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Adsorption of Molecular Gases on Different Porous Surfaces Using the Statistical Associating Fluid Theory Variable Range Approximation

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Abstract

In the thermodynamic framework of coupled statistical associating fluid theory variable range (SAFT-VR) 2D and 3D models we present the theoretical predictions of the adsorption isotherms in real physical units, as it is commonly done in experiments. The systems studied are methane (CH₄), nitrogen (N₂), ethane (C₂H₆), *n*-butane (C₄H₁₀), propane (C₃H₈), and propylene (C₃H₆) adsorbed on silica gel (two classes: NSG and WSG), zeolite (4A and Na-Y), and BDH activated carbon. Employing only two fitting parameters with clear physical meaning in such an approach, we find a better agreement with the experimental data than other semiempirical models with more fitting parameters.

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1 Introduction

A correct interpretation and quantification of the adsorption isotherms in the supercritical region are in much demand for important industrial activities such as in separation processes [1, 2] and adsorptive storage of gaseous fuels [3, 4]. Among a multitude of models, the SAFT-VR thermodynamic model in its two-dimensional (2D) version has been recently shown to work very well not only in the case of adsorption of simple molecules, such as methane and nitrogen on activated carbon and silica gel, but also for molecules as complex as asphaltene on sandstone and limestone [5, 6]. Motivated by those results, we present here a SAFT-VR study of adsorption isotherms for six gases, namely methane, nitrogen, ethane, *n*-butane, propane, and propylene adsorbed on five different types of adsorbents: NSG and WSG silica gels, 4A and Na-Y zeolites, and BDH-activated carbon [7, 8, 9, 10], obtaining the isotherms in real units at different pressures and temperatures.

2 The SAFT-VR model

The main goal of the SAFT-VR model of adsorption is to obtain explicit equations for the Helmholtz free energy, containing several key contributions, for a simple fluid with N spherical particles of diameter σ in the presence of a uniform wall [5, 6]. The interaction exerted by the wall on the particles is of the square well type

$$u_{pw}(z) = \begin{cases} \infty & z < 0 \\ -\epsilon_w & 0 \leq z < \lambda_w \sigma \\ 0 & \lambda_w \sigma \leq z \end{cases} \quad (1)$$

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where z is the perpendicular distance of the particles from the wall, ϵ_w is the depth of the well which is a parameter that varies with the temperature, and $\lambda_w\sigma$ is the range of the attractive potential.

The system is divided into two subsystems: (i) an adsorbed fluid, whose molecules are near the wall and (ii) a bulk fluid, whose molecules are far from the wall. The binary interaction between particles is different in the adsorbed and the bulk phases, though both are of the square-well type. The amount of adsorbed particles Γ is defined as follows

$$\Gamma = \int_0^{\lambda_w\sigma} \rho_{ads}(z)dz - \rho_b\lambda_w\sigma \quad (2)$$

where ρ_b is the particle density in the bulk region and ρ_{ads} is the density of the adsorbed particles. In thermodynamic equilibrium, the chemical potential of the adsorbed phase μ_{ads} and the bulk phase μ_b should be equal

$$\mu_{ads} = \mu_b \quad (3)$$

The latter condition determines ρ_{ads} as a function of ρ_b .

2.1 Adsorption of Monomeric Fluids

The formula for the partition function of an adsorbed monomeric fluid of N molecules that we use has been obtained in previous works [5, 6, 11]

$$Z_{ads} = Z_{2D}^{ideal} Q_{2D} \left(\frac{\lambda_w\sigma}{\Lambda} \right)^N \exp(N\beta u_{pw}) \quad (4)$$

where $Z_{2D}^{ideal} = \frac{S}{N!\Lambda^{2N}}$, $Q_{2D} = \frac{1}{S^N} \int \exp(-\beta u_{2D}(x^{(N)}, y^{(N)})) d^N x d^N y$ is the two-dimensional configurational partition function, S is the adsorption area, Λ is the de Broglie thermal wavelength, u_{pw} is the particle-wall interaction potential of square-well type. Applying the standard relation $A = -kT \ln Z$, the Helmholtz free energy of the adsorbed fluid is given by

