Modelling gas mixture adsorption in active carbons: DFT vs AST

*M.B. Sweatman, N. Quirke and P. Pullumbi**

Department of Chemistry, Imperial College, South Kensington, London, UK. SW7 2AY.
**Air Liquide, Centre de Recherche Claude-Delorme, Les Loges-en-Josas, 78354, Jouy-en-Josas, France.*

Abstract

We describe a slit-pore model and a fast density functional theory (a 'slab-DFT') for predicting gas mixture adsorption in active carbons. The DFT parameters are fitted to reproduce adsorption isotherms of each pure gas in graphitic slit pores generated by Monte-Carlo simulation, and gas - surface interactions are calibrated to a high surface area carbon, rather than a low surface area carbon as in all previous work of this type. Our models are used to predict the adsorption of mixtures of carbon dioxide, methane and nitrogen up to reasonably high pressure in active carbons based on an analysis of one or more probe isotherms. Comparison with experiment and IAST demonstrates that these models are accurate for relatively simple gas mixtures at near-critical or supercritical temperatures.

Introduction

In nature most fluids are mixtures. Active carbons are used on an industrial scale to separate fluid mixtures to yield pure components. A 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 are often to be made quickly so that a wide range of adsorbents can be assessed. Our goal is to solve this 'mixture problem' to provide rapid and accurate results for gas mixture adsorption on active carbons. Every approach to this problem in the literature is based on modelling the adsorption of the pure components accurately and using a fast theory, e.g. ideal adsorbed solution theory[1, 2] (IAST), to make adsorption predictions for the mixture. We use this theory as a benchmark and compare our new approach against it in terms of accuracy, versatility and efficiency.

Previously[3], we described procedures for modelling pure gas adsorption in active carbons based on the polydisperse independent ideal 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 is to show that the same surface and DFT models can also be used to accurately and quickly predict the adsorption of gas mixtures in active carbons. In earlier work[4] we compared the slab-DFT against IAST and found that our novel DFT was significantly more accurate for predicting the adsorption of a model of a non-ideal 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. So we expect the slab-DFT and IAST to provide results of similar accuracy for active carbon and the gases we are interested in because we have already shown[3] that the slit-pore model is a reasonably accurate model for these systems.

A number of other methods have been proposed to solve the mixture problem, including methods based on the Langmuir[5], Dubinin-Radushkevich[6], Dubinin-Astakhov[7] and

Toth[8] isotherms, neural-networks[9] and virial[10] series. However, we 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. There have been no attempts to predict gas mixture adsorption in active carbons with a non-local DFT of the type pioneered by Lastoskie[11] and others[12]. Regarding molecular simulation, Gusev and O'Brien[13], Davies and Seaton[14] and Heuchel and co-workers[15] analysed the adsorption of various simple mixtures in active carbon at ambient temperature up to 17 bar. Overall, their predictions for mixed gas adsorption are somewhat disappointing considering the level of numerical sophistication of their methods. In all of this Monte-Carlo simulation work a likely cause of error is due to calibration of molecular models. In each case gas-surface interaction parameters are fitted to reproduce adsorption on a low-surface area carbon. Results in our earlier work[3] indicate that it is much better to calibrate gas-surface interactions to a reference active carbon, which suggests that the surfaces of active carbons are more similar to each other than to low surface area carbons.

Molecular models and the slab-DFT

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. The adsorption of each component, i, in the mixture is given by the adsorption integral

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

where our kernel of local isotherms, $\{v(H_p, P, \{x\})\}$, for the mixture with composition $\{x\}$ is generated by the slab-DFT. The slab-DFT is described in detail elsewhere[2, 4], but very briefly it symmetrically parameterises density profiles of adsorbed fluid in slit pores in terms of five fluid slabs (a central slab flanked by two further slabs on each side). Our prescription for the excess intrinsic Helmholtz free-energy is effectively a crude non-local approximation. We parameterise the slab-DFT by fitting it separately to each local isotherm in a Monte-Carlo kernel of pure fluid isotherms, $\{v(H_p, P)\}$. We then use these same parameters, together with the Lorentz-Berthelot rules for cross-interactions

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

and a PSD to predict mixture adsorption on a given material. The PSD is optimised to provide the best fit to experimental adsorption isotherms. We compare two sets of results. One obtained using a PSD that provides the best fit to each pure component isotherm, and the other obtained using a PSD that provides the best fit to just the pure carbon dioxide isotherm.

