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External Surface Adsorption on Silicalite-1 Zeolite Studied by Molecular Simulation

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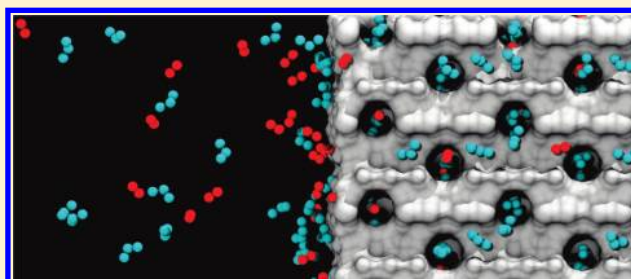
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ABSTRACT: We have studied the adsorption of ethane, propane, and their mixtures on the external surface of silicalite-1 zeolite by molecular simulation using a classical force field. The ideal adsorbed solution theory (IAST) was successfully used to describe mixture adsorption, both on the external surface and inside the zeolite. Propane is preferentially adsorbed inside the zeolite for fugacities from 10^3 to 10^8 Pa, while ethane is favored at higher fugacities. On the zeolite surface, propane is always preferentially adsorbed. We also determined the surface excess concentration for pure ethane and propane, as well as the surface excess of both components in an equimolar mixture. The surface excess concentration is negative or close to zero until the fugacity is approximately 10^5 Pa, when condensation of guest molecules on the external surface becomes important. The surface excess adsorption for ethane in a mixture is different than that for pure ethane, while for propane they are identical.



1. INTRODUCTION

The use of molecular simulations to describe the adsorption of guest molecules inside zeolites is nowadays an important tool in studying microporous systems.^{1–4} Using relatively minor computational resources, detailed models for adsorption can be constructed, resulting in a better understanding of the transport, steric hindrance, location, and orientation of the adsorbed molecules. However, up until now, adsorption of molecules on the external surface of a zeolite has received far less attention. Studying surface adsorption can be quite a challenge experimentally, as the concentration of molecules on the surface can be very low and it is very difficult to distinguish surface adsorption from bulk adsorption in experiments. Therefore, computer simulation seems a natural choice for studying this. For a single zeolite crystal, the number of particles on the external surface will be small compared to those within the pores. Chandross et al.⁵ used molecular dynamics and Monte Carlo simulations to study the dynamic exchange of molecules between a bulk zeolite phase and an adjoining gas phase. The molecules used in this study were *n*-butane and *i*-butane. In their study of the surface, these authors focused on the surface residence time and the importance of the surface as a barrier for transport into the zeolite. It was found that, for thin membranes, the surface resistance can be significant. However, they only studied single component systems. Kortunov et al.⁶ have performed interference microscopy studies of the

surface of ZSM-5. The focus in this study was to investigate the importance of surface defects for transport of molecular species from a gas phase into the surface. These authors found that the surface structure is important for the kinetics of adsorption of *i*-butane in the zeolite crystal, and that surface defects can either increase or decrease the adsorption/desorption on the surface. There is now considerable interest in using a very thin zeolite membrane for separations.⁷ This makes surface effects more important. It is also worth mentioning the work of Zimmermann et al.⁸ These authors define a critical crystal length as

$$L^{\text{crit}} = \gamma \frac{j_{\text{intra}}}{j_{\text{surf}}/\lambda_{\text{surf}}} \quad (1)$$

where j_{intra} and j_{surf} are the flux densities in the zeolite and at the surface, respectively, and λ_{surf} is the distance between the free energy well in the bulk gas phase and the corresponding well in the zeolite phase. The value of γ provides a threshold for when the surface contribution is considered insignificant. The critical crystal length is defined as the width of a membrane, for which the surface resistance will be negligible compared to resistance in the membrane itself. Using methane and ethane (and $\gamma = 200$,

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equivalent to 1% of the total resistance), the critical crystal length was found to be typically 10^2 – 10^4 nm. Inzoli et al.⁹ investigated the surface adsorption isotherm of *n*-butane on silicalite-1. In this work, the focus was exclusively on pure component adsorption. However, these authors calculated the surface adsorption isotherms, along with the surface excess adsorption, which in certain cases was negative.

