Adsorption (2018) 24:233–241
https://doi.org/10.1007/s10450-018-9942-5

On the use of the IAST method for gas separation studies in porous materials with gate-opening behavior

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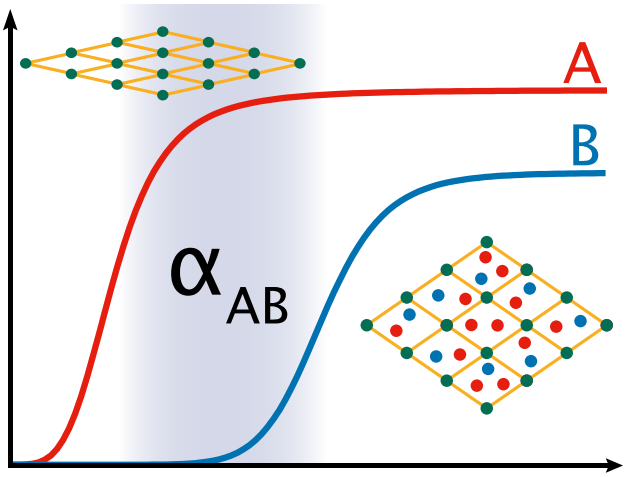
Received: 18 September 2017 / Revised: 17 February 2018 / Accepted: 20 February 2018 / Published online: 6 March 2018

Abstract
Highly flexible nanoporous materials, exhibiting for instance gate opening or breathing behavior, are often presented as candidates for separation processes due to their supposed high adsorption selectivity. But this view, based on "classical" considerations of rigid materials and the use of the Ideal Adsorbed Solution Theory (IAST), does not necessarily hold in the presence of framework deformations. Here, we revisit some results from the published literature and show how proper inclusion of framework flexibility in the osmotic thermodynamic ensemble drastically changes the conclusions, in contrast to what intuition and standard IAST would yield. In all cases, the IAST method does not reproduce the gate-opening behavior in the adsorption of mixtures, and may overestimates the selectivity by up to two orders of magnitude.



Keywords IAST · OFAST · Co-adsorption · Selectivity · Metal–organic frameworks · Flexibility

1 Introduction

Gas separation is an important step in multiple industrial processes, from separation of hydrocarbons in oil chemistry to CO_2 separation and storage or oxygen extraction in the air. The two main methods used for gas separation are cryogenic distillation, mainly used for air separation, and differential adsorption. Adsorption-based processes for gas separation, which rely on microporous materials as an adsorber bed, are very versatile because of the large choice of materials available—and the possibility to tune them for a specific system.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10450-018-9942-5) contains supplementary material, which is available to authorized users.

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Among the porous materials used commercially, one can list inorganic materials (such as zeolites and silica gels), carbon-based compounds (e.g., activated carbon), and hybrid organic–inorganic materials, including the topical family of metal–organic frameworks (MOFs) or porous coordination polymers (PCPs).

Experimental characterization of the co-adsorption of a mixture of gases inside a porous adsorbent is typically done through multi-component gas adsorption studies. This problem is inherently high-dimensional, e.g., for a ternary mixture there are four variables to vary (temperature, total pressure, and two independent variables for the mixture composition). Because such experimental studies of coadsorption equilibrium thermodynamics are typically long and expensive, there has been a great expense of literature devoted to theoretical models for the prediction of mixture co-adsorption based on single-component adsorption data. The most commonly used method in the field is the Ideal Adsorbed Solution Theory (IAST) (Myers and Prausnitz 1965), which is relatively simple to implement and robust, and allows the prediction of multi-component adsorption behavior from individual single-component isotherms. In particular, it is used to predict the potential selectivity of materials based on simple measurements of pure component isotherms.

A novel development in the area of nanoporous materials is the increasing number of flexible materials (Coudert 2015), or *soft porous crystals* (Horike et al. 2009), that can exhibit significant changes in structure upon adsorption of guest molecules. Those materials, which undergo large-scale reversible structural transitions impacting their total volume or internal pore volume, appear to be particular common among metal–organic frameworks based on relatively weaker bonds (coordination bonds, π–π stacking, hydrogen bonds, or some covalent bonds) compared to inorganic dense nanoporous materials (such as zeolites). In particular, some of these materials show transitions between an "open" phase with large pore volume, and a "condensed" or "narrow pore" phase with smaller pore volume—or, in some cases, no microporosity at all. Such transitions, known as *gate opening* (Kitaura 2003; Tanaka 2008; Li and Kaneko 2001) or *breathing* (Serre 2002; Bourrelly 2005) depending on the order in which the phases occur upon adsorption, can lead to stepped adsorption isotherms. In the recent literature, many authors have relied on IAST predictions to predict that several such flexible MOFs would present very good selectivity for gas separation. For example Nijem (2012) reported that "[their] work unveils unexpected hydrocarbon selectivity in a flexible metal–organic framework (MOF), based on differences in their gate opening pressure." In some cases of the published literature, the authors explicitly used IAST to derive such predictions on flexible materials (Banerjee et al. 2015; Mukherjee 2015; Foo 2016; Li 2016). In other cases, IAST was not used explicitly, but the assumptions made for the behavior of mixtures stem from the "classical" understanding of selectivity rules in rigid materials, and would not necessarily be valid in flexible materials (Nijem 2012; Gücüyener 2010; Inubushi 2010; Sanda et al. 2013; Joarder 2014; Soumya Mukherjee 2014).

