



Water vapor adsorption isotherm expressions based on capillary condensation



Xiang Jun Liu^{a,*}, Yun Fei Shi^a, Mohammad Ali Kalbassi^b, Richard Underwood^c, Ying Shu Liu^a

^a School of Mechanical Engineering, University of Science & Technology Beijing, Beijing 100083, China

^b Air Products PLC., Walton-on-Thames, Surrey KT12 4RZ, UK

^c Air Products and Chemicals, Inc., Allentown, PA 18195-1501, USA

ARTICLE INFO

Article history:

Received 30 October 2012

Received in revised form 9 May 2013

Accepted 10 May 2013

Available online 20 May 2013

Keywords:

Water vapor adsorption

Capillary condensation

Isotherm model

ABSTRACT

Four comprehensive isotherm expressions are proposed for various water vapor adsorption mechanisms. Water vapor adsorption in micropores and on macropore walls is described using the Langmuir and Freundlich models, respectively. Water vapor condensation in the pore core volume of macropores is modeled by assuming that the effective pore size follows a Gaussian and uniform distribution. These expressions are used to fit water adsorption data on various kinds of alumina. The results show that the proposed water vapor adsorption isotherm expressions fit the water adsorption data well.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Removal of water vapor from air is receiving increasing attention because of its emerging applications in air reparation, purification, and environmental protection [1,2]. Accurate and reliable models for characterizing water adsorption isotherms are required to improve water removal technologies and processes. Numerous studies have investigated water vapor adsorption on various porous adsorbents [2–5].

Isotherms at low relative humidity can be well-correlated with the commonly used monolayer models, such as Langmuir, Freundlich, and load ratio correlation models [6]. With increased relative humidity, monolayer adsorption is predominated by capillary condensation, and isotherms of water vapor on porous adsorbents over the full partial pressure range are either Type IV or Type II according to the Brunauer classification [7]. A mathematical description for water adsorption isotherms over the full partial pressure range is much more challenging.

Water adsorption isotherms can be characterized over the full partial pressure range by extending the description of monolayer adsorption to multi-layer adsorption. Aranovich and Donohue [8] proposed a general expression for multi-layer adsorption (AD models) by extending monolayer models to multilayer models using an accessory function that describes the adsorption in the second and subsequent layers. Zhang and Wang [9] proposed an extended Langmuir (EL) model by adding a third parameter in the normal

Langmuir equation to describe water adsorption on alumina and 13X. Kim et al. [10] used the n-layer BET equation to correlate the adsorption equilibrium data of water vapor on alumina, zeolite 13X, and on the composite of zeolite and activated carbon. Desai et al. [3] used a combined Langmuir and BET model to correlate the adsorption equilibrium data for water vapor on several types of activated alumina.

The adsorption potential theory is an alternative method to characterize water adsorption isotherms over the full partial pressure range. Kotoh et al. [4] proposed a dual mechanism adsorption potential (DMAP) model by extending the adsorption potential theory to situations with more than one adsorption mechanism.

The performances of the aforementioned models are adsorbent-dependent. They may work well for certain types of adsorbent but may also introduce several deviations for other kinds of adsorbents.

Industrial water adsorbents, such as alumina and silica gel, are pellets with abundant porous structures. Capillary condensation of water vapor may occur at low H₂O partial pressures. Moore and Serbezov [11] reported that capillary condensation is significant when the relative humidity is higher than 25% for F-200 activated alumina. Carniglia [12] divided A-201 alumina/H₂O equilibrium isotherms into three zones according to H₂O loading denoted by λ and suggested that the capillary condensation should be considered at H₂O loading $\lambda > 9$. Machin and Stuckless [13] reported that capillary condensation is significant at relative pressures near 0.3 for Davison grade 03 silica gel. Capillary condensation plays a vital role in water vapor adsorption. A comprehensive model to describe water vapor adsorption on porous adsorbents should include the

* Corresponding author. Tel.: +86 10 62333792.

E-mail address: liuxj@me.ustb.edu.cn (X.J. Liu).

