Confined fluid model to obtain high-pressure absolute adsorption isotherms for CO_2

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Abstract

This study presents a comprehensive approach to describe high-pressure absolute adsorption isotherms for CO_2 using a confined fluid model based on the extended Peng-Robinson equation of state. The experimental equilibrium data were acquired using a magnetic suspension balance for CO_2 adsorption on zeolite 4A across a pressure range of 1 to 50 bar at various temperatures (303-343 K). The conversion of excess adsorption data to absolute adsorption is significant for accurate mass balances in adsorption process simulations. The Peng-Robinson model for confined fluids (PR-C) effectively accounts for molecule-wall interactions within cylindrical pores, leading to accurate estimations of the adsorbed phase volume. Our results demonstrate a strong agreement between the calculated absolute isotherms and those obtained from well-established methodologies. The PR-C model offers a thermodynamically consistent alternative with parameters of clear physical significance, contributing to the optimization of adsorption-based separation processes. This work supports the development of more accurate models for high-pressure adsorption, which are essential for advancing the efficiency of CO_2 capture and storage technologies.

Keywords: adsorption equilibria; high-pressure; carbon dioxide; confined fluids, Peng-Robinson.

1. Introduction

Adsorption isotherms provide essential information for two primary applications: (I) characterization of porous solids and (II) design of adsorption processes [1]. Regarding the first aspect, adsorption equilibrium experiments are among the most popular techniques for obtaining pore size information and surface characterization [1,2]. Moreover, adsorption has become increasingly prevalent in various chemical and biochemical separation processes, primarily due to its relatively low cost and high efficiency in component separation [3]. In this context, the experimental determination of isotherms is the first step in studying an adsorbate/adsorbent system.

Among the separation processes that utilize adsorption, there is a significant presence in the literature regarding technologies for the removal of contaminants from natural gas, such as carbon dioxide (CO_2), water vapor (H_2O), nitrogen (N_2), and other sulfur compounds [4]. Thus, within the context of the natural gas production chain, achieving a better molecular-level understanding and development of the various stages inherent in

adsorption-based separation processes is of great interest.

Therefore, this work proposes using a model based on statistical thermodynamics, specifically an extended Peng-Robinson model, to obtain absolute adsorption isotherms at high pressures. In experimental terms, adsorption equilibrium data in porous solids are generally obtained through gravimetric or volumetric techniques. However, neither of these methods can directly measure the absolute adsorbed amount. The absolute adsorption isotherm is recognized as a fundamental thermodynamic property for mass balances and also provides data about the maximum storage capacity of a solid material [5].

2. Methodology

2.1. Experimental determination of adsorption equilibrium data

The adsorption equilibrium isotherms of CO_2 were obtained at the ATOMS Laboratory (Applied Thermodynamics and Molecular Simulation) of the Federal University of Rio de Janeiro (UFRJ), Brazil. A Rubotherm IsoSORP magnetic

suspension balance (MSB) was used to conduct adsorption measurements on zeolite 4A within the 1 to 50 bar pressure range.

The MSB keeps the sample magnetically suspended, facilitating communication between the measuring apparatus (microbalance) and the equilibrium cell, allowing the two environments to remain physically separated. The amount measured directly by this equipment results from the balance of forces experienced by the magnet, namely weight and buoyancy forces [1]. By isolating these forces into contributions from the sample container (SC), the adsorbent sample (S), and the adsorbed phase (ADS), we have Eq. 1:

$$m_{ADS} = \Delta m - m_{SC} - m_S + (V_{SC} + V_S + V_{ADS})\, \rho_b$$

In this equation, Δm is the mass displayed on the equipment screen, and ρ_b is the gas density in the bulk phase. The mass and volume information related to the sample container (SC) is obtained from the blank test with helium gas under vacuum. The adsorbent sample (S) measurements are obtained under vacuum through the buoyancy test. About Equation 1, if the adsorbed volume (V_{ADS}) is considered negligible, the so-called excess isotherm is obtained. On the other hand, if such volume is accounted for, the absolute isotherm is calculated. However, one should note that V_{ADS} is not obtained experimentally, leading to the need for theoretical models for its prediction (see item 2.3).

2.2. Verification of bulk density (ρ_b)

In this work, the magnetic suspension balance is equipped with a mechanism for measuring the density at each experimental point. Thus, we validate the experimental gas density results with the Peng-Robinson and PC-SAFT equations of state.

2.3. Calculation of adsorbed phase volume (V_{ads})

The conversion of excess adsorbed mass to absolute adsorbed mass remains a topic of ongoing debate in the literature, especially for data at high pressures [6,9]. In this context, the literature provides methodologies for determining the volume or average density of the adsorbed phase described by one of the following approximations:

- Van der Walls approximation - Dubinin [7]

$$v_{ADS} = \frac{b - v_0}{T_c - T_0}(T - T_0) + v_0 \qquad (2)$$

In this equation, b is the van der Waals constant, v_0 is the molar volume at the boiling temperature (T_0), and T_c is the critical temperature of the component.

