

Monte Carlo Simulation Strategies for Predicting CO₂/CH₄ Adsorption onto Activated Carbons from Pure Gas Isotherms[†]

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ABSTRACT: The problem of predicting the adsorptive properties of activated carbon (AC) towards a mixture of gases from the simple knowledge of the adsorption properties of the pure components is addressed, with special reference to the CO₂/CH₄ mixture. The adsorption process for the pure gases and their mixtures was simulated using the Grand Canonical Monte Carlo (GCMC) method and the calculations were then used to analyze experimental isotherms for the pure gases and for mixtures with different molar fractions in the gaseous phase. It was shown that the pore-size distributions (PSDs) “sensed” by each of the pure probe gases was different one from the other and also from the PSDs “seen” by the mixture. A mixing rule for combining the PSDs corresponding to the pure gases is proposed for obtaining predictions regarding the adsorption of the corresponding mixtures, which are then compared with those arising from the classical IAST approximation. For this purpose, selectivity curves for CO₂ relative to CH₄ have been calculated and compared with experimental values. It was concluded that, for the adsorbate/adsorbent system under study, the proposed GCMC mixed model was capable of predicting the binary adsorption equilibrium, and especially the selectivity, more accurately than the IAST.

INTRODUCTION

The adsorptive separation of gases is an important process in many industrial and environmental applications. In particular, the separation of CO₂ from CO₂/CH₄ mixtures is a fundamental problem in natural gas and biogas purification/upgrading in energy-generation applications (Barbarao *et al.* 2007; Bae *et al.* 2008). The adequate design of such processes depends on a knowledge of the behaviour of multicomponent adsorption equilibria. Efforts to predict multicomponent adsorption equilibria based on the adsorption isotherms of each of the pure components of the mixture have frequently appeared in the scientific literature. However, in practice, multicomponent adsorption experiments are tedious and time-consuming. Indeed, design/process engineers seek reliable methods which enable such experiments to be avoided.

Since it was proposed some 50 years ago (Myers and Prauznitz 1965), the classical Ideal Adsorbed Solution Theory (IAST) has been by far the method most usually employed to achieve

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this goal. More recently, the Density Functional Theory (DFT) and Grand Canonical Monte Carlo (GCMC) simulations have been used in the search for a more accurate approach (Yan and Yang 2005; Heuchel *et al.* 1999; Sweatman and Quirke 2005). The main difficulty which has to be overcome in this new approach is the problem of differing PSDs for a given AC sample when determined using different probe gases (Blanco *et al.* 2010; Soares Maia *et al.* 2011; Scaife *et al.* 2000; Ravikovitch *et al.* 2000). In other words, different adsorbates “sense” different PSDs for the same AC sample. In fact, workers are usually faced with the problem that gas A “sees” a PSD(A), gas B “sees” a PSD(B), and, even further, a mixture of A and B with molar fractions in the gaseous phase of Y_A and $Y_B = 1 - Y_A$, “sees” a different PSD(Y_A). Hence, the question which must be faced is which combination of PSD(A) and PSD(B) should be used to predict a reliable selectivity behaviour without performing gas-mixture experiments?

In the present work, we propose the use of a linear combination of PSD(A) and PSD(B) weighted according to the respective molar fractions of A and B in the gaseous phase. Experimental data obtained from measurements of pure component isotherms as well as of mixtures with different gaseous phase compositions for the CO₂/CH₄ mixture on a microporous hydrophobic activated carbon (AC) at 293 K — a temperature of interest for industrial applications — were combined with GCMC simulation studies in order to test our proposition, as a step towards finding an answer to the above fundamental question. GCMC simulation has proved to be an appropriate and accurate method for the determination of PSDs of pure gases and their mixtures, which are obtained by fitting experimental adsorption isotherms with a theoretical isotherm constructed as a superposition of simulated isotherms for each individual pore size.

EXPERIMENTAL

Pure and binary adsorption equilibria of CO₂ and CH₄ onto AC WV1050 (MeadWestvaco, U.S.A.; BET surface area = 1615 m²/g; micropore volume = 0.76 cm³/g) were measured at 293 K, employing total pressures of 2.5, 5.0 and 10 bar, and different gaseous phase compositions.

