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Semiclassical SAFT-VR-2D modeling of adsorption selectivities for binary mixtures of hydrogen and methane adsorbed onto MOFs

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ABSTRACT

Semiclassical versions of the statistical associating fluid theory for three- and two-dimensional chain molecules with attractive potentials of variable range (SAFT-VRQ) are applied to model selectivities and adsorption isotherms of mixtures containing hydrogen (H_2) and methane (CH_4) onto metal-organic frameworks (MOFs). The theoretical model for mixtures relies on eight molecular parameters and their corresponding combining rules. Six of the eight parameters are obtained from the bulk properties of pure components and only the other two, related to the energy depth of the surface-particle potential, ε_W, and the surface area S, are determined from fitting to experimental data of adsorption isotherms of pure components. The obtained S values are in agreement with reported BET surface areas. Satisfactory results are obtained for the prediction of adsorption isotherms for pure substances and mixtures containing hydrogen and methane compared with experimental data. This molecular thermodynamic model is also able to describe adsorption selectivities in mixtures and the relevance of the quantum description as the molar fraction of hydrogen is increased. Finally, we include detailed information about all the mathematical expressions used to describe the adsorption isotherms of mixtures.

1. Introduction

Currently, hydrogen is one of the main sources of energy and a powerful candidate to replace fossil fuels for green and clean hydrogen-technologies. Hydrogen is recognized as a very promising energy carrier and one of the potential replacements for fossil fuels that could help to control global warming [1]. Liquid and gas hydrogen are already being used as a fuel in vehicles equipped with a combustion engine but safety storage of hydrogen and the manufacturing cost of fuel cell vehicles are the major issues addressed by automakers. The storage techniques available commercially cannot afford a potentially competitive hydrogen vehicle compared with vehicles fueled by petroleum products [2]. Additionally, conventional storage of large amounts of hydrogen is difficult and expensive because it requires to employ either extremely high pressures as a gas or very low temperatures as a liquid [3].

Thus, more resistant materials with a high specific surface area and non-reactive behavior are needed and depending on the material where adsorption occurs the size and weight of these components will vary substantially [4]. Current promising adsorbent materials such as carbon [2], metal organic frameworks (MOF) [4,5], graphene nanosheets [6], among others have been studied in detail. All of them have different features such as surface area, porosity, size and shape that are tunable [7]; MOFs have large storage capacity of adsorption and a very large contact area [8–10].

Hydrogen production is obtained from methane steam reforming, $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$, and methane dry reforming, $CH_4 + CO_2 \rightarrow 2CO + 2H_2$, where the hydrogen has to be separated from methane, carbon dioxide, and smaller amounts of other gases before it can be used effectively in a fuel cell. Over the years there has been a lot of interest in implementing separation systems, such as separation membranes made of palladium or polymers [11].

Mathematical models based on molecular equations of state can be applied to describe confined fluids like hydrogen and methane, for a broad range of porous materials, a subject that is of increasing

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interest due to the quick pace at which new solid-porous surfaces are being designed. Since the introduction of the Langmuir [12] and Brunauer-Emmet-Teller (BET) [13] theories to describe the adsorption of dilute gases into a lattice of sites on a substrate surface, more elaborated and detailed models have been proposed to describe several adsorption features, including the effect of adsorbed multilayers, such as the extended version of the BET and Guggenheim-Anderson-de Boer (GAB) model to include additional adsorbed monolayers in the prediction of adsorption isotherms [14] as well multiple solutes [15].

Predictions of adsorption isotherms using equations of state is mainly restricted to semi-empirical models that can be used for mixtures whose parameters are adjusted to each particular case. On the other hand, Molecular Thermodynamics models based on a two-dimensional van der Waals EoS (vdW-2D) have a long history in Statistical Mechanics and Adsorption Science and have been used successfully to model adsorption isotherms of real substances [16–23]. The statistical associating fluid theory of variable range (SAFT-VR) [24] and its two-dimensional version (SAFT-VR-2D) [25,26] have extended this vdW-2D approach to chain and branched molecular models of adsorbed fluids, such as methane, nitrogen, carbon dioxide, water, methanol, asphaltenes and hydrogen, among other substances [27–30]. Extensions for the SAFT-VR-2D for adsorption onto heterogenous substrates have been considered by Kern and Johannsen [31]. More recently the use of the SAFT-VR-Mie approach in adsorption process has been proposed by Economou and coworkers [32].

In this work we present a SAFT-VR-2D study on the adsorption of mixtures of hydrogen and methane onto MOFs materials, using the classical and semiclassical versions of this theory [29] but now extended to mixtures, following our previous work on mixtures of classical systems [28]. Results are presented for adsorption isotherms and selectivity. In Sec. 2 the fundamentals of the SAFT-VR-2D approach are revised. Adsorption isotherms of pure components and mixtures onto MOFs substrates are presented in Sec. 3, including the modeling of adsorption selectivity of hydrogen in the mixture hydrogen/methane. Finally, in Sec. 4 we provide some conclusions of this work. To facilitate the application of the SAFT-VR-2D approach with quantum corrections, we summarize in Appendix A and B the expressions for the calculation of the chemical potentials in three and two dimensions.

