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

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Using Molecular Simulations for Elucidation of Thermodynamic Nonidealities in Adsorption of CO$_2$-Containing Mixtures in NaX Zeolite

Rajamani Krishna* and Jasper M. van Baten

ABSTRACT: Cation-exchanged zeolites are of potential use in pressure swing adsorption (PSA) technologies for CO$_2$ capture applications. Published experimental data for CO$_2$/CH$_4$, CO$_2$/N$_2$, and CO$_2$/C$_3$H$_8$ mixture adsorption in NaX zeolite, also commonly referred to by its trade name 13X, have demonstrated that the ideal adsorbed solution theory (IAST) fails to provide adequately accurate estimates of mixture adsorption equilibrium. In particular, the IAST estimates of CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivities are significantly higher than those realized in experiments. For CO$_2$/C$_3$H$_8$ mixtures, the IAST fails to anticipate the selectivity reversal phenomena observed in experiments. In this article, configurational-bias Monte Carlo (CBMC) simulations are employed to provide confirmation of the observed thermodynamic nonidealities in adsorption of CO$_2$/CH$_4$, CO$_2$/N$_2$, and CO$_2$/C$_3$H$_8$ mixtures in NaX zeolite. The CBMC simulations provide valuable insights into the root cause of the failure of the IAST, whose applicability mandates a homogeneous distribution of adsorbates within the pore landscape. By sampling $10^5$ equilibrated spatial locations of individual guest molecules within the cages of NaX zeolite, the radial distribution functions (RDFs) of each of the pairs of guest molecules are determined. Examination of the RDFs clearly reveals congregation effects, wherein the CO$_2$ guests occupy positions in close proximity to the Na$^+$ cations. The positioning of the partner molecules (CH$_4$, N$_2$, or C$_3$H$_8$) is further removed from the CO$_2$ guest molecules; consequently, the competition in mixture adsorption faced by the partner molecules is less severe than that anticipated by the IAST. The important message to emerge from this article is the need for quantification of thermodynamic nonideality effects in mixture adsorption.

1. INTRODUCTION

In current industrial practice, amine absorption technologies, which are energy intensive, are used for capture of CO$_2$ from a variety of gaseous mixtures. Potential reduction in the energy consumption is achievable using pressure swing adsorption (PSA) processes, which are normally conducted in fixed-bed adsorbers. A variety of microporous crystalline adsorbents such as zeolites and metal−organic frameworks (MOFs) can be employed in fixed-bed devices. For postcombustion CO$_2$ capture, 13X zeolite is considered to be the benchmark adsorbent, with the ability to meet the U.S. Department of Energy (US-DOE) targets for CO$_2$ purity and recovery. The commercially available 13X, a Na$^+$ cation-exchanged faujasite (FAU) zeolite with Si/Al $\approx$ 1.2, has wider applicability in natural gas purification and alkane/alkene separations.

For the design and development of PSA technologies, reliable procedures are required for the calculation of mixture adsorption equilibrium. For a microporous crystalline adsorbent with surface area $A$, we consider $n$-component adsorption equilibrium between a bulk fluid phase mixture with partial fugacities $f_i$ and an adsorbed phase with component molar loadings $q_i$. The requirement of thermodynamic equilibrium demands equality of the chemical potentials of each component, $\mu_i$, in the adsorbed phase and the bulk fluid phase

$$\mu_i = RT \ln f_i \quad i = 1, 2, ..., n \tag{1}$$

The Gibbs adsorption equation$^{14-17}$ relates the spreading pressure $\pi$ to the chemical potentials $\mu_i$ by the differential expression

$$Ad \pi = \sum_{i=1}^{n} q_i d\mu_i \tag{2}$$

In the ideal adsorbed solution theory (IAST),$^{14}$ the partial fugacities $f_i$ are related to the mole fractions $x_i$ in the adsorbed phase mixture

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\[ x_i = q_i / q_i^0; \quad q_i = q_1 + q_2 + \cdots + q_n; \quad i = 1, 2, \ldots, n \]  

