

Gas Adsorption in Active Carbons and the Slit-Pore Model 2: Mixture Adsorption Prediction with DFT and IAST

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Received: October 15, 2004; In Final Form: March 22, 2005

We use a fast density functional theory (a “slab-DFT”) and the polydisperse independent ideal slit-pore model to predict gas mixture adsorption in active carbons. The DFT is parametrized by fitting to pure gas isotherms generated by Monte Carlo simulation of adsorption in model graphitic slit-pores. Accurate gas molecular models are used in our Monte Carlo simulations with gas–surface interactions calibrated to a high surface area carbon, rather than a low surface area carbon as in all previous work of this type, as described in part 1 of this work (Sweatman, M. B.; Quirke, N. *J. Phys. Chem. B* 2005, 109, 10381). We predict the adsorption of binary mixtures of carbon dioxide, methane, and nitrogen on two active carbons up to about 30 bar at near-ambient temperatures. We compare two sets of results; one set obtained using only the pure carbon dioxide adsorption isotherm as input to our pore characterization process, and the other obtained using both pure gas isotherms as input. We also compare these results with ideal adsorbed solution theory (IAST). We find that our methods are at least as accurate as IAST for these relatively simple gas mixtures and have the advantage of much greater versatility. We expect similar results for other active carbons and further performance gains for less ideal mixtures.

Introduction

Active carbons have many uses including separation of fluid mixtures on an industrial scale. So there is a substantial body of research directed to understanding the behavior of fluid mixtures in active carbons. A major problem posed by fluid mixtures concerns the additional degrees of freedom generated by each component after the first. For pure fluids we need specify only the bulk pressure and temperature, in the absence of hysteresis, to map the phase diagram. But for mixtures it becomes increasingly difficult and time-consuming to map the adsorbed phase diagram as the number of fluid components increases. Yet in industry predictions of the behavior of gas mixtures in active carbons are often to be made quickly so that a wide range of adsorbents and adsorbates can be assessed.

One approach for predicting mixed gas adsorption in active carbons is based on the adsorption integral

$$N_i(P) = \int_0^\infty dH_p f(H_p) v_i(H_p, P\{x\}) \quad (1)$$

where N_i is the amount of component i adsorbed at pressure P , f is a pore-size distribution (PSD), and v_i is a “kernel” of isotherms describing the adsorption of component i in a range of pore-widths, H_p , for a mixture of bulk composition $\{x\}$. To provide a very fast interactive software tool we would need to map the entire phase diagram for arbitrary mole fractions of the mixture. This could involve specification of an $n+1$ -dimensional kernel (at a fixed temperature) for an n -component mixture. If we represent the kernel at a fixed temperature by a matrix of, say, only 10 elements each for pressure, pore width, and bulk mole fraction, we find that the number of data entries is of the order 10^{n+1} , a rather large number, even for small n .

So it is quite impractical to try to pre-generate the mixture kernel by any but the most efficient methods. Usually, a much more sensible approach is to calculate mixture adsorption isotherms for each pore width for the specific mixture in question. But even this is a slow process if nonlocal DFT, and particularly Monte Carlo simulation, is employed and if many mixtures are to be investigated. On the other hand, it is unlikely that any method for predicting mixture adsorption in active carbons will be successful generally unless it models the behavior of fluid mixtures at the nanoscale. So our goal is to create a method that is both accurate at the nanoscale and quick.

By far the most popular method for solving this ‘mixture problem’, i.e., fast prediction of mixture adsorption given the pure component isotherms as input, is “ideal adsorbed solution theory,”^{1,2} or IAST. This theory has been developed over many years and has been applied extensively in the literature to predict mixture adsorption. We use this theory as a benchmark and compare our approach against it in terms of accuracy, versatility, and efficiency.

In part 1 of this work³ we described procedures for modeling pure gas adsorption in active carbons based on a slit-pore model, Monte Carlo simulation, and a “slab-DFT”. We demonstrated the accuracy of our methods for predicting pure gas adsorption in active carbons up to reasonably high pressure at a range of super- or near-critical temperatures given a *single* carbon dioxide isotherm only, at similar temperatures, as input. The aim of this work, part 2, is to show that the same approach can also be used to quickly predict the adsorption of gas mixtures in active carbons with good accuracy.

