Predicting mixed-gas adsorption equilibria on activated carbon for pre-combustion CO₂ capture

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ABSTRACT

In this work, we present experimentally measured adsorption isotherms of CO₂, H₂ and N₂ on a phenol-formaldehyde resin-based activated carbon, which had been previously synthesized for the separation of CO₂ in a pre-combustion capture process. The single component adsorption isotherms were measured in a magnetic suspension balance at three different temperatures (298, 318 and 338 K) and over a large range of pressures (from 0 to 3000-4000 kPa). These values cover the temperature and pressure conditions likely to be found in a pre-combustion capture scenario, where CO₂ needs to be separated from a CO₂/H₂/N₂ gas stream at high pressure (~1000-1500 kPa) and with a high CO₂ concentration (~20-40% vol.).

Data on the pure component isotherms were correlated using the Langmuir, Sips and dual-site Langmuir (DSL) models, i.e., a two, three and four-parameter model, respectively. By using the pure component isotherm fitting parameters, adsorption equilibrium was then predicted for multicomponent gas mixtures by the extended models. The DSL model was formulated considering the energetic site-matching concept, recently addressed in the literature. Experimental gas-mixture adsorption

equilibrium data were calculated from breakthrough experiments conducted in a lab-scale fixed-bed reactor and compared with the predictions from the models. Breakthrough experiments were carried out at a temperature of 318 K and five different pressures (300, 500, 1000, 1500 and 2000 kPa) where two different CO₂/H₂/N₂ gas mixtures were used as the feed gas in the adsorption step. The DSL model was found to be the one that most accurately predicted the CO₂ adsorption equilibrium in the multicomponent mixture.

The results presented in this work highlight the importance of performing experimental measurements of mixture adsorption equilibria, as they are of utmost importance to discriminate between models and to correctly select the one that most closely reflects the actual process.

KEYWORDS: pre-combustion capture; ternary mixtures; multicomponent adsorption equilibria; breakthrough experiments; activated carbon.

1. INTRODUCTION

Amongst the various CO₂ capture strategies currently considered to be applied in a future decarbonised energy system, pre-combustion capture, i.e., fuel gasification followed by the shifted-syngas reaction to yield hydrogen (integrated gasification combined cycle, IGCC), could become the technology of choice for new-build power plants. A mixture of mainly CO₂ and H₂ is obtained as the gas stream to be processed, with minor quantities of H₂O and N₂ and some other impurities such as CO and H₂S. Large-scale high purity H₂ (99.9999%) is generally produced by pressure swing adsorption (PSA) of the shifted-syngas ¹. However, in a carbon capture scenario high purity CO₂ (>95%), that meets the specifications for its subsequent transport to a safe storage location, is the target of the separation process. The high concentrations (~20-40%) of CO₂ in the feed stream as well as its pressure of ~1000-1500 kPa are beneficial for an adsorption-based separation process where adsorbent regeneration is performed by a pressure swing, i.e., PSA.

Some of the requirements of an adsorbent for a pre-combustion CO₂ capture process would be: 1) a high cyclic CO₂ working capacity (difference between the amount of the heavy component adsorbed at the adsorption pressure and the amount that remains adsorbed at the desorption/evacuation pressure); 2) high selectivity so the CO₂ will be strongly retained while “light” components such as H₂ and N₂ will be less retained or not retained at all on the adsorbent, and 3) high CO₂ recovery or total mass of CO₂ adsorbed in the adsorption step that is recovered in the desorption step. Physisorbents such as phenolic resin-derived activated carbons are ideally suited for the above application due to their low cost, high surface area and amenability to pore structure modification and surface functionalization ². Additionally, at high pressures, the CO₂

uptake of activated carbons can surpass that of other promising materials like zeolites³,
⁴. Phenolic resin-derived activated carbons offer further advantages in that they can be produced in a wide variety of physical forms, allow a close control of porosity, and present a very low level of impurities and good physical strength⁵⁻⁷.

The evaluation of suitable adsorbents for selective removal of CO₂ from an IGCC pre-combustion gas stream requires knowledge of reliable and extensive pure components adsorption equilibrium data. Furthermore, the design of a technical and economically viable adsorption process for the CO₂ separation involves dealing with gas mixtures so knowledge of mixture equilibria is required. Currently, the results that can be obtained from adsorption process simulators depend heavily on the model used for predicting the mixed-gas adsorption equilibria. There are models available in the literature which can predict the mixture behaviour from pure component isotherms^{8, 9}. Experimental measurement of multicomponent adsorption isotherms is time consuming because of the large number of variables involved, and reliable ternary and multicomponent adsorption equilibria are extremely rare in the literature. Then, predicting multicomponent equilibria from single-component adsorption data has therefore attracted much attention. However, these multi-component adsorption models need to be validated, so accurate gas mixture adsorption data is required to check the accuracy of the models against. Only recently, adsorption isotherms of CO₂, N₂ and H₂ on an activated carbon have been presented to be applied in a pre-combustion CO₂ capture process, and experimental adsorption data of binary mixtures CO₂/H₂ and CO₂/N₂ have been reported for model validation purposes¹⁰.

