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Thermodynamic formalism of water uptakes on solid porous adsorbents for adsorption cooling applications

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This Letter presents a thermodynamic formulation to calculate the amount of water vapor uptakes on various adsorbents such as zeolites, metal organic frameworks, and silica gel for the development of an advanced adsorption chiller. This formalism is developed from the rigor of the partition distribution function of each water vapor adsorptive site on adsorbents and the condensation approximation of adsorptive water molecules and is validated with experimental data. An interesting and useful finding has been established that the proposed model is thermodynamically connected with the pore structures of adsorbent materials, and the water vapor uptake highly depends on the isosteric heat of adsorption at zero surface coverage and the adsorptive sites of the adsorbent materials. Employing the proposed model, the thermodynamic trends of water vapor uptakes on various adsorbents can be estimated. © 2014 AIP Publishing LLC.
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The physical adsorption process occurs mainly within the pores of adsorbent and external adsorbent surface and requires the knowledge of adsorption isotherms and kinetics over wide ranges of pressures and temperatures for various applications like adsorption cooling (ADC). Extensive works have been done to establish the knowledge of adsorption isotherms, which laid the foundation of understanding adsorption phenomenon. The choice of adsorbent-adsorbate pair depends on the amount of heat that can be extracted from the low temperature heat source for the production of cooling effects at the evaporator, which, in turn, depends mainly on the higher (i) the latent heat of evaporation (h_{fg}) of the adsorbate, and (ii) difference between the adsorbate uptake and offtake per adsorption cycle.[1] The amount of adsorbate uptake is calculated by adsorption isotherm equation such as Langmuir,[2] Toth,[3] or Dubinin[4–7] equations, and the parameters of these equations are measured by experimental data. Guggenheim[8] proposed a general adsorption isotherm model with heat and work exchange, and Myers and Monson[9] established the thermodynamic framework of adsorption employing Gibbs free energy, enthalpy, and entropy. Following these works, Chakraborty *et al.*[10,11] developed thermodynamic property surfaces of a single component adsorbent-adsorbate system for an estimation of isosteric heat of adsorption.[12] Most of the classical adsorption uptake equations are limited by their individual thermodynamic inconsistence within the complete adsorption isotherm ranges such as (a) Henry or Langmuir isotherm model is thermodynamically correct only at low pressure region and (b) Dubinin isotherm shows good agreement with experimental data at higher pressure ranges.[13] However, both Dubinin Raduskevich (DR) and Dubinin Astakhov (DA) isotherm models are thermodynamically incorrect at Henry's region. To overcome these limitations, many empirical or semi-empirical isotherms were proposed, including:[14] Toth, Frendlich, Sips, Unilan, Jovanovich equations, etc. These isotherms correlate experimental data with empirical parameters with little or no physical meanings. This paper aims to develop a formalism of adsorption isotherm from the rigor of partition distribution function of each adsorptive site and the isosteric heat of adsorption at zero surface coverage for the calculation of adsorbate uptakes on various adsorbent materials. The proposed thermodynamic framework ranges from Henry's to the saturated pressure and is applied to water vapor adsorption for the design and development into advanced materials for adsorption cooling applications.

It is assumed that s numbers of adsorbate molecules are adsorbed on each adsorbent site of an adsorbent-adsorbate system, where s varies from 0 to its maximum value m.[15] As the van der Waals force is short-range for physical adsorption, the partition function of each isothermal site is $q(s) = q^s(1)$ and the absolute activity is given by $\lambda = \exp(\mu/kT)$, where μ is the chemical potential of the adsorbed molecules and comprises the bulk chemical potential (μ_{gas}) and the external adsorbent wall potential (V_{ext}) or $\mu = \mu_{gas} - V_{ext}$.[16] The grand partition function of each single adsorptive site is[15] $\xi_m = q(0) + q(1)\lambda + \ldots\ldots\ldots + q(m)\lambda^m = \sum_{s=0}^{m} q(s)\lambda^s$, where $q(0) = 1$. The average number of molecules within each adsorbent site is[15]

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

From the definition of the Helmholtz free energy (A),[17] we have $A(N,V,T) = -kT\ln q(N,V,T)$, where V is the volume of N molecules. The Grand potential of one particle is,[16,18] $\phi_G = -kT\ln\{q(1)\lambda\} = A(1, v_1, T) - \mu_{gas} + V_{ext}$, where k is the Boltzmann constant, T is the absolute temperature, and v_1 is the volume occupied by 1 particle. Therefore,

