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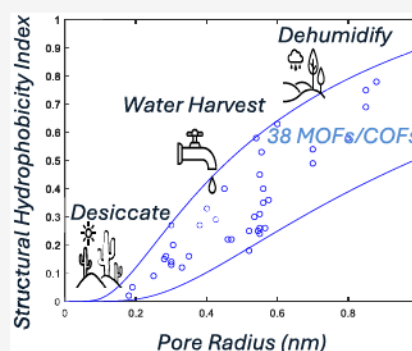


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ABSTRACT: Global challenges posed by freshwater scarcity and the water–energy nexus drive demand for novel macromolecular design of tailored nanostructures endowed with a variety of hydrophilic and hydrophobic features. Offering potential to meet this demand, metal–organic framework (MOF) materials are synthesized from coordinated formations that create versatile reticular structures with variable water adsorption affinities. However, advances in the fundamental understanding of water interactions within these structures are impeded by the failure of classical analyses to identify mechanisms of interaction, connect fundamental isotherm types, and provide appropriate benchmarks for assessment. Proposed herein is a novel definition of hydrophobicity that is coherently coupled with a unified isotherm analysis to connect a wide array of rigorous equilibrium isotherm types bounded by asymptotic limits dictated by hydrophilic rectangular Type I and hydrophobic stepwise Type V (unimodal Type VI). Moreover, distinct forms of hydrophobicity, associated benchmarks and discrete classes of material behavior are introduced to characterize hydrophobic to hydrophilic transitions. Simplification of the analysis for application to microporous MOF materials displaying nominally stepwise water adsorption isotherms yields Ising-Model-Modified-Kelvin-Analysis (IMMKA) that is delivered in a simple, rigorous, analytic form. Mechanisms of pore filling are characterized, allowing verification of widely accepted protocols and “rules of thumb” for the prediction of micropore filling pressures. The analysis successfully captures the foundational features of water in extreme confinement, including the role of pore morphology in directing the molecular and fluidic interactions that underpin the pseudocondensation mechanism of water in micropores.



INTRODUCTION

The ubiquitous presence of water drives the need for fundamental understanding of hydrophobicity of surfaces and porous materials.¹ Despite some advances,² there are still significant challenges associated with capturing and applying the foundational physics of confined water for characterization of hydrophobic phenomena.³ A major obstacle results from the disparity of length scales for which molecular-level consideration of fluid–solid interaction must be coupled with macroscopic interpretation of fluid–fluid–solid interaction.⁴ The challenges are amplified when considering the behavior of water under extreme confinement in microporous materials⁵ that contain pores of diameter less than 2 nm. For these materials, hydrophobic and hydrophilic behaviors are often assumed to be governed by the chemistry of the material and the density of hydrophilic moieties contained within the structure.^{1–6} As a result, the morphological properties of the host⁷ are often overshadowed by chemistry in the assessment of water uptake.⁵ Metal–organic framework (MOF) materials, for example, are often assessed by their chemical nature but lack robust relationships connecting hydrophobicity with MOF morphology.^{8–12} Considering the already vast array of MOFs and rapidly expanding library of new materials and water adsorption

isotherms emerging, MOFs provide ideal materials for advancing knowledge of hydrophobicity at the molecular level. Moreover, a comprehensive fundamental understanding of the behavior of water in MOFs could deliver major impacts on a wide range of technologies used for energy storage,¹³ heat reallocation for energy optimization,^{8,9} or water harvesting applications that have potential to address the water–energy nexus¹⁴ and offer promising solutions for global water crises.¹⁵

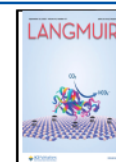
Each of these applications is ideally designed for materials that display sigmoidal, S-shaped, equilibrium isotherms as represented in Figure 1d–f. The unique shape of the isotherm is considered under IUPAC classification to be Type V.⁵ At low humidities (or relative pressures), only small amounts of water are adsorbed, and the isotherm appears concave upward. Characteristic of materials that offer little surface affinity for water molecules, this behavior is defined herein as surface

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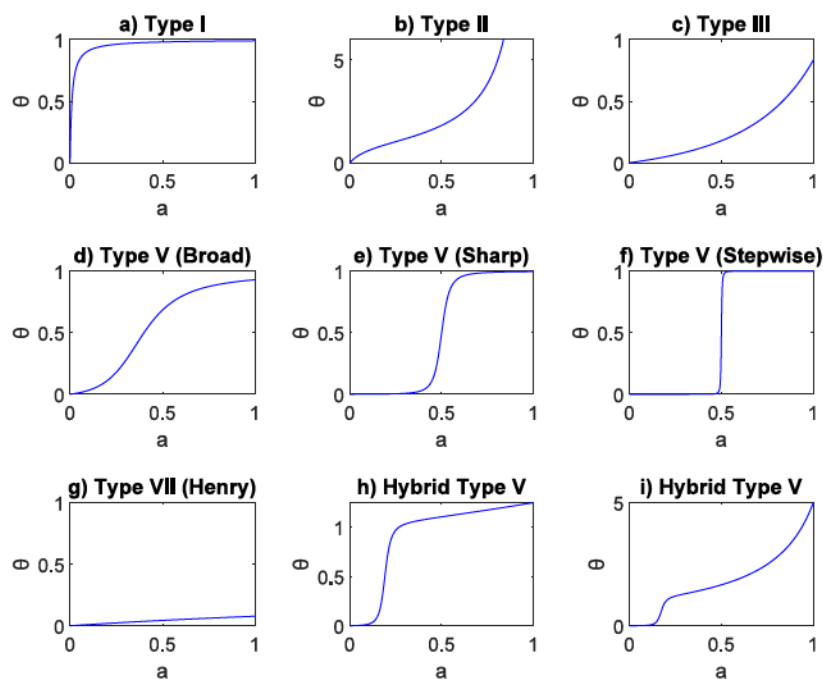


Figure 1. Isotherms of fractional loading (θ) and relative pressure (a) indicating IUPAC types from eq 1 under the following simplifications: (a) $K_{as} = 0$, $K_0 = K_1 = 100$; (b) $K_{as} = 1$, $K_0 = K_1 = 10$; (c) $K_{as} = 0.6$, $K_0 = K_1 = 0.2$; (d) $K_{as} = 0$, $K_0 = 0.2$, $K_1 = 2.5$; (e) $K_{as} = 0$, $K_0 = 0.004$, $K_1 = 2$; (f) $K_{as} = 0$, $K_0 = 0.00004$, $K_1 = 2$; (g) $K_{as} = K_1 = 0$, $K_0 = 0.01$; (h) $K_{as} = 0.2$, $K_0 = 0.04$, $K_1 = 5$; and (i) $K_{as} = 0.8$, $K_0 = 0.04$, $K_1 = 5$.

hydrophobicity. At higher humidities, however, cooperative interaction via hydrogen bonding allows much more water to interact in a fashion that generates a dramatic increase in the amount adsorbed. As pore filling occurs, the amount adsorbed drastically tapers, the concavity pivots from upward to downward, and the sigmoidal shape is produced. These features are clearly indicated in Figure 1d,e. Figure 1f displays a Type V isotherm whose concavity transition is so sharp that it presents a stepwise, unimodal Type VI behavior.⁵ Under these conditions, the concavity transition can be represented by a point of inflection (POI) that is characteristic of the onset of pore filling processes.

The humidity (or relative pressure) at which the POI is observed governs the working range for a given humidity control application.^{8,9} Desiccant applications require the removal of water at low humidity, and dehumidification applications require the control of water content at higher humidities.^{8,9} Notably, many studies report the POI as a characterizing marker that offers a convenient means for representing the complete isotherm.^{8–12} However, despite its wide usage, no rigorous evaluation of this marker for micropore filling has been undertaken in support of its application for characterization of MOF materials.^{8–12} Moreover, the humidity location of this pore filling marker is reported to be affected by pore wall geometry, polarity, and relative strength of fluid–fluid and fluid–solid interactions.⁸ However, it is currently unclear how these factors affect this marker and to what extent. Efforts to explore this by incorporating both pore size and surface chemistry have been proposed in a model¹⁶ that is reported to be unable to account for pore wetting, statistical thickness associated with wetting, or cooperative interactions of water. Additionally, there are currently no widely embraced, validated analyses that can relate fundamental hydrophilic and hydrophobic isotherm relations, including challenging Type V and stepwise isotherms for microporous materials. Furthermore,

methods for benchmarking hydrophobicity of microporous materials with metrics that are consistent with the observed isotherm type are currently critically lacking. The establishment of a successful analysis that is capable of capturing the fundamental behavior of confined water could foreseeably fill these substantial knowledge gaps.

