Elucidation of Selectivity Reversals for Binary Mixture Adsorption in Microporous Adsorbents

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ABSTRACT: The adsorption selectivity, \( S_{ads} \), is a key metric that quantifies the efficacy of any adsorbent in mixture separations. It is common practice to use ideal adsorbed solution theory (IAST) for estimating the value of \( S_{ads} \), using unary isotherm data inputs. In a number of experimental investigations, the phenomena of selectivity reversals and adsorption azeotropy (\( S_{ads} = 1 \)) have been reported in the published literature; such reversals may result from changes in mixture compositions, pressures, or pore loadings. In many cases, IAST is unable to anticipate such selectivity reversals. In this article, configurational-bias Monte Carlo simulations are used to gain insights into the phenomena of selectivity reversals. Two fundamentally different scenarios of selectivity reversals have been identified. In the first scenario, selectivity reversals are caused by inhomogeneous distribution of adsorbates due to preferential location and siting of a guest species in the pore space. For example, CO\(_2\) locates preferentially in the side pockets of mordenite and in window regions of DDR, CHA, and LTA zeolites. CO\(_2\) also congregates around the extra-framework cations of NaX zeolite. IAST fails to anticipate such selectivity reversals because its development relies on the assumption that the competition between guest species is uniform within the pore space. In the second scenario, selectivity reversals are caused by entropy effects that manifest near pore saturation conditions; the component that is preferentially adsorbed is the one that has the higher packing efficiency. For a homologous series of compounds, the component with the smaller chain length is favored at high pore occupancies. For adsorption of mixtures of alkane isomers within the intersecting channel network of MFI zeolite, the linear isomer is favored on the basis of entropic considerations.

1. INTRODUCTION

Microporous adsorbents such as zeolites and metal--organic frameworks (MOFs) offer energy-efficient alternatives to conventional separation technologies such as distillation. There has been a tremendous upsurge in research on the development of MOFs for a variety of applications such as CO\(_2\) capture and alkene/alkane, alkyne/alkene, and water/alcohol mixture separations.\(^1\)\(^-\)\(^6\)

A key metric that quantifies the efficacy of a microporous adsorbent for separation of a binary mixture consisting of components 1 and 2 is the adsorption selectivity, \( S_{ads} \), defined by

\[
S_{ads} = \frac{q_1}{q_2} \frac{f_1}{f_2}
\]

(1)

where \( q_1 \) and \( q_2 \) are the molar loadings of the components 1 and 2 in the adsorbed phase in equilibrium with a bulk fluid phase mixture with partial fugacities \( f_1 \) and \( f_2 \).

The adsorption selectivity is dictated by dispersion and electrostatic interactions between the guest molecules and the framework material.\(^7\)\(^-\)\(^10\) The London–van der Waals dispersion interaction energies are largely dictated by the polarizabilities of the guest molecules and surfaces atoms of the adsorbent materials. The electrostatic interactions arise from charges (which create electric fields) of the extra-framework cations in zeolites or unsaturated metal atoms in MOFs. Because of the large quadrupole moment of CO\(_2\), cation-exchanged zeolites such as NaX, LTA-4A, and LTA-5A offer high selectivities in CO\(_2\)-capture applications. Generally speaking, high values of \( S_{ads} \) are desirable because this leads to sharper separations in fixed bed adsorption devices.\(^11\)\(^,\)\(^12\)

A number of experimental investigations report the phenomena of reversal of selectivity values with changes in the operating conditions.\(^13\)\(^-\)\(^17\) Figure 1a plots data on the selectivity for adsorption of CO\(_2\)/hydrocarbon mixtures in a variety of cation-exchanged zeolites: LTA-5A,\(^18\) NaX,\(^19\) H-MOR,\(^20\) and ZSM-5.\(^21\) In all of these experiments, the total pressure and temperature are held constant and the bulk gas phase composition of CO\(_2\), \( y_1 \), is varied. In each case, the values of \( S_{ads} \) experience a selectivity reversal phenomenon at a certain value of \( y_1 \).

