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2D-SAFT-VR approach to study of the adsorption isotherms for binary mixtures

Martin Castro · Alejandro Martínez

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Abstract In this article we present results of approximating molecular modeling of the gas mixtures methane-nitrogen, methane-carbon dioxide, and nitrogen-carbon dioxide adsorbed on activated carbon at a temperature of 318.2 K, based on the Statistical Associating Fluid Theory for potentials of Variable Range. Unlike the previous work (Castro et al.) showing the results in rescaled units, in this work the results obtained are shown in real units as obtained in the experiments.

Keywords Adsorption · Isotherms · 2D-SAFT-VR · Mixtures · Carbon actived

1 Introduction

In recent decades several theories (e.g., Langmuir (Grande et al. 2003) and Zhou-Gasem-Robinson (Zhou et al. 1994)) have been developed to describe adsorption of pure and mixed systems at equilibrium. One of the main interests in the study of adsorption is in the environmental remediation. Recently, adsorption isotherms of mixture fluids have been studied using the Statistical Associating Fluid Theory for Potentials of Variable Range adapted for mixtures two-dimensional (Castro et al. 2011) within a one-fluid van der Waals approximation (Lee 1988 and Galindo et al. 1998), that has been used previously for 3D mixtures modeled by SAFT-VR (Gil-Villegas et al. 1997 and McCabe et al. 1998). This approach has been applied to model adsorption isotherms of mixture fluids, such CH_4–N_2, CH_4–CO_2, and N_2–CO_2 mixtures adsorbed on dry activated carbon at 318.2 K and pressures up to 13.6 MPa (Castro et al. 2011). Predictions are compared with experimental data reported for these systems (Sudibandriyo et al. 2003). In the three cases very good agreement was found.

In this work we applied the 2D-SAFT-VR approach to model the adsorption isotherms for binary mixtures obtained in real units such as the experimental data reported (Sudibandriyo et al. 2003), achieving a better agreement with experimental data than obtained in previous work (Castro et al. 2011).

2 Theory

In this section we present briefly the theory used to describe the adsorption of a mixture of fluids on a uniform wall, assuming a 2D approximation of the approach within SAFT-VR, for more details see the reference (Castro et al. 2011).

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

$$u_{pw}(z) = \begin{cases} \infty, & z < 0 \\ -\epsilon_w, & 0 < z < \lambda_w \sigma_{ii} \\ 0, & \lambda_w \sigma_{ii} < z \end{cases} \tag{1}$$

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

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M. Castro (✉)
IPICyT, Instituto Potosino de Investigación Científica y Tecnologíca, Camino a la Presa san José, Lomas Tercera Sección, San Luis Potosí, 78216, S.L.P., Mexico
e-mail: mgcastro13@gmail.com

A. Martínez
Department of Physical Engineering, Sciences and Engineering Division, University of Guanajauto Campus León, Lomas del Bosque 103, Fracc. Lomas del Campestre, León 37150, Guanajuato, Mexico

SW parameters for the wall-particle interaction. The cross parameters are given by the following combining rules

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

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

and

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

The first two rules correspond to the standard Lorentz-Berthelot expressions (Lee 1988) whereas Eq. (4) is derived from the van der Waals energy constant α_{ij} according to the Berthelot rule.

The total system, wall + particles, can be divided into two subsystems 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 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), and therefore the binary interaction between particles is different depending on the phase to which they belong to. To describe the amount of particles adsorbed onto the wall we use the following expression for the coverage of a specie i, Γ_i, defined as

$$\Gamma_i = \int_0^{\lambda_i^w\sigma_{ii}} \rho_i(z_i)dz_i - \rho_i^b\lambda_i^w\sigma_{ii} \tag{5}$$

where ρ_i is the density of particles of specie i, and ρ_i^b is the bulk density, i.e., $\rho_i(z_i \to \infty)$. Where the first term of this equation can be identified as absolute adsorption of particles for specie i,

$$\rho_i^{ads} = \int_0^{\lambda_i^w\sigma_{ii}} \rho_i(z_i)dz_i \tag{6}$$

Equation (6) is a 2D density and can be used to obtain a corresponding 2D packing fraction,

$$\gamma_i^{ads} = \frac{m_i\pi\rho_i^{ads}\sigma_{ii}^2}{4} \tag{7}$$

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.,

$$\mu_i^{ads} = \mu_i^b \tag{8}$$

where

$$\mu_i^{ads} = \frac{\partial A_{ads}}{\partial N_i^{ads}} \tag{9}$$

$$\mu_i^b = \frac{\partial A_b}{\partial N_i^b} \tag{10}$$

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 specie i, N_i^{ads} and N_i^b.

