-file motion can be exploited to effect a kinetic separation [5]. Single-component studies, both from pulse-field-gradient (PFG) NMR experiment and molecular dynamics (MD) simulation, have shown that methane undergoes ordinary uni-directional diffusion in $AlPO_4$-5 [6–8]. It has also been demonstrated using both, PFG-NMR and MD techniques that ethane undergoes single-file motion when adsorbed in the pores of $AlPO_4$-5 [7–12]. The single-component studies indicate that single-file motion is a much slower mode of motion than is ordinary diffusion. It is not obvious on what basis one should compare the rapidity of the motion exhibited by methane and ethane because one is described by a diffusivity and the other by a single-file mobility. However, on a time basis as short as one second, we already see a mean-square displacement that varies by a factor of over 200. This factor will increase rapidly as the observation time increases. The most important point is that single-file motion is a much slower mode of motion than ordinary uni-directional diffusion.

It should be noted that there are published quasi-elastic neutron scattering (QENS) results that indicate both, methane and ethane exhibit ordinary diffusion in $AlPO_4$-5 [13]. The QENS ordinary diffusion results for ethane contradict the single-file results for ethane obtained from PFG-NMR. These contradictory experimental results have yet to be reconciled. In the QENS study, the authors cite the fact that different crystals were used (the PFG-NMR study used $AlPO_4$-5 synthesized by Mark Davis) and that crystals defects formed during synthesis or due to exposure to the atmosphere could cause the channels to deteriorate, thus creating a three-dimensional porous network where single-file motion would not be observed.

In order to exploit this difference in diffusivities, we investigated a mixture of methane and ethane in the molecular sieve $AlPO_4$-5 [5]. We have shown that, in a system where methane can pass ethane in the pores, methane retains its high ordinary diffusivity, while ethane remains single-file. However, in a system where methane cannot pass ethane, both are reduced to slow single-file motion. The former case avails itself to kinetic separation.

In this work, we investigate the temperature dependence of the diffusivity/mobility of pure methane, pure ethane, and a binary mixture adsorbed in $AlPO_4$-5. We draw the following three points from our data:

1. Adsorbate motion in the $AlPO_4$-5 nanopore, whether it is ordinary diffusion or single- file motion, can be described by an activation model, where net movement down the pore can be viewed as adsorbates hopping from one energy well (physisorption site) to an adjacent well.
2. The transition from ordinary diffusion to single-file motion can be controlled, in select cases, by the operating temperature.
3. The success of a separation scheme of a binary mixture in a nanoporous material is dependent upon the operating temperature.

2. Methodology

2.1. Potentials

The simulation techniques employed in this work were molecular dynamics simulations. The details of the simula-

Table 1
Lennard–Jones 20-6 parameters

	Methane–methane	Methane–ethane	Ethane–ethane	Methane–oxygen	Ethane–oxygen
σ(Å)	3.882	4.941	5.000	3.083	4.832
ε(aJ)	0.00189150	0.00245081	0.00317552	0.00194768	0.00068564

tion have been described previously [7]. Both, methane and ethane are modeled as single-center spheres. In line with the previous work, all interactions (Me–Me, Me–Et, Et–Et, Me–O, and Et–O) obey a Lennard–Jones 20-6 (LJ20-6) potential [5,7,8]. The LJ12-6 methane and ethane parameters were obtained from the literature [14]. The methane–oxygen and ethane–oxygen parameters were obtained using the Kirkwood–Muller formulas [7]. The cut-off for the LJ potential was 12.0 Å. The parameters for this potential are given in Table 1.

The ethane and methane only interact with the oxygen of the $AlPO_4$-5 framework, following the suggestion of Beezus et al. [15] that the oxygen contributes the most significant term to the potential. The oxygen positions in the framework were taken from the X-ray crystallography data of Bennett et al. [2]. The framework is rigid. While the assumptions of a single-center methane and ethane as well as a rigid lattice are relatively unsophisticated models, we have established previously that these models can capture the fundamental physics governing the transition from ordinary diffusion to single-file motion [7]. However, we discuss some likely implications of these assumptions in Section 5.

2.2. Simulation techniques

The simulations used 256 adsorbate atoms (ethane + methane). The $AlPO_4$-5 unit cell contains 72 atoms. A $2 \times 2 \times 1$ (xyz) block of the unit cell creates the boundary for a central channel in the z-direction (as shown in Fig. 1). For 256 adsorbate atoms at a loading of 1.0 adsorbate atoms per unit-cell length, a block of $2 \times 2 \times 256 = 1024$ $AlPO_4$-5 unit cells (i.e. 73 728 atoms) composed the simulation volume. This volume was bounded in all the three dimensions by periodic images. The size of our fluid, 256 adsorbate molecules, is small. We are constrained, however, by the larger number of 73 728 adsorbent atoms needed to give a complete crystalline structure around the fluid. Simulations of 512 adsorbate molecules confirmed the results of the 256-molecule system within simulation error.