In this paper, we look at the hypotheses of the IAST method and show why they are not fulfilled when adsorption takes place in flexible nanoporous materials. We summarize an alternative method, the Osmotic Framework Adsorbed Solution Theory (OFAST), Coudert (2009) that can be used when structural transitions occur upon adsorption. We then compare the results of IAST and OFAST on two sets of adsorption data from the published literature on gate-opening materials, and show that the IAST method gives unrealistic results: it does not reproduce the gate-opening behavior upon mixture adsorption, and overestimates the selectivity by up to two orders of magnitude.

2 Predicting multi-components adsorption

2.1 Ideal Adsorbed Solution Theory

The Ideal Adsorbed Solution Theory (IAST) starts by assuming that for a given adsorbent and at fixed temperature T, the pure-component isotherms $n_i(P)$ for each gas i of interest is known. Then, given a mixture of ideal gases adsorbing at total pressure P in an host framework and the composition of the gas phases (y_i)—such that the partial pressures are $P_i = y_i P$—the goal of the method is to predict the total adsorbed quantity n_{tot} and the molar fractions (x_i) in the adsorbed phase.

In order to do so, Myers and Prausnitz (1965) introduced for each mixture component a quantity homogeneous to a pressure, P_i^*. The IAST method links this pressure to the compositions of the gas and adsorbed phases with two equations for each component:

$$Py_i = P_i^* x_i; \tag{1}$$

for all i and j,

$$\int_0^{P_i^*} \frac{n_i(p)}{p}\mathrm{d}p = \int_0^{P_j^*} \frac{n_j(p)}{p}\mathrm{d}p. \tag{2}$$

Equation (1) defines the link between P_i^* the total pressure P, the gas phase molar fraction y_i and the adsorbed phase molar fraction x_i. Equation (2) is an expression of the equality of chemical potentials at thermodynamic equilibrium.

In the simpler case of two-component gas mixture (B, C), these two equations and the conservation of matter, can be rewritten to a set of four equations:

$$Py_B = P_B^* x_B \tag{3}$$

$$x_B = \frac{P_C^* - P}{P_C^* - P_B^*} \tag{4}$$

$$\frac{1}{n_{\text{tot}}} = \frac{x_B}{n_B(P_B^*)} + \frac{1 - x_B}{n_C(P_C^*)} \tag{5}$$

$$\int_0^{P_B^*} \frac{n_B(p)}{p} \mathrm{d}p = \int_0^{P_C^*} \frac{n_C(p)}{p} \mathrm{d}p \tag{6}$$

Solving these equations for P_B^* and P_C^* will give all the information on the system composition. It can be done with either numerical integration of the isotherms, or by fitting the isotherms to a model, and then integrating the model analytically.

The IAST model for the prediction of coadsorption of mixtures in nanoporous materials is no panacea, and more involved theories have been developped for cases where ideality cannot be assumed: nonideal adsorbed solution models (Yang 1997; Sweatman and Quirke 2002) the vacancy solution theory (VST), Suwanayuen and Danner (1980) etc. However, IAST has been extensively studied and both its areas of validity and its weaknesses have been well assessed. In particular, it is known to be fairly reliable for adsorption of small gas molecules, or mixtures of apolar fluids of a similar chemical nature (such as mixtures of hydrocarbons). However, one limitation is that if there are big differences in the sorption capacity, extrapolations to high pressures are necessary and thus, the resulting mixture behavior predicted can be far off.

2.2 IAST and flexible frameworks

The original derivation of the IAST equations Myers and Prausnitz (1965) highlights three hypotheses on the co-adsorption process, on which the model is built:

(h1) The adsorbing framework is inert from a thermodynamic point of view;
(h2) The adsorbing framework specific area is constant with respect to temperature and the same for all adsorbed species;
(h3) The Gibbs definition of adsorption applies.