$$\frac{A_{ads}}{NkT} = \frac{A_{2D}}{NkT} - \ln \left(\frac{\lambda_w\sigma}{\Lambda} \right) - \beta u_{pw} \quad (5)$$

where A_{2D} is the Helmholtz free energy of a two-dimensional fluid with interactions given by the binary potential u_{2D} . In perturbation theory up to second order, the dimensionless Helmholtz free energy per particle, A_{2D}/NkT , can be written as follows

$$\frac{A_{2D}}{NkT} = \ln(\rho_{ads}\Lambda^2) - 1 + \frac{A_{HD}}{NkT} + \beta a_{1_{2D}} + \beta^2 a_{2_{2D}}. \quad (6)$$

In the case of the bulk fluid, one can write similarly [12]

$$\frac{A_{3D}}{NkT} = \ln(\rho_b\Lambda^3) - 1 + \frac{A_{HS}}{NkT} + \beta a_{1_{3D}} + \beta^2 a_{2_{3D}}. \quad (7)$$

Here A_{HD} and A_{HS} are the Helmholtz free energy for hard disks and spheres, respectively, $\beta = 1/kT$, $a_{1_{2D}}$, $a_{2_{2D}}$, $a_{1_{3D}}$, $a_{2_{3D}}$ are the first two terms of the 2D and 3D perturbation expansions, respectively. Their expressions have been taken from a previous SAFT-VR study [13].

Getting the chemical potentials μ_{ads} and μ_b from eqs (5), (6), and (7), we can rewrite the condition (3) as follows

$$\mu_{3D} = \mu_{2D} + \mu_w \quad (8)$$

where μ_{3D} and μ_{2D} are the chemical potentials in 3D and 2D, respectively, and μ_w is the wall contribution to the chemical potential [13]

$$\mu_w = -\frac{1}{\beta} \ln(\lambda_w) + u_{pw}(z). \quad (9)$$

2.2 Adsorption of Chain Molecules

The theory presented in subsection 2.1 can be easily extended to the adsorption of fluids composed of chain molecules [5, 6, 13], which is the main application of this paper. In the SAFT-VR approach, the Helmholtz free energy A of chain molecules is composed of three separate terms [12]: the ideal gas free energy given by the first two logarithmic terms in eq (10), the free energy of m monomeric units (the middle term in the same equation), and finally a term corresponding to the formation of chain molecules expressed through the last two logarithmic terms in eq (10)

$$\frac{A}{N_b kT} = \ln(\rho_b \Lambda^3) - 1 + m \frac{A_{3D}}{N_{s,b} kT} - (m-1) [\ln y_{3D}(\sigma)] \quad (10)$$

$$\frac{A_{ads}}{N_{ads} kT} = \ln(\rho_{ads} \Lambda^2) - 1 + m \frac{A_{2D}}{N_{s,ads} kT} - (m-1) [\ln y_{2D}(\sigma)] - \ln \left(\frac{\lambda_w \sigma}{\Lambda} \right) - \beta m \epsilon_w, \quad (11)$$

where $N_{(s,b)}$ and $N_{(s,b)}$ are the number of monomeric units of the bulk and adsorbed phases, respectively, and A_{3D} and A_{2D} are the free energy of monomer fluids in 3D and 2D, respectively, which can be obtained from perturbation theory according to eqs (5) and (7); y_{3D} and y_{2D} are the correlation functions in the 3D and 2D backgrounds obtained from the corresponding radial distribution functions through the well known relationship $y(r) = g(r)e^{\beta u(r)}$. In the SAFT-VR procedure, the functions $g(r)$ are obtained as perturbation expansions:

$$g_{3D}(\sigma) = g_{HS}(\sigma) + \beta \epsilon g_{13D}(\sigma), \quad g_{2D}(\sigma) = g_{HD}(\sigma) + \beta \epsilon g_{22D}(\sigma) \quad (12)$$

where g_{HS} and g_{HD} are the radial distribution functions of the hard spheres and hard disks, respectively, whose analytical expressions can be found in references [12, 13].

