Full Length Article

# Absolute adsorption of light hydrocarbons and carbon dioxide in shale rock and isolated kerogen

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## ABSTRACT

Natural gas production from shale formations has changed the energy landscape. Knowledge of adsorption in the subsurface shale formations improves resource assessment. The excess adsorption is directly measurable from experiments. Evaluation of fluid content in shale is based on the absolute adsorption. At high pressure relevant to subsurface conditions, the computation of absolute adsorption from excess adsorption has shortcomings when the conventional models are used. In this work, we first present the excess sorption data of light hydrocarbons and carbon dioxide in subsurface shale rock and in isolated kerogen. Gravimetric method was used in our measurements. The results show that, at high pressure, the excess adsorption of ethane and carbon dioxide decreases significantly as pressure increases. Excess adsorption of ethane at 60 °C for the shale sample investigated becomes negative at high pressure. The conventional models may provide a non-monotonic absolute adsorption and even magnify the unphysical negative adsorption. In addition to the proposed model based on adsorbed layer volume, we also account for effective sample volume due to the pore volume accessibility by different molecules, as well as the swelling of kerogen. The adsorption data from subsurface shale and the method for analysis presented in this work set the stage for prediction capability in hydrocarbon production from shale reservoirs.

## 1. Introduction

Production of natural gas, a clean-burning fuel, from shale formations has changed the energy landscape in the last few years. Fracturing of tight shale formations, flow in the shale subsurface, and fluid content in the formation are the key elements. This investigation focuses on the absolute adsorption which has significant effect on fluid content in shale formations. Knowledge of adsorption is important in shale oil and gas reservoirs for resource assessment. Shale rock is comprised of two distinct media: organic and inorganic matters, both may contain nanoscale pores [1]. Generally, kerogen is the predominant component of organic matter in most shale formations. The amount of hydrocarbons in shale is often associated with organic matter [2–4].

There are two main methods for measuring gas adsorption: gravimetric and manometric/volumetric [5]. The excess adsorption is directly measured in experiments. The absolute adsorption can be estimated based on excess adsorption. Much work has been done in various experimental measurements of excess adsorption. However, the calculation of absolute adsorption from excess adsorption in shale has not

advanced much. The main reason may be that at low and moderate pressures the absolute adsorption and excess adsorption are close. The absolute adsorption of methane and/or carbon dioxide in various shale samples has been investigated based on the conventional models where the main parameter is the adsorbed layer density [2,6–11]. The absolute adsorption can also be estimated based on the adsorbed layer volume [12–14].

Negative excess adsorption has been reported in different materials. Gasparik et al. [15] reported extensive excess adsorption measurements in shale by gravimetric and volumetric methods and discussed the uncertainty in measurements. They presented negative excess adsorption of carbon dioxide in Posidonia shale and reasoned that the negative data is due to the deviation from bulk fluid density calculation and cross-contamination of the carbon dioxide with residual helium. The negative excess adsorption of methane has been reported by Ross and Bustin [16]. The authors believed that negative excess adsorption was due to the error of void volume calibration from the different pore-space accessibility by helium and methane. Helium can access small pores where the larger molecules may not access. Negative excess

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adsorption of carbon dioxide in coal has also been reported [17]. As we will show in this work an alternative explanation is warranted.

In general, the fluid-in-place (FIP) in shale rock can be divided into three categories: free molecules in the pores; adsorbed species on the inner surfaces of the microscale and nanoscale pores; and dissolved species in the organic matter [18]. The former two categories may have major contribution to the total FIP [4,10,19]. Kerogen may swell due to complex mechanisms, such as structural trapping, adsorption, and dissolution. A number of authors have studied shale/kerogen swelling by organic solvents including aliphatic, alicyclic and aromatic hydrocarbons [20–25]. Kerogens are cross-linked macromolecular systems. Regular solution theory has been used to describe the solvent swelling of kerogens [22]. Heller and Zoback [6] studied the volumetric swelling as a function of methane and carbon dioxide adsorption in activated carbon, illite, and kaolinite. They observed increased swelling when the amount of adsorption increased. The volumetric swelling with slight anisotropy due to methane adsorption has been reported in other studies [19]. Yang et al. [26] have done sensitivity analysis on the effect of shale swelling and shrinkage as wells adsorbed phase volume and excess adsorption and absolute adsorption from methane in several shale samples. The assumptions in their work include a constant adsorbed density and variable adsorb phase volume which are different from our work.

In this work, we first report excess adsorption/desorption data and then propose a model for absolute adsorption estimation from measured excess adsorption. We estimate absolute adsorption based on adsorbed layer volume, and the effects of pore volume accessibility and effective sample volume, as well as swelling. Our data is based on the gravimetric method in reservoir shale samples and the isolated kerogen for methane, ethane, propane, normal-butane (n-butane), iso-butane (i-butane), and carbon dioxide. The pressure in methane, ethane and carbon dioxide is to 150 bar, and the temperature ranges from 60 °C to 120 °C. For propane, n-butane, and i-butane the pressure is set by the vapor pressure at experimental temperature conditions. At the end, we draw conclusions.