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$q(1)\lambda = \exp\{-(A - \mu_{gas} + V_{ext})/kT\}$. Employing $\mu_{gas} = \mu^{\Theta} + kT\ln(P/P^{\Theta})$ (here, μ^{Θ} indicates the reference chemical potential of gas at reference pressure P^{Θ}), we have $q(1)\lambda = \exp\{(-A + \mu^{\Theta} + kT\ln(P/P^{\Theta}) - V_{ext})/kT\} = \exp\{(kT - V_{ext} - h_{fg}(1))/kT\}(P/P_s)$ or $q(1)\lambda = \exp\{(RT - V_{ext} - h_{fg})/RT\}(P/P_s)$, where P_s is the saturated pressure. $A - \mu^{\Theta} = -kT$ indicates the work done of the system, and $R(= N_A k)$ is the gas constant. The isosteric heat of adsorption at zero surface coverage is written by[1,16] $Q_{st}^* = RT - V_{ext}$. To connect the nature of adsorbent surface with the proposed model, the expression of Q_{st}^* as a function of pore width should be included.[16,19] The expression of Q_{st}^* is given by

$$Q_{st}^* = RT - \frac{\int_0^{H_c} V_{ext}(z)\exp[-V_{ext}(z)/RT]dz}{\int_0^{H_c} \exp[-V_{ext}(z)/RT]dz}, \quad (2)$$

where H_c is the pore width of solid adsorbents.[1] The adsorbent wall potential is described by $V_{ext}(z) = U_{sf}(z) + U_{sf}(h - z)$, where U_{sf} defines the adsorbent-adsorbate interaction potential and h is the distance between the nuclei of the outer adsorbent atoms on opposite walls. The value of U_{sf} along the pore width direction (z) is written as[19] $U_{sf} = 2\pi\varepsilon_{sf}\rho_s\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^4 - \frac{\sigma_{sf}^4}{3\Delta(0.61\Delta+z)^3}\right]$, where σ_{sf} and ε_{sf} are the solid-fluid collision diameter and the solid-fluid well depth potential, respectively. Δ defines the separation between the adsorbent planes and ρ_s is the density of solid adsorbent.[1] For water adsorption cases $\sigma_{sf} = 3.43$ Å, $\varepsilon_{sf} = 8.119 \times 10^{-21}$ J/mol, $\Delta = 3.35$ Å, and $\rho_s = 0.055$. It should be noted here that $(Q_{st}^* - h_{fg})$ is the extreme constant of grand potential and it corresponds to the adsorption characteristics energy, and it is a function of pressure, temperature, and pore width of solid adsorbent.[1] Substituting the values of $q(1)\lambda$ and Q_{st}^* in Eq. (1), $\bar{s}$ is calculated. Therefore, Eq. (1) is connected with the porous structure of adsorbent materials. The surface coverage (θ) of adsorbent-adsorbate system is written as

$$\theta = \frac{\bar{s}}{\bar{s}_{max}} = \frac{1}{\bar{s}_{max}}\frac{\sum_{s=0}^m s\exp[s(Q_{st}^* - h_{fg})/RT](P/P_s)^s}{\sum_{s=0}^m \exp[s(Q_{st}^* - h_{fg})/RT](P/P_s)^s}. \quad (3)$$

Here, $\bar{s}_{max} = \rho_l . v_p$, ρ_l is the liquid density and v_p is the pore volume. To simplify Eq. (3), the numerator curve is defined here by a power function. $(1/\bar{s}_{max})\sum_{s=0}^m s\exp[s(Q_{st}^* - h_{fg})/RT](P/P_s)^s \cong \alpha\exp[m(Q_{st}^* - h_{fg})/RT](P/P_s)^m$, where the pre-exponential coefficient α is determined by $\exp[m(Q_{st}^* - h_{fg})/RT]$ and the heterogeneity factor, m. Similarly, the denominator of Eq. (3) can be indicated by another power function with intercept 1, i.e., $\sum_{s=0}^m \exp[s(Q_{st}^* - h_{fg})/RT](P/P_s)^s \cong 1 + [\alpha\exp\{m(Q_{st}^* - h_{fg})/RT\} - 1](P/P_s)^m$. Employing the numerator and the denominator of Eq. (3), a simple adsorbate uptake equation can be presented. Substituting $K = \alpha\exp[m(Q_{st}^* - h_{fg})/RT]$, we have

