Applied Thermal Engineering 105 (2016) 189–197

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

Thermodynamic trends for the adsorption of non polar gases on activated carbons employing a new adsorption isotherm modelling

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HIGHLIGHTS

- Development of a novel adsorption isotherm equation.
- Behaviors of non-polar gases on activated carbons.
- Minimum RMS errors are obtained between the model and the experimental data.
- Enthalpy and entropy of adsorbent – adsorbate system are closely related to the kinetic diameter of adsorbate molecules.
- The model captures adsorption for more than one molecule.

ARTICLE INFO

Article history:
Received 15 March 2016
Revised 19 May 2016
Accepted 26 May 2016
Available online 27 May 2016

Keywords:
Activated carbons
Adsorbate sizes
Adsorption
Non-polar gases
Thermodynamic framework

ABSTRACT

In this paper, the author reports a thermodynamic framework for understanding the surface – energy and the surface – structural interaction factors of activated carbons with various non polar adsorbate molecules. For better understanding, the author employs adsorption uptakes data of activated carbons and some non-polar gases such as H_2, Ar, N_2, CO_2, O_2 and CH_4 to calculate the enthalpy and entropy of adsorption in pressure-temperature-uptake coordinate systems. The RMS errors are calculated with respect to the proposed model and the experimental data. The minimum RMSEs are found as the model fits well with the experimental data. From theoretical observations, the heterogeneity factors (m) are obtained 1 for microporous and 2 for mesoporous activated carbons, and the interactions of non-polar gases on activated carbons are found to be more sensitive to the adsorbent pore geometry and the adsorbate size. It is also established that the enthalpy and entropy of adsorbent – adsorbate system are closely related to the kinetic diameter of adsorbate molecules, and the pore size equivalent to adsorbate kinetic diameter is the key to store more adsorbate at low pressures. For example, the pore width of activated carbon is roughly maintained 3.8 Å for more methane storage and 3.3 Å for more CO_2 captures.

1. Introduction

With increasing concerns over the global warming potentials, the augmented energy demand and the CO_2 emissions, the interests in gas storage, CO_2 capture and heat transmission technology have been grown rapidly. Adsorption phenomena are well known to mankind and they are increasingly utilized to perform separation process, purification of gases, adsorption chiller, cryocooler design, hydrogen driven vehicle and more recently gas storage [1–6]. The physical adsorption process occurs mainly within the pores of adsorbent and external adsorbent surface, and it requires the knowledge of adsorbent – adsorbate and adsorbate – adsorbate interactions over wide ranges of pressures and temperatures. The mass of adsorbate uptakes on porous adsorbents depends on the nature of adsorbates and porous adsorbent structure. For higher adsorptive capacity, the adsorbents should have very high surface area and high micropore volume with an optimal pore width that varies from super micropore to mesopores [7,8]. The porous medium is naturally associated with very small pores, and during adsorption, the adsorbate molecules move into the interior surface area or the pore volume. Therefore, the path finding provides the concept of adsorbent – adsorbate interaction factors. These interaction factors are related to the enthalpy and the entropy of adsorption. Understanding the thermodynamics of adsorptive capacity, the nature of adsorbent surface and the adsorbate interactions within the adsorbents pores, a thermodynamic framework is obliged to be developed and formulated.

In a physisorption of an adsorbate onto micro, meso and macropore surfaces of an adsorbent, the adsorption force field is held in

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http://dx.doi.org/10.1016/j.applthermaleng.2016.05.160
1359-4311/

Nomenclature

M	no of distinguishable sites
n	number of adsorbate molecules in one site
m	number of maximum molecules in one site
m	heterogeneity factor
N	number of molecules bound to M sites
Q	canonical partition function
q(n)	the site partition function for n molecules
q(1)	the site partition function for one molecule
λ	absolute activity
μ	chemical potential
k	Boltzmann constant
Ξ	grand canonical partition function
a_n	the number of sites having n molecules
a_m	the number of sites having m molecules
$\xi(\lambda, T)$	grand partition function of each individual adsorptive site
ΔG^o	Gibbs free energy
ΔH^o	enthalpy of adsorption
ΔS^o	entropy of adsorption
K	binding constant
M_s	mass of adsorbent
m_a	mass of adsorbate
V	total volume
m_{rec}	mass of adsorptive gas in the adsorption cell
m_{char}	mass of adsorptive gas in the charging cell
m_{red}	mass of residual gas in the adsorption cell
ρ	density of adsorptive gas
n	number of experimental data of RMSE equation
i	experimental data range (vary from 1 to any number n)
θ	surface coverage\
c	the amount of adsorbate uptake
c^o	the limiting uptake