3 Results

Our results are a comparison of the SAFT-VR model with the experimental results of the following gases: methane, nitrogen, ethane, n-butane, propane, and propylene on five different types of adsorbents, whose surface areas are given in Table 1 being taken from refs 14 to 22. The results are displayed in Figures 1-10 at different temperatures and pressures. Table 2 contains the parameters used to describe the gases treated as simple fluids both in the bulk phase and the adsorbed phase within the SAFT-VR approximation. The molecular diameters σ are the same both in the bulk and the adsorbed phases at equilibrium, while the parameters of the square-well attractive potential are different from case to case and were taken from refs 12, 13, and 23 to 25. These differences are due to the influence of the wall on the substrate of adsorbed particles. We use the old result of Pitzer for a monolayer of adsorbed Lennard-Jones fluid [?] and reduce the energy well depth of the adsorbed particles by 20% to 40% with respect to the fluid bulk. In our case we take the 20%, which is the value that worked well for us in obtaining adsorption isotherms. Once ϵ_{ads} is selected in this way, the range λ_{ads} can be determined by reproducing the experimental ratios $R_c = T_c^{ads}/T_c^b$ between the critical temperatures of the bulk phase, T_c^b , and the adsorbed phase, T_c^{ads} . The value of this ratio is known for the case of noble gases and methane adsorbed on graphite surfaces, $R_c \approx 0.4$. Next, from the values of R_c and of the parameters ϵ_b , λ_b , and ϵ_{ads} , one determines λ_{ads} for each gas. The latter are reported in Table 2. A value of 0.8165 was used for the range λ_w that corresponds to the upper limit for describing the monolayer adsorption according to mean field criteria. [27] We take this limit because in the quasi-2D approximation for an adsorbed fluid it is the correct one when the monolayer is formed; see ref 13.

The energy parameter of the wall, ϵ_w , was fitted to reproduce the experimental adsorption isotherms, [7-10] and also the BET area was adjusted according to refs 14-22 and respecting the orders of magnitude for each case. Figures 1 to 10 present the reported experimental results for the absolute adsorption (first term in eq 2) in the case of different adsorbate/adsorbent pairs at two different values of the temperature in the range from 303 K up to 473 K and at pressures going up as far as to 0.8 MPa in some cases, while the continuous lines are our SAFT-VR calculations. Looking at the plots, one can notice a very good agreement between this version of the SAFT-VR model and the experimental data, showing that the predictive power of this model is remarkably good. We are of course aware that we need to consider some other properties of an adsorbed fluid or gas (for example: associating, reaction, quadrupole contribution, etc.), but even the simplified approach adopted here provides very satisfactory results. An important feature, different from the previous SAFT-VR works [6,13] devoted to the study of adsorption processes, is that we provide the results

directly in experimental units. For this, we employed the following conversions

$$\rho_{ads} = \frac{\Gamma}{A^*} (N_{AV}) \quad (13)$$

$$\gamma = \frac{\pi \rho_{ads} \sigma^2}{4} \quad (14)$$

where Γ is the absolute adsorption taking the first term of eq 2, $A^* = A/m$ where m is the number of monomeric segments of the chain, A is the surface area of the porous material for which we used the experimental results in Table 1, N_{AV} is the Avogadro number, and γ is the packing fraction of the adsorbate in 2D.

