



# Molecular simulation and modelisation of methane/ethane mixtures adsorption onto a microporous molecular model of kerogen under typical reservoir conditions



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## ABSTRACT

The prediction of mixture adsorption is a challenging task in gas industry when dealing with shales for both resources prospect or production forecast. In this work, we used molecular simulation and models to study the adsorption of methane/ethane mixtures onto a mature kerogen model under typical reservoir conditions (338 K, up to 20 MPa). Using Molecular Dynamics, we first generated microporous structures of kerogen, representative of field samples. Monte Carlo simulations in the Grand Canonical ensemble were used to produce pure compound and mixture adsorption isotherms on these adsorbent structures. The ability to predict simulation results of the Ideal Adsorbed Solution model and a modified statistical mechanical derivation of the Extended Langmuir model have been studied at low pressures (up to 1 MPa) where species are supposed ideal and at higher pressures (up to 20 MPa) where species non-ideality is partially introduced in the models. At low pressures, the adsorption isotherms predicted by the two models are in good agreement with the results from molecular simulation, independently of the confinement. At higher pressures, this agreement is only valid for the less confined structures and worsened as the micropore size decreases.

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## 1. Introduction

From the industrial revolution and the middle of the eighteenth century, the global energy consumption has been constantly increasing. Forecasts up to 2035 do not expect any change in this evolution [1]. Moreover natural gas represents almost a quarter of the global primary energy consumption. Up to now, the conventional resources have been the most exploited because it was not economically viable to produce gas from unconventional resources. However, as the conventional resources become scarce, the resulting rise of the gas price allows the profitable exploitation of unconventional resources (deep off-shore, tight gas or Shale gas). According to the annual report of the International Energy Agency [2], the shale gas production has led to a decrease of the US natural gas price, of approximately 65%, between 2010 and 2012.

From a geochemical point of view, organic rich shales are grained materials composed of an organic phase known as kerogen

spread in an inorganic matrix (mainly made of quartz, clays and carbonates) [3]. Contrary to conventional resources, shales exhibit a poorly connected microporous network mainly located in the organic phase. The high degree of confinement suggests that in some shales approximately 50% of the stored fluid is adsorbed onto the kerogen (as in Barnett) [4], whereas the adsorbed gas in the inorganic matrix is generally supposed to be negligible [5,6]. Adsorption Selectivity and Non-Darcy gas flow through microporous medium [7] are likely to induce an evolution of the produced gas composition. Thus, mixture adsorption is a leading criteria governing shale gas production. This work provides a path of combining adsorption data (from experimental or simulation work) and theoretical models in order to shed light to the mechanisms governing the sorption of gas on kerogen and therefore promotes understanding and predicting the behavior of such systems, at typical reservoir conditions (338 K and pressure up to 20 MPa). Under these thermodynamical conditions, the stored fluid (mostly composed of methane, ethane and carbon dioxide) is in a supercritical state.

This work is based on atomistic molecular simulations [8,9] with the use of both Monte Carlo (MC) and Molecular Dynamics

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(MD) simulations of kerogen model structures. To do so, we used the molecular models of mature kerogen proposed by Yiannourakou et al. [10]. The kerogen models are created by MD in the isobar-isotherm (NPT) ensemble, starting from a low density configuration and being compressed under typical reservoir conditions. The final densities are comparable to those that are experimentally observed. These models are subsequently used to obtain adsorption isotherms, using MC simulations in the Grand Canonical ensemble (GCMC). The simulations presented here have been computed using the Medea© simulation package. MD simulations are conducted with Medea/LAMMPS [11] software and MC simulations with Medea/GIBBS<sup>1</sup> software. In the following, we use Molecular Simulations to generate adsorption data of mixtures under typical reservoir conditions on structures that aims to reproduce the chemical and structural heterogeneity of kerogen, and we then study the ability of the Extended Langmuir (EL) model [12] and the Ideal Adsorbed Solution [13] (IAS) model to predict mixture adsorption in kerogen structures presenting different degrees of confinement.

The EL model is an empirical extension of the pure compound Langmuir model that describes the monolayer coverage of  $N_s$  adsorption sites on a flat surface by a mixture. Several implementations of the Extended Langmuir model, that include heterogeneities in the adsorbate–adsorbent interactions, have been proposed in the literature. The Multi-Site (MS) Langmuir model developed by Nitta et al. [14] allows adsorbed molecules to occupy more than one adsorption sites on a homogeneous surface. On the other hand, the Multi-Region (MR) Langmuir developed by Bai and Yang [15] assumes the possible existence of several regions. On some regions all the species present in the mixture can be adsorbed, while adsorption on other regions is species specific, due to entropic or energetic effects. Bai and Yang [16] coupled both Multi-Site and Multi-Region (MR-MS) Extended Langmuir model. They concluded that for similar species (mixtures of hydrocarbons) the MR-MS Extended Langmuir model only provides minor improvements over the MS Langmuir model.

