

Influence of CO₂ content in natural gas adsorption on CHA for IAST predictions

H.M. Levy^a, D.V. Gonçalves^a, A.S. Pereira^a, M. Bastos-Neto^a, S.M.P. Lucena^{a*}

^a Federal University of Ceará, bloco 709 - Campos do Pici, Fortaleza (60455-760), Brazil

*Corresponding author: Department of Chemical Engineering, Federal University of Ceará, Building 709, Pici, Fortaleza. Zip code: 60455-760. E-mail: lucena@ufc.br

Abstract

Given the significant natural gas production of Brazil and the challenges posed by high CO₂ content in its reservoirs, efficient separation techniques such as Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA) are crucial. This study investigates the application of the Ideal Adsorbed Solution Theory (IAST) for modeling the adsorption of natural gas components, specifically CO₂, methane (C1), ethane (C2), and propane (C3), using chabazite (CHA) as an adsorbent. The study combines experimental adsorption isotherm data with molecular simulations to validate the forcefield employed in the IAST model. The simulations, performed using Grand Canonical Monte Carlo method, exhibited good agreement with experimental data, supporting the accuracy of the forcefield for the selected adsorbate-adsorbent system. However, when applied to multicomponent gas mixtures, the IAST model demonstrated reduced accuracy, particularly with increasing CO₂ content. This reduction is likely due to unaccounted dipole-dipole interactions between CO₂ molecules and cations in the CHA framework. The findings suggest that while IAST is suitable for light hydrocarbons, its application to CO₂-rich mixtures is limited unless additional correction factors.

Keywords: Natural gas, molecular simulation, IAST, adsorption isotherm;

1. Introduction

Natural gas is a primary energy resource with a global consumption of 40,102 TWh in 2023, representing 21.9% of all primary energy consumption. The United States led this consumption (8,860 TWh), followed by Russia (4,530 TWh) and China (4,048 TWh) [1,2]. Brazil has as relevant production of $119 \cdot 10^6$ m³/day in 2015 and intends to increase to $205 \cdot 10^6$ m³/day in 2030 [3]. However, one of the major Brazilian oil and gas reservoir has a high CO₂ content which results in a monthly production of 600,000 t [4]. Due its high content, separation processes such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) offer an alternative to the energy-intensive absorption using liquid amines. These models also help to mitigate the potential dangers associated with O₂ content, which can lead to corrosion and amine degradation [5,6].

To avoid unnecessary expenses in the TSA/PSA projecting and building, modelling these processes using a well-known thermodynamic and phenomenological approach is required. The ideal

adsorbed solution theory (IAST) was developed by Myers and Prausnitz and is a well-studied method to predict multicomponent adsorption equilibrium based on monocomponent data [7,8].

IAST considers the adsorbed phase behavior as ideal while the gas phase can be corrected using fugacity coefficients through Raoult's law [9]. This thermodynamic model uses the reduced spreading pressure concept to predict the adsorption of a gas mixture using adsorption isotherms of each component [10].

While adsorption isotherms are often obtained from experiments, molecular simulation offer an alternative method, allowing for direct comparison between thermodynamics calculations and experiments [11].

Zeolites such as chabazite (CHA) are commonly used as frameworks on molecular simulation for CO₂ separation and capture process as observed in the studies of Hasegawa et al. (2023) [13], Vega and Bahamon (2023) [14] and Wang et al. (2023) [15]. In addition, zeolites are the most used material in catalysis industry, adsorptive separation and ion exchange processes [16].

Thus, the current study applied three adsorption isotherm models (Langmuir, Freundlich and Langmuir-Freundlich) within an IAST model, incorporating gas phase correction using fugacity coefficients. These coefficients were derived from monocomponent adsorption isotherms, obtained through molecular simulations and validated with experimental data.

2. Material and methods

Experimental section

The monocomponent isotherms of CO₂, methane (C1), ethane (C2) and propane (C3) were measured according to Nascimento et al. (2021) [17] using an Intelligent Gravimetric Analyzer—IGA (Hidden Isochema Ltd.,UK) equipped with a balance, pressure and temperature control system and a high vacuum system. Before the analysis the chamber was degassed at 573 K and 10⁻⁹ bar for 8 h. Then CO₂ isotherm was measured at 323 ± 0.5 K in a 0.21-10 bar pressure range. Pressure ranges of 0.05-10 bar were used for C1, 0.14-10 bar for C2 and 0.14-5 bar for C3 at 298 ± 0.5 K. The results of mass gain in each pressure were used in the following section to validate a proposed forcefield.