The volumetric/chromatographic apparatus used to measure the multicomponent and pure gas adsorption equilibria is illustrated in Figure 1 overleaf. It basically consisted of a closed loop containing a dosing system and an adsorption chamber, where the adsorbent sample was tested. The experimental set-up included a gas circulation pump (GK-M 24/02; Rietschle Thomas, Germany) between the dosing and the adsorption chambers in order to ensure a homogeneous gas-phase composition throughout the system and to reduce the time necessary to attain equilibrium conditions. Gas pressures were measured with pressure sensors (P-10; WIKA, Germany) with an accuracy higher than 0.1%. The laboratory where the set-up was installed was air-conditioned in order to maintain a nearly constant temperature of 293 ± 1 K. Two temperature sensors (PT-100; Garlock, Brazil) were connected to the apparatus. The gas-phase composition at equilibrium was analyzed by gas chromatography (GC) (CP4900; Varian, U.S.A.).

Initially, the sample was regenerated *in situ* at 373 K under vacuum (1.3×10^{-8} MPa) until no pressure variation was observed in the system. Then, a gas mixture was prepared in the dosing chamber and its composition analyzed by GC. The PVT data were registered and the gas mixture was allowed to expand into the adsorption chamber containing the AC. After the temperature and pressure had attained constant values, the gas concentration was constantly monitored by GC until no significant variation was detected. Adsorption equilibrium was achieved within 3 h for all experimental points when the gas-circulation pump was employed. The equilibrium composition of the gaseous phase (in mole fractions), Y_{CO_2} and $Y_{\text{CH}_4} = 1 - Y_{\text{CO}_2}$, was obtained by gas chromatography and registered along with the new PVT data. From mass-balance considerations, it was possible to

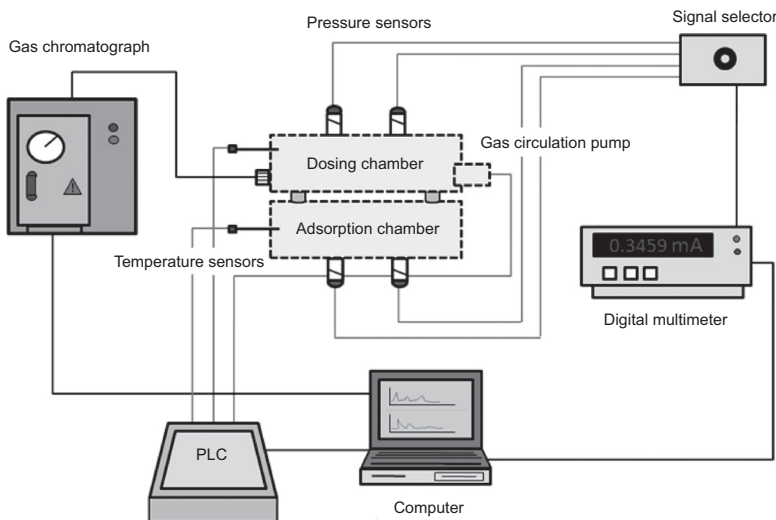


Figure 1. Experimental device for volumetric/chromatographic measurements.

relate the mass of each component present in the gaseous phase both initially and after adsorption equilibrium had been achieved, thereby allowing the concentration of each component and that of the total adsorbed phase to be calculated. Further details on the volumetric/chromatographic method may be found elsewhere (Dreisbach *et al.* 1999; Bazan *et al.* 2008; Goetz *et al.* 2006).

The selectivity of the AC towards the pure components and the CO₂/CH₄ mixture was calculated via the equation described in Kurniawan *et al.* (2006). Figures 2(a) and 3(a) show the experimental adsorption isotherms for the pure components CO₂ and CH₄, respectively, while the data corresponding to the adsorption of the mixture at Y_{CO₂} = 0.18 and 0.78 are presented in Figures 4(a) and 5(a), respectively.

