Elucidation of Selectivity Reversals for Binary Mixture Adsorption in Microporous Adsorbents

Krishna, R.; van Baten, J.M.

DOI
10.1021/acsomega.0c01051

Publication date
2020

Document Version
Final published version

Published in
ACS Omega

License
CC BY-NC-ND

Citation for published version (APA):
Krishna, R., & van Baten, J. M. (2020). Elucidation of Selectivity Reversals for Binary Mixture Adsorption in Microporous Adsorbents. ACS Omega, 5(15), 9031-9040. https://doi.org/10.1021/acsomega.0c01051

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)

Download date: 16 Jan 2022
Elucidation of Selectivity Reversals for Binary Mixture Adsorption in Microporous Adsorbents

Rajamani Krishna* and Jasper M. van Baten

ABSTRACT: The adsorption selectivity, $S_{\text{ads}}$, 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 $S_{\text{ads}}$ using unary isotherm data inputs. In a number of experimental investigations, the phenomena of selectivity reversals and adsorption azeotropy ($S_{\text{ads}} = 1$) 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, $S_{\text{ads}}$, defined by

$$S_{\text{ads}} = \frac{q_1}{q_2} \frac{f_1}{f_2}$$

(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 $S_{\text{ads}}$ 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 $S_{\text{ads}}$ 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 and p-xylene/1-butanol 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 polarization 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, 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

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

(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\(^{-1}\). 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, the partial fugacities in the bulk fluid mixture are related to the mole fractions \(x_i\) in the adsorbed phase mixture

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

(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

\[
\frac{\pi A}{RT} = \int_{0}^{P_i^0} \frac{q_i^0(f)}{f} \, df = \int_{0}^{P_f^0} \frac{f}{q_i^0(f)} \, df = \int_{0}^{P_i^0} \frac{q_i^0(f)}{f} \, df = \ldots
\]  

(6)

In eq 6, \(q_i^0(f)\) 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
limits of integration must yield the same value of $\pi A/RT$ for each component; this ensures that the obtained solution is the correct one.

The adsorbed phase mole fractions $x_i$ are then determined from

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

(7)

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

$$S_{ads} = \frac{x_i f_i}{x_2 f_2} = \frac{P_i^0}{P_2^0} \quad i = 1, 2$$

(8)

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

2.2. CO$_2$/C$_3$H$_8$ Mixture Adsorption in Mordenite. Talu and Zwiebel$^{20}$ report two sets of experimental data for adsorption of CO$_2$/C$_3$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 CO$_2$(1)/C$_3$H$_8$(2) mixture adsorption as a function of the mole fraction of CO$_2$ in the bulk gas phase, $y_1$; the total gas phase pressure $p_1 = p_1 + p_2 = 41$ kPa. For $y_1 < 0.6$, the selectivity is in favor of CO$_2$(1), whereas for bulk gas phase mole fractions $y_1 > 0.6$, $S_{ads} < 1$ and the mixture adsorption is C$_3$H$_8$-selective. The experimental data clearly show the phenomenon of azeotropy, $S_{ads} = 1$, at $y_1 \approx 0.6$. IAST estimations using the unary isotherm data (indicated by the dashed lines) do not anticipate selectivity reversal phenomena, and the adsorption is anticipated to be CO$_2$-selective over the entire composition range.

Figure 2b presents the data on $S_{ ads}$ for 17/83 CO$_2$(1)/C$_3$H$_8$(2) mixture adsorption in H-MOR in which the total gas phase pressure $p_1 = p_1 + p_2 = 41$ kPa. 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

$$\ln(\gamma_i) = \left(1 - \ln(x_i \Lambda_{11} + x_2 \Lambda_{12}) - \frac{x_i \Lambda_{11}}{x_1 \Lambda_{11} + x_2 \Lambda_{12}} \right) - \frac{x_2 \Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \left(1 - \exp\left(-C \frac{\pi A}{RT}\right)\right)$$

$$\ln(\gamma_2) = \left(1 - \ln(x_1 \Lambda_{11} + x_2 \Lambda_{12}) - \frac{x_1 \Lambda_{12}}{x_1 \Lambda_{11} + x_2 \Lambda_{12}} \right) - \frac{x_2 \Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \left(1 - \exp\left(-C \frac{\pi A}{RT}\right)\right)$$