To this end, the study herein is implemented by consideration of a globally unifying isotherm analysis, definition of a novel hydrophobicity metric, simplification for observed stepwise isotherms, and rigorous evaluation and validation of the use of the POI for characterization of stepwise behavior. Critically selected literature data reporting water adsorption in MOFs are assessed not only to establish connections between pore morphology, pore wetting, and cooperative interactions of water but also to gain insight into the mechanisms of micropore filling and origins of hydrophobic behavior in nanostructured materials.

THEORY

Apolar nanochannels embedded in proteins and nanotubes allow water to form hydrogen-bonded multimolecular chains that are collectively oriented.¹⁷ Although under extreme confinement, the molecular interaction produces staggered configurations¹⁷ of water, which give rise to Ising model representation.^{17,18} Under these conditions, fluid–solid as well as fluid–fluid–solid interaction might be expected to influence these systems that exhibit no true phase transition in the thermodynamic limit.¹⁸ Moreover, chains not only can be macroscopically ordered^{17,18} but can display bulk fluid-like properties when coordinated by hydrogen bonding of more than four water molecules.¹⁹ Furthermore, in ultranarrow spacings of molecular dimensions that are formed between deformable graphene layers ranging from 4 to 20 Å,²⁰ water is reported to show behavior akin to bulk fluid.²⁰ Showcasing the importance of fluid–fluid in comparison to fluid–solid interaction, the

Kelvin relation has been applied to predict the relative pressure for pore filling of water between these layers.²⁰ The apparent fluid-like behavior of water under extreme confinement in pores of molecular dimensions allows water to be viewed as an angstrofluid. Currently, angstrofluidics is an evolving field²¹ in which theoretical tools are lacking due to the fact that “fluid structuring effects and correlations play an overwhelming role”,²² and therefore, “new theoretical descriptions are required to understand the emerging physics behind these effects”.²³ Possible developments in this field could be enabled by the rapid emergence of novel microporous materials such as microporous MOF crystals²⁴ whose structure consists of ordered angstrom-sized channels.

Molecular simulations have provided insights into the wide array of associative behaviors observed in these materials. In microporous MOF-303,²⁵ clusters beyond four water molecules have been simulated, and water is seen to coordinate by forming hydrogen bonds with the framework and with each other. Hanikel et al.²⁶ have also simulated MOF-303 where water is shown to hydrogen-bond and form three-dimensional chains within a water network. Similar results are seen for microporous CAU-10²⁷ and NU-1500-Cr²⁸ in which “hydration is initiated by water molecule adsorption at primary sites within the framework followed by the formation of water chains that extend along the MOF channels”.²⁸

These studies highlight the complex underlying behavior of water in extreme confinement that involves fluid–solid and fluid–fluid–solid interactions as well as pore network effects that require assessment at the molecular and supramolecular level.

Shortcomings in the Current Assessment of Hydrophobicity. Fundamental features embedded in adsorption mechanisms and the nature of water interactions can be viewed at two disparate length scales involving both molecular and supramolecular interpretation. However, the disparity of length scales confounds simple metrics for assessment that have been proposed for mesoporous materials with pores larger than 20 Å²⁹ but are currently lacking for microporous solids. Moreover, the disparity of scale produces distinct differences between the internal and external interaction of water with microporous materials.³⁰ In fact, some studies view the external surface as a form of crystal defect,³¹ which generates a need to partition internal from external interactions.³²

Additionally confounding the issue is the lack of broad consensus on simple definitions distinguishing hydrophilic from hydrophobic behavior. To improve classical definitions of hydrophobicity, some studies have suggested benchmarks based on the free energy of hydration.³³ Moreover, it has been argued that hydrophobic behavior should not be based on discrete criteria³⁴ and that robust definitions should be capable of displaying shifting behavior that is benchmarked on a continuous scale.³⁴ Furthermore, there is also a lack of consensus in the literature regarding the application of hydrophobicity and hydrophilicity benchmarks for MOFs. A notable example applies to UiO-66 that is considered hydrophilic by benchmarks that assess steep uptakes occurring at low humidities.³⁵ However, by other benchmarks, UiO-66 is considered hydrophobic.³¹

Despite shortcomings in the simple definition of hydrophobicity, the current suite of tools for its assessment in MOFs has been reviewed by Xie et al.³¹ Henry’s constant and relative pressure where the concavity pivots are featured tools. These can be coupled with standard tools for characterizing MOFs by

adsorptive probes other than water including simple molecules such as nitrogen and argon at subambient temperatures.³¹ Notably, these same tools have been employed to characterize the adsorption and underlying behavior of water in microporous carbon.^{36,37} Surface chemistry is reported to play a role in this behavior when the density of moieties capable of hydrogen bonding with water molecules (e.g., hydroxyl, amine, sulfonic acid groups, as well as open metal sites) is high.³¹ Surfaces composed of nonpolar or weakly polar groups generate internally hydrophobic MOFs.³¹ These surfaces can be generated from presynthetic ligand design or postsynthetic hydrophobization and generally display Type V isotherms.³¹ However, MOFs broadly considered to be hydrophobic constitute only a small percentage of catalogued materials³¹ but are essential to humidity control applications such as water harvesting. For these materials, pore filling is initiated by mechanisms based on relatively weak fluid–solid interaction that is generally accompanied by fluid–fluid–solid interaction at higher pressures.³¹

Clear from assessment of the literature is the current dearth of rigorous studies that simultaneously:

- 1) Demonstrate clear relationships between internal hydrophobicity and the variety of observed water adsorption isotherm types including Type III (Figure 1c), Type V (Figure 1d,e), and stepwise isotherms (Figure 1f) observed in a variety of microporous materials.
- 2) Deliver a definition of hydrophobicity that is based on a continuous scale and is inherently linked to isotherm type.
- 3) Demonstrate clear relationships between the molecular behavior of water, isotherm features of water, and isotherm features displayed by simple molecules such as nitrogen and argon that are commonly employed for pore size analysis.
- 4) Discriminate effects of pore morphology from surface chemistry, network effects of water chains, and fluid–solid from fluid–fluid–solid interaction while incorporating features of pore wetting, statistical thickness associated with wetting, and cooperative interactions of water.

These current voids in fundamental understanding will be individually addressed in the context of rigorous mechanistic isotherm types and are showcased by relevant examples in subsequent sections.

Hydrophilic and Hydrophobic Behavior and Isotherm Types. Apart from industrially relevant applications in humidity control and energy storage, an understanding of the behavior of water in microporous materials is necessary for important niche applications. A prime example resides in decontamination studies¹⁰ in which material compatibility assessments are required to determine the presence of specific compounds that are capable of system degradation. Hydrated materials employed for packaging,³⁸ for instance, are considered incompatible with systems containing metals due to the potential for corrosive degradation.

The amount of water residing within a hydrated material can be characterized by equilibrium isotherm relations, which aid in the assessment of hydration levels. This information is required not only at system temperatures but also at elevated temperatures that allow accelerated contaminant removal.³⁸ These equilibrium isotherms can vary greatly for different hydrophilic microporous materials, which contain pores of radius (or half-width for slit structures) less than 1 nm. Some zeolites, for