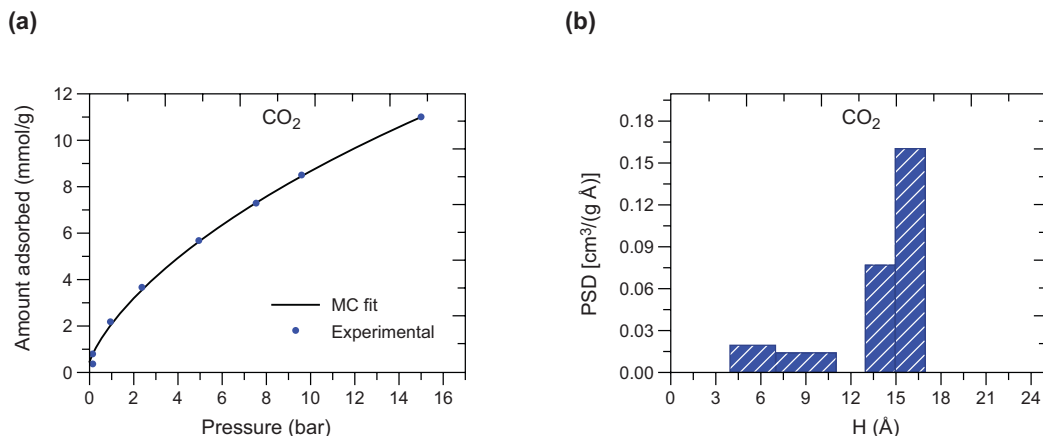


Figure 2. (a) Single-component isotherm for CO₂. The data points correspond to the experimental data while the line is the result of GCMC simulations. (b) Pore-size distribution calculated from the CO₂ adsorption isotherm using GCMC simulations.

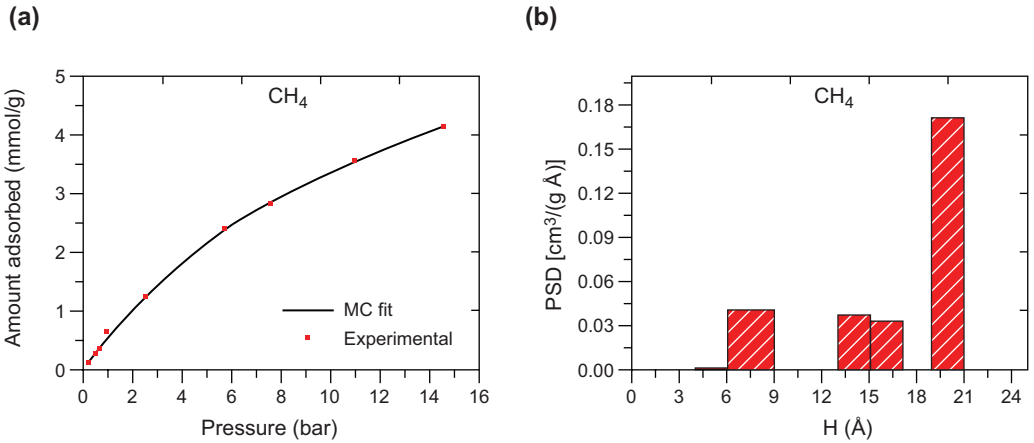


Figure 3. (a) Single-component isotherm for CH₄. The data points correspond to the experimental data while the line is the result of GCMC simulations. (b) Pore-size distribution calculated from the CH₄ adsorption isotherm using GCMC simulations.