In this study, however, successful prediction of mixed-gas adsorption data in ternary CO₂-H₂-N₂ systems relevant to pre-combustion CO₂ capture is targeted. To this aim, single gas adsorption isotherms of the main shifted-syngas components, CO₂ and H₂, as well as N₂, on a phenolic resin-derived activated carbon have been measured gravimetrically with a magnetic suspension balance. A wide range of pressures, up to 3000 or 4000 kPa depending on the adsorbate, and three different temperatures (298, 318 and 338 K) were used for the measurements, so pressure and temperature conditions relevant to a pre-combustion CO₂ capture process could be reproduced. Three different isotherm models (Langmuir, Sips and DSL) were then fitted to the experimental data. Adsorption equilibria of ternary CO₂/H₂/N₂ mixtures were estimated from dynamic experiments conducted in a lab-scale fixed-bed reactor and compared with the predictions obtained from the extended equations of the aforementioned models, which were only based in the fitting parameters derived from the single gas adsorption isotherms.

2. MATERIALS AND METHODS

2.1. Materials

In this work a highly microporous (total micropore volume ~ 0.5 cm³/g) activated carbon prepared from a phenol-formaldehyde resin has been used. The fully detailed synthesis as well as the chemical and textural characterization of this carbon can be found elsewhere ⁷. The well-developed microporosity of this adsorbent, that determines and limits the CO₂ capture capacity at high pressure ¹¹, along with its suitable characteristics for the separation of CO₂ and H₂ under high pressure conditions, makes

it ideal for the separation of CO₂ in pre-combustion processes ¹². The particle size of the activated carbon was between 1 and 3 mm.

CO₂, N₂ and H₂ were used as adsorptive gases and were all provided by Air Products with a purity of more than 99.995%. Helium was used as a non-adsorptive gas in the gravimetric measurements to correct for the buoyancy effect due to the volume of the adsorbent and cell system, i.e., the so-called He-volume, as well as a purge gas in the adsorption column.

2.2. Experimental methods

2.2.1. Pure gas adsorption measurements: magnetic suspension balance

Pure component adsorption isotherms were measured in a high pressure gravimetric Rubotherm-VTI magnetic suspension balance, where a clean adsorbent sample is exposed to a pure gas at constant temperature. Prior to adsorption, the measuring cell is filled with the adsorbent (~ 1 g), which is dried under vacuum at 373 K for 120 min. The cell is then cooled down to the measuring temperature and pressurization is attained with the desired adsorbate in a stepwise mode, so the change in the weight of the adsorbent sample as well as pressure and temperature are measured and recorded when equilibrium is reached. Single gas adsorption isotherms were measured at three different temperatures (298, 318 and 338 K) in a pressure range from 0 to 3000 kPa for CO₂ and N₂, and from 0 to 4000 kPa for H₂.

2.2.2. Ternary gas mixture adsorption measurements: column breakthrough experiments

Ternary adsorption equilibrium data were obtained in a single-bed adsorption unit packed with 3.4 g of adsorbent (length: 9.5 cm, diameter: 0.9 cm, porosity: 0.39). The schematic and detailed description of the system have been reported previously¹³.

The adsorption unit was used to monitor the breakthrough curves of CO₂, N₂ and H₂. Each experimental run involved the following steps: (i) drying of the adsorbent before each experiment by flowing He (100 mL min⁻¹ STP) for 60 min at 473 K and atmospheric pressure, (ii) pressurization and cooling of the bed in a pre-conditioning step of 15 min, where 60 mL min⁻¹ (STP) of He were allowed to flow through the system, (iii) feed gas switch to a CO₂/H₂/N₂ gas mixture to initiate the adsorption step for 60 min, and (iv) depressurization of the unit and atmospheric pressure purge with 100 mL/min (STP) of He at 473 K for 60 min to fully desorb the adsorptive gases from the column. A total flowrate of 100 mL min⁻¹ (STP) was kept constant during the adsorption step so all experiments were performed at the same feed velocity. Measurements of the CO₂, H₂ and N₂ elution profiles (tracked by a dual channel micro-gas chromatograph) enabled to calculate the adsorbed amounts of CO₂, H₂ and N₂ by mass balances to the system. For each experimental run the adsorbent was subjected to a maximum of six consecutive adsorption-desorption cycles to test the reproducibility of the system.

Breakthrough experiments were carried out at a temperature of 318 K and five different pressures (300, 500, 1000, 1500 and 2000 kPa) where two different CO₂/H₂/N₂ gas mixtures with concentrations of 25/67/8 and 44/46/10 % by volume, were used as the feed gas in the adsorption step.

3. ADSORPTION EQUILIBRIUM MODELS: THEORY AND DATA HANDLING

3.1. Single component adsorption: data handling and equilibrium description equations

3.1.1. Data handling

As a first step and prior to any fit of the experimental data to an adsorption model, we need to distinguish between absolute and excess adsorption. In the high pressure magnetic suspension balance, absolute adsorption cannot be obtained directly from the gravimetric measurement and the excess mass adsorbed is obtained instead. Recent works have highlighted the need of converting excess loadings to absolute loadings before fitting to any Langmuir-type models and properly calculate isosteric heats of adsorption and adsorption selectivities¹⁴. To estimate the absolute adsorption from the excess adsorption data is a major challenge in applying most modeling procedures. The excess and absolute adsorption are correlated as follows¹⁵:

