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Predicting Multicomponent Adsorption: 50 Years of the Ideal Adsorbed Solution Theory

Krista S. Walton and David S. Sholl
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, 30332

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Describing multi-component adsorption is fundamental to using sorption in any chemical separation. 50 years ago, Myers and Prausnitz made a seminal contribution to characterization and prediction of multi-component adsorption by introducing Ideal Adsorbed Solution Theory (IAST). Here, we give an overview of IAST, highlighting its continued role as a benchmark method in describing adsorption using illustrative examples from a variety of experimental and molecular modeling studies. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2757–2762, 2015

Keywords: mixture adsorption, molecular modeling, ideal adsorbed solution theory

Introduction

The measurement of mixed-gas adsorption equilibrium remains one of the most difficult experimental techniques in the adsorption field today. Nevertheless, these data are critical to the design of adsorption separation and storage processes. Over the past several decades, a variety of models have been proposed for predicting multicomponent adsorption data using only pure-component adsorption isotherms. However, none of these theories have matched the influence and applicability of the Ideal Adsorbed Solution Theory (IAST) put forth 50 years ago by Alan Myers and John Prausnitz in 1965.[1] The Myers and Prausnitz paper has been cited over 1200 times, including over 100 citations per year in the past several years, and it continues to find new users as classical adsorption science expands into emerging areas.

IAST is one of the most reliable and often-used methods for predicting gas mixture adsorption equilibrium using only pure-component adsorption isotherms. The theory was developed using three major assumptions: (1) adsorbate molecules in the mixture have equal access to the entire surface area of the adsorbent, (2) the adsorbent is homogeneous, and (3) the adsorbed phase is an ideal solution in which interactions between molecules are equivalent in strength. These assumptions were applied in the original IAST development, but recent work by Talu[2] and Myers and Monson[3] show that the first two assumptions are actually not required for IAST. Furthermore, the two-dimensional view of spreading pressure was also found to be unnecessary. Adsorption equilibria of mixtures containing molecules that vary significantly in size, polarity, or adsorption interactions (e.g., one component adsorbs very strongly over the other species) tend to be poorly predicted by IAST. IAST also does not provide accurate predictions for adsorbents with heterogenous surfaces, such as cationic zeolites. In spite of these shortcomings, IAST is widely used in the adsorption literature and is the standard in mixture adsorption predictions. In this perspective, we highlight the development of IAST and its usage, and the contribution of molecular modeling to understanding its limits in accurately predicting multicomponent adsorption.

Understanding IAST

Multicomponent adsorption theories can be categorized into three types: thermodynamic theories, extensions of the Langmuir model, and the potential adsorption theory. Bartholdy et al.[4] provide a good overview and comparison of capabilities and limitations of these theories. IAST is a thermodynamic approach that assumes an ideal solution is formed by the adsorbed phase. It is essentially an adsorption analog to Raoult's law for vapor-liquid equilibrium. To meet the ideal requirement, there must be no interactions between the adsorbate molecules in the adsorbed phase mixture, and the spreading pressures of the components must be equal at constant temperature. The method for determining mixed gas adsorption using IAST has been discussed in detail in a variety of articles and books.[5–8] We will provide highlights of the calculation here and refer the reader to these other detailed texts for more information.

The spreading pressure can be calculated for pure components using

$$\frac{\pi A}{RT}=\int_0^{p_i^0}\frac{n_i}{P_i}dP_i \tag{1}$$

where π is the spreading pressure, and the partial pressure is calculated using an analog to Raoult's law:

$$P_i=y_iP=x_ip_i^0(\pi) \quad (\text{Constant}\,T\text{ and }\pi) \tag{2}$$

where $p_i^0(\pi)$ is the partial pressure of pure component i calculated at the spreading pressure and temperature of the mixture. Spreading pressure is two-dimensional and can be thought of as the negative of surface tension. For adsorption, this term is positive and is an intensive variable that can be calculated from the experimental isotherm and is not dependent on any adsorbed-phase physical model. The total adsorbed amount, n_T, is calculated using standard state loadings from the pure component isotherm

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Corresponding concerning this article should be addressed to K. S. Walton at krista.walton@chbe.gatech.edu or D. S. Sholl at david.sholl@chbe.gatech.edu

