



An adsorption isotherm equation for multi-types adsorption with thermodynamic correctness

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ARTICLE INFO

Article history:

Received 1 November 2013

Received in revised form

1 April 2014

Accepted 10 April 2014

Available online 2 May 2014

Keywords:

Adsorption

Isotherms

Fermi–Dirac distribution

Langmuir equation

Heterogeneity factor

Load factor

Tóth equation

ABSTRACT

From the perspective of adsorption energy distribution, the Langmuir adsorption isotherm equation is modified and reformulated on the basis of Fermi–Dirac distribution function. The proposed isotherm model including the loading, the adsorbent–adsorbate interaction and the surface structural heterogeneity factors, overcomes the limitations of the existing isotherm models such as Langmuir, Tóth or Dubinin equations. The proposed equation is validated with experimentally measured multi-types of adsorption isotherms according to IUPAC. Non-monotonic adsorption isotherms stemming from Gibbs adsorption could also be described by the proposed adsorption isotherm directly and it is verified with experimental data. The surface energy and structural factors of the modified equation are demonstrated by the energy distribution functions.

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1. Introduction

The adsorption isotherms of gas on the adsorbent surface provide all information needed to study the adsorption equilibrium since both the isobars and the isosteres are obtained from a series of isotherms. The adsorption isotherm can be considered as the experimental piece of information, while the adsorption model is the theory of the adsorption equilibrium. Up to now, extensive works for adsorption isotherms modeling have already been done. Langmuir [1,2] derived, for the first time, an adsorption isotherm equation for energetically homogeneous surface adsorption from the rigor of adsorption kinetics. Later Brunauer, Emmett and Teller [3] generalized Langmuir's work for multilayer adsorption situation and proposed a universal theory of physical adsorption named BET isotherms. Polanyi [4] defined the adsorption potential from the differential molar work of adsorption, and employing this theory, isotherms of micro-pore filling mechanism were developed [5–13], which are known as Dubinin Radushkievich (DR) and

Dubinin Astakhov (DA) equations. Cerofolini [14,15] studied the theoretical foundation of DR equation, and reviewed the mathematical theory of adsorption on heterogeneous adsorbent surface. In 2005, U. von Gemmingen [16] reviewed the integral isotherm equations for heterogeneous surfaces based on Fermi–Dirac function, which is applied as occupation index for mono sites. From Gibbs approach, Guggenheim [17] proposed a general treatment to adsorption with heat and work exchange, and Myers [18] established the thermodynamic framework of adsorption by expressing adsorption thermodynamic properties including Gibbs free energy, enthalpy and entropy. Following these works, Chakraborty et al. developed thermodynamic property fields as a function of pressure, temperature and the amount of adsorbate uptake [19,20], and based on this work an estimation of isosteric heat of adsorption was proposed which is verified against all categories of adsorbent + adsorbate pairs [21].

It should be noted here that the existing classical adsorption isotherms are limited by their individual thermodynamic inconsistency from being used within the complete adsorption isotherm range. For isotherms that are valid at Henry's region, seldom would they be valid at high pressure range, such as Henry, Tóth and Langmuir equations [16,22,23] as to those isotherms perform nicely when pressure reaches saturated value, most of them failed to be consistent with experimental data at low pressure range such as DA and DR equations [10–13].

Abbreviations: DR, Dubinin and Radushkievich equation; IUPAC, International Union of Applied Chemistry; BET, Brunauer–Emmett–Teller theory; SWNT, single-walled carbon nanotube.

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To overcome these limitations, many empirical or semi-empirical isotherms were proposed, including [23]: Tóth, Freundlich, Sips, Unilan, Fowler, and Jovanovich equations, etc. These isotherms are correlated with experimental data to calculate empirical parameters, which gives little or no physical meanings. In general, the more parameters in the model, the better are the fitting results. All of these empirical isotherms are qualified with insufficient physical meanings [24]. In the 1980s, Tóth proposed empirically an isotherm equation based on a power function relation between the adsorption uptake and the surface adsorption potential [25]. Jaroniec and Marczewski also proposed isotherm equation as a power function [26,27]. Nevertheless, it is found that Tóth equation [22] is also incorrect and limited, as this equation fails to explain surface energy distribution as a function of pressure ranging from Henry to the saturated region.

Adsorption on practical adsorbent solid exhibits diverse isotherm shapes. Established by Brunauer et al., isotherms were identified by IUPAC into five classical types [28]. Type I isotherm describes adsorption on microporous adsorbent. Type II represents adsorption on macroporous adsorbent with strong adsorbent + adsorbate interactions, while type III works with the weak interaction. Type IV and V isotherms correspond to mono- and multilayer adsorption with capillary condensation. However, IUPAC classification was established half a century ago based on “absolute” adsorption rather than on Gibbs adsorption. From an up-to-date view points, IUPAC classification is suffered from two deficiencies [29]: (i) with the development of novel adsorbent materials and experimental condition, there are many adsorption isotherms that do not fall into any of IUPAC classes; and (ii) the IUPAC classification ‘gives incorrect impression that adsorption isotherms are always monotonic function of pressure’, while some experimental isotherms show maxima. Currently, almost all existing isotherms are monotonic, and most isotherm theories are able to simulate at most one or two types of adsorption isotherms. Those isotherm models which are capable to deal with more isotherm types, on the other hand, has been proven manifestly difficult to manipulate [15].

