Journal of Colloid and Interface Science 331 (2009) 302–311

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

A thermodynamic analysis of gas adsorption on microporous materials: Evaluation of energy heterogeneity

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ARTICLE INFO

Article history:
Received 11 September 2008
Accepted 30 October 2008
Available online 19 December 2008

Keywords:
Microporous material
Gas adsorption
Energy heterogeneity
Fractal
Dubinin–Astakhov
Langmuir

ABSTRACT

This paper presents a thermodynamic isotherm derived from solution thermodynamics principles to describe gas adsorption on microporous materials. This isotherm relies on a potential relationship between the integral free energy of adsorption relative to saturation, Ψ/RT, expressed by the Kiselev equation, and the variable $Z = 1/-\mathrm{Ln}(\Pi)$, being Π the relative pressure. A mathematical analysis reveals that the adsorption energy heterogeneity in the micropores is collected in a characteristic parameter of the isotherm, m, that can be related to the α parameter of the Dubinin–Astakhov isotherm in a simple way ($m = \alpha + 1$). The isotherm also predicts a plateau in Ψ/RT at extremely low pressures ($\Pi < 10^{-7}$). Neimark's thermodynamic equation accounting for gas adsorption on mesoporous solids is found to be a particular case of the isotherm presented in this study. The Langmuir isotherm only shows consistency with the thermodynamic isotherm for a reduced combination of values of the relevant parameters, not usually found in common adsorbents. The suitability of the thermodynamic isotherm is experimentally assessed by testing a collection of microporous materials, including activated carbons, carbon nanotubes, and zeolites.

1. Introduction

Microporous materials (e.g., activated carbons, zeolites) are used in a great variety of gas separation, purification, and catalytic processes. The adsorption capacity of these materials is strongly determined by their textural properties, such as their "apparent" internal surface, pore geometry, pore size distribution, and surface irregularity. The microstructure of microporous materials can be inferred from physical adsorption of gases and vapors of different sizes and polarities (most often nitrogen at 77 K). A critical review about porous material characterization by gas adsorption methods can be found in Ref. [1].

Considerable attention has been devoted in the past to the development of suitable isotherm models to describe gas adsorption on microporous materials. Early models such as the Langmuir isotherm of idealized monolayer adsorption are not applicable to physical adsorption by microporous adsorbents despite the characteristic form of the isotherm (Type I) [1–3]. In fact, the form of this isotherm is ascribed to a micropore volume-filling process (3D) instead of a layer-by-layer surface coverage (2D) [2,4], and the plateau does not correspond to monolayer completion.

The vacancy solution theory (VST) [5–9] is one of the first approaches to describe gas adsorption on homogeneous microporous solids as a pore-filling process. In this theory, the adsorbed and gas phases are treated as two vacancy solutions. The vacancy is an imaginary solvent occupying spaces that will be filled by the sorbate. The composition relationship between the two phases is derived from "osmotic" equilibrium criteria. Additional assumptions concerning vacancy properties and activity coefficients of the vacancy solution lead to some fundamental isotherm equations (e.g., Langmuir, Henry, Volmer, and Fowler–Guggenheim) [10]. This theory offers a unified representation of single as well as mixture adsorption within the same framework.

Another approach is based on the volume-filling theory of micropores (TVFM) developed by Dubinin and co-workers [11–13]. The well-known Dubinin–Radushkevich (DR) isotherm [14,15] can be deduced from this theory combined with the Polayni's adsorption potential. Several authors have postulated that the DR isotherm applies only to solids with a uniform structure of micropores [16,17]. Alternative models such as the Dubinin–Astakhov (DA) isotherm [12,18] have been proposed to account for gas adsorption in microporous solids, including bound impurities and functional groups. The Dubinin–Astakhov isotherm has two parameters: the characteristic exponent, α, and the energy of adsorption, E^0. The characteristic exponent of this isotherm (usually in the range 1–5) can be linked to the degree of heterogeneity of the microporous

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doi:10.1016/j.jcis.2008.10.086

system [19–21]. On the other hand, the energy of adsorption can be linked to the average micropore width [22]. The DR equation can be regarded as a particular case of the DA isotherm for $\alpha = 2$. Energy heterogeneity can also arise from structural heterogeneity in the form of the micropore size distribution, with adsorption energy varying with pore size. According to the theory of adsorption in micropores, such a distribution can be obtained by solving the Fredholm equation of the first kind defined by [2,23]

$$\theta_t = \int_{z_{\min}}^{z_{\max}} \theta_{\text{theor}}(z, p) f(z) \delta z, \tag{1}$$

where z describes the structural heterogeneity of the adsorbent, $f(z)$ is the pore size distribution designed in the micropore region ($z_{\min}$, $z_{\max}$), and θ_{theor} is the local adsorption isotherm (i.e., kernel) that describes adsorption on a homogeneous patch of the adsorbent. The function $f(z)$ can be selected to include the effect of surface impurities and irregularities embedded in model constants [24,25].

As proposed by Pfeifer and Avnir [26–28], fractal geometry can be applied in combination with Eq. (1) to account for gas adsorption on heterogeneous materials. In this way, fractal analogues of the Frenkel–Hasley–Hill (f-FHH), Brunauer–Emmet–Teller (fn-BET), and DA (FRDA) isotherms have been obtained [29–32]. The fractal dimension of a surface accessible to adsorption, D_S, is a global measure of structural and surface irregularities of a given solid, remaining invariant over a certain degree of resolution (self-similitude) [33]. It should be emphasized that, for highly porous systems, the fractal dimension does not reflect the structure of the basic objects such as pores or clusters, but their distribution [34]. The fractal dimension can vary from 2 for a perfectly regular smooth surface to 3 for a complex surface. In addition to gas adsorption, the fractal dimension of a surface can be determined from several types of experiments, including porosimetry, small-angle X-ray and neutron scattering (SAXS and SANS), and nuclear magnetic resonance (NMR) [28,29,35–37].