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$$\frac{1}{n_T} = \sum_{i=1}^{N} \frac{x_i}{n_i^0} \tag{3}$$

where N is the number of species in the mixture, x_i is the mole fraction of component i in the adsorbed phase. The standard state loading, n_i^0, is the amount of component i adsorbed at constant temperature and spreading pressure in the absence of the other components. The adsorption of pure species is calculated by

$$n_i = x_i n_T \tag{4}$$

Carrying out these calculations requires that the integral in Eq. 1 be evaluated to obtain the spreading pressure. This can introduce complexity because some pure-component adsorption isotherm models do not have analytical solutions. However, this is simply a point of convenience as obtaining mixture adsorption data from IAST is independent of the model used to describe the pure component data. The main requirement for the pure isotherms is that the data at low pressure or concentration must be known accurately. Poor quality low coverage data will lead to low accuracies in determining the spreading pressure. The isotherm equation being used must also have a finite slope at the origin to be thermodynamically consistent.

In general, IAST cannot be solved in closed form and solutions must be found numerically.[7] This is not a challenge when IAST is used to interpret individual situations, but it can limit the applicability of IAST in process optimization calculations where calculation of mixture isotherm data is deeply embedded within other complex iterative calculations.[10] Several efforts have been made to develop efficient and robust numerical solvers for IAST for use in these contexts.[11,12]

It is generally known that IAST provides good predictions of mixture adsorption and selectivities for mixtures that are close to ideal and for mixtures in which the components are adsorbed at similar levels. However, IAST often does not capture the proper behavior for mixtures of polar species or for mixtures in which one component is adsorbed strongly and the other component is weakly adsorbed, for example, CO_2 and water vapor. Heterogeneity of the adsorbent can also play a significant role in causing poor predictions of mixture adsorption. Multicomponent adsorption predictions for mixtures such as CO_2/CH_4, CH_4/N_2, hydrocarbons, and noble gases are relatively accurate.

Limiting Cases: Selectivity in Limit of Infinite Dilution, Solutions for Langmuir Isotherms

Before using IAST in any context, it is useful to understand several simple limits in which IAST can be solved exactly. The simplest of these is in the limit of low loading. At conditions where each adsorbed component is accurately described by Henry's law, interactions between adsorbed molecules are (by definition) negligible. In this limit, the selectivity of species i relative to species j for any bulk phase composition is simply the ratio of the Henry's constants, $K_{H,i}/K_{H,j}$. This limit can be deduced mathematically from IAST, but its validity is clear from the physical reasoning just given. An important implication of this result is that if IAST is used with fitted isotherms that do not accurately reproduce the Henry's constant for each species, the resulting calculations will be systematically incorrect in their prediction of adsorption selectivity at low loadings. We therefore recommend that Henry's constants be included in fitted isotherms as constraints rather than be obtained from a global fit to isotherm data when this is feasible.[13]

IAST can be solved in closed form for two adsorbed components that are each described by a single-component Langmuir isotherm.[14] If the two components have the same saturation capacity, the selectivity of the adsorbed mixture is the same at all bulk phase pressures and compositions (and is equal to the Henry's law limit stated above). This is a remarkable result because of its simplicity. Although treating the saturation capacity of different components as equal is clearly an approximation, there are many examples of exactly this approach being used. If the saturation capacity of one component is larger than the other, then the selectivity of adsorption for this component as predicted by IAST increases without bound as the chemical potential of the bulk phase increases.[14] This phenomenon reflects the fact that at sufficiently high chemical potentials (albeit at unphysically high values in same cases), entropy dominates over enthalpy and the species that allows adsorption of more molecules in the same volume will dominate. Uses of this effect to achieve molecular separations have been discussed recently by Krishna.[15]

Highlighting the Use of IAST: From Carbons to Metal Organic Frameworks

IAST has been used to calculate mixture adsorption in a large variety of materials including activated carbon, zeolites, and metal-organic frameworks. The literature on experimental mixture adsorption equilibrium is much smaller than the number of reported pure isotherms. The most studied systems include mixtures of CO_2, N_2, and various hydrocarbons. In 1998, Do and coworkers[16] reported IAST predictions with experimental measurements for adsorption of mixtures of methane, ethane, propane, and carbon dioxide on activated carbons. The carbons were derived from KOH activation of macadamia nut shells. The results show that the CO_2/CH_4

