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Corresponding states interpretation of adsorption in gate-opening metal–organic framework $Cu(dhbc)_2(4,4'\text{-}bpy)$

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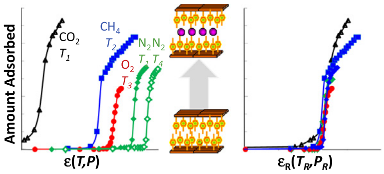
GRAPHICAL ABSTRACT



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ABSTRACT

The "universal adsorption theory" (UAT) extends the principle of corresponding states for gas compressibility to describe the excess density of an adsorbed phase at comparable reduced conditions. The UAT helps to describe experimental trends and provide predictive capacity for extrapolation from one adsorption isotherm to that of a different adsorbate. Here, we extend the UAT to a flexible metal–organic framework (MOF) as a function of adsorbate, temperature, and pressure. When considered via the UAT, the adsorption capacity and GO pressure of multiple gases to $Cu(dhbc)_2(4,4'\text{-}bpy)$ [H_2dhbc = 2,5-dihydroxybenzoic acid, bpy = bipyridine] show quantifiable trends over a considerable temperature and pressure range, despite the chemical and structural heterogeneity of the adsorbent. Exceptions include quantum gases (such as H_2) and prediction of maximum capacity for large and/or polar adsorbates. A method to derive the heat of gate opening and heat of expansion from experimental trends is also presented, and the parameters can be treated as separable and independent over the temperature and pressure range studied. We demonstrate the relationship between the UAT and the common Dubinin analysis, which was not previously noted.

1. Introduction

Metal–organic frameworks (MOFs) are promising for a variety of applications including adsorptive gas storage, gas separations, catalysis, and sensing and detection devices [1]. A subclass of MOFs, subsequently referred to as Gate-Opening (GO)-MOFs, have flexible structures that change shape to accommodate guest molecules [2]. GO–MOFs have unique adsorption isotherms, which are typified by a sharp discontinuity at a pressure associated with GO (P_{GO}), giving rise to an unusual isotherm with a pronounced S-shape. A similar

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Abbreviations: GO, Gate-Opening; GC, gate-closing; MOF, metal–organic framework; Pc, critical pressure; Tc, critical temperature; UAT, universal adsorption theory.

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discontinuity is observed in the desorption branch at a 'gate closing' pressure (P_{GC}). The adsorption and desorption branches show considerable hysteresis, such that $P_{GO} > P_{GC}$. Although this unusual S-shaped isotherm is certainly distinctive in the field of adsorption, isotherm discontinuities alone are insufficient evidence to demonstrate structural transformations, as other conditions (e.g. capillary condensation without structural change) also may exhibit such features. Slow diffusion into the material, accompanied by insufficient experimental time, may also lead to similar S-shaped isotherms [3], and molecular sieving effects have been invoked to explain hysteretic adsorption of H_2 at 77 K to $Ni_2(bipy)_3(NO_3)_4$ [4]. In certain cases, significant adsorption below P_{GO} may occur, given sufficient induction time [5] Despite these alternative explanations, structural transformations in GO–MOFs have been confirmed by *in situ* characterization techniques, including powder X-ray diffraction (XRD) [6], neutron diffraction [7], and spectroscopy [8–11]. The structural transformations have been attributed to specific chemical interactions (e.g. H-bonding [12], $\pi-\pi$ stacking interactions with polar molecules [2]) that are disrupted by the adsorbate, leading to subsequent changes in channel or pore or window sizes [2,4,12,13]. In this paper, we focus our analysis on the *P* and *T* of the GO transition and the maximum capacity of the adsorption branch (which will converge with the desorption branch at sufficient pressure).

There are multiple emerging theoretical explanations of the thermodynamics of the GO phenomenon. Early work described adsorption to GO–MOFs as the superposition of the isotherms of a first ('closed') structure and a second ('open') structure [2]. First principle considerations of structural changes associated with an 'imbibition-transition' for the model graphene–silica slit pore system found pore dilation to be a consequence of Newton's third law [14]. To generalize to any size pore, structural changes and/or pore expansion or contraction occur when the change leads to minimization of the free energy of the system. Specifically, insertion of an adsorbed film into the graphene–silica slit pore will occur when the energetics of film formation exceed the energy cost of expanding the slit [14,15]. At low pressure, low film coverage is insufficient to drive pore expansion, but at higher pressure, there is enough net free energy incentive to adsorb additional molecules to drive the pore expansion. The pore expansion is proportional to gas density, a force imparted to the pore by the adsorbate, and inversely related to compressibility modulus (or spring constant) of the material. This treatment suggests that pore expansion/contraction is a universal phenomenon, although it will be particularly pronounced in materials that have a small spring constant due to weak cohesive interactions and/or variable conformations. This theory also suggests that a force imparted by a particular gas–surface interaction can be useful in predicting behavior of all gases. Similarly, Neimark et al. argued that breathing transitions are a response to the development of a threshold adsorption stress within pores which corresponds to the external pressure that triggers the transition [16–19].