(12)

In eq 12, $\Lambda_{11} = 1$; $\Lambda_{12} = 1$ and C is a constant with the unit kg mol$^{-1}$. The choice of $\Lambda_{12} = \Lambda_{21} = 1$ 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 $\left(1 - \exp\left(-\frac{\pi A}{RT}\right)\right)$ imparts the correct limiting behaviors $\gamma_i \to 1$; $\pi A/RT \to 0$ for the activity coefficients in the Henry regime, $p_i \to 0$; $\pi A/RT \to 0$. As pore saturation conditions are approached, this correction factor tends to unity $\left(1 - \exp\left(-\frac{C x_i}{RT}\right)\right) \to 1$.13 The experimental data for CO$_2$/C$_3$H$_8$ mixture adsorption in H-MOR are well-matched by the choice of the Wilson parameters $\Lambda_{12} = 4.2$; $\Lambda_{21} = 6.5$; $C = 1$ mol kg$^{-1}$, as evidenced by the RAST calculations represented by the solid black lines in Figure 3a. The RAST calculations of the activity coefficients are plotted in Figure 3b as a function of the mole fraction of CO$_2$ in the adsorbed phase. It is evident that both components are nearly equally influenced by thermodynamic nonidealities. The Wilson model must be viewed as providing a thermodynamically consistent approach to quantify the departures from the IAST estimates.

Having established the need to introduce activity coefficients in the description of mixture adsorption, the next step is to gain insights into the origins of nonidealities by resorting to CBMC simulations. Figure 4a presents CBMC simulation data for CO$_2$(1)/C$_3$H$_8$(2) mixture adsorption in MOR zeolite at 300 K and total fugacity $f_t = 40$ kPa, as a function of the mole fraction of CO$_2$ in the bulk gas phase, $y_1$. For $y_1 < 0.2$, $S_{ads} > 1$ and the selectivity is in favor of CO$_2$. 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 CO$_2$ in the bulk gas phase. Computational snapshots are shown in Figure 4b. CO$_2$ gets preferentially ensconced in the side pockets, but when the side pockets are fully occupied, the CO$_2$ can also locate in the 12-ring 1D channels. The C$_3$H$_8$ 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 C$_3$H$_8$ molecules compete with all of the CO$_2$, making no allowance for segregation. Because of segregation effects, the competition faced by C$_3$H$_8$ molecules within the 12-ring channels, where C$_3$H$_8$ exclusively resides, is smaller than that in the entire pore space. IAST anticipates a stiffer competition between CO$_2$ and C$_3$H$_8$ 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 CO$_2$ from gaseous mixtures, cage-type zeolites such as DDR, CHA, LTA, and ERI are of practical interest.4,30,38−40 These materials consist of cages separated by 8-ring windows in the 3.3−4.5 Å range. For adsorption of CO$_2$/CH$_4$ mixtures, published CBMC simulations41 show that the
window regions of cage-type zeolites have a significantly higher proportion of CO$_2$ than within the cages. For all four zeolites, CO$_2$ has the highest probability, about 30–40%, of locating in the window regions. As illustration, Figures 5a and 6a present computational snapshots for the location of CO$_2$ and CH$_4$ in DDR and CHA zeolites.

![Computational snapshot showing the location of CO$_2$ and CH$_4$ within the cage/window structure of DDR zeolite.](image)

**Figure 5.** (a) Computational snapshot showing the location of CO$_2$ and CH$_4$ within the cage/window structure of DDR zeolite. (b) CBMC simulations of the adsorption selectivity, $S_{ads}$, for CO$_2$(1)/CH$_4$(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 $y_1 = y_2 = 0.5$, and the mixture fugacity $f_t = f_1 + f_2$ is varied, and (ii) the total bulk gas mixture fugacity is held constant, $f_t = f_1 + f_2 = 10^6$ Pa, and the mole fraction of CO$_2$ in the bulk gas mixture, $y_1$, is varied. Both data sets are plotted as a function of the adsorption potential $\pi A/RT$. The dashed lines are the IAST calculations; all calculation details and input data are provided in the Supporting Information accompanying this publication.

