

Effect of adsorbate loading on selectivity during adsorption of C₁₄/C₁₅ and C₁₅/C₁₆ *n*-alkane binary mixtures in silicalite

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Abstract Adsorption experiments of mixtures of long chain alkanes into silicalite under liquid phase conditions show selectivity inversion and azeotrope formation. These effects are due to the subtle interplay between the size of the adsorbed molecules and pore topology of the adsorbent. In this study, the selective uptake of lighter component during liquid phase adsorption of C₁₄/C₁₅ and C₁₅/C₁₆ *n*-alkane binary mixtures in the zeolite silicalite is understood through configurational bias grand-canonical Monte Carlo molecular simulation technique and a coarse-grained siting analysis. The simulations are conducted under conditions of low and intermediate levels of loading. The siting pattern of the adsorbates inside the zeolite pores explain the selectivity as seen in experiments.

Keywords Liquid phase adsorption · Silicalite · Configurational bias Monte Carlo · Molecular simulations

1 Introduction

The study of adsorption in microporous materials such as zeolites is interesting from a theoretical viewpoint and useful for practical applications. Zeolites are porous crystalline aluminosilicates with pore diameters in the range of 0.3–2.0 nm (Ruthven 1984). They are widely used in selective separation of *n*-alkane, iso-alkane, alkene and

aromatic mixtures in petroleum refining and petrochemical industry (Ruthven 1984; Broughton 1984; Yang 1986; Kulprathipanja and Johnson 2008; Gump et al. 2001; Hedlund et al. 2002; Min et al. 2003; Sakai et al. 2001; Xomeritakis et al. 2001). Preferential adsorption in zeolite pores is an attractive alternative to distillation for achieving desired selectivity of close boiling mixtures that have a low relative volatility (Ruthven 1984). Selectivity may depend on a difference in interactions of sorbates with the zeolite surface or a difference in intracrystalline diffusivity due to geometrical constraints. Studies (Denayer et al. 2003; Chempath et al. 2004; Krishna et al. 2002, 2002; Daems et al. 2005; Denayer et al. 2006; Daems et al. 2007; Punathanam et al. 2010) on adsorption of binary mixtures of *n*-alkanes on to zeolites have shown a pronounced selectivity of one of the components even when it differs by one CH_x group compared to the other component. An explanation of such selectivities will require an understanding of siting of adsorbate molecules inside the zeolite pores. Such molecular-level information is hard to realize through experiments but can be readily obtained from molecular simulations. The development of efficient algorithms and accurate force fields combined with the computational power of present day computer have resulted in molecular simulations becoming a viable tool in the study of adsorption on microporous materials (Fuchs and Cheetham 2001). Besides providing useful data, molecular simulation provides insight into experimental observations and helps to explore conditions where it is tough or impossible to conduct experiments. Grand-canonical Monte Carlo simulations with configurational biased techniques (CB-GCMC) (Frenkel and Smit 2001), based on Rosenbluth sampling (Rosenbluth and Rosenbluth 1955), have been widely used to study adsorption of chain molecules such as *n*-alkanes in zeolites (Mezei 1980; Snurr et al. 1993; Siepmann and

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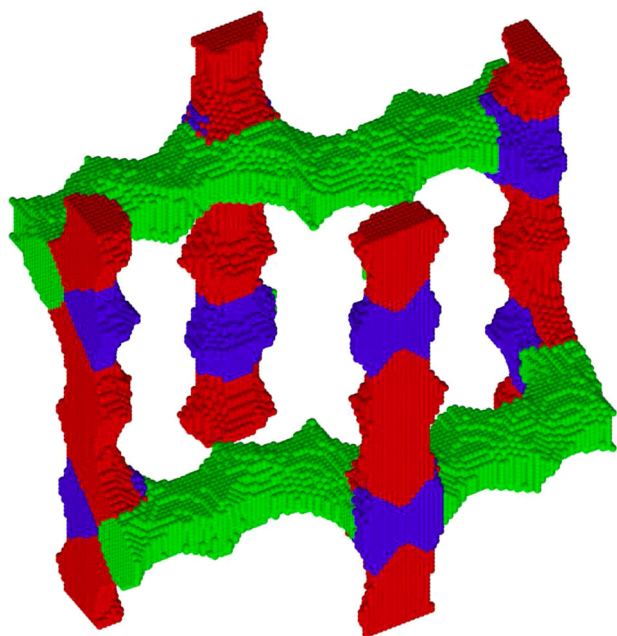


Fig. 1 Schematic representation of different sections in the channel structure of silicalite. *Red* color indicates straight channels, *green* color indicates the sinusoidal channels and *purple* color indicates the intersections (Color figure online)

Frenkel 1992; Frenkel et al. 1992; Laso et al. 1992). Such studies have contributed greatly to our understanding of adsorption in zeolites.

In this study, we have used CB-GCMC simulations to obtain molecular-level insights into adsorption of long chain *n*-alkanes in silicate under liquid phase conditions. Silicalite (see Fig. 1) has a pore structure consisting of linear channels having a pore diameter of 0.56×0.53 nm intersecting with sinusoidal channels, with diameters of 0.55×0.51 nm (Denayer et al. 2003). The length of a linear channel segment and a sinusoidal channel segment between two intersections is 0.45 and 0.665 nm respectively. Each unit cell consists of four linear segments, four intersections and four sinusoidal segments.