In this paper, we point out how the isotherm shape is a source of direct information for adsorbent–adsorbate system. This paper aims at developing an adsorption isotherm formulation, which is valid from the Henry’s region to the saturated region, and is also able to be applied to various adsorption isotherm types within IUPAC classifications or out of it such as Gibbs adsorption. The distribution functions, characterizing the energetic and structural heterogeneity of adsorbents are evaluated from experimentally measured adsorption isotherm data and the proposed isotherm. A comparison study of various isotherms is also performed. The information gap between the conventional isotherm equations and the actual physical adsorption isotherm process is expected to be filled by this work, presented herein.

2. Modified adsorption isotherm model

The driving forces for physical adsorption are predominantly the attractive “dispersion forces” and short range repulsive forces. In addition, the electrostatic forces are responsible for the adsorption of adsorbate molecules by the surface. Altogether, these forces are the van der Waals interaction field between adsorbent–adsorbate pair and could be represented by the Lennard–Jones potential function. From the adsorption isotherm of adsorbent–adsorbate pair, a distribution of adsorption potential can be derived in the form of $\phi = f(r)$, ϕ is the adsorption potential energy and r is the space enclosed by the adsorbate molecule and the adjacent adsorptive site. The relationship is now simplified to be power function, as [30]:

$$\phi = Kr^{-t} \quad (1)$$

where K is the force coefficient, and t is a constant. It should be noted here that t is generally positive as ϕ decreases gradually with increasing r . At far distance ($r \gg r_m$), the magnitude of the interaction potential is negligible, where r_m is the minimum distance between adsorbent adsorbate molecules. If the adsorbate species become spontaneously closer together at a specific distance apart of $r = r_m$, the adsorption potential ϕ may increase due to repulsion effects of adsorbent–adsorbate molecules, and the unfavorable adsorption takes place. Generally, at r_m , the absolute value of ϕ equals to ϕ_m , and ϕ_m is given by $\phi_m = Kr_m^{-t}$. Hence we get:

$$\phi = \phi_m \left(\frac{r_m}{r} \right)^t \quad (2)$$

In case of the adsorption process, a certain finite pressure P of the vapor corresponds to a certain adsorption potential value, ϕ . From Equation (2), it is concluded here that the adsorption potential is maximum at r_m or Henry region where the pressure approaches $P \rightarrow 0$ or P_0 . With increasing pressure, the vapor molecules are considered to move near to the adsorption site and when it approaches saturated pressure (P_s), ϕ becomes its lowest value [31,32]. It is reasonable to conclude that P is proportional to r . Equation (2) can be written as

$$\frac{\phi}{\phi_m} = \left(\frac{P_0}{P} \right)^n, \text{ for } P \geq P_0. \quad (3)$$

As Equation (3) is a power function. The modified form of Equation (3) can be expressed as

$$\frac{\phi}{\phi_m} = 1 - \left(\frac{\gamma P}{P_s} \right)^n \text{ for } P \leq P_s, \quad (4)$$

where γ is a correction factor and n indicates the surface energy heterogeneity factor that depends on the nature of adsorbent–adsorbate interactions. Equation (4) holds true for all pressures ranging from Henry region to saturated pressure. ϕ_m is calculated as a function of adsorbent pore width [31]. Polanyi [4] observed an adsorption potential for monolayer adsorption on homogeneous adsorbents as a function of pressure and temperature and is expressed by $RT \ln(P_s/P)$. Tóth modified this equation [22] by including a correction factor χ and is given by $RT \ln(\chi P_s/P)$. The value of χ depends on experimentally measured adsorption isotherms data. Equation (4) indicates a power function and is similar to $RT \ln(P_s/P)$. Various sources [21,33–35] explain the derivations of both the differential and the isosteric heat of adsorption (Q_{st}). The general form of isosteric heat of adsorption is typically approximated as [36]

$$Q_{st} = Q_0 + \phi + zRT, \quad (5)$$

where Q_0 indicates the latent heat of vaporization, z represents the compressibility factor and R is the gas constant. n of Equation (4) depends on the nature of adsorbent–adsorbate interaction factors. The energetically homogeneous adsorbent, when exposed to a certain type of adsorbate, would exhibit a constant Q_{st} with increasing adsorbate loading or uptake. In that case, the value of n approaches zero or even more than 1 depending on the nature of adsorbate–adsorbent interactions. Secondly, the Q_{st} may decrease with increasing adsorbate uptake due to variability in the energetic heterogeneity, n is positive and generally less than 1. Thirdly, the Q_{st} may also increase with increasing adsorbate loading due to the stronger lateral interactions between the adsorbed molecules at higher surface coverage, in that case, n is more than 1 and the non

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