For each data point in the following graphs, the first 5000 simulation steps were used for equilibration and discarded. Following equilibration, 1 000 000 simulation steps were conducted with a time step of 2.0 fs, yielding a total simulation time of 2 ns. Two nanoseconds has been shown to be sufficiently to establish the long-time behavior of either ordinary diffusion (which is established in ca. 10 ps) or single-file motion (which takes much longer) [9]. During data production, the Berendson thermostat was employed to maintain a constant temperature [16]. Newton's equations were integrated using the fifth-order Gear-predictor corrector [17].

The simulations were conducted on a dual processor SGI workstation, using the 'message passing interface' (MPI) library of communication subroutines. Each simulation took ≈48 h of cpu time.

The diffusivities reported in this paper were calculated using the Einstein relation [3]. During the simulation, positions were periodically saved. After the simulation was completed, mean-square displacements were computed as a function of observation time. A least-squares linear regression was performed for all observation times >4.0 ps. (The extremely short-time behavior is free-motion, where the mean-square displacement scales as the square of the observation time.) This short-time regime should not contribute to the long-time behavior used to determine the diffusivity. The standard deviations of the diffusivities were calculated from the coefficients of the linear regression [18]. The measure of fit of the least-squares regression to the mean-square displacement vs. time data was calculated to demonstrate the appropriateness of either the ordinary or single-file model [19].

In cases where the adsorbates do not undergo ordinary motion but rather a single-file motion, the same data used to calculate the diffusivities can be used to perform a least-squares linear regression for the single-file mobilities, except that now the regression must be made on the mean-square displacement vs. the square root of the observation time. The mobilities, standard deviations, and measures of fit are then taken from the regression.

3. Activation theory

Given that the molecular sieve, $AlPO_4$-5, has a unidimensional porous network, decorated with energy wells (physisorption sites) twice per unit channel length (8.48 Å) in the axial direction, the motion of adsorbates in the pore should be considered an activated process. To demonstrate that diffusion of an adsorbate in $AlPO_4$-5 is, in fact, an activated process, we must show that the standard temperature dependence for activated processes,

$$D_i(T,n) = c(T,n)\mathrm{e}^{-\Delta G_{\mathrm{act},i}/kT} \tag{4}$$

is obeyed, where D_i is the diffusivity of species i at temperature, T, and molar density n, c the exponential pre-factor with units of diffusivity, a weak dependence on

T and presumably all of the n dependence; $\Delta G_{\mathrm{act},i}$ the molar free energy of activation for diffusion of species i, and k the Boltzmann constant.

Since our ultimate goal is to develop a predictive model of diffusion in nanoporous materials, it is necessary to rearrange Eq. (1) into a form that is useful for comparison with data. The Gibbs' free energy of activation can be written as

$$\begin{aligned}\Delta G_{\mathrm{act},i} &\equiv \Delta H_{\mathrm{act},i} - T\Delta S_{\mathrm{act},i} \\ &= \Delta U_{\mathrm{act},i} + \Delta(PV)_{\mathrm{act},i} - T\Delta S_{\mathrm{act},i}\end{aligned} \tag{5}$$

where P is the pressure, V the molar volume, U the molar internal energy, H the molar enthalpy, and S the molar entropy. Substituting Eq. (5) into Eq. (4) we have

$$D_i(T,n) = D_i^0(T,n)\mathrm{e}^{-\Delta H_{\mathrm{act},i}/kT} \tag{6}$$

where

$$D_i^0(T,n) = c\mathrm{e}^{(\Delta S_{\mathrm{act},i}/k)} \tag{7}$$

This rearrangement is useful because it allows us to distinguish between enthalpic and entropic contributions to changes in the diffusivity as a function of temperature.

One-dimensional hard-rod theory predicts that the functional form of the temperature dependence of an adsorbate undergoing single-file motion should be the same as that undergoing ordinary diffusion because, looking at Eq. (3), we see all of the temperature dependence in the infinite dilution diffusivity.

4. Results and discussion

4.1. Temperature dependence of the mobility of infinitely dilute pure fluids

In Fig. 2, we plot the natural log of the infinite dilution diffusivity as a function of ($1/kT$) The data points fit a least-squares model. The slope of the fit is the negative of the activation enthalpy, $\Delta H_{\mathrm{act},i}$. The y-intercept is the natural log of the pre-factor. D_i^0, or the diffusivity in the absence of an activation enthalpy. The data points were simulated over a range from 98 to 498 K, at infinite dilution. For both, methane and ethane the temperature dependence of the infinite dilution diffusivity is in good agreement with the activation theory of Eq. (6).

This demonstration of an activation model is important for two reasons. First, it shows that we are correct in assuming that the movement of adsorbates in a molecular sieve like $AlPO_4$-5 is an activated process. Second, since all of the temperature dependence of the single-file mobility is contained in the infinite dilution diffusivity (Eq. (3)), we can use this data to predict that single-file motion is also an activated process.

