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**Analysis of gas adsorption in Kureha active carbon based on the slit-pore model and Monte-Carlo simulations**

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3 **Analysis of gas adsorption in Kureha active carbon based on the slit-pore**  
4 **model and Monte-Carlo simulations**  
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26 **ABSTRACT**  
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29 We analyse the adsorption of carbon dioxide and several light alkenes and alkanes on Kureha  
30 active carbon at a range of temperatures. We find generally good agreement between the  
31 alkene and alkane isotherms at moderate to high pressure, but find that at the lowest relative  
32 pressures for each gas there are significant discrepancies that seem to be correlated with the  
33 strength of gas – surface interactions. This pattern is similar to that observed in our previous  
34 work on the adsorption of light alkenes and alkanes on active carbon, except the errors here  
35 are much smaller. One possible explanation for this error is poor diffusion in the experiments  
36 at the lowest relative pressures, leading to measurements of non-equilibrium states. We  
37 suggest that this poor diffusion might be caused by potential barriers (i.e. it is activated  
38 diffusion) in the narrowest pores. We also find that our analysis of the adsorption of carbon  
39 dioxide at 273 K is inconsistent with all the alkene and alkane data. We suggest this  
40 discrepancy arises because our model of gas – surface interactions does not take contributions  
41 from polar surface sites into account. Although this study is specific to Kureha active carbon,  
42 we expect that our conclusions are relevant to other studies of gas adsorption on active  
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3 carbon; they highlight the need for great care when taking measurements at low pressures, and  
4 motivate improvements in molecular models for gas adsorption in active carbons.  
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## 7 **INTRODUCTION**

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10 We are interested in understanding how to model a complex and important class of adsorption  
11 systems, i.e. active carbons. An important step towards this aim would be a fast and reliable  
12 method for predicting equilibrium gas adsorption on the basis of a straightforward  
13 characterisation. We aim to develop methods that allow the prediction of pure and mixed gas  
14 adsorption on the basis of one or more 'probe' adsorption isotherms.  
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19 In our early work [1, 2] we found that predictions could be improved, over standard  
20 techniques described in the literature [3-6], if Monte-Carlo simulation was used to model  
21 adsorption in pores, and if the porosity of the reference material (a low surface area carbon,  
22 Vulcan 3G) was taken into account. However, in later work [7, 8] we found that we could  
23 improve predictions dramatically, generally to within just a few percent for prediction of  
24 nitrogen and methane on the basis of a carbon dioxide probe isotherm (at ambient  
25 temperatures up to about 50 bar) if we used an active carbon as our reference material rather  
26 than a low surface area carbon. Our understanding of this finding is that generally the surfaces  
27 of active carbons [9, 10] (of which there are a multitude of different types, prepared from  
28 different precursors in different ways) are more similar to each other than to the surfaces of  
29 low surface area carbons (surface area aside, of course). Although a significant step forward  
30 in modelling procedures, this work should be seen in its proper context. That is, prediction of  
31 the adsorption of supercritical gases on the basis of the adsorption of a near-critical gas should  
32 not be seen as a particularly stringent test. A more interesting challenge is prediction of sub-  
33 critical gas adsorption. To this end we recently reported [11] predictions for the adsorption of  
34 several light alkenes and alkanes at ambient temperatures on several quite different active  
35 carbons based, once again, on a carbon dioxide probe isotherm at 293 K. The respective bulk  
36 critical temperatures of the gases involved are [12] 304 K, 191 K, 282 K, 305 K, 366 K and  
37 370 K for carbon dioxide, methane, ethene, ethane, propene and propane respectively. We  
38 found a complex pattern of agreement. For carbons that had a wide range of pores, including  
39 some significant mesoporosity, we found good agreement between theory and experiment  
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3 over a wide pressure range. However, for carbons with PSDs dominated by pore widths less  
4 than 1 nm we found considerably worse agreement, particularly at low pressure where errors  
5 were seen to be very large. For carbons with intermediate types of PSD the quality of  
6 agreement varied from reasonably good to poor, but again errors at low pressure were often  
7 very large. We attributed these errors to two main sources. First, we suggested that our  
8 procedures were sensitive to the polarity of active carbons and the moderately strong  
9 electrostatic quadrupole on carbon-dioxide (the other gases analysed have much smaller  
10 quadrupoles), but that the major errors seen at low pressure were caused by experimental  
11 error. That is, there seemed to be a strong correlation between these low pressure errors, the  
12 pore-size-distribution (PSD) and the molecular 'size' of the gas that we suggested could be  
13 caused by taking experimental measurements too quickly, i.e. before the system could reach  
14 equilibrium.  
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22 In this present work we analyse a different set of experimental data for adsorption of these  
23 gases (except methane) on Kureha active carbon. Our aim here is to test our modelling  
24 procedures on this new data. Overall, we find that agreement between theory and experiment  
25 is generally good for the alkenes and alkanes, comparable to the better results in reference  
26 [11] corresponding to carbons with some mesoporosity. However, we again find some  
27 inconsistency at the lowest relative pressures, although this is much reduced compared to  
28 most results in reference [11]. Moreover, we find a significant discrepancy between our  
29 analysis of the carbon dioxide isotherm at 273 K and all the other isotherms. We suggest that  
30 this is a result of not including polar gas – surface interactions in our models. In the following  
31 we provide a brief description of our experimental and modelling procedures, which are given  
32 in detail elsewhere[7, 8, 13-16]. We concentrate on analysis of our results.  
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### 39 **EXPERIMENTAL PROCEDURES**

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42 The commercial sample, spherical bead activated carbon, was supplied by Kureha Chemical  
43 Industry. This activated carbon is referred to as Kureha active carbon. A Micromeritics ASAP  
44 2010 gas adsorption analyser (stainless steel version) was used to measure the adsorption  
45 isotherms of ethene, ethane, propane, and propene on Kureha carbon in the pressure range  
46 from 0.002 to 120 kPa. The instrument was equipped with a turbomolecular vacuum pump  
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and three different pressure transducers (0.13, 1.33, and 133 kPa, respectively) to enhance the sensitivity in different pressure ranges. The static-volumetric technique was used to determine the volume of the gas adsorbed at different partial pressures: upon adsorption a pressure decrease was observed in the gas phase, which is a direct measure for the amount adsorbed.

The sample cell was loaded with 155.7 mg of Kureha carbon particles. Prior to the adsorption measurements the adsorbent particles were outgassed in situ in vacuum at 623 K for 16 h to remove any adsorbed impurities. The obtained dry sample weight was used in the calculation of isotherm data.

The gaseous adsorbates such as ethene, ethane, propane, and propene were 3.5 grade (>99.95%).