While the meaning of the last assumption (h3) has been diversely interpreted by different authors, Myers and Prausnitz originaly meant it to qualify the method by which the adsorption isotherms are measured. There is, however, consensus on the fact that absolute adsorption should be used in IAST calculations—as opposed to excess or net adsorption (Myers and Monson 2014; Brandani et al. 2016). This assumption thus applies equally to both rigid and flexible adsorbents. However, the first two hypothesis are not valid for flexible nanoporous materials. (h2) is clearly invalid, as modifications in both the host's volume and internal structure lead to variations of pore size and specific area upon structural transitions. We note here, in passing, that (h2) should already be ruled out for systems of pore size close to the adsorbate diameter, as well as gas mixtures of widely different size or shape. It should, for example, not apply to molecular sieves systems, yet those can often be described reasonably well by IAST in practice. Finally, (h1) is violated by all the systems that feature adsorption-induced deformation, and in particular by systems presenting a gate-opening or a breathing behavior. As a conclusion, IAST has no theoretical foundation for those systems and should not be used for co-adsorption prediction in flexible frameworks.

Aside from the mathematical treatment and thermodynamic hypotheses, we can show in an qualitative way why it is not possible, in flexible host frameworks, to use the single-component isotherm directly to predict multi-components adsorption. We address here a common misconception, due to an invalid graphical interpretation of the isotherms. Figure 1 depicts the equilibrium adsorption isotherms for two different guests in a material presenting a gate-opening behavior. The gate opening is an adsorption-induced structural transition from a nonporous to a porous phase of the host, leading to a step in the single-component adsorption isotherm. Gate opening occurs at two different pressures for the two adsorbates, due to the specific host–guest interactions of the two gases (characterized notably by the enthalpy of adsorption and saturation uptake). In the pressure range in-between the transition pressures (in gray in Fig. 1), the uptake of one species is close to 0—*in the single-component*

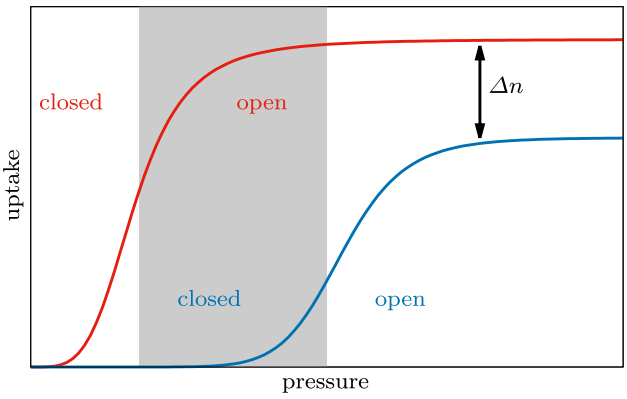

Fig. 1 Typical single-component isotherms for adsorption of two gases (red and blue) in a material with gate opening. The gate opening pressure is not the same for the two adsorbates, creating a pressure range with a high difference in the adsorption capacity for single-components isotherms (gray zone in the figure). Contrary to intuition, selectivity will not necessarily by high in this pressure range, but will depend on difference in saturation uptake Δn. (Color figure online)

isotherm—and the uptake of the other species is close to its maximum value. If these isotherms were encountered for a rigid host material, the selectivity would be extremely high in this range, with one guest adsorbing but not the other.

Yet, the step in the isotherms here is not simply linked to host–guest interactions but indeed due to a change in the host structure. In particular, upon adsorption of a gas mixture in this gate-opening framework, a phase transition will occur at a given pressure. Before this transition, the structure will be contracted and show no (or little) adsorption for either guest, and thus no usable selectivity. After the transition, *both species* will adsorb into the open pore framework. The selectivity is then governed—at least qualitatively—by the respective saturation uptakes of the two fluids (Δn in the figure). While the difference in adsorbed quantities in the intermediate pressure range visually suggests great selectivity, it is not possible for one component to adsorb inside the close phase framework while at the same time the other component adsorb inside the open phase of the framework. The framework is either in one phase or in the other, at any given time.

The whole issue with using single-component isotherms to predict multi-component adsorption in frameworks with phase transition boils down to the origin of the stepped isotherms. The single-component isotherm (represented in Fig. 2) is a combination of two isotherms: one in the first phase (the contracted pore phase), and one in the second phase (the open pore phase). Both phases—and the thermodynamic equilibrium between them—need to be taken in account to predict the multi-component adsorption.

2.3 The OFAST theory

The thermodynamic ensemble suited for the study of adsorption in flexible materials is the so-called "osmotic ensemble",

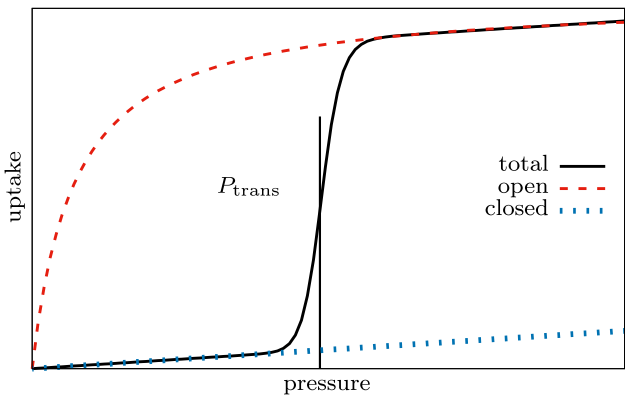

Fig. 2 Generation of the total isotherm in gate-opening materials by the combination of two single-phase isotherms: an open pores isotherm, and an closed pores isotherm. The transition between the two host phases occurs at P_{trans}. (Color figure online)