The values for the activation enthalpy for methane and ethane in $AlPO_4$-5 are 4.47 and 2.89 kJ/mol, respectively. We are currently in the process of developing a predictive theory to obtain these activation enthalpies without simulation. At the present time, we will say no more than that the higher activation enthalpy for the smaller molecule,

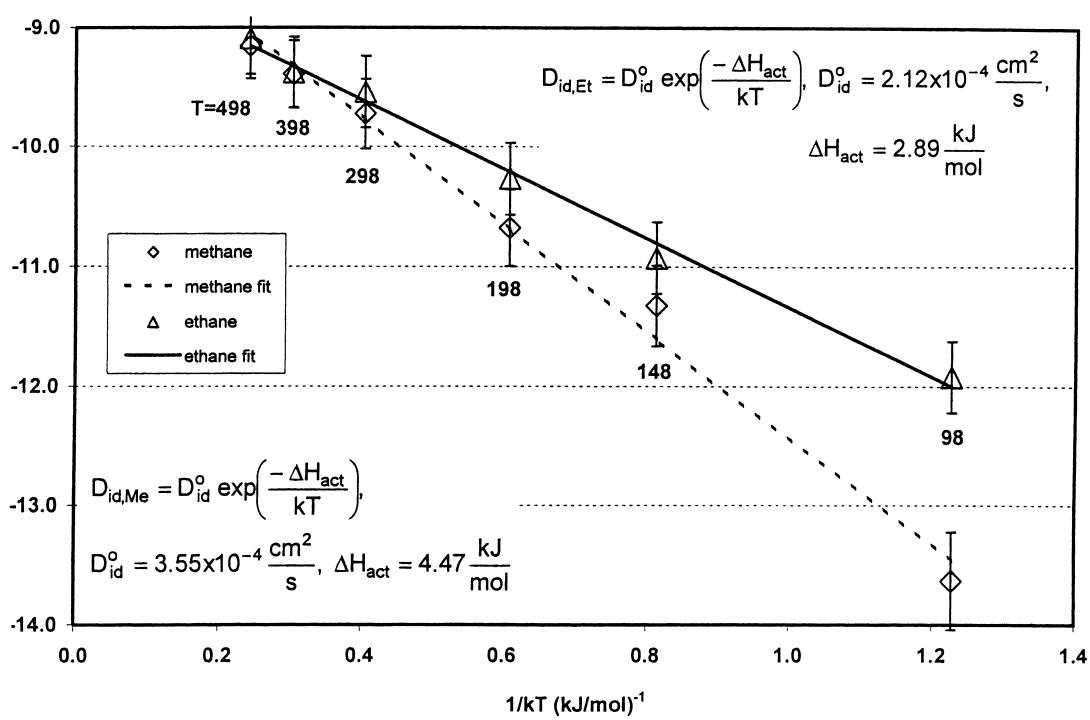

Fig. 2. Natural logarithm of the *infinite-dilution* diffusivities of methane and ethane *pure fluids* as a function of temperature, where $\sigma_M = 3.882$ Å and $\sigma_E = 5.0$ Å.

methane, is a result of the smaller molecule being able to move farther into the physisorption site (closer to the wall of the pore), where the energy well is deeper. The resulting lower activation enthalpy gives ethane a higher infinite dilution diffusivity at low temperatures. However, as the temperature increases, the effect of the activation barrier is reduced and the smaller, lighter molecule, methane, has the higher diffusivity, and thus the higher y-intercept.

From kinetic theory, one expects that the diffusivity is inversely proportional to the square root of the molecular weight [20]. From this estimate, we predict a ratio of methane to ethane diffusivities of 1.37 in the absence of an activation barrier, that is the high temperature limit. The ratio of our y-intercepts is 1.67, a higher value than that due purely to mass, because, in addition to the mass difference, there is also a size advantage for the smaller methane.

4.2. *Temperature dependence of the mobility of pure fluids at finite loadings*

Moving from an infinitely dilute pure component to one at finite density, the motion of methane changes only quantitatively. Methane molecules at both, infinite dilution and finite loadings undergo ordinary diffusion. However, when shifting from infinite dilution to finite loadings, the ethane undergoes a qualitative change in motion. At infinite dilution, there is no question of one ethane molecules passing another, and thus ordinary diffusion is observed. At finite loadings, the ethane cannot pass, and one observes single-file motion. In fact, at all temperatures in the range studied, ethane at the finite loading was observed to undergo single-file motion.