## MODELLING PROCEDURES

As in previous work [7, 8], we employ the polydisperse independent ideal slit-pore model to model the surface of active carbons. The pore-size distribution (PSD) is calculated by analysis of a single experimental probe adsorption isotherm according to the adsorption equation

$$N(P) = \int_0^{\infty} dH f(H) v(H, P) \quad (1)$$

where  $N$  is the *excess* adsorption (after subtraction of a helium calibrated pore volume, which we model by setting the ‘chemical’ pore width  $H = H_p - 0.285$  nm),  $P$  is pressure,  $H$  is slit-pore (chemical) width ( $H_p$  is ‘physical’ pore width defined as the distance between atom centres in the first layer of opposing slit-pore walls),  $f$  is the PSD and  $v$  is a kernel of local isotherms for each pore width. Adsorption isotherms for other gases are then predicted using the appropriate kernel with the same PSD. The PSD is obtained using the procedures described in reference [7], i.e. the PSD is constrained to a sum of log-normal modes, and a downhill simplex algorithm is applied to obtain the smoothest PSD that produces a fit to the experimental adsorption isotherm within experimental error. The PSD is defined over a range of pore widths consistent with the kernel of the probe gas, as described previously [7] and by

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3 Seaton and colleagues[17]. So in this work we limit the PSD to the range  $0.315 \leq H_c \leq 2.715$   
4 nm, and, for convenience, at most 3 log-normal modes.  
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8 We use Monte-Carlo simulation[18] to generate the appropriate kernels[19]. We model gas  
9 molecules as rigid assemblies of Lennard-Jones and partial charge sites. We tailor the  
10 Lennard-Jones (LJ) parameters until good agreement with experimental data for saturation  
11 properties (coexisting gas and liquid densities and pressures) is obtained by Gibbs ensemble  
12 simulation[18, 20, 21]. We employ a cutoff in gas-gas interactions to avoid interactions  
13 between periodic images, and also use a ‘ramp’ [7] (starting at 0.9 times the cutoff distance)  
14 to smooth these interactions near the cutoff. Our gas molecular models are identical to those  
15 used in preceding work [7, 11] and are detailed in Table 1. Gibbs ensemble Monte Carlo  
16 simulation data for the saturation properties of the ethene, ethane, propene and propane  
17 models are displayed in Figures 1a-d (similar data for carbon dioxide can be found in  
18 reference [7]) and compared with reference data[12].  
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25 Our slit pores are formed from two identical opposing walls, whose mass centres are  
26 separated by a ‘physical’ pore width  $H_p$ , each described by the Steele potential [14, 22, 23]. If  
27 we use the Lorentz-Berthelot combining rules [14] then for a given gas molecular model our  
28 surface model is fully defined by definition of the surface – surface interaction length and  
29 strength parameters respectively. The length parameter is fixed at the commonly used value of  
30 0.34 nm while the strength parameter is adjusted, or calibrated [7], separately for each gas.  
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35 We use grand canonical ensemble Monte-Carlo simulations to generate the appropriate  
36 kernels for adsorption in slit-pores at the required temperatures. That is, we have generated  
37 kernels for all the gases in this study at 273 K, and for ethene and ethane at 194 K. To predict  
38 adsorption of ethene and ethane at 298 K we use the same 293 K kernels generated for  
39 previous work [7], and then use our ‘slab-DFT’ methodology [7, 13] to convert these  
40 databases from 293 K to 298 K. We use the same gas molecular models calibrated to  
41 reproduce bulk fluid saturation properties in our slit-pore simulations.  
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46 Gas – surface interactions for these gases were calibrated in previous work [7, 11] by fitting to  
47 PNC active carbon on the basis of a PSD generated from a carbon dioxide probe isotherm,  
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3 with the surface – surface interaction strength for nitrogen held fixed at the commonly used  
4 value of  $\varepsilon_{ss}/k_B = 28.0$  K. However, these gas-surface calibrations were performed at 293 K,  
5 while the data set under analysis here comprises adsorption isotherms at a range of  
6 temperatures. Specifically, ethene and ethane at 194 K and 298 K, and all the gases at 273 K.  
7 We expect our calibration procedure at 293 K to remain accurate (i.e. we expect to be able to  
8 use the same values for  $\varepsilon_{ss}$ ) at 273 K, but for ethene and ethane at 194 K we have performed a  
9 separate calibration study. For each respective gas at 194 K, we tailored  $\varepsilon_{ss}$  until good  
10 agreement was obtained for adsorption at 273 K and 298 K (using the values for  $\varepsilon_{ss}$  obtained  
11 in earlier work for 293 K) on the basis of a PSD generated by the respective 194 K isotherm.  
12 The results of this calibration exercise are also recorded in Table 1. Figure 2a shows how the  
13 predicted adsorption of ethene at 273 K and 298 K varies with the strength of  $\varepsilon_{ss}$  at 194 K.  
14 Figure 2b shows the corresponding variation for ethane, while Figure 2c shows the variation  
15 in the PSD, generated using the method described above.  
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24 Figure 2a shows that at moderate and higher pressures the prediction of ethene at 273 K and  
25 298 K is more accurate when  $\varepsilon_{ss}/k_B = 28.5$  K at 194 K, compared to  $\varepsilon_{ss}/k_B = 28.0$  K which is  
26 the value calibrated in reference [7] and used to generate the 273 K and 298 K databases.  
27 Similarly, Figure 2b shows that for ethane  $\varepsilon_{ss}/k_B = 26.5$  K at 194 K is better than  $\varepsilon_{ss}/k_B = 25.5$   
28 K, or  $\varepsilon_{ss}/k_B = 23.0$  K. However, in the insets to these Figures it can be seen that the predictions  
29 at low pressure are not as good, i.e. there is consistent under-prediction of ethene, and  
30 especially ethane, at 273 K and 298 K on the basis of the PSDs generated from the respective  
31 194 K isotherms, except for ethane when  $\varepsilon_{ss}/k_B = 23.0$  K at 194 K. For this value of  $\varepsilon_{ss}$  at 194  
32 K we find that ethane adsorption at 273 and 298 K is well predicted at low pressure, but not at  
33 moderate or higher pressure. So, we find that it is not possible to accurately reproduce the  
34 entire isotherms at 273 K and 298 K using the 194 K isotherms as probes. We will come back  
35 to this point later.  
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### 43 ANALYSIS OF ADSORPTION ISOTHERMS