Table 1. Isotherm Selection Criteria Showing Isotherm Types (I–VII), Various Simplifications of eq 1, and the Resulting Relationships between the Specified, Mechanistically Based, Isotherm Models

model	isotherm types and features	relationship between $\theta = \frac{C}{C_{\text{SAT}}}$ and $a = \frac{P}{P_V}$	condition	H
CMMS	hybrid isotherm types (e.g., Figure 1h,i)	$\theta = \frac{K_{0a}}{1 - K_{0a}[K_{0a} + w^2(1 - K_{0a})]}$ with $w = \frac{1}{2} \left\{ 1 - \frac{K_{1a}}{(1 - K_{0a})} + \sqrt{\left(1 - \frac{K_{1a}}{1 - K_{0a}} \right)^2 + \frac{4K_{0a}}{1 - K_{0a}}} \right\}$		
Henry	VII (linear: Figure 1g)	$\theta = K_{0a}$	$a \rightarrow 0$	
BET	II (downward concavity at low pressure: Figure 1b)	$\theta = \frac{K_{0a}}{[1 - a][1 - a + K_{0a}]}$	large $K_0 = K_1$; $K_{as} = 1$	$H = 1$
GAB	II (downward concavity at low pressure: shape of Figure 1b)	$\theta = \frac{K_{0a}}{[1 - K_{as}a][1 + (K_0 - K_{as})a]}$	large $K_0 = K_1$; $0 \leq K_{as} \leq 1$	$H = 1$
GAB	III (upward concavity: Figure 1c)	$\theta = \frac{K_{0a}}{[1 - K_{as}a][1 + (K_0 - K_{as})a]}$	small $K_0 = K_1$; $0 \leq K_{as} \leq 1$	$H = 1$
Langmuir	I (downward concavity: Figure 1a)	$\theta = \frac{K_{0a}}{[1 + K_{0a}]}$	large $K_0 = K_1$; $K_{as} = 0$	$H = 1$
Rectangular	I (sharpened shape of Figure 1a)	$\theta = 1$	$K_0 = K_1 \rightarrow \infty$; $K_{as} = 0$	$H = 1$
Ising	V (upward concavity at low pressures turns to downward concavity: Figure 1d,e)	$\theta = \frac{K_{0a}}{K_{0a} + \frac{1}{4} \{ 1 - K_{1a} + \sqrt{(1 - K_{1a})^2 + 4K_{0a}} \}^2}$	$K_{as} = 0$; $K_1 > 1$; $K_0 < K_1$	$H > 1$
Ising	III (upward concavity: shape of Figure 1c)	$\theta = \frac{K_{0a}}{K_{0a} + \frac{1}{4} \{ 1 - K_{1a} + \sqrt{(1 - K_{1a})^2 + 4K_{0a}} \}^2}$	$K_{as} = 0$; $K_1 < 1$; $K_0 < K_1$	$H > 1$
Ising	I (downward concavity: shape of Figure 1a)	$\theta = \frac{K_{0a}}{K_{0a} + \frac{1}{4} \{ 1 - K_{1a} + \sqrt{(1 - K_{1a})^2 + 4K_{0a}} \}^2}$	$K_{as} = 0$; $K_0 > K_1$	$H < 1$
Ising	VI (unimodal)/Stepwise V (Figure 1f)	$a = \frac{1}{K_1}$	$K_{as} = 0$; $K_0 \ll K_1$	$H \rightarrow \infty$

example, display hydrophilic behavior that leads mostly to Type I equilibrium isotherms by the IUPAC classification scheme⁵ that are shown in Figure 1a. Notably, Type I isotherms are also seen with subambient adsorption of species such as carbon dioxide, argon, and nitrogen in microporous materials and have also been reported for water in MOF materials.³¹

In other zeolites such as ZSM-5, Type II water adsorption equilibrium³⁹ is displayed as shown in Figure 1b and has also been reported for water in MOF materials.³¹ Extending the variety of observed behavior is another zeolite, known as silicalite, which displays Type III equilibrium⁵ that is also reported for MOF materials.³¹ Additionally, some microporous materials such as aluminophosphates, titanosilicates,⁵ and nonfunctionalized carbon display Type V water adsorption isotherms.^{36,37} However, Type V isotherms for water are not a phenomenon exclusive to microporous materials. Mesoporous materials such as MCM-41 that contain pores of radius between 1 and 25 nm are also capable of displaying Type V behavior.^{40,41}

The large variability in observed equilibrium types requires the consideration of a variety of isotherm analyses. Aumond et al.¹⁰ have reviewed isotherms relevant to decontamination with considerable emphasis on water adsorption. The Type I and II behavior displayed by hydrophilic materials is reasonably well understood.^{5,10,29} However, nominally hydrophobic materials have a more complex behavior that is not well understood. For these materials, molecular interaction with water is believed to be governed by the formation of primary adsorption sites and is characterized by the observation of Henry's law^{8–12} at low pressures. At higher pressures or humidities, cooperative effects from hydrogen bonding are believed to promote the uptake of water until the pore has reached saturation.

Enabling Comparison of Isotherms of Water and Simple Molecules. To successfully connect the simple behavior of nonpolar molecules with the complex behavior of polar molecules in hydrophilic and hydrophobic materials, a unifying isotherm is required to rigorously link observed

equilibrium relationships. In the review of Aumond et al.,¹⁰ there are several key foundational isotherm models presented including the mechanistically based Henry, Langmuir, and Brunauer–Emmett–Teller (BET) as well as the thermodynamically based Derjaguin analysis. The review does not consider models that fail to meet the thermodynamic requirement of reduction to Henry's law at low concentrations. Ultimately, this condition explicitly precludes consideration of commonly applied variants of Dubinin's theory.^{8,9} Furthermore, the review does not include forms with empirical exponents such as Freundlich, Langmuir–Freundlich, Sips, Toth and associated clustering isotherms whose “scientific foundations often remain questionable”.¹⁰ Moreover, these models inadequately represent pore morphology and are often applied to isolated data sets of unspecified error with justification implicitly rendered simply by goodness of fit. A more reliable assessment of underlying behavior can be delivered by the establishment of global relationships assessed across multiple materials with various morphological features. To this end, the cooperative multi-molecular sorption (CMMS) model offers a viable option for both the elucidation of underlying interaction mechanisms as well as the unification of key foundational isotherms. Based on a Markov copolymer,⁴² the CMMS isotherm has been applied to represent Type V water adsorption in carbon micropores^{43–45} as well as unique, hybrid, Type V isotherms of polar alcohol molecules in a microporous MOF, ZIF-8, and a polymer of intrinsic microporosity (PIM).⁴⁶

Ising Model from CMMS Relation. As shown in Figure 1, isotherms for vapors are generally represented by a relationship between relative pressure, a (defined as the ratio of the pressure, P , to the saturated vapor pressure, P_V), and fractional loading, θ , which is the ratio of the adsorbed phase concentration to that at saturation. The CMMS relationship, presented in Table 1, relates θ to a by:⁴²

$$\theta = \frac{K_0 a}{(1 - K_{as} a)[K_0 a + w^2(1 - K_{as} a)]} \quad (1a)$$

with the parameter w given by:

$$w = \frac{1}{2} \left\{ 1 - \frac{K_1 a}{(1 - K_{as} a)} + \sqrt{\left(1 - \frac{K_1 a}{1 - K_{as} a} \right)^2 + \frac{4K_0 a}{1 - K_{as} a}} \right\} \quad (1b)$$

Further captured in Table 1 are the multiple transitions in concavity and complex isotherm types, represented by the CMMS model. Also captured are the varieties of simplified forms, together with isotherm features, corresponding isotherm types, and simplification criteria associated with each type. Notably, the thermodynamic requirement of reduction to Henry's law is satisfied by consideration of the low-pressure limit ($a \rightarrow 0$) of the CMMS model with the result also presented in Table 1. This table clearly demonstrates the ability of the model to represent a multitude of compatible equilibrium types in a simple analytic form. It also highlights the potential that this model offers for consideration as a globally unifying isotherm that might be capable of representing the simple behavior of nonpolar molecules as well as the complex behavior of polar molecules in hydrophilic and hydrophobic materials.

In alignment with previous discussion, the CMMS model proposes variable forms of interaction with the host material's surface. Initial fluid–solid interaction, referred to as primary site adsorption, is characterized by an affinity parameter noted as K_0 to represent Henry's law. Beyond Henry's law, subsequent interactions depend on the probe molecule. For water in nominally hydrophobic materials, primary sites can enhance the formation of neighboring secondary sites through hydrogen bonding in addition to surface interaction. These fluid–fluid–solid interactions are represented by the secondary site affinity parameter noted as K_1 .⁴²

For weakly hydrophilic materials, adsorption of polar molecules can generate adsorbate networks that grow via primary and secondary interactions to form hydrogen-bonded multimolecular chains. Interaction occurs not only with the surface as a fluid–solid interaction but also with other adsorbed molecules in a fashion that additionally promotes a fluid–fluid interaction. Hydrogen-bonded water chains can continue to grow through the process of side association that is represented by the affinity parameter K_{as} .⁴² This process occurs adjacent to the main chains in systems such as open surfaces that have geometric allowance to accommodate such growth at high relative pressure.⁴² The side association parameter K_{as} represents the fraction of primary site molecules that allow subsequent layering in a fashion consistent with the Guggenheim–Anderson–de Boer (GAB) analysis of Andersen.⁴⁷

For a homogeneous, uniform first layer in which $K_0 = K_1$, the classical BET, GAB, and Langmuir isotherms⁴⁸ are applicable as shown in Table 1. The Langmuir isotherm is limited to monolayer formation only. However, materials that offer uniform first layer formation and can accommodate multilayers, complete ($K_{as} = 1$) or incomplete multilayering ($K_{as} \neq 1$) dictates the applicability of BET or GAB analyses, respectively. This is captured in Table 1. BET analysis is classically applied for

determination of surface area⁴⁸ by adsorption of simple molecules on surfaces that allow uniform layer formation.