A vast majority of studies of adsorption of *n*-alkanes in silicalite were done under conditions of low loading. In such cases, valuable insights into the equilibrium packing of alkanes in different channel segments of zeolite pores have been obtained through CB-GCMC simulations (Maginn et al. 1995; Smit and Siepmann 1994; Smit and Maesen 1995; Macedonia and Maginn 1999; Vlucht et al. 1998; Du et al. 1998; Schenk et al. 2001; Krishna et al. 2002; Vlucht et al. 1999). Studies of adsorption of binary mixtures of *n*-alkanes in silicalite under liquid phase conditions reveal interesting results such as selectivity inversion and azeotrope formation. Denayer et al. (2003) conducted experiments to study liquid phase adsorption of binary mixtures of linear alkanes ranging in length from C_5 to C_{22} in silicalite. Selective adsorption of heavier alkane

occurred with C_5/C_6 , C_6/C_{14} , C_8/C_9 , C_8/C_{12} , C_9/C_{11} , C_9/C_{12} and C_9/C_{13} , lighter molecules with C_{14}/C_{15} and C_{15}/C_{16} and azeotropic behavior with C_5/C_7 , C_6/C_7 , C_6/C_8 , C_7/C_8 , C_6/C_{10} , C_{13}/C_{14} , C_{17}/C_{18} and C_{20}/C_{22} . A CB-GCMC study that aimed to predict these observations was done by Chempath et al. (2004). These simulations under liquid phase conditions, run for representative mixture samples of *n*-alkanes up to C_{12} , showed good agreement with experimental observations.

The results obtained from liquid phase adsorption of *n*-alkanes with size equal or larger than C_{14} are quite interesting. Experiments of adsorption of pure *n*-alkanes in silicalite under liquid phase conditions by De Meyer et al. (2003) revealed that the adsorption capacity measured as the number of CH_x groups per unit cell of zeolite is nearly constant between 53 and 54 for alkanes from C_{14} to C_{22} . Under these conditions, the pores are completely filled with sorbate molecules. However, experiments conducted by Denayer et al. (2003) for binary *n*-alkane mixtures show selectivity towards one of the components. For example, silicalite is selective towards the shorter chains in C_{14}/C_{15} and C_{15}/C_{16} mixtures. Selectivity towards one of the components under liquid phase conditions is attributed to differences in the nature of packing of alkanes with varying lengths inside the pores of the adsorbent. Chempath et al. (2004) did not conduct simulations for alkane chains higher than C_{12} under liquid phase conditions because even with configurational-bias techniques it was very difficult to equilibrate simulations of longer alkanes at high loading (De Meyer et al. 2003). From a statistical mechanical perspective, there is little difference between adsorption from a gas phase of alkanes and that from a liquid phase. But, performing Monte Carlo simulations, even with configurational bias, becomes extremely difficult under liquid phase conditions because the adsorbent pores are almost saturated with sorbate molecules. As a result, the values of acceptance rates for insertion and deletion moves in the GCMC simulations are extremely low which results in an inefficient sampling of the configuration space. Hence, extremely long simulations beyond the capacity of present day computers are required to obtain good statistics under liquid phase conditions. The sampling efficiencies can be improved with advanced techniques such as parallel-tempering (Geyer and Thompson 1995; Hansmann 1997) which had been previously applied to simulate liquid phase alkane adsorption in LTA-5A zeolite (Punnathanam et al. 2010). However, even with parallel tempering technique, our preliminary investigations revealed that the improvements in sampling were insufficient to study the liquid phase adsorption simulations of C_{14} and longer alkanes in silicalite.

Our aim was to understand the molecular mechanism for selectivity inversion seen in the adsorption experiments on

C₁₄/C₁₅ and C₁₅/C₁₆ mixtures. Since simulations under liquid phase conditions were difficult, they were instead done at low and intermediate loadings in order to study the effect of adsorbate loading on selectivity. As will be seen in subsequent sections, the extrapolation of these simulation results to high loading gives reasonable explanation for selectivities seen under liquid phase conditions.

2 Methodology

2.1 Simulation details

CB-GCMC simulation technique is used to study the adsorption of *n*-alkanes in zeolite pores. Alkanes are modeled as flexible molecules treating methyl (CH₃) and methylene (CH₂) groups as united atoms. The bond lengths between adjacent CH_x groups are kept fixed to 1.54 Å. The atomic coordinates of silicalite atoms are obtained from Olson et al. (1981). Silicalite is modeled as a rigid framework of oxygen atoms only as proposed by Bezus et al. (1978). The intermolecular interactions between the adsorbates and the adsorbate-adsorbent interactions consists of van der Waals interactions and are modeled by Lennard–Jones potentials. The intra-molecular interactions in the adsorbates consist of bending and torsion interactions plus non-bonded van der Waals interactions between pairs of atoms separated by more than three bonds. The forcefield parameters are taken from Macedonia and Maginn (1999) and are listed in Table 1. All non-bonded interactions are truncated at 13 Å and tail corrections are not included for reasons explained in Macedonia and Maginn (1999).