3

by introducing the sorption pressures, \( P_i^0 \), and invoking an analogy to Raoult’s law for vapor–liquid equilibrium

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

4

If \( q_i^0(f) \) represents the pure component adsorption isotherms for each guest constituent in the mixture, the sorption pressures \( P_i^0 \) for each component in the mixture must satisfy the constraint

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

5

An equation solver is required to determine the set of \( n \) values \( P_i^0 \). When \( P_i^0 \) are used as the upper limits in the definite integrals in eq 5, these result in the same value of the adsorption potential \( \pi A/RT \), which serves as a practical proxy for the spreading pressure \( \pi \). The adsorbed phase mole fractions \( x_i \) are then determined from

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

6

A number of experimental investigations\textsuperscript{2,16–26} for adsorption of \( CO_2 \)-containing binary mixtures in cation-exchanged zeolites demonstrate that the IAST does not provide quantitatively accurate estimates of component loadings and adsorption selectivities, \( S_{ads} \), defined by

\[ S_{ads} = \frac{q_i / q_j}{f_i / f_j} \]  

7

As an illustration, Figure 1a presents the experimental data of Wilkins and Rajendran\textsuperscript{7} for component loadings, \( q_i \) of \( CO_2 \) and \( N_2 \) for adsorption of \( CO_2/N_2 \) mixtures in 13X zeolite at 296 K and total pressure \( p_t = 97 \, kPa \) as a function of the mole fraction of \( CO_2 \) in the bulk gas phase, \( y_1 \). The dashed lines are the IAST estimations using the experimental data on the unary isotherms. The IAST estimations of the component loadings for \( N_2 \) are not in good agreement with the experimental data.

Figure 1b plots the experimental data on the \( CO_2/N_2 \) adsorption selectivity as a function of the mole fraction of \( CO_2 \) in the bulk gas phase. The IAST severely overestimates the values of \( S_{ads} \).

Gholipour and Mofarahi\textsuperscript{19} reported the results of a comprehensive experimental investigation of adsorption equilibrium of \( CO_2/CH_4 \) mixture adsorption in 13X zeolite; Figure 2a presents a plot of the \( CO_2/CH_4 \) adsorption selectivity as a function of the mole fraction of \( CO_2 \) in the bulk gas mixture. As compared to the experimental data, the IAST overpredicts the selectivity values to a significant extent.

For adsorption of \( CO_2/C_3H_8 \) mixtures in 13X zeolite, the experimental data of Costa et al.\textsuperscript{20} show selectivity reversal in favor of \( C_3H_8 \) when the mole fraction of \( CO_2 \) in the bulk gas phase, \( y_1 \), > 0.8; see Figure 2b. The phenomena of selectivity reversal are not anticipated by the IAST, which expects \( S_{ads} > 1 \) over the entire composition range.

The primary objective of this article is to gain some insights into the reasons for the failure of the IAST to match the experimental data, such as that illustrated in Figures 1 and 2. Toward this end, configurational-bias Monte Carlo (CBMC) simulations for adsorption of \( CO_2/N_2 \), \( CO_2/CH_4 \), and \( CO_2/C_3H_8 \) mixtures in NaX zeolite (per unit cell: 106 Si, 86 Al, and 86 Na\textsuperscript{+} with Si/Al = 1.23) are performed using the simulation methodology that is firmly established in the literature\textsuperscript{3,10,27–29}.

The force field information are taken from Garcia-Sánchez et al.\textsuperscript{30} and Dubbeldam et al.\textsuperscript{31} The Supporting Information accompanying this publication provides (a) details of the CBMC simulation methodology, (b) unary isotherm fits for all of the guest/host combinations, (c) details of the IAST and real adsorbed solution theory (RAST) calculations for mixture adsorption equilibrium, and (d) Wilson parameter fits for thermodynamic nonidealities.