- Liquid phase approximation - Ozawa [8]

$$\rho_{ADS} = \rho_0^L \exp\big(\alpha\,(T - T_0)\big) \qquad (3)$$

In this equation , ρ_0^L is the density of the component in the liquid phase at its boiling point under ambient pressure and α is the thermal expansion coefficient of the superheated fluid. For gas adsorption, this methodology is widely cited in the literature [1]. However, when the component does not have a standard boiling point, it is convenient to use the data from the triple point [8,9].

- Models based on statistical thermodynamics

The previous methodologies arise from empirical relationships. Therefore, thermodynamically consistent methods thermodynamically consistent methods are pursued, such as molecular simulation and classical density functional theory (DFT) [6,9]. In this sense, item 2.4 presents an equation of state (EoS) for confined fluids for calculating adsorbed density information.

2.4. EoS for confined fluids

This study evaluated the Peng-Robinson equation extended for confined fluids, considering cylindrical pores (PR-C). The PR-C model was formulated using the generalized van der Waals theory, using the canonical ensemble (N, V, T). More details are presented in previous works [10].

The model includes a modeling for the molecule-wall interaction in cylindrical pores. A square well potential was established, described by
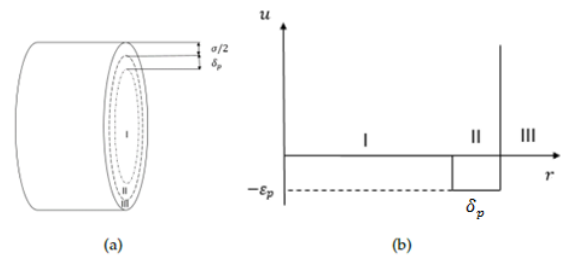
the radial coordinate relative to the center of the pore, as shown in Figure 1.

Fig. 1: Square well potential for cylindrical pores.

From the thermodynamic relations provided by the canonical ensemble, it is possible to derive the mathematical expressions for the equilibrium condition of adsorption for a pure fluid. The thermodynamics of adsorption can be addressed by equating the chemical potentials in each phase:

$$\mu_b(T,P) = \mu_{ADS}(T,\rho_{ADS}) \qquad (4)$$

This equality of chemical potentials is solved to obtain the thermodynamically stable value of ρ_{ADS}. Finally, using the textural properties of the adsorbent (V_p and r_p), the absolute and excess number of moles adsorbed are respectively obtained through Eqs. 5 or 6:

$$n_{ADS}(T,P) = V_p\,\rho_{ADS} \qquad (5)$$

$$n_{EXC}(T,P) = V_p\,(\rho_{ADS} - \rho_b) \qquad (6)$$

3. Results and Discussion

Figure 2 shows the equilibrium data obtained for the adsorption of CO_2 on 4A zeolite at different temperatures: 303, 313, 323, 333, and 343 K. The experiments were conducted at pressures up to 50 bar in triplicates.
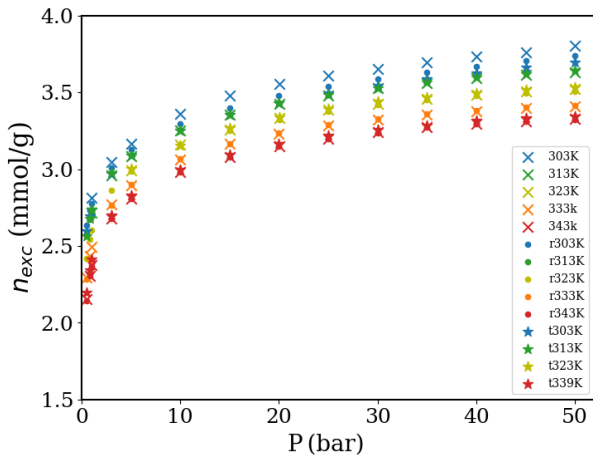

Fig.2: Experimental equilibrium adsorption isotherms of CO_2 on zeolite 4A. Markers in 'x' represent the 1st measurement, dots represent replicates, and stars represent triplicates.

One key observation is the reproducibility of the adsorption equilibrium measurements, confirming the high precision of the equipment, even at the highest pressure condition. Except a few

measurements on the 303K isotherm, all repetitions showed relative errors of less than 2%.

