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Potential theory for prediction of high-pressure gas mixture adsorption on activated carbon and MOFs

E. Dundar [a,*], R. Zacharia [b], R. Chahine [b], P. Bénard [b]

[a] Aix Marseille Université, CNRS, MADIREL UMR 7246, 13397, Marseille, France
[b] Hydrogen Research Institute, Université du Québec à Trois-Rivières, (P.O. Box 500), Trois-Rivières, Québec G9A 5H7, Canada

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ABSTRACT

While selective adsorption of carbon dioxide has recently attracted special interest due to concerns over greenhouse emissions, separation of methane from its mixtures with carbon dioxide and nitrogen is a key operation for biogas and natural gas enrichment. Herein we present a detailed study of the multicomponent potential theory of adsorption's (MPTA) capabilities to predict published experimental adsorption data of binary and ternary mixtures of carbon dioxide, methane and nitrogen from each gas' pure component adsorption data on activated carbons Norit R1 and Calgon F-400 and on the metal–organic frameworks (MOFs) MOF-508b and MOF-5. It is observed that at temperatures below its critical temperature (304 K), and pressures in the vicinity of its critical pressure (7.37 MPa), carbon dioxide content in the binary mixtures adsorbed on Norit R1 has significant influence on the accuracy of MPTA's predictions, as sharp mixture density increases due to possible carbon dioxide phase changes cause convergence difficulties in the model's numerical iterations. This phenomenon is not observed in the studied ternary mixtures' case. Here, discrepancies are rather attributed to the inherent limitations of using four adjustable parameters to describe multicomponent adsorption at high pressure, and to the additive errors associated with the volumetric experimental measurement technique. Carbon dioxide's high selectivity due to its strong quadrupole moment is well predicted by the MPTA, on activated carbon as well as on MOFs.

1. Introduction

Selective adsorption of certain gases from gaseous mixtures forms the fundamental basis of several industrial gas separation and purification processes, such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) [1,2]. These processes make use of the different adsorption affinities exerted by each component in a gas mixture to an adsorbent material like activated carbon, porous alumina or zeolite, for various applications such as the design of heterogeneous chemical reactors and removal of low-concentration impurities and pollutants from fluid streams [3,4]. The discovery of metal–organic frameworks (MOFs), a novel class of extended network materials whose pore size and functionality can be tailored for specific applications, has a significant impact in separation/purification since an endless number of these materials' properties can readily be adapted to the requirements of the mixtures they are combined with [5].

Selection of a sorbent material for separation and purification applications and tuning of the process parameters depend ultimately on the sorption uptake, selectivity, kinetics, and isosteric heats of adsorption of gas mixtures. In order to properly choose the optimal adsorbent for specific separation purposes, rather than experimentally measuring adsorption equilibria which can be cumbersome and time consuming, theoretical models using published experimental data are often used to predict adsorption isotherms and screen different adsorptive materials [6]. However, although multicomponent gas adsorption data on activated carbon and high-quality single-component gas adsorption data on MOFs are easily found in the literature [7–9], experimental data on the direct separation of multicomponent gas adsorption on MOFs are rather scarce [10]. Hence, the most convenient approach for studying gas mixture adsorption on MOFs is to develop theoretical adsorption models that fit available experimental single-component data, which can then be extended in an easy and reliable manner to multicomponent adsorption systems [3,11]. Theoretical approaches to understanding and predicting adsorption range from simple empirical correlations like the Langmuir or Toth equations [12], to computationally intensive methods grounded in statistical

* Corresponding author. Tel.: +33 04 13 55 18 47.
E-mail addresses: ege.dundar@univ-amu.fr (E. Dundar), Renju.Zacharia@uqtr.ca (R. Zacharia), Richard.Chahine@uqtr.ca (R. Chahine), Pierre.Benard@uqtr.ca (P. Bénard).

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mechanics, such as the density functional theory (DFT) [13]. For many years, one of the most commonly used models for predicting multicomponent adsorption equilibria has been the ideal adsorption solution theory (IAST) proposed by Myers and Prausnitz [14]. In IAST, both the adsorbed and bulk phases are assumed to be ideal, and the model attempts to describe adsorption looking only at its thermodynamic aspects while ignoring the molecular interactions in the adsorbed layer. However, since in many industrial cases the mixtures are complex, and involve pressures or temperatures that deviate from ideality, this approach can in some cases lack accuracy [3,15]. The corrected Langmuir model [16] has had some success for studying non-ideal mixture adsorption but it was found that it could not correctly predict adsorption at high pressure [17]. Finally, although computational methods like DFT and the grand canonical Monte Carlo (GCMC) simulations are very rigorous, they are also computationally demanding and require significant resources to implement [11,18].

An alternative thermodynamic approach for modeling non-ideal gas mixture adsorption is a treatment based on Polanyi's potential theory of adsorption [19,20]. The original Polanyi theory had been extended by Grant and Manes [21] to predict the adsorption of gas mixtures containing methane, propane, butane, and hexane on activated carbon at room temperature. Significant contributions were also made by, among others, Greenback and Manes [22] Manes [23], and Moon and Tien [24]. Further advances came when Shapiro and Stenby extended the potential theory and enabled it to predict adsorption equilibria for a large variety of gas and liquid mixtures on several porous materials over a wide range of conditions [17,25]. Moreover, while the number of adjustable parameters in this extended version of the theory is comparable to the simpler macroscopic models such as IAST [14,17], the approach may be applied in a much wider range of practically important conditions [4,17,26]. This treatment, called the multicomponent potential theory of adsorption (MPTA), considers the mixture as a heterogenous substance segregated in the external field emitted by the adsorbent and uses a thermodynamic model to describe the equilibrium between the bulk and adsorbed phases (fluid–fluid interactions) while the fluid–solid interactions are described by potential models [17,25]. A crucial advantage of MPTA is its ability to accurately predict excess adsorption of various gases on adsorbents with few fitting parameters due to the use of the same equation of state for both the bulk and the adsorbed phases [25].

