Journal of Molecular Liquids 252 (2018) 399–407

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Adsorption process of *n*-alkanes onto BAX-1100 activated carbon: Theoretical estimation of isosteric heat of adsorption and energy distribution of heterogeneous surfaces

Manel Bergaoui [a], Asma Nakhli [a], Shaheen Al-Muhtaseb [b], Mohamed Khalfaoui [c,*]

[a] University of Monastir, Faculty of Sciences, Laboratory of Quantum Physics Research UR11ES54, Monastir 5000, Tunisia
[b] Qatar University, Department of Chemical Engineering, P.O. Box 2713, Doha, Qatar
[c] University of Monastir, Higher Institute of Computer Sciences and Mathematics of Monastir, Department of Technology, Monastir 5000, Tunisia

ARTICLE INFO

Article history:
Received 7 November 2017
Received in revised form 28 December 2017
Accepted 3 January 2018
Available online 04 January 2018

Keywords:
Activated carbon
n-Alkanes
Heterogeneous surface
Isosteric heats
Statistical physics approach
Adsorption energy distribution

ABSTRACT

Adsorption of the *n*-alkane series, C_1–C_7, on Westvaco BAX-1100 activated carbon were measured over very broad ranges of temperature (293–393 K) and pressure (0.06–4964 Torr), depending on the *n*-alkane. Different behaviors of experimental adsorption isotherms were observed where various steps were noticed depending on the adsorbate length. A heterogeneous Gauss-monolayer model was developed based on statistical physics approach to evaluate the adsorption energy distribution (AED). Surface heterogeneity was evaluated and confirmed from isosteric heat of adsorption; where the adsorption of longer *n*-alkanes is energetically more favorable. A new equation was obtained from AED analysis to calculate the isosteric heat of adsorption. A notable difference between the adsorption isosteric heats estimated from AEDs and those obtained from classical Clausius-Clapeyron equation was observed at very low and high capacities. This difference was explained by the fact that, the gas behaves non-ideally at high pressure range. On the other hand, the absolute percentage deviation in adsorbed phase heat capacity was evaluated from the isosteric heat of adsorption predicted from the AED analysis. This percentage deviation increases when increasing the chain length of the alkane.

1. Introduction

Activated carbon studies as potential natural gas storage medium have been commonly reported for different kinds of carbon materials [1–3], usually focusing on methane as the major constituent of natural gas [4]. Several authors studied the adsorption of *n*-alkanes on activated carbon, using available standard commercial carbons [5–7]. *n*-Alkanes are important constituents of organic matter and are commonly distributed in the environment [8–12].

The interest and applications of activated carbon relies on their surface properties and porous structure, where the surface heterogeneity has direct implications on its adsorption properties [13–16]. The term “surface heterogeneity” is a well-established concept in surface science, which always refers to a specified adsorption system (adsorbate/adsorbent) [17]. It is related to the lack of geometric and energetic uniformity of actual solid surfaces. The heterogeneity of adsorbents is essentially attributed to their surface characteristics, such as pore shapes and pore size distributions, whereas the contribution of adsorbate molecules is their shapes, sizes, and conformations [18,19]. The heat amount released per molecule added to the adsorbed phase at constant temperature and capacity is widely known as the isosteric heat of adsorption [20,21]. This thermodynamic parameter can be calculated by applying the Clausius-Clapeyron equation onto adsorption isotherms measured at different temperatures [22]. The reliable estimation of the isosteric heat of adsorption, and also the adsorbed-phase heat capacity, provide significant information about the physical characters of specific adsorption systems, including adsorbent surface heterogeneity and adsorbate-adsorbate lateral interactions [23].

In this context, the aim of this work is to provide a description of structural energetic heterogeneity of BAX-1100 activated carbon by evaluating the adsorption energy distribution (AED) function, $f(\varepsilon)$. The majority of studies that describe the surface heterogeneity utilize several local adsorption isotherm models suggesting, Langmuir [24,25], Fowler Guggenheim (FG) [26], BET [27] and others [28]. In the present work, the AEDs are obtained from integral equation with a monolayer model as local isotherm [29–37]. Such model has proven useful to make new insights for the microscopic interpretations of the adsorption process [33]. Specifically, the experimental adsorption isotherms obtained for

---

* Corresponding author.
E-mail address: mohamed.khalfaoui@isimm.rnu.tn (M. Khalfaoui).

https://doi.org/10.1016/j.molliq.2018.01.016

the normal alkane series C_1–C_7 over a wide range of temperatures and pressures on Westvaco BAX-1100 activated carbon [6] are correlated with the developed integral equation model. Therefore, the corresponding heats of adsorption and adsorbed-phase heat capacities are predicted from the integral expression of AED analysis adapted to heterogeneous model. This heat of adsorption is compared to that calculated directly from Clausius-Clapeyron equation. The comparison between isosteric heat of adsorption resulting from the integral equation model versus that resulting from the monolayer adsorption model is evaluated and discussed.

2. Experimental

The materials and experimental study description of *n*-alkanes adsorption onto BAX-1100 activated carbon were presented in a previous publication [6]. Methane, ethane and *n*-butane were obtained from National Welders. Propane was received from Matheson Gas Products, Inc. *n*-Pentane and *n*-heptane were >99% pure and were obtained from Alfa AESAR, whereas *n*-hexane (>99%, pure) was obtained from sigma Chemicals Company. All of these adsorbates were used as received. The BAX-1100 activated carbon was collected from Westvaco in the form of pellets and used as received, except for regeneration [6].