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46 Our data set of adsorption isotherms on Kureha active carbon consists of ethene and ethane at  
47 194 K, 273 K and 298 K, and propene, propane and carbon dioxide at 273 K. The 194 K  
48 isotherms and the propene and propane isotherms are measured from very low pressure ( $\sim 10^{-5}$   
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3<sup>5</sup> bar). All isotherms are measured up to 1.2 bar. This upper pressure limit corresponds to  
4 relative pressures (relative to the saturation pressure) of 0.34 and 0.73 for ethene and ethane at  
5 194 K, 0.029, 0.050, 0.206, 0.254 and 0.035 for ethene, ethane, propene, propane, and carbon  
6 dioxide at 273 K respectively, and 0.029 for ethane at 298 K. Ethene is supercritical at 298 K.  
7 This means that we should expect the ethane isotherm at 194 K to be the most sensitive probe  
8 of porosity, followed by ethene at 194 K. Not only are gas – surface interactions more  
9 significant at this temperature, but the range of pore widths that can be resolved with capillary  
10 condensation is greatest (compared to the other gases studied here) at this temperature and  
11 upper pressure limit. This temperature is well above the bulk triple point temperature (90 K  
12 for ethane), so freezing should not cause a problem here, as might be the case with nitrogen at  
13 77 K for example [2, 14, 19]. Because of the relatively low upper pressure limit the carbon  
14 dioxide isotherm carries limited information. So, unfortunately, we cannot use the carbon  
15 dioxide isotherm as the main probe, which means that we cannot be entirely consistent with  
16 our previous work [7].  
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25 Figures 3a and 3b show theoretical predictions compared with experiment for adsorption on  
26 Kureha active carbon based on PSDs generated by fitting to ethene and ethane respectively at  
27 194 K. In Figure 3a it can be seen that ethane adsorption at 194 K at the lowest pressures is  
28 significantly over-predicted, while it is generally good at moderate pressures and higher. The  
29 propene and propane isotherms at 273 K are well predicted over the whole pressure range.  
30 Ethene and ethane are predicted quite well at 273 K, although there is a degree of under-  
31 prediction at the lowest relative pressures. Carbon dioxide at 273 K is significantly under-  
32 predicted at the lowest relative pressures, although agreement improves at higher pressures.  
33 Overall, these are satisfactory results, except for ethane at 194 K and carbon dioxide at 273 K  
34 at the lowest relative pressures. The situation in Figure 3b is not as good, particularly at the  
35 lowest relative pressures. Although predictions for all gases and temperatures are acceptable  
36 at moderate to high pressures, at the lowest pressures there is consistent under-prediction.  
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43 Figure 2c compares the PSDs from this analysis; we will use it to help interpret these results.  
44 We are interested here in comparing the solid lines with (ethene) and without (ethane) the  
45 solid symbols. The most obvious conclusion from this analysis is that there are some pores,  
46 less than about 6.0 Å in width, that ethane at 194 K at low pressure has not accessed,  
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3 compared to ethene at 194 K. However, the pore volume calculated from the PSDs is slightly  
4 larger for ethane (0.568 cm<sup>3</sup>/g) than for ethene (0.553 cm<sup>3</sup>/g) (note that in reference [16] the  
5 reported pore volume of Kureha active carbon is higher because the *bulk* molar volume of the  
6 respective adsorbate at its *saturated liquid density* is used in the analysis). So it appears that  
7 these small pores, which are not accessed by ethane at 194 K at the lowest pressures, are  
8 actually filled at higher pressure and interpreted as slightly wider pores, i.e. as being 6.5 Å in  
9 width. Generally, the agreement between the PSDs corresponding to ethene and ethane at 194  
10 K is good, with both PSDs having secondary and tertiary peaks at about 8.5 to 9.5 Å and 14.0  
11 to 15.0 Å respectively. Of course, to make these detailed comparisons requires our modelling  
12 and gas–surface interaction calibration procedures to be accurate. That alkene and alkane  
13 isotherms across a wide range of temperatures seem to be consistent at moderate pressure and  
14 higher indicates that this is so, but we should not be too confident in this analysis given the  
15 simplicity of our surface model. This is highlighted by the apparent inconsistency between the  
16 carbon dioxide isotherm and the other isotherms.  
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25 To analyse this data further, Figure 4a shows prediction versus experiment when the PSD is  
26 fitted simultaneously to both ethene at 194 K and carbon dioxide at 273 K, with equal  
27 weighting. Once again the most serious error is for ethane at 194 K and the lowest pressures,  
28 which is significantly over-predicted. Interestingly, predictions for all the other isotherms,  
29 including the fit to carbon dioxide at 273 K, are reasonably good over the whole range of  
30 pressures. To explain this result we again consider the PSD generated from this simultaneous  
31 fitting exercise, shown in Figure 4b. If we analyse this result in the same terms as before, we  
32 should conclude that carbon dioxide at 273 K is accessing many pores about 3.5 Å in  
33 width that the other gasses cannot access. Physically, it might be thought that these pores  
34 correspond to the inter-layer distance in graphite, and are formed where a portion of a layer is  
35 absent in a stack of graphene layers. However, if such pores exist then, using an interlayer  
36 distance of 3.35 Å for graphite, their chemical pore width would be 3.85 Å according to the  
37 definition of chemical pore width used here (remember, we use  $H = H_p - 0.285$  nm). So in our  
38 view there is no physical reason to expect a significant fraction of pores with chemical width  
39 3.5 Å to exist in any active carbon. In our view, this first peak at about 3.5 Å in Figure 4b is  
40 an artefact of our surface model; by introducing such a peak into the PSD our model is able  
41 to account for the observed behaviour of the carbon dioxide  
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3 and other isotherms (except for ethane at 194 K). It can achieve this because at about 3.5  
4 Angstroms the low pressure adsorption of ethene and ethane changes from being weak to  
5 strong, whereas the adsorption of carbon dioxide is already strong at this pressure (this is  
6 simply a steric effect, concerned with how easy it is to 'fit' a given molecule inside such  
7 narrow pores). Conversely, ethene and ethane can easily fit into 3.85 Angstrom pores. We  
8 instead interpret this peak in the PSD as a signal of a deficiency in our surface model. We  
9 suspect, this deficiency arises because of the lack of polar surface sites in our model that  
10 could interact strongly with the relatively large (compared to the other gases) permanent  
11 electric quadrupole of carbon dioxide. This is the most significant differentiating factor  
12 between carbon dioxide, and the alkenes and alkanes that we know of. Essentially, we suspect  
13 that carbon dioxide's quadrupole might well be interacting quite strongly with polar sites on  
14 the active carbon surface that are interpreted by the slit pore model as narrow pores.  
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## 21 **DISCUSSION**

