Modified GAB model for correlating multilayer adsorption equilibrium data

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A B S T R A C T

A new multilayer gas adsorption model is built based on the GAB (Guggenheim–Anderson–de Boer) model and L–F isotherm (Langmuir–Freundlich isotherm). Accounting for the heterogeneity of the adsorption system, the adsorption rate is assumed to be αth power of the surface area as demonstrated in L–F isotherm; the modified GAB model has the same form as that of the GAB equation with the difference lying on the relative pressure form; the nominal relative pressure is the α th power of the relative pressure. Different adsorption isotherm models are applied to correlate the adsorption data of microporous materials. The modified GAB model has the best conformity with the experimental data and can get almost the same so called "BET monolayer capacity" with that of the original BET equation using consistence criteria. The parameters in the modified GAB model were calculated as well; the non-unity of α indicated that the heterogeneity of the adsorption system is un-negligible even on the highly homogeneous surface.

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1. Introduction

Adsorption is a common technology to study the characteristic of porous material and adsorption isotherm is mostly used to describe the adsorption process. There are many famous models available to describe the pure component adsorption, such as the Langmuir model [1], Freundlich, BET [2], Langmuir–Freundlich isotherm [3], Toth model [4] and DR (DA) equation [5]. The BET model is usually used to evaluate the specific area of the non-porous and mesoporous material and it's applicable when the relative pressure is 0.05–0.35. Because the existence of micropores can lead to nonlinear BET plot [6] and capillary condensation may occur in high pressure. A modified BET equation is built by Anderson [7] and Brunauer et al. [8] respectively by employing a third parameter k, which is a measurement of the attractive force field of the adsorbent. And it greatly extends the applicability of the BET model with P/P_0 or c/c_0 up to at least 0.9 [9] while the BET areas are almost the same for the two models. Timmermann [10] did more research about the parameters in GAB (Guggenheim–Anderson–de Boer) isotherms (that is the modified BET model derived by Anderson and Brunauer) and found that although the GAB isotherm can reproduce the results of the BET equation, the GAB monolayer

value is about 15% higher than the BET value and the GAB energy constant C reduces 35–40% or more than the BET constant. That is huge difference. And these two models are unable to explain and represent the sorption at very low activities (relative pressure $P/P_0 < 0.1$). Bashiri and Orouji [11] derived a new multilayer adsorption model based on the BET model and accounting for the heterogeneity by assuming the first layer being heterogeneous and the lateral layers being homogeneous. And it shows it has a good conformity with experimental data in some system.

BET equation is traditionally used to evaluate the specific surface area of non-microporous materials. But still, it's routinely used in microporous system. There're several problems applying the BET model to microporous materials [12]; (1) the BET monolayer capacity is doubtful, (2) monolayer structure is different for different materials, (3) localized monolayer adsorption or micropore filling could occur in low relative pressure. Rouquerol et al. [13] did further study about the applicability of BET equation in microporous adsorbent. They found that two other criteria (consistency criteria) besides the relative pressure range being 0.05–0.35 should be included if the BET equation was used to microporous adsorbent and the monolayer capacity was more like "BET strong retention capacity". Bae et al. [12] and Walton and Snurr [14] did molecular simulation to predict nitrogen adsorption in MOFs and zeolite with micropores and even ultra-micropores. The BET surface area calculated with the consistency criteria agreed well with the accessible

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Nomenclature

a_i	BET constant ($i = 1, 2, \ldots, \infty$)
a_m	projected area occupied by one molecule (nm^2/molecule)
A	the specific surface area (m^2/kg)
b	equilibrium constant (1/Pa)
b_i	evaporation coefficients in BET equation ($i = 1, 2, \ldots, \infty$)
c	solute concentration in the liquid phase (mole/kg)
c_0	solute saturation concentration in the liquid phase (mole/kg)
d	adsorption enthalpy deviation from that of liquefaction (J/mole)
C	energy constant
E_i	adsorption enthalpy in the ith layer (J/mole, $i = 1, 2, \ldots, \infty$)
GAB	Guggenheim–Anderson–de Boer
k	GAB model constant
k_a	the adsorption rate (1/(s Pa))
k_d	the desorption rate (1/s)
K	GAB model constant (k/P_0^α)
L–F	Langmuir–Freundlich

N_A	Avogadro number
n	adsorption equilibrium amount (mole/kg)
n_{max}	monolayer saturation capacity (mole/kg)
V	adsorption equilibrium amount (m^3/kg)
V_m	monolayer saturation capacity (m^3/kg)
P	gas pressure (Pa)
P_0	saturated vapor pressure (Pa)
Q_{st}	adsorption enthalpy (kJ/mole)
R	universal gas constant (J mole^{-1} K^{-1})
S_i	number of adsorption sites in the ith layer ($i = 1, 2, \ldots, \infty$)
T	temperature (K)

Greek symbol

α	display of the heterogeneity of the adsorption system
θ	surface coverage

Subscripts

N	equivalent of surface loading when calculating the isosteric heat

surfaces areas obtained from crystal structures, indicating that BET theory can be applied to microporous materials on heterogeneous surface.