In Fig. 3, we find plots of the natural logarithm of the diffusivity of methane and the single-file mobility of ethane as a function of ($1/kT$). The data points were simulated over a range from 98 to 498 K, at a loading of 1.0 adsorbate molecules per unit cell of $AlPO_4$-5. The fit of Eq. (6) with the diffusivity of methane is again in good agreement, within 3%. The ethane data points have larger error bars, because the single-file mode of motion has consistently shown to be more difficult to smoothly capture in simulations. The noise can be attributed to the elements of the slower mode of motion not being averaged out as well over the course of the simulation.

The key point, however, is that the single-file system still obeys the temperature dependence predicted by the activation theory for ordinary diffusion.

The ratio of the activation enthalpy of methane at 1.0 molecules per unit cell to that at infinite dilution is 0.61. This indicates that the adsorbate–adsorbate interactions substantially lower the activation barrier. From this observation and from the movies taken of the simulation, we see that the physisorption sites are multiply occupied, even though there is 1.0 adsorbate per 2.0 sites. The methane forms clusters of two to four atoms. The clusters are bound only by the (weak) Lennard–Jones attractive interaction. The presence of a second or third adsorbate changes the energetic and local pressure profile of the pore in such a way that the activation enthalpy is reduced. Similarly, the prefactor in Eq. (6), a measure of the entropy of activation, is

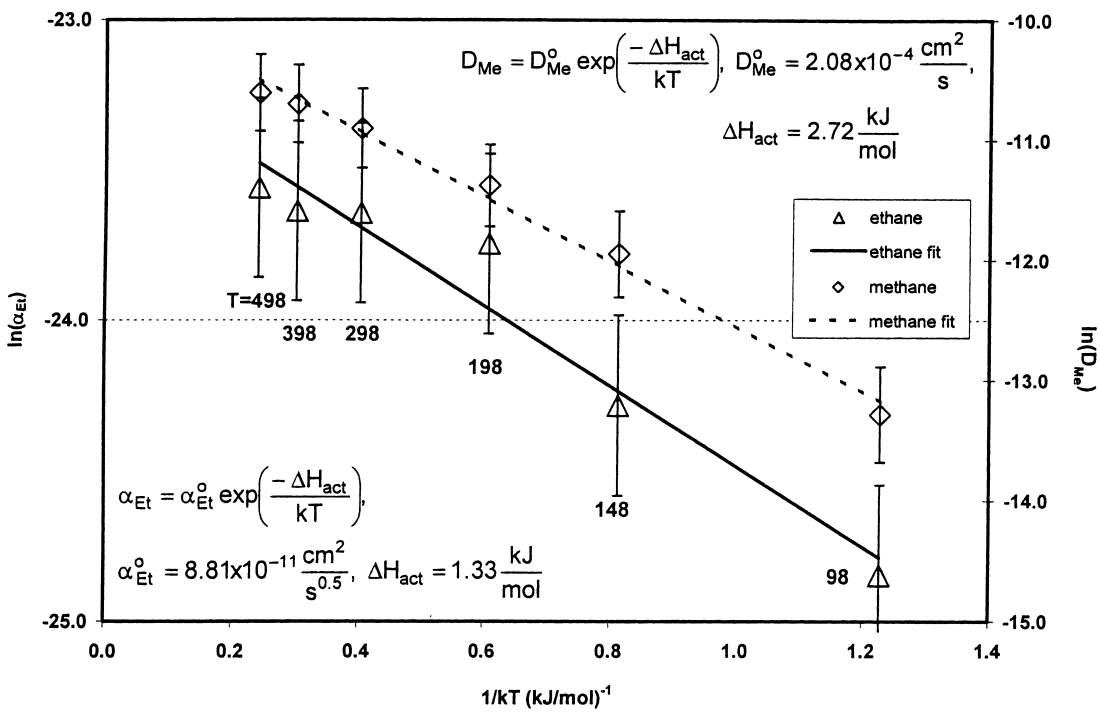

Fig. 3. Natural logarithm of the diffusivity of methane and the single-file mobility of ethane *pure fluids* as a function of temperature, where $\sigma_M = 3.882$ Å, $\sigma_E = 5.0$ Å, and a *finite loading* of 1.0 adsorbate molecules per unit cell $AlPO_4$-5.

reduced. This data suggests that, at finite loadings, the adsorbate begins the activated hop, not from the deepest portion of the adsorption site, but from a point closer to the radial center of the pore. An activated hop from this point has a lower enthalpy and entropy of activation, as predicted by potential energy and external pressure maps of the pore space [1]. Sholl and Fichthorn [21] have investigated the movement of adsorbate clusters in idealized systems and have characterized the change in energy of activation with cluster size, based on potential energy maps. They predict non-monatomic trends in the energy of activation with cluster size. We see a general decrease in the activation energy as loading increases.

The ratio of the activation enthalpy of ethane at 1.0 molecules per unit cell to that at infinite dilution is 0.46, and can be attributed to analogous reasons as those given above for methane.

