Modelling Adsorption Isotherms of Binary Mixtures of Carbon Dioxide, Methane and Nitrogen

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ABSTRACT: A molecular-based approach for modelling mixtures adsorbed onto solid surfaces using the Statistical Associating Fluid Theory for Potentials of Variable Range (SAFT-VR) for three- and two-dimensional systems is presented in this work. The theory is used to describe the adsorption of binary mixtures of carbon dioxide, methane and nitrogen onto dry activated carbon, describing the overall adsorption phase diagram reported for these systems even at high pressures.

INTRODUCTION

The processes of adsorption and diffusion of fluids in porous media is of great interest in the chemical industry, with applications on environmental remediation being of specific concern (Patel *et al.* 1972; Ruthven 1984; Yang 1987). The design of the optimized process requires a good understanding of the adsorption equilibrium of mixtures. Theories of adsorption where systems are composed of several compounds have been developed on the basis of classical thermodynamics and statistical mechanics. At low pressures, theories for ideal adsorption solutions (Myers and Prausnitz 1965) or simplified statistical thermodynamic models (Ruthven and Wong 1985) can reproduce experimental systems. However, more robust equations of state are required at high pressures.

Recently, adsorption isotherms for simple single-component fluids have been studied using the Statistical Associating Fluid Theory for Potentials of Variable Range (SAFT-VR) (Gil-Villegas *et al.* 1997) adapted for two-dimensional (2D) fluids interacting with discrete potentials (Martínez *et al.* 2007; Jiménez *et al.* 2008). This approach has been applied to model adsorption isotherms for pure molecular fluids, such as methane, nitrogen, carbon dioxide, ethane, ethylene and propane, adsorbed onto activated carbon and silica gel (Martínez *et al.* 2007; Jiménez *et al.* 2008; Castro *et al.* 2010), as well as asphaltenes adsorbed onto Berea sandstone, Bedford limestone and dolomite rock (Castro *et al.* 2009). In all cases, very good agreement was found.

In the present work, we present an extension of this approach in order to model mixtures within a one-fluid van der Waals approximation (Lee 1988; Galindo *et al.* 1998) that has been used previously for 3D mixtures modelled by SAFT-VR (Galindo *et al.* 1998; McCabe *et al.* 1999). This theory is applied to describe adsorption isotherms of methane/nitrogen, methane/carbon

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dioxide and carbon dioxide/nitrogen mixtures adsorbed onto dry activated carbon at a temperature of 318.2 K and pressures up to 13.6 MPa. The predictions obtained are compared with the experimental data reported for these systems (Sudibandriyo *et al.* 2003).

THEORY

In this section, we present the theory used to describe the adsorption of a mixture of fluids onto a uniform wall, assuming a 2D approximation within the SAFT-VR approach.

Let assume the existence of a fluid composed of a binary mixture of M components, each i-species being formed by N_i spherical particles of diameter σ_{ii}. The particle–particle and particle–wall interactions are modelled by square-well potentials (SW). The particle–particle SW interaction is given by:

$$u_{pp}(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma_{ij} \\ -\varepsilon_{ij}, & \sigma_{ij} < r_{ij} < \lambda_{ij}\sigma_{ij} \\ 0, & \lambda_{ij}\sigma_{ij} < r_{ij} \end{cases} \tag{1}$$

where r_{ij} is the interparticle distance between particles of species i and j, ε_{ij} and $\lambda_{ij}\sigma_{ij}$ are the energy-depth well and attractive-potential range, respectively, and σ_{ij} is the mixture diameter. The cross-parameters are given by the following combining rules:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{3}$$

and

$$\lambda_{ij}^3 = 1 + \frac{1}{\sigma_{ij}^3}\left[(\lambda_{ii}^3 - 1)(\lambda_{jj}^3 - 1)\sigma_{ii}^3\sigma_{jj}^3\right]^{1/2} \tag{4}$$

The first two rules correspond to the standard Lorentz–Berthelot expressions (Lee 1988), whereas equation (4) is derived from the van der Waals energy constant α_{ij} according to the Berthelot rule (Galindo *et al.* 1998).

On the other hand, the particle–wall SW interaction is given by:

$$u_{pw}(z) = \begin{cases} \infty, & z < 0 \\ -\varepsilon_w, & 0 < z < \lambda_w\sigma_{ii} \\ 0, & \lambda_w\sigma_{ii} < z \end{cases} \tag{5}$$

where z is the perpendicular distance of a particle of diameter σ_{ii} to the wall, and ε_w and $\lambda_w\sigma_{ii}$ are the corresponding SW parameters for the wall–particle interaction.

The total system, wall + particles, can be divided into two sub-systems according to the distance z: if $z < \lambda_w\sigma_{ii}$, then the particles can adsorb onto the wall, forming the adsorbed phase; if $z > \lambda_w\sigma_{ii}$, then the particles are in the bulk phase.