Simulation section

CHA framework group of type R-3m with $a = b = 13.5799 \text{ \AA}$ and $c = 14.7472 \text{ \AA}$ and a Si/Al ratio = 3 was used to simulate an adsorption isotherm calculated by Monte Carlo simulations applied to grand canonical ensemble (GCMC) through RASPA code 2.0 [18]. The gas phase molecules forcefield was used according to the study by Gomes et al. (2015) [19] study and the solid phase (chabazite) forcefield was based on UFF [20] adjusting Si and Al well depth potential (ϵ) for each gas phase component. To validate the forcefield proposed, the same conditions applied in experimental section were used in the simulation input.

After validating the forcefield proposed, a monocomponent isotherm was performed for CO₂, C1, C2 and C3 at 318 K using pressure ranges that varies according to the partial pressure of each component based on CO₂ proposed content in gas phase. A multicomponent isotherm was also performed in the same simulation setting previously described using the composition described in Table

1.

Table 1. Adsorbate compositions evaluated.

Simulation	% CO ₂	% C1	% C2	% C3
1	0	89.02	10.07	0.91
2	1.00	88.13	9.97	0.90
3	10.00	80.12	9.06	0.82
4	20.00	71.22	8.06	0.73

All the simulations performed used 10⁴ Monte Carlo cycles was performed using Lennard-Jones potential truncated at 12.8 Å to calculate van der Waals interaction.

IAST modelling section

For modelling the IAST thermodynamic model, Langmuir (1), Freundlich (2) and Langmuir-Freundlich (3) isotherm models were adjusted under the isotherms obtained via molecular simulation at 318 K using a validated forcefield and had its gas phase corrected with fugacity coefficients obtained by Peng-Robinson equation of state.

$$q = \frac{q_s b \varphi P}{1 + b \varphi P} \quad (1)$$

$$q = b(\varphi P)^n \quad (2)$$

$$q = \frac{q_s b(\varphi P)^n}{1 + b(\varphi P)^n} \quad (3)$$

Where q_s , b and n are the adsorption parameters, q , φ and P are the loading, fugacity coefficient and the pressure respectively. Using the fugacity definition, the IAST model proposed initially by Myers and Prausnitz [8] was modified by (4) for moderate and high pressures.

$$\frac{\pi A}{RT} = \int_0^{P_i^0} \frac{q(f)}{f} df \quad (4)$$

Since the left side of the equality is constant for each component in the same fugacity, we can determine the vapor pressure at the spreading pressure for each component (P_i^0) and subsequently calculate the composition and loading of each component adsorbed in the solid phase. All the calculations were performed using the Python programming language.

3. Results and discussion

Experimental and simulated isotherms

Figure 1 shows the simulated isotherms for pure components at 323 K in CHA, alongside the

experimental data. It was observed that the simulated isotherms slightly overestimated the experimental values for all four components. This behavior can be attributed to the idealized CHA crystal used in the simulations, which is perfect, while the real crystal contains imperfections due to the synthesis process. Despite this, both curves exhibit similar behavior, which supports the proposed forcefield. The forcefield reparameterization include modifications to the well depth potential for Si and Al, based on the UFF parameters. 1.15%, 17.5%, 5%, and 1% of the original UFF ϵ parameter were applied for CO₂, C1, C2 and C3, respectively.

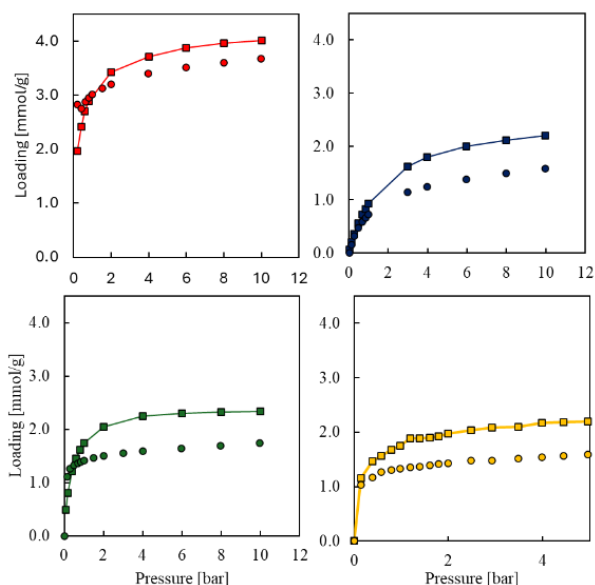


Fig. 1: Simulated (■) and experimental (●) adsorption isotherms at 323 K for CO₂ and 298 K for C1-C4 in CHA.

Adsorption parameters evaluation

After applying the 3 monocomponent adsorption models and obtain its parameters, was achieved the curves showed in Figure 2.

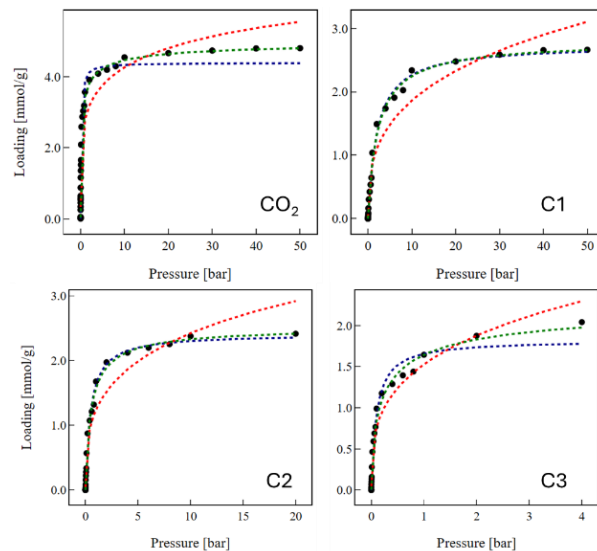


Fig. 2: Langmuir (---), Freundlich (···) and Langmuir-Freundlich (-·-) adsorption isotherm model with parameters adjusted using molecular simulation data (●) at 318 K in CHA.

The R^2 values obtained using Freundlich model were above 0.94, while those from the Langmuir were above 0.96. The Langmuir-Freundlich model achieved the highest R^2 values, exceeding 0.99. That is also expected since Langmuir-Freundlich present one more adjust parameter than the others. Then Langmuir-Freundlich was the isotherm model selected to be applied on IAST.

IAST model

As shown in Figure 3, the accuracy of the proposed IAST decreases as the CO₂ content in the mixture increases. A similar behavior was reported by de Oliveira et al. (2011) [21]. This decline in accuracy is likely due to the partial polarity of the CO₂ molecules, which can induce strong dipole-dipole interactions with the cations in CHA. Such strong interactions highlight the energetic heterogeneity of the adsorbent phase, which the IAST model does not account for, resulting in the significant errors illustrated in Figure 3.

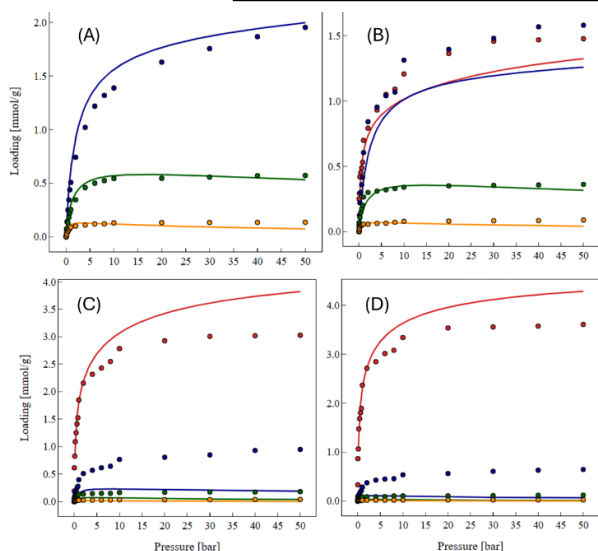


Figure 3: IAST CO₂ (—), C1 (—), C2 (—) e C3 (—) prediction in CHA compared to simulated data (●●●●) using 0% (A), 1% (B), 10% (C) and 20% (D) of CO₂.

4. Conclusion

Therefore, the IAST model effectively predicts multicomponent adsorption for light hydrocarbons like C1–C3 in CHA zeolite, but it is less accurate for mixtures containing CO₂. To address this limitation, it would be necessary to incorporate a factor that accounts for the energetic heterogeneity of the adsorbent.

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