2. CBMC SIMULATION RESULTS AND DISCUSSION

2.1. \( CO_2/N_2 \), \( CO_2/CH_4 \), and \( CO_2/C_3H_8 \) Mixture Adsorption in NaX. Figure 3a presents the CBMC simulation data of component loadings, \( q_i \) of \( CO_2 \) and \( N_2 \) for adsorption of \( CO_2/N_2 \) mixtures in NaX zeolite at 300 K and total gas-phase fugacity \( f_i = f_1 + f_2 = 100 \, kPa \), plotted as a function of the mole fraction of \( CO_2 \) in the bulk gas phase, \( y_1 \). The IAST estimations of the component loadings for \( N_2 \) are not in good agreement with the CBMC mixture simulations. Figure 3b plots the CBMC data on the \( CO_2/N_2 \) adsorption selectivity as a function of the mole fraction of \( CO_2 \) in the bulk gas phase.
IAST severely overestimates the adsorption selectivity, in qualitative agreement with the experimental data in Figure 1. Figure 4a,b presents the corresponding CBMC simulation data for adsorption of CO$_2$/CH$_4$ mixtures in NaX zeolite at 300 K and total gas phase fugacity $f_t = f_1 + f_2 = 100$ kPa. The IAST overestimates the adsorption selectivity, in qualitative agreement with the experimental data in Figure 2a.

For adsorption of CO$_2$/C$_3$H$_8$ mixtures in NaX zeolite, CBMC simulation data for the adsorption selectivities are plotted in Figure 5 for two different total gas-phase fugacities $f_1 = 50$ kPa and $f_1 = 1$ MPa. The CBMC data for $f_1 = 50$ kPa display selectivity reversals in favor of the saturated alkane for $y_1 > 0.8$, in agreement with the experimental data of Costa et al. The IAST calculations, shown by the dashed lines, are in poor agreement with the CBMC data and do not anticipate the selectivity reversal phenomena.

The failure of the IAST to provide a quantitative description of mixture adsorption in NaX zeolite is traceable to the use of Raoult’s law analogue, eq 4, whose applicability mandates that all of the adsorption sites within the microporous material are equally accessible to each of the guest molecules, implying a homogeneous distribution of guest adsorbates within the pore landscape, with no preferential locations of any guest species. To test this requirement, CBMC simulation data on the spatial locations of the guest molecules were sampled to determine the intermolecular distances. By sampling a total of $10^5$ equilibrated simulation steps, the radial distribution of the separation distances between the various molecular pairs was determined for CO$_2$/N$_2$, CO$_2$/CH$_4$, and CO$_2$/C$_3$H$_8$ mixtures. The data on the radial distribution functions (RDFs) are presented in Figure 6a-c. If we compare the first peaks, it is noteworthy that for all three mixtures, the CO$_2$−CO$_2$ and CO$_2$−Na$^+$ pairs are close together, indicating that the major proportion of CO$_2$ congregates around the cations. A further point to note is that the CO$_2$−N$_2$, CO$_2$−CH$_4$, and CO$_2$−C$_3$H$_8$ separation distances are significantly larger than the corresponding CO$_2$−CO$_2$ separation distances. This implies that the partner molecules, N$_2$, CH$_4$, and C$_3$H$_8$, endure less severe competitive adsorption with CO$_2$ than that anticipated by the IAST; as a consequence, the IAST overestimates the values of $S_{ab}$.

A visual appreciation of the congregation of CO$_2$ around the cations can be gained from the snapshots for CO$_2$/CH$_4$ Figure 2. Comparison of experimental data on the adsorption selectivity with IAST estimates for (a) CO$_2$/CH$_4$ in 13X zeolite at $T = 303$ K and $p_t = 0.6$ MPa and (b) CO$_2$/C$_3$H$_8$ in 13X zeolite at $T = 293$ K and $p_t = 50$ kPa. The $x$-axis represents the mole fraction of CO$_2$ in the bulk gas phase, maintained at constant total pressure, $p_t$, and temperature, $T$. All calculation details and input data are provided in the Supporting Information accompanying this publication.