$$q = q_{exc} + \frac{\rho_g V_{ads}}{m_s M} \quad (1)$$

where q is the absolute amount adsorbed, q_{exc} is the excess amount adsorbed, ρ_g is the density of the gas phase, V_{ads} is the volume of the adsorbed phase, m_s is the mass of adsorbent and M is the adsorbate molecular weight. Although in gas adsorption under a subatmospheric pressure range V_{ads} is negligible, it cannot be neglected in a high pressure range^{16, 17}. In this case, either the density or volume of the adsorbed phase has to be known, which are not readily accessible by an experimental measurement. Thus, estimates of the adsorbed phase density or volume are usually employed¹⁸⁻²⁵. Herein, the volume of the adsorbed phase is approximated by²⁶:

$$V_{ads} \cong \frac{m_{ads}}{\rho_L} \quad (2)$$

where m_{ads} is the mass of the adsorbed phase and ρ_L is the adsorbed phase density, which is assumed to present a density similar to that of the liquid phase at the adsorption temperature (T_{ads}). The adsorbate liquid phase density is then calculated as:

$$\rho_L = \frac{M}{V_m} \quad (3)$$

V_m is the molar volume calculated by the Gunn-Yamada method²⁷ when $T_{ads} < T_c$ (T_c is the critical temperature of the adsorbate), and equals the van der Waals co-volume of the adsorbate, b , when $T_{ads} \geq T_c$ ^{22, 28}. Numerical values of V_m and pure liquid densities of CO_2 , H_2 and N_2 at the different experimental adsorption temperatures as calculated by eq. (3) are shown in Table 1. By replacing eq.2 into eq.1 we get that the absolute adsorption capacity can be calculated from the following equation²⁹:

$$q = \frac{\Delta m + \rho_g (V_s + V_i)}{m_s M} \frac{\rho_L}{\rho_L - \rho_g} \quad (4)$$

where Δm is the microbalance signal when adsorption equilibrium is reached, ρ_g is the density of the gas at measuring conditions and $(V_s + V_i)$ are the adsorbent volume and measuring cell volume, respectively. These volumes are measured by adsorption isotherm measurements with helium as adsorptive and assuming that it accesses the total pore volume of the sample without being adsorbed. Helium measurements were done at 338 K and pressures that were similar to conditions during an adsorption run with adsorptive gases. Prior to the measurements, the measuring cell with the adsorbent was dried under vacuum at 373 K for 120 min. The cell was then cooled down to the measuring temperature and pressurization was attained with He in a stepwise mode.

3.1.2. Equilibrium description equations

The experimental data of adsorption equilibria (absolute amounts adsorbed) of the pure gases on the activated carbon were correlated with Langmuir, Sips and dual-site Langmuir isotherm models. The Langmuir equation (eq. 5) is fundamentally sound and it describes monolayer surface adsorption on an ideal and flat surface assuming surface homogeneity, localized adsorption on the solid surface and energetically equivalent adsorption sites^{8, 9, 30}. The equation contains two parameters, the saturation capacity, q_s , and the affinity constant, b . Also, it is important to have the temperature dependence form of an isotherm equation, so that adsorption equilibrium at various temperatures can be described. The affinity constant dependence with temperature is described using an Arrhenius-type equation (eq. 6) with parameters A_i and B_i , which correspond to a pre-exponential factor and the isosteric heat of sorption, respectively.

$$q = \frac{q_s b P}{1 + b P} \quad (5)$$

$$b_i = A_i \exp\left(\frac{-B_i}{RT}\right) \quad (6)$$

Adsorption in real solids, however, is a heterogeneous process because solids present complex pore and surface structures, which rarely satisfy the basic assumptions made in the Langmuir theory. This heterogeneity is characteristic of the specific solid-adsorbate pair rather than the solid alone. Thereby, many semi-empirical approaches have been successfully developed to describe equilibrium data, as the ones described next.

The Sips equation (eq. 7) is a three parameters one, q_s , b and n , and it only differs from the Langmuir equation in the additional parameter “ n ”, which characterizes the

system heterogeneity. The latter one could stem from the solid or the adsorbate or a combination of both. If the parameter “ n ” is unity the Langmuir equation is recovered.

$$q = \frac{q_s (bP)^{1/n}}{1 + (bP)^{1/n}} \quad (7)$$

The temperature dependence of b is taken from that of the Langmuir equation. As for the exponent n , its temperature-dependent form is empirical and eq. 8 is chosen from the literature⁸ because of its simplicity. In this equation, n_0 is the parameter n at some reference temperature T_0 (taken here as 298 K) and α is a constant parameter.

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T} \right) \quad (8)$$

An alternative model to fit the pure component data is the single-gas dual-site Langmuir (DSL) four parameters (q_{s1} , q_{s2} , b_1 and b_2) model, which describes the adsorption of a pure component on a heterogeneous adsorbent that is composed of two homogeneous but energetically different patches (or sites)³⁰⁻³². All of the assumptions of the Langmuir model apply to each patch, with no interactions between the two patches. The amount adsorbed would be given by eq. 9 below:

$$q = \frac{q_{s1} b_1 P}{1 + b_1 P} + \frac{q_{s2} b_2 P}{1 + b_2 P} \quad (9)$$

where q_{s1} and q_{s2} are the saturation capacities at site 1 and 2, respectively, so the total saturation capacity is the sum of those on each patch or site ($q_s = q_{s1} + q_{s2}$); b_1 and b_2 are the affinity parameters or free energy for site 1 and 2, respectively, which are considered to be temperature-dependent as expressed in eq. 10, where the subscript j represents the free-energy level of site 1 or 2, $b_{0,j}$ are the pre-exponential factors or adsorption entropies, and E_j are their corresponding adsorption energies.

$$b_j = b_{0,j} \exp\left(\frac{E_j}{RT}\right) \quad j = 1, 2 \quad (10)$$

In eq. 10, $j=1$ always denotes the higher adsorbate-adsorbent free energy as opposed to $j=2$ that always denotes the lower adsorbate-adsorbent free energy. The free energy of site 1 is always higher than that of site 2 for single-gas adsorption³¹.