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24 Overall, the level of agreement between theoretical prediction and experiment, at least for the  
25 alkanes and alkenes, shown in Figures 2a, 2b, 3a and 3b is encouraging. The slit-pore model  
26 has been subjected to a more demanding test than in our previous work [7], and overall it has  
27 performed quite well. Consistency between isotherms of near-supercritical and substantially  
28 sub-critical gases is generally good, except for some remaining errors that we will discuss  
29 below. Indeed, it might be surprising to see this level of agreement considering the simplicity  
30 of the slit-pore model. It is tempting to conclude that these results indicate that the slit-pore  
31 model is not such a gross approximation for some active carbons after all. The main  
32 approximations of this model concern the independence and uniformity of the pores, the  
33 'universality' of the PSD for all gases, temperatures and pressures, the use of the Steele  
34 potential to represent gas-surface interactions, and the use of gas molecular models tuned to  
35 reproduce bulk fluid behaviour to model adsorption in slit pores. For Kureha active carbon  
36 these choices appear to be quite reasonable, possibly because for this material and these gases  
37 adsorption is dominated by gas-surface interactions, and we have calibrated these interactions  
38 for each gas. Any imperfections in the model, i.e. the absence of pore non-uniformity and  
39 pore-pore interactions[14], non-universality of the PSD, use of the Steele potential etc., are  
40 largely compensated by this calibration procedure. But we should be careful about drawing  
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3 wider conclusions regarding the use of our procedures to model other materials where such  
4 factors might have more influence.  
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7 Regarding the remaining errors, we suspect that the low pressure experimental measurements  
8 for all the gases, and particularly ethane at 194 K, might be in error, resulting from poor  
9 diffusion. A potential mechanism for this error arises from the same source that seems to  
10 make the slit-pore model so surprisingly successful, that is, diffusion (as well as adsorption) is  
11 dominated by gas-surface interactions. In such narrow pores as occur in the present material,  
12 pore sizes frequently correspond to only one or two adsorbed layers. The external potential,  
13 (i.e. the gas-surface interaction),  $V^{ext}$ , in these pores is large and negative, and its effect is  
14 enhanced as temperature decreases, i.e. as molecular thermal energy reduces. If there is  
15 significant variation in the Boltzmann factor ( $\exp(-V^{ext}/k_B T)$ ) along a diffusion path then the  
16 diffusion will effectively become 'activated diffusion' [18], i.e. it will be controlled by the  
17 number and severity of the 'potential barriers'. So, in this situation the flux of gas into the  
18 carbon material will be influenced by the number and type of non-uniformities present in  
19 these narrowest pores, including pore junctions, openings, pits, constrictions etc., which  
20 would act like a network of resistors in an electrical circuit. To justify this interpretation,  
21 consider estimates (shown in Table 2) of the natural logarithm of the Boltzmann factor for  
22 each gas and temperature on a single surface defined by our surface model. The estimates in  
23 Table 2 indicate that, if we accept this explanation, then we should expect similar behaviour  
24 for ethene and ethane at 194 K and propene and propane at 273 K, and for ethene, ethane and  
25 carbon dioxide at 273 K. Looking again at Figure 3a, we see that the low pressure behaviour  
26 of ethene at 194 K and propene and propane at 273 K does appear to be consistent. However,  
27 ethane at 194 K appears to be inconsistent with this hypothesis in that it seems to be much  
28 less mobile at the lowest pressures in Kureha active carbon than ethene at 194 K or propene  
29 and propane at 273 K. To be clear, in Figure 3a while theory and experiment agree, even at  
30 low pressure, for ethane at 194 K and propene and propane at 273 K, theory and experiment  
31 do not agree at the lowest pressures for ethane at 194 K. We cannot explain this within our  
32 hypothesis. Of course, diffusion in nanoporous materials is a very complex process and is  
33 influenced, like adsorption, by fine details of both pore geometry and adsorbate molecular  
34 model [24, 25]. Nevertheless, we cannot explain the difference seen in the low-pressure  
35 adsorption of ethane at 194 K compared to the other gases. In particular, we cannot account  
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Comment [c4]: this is added

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3 for the differences seen between ethene and ethane at 194 K, and ethane at 194 K and 273 K.  
4 To  ar, we cannot explain why the level of agreement at low pressure between theory and  
5 experiment for ethene at 194 K and ethene and ethane at 273 K seems to support our  
6 hypothesis regarding activated diffusion at low pressure, while the poor agreement between  
7 theory and experiment at low pressure for ethane at 194 K does not. Note that this discrepancy  
8 cannot be due solely to any difference between ethene and ethane (for example, any specific  
9 difference in gas-surface interactions), because it also occurs for ethane at two different  
10 temperatures (194 K and 273 K). This means that it can only be caused by inconsistencies in  
11 experimental measurement techniques, or by a process that applies only to ethane adsorption  
12 at low temperature and pressure of which we are unaware. 

Comment [c5]: this is added

Comment [c6]: this is changed - the previous wording was too vague and the referee picked up on this.

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19 In our view, this diffusion mechanism does not explain the inconsistency between carbon  
20 dioxide and the other gases because there is little difference between the factors in Table 2 for  
21 carbon dioxide, ethene and ethane at 273 K. In addition, because these molecules are of a  
22 reasonably similar size it seems unlikely to us that molecular sieving could be significant. A  
23 simple estimate of the interaction energy of a carbon dioxide molecule on a graphitic surface  
24 with an embedded point dipole of 1 Debye shows that the surface dipole – gas molecule  
25 electrostatic quadrupole interaction energy can amount to as much as 20% of the total  
26 interaction energy, depending on pore width and molecular orientation. This is a significant  
27 contribution that will, of course, scale linearly with the size of the embedded dipole. So it is  
28 clear that the polarity of the surface should be included in the surface model if the adsorption  
29 of gases with significant permanent electric quadrupoles, such as carbon dioxide, or dipoles,  
30 such as water, are to be modelled.