In this work, we use MPTA to predict the adsorption isotherms of gas mixtures containing carbon dioxide, methane and nitrogen on Norit R1 and Calgon F-400 activated carbons, and MOF-508b and MOF-5 metal–organic frameworks. To our knowledge, the use of MPTA for multicomponent adsorption prediction on MOFs is done for the first time [3,4,15,17,25–29]. The experimental data required for the modeling is adapted from published literature. MPTA is particularly disposed for modeling non-ideal gas mixture adsorption as it can accurately predict multicomponent adsorption behavior from pure gas experimental data [17,25,28]. Parameters obtained from the modeling of excess mixture adsorption isotherms on MOFs are compared with those obtained for similar mixtures on activated carbon adsorbents used in the separation and purification industry. Influence of different pore structures and heterogeneity of adsorbents on model predictions is discussed. Emphasis is put on carbon dioxide content's influence, especially in subcritical conditions, on MPTA's excess adsorption isotherm predictions. The equations of state (EOSs) used in this work for carbon dioxide, methane, nitrogen, and their mixtures are the ones included in NIST's thermodynamic property database (REFPROP [30]). For mixtures, the default mixing rules implemented in REFPROP were used.

2. Description of the MPTA

The MPTA is a thermodynamic approach developed by Shapiro and Stenby [25] to model both single-component non-ideal gas adsorption and non-ideal gas mixture adsorption in terms of pure gas experimental data. Originating from Polanyi's potential theory of adsorption [19], it considers the adsorbate as a distributed fluid subjected to the external attractive potential field $\varepsilon(z)$ of the adsorbent. This potential which describes the fluid–solid interactions between the adsorbate and the adsorbent drives the physisorption. As stated in the introduction and in the case of gas mixtures, the main difference between the assumptions made by the MPTA and that of the potential theory applied by Grant and Manes [21] is that the MPTA does not consider the adsorbate behavior to be ideal. Here, the magnitude of adsorption potential is assumed to depend only on the adsorbate's position in the porous space, and is independent of other molecules within the field, including those already adsorbed [19]. The fundamental basis of predicting sorption characteristics using MPTA is the calculation of the fluid's thermodynamic properties in the presence of the potential; by doing so, the effects introduced by the microporous materials are accounted for. The bulk phase gas, characterized by a uniform gas density ρ_B, is described using a non-ideal gas EOS while the adsorbed phase and all its thermodynamic properties, such as density, fugacity, pressure, and compressibility factor are functions of the potential $\varepsilon(z)$ [11,17,25]. The equilibrium between the bulk phase gas and the adsorbed phase at a given temperature and pressure can be expressed by including a perturbation term in the chemical potential of the bulk phase gas [17]. In the case of an N-component mixture, we assume that the ith component is subjected to the adsorption potential $\varepsilon_i(z)$. Since these potentials vary from one component to another due to the different interaction forces with the solid, the equilibrium state of the mixture within the potential field is described by the system of equations for the chemical potentials μ_i:

$$\mu_i(x(z),\rho(z)) - \varepsilon_i(z) = \mu_{Bi}(x_{B.}\rho_B), \tag{1}$$

where $i = [1,\ldots,N]$, subscript B represents the bulk gas phase, and notation $x(z)$, $\rho(z)$ is used to emphasize that the properties in the adsorbed phase depend on volume element z. For example, in Eq. (1), x_B and ρ_B respectively represent the molar fraction and density in the bulk phase while $x(z)$ and $\rho(z)$ represent the same variables in the adsorbed phase. Although z can also be interpreted as the distance from an adsorbent surface [15,25], in the theory of volume filling of micropores (TVFM) which we base our work on, it takes a meaning of volume [3,4,17,25,31]. For a given gaseous bulk phase condition ρ_B, all thermodynamic properties of the adsorbed phase corresponding to each micropore volume z are uniquely determined by Eq. (1). If put in a more convenient form in terms of the respective fugacities, Eq. (1) becomes:

$$f_i(x(z),\rho(z)) = f_{Bi}(x_B,\rho_B)exp\left(\frac{\varepsilon_i(z)}{RT}\right), \tag{2}$$

where $f_i(x(z), \rho(z))$ is the fugacity of ith component in the adsorbed phase, $f_{Bi}(x_B, \rho_B)$ is its fugacity in the bulk phase, R is the universal gas constant, and T is the equilibrium temperature. The fluid–solid interactions in Eq. (1) are described using potential functions, such as the Dubinin–Radushkevich–Astakhov (DRA) potential [17,32], or the 10–4–3 Steele potential [11,17,33]. In this work we use the former, since it is easy to implement and it has been used successfully for predicting adsorption on many activated carbons and MOFs [11,17]. DRA potentials are semi-empirical potentials based on Dubinin's theory of TVFM which take into account the heterogeneity of adsorbent materials, and allow the calculation of the adsorption