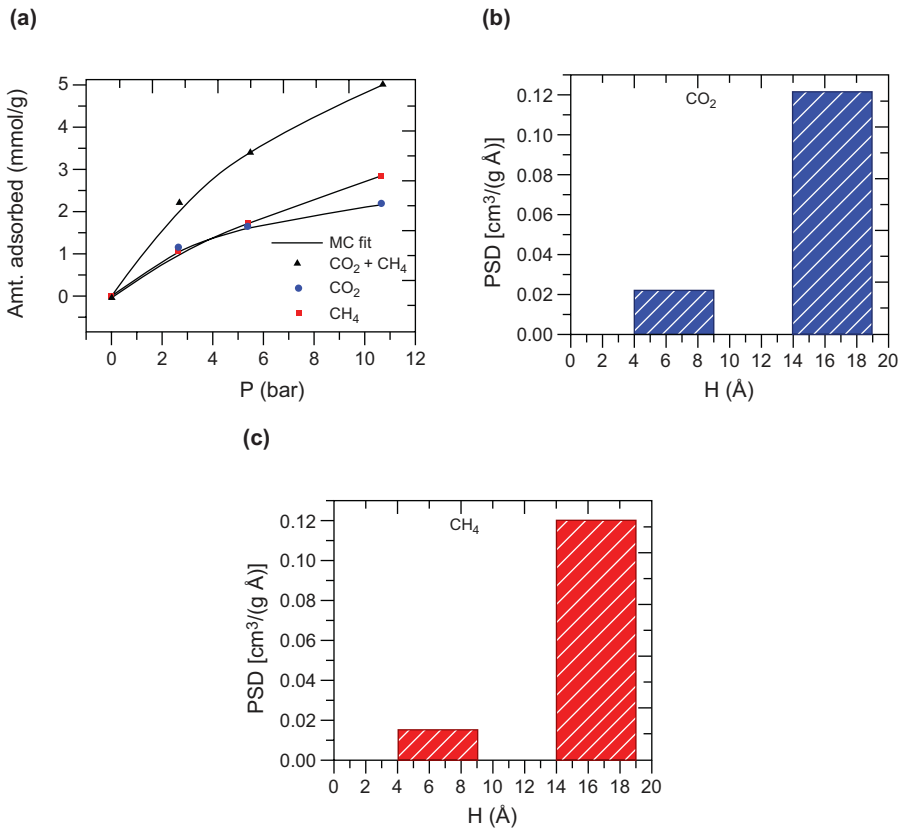


Figure 4. (a) Single-component isotherms for (■) CH₄ and (●) CO₂ together with the adsorption isotherm (▲) for a binary mixture of CH₄ and CO₂ with Y_{CO₂} = 0.18. The symbols correspond to experimental data while the line is the result of GCMC simulations. (b) Pore-size distribution for CO₂ in the mixture. (c) Pore-size distribution for CH₄ in the mixture.

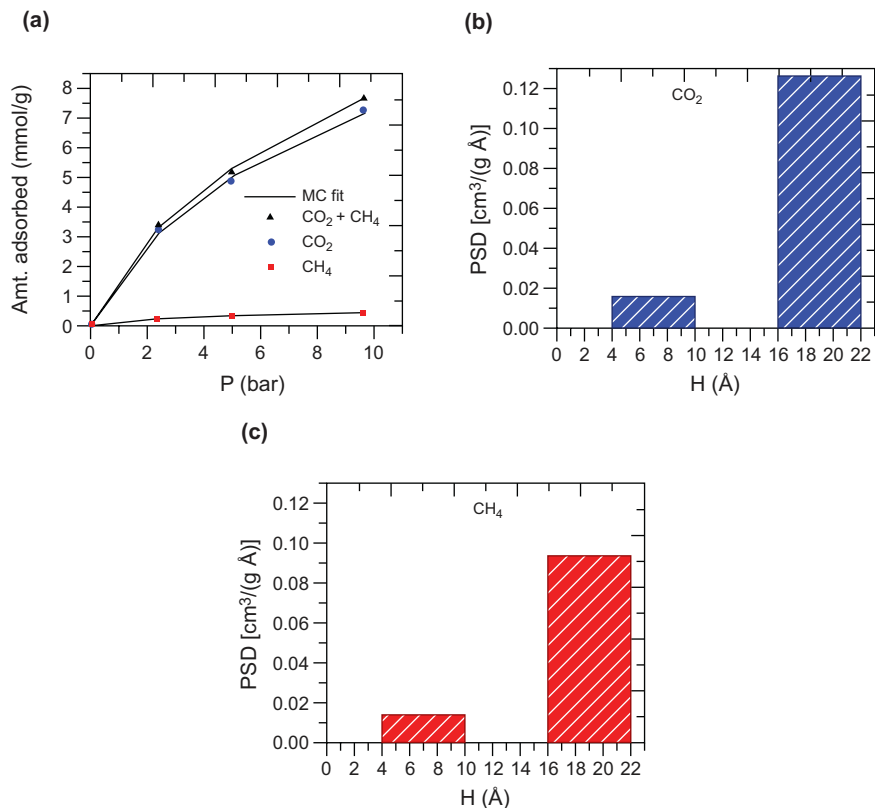


Figure 5. (a) Single-component isotherms for (■) CH₄ and (●) CO₂ together with the adsorption isotherm (▲) for a binary mixture of CH₄ and CO₂ with $Y_{\text{CO}_2} = 0.78$. The symbols correspond to experimental data while the line is the result of GCMC simulations. (b) Pore-size distribution for CO₂ in the mixture. (c) Pore-size distribution for CH₄ in the mixture.

GCMC ANALYSIS OF PURE AND MIXTURE ADSORPTION ISOTHERMS

The adsorption of gases in slit-like micropores has been investigated by GCMC simulations because these allow for a direct calculation of the phase equilibrium between a gaseous phase and an adsorbed phase. The use of this simulation method is well-established (Steele 1977; Nicholson and Parsonage 1982).