![Computational snapshot showing the location of CO$_2$ and CH$_4$ within the cage/window structure of CHA zeolite.](image)

**Figure 6.** (a) Computational snapshot showing the location of CO$_2$ and CH$_4$ within the cage/window structure of CHA zeolite. (b) CBMC simulations of the adsorption selectivity, $S_{ads}$, for CO$_2$(1)/CH$_4$(2) mixture adsorption in all-silica CHA zeolite at 300 K. Two sets of simulation data are presented: (i) the bulk gas phase mole fractions are maintained at $y_1 = y_2 = 0.5$, and the mixture fugacity $f_t = f_1 + f_2$ is varied, and (ii) the total bulk gas mixture fugacity is held constant, $f_t = f_1 + f_2 = 10^6$ Pa, and the mole fraction of CO$_2$ in the bulk gas mixture, $y_1$, is varied. Both data sets are plotted as a function of the adsorption potential $\pi A/RT$. The dashed lines are the IAST 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 CO$_2$(1)/CH$_4$(2) mixtures in DDR zeolite that consists of cages of 277.8 Å$^3$ 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 $y_1 = y_2 = 0.5$, and mixture fugacity $f_t = f_1 + f_2$ is varied, and (ii) the total bulk gas mixture fugacity is held constant, $f_t = f_1 + f_2 = 10^6$ Pa, and the mole fraction of CO$_2$ in the bulk gas mixture, $y_1$, is varied. Both CBMC data sets on $S_{ads}$ are plotted as a function of the adsorption potential $\pi A/RT$. The IAST calculations (shown by the dashed line) anticipate that $S_{ads}$ is uniquely determined by $\pi A/RT$, whereas the CBMC data show that the two data sets for $S_{ads}$ do not coincide when plotted against $\pi A/RT$. Furthermore, IAST significantly overestimates the $S_{ads}$ values at $\pi A/RT > 5$ mol kg$^{-1}$. The IAST calculation assumes that CH$_4$ molecules compete with all of the CO$_2$ molecules, making no allowance for segregation. Because of segregation effects, the competition faced by CH$_4$ 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 $\Lambda_{12} = 0.81$; $\Lambda_{11} = 3$; $C = 0.34$ mol kg$^{-1}$, as evidenced by the RAST calculations indicated by the continuous solid lines in Figure 5b.
The corresponding CBMC simulation data for CO₂/CH₄ mixture adsorption in CHA zeolite that consists of cages of volume 316 Å³ separated by 3.8 Å × 4.2 Å; 8-ring windows are presented in Figure 6b. Because of segregation effects, IAST overestimates the S_ads values for πA/RT > 0.5 mol kg⁻¹. Figure 7 shows snapshots of the location of CO₂ and C₃H₈ molecules within the pore topology of LTA-4A zeolite that consists of cages of 743 Å³ volume separated by 4.11 Å × 4.47 Å; 8-ring windows. We note that the CO₂ is almost exclusively located at the windows or near the window entrance regions. Because of configurational restraints, C₃H₈ can only be located at the cage interiors. Consequently, the competition between the adsorption of CO₂ and C₃H₈ 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 CO₂(1)/C₃H₈(2) mixture adsorption in LTA-4A zeolite at 300 K. The CBMC simulations for CO₂(1)/C₃H₈(2) mixture adsorption in LTA-4A zeolite at f₁ = 1 MPa and varying mole fractions of CO₂(1) in the bulk gas phase, y₁, are shown in Figure 8a. For y₁ < 0.1, S_ads > 1, and the selectivity is in favor of CO₂. The CBMC simulations 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; IAST anticipates S_ads to be virtually independent of y₁. 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 CO₂/C₂H₆ mixture adsorption in LTA-5A reported by Basmajian and Hsieh¹⁸ and plotted in Figure 1. Such selectivity reversals are also experienced in the transient breakthrough experiments reported by van Zandvoort et al.¹⁵,¹⁶

The CBMC simulations for CO₂/C₃H₈ mixture adsorption in LTA-4A zeolite in which the mole fraction of CO₂ in the bulk gas phase is held constant, y₁ = 0.1, and the bulk gas phase fugacity f₁ = f₁ + f₂ was varied are shown by the square symbols in Figure 8b. For πA/RT < 25 mol kg⁻¹, the selectivity is in favor of C₃H₈ with increasing values of the adsorption potential πA/RT > 25 mol kg⁻¹. The adsorption selectivity S_ads switches in favor of CO₂ because of strong Coulombic interactions with the extra-framework cations Na⁺. IAST does not anticipate this selectivity reversal in favor of CO₂. The CBMC simulations can be matched by quantification of thermodynamic nonidealities using the Wilson parameters Λ₁₂ = 1; Λ₂₁ = 5.65; C = 0.1 mol kg⁻¹; see RAST calculations indicated by continuous solid lines in Figure 8a.b.