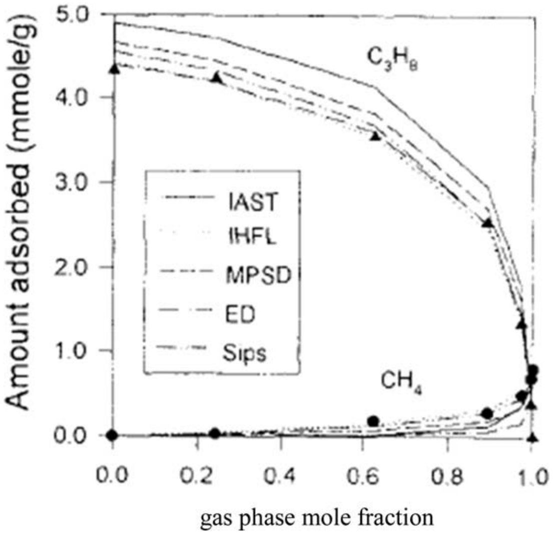

Figure 1. Binary adsorption data and model predictions for CH_4/C_3H_8 in Ajax activated carbon at 303 K.

The models are ideal adsorbed solution theory (IAST), loading-dependent isosteric heat, (IHFL), micropore-size distribution (MPSD), energy distribution (ED), extended Langmuir, and extended Sips (Reproduced from Ref 16 with permission from AIChE J).

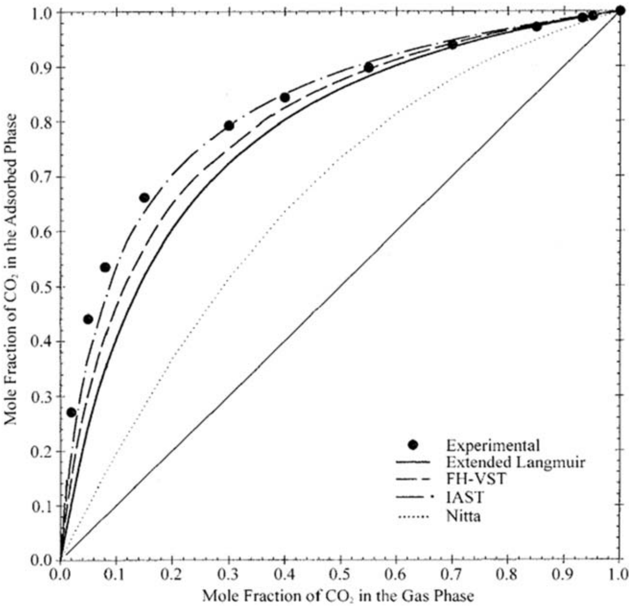

Figure 2. Experimental and predicted *x–y* adsorption phase diagrams for CO_2–CH_4 binary system with H-ZSM-5 at 40°C. (Reproduced from Ref 17, with permission from Sep. Sci. Tech).

system is modeled well by IAST. However, the methane/propane mixture is less ideal, and IAST over-predicts the adsorption loadings in the mixture (Figure 1). This behavior is common for mixtures with species that have large differences in size and/or adsorption interactions. It was pointed out by Do et al.[16] that the differences between the different model predictions appear to be a function of how accurately the pure-component models fit the pure isotherm data. This is a common result in the mixture adsorption literature, and it is important to reiterate that if IAST is applied using pure-component isotherms that fit experimental data relatively poorly then it is to be expected that multicomponent predictions will have systematic inaccuracies, even when IAST itself is accurate for the system of interest.

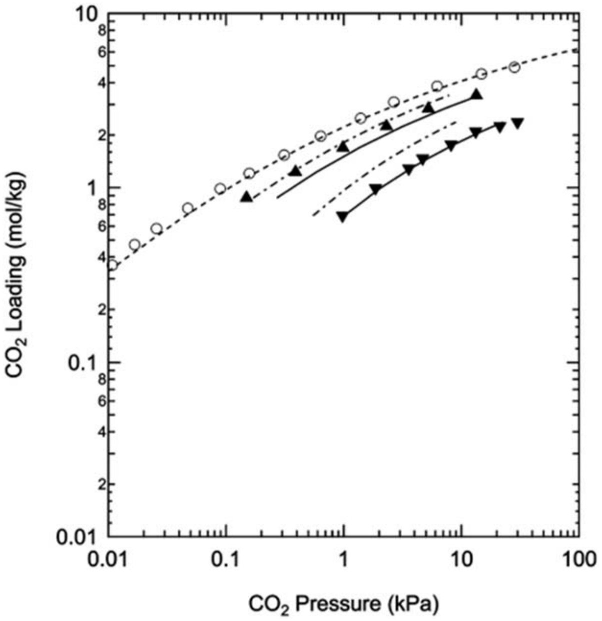

Figure 3. CO_2 adsorption isotherms on zeolite 5A at 0°C.