In this work, a new multilayer adsorption isotherm is built based on the GAB model and the BET model; the adsorption surface is heterogeneous, not just for the first layer. And it shows that the new modified GAB model can be applied to describe the adsorption process in microporous material and can get the almost the same so called "BET monolayer capacity" with original BET model in the full relative pressure range.

2. Theory

Assume that one molecule occupies α sites when being adsorbed, then the rates of adsorption and desorption rate are proportional to $(1 - \theta)^\alpha$ and θ^α respectively (θ is the surface coverage); similar to the derivation of Langmuir model, from adsorption and desorption kinetics:

$$\frac{d\theta}{dt} = k_a P (1 - \theta)^\alpha - k_d \theta^\alpha \tag{1}$$

When adsorption equilibrium is arrived, $\frac{d\theta}{dt} = 0$

Thus:

$$n = n_{max} \cdot \frac{(bP)^{\frac{1}{\alpha}}}{1 + (bP)^{\frac{1}{\alpha}}}, \theta = \frac{V}{V_m}, \frac{V}{V_m} = \frac{n}{n_{max}} \tag{2}$$

This is the L–F isotherm [3], $b = (k_a/k_d)$. k_a is the adsorption rate while k_d is the desorption rate. n is the adsorption amount when adsorption equilibrium is reached. n_{max} is the saturation capacity.

When α is unity, the Langmuir–Freundlich isotherm reduces to Langmuir model. Thus α can be a symbol of heterogeneity. Based on the concept of multisite occupation of one molecule when being adsorbed, the adsorption rate is proportional to surface coverage. And the new multilayer adsorption model is built. There are several assumptions need to make before the derivation.

(1) One molecule occupies α sites when being adsorbed.
(2) The adsorption occurs at second and further layers before the completion of the first one [15].

(3) The heat of adsorption differs from that of liquefaction by a constant amount d from the second layer and above [7].
(4) The number of adsorbed layer is infinite when adsorption equilibrium is reached.

Accounting for the heterogeneity of the system whether it is the heterogeneous surface or the force between adsorbed molecules, all is displayed in the parameter α. When adsorption equilibrium is reached, the adsorption rate on the free surface (not occupied by molecules) is equal to the desorption rate of the first layer, that is [11]:

$$a_1 P S_0^{\frac{1}{\alpha}} = b_1 S_1^{\frac{1}{\alpha}} \exp\left(-\frac{E_1}{RT}\right) \tag{3}$$

Here a_1 and b_1 are constants. P is the equilibrium pressure, E_1 is the heat of adsorption. S_i is the number of adsorption sites on each layer of the multilayer adsorption.

For the second layer:

$$a_2 P S_1^{\frac{1}{\alpha}} = b_2 S_2^{\frac{1}{\alpha}} \exp\left(-\frac{E_2 + d}{RT}\right) \tag{4}$$

The quantity d will be added to the adsorption heat of the first layer as well for convenience [7].

For the ith layer:

$$S_i = \left(\frac{a_1}{b_1} \cdot \frac{a_2}{b_2} \cdots \frac{a_i}{b_i} \exp\left(\frac{E_1 + d}{RT} + \frac{E_2 + d}{RT} + \ldots + \frac{E_i + d}{RT}\right)\right)^\alpha P^{i\alpha} S_0 \tag{5}$$

We know from the derivation of BET equation, $E_2, E_3, \ldots E_i$ is assumed to be equal to the heat of liquefaction. From the second layers and above, the adsorption is mainly due to the attracting force among adsorbed molecules, the interaction among adsorbed molecules is similar (not equal) to the interactions in a pure liquid, so it is expected that $d \ll E_i$ and a_i/b_i is constant.

$$\frac{a_2}{b_2} = \frac{a_3}{b_3} = \cdots = \frac{a_i}{b_i} = \cdots \frac{a_\infty}{b_\infty} \tag{6}$$

Define:

$$x = \frac{a_2}{b_2} \exp\left(\frac{E_2 + d}{RT}\right) \cdot P^\alpha \tag{7}$$