Nomenclature

b	adsorption equilibrium constant in Langmuir equation, 1/kPa	t	thickness of the adsorbed layer, m
n	adsorption equilibrium constant in Freundlich equation	T	temperature, K
N	number of experimental points	v_m	molar volume of sorbate, m ³ /mol
p	partial pressure, kPa	V_0	total pore volume per unit of adsorbent, m ³ /kg
p_s	saturation vapor pressure for a plane liquid surface, kPa	V_1	volume of micropores in an adsorbent, m ³ /kg
q	adsorbed amount per unit weight of sorbent, mol/kg	V_2	volume of the adsorbed layer on macropore walls, m ³ /kg
q_{12}	amount adsorbed in micropores and on macropore walls, mol/kg	V_3	remnant pore core volume of the macropores, m ³ /kg
q_3	amount adsorbed due to capillary condensation, mol/kg	<i>Greek letters</i>	
q_{cm}	limit of the amount adsorbed due to capillary condensation, mol/kg	γ	surface tension of liquid sorbate, N/m
q_m	monolayer adsorbed amount, mol/kg	η	modification factor in L–U and F–U models
r	pore radius, m	μ_1	parameter corresponding to adsorption potential, J/mol
r_0	expected pore radius in Gaussian distribution, m	μ_2	parameter in uniform distribution models, J/kg
r_k	Kelvin pore radius, m	σ	variance of pore radius in Gaussian distribution
r_m	maximal pore radius in uniform distribution, m	<i>Subscripts</i>	
r_p	real pore radius, m	cal	calculated
R	general gas constant, J/mol K	exp	experimental
S_{mac}	specific surface area of the macropores, m ² /kg		

description of capillary condensation occurring in the adsorbent pores.

In this study, we divide the total pore volume of a porous adsorbent into three parts as follows: the pore volume of very small pores (micropores) where capillary condensation may not take place [14], the region next to the macropore walls, and the remnant pore core volume of the macropores. The Langmuir and Freundlich models are used to describe both the micropore adsorption and the surface adsorption on the macropore walls. Water vapor condensation in the pore core volume of macropores is described based on the Kelvin theory without considering the interferences between vapor condensation and surface adsorption. Consequently, four expressions for water vapor adsorption are derived and their applications are further developed.

2. Basic theory and assumptions

Surface tension weakens the saturation vapor pressure in a small pore. Therefore, smaller pores in a porous adsorbent may be filled with liquid sorbate with lower pressure than the saturation vapor for pure plane liquid surface at the same temperature. This phenomenon is the so-called capillary condensation, which plays a vital role in water vapor adsorption.

Kelvin proposed the following equation, which is widely used to illustrate the relations between the pore radius and the corresponding equilibrium vapor pressure [14,15]:

$$\ln(p/p_s) = -\frac{\gamma v_m}{RT r} \quad (1)$$

where p_s is the saturation vapor pressure for a plane liquid surface, r is the pore radius, R is the universal gas constant (J/mol K), and v_m and γ are the liquid molecular volume (m³/mol) and surface tension (N/m), respectively.

However, the size of pores in real porous adsorbents varies widely. Capillary condensation may not occur in very small pores because the concept of a liquid meniscus is no longer meaningful [14]. These pores are called micropores, and the volume of micropores in a porous adsorbent is denoted as V_1 and expressed in m³/kg. Water vapor adsorption in micropores is usually interpreted by the “pore filling” mechanism [16].

The relations between the pore radius and the corresponding equilibrium vapor pressure are described in Eq. (1). Interestingly,

surface adsorption occurs on the macropore walls sooner than capillary condensation such that the effective pore radius becomes smaller prior to the occurrence of capillary condensation [17]. The effective pore radius available for condensation is related to the true radius as follows:

$$r_k = r_p - t \quad (2)$$

where t is the thickness of the adsorbed layer.

The volume of this adsorbed layer (V_2) is calculated as follows:

$$V_2 = S_{mac} \times t \quad (3)$$

where S_{mac} is the specific surface area of the macropores (m²/kg). The remnant pore core volume of the macropores (V_3) can be calculated by subtracting the volume of the adsorbed layer on the pore walls. The total pore volume of a porous adsorbent with three parts can be written as follows:

$$V_0 = V_1 + V_2 + V_3 \quad (4)$$

Water vapor adsorption in micropores and on macropore walls can be described by existing classical models [6]. We assume that the combined contributions from these two parts can be expressed by one model and that the surface adsorption and the vapor condensation of the macropores have no interferences. Therefore, a comprehensive adsorption isotherm model considering the joint contributions from these three parts can be formulated as follows:

$$q = q_{12}(p) + q_3(p) \quad (5)$$

Water vapor adsorption in micropores and on macropore walls is dominant at low pressures, whereas capillary condensation is more significant at higher relative pressure. An expression to describe the amount adsorbed due to capillary condensation is the key in Eq. (5).

The effective radius of the remnant pore volume (V_3) is calculated as follows: $r_k = r_p - t$. The amount adsorbed due to capillary condensation at vapor pressure (p) can be calculated by the distribution of the effective pore size of an adsorbent [$f(r_k)$] as follows:

$$q_3 = \frac{1}{v_m} \int_0^{r_k} f(r_k) dr_k \quad (6)$$

where q_3 is the adsorbed amount per unit of adsorbent (mol/kg). r_k can be obtained from Eq. (1) as follows:

Download English Version:

<https://daneshyari.com/en/article/641636>

Download Persian Version:

<https://daneshyari.com/article/641636>

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