Fluids from the adsorbed and bulk phases have different properties, since the interaction between molecules is modified by the presence of the wall (Sinanoglu and Pitzer 1960); hence, the binary interaction between particles is different depending on the phase to which they belong. We will consider that equation (1) gives the particle–particle interaction in the bulk or adsorbed phases using different potential parameters for each case: ε and λ for the particles in the bulk and ε_{ads} and λ_{ads} for the adsorbed particles. The particle size σ_{ii} is not modified by the presence of the wall. We assume that in both cases the same type of combining rules are used, as given by equations (2)–(4).

To describe the amount of particles adsorbed onto the wall, we use the following expression for the coverage of a species i, Γ_i, defined as:

$$\Gamma_i = \int_0^\infty \left[\rho_i(z_i) - \rho_i^b \right] dz_i \tag{6}$$

where ρ_i is the density of particles of species i, and ρ_i^b is the bulk density, i.e. $\rho_i(z_i \to \infty)$. Since the length scale of the adsorbed phase for species i is defined by $\lambda_i^w \sigma_{ii}$, we can re-write equation (6) as:

$$\Gamma_i = \int_0^{\lambda_w \sigma_{ii}} \rho_i(z_i) dz_i - \rho_i^b \lambda_w \sigma_{ii} \tag{7}$$

where the first term of this equation can be identified as an adsorbed density of particles for species i,

$$\rho_i^{ads} = \int_0^{\lambda_w \sigma_{ii}} \rho_i(z_i) dz_i \tag{8}$$

Equation (8) is a 2D density and can be used to obtain the corresponding 2D packing fraction:

$$\gamma_i = \pi \rho_i^{ads} \sigma_{ii}^2 / 4 \tag{9}$$

In order to obtain the adsorbed density ρ_i^{ads} for a given value of the density and temperature of the bulk phase, the chemical potentials of the adsorbed and bulk phases, given by μ_i^{ads} and μ_i^b respectively, must be equal, i.e.

$$\mu_i^{ads} = \mu_i^b \tag{10}$$

where

$$\mu_i^{ads} = \frac{\partial A_{ads}}{\partial N_i^{ads}} \tag{11}$$

$$\mu_i^b = \frac{\partial A_b}{\partial N_i^b} \tag{12}$$

where A_{ads} and A_b are the Helmholtz free energies for the adsorbed and bulk phases obtained from the corresponding number of particles of species i, N_i^{ads} and N_i^b.

For the case of the adsorbed phase, A_{ads} can be derived from a 2D approximation. First, we express the partition function of the mixture of fluids adsorbed onto the surface in the following way:

$$Z_{ads} = \left[\Pi_{i=1}^{M} \frac{V_i^{N_i}}{N_i! \Lambda_i^{3N_i}} \right] Q_{ads} \tag{13}$$

where V_i is the volume of the adsorbed phase with an adsorption area S_i for component i, given by $V_i = S_i \lambda_w \sigma_{ii}$, and $\Lambda_i = h/(2\pi m_i kT)^{1/2}$ is the de Broglie's thermal wavelength at temperature T, given in terms of the Planck and Boltzmann constants, h and k, respectively, and the particle mass m_i of species i. The configurational partition Q_{ads} is defined by:

$$Q_{ads} = \frac{1}{\Pi_i^M V_i^{N_i}} \int e^{-\beta U_{ads}(x^N, y^N, z^N)} \Pi_i^M dx_i^{N_i} dy_i^{N_i} dz_i^{N_i} \tag{14}$$

where $U_{ads}(x^N, y^N, z^N)$ is the total potential function for the adsorbed particles, and $\beta = 1/kT$. This potential is given by the sum of all the pair interactions between particles of different species, plus the particle–wall interaction, i.e.

$$U_{ads}(x^N, y^N, z^N) = \frac{1}{2} \sum_{\omega}^{M} \sum_{\nu}^{M} \sum_{s_\omega}^{N_\omega} \sum_{s_\nu}^{N_\nu} u_{pp}(r_{s_\omega s_\nu}) + \sum_{\omega}^{M} \sum_{s_\omega}^{N_\omega} u_{pw}(z_{s_\omega}) \tag{15}$$

where $r_{s_\omega s_\nu}$ denotes the distance between particles s_ω and s_ν corresponding to species ω and ν, respectively, and the pair potentials u_{pp} and u_{pw} are given by equations (1) and (5), respectively. Because of the presence of the wall, interaction u_{pw} dominates the dynamical behaviour of the particles along the z-direction, and then we can justify a 2D approximation to describe the particle–particle potential, viz.

$$u_{pp}(r_{s_\omega s_\nu}) \approx u_{pp}(x_{s_\omega s_\nu}, y_{s_\omega s_\nu}) \tag{16}$$