4.3. Controlling the single-file transition of a pure fluid with temperature

Using several criteria described elsewhere, we were able to make confident statements about whether methane and ethane pure components systems were undergoing uni-directional diffusion or single-file motion [5]. At all temperatures, pure methane exhibited ordinary uni-directional motion and pure ethane exhibited single-file motion. However, this may not always be the case; some molecules may change modes of motion with temperature. The operating temperature can determine, in some cases, the mode of motion of an adsorbate.

The mechanism for this temperature-induced transition from single-file motion to ordinary diffusion, or vice-versa, is based on adsorbates having the necessary kinetic energy to squeeze past each other in the pore. In effect, there is a second activation energy which is the passing activation energy. At low temperatures, adsorbates will not have the necessary kinetic energy to overcome the passing barrier, and thus they will back-scatter from a collision, resulting in single-file motion for the entire system. At high temperatures, adsorbates will be able to pass more easily, and thus undergo ordinary diffusion.

(One should add that, as the temperature increases, the equilibrium distribution of the fluid within the pore shifts toward volumes of higher potential energy. In effect, this slightly expands the accessible pore volume with increasing temperature. Clearly this effect is of secondary consideration relative to the kinetic energy in considering the transition from single-file motion to ordinary diffusion.)

If ethane were to be placed in a pore with a slightly larger cross-sectional area than $AlPO_4$-5 (e.g. zeolite-L or $AlPO_4$-8), this kind of a situation, where we observed a temperature-induced transition from single-file motion at low temperature to ordinary diffusion at high temperatures, might occur. However, introducing a new crystal structure also introduces a variety of other parameter changes, for example the shapes and distribution of the adsorption sites. Therefore, in order to obtain the cleanest comparison possible, rather than examine ethane in a larger one-dimensional molecular sieve, we reduce the ethane diameter and continue to simulate in $AlPO_4$-5. This change of parameters has the same effect and simulates the same phenomenon as simulating ethane in a larger pore. We change the diameter of ethane from 5.0 to 4.5 Å, and will refer to this molecule as $\text{ethane}_{4.5}$.

On comparing the initial and final order of the molecules, we can determine whether there was any passing during the simulation of $\text{ethane}_{4.5}$. This determination then indicates whether the mean-square displacement data should be fit with a diffusion coefficient (Eq. (1)) or a single-file mobility (Eq. (2)).

In Fig. 4, we plot the natural logarithm of the diffusivity or single-file mobility of $\text{ethane}_{4.5}$ as a function of $(1/kT)$. The data points were simulated over a range from 98 to 498 K, at a loading of 1.0 $\text{ethane}_{4.5}$ per unit cell of $AlPO_4$-5. At a temperature of 98 K, $\text{ethane}_{4.5}$ molecules were not able to pass each other and thus exhibited single-file motion. At all temperatures above that, some passing was observed. At 148 K, two passing events were observed. At 198, 15 passing events were observed. At higher temperatures, the final order of the adsorbates had completely changed from the initial order. In this case, the 148 and 198 K data points are in a 'transitional regime' of motion, between single-file motion and ordinary diffusion. The plots of mean-square displacement vs. time fall somewhere between the exponent 1.0, predicted for ordinary diffusion (Eq. (1)), and 0.5, predicted for single file motion (Eq. (2)). However, we choose to interpret a case like this as ordinary diffusion, since the mean square of ordinary diffusion is orders of magnitude greater than single-file motion; the mean-square displacement of rare passing-events outweigh the small mean-square displacements of the local single-file motion in the system [7].

It is not essential to reduce the system to very low temperatures in order to observe this transition. On the contrary, the temperature of the transition is determined by some function of the ratio of adsorbate size to pore size. Thus, while in the case of $\text{ethane}_{4.5}$ the transition was observed between 98 and 148 K, in the case of $\text{ethane}_{5.0}$, which exhibits single-file motion up to 498 K, we might yet see a temperature-induced transition to ordinary motion at a temperature >498 K.

4.4. Temperature dependence of the mobility of a binary mixture

In order to effect a kinetic separation, we require (1) that one component of the binary mixture (methane) be able to pass both other methane and ethane molecules, and (2) that ethane not be able to pass other ethane. We simulated a mixture of 50% methane and 50% ethane at a total loading of 1.0 adsorbate per unit cell.