first introduced in 1994 (Mehta and Kofke 1994) for the study of fluid mixtures, and adapted to multi-components phase equilibrium in 1998 (Fernando 1998). The thermodynamic potential Ω associated with this ensemble is a function of the mechanical pressure P, the temperature T, the number of atoms in a given host phase α and the adsorbed species chemical potentials μ_i:

$$\Omega(T, P, \mu_i) = F_\alpha + PV_\alpha - \sum_i \mu_i N_i, \tag{7}$$

where F_α is the Helmholtz free energy of the empty host in phase α, V_α the volume of the host in this phase, and N_i the molar uptake of guest i. This expression can be reworked and expressed as a function not of chemical potentials, but of fluid pressure (taken equal to mechanical pressure P) and adsorption isotherms: (Coudert 2008),

$$\Omega(T, P, \mu_i) = F_\alpha + PV_\alpha - \sum_i \int_0^P n_i(T, p) V_i^m(T, p)\, \mathrm{d}p \tag{8}$$

here $n_i(T, P)$ are the coadsorption isotherms for each component and $V_i^m(T, P)$ the molar volume for the species i in the bulk phase. If we supposed that the gases are ideal, the molar volume is given by RT / P, with R the ideal gas constant.

We have shown above that IAST cannot be used for the study of co-adsorption in frameworks with adsorption-induced phases transition, because the framework is not inert during adsorption. However, the IAST assumptions are still valid for each individual phase of the host matrix, if they are considered in the absence of a transition. As a consequence, it means that the IAST model can be used, for each possible host phase α, to calculate the co-adsorption isotherms $n_{\alpha,i}(P, T)$ in this given phase. Then, the thermodynamic potential of each phase Ω_α can be calculated from these isotherms through Eq. 8, allowing to predict which phase is the more stable at a given gas phase pressure and composition—and where the structural transition(s) occur. This method, extending the IAST theory in the osmotic ensemble to account for host flexibility, is called Osmotic Framework Adsorbed Solution Theory (OFAST) (Coudert 2009, 2010). Although the amount of published data from direct experimental measurements of coadsorption of gas mixtures in flexible MOFs is very limited, the OFAST method has been well validated in the past against experimental data (Ortiz 2012; Hoffmann 2011; Zang et al. 2011).

In practice, the use of OFAST follows the following steps. First, the host phases of interest are identified and the single-component adsorption isotherms $n_{\alpha,i}(T, p)$ for these are obtained: this can be achieved from a fit of experimental isotherms (see Fig. 2) or from molecular simulation.

Secondly, the relative free energies of the host phases (which reduces to a single ΔF_{host} in our case of two host phases) can be computed from Eq. (8) and the experimental

single-component stepped isotherm. For example, with two phases α and β, and considering ideal gas, we can express Eq. (8) for each phase:

$$\Omega_\alpha(T,P,\mu_i) = F_\alpha + PV_\alpha - RT\sum_i \int_0^P \frac{n_{\alpha,i}(p)}{p}\,\mathrm{d}p \tag{9}$$

$$\Omega_\beta(T,P,\mu_i) = F_\beta + PV_\beta - RT\sum_i \int_0^P \frac{n_{\beta,i}(p)}{p}\,\mathrm{d}p \tag{10}$$

At the transition ($P = P_{\text{trans}}$ in Fig. 2, which is typically known experimentally) the two thermodynamic potentials will be equal, which gives us a way to evaluate the free energy difference between the phases:

$$\Delta F_{\text{host}} = RT\sum_i \int_0^{P_{\text{trans}}} \frac{\Delta n_i(T,p)}{p}\mathrm{d}p - P_{\text{trans}}\Delta V_{\text{host}} \tag{11}$$

Then, for all values of thermodynamic parameters of interest (pressure and gas mixture composition) the osmotic potential of the host phases is computed, enabling the identification of the most stable phase: the phase with the lowest osmotic potential is the most stable at this pressure and composition. The pressure at which the osmotic potential in both phases are equal is the phase transition pressure for a given composition.

Finally, we can compute adsorption properties (guest uptake and selectivity) using IAST in this most stable phase.