In addition, for comparison purposes, we calculate the average relative error (ARE) according to the following equation

$$\text{ARE}(\%) = \frac{100\%}{N_c} \sum_{j=1}^{N_c} \left[\frac{|n_{exp} - n_{calc}|}{n_{exp}} \right]_j \quad (15)$$

where N_c is the corresponding number of experimental data points. Table 3 shows the values of ARE for the predictions of adsorption isotherms with SAFT-VR and in the case of the Langmuir model; see ref 7 for activated carbon. In conclusion, to obtain predictions of adsorption isotherms in confined spaces, we used a SAFT-VR framework in which one needs to vary only two parameters, namely, ϵ_w and A^* see Tables 4 and 1, respectively. The parameter ϵ_w is not chosen arbitrarily, but comes from experimental results. For example, in the case of krypton adsorbed on graphite, the experimental value, $U_w=11.72$ kJ·mol⁻¹, corresponds to $\epsilon_w=8.168$ [?]. On the contrary, other models use at least three or four parameters to make adjustments and to reproduce the experimental data of the adsorption isotherms, and usually these models have strong semiempirical features.[10,14] Superficial area values were fitted based on the results obtained in refs 14 to 22, taking care of the order of magnitude, for example, in the case of Na-Y zeolite where the range is between (360 and 690) m²·g⁻¹, while our result is 528 m²·g⁻¹, taking for reference the adsorption of nitrogen where $m = 1.33$.

4 Conclusions

We have applied the SAFT-VR-2D model to the adsorption isotherms of several important gases treated as simple fluids composed of chain molecules of nonspherical shape. To achieve this goal, we used a SAFT-VR approach in which the chemical equilibrium condition in both 3D and 2D has been employed. As in previous works [5, 6, 11], To obtain a good fit with experimental data two parameters were adjusted, ϵ_w and A^* , both of them having a physical meaning, and also taking care not to get out of the range allowed by the experimental data. Moreover, the comparison is made in real units, such as given in the experiments. Thus, we have been able to show that this version of SAFT-VR model reproduces appropriately the experimental adsorption isotherms of these gases on the porous materials used in experiments.

Notes

The authors declare no competing financial interest.

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Table 1: Surface Area of Different Adsorbents Used in this Study

adsorbent	surface area = $A^* = A/m$ ($\text{m}^2 \cdot \text{g}^{-1}$)
BDH-activated carbon	410 Na-Y zeolite
4A zeolite	347
NSG silica gel	540
WSG silica gel	240

Table 2: Values of Molecular Parameters Used to Describe the Adsorption of Methane, Nitrogen, Ethane, *n*-Butane, Propane, and Propylene Both in the Bulk and the Adsorbed Phase

adsorbate (m)	$\sigma(\text{\AA})$	λ	$\epsilon/k(\text{K})$	λ_{ads}	$\epsilon_{ads}/k(\text{K})$
CH_4 (1)	3.67	1.444	168.8	1.2	133.1
N_2 (1.33)	3.159	1.55	81.4851	1.4737	65.188
C_2H_6 (1.33)	3.788	1.449	241.8	1.2	193.44
C_4H_{10} (2.0)	3.887	1.501	256.3	1.2	205.04
C_3H_8 (1.67)	3.873	1.452	261.9	1.1616	209.52
C_3H_6 (1.015)	4.412	1.817	142.219	1.4538	113.775

Table 3: Average Relative Error (ARE) Values Found in This Work and in Ref. 7 for BDH-Activated Carbon in the Langmuir Model

substance	ARE % (this work)	ARE % (ref 7)
methane	5.35	3.42
nitrogen	4.65	6.51
ethane	5.73	3.06

Table 4: Values of Molecular Parameters Used to Describe the Adsorption of Methane, Nitrogen, Ethane, *n*-Butane, Propane, and Propylene on Different Surfaces and Temperatures; Only ϵ_w Values Were Found in This Work