Fitting of the models to the experimental data was done with the Excel tool Solver and the values of the different fitting parameters were found by minimizing the sum of the squared relative errors (SSE), i.e., by minimizing the relative differences between the predicted and experimental amounts adsorbed at all temperatures for a particular adsorbate-adsorbent system. The objective function that was used in Solver is given by:

$$SSE(\%) = \sqrt{\frac{\sum [(q_{\text{exp},i} - q_{\text{mod},i})/q_{\text{exp},i}]^2}{N-1}} \times 100 \quad (11)$$

where $q_{\text{exp},i}$ and $q_{\text{mod},i}$ are the experimental and predicted amounts adsorbed, respectively, and N is the number of data points. Hence, the goodness-of-fit of the different models can be judged by the model with the minimum SSE as the best-fit.

3.2. Multicomponent adsorption

Successful prediction of multicomponent adsorption equilibria relies entirely on an accurate measurement of single component data, and on a reliable correlation of these data with an isotherm model. Using the pure component isotherm parameters, adsorption equilibria of ternary mixtures can be predicted by extending the corresponding single component equations to multicomponent adsorption equations. Thus, the amount adsorbed of component i of a ternary mixture is given by eq. 12, 13

and 14, which are known as the extended multicomponent Langmuir, Sips and DSL equations respectively.

$$q_i = \frac{q_{s,i} b_i y_i P}{1 + \left(\sum_{k=1}^n b_k y_k P \right)} \quad (12)$$

$$q_i = \frac{q_{s,i} (b_i y_i P)^{1/n_i}}{1 + \left(\sum_{k=1}^n b_k y_k P \right)^{1/n_i}} \quad (13)$$

$$q_i = \frac{q_{s1,i} b_{1,i} y_i P}{1 + \left(\sum_{k=1}^n b_{1,k} y_k P \right)} + \frac{q_{s2,i} b_{2,i} y_i P}{1 + \left(\sum_{k=1}^n b_{2,k} y_k P \right)} \quad (14)$$

In eqs. 12, 13 and 14, i stands for the species for which the isotherm q_i is being evaluated, y would be the gas mole fraction of the corresponding component (denoted by subscript i or k) and n is the total number of components in the gas mixture. Eq. 14 only describes one of the possible cases (the simplest one) in a multicomponent system; however, to correctly apply the DSL formulation, the energetic site-matching issue, recently addressed in the literature for ternary and higher-order systems^{31, 32}, needs to be considered, so possible erroneous predictions are avoided. The energetic site-matching issue refers to the fact that in a multicomponent system, all the adsorbates do not necessarily see the site 1 as the high-free-energy site ($j=1$ in eq. 10) and site 2 as the low-free energy site ($j=2$). For instance, in a binary system there are four different adsorbate-adsorbent free energies corresponding to the free energies of the two components on each site. When both components see site 1 as the high-free-energy site ($j=1$), then their adsorbate-adsorbent free energies correlate in a perfect positive (PP)

fashion, as opposed to the case where site 1 is the high-free-energy site for one component but a low-free energy site for the other component. In the latter case the adsorbate-adsorbent free energies correlate in a perfect negative (PN) fashion. In multicomponent equilibria, it is assumed that the binary adsorbate-adsorbent interactions defined through the affinity parameter, $b_{j,i}$, are pairwise additive³¹. When each binary pair in the gas mixture correlates in a PP fashion the extension to ternary and higher-order systems is straightforward and eq. 14 is derived. However, when the correlation of any of the binary pairs is in a PN fashion, the pairwise additivity has to follow two rules of logic. These two rules are explained next for a ternary system with components A, B and C, and therefore three binary pairs, A-B, A-C and B-C. When evaluating component A in the mixture, two different possibilities arise when it comes to correlation between the components: 1) A and B and A and C correlation is of the same type, i.e., either PP or PN, or 2) A and B and A and C correlation is of different type, i.e., one is PP and the other one is PN or vice versa. To correctly apply the DSL formulation, in case 1), B and C correlation would have to be PP and, in case 2), B and C correlation would be PN, as a consequence of different type of correlations between the other two binary pairs. Hence, for a ternary system, like the one considered here, four viable correlations are possible (Table 2). The corresponding amount adsorbed of each component for each case is given by equations presented in the Supporting Information.