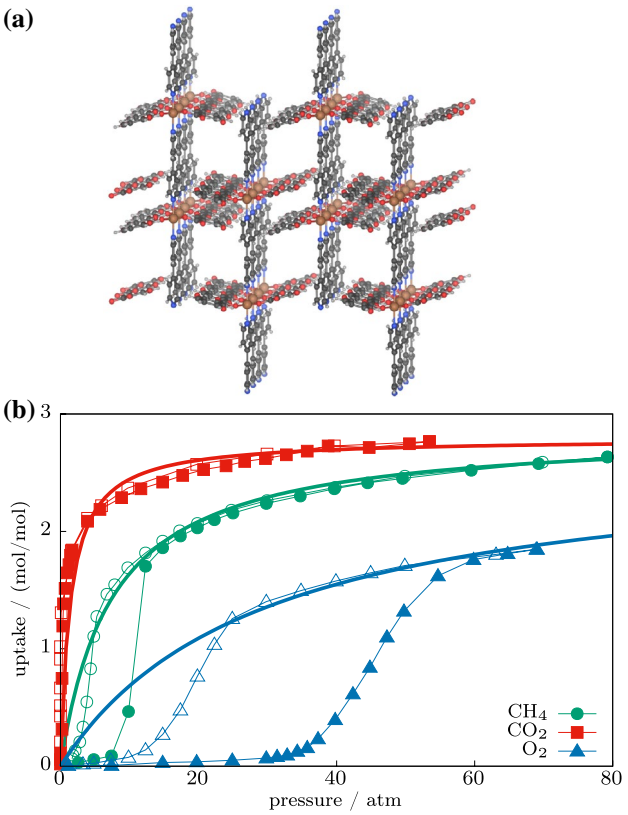

Fig. 3 **a** $Cu(dhbc)_2(4,4'\text{-bpy})$ structure from Kitaura (2003). **a** Sorption isotherms and model isotherms fit at 298 K in $Cu(dhbc)_2(4,4'\text{-bpy})$ for various gas compounds. Adsorption data are presented using filled symbols, and desorption data using empty symbols. Thick lines are Langmuir isotherms fitted at high loading. Experimental data published by Kitaura (2003). (Color figure online)

3 Results and discussion

We present here two examples of co-adsorption of gas mixtures in metal–organic frameworks with gate opening behavior, based on experimental data from the published literature, comparing the predictions of IAST with those of OFAST. The first example deals with the adsorption of CO_2, CH_4, and O_2 in the $Cu(dhbc)_2(4,4'\text{-bpy})$ MOF (Kitaura 2003, see Fig. 3; dhbc = 2,5-dihydroxybenzoate; bpy = bipyridine). These isotherms correspond very closely to the archetypal "gate opening" scenario described above. The second example deals with linear alkanes (ethane, propane, and butane) adsorption in RPM3-Zn MOF (Nijem 2012); Fig. 4 presents the framework structure of RPM3-Zn and relevant experimental adsorption and desorption isotherms, from Nijem (2012).

For both structures, we fitted the isotherms at high loading using a Langmuir model for the isotherm in the open pores structure; and at low loading using a Henry isotherm model for the closed pores structure. This choice is discussed in the next section. The fit coefficients are given in supplementary information, Tables S1 and S2. We performed OFAST calculations using Wolfram Mathematica, the code is reproduced in the supplementary information, and available as a full notebook online at https://github.com/fxcoudert/citable-data. We computed the difference in free energy between the two phases of the structures using these isotherms models. We performed the pure IAST calculations using the PyIAST Python package (Simon et al. 2016). For the IAST calculations, we did not fit the isotherms to a specific model, but rather the IAST equations were solved by numerical integration and interpolation between experimental data points. At partial pressures higher than the last point in the experimental isotherm, that last point was used as saturation uptake. We only discuss selectivity curves in the following section, as selectivity is often what people are looking for when working with flexible porous media for the separation of gas. The total and partial loading curves are also available in supplementary information, Figures S2 to S7.