For studying transport into and through zeolites, making models of such transport, and modifying the zeolite to act as a better membrane, knowledge on what happens on and in the different parts of the zeolite is very important. The whole path, from molecules residing in the gas phase, adsorbing on the surface, entering zeolite, and finally desorbing from the zeolite needs to be considered when constructing models for membrane transport. The surface acts as a barrier to transport,¹⁰ and a negative surface excess may be one of the contributors to this resistance. It is therefore necessary to have models accurately describing adsorption and composition of binary or multicomponent adsorption at the surface. In this work, we have used Monte Carlo simulations in the grand-canonical ensemble to obtain equilibrium adsorption data for surface adsorption. This should lead to a better molecular understanding of surface adsorption and barriers for mass transport at the surface. The simulations are performed with ethane, propane, and their equimolar mixture. The ideal adsorbed solution theory (IAST) of Myers and Prausnitz¹¹ is applied to the pure component adsorption isotherms, in order to predict the surface adsorption of a mixture of these two components. The ideal adsorbed solution theory is a fairly simple model, in which two (or more) pure component isotherms can be used to predict the adsorbed mixture composition for any gas mixture composition. In addition, we find the surface excess concentration of ethane, propane, and their equimolar mixture on the surface.

The remainder of this paper is organized as follows: In section 2, we describe the simulation method and the force field and provide details on the description of the surface. We explain how the simulations are performed, and how the absolute concentration and surface excess concentration are determined. In section 3, we present our results—adsorption isotherms, mixture isotherms, surface excess adsorption—and we show that the IAST describes the mixture adsorption on the surface. In the final section, we summarize our findings.

2. METHODOLOGY

The computed adsorption isotherms were obtained using grand-canonical Monte Carlo (GCMC) simulations, in which the chemical potential of each component, the temperature, and the volume are fixed.¹² The imposed chemical potential of a component is directly related to its fugacity.¹³ The simulations were performed in cycles, and in each cycle, a Monte Carlo move was chosen at random with a fixed probability: translation (20%), regrowth (20%), rotation (20%), and insertion/deletion of molecules (40%). In the case of mixtures, identity changes were also performed with the same probability as the insertion/deletion of molecules.¹⁴ Monte Carlo simulations of surface adsorption are computationally much more expensive than simulations for a corresponding bulk phase with periodic boundary conditions. Due to very large memory requirements, it is not practical to use grid interpolation techniques for computing guest–host interactions. More details on the simulation methods can be found elsewhere.^{12,15,16}

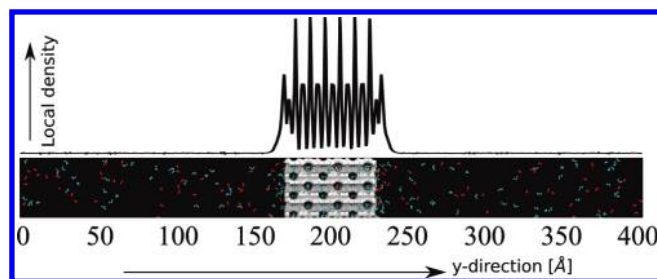


Figure 1. Typical simulation snapshots for the adsorption of ethane and propane, along with the density distribution. Both were taken at a high fugacity. We clearly see that the concentration of guest molecules in the gas phase is low compared to the zeolite. Silicalite-1 has a high affinity for linear organic molecules, so inside the zeolite the concentration of guest molecules is very large, even at moderate fugacities. The sinusoidal channels can clearly be distinguished as the sharp peaks in the density distribution.

The ethane and propane molecules were modeled using the united atom approach, in which the CH_n beads (pseudoatoms) are considered as single, chargeless interaction sites. The interactions of the adsorbed molecules with the zeolite are dominated by the dispersive forces between the pseudoatoms and the oxygen atoms of the zeolite.^{4,17,18} These dispersive interactions are modeled by truncated and shifted Lennard-Jones potentials^{16,19} with a cutoff distance of 12 Å. All Lennard-Jones parameters were taken from the work of Dubbeldam et al.¹⁶ Lorentz–Berthelot mixing rules were used to calculate Lennard-Jones interactions between unlike atoms.