## 2. Experimental method

### 2.1. Basic properties

The sorption in shale reservoir rocks from Vaca Muerta formation, Neuquén Basin in Argentina, was investigated in this study. The geological formation is Jurassic and Cretaceous age and considered to have high potential for the production of oil and gas [27]. The basic properties were analyzed systematically, including density, pore size distribution, mineral composition, organic petrography, and thermal maturity. Kerogen was isolated from the shale sample by acid treatment and Soxhlet extraction process [28]. The details and procedures of basic property tests and kerogen isolation are provided in the SI.

### 2.2. Gas adsorption/desorption by gravimetric method

Adsorption/desorption of various light hydrocarbons, including methane (99.97%), ethane (99%), propane (99.5%), n-butane (99.999%), i-butane (99.999%), and carbon dioxide (99.5%) in the shale and isolated kerogen were investigated using an ISOSORP® STATIC (SC-HPII) Automatic Gravimetric High Pressure Sorption Analyzer. The instrument is manufactured by RUBOTHERM. The schematic diagram of the gravimetric adsorption analyzer is presented in Fig. S1. The sorption amount is determined gravimetrically by weighing the sample using the patented magnetic suspension balance. Resolution of the magnetic suspension balance is 0.01 mg and the reproducibility is ± 0.04 mg (standard deviation).

First, the weight ($m^{SC}$) and volume ($V^{SC}$) of the empty sample container were measured with helium (99.999%) at 60 °C. This step is known as the blank measurement. Second, around 0.3 to 2.5 g of

sample was loaded to the sample container and was vacuum (ultimate vacuum with gas ballast is 0.01 mbar) dried at 200 °C until there was no weight change. This step is known as the sample pretreatment. In the third step, the weight ($m^S$) and the volume ($V^S$) of the loaded sample were determined with helium at 60 °C. $V^S$ is the volume of the grain matrix and does not include the pore volume measured from low temperature adsorption analysis. This step is known as the buoyancy measurement. In the fourth step, the loaded sample was evacuated again at 200 °C until there was no weight change, and then the adsorption/desorption measurements were conducted. In the adsorption (desorption) measurement, the pressure of the gas was increased (decreased) stepwise at a constant temperature. After each adsorption/desorption measurement cycle, the loaded sample was reprocessed by vacuum dry at 200 °C, followed by the next adsorption/desorption measurement. Adsorption and desorption were measured at equilibrium. For each of the measuring point, the pressure and temperature were in the tolerance of ± 0.1 bar for setting pressure and ± 0.1 °C for setting temperature, respectively. Each adsorption/desorption point was measured after 0.5–3 h depending on the gas species [29].

### 2.3. Excess adsorption and conventional model for absolute adsorption

There are two forces acting on the sample in the gravimetric method: gravity ($F_A$) and buoyancy ($F_B$) are given by,

$$F_A = (m^{SC} + m^S + m^A)g \tag{1}$$

$$F_B = (V^{SC} + V^S + V^A)\rho^B g \tag{2}$$

where $m^A$ is the absolute adsorption, $V^A$ is the volume of the adsorbed layer, $\rho^B$ is the bulk density of the fluid, and $g$ is the gravity acceleration. Bulk density of the fluid is determined by a sinker, which has a known weight and volume. $m^{SC}$, $V^{SC}$, $m^S$, and $V^S$ are obtained using helium in the blank measurement and buoyancy measurement. In sorption measurements, the balance reading, $\Delta m$, and the mass of adsorbate $m^A$ are given by,

$$\Delta m = (F_A - F_B)/g = m^{SC} + m^S + m^A - (V^{SC} + V^S + V^A)\rho^B \tag{3}$$

$$m^A = \Delta m - m^{SC} - m^S + (V^{SC} + V^S + V^A)\rho^B \tag{4}$$

The excess adsorption can be expressed as

$$m^E = \Delta m - m^{SC} - m^S + (V^{SC} + V^S)\rho^B \tag{5}$$

Eq. (5) has the same form as $m^A$ in Eq. (4) when $V^A = 0$. The relationship between absolute adsorption and excess adsorption can be written as

$$m^A = m^E + V^A \rho^B \tag{6}$$

The adsorbed layer volume can be expressed by,

$$V^A = \frac{m^A}{\rho^A} \tag{7}$$

where $\rho^A$ is the average adsorbed layer density. By substituting Eq. (7) into Eq. (6), the relationship between absolute adsorption and excess adsorption can also be given as

$$m^A = \frac{m^E}{1 - \rho^B/\rho^A} \tag{8}$$

The excess adsorption is obtained from experimental measurements based on Eq. (5). The absolute adsorption can be estimated based on either Eqs. (6) or (8) [30]. In Eq. (6), because the adsorbed layer volume $V^A$ cannot be measured directly, many assumptions have been made by various authors. Payne et al. [31] introduced the approximation based on surface area and effective adsorbed layer thickness. Rexer et al. [12] applied the sorption pore volume estimated from $CO_2$ isotherms at −78 °C (195.15 K) as an upper limit. Zhang et al. [13] and Tian et al. [14] estimated adsorbed layer volume based on linear