Introducing equation (15) into equation (14), and assuming this 2D approximation, then Q_{ads} can be factorized as the product of a 1D and 2D partition function, Q^{1D} and Q^{2D}, respectively, i.e.

$$Q_{ads} = Q^{1D} Q^{2D} \tag{17}$$

where Q^{1D} and Q^{2D} are given by:

$$Q^{1D} = \frac{1}{\Pi_{i=1}^{M} (\lambda_w \sigma_i)^{N_i}} \int \exp \left[-\beta \sum_{\omega}^{M} \sum_{s_\omega}^{N_\omega} u_{pw}(z_{s_\omega}) \right] \Pi_i^M dz_i^{N_i} \tag{18}$$

and

$$Q^{2D} = \frac{1}{\Pi_i^M S^{N_i}} \int \exp \left[-\frac{\beta}{2} \sum_{\omega}^{M} \sum_{\nu}^{M} \sum_{s_\omega}^{N_\omega} \sum_{s_\nu}^{N_\nu} u_{pp}(x_{s_\omega s_\nu}, y_{s_\omega s_\nu}) \right] \Pi_i^M dx_i^{N_i} dy_i^{N_i} \tag{19}$$

Using equations (5), (17), (18) and (19) in equation (14), we finally obtain the following expression for Z_{ads}:

$$Z_{ads} = Z_{2D}^{ideal} Q^{2D} \Pi_i^M \left(\frac{\lambda_w \sigma_i}{\Lambda_i} \right)^{N_i} e^{\beta N_i \varepsilon_i^w} \tag{20}$$

where Z_{2D}^{ideal} is the 2D partition function for a mixture of ideal gases, viz.

$$Z_{2D}^{ideal} = \Pi_{i=1}^M \frac{S_i^{N_i}}{N_i! \Lambda_i^{2N_i}} \tag{21}$$

Since $A_{ads} = kT \ln Z_{ads}$, from equation (20) we obtain:

$$\frac{A_{ads}}{NkT} = \frac{A_{2D}}{NkT} - \sum_{i=1}^M x_i \left[\ln \left(\frac{\lambda_w \sigma_i^w}{\Lambda_i} \right) + \beta \varepsilon_i^w \right] \tag{22}$$

where $x_i = N_i/N$ is the mole fraction of species i, and $A_{2D} = -kT \ln [Z_{2D}^{ideal} Q^{2D}]$ denotes the Helmholtz free energy for the 2D-mixture system, which can be obtained by perturbation theory following the high-temperature expansion theory of Barker and Henderson (1967):

$$\frac{A_{2D}}{NkT} = \sum_i^M x_i \ln(\rho_i^{ads} \Lambda_i^2) - 1 + \frac{A_{HD}}{NkT} + \beta a_1^{(2D)} + \beta^2 a_2^{(2D)} \tag{23}$$

Here A_{HD} is the Helmholtz excess free energy for a fluid mixture of hard disks, $a_1^{(2D)}$ and $a_2^{(2D)}$ are the first- and second-order perturbation terms, respectively.

The properties of the bulk fluid may also be obtained by perturbation theory at the same expansion order in β (Galindo *et al.* 1998):

$$\frac{A_b}{NkT} = \sum_i^M x_i \ln(\rho_i^b \Lambda_i^3) - 1 + \frac{A_{HS}}{NkT} + \beta a_1^{(3D)} + \beta^2 a_2^{(3D)} \tag{24}$$

It should be pointed out that the method presented in this section can also be applied when the particle–particle and particle–wall interactions are described by discontinous potentials (Jiménez *et al.* 2008).

ADSORPTION OF A MIXTURE OF CHAIN MOLECULES

In the previous section, we presented a theory for the modelling of adsorption isotherms of mixtures of monomeric fluids. We now extend this study to the case of the adsorption of chain molecule fluids, following the SAFT-VR approach in 3D (Galindo *et al.* 1998) and assuming that the monomer–monomer and monomer–wall interactions can be described via square-well potentials.

Mixtures of 2D chain molecules

The Helmholtz free energy A_{2D}^{mix} for a mixture of M-component fluids of 2D chain molecules consists of three different contributions, i.e.

$$\frac{A_{2D}^{mix}}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} \tag{25}$$

where N is the total number of chain molecules in the mixture, A^{ideal} is the ideal contribution, A^{mono} is the residual free energy of the monomeric segments and A^{chain} is the contribution due to the formation of chains.

The ideal contribution to the free energy is given by:

$$\frac{A^{ideal}}{NkT} = \sum_{i=1}^{M} x_i \ln\left(\rho_i \Lambda_i^2\right) - 1 \tag{26}$$

where the sum is over all species i in the mixture, $x_i = N_i/N$ is the mole fraction of chain molecules and $\rho_i^{ads} = N_i/S$ is the 2D density of chain molecules adsorbed onto a surface of area S.