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38 Similar conclusions have been reached recently [26] in respect of surface quadrupole – gas  
39 molecule dipole interactions. Zhao and Johnson [26] provided details of how the interaction  
40 of polar adsorbate molecules with the permanent electric quadrupole (and any induced, or  
41 image, dipole) of carbon in graphitic walls can be represented in an efficient yet accurate  
42 manner in terms of effective potentials. Their effective potentials are developed by techniques  
43 very similar to the original Steele potential for Lennard-Jones interactions, resulting in  
44 ‘smeared’ or surface averaged effective potentials. They find that these interactions are  
45 significant for strongly dipolar and quadrupolar adsorbate molecules. These particular  
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3 electrostatic contributions to the total energy, resulting from adsorbate interactions with the  
4 permanent quadrupole of carbon in graphitic walls, are effectively included in our molecular  
5 models by our gas – surface calibration procedure. But their work does suggest an efficient  
6 method that could account for the interaction of polar adsorbate molecules with the permanent  
7 electric dipoles or quadrupoles of *impurities*, or active sites, that are known to occur in  
8 varying quantities in active carbons [27], provided these impurities have sufficiently high  
9 surface density. A high surface density is desired in this case because of the surface averaging  
10 technique employed. If the surface density is not sufficiently high then this approach could  
11 lead to inaccuracies because the real external potential would have highly localised sites,  
12 whereas this averaging procedure leads to an average ‘smooth’ potential, and these different  
13 situations can lead to different adsorption phenomena, depending on the temperature.  
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20 Alternatively, explicit dipolar or quadrupolar surface sites could be included in the surface  
21 model. This is the approach described by Jorge and Seaton [28] who represent all such ‘active  
22 sites’ in terms of C=O surface groups, and use grand canonical MC simulation to determine  
23 the adsorption kernel,  $\nu(H,P)$ , (see equation 1) of water and ethane in slit pores with  
24 distributions of these sites. They then use the pure isotherms of water and ethane to  
25 characterise BPL active carbon in terms of a PSD and a distribution of active surface sites. To  
26 our knowledge, this is the first time that this technique, i.e. combining the slit-pore model  
27 with a model of active surface sites, MC simulation of adsorption, and differential adsorption  
28 of polar and non-polar adsorbates, has been attempted to characterise an active carbon. They  
29 find that this approach is able to predict co-adsorption of water and ethane on BPL active  
30 carbon quite well, and much better than theories based on, for example, ideal adsorbed  
31 solution theory (IAST). Unfortunately, they also find that satisfactory accuracy can only be  
32 achieved if the density of active surface sites is allowed to depend on pore width, which  
33 produces significant additional model complexity and contradicts other work [29] using more  
34 empirical methods. In our view, their results for water adsorption are likely to be sensitive to  
35 their particular PSD, which in turn is sensitive to their particular choice of ethane and  
36 graphitic wall molecular models (Figures 2a to 2c in this work demonstrate the sensitivity of  
37 the PSD to molecular model parameters), and they did not analyse this sensitivity. So it is still  
38 conceivable that a pore-width independent distribution of active surface sites could be  
39 sufficient in such a model for characterisation studies, and further work should be performed  
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3 to examine this. Of course, explicit representation of these polar surface sites is possible with  
4 more detailed 3D surface models as well [30, 31]. But to our knowledge, this ‘reverse Monte-  
5 Carlo’ approach has not been employed to characterise, or make adsorption predictions, for  
6 active carbons.  
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10 Whichever approach is adopted, the conclusion of this work is that surface models that  
11 account for surface polarity are necessary for accurate description of the adsorption of carbon  
12 dioxide in active carbons at ambient temperatures. Very likely, they will be important for  
13 other strongly quadrupolar gases as well, and are not only useful for describing the adsorption  
14 of strongly *dipolar* gases. So it seems, after all, that carbon dioxide is not such a good probe  
15 of active carbons because it cannot by itself distinguish between adsorption on polar sites and  
16 in slit-pores of various widths. This clearly did not present a problem in our earlier work  
17 where we were interested in predicting the adsorption of super-critical gases such as nitrogen  
18 and methane at 293 K. But for subcritical adsorption it becomes more important to distinguish  
19 competing effects, because such adsorption is more sensitive to these effects. This work also  
20 highlights the need for care when interpreting 77 K nitrogen adsorption measurements. At this  
21 temperature there has been speculation [2, 14, 15] that nitrogen could potentially freeze, or at  
22 least become glassy or highly viscous, in the narrowest pores in active carbons. This  
23 speculation is based on analysis of data in work of Radhakrishnan et.al. [32]. Further,  $-V^{ext} /$   
24  $k_B T$  for this gas at this temperature is 15.2, based on the nitrogen model in reference [7],  
25 which is significantly higher than any of the values in Table 2. So if low pressure adsorption  
26 measurements are sensitive to activated diffusion, as is proposed above in relation to results  
27 shown here in Figures 3 and 4a, then great care should be exercised with interpreting 77 K  
28 nitrogen adsorption. Moreover, nitrogen has an electrostatic quadrupole moment about 1/3<sup>rd</sup>  
29 the size of carbon dioxide’s (according to the molecular models in [7]), which indicates that  
30 electrostatic interactions could also play a significant role in its adsorption in active carbons.  
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42 From a purely theoretical perspective, it appears that an inert gas, like argon, which is quite  
43 small, spherical and non-polar should be used to characterise pore geometries in active  
44 carbons. In this case, a temperature of about 120 K, which is about half way between argon’s  
45 triple and critical points and, using the model of argon in [33], has a corresponding  
46 Boltzmann factor of about 9.2, could be used. Alternatively, a small non-polar organic gas,  
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such as ethane (as used by Jorge and Seaton [28]) could be employed at an appropriate temperature. Water could then be used to characterise surface polarity.

**Acknowledgements** This work was performed as part of the EU Network of Excellence, 'Innovative Pores' ( see <http://www.pores.gr>)

**Comment [c11]:** Is this actually appropriate given that I performed most of the analysis, wrote most of the paper, but am not yet part of the NOE?

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Table 1

Model parameters used in MC simulations.  $\sigma_{ff}$  and  $\varepsilon_{ff}$  are the Lennard-Jones interaction length and energy parameters respectively,  $L$  and  $\theta$  denote bond lengths and angles respectively,  $q$  is the partial charge centred on a Lennard-Jones site,  $r_c$  denotes the cutoff distance between molecular centres (the CH site in the case of propene), while  $\varepsilon_{ss}$  is the calibrated strength of surface – surface interactions.

Parameter	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
$\sigma_{ff}$ (nm)	C: 0.275	CH <sub>2</sub> : 0.3483	CH <sub>3</sub> : 0.3625	CH <sub>3</sub> : 0.3561	CH <sub>3</sub> : 0.3608
	O: 0.304			CH: 0.3431	CH <sub>2</sub> : 0.3458
				CH <sub>2</sub> : 0.3391	
$L$ (nm)	C-O: 0.1149	CH <sub>2</sub> -CH <sub>2</sub> : 0.1922	CH <sub>3</sub> -CH <sub>3</sub> : 0.1976	CH <sub>3</sub> : 0.1936	CH <sub>3</sub> -CH <sub>2</sub> : 0.1966
				CH: 0	
				CH <sub>2</sub> : 0.1896	
$\theta$ (deg)	O-C-O: 0	0	0	CH <sub>3</sub> -CH-CH <sub>2</sub> : 124.0	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub> : 114.0
$r_c$ (nm)	1.5	1.6	1.6	1.75	1.75
$\varepsilon_{ff}/k_B$ (K)	C: 28.3	CH <sub>2</sub> : 112.6	CH <sub>3</sub> : 121.3	CH <sub>3</sub> : 122.8	CH <sub>3</sub> : 123.4
	O: 84.2			CH: 92.6	CH <sub>2</sub> : 88.7
				CH <sub>2</sub> : 112	
$q$ (e)	C: 0.6512	CH <sub>2</sub> : 0	CH <sub>3</sub> : 0	CH <sub>3</sub> : 0	CH <sub>3</sub> : 0
	O: -0.3256			CH: 0	CH <sub>2</sub> : 0
				CH <sub>2</sub> : 0	
$\varepsilon_{ss}/k_B$ (K)	24.0	194 K: 28.5	194 K: 26.5	28.0	26.0
		273+ K: 28.0	273+ K: 25.5		

Table 2

Estimates of  $-V^{ext} / k_B T$  (see text) for gases on an isolated surface defined by our molecular models.