In structures that cannot offer uniform monolayer and multilayer formation ($K_0 \neq K_1$; $K_{as} = 0$), Table 1 indicates that the Ising model is a valid simplification of the more general unifying CMMS isotherm.^{43–45} The Ising model can be represented as:

$$\theta = \frac{C}{C_{SAT}} = \frac{K_0 a}{K_0 a + \frac{1}{4} \{ 1 - K_1 a + \sqrt{(1 - K_1 a)^2 + 4K_0 a} \}^2} \quad (2)$$

Largely underutilized in comparison to other models represented in Table 1, the Ising model can represent a variety of isotherm types relevant to water in hydrophobic and hydrophilic materials including Types I, III, and V.

For materials with differing degrees of hydrophobicity, the Ising model captures water's weak fluid–solid interaction and the associated lack of uniform layering ($K_0 \neq K_1$). In alignment with Ising model conditions, water molecules on hydrophobic silicon surfaces⁴⁹ have been directly observed in disordered ($K_0 \neq K_1$), cluster-like structures.⁴⁹ To quantify the degree of hydrophobicity offered by various materials, an appropriate definition that captures both fluid–solid and fluid–fluid–solid interactions is required.

Hydrophobic Materials and Stepwise Isotherms. To fill the void in hydrophobicity metrics that are capable of distinguishing various equilibrium types, including Type V isotherms applicable to microporous materials, a hydrophobicity ratio, H , is introduced herein. It is novelly defined on a continuous scale as the ratio of secondary site to primary site affinity as:

$$H = \frac{K_1}{K_0} \quad (3)$$

Representing the ratio of fluid–fluid–solid to fluid–solid interaction, the hydrophobicity ratio can be large for materials offering little surface affinity and considerable fluid–fluid–solid interaction. Additionally, increasingly larger hydrophobicity ratios affect the Type V isotherm shape by sharpening the transition from an upward to downward concavity. This generates a steeper sigmoidal shape as shown in Figure 1 d–f. Figure 1d represents a broad Type V isotherm from a K_0 value of 0.2 and $H = 12.5$. Figure 1e indicates that a smaller K_0 and therefore higher H value produce a transition to a steeper Type V shape. Extreme values of $K_0 = 0.00004$ and $H = 50,000$ produce a nominally stepwise Type V isotherm shown in Figure 1f. Under the IUPAC classification, this isotherm could also be interpreted as a unimodal form of Type VI isotherm.

It is clear from Figure 1 that large values of the hydrophobicity ratio generate isotherms so steep that a simple POI represents the isotherm. Many of the same studies reporting a sharp Type V behavior utilize the POI as the characterizing feature^{8–12} of the observed isotherm. Currently, there are no established means to rigorously relate this point to any fundamental quantity that characterizes the MOF system.^{8–12} To relate it to a fundamental isotherm parameter, this study looks at the behavior of the Ising model (as represented by eq 2). To find the POI, the first derivative of the isotherm (eq 2) is taken and represented as follows:

$$\frac{\partial \theta}{\partial a} = \frac{K_0 K_1 a + K_0}{\{4K_0 a + (K_1 - 1)^2\}^{3/2}} \quad (4a)$$

The second derivative is found and given as:

$$\frac{\partial^2 \theta}{\partial a^2} = -\frac{2K_0\{K_1^3 a^2 + K_1^2 a + K_1(K_0 a - 2) + 3K_0\}}{\{4K_0 a + (K_1 - 1)^2\}^{5/2}} \quad (4b)$$

Setting the second derivative to zero and rejecting the negative root result in:

$$a_{\text{POI}} = \frac{-\frac{K_0}{K_1} - 1 + \sqrt{9 - 10\frac{K_0}{K_1} + \left(\frac{K_0}{K_1}\right)^2}}{2K_1} \quad (5)$$

where a_{POI} is the value of relative pressure where the inflection point occurs and is expressed in terms of the values of K_1 and K_0 . To examine the result of large values of the hydrophobicity ratio, this study looks at a limit. At the infinitely large limit of hydrophobicity, $H \rightarrow \infty$, or alternatively, $\frac{K_0}{K_1} \rightarrow 0$, the POI expressed in eq 5 simplifies to be inversely related to K_1 only:

$$\lim_{K_0/K_1 \rightarrow 0} a_{\text{POI}} = \frac{1}{K_1} \quad (6)$$

This analysis indicates that, for noninteracting solids where $K_0 \rightarrow 0$ or for extremely hydrophobic materials where K_0 is much smaller than K_1 , extremely large values of the ratio result in $H \rightarrow \infty$, and the isotherm collapses to a single POI that is inversely related to K_1 . Additionally, under this limit, the isotherm will appear as a step change whose location will depend only on K_1 and not on K_0 . This analysis provides a novel verification of the use of a_{POI} as a parameter that characterizes the water/MOF system. The result is summarized in Table 1 as the stepwise Ising model. Contrasted with stepwise behavior observed with extreme hydrophobicity ($K_0 \rightarrow 0$) is irreversible, rectangular behavior⁴⁸ that represents extreme hydrophilicity ($K_0 = K_1 \rightarrow \infty$). Both are indicated on Table 1 which also considers the hydrophobicity ratio and applicability conditions for isotherm relations commonly applied between these extremes.

Hydrophobicity Ratio and Isotherm Types. Table 1 indicates that the novel defined hydrophobicity ratio ranges in value to capture classically defined hydrophobic and hydrophilic isotherms. The value of the ratio dictates the type of isotherm for the following specific classes of materials:

Class A: strongly hydrophilic materials (K_0 large and $H = 1$).

Isotherms for *strongly hydrophilic materials* reflect solids offering significant fluid–solid interaction (K_0 large) that is considerably larger than the fluid–fluid–solid interaction. As a result, these materials effectively offer equal affinity for all surface sites. Primary and secondary sites become indistinguishable, uniform layering can occur, and $K_0 = K_1$, resulting in $H = 1$. In the absence of side association ($K_{\text{as}} = 0$), a homogeneous monolayer could form, resulting in the Type I, Langmuir isotherm. With the inclusion of side association, GAB and BET isotherms are applicable. These isotherms have been classically defined as hydrophilic and often used for analysis of layering of simple molecules. Very strongly hydrophilic materials ($K_0 = K_1 \rightarrow \infty$; $H = 1$) display sharp Type 1 or rectangular, irreversible isotherms.

Class B: moderately hydrophilic materials ($H < 1$).

In contrast, *moderately hydrophilic materials* offer both fluid–solid and fluid–fluid–solid interactions that are enabled by hydrogen bonding. If the hydrogen bonding is weak in comparison to surface interaction, then $K_0 > K_1$ and $H < 1$, resulting in the application of Type I Ising or CMMS models for the absence or inclusion of side association, respectively.

Class C: moderately and strongly hydrophobic materials ($H > 1$).

In further contrast, *moderately hydrophobic materials* present primary sites that offer limited fluid–solid interaction reflected by a small Henry's constant. Fluid–fluid–solid interaction is driven by the significant hydrogen bonding capability of water, and hence, $K_0 < K_1$, resulting in $H > 1$. Broad Type V or Type III Ising models can be applied in the absence of side association, and these isotherms have been classically defined as hydrophobic.

In stark contrast, *strongly hydrophobic materials* generate sharp Type V or nominally stepwise isotherms that are indicative of pore filling processes that are driven by condensation. These materials offer very little fluid–solid interaction ($K_0 \rightarrow 0$) or offer much larger fluid–fluid–solid interaction ($K_1 \gg K_0$). As a result, $H \rightarrow \infty$, and isotherms captured by the stepwise Ising model are predicted.

It is evident from Table 1 that the hydrophobicity ratio provides a definition of hydrophobicity that is based on a continuous scale and can explain the variety of water adsorption isotherm types broadly observed in a range of microporous materials. It is also evident that the hydrophobicity ratio provides a benchmark that can explain transitions from extremely hydrophilic isotherms that are dominated by fluid–solid interactions to extremely hydrophobic isotherms that offer very little fluid–solid interaction.