Open circles, pure CO_2; triangles, binary CO_2 with 1 mol kg^{-1} H_2O; upside down triangles, binary CO_2 with 3.4 mol kg^{-1} H_2O; dotted curve is the Toth isotherm for pure CO_2; dashed curves are the IAST model; and solid curves are the VEMC model for mixtures (Reproduced from Ref 18, with permission from J. Chem. Eng. Data).

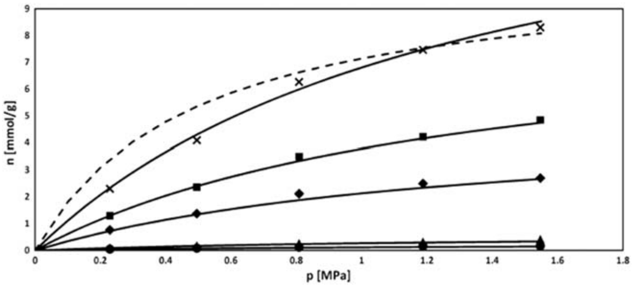

Figure 4. Measured multicomponent sorption data on Basolite C300 containing the total adsorbed amount (crosses) and the partial adsorbed amounts of CH_4 (black square), CO_2 (black diamond), N_2 (black triangle) and H_2 (black circle), total adsorbed amount predicted with IAST (dotted line) (Reproduced from Ref 19, with permission from Adsorption).

Tezel and coworkers[17] measured binary adsorption data for mixtures of CO_2-CH_4, CO_2-N_2, and CH_4-N_2 on H-ZSM-5 at 40°C. Mixture adsorption predictions were performed with several models including Extended Langmuir, Extended Nitta (Nitta), IAST, and the Flory–Huggins form of the Vacancy Solution Theory. Similar to the results found for activated carbon, the CO_2-CH_4 mixtures were modeled very well by IAST (Figure 2). However, the models significantly under predicted the CO_2-N_2 mixture adsorption data, which is the result of differences in adsorption strength. When one component is adsorbed strongly over another, the adsorbed phase deviates from an ideal mixture, and IAST cannot accurately describe the mixture without corrections to the model.

Wang and LeVan[18] reported an experimental study of CO_2 and water vapor adsorption on zeolites 5A and 13X at 0, 25, and 50°C, at various water loadings. These zeolites have accessible Ca^{2+} and Na^+ cations, respectively, in the pore space, which leads to a heterogenous adsorbent surface. IAST was found to predict mixture adsorption correctly in 5A when the water loading was small (1 mol/kg). However, at higher water adsorption loadings, the CO_2 coadsorption is not accurately captured by IAST. A virial excess mixing coefficient model (VEMC) was used to add corrective terms to IAST and account for the nonideality of the CO_2-H_2O mixtures. As shown in Figure 3, the corrected model was found to describe the mixture data with high water loadings with greater accuracy than IAST alone (although IAST and the corrected model had similar accuracy at lower water loadings).

Experimental investigations of multicomponent adsorption in metal-organic frameworks are less prevalent in the literature compared with carbons and zeolites. One of the few investigations of this type was reported by Rother and Fieback in 2013.[19] They conducted adsorption experiments of quaternary gas mixtures on activated carbon, 13X zeolite, and the metal-organic framework Cu-BTC (available commercially as

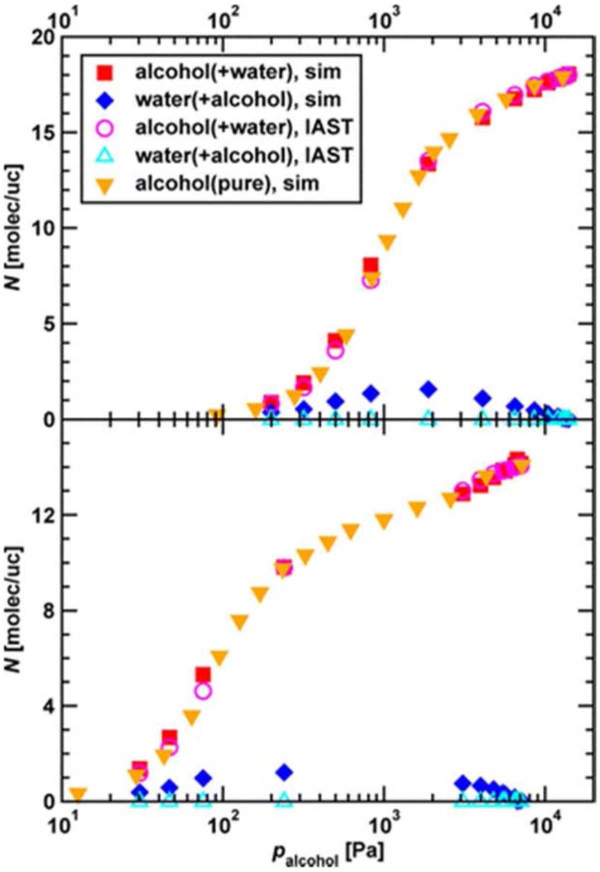

Figure 5. Binary adsorption isotherms for water/methanol (top) and water/ethanol (bottom) in silicalite at 298 K.