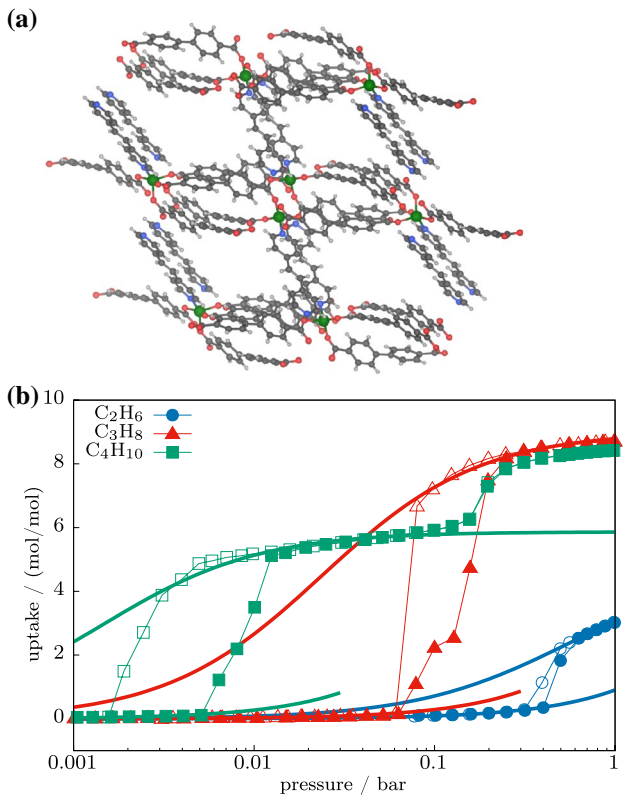

Fig. 4 **a** RPM3-Zn structure from Lan (2009). **b** Sorption isotherms at 298 K for short alkanes in RPM3-Zn. Blue circles are for C_2H_6, red triangles for C_3H_8, and green squares for C_4H_{10}. Filled symbols for adsorption, empty symbols for desorption. Thick lines are the open and closed phases fit of the isotherms. Experimental data published by Nijem (2012). (Color figure online)

3.1 Simple isotherms in Cu(dhbc)$_2$(4,4′-bpy)

Cu(dhbc)$_2$(4,4′-bpy) is a textbook example of gate opening upon adsorption, with single-component adsorption isotherms (reproduced in Fig. 3) that clearly show the transition from a nonporous (at low gas pressure) to a microporous (at higher pressure) host phase. From the experimental data (Kitaura 2003) we computed the free energy difference for all the isotherms, and they all agree on the value of -3.5 ± 0.1 kJ/mol. The exact values are given in the supplementary Table S3.

Figure 5 presents the selectivity obtained with IAST and OFAST for various gas mixtures and compositions in Cu(dhbc)$_2$(4,4′-bpy). The adsorption selectivity, calculated with OFAST, follow what one would expect: at low pressure, the pores are closed and no gas enter the structure, making the selectivity ill-defined—the isotherms at low pressure cannot be fitted and exploited for calculation of separation. Then, at a pressure depending on the composition of the gas phase, the gate opening transition occurs. At pressure higher than gate opening pressure, the framework is in its open pore form, and the value of selectivity depends on the relative saturation uptake of the two phases. The selectivities observed are almost independent of the fluid mixture composition, they are ≈ 20 for CO_2/O_2 and ≈ 4 for CH_4/O_2 mixtures.

In stark contrast with this picture, the selectivities calculated by IAST are clearly non-physical. All selectivity curves present a maximum in the pressure range where gate opening occurs, with selectivities that can be several orders of magnitude too high, with for example 2000 instead of 20 for CO_2/O_2. Even at higher pressure—above the gate opening pressure range—the behavior is not identical to the OFAST calculations, because the incorrect behavior at low pressure affects IAST directly in the integration of the isotherms (Eq. 6). Moreover, the IAST selectivity for CO_2/O_2 presents a big jump around 40 atm when $y_{CO_2} = 0.1$. Looking at the partial loading in figure S4, we can attribute this jump to an equilibrium displacement, O_2 replacing CO_2 in the structure. This shows again the fact that IAST behaves as if the structure was closed for O_2, while being open for CO_2 at lower pressure range. We thus confirm by a quantitative study the inapplicability of IAST in flexible nanoporous materials.

3.2 More complex isotherms: the case of RPM3-Zn

We now turn to a second example of gate opening material, RPM3-Zn (Lan 2009), which presents more complex adsorption–desorption isotherms for short alkanes (ethane, propane, butane)—depicted on the right panel of Fig. 6. While adsorption of C_2H_6, and C_3H_8 in this material display a typical gate opening behavior, with a well-marked single transition from a nonporous to a microporous phase, the adsorption of C_4H_{10} present two steps at 0.01 and 0.2 atm. There, the first transition can be attributed to the structural transition (gate opening), but the second one is of a different nature. Because there is no hysteresis loop for the second step, and because it occurs for the larger and more anisotropic guest molecule, it can be attributed to a fluid reorganization (or fluid packing) transition inside the pores. Because experimental in situ characterization (such as single X-ray diffraction) would be necessary to definitely affirm the character of this second step, we chose in the current analysis to work in a reduced pressure range—although the OFAST method itself works with host materials with more than two phases. We thus fitted the C_4H_{10} isotherm using a Langmuir isotherm for pressures below 0.2 atm. The OFAST selectivity after this pressure will thus not be quantitatively accurate, but will be sufficient for the physical insight we need. We also performed tests by computing the selectivity under the assumption that the second jump is due to fluid reorganization by using Langmuir–Freundlich isotherms instead of single site Langmuir isotherm in the open phase,