A number of other methods have been proposed to solve the mixture problem based on extending pure adsorption equations to mixtures. For example, the Langmuir,^{4–8} Dubinin–Radushkevich,⁹ Dubinin–Astakhov,¹⁰ and Toth¹¹ isotherms and neural-network¹² and virial^{8,13–15} methods have been adapted in this way to analyze a variety of gas mixture systems. However, we

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do not expect these approaches will be successful generally as either (a) they are not based on statistical mechanics, or (b) they are limited to low pressure where gas–gas interactions are described at a trivial level.

To our knowledge, there have been no attempts to predict gas mixture adsorption in active carbons with a nonlocal DFT of the type pioneered by Lastoskie et al.¹⁶ and others.¹⁷ Regarding molecular simulation, Gusev and O'Brien¹⁸ find that they are unable to satisfactorily predict the adsorption of methane/ethane gas mixtures at 308 K in BPL-6 activated carbon at moderate to high pressures using the polydisperse independent ideal slit-pore model and GCMC, although they find better agreement with experiment at low pressure. Davies and Seaton¹⁹ used the same methods to study these gases on a range of activated carbons. They found that selectivity is predicted quite well at relatively low pressure (1 bar or less), but is less satisfactory at higher pressures. They compared the use of MC simulation with IAST for predicting mixture adsorption and found close agreement, indicating that the mixture is relatively ideal under the conditions analyzed. Heuchel and co-workers²⁰ analyzed carbon dioxide/methane mixtures at ambient temperature up to 17 bar. They found that, generally, better predictions for gas mixture adsorption can be obtained as more and more input data are used, i.e., using several pure gas isotherms as input is better than using just one. They attributed this to obtaining a more accurate pore-size characterization as more input data is used. However, they could not accurately predict all their experimental data, including the mixture data.

In our view these predictions for mixed gas adsorption using numerically intensive methods are somewhat disappointing considering the level of sophistication. We consider it likely that in all of this Monte Carlo simulation work a major contribution to inaccuracy is the technique used to calibrate molecular models. In each case gas–surface interaction parameters are fitted to reproduce adsorption on a low surface area carbon. The assumption is that this parametrization is accurate for high surface area carbons. The results in part 1 of this present work³ suggest that this is not the case.

The remainder of this paper is structured as follows. First, we discuss ideal adsorbed solution theory²¹ (IAST). Then we briefly describe our models and methods for predicting gas mixture adsorption in active carbons, including the slab-DFT. More comprehensive detail concerning this DFT model can be found in earlier work.²² We test our approach in two ways. First, to make direct comparison with IAST, we use experimental pure adsorption isotherms for each component of the mixture as input to our characterization and prediction process. Then, to realize our ultimate aim, we repeat our analysis using only a single (carbon dioxide) experimental isotherm as input. We provide results for two sample active carbons, presented in terms of the error between prediction and experiment for the adsorbed mole fraction of carbon dioxide.

IAST

Probably the most popular theory for predicting gas mixture adsorption, ideal adsorbed solution theory, is a thermodynamic treatment of adsorption at a surface. This theory for the adsorbed mixture takes as its only input the pure component isotherms, all at the same temperature. It is able to make predictions for gas mixture adsorption at this temperature up to a pressure that is limited by the input data. Cracknell and Nicholson²³ suggested the original theory should be recast in terms of the total, or absolute, grand potential rather than the “spreading pressure”, which they describe as the negative of the excess grand-potential

per unit area. Vuong and Monson²⁴ arrived at the same conclusion, which was later proved by us.²² However, there is no mention of excess or absolute quantities in Myers and Prausnitz's original work¹ and, indeed, their fundamental thermodynamic relation is based on absolute quantities.

There is no constraint on how the isotherms that are input to AST are described, but often they are described in terms of a smooth adsorption equation such as the Langmuir^{4,25,26}, Dubinin–Radushkevich,²⁷ or Toth²⁵ isotherms. One could also fit straight-line segments, or “splines”, between the data-points and, actually, this may well be preferable if the particular engineering adsorption equation fits the data poorly. Neither does AST make any assumption about the nature of the adsorbent, other than it is inert. AST itself is not based on any molecular or microscopic model, but the pure component isotherms can be. This means that AST can be combined with a model of the surface, such as a polydisperse pore model. This seemingly attractive feature has been used by several groups^{28–31} to study gas mixture adsorption. However, we note that this approach, sometimes called HIAST (heterogeneous IAST), can generate severe problems if adsorption in the narrowest pores is strongly favored by one component because in this case solution of IAST in these pores can be limited to unacceptably low pressures. So we apply IAST without use of a PSD, i.e., we avoid the HIAST route.