Received: March 9, 2020
Accepted: March 31, 2020
Published: April 7, 2020
For adsorption of mixtures of toluene/1-propanol\(^{22}\) and \(p\)-xylene/1-butanol\(^{23}\) mixtures in Y zeolite, selectivity reversals occur as the mole fraction of the aromatic compound in the bulk vapor phase increases, see Figure 1b.

For adsorption of mixtures of homologous series of compounds, such as alkanes, alkenes, and 1-alcohols, the polarizability of the molecules increases with increasing chain length. Consequently, in the Henry regime of adsorption, the binding strengths of the molecules increase with increasing chain length.\(^{24 - 26}\) Remy et al.\(^{27}\) report data on transient breakthroughs of ethanol/1-propanol and ethanol/1-hexanol liquid mixtures in a fixed bed adsorber packed with SAPO-34 that has the same structural topology as CHA zeolite. The experiments show that the component that is eluted first from the adsorber is the alcohol with the longer chain length, implying that the selectivity is in favor of the shorter 1-alcohol.

Two major questions arise from the foregoing set of experimental observations: (i) what is the root cause of the selectivity reversals in the experiments mentioned in foregoing paragraphs? and (ii) what are the selectivity reversals amenable to quantitative description using ideal adsorbed solution theory (IAST) of Myers and Prausnitz\(^{28}\) that is widely used to estimate mixture adsorption characteristics? The primary objective of this article is to elucidate the phenomena of selectivity reversals. Toward this end, configurational-bias Monte Carlo (CBMC) simulations on mixture adsorption equilibrium were performed using the simulation methodology that is firmly established in the literature.\(^{29 - 33}\) The force field information is taken from García-Sánchez et al.\(^{34}\) and Dubbeldam et al.\(^{35}\)

The Supporting Information accompanying this publication provides (a) a detailed structural information on all of the zeolites and MOFs analyzed and discussed in the article, (b) details of the IAST and real adsorbed solution theory (RAST) methodologies and calculations for mixture adsorption equilibria, and (c) input data on unary isotherm fits for the wide variety of guest/host combinations examined in this article.

2. RESULTS AND DISCUSSION

2.1. Thermodynamics of Mixture Adsorption. The appropriate starting point for setting up the theory for mixture adsorption is the Gibbs adsorption equation, written in the differential form\(^{7,13,14,28}\)

\[
A \frac{d\pi}{d\gamma} = \sum_{i=1}^{n} \frac{q_i \, d\mu_i}{\gamma_i}
\]  

(2)

In eq 2, \(A\) represents the surface area per kg of framework, \(q_i\) is the molar loading, \(\mu_i\) is the molar chemical potential, and \(\pi\) is the spreading pressure. The spreading pressure \(\pi\) has the same unit as surface tension, that is, \(N / m^2\). At phase equilibrium, equating the component chemical potentials, \(\mu_i\) in the adsorbed phase equals that in the bulk fluid phase mixture. If the partial fugacities in the bulk fluid phase are \(f_i\)

\[
d\mu_i = RT \, d\ln f_i; \quad i = 1, 2, \ldots, n
\]

(3)

In the Myers–Prausnitz development of IAST,\(^{28}\) the partial fugacities in the bulk fluid mixture are related to the mole fractions \(x_i\) in the adsorbed phase mixture

\[
x_i = \frac{q_i}{\gamma_i}; \quad q_i = q_1 + q_2 + \ldots + q_n
\]

(4)

by the analogue of Raoult’s law for vapor–liquid equilibrium, that is,

\[
f_i = x_i P_i^0; \quad i = 1, 2, \ldots n
\]

(5)

where \(P_i^0\) is the pressure for sorption of every component \(i\), which yields the same spreading pressure \(\pi\) for each of the pure components, as that for the mixture

\[
\frac{\pi A}{RT} = \int_0^{P_i^0} \frac{\rho_i^C(f)}{f} \, df = \int_0^{P_i^0} \frac{\rho_i^C(f)}{f} \, df = \int_0^{P_i^0} \frac{\rho_i^C(f)}{f} \, df = \ldots
\]

(6)

In eq 6, \(\rho_i^C(f)\) is the pure component adsorption isotherm. Because the surface area \(A\) is not directly accessible from experimental data, the adsorption potential \(\pi A/RT\), with the units mol kg\(^{-1}\), serves as a convenient and practical proxy for the spreading pressure \(\pi\).