4. RESULTS AND DISCUSSION

4.1. Single gas adsorption isotherms of CO₂, H₂ and N₂ on activated carbon

The experimental absolute adsorption isotherms of pure CO₂, N₂ and H₂ on activated carbon at 298, 318 and 338 K are shown as symbols in Figures 1, 2 and 3. CO₂ always adsorbs more strongly than N₂ and H₂ on the activated carbon at all temperatures. The absolute adsorbed amount increases linearly with pressure for CO₂ and N₂, and a gradual flattening is observed when pressure is sufficiently high; however, the H₂ isotherm is almost linear. The low-pressure region for all the adsorbates is depicted in inner graphs of Figures 1, 2 and 3 for the sake of clarity. Experimental data are used to fit the parameters of Langmuir, Sips and Dual-site Langmuir (DSL) equations. From a thermodynamic consistency point of view, the saturation capacity (q_s) for each component should not be temperature-dependent. Hence, this restriction has been taken into account when conducting the non-linear regression procedure to minimize the error function in Solver. The above fittings will be used later for the prediction of ternary adsorption via the extended models, previously described in section 3.2. Figures 1, 2 and 3 show the degree of goodness of the fit between experimental values and the Langmuir, Sips and DSL equations, respectively. The optimal parameters from the fit as well as the sum of the squared relative errors (SSE) are tabulated in Tables S1, S2 and S3 (Supporting Information).

Although the Langmuir isotherm is fundamentally sound and it shows the correct asymptotic behaviour because it approaches Henry's law in the low-concentration region (the amount adsorbed increases linearly with pressure) and the saturation limit q_s at high concentrations, it fails to describe well the experimental values for CO₂ uptake at 298 K at high pressures (>1000 kPa) (Figure 1a). In this case, experimental data differ considerably from those values predicted by the fitted equation. Adsorption of CO₂ and N₂ at low pressures is quite well described (Figures 1a and 1b), as opposed to

the H₂ behaviour, which fitting in the low-pressure domain is grossly erroneous (Figure 1c). It is important pointing out the fact that uncertainties in gravimetric measurements become more important when dealing with light gases. In this particular case, H₂ is not only a light gas, but also it barely adsorbs on the activated carbon. This actually yields bad quality experimental data in the low-pressure region where the amount adsorbed per unit mass of adsorbent is almost negligible. Hence, deviations from the equation could be then also derived from the aforementioned observation. The SSE(%) are always higher for H₂ than for CO₂ and N₂ at all temperatures and for all models (Tables S1, S2 and S3 in Supporting Information). The bad quality of the experimental data for H₂ adsorption in the low-pressure region is indeed responsible for a large percentage of those discrepancies.

The affinity constant, b , for CO₂ is larger than the one for N₂, which in turn is also larger than the one for H₂ at all temperatures and for all models (Tables S1, S2 and S3 in Supporting Information). This constant is a measure of how strong adsorbate molecules are attracted onto a surface and it is also directly related to the Henry constant ($K=b q_s$). Hence, it seems obvious that CO₂ is more strongly attracted to the surface than N₂ and H₂. In an exothermic process like adsorption, b decreases with temperature for all the adsorbates, so at higher temperature the isotherms become less sharply curved (Figures 1, 2 and 3).

The Sips equation (Figure 2) fits the experimental data significantly better than the Langmuir equation, as it can be seen in the SSE values for each adsorbate at each temperature (Table S2 in Supporting Information). Even though the fitting significantly improves, an important feature to note is, again, the high scatter for the H₂ fitting in the

low-pressure region (Figure 2c). The parameter n is greater than unity (Table S2 in Supporting Information), suggesting some degree of heterogeneity of the gas/activated carbon system. The larger is this parameter, the higher is the degree of heterogeneity. However, this information does not reveal the source of the heterogeneity, which could be in the solid structure, in the solid energetical properties or in the adsorbate.

When considering the whole experimental pressure range, the DSL isotherm fit (Figure 3) is much better than the Langmuir and Sips ones. This is confirmed by the lower SSE values obtained for the CO₂ and N₂ fitting (Table S3 in Supporting Information) when compared with the ones obtained for the Langmuir and Sips models (except for the N₂ fitting at 298 K, which best fitting corresponds to the Sips model). However, the SSE values for the H₂ fitting increase in the DSL model with respect to the other two models. This is due to the fact that, although the high domain of pressure of the adsorption isotherms is quite well described by the DSL model, there is a significant discrepancy in the low-pressure domain (Figure 3 – inner graph), which is responsible for the high SSE values in Table S3 in Supporting Information (ranging from 26 to 39%). It is well known that a correct fitting of the low-pressure region is important for predicting multicomponent adsorption data from the pure component isotherms³³. This statement will be assessed in the following section for our three adsorbate-adsorbent system, when comparing multicomponent adsorption equilibria predictions with the corresponding experimental data.

4.2. Prediction of multicomponent adsorption equilibria from single component data: Comparison of models

A set of n -P diagrams of mixed-gas adsorption equilibria predicted from the extended Langmuir, Sips and DSL models for a gas mixture composition of 25/67/8 vol.% of CO₂, H₂ and N₂, respectively, and by using only the single-gas fitting parameters in Tables S1, S2 and S3 (Supporting Information) is presented in Figure 4. For the extended Langmuir equation, thermodynamic consistency requires q_s to be the same for all the components⁹. Analogously, the quantities q_{s1} and q_{s2} in the DSL model would not depend on the component³⁴. However, with a constant value of the saturation capacity for the three components, the experimental values cannot be described satisfactorily. Furthermore, for physical adsorption of molecules of widely different size such an assumption is unrealistic. Then, if we consider the Langmuir and DSL equations as an analytical description rather than physical models, the use of different values for q_s for each component becomes permissible. Caution must be taken though when extrapolations are made based on such a basis, as the equations cannot be expected to apply over the entire concentration range.

