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LETTERS

Sorption-Induced Diffusion-Selective Separation of Hydrocarbon Isomers Using Silicalite

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In this paper we demonstrate a new principle for separation of linear and branched (2-methyl)alkanes, in the five to seven carbon atom range, by means of permeation through a silicalite membrane. The permeation selectivity relies on subtle interplay between sorption and diffusion. The required sorption isotherms for the pure components and mixtures are generated using configurational-bias Monte Carlo (CBMC) simulations. The CBMC simulations of the mixture isotherm show a curious maximum in the loading of 2-methyl alkane; this loading decreases to almost zero with increased pressures. The high sorption selectivity for the linear alkane is due to entropic effects; the linear alkane has a higher "packing" efficiency than the branched alkane within the zeolite structure. Calculations for a 50−50 mixture of *n*-hexane (*n*-C_6) and 2-methylpentane (2MP), for example, show that the higher sorption selectivity for the linear alkane has the effect of enhancing the flux of *n*-C_6 through the silicalite membrane by up to a factor of 60 above that of 2MP. Experimental evidence to support our new separation principle is provided by permeation data of Funke et al.[2]

Branched hydrocarbons are preferred to straight-chain hydrocarbons as ingredients in petrol because branched hydrocarbons burn more efficiently and have a higher octane number. Catalytic isomerization is used to convert straight-chain hydrocarbons to their mono- or dibranched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons that are in thermodynamic equilibrium, and the separation of linear hydrocarbons from their branched isomers becomes necessary. A variety of zeolites offer a possibility for hydrocarbon isomer separations relying on differences in their sorption capacities.[1] Recently there has been considerable research interest in the development of silicalite membranes for separating hydrocarbon mixtures.[2,3] The basis of separation is the difference in the permeation rates, or fluxes, of the components across the membrane. For separation of components 1 (linear isomer) and 2 (branched isomer), the Maxwell−Stefan formulation for the fluxes across the membrane is[3,4]

$$N_i = \rho Đ_{i0} \frac{\theta_i}{RT} \frac{\Delta\mu_i}{\delta}; \quad i = 1, 2 \tag{1}$$

where θ_i is the component loading, expressed as molecules per unit cell of silicalite. The $Đ_{i0}$ represents the Maxwell−Stefan diffusivity of the pure component i; these are also termed "corrected" diffusivities in the literature.[5] The fluxes N_i in eq 1 are expressed in molecules per second per m^2 of membrane cross section. Other symbols used in eq 1: δ is the thickness of the membrane layer, ρ is the number of unit cells per m^3, R is the gas constant; T is the absolute temperature. The chemical potential differences $\Delta\mu_i$ across the membrane are related to the differences in the component loadings $\Delta\theta_i$ by

$$\frac{\theta_i}{RT}\Delta\mu_i = \sum_{j=1}^{2}\Gamma_{ij}\Delta\theta_j; \quad \Gamma_{ij} \equiv \frac{\theta_i}{p_i}\frac{\partial p_i}{\partial \theta_j}; \quad i, j = 1, 2 \tag{2}$$

The elements of the matrix Γ_{ij} can be determined from knowledge of the mixture isotherm that relates the molecular loadings θ_i to the partial pressures p_i. Combining equations

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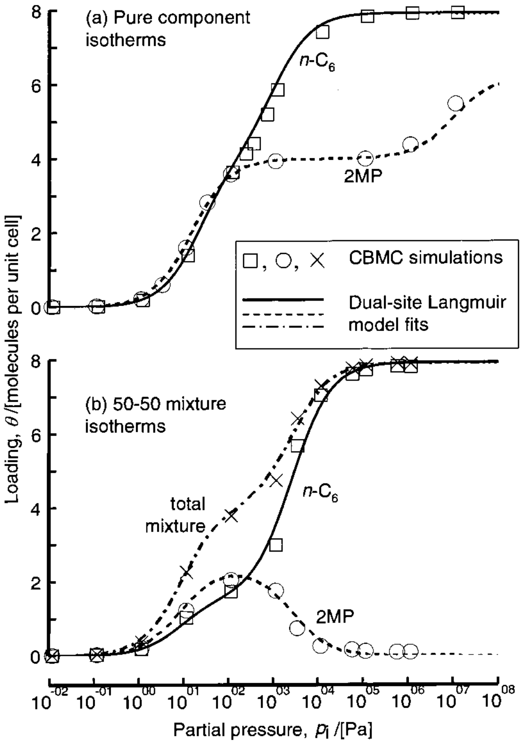