Simulations are carried out using the MUSIC code (Gupta et al. 2003). The different moves of CB-GCMC simulations are: (1) Translation, (2) Insertion, (3) Deletion, (4) Cut-Regrow and (5) Identity swap. The sampling techniques and the acceptance/rejection criteria of CB-GCMC moves are described in detail in Maginn et al. (1995) and Macedonia and Maginn (1999). In identity swap move, a molecule of a component is randomly chosen and an attempt is made to convert it in to a molecule of other component. This method is used for mixture simulation and described in Chempath et al. (2004). The simulations were performed on a system consisting of 3×3×4 unit cells of silicalite with a periodic boundary conditions. This corresponded to simulation box with dimensions of 62.1 × 59.76 × 53.68 Å³. In comparison, the length of the largest *n*-alkane (De Meyer et al. 2003), i.e., C₁₆ is 22.79 Å. Simulations with pure alkanes consisted of 5 million Monte Carlo steps and those with mixtures consisted of 12 million Monte Carlo steps. The first 30 % of Monte Carlo moves are kept for equilibration and the averages for

Table 1 United atom forcefield parameters (Macedonia and Maginn 1999) used in the simulations

Non-bonded	ϵ/k_B (K)	σ (Å)
CH ₃ –CH ₃	98.1	3.77
CH ₃ –CH ₂	67.9	3.84
CH ₂ –CH ₂	47.0	3.93
CH ₃ –O	80.0	3.60
CH ₂ –O	58.0	3.60

Bond angle	k_θ (kcal rad ^{−2})	θ_0 (°)
CH ₃ –CH ₂ –CH ₂	62.1	114
CH ₂ –CH ₂ –CH ₂	62.1	114

Torsion	a_1/k_B (K)	a_2/k_B (K)	a_3/k_B (K)
CH ₃ –CH ₂ –CH ₂ –CH ₂	355.0	−68.2	791.3
CH ₂ –CH ₂ –CH ₂ –CH ₂	355.0	−68.2	791.3

Bond lengths are fixed at a value of 1.54 Å. Non-bonded interactions are calculated by 12–6 Lennard–Jones potential function. A harmonic bending potential $U(\theta) = k_\theta(\theta - \theta_0)^2$ is used for bond angle potentials while cosine-expansion form $U(\phi) = a_1[1 + \cos(\phi)] + a_2[1 - \cos(2\phi)] + a_3[1 + \cos(3\phi)]$ is used for torsion angle potentials

various quantities are sampled over the remaining 70 % of the Monte Carlo moves.

2.2 Siting

The space inside the crystal accessible to sorbates consists of three types of regions: the interiors of the straight channels, the interiors of the sinusoidal channels and the region where the linear and sinusoidal channels intersect. The method to quantitatively define these sites, initially done by June et al. (1991) to study Xenon and SF₆ diffusion in silicalite, is described here. The zeolite is discretized into cubelets of dimensions approximately 0.2×0.2×0.2 Å³. The energy of each of these cubelets is calculated by placing a probe Lennard–Jones sphere with $\epsilon/k = 148$ K and $\sigma = 3.73$ Å on its center and computing the total interaction with the zeolite framework. The boxes having very high energies are discarded as these would lie on the crystal atoms. A steepest descent energy minimization is done starting from each of the grid points. All points that minimize to the same minimum value belong to a particular site. The minima and its associated grid points are visually inspected and categorized into either linear, sinusoidal or intersection. Thus the entire pore volume of silicalite can be divided into three regions, namely, *linear*, *sinusoidal* and *intersection*.

Once the pore regions have been identified, the adsorbed molecules can be classified according to the configurations

adopted by them inside the pores. It can be seen from Fig. 1 that sinusoidal channel segments touch linear channel segments at intersections. Therefore, the region of intersection can be lumped with linear. If an *n*-alkane chain starts from a linear channel segment, pass through the intersection and ends in another linear section without going through sinusoidal channels, it is said to be *straight*; if it starts and ends in sinusoidal pore segments without passing through linear or intersection, it is said to be *zig-zag* and if it pass through both linear and sinusoidal channels, it is said to be *bent*.

3 Results and discussion

3.1 Adsorption of pure *n*-alkanes

GCMC simulations of C₁₄, C₁₅ and C₁₆ in silicalite were performed at pressures ranging from very low values till the vapor pressure at a temperature of 277 K. The computed isotherms are shown in Fig. 2 where the adsorbate loading in terms of number of CH_x groups per unit cell is plotted against the pressure. The values of the fraction of the insertion moves accepted in the latter 70 % of GCMC simulations (the production stage) are shown in Table 2. As expected, the acceptance rates decrease with increased loading. From this data we conclude that the sampling in the GCMC simulations is inefficient for fugacities with values greater than 10^{−14} kPa. Under these conditions, all the three *n*-alkanes give a loading of approximately 30 groups per unit cell and there are significant packing effects that make it difficult to simulate adsorption at higher loadings. Hence, further GCMC simulations of C₁₄, C₁₅ and C₁₆ and their mixtures in silicalite were performed at a pressure of 10^{−14} kPa. These results are also compared with simulations at a pressure of 10^{−18} kPa which correspond to conditions of low loading.

From the simulation data, a siting analysis of the adsorbed alkanes inside the pores were performed. These results are shown in Table 3 and Fig. 3. These results, which are in agreement with previous studies (Maginn et al. 1995), show that under conditions of low loading, majority of the alkanes molecules lie in the straight channels of silicate. Inside the straight channels, the *n*-alkanes are in the all-trans configuration which has the lowest intramolecular energy. Most of the remaining molecules are in the bent configuration where a part on the *n*-alkane is in the straight channel and the remaining part in the zigzag channel. The zig-zag channels are clearly not favored and contain only a tiny fraction of the adsorbed molecules. In contrast, the results at high loading show that a large fraction of the molecules are in the bent configuration (see Fig. 3). In fact, the bent configurations constitute a majority