The extended model predictions trends for the component loadings in the gas mixture are not very different for the extended Langmuir, Sips and Case 1 and 2 of DSL model, i.e., the CO₂ remains as the most adsorbed component, followed by H₂ and N₂ (Figures 4a, 4b, 4c and 4d). Even though as a single gas N₂ adsorption is higher than H₂ one, predictions foresee a different behaviour when the adsorbates are assessed in the gas mixture considered here. This might be probably due to their different concentrations in the mixture, where H₂ is a major component (67%vol.) as opposed to N₂, which is only present in an 8%vol. Contrarily, predictions from Case 3 and 4 of the DSL model (Figure 4e and Figure 4f, respectively) exhibit a higher N₂ adsorption versus H₂ one. This fact is related to the different correlation between the binary pairs.

4.3. Multicomponent adsorption equilibria from breakthrough curves: Comparison between experimental and predicted values

To evaluate which predicted behaviour is the most reliable and accurate one, mixed-gas adsorption data calculated from breakthrough experiments carried out at a temperature of 318 K, two different concentrations of a ternary CO₂-H₂-N₂ gas mixture, and five different pressures (300, 500, 1000, 1500 and 2000 kPa), are compared with the predictions of multi-component adsorption equilibria. Figure 5 shows an example of the breakthrough curves of a CO₂/H₂/N₂ mixture at 318 K and 1000 kPa of total pressure for the two different tested compositions. The less adsorbed components, H₂ and N₂, always break first than CO₂ and their breakthrough curves exhibit a so-called roll-up, that is, the flow rate or concentration of those components at the column exit temporarily exceeds the feed flow rate/concentration. The exit profiles in Figure 5 can be explained as follows: the concentration front of H₂ advances faster through the column than the concentration front of N₂ and CO₂. Thereby, the outlet end of the column is initially only in contact with H₂. However, as the concentration front of N₂ advances further through the column, N₂ replaces H₂ that was initially adsorbed, so H₂ is desorbed by incoming N₂, leading to the aforementioned roll-up effect. Likewise, CO₂ replaces N₂ initially adsorbed, resulting in another roll-up effect for N₂. An additional peak is also detected in the roll-up of H₂, just before N₂ breaks through the column. This is due to the thermal wave that accompanies the concentration front of N₂, triggering further desorption of H₂ and therefore, an additional peak in its roll-up.

The absolute component adsorbed quantity at equilibrium was calculated by integration of the breakthrough curve, which was corrected with a blank experiment to account for the dead volume of the setup, and subtracting the amount of gas that has accumulated in the inter- and intra-particle voids. In the integration of the breakthrough curves of H₂ and N₂, the net amount of gas adsorbed at equilibrium is computed as the amount that is adsorbed minus the amount desorbed by the incoming gas (i.e., the roll-up area or area above C/C₀=1). In these cases, the net amounts of H₂ and N₂ are difficult to estimate from the breakthrough curves reliably due to the relatively large error in the calculation. Then, only the equilibrium CO₂ uptake in the ternary mixture is utilized for the comparison with models predictions.

Predictions of mixed-gas adsorption equilibria for CO₂ on phenol-formaldehyde resin-based activated carbon are compared to experimental data in Figure 6. The experimental error for each data point obtained from breakthrough experiments is also depicted in Figure 6 but, in most cases, the error bar is smaller than the symbol size. The relative errors (RE) for each model are also presented in Figure 6 where the RE for the amount of CO₂ adsorbed is defined as:

$$RE (\%) = \left| \frac{q_{meas} - q_{calc}}{q_{meas}} \right| \times 100 \quad (15)$$

In eq. (15) q_{meas} is the experimental or measured CO₂ uptake, and q_{calc} is the calculated or predicted value. Two different gas-mixture compositions are shown at constant temperature and varying pressures (Figures 6a and 6c). In both cases, the qualitative behaviour from the experiments is well predicted by the models; however, they differ quantitatively, with the largest discrepancies between the predictions and

experimental values corresponding to the Sips model. For this model, RE values above 30% are obtained for the two gas mixture compositions at all pressures, with RE values increasing up to between 50 and 80% in some instances (Figures 6b and 6d). Thereby, although the Sips equation has been proved to provide a reasonable good empirical correlation of binary equilibrium data for a number of simple gases on adsorbents like molecular sieves, it clearly fails to predict gas-mixture adsorption in our system.

The REs decrease significantly for the other models, although they are still significant for the Langmuir and DSL_Case 1 models (normally higher than 10%). Predictions from Case 2, 3 and 4 of the DSL model differ very slightly with relevant differences only observed above a total pressure of 1000 kPa. Actually, Case 2 and Case 4 practically overlap for the two different gas-mixture compositions, and Case 3 is the one that differs at higher pressures (> 1000 kPa). This latter case seems to be the one that better predicts the CO₂ uptake as it is reflected in the RE values, which were never higher than 5% in most of the cases. Nevertheless, even for this model, REs at lower pressures (300 and 500 kPa) are significant ($\sim 20\%$ for the gas-mixture containing 44% of CO₂ and $\sim 45\%$ for the gas-mixture containing 25% of CO₂ and a total pressure of 300 kPa). Deviations might be derived from the quality of the single-gas adsorption experimental data in the low-pressure domain, especially for H₂, which have been previously used to fit the pure component isotherm parameters considered for the mixed-gas predictions.