The contribution to the free energy due to monomers is:

$$\frac{A^{mono}}{NkT} = \left[\sum_{i=1}^{M} x_i m_i\right]\frac{A^{mono}}{N_s kT} = \left[\sum_{i=1}^{M} x_i m_i\right] a^{mono} \tag{27}$$

where m_i is the number of monomer segments of chain i, N_s is the total number of hard-disk monomers and a^{mono} is the 2D free energy per monomer. In our case, a^{mono} is given by equation (23). In the present study, the hard-disk fluid properties were obtained from the equation of state proposed by Santos *et al.* (1999), viz.

$$Z_{HD} = \frac{1 - (1 - w)\gamma + (B_3 - 3)w\gamma^2}{(1 - \gamma)^2} \tag{28}$$

where Z_{HD} and γ are the compressibility factor and packing fraction for a HD mixture, respectively, $w = <\sigma>^2/<\sigma^2>, <\sigma^2> = \sum_{i=1}^{M} x_i \sigma_i^2$ and $B_3 = \frac{16}{3} - \frac{4}{\pi}\sqrt{3}$ is the third virial coefficient of this system. From equation(9), γ is given by:

$$\gamma = \frac{\pi\rho_s^{ads}}{4}\left[\sum_{i=1}^{M} x_{s,i} \sigma_{ii}^2\right] \tag{29}$$

where $\rho_s^{ads} = N_s/S$ and $x_{s,i}$ is the mole fraction of disk segments of type i in the mixture, defined by:

$$x_{s,i} = \frac{m_i x_i}{\sum_{k=1}^{M} m_k x_k} \tag{30}$$

The excess free energy per hard disk, $a_{HD} = A_{HD}/N_s kT$, is obtained from equation (28) and the following relationship:

$$Z_{HD} = 1 + \gamma\left(\frac{\partial a_{HD}}{\partial \gamma}\right)_{N,T} \tag{31}$$

to give

$$a_{HD} = -w + \ln(1 - \gamma)[(B_3 - 3)w - 1] + \frac{w[1 + (B_3 - 3)\gamma]}{1 - \gamma} \tag{32}$$

The perturbation terms a_1 and a_2 are calculated within the van der Waals one-fluid approximation. In the case of the first-order term, we have that:

$$a_1 = \sum_{i=1}^{M}\sum_{j=1}^{M} x_{s,i} x_{s,j} a_1^{ij} \tag{33}$$

where a_1^{ij} is the mean attractive energy associated to the pair potential $u_{pp}(r_{ij})$.

The second-order term is:

$$a_2 = \sum_{i=1}^{M}\sum_{j=1}^{M} x_{s,i} x_{s,j} a_2^{ij} \tag{34}$$

where a_2^{ij} is obtained from the local compressiblity approximation for mixtures, i.e.

$$a_2^{ij} = \tfrac{1}{2}\varepsilon_{ij}\kappa_{HD}\rho_s^{ads}\frac{\partial a_1^{ij}}{\partial \rho_s^{ads}} \tag{35}$$

where

$$\kappa_{HD} = \frac{(1 - \gamma)^3}{1 - \gamma + 3\gamma^2 w(B_3 - 3) - \gamma^3 w(B_3 - 3)} \tag{36}$$

Introducing the vdW – 1 fluid approximation, and following the 2D SAFT-VR mapping procedure for the evaluation of a_1^{ij} (Martínez *et al.* 2007), we have that:

$$a_1^{ij} = \tfrac{\pi}{2}\rho_s\varepsilon_{ij}(\lambda_{ij}^2 - 1)\sigma_{ij}^2 g_0^{HD}(\gamma_x^{eff}) \tag{37}$$

where g_0^{HD} is the contact value of the hard-disk radial distribution function obtained from the Henderson equation [equation (18)] for pure fluids:

$$g_0^{HD}(\gamma_x^{eff}) = \frac{1 - 7\gamma_x^{eff}/16}{(1 - \gamma_x^{eff})^2} \tag{38}$$

and the effective packing fraction is given by:

$$\gamma_x^{eff}(\gamma_x,\lambda_x) = d_1(\lambda_x)\gamma_x + d_2(\lambda_x)\gamma_x^2 \tag{39}$$

where

$$d_1 = 1.4215 - 0.405625\lambda_x - 0.03869981\lambda_x^2 \tag{40}$$

$$d_2 = 1.5582 - 1.89768\lambda_x + 0.405215\lambda_x^2 \tag{41}$$

$$\gamma_x = \tfrac{\pi}{4}\rho_s^{ads}\sum_{i=1}^{M}\sum_{j=1}^{M} x_{s,i} x_{s,j}\sigma_{ij}^2 \tag{42}$$

and

$$\lambda_x^2 = \frac{\sum_{i=1}^{M}\sum_{j=1}^{M} x_{s,i} x_{s,j} \varepsilon_{ij} \lambda_{ij}^2 \sigma_{ij}^2}{\sum_{i=1}^{M}\sum_{j=1}^{M} x_{s,i} x_{s,j} \varepsilon_{ij} \sigma_{ij}^2} \tag{43}$$