2. SAFT-VR-2D model

In this section, we describe the SAFT-VR-2D approach for modeling the adsorption of a mixture of classical and quantum fluids onto a planar wall. In this study, we consider a multicomponent mixture with i-species being formed by N_i-spherical particles of diameter σ_{ii} interacting with a planar wall. The particle-particle interaction (u_{pp}) is modeled by a square-well potential (SW),

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

where r_{ij} is the distance between particles of species i and j, σ_{ij} is the mixture diameter, ε_{ij} and $\lambda_{ij}\sigma_{ij}$ are the energy-depth well and attractive-potential range, respectively. In our approximation, we describe the system as being composed of two subsystems: a fluid whose particles are near to the wall, i.e., when $z \le \lambda_w\sigma_{ii}$, which we shall refer to as the *adsorbed fluid*, and a fluid whose particles are far away from the wall, *i.e*, *bulkfluid*. The interaction potential exerted by the wall on a particle is denoted as u_{pw},

$$u_{pw}(z,\sigma_{ii},\lambda_w) = \begin{cases} \infty & \text{if } z < 0 \\ -\varepsilon_w & \text{if } 0 < z \le \lambda_w\sigma_{ii} \\ 0 & \text{if } z > \lambda_w\sigma_{ii} \end{cases} \tag{2}$$

where z is the perpendicular distance of the particles from the wall, ε_w is the depth energy parameter per monomeric-segment, and $\lambda_w\sigma_{ii}$ is the range of the attractive potential. The adsorbed particles interact laterally via a SW potential with parameters $(\lambda_{ads},\varepsilon_{ads})$ for each component ij.

The prediction of the adsorption isotherms is obtained from the chemical potential of the adsorbed (μ_i^{ads}) and bulk phases (μ_i^{bulk}), that have the same value at equilibrium for a given temperature T [16],

$$\mu_i^b = \mu_i^{ads} \tag{3}$$

where

$$\mu_i^{ads} = \left(\frac{\partial A_{ads}}{\partial N_i^{ads}}\right)_{T,V,N_{i\ne j}} \tag{4}$$

$$\mu_i^b = \left(\frac{\partial A_b}{\partial N_i^b}\right)_{T,V,N_{i\ne j}} \tag{5}$$

where A_b and A_{ads} are the Helmholtz free energies for the bulk and adsorbed systems formed by N_b and N_{ads} particles, respectively. These energies are given by Ref. [29],

$$\frac{A_b}{NkT} = \frac{A_{3D}^C}{NkT} + \frac{A_{3D}^Q}{NkT} \tag{6}$$

and

$$\frac{A_{ads}}{NkT} = \frac{A_{2D}^C}{NkT} + \frac{A_{2D}^Q}{NkT} - \sum_i x_i\left[\ln\left(\frac{\lambda_w\sigma_{ii}}{\lambda_B}\right) + \beta m_i\varepsilon_{wi}\right]. \tag{7}$$

where $x_i = N_i/N$ is the molar fraction of species i, λ_B is the de Broglie's thermal wavelength, $\beta = 1/kT$ and k is the Boltzmann constant, and the superscripts C and Q denote classical and quantum contributions, respectively. The classical Helmholtz free energies A_{2D}^C and A_{3D}^C for 2D and 3D fluids are given by

$$\frac{A_{2D}^C}{NkT} = \frac{A_{2D}^{\mathrm{ideal}}}{NkT} + \frac{A_{2D}^{\mathrm{mono}}}{NkT} + \frac{A_{2D}^{\mathrm{chain}}}{NkT}, \tag{8}$$

and

$$\frac{A_{3D}^C}{NkT} = \frac{A_{3D}^{\mathrm{ideal}}}{NkT} + \frac{A_{3D}^{\mathrm{mono}}}{NkT} + \frac{A_{3D}^{\mathrm{chain}}}{NkT}, \tag{9}$$

where A^{ideal} is the ideal free energy, A^{mono} is the excess free energy due to monomer segments and A^{chain} is the contribution due to the formation of the molecular chains. The quantum Helmholtz free energies A_{2D}^Q and A_{3D}^Q are given by Refs. [29,33]

$$\frac{A_{2D}^Q}{NkT} = \gamma_x\left(\frac{\beta\varepsilon_x}{\pi}\right)^{1/2}\sum_k\sum_j x_{s,k}x_{s,j}\Lambda_{kj}g_{2D}^{SW}(\sigma_x;\lambda_x) \tag{10}$$

and