Red and blue symbols show results from molecular simulations of binary adsorption for alcohol and water, respectively. Open symbols show the predictions of IAST for the same mixtures. Water adsorption is severely underestimated by IAST. (Reproduced from Ref 27, with permission from J. Phys. Chem. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Basolite C300). Multicomponent adsorption data were measured for mixtures consisting of 60 mol % CH_4, 33 mol % CO_2, 5 mol % N_2, and 2 mol % H_2. IAST predicted the total adsorption loading of this gas mixture with very good accuracy for Norit R1 activated carbon. However, strong deviations from IAST were exhibited by 13X, where the total adsorption loadings were over predicted. Experiments performed on Cu-BTC indicate that a slight nonideality exists, but the IAST predictions are closer to the experimental data. As shown in Figure 4, IAST slightly over predicts loadings at low pressure, but is more accurate as total pressure increases. This is a somewhat surprising result considering the nonideality that should be introduced into the system by heterogeneity of the material (Cu-BTC has two types of pore cavities and open metal sites that create heterogeneity in terms of local adsorption strength) and by differences in loadings of the molecules in the mixture (CH_4 adsorbs more strongly than N_2 or H_2).

These studies highlight the applicability of IAST in providing good mixture adsorption predictions over a variety of materials and molecules. There are other mixture studies with high industrial relevance including for example hydrogen purification[20] and xylene separations[21]. However, the difficulty in measuring mixed gas adsorption means that there are relatively few systematic studies in the literature that would allow a comprehensive evaluation of the accuracy of IAST over wide ranges of mixture compositions, adsorbents, and conditions. This type of study lends itself to taking advantage of molecular modeling methods.

Contributions of Molecular Modeling to Understanding IAST

Molecular simulation of adsorption has played an important role in testing the accuracy and applicability of IAST. Adsorption equilibrium can be simulated in porous materials using Grand Canonical Monte Carlo (GCMC).[22] Crucially, the computational cost of predicting a single state point of a multicomponent adsorption isotherm with GCMC is roughly the same as finding a point on a single-component isotherm. This situation strongly contrasts with experimental measurements, and as a result the vast majority of extant mixture isotherm data comes from molecular simulations.

Early examples of using molecular simulations to test the accuracy of IAST were reported by Karavias and Myers[23] and by Heuchel et al.[24] The former included a detailed study on binary adsorption data for C_2H_4/CO_2, CH_4/CO_2, and iC_4H_6/C_2H_4 in zeolite X. Phase diagrams and total coverages were calculated using Monte Carlo simulations and results were compared with experimental data. The simulations modeled the two CO_2 mixtures very well, but negative deviations from ideality were found for the iC_4H_6/C_2H_4 mixtures. These deviations were explained as resulting from energetic heterogeneity and size effects. Heuchel et al. reported on CH_4/CF_4 mixtures in silicalite. Comparisons were made between mixture adsorption data from GCMC simulations, IAST predictions made using single-component adsorption data from GCMC, and gravimetric experimental data for both single-component and mixture adsorption for a wide range of bulk phase compositions and pressures up to 20 bar at room temperature. The agreement between IAST and the mixture GCMC data was quantitative, indicating that IAST is a good approximation for this system. Small deviations were observed between GCMC and experimental data for mixture adsorption, but it is important to note that this implies imprecision in the force fields used for the GCMC simulations, not a failing of IAST.

Combining IAST with molecular simulation data has now become a relatively common tool in computational screening of porous materials for adsorption applications. Van Heest et al. combined single-component GCMC data and IAST to predict mixture adsorption for Ar/Kr, Kr/Xe, and Xe/Rn mixtures in 70 MOFs that had been selected from an initial library of more than 3000 materials.[25] They showed for selected materials that agreement between IAST and binary isotherm data from GCMC was quantitative over the full range of pore loadings provided that IAST was applied by directly integrating high quality single-component adsorption data. An example was given where curve-fitting to single-component isotherms could lead to the spurious conclusion that IAST was inaccurate. Haldoupis et al. combined molecular simulations and IAST to identify MOFs with very high selectivities for CO_2 over N_2 after performing initial single-component calculations for ~500 materials.[26] IAST was found to be quantitatively accurate for bulk pressures up to ~10 bar at room temperature for several materials with CO_2/N_2 selectivities of 200–300.