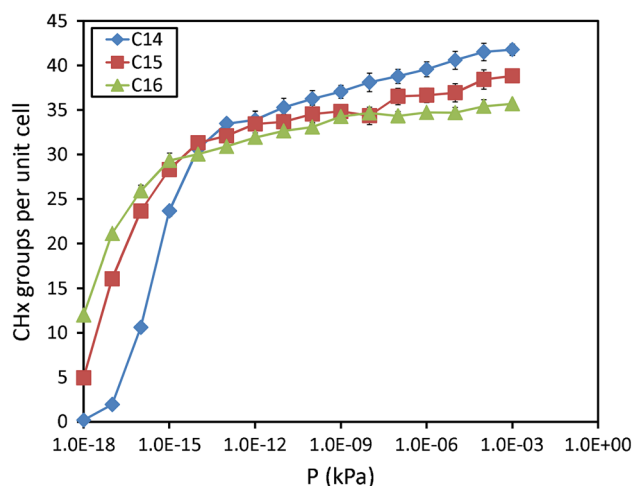


Fig. 2 Number of CH_x groups of C₁₄, C₁₅ and C₁₆ alkanes adsorbed in a unit cell of zeolite at 277 K for various pressures as predicted by CB-GCMC simulations. The size of the error bars are estimated from five independent simulations and correspond to 90 % confidence

Table 2 Fraction of insertion moves accepted during GCMC simulations of C₁₄, C₁₅ and C₁₆ at various pressures

Pressure (kPa)	C ₁₄	C ₁₅	C ₁₆
10 ^{−18}	7.30×10^{-3}	5.84×10^{-3}	2.68×10^{-3}
10 ^{−16}	5.42×10^{-3}	8.11×10^{-4}	3.65×10^{-4}
10 ^{−14}	4.27×10^{-4}	7.86×10^{-5}	6.14×10^{-5}
10 ^{−9}	1.57×10^{-5}	9.98×10^{-6}	5.72×10^{-6}
10 ^{−5}	1.29×10^{-5}	1.14×10^{-5}	2.85×10^{-6}
10 ^{−3}	1.14×10^{-5}	1.57×10^{-5}	7.15×10^{-6}

Table 3 Fraction of adsorbed molecules in straight, zig-zag and bent configurations of C₁₄, C₁₅ and C₁₆ alkanes at high (10^{−14} kPa) and low (10^{−18} kPa) pressures

Loading	Alkane	Straight	Zig-zag	Bent
High	C ₁₄	0.49	0.23	0.27
	C ₁₅	0.40	0.16	0.44
	C ₁₆	0.38	5.61×10^{-2}	0.56
Low	C ₁₄	0.87	4.76×10^{-3}	1.22×10^{-1}
	C ₁₅	0.83	3.53×10^{-3}	0.16
	C ₁₆	0.85	4.51×10^{-3}	0.14

for C₁₅ and C₁₆. There is also a significant increase in the number of molecules that lie completely in the zig-zag channel. Among the three *n*-alkanes simulated, the fraction of adsorbed molecules that completely lie in the zig-zag channel is the highest for C₁₄ followed by C₁₅ and C₁₆. Overall, these simulations show that the *n*-alkane molecules prefer the straight channels and are forced into the zig-zag channel only at high loading. In Fig. 4, the number

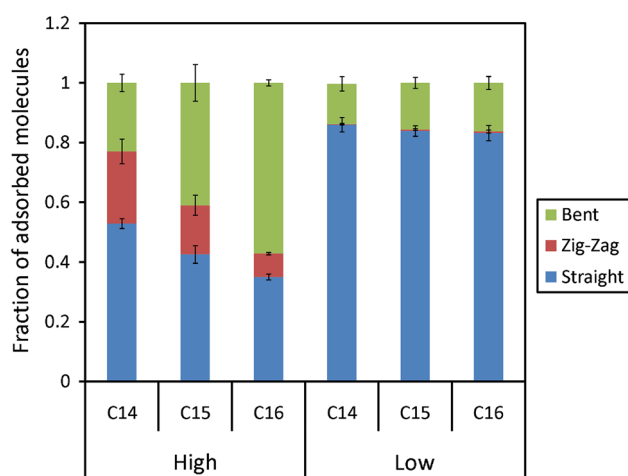


Fig. 3 Fraction of adsorbed molecules in straight, zig-zag and bent configurations of C₁₄, C₁₅ and C₁₆ alkanes under conditions of high and low loading. The high loading corresponds to an external gas phase pressure of 10^{−14} kPa and the low loading corresponds to 10^{−18} kPa. The size of the error bars correspond to 90 % confidence

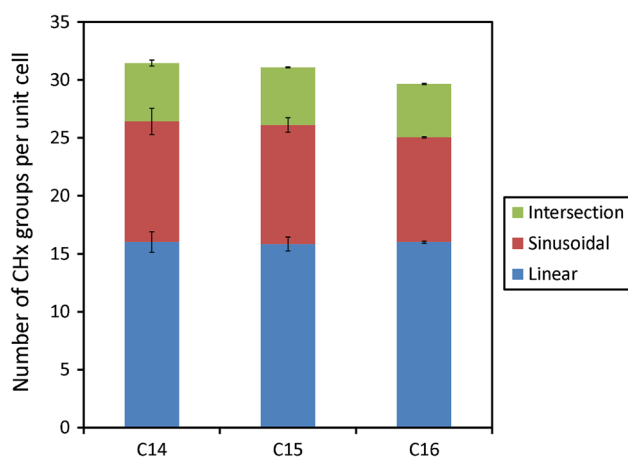


Fig. 4 Number of CH_x groups adsorbed in linear, sinusoidal and intersection sites of silicalite pores at high loading. The size of the error bars correspond to 90 % confidence

of CH_x groups adsorbed in different regions of the silicates pores are plotted. Interestingly, even though the distribution of molecular siting (see Fig. 3) varies across the different *n*-alkanes, the distribution of the CH_x groups in the various sections of the zeolites pores are nearly the same.