Results

First, we test the performance of the slab-DFT using a PSD that is fitted only to the pure carbon dioxide isotherm for a mixture of carbon dioxide and nitrogen at 303 K adsorbed in an active carbon sample at pressures up to 50 bar (the 303 K kernels are generated by the slab-DFT which is fitted to Monte-Carlo kernels at 293 K). The rms error in the CO2 fit is 0.6 cm³(STP)/g which results in a predicted N2 isotherm with rms error of 3.1 cm³(STP)/g. Predictions for mixture adsorption with a range of bulk mole fractions at 1, 6

and 30 bar are shown in Figure 1. We see that the slab-DFT makes quite accurate predictions for a wide range of bulk mole fractions at each pressure, with accuracy deteriorating somewhat at low CO2 compositions.
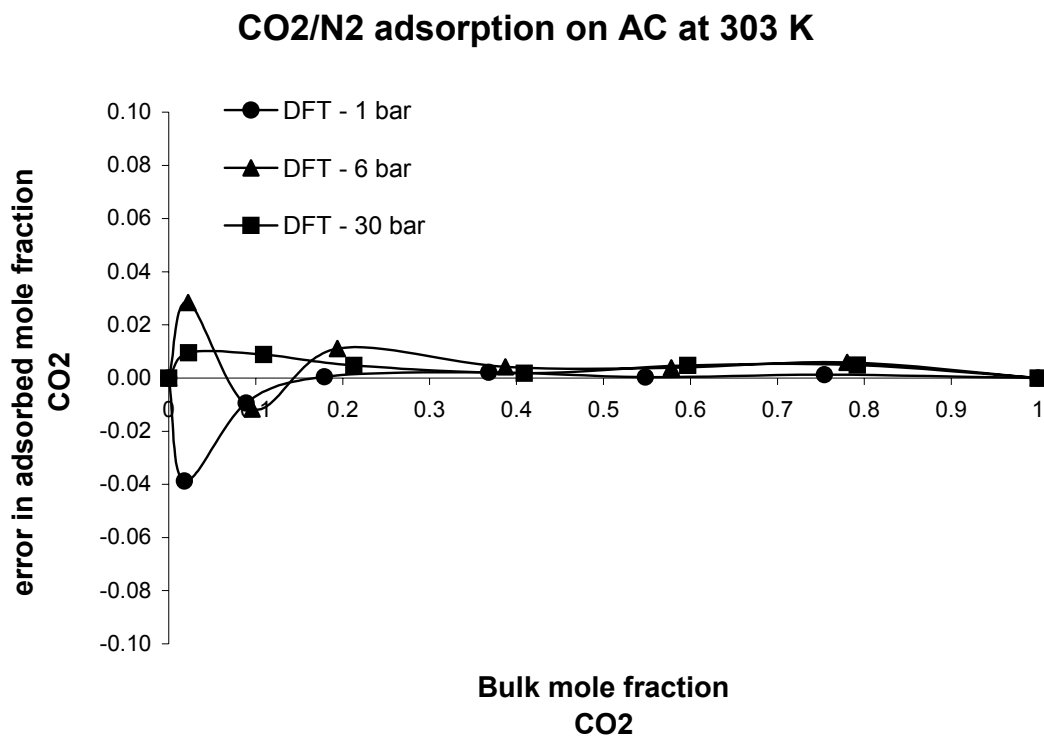
CO2/N2 adsorption on AC at 303 K

Figure 1. Adsorption of mixtures of carbon dioxide and nitrogen in an active carbon sample at 303 K and three different pressures. The symbols show the error in prediction of the adsorbed mole fraction of carbon dioxide with the slab-DFT compared to experiment (lines are a guide to the eye). These results are based on a PSD that is calculated from analysis of the pure carbon dioxide adsorption isotherm only.