$$\theta = \frac{K(P/P_s)^m}{1 + (K - 1)(P/P_s)^m}. \quad (4)$$

The proposed adsorption uptake formulation as shown in Eq. (4) is verified with experimentally measured isotherm data[20–25] of various adsorbents such as silica gel, zeolites (type AQSOA Z02), and metal organic frameworks (MOFs) (type Mil-100), and these are shown in Fig. 1. From experimental data of water adsorption, the value α is predicted 9×10^{-7} as the effect of α is not very significant on the shape of adsorption isotherm. Q_{st}^* is calculated from Eq. (2) as a function of pore width. For silica gel + water system, $Q_{st}^* = 4000$ kJ/kg due to the fact that silica gel is mainly the combination of micro and meso-porous structure. Q_{st}^* is estimated as 3600 kJ/kg for AQSOAZ02 and 2960 kJ/kg for Mil-100(Cu) MOFs. AQSOA-Z02 is a chabazite (CHA) type molecular sieve with three-dimensional structure, where small guest molecules, such as water, can enter the cages through 0.38 nm windows. For comparison purposes, Langmuir, Brunauer–Emmett–Teller (BET), and DA isotherm models are included in Fig. 1. It is found that the amount of water vapor uptake increases from Henry's region to the saturated pressure for silica gel and AQSOA-Z02 zeolites. However, Mil-100 shows the S-shaped isotherm with hydrophobic behaviors for the relative pressures (P/P_s) varying from 0 to 0.15. Fig. 2 shows the uptakes of water vapor against P/P_s on two types of zeolites, namely, AQSOA-Z01 and AQSOA-Z05. The S-shaped isotherms are found, and it should be noted that AQSOA-Z05 structure consists of AlO4, PO4 tetrahedrons with 0.73 nm pores and it shows hydrophobic nature when P/P_s varies from 0 to 0.2. On the other hand, the structural framework of AQSOA-Z01 comprises AlO4, PO4, and FeO4 tetrahedrons, where Al and P atoms are partially substituted by Fe atoms. From Fig. 2, it is found that AQSOAZ01 behaves hydrophobic from Henry region to P/Ps = 0.1 and this is suitable for adsorption chiller design. Employing the present thermodynamic formulation, it is observed that for AQSOA-Z05 + water
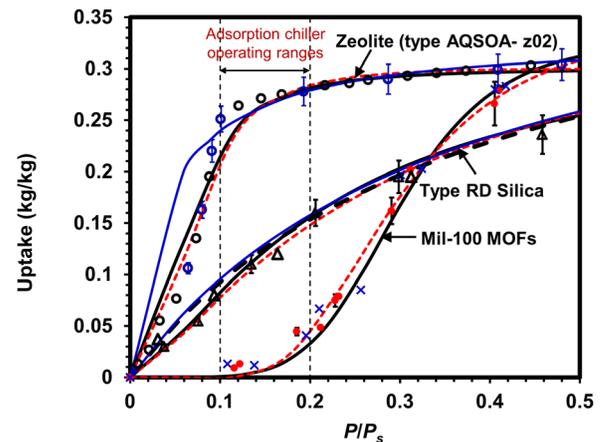

FIG. 1. Adsorption characteristics of various hydrophilic and hydrophobic porous adsorbents with adsorption cooling operating ranges. Here, the red dotted lines (- - - -) indicate the DA isotherm model, the blue lines (—) define the isotherms models of BET theory, and the black dotted lines (- - -) refer to Langmuir isotherm model. The proposed adsorption uptake modeling (—) agrees well with experimental data (±5% error). Langmuir and BET fail to fit with the experimental data of S-shaped isotherms.
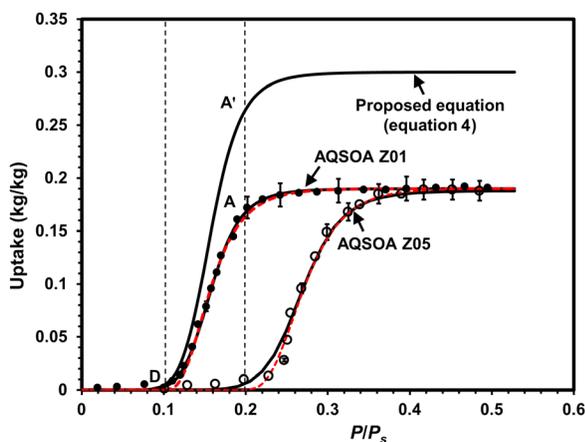
FIG. 2. Water vapor uptakes on AQSOA-Z01 and AQSOA-Z05 with adsorption-desorption operating points. A and A′ indicate adsorption and D indicates desorption. The experimental data are fitted with the proposed adsorption isotherm equation and the DA isotherm model (red dotted lines - - -). Employing the proposed thermodynamic equation (4), the water vapor uptakes (——) is shown here (it can be predicted by improving the surface area and pore volume of AQSOA-Z01).