Adsorbed solution theory (AST) is easily derived²² using thermodynamic arguments together with Henry's Law (which concerns adsorption in the low-density limit). Note that Henry's law can be obtained quite easily² from density functional theory. IAST is then obtained from AST by two approximations,^{2,22} namely, that mixing is ideal and that the bulk gas is ideal. IAST is defined by two equations:

$$x_{ai} = \frac{P(\Omega)x_{bi}}{P_i^0(\Omega)}$$

$$N_{ai} = x_{ai} \left(\sum_i \frac{x_{ai}}{N_{ai}^0(\Omega)} \right) \quad (2)$$

The first is used to calculate adsorbed phase mole fractions, $\{x_{ai}\}$, at a particular grand potential Ω , while the second gives the total adsorption of each component, N_{ai} . Here, $\{x_{bi}\}$ are the bulk phase mole fractions and P , $\{P_i^0\}$ and $\{N_{ai}^0\}$ are the bulk mixture pressure, the pure component bulk pressures, and the adsorptions of the pure components all expressed as functions of the grand potential of the adsorbed phase.

We compared²² IAST against the slab-DFT described below and found that, as expected, our novel DFT was significantly more accurate for predicting the adsorption of a model of a nonideal gas mixture, carbon dioxide and hydrogen, in ideal graphitic slit-pores. But for relatively ideal gas mixtures, such as a model of methane and carbon dioxide, there was naturally little difference in accuracy. We describe this DFT approach next.

Molecular Models and the Slab-DFT

This work uses the same models and methods³ used in part 1 to model the adsorption of gases in active carbons. We describe them very briefly here and direct the reader to part 1 and ref 22 for more detail.

We model the pore space of active carbon with the polydisperse independent ideal slit-pore model, which describes a material in terms of a pore-size distribution (PSD). Each pore is constructed from two parallel inert graphitic walls separated

by a distance H_p , where gas–surface interactions are described by the Steele potential.^{32,33}

The first DFT study to use a slit-pore model³⁴ employed a “local” DFT to generate the local isotherms, $\nu(H_p, P)$, which describe gas adsorption in each pore. But more recent DFT studies^{16,35–40} have used a nonlocal theory based on accurate hard-sphere functionals.^{41–44} While these DFTs have proved popular for fundamental studies of fluid behavior in pores and for characterization studies, there are no studies, to our knowledge, that make predictions for either pure or mixed gas adsorption in real materials using these nonlocal DFT. We can expect, given the accuracy of these DFTs in ideal pores for simple fluids, that they might be quite accurate for predicting adsorption of simple fluids in active carbons, but we have no right to expect similar accuracy for more complex fluids with significantly nonspherical molecular shapes or with electrostatic moments, such as butane and water. Further work is needed to establish whether current DFT methods are sufficient to model a range of gases in active carbons, or whether more sophisticated functionals and models are required. Whatever the result, these DFTs are too numerically demanding for our present purpose.

Several studies^{45–50} use the polydisperse ideal-pore model and GCMC simulation to generate the kernel, where gas–surface interactions are calibrated to reproduce adsorption on a low-surface area carbon. Part 1 of this current work³ demonstrated that much greater accuracy can be obtained if gas–surface interactions are calibrated to a high surface area carbon, and we follow the same approach here. So our kernel of local isotherms for pure fluid adsorption is generated by Monte Carlo simulation together with the Steele potential, where gas–surface interactions are calibrated to a high surface area carbon. Details of our gas molecular models can be found in part 1.³

To predict mixture adsorption we employ a slab-DFT, using the same model and methods as in previous work.^{3,22} That is, we parametrize the slab-DFT by fitting it to each local isotherm in our MC kernel of pure fluid isotherms, $\nu(H_p, P)$. We then use these same parameters, together with the Lorentz–Berthelot rules for cross-interactions

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2; \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (3)$$

and a PSD to predict mixture adsorption on a given material. PSDs are generated using the same methods as in part 1 of this work, i.e., we optimize the PSD to obtain the most robust solution that fits the experimental adsorption isotherm well, where each PSD is constrained to consist of a number of log-normal modes. We compare two sets of results. One obtained using a PSD generated using both pure component isotherm, and the other obtained using a PSD generated from just the pure carbon dioxide isotherm.