The experimental data of Costa et al.¹⁹ for CO₂/C₃H₈ mixture adsorption in NaX zeolite, which consists of cages of 786 Å³ volume separated by 7.3 Å; 12-ring windows, demonstrate the selectivity reversal in favor of the saturated alkane at high mole fractions of CO₂ in the bulk gas mixture: see Figure 1. Most likely, this selectivity reversal is caused by the inhomogeneous distribution of guest molecules, with CO₂ congregating around the cations: see the computational snapshot in Figure 9. We note that the bottom cage contains only CO₂ and there is no C₃H₈ present in that cage, underscoring the fact that the distribution of adsorbates is not uniform within the pore space. The competition faced by C₃H₈ in the entire pore space is effectively reduced, and this engenders a reversal in selectivity in favor of
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 πA/RT < 30 mol kg⁻¹, the adsorption selectivity is strongly in favor of the longer 1-propanol molecule that has the higher binding strength. However, πA/RT > 30 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 the alkane; for detailed analyses, see Figures S53 and S54 of the Supporting Information.

Figure 9. Computational snapshots showing the location of CO₂ and C₃H₈ within the cages of NaX zeolite at 300 K and partial fugacities are f₁ = f₂ = 0.5 MPa.

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_{ads}, plotted as a function of the adsorption potential πA/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 $\pi/RT > 20 \text{ mol kg}^{-1}$. 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 $\pi/RT$ 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, CO$_2$ locates preferentially in the side pockets of MOR 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.
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 $\alpha A/RT$. 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**

**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)

**AUTHOR INFORMATION**

**Corresponding Author**

Rajamani Krishna — Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands; orcid.org/0000-0002-4784-8530; Email: r.krishna@contact.uva.nl

**Author**

Jasper M. van Baten — Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c01051

**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, m$^2$ kg$^{-1}$; $C$, constant used in eq $^{12}$, kg mol$^{-1}$; $f_p$ partial fugacity of species i, Pa; $f_t$, total fugacity of the bulk fluid mixture, Pa; $G^{excess}$ excess Gibbs free energy, J mol$^{-1}$; $n$, number of species in the mixture, dimensionless; $p_i$, partial pressure of species i, Pa; $p_t$, total system pressure, Pa; $P_i^*$, sorption pressure, Pa; $q_i$, molar loading of species i, mol kg$^{-1}$; $q_t$, total molar loading of the mixture, mol kg$^{-1}$; $R$, gas constant, 8.314 J mol$^{-1}$ K$^{-1}$; $S_{ads}$, adsorption selectivity, dimensionless; $T$, absolute temperature, K; $x_i$, mole fraction of species i in the adsorbed phase, dimensionless; $y_i$, mole fraction of species i in the bulk fluid mixture, dimensionless

**Greek Alphabet**

$\gamma$, activity coefficient of component i in the adsorbed phase, dimensionless; $\Lambda_a$, Wilson parameters, dimensionless; $\mu_i$, molar chemical potential, J mol$^{-1}$; $\sigma_i$, spreading pressure, N m$^{-1}$

**REFERENCES**

(1) Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M. J.; Chen, B. Pore Chemistry and Size Control in Hybrid Porous Materials for Acetylene Capture from Ethylene. Science 2016, 353, 141–144.

(2) Cadiau, A.; Adil, K.; Bhatt, P. M.; Belmahbouk, Y.; Eddaoudi, M. A Metal-Organic Framework—Based Splitter for Separating Propylene from Propane. Science 2016, 353, 137–140.

(3) Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. Hydrocarbon Separations in a Metal-Organic Framework with Open Iron(I) Coordination Sites. Science 2012, 335, 1606–1610.