Simulations of the GO process include the statistical osmotic ensemble, which extends the Grand Canonical ensemble to account for the possibility of a flexible host by varying the unit cell [19–21]. This treatment assumes energies of adsorption and the host configuration as separable additive variables (which is common). Application of the osmotic potential ensemble has relied on fits of experimental isotherm data to yield host free interaction energies of expansion for the structure, i.e. the material "spring constant" [20]. Experimental data at the distinct P_{GO} transition point is used to account for the free energy of GO, as it is presumed the open and closed structures have equal free energies at this condition. To apply this model, adsorption to the rigid host (had it not opened) is extrapolated from the 'flat' portion of the isotherm (i.e. the lower portion of the 'S'-shaped isotherm). Alternatively, the host's free energy of interaction with the adsorbate can be calculated from molecular dynamics or Monte Carlo simulations of the GO process [22–24]. Molecular-level first principle simulations of adsorption to GO–MOFs come with considerable computational expense, however, particularly when/if structural dynamics are included. It is often desirable to perform a preliminary estimate of adsorption behavior to down-select materials that warrant a detailed study, and furthermore, to have a reliable means to extrapolate from the modeling study (and/or experimental isotherm) of one adsorbate to another.

A unifying theory that would include predictive behavior of the effects of *T*, *P*, and adsorbate on both the capacity and the GO transition point of GO–MOFs would provide insight into the gas–surface potential and the mechanism for adsorption-induced structural transformations. From a practical standpoint, predictive relationships would greatly facilitate optimization of adsorption conditions, as well as provide a means to design a system for a given gas separation. A means to extend the molecular-level thermodynamic theories (described in the preceding paragraph) to predict experimental trends, and extrapolate from one gas measurement to another, has not yet emerged, to the best of our knowledge. An alternative approach is to apply relationships that are grounded in theory, but tend to be more empirical. For example, Yamakazi et al. [25] attempted to correlate extensive experimental data by use of the Dubinin-type analysis. Discussed further below, this treatment relates the 'adsorption potential' (i.e. chemical potential of the adsorbate) to a characteristic adsorption curve for a solid, generally over a limited temperature range. In the development below, we show how the Dubinin-type analysis is quite similar to the universal adsorption theory (UAT) previously observed by Quinn to describe adsorption of six gases to four different activated carbons [26]. The convergence of adsorption isotherms shown in Quinn's treatment suggests that when thermodynamic variables are scaled appropriately, the guest–host surface potential exerted is possibly the same irrespective of the guest [27,28]. This is the same principle applied in the Dubinin-type analysis; although the analogy between the two theories has not previously been noted. Our previous development of the UAT [27] (described further in the theory section below) extends the law of corresponding states to consideration of excess adsorption, demonstrating a novel approach to arrive at the Dubinin treatment. Although MOFs and GO–MOFs have a significantly more complex and non-uniform surface potential than the activated carbons studied by Quinn, previous adsorption data for GO–MOFs from our laboratory hint towards the applicability of the UAT to these more complex materials. Specifically, adsorption capacities of N_2 and Ar for adsorption to $[Zn_2(bpdc)_2(bpee)]\cdot 2DMF$ (bpdc = biphenyldicarboxylate, bpee = 1,2-bipyridylethene; DMF = N,N-dimethyl formamide) converged at their boiling points, which corresponded to a T_R of ~0.6 [3]. Here, we further explore the applicability of the UAT to adsorption to $Cu(dhbc)_2(4,4'\text{-bpy})$ [H_2-dhbc = 2,5-dihydroxybenzoic acid, bpy = bipyridine], subsequently abbreviated as Cu(db), which is perhaps the most extensively studied GO–MOF, including published experimental adsorption isotherms by Kitagawa et al. [2] and Yamakazi et al. [25] We extend this published data set to include additional high- and low-pressure data. Although the UAT is approximate, our overall goal is to develop predictive relationships to explain key features of the adsorption isotherms and adsorption energetics, which are applicable to a multitude of adsorbates, temperatures, and pressures. Unlike previous treatment with limited temperature- and pressure-applicability, our results suggest the existence of a *universal gate-opening adsorption behavior* that implies scaling behavior of the corresponding force imparted by the gas–surface interaction.