3.1. Verification of Fluid Phase (Bulk) Density

Figure 3 presents the molar density data of CO_2 measured by the magnetic balance with increasing pressure and compared with the results from the thermodynamic models. One can note a remarkable agreement between the experimental data and the thermodynamic models, confirming the high precision of the equipment in obtaining density information.
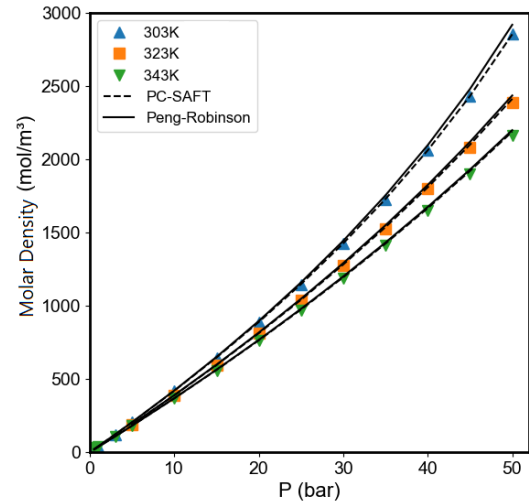

Fig. 3: Molar density of CO_2 for different pressures at 303, 323 and 343K. Markers represent the experimental data, and the solid and dashed lines represent the Peng-Robinson and PC-SAFT models, respectively.

3.2. Calculation of absolute adsorption isotherms

Subsequently, Figure 4 shows the adjustment of the PR-C model with the excess experimental data at 303K. With the proper estimation of the model parameters, it becomes possible to calculate the respective absolute isotherm.

Figure 5 presents the absolute isotherms obtained by the methodologies reported in this work. The adsorbed absolute concentrations (n_{ADS}) were obtained from the average values of excess adsorption (n_{EXC}). Initially, a close match is observed between the absolute isotherms and the excess isotherm at pressures up to 10 bar. Beyond this value, there is a growing divergence between the curves, which justifies the need to include a methodology for calculating the density (or volume) of the adsorbed phase.
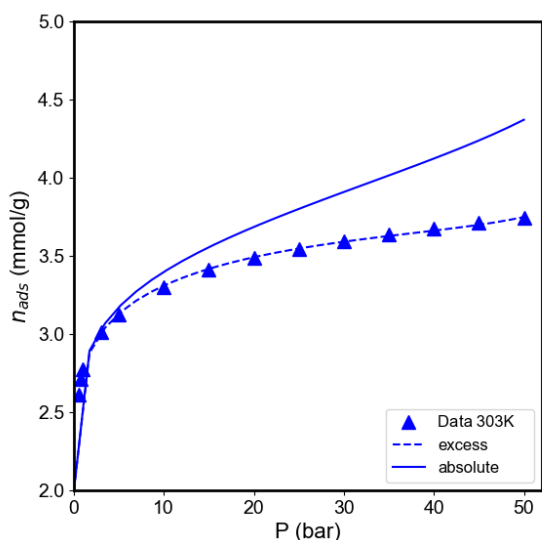
Fig. 4: Experimental adsorption data and absolute and excess isotherms calculated by the PR-C model with optimal parameters $(\delta_p = 0.15nm, \varepsilon_p = 9834K, r_p = 0.55nm, V_p = 0.22nm)$.
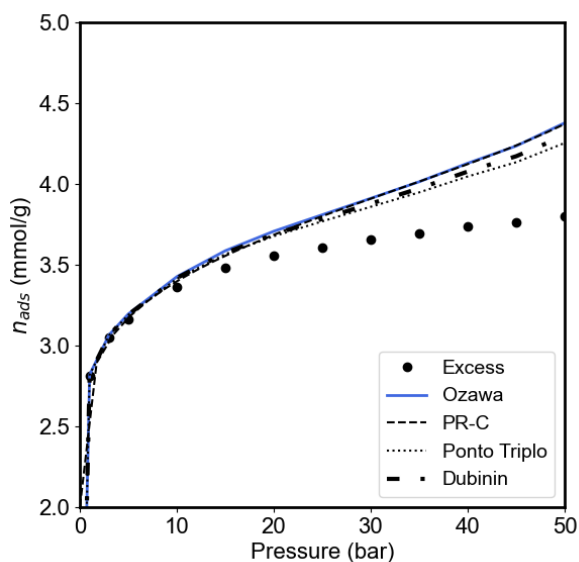

Fig. 5: Comparison of absolute isotherms calculated by different methodologies for the adsorption of CO_2 on zeolite 4A at 303K.

Finally, one should note that the absolute isotherm calculated by the PR-C confined fluid model presents great similarity with well-established Ozawa's methodology, which is a reference in the literature.

4. Conclusions

The conversion of the excess adsorbed concentration to the absolute concentration is a crucial procedure for using adsorption equilibrium information in the mass balances of column simulators. In this sense, the present work successfully presents an alternative of a thermodynamically consistent model with parameters with well-defined physical meaning for calculating high-pressure absolute adsorption isotherms. Additionally, the PR-C model can still be modified and enriched with textural information about the zeolite of interest.

Acknowledgements

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