Thereby, and according to the results presented herein, the extended DSL model with the binary pairs CO₂-N₂ and CO₂-H₂ correlating in a PN fashion and the correlation for

the binary pair $\text{N}_2\text{-H}_2$ being of PP form, is the one that most accurately predicts the gas-mixture behaviour of this three adsorbate-adsorbent system.

The DSL model has already been claimed to be one of the most powerful and predictive equilibrium models to be used in gas-phase adsorption process simulation, after being tested in various ideal and non-ideal systems ³¹. In an aim to elucidate whether the nature of the binary pair interactions for our adsorbates is adsorbent-dependent or not, adsorption equilibria for two binary systems from the literature ¹⁰, $\text{CO}_2\text{-N}_2$ and $\text{CO}_2\text{-H}_2$ on activated carbon AP3-60, were tested against the DSL model, by using only the single-gas fitting parameters obtained from the experimental isotherms. The optimal parameters from the fit as well as the sum of the squared relative errors (SSE) are tabulated in Table S4 (Supporting Information), and Figure 7 shows the degree of goodness of the fit between experimental values and the DSL equation.

When applying the extended DSL model to a binary system, either both components correlation is of the same type, i.e., PP, or of different type, i.e., PN. Results presented in Figures 8 and 9 show that experimental points correlate with the DSL model in a PP fashion, demonstrating that perfect positive (PP) is the correct correlation for these binary systems. For the $\text{CO}_2\text{-N}_2$ binary system the correlation is even quantitatively quite accurate and for the $\text{CO}_2\text{-H}_2$ binary system, although the predicted values are not as accurate as in the $\text{CO}_2\text{-N}_2$ system, they perfectly follow the trend predicted by the PP correlation. Again, this observation highlights the fact that reliable and accurate H_2 adsorption equilibrium data is, indeed, a challenging task. The bounding behaviour, i.e., PP or PN site-matching correlation, of each binary pair in the mixture should prevail, regardless of temperature, pressure and composition, so the DSL model would be easily

extendable to predicting adsorption equilibria in higher-order systems. This implies that in a $\text{CO}_2\text{-H}_2\text{-N}_2$ ternary system and activated carbon AP3-60, Case 1 (i.e., all binary pairs correlate in a PP fashion) would be the correct behaviour to predict mixed-gas adsorption equilibria. In this study, the same ternary system tested on a different activated carbon is best described by the DSL model but with a different correlation behaviour between the binary pairs (Case 3 versus Case 1). Therefore, it has been demonstrated that for a fixed mixed-gas, the binary pair interactions between the adsorbates are related to how the adsorbed gas components interact on the solid surface, i.e., the adsorbent and/or its heterogeneity seems to dictate the nature of those interactions.

The extended models presented here will be applied to dynamic studies of adsorption columns, where the suitability of the activated carbon used in this study can be evaluated and optimized for separating high-pressure CO_2 gas streams in pre-combustion capture applications.

5. CONCLUSIONS

In this paper, gravimetrically measured adsorption isotherms for pure CO_2 , H_2 and N_2 , on a phenol-formaldehyde resin-based activated carbon for pressures ranging from 0 to 3000-4000 kPa and for temperatures ranging from 298 to 338 K are presented. The experimental data were described with the Langmuir, Sips and DSL isotherms by fitting of the models to the data. Next, co-adsorption equilibria of $\text{CO}_2\text{-H}_2\text{-N}_2$ mixtures were measured at 318 K, two different gas phase compositions and varying total pressure in a fixed-bed reactor. Experimental data from mixed-gas adsorption were compared to

isotherms calculated by the extended Langmuir, Sips and DSL models. The site-matching correlation between each binary pair of the gas mixture was taken into account when formulating the extended DSL model equations.

The most accurate predictions of CO₂ loadings in the gas mixture-adsorbent system, which is an important parameter in adsorption process simulation, were attained by the extended DSL model. The correct correlation behaviour between the three binary pairs involved in the process proved to be of PN fashion for CO₂-N₂ and CO₂-H₂, and of PP form for N₂-H₂. Furthermore, this correlation behaviour was demonstrated to be adsorbent-dependant.

The equilibrium specified by the isotherm model affects the driving force for mass transfer, so significantly different simulation results can be obtained when using different models, even if the model parameters are derived from exactly the same set of data. Hence, it is a key issue to choose a model that closely reflects the actual process. The results presented in this work highlight the importance of performing measurements of mixture adsorption equilibria. These experimental data, although tedious and time-consuming to obtain, help to discriminate between models and to correctly select an appropriate one to be further used in simulations of gas phase adsorption processes.

ASSOCIATED CONTENT

Supporting Information

Extended multicomponent DSL equations for a ternary system considering the energetic site-matching concept, three tables listing Langmuir, Sips and Dual-site Langmuir (DSL) model parameters and sum of the squared relative errors (SSE) for single-

component adsorption on activated carbon at different temperatures, and one table listing Dual-site Langmuir (DSL) model parameters and sum of the squared relative errors (SSE) for single-component adsorption on AC AP3-60 at different temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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FIGURE CAPTIONS

Figure 1. Fitting of pure CO₂ (a), N₂ (b) and H₂ (c) adsorption data on phenol-formaldehyde resin-based activated carbon with the Langmuir equation at different temperatures (symbols – absolute experimental loading; lines – fitted Langmuir equation): 298 K-squares, 318 K-triangles, 338 K-circles. Parameter values are given in Table S1 (Supporting Information).