For multicomponent mixture adsorption, each of the equalities on the right hand side of eq 6 must be satisfied. These constraints may be solved using a suitable equation solver to yield the set of values of \(P_1^0, P_2^0, P_3^0, \ldots, P_n^0\), all of which satisfy eq 6. The corresponding values of the integrals using these as upper
Contrary to this expectation, the experimental data follow two experimental data to coincide and follow the dashed lines.

MOR zeolite, we need to introduce activity coefficients; this ensures that the obtained solution is the correct one. The adsorbed phase mole fractions \( x_i \) are then determined from

\[
x_i = \frac{f_i}{P_i^0} \quad i = 1, 2, \ldots n
\]

In view of eq 7, we rewrite eq 1 as the ratio of the sorption pressures

\[
S_{ads} = \frac{x_i/f_i}{x_2/f_2} = \frac{P_1^0}{P_2^0}
\]

Applying the restriction specified by eq 6, it follows that \( S_{ads} \) is uniquely determined by the adsorption potential \( \pi A/RT \).

2.2. \( \text{CO}_2/\text{C}_3\text{H}_8 \) Mixture Adsorption in Mordenite. Talu and Zwiebel report two sets of experimental data for adsorption of \( \text{CO}_2/\text{C}_3\text{H}_8 \) mixtures in H-MOR (=H-mordenite) at 303 K; this zeolite consists of 12-ring (7.0 Å × 6.5 Å) 1D channels connected to 8-ring (5.7 Å; 2.6 Å) pockets, see pore landscapes and structural details in Figures S11 and S12. Figure 2a presents the data on the adsorption selectivity \( S_{ads} \) for \( \text{CO}_2(1)/\text{C}_3\text{H}_8(2) \) mixture adsorption as a function of the mole fraction of \( \text{CO}_2 \) in the bulk gas phase, \( y_1 \), the total gas phase pressure \( p_1 = p_1^* + p_2 \) is varied. The IAST estimations using the unary isotherm (indicated by the dashed lines) do not anticipate selectivity reversal phenomena, and the adsorption is anticipated to be \( \text{CO}_2 \)-selective over the entire composition range.

Figure 2b presents the data on \( S_{ads} \) for 17/83 \( \text{CO}_2(1)/\text{C}_3\text{H}_8(2) \) mixture adsorption in H-MOR in which the total gas phase pressure \( p_1 = p_1^* + p_2^* \) is varied. The IAST estimations of \( S_{ads} \) (indicated by dashed lines) show C\_3H\_8-selective adsorption; for \( p_1 = p_1^* + p_2^* > 18 \text{ kPa} \), the selectivity reverses in favor of \( \text{CO}_2 \).

The two sets of experimental data for the adsorption selectivity in Figure 2a,b are replotted in Figure 3a as a function of the mole fraction of \( \text{CO}_2 \) in the bulk gas phase, \( y_1 \), the total gas phase pressure \( p_1 = p_1^* + p_2 \) is varied. Also shown in (a,b) are IAST (dashed lines) and RAST calculations (continuous solid lines). All calculation details and input data are provided in the Supporting Information accompanying this publication.

The Wilson model for activity coefficients is given for binary mixtures by

\[
\ln(\gamma_1) = \left(1 - \ln(x_1 \Lambda_{11} + x_2 \Lambda_{12}) - \frac{x_1 \Lambda_{11}}{x_1 \Lambda_{11} + x_2 \Lambda_{12}} \right) - \frac{x_2 \Lambda_{21}}{x_2 \Lambda_{21} + x_1 \Lambda_{12}} (1 - \exp(-C \pi A/RT))
\]

\[
\ln(\gamma_2) = \left(1 - \ln(x_1 \Lambda_{12} + x_2 \Lambda_{22}) - \frac{x_1 \Lambda_{12}}{x_1 \Lambda_{12} + x_2 \Lambda_{22}} \right) - \frac{x_2 \Lambda_{21}}{x_2 \Lambda_{21} + x_1 \Lambda_{12}} (1 - \exp(-C \pi A/RT))
\]

In eq 12, \( \Lambda_{11} = 1; \Lambda_{12} = 1 \) and \( C \) is a constant with the unit kg mol\(^{-1}\). The choice of \( \Lambda_{11} = \Lambda_{21} = 1 \) in eq 12 yields unity values.
for the activity coefficients and reduces to IAST. The Wilson model has the right limiting behaviors: \( \gamma_i \to 1; \ x_i \to 1 \). The introduction of \( 1 - \exp(-C A / RT) \) imparts the correct limiting behaviors \( \gamma_i \to 1; \ x_i \to 1 \). For \( y_1 < 0.2; \ S_{ads} > 1 \) and the selectivity is in favor of CO2. The CBMC simulation data, that are in remarkably good agreement with the experimental data plotted in Figure 2a, show that the adsorption selectivity \( S_{ads} \) is increasingly lowered below unity, that is, in favor of the alkane, with increasing proportion of CO2 in the bulk gas phase. Computational snapshots are shown in Figure 4b. CO2 gets preferentially ensconced in the side pockets, but when the side pockets are fully occupied, the CO2 can also locate in the 12-ring 1D channels. The C3H8 molecules are unable to occupy the side pockets and are exclusively located in the 12-ring 1D channels. IAST anticipates \( S_{ads} \) to be virtually independent of \( y_1 \). The conventional IAST calculation assumes that C3H8 molecules compete with all of the CO2, making no allowance for segregation. Because of segregation effects, the competition faced by C3H8 molecules within the 12-ring channels, where C3H8 exclusively resides, is smaller than that in the entire pore space. IAST anticipates a stiffer competition between CO2 and C3H8 as it assumes a uniform distribution of composition; consequently, \( S_{ads} \) is overestimated to a significant extent.

2.3. Segregated Mixture Adsorption in Cage-Type Zeolites. For separation of CO2 from gaseous mixtures, cage-type zeolites such as DDR, CHA, LTA, and ERI are of practical interest. These materials consist of cages separated by 8-ring windows in the 3.3–4.5 Å range. For adsorption of CO2/CH4 mixtures, published CBMC simulations show that the...
window regions of cage-type zeolites have a significantly higher proportion of CO₂ than within the cages. For all four zeolites, CO₂ has the highest probability, about 30–40%, of locating in the window regions.41 As illustration, Figures 5a and 6a present computational snapshots for the location of CO₂ and CH₄ in DDR and CHA zeolites.

Figure 5. (a) Computational snapshot showing the location of CO₂ and CH₄ within the cage/window structure of DDR zeolite. (b) CBMC simulations of the adsorption selectivity, S_ads, for CO₂(1)/CH₄(2) mixture adsorption in all-silica DDR zeolite at 300 K. Two sets of simulation data are presented: (i) the bulk gas phase mole fractions are maintained at y₁ = y₂ = 0.5, and the mixture fugacity f₁ + f₂ is varied, and (ii) the total bulk gas mixture fugacity is held constant, f₁ + f₂ = 10⁶ Pa, and the mole fraction of CO₂ in the bulk gas mixture, y₁, is varied. Both data sets are plotted as a function of the adsorption potential πA/RT. The dashed lines are the IAST calculations, and the continuous solid lines are the RAST calculations. All calculation details and input data are provided in the Supporting Information accompanying this publication.

Figure 5b shows CBMC simulation data of the adsorption selectivity, S_ads, for CO₂(1)/CH₄(2) mixtures in DDR zeolite that consists of cages of 277.8 Å³ volume, separated by 3.65 Å × 4.37 Å; 8-ring windows. Two sets of simulation data are presented: (i) the bulk gas phase mole fractions are maintained at y₁ = y₂ = 0.5, and mixture fugacity f₁ + f₂ is varied, and (ii) the total bulk gas mixture fugacity is held constant, f₁ + f₂ = 10⁶ Pa, and the mole fraction of CO₂ in the bulk gas mixture, y₁, is varied. Both CBMC data sets on S_ads are plotted as a function of the adsorption potential πA/RT. The IAST calculations (shown by the dashed line) anticipate that S_ads is uniquely determined by πA/RT, whereas the CBMC data show that the two data sets for S_ads do not coincide when plotted against πA/RT. Furthermore, IAST significantly overestimates the S_ads values at πA/RT > 5 mol kg⁻¹. The IAST calculation assumes that CH₄ molecules compete with all of the CO₂, making no allowance for segregation. Because of segregation effects, the competition faced by CH₄ molecules within the cages, where they almost exclusively reside, is smaller than that in the entire pore space. The two sets of CBMC data are adequately captured by the choice of the Wilson parameters Λ₁₂ = 0.81; Λ₁₁ = 3; C = 0.34 mol kg⁻¹, as evidenced by the RAST calculations indicated by the continuous solid lines in Figure 5b.
The corresponding CBMC simulation data for CO\textsubscript{2}/CH\textsubscript{4} mixture adsorption in CHA zeolite that consists of cages of volume 316 Å\textsuperscript{3} separated by 3.8 Å × 4.2 Å; 8-ring windows are presented in Figure 6b. Because of segregation effects, IAST overestimates the \( S_{\text{ads}} \) values for \( \pi A/RT > 0.5 \text{ mol kg}^{-1} \).

Figure 7 shows snapshots of the location of CO\textsubscript{2} and C\textsubscript{3}H\textsubscript{8} molecules within the pore topology of LTA-4A zeolite that consists of cages of 743 Å\textsuperscript{3} volume separated by 4.11 Å × 4.47 Å; 8-ring windows. We note that the CO\textsubscript{2} is almost exclusively located at the windows or near the window entrance regions. Because of configurational restraints, C\textsubscript{3}H\textsubscript{8} can only be located at the cage interiors. Consequently, the competition between the adsorption of CO\textsubscript{2} and C\textsubscript{3}H\textsubscript{8} is less severe than assumed in the homogenous distribution that is inherent in the IAST prescription.

Two different campaigns were carried out for CBMC simulations of CO\textsubscript{2}(1)/C\textsubscript{3}H\textsubscript{8}(2) mixture adsorption in LTA-4A zeolite at 300 K. The CBMC simulations for CO\textsubscript{2}(1)/C\textsubscript{3}H\textsubscript{8}(2) mixture adsorption in LTA-4A zeolite at \( f_1 = 1 \text{ MPa} \) and varying mole fractions of CO\textsubscript{2}(1) in the bulk gas phase, \( y_1 \), are shown in Figure 8a. For \( y_1 < 0.1, S_{\text{ads}} > 1 \), and the selectivity is in favor of CO\textsubscript{2}. The CBMC simulations show that the adsorption selectivity \( S_{\text{ads}} \) is increasingly lowered below unity, that is, in favor of the alkane, with increasing proportion of CO\textsubscript{2} in the bulk gas phase; IAST anticipates \( S_{\text{ads}} \) to be virtually independent of \( y_1 \). The observed selectivity reversal phenomena, arising out of inhomogeneous distribution of guest molecules in the cage/window structure of LTA, are entirely analogous to those observed for CO\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} mixture adsorption in LTA-5A reported by Basmajian and Hsieh\textsuperscript{18} and plotted in Figure 1. Such selectivity reversals are also experienced in the transient breakthrough experiments reported by van Zandvoort et al.\textsuperscript{15,16}

The CBMC simulations for CO\textsubscript{2}/C\textsubscript{3}H\textsubscript{8} mixture adsorption in LTA-4A zeolite in which the mole fraction of CO\textsubscript{2} in the bulk gas phase is held constant, \( y_1 = 0.1 \), and the bulk gas phase fugacity \( f_1 = f_1 + f_2 \) was varied are shown by the square symbols in Figure 8b. For \( \pi A/RT < 25 \text{ mol kg}^{-1} \), the selectivity is in favor of C\textsubscript{3}H\textsubscript{8}; with increasing values of the adsorption potential \( \pi A/RT > 25 \text{ mol kg}^{-1} \), the adsorption selectivity \( S_{\text{ads}} \) switches in favor of CO\textsubscript{2} because of strong Coulombic interactions with the extra-framework cations Na\textsuperscript{+}. IAST does not anticipate this selectivity reversal in favor of CO\textsubscript{2}. The CBMC simulations can be matched by quantification of thermodynamic nonidealities using the Wilson parameters \( \Lambda_2 = 1 \); \( \Lambda_3 = 5.65 \); \( C = 0.1 \text{ mol kg}^{-1} \); see RAST calculations indicated by continuous solid lines in Figure 8a,b.

The experimental data of Costa et al.\textsuperscript{19} for CO\textsubscript{2}/C\textsubscript{3}H\textsubscript{8} mixture adsorption in NaX zeolite, which consists of cages of 786 Å\textsuperscript{3} volume separated by 7.3 Å; 12-ring windows, demonstrate the selectivity reversal in favor of the saturated alkane at high mole fractions of CO\textsubscript{2} in the bulk gas mixture: see Figure 1. Most likely, this selectivity reversal is caused by the inhomogeneous distribution of guest molecules, with CO\textsubscript{2} congregating around the cations: see the computational snapshot in Figure 9. We note that the bottom cage contains only CO\textsubscript{2} and there is no C\textsubscript{3}H\textsubscript{8} present in that cage, underscoring the fact that the distribution of adsorbates is not uniform within the pore space. The competition faced by C\textsubscript{3}H\textsubscript{8} in the entire pore space is effectively reduced, and this engenders a reversal in selectivity in favor of CO\textsubscript{2}. The observed selectivity reversal phenomena, arising out of inhomogeneous distribution of guest molecules in the cage/window structure of LTA, are entirely analogous to those observed for CO\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} mixture adsorption in LTA-5A reported by Basmajian and Hsieh\textsuperscript{18} and plotted in Figure 1. Such selectivity reversals are also experienced in the transient breakthrough experiments reported by van Zandvoort et al.\textsuperscript{15,16}

The CBMC simulations for CO\textsubscript{2}/C\textsubscript{3}H\textsubscript{8} mixture adsorption in LTA-4A zeolite in which the mole fraction of CO\textsubscript{2} in the bulk gas phase is held constant, \( y_1 = 0.1 \), and the bulk gas phase fugacity \( f_1 = f_1 + f_2 \) was varied are shown by the square symbols in Figure 8b. For \( \pi A/RT < 25 \text{ mol kg}^{-1} \), the selectivity is in favor of C\textsubscript{3}H\textsubscript{8}; with increasing values of the adsorption potential \( \pi A/RT > 25 \text{ mol kg}^{-1} \), the adsorption selectivity \( S_{\text{ads}} \) switches in favor of CO\textsubscript{2} because of strong Coulombic interactions with the extra-framework cations Na\textsuperscript{+}. IAST does not anticipate this selectivity reversal in favor of CO\textsubscript{2}. The CBMC simulations can be matched by quantification of thermodynamic nonidealities using the Wilson parameters \( \Lambda_2 = 1 \); \( \Lambda_3 = 5.65 \); \( C = 0.1 \text{ mol kg}^{-1} \); see RAST calculations indicated by continuous solid lines in Figure 8a,b.
the alkane; for detailed analyses, see Figures S39–S42, S49, and S50 of the Supporting Information.

The experimentally observed selectivity reversals for aromatic/1-alcohol mixtures in Y zeolite (cf. Figure 1b) are most likely caused because of congregation of the aromatic molecules around the extra-framework cations; for detailed analyses, see Figures S53 and S54 of the Supporting Information.

2.4. Selectivity Reversals Caused by Molecular Packing Effects. We now attempt to gain insights into the selectivity reversals for ethanol/1-propanol and ethanol/1-hexanol mixture adsorption in SAPO-34 as evidenced in the liquid phase breakthrough experiments of Remy et al.27 For operations with feed mixtures in the liquid phase, the pore space of the adsorbent is expected to be saturated with guest molecules.28 Computational snapshots of the conformations of ethanol, 1-propanol, and 1-hexanol under pore saturation conditions in CHA (structural analogue of SAPO-34) are shown in Figure 10a. Because of the limited capacity of the cages of CHA, each having a volume of 316 Å³, the maximum number of molecules that can be accommodated is, respectively, 4, 2, and 1 per cage. Near pore saturation conditions, entropic considerations favor the adsorption of the shorter ethanol because it is easier to fill in the few available vacant spaces.25,26

The entropic preference for ethanol near saturation loadings is confirmed by the CBMC simulations for ethanol/1-propanol mixtures, as shown in Figure 10b. For adsorption potentials \( \pi_A/RT < 30 \text{ mol kg}^{-1} \), the adsorption selectivity is strongly in favor of the longer 1-propanol molecule that has the higher binding strength. However, \( \pi_A/RT > 30 \text{ mol kg}^{-1} \), corresponding to conditions in which the bulk fluid is in the liquid phase, we find a reversal of selectivity in favor of ethanol. This selectivity reversal is entropy-based and is ascribable to the significantly higher saturation capacity of ethanol (4 molecules per cage) in

![Figure 9](image-url)

*Figure 9.* Computational snapshots showing the location of CO\(_2\) and C\(_3\)H\(_8\) within the cages of NaX zeolite at 300 K and partial fugacities are \( f_1 = f_2 = 0.5 \) MPa.

![Figure 10](image-url)

*Figure 10.* (a) Snapshots showing the conformations of ethanol, 1-propanol, and 1-hexanol in CHA under saturation conditions in CHA zeolite. (b,c) Selectivity of adsorption of (b) ethanol/1-propanol and (c) ethanol/1-hexanol mixtures in CHA zeolite, \( S_{\text{ads}} \), plotted as a function of the adsorption potential \( \pi_A/RT \). The dashed lines represent the IAST calculations; all calculation details and input data are provided in the Supporting Information accompanying this publication.
comparison with that of 1-propanol (2 molecules per cage). The IAST calculations, shown by the dashed lines, are in good agreement with the CBMC data.

The corresponding CBMC data for selectivity for ethanol/1-hexanol mixture adsorption are shown in Figure 10c. Selectivity reversal in favor of ethanol is realized for \( \pi_A/RT > 20 \text{ mol kg}^{-1} \).

Although IAST also anticipates selectivity reversal, the agreement of IAST estimates of \( S_{ads} \) is quantitatively poor. The reason for the poor IAST estimates is that only one molecule of 1-hexanol can occupy a single cage; consequently, within a single cage, there is no competitive adsorption with ethanol because of the inhomogeneous nature of the distribution of guest molecules in the pore space.

Analogous entropy-driven selectivity reversals are also found for methanol/ethanol mixture adsorption in CuBTC. \(^{42,43}\) see Figures S30 and S31.