Figure 1. Pure component and 50−50 mixture isotherms at 362 K in silicalite. The open square and circle symbols represent the CBMC simulations for (1) n-C_6 and (2) 2MP, respectively. The statistical uncertainties in the simulations are smaller than the size of symbols used. The continuous and dashed lines are the dual-site Langmuir fits with the parameter values determined only from pure component CBMC simulation data. The dual-site Langmuir parameter values are for n-C_6, $\theta_{1A} = 4$, $\theta_{1B} = 3.93$, $k_{1A} = 0.045$ Pa^{-1}, $k_{1B} = 1 \times 10^{-3}$ Pa and for 2MP, $\theta_{2A} = 4$, $\theta_{2B} = 2.2$, $k_{2A} = 0.07$, $k_{2B} = 1 \times 10^{-7}$.

(1) and (2) we obtain the following expression for the selectivityof separation

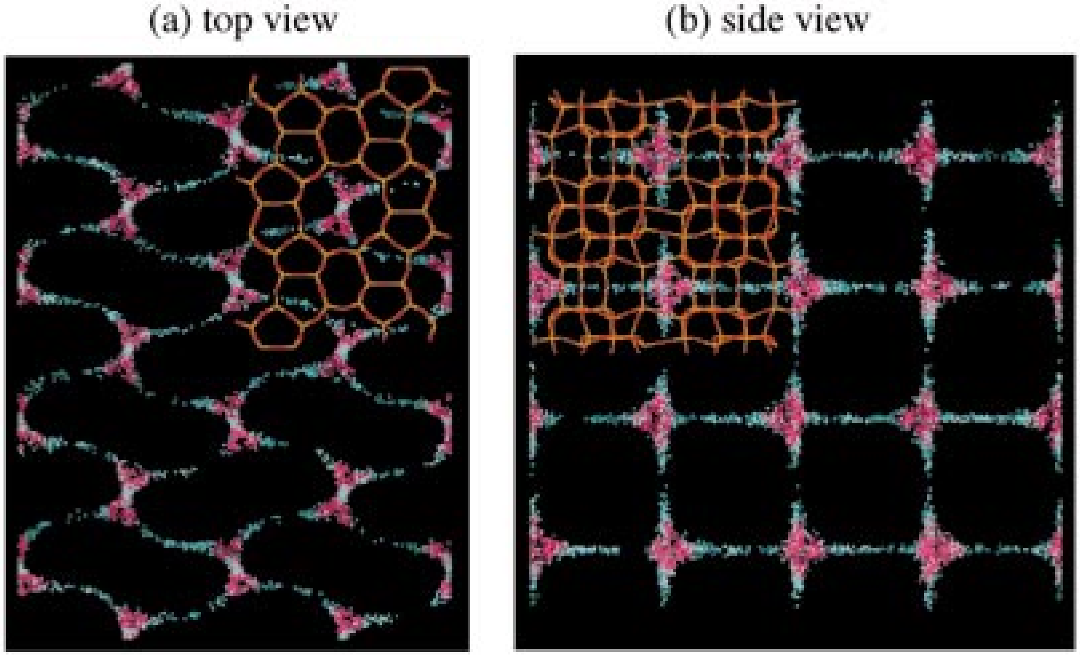
$$S = \frac{N_1}{N_2} \equiv S_{\mathrm{MS}} S_{\mathrm{T}}; \quad S_{\mathrm{MS}} = \frac{\text{Đ}_{10}}{\text{Đ}_{20}}; \quad S_{\mathrm{T}} = \left(\frac{\Gamma_{11}\Delta\theta_1 + \Gamma_{12}\Delta\theta_2}{\Gamma_{21}\Delta\theta_1 + \Gamma_{22}\Delta\theta_2} \right) \tag{3}$$

The separation selectivity S is the product of two factors: (i) S_{MS}, which is the ratio of the Maxwell−Stefan diffusivities, and (ii) the thermodynamic selectivity factor S_{T}. For hydrocarbon isomer separation, we may expect Đ_{10} to be larger than Đ_{20}, and indeed this is the basic principle used in size selective sieving processes with small pore 5A zeolites.[5] Here we will demonstrate that high selectivities can be realized with medium pore size silicalite by ensuring conditions such that S_{T} is large and supplements S_{MS}. This can be of potential commercial interest because the diffusivities, and hence the fluxes, in medium pore size zeolites are considerably higher than in small pore zeolites.[5] To exploit S_{T} for separation of hydrocarbon isomers, we need to compute the Γ_{ij} and $\Delta\theta_i$; this requires detailed knowledge of the adsorption isotherms of the hydrocarbon mixture. As the experimental determination of such isotherms is significantly more complicated and time-consuming than the measurements for the pure components, mixture isotherm data is rarely available. Traditionally, the factor S_{T} is taken to be equal to the ratio of the Henry coefficients of the two isomers, estimated from pure component data at low molecular loadings. We will show that this approach ignores some exciting new separation opportunities that arise from knowledge of the complete mixture isotherm.