Our slab-DFT model is a crude nonlocal theory that can be solved quickly, yet it exhibits complex size-related energy and entropic effects, which are important for mixtures. It is essentially a DFT analogue of the many popular empirical or semiempirical “isotherm equations” for mixtures, but it has the advantage of being founded on statistical mechanics and developed by a series of approximations whose impact is understood. In part 1 of this current work we showed³ that this slab-DFT and the polydisperse independent ideal slit-pore model could also be used to predict how adsorption isotherms of some relatively simple near- and super-critical gases in active carbons vary with temperature (thereby allowing prediction of the isosteric heat). Although the IAST approach is quicker by far, our DFT method was sufficiently quick to be considered

TABLE 1: Results for Pure Gas Isotherms^a

carbon (probe gas)	rms error in fitted isotherm (cm ³ (STP)/g)	rms error in predicted isotherm (cm ³ (STP)/g)
AC1 (CO ₂ only)	CO ₂ (293K): 1.0	CH ₄ (293K): 2.4 CO ₂ (333K): 1.0 CH ₄ (333K): 1.2
AC1 (CO ₂ and CH ₄)	CO ₂ (293K): 1.2 CH ₄ (293K): 0.8	CO ₂ (333K): 1.0 CH ₄ (333K): 2.4
AC2 (CO ₂ only)	CO ₂ (303K): 1.0	N ₂ (303K): 2.7 CO ₂ (323K): 5.7 N ₂ (323K): 2.1
AC2 (CO ₂ and N ₂)	CO ₂ (303K): 1.3 N ₂ (303K): 0.6	CO ₂ (323K): 5.8 N ₂ (323K): 0.7

^a Note how using both isotherms as input improves the fit to the other gas at the expense of the fit to carbon dioxide. Also note the relatively large rms (root-mean-square) error (between theory and experiment) in the carbon dioxide predictions at 323 K on AC2. This large error is inconsistent with results from around 20 other active carbon samples (some of which are described in part 1 of this work³), and so we believe the error is in the experimental results in this case. Obtained using two different methods for the characterization process: one uses just a single carbon dioxide isotherm as input, the other uses both pure gas isotherms as input.

interactive, i.e., an isotherm for a gas mixture adsorbed in an ideal slit pore can be generated in under a second on a desktop PC.

Results

To test the slab-DFT’s performance for active carbons it is applied to predict the adsorption of mixtures of (a) carbon dioxide and methane at 293 and 333 K in one active carbon (AC1) at 2 and 10 bar, and (b) carbon dioxide and nitrogen at 303 and 323 K in another activated carbon (AC2) at 1, 6, and 30 bar. We compare with experimental results⁵⁶ and also IAST when each pure component isotherm is used as input. Our experimental data is obtained from a third party. We generate MC simulation kernels at 293 K and, rather than generating another set of MC kernels at 303, 323, and 333 K, we instead convert these kernels from 293 K using the slab-DFT for each bulk gas isotherm and each pure gas isotherm for each pore. We choose $\delta H = 0.285$ nm and $\delta\sigma_{bi} = 0.25 \sigma_{bi}$ as in reference.²²

Table 1 displays the rms error in the fitted and predicted pure gas isotherms for each active carbon at each temperature and for the two characterization methods (i.e., using both pure isotherms or just the carbon dioxide isotherm as input to the characterization process). We see that, as expected, fitting to both pure isotherms reduces the accuracy of the fit to the carbon dioxide isotherm slightly but significantly improves the fit to the other gas. This difference is particularly significant for nitrogen on AC2.

Figure 1 shows the mixture prediction results⁵⁷ for AC1 at two pressures: 2 bar (a) and 10 bar (b). Due to restrictions on the data we can present, we have decided that displaying the difference in the adsorbed mole fraction between theoretical prediction and experiment is clearest. This avoids showing the experimental data directly. Experimental errors are unknown. The symbols are our data while lines guide the eye. At both pressures we see that the accuracy of IAST and the slab-DFT, regardless of how the material is characterized, are comparable. Note how the predictions made with the slab-DFT at 333 K are shifted consistently with respect to those at 293 K (the temperature of the MC kernel).

