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# Hydrogen storage in a series of Zn-based IRMOFs studied by Sanchez–Lacombe equation of state

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ABSTRACT

In this work, the adsorptive behaviors of molecular hydrogen in 10 different isoreticular metal-organic frameworks, namely, IRMOF-1, -2, -3, -6, -8, -10, -11, -13, -18 and -20 have been studied using Sanchez–Lacombe equation of state. Sanchez–Lacombe equation of state has three characteristic parameters: characteristic density, characteristic pressure, and characteristic temperature which have been calculated from group contribution procedure. The amount of hydrogen uptake in IRMOFs has been obtained through gas-adsorbents phase equilibrium calculations at temperature 77 K and various pressures up to $80 \times 10^5$ Pa. Finally, the results have been compared with the experimental data to show the precision of SL equation of state in predicting the hydrogen sorption data.

## Introduction

The rapid consumption of petroleum deposits and severe environmental impacts caused by burning fuel cells have driven the global research community to look for an alternative power source that is clean and sustainable [1,2]. Among many emerging new sources in the future, hydrogen is probably the best candidate [3–5]. However, the main bottleneck of hydrogen fuel cells is developing efficient, economic and safe hydrogen storing systems [6–8]. Without the new hydrogen storage system, it is difficult to switch to the hydrogen fuel cell engine because the existing hydrogen storage systems including compression orcryogenic storage are not economically viable and difficult to implement [9]. There is a third potential solution for hydrogen storage such as hydrogen adsorption in a new class of microporous adsorbents named Metal Organic Frameworks (MOFs). Application of these functional materials is now a focus of considerable research due to their greater surface area and pore volumes [10–13]. Among all MOFs, Isoreticular Metal Organic Frameworks (IRMOFs) are a branch of MOFs which reticulated through the connection of octahedral $Zn_4O(O_2C-)_6$ secondary building units, resulting in frameworks based on the same primitive cubic topology. The alteration of linear ditopic carboxylate ligands has been shown to improve the hydrogen uptake level through the controlling specific surface area and pore sizes in the framework. In this study, IRMOF-1 prepared from benzene-1,4-dicarboxylic acid (BDC) and its bromo-, amino- and dihydrocyclobuta-derivatives i.e. IRMOF-2, -3 and -6 are viewed [14]. Other designs such as IRMOF-8 with naphthalene-2,6-dicarboxylate (NDC) organic linker can also be wielded by the extension of the length between the metal centers leading to large void regions [15,16]. When the length of the linker

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reaches two phenyl rings as biphenyl-dicarboxylate (BPTC) in IRMOF-9 [14], interpenetration i.e. filling the void in one net by another net passing through it, is observed. The degree of interpenetration can be as high as fourfold when the linker contains a linear quarter-phenyl chain as 4,5,9,10-tetrahydropyrene–2,7-dicarboxylate (HPDC) in IRMOF-11 [15,16] and pyrene–2,7-dicarboxylate (PDC) in IRMOF-13 [14].

An organic ligand with four methyl functional groups, 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate (TMBDC), is considered in IRMOF-18 to study the effect of pore volume occupation [16]. Heteroatoms can be also incorporated in the aromatic backbone of the organic links, by using thieno[3,2-b] thiophene-2,5-dicarboxylic acid (TTDC) as the precursor IRMOF-20 [14].

Calculating the thermodynamic properties of gaseous processes such as exergy analysis has been performed for air, nitrogen and oxygen using three kinds of cubic equations of state [17]. Investigation on the solubility of gases in organic frameworks through the equation of state (EoS) was started in our group by publishing the work on the sorption of $CO_2$, $C_2H_2$ and $C_2H_4$ in hydrogen-bonded organic framework (HOF-1a) using Perturbed Hard Sphere Chain Equation of State (PHSC EoS) [18]. This model has been also adopted to predict the hydrogen [19] and methane [20] storage in five adsorbents including MOF-5, MOF-177, MOF-200, MOF-205 and MOF-210. In this work, the Sanchez–Lacombe (SL) equation of state has been employed to examine its capability for interpreting hydrogen sorption data in above-mentioned macromolecules. The well-known lattice-fluid model of SL has been previously applied to describe properties of binary or multi-component ordinary compounds and polymeric systems [21–24]. For gas solubility prediction, the knowledge of three characteristic parameters, i.e. the characteristic density, $\rho^*$, the characteristic pressure, $P^*$, and the characteristic temperature, $T^*$, is required. These parameters have been calculated for both hydrogen molecules and IRMOFs in order to use as scaling constants to correlate sorption data. Comparison of experimental and theoretical coexistence curves shows that SL EoS works very well in predicting hydrogen sorption behavior.