Finally, the 2D SAFT-VR expression for the contribution to the free energy due to chain formation is:

$$\frac{A^{chain}}{NkT} = -\sum_{i=1}^{M} x_i (m_i - 1) \ln y_{ii}^m(\sigma_i) \tag{44}$$

where y_{ii}^m is the contact value of the background function of the monomeric fluid defined by:

$$y_{ii}^m(\sigma_{ii}) = g_{ii}^m(\sigma_{ii}) e^{-\beta\varepsilon_{ii}} \tag{45}$$

where g_{ii}^m is the corresponding radial distribution function which is determined by perturbation theory as:

$$g_{ii}^m(\sigma_{ii}) = g_{ii}^{HD}(\sigma_{ii}) + \beta\varepsilon_{ii} g_1^{ii}(\sigma_{ii}) \tag{46}$$

where g_{ij}^{HD} is the contact value of the HD radial distribution function given by:

$$g_{ij}^{HD}(\sigma_{ij}) = \frac{1}{2(1 - \gamma)} + \frac{[1 + (B_3 - 3)\gamma]\sigma_i\sigma_j}{2(1 - \gamma)^2 \sum_{i=1}^{M} x_i \sigma_i^2} \tag{47}$$

and the first-order perturbation term $g_1^{ii}(\sigma_{ii})$ is given by:

$$g_1^{ii}(\sigma_{ij}) = \frac{2}{\pi\sigma_{ii}^2\varepsilon_{ii}} \left[\frac{\partial a_1^{ii}}{\partial\rho_s^{ads}} - \frac{\lambda_{ii}}{4\rho_s^{ads}} \frac{\partial a_1^{ii}}{\partial\lambda_{ii}} \right] \tag{48}$$

The last result is obtained from a self-consistent method for obtaining the pressure p, using the Clausius virial theorem and the density derivative of the Helmholtz free energy. Using the vdW – 1 fluid approximation and equations (32)–(36), we have that:

$$g_1^{ii} = g_0^{HD}(\gamma_x^{eff}) + (\lambda_{ii}^2 - 1)\frac{\partial g_0^{HD}(\gamma_x^{eff})}{\partial\gamma_x^{eff}}\left(\frac{\lambda_{ii}}{2} \frac{\partial\gamma_x^{eff}}{\partial\lambda_{ii}} - \gamma \frac{\partial\gamma_x^{eff}}{\partial\gamma} \right) \tag{49}$$

Adsorption equation

Once we have detailed how the free energy A_{2D}^{mix} is obtained following previous developments for 3D and 2D chain molecules fluids (Galindo *et al.* 1998; Martínez *et al.* 2007; Jiménez *et al.* 2008), equation (22) can be re-written for the case of the adsorption of fluid mixtures of chain molecules as:

$$\frac{A_{ads}^{mix}}{NkT} = \frac{A_{2D}^{mix}}{NkT} - \sum_{i=1}^{M} x_i \left[\ln\left(\frac{\lambda_w \sigma_i^w}{\Lambda_i}\right) + \beta m_i \varepsilon_i^w \right] \tag{50}$$

where it should be borne in mind that x_i is the mole fraction of chain molecules of species i and ε_i^w is the corresponding chain-segment/wall energy parameter.

RESULTS

The theory presented in this paper was applied to three different systems adsorbed onto an activated carbon which had been characterized previously experimentally (Sudibandriyo *et al.* 2003). The systems studied were methane/nitrogen, methane/carbon dioxide and carbon dioxide/nitrogen. The molecular parameters for the pure components are reported in Table 1. The theory requires eight molecular parameters for each pure compound; four of these were taken from previous studies using the SAFT-VR approach for the bulk phases of methane (Gil-Villegas *et al.* 1997; McCabe *et al.* 1998), nitrogen (Zhao *et al.* 2006) and carbon dioxide (Colina *et al.* 2004). These parameters were the number of segments, m, the diameters of the monomers, σ, the energy well depth, ε, and the range, λ, of the SW particle–particle interactions. The first two parameters are the same for the adsorbed and bulk fluids. The criteria for the selection of the other four parameters, which were related to the SW particle–particle interaction for the adsorbed phase and the SW particle–wall interaction, have been explained elsewhere (Martínez *et al.* 2007; Galindo *et al.* 1998). We summarize here the procedure followed in order to clarify the presentation of the results.