Figure 2 shows the mixture prediction results for AC2 at three pressures; 1 bar (a), 6 bar (b) and 30 bar (c). This time, we see that the accuracy of IAST and the slab-DFT are comparable

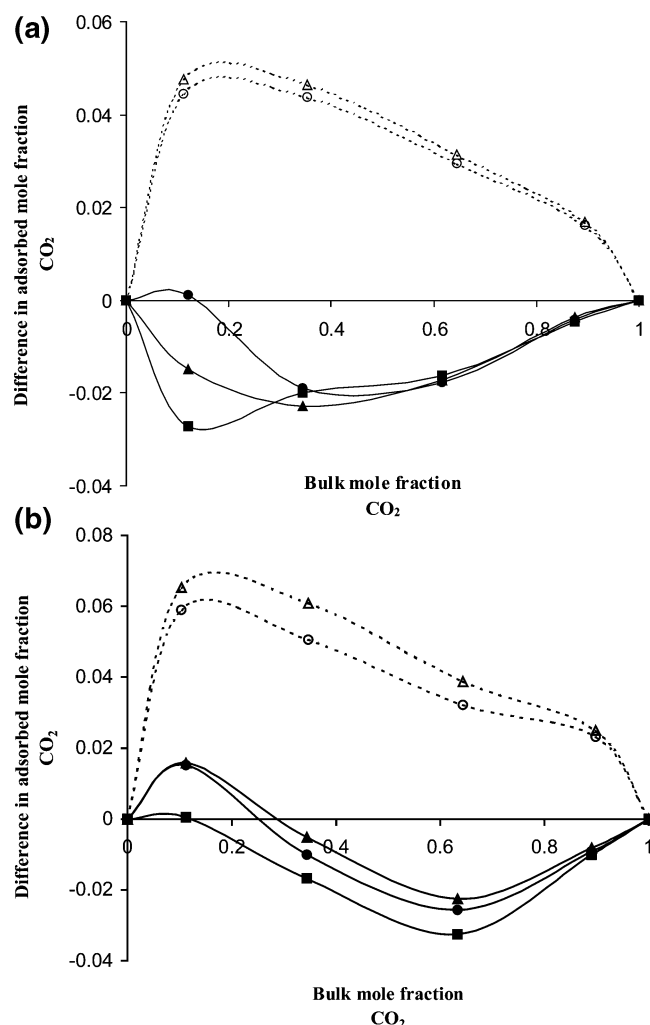


Figure 1. (a) Results for the adsorption of mixtures of carbon dioxide and methane in AC1 at 2 bar. Symbols show the difference in the adsorbed mole fraction of carbon dioxide between theoretical prediction and experiment (lines are a guide to the eye). The symbols denote results from IAST (squares), the slab-DFT with a PSD based on just the pure carbon dioxide isotherm (circles), and the slab-DFT with a PSD based on both pure isotherms (triangles). Solid lines and symbols are for 293 K while dotted lines with open symbols are for 333 K. Note that the slab-DFT is parametrized by fitting to a 293 K MC kernel. (b) As for Figure 1a except that the pressure is 10 bar.

when only the carbon dioxide isotherm, not both pure gas isotherms, is used as input to the characterization process. Predictions based on the slab-DFT and both gas isotherms as input are much worse. These conclusions hold at both 303 and 323 K. Once again, predictions made with the slab-DFT at 323 K are shifted consistently with respect to those at 293 K. Note that IAST cannot be used to make predictions for bulk mole fractions of carbon dioxide above 0.4 at 6 bar and above 0.01 at 30 bar.

Discussion

The above results appear to be inconclusive — it is not clear whether it is better to base the characterization process on both the pure gas isotherms or just the carbon dioxide isotherm. In particular, contrast the results in Figure 2 with those obtained by Seaton and others^{18–20} that suggest greater predictive accuracy is achieved as more input isotherms, not fewer, are employed as this leads to a more accurate PSD.