The interaction between adsorbate molecules was modelled using the truncated Lennard-Jones (LJ) potential:

$$U_{\text{gg}}(r) = -4\epsilon_{\text{gg}} \left[\left(\frac{\sigma_{\text{gg}}}{r} \right)^6 - \left(\frac{\sigma_{\text{gg}}}{r} \right)^{12} \right] \quad (1)$$

where ϵ_{gg} and σ_{gg} are the energetic and geometrical parameters of the LJ potential and r is the distance between the molecules. Each wall of the model graphitic slit pore was represented by a series of stacked planes of LJ carbon atoms. The interaction energy between a fluid particle and a

TABLE 1. Lennard-Jones Parameters Used in the GCMC Simulations

Molecule	σ_{gg} (nm) ^a	ϵ_{gg}/k_B (K) ^a	σ_{gs} (nm) ^a	ϵ_{gs}/k_B (K) ^a
CO ₂	0.3615	242.0	0.35075	82.3165
CH ₄	0.3751	148.0	0.35755	64.3739
Carbon	0.340	28.0	–	–

^aSteele (1974). ^bBoltzmann constant: $k_B = 1.380/650424 \times 10^{-23}$ J/K.

single pore wall at a distance z (measured between the centres of the fluid atom and the atoms in the outer layer of the solid) was described by the Steele 10–4–3 potential (Steele 1974):

$$U_{gs\text{-STEELE}}(z) = 2\pi\epsilon_{gs}\rho_C\sigma_{gs}^2\Delta \left\{ \frac{2}{5} \left(\frac{\sigma_{gs}}{z} \right)^{10} + \left(\frac{\sigma_{gs}}{z} \right)^4 - \frac{\sigma_{gs}^4}{3\Delta(z + 0.61\Delta)^3} \right\} \quad (2)$$

where Δ is the distance between the layers in graphite (0.335 nm), ρ_C is the density of carbon atoms per unit volume of graphite (114 atoms/nm³), z is the distance from the site of a fluid molecule to the nuclei of the carbon atoms in the surface graphitic plane, and ϵ_{gs} and σ_{gs} are the LJ parameters for a molecule and a graphite carbon atom. The values of the parameters included in the interaction potentials described in equations (1) and (2) are listed in Table 1 (Kurniawan *et al.* 2006), where the parameter σ represents the LJ collision diameter, viz. σ_{gg} for the gas and σ_{ss} for carbon. The cross-LJ parameters (arithmetic mean for the collision diameter, σ_{gs} , and the geometric mean for the well depth, ϵ_{gs}) were determined using the standard Lorentz–Berthelot combining rules.

In each GCMC simulation attempt in binary-gas adsorption, four types of operations are performed randomly with equal probability (Frenkel and Smit 1996; Allen and Tildesley 1991): displacement, adsorption, identity-swapping and desorption. The use of identity-swapping trials did not affect the GCMC averages; however, as was expected (Tant and Gubbins 1992; Cracknell *et al.* 1993), it improved convergence, considerably reducing the magnitude of standard deviations. For the adsorption step, a species is chosen from the gas phase at random with a probability given by its molar fraction. Transition probabilities for each Monte Carlo attempt are given by the usual Metropolis rules. The lateral dimension of the cell for the slit geometry was taken as $L = 10.3$ nm and periodic boundary conditions were used in these directions. The cut-off distance, beyond which the potential is neglected, was set at 5σ . Equilibrium was generally achieved after 2×10^7 MC attempts, after which mean values were taken over the following 2×10^7 MC attempts for configurations spaced by 10^3 MC attempts in order to ensure statistical independence. An MC step is an attempted creation, or destruction, of a molecule in a unit cell of size $L \times L \times H$, where H is the width of the unit cell.

In order to compare theoretical with experimental adsorption isotherms, the absolute adsorption obtained by GCMC simulation was converted to excess adsorption — the quantity determined by experimental measurements — by using a bulk equation of state to determine the number of molecules that would have been present in the absence of adsorbate–adsorbent interactions. The conversion was carried out using the equation:

$$N_i^{\text{ex}}(H, T, P, y) = N_i^{\text{abs}}(H, T, P, y) - y_i \rho_i^{\text{bulk}}(T, P) V_{\text{br}}(H) \quad (3)$$

where, for one-component adsorption, the bulk gas phase composition y is equal to one (Heuchel *et al.* 1999); $N_i^{\text{ex}}(H, T, P, y)$ is the excess number of adsorbed molecules of species i in a model pore of width H at temperature T , pressure P and bulk gas-phase composition y ; $N_i^{\text{abs}}(H, T, P, y)$ is the

TABLE 2. Critical Constants Used in the Peng–Robinson Equation of State for Methane and Carbon Dioxide^a

Molecule	Critical temperature (K)	Critical pressure (bar)	Accentricity factor
CO ₂	304.2	73.83	0.224
CH ₄	190.6	45.66	0.012