As demonstrated by Sinanoglu and Pitzer (1960), for a Lennard-Jones fluid using quantum mechanical third-order perturbation theory, the depth of the attractive energy well of the particle–particle potential in an adsorbed monolayer is reduced by 20–40% from its value in the bulk. This effect is due to fluctuations in the surface fields and has the same origin as dispersion forces that yield an additional long-range repulsion. As a consequence of this repulsive barrier, the system can be modelled by an effective potential with a reduced attractive energy well. The same type of behaviour has also been predicted theoretically and observed experimentally at the air/water interface in two-dimensional colloids (Ruíz-García and Ivlev 1998; Mejía-Rosales *et al.* 2001; Ruiz-García *et al.* 2008). In the present work, we have selected a 20% reduction for all the systems, i.e. $\varepsilon_{ads} = 0.8\varepsilon$.

From a knowledge of all the other five parameters (m, σ, ε, λ and ε_{ads}), the experimental ratio between the critical temperatures of the bulk and adsorbed phases, T_c^b and T_c^{ads}, i.e. $R_c = T_c^{ads}/T_c^b$, can be reproduced by selecting a specific value of λ_{ads}. For noble gases and methane adsorbed onto graphite surfaces, $R_c \approx 0.4$, and this value has been taken for all the systems studied here. The

TABLE 1. Molecular Parameter Values Used to Describe the Adsorption of Methane, Nitrogen and Carbon Dioxide onto Dry Activated Carbon

Substance	m	σ (Å)	λ	ε/k (K)	λ_{ads}	ε_{ads}/k	λ_w	$\varepsilon_w/\varepsilon$
CH_4	1.0	3.670	1.444	168.8	1.2	133.1	0.8165	7.80
N_2	1.33	3.159	1.550	81.4851	1.4737	65.188	0.8165	9.85
CO_2	2.0	2.7864	1.5257	179.27	1.262	143.416	0.8165	4.1

corresponding values of λ_{ads} that reproduce R_c are listed in Table 1. Finally, as explained elsewhere (Martínez *et al.* 2007; Jiménez *et al.* 2008), the wall–particle potential parameters were chosen so that both the theoretical limit that determines monolayer adsorption ($\lambda_w = 0.8165$) and the experimental adsorption isotherms (ε_w) could be reproduced.

Figures 1–3 present a comparison between the theoretical and experimental adsorption isotherms (Sudibandriyo *et al.* 2003) for a temperature, T, of 318.2 K and a pressure, P, of 13.8 MPa.

(a)   **(b)**
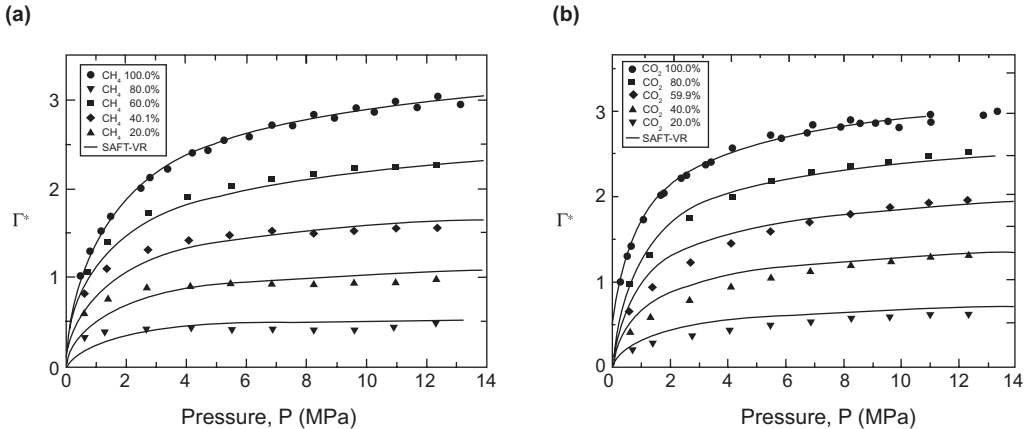
Figure 1. Absolute isotherms for the adsorption of a CH_4/CO_2 mixture onto dry activated carbon at 318.2 K. The solid lines and symbols correspond to the SAFT-VR prediction and the experimental data (Sudibandriyo *et al.* 2003), respectively. In part (a), the adsorption isotherms correspond to methane whereas in part (b) they correspond to carbon dioxide. The amount of substance adsorbed, Γ^*, is shown scaled with respect to the lowest-pressure experimental data for the pure substance.

(a)   **(b)**
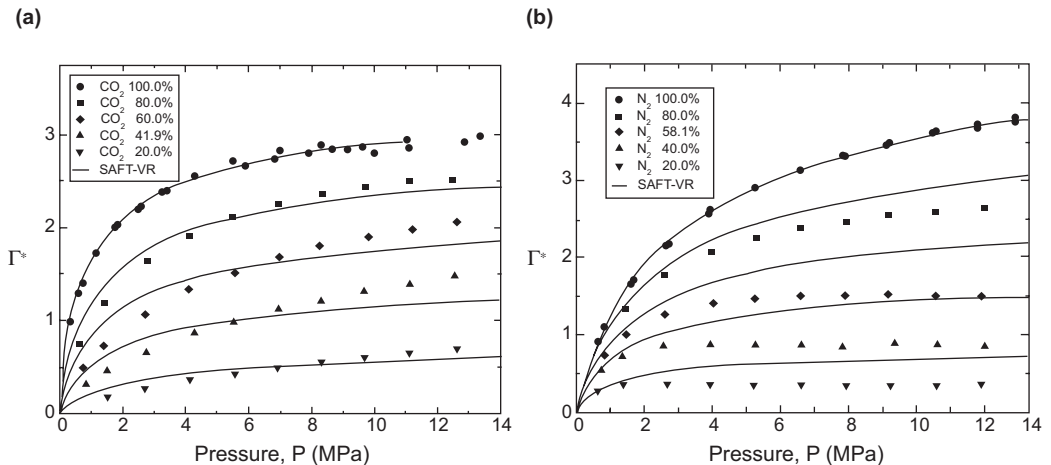
Figure 2. Absolute isotherms for the adsorption of a CO_2/N_2 mixture onto dry activated carbon at 318.2 K. The solid lines and symbols correspond to the SAFT-VR prediction and the experimental data (Sudibandriyo *et al.* 2003), respectively. In part (a), the adsorption isotherms correspond to carbon dioxide whereas in part (b) they correspond to nitrogen. The amount of substance adsorbed, Γ^*, is shown scaled with respect to the lowest-pressure experimental data for the pure substance.
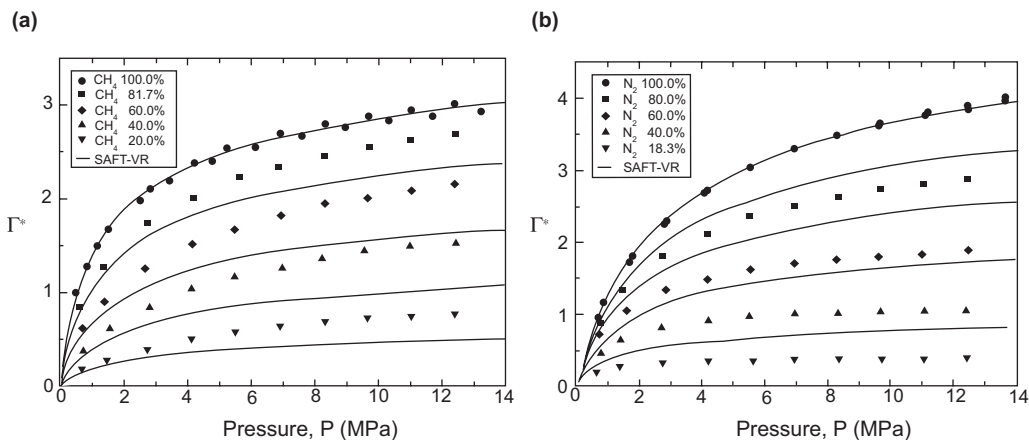
Figure 3. Absolute isotherms for the adsorption of a CH_4/N_2 mixture onto dry activated carbon at 318.2 K. The solid lines and symbols correspond to the SAFT-VR prediction and the experimental data (Sudibandriyo *et al.* 2003), respectively. In part (a), the adsorption isotherms correspond to methane whereas in part (b) they correspond to nitrogen. The amount of substance adsorbed, Γ^*, is shown scaled with respect to the lowest-pressure experimental data for the pure substance.

The results are reported as absolute adsorption isotherms, viz. the amount of adsorbed substance scaled by the low-pressure value for the pure component as a function of the bulk pressure. The theoretical modelling of the CH_4/CO_2 mixture (Figure 1) agrees very well with the experimental data at all the different compositions studied. However, for the mixtures with nitrogen, CO_2/N_2 (Figure 2) and CH_4/N_2 (Figure 3), discrepancies arise between theory and experiment which appear to be caused by competition between nitrogen and carbon dioxide or methane molecules. We do not have a clear explanation for this behaviour, although it is clear that the approach followed was the simplest one since no account was taken of a correction factor for the cross-energy interaction in the Lorentz relation, neither was the quadrupolar nature of the molecules considered. A study of these effects is required. However, preliminary results obtained by our group indicate that the new molecular parameters introduced in this way do not have a simple relationship with the pure compound values and that more fundamental work is required, as has been done, for example, for 3D mixtures by Haslam *et al.* (2008).

Our interest has been to develop a systematic way of describing adsorption isotherms using pure-compound molecular values and the minimum of fitting parameters. However, the general description for all the cases is very good, since the theory is able to follow the right tendency of the adsorption isotherms as the pressure increases to very high values.