Our earlier studies have demonstrated the power of CBMC simulations in the grand canonical ensemble for calculation of sorption isotherms of pure components in zeolites;[6−9] we shall use the same simulation technique here to calculate the isotherms of the pure components and of the mixture. As a test case to illustrate our concept, we take the separation of n-C_6 and 2MP using silicalite. The CBMC calculations of the pure component and mixture isotherms at 362 K are shown in Figure 1. Our simulations have been performed in the grand canonical ensemble wherein the zeolite is in contact with a reservoir that fixes the chemical potential of each component and also the temperature. In a CBMC simulation, it is essential to successfully exchange particles with the reservoir. With this technique we grow a flexible alkane molecule atom by atom in such a way that the “empty spaces” in the zeolite are found. The bias of this growing scheme is removed exactly by a modification of the acceptance rules.[9] The acceptance ratio of the particle exchange move is increased by 10−100 orders of magnitude and thus makes these simulations possible. To increase the efficiency for the mixture simulations, we also performed trial moves that change the identity of a particle.[8] In the simulations presented in this work the linear and branched alkanes are described with a united-atom model; i.e., CH_3, CH_2, and CH groups are considered as single interaction centers. The zeolite is assumed to be rigid, and the interactions of the alkane with the zeolite are dominated by the oxygen atoms of the zeolite. The alkane−zeolite and alkane−alkane interactions are described by a Lennard-Jones potential. The intramolecular interactions include bond-bending and torsion potentials and a fixed C−C bond length.

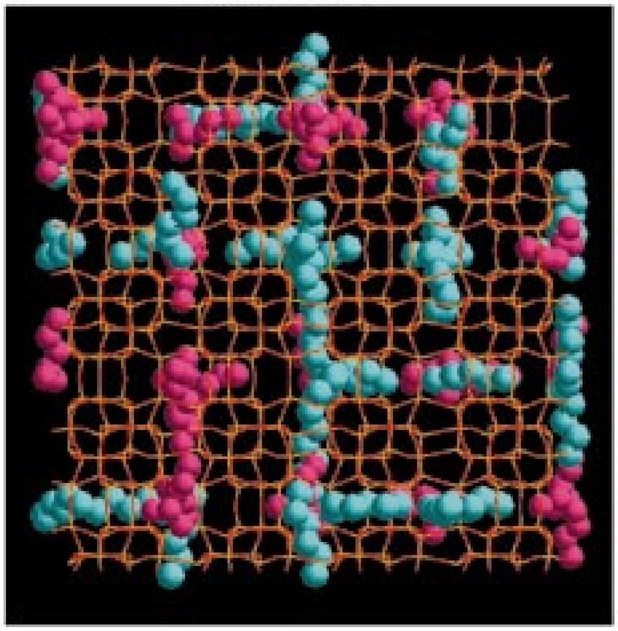
Our simulation box consists of 16 (2 × 2 × 4) unit cells of silicalite. The simulations are performed in cycles; in each cycle an attempt is made to perform one of the following moves: (1) displacement of a chain; a chain is selected at random and given a random displacement, (2) rotation of a chain; a chain is selected at random and given a random rotation around the center of mass, (3) partial regrowing of a chain; a chain is selected at random, and part of the molecule is regrown using the CBMC scheme, (4) exchange with reservoir using the CBMC scheme; it is decided at random whether to add or to remove a molecule from the zeolite, and (5) change of identity (only in the case of mixtures); one of the components is selected at random, and an attempt is made to change its identity. The acceptance rules for this type of move are given in ref 8. A total simulation consisted of at least 10^7 Monte Carlo cycles. Further details of the simulation and model are to be found in our earlier publications.[6,7,9,10]