Substance	Adsorbent	ϵ_w	T/K	ϵ_w	T/K
CH_4	BDH-activated carbon	9.0	303	8.5	333
N_2		8.8	303	8.3	333
C_2H_6		7.1	310	6.9	333
C_4H_{10}	Na-Y zeolite	7.5	343	7.1	423
C_3H_8	4A zeolite	4.9	423	5.1	473
C_3H_6		22.0	373	22.5	473
C_3H_8	NSG silica gel	3.8	303	3.55	343
C_3H_8	WSG silica gel	3.7	303	3.25	343
C_3H_6	WSG silica gel	14.5	303	13.8	343
C_3H_6	NSG silica gel	13.1	303	12.7	343

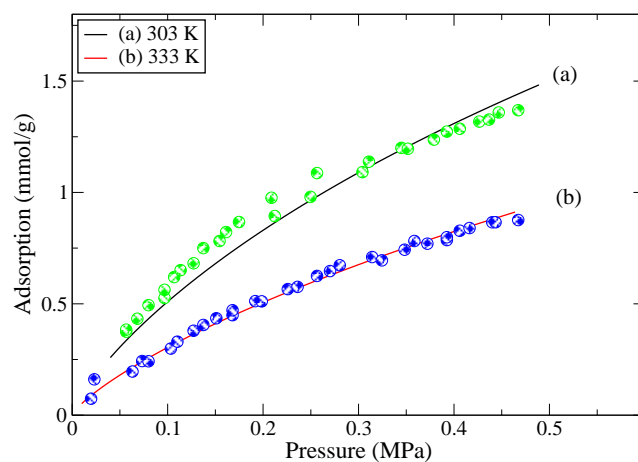


Fig. 1: Adsorption of methane on BDH-activated carbon vs pressure at temperatures (a) 303 K and (b) 333 K. The circles are experimental data from ref [7] and the continuous line corresponds to the SAFT-VR-2D model.

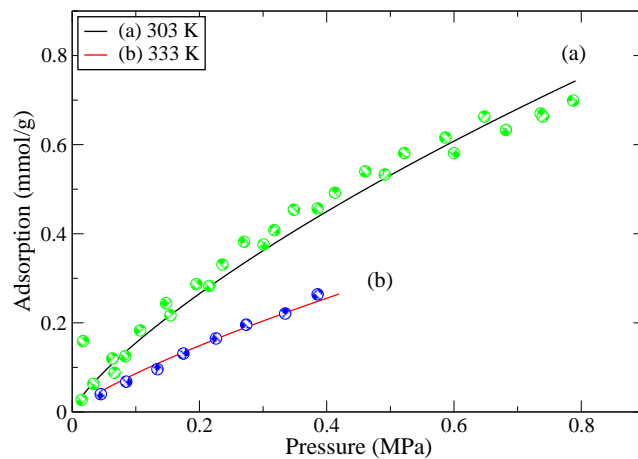


Fig. 2: Same as in Figure 1, but for nitrogen.

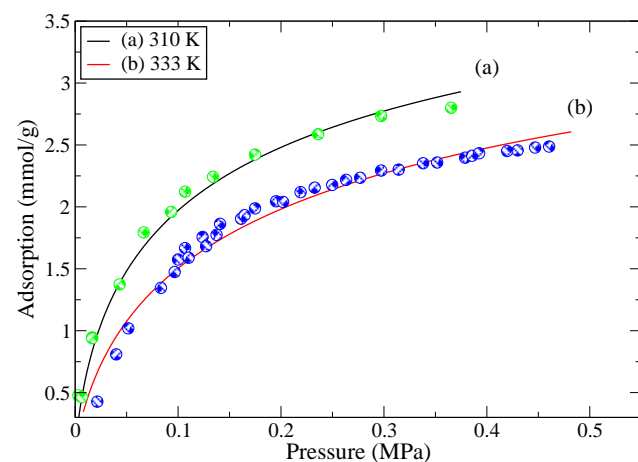


Fig. 3: Same as in Figure 1, but for ethane at the temperatures indicated in the inset.