We believe the correct interpretation of these results is as follows. First, consider the quite different predictions obtained

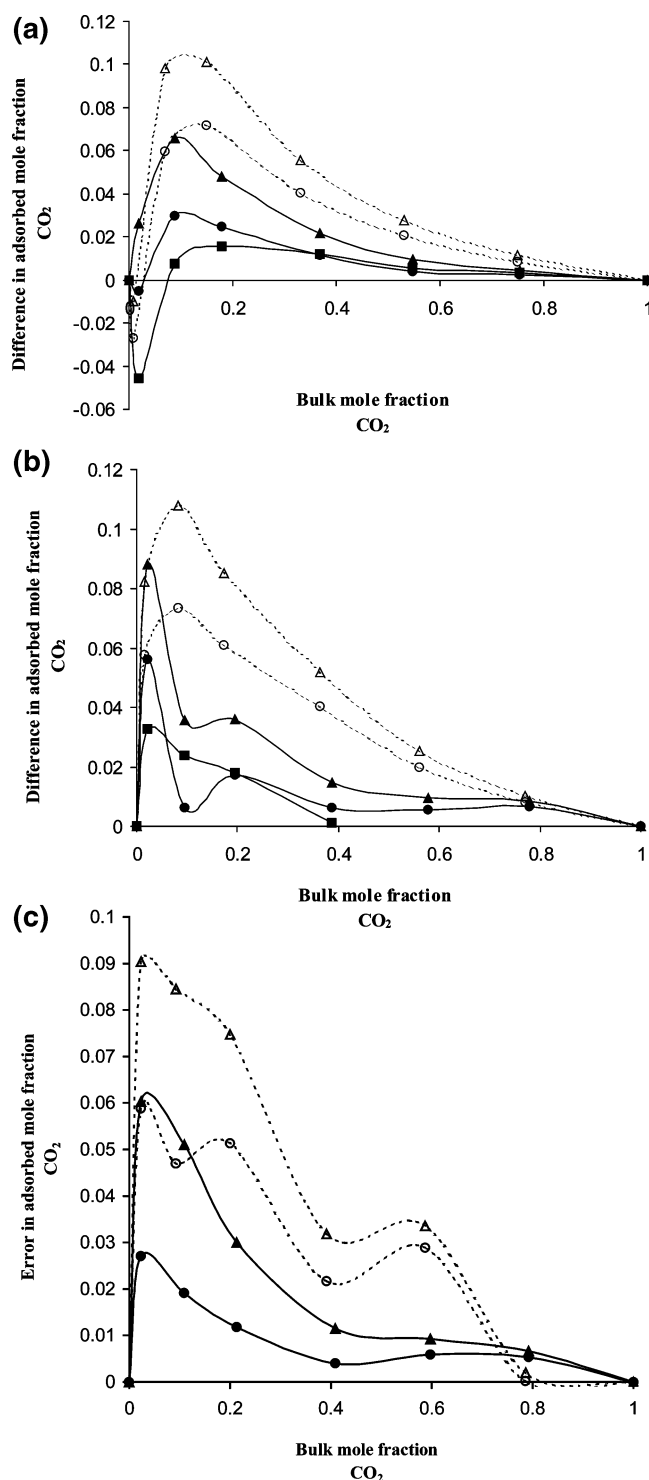


Figure 2. (a) As for Figure 1a except that results are for mixtures of carbon dioxide and nitrogen in AC2 at 1 bar, and solid lines and symbols are for 303 K while dotted lines with open symbols are for 323 K. (b) As for Figure 2a except the pressure is 6 bar. Note that IAST fails for bulk mole fractions of carbon dioxide above 0.4 at this pressure. (c) As for Figure 2a except the pressure is 30 bar. Note that IAST fails for bulk mole fractions of carbon dioxide above 0.01 at this pressure.

from the slab-DFT in Figure 2 based on different pore characterizations. These differences are a direct result of the different PSDs obtained in each case. So we can immediately conclude that, in the language of adsorbed solution theory, the activity coefficient of the CO_2/N_2 mixture is dependent on the PSD of the material, in agreement with the conclusions of Van der Vaart et al.⁵¹ In fact, we find that the ideality of this mixture

increases with increasing pore width, which indicates that IAST will be less accurate for carbon molecular sieves than for mesoporous carbons. This means that we cannot have much confidence in IAST for this mixture (at least at the higher pressures) because IAST is independent of the PSD. Further, without an analysis of the PSD, it is unlikely that activity coefficients can be predicted with confidence (which is a justification for HIAST). However, for more ideal mixtures (for example the CO₂/CH₄ mixture is more ideal than the CO₂/N₂ mixture in the narrower pores) the PSD will have less influence and it will be difficult for any theory, no matter how complex, to outperform IAST (provided the ideal gas approximation is valid). So for nearly ideal mixtures other considerations, such as efficiency and versatility will be key. Briefly, IAST is much quicker than our slab-DFT (which is still very rapid compared to more complex density functional and molecular simulation methods) but the slab-DFT is much more versatile in that it is not limited to pressures and temperatures defined by the input pure component isotherms. Of course, the difficulty with IAST is that often one does not know in advance the ideality of a mixture adsorbed in a particular material.