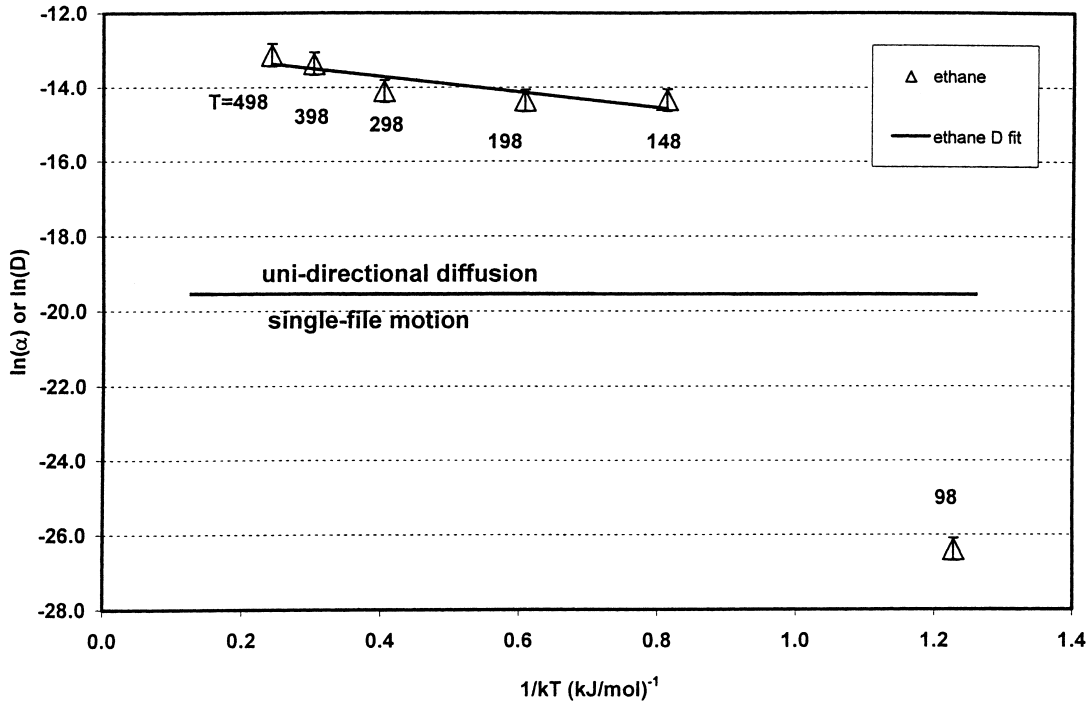

Fig. 4. Natural logarithm of the diffusivity and the single-file mobility of ethane$_{4.5}$ *pure fluid* as a function of temperature, where $\sigma_E = 4.5$ Å and a *finite loading* of 1.0 molecules per unit cell $AlPO_4$-5.

For this size of ethane (5.0 Å), the methane can pass ethane at all temperatures. Thus, the methane exhibits ordinary diffusion. From the pure component data, we know that ethane cannot pass other ethane, and thus undergoes single-file motion. In Fig. 5, we plot the natural logarithm of the diffusivity of methane and the single-file mobility of ethane for the mixture. Both continue to yield relatively good fits to the activation theory of Eq. (6).

The ratio of the activation enthalpy of ethane in the mixture to that in the pure component (at the same total loading of 1.0 molecules per unit cell) is 1.32. In other words, methane molecules are not as effective in reducing the activation enthalpy for ethane motion as are other ethane. However, the methane still reduces the activation enthalpy for ethane motion, over what it was at infinite dilution (by a factor of 0.62).

The ratio of the activation enthalpy of methane in the mixture to that in the pure component (at the same total loading of 1.0 molecules per unit cell) is 0.81. Again, the ethane molecules are better than methane molecules at reducing the activation enthalpy, whether it be for the motion of ethane or methane.

The reason that ethane is better than methane at reducing the activation barrier for other adsorbates is not precisely known. However, we speculate that the larger ethane, with the deeper Lennard–Jones energy well changes the potential-energy distribution in the pore to a greater extent. This change is evidently made in such a way as to reduce the activation barrier for a nearby adsorbate.

The point to draw from this is that, in a mixture, the motion of each species is still a series of activated hops. The enthalpy of activation is affected by the presence of the other component in the same functional manner that the enthalpy of activation is affected by changes in the total diffusivity. The magnitude of the changes in the enthalpy of activation are affected by the composition of the mixture.

4.5. *Controlling the kinetic separation of a binary mixture with temperature*

We see that. for a mixture of methane and ethane$_{5.0}$ in $AlPO_4$-5, methane can pass the ethane at all temperatures studied. In a smaller pore than $AlPO_4$-5, it would be more difficult for methane to pass ethane, and thus one might expect the methane to be unable to pass ethane at some temperatures. If this were the case, the methane would lose its high ordinary diffusivity and a separation scheme based on one component having an ordinary diffusivity and the other having a single-file mobility would not be feasible. By raising the temperature, one would be able to introduce the change in modes of motion. This would be a case of a temperature-induced transition of the mixture to a state where kinetic separation was possible.