Gas	194 K	273 K
Carbon dioxide		7.0
Ethene	11.3	8.0
Ethane	11.7	8.3
Propene		11.7
Propane		11.8

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6 Figure 1. Gibbs ensemble simulation results for a) ethene, b) ethane, c) propene, and d)  
7 propane, based on the molecular models in Table 1. Solid lines (reference data[12]) and  
8 symbols (simulation data) denote saturated densities, while dotted lines[12] and symbols with  
9 error bars show saturated pressures. The saturated density error from simulation is less than or  
10 equal to the symbol size.  
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14 Figure 2. Calibration of the gas-surface interactions at 194 K. Lines are theory (fits or  
15 predictions) and symbols are experiment. Circles correspond to measured adsorption on  
16 Kureha active carbon at 194 K. This isotherm is used to generate a PSD, which in turn is used  
17 to predict the other isotherms, via equation (1). Diamonds denote adsorption at 273 K, while  
18 triangles are for adsorption at 298 K. Figure a) is for ethene while b) is for ethane. In Figure a)  
19 full lines correspond to predictions based on  $\epsilon_{ss} / k_B = 28.5$  K (see Table 1), while the dashed  
20 lines are for 28.0 K. In Figure b) full lines correspond to predictions based on  $\epsilon_{ss} / k_B = 26.5$  K  
21 (see Table 1), while the dashed lines are for 25.5 K and the dashed-dot lines are for  $\epsilon_{ss} / k_B =$   
22 23.0 K. Pressure is on a logarithmic scale. For the inserts adsorption is also shown on a  
23 logarithmic scale.  
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31 Figure 2c. PSDs corresponding to the various values of  $\epsilon_{ss}$  for ethene and ethane in Figures 2a  
32 and 2b. Lines with symbols are for ethene, those without are for ethane. The solid symbols are  
33 for  $\epsilon_{ss} / k_B = 28.5$ , the open symbols are for  $\epsilon_{ss} / k_B = 28.0$ . The solid line is for  $\epsilon_{ss} / k_B = 26.5$ ,  
34 the dotted line is for  $\epsilon_{ss} / k_B = 25.5$ , and the dashed-dot line is for  $\epsilon_{ss} / k_B = 23.0$ .  
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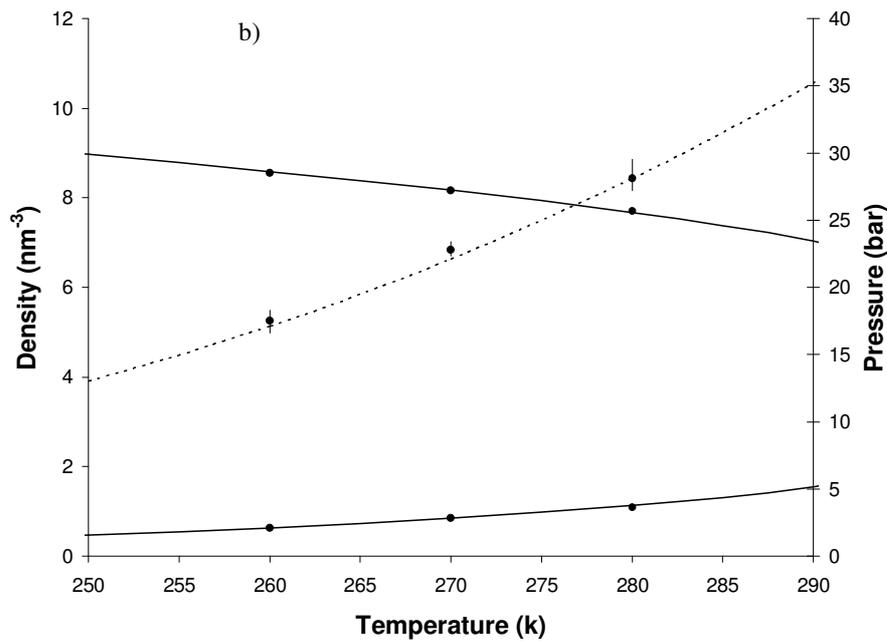
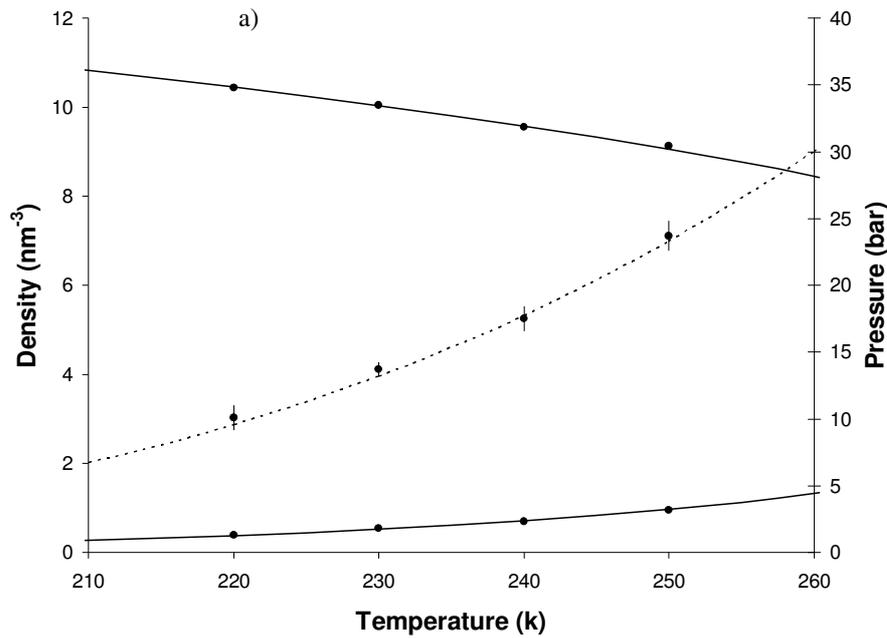
38 Figure 3. Adsorption isotherms for carbon dioxide at 273 K (squares and full line), ethene at  
39 194 K (open circles and dotted line), ethane at 194 K (full circles and solid line), ethene at  
40 273 K (open triangles and dotted line), ethane at 273 K (solid triangles and dotted line),  
41 propene at 273 K (open diamonds and dotted line) and propane at 273 K (solid diamonds and  
42 dotted line) on Kureha active carbon. Symbols are experiment, lines are fits (to ethene at 194  
43 K in part a), and ethane at 194 K in part b)) or predictions based on the fits and the  
44 corresponding PSDs (see Figure 2c). Pressure is on a logarithmic scale. For the inserts  
45 adsorption is also shown on a logarithmic scale.  
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Figure 4. Part a) is the same as Figure 3a, except that the PSD used to generate the predictions is based on a simultaneous fit to ethene at 194 K and carbon dioxide at 273 K. Part b) shows the corresponding PSD.