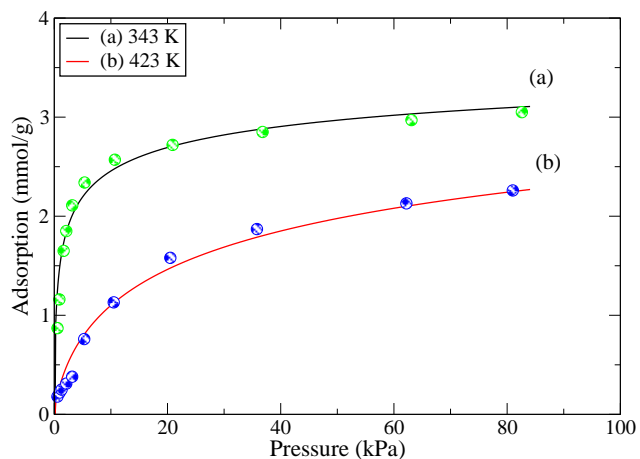


Fig. 4: Adsorption of n-butane on Na-Y zeolite vs pressure at temperatures shown in the inset. The circles are experimental data from ref [8] and the continuous line corresponds to the SAFT-VR-2D model.

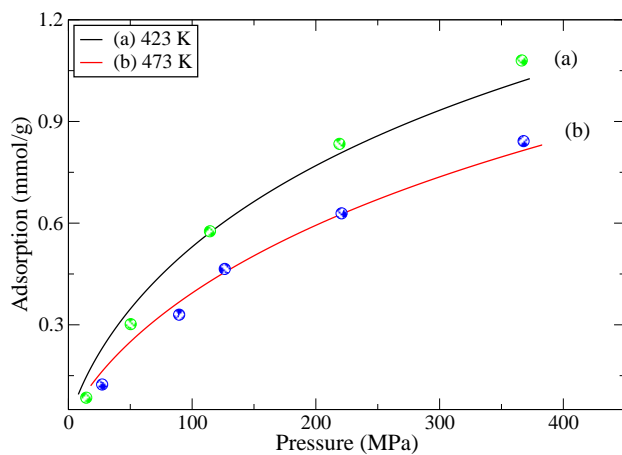


Fig. 5: Adsorption of propane on zeolite 4A vs pressure at temperatures of (a) 423 K and (b) 473 K. The circles are experimental data from ref [9] and the continuous line is generated by the SAFT-VR-2D model.

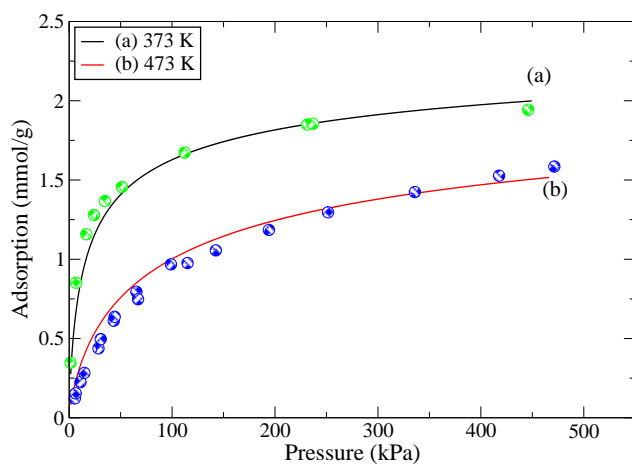


Fig. 6: Same as in Figure 5, but for propylene at the inset temperatures.