For the case of the adsorbed phase, A_{ads} can be derived from a 2D approximation, from partition function of the mixture of fluids adsorbed onto the surface,

$$Z_{ads} = Z_{2D}^{ideal}Q^{2D}\prod_{i=1}^{M}\left(\frac{\lambda_i^w\sigma_i}{\Lambda_i}\right)^{N_i} e^{\beta N_i\epsilon_i^w} \tag{11}$$

where Z_{2D}^{ideal} is the 2D partition function for a mixture of ideal gases and Q^{2D} is the 2D partition function configurational (Castro et al. 2011).

Since $A_{ads} = -kT\ln Z_{ads}$, from Eq. (11) we obtain

$$\frac{A_{ads}}{NkT} = \frac{A_{2D}}{NkT} - \sum_{i=1}^{M} x_i\left[\ln\left(\frac{\lambda_i^w\sigma_i^w}{\Lambda_i}\right) + \beta\epsilon_i^w\right] \tag{12}$$

where $x_i = N_i/N$ is the mole fraction of specie 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), similarly for two-dimensional

$$\frac{A_{2D}}{NkT} = \sum_{i=1}^{M} x_i\ln\left(\rho_i^{ads}\Lambda_i^2\right) - 1 + a^{mono} \tag{13}$$

where the first term is the free energy of ideal gases and a^{mono} is the 2D free energy molar per monomer, is given by

$$a^{mono} = \frac{A_{HD}}{NkT} + \beta a_1^{(2D)} + \beta^2 a_2^{(2D)} \tag{14}$$

Here A_{HD} is the Helmholtz excess free energy for a hard disks mixture fluid, and $a_1^{(2D)}$ and $a_2^{(2D)}$ are the first and second order perturbation terms, respectively. These last two terms can be seen in more detail in reference (Castro et al. 2011).

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

$$\frac{A_b}{NkT} = \sum_{i=1}^{M}\ln\left(\rho_i^b\Lambda_i^3\right) - 1 + \frac{A_{HS}}{NkT} + \beta a_1^{(3D)} + \beta^2 a_2^{(3D)} \tag{15}$$

3 Adsorption of a mixture of chain molecules

In the previous section we presented a theory for adsorption isotherms of a mixtures of monomeric fluids; now we extend the study for the case of adsorption of chain molecules fluids, following the SAFT-VR approach in 3D (Galindo et al. 1998), and assuming that the monomer-monomer and monomer-wall interactions are described via square-well potentials.

3.1 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, the ideal, monomeric, and chain

$$\frac{A_{2D}^{mix}}{NkT} = \sum_{i=1}^{M} x_i \ln\left(\rho_i^{ads} \Lambda_i^2\right) - 1 + \left[\sum_{i=1}^{M} x_i m_i\right] a^{mono} + \frac{A^{chain}}{NkT} \tag{16}$$

where N is the total number of chain molecules in the mixture, m_i is the number of monomer segments of chain i, the first and second term is defined in Eq. (14), and A^{chain} is the contribution due to the formation of chains, is given by

$$\frac{A^{chain}}{NkT} = -\sum_{i=1}^{M} x_i (m_i - 1) \ln y_{ii}^{m}(\sigma_i) \tag{17}$$

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

$$y_{ii}^{m}(\sigma_{ii}) = g_{ii}^{m}(\sigma_{ii}) e^{-\beta\epsilon_{ii}} \tag{18}$$

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

$$g_{ii}^{m}(\sigma_{ii}) = g_0^{HD}\left(\gamma_x^{ef}\right) + \beta\epsilon_{ii} g_1^{ii}(\sigma_{ii}) \tag{19}$$