3.2 Adsorption of binary mixtures of *n*-alkanes

As mentioned earlier, the experiments by Denayer et al. (2003) indicate that the shorter alkane is selectively adsorbed for both C₁₄/C₁₅ and C₁₅/C₁₆ mixtures. Since the

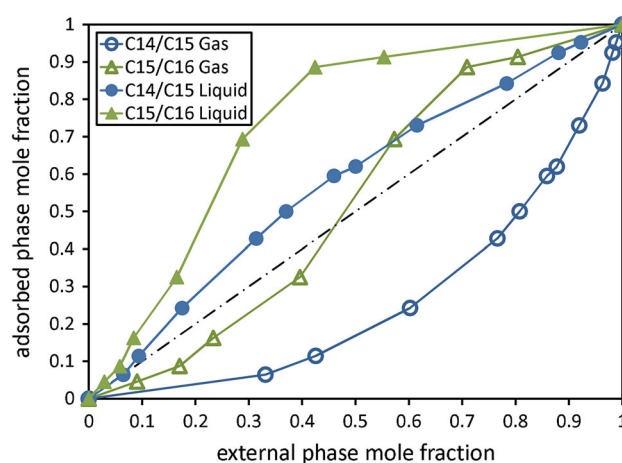


Fig. 5 Comparison of mole fraction of the shorter alkane in the adsorbed phase versus the mole fraction in the external phase. The filled symbols represent data obtained from Denayer et al. (2003) The open symbols represent comparison with composition in the corresponding gas phase at the bubble point

longer alkanes have stronger energetic interaction with the zeolite, the preference for the shorter alkanes at conditions of high loading is usually attributed to packing effects. However, in our view, this reasoning is incomplete since the liquid phase is also a dense phase with significant confinement constraints. Hence the selectivities seen during adsorption from a liquid phase will be a result of the relative energetic-entropic effects in each phase. Since fugacities of the various components in the liquid phase are nearly independent of the pressure, their values will be close to the liquid phase fugacities at the bubble point which in turn will be equal to the fugacities in the corresponding equilibrium vapor phase. We, therefore, compared the compositions of the adsorbed phase reported in Denayer et al. (2003) with the composition of the equilibrium vapor phase at the bubble point. Calculations using the Peng-Robinson equation of state showed that it is reasonable to consider the vapor phase as an ideal gas mixture and the liquid phase as an ideal solution. Hence, the bubble points were calculated using Raoult's law. The vapor pressures for C₁₄, C₁₅ and C₁₆ used in these calculations are 6.86×10^{-4} , 9.60×10^{-5} and 2.90×10^{-5} kPa respectively. The comparison with the vapor phase composition is shown in Fig. 5. The comparison with the saturated vapor phase compositions now show that the longer C₁₅ alkane is preferably adsorbed from a C₁₄/C₁₅ mixture. In the case of the C₁₅/C₁₆ mixture, we see the formation of an azeotrope with preference for the shorter C₁₅ when the vapor phase is rich in C₁₅.

In order to understand the reasons for selectivity inversion in the C₁₅/C₁₆ mixture and its absence for the C₁₄/C₁₅

Table 4 Total number of CH_x groups per unit cell in the adsorbed phase against molefraction of the shorter alkane in the external vapor phase for $\text{C}_{14}/\text{C}_{15}$ and $\text{C}_{15}/\text{C}_{16}$ mixtures

x	$\text{C}_{14}/\text{C}_{15}$	$\text{C}_{15}/\text{C}_{16}$
0.1	31.8	29.6
0.2	30.6	29.1
0.3	33.0	30.1
0.4	32.2	29.4
0.5	33.9	30.8
0.6	32.1	30.7
0.7	33.6	30.0
0.8	32.1	28.9
0.9	32.2	29.8

mixture, we performed GCMC simulations of adsorption from binary mixtures. Again, similar to simulations of pure alkane adsorption, the pressure of the external gas phase for conditions of high loading was kept equal to 10^{-14} kPa. The total loading for all compositions of the external gas phase is approximately equal to 30 CH_x groups per unit cell (see Table 4). As the vapor phase is ideal, fugacity of each component is equal to its partial pressure. Figures 6 and 7 show the composition of the adsorbed phase versus the composition of the external gas phase. These results are also compared with those obtained from GCMC mixture simulations with the gas phase pressure equal to 10^{-18} kPa which correspond to low loading conditions. The comparison shows that for both $\text{C}_{14}/\text{C}_{15}$ and $\text{C}_{15}/\text{C}_{16}$ mixtures, an increase in the loading favors the adsorption of the shorter chain. The selectivity of the shorter chain in the simulations, however, is lower than that obtained in experiments. The azeotrope formation in the $\text{C}_{15}/\text{C}_{16}$ mixture is also not seen in simulations indicating that selectivity inversion is possible only at even higher adsorbate loading than the one considered in these simulations.