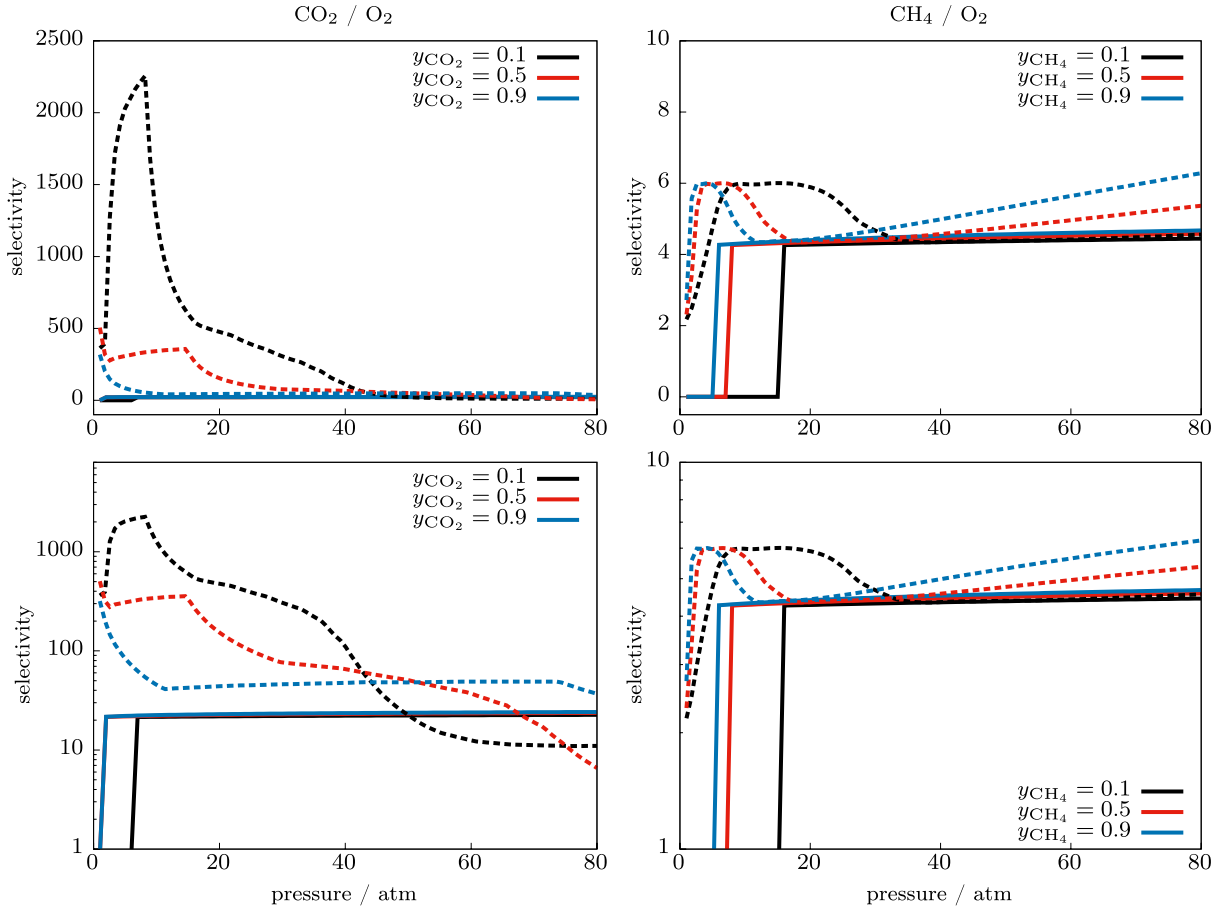

Fig. 5 Comparison of IAST (dashed lines) and OFAST (solid lines) adsorption selectivity for CO_2/O_2 (left) and CH_4/O_2 (right) mixtures in $Cu(dhbc)_2(4,4'\text{-bpy})$. The same curves are presented twice, using linear scale for the y axis on the top panels, and logarithmic scale on the bottom panels. (Color figure online)

