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# Investigating the non-idealities in adsorption of CO<sub>2</sub>-bearing mixtures in cation-exchanged zeolites

Rajamani Krishna<sup>a,\*</sup>, Jasper M. van Baten<sup>b</sup>

<sup>a</sup> Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, Amsterdam 1098 XH, The Netherlands

<sup>b</sup> AmsterCHEM, Almería, Spain



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## ABSTRACT

Cation-exchanged zeolites have significant potential for capture of CO<sub>2</sub> from a wide variety of mixtures containing N<sub>2</sub>, H<sub>2</sub>, alkanes and alkenes. The strong coulombic interactions of CO<sub>2</sub> with extra-framework cations result in strong binding and selective capture. Published experimental data on mixture adsorption indicate that the Ideal Adsorbed Solution Theory (IAST) fails to provide accurate estimates of mixture adsorption equilibrium. The reasons for the quantitative failure of IAST estimates are investigated with the aid of Configurational-Bias Monte Carlo (CBMC) simulations of mixture adsorption. Computational snapshots indicate that the failure of the IAST is traceable to inhomogeneous distribution of adsorbates within the zeolite framework.

## 1. Introduction

Cation-exchanged zeolites are potent adsorbents for selective capture of CO<sub>2</sub> in natural gas purification, flue gas cleaning, and hydrogen purification processes [1–16]. Coulombic interactions of CO<sub>2</sub> with the extra-framework cations result in strong binding; the binding strength and selectivity can be tuned by appropriate choice of the extra-framework cations, and adjustment of the Si/Al ratios [3,13,17]. For the design and development of CO<sub>2</sub>-capture technologies, that are normally conducted in fixed-bed adsorbents [18–20], the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz [21] is widely used for calculation of mixture adsorption equilibrium [2,8,15,17,22–26].

Briefly, in the IAST, the partial fugacities in the bulk fluid mixture are related to the mole fraction in the adsorbed phase  $x_i = \frac{q_i}{q_1 + q_2}$  by the analogue of Raoult's law for vapor-liquid equilibrium, i.e.  $f_i = P_i^0 x_i$ ;  $i = 1, 2$  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:

$$\frac{\pi A}{RT} = \int_0^{P_1^0} \frac{q_1^0(f)}{f} df = \int_0^{P_2^0} \frac{q_2^0(f)}{f} df \quad (1)$$

The units of  $\frac{\pi A}{RT}$ , also called the adsorption potential [23,27–29], are

mol kg<sup>-1</sup>. If the pure component adsorption  $q_i^0(f)$  isotherm are described by, say, the dual-site Langmuir-Freundlich isotherm  $q^0(f) = q_{A,sat} \frac{b_A f^{v_A}}{1 + b_A f^{v_A}} + q_{B,sat} \frac{b_B f^{v_B}}{1 + b_B f^{v_B}}$ , each of the integrals in Eq. (1) can be evaluated analytically. For specified partial fugacities in the bulk fluid phase,  $f_i$ , these constraints may be solved simultaneously, to yield the set of values of the adsorbed phase mole fractions,  $x_i$ , and  $P_i^0$ , all of which must satisfy Eq. (1). The corresponding values of the integrals using these values of  $P_i^0$  as upper limits of integration must yield the same value of  $\frac{\pi A}{RT}$  for each component.

A number of experimental data on mixture adsorption equilibrium reveal the IAST does not provide accurate estimates of component loadings, and adsorption selectivities, especially for operations at high guest occupancies [27,29]. As illustration, Fig. 1a,b,c present comparisons of experimental data on adsorption selectivity with IAST estimates for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> mixtures in NaX (trade name = 13X) and LTA-5A zeolites. The IAST selectivity estimates are about an order of magnitude higher than those determined experimentally. The experimental data for selectivity of adsorption of CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> mixtures in 13X, ZSM-5 (Si/Al = 15), and H-MOR zeolites show that the selectivity decreases with increased mole fraction of CO<sub>2</sub> in the bulk gas mixture,  $y_1 = \frac{f_1}{f_1 + f_2}$ . On the other hand, the IAST predicts the selectivity to increase, albeit slightly, with the mole fraction of CO<sub>2</sub> in the bulk gas

\* Corresponding author.

E-mail address: [r.krishna@contact.uva.nl](mailto:r.krishna@contact.uva.nl) (R. Krishna).

Nomenclature		Greek letters	
$A$	surface area per kg of framework, $\text{m}^2 \text{kg}^{-1}$	$\gamma_i$	activity coefficient of component $i$ in adsorbed phase, dimensionless
$b_i$	Langmuir-Freundlich parameter, $\text{Pa}^{-\nu}$	$\Lambda_{ij}$	Wilson parameters, dimensionless
$C$	constant used in Eq. (3), $\text{kg mol}^{-1}$	$\nu$	Freundlich exponent in unary isotherm, dimensionless
$f_i$	partial fugacity of species $i$ , Pa	$\pi$	spreading pressure, $\text{N m}^{-1}$
$f_t$	total fugacity of bulk fluid mixture, Pa	$\rho$	framework density, $\text{kg m}^{-3}$
$p_i$	partial pressure of species $i$ , Pa	<b>Subscripts</b>	
$p_t$	total system pressure, Pa	1	referring to species 1
$P_i^0$	sorption pressure, Pa	2	referring to species 2
$q_i$	molar loading species of species $i$ , $\text{mol kg}^{-1}$	$i, j$	components in mixture
$q_{i, \text{sat}}$	molar loading of species $i$ at saturation, $\text{mol kg}^{-1}$	$i$	referring to component $i$
$q_t$	total molar loading of mixture, $\text{mol kg}^{-1}$	$t$	referring to total mixture
$Q_i$	volumetric uptake of species $i$ , $Q_i = \rho q_i$ , $\text{mol m}^{-3}$	$\text{sat}$	referring to saturation conditions
$\Delta Q$	separation potential, $\text{mol m}^{-3}$	<b>Superscripts</b>	
$R$	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	0	referring to pure component loading
$S_{\text{ads}}$	adsorption selectivity, dimensionless		
$T$	absolute temperature, K		
$x_i$	mole fraction of species $i$ in adsorbed phase, dimensionless		
$y_i$	mole fraction of species $i$ in bulk fluid mixture, dimensionless		

mixture; see Fig. 1 d,e,f. There are several other examples of failures of the IAST estimations for mixture adsorption in a variety of cation-exchanged zeolites [4,30,31].

The primary objective of this communication is to gain some insights into the reasons for the failure of the IAST to match the experimental data, as witnessed in Fig. 1. Towards this end, Configurational-Bias Monte Carlo (CBMC) simulations on unary isotherms and mixture adsorption equilibrium were performed using the simulation methodology that is firmly established in the literature [6,7,32–34]. The force field information are taken from García-Sánchez et al. [35], and Dubbedam et al. [36].

The Supplementary Material accompanying this publication provides (a) details of experimental data and CBMC simulation data for mixture adsorption, (b) unary isotherm fits for all the guest/host combinations examined in this article, (c) details of the IAST, and Real Adsorbed Solution Theory (RAST) methodologies and calculations for mixture adsorption equilibrium, and (d) Wilson parameter fits for thermodynamic non-idealities.

## 2. CBMC simulations of mixture adsorption in cation-exchanged FAU zeolites

We first investigate  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in NaX zeolite, that has the Faujasite (FAU) topology consisting of cages of  $786 \text{ \AA}^3$  volume, separated by  $7.3 \text{ \AA}$  12-ring windows. Each unit cell of NaX zeolite has 106 Si, 86 Al, 86  $\text{Na}^+$  with  $\text{Si}/\text{Al} = 1.23$ . Two different CBMC simulation campaigns were conducted:

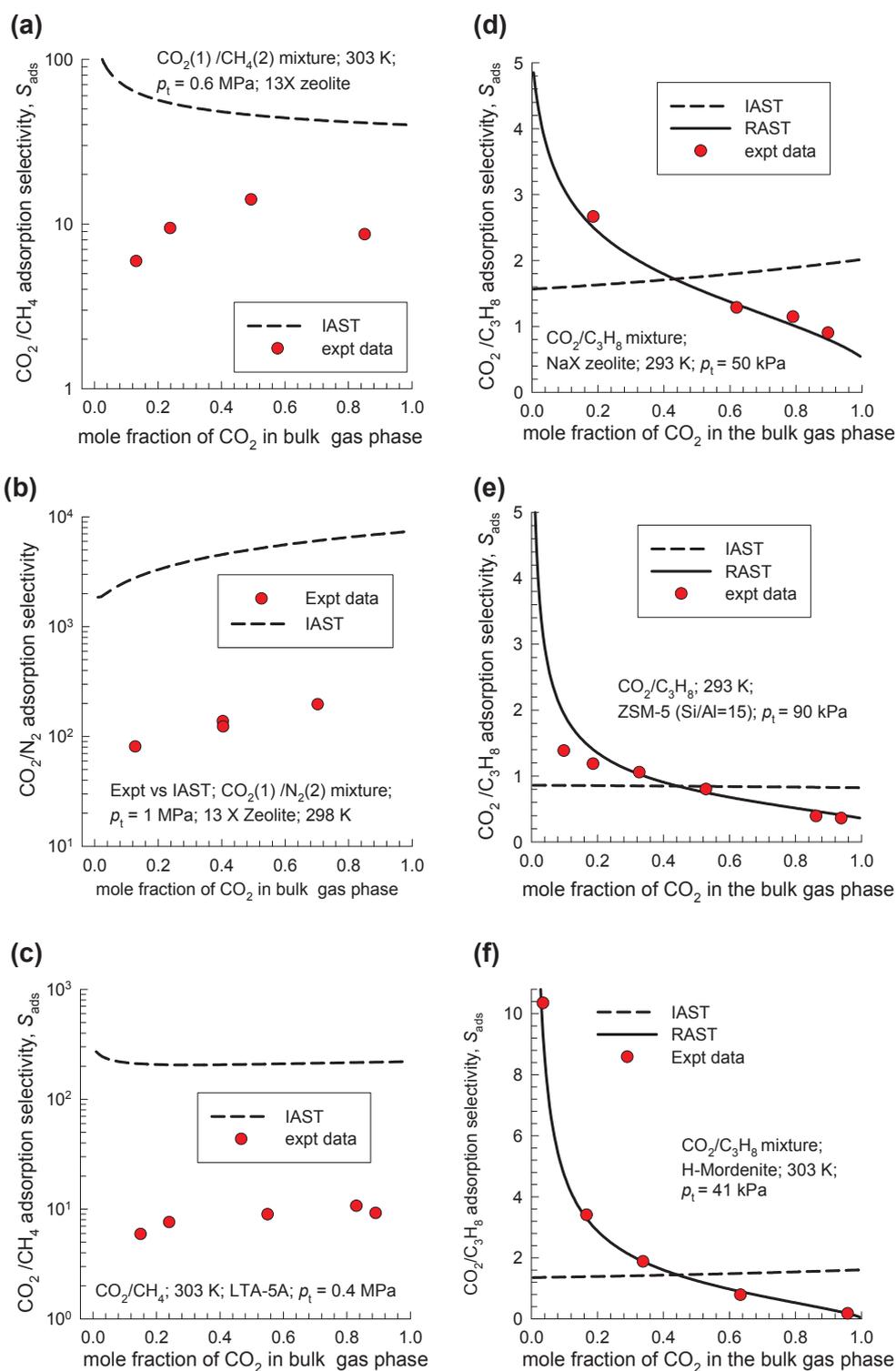
- (i) The mole fraction of  $\text{CO}_2(1)$  in the bulk gas phase is held constant,  $y_1 = 0.5$ , and the bulk gas phase fugacity  $f_t = f_1 + f_2$  was varied, and
- (ii) The mole fraction of  $\text{CO}_2(1)$  in the bulk gas phase,  $y_1$  was varied from 0 to 1, keeping the bulk gas phase mixture fugacity  $f_t = f_1 + f_2$  constant at a value of 1 MPa.

The results of these two separate campaigns are presented in Fig. 2. In the Henry regime of adsorption, prevailing at  $f_t < 10 \text{ kPa}$ , the component loadings of  $\text{CO}_2$ , and  $\text{C}_3\text{H}_8$  are nearly equal to each other (cf. Fig. 2a), and the  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  adsorption selectivity,  $S_{\text{ads}}$ , is close to unity (cf. Fig. 2b). With increasing values of the bulk gas phase fugacity  $f_t$ , above about 100 kPa, the adsorption becomes increasingly in favor of  $\text{CO}_2$ , due to strong Coulombic interactions with the extra-framework  $\text{Na}^+$  cations. The IAST estimates for the adsorption selectivity are plotted as dashed lines in Fig. 2b. At  $f_t = 1 \text{ MPa}$ , the value of  $S_{\text{ads}} \approx 4$ ; the IAST estimate is a factor two higher than those determined from CBMC simulations.

The CBMC simulations for  $f_t = 1 \text{ MPa}$ , and varying mole fractions of  $\text{CO}_2(1)$  in the bulk gas phase,  $y_1$ , are shown in Fig. 2c. The CBMC simulations show that the adsorption selectivity decreases with increasing proportion of  $\text{CO}_2(1)$  in the bulk gas phase; see Fig. 2d. On the other hand, the IAST anticipates  $S_{\text{ads}}$  to increase with increasing  $y_1$ . This trend is the same as that witnessed for the experimental data for  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in NaX zeolite; see Fig. 1d.

The failure of the IAST to provide quantitatively accurate estimates of component loadings, and adsorption selectivities is attributable to the inhomogeneous distribution of adsorbates in the pore space of NaX zeolite, caused by strong binding of  $\text{CO}_2$  with the extra-framework cations. The inhomogeneous distribution is clearly visualized in the computational snapshot in Fig. 3 for  $f_1 = 0.45 \text{ MPa}$ , and  $f_2 = 0.55 \text{ MPa}$ . We note that the top left cage contains only  $\text{CO}_2$ , and there is no  $\text{C}_3\text{H}_8$  present in that cage. One of the key assumptions of the IAST is that the distribution of adsorbates within the pore space is homogenous; this assumption is violated causing the quantitative failure of the IAST.

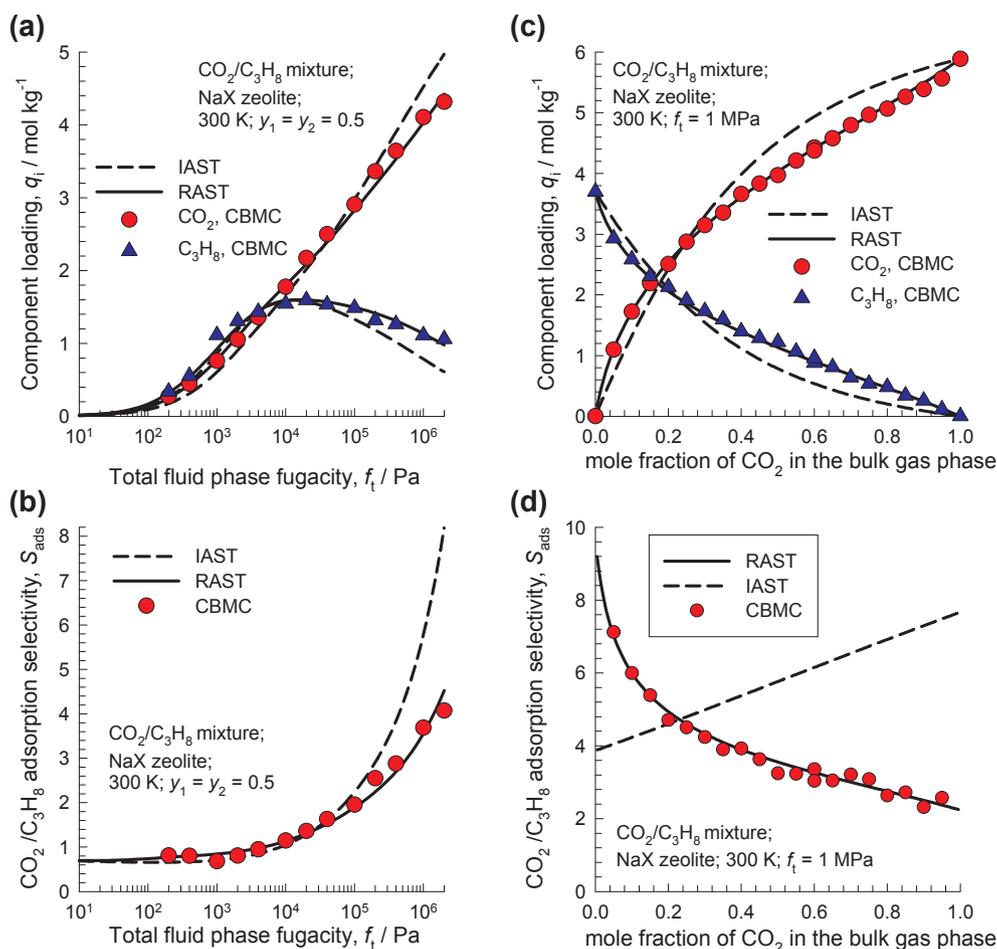
Since the root cause of the failure of the IAST is the inhomogeneous distribution of adsorbates engendered by strong binding of  $\text{CO}_2$  with the extra-framework cations, we should expect the non-ideality effects to be negligibly small in all-silica zeolites, with no extra-framework cations. In order to verify this, we performed CBMC simulations  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in all-silica FAU zeolite, with  $\text{Si}/\text{Al} \rightarrow \infty$ , at 300 K and total fugacity  $f_t = 1 \text{ MPa}$ , with varying  $\text{CO}_2$  in the



**Fig. 1.** Comparison of experimental data on mixture adsorption selectivity with IAST estimates for (a)  $\text{CO}_2/\text{CH}_4$  in 13X zeolite at  $T = 298$  K and  $p_t = 1$  MPa [10], (b)  $\text{CO}_2/\text{N}_2$  in 13X zeolite at  $T = 298$  K and  $p_t = 1$  MPa [11], (c)  $\text{CO}_2/\text{CH}_4$  in LTA-5A zeolite at  $T = 303$  K and  $p_t = 0.4$  MPa [12], (d)  $\text{CO}_2/\text{C}_3\text{H}_8$  in 13X zeolite at  $T = 293$  K and  $p_t = 50$  kPa [40], (e)  $\text{CO}_2/\text{C}_3\text{H}_8$  in ZSM-5 (Si/Al = 15) at  $T = 293$  K and  $p_t = 90$  kPa [41], and (f)  $\text{CO}_2/\text{C}_3\text{H}_8$  in H-MOR (= H-Mordenite) at  $T = 303$  K and  $p_t = 41$  kPa and [29]. In all cases, the x-axis represents the mole fraction of  $\text{CO}_2$  in the bulk gas phase, maintained at constant total pressure,  $p_t$ , and temperature,  $T$ . All data inputs and computational details are provided in the Supplementary Material.

bulk gas phase; the results are presented in Fig. 4a. As anticipated, the IAST estimates of component loadings, and adsorption selectivities are in good agreement with CBMC data. Similar good agreement is also obtained for  $\text{CO}_2(1)/\text{C}_2\text{H}_6(2)$  mixture adsorption in all-silica FAU zeolite; see Fig. 4b.

From the data in Figs. 2 and 4, we must conclude that the accuracy of IAST estimates should also depend on the Si/Al ratio of cation-exchanged zeolites. To test this hypothesis Fig. 5 presents a comparison of  $\text{CO}_2/\text{CH}_4$  adsorption selectivities determined from CBMC simulations at 300 K for all-silica FAU (Si/Al =  $\infty$  with 192 Si, 0 Al, 0  $\text{Na}^+$  per unit



**Fig. 2.** (a, c) CBMC simulations (symbols) of the component loadings for  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in NaX zeolite at 300 K. (b, d) CBMC simulations (symbols) of the  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  adsorption selectivity. In (a, b), the x-axis is the total fugacity  $f_t$  in the bulk gas phase; the mole fraction of  $\text{CO}_2(1)$  in the bulk gas phase is held constant,  $y_1 = 0.5$ . In (c, d), The IAST and RAST estimates are indicated by dashed and continuous solid lines, respectively. All data inputs and computational details are provided in the Supplementary Material.

cell), NaY (Si/Al = 2.56 with 138 Si, 54 Al, 54  $\text{Na}^+$  per unit cell), and NaX (Si/Al = 1.23 with 106 Si, 86 Al, 86  $\text{Na}^+$  per unit cell) zeolites with IAST estimations. For all-silica FAU, the IAST estimates are in perfect agreement with CBMC simulations. The agreement of IAST estimates with CBMC simulated data becomes progressively worse with decreasing Si/Al ratios. This trend confirms our contention that the failure of IAST is due to the strong interactions of  $\text{CO}_2$  with extra-framework cations.