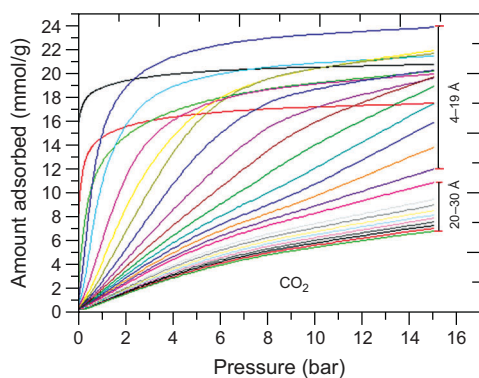
^aSandler (1989).

absolute (i.e. simulated) number of adsorbed molecules under these conditions; $\rho_i^{\text{bulk}}(P,T)$ is the bulk fluid density of species i at the temperature and pressure of concern; and $V_{\text{bf}}(H)$ is the volume in the model pore of width H accessible to the bulk fluid (Oliveira *et al.* 2011). The calculations were performed at a defined temperature and pressure by using the equation of state for ideal gases at low pressures (up to 0.1 MPa) and the Peng–Robinson equation of state (1976) for high pressures, employing the parameters listed in Table 2 (Sandler 1989).

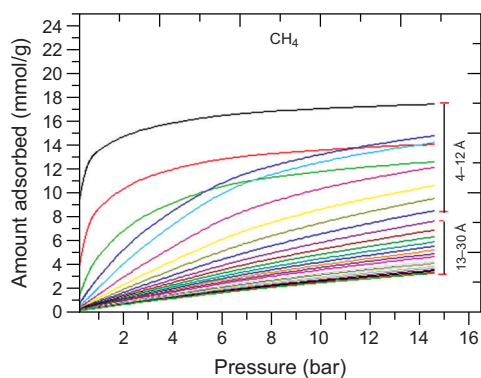
An important issue in the process of determining the PSD is the correct use of simulated local isotherms within the “reliability window”, RW (Davies and Seaton 2000; Gusev *et al.* 1997). As the pore size increases, the adsorption isotherms becomes less and less sensitive to the size, and from a critical size onwards (this defining the RW) they become linearly dependent; hence, determination of the PSD will not be reliable above the RW. The critical size, and therefore the RW, can be determined numerically by the procedure explained by Gusev *et al.* (1997).

Figures 6(a) and (b) show the simulated pure CO₂ and CH₄ local isotherms, respectively, at 293 K for pore sizes ranging from 4 Å to 30 Å in steps of 1 Å. In each case, the set of isotherms is separated into two sub-sets — the upper sub-set includes isotherms belonging to the RW, whereas the lower sub-set represents isotherms that become linearly dependent and whose contribution to the PSD will be accumulated at the pore size immediately after the S_{max} corresponding to the size limit of the RW. It can be observed that $S_{\text{max}} = 19$ Å for CO₂ and $S_{\text{max}} = 12$ Å for CH₄. The local isotherms for the adsorption of the mixture are presented in Figures 7(a) and (b) for CO₂ and CH₄, respectively, corresponding to $Y_{\text{CO}_2} = 0.18$, while the data for $Y_{\text{CO}_2} = 0.78$ are shown in Figures 8(a) and (b), respectively. It can be seen that $S_{\text{max}} = 14$ Å for both species at $Y_{\text{CO}_2} = 0.18$ while $S_{\text{max}} = 16$ Å for both species at $Y_{\text{CO}_2} = 0.78$.

(a)



(b)

**Figure 6.** Single-component local isotherms at 293 K for pore sizes ranging from 4 Å to 30 Å for (a) CO₂ and (b) CH₄.

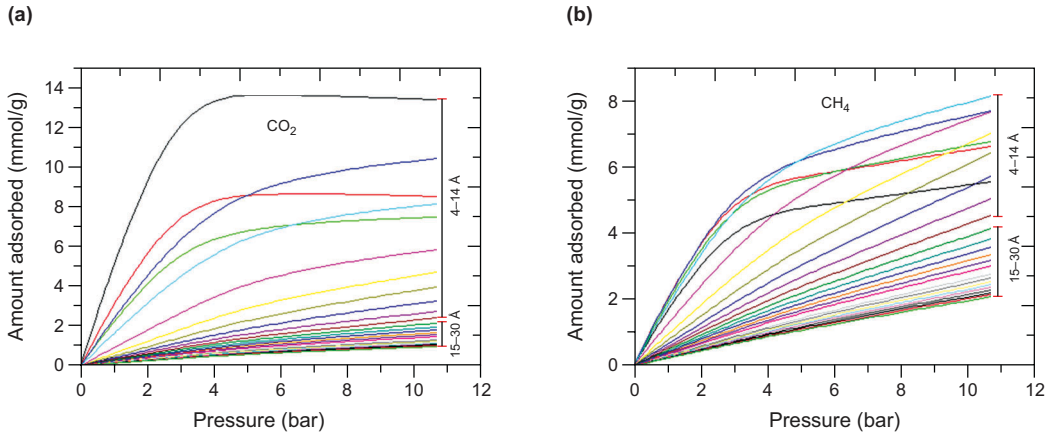


Figure 7. Adsorption local isotherms for a binary mixture at 293 K for pore sizes ranging from 4 Å to 3 Å corresponding to $Y_{\text{CO}_2} = 0.18$ for (a) CO₂ and (b) CH₄.