Classically defined hydrophobic isotherms for nanoporous materials such as Type III and V isotherms offered by “Class C” materials are captured by $H > 1$. By this benchmark, hydrophobicity can be defined by the condition $H > 1$. Moreover, sharp Type V isotherms (Figure 1e,f) also offered by “Class C” materials have very high values of hydrophobicity ratio due to comparatively little fluid–solid interaction. An example of a sharp Type V isotherm is shown in Figure 2 for MWH-1 at 293 K.⁵⁰ The figure displays features of Figure 1f that could be represented by the stepwise Ising model. The relative filling pressure clearly resides at 0.02 ($a_{\text{POI}} = 2\%$), and application of eq 6 translates this to an estimate of $K_1 = 50$.

Challenges Finding Henry's Constant with Nominally Stepwise Isotherms. Figure 2 formally represents a hydrophobic “Class C” isotherm of Type V that could be fully represented by the Ising model shown in eq 2. However, Figure 2 also shows bounds for the data that are indicated by two curves with disparate values of the hydrophobicity ratio H at 90 and 3000. The large disparity in values of H translates to a large variation in the estimate of K_0 that could feasibly range over an order of magnitude from 0.017 to 0.55. It is therefore clear from Figure 2 that nominally stepwise isotherms are sensitive to changes in K_1 but largely insensitive to changes in Henry's constant K_0 . As a result, a precise assessment of Henry's constant across a wide range of MOFs is not feasible. Coupling this limitation with the fact that the relative filling pressure (a_{POI}) is clearly indicated on sharp isotherms, the use of a_{POI} and K_1 as a

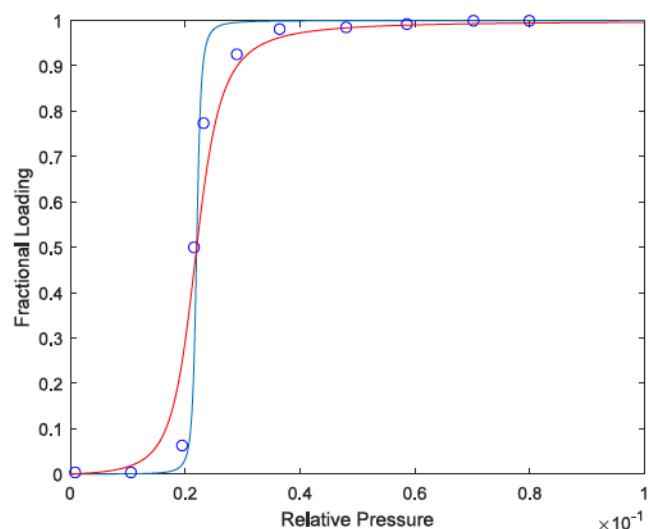


Figure 2. Nominally stepwise water equilibrium in MWH-1⁵⁰ at 293 K is represented as blue circles. Data bounds are indicated by two lines representing the Ising model of eq 2 with $K_1 = 50$ together with $H = 3000$ (blue line) and $H = 90$ (red line).

characterizing system variable appears to be highly advantageous in terms of simplicity and precision.

Moreover, the use of secondary site affinity (K_1) as a characterizing system variable delivers a methodology capable of circumventing the need for an entire isotherm data set and could offer the potential for application to large-scale screening studies. In fact, it has been reported that computational screening algorithms can become trapped in local energy minima primarily as a result of hydrogen bonding in simulations of nominally stepwise behavior of water in MOF materials.⁵¹ The analysis proposed herein could be applied to rationalize simulations and possibly permit an efficient computational strategy in the search for optimal materials for atmospheric water harvesting.

Although the preceding analysis is capable of interpreting molecular-level interactions and isotherm types, it does not fully identify mechanisms of pore filling. However, scrutiny of the scaling behavior of isotherm features with pore size offers the potential to characterize these mechanisms.

Pore Filling Mechanisms and Scaling Behavior with Pore Size. Nominally stepwise isotherms, noted for strongly hydrophobic “Class C” materials, are observed in microporous MOFs that exhibit high values of hydrophobicity ratio due to comparatively little surface interaction. The stepwise features are reminiscent of condensation in porous solids. In terms of pore size, simple condensation with wetting is classically characterized by the Kelvin relation that can be expressed in arbitrary geometry by the following:⁵²

$$\frac{\partial V}{\partial S} = -\frac{\sigma v_M}{R_g T \ln\left(\frac{P}{P_v}\right)} \quad (7)$$

where R_g is the universal gas constant, T is the absolute temperature, v_M is the liquid molar volume, and σ is the surface tension of fluid within the pore. The term $\frac{\partial V}{\partial S}$ represents the change in pore volume with respect to the interfacial area of the fluid and is therefore dependent on geometry. For fluid lodged between two parallel plates, slab geometry reduces this term to slit half-width, and for cylinders, it equates to half the pore

radius. To align with other publications, an effective pore radius r_{pore} is applied and is equivalent to slit half-width for slab geometry. A geometric factor f is also assigned such that $f = 1$ for an ideal slab and $f = 2$ for an ideal cylinder such that:

$$\frac{\partial V}{\partial S} = \frac{r_{\text{pore}}}{f} \quad (8)$$

For real materials, pore morphologies are not perfectly uniform. In MOFs, differences can be seen between pore limiting diameter (PLD) and largest cavity diameter (LCD). In fact, simulations indicate that MOFs exhibit tube-like pore morphologies when their LCD/PLD ratios fall between 1 and 2.⁵³ Cylindrical geometry might be appropriate for these materials; however, slab geometry is often applied for the assessment of pore size via nitrogen adsorption. In UiO-based MOFs,⁵⁴ for example, octahedral and tetrahedral pores of differing size have been modeled as slit shaped channels ($f = 1$) for purposes of pore size assessment with nitrogen adsorption data. Conversely, alternate geometry ($f = 2$) has been applied for the assessment of water adsorption in the same materials. The interchangeability of geometry suggests that MOF channels may fall into a hybrid situation where pore morphology might allow f to span a value from 1 to 2.

Although simple condensation dictated by the Kelvin relation can account for geometry, it does not explicitly account for fluid–fluid–solid interaction. To rectify this, the conditions of mechanical and chemical equilibrium should be considered.

Conditions for Mechanical Equilibrium: Wetting and Disjoining Pressure. In prior decades, the creation of ordered mesoporous materials such as MCM-41 stimulated new interest and propelled the advancement of theories for adsorption of simple molecules in nanoporous interacting solids. One theory applied to adsorption within mesopores has been described by Broekhoff and de Boer⁵⁵ and accounts for film thickness denoted as t . It also includes allowance for interaction with the solid, denoted herein as u , as well as a geometric factor f . The resulting relation is given as:⁵⁶

$$-R_g T \ln\left(\frac{P}{P_v}\right) = \frac{f \sigma v_M}{r_{\text{pore}} - t} + u R_g T \quad (9)$$

The approach of Broekhoff and de Boer⁵⁵ is similar in principle to that proposed by Derjaguin (for example see 57) when conditions of mechanical equilibrium are imposed on fluid and surface forces. For water in microporous materials, surface forces as a result of adsorption and wetting can generate a “disjoining pressure”, π . The resulting Derjaguin relation is equivalent to eq 9 under the assignment $u R_g T = \pi v_M$. A negative disjoining (conjoining) pressure as a result of wetting can reduce the observed filling pressure to values well below those expected for a given pore size based on simple condensation.

The two approaches of Broekhoff and de Boer⁵⁵ and Derjaguin⁵⁷ have been fused and referred to as Derjaguin–Broekhoff–de Boer (DBdB) analysis⁵⁸ that describes many model mesoporous solids such as SBA-15 and MCM-41.⁵⁹

Consideration of Layer Thickness in Hydrophobic Materials. Extremely hydrophilic materials that offer a strong fluid–solid interaction may also allow uniform layering of adsorbed water. The adsorbed layer may occupy a volume that reduces the volume available for condensed fluid within the pore. Under these conditions, the effective pore radius is reduced, and adsorption analysis may require allowance for film thickness. However, hydrophobic isotherms of Type III, V, VI,

or VI indicate weak fluid–solid interaction in which uniform layering is not observed. This is supported by direct observations of water on hydrophobic silicon surfaces that reflect the disordered nature of water adsorption and inability for water to form a uniform layer.⁴⁹ As a result, the statistical thickness is considered negligible ($t = 0$) for this type of interaction. To account for this, eq 9 is simplified as:

$$-R^g T \ln \left(\frac{p}{p^*} \right) = \frac{f_{\text{ov}}^g}{p^*} + u R^g T \quad (10)$$

Equation 10 represents mechanical equilibrium between cohesive and adhesive forces for confined water and reduces to the classical Kelvin relation for simple condensation when $u \rightarrow 0$. As a result, this relation can be considered a modified Kelvin analysis that accounts for analogous adsorption, confining, and wetting forces that are generated by interaction with the surface. Modified Kelvin analysis has not only been extensively applied to mesopores⁵² but also been applied to micropores as small as 4 Å.^{36,37,60,61} This encourages further application to microporous solids, such as MOFs studied in this investigation.

