



Interpretation of net and excess adsorption isotherms in microporous adsorbents



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ABSTRACT

Adsorption data are routinely reported as net or excess amounts adsorbed; although measuring techniques are nowadays well established, the interpretation and further use of these two measures is limited by the uncertainty on the estimated internal pore volume of the material and, accordingly, the volume (or density) of the adsorbed fluid. In this study, adsorption data are presented that have been measured with CO₂ on 13X zeolite in both crystal and pellet forms at 50 °C and in the pressure range 0.02–14 MPa by using a magnetic suspension balance. The adsorbents' structural parameters have been obtained through a combination of independent measuring techniques, including low-pressure adsorption and mercury intrusion porosimetry, and a methodology is presented where both net and excess adsorption isotherms are simultaneously evaluated through a graphical method. While providing additional insights on the meaning of these two different frameworks, the application of such an integrated approach allows for a more consistent interpretation of the obtained adsorption data. It is shown that for both materials the adsorption process is entirely controlled by the filling of the micropores and that the adsorbent's volume is overestimated when helium is used as a probing gas. The statistical adsorption isotherm model proposed by Ruthven is applied to describe the measured adsorption isotherms and provides a much better fit than the Langmuir model. For both crystals and pellets, and over the whole pressure range, CO₂ adsorbs as a dense liquid with density values starting from the critical density of the fluid and reaching ~27 mol/L (i.e. 15 molecules/cage) at the highest pressure of the experiment.

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1. Introduction

The interest in applications of adsorption at high pressure is increasing and spans both industrial processes, such as the capture of carbon dioxide (CO₂) from flue gas [1] or the storage of hydrogen [2], and processes in the subsurface, where these conditions are attained naturally, such as the underground storage of CO₂ [3] or the recovery of natural gas from shales [4]. The adsorption isotherm plays a central role in the design of all these operations, as it controls process-relevant parameters such as elution profiles, displacement efficiencies and storage capacities. This shift towards high-pressure applications has set new challenges with respect to both the measurement and the interpretation of the experimentally obtained adsorption data. In fact, despite significant advances have been made in the accuracy of the most common measuring techniques and data are becoming more available, the actual mechanism of adsorption at high pressure is still far from being understood [5]. As expanded in the sections

that follow, a complete characterization of the adsorption equilibrium includes the quantification of the volume or the density of the adsorbed phase, which can be significantly different from the corresponding properties in the bulk phase, as in the first case the fluid is subject to a molecular-level confinement in the pores of the adsorbent material [6]. The point of contention here is that an assumption has to be typically made with respect to the value of either the density or the volume of the adsorbed fluid [7]; for measurements carried out below the critical temperature of the adsorbate, the adsorption process is controlled by the vapor–liquid transition and accordingly the adsorbed fluid takes the density corresponding to the one of the saturated liquid [8]. On the contrary, when the adsorbate is in the supercritical state (which is achieved at high pressures for many gases), a well-defined phase transition is absent, and the estimation of the required parameter is left to a more or less arbitrary choice. As a matter of fact, density values are reported that range between the liquid and the solid state of the adsorbate even for very similar pressure and temperature conditions (see Table 1 and discussion in the next section), this representing the main reason for the current uncertainty regarding the mechanism of adsorption at high pressure. In particular, it is not clear whether these differ-

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Nomenclature

b	Van der Waals co-volume [L/mol]
b_L	Langmuir equilibrium constant [L/mol]
K'	Henry's constant [-], $K' = K/N_A/v_c$
m	mass [g]
M_1	mass at measuring point 1 [g]
M_1^0	mass at measuring point 1 under vacuum [g]
M_m	molar mass of CO ₂ [g/mol], $M_m = 44.0$ g/mol
n	moles (experiment) [mmol]
\hat{n}	moles (model) [mmol]
n_{cry}^∞	saturation capacity (Langmuir isotherm) [mmol/g _{cry}]
N_A	Avogadro's number [molec./mol], $N_A = 6.022 \times 10^{23}$ molec./mol
N_{exp}	number of experimental data points [-]
P	pressure [MPa]
P_0	saturation pressure [kPa]
q^a	adsorbed amount [molec./cavity]
T	temperature [°C or K]
V	volume [cm ³]
V^0	combined volume of lifted metal parts and adsorbent [cm ³], $V^0 = V^{\text{met}} + V^s$
w_{cry}	crystal content [wt.%]
<i>sub- and superscripts</i>	
a	adsorbed

b	boiling point
c	critical
cry	crystals
env	envelope
He	helium
Ma	macropores
met	metal parts
mi	micropores
pel	pellets
s	solid adsorbent