### 3. CBMC simulations of mixture adsorption in cation-exchanged LTA zeolite

We now investigate the accuracy of IAST estimates of  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in LTA-4A zeolite, that consists of cages of  $743 \text{ \AA}^3$  volume, separated by  $4.11 \text{ \AA} \times 4.47 \text{ \AA}$  8-ring windows. Per unit cell LTA-4A has 96 Si, 96 Al, 96  $\text{Na}^+$ , with Si/Al = 1. In the CBMC simulations of  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption the mole fraction of  $\text{CO}_2(1)$  in the bulk gas phase,  $y_1$  was varied from 0 to 1, keeping the

bulk gas phase mixture fugacity  $f_t = f_1 + f_2$  constant at a value of 1 MPa; the results are summarized in Fig. 6a. The CBMC simulations show that the adsorption selectivity decreases with increasing proportion of  $\text{CO}_2(1)$  in the bulk gas phase; see Fig. 6b. On the other hand, the IAST anticipates  $S_{\text{ads}}$  to be practically independent of  $y_1$ ; this trend is similar to that witnessed in Fig. 1 e,f for the experimental data for  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption in ZSM-5 (Si/Al = 15), and HMOR.

Fig. 7 shows computational snapshots of the location of  $\text{CO}_2(1)$ , and  $\text{C}_3\text{H}_8(2)$  molecules within the pore topology of LTA-4A zeolite. We note that the  $\text{CO}_2$  is almost exclusively located at the windows, or near the window entrance regions. Due to configurational restraints  $\text{C}_3\text{H}_8$  can only be located at the cage interiors. Consequently, the competition between the adsorption of  $\text{CO}_2$  and  $\text{C}_3\text{H}_8$  is less severe than assumed in the homogenous distribution that is inherent in the IAST prescription. The preferential perching of  $\text{CO}_2$  at the window sites also manifests for other cage-window structures such as DDR, ERI, and CHA [23,37,38].

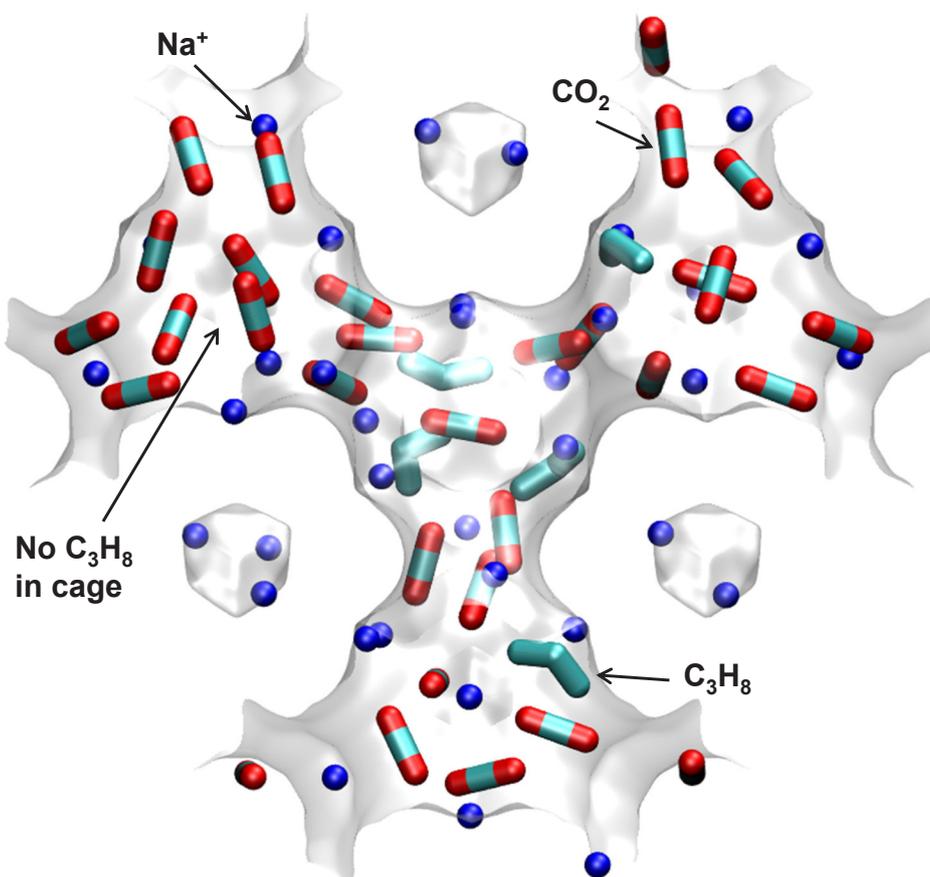


Fig. 3. Computational snapshots showing the location of  $\text{CO}_2$ , and  $\text{C}_3\text{H}_8$  within the cages of NaX zeolite at 300 K and total fugacity  $f_t = 1$  MPa. The component partial fugacities are  $f_1 = 0.45$  MPa, and  $f_2 = 0.55$  MPa.

#### 4. Modelling non-ideal mixture adsorption using the RAST

For quantifying the departures of the IAST from CBMC data, we use the Real Adsorbed Solution Theory (RAST) [21,23,27–29,39], in which the partial fugacity of any component in the bulk fluid phase is related to the mole fraction  $x_i$  in the adsorbed phase by introduction of activity coefficients describing non-idealities in the adsorbed phase

$$f_i = P_i^0 x_i \gamma_i \quad (2)$$

From the CBMC data on  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$  mixture adsorption data in Fig. 2, the quantities  $f_i / P_i^0 x_{i,\text{CBMC}}$  may be determined; these are plotted in Fig. 8a,b as function of (a) the mole fraction of  $\text{CO}_2$  in the adsorbed phase,  $x_{1,\text{CBMC}}$ , and (b) the adsorption potential,  $\frac{\pi A}{RT}$ . The plots show that appropriate models for the activity coefficient must also include the dependence on the adsorption potential [21,23,27–29,39]. The Wilson model, for example, may be written as

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

$$\ln(\gamma_2) = \left(1 - \ln(x_2 + x_1 \Lambda_{21}) - \frac{x_2}{x_2 + x_1 \Lambda_{21}} - \frac{x_1 \Lambda_{12}}{x_1 + x_2 \Lambda_{12}}\right) \left(1 - \exp\left(-C \frac{\pi A}{RT}\right)\right) \quad (3)$$

In Eq. (3),  $C$  is a constant with the units  $\text{kg mol}^{-1}$ . The introduction of  $\left(1 - \exp\left(-C \frac{\pi A}{RT}\right)\right)$  imparts the correct limiting behaviors  $\gamma_i \rightarrow 1$ ;  $f_i \rightarrow 0$

for the activity coefficients in the Henry regime. As pore saturation conditions are approached, this correction factor tends to unity,  $\left(1 - \exp\left(-C \frac{\pi A}{RT}\right)\right) \rightarrow 1$ . The total mixture loading is given by

$$q_t \equiv q_1 + q_2 = \frac{1}{\frac{x_1}{q_1^0(P_1^0)} + \frac{x_2}{q_2^0(P_2^0)} + [-x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})] C \exp\left(-C \frac{\pi A}{RT}\right)} \quad (4)$$

The set of Eqs. (1), (2), (3), and (4) must be solved simultaneously to obtain the values of the component loadings  $q_1$ , and  $q_2$ , for a specified set of values of  $f_1$ , and  $f_2$ .

The continuous solid lines in Figs. 1, 2, and 6 represent RAST calculations in which the parameters in the Wilson model are obtained by fitting to match CBMC or experimental data on component loadings.

As illustration of the influence of thermodynamic non-idealities on the separation performance in fixed beds, let us consider  $\text{CO}_2/\text{C}_3\text{H}_8$  separations in an adsorber packed with NaX zeolite operating at 300 K. Using the theory of shock waves for separations in fixed bed adsorbers [8,19], the maximum amount of pure  $\text{C}_3\text{H}_8$  that can be recovered during the adsorption cycle is given by the separation potential,  $\Delta Q = Q_{\text{CO}_2} \frac{y_{\text{C}_3\text{H}_8}}{1 - y_{\text{C}_3\text{H}_8}} - Q_{\text{C}_3\text{H}_8}$ , expressed in the units mol per L of adsorbent; for these calculations the crystal framework density of NaX zeolite is taken as  $\rho = 1421 \text{ kg m}^{-3}$ . Fig. 9. presents a comparison of the

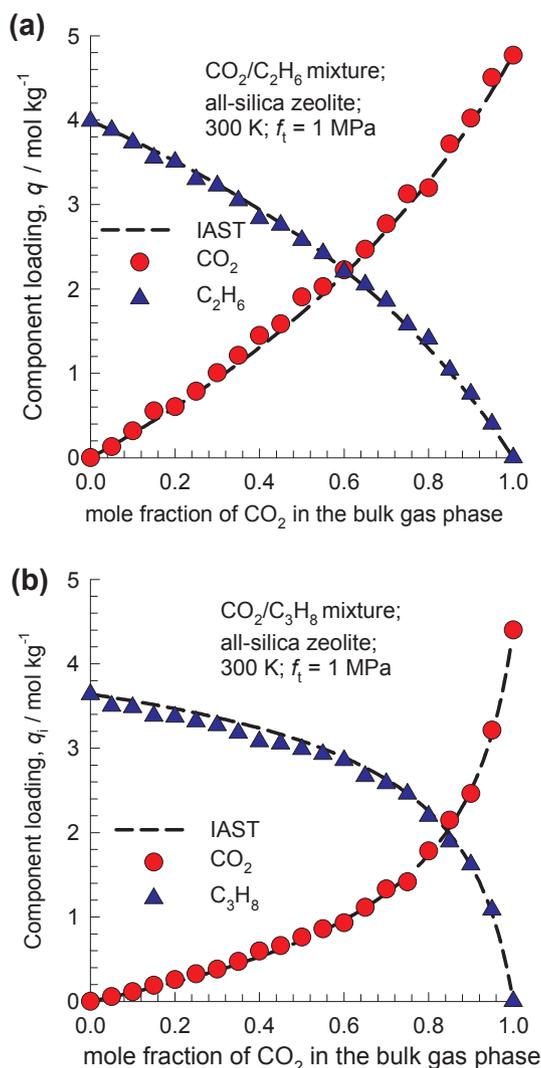


Fig. 4. CBMC simulations (symbols) of the component loadings for adsorption of (a)  $\text{CO}_2(1)/\text{C}_3\text{H}_8(2)$ , and (b)  $\text{CO}_2(1)/\text{C}_2\text{H}_6(2)$  mixtures in all-silica FAU zeolite at 300 K and total fugacity  $f_t = 1$  MPa. The x-axis represents the mole fraction of  $\text{CO}_2$  in the bulk gas phase. The dashed line represent IAST estimates. All data inputs and computational details are provided in the Supplementary Material.

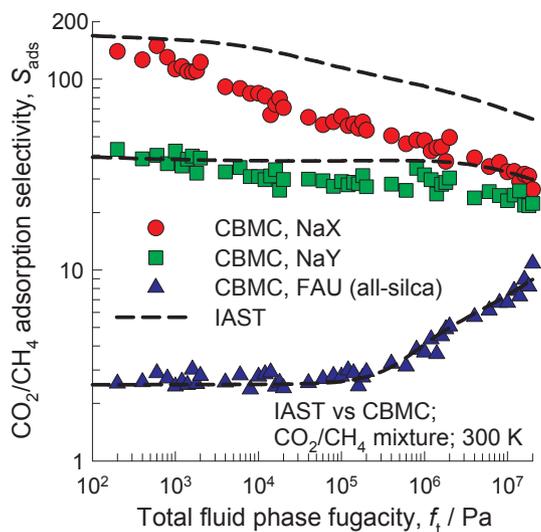
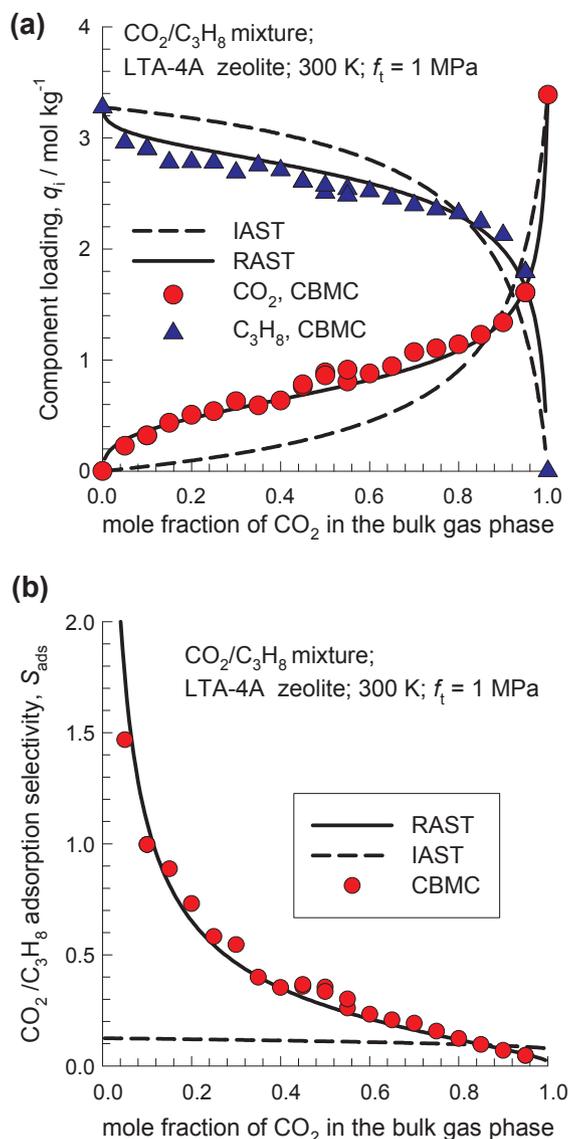


Fig. 5. Comparison  $\text{CO}_2/\text{CH}_4$  adsorption selectivities determined from CBMC simulations 300 K for all-silica FAU (192 Si, 0 Al, 0  $\text{Na}^+$ ,  $\text{Si}/\text{Al} = \infty$ ), NaY (138 Si, 54 Al, 54  $\text{Na}^+$ ,  $\text{Si}/\text{Al} = 2.56$ ), and NaX (106 Si, 86 Al, 86  $\text{Na}^+$ ,  $\text{Si}/\text{Al} = 1.23$ ) zeolites with IAST estimations. All data inputs and computational details are provided in the Supplementary Material.



**Fig. 6.** (a) CBMC simulations (symbols) of the component loadings for CO<sub>2</sub>(1)/C<sub>3</sub>H<sub>8</sub>(2) mixture adsorption in LTA-4A zeolite at 300 K. The x-axis is mole fraction of CO<sub>2</sub> in the bulk gas phase; the total fugacity is held constant at  $f_t = 1$  MPa. (b) CBMC simulations (symbols) of the CO<sub>2</sub>(1)/C<sub>3</sub>H<sub>8</sub>(2) adsorption selectivity. The IAST and RAST estimates are indicated by dashed and continuous solid lines, respectively. All data inputs and computational details are provided in the Supplementary Material.

IAST and RAST calculations of  $\Delta Q$ ; for a total mixture fugacity,  $f_t = 1$  MPa, the values of  $\Delta Q$ , are respectively 5.2, and 4 mol L<sup>-1</sup>, respectively. Thermodynamic non-idealities reduce the productivity of pure C<sub>3</sub>H<sub>8</sub> in a fixed bed adsorber by about 20%.

## 5. Conclusions

The following major conclusions emerge from the foregoing analysis of adsorption of CO<sub>2</sub>-bearing mixtures in cation-exchanged zeolites. The failure of the IAST to provide quantitatively accurate estimates of mixture adsorption, as witnessed in the experimental data in Fig. 1, is ascribable to inhomogeneous distribution of adsorbates within the

zeolite pores. In NaX zeolite, the inhomogeneity is a direct consequence of strong binding of CO<sub>2</sub> with extra-framework cations, leading to congregation effects around cations. In LTA zeolites, CO<sub>2</sub> locates preferentially at the window regions, causing an inhomogeneous distribution of adsorbates. In the RAST description of mixture adsorption, the chosen model for activity coefficients must also include the dependence on the adsorption potential  $\frac{\pi A}{RT}$ .

The overall conclusion to be drawn from this study is that thermodynamic non-idealities may have a significant influence on the separations in fixed bed adsorption devices. For CO<sub>2</sub> capture applications with cation-exchanged zeolites, departures from idealities generally tend to reduce the separation effectiveness.

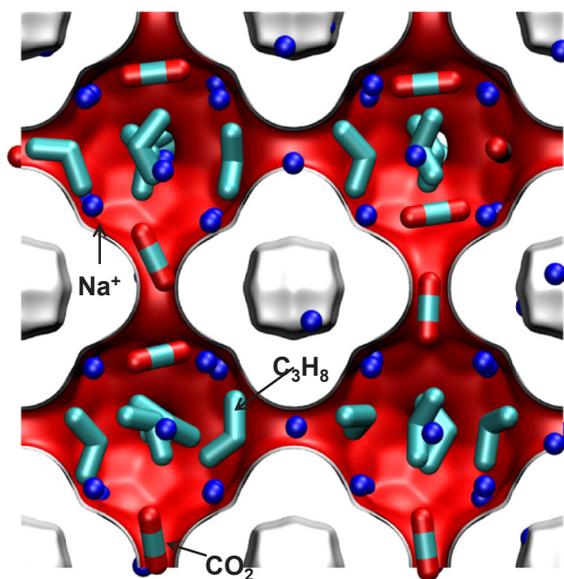


Fig. 7. Computational snapshots showing the location of CO<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub> within the cages of LTA-4A zeolite at 300 K and total fugacity  $f_t = 1$  MPa. The component partial fugacities are  $f_1 = 0.85$  MPa, and  $f_2 = 0.15$  MPa.

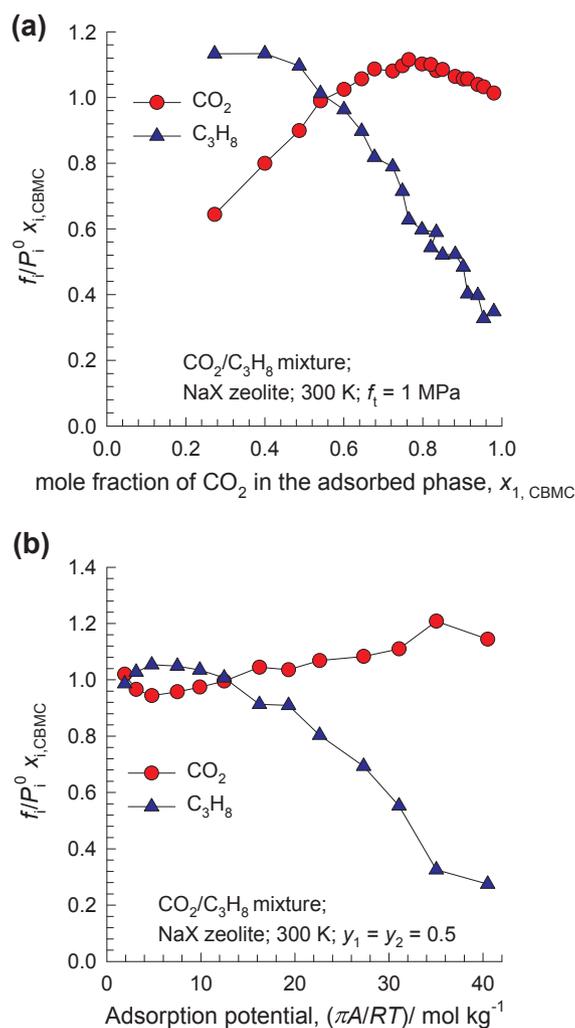


Fig. 8. Analysis of the non-idealities in CO<sub>2</sub>(1)/C<sub>3</sub>H<sub>8</sub>(2) mixture adsorption in NaX zeolite at 300 K. Dependence of  $f_i/P_i^0 x_{i,CBMC}$  on (a) the mole fraction of CO<sub>2</sub> in the adsorbed phase as determined from CBMC simulations,  $x_{1,CBMC}$ , and (b) the adsorption potential,  $\frac{\pi A}{RT}$ . All data inputs and computational details are provided in the Supplementary Material.

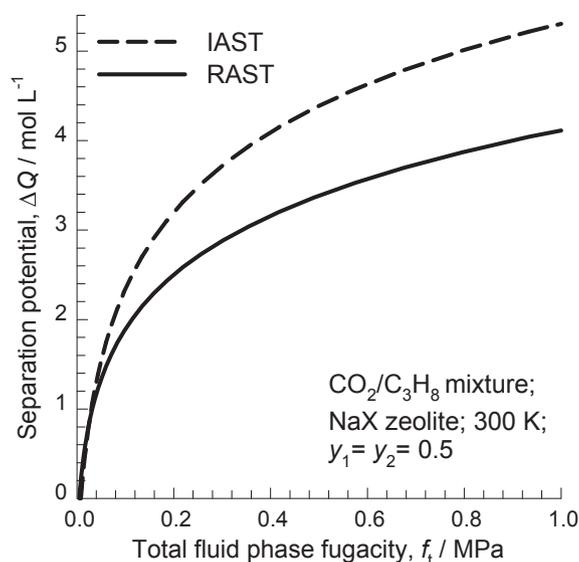


Fig. 9. Comparison of IAST and RAST calculations of the separation potential,  $\Delta Q = Q_1 \frac{y_2}{y_1} - Q_2$  for separation of 50/50 CO<sub>2</sub>(1)/C<sub>3</sub>H<sub>8</sub>(2) feed mixtures in NaX zeolite at 300 K.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.seppur.2018.06.009>.

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