CONCLUSIONS

An extension of the 2D SAFT-VR approach (Martínez *et al.* 2007) to modelling mixtures of chain molecules is described, with specific application to the adsorption of three different mixture systems, viz. CH_4/N_2, CH_4/CO_2 and CO_2/N_2. Adsorption isotherms for these systems were well reproduced when compared to experimental data (Sudibandriyo *et al.* 2003), using pure-compound parameters studied previously elsewhere (Martínez *et al.* 2007; Jiménez *et al.* 2008) and high bulk-pressure values. Although the thermodynamic approach followed here required

eight parameters, seven of these could be specified independently from the bulk-hase modellng (m, σ, λ and ε), the theoretical prediction of the effect of the substrate on the particle–particle interaction (ε_{ads}), the behaviour of the ratio of the critical temperatures (λ_{ads}) and the geometrical restriction for the adsorption of a monolayer (λ_w). The only fitting parameter was the particle–wall interaction energy ($\varepsilon_w/\varepsilon$). We have found that the theory is capable of predicting the overall phase diagram for real mixtures. The role played by dipolar, quadrupolar and hydrogen-bonding interactions is under study and will be presented in future communications.

REFERENCES

Barker, J.A. and Henderson, D. (1967) *J. Chem. Phys.* **47,** 2856.

Castro, M., Martínez, R., Martínez, A. and Rosu, H. (2010) *Physica A* **389,** 3140.

Castro, M., Mendoza de la Cruz, J.L., Buenrostro-González, E., Lopéz-Ramírez, S. and Gil-Villegas, A. (2009) *Fluid Phase Equilib.* **87,** 113.

Colina, C.M., Galindo, A., Blas, F.J. and Gubbins, K.E. (2004) *Fluid Phase Equilib.* **77,** 222.

Galindo, A., Davies, L., Gil-Villegas, A. and Jackson, G. (1998) *Mol. Phys.* **93,** 241.

Gil-Villegas, A., Galindo, A., Whitehead, P.J., Mills, S.J., Jackson, G. and Burgess, A.N. (1997) *J. Chem. Phys.* **106,** 4168.

Haslam, A., Galindo, A. and Jackson, G. (2008) *Fluid Phase Equilib.* **266,** 105.

Henderson, D. (1975) *Mol. Phys.* **30,** 71.

Jiménez, A., Santillán, S., Avendaño, C., Castro, M. and Gil-Villegas, A. (2008) *Oil Gas Sci. Technol.* **63,** 329.

Lee, L.L. (1988) *Molecular Thermodynamics of Nonideal Fluids*, Butterworth Publishers, Boston, MA, U.S.A.

Martínez, A., Castro, M., McCabe, C. and Gil-Villegas, A. (2007) *J. Chem. Phys.* **126,** 074 707.

McCabe, C., Galindo, A., Gil-Villegas, A. and Jackson, G. (1998) *Int. J. Thermophys.* **19,** 1511.

McCabe, C., Gil-Villegas, A. and Jackson, G. (1999) *Chem. Phys. Lett.* **303,** 27.

Mejía-Rosales, S.J., Gil-Villegas, A., Ivlev, B.I. and Ruiz-García, J. (2001) *J. Phys. Condens. Mater.* **14,** 4795.

Myers, A.L. and Prausnitz, J.M. (1965) *AIChE J.* **11,** 121.

Patel, R.L., Nandi, S.P. and Walker, P.L. (1972) *Fuel* **51,** 47.

Ruiz-García, J. and Ivlev, B.I. (1998) *Mol. Phys.* **95,** 371.

Ruiz-García, J., Ivlev, B.I.J. and Gil-Villegas, A. (2008) in *Third Mexican Meeting on Mathematical and Experimental Physics*, México City (México), 10–14 September 2007, *AIP Conference Proceedings 979*, pp. 138–155.

Ruthven, D.M. (1984) *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York.

Ruthven, D.M. and Wong, F. (1985) *Ind. Eng. Chem., Fundam.* **24,** 27.

Santos, A., Yuste, S.B. and Haro, M.L. (1999) *Mol. Phys.* **96,** 1.

Sinanoglu, O. and Pitzer, K.S. (1960) *J. Chem. Phys.* **32,** 1279.

Sudibandriyo, M., Pan, Z., Fitzgerald, J.E., Robinson Jr., R.L. and Gasem, K.A.M. (2003) *Langmuir* **19,** 5323.

Yang, R.T. (1987) *Gas Separation by Adsorption Processes*, Butterworth Publishers, Boston, MA, U.S.A.

Zhao, H., Morgado, P., Gil-Villegas, A. and McCabe, C. (2006) *J. Phys. Chem. B* **110,** 24 083.