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Thermodynamic frameworks of adsorption kinetics modeling: Dynamic water uptakes on silica gel for adsorption cooling applications

Baichuan Sun, Anutosh Chakraborty*

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Republic of Singapore

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ABSTRACT

This paper presents the thermodynamic frameworks to describe the dynamic uptakes of water vapor on various sizes and layers of silica gels for adsorption cooling applications. The proposed kinetic formulation is developed from the rigor of the partition function of each adsorptive sites and the kinetics theory of adsorbate molecules with the analogy of Langmuir kinetics. The simulation results calculated from the proposed formulation are compared with experimentally measured kinetics data of various single and multi layers configuration of silica gels–water systems. An interesting and useful finding has been established that the proposed model is thermodynamically consistent from the Henry's region to the saturated pressure, and also is connected with the surface structural heterogeneity factors of adsorbents.

1. Introduction

It is well known that the adsorption chiller (ADC) utilizes the adsorbent–adsorbate characteristics to achieve useful cooling effects at the evaporator by the amalgamation of two processes namely 'adsorption-triggered-evaporation' and 'desorption-activated-condensation' [1]. The ADC works as a batch wise process i.e. adsorption and desorption occur alternatively in the adsorption bed and is also time dependent [2–6]. So, the adsorption rate or kinetic equations are widely used to describe adsorption data at non-equilibrium conditions, and are significant to investigate the basic understanding of adsorption process that ranges from transient to the cyclic steady state. The simplest kinetics equation is commonly expressed by $\mathrm{d}\theta_t/\mathrm{d}t = \alpha(\theta^* - \theta_t)$, where θ_t is the amount of adsorbate uptake at time t, θ^* is its value at equilibrium, and α is the temperature dependent constant. This rate equation indeed is in line with the concept of LDF (linear driving force) model or the first order kinetic equation [7,8]. The basic mathematic model for the diffusive transport of adsorbates within complex adsorbent structures is the Fick's equations [9], and is difficult to solve analytically under practical situation [9,10]. The LDF model [11] correlates experimental data in simple equation forms [11–13] employing data fitting parameters. The LDF model assumes that the adsorbent particle temperature is uniform, and its thermal conductivity is infinity, which means that the heat transfer effect is neglected. The LDF models also involve the intra-particle diffusion for mass transfer process. The physical evidence of the LDF coefficient is obtained thermodynamically from Langmuirian kinetics. It should be noted here that the Langmuir kinetics [14–18] are used to describe the non-equilibrium conditions of adsorbent + adsorbate system. However, the Langmuir isotherm is limited to one site occupancy adsorption onto the homogeneous adsorbent surface. Moreover, the Langmuir isotherm gives inconsistency thermodynamic behavior at higher pressure ranges [19].

Bhatia et al. [9] gave a comprehensive theoretical perspective of molecular transport in nanopores with the proposal of an oscillator model and a distributed friction models. Sircar and Hufton [12] analyzed the connection between the linear driving force (LDF) model and the FD (Fickian Diffusion) model but the detailed characteristics of local adsorption kinetic model are neglected during integrations. The Fick's differential equation is difficult to solve analytically under practical situation, because the diffusivity, which considers sophisticate diffusion mechanisms within complex

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* Corresponding author. Tel.: +65 6790 4222.
E-mail address: AChakraborty@ntu.edu.sg (A. Chakraborty).

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adsorbent structures, is highly computational time consuming to determine its integration form over the complete time and space domain [12].

Based on Langmuirian adsorption theory, Azizian [10] analyzed the general analytical solution of two extreme cases theoretically with high initial concentration of adsorbate, and lower initial concentration of solute, where the first one converts into a pseudo-first-order LDF model, while the latter follows a pseudo-second-order equation. Liu and Shen [8] also gave a similar conclusion of Azizian [10]. Employing Langmuir model, Marczewski [17] derived the integrated form of kinetics Langmuir equation (IKL), and compared it with the *n*th-order, mixed 1, 2-order, and multi-exponential kinetic equations. Marczewski et al. [18] also proposed a generalization form of Langmuir kinetics (gIKL), and LF (Langmuir–Freundlich) isotherm was applied to describe the non-ideal behavior of adsorption phenomena. Later, Azizian and Bashiri [13] developed the adsorption kinetics with SRT (statistical rate theory) approach, and studied the solute adsorption at the solid/solution. The MPFO (modified pseudo-first-order) kinetic equation, proposed by Yang and Al-Duri [20], was interpreted theoretically [13]. By applying different adsorptive site energy distribution, Rudzinski and Panczyk [21] derived the power form of Elovich equation from Langmuir–Freundlich and the Temkin isotherms. Corresponding to practical experimental conditions, Loh et al. proposed [22] a theoretical framework to describe the adsorption kinetics for the non-isothermal system. Babrao and Jiang [23] investigated the transport diffusivities of CO_2 and CH_4 in silicalite, C_{168} schwarzite, and IRMOF-1 employing molecular dynamics simulation, and it was found that the computational results match well with the Maxwell–Stefan formulation for pure CO_2 and CH_4. To utilize the adsorption kinetics with adsorption chiller system, Aristov et al. [15,16] studied the water adsorption kinetics on silica gel (type Fuji RD) under real operating conditions with the optimization of various loose grains silica gel configuration.