Considered above are conditions for mechanical equilibrium that can identify the filling pressure for a given pore size. For a complete description, however, mechanical equilibrium conditions must be complemented with corresponding appropriate conditions for chemical equilibrium.

Tracking the Filling Pressure of Water: Mechanical and Chemical Equilibrium

Large hydrophobicity ratios display a nominal stepwise behavior that is characterized by the stepwise Ising model. This model provides a simple relationship between filling pressure and the secondary site affinity parameter K_1 represented as $\frac{K_1}{p} = \frac{1}{p}$. Applying this condition for chemical equilibrium to the conditions for mechanical equilibrium, eq 10 becomes:

$$R^g T \ln(K_1) = \frac{f_{\text{ov}}^g}{p^*} + u R^g T \quad (11)$$

Notably, this relation represents an Ising Model coupled with Modified Kelvin Analysis that has previously been proposed as Ising-Model-Modified-Kelvin-Analysis (IMMKA).⁵⁷ It represents not only a Kelvin relation modified for wetting but also a simplification of DBB analysis. The two components of IMMKA indicated in eq 11 include a nanocapillary contribution that represents the condensation-driven behavior of secondary site interaction. The wetting component of the analysis is represented by the wetting energy for secondary site interaction, $u R^g T$.

Application to Microporous MOFs Displaying Type V Isotherms. For MOFs, the relationship between pore size and water adsorption behavior is known to follow a general “rule of thumb” that suggests that contracted pores of isoteric MOFs result in Type V water isotherms with lower relative inflection points and higher steepness.⁶² Although generally accepted, no simple, rigorous, and widely applicable validation has appeared in support of this “rule of thumb”. However, this rule can be directly verified by consideration of the IMMKA relation presented as eq 11. The nanocapillary component of IMMKA suggests that contraction of the pore radius delivers both a larger value of secondary site affinity (K_1) and lower inflection point. Additionally, the increase in K_1 directly increases the value of the hydrophobicity ratio when accompanied by insignificant changes in surface chemistry and Henry’s law constant K_0 .

RESULTS AND DISCUSSION

Moreover, the increased hydrophobicity ratio delivers steeper isotherms, as shown in Figure 1. As a result, IMMKA affirms the “rule of thumb” by directly predicting that contracted pore size is related to lower a_{POI} values as well as steeper isotherms. However, application of IMMKA to characterize water adsorption requires assessment of the micropore size. It has been demonstrated in this study that the behaviors of water and simple molecules such as nitrogen are fundamentally comparable and only differ by the relative contribution of fluid–solid versus fluid–fluid–solid behavior. Therefore, in principle, pore features probed by simple molecules should be comparable to those probed by water. As a result, the analysis proposed herein is appropriately applied to microporous materials that:

- (1) have their pore size independently determined by standard adsorption of simple molecules such as nitrogen or argon adsorption at 77 and 87 K, respectively.
- (2) have water adsorption isotherms displaying a clear inflection point.
- (3) have water adsorption isotherms displaying significant isotherm steepness enabled by high hydrophobicity ratios that are reflective of high secondary site affinity constant, low Henry’s law constant, or both.

The behavior of water in MOF micropores can be elucidated by consideration of the scaling behavior of secondary site affinity with micropore size. This requires the collation of a series of MOF materials for which the points of inflection in the water adsorption isotherm and micropore size are reported. Moreover, with the assignment of $\delta = \frac{f_{\text{ov}}^g}{R^g T}$, eq 11 can be expressed in the simple form:

$$\ln(K_1) = \frac{\delta}{\delta} + u \quad (12)$$

which provides a convenient representation for the application of linear regression of collated values for $\ln(K_1)$ and inverse micropore size. However, criteria for material selection must be introduced to permit a reliable analysis across a series of materials.

Criteria for Analysis of Water Isotherms and Limitations. Water adsorption in porous materials involves numerous competing phenomena that are governed by the MOF pore dimensionality, size, shape, and chemical nature,^{62,63} which are subsequently individually addressed.

The chemical nature is affected by the presence of framework moieties that can increase the fluid–solid interaction. This interaction is largely captured by Henry’s law constant K_0 . However, the analysis proposed herein is limited to steep isotherms that are sensitive to changes in K_1 but largely insensitive to changes in Henry’s constant. This is supported by the limit analysis at large values of H , which indicates that the filling relative pressure (a_{POI}) is independent of Henry’s constant for nominally stepwise isotherms. This is further supported by a simple informal comparison of MOF samples. Shown in Table S1,⁶⁴ are two samples of MOF-303,^{64,65} CUK-1,⁶⁶ and CAU-10-H,⁶⁷ which all have similar pore size and filling pressures (a_{POI}) in the range of 10 to 15% but differ greatly in formulation chemistry. It is apparent from the analysis that the selection of microporous materials with steep isotherms not only allows the influence of the chemical nature to be minimized but also promotes the role of micropore morphology.

The effect of pore dimensionality can be minimized by selecting MOFs that report unimodal pore size obtained from standard adsorption of simple molecules such as nitrogen at 77 K. This leaves the geometry of micropore filling as a parameter that is represented by the geometric factor f , which can be evaluated from data assessment.

Beyond the previously mentioned analysis requirements, other limitations and associated criteria are listed below:

1. Exclusively microporous MOF materials are studied.

Adsorption of simple molecules in mesopores is relatively well characterized and understood to be initiated by the formation of multilayers for which consideration of statistical thickness⁴⁸ is required. Multilayering is generally followed by bulk mechanisms such as Kelvin-like condensation, meniscus formation, and associated hysteresis.⁴⁸ Contrastingly, water adsorption mechanisms in micropores are theoretically considered to be continuous and reversible at near-ambient temperatures,⁶⁸ which yield hysteresis-free Type V isotherms relevant to humidity control applications. Micropores can also allow potential overlap from pore walls to enhance fluid–fluid–solid interaction throughout the entire channel volume; an effect that may not be offered in larger pores. For these reasons, microporous MOFs are exclusively considered in this study.

2. MOFs reported to contain channels of unimodal size are studied.

Further complicating the global adsorption phenomena is pore size distribution that distorts isotherm shapes.⁴⁸ To minimize this effect, nominally nondefective MOFs reported to contain pores with unimodal effective size are collated in Table S1. However, pore size assessment currently requires a specification of geometry in the form of either a slab or a cylinder. For irregular microporous materials that do not conform to either, substantial variability can be introduced in the assessment of pore size simply from the analysis methodology. As a possible result of the variability in pore size assessment, UiO-67-4Me-NH₂-38 is reported to have differing unimodal pore size in two review articles.^{8,12} Considered as replicates, both pore sizes are included separately in the analysis in a basic effort to capture the uncertainty associated with pore size estimation.

3. Ambient temperatures are studied.

Adsorption isotherms can be influenced by the temperature. To minimize any possible influence of the temperature, assessment of data at around 298 K is undertaken in this study.

4. MOFs with demonstrated water stability are studied.

Not all MOF materials are stable upon water exposure. In general, MOFs can experience framework collapse due to water's ability to break coordination bonds between organic linkers and inorganic metal ions.³⁵ For the purposes of this study, the demonstrated water stability of the selected materials is a requirement for data reproducibility.

Judicious selection of appropriate materials and associated analysis yields selection criteria that are designed to create a univariate exploration of the effect of pore size on the secondary site affinity parameter. Using these selection criteria, a literature search has located studies of 26 relevant MOF materials, including replicate UiO-67-4Me-NH₂-38. The secondary site

affinity parameter K_1 and reported micropore size are presented in Table S1. Assessment of these data can be undertaken for the purpose of determining the applicability of IMMKA for microporous MOF materials and subsequent evaluation of pore filling mechanisms.

