



Modeling adsorption equilibria of xylene isomers in a microporous metal–organic framework

Patrick S. Barcia^{a,c}, Marco P.M. Nicolau^a, Jose M. Gallegos^b, Banglin Chen^b, Alırio E. Rodrigues^{c,*}, Jose A.C. Silva^{a,*}

^a Escola Superior de Tecnologia e Gestao, Instituto Politecnico de Braganca, 5301-857 Braganca, Portugal

^b Univ. Texas San Antonio, Dept. Chem., San Antonio, TX 78249, USA

^c Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Quımica, Faculdade de Engenharia, Universidade do Porto, Rua do Dr. Roberto Frias, S/N, Portugal

ARTICLE INFO

Article history:

Received 13 December 2011

Received in revised form 19 January 2012

Accepted 20 January 2012

Available online 6 February 2012

Keywords:

Metal–organic framework

Xylene isomers

Adsorption equilibrium

Dual-Site Langmuir model

Isosteric heat of sorption

ABSTRACT

Single and multicomponent adsorption equilibria of xylene isomers: *o*-xylene (*o*-x), *m*-xylene (*m*-x), *p*-xylene (*p*-x) and ethylbenzene (eb) was investigated on the three dimensional microporous metal–organic framework Zn(BDC)(Dabco)_{0.5} (BDC = 1,4-benzenedicarboxylate, Dabco = 1,4-diazabicyclo[2.2.2]-octane), MOF **1**, in the range of temperatures between 398 and 448 K and partial pressures up to 0.1 bar. The equilibrium data show that a significant amount (around 34 g/100g_{ads} at 398 K) of xylene isomers can be adsorbed in MOF **1**. The affinity to the adsorbent measured by the Henry's constants decreases in the order *o*-x > *m*-x > eb > *p*-x for all temperatures. The zero coverage adsorption enthalpies are all similar and range from 77.4 (eb) to 79.8 kJ/mol (*o*-x). The Dual-Site Langmuir model (DSL) was used for the interpretation and correlation of the experimental data. The parameters obtained from the pure component isotherms fitting were also used to predict the multicomponent equilibrium data by an extended DSL model. A good agreement was obtained between the predictions and the experimental data. It was also demonstrated that the DSL model is also capable to explain the increase in the isosteric heat of sorption with increasing coverage.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The benzene homologs of general formula C₈H₁₀ are generally known as mixed xylenes. The mixture of isomers mainly consists of the three isomeric dimethylbenzenes (*ortho*-, *meta*-, and *para*-xylene) and ethylbenzene. The feedstocks used for xylene production give rise to a mixture containing the four isomers [1].

Para-xylene has by far the largest market of the three isomers. *p*-x is mainly oxidized to terephthalic acid, which can be esterified to dimethyl terephthalate (precursor for polyesters). *o*-x is oxidized to phthalic anhydride (precursor for plasticizers) and *m*-x to isophthalic acid (precursor for polyesters). EB is dehydrogenated to styrene, which is converted to polystyrene and other polymers [1,2].

These isomers boil so closely together that separating them by conventional distillation is not feasible [2]. Actually, the separation of high-purity *p*-x from a mixture of mixed xylenes is industrially performed by three main processes: crystallization, adsorption, and a hybrid crystallization/adsorption process [3]. However, about 60% of the *p*-x produced worldwide is by adsorption technology.

Adsorption processes are operated using Simulated Moving Bed technology (SMB), which allows a continuous separation, using zeolites exchanged with cations such as Na⁺, K⁺, Ba²⁺ [2,4–11]. This process is being studied and simulated in order to provide tools for process understanding, operations and optimization [3,9,12–16]. Those authors have also investigated a Simulated Moving Bed Reactor (SMBR) applied for *p*-xylene production, combining xylene isomerization and selective adsorption operating in liquid phase [17,18].

Porous metal–organic frameworks (MOFs) are crystalline microporous materials and consists of small metal-containing clusters connected three dimensionally by organic ligands. Contrasting to zeolites, which have pores confined by tetrahedral oxide skeletons, the pores within MOFs can be systematically varied by the judicious choice of the metal-containing and/or organic ligands [19]. Due to their unusual features, MOFs are considered promising materials for gas storage, adsorption separations and catalysis [20–32].

Despite the large interest in xylene separations and the potential of MOFs for adsorption separations, experimental data about xylene separation using MOFs are almost inexistent. The few studies found in the literature show promising results. Alaerts et al. [33] demonstrates the first successful use of MOF as selective adsorbent for this difficult task. Vapor-phase experiments carried out by Finsy et al., showed that the selectivity of MIL-47 increases

* Corresponding authors. Address: Campus de Santa Apolonia, Apartado 134, 5301-857 Braganca, Portugal. Tel.: +351 273 303 125; fax: +351 273 313 051.

E-mail address: jsilva@ipb.pt (J.A.C. Silva).

Nomenclature

b	Langmuir constant or adsorption affinity constant, Pa ⁻¹	q_s	saturation capacity of each type of sites, respectively, g/100g _{ads}
b_0	frequency factor of the affinity constant, Pa ⁻¹	N	total number of measurements, dimensionless
ΔH	heat of adsorption, kJ/mol	R	ideal gas constant, Pa m ³ mol ⁻¹ K ⁻¹
ΔH_{st}	isosteric heat of sorption, kJ/mol	T	temperature, K
n	number of active sites of adsorption, dimensionless		
q	amount adsorbed, p is the pressure of sorbate, g/100g _{ads}		

with the degree of pore filling, due to efficient packing effects [34]. Alaerts et al. have investigated MIL-53 and found that this MOF is ortho-selective [35]. Ramesh et al. [36], have carried out effectively the separation of *o*-*x*/*p*-*x* mixture using the hydrotropy technique. This technique is used to separate near boiling point isomeric/non-isomeric mixtures and its possible mechanism of separation effect of hydrotropes may be due to the formation of organized aggregates of hydrotrope molecules at a critical concentration.