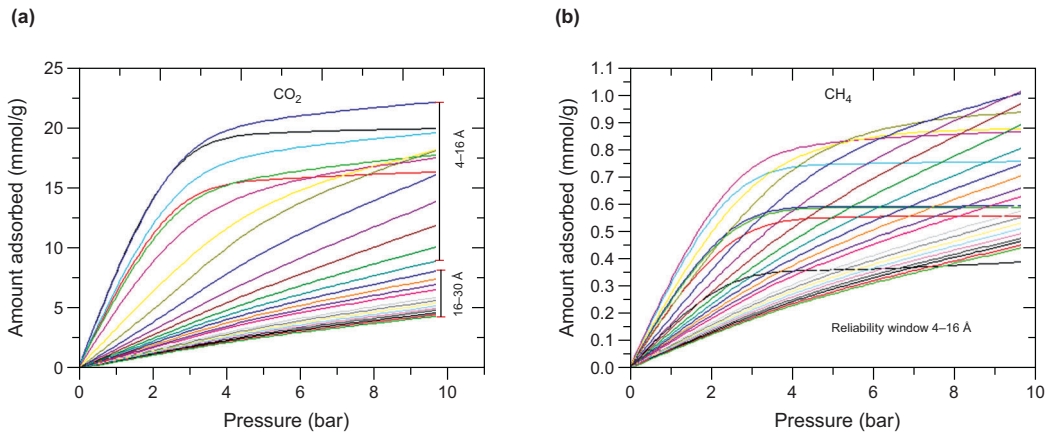


Figure 8. Adsorption local isotherms for a binary mixture at 293 K for pore sizes ranging from 4 Å to 30 Å corresponding to $Y_{\text{CO}_2} = 0.78$ for (a) CO₂ and (b) CH₄.

The local simulated isotherm sets are now used to fit the experimental adsorption data to obtain the PSDs, following the fitting procedure with a regularization term as indicated in Davies and Seaton (1998) and Davies *et al.* (1999). This is achieved by performing a mean-square fitting of the experimental isotherm with a theoretical isotherm. The latter is a linear superposition of local simulated isotherms for different sizes — each one weighted according to the relative abundance of the size (the PSD) — plus a regularization factor depending on the changes in the curvature of the PSD, which has the effect of conveniently smoothing the resulting PSD [Davies and Seaton (1998); Davies *et al.* (1999)].

At this stage, it is important to point out that, in each case, the value of S_{max} corresponding to the strongest adsorbing species should be used for both species. With this in mind, the PSDs for the pure species shown in Figures 2(b) and 3(b), and the PSDs for their mixtures shown in Figures 4(b) and (c) ($Y_{\text{CO}_2} = 0.18$) and in Figures 5(b) and (c) ($Y_{\text{CO}_2} = 0.78$) were obtained. The respective fittings of experimental data by the theoretical adsorption isotherms are shown in Figures 2(a), 3(a), 4(a) and 5(a).

PROPOSITION OF A MIXING MODEL FOR PREDICTING THE ADSORPTIVE BEHAVIOUR OF THE MIXTURE

As the above results show, PSDs corresponding to the pure components are different amongst themselves, and they are also different from the PSDs corresponding to the components in the mixture. It is of interest for industrial applications that the adsorptive properties of the mixture be predicted as precisely as possible, based only on the adsorption isotherms of the pure components without the need for performing experiments for the adsorption of the mixture. Consequently, the PSDs of the components in the mixture, obtained by fitting the experimental data, are only used here as a guide to propose a “mixing rule” for the PSDs of the pure components.