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Figure 1



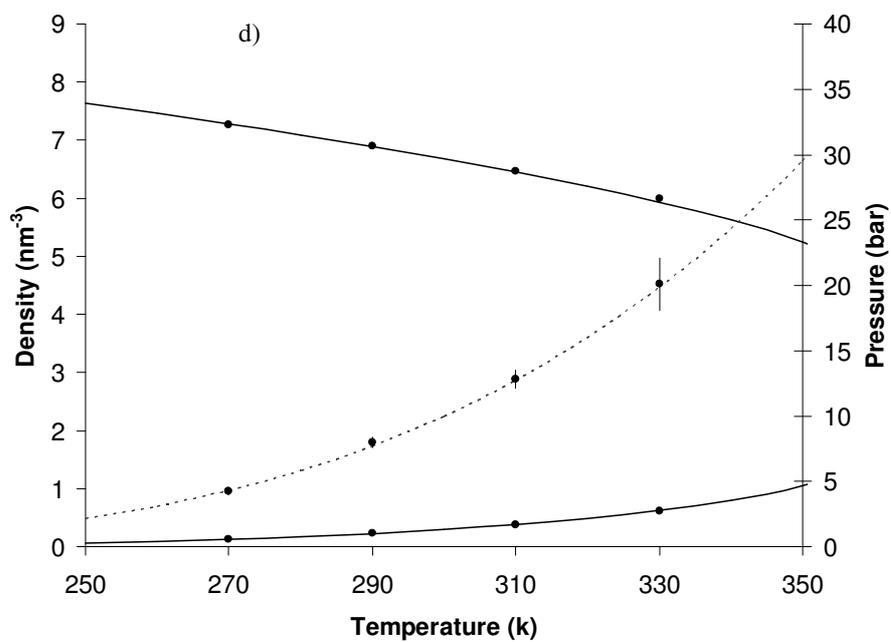
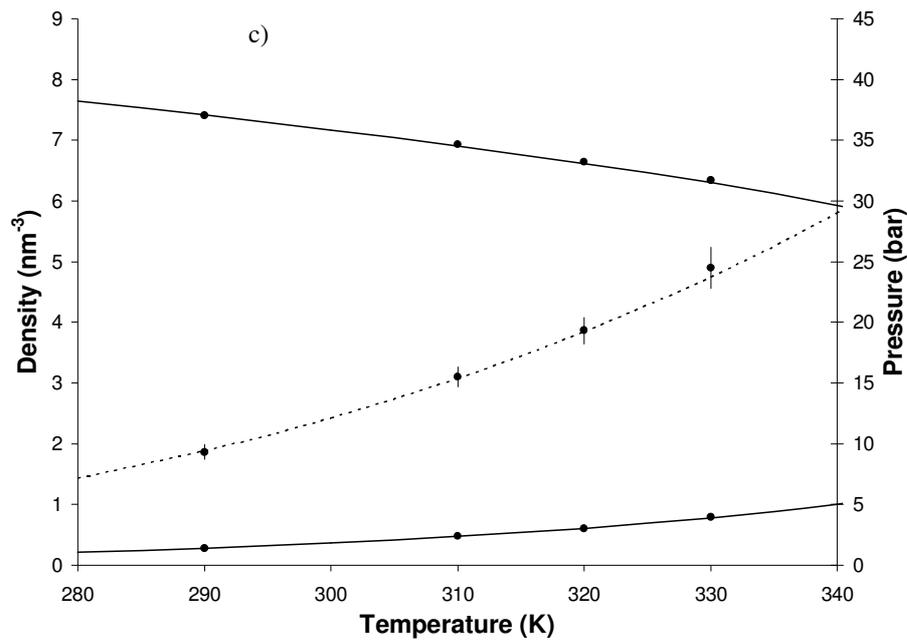
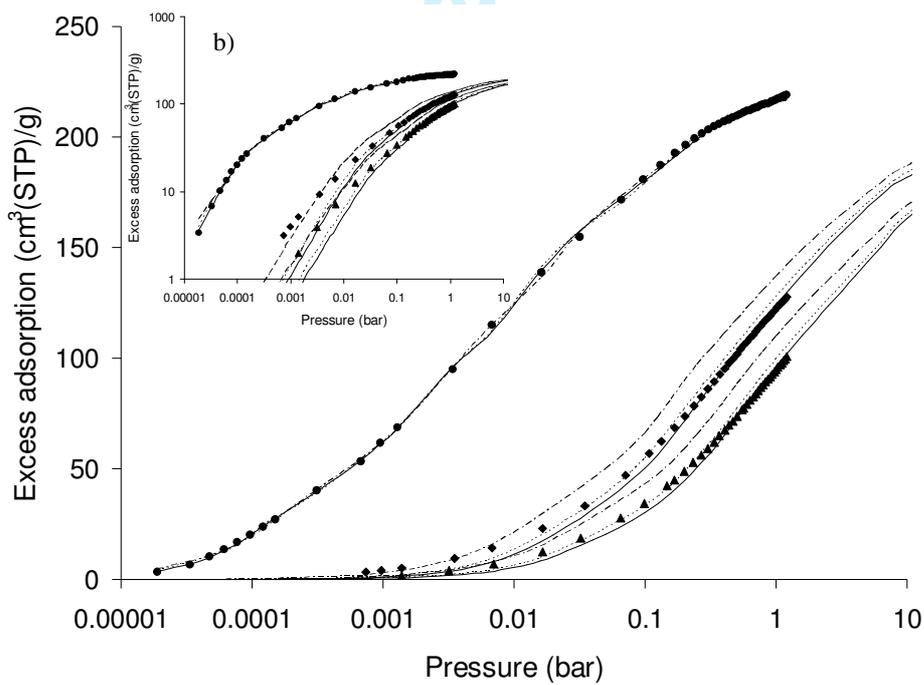
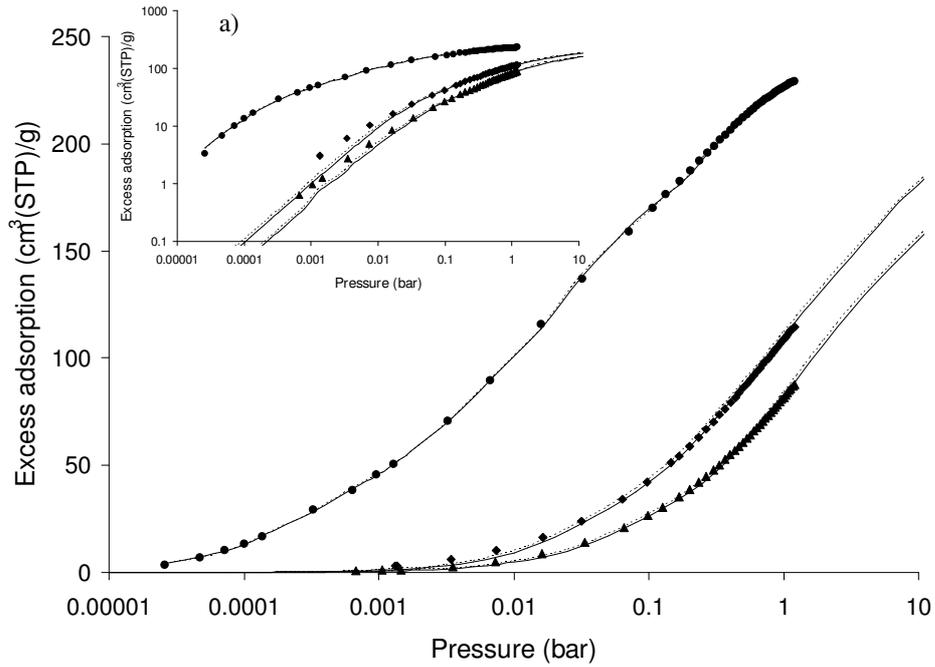