Figure 3. (a) CBMC simulation data (indicated by symbols) for component loadings, $q_i$, of CO$_2$ and N$_2$ for adsorption of CO$_2$/N$_2$ mixtures in NaX zeolite (106 Si, 86 Al, 86 Na$^+$, Si/Al = 1.23) at 300 K and total fugacity $f_t = 100$ kPa as a function of the mole fraction of CO$_2$ in the bulk gas phase, $y_1$. (b) CO$_2$/N$_2$ adsorption selectivity as a function of the mole fraction of CO$_2$ in the bulk gas phase. IAST (dashed lines) and RAST calculations (continuous solid lines) are also shown. All calculation details and input data are provided in the Supporting Information accompanying this publication.
mixture presented in Figure 7. It is also noteworthy that the CH$_4$ are further removed from the CO$_2$ guests. Since the primary reason for the congregation of CO$_2$ molecules is the presence of cations, we should expect that for mixture adsorption in all-silica zeolites without extra-framework cations (i.e., with Si/Al $\to \infty$), there would be no congregation or segregation effects. To confirm this expect-
ation, we also examined the radial distribution of adsorbates for CO₂/N₂ and CO₂/CH₄ mixtures in all-silica FAU zeolites; see Figure 8a,b. For both mixtures, the first peaks of the CO₂–CO₂, CO₂–partner, and partner–partner pairs occur at nearly the same separation distances. This indicates that there are no congregation/segregation effects and that the guest molecules are homogeneously distributed within the pore landscape. Such a homogeneous distribution of guest molecules fulfills the requirement of the IAST. Consequently, we should expect the IAST to provide a good quantitative description of CO₂/N₂ and CO₂/CH₄ mixture adsorption in all-silica zeolites. To confirm this expectation, we performed CBMC simulations for adsorption of 15/85 CO₂/N₂ and 50/50 CO₂/CH₄ mixtures in all-silica FAU, in which the total fugacity of the bulk gas phase mixture \( f_t = f_1 + f_2 \) is varied from 10² Pa to 10⁷ Pa. Figure 9a,b compares the CBMC simulated values of the adsorption selectivities with the corresponding IAST calculations; there is excellent agreement between the two data sets. In sharp contrast, the IAST calculations severely overpredict the adsorption selectivities for both mixtures in NaX zeolite. Evidence of inhomogeneous distribution of adsorbates in other zeolites such as LTA-4A and DDR is provided in Figures S29-S33 of the Supporting Information.

2.2. Modeling Nonidealities for Mixture Adsorption.

For quantitative modeling of nonideality effects in mixture adsorption arising out of congregation/segregation effects, we need to introduce activity coefficients \( \gamma_i \) in eq (4).
The implementation of the activity coefficients is termed as the real adsorbed solution theory (RAST). For parametrization of the activity coefficients, the well-known Wilson model for vapor–liquid equilibria can be adapted for binary mixture adsorption as follows

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

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

The introduction of \(1 - \exp\left(-\frac{C\pi A}{RT}\right)\), where \(C\) is a constant with the unit kg mol\(^{-1}\), imparts the correct limiting behaviors \(\gamma_i \to 1; \frac{\pi A}{RT} \to 0\) for the activity coefficients in the Henry regime, \(f_i \to 0; \frac{\pi A}{RT} \to 0\). The three parameters \(\Lambda_{12}, \Lambda_{21}\), and \(C\) can be determined by fitting experimental or CBMC simulated data sets. For the CBMC simulated data for \(\text{CO}_2(1)/\text{N}_2(2)\) mixture adsorption in \(\text{NaX}\) (cf. Figure 3a), the fitted Wilson parameters are \(\Lambda_{12} = 8.6, \Lambda_{21} = 0.12\), and \(C = 0.025\) mol kg\(^{-1}\); and Figure 10a presents the RAST calculations of the activity coefficients. It is noteworthy that \(\gamma_i\) is practically unity over the entire composition range, implying that congregation effects have practically no influence on \(\text{CO}_2\) adsorption. On the other hand, \(\gamma_1\) shows increasing departure from unity as the molar fraction of \(\text{CO}_2\) in the bulk gas phase, \(y_1\), increases. The inhomogeneous distribution of adsorbates influences the adsorption of \(\text{N}_2\) to a significant extent. Analogous results are obtained for \(\text{CO}_2(1)/\text{CH}_4(2)\) mixture adsorption; see Figure 10b. For \(\text{CO}_2/\text{C}_3\text{H}_8\) mixtures, thermodynamic nonidealities influence the adsorption of both guests, and both \(\gamma_1\) and \(\gamma_2\) have values lower than unity; see Figure 10c.