Adsorption isotherms of *n*-alkanes on BAX-1100 activated carbon were measured gravimetrically using a VTI integrated microbalance system driven with in-house-developed National Instruments LabView hardware and software [6]. Further experimental details are described by Charles et al. [6].

3. Methodology

In this work, the statistical mechanics approach is used to simulate the adsorption of *n*-alkanes on heterogeneous BAX-1100 activated carbon surface. Indeed, the degree of heterogeneity has been described in terms of the adsorption energy distribution (AED) and the variation of isosteric heat of adsorption with respect to surface coverage [18,38]. Essentially, the heterogeneity of adsorbents is attributed to their surface characteristics, like pore shapes and pore size distributions, whereas the contribution of adsorbate is its molecular shape, size, and conformation [18,19].

The AED of heterogeneous surface can be easily determined form the theoretical isotherm representing the experimental equilibrium data. This requires the solution of the adsorption integral equation [39,40] to generate the corresponding affinity distribution (Eq. (1)):

$$Q_a(\varepsilon, T, p) = \int_D \theta(\varepsilon, T, p) f(\varepsilon) d\varepsilon \tag{1}$$

where Q_a (mol/kg) as the adsorbed quantity, D is the physical domain of adsorption energies that exist at the gas solid interface, θ is the local isotherm and $f(\varepsilon)$ represents the AED function.

Then, a majority of studies use the patchwise heterogeneity model [18,19,41], suggesting Langmuir model as local isotherm [42,43]. In this work, we used the monolayer model [33] as local isotherm developed from statistical physics approach to evaluate the surface heterogeneity. Indeed, we propose here a new method which is more accurate and flexible then existing alternatives. For this goal, it was demonstrated that statistical physics approach is a powerful tool to establish flexible models [29–33,44–46]. The heterogeneity has been evaluated from both adsorption energy distribution and isosteric heat of adsorption as will be presented in the following sections.

3.1. Adsorption energy distribution (AED)

In this section, we develop a theoretical approach that considers both surface heterogeneity and multi-step isotherms shape. The AED function was calculated from Eq. (1).

As a local adsorption isotherm, we use a monolayer model (Eq. (2)) where we present here just its equation; statistical physics approach details are reported elsewhere [30,31,33,44,45]:

$$Q_a\left(\frac{p}{p^0}\right) = \frac{n \times N_m}{1 + \left(\frac{p_{1/2}}{p}\right)^n} \tag{2}$$

where n is the number of adsorbed molecule(s) per site and N_m is the receptor sites density. $p_{1/2}$ is the half-saturation pressure which expressed as $p_{1/2} = p^0 e^{\frac{\Delta E^a}{RT}}$, where p^0(Torr) is the saturated vapor pressure, ΔE^a(kJ/mol) is the molar adsorption energy, R (0.008314 kJ/K · mol) is the universal gas constant and T (K) is the absolute temperature.

This last equation can be rewritten as follows [31]:

$$Q_a\left(\frac{p}{p^0}\right) = \frac{n \times N_m}{1 + e^{\frac{\varepsilon}{RT}}\left(\frac{p^0}{p}\right)^n} \tag{3}$$

where $\frac{p}{p^0}$ is the relative pressure and ε (kJ/mol) is the adsorption site energy.

Eq. (3) has been extended for predicting the adsorption energy distribution as AED function *f(ε)*. The most commonly used form of adsorption energy distribution is a Gaussian function:

$$f(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}}\, exp\left(-\frac{(\varepsilon - \varepsilon_m)^2}{2\sigma^2}\right) \tag{4}$$

with ε_m(kJ/mol) as the most probable energy, $\mathcal{E}$(kJ/mol) is the adsorption site energy and σ(kJ/mol) as the dispersion of the Gaussian distribution, which allows us to indicate the degree of heterogeneity for the model materials [47].

Finally, the integral equation that uses the monolayer model as local isotherm to fit our experimental data can be written as follows:

$$Q_{ia-GM}\left(\frac{p}{p_i^0}\right) = \frac{n_i \times N_{im}}{\sigma_i\sqrt{2\pi}} \int_{\varepsilon_{imin}}^{\varepsilon_{imax}} \frac{exp\left(-\frac{(\varepsilon_i - \varepsilon_{im})^2}{2\sigma_i^2}\right)}{1 + e^{\frac{\varepsilon_i}{RT}}\left(\frac{p_i^0}{p}\right)^n} d\varepsilon_i \tag{5}$$

where ε_{imin} and ε_{imax} are the minimum and the maximum of energy, respectively, and i is the index of a given step.

Then, the AED are obtained by the fitting procedure of the adsorption equilibrium data with the Gauss-monolayer model (Eq. (5)) using the Solver add-in of Microsoft Excel (Microsoft Corporation, 2007), which is based on the Generalized Reduced Gradient algorithm with nonlinear optimization. This fitting procedure was made by minimizing the sum of the squares of the errors (ERRSQ) [48]:

$$ERRSQ = \sum_{i=1}^{j} (Q_{calc} - Q_{meas})_i^2 \tag{6}$$

where Q_{calc} is the theoretical amount adsorbed, which has been calculated with the local isotherm models, Q_{meas} is the experimentally determined amount adsorbed, i is the data point number, and j is the total number of data points.

The corresponding absolute relative error (ARE) values were estimated from Eq. (7) [49] and the optimum fitting parameters, namely,