In order to demonstrate this concept, we could examine methane and ethane in a one-dimensional molecular sieve with a smaller cross section, e.g. zeolite-θ, ZSM-12, or zeolite-ω. However, as we did above, to allow for a cleaner comparison, we can demonstrate the same concept by

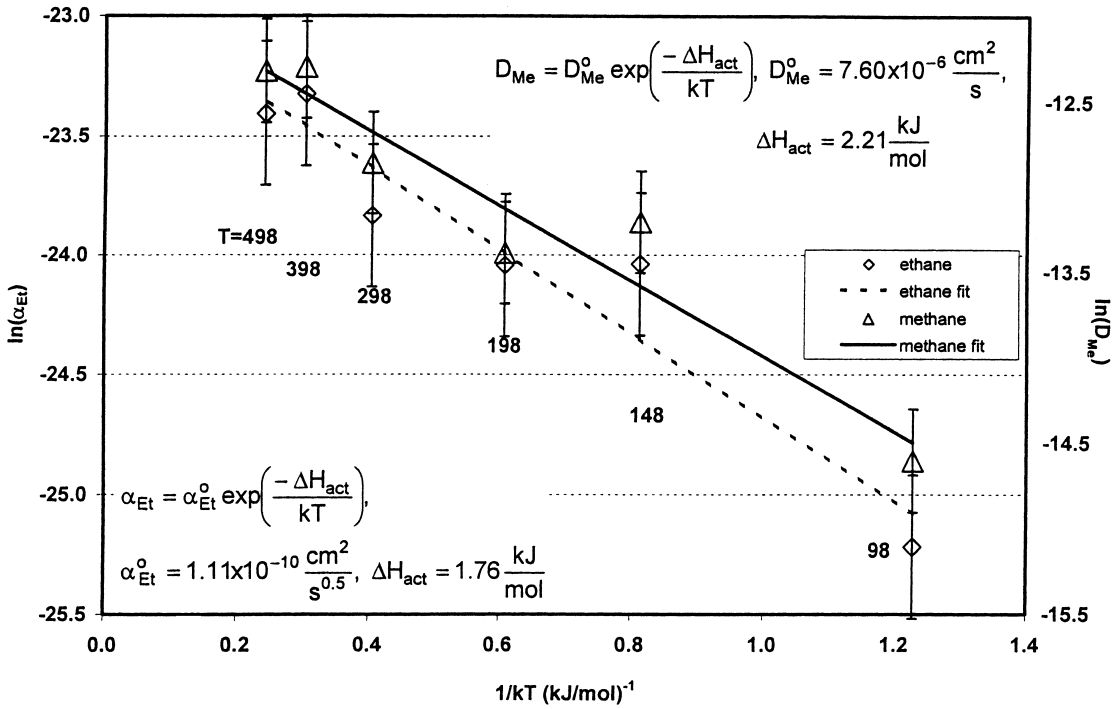

Fig. 5. Natural logarithm of the diffusivity of methane and the single-file mobility of ethane in a 50%/50% *mixture* as a function of temperature, where $\sigma_M = 3.882$ Å, $\sigma_E = 5.0$ Å, and a *finite loading* of 1.0 molecules per unit cell $AlPO_4$-5.

inflating the radius of ethane. In this case, we increase the ethane diameter from 5.0 to 5.5 A, and refer to the molecule as ethane$_{5.5}$. In Fig. 6, we plot the natural logarithm of the diffusivity of methane and the single-file mobility of ethane$_{5.5}$ for a mixture of 50% methane and 50% ethane$_{5.5}$ at a total loading of 1.0 molecules per unit cell.

At low temperatures, below 148 K, methane cannot pass ethane$_{5.5}$ and thus undergoes a single-file motion. Even