CBMC simulations for adsorption of \( n \)-butane (\( nC_4 \))/iso-butane (\( iC_4 \)) and \( n \)-hexane (\( nC_6 \))/2-methylpentane (2MP) mixtures in MFI zeolite show that as saturation conditions are approached, the selectivity values are increasingly in favor of the linear isomers: see Figure 11a,b. The linear isomers pack more efficiently because these can be located along both the straight channels and zigzag channels. The branched isomers can only occupy the channel intersections because these demand more leg room: see computational snapshots in Figure 11c,d.

Although IAST predicts the correct trends in the \( S_{ads} \) versus \( \pi_A/RT \) characteristics, the quantitative agreement with CBMC data is not very good because of the segregated nature of mixture adsorption with the intersecting network of channels.

The experimental data of Titze et al. \(^{44}\) provide quantitative confirmation of the CBMC data and IAST estimates in Figure 11.

3. CONCLUSIONS

CBMC simulations have been used to gain insights into the phenomena of selectivity reversals for mixture adsorption in zeolites, as witnessed in a number of experimental investigations. Two fundamental different scenarios of selectivity reversals have been identified.

1. In the first scenario, selectivity reversals are caused by inhomogeneous distribution of adsorbates because of preferential location and siting of a guest species in the pore space. For example, CO₂ locates preferentially in the side pockets of MOR and in window regions of DDR, CHA, and LTA zeolites. CO₂ also congregates around the extra-framework cations of NaX zeolite. IAST fails to anticipate such selectivity reversals because its development relies on the assumption that the competition between guest species is uniform within the pore space.
For quantitative modeling, the use of the RAST with the introduction of activity coefficients becomes necessary.

(2) In the second scenario, selectivity reversals are caused by entropy effects that manifest near pore saturation conditions; the component that is preferentially adsorbed is the one that has the higher packing efficiency. For a homologous series of molecules, the component with the smaller chain length is favored at high values of the adsorption potential $\pi A/RT$. For adsorption of mixtures of alkane isomers within the intersecting channel network of MFI zeolite, the linear isomer is favored on the basis of entropic considerations. IAST is able to anticipate entropy-driven selectivity reversals but the IAST estimates of selectivities are not of adequate accuracy if there is nonuniform distribution of guest molecules in the pore space.

**ASSOCIATED CONTENT**

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01051. Detailed structural information on all of the zeolites and MOFs analyzed and discussed in the article; details of the IAST and RAST methodologies and calculations for mixture adsorption equilibria, selectivities, and activity coefficients; and input data on unary isotherm fits for the wide variety of guest/host combinations examined in this article (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge the constructive remarks and suggestions of the reviewers.

**NOMENCLATURE**

Latin Alphabet

- $A$, surface area per kg of framework, m² kg⁻¹;
- $C$, constant used in eq 12, kg mol⁻¹;
- $f_p$, partial fugacity of species $i$, Pa;
- $f_o$, total fugacity of the bulk fluid mixture, Pa;
- $G_{\text{exc}}$, excess Gibbs free energy, J mol⁻¹;
- $n$, number of species in the mixture, dimensionless;
- $p_p$, partial pressure of species $i$, Pa;
- $p_s$, total system pressure, Pa;
- $P_i$, sorption pressure, Pa;
- $q_o$, molar loading of species $i$, mol kg⁻¹;
- $q_m$, total molar loading of the mixture, mol kg⁻¹;
- $R$, gas constant, 8.314 J mol⁻¹ K⁻¹;
- $S_{\text{ads}}$, adsorption selectivity, dimensionless;
- $T$, absolute temperature, K;
- $x_o$, mole fraction of species $i$ in the adsorbed phase, dimensionless;
- $y_o$, mole fraction of species $i$ in the bulk fluid mixture, dimensionless

Greek Alphabet

- $\alpha$, activity coefficient of component $i$ in the adsorbed phase, dimensionless;
- $\Lambda$, Wilson parameters, dimensionless;
- $\mu$, molar chemical potential, J mol⁻¹;
- $\gamma$, spreading pressure, N m⁻¹

**REFERENCES**