In addition to these fractal analogue adsorption isotherms, Neimark [38] has proposed a thermodynamic equation for the determination of the fractal dimension of mesoporous solids from adsorption data. The theoretical basis for this method is a relationship between the surface area of the adsorbed liquid film, S, and the mean pore radius, r:

$$\mathrm{Ln}(S) = \text{const} + (D_s - 2)\,\mathrm{Ln}(r). \tag{2}$$

Equation (2) can be expressed as a function of the relative pressure, P/P^0, by relating it to the mean pore radius,

$$\mathrm{Ln}(S) = \text{const} + (D_s - 2)\,\mathrm{Ln}\left[-\mathrm{Ln}\left(\frac{P}{P^0}\right)\right]. \tag{3}$$

The surface area of the adsorbed film can be calculated by the Kiselev equation,

$$S(\Pi) = \frac{RT}{\gamma} \int_{q}^{q_{\max}} \left[-\mathrm{Ln}\left(\frac{P}{P^0}\right)\right] \delta q, \tag{4}$$

where $q_{\max}$ denotes the amount adsorbed at $P/P^0 \to 1$, and γ is the surface tension of the sorbate. This thermodynamic method is compatible with the classical FHH theory in the capillary condensation regime, since both rely on the Kelvin equation in a fractal context [35,38].

In this paper, we present a thermodynamic model to describe gas adsorption on microporous materials, relying on the DA isotherm and the solution thermodynamics approach proposed by Myers for pure [39] and mixture adsorption [40]. In this analysis, the concept of surface potential, Φ, instead of the classical spreading pressure, collects the information related to the energy at which the sorbate molecules adsorb. This isotherm provides relevant information about the adsorption energy heterogeneity of the material, involving a separate analysis of the contribution of the physical structure of the adsorbent and the sorbate–adsorbent interaction. Neimark's equation can be obtained as a particular case of the thermodynamic isotherm presented here when applied to mesoporous materials with surface heterogeneity. This analysis has proven useful to correlate the reaction yields for the Si dissolution process of dealuminated kaolin in sodium–potassium hydroxide [41].

2. Theory

2.1. Description of adsorption on microporous materials using solution thermodynamics

From the standpoint of solution thermodynamics, an adsorption system is regarded as consisting of three phases: a gas phase (g), a solid phase or "solvent" (s), and an adsorbed phase or "solute" (a). The adsorbed phase has no volume; i.e., $V_a = 0$. This phase, together with the solid phase, constitutes the "condensed phase" (v). The volumes of all phases are assumed not to change during the adsorption process. The volume of the gas phase, V_g, including that related to micropores, is determined assuming that helium, as a reference gas, does not adsorb at near-ambient temperature and atmospheric pressure. For such a system, the specific free energy of the adsorbed phase is given by [40]

$$\bar{G}^a = \bar{U}^a - T\bar{S}^a = \mu q + \Phi, \tag{5}$$

where U is the internal energy, S the entropy, μ the chemical potential, and Φ the surface potential, which equals the difference between the actual surface potential of the adsorbent and the chemical potential of the adsorbent without loading, i.e., $\mu' - \mu'^S$. The symbol '–' on top refers to specific variables related to the mass of adsorbent. The specific free energy of the adsorbed phase includes two contributions: (1) the free energy of q moles per kg of adsorbent adsorbed at equilibrium with the gas phase, namely with the same chemical potential, and (2) the surface potential, Φ, which depends on the sorbate–adsorbent interaction and tends to zero when there is no adsorption. The sorbate–adsorbent interaction alters the surface potential of the adsorbed phase. The differentiation of Eq. (5) at constant temperature allows obtaining $\delta\bar{G}^a = \mu\delta q$ and $\delta\Phi = -q \cdot \delta\mu$ (Gibbs–Duhem equation), relating the surface potential to the chemical potential of the condensed phase. Assuming $\delta\mu = RT\delta\,\mathrm{Ln}(P)$ in the case of ideal gases (otherwise the pressure has to be substituted by a fugacity), we can obtain

$$\frac{\Phi}{RT} = -\int_0^P q\delta\,\mathrm{Ln}(P) = -q_M \int_0^P \theta\delta\,\mathrm{Ln}(P), \tag{6}$$

where $\theta = q/q_M$ and $q_M = q(P^0)$. As can be deduced from Eq. (6), the surface potential is always negative and increases in absolute value as this approaches 0.

The integral free energy of the adsorbed phase, $\Delta\bar{G}^a$, is defined as the difference between the internal free energy of the adsorbed phase and the free energy of the same amount of sorbate at saturation pressure, μ^0,

$$\Delta\bar{G}^a = \bar{G}^a - q\mu^0. \tag{7}$$

Combining Eqs. (6) and (7), we obtain

$$\Delta\bar{G}^a = q(\mu - \mu^0) + \Phi. \tag{8}$$

The differential free energy of adsorption, $\Delta\bar{g}^a$, can be obtained by differentiating the integral free energy,

$$\Delta\bar{g}^a = \left.\frac{\partial\Delta G^a}{\partial q}\right|_T = \mu - \mu^0 = RT\,\mathrm{Ln}\left(\frac{P}{P^0}\right). \tag{9}$$