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

$$g_1^{ii}(\sigma_{ij}) = \frac{2}{\pi\sigma_{ii}^2\epsilon_{ii}} \left[\frac{\partial a_1^{ii}}{\partial \rho_s^{ads}} - \frac{\lambda_{ii}}{4\rho_s^{ads}} \frac{\partial a_1^{ii}}{\partial \lambda_{ii}}\right] \tag{20}$$

Last result is obtained from a self-consistent method for the obtention of the pressure p, using Clausius virial theorem and the density derivative of the Helmholtz free energy.

3.2 Adsorption equation

Once we have detailed how the free energy A_{2D}^{mix} is obtained following previous developments for 3D (Galindo et al. 1998) and 2D chain molecules fluids (Castro et al. 2011), Eq. (12) can be rewritten for the case of adsorption of mixtures of chain molecules fluids as

$$\frac{A_{ads}^{mix}}{NkT} = \frac{A_{2D}^{mix}}{NkT} - \sum_{i=1}^{M} x_i \left[\ln\left(\frac{\lambda_i^w \sigma_i^w}{\Lambda_i}\right) + \beta m_i \epsilon_i^w\right] \tag{21}$$

where we have to bear 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.

4 Results

The theory presented in this article was applied to three different systems adsorbed on activated carbon at 318.2 K, which have been previously experimentally characterized by Sudibandriyo (Sudibandriyo et al. 2003): methane/nitrogen, methane/carbon dioxide and carbon dioxide/nitrogen. The theory requires eight molecular parameters for each pure compound, and four of them were taken from previous studies using the SAFT-VR approach for bulk phases: methane (Martínez et al. 2007 and McCabe et al. 1999), nitrogen (Zhao et al. 2006), carbon dioxide (Colina et al. 2004). These parameters are: the number of segments, m, the diameter of monomers, σ, the energy depth, ϵ, and the range, λ, of the SW particle-particle interaction. The first two parameters are the same for the adsorbed and bulk fluids. The criteria for the selection of the other four parameters, related to the SW particle-particle interaction for the adsorbed phase and the SW particle-wall interaction, has been explained elsewhere (Galindo et al. 1998 and Martínez et al. 2007) and we summarize the procedure followed to clarify the presentation of results.

As demonstrated by Sinanoglu and Pitzer (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 their value on the bulk. This effect is due to fluctuations of the surface fields and is of the same origin as dispersion forces, that yield an additional long-range repulsion. As a consequence of this repulsive barrier, the system can be modeled by an effective potential with a reduced attractive energy well.

In this work we selected a 20 % reduction for all the systems, i.e., $\epsilon_{ads} = 0.8\epsilon$. Knowing all the previous 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}, respectively, 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 on graphite surfaces, $R_c \approx 0.4$, and this value is taken for all the systems studied here. The corresponding values of λ_{ads} that reproduces R_c are reported in Table 1. Finally, as explained in references (Martínez

Table 1 Values of molecular parameters used to describe the adsorption of methane, nitrogen and dioxide carbon on dry activated carbon

Substance	m	σ (Å)	λ	ϵ/k (K)	λ_{ads}	ϵ_{ads}/k	λ_w	ϵ_w/ϵ
CH_4	1.0	3.670	1.444	168.8	1.2	133.1	0.8165	7.6
N_2	1.33	3.159	1.550	81.4851	1.4737	65.188	0.8165	9.1
CO_2	2.0	2.7864	1.5257	179.27	1.262	143.416	0.8165	4.0