Recently, Nicolau et al. [37] have shown that the separation of *o*-*x* from the other C₈ components in Zn(1,4-BDC)(Dabco)_{0.5} MOF, denoted as MOF **1**, is quite efficient. “BDC” denotes 1,4-benzenedicarboxylate and “Dabco” denotes 1,4-diazabicyclo[2.2.2]-octane. For the adsorbates in this study, the structure of MOF **1** is in effect a one-dimensional channel system, despite the three dimensional structure, and is thermally stable. Dubbeldam et al. have reported that MOF **1** presents two energetically different sites of adsorption [38].

This work focuses on the experimental and modeling of the single and multicomponent adsorption equilibrium data of C₈ isomers in MOF **1** structure. The pure component experimental data was fitted with the Dual-Site Langmuir model (DSL), and then the model was extended to predict the multicomponent sorption data. Thereafter, the DSL model was used to predict the variation of isosteric heat of sorption with the coverage.

2. Experimental section

2.1. MOF **1** structure

As revealed in the X-ray single-crystal structure by Kim et al., MOF **1** is constructed of paddle-wheel Zn₂(COO)₄ clusters bridged by BDC dianions and Dabco pillar linkers to form a three-dimensional framework of a primitive cubic (α -Po) net. There exist two types of intersecting channels of about 7.5 × 7.5 Å along the *a*-axis and channels of 3.8 × 4.7 Å along *b* and *c* axes, respectively (Fig. 1) [39].

Due to the large kinetic diameters of the adsorbates (see Table 1), it is expected that they can go only through the large channels of 7.5 × 7.5 Å along *a*-axis. MOF **1** was synthesized according to the procedure described by Kim et al. The information about experimental setup and procedure is reported elsewhere [40,41].

2.2. Xylene isomers structure

Fig. 2 shows an approximate three dimensional structure of xylene isomers. From the view along the [100] axis it can be clearly seen that their molecular structure is very similar. The difference lies in where the two methyl groups are attached to the benzenic ring. Counting the carbons atoms from one of the ring carbons bonded to a methyl group, and counting towards the second ring carbon bonded to a methyl group, the *o*-isomer has the IUPAC name of 1,2-dimethylbenzene, the *m*-isomer has the name of 1,3-dimethylbenzene, and the *p*-isomer has the name of 1,4-dimethylbenzene. *eb* has one ethyl group attached to the benzenic ring. All

the C₈ alkylaromatics used in this work were of analytical grade purchased from Sigma–Aldrich.

2.3. Adsorption equilibrium apparatus

The experimental data was obtained in an apparatus developed at the LSRE for the measurement of single and multicomponent breakthrough curves consisting of three main sections. The preparation section includes a syringe pump used to introduce the adsorbable species in the carrier gas followed by a heating chamber where this stream is completely vaporized. The adsorption section consists of a stainless steel column ($L = 100$ mm, $d_i = 4.6$ mm) packed with MOF **1**, placed in a ventilated chromatographic oven, as well as a heated 10 loops sample collector, to collect samples at the outlet of the column. The third part is an analytical section composed by a chromatographic column and a flame ionization detector (FID).

The adsorption column was operated by introducing continuously a known composition of hydrocarbons in a helium stream of minimum purity 99.999% (ALPHAGAZ 1, Air Liquide, France). A flame ionization detector measures the concentration history at the outlet of the packed bed. During the multicomponent experiments, a 100 μ l-loop collector is used to trap samples from the effluent of the column. After the saturation is reached, the composition of the collected samples is evaluated by chromatography using a 2 m long, 2 mm ID, Chromosorb W-HP packed column 5% Bentone 34, 5% SP-1200 on Chromosorb 100/120 mesh (Restek Corporation, Bellefonte, PA, USA). Complete information about the experimental apparatus and operating procedure is reported elsewhere [40,41].

3. Modeling adsorption equilibrium

For the development of an adsorptive process, it is essential to obtain a good analytical description of the experimental sorption data. Dubbeldam et al. [38] have reported using grand canonical Monte Carlo simulations (GCMC), that MOF **1** presents two energetically different sites of adsorption. At low loading, the bulkier molecules adsorb along the 7.5 × 7.5 Å 1D channels, preferentially near the “boxes” formed by the “BDC” ligands. At high loadings, they adsorb within those “boxes”. Therefore, to model equilibrium sorption data we decided to make use of the DSL model, which distinguishes two categories of sorption sites, each one following a Langmuir behavior, reflecting in this way the heterogeneity of the adsorbent. This model was used successfully to predict pure component data of several alkanes in zeolites [42–45]. The adsorption isotherm is

$$q(p, T) = q_A + q_B = q_s^A \frac{b^A(T)p}{1 + b^A(T)p} + q_s^B \frac{b^B(T)p}{1 + b^B(T)p} \quad (1a)$$

where q is the amount adsorbed, p is the pressure of sorbate, b and q_s are the adsorption affinity constant (Langmuir constant) and the

Download English Version:

<https://daneshyari.com/en/article/73889>

Download Persian Version:

<https://daneshyari.com/article/73889>

[Daneshyari.com](https://daneshyari.com)