Subscripts

gas	gaseous phase
ext	external adsorbate wall
exp	experimental data

the adsorbent pores by the existence of van der Waal force for the pressures ranging from the Henry's region (pressure, P → 0) to the saturated pressure. However the adsorption force distribution at Henry's region is narrower than at higher pressures. This means that the adsorbate molecules can attract the pores of adsorbents independently with high energies, and the heat generated during adsorption process depends on pore structures and the applied pressures on the adsorbent-adsorbate system. So the knowledge of heat of adsorption for a molecule can help in the design of new materials with different pore widths [9]. On the other hand, the entropy of adsorbed phase is linked with the binding or repulsive forces and is also associated with the spatial arrangements at the adsorbate – adsorbent interface. Thus the adsorption is related to the "enthalpy – entropy" compensation phenomenon [10]. Up to now, extensive works have been done to develop the formulations of adsorption isotherms such as Langmuir, Toth, Dubinin, Freundlich, and Sips for understanding adsorption phenomenon [11]. Brunauer et al. [12] generalized Langmuir's work for multilayer adsorption situation with five classical types of adsorption uptakes. Employing micropore filling theory, Polanyi defined the adsorption potential from differential molar work of adsorption [13], and following this theory, the amount of adsorbate uptakes as a function of pressure and temperature were developed [14,15]. Employing the adsorbate uptake formulation and the thermodynamic equation of states for adsorbent-adsorbate system, Chakraborty et al. [16,17] calculated an estimation of various shapes of isosteric heat of adsorption as a function of adsorbate uptakes. In one study, Srinivasan et al. [18] proposed a hypothesis for the calculation of adsorbed phase volume employing over 50 combinations of experimentally measured activated carbons and various adsorbates data and the Dubinin-Astakhov equation.

The selectivity of adsorption sites is based on the steric constrains defined by the adsorbent pore geometry and the size of the adsorbate as a dominant factor. So it is important to establish the relationships between the enthalpy of adsorption and the kinetic diameter of adsorbate as they provide necessary information about the affinity of adsorbent – adsorbate interactions. This paper aims to develop a thermodynamic framework that calculates the amount of adsorbate uptakes with the enthalpy-entropy compensation effects. The main feature of the proposed model is that it allows adsorption for more than one molecule per adsorption site with a better theoretical foundation. The proposed model is fitted with a good number of experimentally measured carbonaceous adsorbents + non-polar adsorbates isotherms data to find (i) the compensation effects between enthalpy (ΔH^o) and entropy of adsorption (ΔS^o), and (ii) the surface-structural heterogeneity factor. Employing the data of ΔH^o and ΔS^o, the thermodynamic trends of $\Delta H^o/\Delta S^o$ against adsorbate kinetic diameter are established, i.e. the binding constant (K) of the proposed model can be expressed in terms of kinetic diameter as a general trend for estimating the selectivity of adsorption sites.

2. Theoretical modelling

The present author consider a macroscopie adsorbent system that comprises M equivalent, independent and distinguishable sites, and n number of adsorbate molecules that ranges from 0 to m are adsorbed on each adsorbent site. Here $q(n)$ is the site partition function in which n molecules are bound. From macroscopic viewpoints, if N molecules are bound to the total M sites of the adsorbent, and if the number of sites with n molecules each is a_n, the canonical partition function (Q) for the system of M sites becomes [19]

$$Q(N, M, T) = \sum \frac{M! q(0)^{a_0}\, q(1)^{a_1} q(2)^{a_2} \ldots q(m)^{a_m}}{a_0 a_1 a_2 \ldots a_m},$$

where $M = \sum_{n=0}^{m} a_n$ and $N = \sum_{n=0}^{m} n a_n$. By definition, the grand canonical partition function of all sites is defined as $\Xi = \sum_{N=0}^{m,M} Q(N, M, T)\lambda^N$, where the absolute activity is given by $\lambda = \exp(\mu/kT)$. μ the chemical potential of the adsorbed molecules and it comprises the bulk chemical potential μ_{gas} and the external adsorbent wall potential μ_{ext}, or $\mu = \mu_{gas} - \mu_{ext} \approx \mu_{gas}$ [20]. The Ξ can be expressed as

$$\Xi(\lambda, M, T) = \sum \frac{M! q(0)^{a_0} \{q(1)\lambda\}^{a_1} \{q(2)\lambda^2\}^{a_2} \ldots \{q(m)^{a_m}\lambda^m\}^{a_m}}{a_0 a_1 a_2 \ldots a_m}. \tag{1}$$

Employing the concept of multinomial theorem, $\Xi(\lambda, M, T) = \xi(\lambda, T)^M$ [19], where $\xi(\lambda, T)$ defines the grand partition function of each individual adsorptive site and is given by