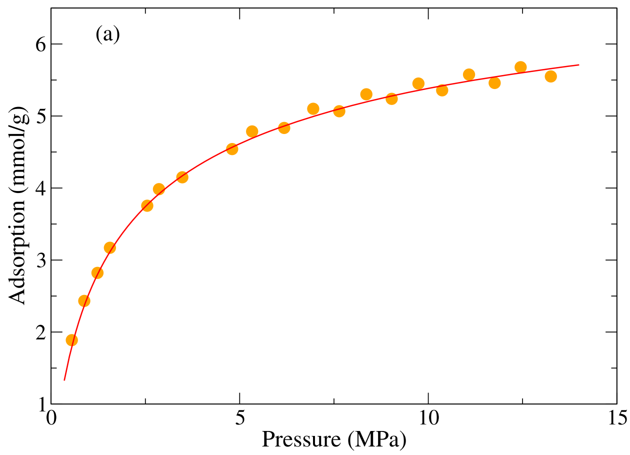

Fig. 1 Absolute adsorption of CH_4 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively

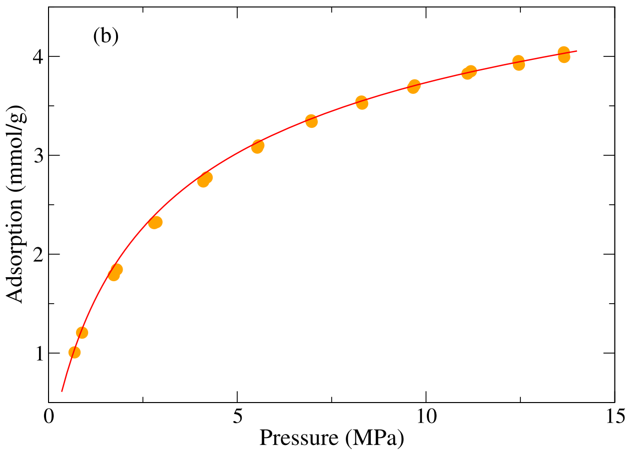

Fig. 2 Absolute adsorption of N_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively

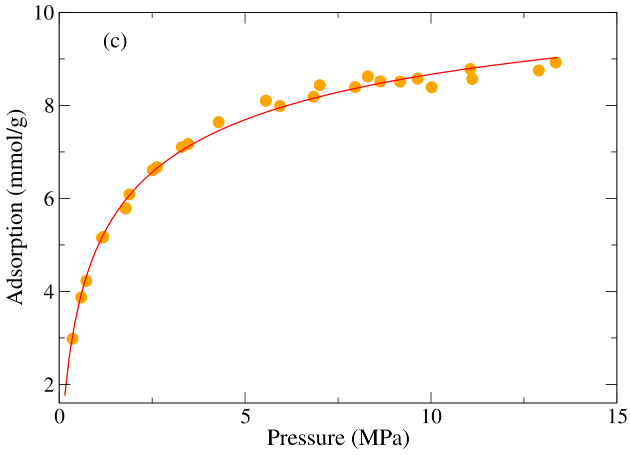

Fig. 3 Absolute adsorption of CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively

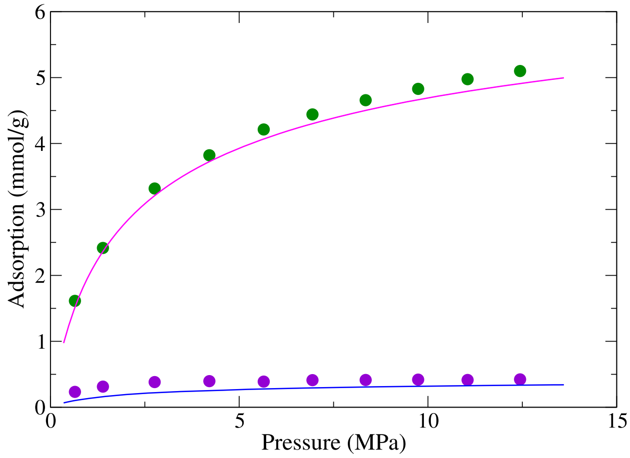

Fig. 4 Absolute adsorption of mixture CH_4–N_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 80 %–nitrogen 20 %

et al. 2007 and Jiménez et al. 2008), the particle-wall potential parameters were chosen in order to reproduce the theoretical limit that determines the adsorption of a monolayer ($\lambda_w = 0.8165$) and the reproduction of the experimental adsorption isotherms (ϵ_w).

Our results are obtained from Eq. (6), getting only absolute adsorption. The density ρ_i^{ads} present in this equation is obtained by a chemical equilibrium between bulk and adsorbed phase fluid. To perform theoretical and experimental comparison and to obtain results in real units we use the follow equation

$$\Gamma_i^{ads} = \frac{4A_i^* m_i \gamma_i^{ads}}{\pi(\sum_{i=1}^{m} m_i x_i \sigma_i^2) N_{av}} \tag{22}$$

where Γ_i^{ads} is the absolute adsorption for component, A_i^* is the surface area (commonly called BET), this value was taken from Sudibandriyo (Sudibandriyo et al. 2003) which

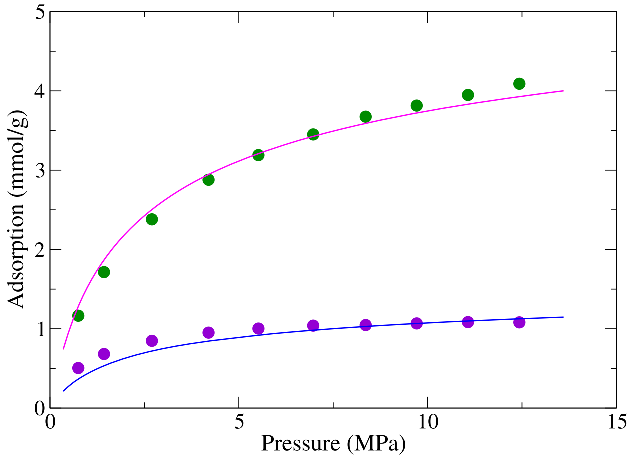

Fig. 5 Absolute adsorption of mixture CH_4–N_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture methane 60 %–nitrogen 40 %

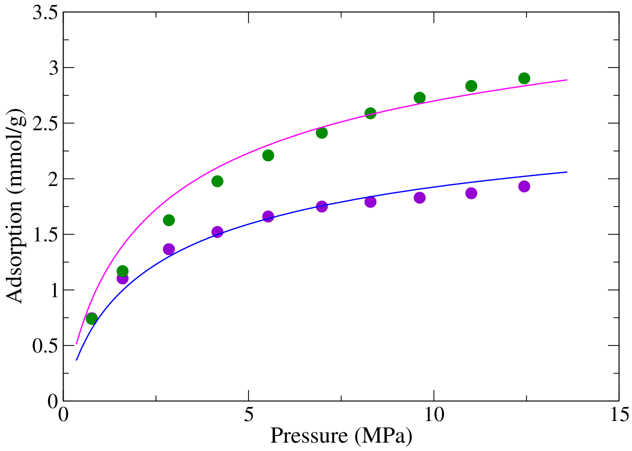

Fig. 6 Absolute adsorption of mixture CH_4–N_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond the mixture is methane 40 %–nitrogen 60 %

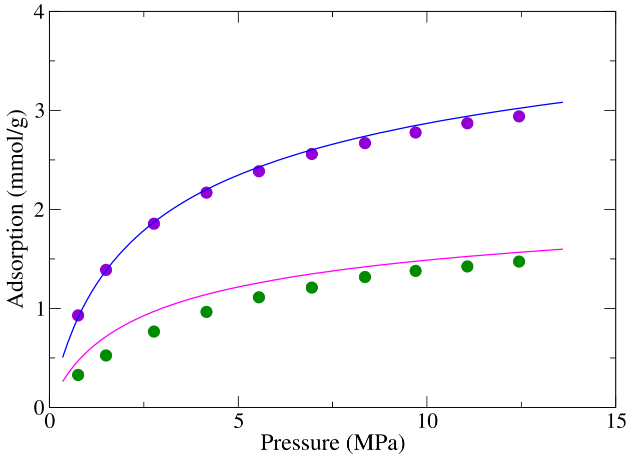

Fig. 7 Absolute adsorption of mixture CH_4–N_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 20 %–nitrogen 80 %

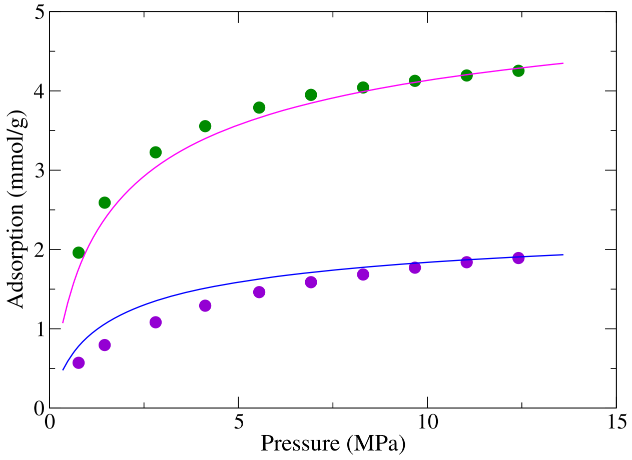

Fig. 8 Absolute adsorption of mixture CH_4–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 80 %–carbon dioxide 20 %

has value of 850 m^2/g, for this work we found that methane BET value is 850, 580 for nitrogen, and carbon dioxide is 830, N_{av} is the Avogadro number. Now for the mixture systems, we are proposing the following equation

$$\Gamma_i^{mix} = \Gamma_i^{ads} \times (1 - x_j \Upsilon_i) \tag{23}$$

where Γ_i^{ads} is given by Eq. (22), x_j corresponds to the concentration of the different components of the binary mixture and Υ_i is the parameter selection, and indicates the preferences of adsorption of the components, i.e. the presence of one component affects the other component. Furthermore, this parameter has implied contributions not taken into account, such as quadrupole interactions, chemical reactions and so on.

In Figs. 1, 2, and 3, we present the comparison between theory and experimental data of the adsorption isotherms for temperature $T = 318.2$ K and pressure $P = 13.8$ MPa of pure substances, methane, nitrogen and carbon dioxide, in real units. The results of these three substances are the first step before obtaining mixture results. Figure 1 shows the good agreement between theory and experiment. Figures 4–15 present the comparison between theoretical and experimental adsorption isotherms (Sudibandriyo et al. 2003), for the same temperature and pressure for the case of pure substances.

Results are reported as absolute adsorption isotherms, in real units. The theoretical modeling of the mixtures CH_4–N_2 and CH_4–CO_2 (Figs. 4, 5, 6, 7, 8, 9, 10, 11) agrees very well with the experimental data for all the different compo-

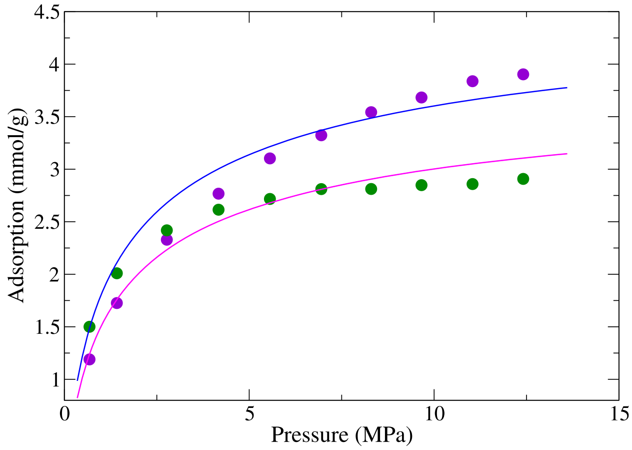

Fig. 9 Absolute adsorption of mixture CH_4–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 60 %–carbon dioxide 40 %

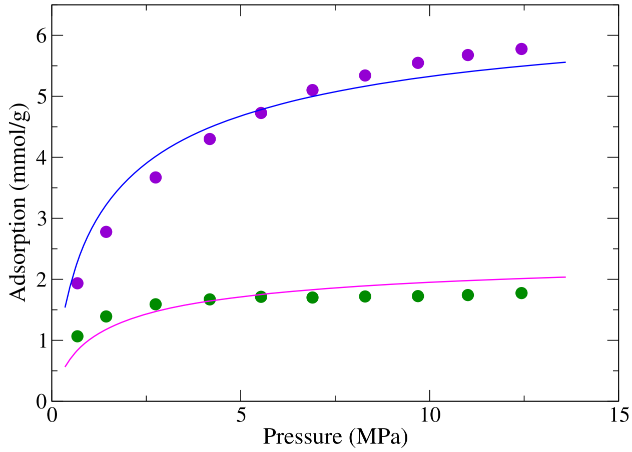

Fig. 10 Absolute adsorption of mixture CH_4–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 40 %–carbon dioxide 60 %

sitions, whereas for the mixture N_2–CO_2 (Figs. 12, 13, 14, and 15) discrepancies arise between theory and experiment, probably due to not considering the quadrupolar nature of nitrogen and carbon dioxide. A study of these effects is required although preliminary results obtained by our group indicate that the new molecular parameters 2D introduced in this way do not have a simple relation ship and that more fundamental work is required, as for example has been done for 3D mixtures (Haslam et al. 2008). Another very important difference from previous work where the results were in rescaled units, is that it is possible to obtain results of adsorption isotherms in real units such as used for presenting experimental results. Very good agreement with experimental data was achieved using the surface area (BET) of each pure system in Eq. (22). Furthermore, as the deviations in

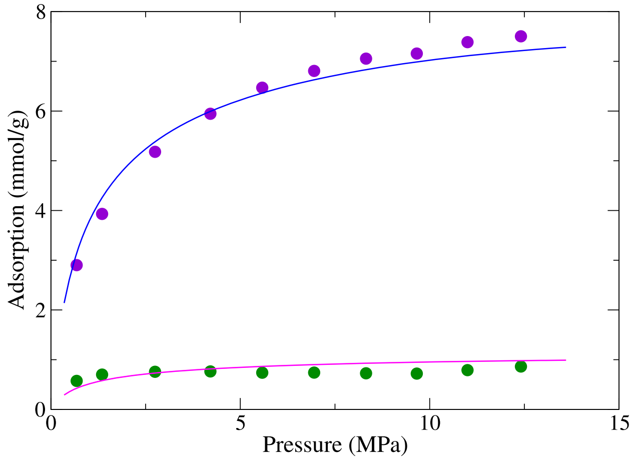

Fig. 11 Absolute adsorption of mixture CH_4–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is methane 20 %–carbon dioxide 80 %

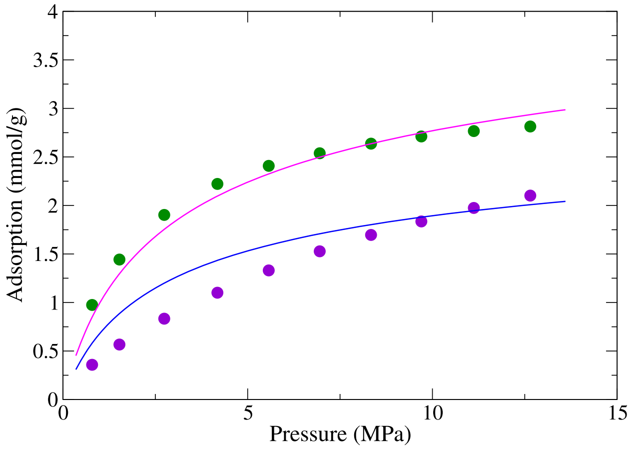

Fig. 12 Absolute adsorption of mixture N_2–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is nitrogen 80 %–carbon dioxide 20 %

the fits are small (see Eq. (23)), the parameters of the pure substances are good for predicting binary mixtures studied in this work.

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.