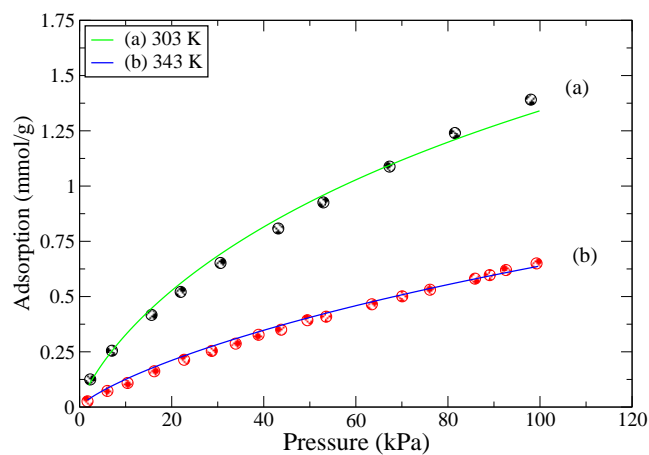


Fig. 7: Adsorption of propane on silica gel (NSG) vs pressure at temperatures (a) 303 K and (b) 343 K. The circles are experimental data from ref [10] and the continuous line is given by the SAFT-VR-2D model.

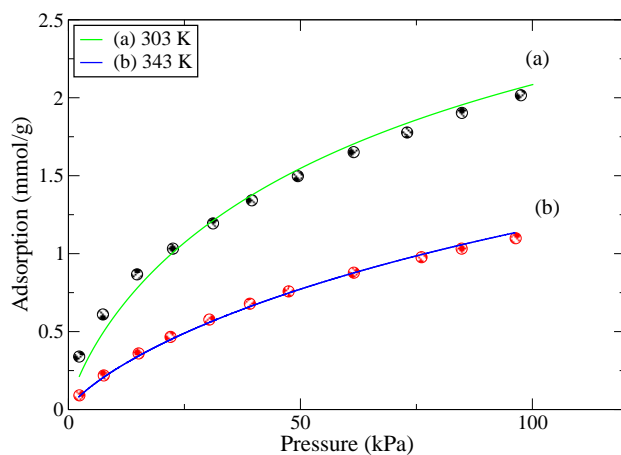


Fig. 8: Same as in Figure 7, but for propylene.

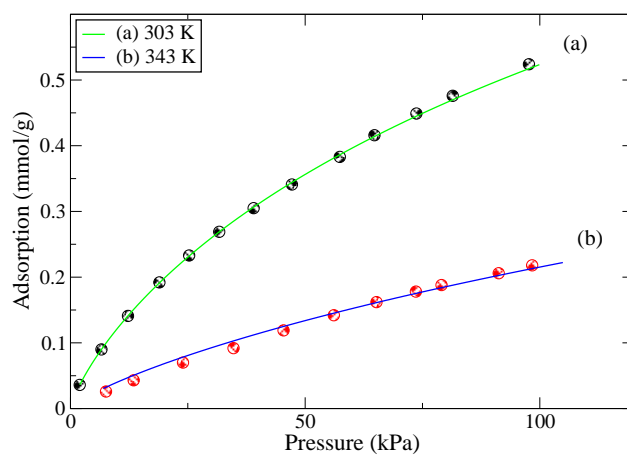


Fig. 9: Adsorption of propane on silica gel (WSG) vs pressure at temperatures of (a) 303 K and (b) 343 K. The circles are experimental data from ref [10] and the continuous line is obtained by applying the SAFT-VR-2D model.

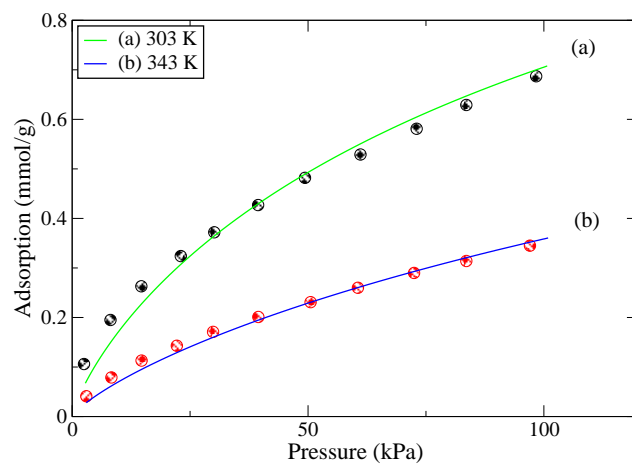


Fig. 10: Same as in Figure 9, but for propylene.