A small inflection is observed for n-C_6 at a loading of four molecules per unit cell (see Figure 1a), due to commensurate “freezing”.[6,11] The branched isomer 2MP shows a pronounced, plateaulike, inflection at $\theta = 4$. At low pressures 2MP is located predominantly at the intersections of the straight and zigzag channels. To obtain loadings higher than $\theta = 4$, 2MP must seek residence in the channel interiors, which is more demanding and therefore requires disproportionately higher pressures; this leads to the inflection for 2MP.[7] It is essential to recognize the distinction in the sorption characteristics of the intersection regions and the channel interiors, and we adopt a dual-site Langmuir isotherm,[12]



(a) top view

(b) side view



(c) side view

Figure 2. (a) Top view and (b) side view of probability distribution functions for n-C_6 (cyan dots) and 2MP (pink dots) at partial pressures of 100 Pa and 362 K. These distributions were obtained by plotting the centers of mass of the molecules every 200 Monte Carlo cycles. (c) Side view of the location of n-C_6 (cyan balls) and 2MP (pink balls) within the silicalite structure.

$$\theta = \frac{\theta_A k_A p}{1 + k_A p} + \frac{\theta_B k_B p}{1 + k_B p} = \frac{(\theta_A k_A + \theta_B k_B)p + (\theta_A + \theta_B) k_A k_B p^2}{1 + (k_A + k_B)p + k_A k_B p^2} \quad (4)$$

for fitting purposes. Here we identify A and B as two sorption sites, channel intersections and channel interiors, respectively, θ_A and θ_B are the maximum loadings, k_A and k_B are the Henry coefficients for the two respective sites, and p is the pressure. It is interesting to note that were S_T to be determined from the pure component data at low loading, we would obtain a value close to unity leading us to conclude that it is not possible to separate the isomers by permeation across a silicalite membrane.

The CBMC simulation results of a 50−50 mixture at 362 K are shown in Figure 1b. We see that the branched isomer exhibits a curious maximum in the loading, which falls to zero at pressures exceeding 10 000 Pa, indicating that 2MP is virtually excluded from the zeolite at higher pressures. The total loading exhibits inflection behavior at $(\theta_1 + \theta_2) = 4$. Until this loading, there is no competition between n-C_6 and 2MP and both are almost equally easily adsorbed. Examination of the probability distributions of the linear and branched isomers 100 Pa (cf. Figure 2a,b) shows that all the 2MP molecules are located at the intersections between the straight channels and the zigzag channels whereas n-C_6 are located everywhere. A further important aspect to note is orientation of the 2MP

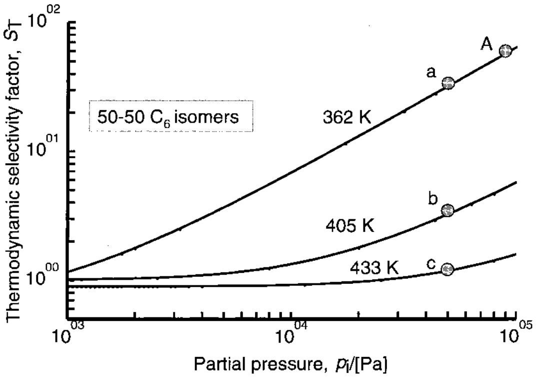


Figure 3. Thermodynamic selectivity factor S_T for separation of a 50−50 mixture of n-C_6 and 2MP as a function of partial pressure of the components upstream of the membrane. For the equimolar feed mixture we have $\Delta p_1 = \Delta p_2$. The driving forces $\Delta\theta_i$ in eq 3 are calculated assuming that the downstream partial pressures are zero for both components. The mixture isotherm (5) is used to calculate the molecular loadings at the upstream face of the membrane.

molecules; these have their heads (i.e. the branched end) at the intersections and their tails sticking out into the zigzag or straight channels; see Figure 2c. The n-C_6 molecules fit nicely into both straight and zigzag channels;[6] these molecules have a higher "packing efficiency" than 2MP. As the pressure is increased beyond 100 Pa, it is more efficient to obtain higher loadings by "replacing" the 2MP with n-C_6; this entropic effect is the reason behind the curious maximum in the 2MP isotherm. This maximum is also predicted by applying the usual mixture rule[12]

$$\theta_i = \frac{(\theta_{iA}k_{iA} + \theta_{iB}k_{iB})p_i + (\theta_{iA} + \theta_{iB})k_{iA}k_{iB}p_i^2}{1 + (k_{1A} + k_{1B})p_1 + k_{1A}k_{1B}p_1^2 + (k_{2A} + k_{2B})p_2 + k_{2A}k_{2B}p_2^2}; \quad i = 1, 2 \quad (5)$$

as can be seen from the continuous lines in Figure 1b, which have been calculated on the basis of pure component data fits.