Our idea is that a given mixture corresponding to a molar fraction of component “i” in the gaseous phase, Y_i , where i stands for either CO₂ or CH₄, possesses a PSD which is a linear combination of the PSDs of the pure components, each one of them weighted according to its molar fraction in the gaseous phase. In other words, if we denote the PSD of component i by f_i , in such a way that $f_i(S_j)\delta S_j$ is the pore volume per gram of the adsorbent corresponding to pores with sizes between S_j and $S_j + \delta S_j$, then the PSD for the mixture of species i and j is assumed to be $f_{\text{mix}} = Y_i f_i + Y_j f_j = Y_i f_i + (1 - Y_i) f_j$. In this way, the PSD of the mixture approaches closer to that obtained by fitting the experimental data of the mixture by GCMC simulation [Figures 4(b) and (c), and Figures 5(b) and (c)] and reduces to that of the corresponding pure component for $Y_i = 0$ or 1. Hence, the proposed mixing rule for predicting the theoretical adsorption properties of a binary mixture will be given by the equation:

$$\theta_i^{\text{mix}}(P_k, T, y_i) = \sum_{j=1}^m \theta_{i,L}^{\text{mix}}(S_j, P_k, T, y_i) [y_i f_i(S_j) + (1 - y_i) f_j(S_j)] \delta S_j \quad (4)$$

where $\theta_i^{\text{mix}}(P_k, T, y_i)$ is the total adsorption isotherm for component i in the mixture, $\theta_{i,L}^{\text{mix}}(S_j, P_k, T, y_i)$ is the corresponding local isotherm for pores of size S_j , and m is the number of pore size intervals.

In order to test the proposed model, it is convenient to work with the *selectivity*, Sel, of CO₂ with respect to CH₄, as defined by:

$$\text{Sel} = \frac{X_{\text{CO}_2}/Y_{\text{CO}_2}}{X_{\text{CH}_4}/Y_{\text{CH}_4}} \quad (5)$$

where X stands for the molar fraction in the adsorbed phase. This parameter turns out to be very convenient for two main reasons: it is directly connected with the design and optimization of industrial processes and it is very sensitive for the purpose of testing theoretical predictions.

Figures 9(a) and (b) overleaf show a comparison between the predictions of the mixing model, those of the IAST and the experimental selectivity values at two compositions in the gaseous phase. As can be seen from the data depicted, the predictions of the mixing model gave a much better agreement with the experimental selectivities than those of the IAST.

CONCLUSIONS

The problem of predicting the adsorptive properties of a binary gas mixture in activated carbons (ACs) from a simple knowledge of the pure gas adsorption isotherms has been addressed and applied to the case of the CO₂/CH₄ mixture. Our study has led us to propose a mixing rule for combining the pure component PSDs in order to obtain the adsorptive behaviour of the mixture.

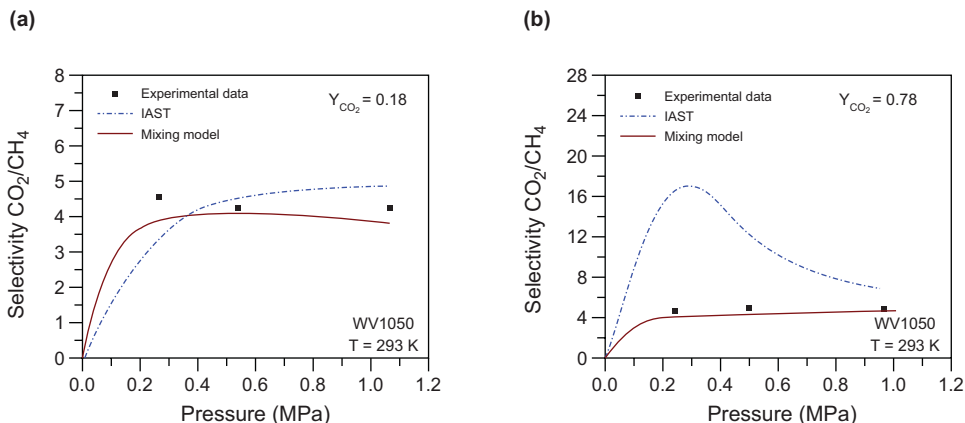


Figure 9. Selectivity in binary mixtures as a function of pressure for (a) $Y_{\text{CO}_2} = 0.18$ and (b) $Y_{\text{CO}_2} = 0.78$. Comparison between the predictions of the mixing model and the IAST, and the experimental data.

At least for the system studied herein, the mixing model was capable of predicting the selectivity more accurately than the IAST when compared to the experimental data. It should be pointed out, however, that an analysis of several other gas-mixture adsorption systems is required in order to evaluate and validate a new model such as that proposed here. For this reason, we conclude that this contribution represents a first stepping stone towards the development of a reliable method for predicting gas-mixture adsorption properties in activated carbons.

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