Results of Regression analysis. Linear regression of $\ln(K_1)$ with inverse micropore size was employed on the data set of 26 materials presented in Table S1, and the results are shown in the inset of Figure 3. The regression relation can be represented as:

$$\ln(K_1) = \frac{0.69}{r_{\text{pore}}} - 0.39 \quad (R^2 = 0.903) \quad (13)$$

with $\delta = 0.69$ nm (standard error = 0.05 nm) and $u = -0.39$ (standard error = 0.13).

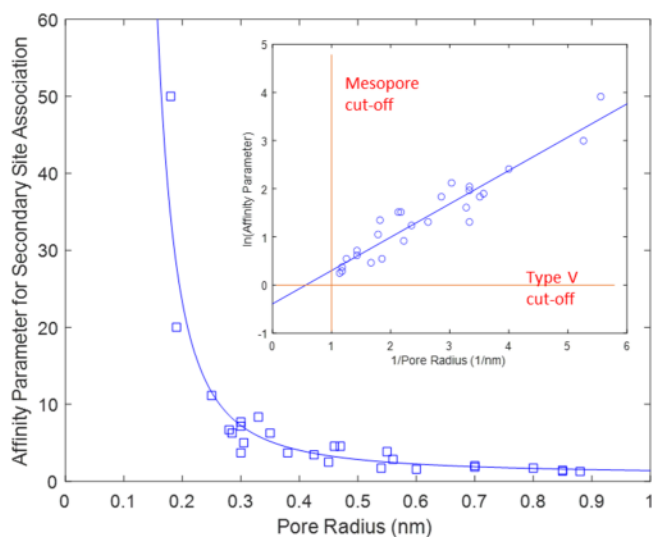


Figure 3. Plot of IMMKA relation posed as eq 11 and represented as a solid line together with data for MOF materials appearing in Table S1. Inset graph plots the natural logarithm of the affinity parameter for secondary site association, $\ln(K_1)$, against the inverse of effective pore radius. Linear regression ($R^2 = 0.903$) result is shown with slope 0.69 nm and intercept -0.39 .

In alignment with previous discussion, the negative disjoining (conjoining) pressure generated by the fluid–fluid–solid interaction is indicative of wetting. Moreover, the corresponding wetting energy (uR_gT) has a magnitude estimated at less than 1 kJ/mol, which is small in comparison to the enthalpy change associated with the condensation of water. Furthermore, the nominally stepwise isotherms, high hydrophobicity ratio, and small wetting energy associated with these materials are consistent with the limited fluid–solid interaction and condensation-driven pore filling mechanisms of “Class C” materials.

In further alignment with earlier discussion, Figure 3 indicates that a small effective radius corresponds to large values of secondary site affinity K_1 . At sizes nearing 2 Å radius, the affinity increases sharply. This observation aligns with the Lennard–Jones 12-6 potential model^{69,70} that also predicts the exclusion of water below dimensions of around 0.2 nm radius. The predicted exclusion of water generates a cutoff that would effectively truncate the relationship appearing in Figure 3 at low values of pore size.

Criteria for Structural Hydrophobicity. Figure 3 indicates

a clear transition in affinity offered by micropores of varying sizes. Small micropores appear to be attractive for water and offer a high affinity for secondary sites. In contrast, large pores are less attractive and offer a lower affinity. In this respect, the behavior that is defined as structural hydrophobicity³⁷ and is distinct from its surface counterpart. Although partitioned, the two forms of hydrophobicity can be tailored by changes in the pore morphology or chemical functionalization. Surface hydrophobicity can be reduced through enhanced primary site affinity (Henry's constant, K_0), which is commonly enabled by increasing hydrophilic heteroatom site density.^{1–12} However, long range van der Waals or shorter-range Coulombic interactions of water that are inversely related to pore size can also drive sharply increasing primary site, pre-wetting affinity in microporous carbon.^{71–73} Structural hydrophobicity can be reduced by increasing secondary site affinity, which can be enabled by decreasing pore size. In this respect, the pore size appears to offer an affinity transforming effect. Notably, a similar affinity transformation has been reported for water adsorption in slit-pore carbon micropores⁷¹ and nanotubes⁷² for which IMMKKA has been successfully applied.⁷³ Moreover, "Class C" isotherms display a range of hydrophobic behavior from broad to sharp Type V and even Type III depending on pore size. To clearly define the conditions for structural hydrophobicity and its effect on the equilibrium isotherm, it is necessary to consider the constraints for capturing this behavior in isotherm assessment. With gas phase analysis, an equilibrium isotherm is limited in span to range from 0 to 100% relative humidity. As a result, for an inflection point to be observed in this range, the following condition must be observed: $0 < a_{\text{POI}} < 1$.

On the basis of eq 6 that suggests an inverse relationship between a_{POI} and K_1 for stepwise isotherms, the condition translates to a bounded range for affinity at $1 < K_1 < \infty$. Therefore, K_1 must be greater than 1 for an equilibrium isotherm to present a transition from upward to downward concavity, display an inflection point, and exhibit Type V.

Alternatively, with K_1 less than 1, hydrophilic concavity transitions are absent, cooperative interactions are minimal, the pore filling process is incomplete, and isotherms with only upward concavity are produced. This results in Type III isotherms dictated by the Ising model, as indicated in Table 1.

Clearly, a transition point exists at $K_1 = 1$ that defines the inclusion or exclusion of sigmoidal, Type V adsorption isotherms and could be used to dictate the absence or presence of structural hydrophobicity in "Class C" materials. Applying this discrete approach, the Type V cutoff for structural hydrophobicity at $K_1 = 1$ is labeled in Figure 3 (inset). The micropore/mesopore cutoff is also labeled at a pore radius of 1 nm.

Structural Hydrophobicity on a Continuous Scale. An

alternative to the classical discrete definition of hydrophobicity is a continuously scaled index, which does not emphasize the Type III/V transition point. Discarding the transition point cutoff at $K_1 = 1$ is a proposed index that is simply based on the location of the point of inflection. As a result, materials that have relatively low observed a_{POI} values would have relatively low index values. The structural hydrophobicity index (SHI) is proposed to capture this behavior that is not only inversely related to K_1 but also related to IMMKKA provided as eq 11. As a result, SHI is defined as:

$$\text{SHI} = a_{\text{POI}} = 1/K_1 = \exp\left(-\frac{f_{\text{VM}}^{\text{po}} R^{\text{g}} T}{f_{\text{VM}}^{\text{g}} T} - n\right) \quad (14)$$

Analogous to the hydrophobicity ratio (H) that provides a continuous scale for the assessment of fluid–fluid–solid and fluid–solid interactions, SHI also provides a continuous scale for a more detailed assessment of the individual components of fluid–fluid–solid interactions. Moreover, this index represents the hydrophobicity transforming effect of pore size and includes a wetting component.

Applying the index to MWH-1⁵⁰ indicates that it has the lowest SHI of all the materials considered in this study. MWH-1 could therefore be considered the most structurally hydrophilic MOF appearing in Table S1. This form of hydrophilic behavior stands in contrast to the large hydrophobicity ratio but is complementary with negative disjoining (conjoining) pressure and surface wetting features. Likewise, the previously mentioned behavior of UIO-66 that presents steep water uptakes at low humidities translates to high H but low SHI. These two scales provide a means to discriminate hydrophilic and hydrophobic components of its equilibrium isotherm features.

At the other end of the spectrum, Cr-soc-MOF-1⁷⁴ presents a high relative filling pressure in the vicinity of unity. The SHI of this material is obviously much higher than that of MWH-1. However, both materials present large hydrophobicity ratios coupled with negative disjoining (conjoining) pressures and surface wetting features.

What Governs the Inflection Point Location: Surface or Structural Hydrophobicity? This study has provided a

clear distinction between the two forms of hydrophobicity. Surface chemistry, primary site affinity, and Henry's constant (K_0) that represent surface hydrophobicity are partitioned from secondary site affinity (K_1) that represents structural hydrophobicity. The distinction between these two forms is necessary to determine the influence of surface chemistry on the location of the inflection point that governs the applicability of a given material for humidity control applications. Although it is currently accepted that the presence of hydrophilic heteroatoms increases Henry's constant (K_0) and allows for a more "hydrophilic pore environment", it has been further reported that this effect shifts the inflection point to lower relative pressures.⁷⁵ In contrast, recent studies report a strong correlation for low Henry's constant with sudden water uptake but not with relative filling pressure a_{POI} .²⁷ This behavior agrees with the limit analysis ($H \rightarrow \infty$) applicable to normally stepwise isotherms and is evident in studies of water in microporous carbon that show a weak effect of surface chemistry and a strong effect of pore size⁷³ on the location of concavity transition. According to the analysis herein, shifts in the inflection point to lower relative pressures reflect increases in structural, as opposed to surface, hydrophobicity. This highlights not only the need to partition the two forms of hydrophobicity but also the need to explicitly address the role of pore morphology.