It is perhaps not surprising that IAST accurately describes adsorption of the relatively ideal mixtures discussed above (noble gas mixtures, CH_4/CF_4, CO_2/N_2). Molecular simulations also provide a useful approach to testing the precision of IAST for mixtures that have stronger nonidealities in the bulk phase. Bai et al. performed thorough simulations of water/methanol and water/ethanol mixtures in silicalite and used their results to examine the validity of IAST.[27] Defect-free silicalite is highly hydrophobic, so water does not adsorb at room temperatures until the bulk phase pressure of liquid water is high, whereas alcohols adsorb appreciably at low partial pressures. Applying IAST to these mixtures predicts the adsorbed amount of alcohols quite accurately, but severely underestimates the water loading at essentially all conditions (see Figure 5). In the adsorbed mixtures, the presence of alcohol molecules allows formation of favorable hydrogen bonds with water molecules, leading to water adsorption that does not occur in the purely hydrophobic environment encountered by water adsorbing as a single component. Bai et al. showed that IAST overestimates the selectivity of silicalite for methanol or ethanol over water by a factor of roughly 5000. As a side note, modeling water adsorption in silicalite is a useful example of the challenges of using molecular simulation to predict adsorption in complex materials; experimental assessments of water adsorption show that the intrusion pressures of water are very strongly influenced by the presence of defects such as silanol nests, a physical phenomenon that is very difficult to describe in a predictive way in simulations.[27]

Molecular simulations can be used to examine fundamental questions about IAST that cannot be probed with experimental data. In applying IAST to experimental data, it is always necessary to fit single-component isotherms to discrete data, so some uncertainty in the prediction of mixture adsorption always results from this data fitting. Moreover, if IAST is applied in regimes where information from the single-component isotherms requires extrapolation beyond the original experimental data there is uncertainty associated with this extrapolation. This latter situation is particularly problematic for systems with large selectivities. The same issues arise in using molecular simulation data from standard GCMC simulations, which give data in a pointwise manner, although direct numerical integration of high precision simulation data can minimize these issues.[25]

Simulation techniques are available, however, that accurately provide adsorption isotherms at arbitrary bulk phase precisions using well-defined reweighting of simulation data. Chen and Sholl used one of these methods, Transition Matrix Monte Carlo, to assess the accuracy of IAST without needing to invoke curve fitting for several examples.[13] They showed for CO_2/CH_4 mixtures that IAST was highly accurate for adsorption in idealized models of carbon nanotubes, but that IAST over predicted the selectivity of CO_2 in CO_2/CH_4 mixtures in the all silica version of the zeolite DDR by a factor of up to 2 at high bulk phase pressures.

Molecular simulations have become a valuable tool in efforts to develop new adsorbents, but the complexities of real materials and real applications means that modeling of this kind can complement but not entirely replace experimental measurements. Molecular simulations are reliant on the precision of the force fields that define interactions between atoms in adsorbates and the adsorbent. Significant progress has been made in recent years using quantum chemistry methods to derive accurate force fields for broad classes of nanoporous materials.[28] Most molecular simulations of adsorption in nanoporous materials assume that the adsorbent is rigid. This is a reasonable assumption for many materials such as zeolites, but there are well-known examples of MOFs were adsorption properties can vary strongly due to adsorption-induced structural changes in the adsorbent.[29] Finally, the great majority of molecular simulations focus on crystalline materials because of the significant challenges associated with generating meaningful atomic-scale models of disordered porous materials. As already shown above multicomponent adsorption in disordered materials such as activated carbons is important in many applications of these materials.

Future Outlook

It has been 50 years since the IAST was introduced to the scientific community, and it continues to be the benchmark theory in multicomponent adsorption studies. Although more complex and presumably more accurate theories for predicting multicomponent adsorption have been advanced since the introduction of IAST, the conceptual and practical simplicity of IAST mean that it is by far the most widely used approach to this phenomenon. After five decades, one would be hard pressed to find a paper on mixture adsorption that does not compare IAST predictions with data or with other mixture theories, and it is difficult to imagine that this will change.

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