system, $Q_{st}^* = 2790$ kJ/kg with the heterogeneity factor (m) of 13. This means that the adsorbent structure is mesoporous, i.e., little or no adsorption occurs at low pressure side. For AQSOA-Z01 zeolite + water systems, Q_{st}^* and m are calculated as 2910 kJ/kg and 9.4, respectively. Here, the surface structure of AQSOA-Z05 is modified by the addition of Fe atoms to form zeolite AQSOA-Z01. Due to the addition of Fe, the pore size is decreased and Q_{st}^* increases. From the proposed thermodynamic modeling, it is established that the pore-surface structure of AQSOA Z01 can further be modified by increasing its pore volume and BET surface area. The proposed isotherm for ADC is shown in Fig. 2. The ADC utilizes the adsorbent-adsorbate characteristics and produces useful cooling effects at the evaporator by the union of "adsorption-triggered-evaporation" and "desorption-activated-condensation."[1] The adsorption-desorption cycles for silica gel (A′B′CD) and AQSOA-Z01 (ABCD) are shown in Fig. 3. Here, the amount of water

vapor uptakes are calculated by the proposed thermodynamic formulation and is found that the S-shaped isotherms are suitable for adsorption chiller design due to the fact that the cycled mass of water vapor for AQSOA-Z01 + water system is higher than that of silica gel + water system. Employing S-shaped isotherm based adsorbent + water system, the size of adsorption/desorption reactor is minimized for the same cooling capacity and coefficient of performance of the conventional adsorption chiller, which indicates a significant breakthrough in cooling science and technology.

To overcome the limitations of the existing adsorption uptake models, such as Langmuir, Toth, and Dubinin Astakhov equations, the proposed isotherm (a) includes thermodynamically consistent boundary conditions that range from the Henry's region to the saturated pressure and (b) is connected with the porous structures of adsorbent materials. However, the derivation of the proposed adsorption uptake equation begins with the lattice gas frameworks and the parallel silt model of adsorbent structures. From the thermodynamic trends of experimentally measured various adsorbents + water systems, it is found that the Q_{st}^* depends on various pore widths, and m defines the shape of the adsorption isotherm. So the knowledge of Q_{st}^* and m helps to design new adsorbent materials. The adsorbent materials such as zeolites, silica gel, or metal organic frameworks should be designed with $Q_{st}^* \sim 3000$ kJ/kg or the combination of micro-mesoporous structure for adsorption cooling applications.

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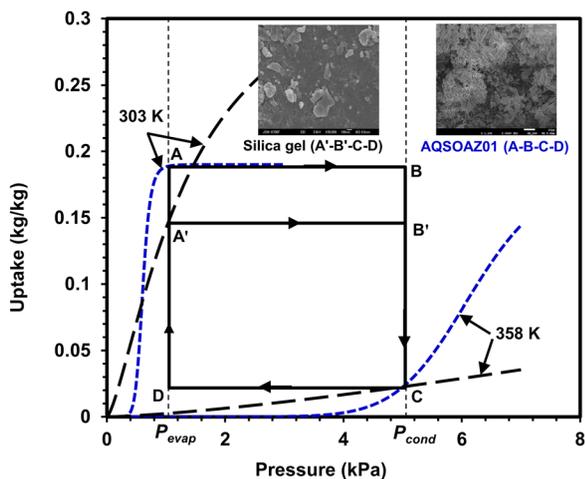

FIG. 3. Adsorption-desorption cycle of silica gel—water (A′B′CD) and AQSOA-Z01—water, where the evaporator pressure is 1 kPa and the condenser pressure is 5 kPa. The SEM pictures of silica gel and AQSOA-Z01 are shown here.

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