The positions of the zeolite atoms of silicalite-1 zeolite were taken from van Koningsveld et al.²⁰ In this characterization of silicalite-1, the unit cell is orthorhombic (space group *Pnma*) with cell parameters $a = 20.022$ Å, $b = 19.899$ Å, and $c = 13.383$ Å. Simulations were performed for three different systems with periodic boundary conditions in all directions: (a) a system comprising $2 \times 2 \times 2$ unit cells of silicalite-1 with periodic boundary conditions, (b) an empty box (without zeolite) with dimensions $L_x = 40.044$ Å, $L_y = 179.091$ Å, and $L_z = 40.149$ Å (taken from the dimensions of a silicalite-1 structure: $L_x = 2a$, $L_y = 9b$, and $L_z = 3c$), (c) a box containing a zeolite membrane, with dimensions $L_x = 40.044$ Å, $L_y = 417.879$ Å, and $L_z = 40.149$ Å (taken from the dimensions of a silicalite-1 unit cell: $L_x = 2a$, $L_y = 21b$, and $L_z = 3c$). This system contains 18 unit cells of silicalite-1 placed at the center of the simulation box, with the straight channels of the zeolite oriented in the *y*-direction. Therefore, in this simulation box, there are two gas regions, a zeolite membrane, and two surfaces separating the zeolite and the gas regions. The two gas regions account for approximately 85% of the total box volume (see Figure 1). Different surface structures appear depending on where the crystal was cut. In our case, the crystal is cut in the middle of two sinusoidal channels, perpendicular to the straight channel. The external surfaces of the zeolite were then flat with the pores emerging at the surfaces (see Figure 2). The positions of the zeolite atoms are kept fixed, as it has been demonstrated that the influence of framework flexibility in the adsorption of small molecules in zeolites is negligible.²¹

In experiments, silicon atoms at the surface are terminated with silanol groups. In our simulations, we did not saturate the silicon atoms at the surface for two reasons: (1) our model for the adsorbed molecules does not consider atomic partial charges, so there are no electrostatic interactions between the adsorbed

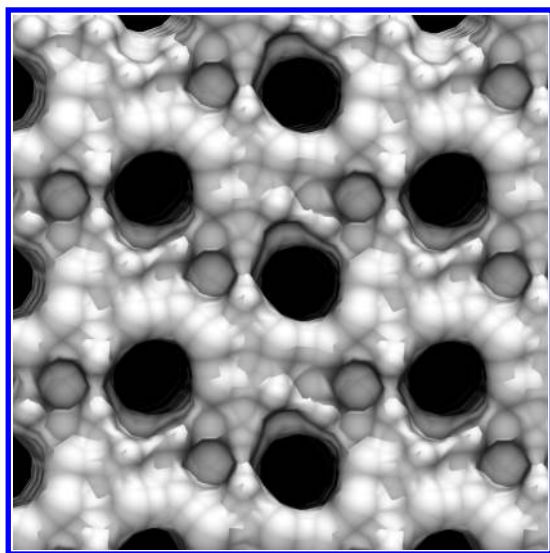


Figure 2. Structure of the external zeolite surface. The zeolite was cut perpendicular to the straight channels, between the sinusoidal channels. This makes the straight channels come out on the flat surface.

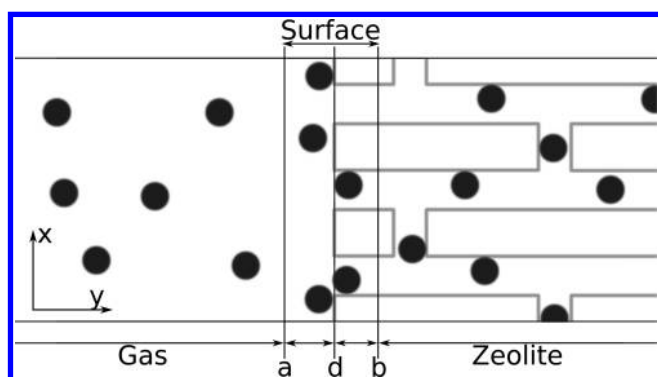


Figure 3. Schematic representation of the external zeolite surface and positions of gas side and host side of the external surface. The crystallographic surface, d , is delimiting between the gas part and the host part. The surface is determined by studying the concentration profile in the y -direction. The typical extent of the surface is 10 Å for the gas side and 7 Å for the host side, leading to a total surface of typically 17 Å. However, when condensation takes place, the gas side can easily extend up to 30 Å into the gas phase.

molecules and the zeolite; (2) the dispersive interactions between the adsorbed molecules and the hydrogen atoms in the silanol group are negligible.