Figure 2



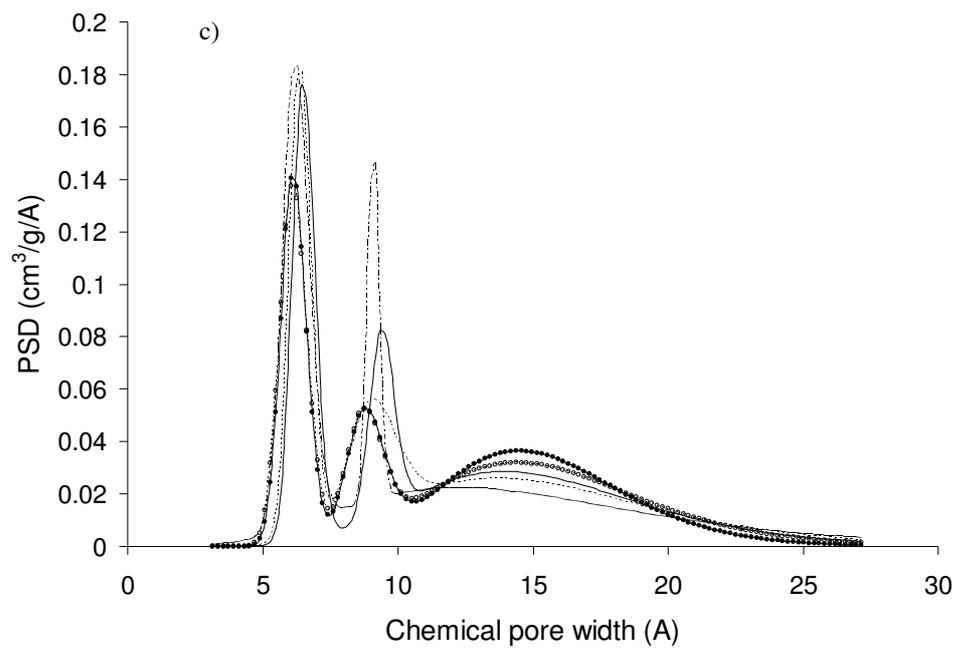


Figure 3

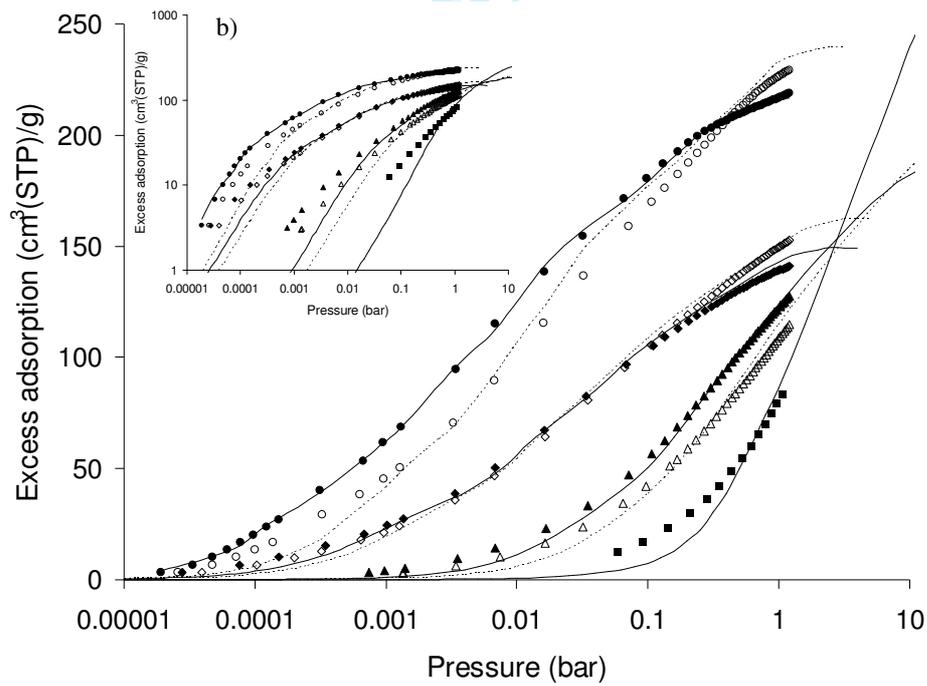
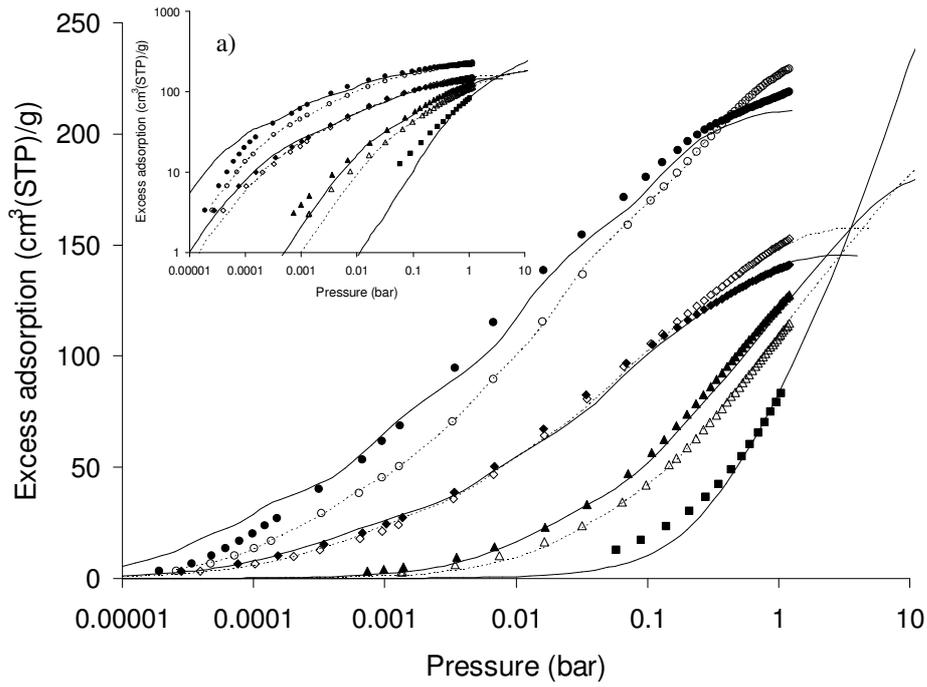


Figure 4