Next, we compare the performance of IAST and the slab-DFT using a PSD that is fitted to both pure isotherms for a mixture of carbon dioxide and nitrogen at 303 K adsorbed in the same active carbon sample at pressures up to 50 bar (we refer the reader to comprehensive articles[1, 2] concerning IAST). The rms error in these fits are 1.2 and .5 cm^3(STP)/g for the pure CO2 and N2 isotherms respectively. Clearly, compared to the case when we fit only to the CO2 isotherm, a much closer fit to the N2 isotherm is gained at the expense of a slightly worse fit to the CO2 isotherm. Predictions for mixture adsorption with a range of bulk mole fractions at 1, 6 and 30 bar are shown in Figure 2 (note that IAST is unable to make predictions for bulk mole fractions higher than 0.4 at 6 bar and .01 at 30 bar respectively). We see that the slab-DFT is now performing much worse, and is even less accurate than IAST. However, comparing Figures 1 and 2 shows that the slab-DFT performs better than IAST when the PSD is obtained from the single CO2 isotherm. This suggests that the CO2/N2 mixture is nearly ideal in this material, at least up to about 6 bar.
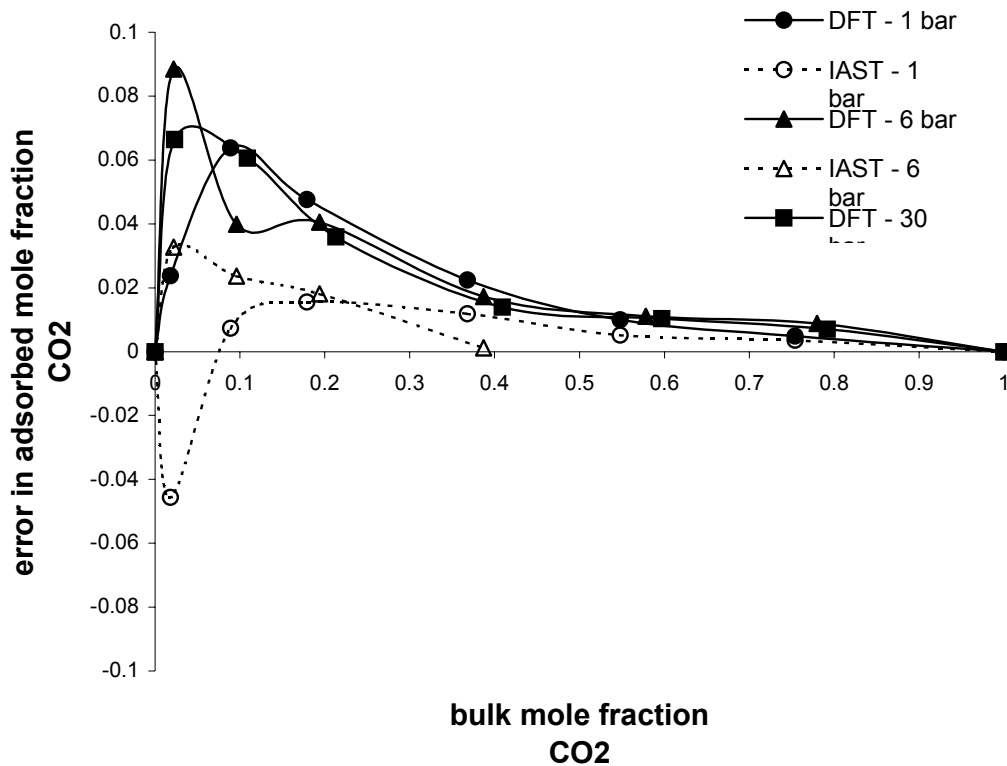
CO2/N2 adsorption on AC at 303 K

Figure 2. As for Figure 1 (using the same AC sample) except that the error in the predictions of IAST are also shown and the slab-DFT results are based on a PSD that is calculated from analysis of both the pure carbon dioxide and nitrogen adsorption isotherms.

Conclusions

From these results alone it might be tempting to conclude 1) that the slab-DFT is more accurate than IAST, and 2) that using one isotherm as input to the PSD calculation is better than using two (or more). However, this second point contradicts work by Seaton and others[13-15] that suggests greater predictive accuracy is achieved as more input isotherms, not less, are employed as this leads to a more accurate PSD. We have obtained results[16] from other active carbon samples that add weight to this argument, but cannot be shown here.

Actually, we believe the truth is much more subtle than any of these conclusions. First, consider the quite different predictions obtained from the slab-DFT in Figures 1 and 2. These differences are a direct result of the different PSDs obtained in each case. So we can immediately conclude that the activity coefficient of the CO2/N2 mixture is dependent on the PSD of the material. In fact, we find that the ideality of this mixture increases with increasing pore width, which is as expected. In turn, this means that IAST will be less accurate for carbon molecular sieves than for mesoporous carbons. Or in other words, 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. However, for mixtures that are close to ideal even in the smallest pores (for example the CO2/CH4 mixture is

much more ideal than CO2/N2) 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 *a priori* the ideality of a mixture.