The Γ_{ij}, required for calculation of the thermodynamic selectivity factor S_T, are obtained by analytic differentiation of eq 5, and Figure 3 shows the results for membrane permeation at temperatures of 362, 405, and 443 K. Exciting separation possibilities emerge at high pressures and lower temperatures. For example, at 362 K with an upstream partial pressure of 50 kPa for each of the components, $S_T = 32$ (point a), a value that drops to 3.3 (point b) and 1.2 (point c) for $T = 405$ and 443 K, respectively. Experimental values of the selectivity S obtained by Funke et al.[2] for a 50−50 mixture of n-C_6 and 3-methylpentane through silicalite confirm the 25-fold increase in selectivity as the temperature is decreased from 443 to 362 K. Our work provides the necessary fundamental background to their experimental observation and also offers clues for enhancing S_T; as can be seen in Figure 3 S_T is increased to 60 by operating at position A.

Our sorption-induced diffusion-selective separation principle is generic in character; this is demonstrated by applying it to C_5 and C_7 hydrocarbon isomers. We performed CBMC simulations of 50−50 mixtures of C_5 isomers (n-pentane (n-C_5) and 2-methylbutane (2MB)) and C_7 isomers (n-heptane (n-C_7) and 2-methylhexane (2MH)) at their respective boiling points, 310 and 374 K. The results shown in Figure 4 display the same qualitative features as for the C_6 isomers; the table mountain maximum for 2MH is striking. For permeation across a silicalite membrane with upstream partial pressures of 50 kPa for each isomer, we calculated S_T for the C_5 and C_7 isomers to be 37 and 1.8, respectively. Improved selectivity for C_7 isomer separation can be achieved by operating the membrane in a pervaporation mode, in which the upstream partial pressures are increased to, say, 150 kPa; this will increase the value of S_T to 4.1, which may be acceptable.

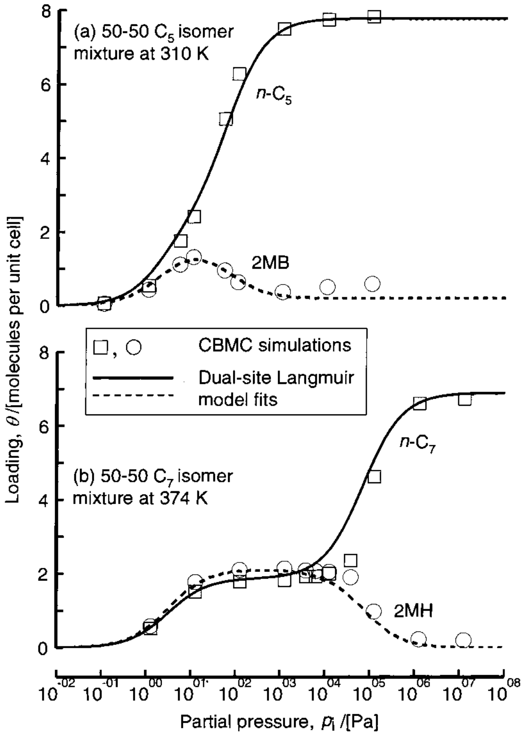


Figure 4. Mixture isotherms for (a) C_5 and (b) C_7 isomers. The open square and circle symbols represent the CBMC simulations, and the continuous and dashed lines are the dual-site Langmuir fits with the following parameter values: n-C_5, $\theta_{1A} = 4$, $\theta_{1B} = 4$, $k_{1A} = 0.25$, $k_{1B} = 3 \times 10^{-2}$; 2MB, $\theta_{2A} = 4$, $\theta_{2B} = 4$, $k_{2A} = 0.20$, $k_{2B} = 1 \times 10^{-3}$; n-C_7, $\theta_{1A} = 4$, $\theta_{1B} = 2.9$, $k_{1A} = 0.15$, $k_{1B} = 3 \times 10^{-5}$; 2MH, $\theta_{2A} = 4$, $\theta_{2B} = 0.7$, $k_{2A} = 0.17$, $k_{2B} = 2 \times 10^{-9}$.

The methodology developed in this paper, consisting of performing CBMC simulations of pure component and mixture isotherms, and linking these with the Maxwell−Stefan theory for mixture diffusion within zeolitic structures is applicable to any mixture in any zeolite. The methodology could be used for screening of promising zeolite structures for separation of single-branched and dibranched isomers.[1]

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