Furthermore, the prevailing view of the importance of surface chemistry on the inflection point location is embedded in a recent analysis⁷⁶ that proposes a hydrophobicity index to track the inflection point location. Long-arm MOFs (LAMOFs)⁷⁷ and covalent organic framework (COF) materials⁷⁶ with hydrophilic functional groups distributed throughout the

micropore network are considered and characterized by the index. Although it does not explicitly account for pore size and incorporates materials with complex pore morphology beyond unimodal micropore size, the index is applied to track changes in the inflection point for water adsorption.⁷⁶

To assess the effect of pore morphology, the suite of materials studied by Nguyen et al.⁷⁶ is reduced to include only materials with unimodal pore size as indicated on Table 2. Notably, the

Table 2. Additional Data Set^{76,77} (at 298K) of MOFs and COFs with Unimodal Pore Size Determined by Nitrogen Adsorption

material	reported effective pore diameter (nm)	a_{POI}
LAMOF-1	1.09	0.25
LAMOF-2	1.15	0.36
LAMOF-3	1.10	0.45
LAMOF-4	1.12	0.40
LAMOF-6	1.04	0.18
LAMOF-7	1.11	0.53
LAMOF-8	1.10	0.31
LAMOF-9	1.13	0.26
HCOF-2	1.06	0.30
HCOF-3	1.04	0.25
COF-432	0.8	0.33
AB-COF	1.1	0.24

reported pore sizes for LAMOF materials are obtained from nitrogen adsorption data by application of the slit-pore model ($f = 1$),⁷⁷ whereas COFs have cylindrical geometry applied ($f = 2$).⁷⁶ Table 2 data are coupled with the data set shown in Table S1 to deliver a validation set totaling 38 materials that span a wide range of micropore size, pore morphological features, and surface chemistry.

Structural Hydrophobicity Index and Validation Data Set. To adequately capture the hydrophobicity transforming effect of pore morphology, the structural hydrophobicity index is applied as a benchmark for the characterization of the validation data set. Figure 4 presents the curated validation data set for 38 materials together with the regression result assessed over the data in Table S1 only. The prediction of eq 14 is enabled by applying water properties of $v_m = 18$ mL/mol, a bulk value for water surface tension at 298 K ($\sigma = 72$ mN/m), and wetting interaction captured by $u = -0.39$. Figure 4 shows eq 14 for two bounding values of the geometric factor (f). Representing ideal uniform slab, an f value of 1 has been successfully applied to characterize graphitic slit-pore carbon,⁷³ while an f value of 2 has been applied to represent uniformly cylindrical carbon nanotubes.⁷³ Although long-arm MOFs and COFs have complex blends of pore morphology, single and multiple linkers, and hydrophilic group densities, the geometric bounds appear to adequately capture the data envelope of 38 materials.

In support of previous discussions highlighting the relevance of pore morphology and irregular geometry, the model proposed herein appears capable of characterizing materials displaying micropore filling processes associated with nominally stepwise isotherms. Moreover, these results could permit improved design strategies for microporous materials for humidity control and capture. A potential pivot away from material chemistry and toward the consideration of channel morphology could deliver improved material selection and process performance.

Furthermore, the geometric bounds indicated in Figure 4 provide material selection guidance for a range of applications

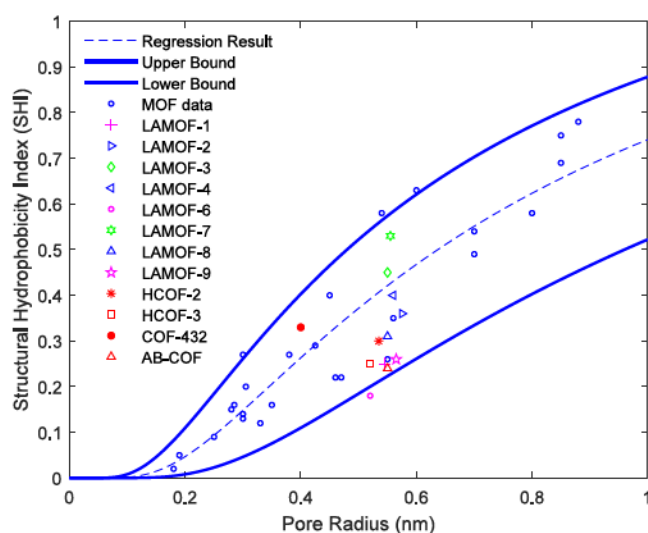


Figure 4. Validation data set of 38 MOFs and COFs presenting unimodal effective pore radius determined by nitrogen adsorption. Dotted line represents regression results across the original data set represented as blue circles from Table S1. Solid lines represent bounds imposed by eq 14 with $u = -0.39$ together with $f = 1$ (ideal slab) and $f = 2$ (ideal cylinder).

from dehumidification for which materials with high values of SHI are sought to desiccant drying processes that require low SHI materials to water harvesting that utilizes materials with intermediate values of SHI.

Condensation-Driven Channel Filling Mechanism. The microporous MOFs and COFs selected in this study display water adsorption equilibrium that is characterized by steep isotherms and large hydrophobicity ratios. These features are not only reminiscent of condensation but also indicative of channel filling with limited fluid–solid interaction in a pseudocondensation process that is observed in carbon micropores.⁷³ This process is characterized by a secondary site affinity that can be tracked by a condensation-driven Kelvin analysis that is modified for wetting. Furthermore, the negative disjoining (conjoining) pressure ($u < 0$) extracted from the modified Kelvin analysis indicates an interaction that not only is influenced by fluidic features but also is favorable to wetting. Consistent with this observation is a low wetting energy that further highlights the limited extent of fluid–solid interaction and condensation-driven channel filling. Moreover, the simple pseudocondensation mechanism observed in these “Class C” materials supports the plausible use of water adsorption as a potential tool for pore size analysis at room temperature.

CONCLUSIONS

The CMMS model connects multiple separate isotherm types, including classical forms applied for pore size analysis with rigorous forms applicable to water adsorption. As a result of its broad general utility, the model is offered as a unified isotherm analysis that bounds extremely hydrophilic rectangular from extremely hydrophobic stepwise limits and connects a multitude of classes of materials and fundamental relations, including Henry, Langmuir, BET, GAB, Ising, as well as the thermodynamically based Derjaguin–Broekhoff–de Boer. Moreover, the ability to account for multiple interaction mechanisms allows unified isotherm analysis to broadly capture features displayed by a series of polar and non-polar molecules

within micropores of MOFs, COFs, PIMs, graphitic carbons and nanotubes.

When uniquely coupled with unified isotherm analysis, the newly defined hydrophobicity ratio quantitatively links hydrophilic Types I and II isotherms with hydrophobic behavior represented by Types III, V, VI, and VII. Superseding classical discrete definitions of hydrophobicity, the hydrophobicity ratio is demonstrably capable of displaying continuous transitions between isotherm types, characterizing fluid–solid and fluid–fluid–solid interactions, and elucidating the role of surface and pore morphological properties. Consideration of fluid–fluid–solid interactions and enforcement of stringent conditions for mechanical and chemical equilibrium deliver IMMKA in a simple analytical form. Further assessment of morphological and nanoscale wetting properties embedded in IMMKA allows forms of hydrophobicity to be partitioned and redefined on continuous scales. The analysis not only represents the fundamental nature of fluid–fluid–solid interactions but is applied herein to validate common assessment protocols for MOF materials whose hydrophobic nature is commercially important but incompletely characterized. It is also capable of affirming “rules of thumb” for prediction of micropore filling pressure, which is crucial to humidity control applications. In contrast to the prevailing viewpoints that elevate consideration of surface chemistry in lieu of pore morphology, the opposite appears to be applicable to the materials studied herein. Tracked by the structural hydrophobicity index, the affinity transforming effect of pore morphology is quantitatively related to the micropore filling pressure via a pseudocondensation mechanism.

The general contributions of this study offer fundamental means for the assessment of emerging physics behind phenomena involving the angstrofluidic behavior of water. The analysis offers potential advancement of material design strategies for water control and capture technologies by permitting insight into foundational mechanisms of water interaction and elucidation of the hydrophobic behavior of microporous materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.5c00853>.

Pore size and K_1 for microporous MOF materials studied (Table S1) (PDF)

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Notes

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