All the simulations were performed at a temperature of 308 K. We computed density profiles along the y -direction of the simulation box; see Figures 1 and 3. The loading on the different parts of the surface is found from integrating the density profile over the different parts of the surface. That is,

$$q_{A, \text{gas}} = \int_a^d c_A(y) dy \quad (2)$$

and

$$q_{A, \text{host}} = \int_d^b c_A(y) dy \quad (3)$$

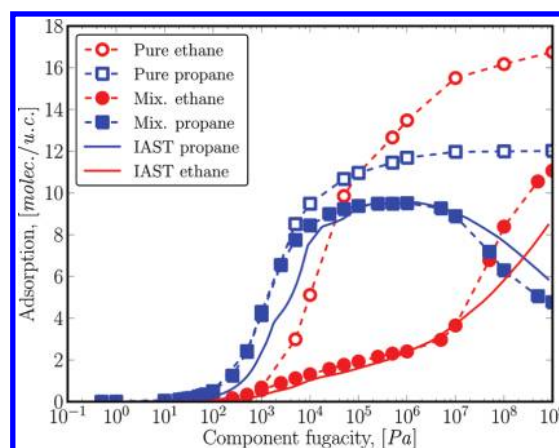


Figure 4. Adsorption isotherms of ethane and propane as pure components and in an equimolar mixture in silicalite-1 zeolite at 308 K. Error bars are smaller than the symbol size.

where c_A is the local concentration of component A. We denote the dividing surface d and take this to be the crystallographic surface (see Figure 3). Positions a and b are determined by comparing the local density profile with the corresponding bulk phase at the same simulation conditions. When the difference between these becomes larger than 1%, we assume that we are in the surface region. In this way, the surface is separated into two parts: the gas part, going from the crystallographic surface and into the gas phase, and the host part, going from the crystallographic surface and into the zeolite structure. We can then study each of these parts individually and, by adding them, the external surface as a whole.

Considering the surface a Gibbs surface, we compute the surface excess concentration by integrating the local density:^{22–24}

$$\Gamma_A(y) = \int_a^b [c_A(y) - c_A^g \theta(d - y) - c_A^z \theta(y - d)] dy \quad (4)$$

where Γ_A is the surface excess concentration of component A, y is the position along the y -axis in the box (perpendicular to the surface), and θ is the usual Heaviside step function. The superscripts g and z refer to the concentration in the bulk gas phase and the bulk zeolite phase, respectively. The integration is performed from a to b , where position a is in the bulk gas phase and b is in the bulk zeolite phase. In this case, the positions of a and b are of no importance, as we are considering excess properties. We take d to be the dividing surface, the crystallographic surface in this case.

3. RESULTS

Figure 4 shows the adsorption isotherms of ethane and propane as pure components and as an equimolar mixture in the bulk zeolite as a function of the fugacity of each component. The isotherms for the equimolar mixture obtained using the ideal adsorption solution theory (IAST) of Myers and Prausnitz¹¹ are shown with solid lines. Regarding the pure components, the adsorption for ethane is lower than that for propane for fugacities lower than 10^5 Pa. At larger fugacities, we observe the opposite behavior, where the adsorption of ethane is notably larger than that of propane. At low fugacity, the larger molecule adsorbs better due to the larger adsorption energy. At higher fugacity, the loading of the smaller ethane molecule is larger because it is much