The RAST calculations of mixture adsorption are shown by the continuous solid lines in Figures 1–4. For \(\text{CO}_2/\text{C}_3\text{H}_8\) mixtures, the RAST calculations in Figure 5 for both \(f_i = 50\) kPa and \(f_i = 1\) MPa are obtained with the same set of fitted Wilson parameters \(\Lambda_{12} = 1.5, \Lambda_{21} = 2.4\), and \(C = 1\) mol kg\(^{-1}\); the selectivity reversal phenomena at \(f_i = 50\) kPa arise “naturally” out of thermodynamic nonidealities.

3. CONCLUSIONS

The failure of the IAST to provide quantitative estimates of component loadings and selectivities for \(\text{CO}_2/\text{CH}_4, \text{CO}_2/\text{N}_2,\) and \(\text{CO}_2/\text{C}_3\text{H}_8\) mixture adsorption in \(\text{NaX}\) zeolite has been investigated and elucidated with the aid of CBMC simulations. CBMC simulations have been used to determine the intermolecular distances for each pair of guest species. The obtained radial distributions reveal that there is congregation of \(\text{CO}_2\) around the extra-framework cations, causing an inhomogeneous distribution of adsorbates in the pore space. Partner molecules such as \(\text{N}_2, \text{CH}_4, \text{C}_3\text{H}_8\) are further removed from the \(\text{CO}_2\) molecules and thereby face less severe competition during mixture adsorption. As a consequence, the IAST generally overestimates the selectivity for adsorption of \(\text{CO}_2\). For \(\text{CO}_2/\text{C}_3\text{H}_8\) mixture adsorption, the inhomogeneous distribution of adsorbates leads to selectivity reversals, which have been established in both experiments (Figure 2b) and simulations (Figure 5).

The important message that emerges from this investigation is the need to incorporate the RAST for quantitative modeling of fixed-bed adsorbers in \(\text{CO}_2\) capture applications.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02730.

Provides (a) structural details of zeolites, (b) details of the CBMC simulation methodology, (c) unary isotherm fits for all of the guest/host combinations, (d) details of the IAST and real adsorbed solution theory (RAST) calculations for mixture adsorption equilibrium, and (d) Wilson parameter fits for thermodynamic nonidealities (PDF)

AUTHOR INFORMATION

Corresponding Author
Rajamani Krishna – Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands; 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/10.1021/acsomega.0c02730

Notes
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NOMENCLATURE

Latin Alphabet
A  surface area per kg of framework, m^2 kg\(^{-1}\)
C  constant used in eq \(^9\), kg mol\(^{-1}\)
f_i  partial fugacity of species \(i\), Pa
f_b  total fugacity of bulk fluid mixture, Pa
n  number of species in the mixture, dimensionless
p_i  partial pressure of species \(i\), Pa
p_s  total system pressure, Pa
p_i^0  sorption pressure, Pa
q_i  molar loading of species \(i\), mol kg\(^{-1}\)
q_b  total molar loading of 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
\(\gamma_i\)  activity coefficient of component \(i\) in the adsorbed phase, dimensionless
\(\Lambda_{ij}\)  Wilson parameters, dimensionless
\(\mu_i\)  molar chemical potential, J mol\(^{-1}\)
\(\pi\)  spreading pressure, N m\(^{-1}\)

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