On the other hand, the IAS model considers a vapor liquid like equilibrium between the adsorbed and free molecules. Species are supposed to behave as ideal gases which can lead to strong deviations from experimental or simulated results as reported by Myers [17]. As for the Extended Langmuir model, several improvements have been proposed. Mixture non-ideality in the adsorbed phase can be introduced [18] (NIAL). Valenzuela et al. [19] introduced species-dependent fluid–solid interactions. In the following, we will apply the EL and the IAS models to describe mixture adsorption in kerogen, because they do not require assumptions on the fluid–solid interaction energy distribution. We then propose modifications to include fluid non-ideality that can be generalized, independently of the system or structure studied.

We discuss in Section 2 the force fields and the process used to generate controlled adsorbent structure of kerogen and characterize their porous volume and pore size distribution. In Section 3, we propose to derive the Extended Langmuir model from a statistical mechanics. We also detail the basic concepts of the Ideal Adsorbed Solution theory. In Section 4, we discuss the comparison of the simulation data and the results predicted by the EL and IAS model. This section is split in two parts: first we discuss the results obtained at low pressure (from 0.1 to 1 MPa), where the fluids and mixtures can be considered as ideal. Secondly, we extend our work to higher pressure (up to 20 MPa) and discuss about the limitations of the ideal mixture model and the ways to reintroduce the non-ideality of the gases. Conclusions of this work are given in Section 5.

## 2. Generation and characterization of kerogen structures

### 2.1. Force fields

Force fields are defined as a set of rules and parameters used to estimate interaction energies (MC) or forces (MD) between interacting particles. In this work, we take into account non-bonded interatomic dispersion/repulsion interactions ( $U_{disp/rep}$ ), electrostatic interactions ( $U_{el}$ ) and intramolecular interactions ( $U_{int}$ ). The total potential, is the sum in this three contributions ( $U = U_{disp/rep} + U_{el} + U_{int}$ ). The all atom pcff+ [20] force field was used for the MD simulations with the Waldman and Hagler [21] combining rules. The TraPPE [22] force field and Möller et al. [23] force field for methane are used for MC simulations with Lorentz–Berthelot [24]. Both force fields are well known for their ability to reproduce with a high accuracy the thermodynamic properties of organic compounds.

### 2.2. Kerogen models

Kerogen is defined as insoluble part of the sedimentary organic matter present in shale reservoirs [25]. Depending on its origin and the burial history of the reservoir, the chemical or topological structure of kerogen samples may strongly differ [26]. Kerogen generation occurs during the maturation of unconsolidated sediments. There are three different types depending on their origin (type I: algal, type II: liptinitic, type III: humic), leading to different elementary composition [27]. Kerogens share similarities with pyrobitumen, coals or asphaltenes depending on their maturity [28,29]. The kerogen molecular model used for this work published by Yiannourakou et al. [10] is based on structural and elemental analysis published from Kelemen et al. [30]: this model mimics a generic type II mature kerogen at the end of the catagenetic process, where chemical composition of the three different sources tends to converge to coals like structure made of polyaromatic clusters [30]. This kerogen is supposed to be a standard of a generic kerogen that can be encountered in mature shale as in the Barnett [31]. The global structure is amorphous but polyaromatic cluster tends to stack in parallel ( $\pi$  stacking) or orthogonal planes [32]. As stacking increases the kerogen density, we used it as a criterion to check the consistency of the supra-molecular structures obtained from molecular simulations.

#### 2.2.1. Building a kerogen molecule

Several attempts have been made in the literature to represent the chemical structure of kerogen depending their type and burial history [33,28] or by predicting the chemical structure of kerogen using molecular simulation and reactive force fields [34]. Our model is based on data from the literature (chemical structure, elementary analysis and physical properties). First, model fragments (polyaromatic units) of kerogen are created which have the following characteristics (see Fig. 1a): H/C ratio from 0.5 to 0.8, O/C ratio from 0.05 to 0.1, and poly-aromatic cluster composed of 4–6 benzene rings with few short lateral alkyl chains. Then, macromolecules of kerogen are created by linking 4–5 cluster units. The molecular weight is approximately 1200 g/mol, quite low for such compounds [35,36] but adequate to describe the basic features of these systems at a reasonable cost. Examples of such cluster units and kerogen molecules are shown on Fig. 1b. Such a workflow has been previously followed by Facelli et al. [37] to study the interaction of less mature type I kerogen and asphaltenes with the inorganic matrix present in shales.

#### 2.2.2. Creation of an adsorbent structure

We created dense kerogen structures with the following process: first kerogen molecules are relaxed individually (random

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