Greek letters

β	effective molecular volume [\AA^3]
η_c	number of cages [cages/uc]
η_{uc}	number of unit cells [uc/g _{cry}]
ρ_m	adsorbate mass density [g/cm ³]
ρ	adsorbate molar density [mol/L]
σ	uncertainty [appropriate units]
v_c	volume of a cage [\AA^3]
v_{uc}	volume of a unit cell (uc) [\AA^3]
Φ	sum of squared residuals [-]
ω	saturation capacity [molec./cage]

ences are caused by the distinct properties of the adsorbent material or by the assumptions underlying the measuring technique, and the traditional protocols are currently being revisited with regards to both the measurement and representation of supercritical adsorption isotherms [2,9].

This last aspect represents the starting point for the analysis developed in this work. The adsorption of CO₂ on 13X zeolite is investigated through an integrated approach, which includes measuring techniques such as mercury intrusion porosimetry, together with low- and high-pressure adsorption experiments. The latter are interpreted through the concepts of net and excess adsorption, thus allowing for an assessment of the consistency of the measured data, while simultaneously gaining additional insights on the meaning of these two different frameworks. Procedures are evaluated that are commonly applied to the interpretation of the obtained isotherms, such as the use of helium to measure the adsorbent's volume or the graphical approach to estimate the volume and the density of the adsorbed phase. To assess the reliability of the experimental data and methods, a thorough analysis of measurement uncertainties is carried out and presented. It is shown that the application of such an approach that combines various independent experimental techniques leads to a physically more sound characterization of the adsorbed phase, this being key to improve our understanding of the behavior of a fluid confined into nanopores.

The remainder of the paper is organized as follows. First, a brief review of literature data on the density of adsorbed CO₂ is presented that covers various techniques and adsorbent materials. Next, the net and excess adsorption frameworks are defined and their differences highlighted, these being the so-called truly measurable quantities in a high-pressure adsorption experiment. Subsequent sections introduce the materials and experimental protocols used in this study, followed by the presentation of the results and the discussion of their implications for the understanding of supercritical adsorption in microporous adsorbents.

2. Density of the adsorbed phase: literature review

We start this analysis by focusing our attention on the adsorption of CO₂ and Table 1 provides a literature overview of densities values of the adsorbed phase (ρ^a) that have been estimated using various adsorbent materials and methods. The latter include traditional experimental techniques (manometric, volumetric or gravimetric methods coupled with a graphical interpretation of the adsorption isotherm), novel approaches (labeled as *Optical techniques*) and molecular simulations. In all the studies considered here, the applied temperature is above the critical temperature of CO₂ ($T_c = 30.98$ °C) and pressures are above 5 MPa. Interesting observations can be gathered from the table. While, generally, the formation of a highly densified state upon adsorption is reported (i.e. with densities larger than 21.1 mol/L, the density of a saturated CO₂ vapor at 0 °C [10]), values obtained from both molecular simulations and optical techniques are significantly lower (less than 20 mol/L). This is always the case for those studies where only moderate pressures were attained (below 7 MPa), thus suggesting that the adsorbed phase density is not constant, but increases with pressure, as a result of a closer packing of the molecules. The dataset from the more conventional adsorption techniques (*Graphical estimates from adsorption experiments* in the table) is larger and the spread of adsorbed phase densities is remarkable: estimates are ranging between 22 mol/L for activated carbons up to almost 40 mol/L for a 13X zeolite, this value being even larger than the density of dry ice (35.5 mol/L [10]). Note that values larger than the solid density of the adsorbate were reported also for N₂ adsorption on alumina in the temperature range 50–100 °C and at pressures up to 300 MPa [7]. These observations are problematic, as they don't find support from independent observations with other supercritical fluids and techniques. In fact, upon application of a chromatographic method on a 13X zeolite ($P = 8$ MPa and ambient temperature), Rolniak and Kobayashi [11] have estimated a density of adsorbed CH₄ that is significantly lower (~ 15 mol/L) than the corresponding liquid density at the

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