(4) Krishna, R. Methodologies for Screening and Selection of Crystalline Microporous Materials in Mixture Separations. Sep. Purif. Technol. 2018, 194, 281–300.

(5) Krishna, R. Methodologies for Evaluation of Metal-Organic Frameworks in Separation Applications. RSC Adv. 2015, 5, 52269–52295.

(6) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. Microporous Metal-Organic Framework with Potential for Carbon Dioxide Capture at Ambient Conditions. Nat. Commun. 2012, 3, 954.

(7) Ruthven, D. M. Principles of Adsorption and Adsorption Processes; John Wiley: New York, 1984.

(8) Yang, R. T. Gas Separation by Adsorption Processes; Butterworth: Boston, 1987.

(9) Yang, R. T. Adsorbents: Fundamentals and Applications; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2003.

(10) Krishna, R. Highlighting the Influence of Thermodynamic Coupling on Kinetic Separations with Microporous Crystalline Materials. ACS Omega 2019, 4, 3409–3419.

(11) Krishna, R. Screening Metal-Organic Frameworks for Mixture Separations in Fixed-Bed Adsorbers using a Combined Selectivity/ Capacity Metric. RSC Adv. 2017, 7, 35724–35737.

(12) Ruthven, D. M.; Farooq, S.; Knaebel, K. S. Pressure Swing Adsorption; VCH Publishers: New York, 1994.

(13) Krishna, R.; van Baten, J. M.; Baur, R. Highlighting the Origins and Consequences of Thermodynamic Nonidealities in Mixture Separations using Zeolites and Metal-Organic Frameworks. Microporous Mesoporous Mater. 2018, 267, 274–292.

(14) Krishna, R.; Van Baten, J. M. Investigating the Non-idealities in Adsorption of CO$_2$-bearing Mixtures in Cation-exchanged Zeolites. Sep. Purif. Technol. 2018, 206, 208–217.

(15) van Zandvoort, I.; Ras, E.-J.; Graaf, R. d.; Krishna, R. Using Transient Breakthrough Experiments for Screening of Adsorbents for Separation of C$_2$H$_4$/CO$_2$ Mixtures. Sep. Purif. Technol. 2020, 241, 116706.

(16) van Zandvoort, I.; van der Waal, J. K.; Ras, E.-J.; de Graaf, R.; Krishna, R. Highlighting non-idealities in C$_2$H$_4$/CO$_2$ mixture adsorption in SA zeolite. Sep. Purif. Technol. 2019, 227, 115730.

(17) Ritter, J. A.; Bhadra, S. J.; Ehner, A. D. On the Use of the Dual-Process Langmuir Model for Correlating Unary Equilibria and Predicting Mixed-Gas Adsorption Equilibria. Langmuir 2011, 27, 4700–4712.

(18) Basmdjian, D.; Hsieh, S. T. Isothermal Column Sorption of Ethylene-Carbon Dioxide Mixtures with Azeotropic Behaviour. Can. J. Chem. Eng. 1980, 58, 185–189.

(19) Costa, E.; Calleja, G.; Jimenez, A.; Pau, J. Adsorption Equilibrium of Ethylene, Propylene, Carbon Dioxide, and Their Mixtures in 13X Zeolite. J. Chem. Eng. Data 1991, 36, 218–224.