5 Conclusions

In this article we apply the 2D SAFT-VR approach (Castro et al. 2011) to model mixtures of chain molecules, with

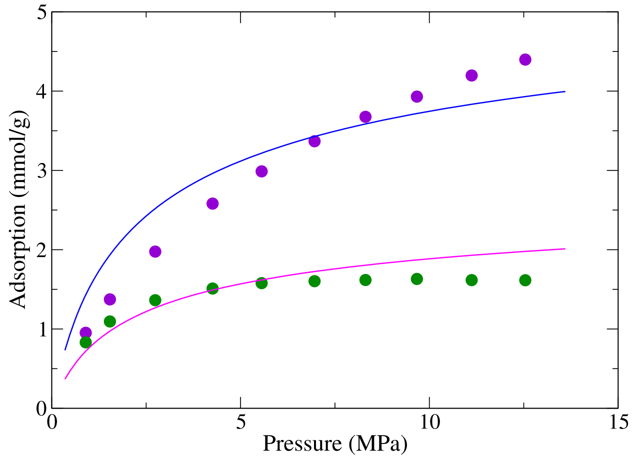

Fig. 13 Absolute adsorption of mixture N_2–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is nitrogen 60 %–carbon dioxide 40 %

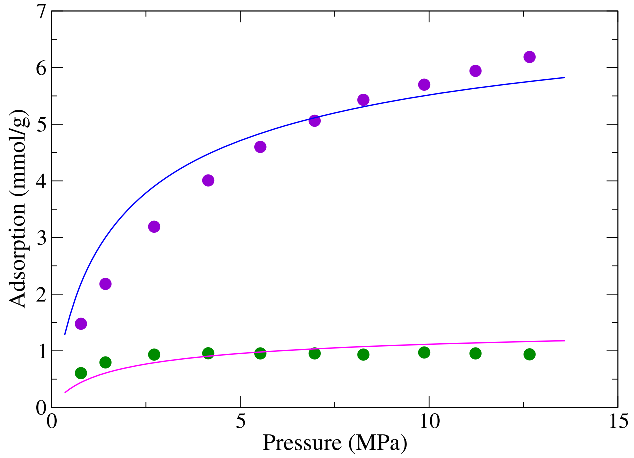

Fig. 14 Absolute adsorption of mixture N_2–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is nitrogen 40 %–carbon dioxide 60 %

a specific application to model adsorption of three different mixture systems: CH_4–N_2, CH_4–CO_2 and CO_2–N_2. Adsorption isotherms for these systems are well reproduced when compared to experimental data (Sudibandriyo et al. 2003), using pure-compound parameters studied previously elsewhere (Martínez et al. 2007 and Jiménez et al. 2008), and for high bulk-pressure values. Although the thermodynamic approach followed here, based on the use of Eq. (8) requires eight parameters, seven of them can be specified independently from the bulk phase modeling (m, σ, λ and ϵ), the theoretical prediction of the effect of the substrate on the particle-particle interaction (ϵ_{ads}), the behavior 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 is the energy of the particle-wall interaction (ϵ_w/ϵ). We have found that the theory is able to predict the overall phase diagram of real mixtures. Another very important difference from the previous work, where the results obtained are shown in rescaled units, is to have achieved the results of adsorption isotherms in real units, such as commonly used in presenting experimental data. Furthermore, the prediction is improved with respect to the results obtained in previous work (Castro et al. 2011).

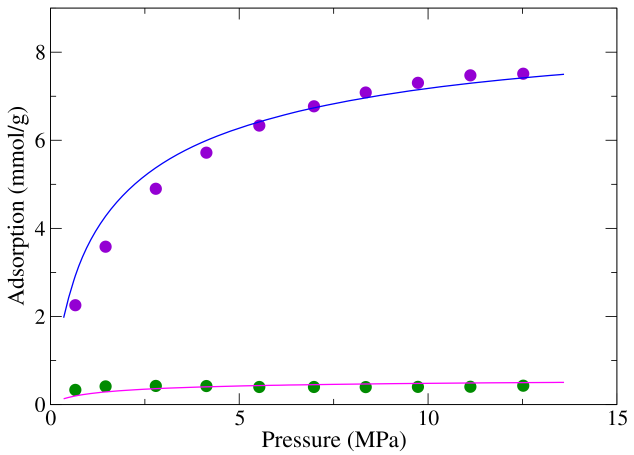

Fig. 15 Absolute adsorption of mixture N_2–CO_2 on dry activated carbon at 318.2 K. *Solid lines* and *symbols* correspond to the SAFT-VR prediction and experimental data (Sudibandriyo et al. 2003), respectively. The correspond mixture is nitrogen 20 %–carbon dioxide 80 %

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