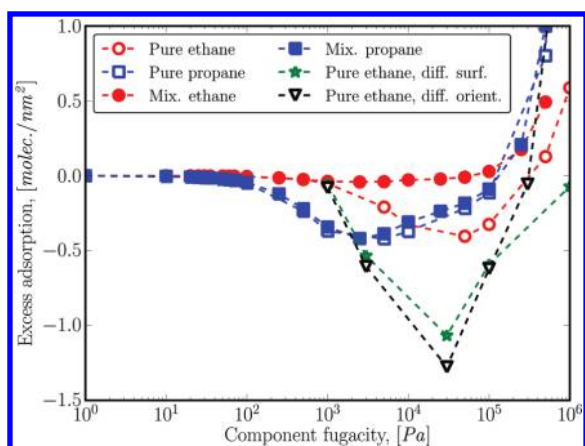


Figure 5. Ethane and propane surface excess adsorption for pure components and for an equimolar mixture in the system with a zeolite membrane. Also shown are results for a different cut of the surface, i.e., perpendicular to the y -axis of the zeolite and crossing the sinusoidal channels, as well as a different surface perpendicular to the x -axis of the zeolite. Results are obtained using eq 4.

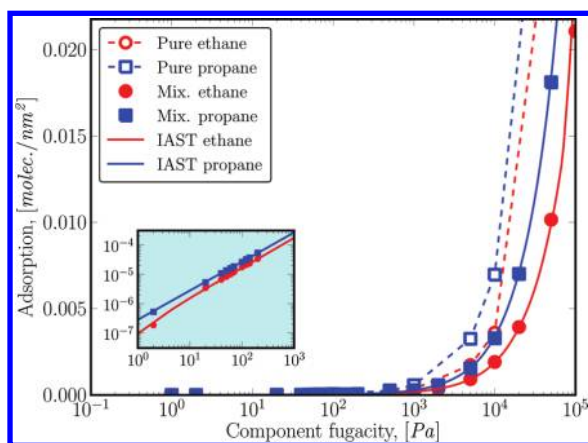


Figure 6. Adsorption on the gas part of the external surface. Isotherms for the equimolar mixture compared to IAST analysis. Results from the IAST are shown as solid lines. The error bars from the simulation data are smaller than the symbol size. The inset shows the data from the left part of the main figure. This is plotted in a log–log plot, to emphasize that IAST does describe the data very well at this low concentration regime. The step increase in adsorption on the right side of the figure indicates that condensation occurs. The IAST give fairly good predictions up to 10^5 Pa.

easier to fill in the pores in the silicalite-1 as the loading increases. These effects are well-known for bulk zeolites and have been observed previously by molecular simulations.^{25–27} These effects also explain the behavior of the mixture isotherm. At low fugacities, we find the same behavior as for the pure components, but there is a reversal of adsorption at 10^8 Pa. This reversal in the adsorption is due to the fact that, under saturation conditions, the ethane adsorbs more as a consequence of a size entropic effect.²⁵ The total mixture loading predicted using IAST compares very well with the CBMC simulations for the equimolar mixture of ethane and propane under these conditions.

In Figure 5, we compare the surface excess adsorption for pure components and for the equimolar mixture as a function of the component fugacity. The number of molecules adsorbed on the

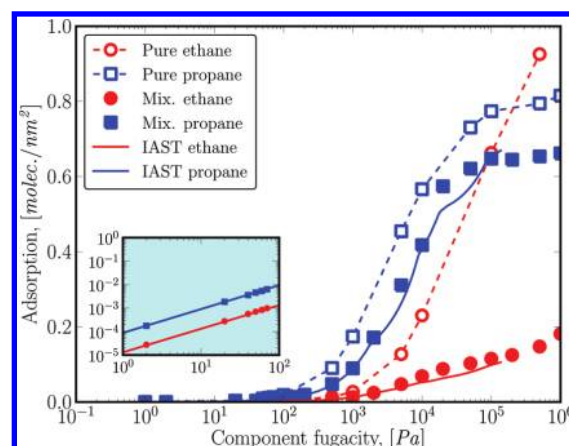


Figure 7. Adsorption on the host part of the external surface. Isotherms for the equimolar mixture compared to IAST analysis. Results from the IAST are shown as solid lines. The error bars from the simulation data are smaller than the symbol size. The inset shows the data from the left part of the main figure. This is plotted in a log–log plot, to emphasize that IAST does describe the data very well at this low concentration regime.