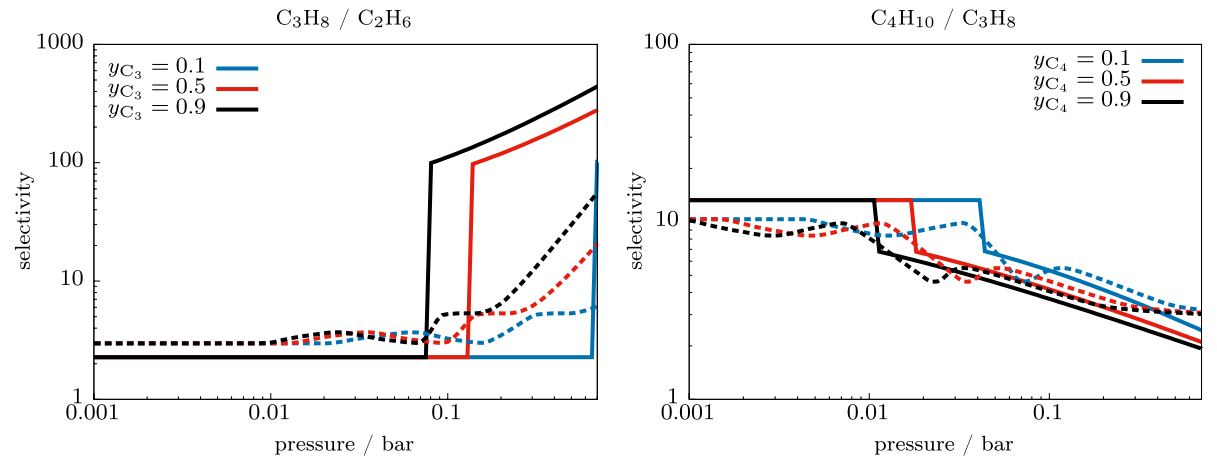

Fig. 6 IAST (dashed lines) versus OFAST (solid lines) adsorption selectivity for C_3H_8/C_2H_6 (left) and C_4H_{10}/C_3H_8 (right) mixtures in RPM3-Zn at different compositions. (Color figure online)

and the selectivity only differs at pressures higher than 0.2 atm.

From the C_3H_8 and C_4H_{10} isotherms, we computed the free energy difference between the nonporous and microporous phases, which we find to be $\Delta F = -30.0 \pm 0.1$ kJ/mol (see supplementary table S4 for details). We did not use the C_2H_6 isotherms for this purpose, as it has only limited data at high loading (at pressure above 1 bar), which increases somewhat the uncertainty of the fit. We were still able to fit the C_2H_6 isotherm with a Langmuir model and use it to compute co-adsorption data, as the free energy difference of the two host phases do not depend on the gas.

Figure 6 displays the selectivity curves obtained with IAST and OFAST for various gas mixtures and compositions in RPM3-Zn. Again, the OFAST selectivity curve follows the expected behavior: it is constant at low loading, where single-component isotherms follow the Henry model. In this low-pressure region, adsorption is negligible and the selectivity cannot be exploited in adsorption-based processes. However, we can see that because IAST is using numerical integration, it is much more sensitive to details in the single-component isotherms than the OFAST method, which is based on fits.

OFAST correctly describes the occurrence of gate opening, at a pressure which depends on mixture composition but is in the range of the pure component gating pressures. After gate opening, the selectivity jumps to its value in the open pore framework. C_3/C_2 mixtures have a behavior similar to that observed in Cu(dhbc)$_2$(4,4′-bpy), with a slowly growing (in log scale) selectivity at high loading. On the other hand, OFAST selectivity for C_4/C_3 mixture displays a different behavior. The selectivity is lower after the transition than before, and further decreases as the pressure and loading increases. This is due to the fact that the single-component isotherms in the open pore structure cross, with C_3H_8 adsorbing more than C_4H_{10} for pressure bigger than 0.03 bar. Thus, the low-pressure selectivity is reversed at high pressure.

In contrast, the IAST fails to describe gate opening, with selectivity showing a continuous evolution. Even the trends displayed by this evolution are in poor agreement and make no physical sense, featuring non-monotonic evolution as a function of pressure and composition. Even their high-pressure limit is often far off from reality, as seen in the case of C_3/C_2.

4 Conclusion

Several published studies of fluid mixture coadsorption in flexible nanoporous material use the IAST method to predict the coadsorption behavior based on single-component adsorption isotherms. This is an invalid application of IAST, which is not adapted to flexible frameworks, as its very first hypothesis is that the framework is inert during adsorption—as clearly stated in the derivation of the method in the seminal IAST paper (Myers and Prausnitz 1965). However, the IAST method can be adapted for frameworks presenting phase transitions induced by adsorption by using the osmotic thermodynamic ensemble. This extension of IAST to flexible materials is called Osmotic Framework Adsorbed Solution Theory (OFAST) (Coudert 2010). It allows the prediction of phases transitions upon co-adsorption, as well as the details of the multi-component co-adsorption isotherms, and is available in commercial software (Tom et al. 2016). Moreover, the use of OFAST with data at various temperatures allows one to produce multi-dimensional temperature, pressure, mixture composition phase diagrams for the flexible host (Ortiz 2012). Finally, while OFAST itself relies on the IAST to describe adsorption in each phase of the host material, this method of accounting for flexibility is not limited to IAST and can be used with other adsorbed solution models, such as real adsorbed solution theory (RAST) or vacancy solution theory (VST).

In this paper, we compared the results given by the IAST and the OFAST method for co-adsorption of fluid mixtures in two different frameworks presenting a gate-opening behavior. In both cases, the selectivities derived by the IAST method are nonphysical and differ widely from the OFAST results, over- or under-estimate the selectivity, sometimes by up to two orders of magnitude. Moreover, we show that even without explicitly using IAST for calculations of selectivity in flexible frameworks, one has to be cautious in comparing single-component isotherms of different guests. Differences in step pressure of stepped isotherms can lead to claims of strong selectivity using flexibility, when applying—without noticing it—concepts that are valid only for rigid host matrices.

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