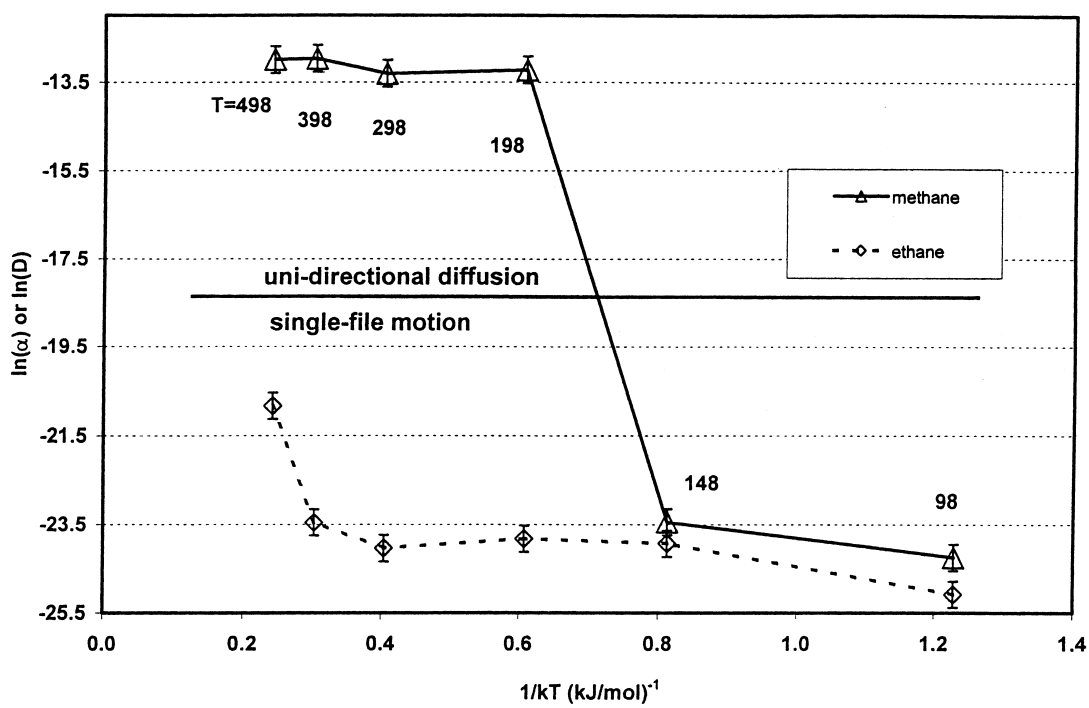

Fig. 6. Natural logarithm of the diffusivity and single-file mobility of methane and ethane$_{5.5}$ in a 50%/50% *mixture* as a function of temperature, where $\sigma_M = 3.882$ Å, $\sigma_E = 5.5$ Å, and a *finite loading* of 1.0 molecules per unit cell $AlPO_4$-5.

though, methane can pass other methane, they are limited by the ethane$_{5.5}$ that surrounds them. In fact, the system is one of methane-clusters randomly distributed among ethane$_{5.5}$ molecules. The motion of this type of complex system has not been studied. However, the one thing that can be said about this type of system is that it does not avail itself to kinetic separations since the mobilities of the methane and ethane are of the same order of magnitude.

As the temperature increases, methane begins to be able to pass ethane$_{5.5}$. This changes the motion of methane from single-file to ordinary diffusion, resulting in a drastic increase in the methane motion. It also produces a sharp increase in the ethane$_{5.5}$ mobility, although not on the same scale as the methane increase, since the ethane$_{5.5}$ motion remains single-file because it cannot pass other ethane$_{5.5}$.

This demonstrates that one can vary the operating temperature to create a system where a kinetic separation based on the single-file versus ordinary diffusion mechanism is feasible, even when the separation is not feasible at all temperatures.

5. Conclusions and applications

In this work, we have demonstrated using molecular dynamics computer simulations of methane and ethane in the one-dimensional molecular sieve, $AlPO_4$-5, that:

1. pure-component ordinary uni-directional diffusion in some crystalline nanoporous materials is a well-characterized activated process;
2. pure component single-file motion in some crystalline nanoporous materials is a well-characterized activated process, as predicted by the temperature dependence of one-dimensional hard-rod theory;
3. ordinary diffusion and single-file motion of components in mixtures adsorbed in crystalline nanoporous materials are activated processes with activation barriers affected by the total loading and composition of the mixture;
4. pure fluids can undergo a shift from single-file motion to ordinary diffusion by an increase in the operating temperature; and
5. a binary mixture with components that cannot pass each other (a system with no promise for kinetic separation) can be converted to a system with components that can pass each other (a system with great promise for kinetic separation) by an increase in the operating temperature.

Statements (4) and (5) rely on a careful balance between the residence time of the adsorbate in the one-dimensional channel and the time between passing events, as predicted by activation theory. So long as the residence time is less than the time between passing events, single-file motion will be observed.

These conclusions have both, theoretical and industrial impact. The fact that all the systems studied (including pure fluids and mixtures, fluids at infinite dilution and at finite loadings, fluids undergoing ordinary diffusion or single-file motion) showed good agreement with standard activation theory, gives direction to the effort to establish a predictive theory for diffusion/single-file motion in nanoporous materials.

Additionally, the fact that temperature can be used to create an environment where kinetic separation based on the ordinary diffusion vs. single-file motion scheme is feasible is of direct industrial use. Moreover, one can imagine that such a scheme involves a separation stage and a regeneration stage of the adsorbent. In the regeneration stage, one would begin with the adsorbent having a high loading of the single-file component of the mixture. Regeneration of this bed would take a long time since the motion of the single-file component is slow. However, by raising the temperature, one could induce a transition from single-file motion to ordinary diffusion, which would regenerate the adsorption bed much more quickly.

6. Nomenclature

c	exponential pre-factor [units of diffusivity
D	diffusivity]
D_{id}	infinite dilution diffusivity
D^0	exponential pre-factor including entropy of activation
ΔG_{act}	molar free energy of activation for diffusion
H	molar enthalpy
k	Boltzmann constant
N	one-dimensional number density [molecules/length]
P	pressure
S	molar entropy
t	time
T	temperature
U	molar internal energy
V	molar volume
x_i	mole fraction of component
z	position
α	single-file mobility factor
σ	Lennard–Jones diameter

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