surface is expressed as the number of molecules per unit of surface area. When the excess adsorption is positive, the adsorption of molecules on the surface is favored. Pure ethane results in an excess adsorption nearly close to zero until we reach a fugacity of 10^3 Pa. The excess adsorption of pure propane is large and negative at low fugacities and becomes positive between 10^5 and 10^6 Pa. There are considerable differences for ethane between the pure component and the equimolar mixture between 5×10^3 and 5×10^5 Pa. Between this range of fugacities, the excess adsorption of the mixture is zero and negative for the pure component. On the other hand, the surface excess adsorption of propane does not show large differences between the pure component and the mixture. In conclusion, pure component ethane tends to adsorb more on the surface for the whole range of fugacities. However, pure component propane provides the largest excess adsorption. Propane has the highest excess adsorption at high fugacities. In Figure 5, we also provided the excess adsorption of ethane for a different cut of the surface, as well as for a different orientation. Clearly, the excess adsorption for these different surfaces is different.

Adsorption on the gas part of the external surface for ethane and propane as pure components and their equimolar mixture are shown in Figure 6. We observe that the adsorption of both ethane and propane is low until the fugacity approaches 10^3 Pa. This is related to condensation. The IAST analysis gives a very good representation of this case at low loadings. However, the IAST breaks down when condensation at the surface becomes important. The inset in Figure 6 shows the left part of the plot on a logarithmic scale for both axes to better distinguish the details. The IAST perfectly predicts mixture adsorption on the surface. In Figure 7, something similar is shown for the host part of the external surface. The agreement is excellent when we compare the mixture's isotherms from simulations to those from IAST analysis. In this system, we have very similar conditions as we have inside the zeolite pores.

Finally, in Figure 8, we study the adsorption on the external surface in total, this being the gas side and the host side considered together. When we compare the mixture's isotherms from simulations to those from the IAST analysis, the IAST

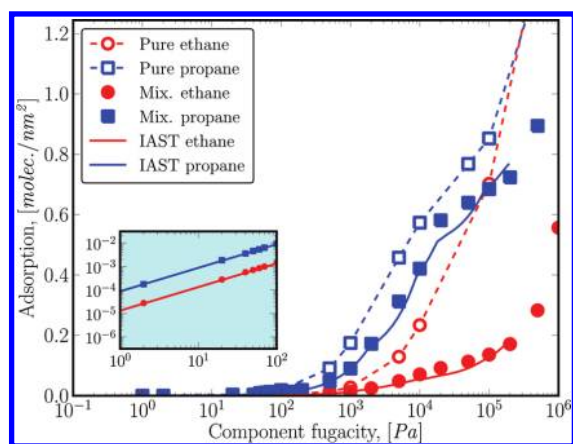


Figure 8. Total surface adsorption as a function of the component fugacity. This is a combination of the data plotted in Figures 6 and 7. The adsorption on the host side is totally dominating up until condensation occurs on the gas side of the surface. The IAST predictions correspond well with data from simulations.

analysis provides similar results as for the host side of the surface. For most of this system, the contribution from the gas side of the surface is minor, until condensation occurs. Again, IAST predicts the adsorbed mixture composition within the expected range.

4. CONCLUSIONS

In this work, we investigated the single component and binary mixture adsorption of ethane and propane on the surface of silicalite-1 zeolite. The external surface is defined as a Gibbs surface, and changes in density lead to a gas side and host side surface. The crystallographic surface is taken as the dividing surface. The IAST is able to predict the mixture adsorption for the different parts of the external surface. We also find that the predictions for the zeolite framework correspond well with previous results. The IAST offers a simple and efficient way to get quantitative information on the mixture at zeolite surfaces. The fact that the IAST method works indicates that we have an ideal adsorption on the surface. In future work, we would like to look at competitive adsorption of branched and linear alkanes, as well as adsorption of polar molecules on the surface of silicalite-1. With polar molecules, it is necessary to describe the structure of the surface with different models and electrostatic interactions will become significant. Our results clearly show that the excess adsorption of molecules on zeolite surfaces depends on the cut as well as the orientation of the zeolite crystal.

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