Figure 2. Fitting of pure CO₂ (a), N₂ (b) and H₂ (c) adsorption data on phenol-formaldehyde resin-based activated carbon with the Sips equation at different temperatures (symbols – absolute experimental loading; lines – fitted Sips equation): 298 K-squares, 318 K-triangles, 338 K-circles. Parameter values are given in Table S2 (Supporting Information).

Figure 3. Fitting of pure CO₂ (a), N₂ (b) and H₂ (c) adsorption data on phenol-formaldehyde resin-based activated carbon with the Dual-site Langmuir (DSL) equation at different temperatures (symbols – absolute experimental loading; lines – fitted DSL equation): 298 K-squares, 318 K-triangles, 338 K-circles. Parameter values are given in Table S3 (Supporting Information).

Figure 4. Component adsorbed amounts of a CO₂/H₂/N₂ gas mixture (25/67/8 vol.%) on phenol-formaldehyde resin-based activated carbon at 318 K predicted from the extended Langmuir (a), Sips (b), and DSL model based on the PP or PN correlation between the binary pairs, Case 1 (c), Case 2 (d), Case 3 (e) and Case 4 (f) of Table 2: CO₂ (red lines), H₂ (green lines) and N₂ (blue lines). The colour reproduction of this figure is available in the on-line version of the article.

Figure 5. Exit profiles of experimental breakthrough data of CO₂-H₂-N₂ gas mixtures on phenol-formaldehyde resin-based activated carbon at 318 K and 1000 kPa of total pressure. Gas phase composition: CO₂/H₂/N₂ 44/46/10% vol. (a) and CO₂/H₂/N₂ 25/67/8 % vol. (b); CO₂ (solid lines), H₂ (dotted lines) and N₂ (dash-dotted lines).

Figure 6. n_{CO_2} -P diagrams for CO₂/H₂/N₂ mixtures at 318 K and two different compositions; symbols are experimental points and lines are predictions with the

extended Langmuir, Sips and DSL equations and parameter values given in Tables S1, S2 and S3 (Supporting Information). RE(%) values obtained for each model are also shown. Gas phase composition: CO₂/H₂/N₂ 25/67/8 %vol. (a and b) and CO₂/H₂/N₂ 44/46/10 %vol. (c and d). The colour reproduction of this figure is available in the on-line version of the article.

Figure 7. Single-gas adsorption equilibrium isotherms for CO₂ (a), N₂ (b) and H₂ (c) on AC AP3-60¹⁰ at different temperatures (symbols – absolute experimental loading; lines – fitted DSL equation): 298 K-squares, 318 K-triangles, 338 K-circles. Parameter values are given in Table S4 (Supporting Information).

Figure 8. Binary CO₂-N₂ adsorption equilibria on AC AP3-60 at 298 K. Symbols represent experimental data¹⁰ and lines represent DSL model predictions: CO₂ uptake (triangles), N₂ uptake (squares) and total uptake (circles); solid lines and dotted and dashed lines represent total and component amounts adsorbed, respectively (CO₂: dotted lines; N₂: dashed lines). Each row represents a different total pressure of the system: 2000 kPa (a and b) and 3000 kPa (c and d).

Figure 9. Binary CO₂-H₂ adsorption equilibria on AC AP3-60 at 298 K. Symbols represent experimental data¹⁰ and lines represent DSL model predictions: CO₂ uptake (triangles), H₂ uptake (squares) and total uptake (circles); solid lines and dotted and dashed lines represent total and component amounts adsorbed, respectively (CO₂: dotted lines; H₂: dashed lines). Each row represents a different total pressure of the system: 2000 kPa (a and b) and 3000 kPa (c and d).

Figure 10. “For table of contents only”.

Table 1. Critical constants, molar volume and adsorbed phase density of the adsorbates at experimental adsorption temperatures.

	T_c	P_c	V_c	T_{ads}	CO ₂		H ₂		N ₂	
	K	bar	cm^3/mol	K	V_m cm^3/mol	ρ_L g/cm^3	V_m cm^3/mol	ρ_L g/cm^3	V_m cm^3/mol	ρ_L g/cm^3
CO ₂	304.12	73.74	94.07	298.15	61.51	0.716	26.51	0.076	38.60	0.726
H ₂	32.98	12.93	64.20	318.15	42.86	1.027	26.51	0.076	38.60	0.726
N ₂	126.20	33.98	90.10	338.15	42.86	1.027	26.51	0.076	38.60	0.726

Table 2. Viable Perfect Positive (PP) and Perfect Negative (PN) correlations for a CO₂-H₂-N₂ ternary system based on pairwise additivity and following the two rules of logic.

<i>site-matching correlations</i>				
<i>binary-pair</i>	<i>Case 1</i>	<i>Case 2</i>	<i>Case 3</i>	<i>Case 4</i>
CO ₂ -N ₂	PP	PN	PN	PP
CO ₂ -H ₂	PP	PP	PN	PN
N ₂ -H ₂	PP	PN	PP	PN

Figure 1. Fitting of pure CO₂ (a), N₂ (b) and H₂ (c) adsorption data on phenol-formaldehyde resin-based activated carbon with the Langmuir equation at different temperatures (symbols – absolute experimental loading; lines – fitted Langmuir equation): 298 K-squares, 318 K-triangles, 338 K-circles. Parameter values are given in Table S1 (Supporting Information).

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