Up to now, no significant attempts are established to explain the theoretical origins of adsorption rate equations for a single component adsorbent + adsorbate system in detail, and the current understanding of adsorption kinetics is not more established as compared with the theoretical description of adsorption isotherms. The present study thus attempts to focus more on the theoretical origins of the adsorption rate equation from the thermodynamics foundation [24] of adsorption uptakes that varies from the Henry's region (Pressure, $P \to 0$) to the saturated pressure (P_s) values. The proposed adsorption kinetics formulation (i) is connected with the pore structures or the heterogeneity factors of adsorbent materials and the isosteric heat of adsorption at zero surface coverage (Q_{st}^*), and (ii) also calculates the adsorption and desorption rates of water vapor onto single and multi-layers of loose grain configuration of silica gel [25,26]. In this paper, we have shown how the number of layers and the adsorbent grain size affect the water adsorption dynamics under conditions close to the isobaric conditions of adsorption cooling cycle [16].

2. Langmuir kinetics model

For better understanding, we start with the kinetics model of Langmuir [27,28]. This is given by

$$\frac{d\theta_t}{dt} = k_{ads} P_t (1 - \theta_t) - k_{des}\theta_t, \tag{1}$$

where θ_t is the fraction of uptake as a function of time, $\theta_t = q_t/q_m$. q_m is the maximum amount of adsorbate uptake. k_{ads} and k_{des} are adsorption and desorption rate coefficients.P_t is the simultaneous equilibrium pressure of the adsorbed phase.

At equilibrium $d\theta_t/dt = 0$, and $\theta_t = \theta$, equation (1) gives the Langmuir's isotherm as:

$$\theta = \frac{KP}{1 + KP}, \tag{2}$$

where $K = k_{ads}/k_{des}$. Under situation where the initial pressure P_{ini} differs no much from the eventually equilibrium pressure$P$, that is$P \approx P_{ini}$, equation (1) turns to be the pseudo-first-order model [10] or

$$\frac{d\theta_t}{dt} = \alpha(\theta - \theta_t), \tag{3}$$

where $\alpha = k_{ads}P + k_{des}$. Both equations (1) and (3) give the same adsorption kinetics expression analytically and is written as

$$\theta_t = \theta\left(1 - e^{-\alpha t}\right) + e^{-\alpha t}\theta_{ini} \tag{4}$$

with the boundary conditions of $\theta_t = \theta_{ini}$ at $t = 0$, and $\theta_t = \theta$ at $t = \infty$.

3. Proposed theory of adsorption kinetics

The adsorbent–adsorbate system consists of equivalent and distinguishable adsorptive sites, where any number, *s*, from 0 to maximum *m*, of molecules can be adsorbed [29]. Considering van der Waals force as short-range for physical adsorption, the partition function of each isothermal site is $q(s) = q^s(1)$. The absolute activity is given by $\lambda = \exp(\mu/kT)$, where μ defines the chemical potential of the adsorbed molecules and it comprises the bulk chemical potential μ_{gas} and the external adsorbent wall potential ν_{ext}, or $\mu = \mu_{gas} - \nu_{ext}$[30]. The grand partition function of each individual adsorptive site is [29]:

$$\xi_m = q(0) + q(1)\lambda + \cdots + q(m)\lambda^m = \sum_{s=0}^{m} q(s)\lambda^s \tag{5}$$

where $q(0) = 1$. The average number of molecules within each adsorptive site can be presented by Ref. [29]:

$$\bar{s} = \lambda\left(\frac{\partial \ln \xi_m}{\partial\lambda}\right) = \frac{\sum_{s=0}^{m} s q(s)\lambda^s}{\sum_{s=0}^{m} q(s)\lambda^s} = \frac{\sum_{s=0}^{m} s\{q(1)\lambda\}^s}{\sum_{s=0}^{m} \{q(1)\lambda\}^s} \tag{6}$$

From the definition of the Helmholtz free energy [31], we have$A(N, V, T) = -kT \ln q(N, V, T)$, where V is the volume of N molecules at temperature T. The Grand potential of one particle is then expressed by $\phi_G = -k_B T \ln\{q(1)\lambda\} = A(1, \nu_1, T) - \mu_{gas} + \nu_{ext}$ [30,32], where k_B is the Boltzmann constant, T is the absolute temperature and ν_1 is the volume occupied by 1 particle. As a result, we have

$$q(1)\lambda = \exp\{-(A - \mu_{gas} + \nu_{ext})/k_B T\}. \tag{7}$$

Using μ^Θ as the reference chemical potential of the gas at reference pressureP^Θ, it is possible to show $\mu_{gas} = \mu^\Theta + k_B T \ln(P/P^\Theta)$ to get

$$\begin{aligned} q(1)\lambda &= \exp\{(-A + \mu^\Theta + k_B T \ln(P/P^\Theta) - \nu_{ext})/k_B T\} \\ &= \exp\left\{\left(k_B T - \nu_{ext} - h_{fg}(1)\right)\Big/ k_B T\right\}(P/P_s) \\ &= \exp\left\{\left(RT - V_{ext} - h_{fg}\right)\Big/ RT\right\}(P/P_s) \end{aligned} \tag{8}$$

Here, P_s is the saturated pressure. $A - \mu^\Theta = -k_B T$ indicates the work done of the system, and $R(= N_A k_B)$ is the gas constant. The isosteric heat of adsorption at zero surface coverage is [1,30]