Figure 8 shows the siting of the adsorbed molecules inside the silicalite pores when the external gas phase is equimolar. The siting analysis shows majority of the molecules in the straight and bent configurations belong to the longer alkane. This is because in the straight channels of silicalite, the n -alkanes are in the trans configuration and the stronger energetic interactions with the zeolites will always favor the longer chain. In contrast, the sinusoidal segments are tortuous and the energetic advantage of the longer alkanes will be decreased. In Fig. 9, the relative mole fraction of the shorter alkane among molecules that lie in the zig-zag configuration is compared with the mole fraction of the shorter alkane in the external vapor phase. It can be seen that the composition in zig-zag channels is close to the composition of the external gas phase. This indicates a fine balance between the energetic advantage of the longer alkane with the entropic advantage of the shorter alkane. However, C_{15} is slightly favored in both $\text{C}_{14}/\text{C}_{15}$

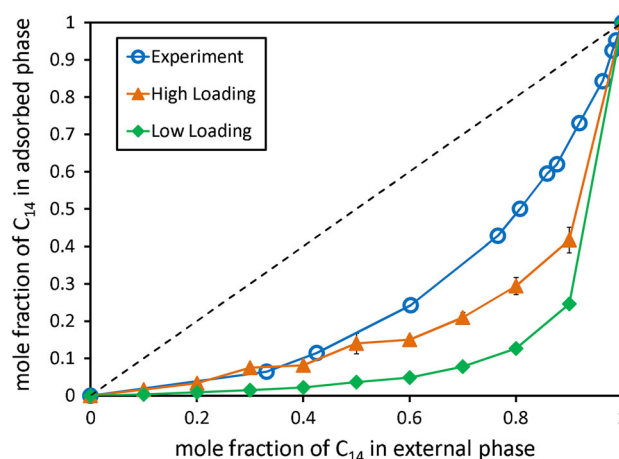


Fig. 6 Composition of C_{14} in $\text{C}_{14}/\text{C}_{15}$ in the adsorbed phase versus that in the external gas phase as predicted by CB-GCMC simulations at 277 K and high and low pressures. The results are compared with the data reported in Denayer et al. (2003) where the vapor phase composition at the bubble point is used for the external phase. The lines are used as a guide to the eye. The size of the error bars correspond to 90 % confidence

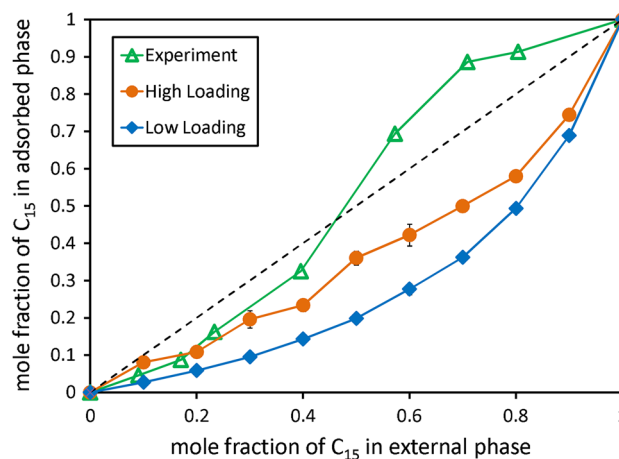


Fig. 7 Composition of C_{15} in $\text{C}_{15}/\text{C}_{16}$ in the adsorbed phase versus that in the external gas phase as predicted by CB-GCMC simulations at 277 K and high and low pressures. The results are compared with the data reported in Denayer et al. (2003) where the vapor phase composition at the bubble point is used for the external phase. The lines are used as a guide to the eye. The size of the error bars correspond to 90 % confidence

and $\text{C}_{15}/\text{C}_{16}$ alkane mixtures. The energetic advantage of longer C_{15} in the zig-zag configuration is strong enough to overcome the entropic advantage of shorter C_{14} but reverse is true for the $\text{C}_{15}/\text{C}_{16}$ mixture. This implies that in the case of $\text{C}_{14}/\text{C}_{15}$ mixture, the longer C_{15} is favored in all the pore regions and hence we observe selectivity towards C_{15} even at the highest loading. In the case of $\text{C}_{15}/\text{C}_{16}$ mixture, C_{15} is favored in the zig-zag channel and C_{16} is favored in the

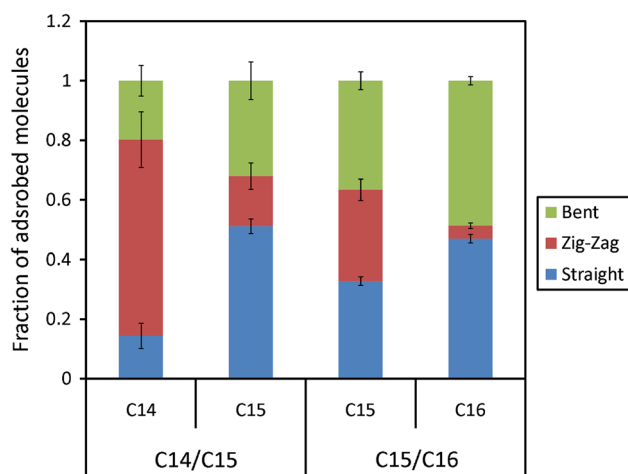


Fig. 8 Fraction of adsorbed molecules in straight, zig-zag and bent configurations from an equimolar binary mixture of C₁₄/C₁₅ and C₁₅/C₁₆ under conditions of high loading. The high loading corresponds to an external gas phase pressure of 10⁻¹⁴ kPa. The size of the error bars correspond to 90 % confidence

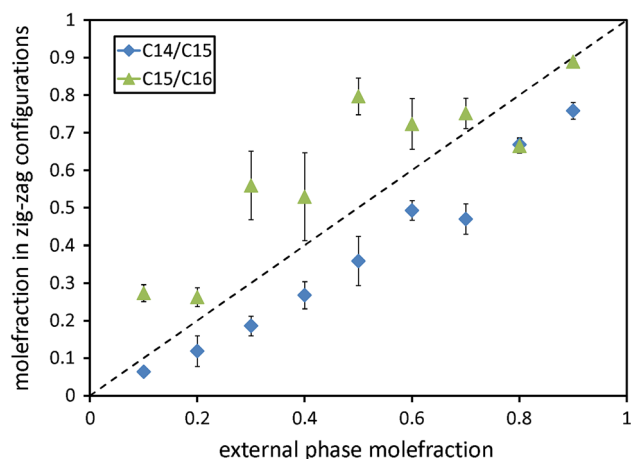


Fig. 9 Mole fraction of shorter alkane in the zig-zag configuration against the same in the external vapor phase. The size of the error bars correspond to 90 % confidence

straight channel. Thus, even though the overall selectivity favors the longer C₁₆, it is lower when compared to C₁₄/C₁₅ mixture. Extrapolating these results to high adsorbate loading can explain the formation of azeotrope under liquid phase conditions as seen in experiments.

4 Conclusions

GCMC simulations of pure C₁₄, C₁₅ and C₁₆ as well as C₁₄/C₁₅ and C₁₅/C₁₆ *n*-alkane binary mixtures in silicalite were performed to study the effects of adsorbate loading on

selectivity. The simulations were performed at low and intermediate levels of loading while those at high loading were unsuccessful. The siting analysis of the adsorbed molecules revealed that under conditions of low loading the adsorbed *n*-alkane molecules predominantly lie in the straight configuration. With increased loading, these molecules adopt the bent configuration and finally the zig-zag configuration. The siting analysis also revealed that the longer alkane is always preferred in the straight channel whereas C₁₅ is favoured over both C₁₄ and C₁₆ in the zig-zag channels. Extrapolation of these simulation results to high adsorbate loading, then explains the selectivity towards C₁₅ in the case of C₁₄/C₁₅ mixture and the azeotrope formation in the case of C₁₅/C₁₆ mixture as seen in experiments.

References

- Bezus, A.G., Kiselev, A.V., Lopkin, A.A., Du, P.Q.J.: Molecular statistical calculation of the thermodynamic adsorption characteristics of zeolites using the atom-atom approximation. Part 1. Adsorption of methane by zeolite NaX. *J. Chem. Soc. Faraday Trans. 2* (74), 367–379 (1978)
- Broughton, D.: Production-scale adsorptive separations of liquid mixtures by simulated moving-bed technology. *Sep. Sci. Technol.* **19**(11–12), 723–736 (1984)
- Chempath, S., Denayer, J.F., De Meyer, K.M., Baron, G.V., Snurr, R.Q.: Adsorption of liquid-phase alkane mixtures in silicalite: simulations and experiment. *Langmuir* **20**(1), 150–156 (2004)
- Daems, I., Leflaive, P., Méthivier, A., Denayer, J.F., Baron, G.V.: A study of packing induced selectivity effects in the liquid phase adsorption of alkane/alkene mixtures on NaY. *Microporous Mesoporous Mater.* **82**(1), 191–199 (2005)
- Daems, I., Baron, G.V., Punathanam, S., Snurr, R.Q., Denayer, J.F.: Molecular cage nesting in the liquid-phase adsorption of *n*-alkanes in 5A zeolite. *J. Phys. Chem. C* **111**(5), 2191–2197 (2007)
- De Meyer, K.M.A., Chempath, S., Denayer, J.F.M., Martens, J.A., Snurr, R.Q., Baron, G.V.: Packing effects in the liquid phase adsorption of C₅–C₂₂ *n*-alkanes on ZSM-5. *J. Phys. Chem. B* **107**, 10760–10766 (2003)
- Denayer, J., Daems, I., Baron, G.: Adsorption and reaction in confined spaces. *Oil Gas Sci. Technol.* **61**(4), 561–569 (2006)
- Denayer, J.F.M., De Meyer, K., Martens, J.A., Baron, G.V.: Molecular competition effects in liquid-phase adsorption of long-chain *n*-alkane mixtures in ZSM-5 zeolite pores. *Angew. Chem. Int. Ed.* **42**, 2774–2777 (2003)
- Du, Z.M., Manos, G., Vlugt, T.J.H., Smit, B.: Adsorption of short linear alkanes and their mixtures in silicalite. *AIChE J.* **44**, 1756–1764 (1998)
- Frenkel, D., Smit, B.: Understanding molecular simulation: from algorithms to applications. Academic press, San Diego (2001)
- Frenkel, D., Mooij, G., Smit, B.: Novel scheme to study structural and thermal properties of continuously deformable molecules. *J. Phys. Chem.* **4**, 3053–3076 (1992)
- Fuchs, A.H., Cheetham, A.K.: Adsorption of guest molecules in zeolitic materials: computational aspects. *J. Phys. Chem. B* **105**, 7375–7383 (2001)

- Geyer, C.J., Thompson, E.A.: Annealing Markov chain Monte Carlo with applications to ancestral inference. *J. Am. Stat. Assoc.* **90**(431), 909–920 (1995)
- Gump, C.J., Tuan, V.A., Noble, R.D., Falconer, J.L.: Aromatic permeation through crystalline molecular sieve membranes. *Ind. Eng. Chem. Res.* **40**(2), 565–577 (2001)
- Gupta, A., Chempath, S., Sanborn, M.J., Clark, L.A., Snurr, R.Q.: Object-oriented programming paradigms for molecular modeling. *Mol. Simul.* **29**, 29–46 (2003)
- Hansmann, U.H.E.: Parallel tempering algorithm for conformation studies of biological molecules. *Chem. Phys. Lett.* **281**(1), 140–150 (1997)
- Hedlund, J., Sterte, J., Anthonis, M., Bons, A.J., Carstensen, B., Corcoran, N., Cox, D., Deckman, H., De Gijnst, W., de Moor, P.P., McHenry, J., Mortier, W., Reinoso, J.: High-flux MFI membranes. *Microporous Mesoporous Mater.* **52**(3), 179–189 (2002)
- June, R.L., Bell, A.T., Theodorou, D.N.: Transition-state studies of xenon and sulfur hexafluoride diffusion in silicalite. *J. Phys. Chem.* **95**, 8866–8878 (1991)
- Krishna, R., Calero, S., Smit, B.: Investigation of entropy effects during sorption of mixtures of alkanes in MFI zeolite. *Chem. Eng. J.* **88**(1), 81–94 (2002a)
- Krishna, R., Smit, B., Calero, S.: Entropy effects during sorption of alkanes in zeolites. *Chem. Soc. Rev.* **31**, 185–194 (2002b)
- Kulprathipanja, S., Johnson, J.A.: *Liquid separations*. Wiley-VCH, Weinheim (2008)
- Laso, M., de Pablo, J.J., Suter, U.W.: Simulation of phase equilibria for chain molecules. *J. Chem. Phys.* **97**, 2817–2819 (1992)
- Macedonia, M.D., Maginn, E.: A biased grand canonical Monte Carlo method for simulating adsorption using all-atom and branched united atom models. *Mol. Phys.* **96**, 1375–1390 (1999)
- Maginn, E.J., Bell, A.T., Theodorou, D.N.: Sorption thermodynamics, siting and conformation of long *n*-alkanes in silicalite as predicted by configurational-bias Monte Carlo integration. *J. Phys. Chem.* **99**, 2057–2079 (1995)
- Mezei, M.: A cavity-biased (T, V, m) Monte Carlo method for the computer simulation of fluids. *Mol. Phys.* **40**, 901–906 (1980)
- Min, J.S., Kiyozumi, Y., Itoh, N.: A sealant-free preparation technique for high-temperature use of a composite zeolite membrane. *Ind. Eng. Chem. Res.* **42**(1), 80–84 (2003)
- Olson, D.H., Kokotailo, G.T., Lawton, S.L., Meier, W.M.: Crystal structure and structure-related properties of ZSM-5. *J. Phys. Chem.* **85**, 2238–2243 (1981)
- Punnathanam, S., Denayer, J.F., Daems, I., Baron, G.V., Snurr, R.Q.: Parallel tempering simulations of liquid-phase adsorption of *n*-alkane mixtures in zeolite LTA-5A. *J. Phys. Chem. C* **115**(3), 762–769 (2010)
- Rosenbluth, M.N., Rosenbluth, A.W.: Monte Carlo calculation of the average extension of molecular chains. *J. Chem. Phys.* **23**, 356–359 (1955)
- Ruthven, D.: *Principles of adsorption and adsorption processes*. Wiley, New York (1984)
- Sakai, H., Tomita, T., Takahashi, T.: *p*-Xylene separation with MFI-type zeolite membrane. *Sep. Purif. Technol.* **25**(1), 297–306 (2001)
- Schenk, M., Vidal, S.L., Vlucht, T.J.H., Smit, B., Krishna, R.: Separation of alkane isomers by exploiting entropy effects during adsorption on silicalite-1: a CBMC simulation study. *Langmuir* **17**, 1558–1570 (2001)
- Siepmann, J.I., Frenkel, D.: Configurational-bias Monte Carlo: a new sampling scheme for flexible chains. *Mol. Phys.* **75**, 59–70 (1992)
- Smit, B., Maesen, T.L.: Commensurate freezing of alkanes in the channels of a zeolite. *Nature* **374**, 42–44 (1995)
- Smit, B., Siepmann, J.I.: Computer simulations of the energetics and siting of *n*-alkanes in zeolites. *J. Phys. Chem.* **98**(34), 8442–8452 (1994)
- Snurr, R.Q., Bell, A.T., Theodorou, D.N.: Prediction of adsorption of aromatic hydrocarbons in silicalite from grand canonical Monte Carlo simulations with biased insertions. *J. Phys. Chem.* **97**, 13,742–13,752 (1993)
- Vlucht, T.J.H., Zhu, W., Kapteijn, F., Moulijn, J.A., Smit, B., Krishna, R.: Adsorption of linear and branched alkanes in the zeolite silicalite-1. *J. Am. Chem. Soc.* **120**, 5599–5600 (1998)
- Vlucht, T.J.H., Krishna, R., Smit, B.: Molecular simulations of adsorption isotherms for linear and branched alkanes and their mixtures in silicalite. *J. Phys. Chem. B* **103**, 1102–1118 (1999)
- Xomeritakis, G., Lai, Z., Tsapatsis, M.: Separation of xylene isomer vapors with oriented MFI membranes made by seeded growth. *Ind. Eng. Chem. Res.* **40**(2), 544–552 (2001)
- Yang, R.T.: *Gas separation by adsorption processes*. Butterworth Publishers, Stoneham (1986)