Second, we believe that it is not possible to say whether using one or many isotherms as input to the PSD calculation will result in more accurate predictions. In some cases (the case presented in Figure 2, for example) using the isotherm of the most sensitive probe will provide more accurate results, whereas in other cases (where the pure gases are equally sensitive to pore width, for example) using more isotherms could be better. It will depend on the material and the probe isotherms in question. We believe this because it is known^{52–54} that the polydisperse independent ideal slit-pore model is a crude model for active carbons. So we cannot know whether fitting to multiple isotherms is actually yielding a more accurate PSD or whether it is leading to a less accurate PSD that is effectively compensating for deficiencies in our surface model. For example, it might be compensating for slight differences in the effective strength of gas–surface interactions between the active carbon in question and our reference carbon. Indeed, we believe this latter point is a factor in the work of Seaton and others.^{18–20} In their work they calibrate gas–surface interactions to a low surface area carbon and then use these models to describe active carbons. But part 1 of this work³ indicates that much greater accuracy is achieved by calibrating to a reference active carbon. So it is likely that in the work of Seaton and others^{18–20} the use of multiple isotherms in the characterization process results in PSDs that are effectively compensating for this difference in effective interaction strengths and are not actually accurate. Since we know that the PSD directly influences activity coefficients, it seems likely that this explains the relatively poor predictions for mixture adsorption.

Using this interpretation to evaluate the results in this work, we see that predictions in Figure 2 based on the slab-DFT where both isotherms are used as input are poor for two reasons: (a) the CO₂/N₂ mixture is sensitive to the PSD, and (b) the resulting PSD is not accurate and is compensating for deficiencies in our surface model (perhaps the difference in the effective strength of gas–surface interactions between our reference material and AC2). However, in contrast, the corresponding predictions in Figure 1 are reasonably accurate because (a) the CO₂/CH₄ mixture is less sensitive to the PSD and (b) the surface of AC1 is more similar to our reference material than AC2, and so there is a smaller compensatory effect in the PSD.

Overall we find that predictions made with the slab-DFT and a PSD based on just the pure carbon dioxide isotherm are

satisfactory, just like the pure gas results in part 1 of this work,³ despite our use of experimental data from different laboratories. However, adsorption predictions for significantly sub-critical gas mixtures would present a more severe test of the model. So it seems that further work is needed covering a range of gases and conditions on a range of carbons using experimental data that is known to be consistent.

It seems somewhat fortunate that for active carbons a relatively simple model of the surface, i.e., the polydisperse independent ideal slit-pore model, is accurate for modeling the adsorption of simple gas mixtures, at least at super- or near-critical temperatures. But this does not mean that this strategy will necessarily be successful for other materials or more complex adsorbates or lower temperatures. For example, materials that swell significantly might well require an altogether different approach.⁵⁵ And even for nonswelling materials the polydisperse independent pore model is likely to be inadequate for a range of other important systems (see part 1).

The novel slab-DFT model developed by us based on the polydisperse independent slit-pore model seems to fulfill many of the requirements outlined in the Introduction, i.e., it is quite fast and accurate, at least for the simple systems analyzed in this work. But its suitability for more complex systems, i.e., sub-critical or polar gas or long-alkane adsorption in active carbons, is yet to be assessed. Very likely, the Lorentz–Berthelot mixing rules, at least, will be inappropriate for some of these systems, and bulk mixture data, such as solubility, might be required to obtain accurate cross-interaction parameters.

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- (56) Note that the gas mixture experiments for AC1 and all the measurements for AC2 were carried out in a different laboratory to that which provided the reference data for our gas-surface interaction calibration. Also, due to confidentiality restrictions we cannot publish the experimental adsorption data or PSD derived from it directly. We appreciate that this reduces the quality of our presentation, but are confident that it does not detract from our conclusions.
- (57) Note that two samples from different batches of this active carbon, AC1, were used: one for the pure gas measurements and another for the mixed gas measurements. Nevertheless, these mixture predictions are quite accurate.