Second, we believe that it is not possible to say whether using one or many isotherms as input to the PSD calculation will results in more accurate predictions. In some cases (the case presented here, for example) using the isotherm of the most sensitive probe will provide more accurate results, in other cases using more isotherms will be better. It will depend on the material and the probe isotherms in question. We believe this because it is known[17-19] that the polydisperse independent ideal slit-pore model is a crude model for active carbons, i.e. this model cannot easily distinguish the effects of pore geometry from surface chemistry. So we cannot know, at least for the gases used here, whether fitting to both the CO2 and N2 isotherms is actually yielding a more accurate PSD or whether it is leading to a less accurate PSD that is effectively compensating for slight differences in the strength of gas-surface interactions between the active carbon in question and our reference carbon. Indeed, we believe this latter point is also a factor in the work of Seaton and others[13-15]. In their work they calibrate gas-surface interactions to a low surface area carbon and then use these models to describe active carbons. But we have shown in our previous work[3] that greater accuracy is achieved by calibrating to a reference active carbon. So it is likely that in their work that when they use more than one isotherm to calculate a PSD that the resulting PSDs are effectively compensating for this difference in 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 in their work.

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 modelling 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 strongly dipolar molecules, like water, Brennan and colleagues[20] find that energetic non-uniformities can lead to pore blocking. And Kierlik and colleagues[21] have demonstrated that pore – pore interactions can significantly influence hysterisis. Materials that swell significantly might well require an altogether different approach[22]. And even for non-swelling materials this pore model is likely to be inadequate for a range of important systems. Our 'slab-DFT' model fulfils many of the requirements outlined in the introduction, i.e. it is quite fast and accurate, at least for the simple systems analysed in this chapter. But its suitability for more complex systems, i.e. significantly sub-critical, polar or long-alkane gases, 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 more accurate results.

References

1. A. L. Myers and J. M. Prausnitz, AICHE **11**, 121 (1965).
2. M. B. Sweatman and N. Quirke, in *Handbook of Theoretical and Computational Nanotehnology* (American Scientific Publishers, in press*.

3.   M. B. Sweatman and N. Quirke, submitted to Langmuir.
4.   M. B. Sweatman and N. Quirke, Langmuir **18**, 10443 (2002).
5.   R. T. Yang, *Gas Separation by Adsorption Processes* (Imperial College Press, Singapore, 1997).
6.   G. O. Wood, Carbon **40**, 231 (2002).
7.   K. Nieszporek, Adsorption-J. Int. Ads. Soc. **8**, 45 (2002).
8.   W. S. Appel, M. D. LeVan, and J. E. Finn, Ind. Eng. Chem. Res. **37**, 4774 (1998).
9.   M. Carsky and D. D. Do, Adsorption **5**, 183 (1999).
10.   J. Ghassemzadeh, L. F. Xu, and T. T. e. a. Tsotsis, J. Phys. Chem. B **104**, 3892 (2000).
11.   M. L. Lastoskie, K. E. Gubbins, and N. Quirke, J. Phys. Chem.-US **97**, 4786 (1993).
12.   J. P. Olivier, W. B. Conklin, and M. von Szombathely, in *Characterization of Porous Solids III*, 1994), Vol. 87, p. 81.
13.   V. Gusev and J. A. O'Brien, Langmuir **14**, 6328 (1998).
14.   G. M. Davies and N. A. Seaton, AICHE **46**, 1753 (2000).
15.   M. Heuchel, G. M. Davies, E. Buss, et al., Langmuir **15**, 8695 (1999).
16.   M. B. Sweatman and N. Quirke, (in preparation).
17.   G. M. Davies and N. A. Seaton, Carbon **36**, 1473 (1998).
18.   M. J. Bojan and W. A. Steele, Carbon **36**, 1417 (1998).
19.   W. Gac, A. Patrykiejew, and S. Sokolowski, Thin Solid Films **298**, 22 (1997).
20.   J. K. Brennan, K. T. Thomson, and K. E. Gubbins, Langmuir **18**, 5438 (2002).
21.   E. Kierlik, P. A. Monson, M. L. Rosinberg, et al., J. Phys.: Condens. Matter **14**, 9295 (2002).
22.   A. L. Myers and P. A. Monson, Langmuir **18**, 10261 (2002).