(20) Tu, O.; Zwiebel, I. Multicomponent Adsorption Equilibria of Nonideal Mixtures. AIChE J. 1986, 32, 1263–1276.
(21) Calleja, G.; Pau, J.; Calles, J. A. Pure and Multicomponent Adsorption Equilibria of Carbon Dioxide, Ethylene, and Propane on ZSM-5 Zeolites with Different Si/Al Ratios. J. Chem. Eng. Data 1998, 43, 994—1003.
(22) Sakuth, M.; Meyer, J.; Gmehling, J. Vapor Phase Adsorption Equilibria of Toluene + 1-Propanol Mixtures on Y-Zeolites with Different Silicon to Aluminum Ratios. J. Chem. Eng. Data 1995, 40, 895—899.
(23) Takeuchi, Y.; Iwamoto, H.; Miyata, N.; Asano, S.; Harada, M. Adsorption of 1-butanol and p-xylene vapor with high silica zeolites. Sep. Technol. 1995, 5, 23—34.
(24) Krishna, R. Separating Mixtures by Exploiting Molecular Packing Effects in Microporous Materials. Phys. Chem. Chem. Phys. 2015, 17, 39—59.
(25) Krishna, R. Elucidation and Characterization of Entropy Effects in Mixture Separations with Micro-porous Crystalline Adsorbents. Sep. Purif. Technol. 2019, 215, 227—241.
(26) Krishna, R.; van Baten, J. M. Commensurate-Incommensurate Adsorption and Diffusion in Ordered Crystalline Microporous Materials. Phys. Chem. Chem. Phys. 2017, 19, 20320—20337.
(27) Remy, T.; Cousin Saint Remi, J.; Singh, R.; Webley, P. A.; Baron, G. V.; Denayer, J. F. M. Adsorption and Separation of C1-C8 Alcohols on SAPO-34. J. Phys. Chem. C 2011, 115, 8117—8125.
(28) Myers, A. L.; Prausnitz, J. M. Thermodynamics of Mixed Gas Adsorption. AIChE J. 1965, 11, 121—127.
(29) Krishna, R.; van Baten, J. M. A comparison of the CO2 capture characteristics of zeolites and metal-organic frameworks. Sep. Purif. Technol. 2012, 87, 120—126.
(30) Krishna, R.; van Baten, J. M. In silico screening of metal-organic frameworks in separation applications. Phys. Chem. Chem. Phys. 2011, 13, 10593—10616.
(31) Frenkel, D.; Smit, B. Understanding Molecular Simulations: From Algorithms to Applications, 2nd ed.; Academic Press: San Diego, 2002.
(32) Smit, B.; Krishna, R. Molecular simulations in zeolitic process design. Chem. Eng. Sci. 2003, 58, 557—568.
(33) Vlugt, 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 1999, 103, 1102—1118.
(34) García-Sánchez, A.; Ania, C. O.; Parra, J. B.; Dubbeldam, D.; Vlugt, T. J. H.; Krishna, R.; Calero, S. Development of a Transferable Force Field for Carbon Dioxide Adsorption in Zeolites. J. Phys. Chem. C 2009, 113, 8814—8820.
(35) Dubbeldam, D.; Calero, S.; Vlugt, T. J. H.; Krishna, R.; Maesen, T. L. M.; Smit, B. United Atom Forcefield for Alkanes in Nanoporous Materials. J. Phys. Chem. B 2004, 108, 12301—12313.
(36) Talu, O.; Myers, A. L. Rigorous Thermodynamic Treatment of Gas-Adsorption. AIChE J. 1988, 34, 1887—1893.
(37) Siperstein, F. R.; Myers, A. L. Mixed-Gas Adsorption. AIChE J. 2001, 47, 1141—1159.
(38) Krishna, R.; van Baten, J. M. In Silico Screening of Zeolite Membranes for CO2 Capture. J. Membr. Sci. 2010, 360, 323—333.
(39) Krishna, R.; van Baten, J. M. A molecular dynamics investigation of the diffusion characteristics of cavity-type zeolites with 8-ring windows. Microporous Mesoporous Mater. 2011, 137, 83—91.
(40) Krishna, R.; van Baten, J. M. Using Molecular Dynamics Simulations for Elucidation of Molecular Traffic in Ordered Crystalline Microporous Materials. Microporous Mesoporous Mater. 2018, 258, 151—169.
(41) Krishna, R.; van Baten, J. M. Segregation effects in adsorption of CO2 containing mixtures and their consequences for separation selectivities in cage-type zeolites. Sep. Purif. Technol. 2008, 61, 414—423.
(42) Gutiérrez-Sevillano, J. J.; Calero, S.; Krishna, R. Selective Adsorption of Water from Mixtures with 1-Alcohols by Exploitation of Molecular Packing Effects in CuBTC. J. Phys. Chem. C 2015, 119, 3658—3666.
(43) Gutiérrez-Sevillano, J. J.; Calero, S.; Krishna, R. Separation of Benzene from Mixtures with Water, Methanol, Ethanol, and Acetone: Highlighting Hydrogen Bonding and Molecular Clustering Influences in CuBTC. Phys. Chem. Chem. Phys. 2015, 17, 20114—20124.