## Theory

Sanchez–Lacombe EoS is based on lattice-fluid theory that treats the polymer chains as a set of interacting beads in a lattice. Following the original developments of Sanchez and Lacombe the general SL EoS can be written as [25,26]:

$$\bar{\rho}^2 + \bar{P} + \bar{T}\left[\ln\left(1-\bar{\rho}\right) + \left(1-\frac{1}{r}\right)\bar{\rho}\right] = 0 \tag{1}$$

where $\bar{\rho}$ is the reduced density, $\bar{P}$ the reduced pressure and $\bar{T}$ the reduced temperature of a pure component. The parameters are reduced by characteristic constants as follows:

$$\bar{\rho} = \frac{\rho}{\rho^*} = \frac{1}{\bar{v}} = \frac{V^*}{V}, \quad \bar{P} = \frac{P}{P^*}, \quad \bar{T} = \frac{T}{T^*} \tag{2}$$

$r$ is a size parameter that represents the number of lattice sites occupied by a molecule and can be related to the molecular weight according to the following equation:

$$r = P^*M/\left(RT^*\rho^*\right) \tag{3}$$

Note that for a high molecular weight polymer the value of $r$ can be considered to be infinite, then $(1/r)$ can be neglected. $T^*$, $P^*$, $\rho^*$ and $V^*$are characteristic parameters which defined as [23]:

$$T^* = \frac{\varepsilon^*}{R}, \quad P^* = \frac{\varepsilon^*}{\nu^*}, \quad V^* = N\left(r\nu^*\right), \quad \rho^* = \frac{M}{r\nu^*} \tag{4}$$

Where $\varepsilon^*$ and $\nu^*$ are the characteristic interaction energy per mer and the close-packed volume of a mer, respectively. $N$ is the number of molecules.

For a polymer-gas mixture it is necessary to use a mixing rule for the calculation of $\nu^*_{mix}$, $\varepsilon^*_{mix}$ and $r_{mix}$ based on the corresponding values of the pure component parameters. There are different types of mixing rules for calculating mixture properties [23]. In this research work, the van der Waals mixing rule has been used for calculating the mixture properties as follows:

$$\nu^*_{mix} = \sum_{i=1}^{N_c}\sum_{j=1}^{N_c}\phi_i\phi_j\nu^*_{ij} \tag{5}$$

where

$$\nu^*_{ij} = \frac{\nu^*_{ii} + \nu^*_{jj}}{2}\left(1 - n_{ij}\right) \tag{6}$$

with the parameter $n_{ij}$ which accounts for the possible deviation of$\nu^*_{ij}$ from the arithmetic mean of the corresponding values,$\nu^*_{ii}$ and $\nu^*_{jj}$, of the pure components. In this work, the value of the interaction parameter $n_{ij}$ was assumed to be equal to zero. Accordingly, the values of$\varepsilon^*_{mix}$ and $r_{mix}$ of the mixture will be obtained by the following equations:

$$\varepsilon^*_{mix} = \frac{1}{\nu^*_{mix}}\sum_{i=1}^{N_c}\sum_{j=1}^{N_c}\phi_i\phi_j\left(\left(\varepsilon^*_{ii}\varepsilon^*_{jj}\right)^{0.5}\left(1-k_{ij}\right)\right)\nu^*_{ij} \tag{7}$$

$$r^{-1}_{mix} = \sum_{j=1}^{N_c}\left(\phi_j/r_j\right) \tag{8}$$

where $k_{ij}$ is a binary interaction parameter which represents the interaction energy between the $i$th and $j$th species in the mixture. $\phi_i$ is the volume fraction of the $i$th component in the mixture that can be expressed in terms of the mass fraction $\omega_i$, the characteristic density$\rho^*_i$ and the characteristic volume $\nu^*_i$ of the pure components:

$$\phi_i = \frac{\omega_i}{\rho^*_i\nu^*_i}\left[\sum_{j=1}^{N_c}\left(\frac{\omega_j}{\rho^*_j\nu^*_j}\right)\right]^{-1} \tag{9}$$

The chemical potential of each component in the two phases, one phase is gas and the other one consists of polymer and the sorbed gaseous molecules, must be set equal at the equilibrium state, i.e. $\mu^G_i = \mu^P_i$. Following the developments of McHugh and Krukonis [27], the chemical potential of the $i$th component in a multi-component system can be expressed as: