Adsorption of Associating Molecules in Micropores and Application to Water on Carbon

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A general theory for the adsorption of self-associating molecules in microporous structures is developed. The approach is similar to the "chemical" interpretation of nonideality of vapor and liquid phases. The theory displays Type 5 isotherm behavior and can explain Types 1 and 5 transition. Isothermal data are represented by only three parameters: Henry's law constant, saturation capacity, and reaction constant for "cluster" formation in the micropores. When isotherms at different temperatures are available, the theory can be used with five temperature-independent parameters to describe the entire phase behavior including the heat of adsorption. Water adsorption on activated carbon, the most common display of Type 5 behavior, is used to test the theory. Analysis of several data sets indicates that the theory can closely correlate data, provide physically meaningful parameter values in line with carbon properties, and it is highly effective in correlating temperature variation. The reaction enthalpy for water dimerization in the carbon micropores is lower than that in vapor phase. This preliminary conclusion with the theory needs to be supported with more accurate data when available.

Introduction

There is a need for better understanding and correlation of water vapor adsorption on hydrophobic surfaces, especially on activated carbon. Water vapor is present in most air-pollution control problems, since it is one of the major impurities in atmospheric air (Mahle and Friday, 1989). Treatment of polluted air streams with active carbon is gaining ever increasing importance as the only technology which can perform at a satisfactory level mandated by strict worldwide environmental regulations.

Besides practical importance, water adsorption on activated carbon is a very good and common example of systems where the molecules "like" each other more than they "like" the surface. This results in the S-shaped isotherm classified as Type 5. The word hydrophobic does not mean that graphite planes actually repel water; there is always the dispersion attraction between the carbon and water molecules. Water molecules simply prefer to stay in the vapor phase rather than in the contained environment of carbon micropores.

Contrasted with adsorption systems where there is relatively high interaction between the solid and the guest molecules (Type 1 isotherm), water in microporous carbon displays Type 5 isotherm (Bansal et al., 1988) with an inflection point at about half the saturation pressure. Here, we present a new and novel approach to formulate the behavior displayed in Type 5 isotherms. Furthermore, the theory is also capable of explaining Types 1 to 5 transition. We will detail a general theoretical framework on the adsorption of self-associating molecules in micropores and apply it to water adsorption data on several activated carbons at several different temperatures.

The theory is applicable on the adsorption branch of water/carbon isotherms which commonly show hysteresis loops (Pierce and Smith, 1950). Hysteresis phenomena is well-examined in literature: Dubinin (1980), Evans and Marconi (1986), Peterson et al. (1986), Peterson and Gubbins (1987), and Heffelfinger et al. (1988). Formulation of hysteresis loops is beyond the scope of this work. Furthermore, the theory, as presented here, does not include any mesopore or macropore condensation mechanism. It cannot mimic the "tail" observed in some water adsorption data at very high relative pressures exceeding 0.95. If the tail is to be included, the theory can be combined with formulations based on the Kelvin equation (Sircar, 1985, 1987) to incorporate the onset of condensation in meso- and macropores. As stated above, our purpose is to

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formulate a general theory for Type 5 isotherms, not just for water adsorption on carbon. Water on carbon is in fact the most commonly known display of Type 5 behavior.

Mechanism of Water Adsorption

Water adsorption around ambient temperature corresponds to adsorption from a vapor phase under its critical temperature. It is instructive to review the two commonly used and accepted models for vapor adsorption: (1) The BET model (Brunauer et al., 1938); and (2) The Polanyi potential theory or its more recent extensions by Dubinin and his coresearchers (Dubinin, 1960; Dubinin and Astakhov, 1971; Radushkevich, 1949). Later, a model specific to water adsorption on carbon will also be examined.

The BET equation is the most commonly known vapor adsorption model. The molecular interpretation of the BET model is depicted in Figure 1, where the already adsorbed molecules provide sites for more molecules to adsorb resulting in tower like structures. The towers do not interact with each other, but there is interaction between the molecules at consecutive levels in a tower. This interaction energy is set equal to the heat of vaporization. Thus, the molecules beyond the first layer are actually assumed to be in the condensed liquid state. The number of sites (or towers) on the surface are fixed following the well-known Langmuir assumption. Figure 1 is for an open surface where the height of each tower reach infinity as saturation pressure is approached, or when condensation to bulk liquid phase occurs. In a later work (Joyner et al., 1945), the BET model was extensively studied when limited to a finite number of layers. This provides a better representation of finite adsorption space in micropores.

The BET model is not applicable to water adsorption on carbon. The major shortcoming is the assumption that the molecules wet the surface; that is, the molecules interact more strongly with the surface than they do with each other. This assumption is inherent in the BET model since the heat of adsorption for the first layer of molecules is always larger than the heat of condensation for the second and higher layers of molecules. A Type 2 isotherm results when the heat of adsorption is much larger than the heat of condensation. As the difference in between the two energies diminish, the isotherm becomes Type 3 which is similar to water adsorption on carbon at low loadings; however the BET model cannot display the trademark inflection point of water adsorption on carbon.

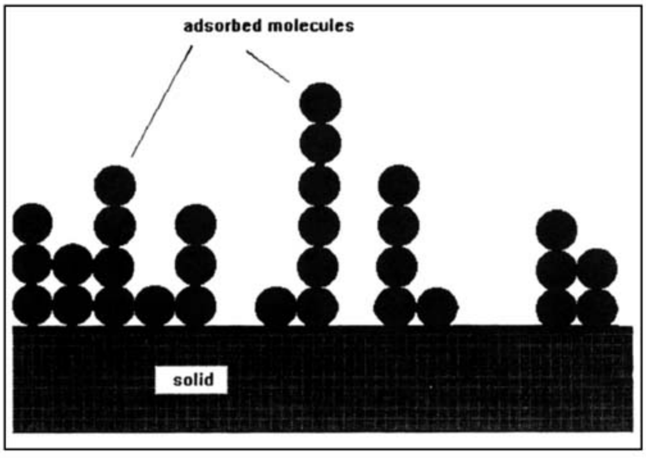

Figure 1. BET model.

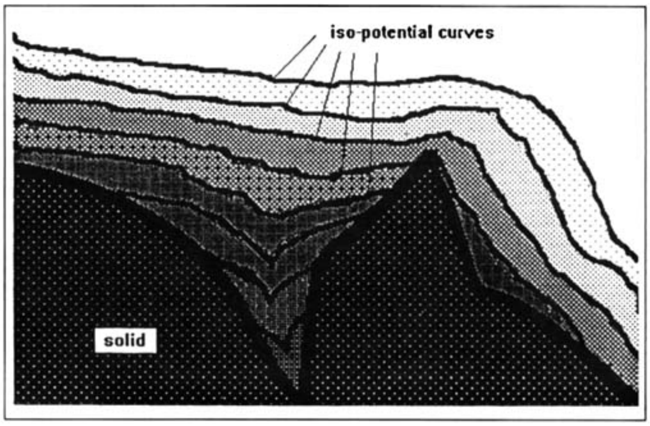

Figure 2. Potential theory.

The other very commonly used theory for adsorption from vapors is the Polanyi potential theory (Polanyi, 1932), and its extensions by Dubinin and coresearchers especially for adsorption in carbons. The potential theory stipulates that the solid imposes a potential field in the adjacent bulk phase where the vapor molecules are captured. The density of the surface layers decrease with distance from the solid as depicted in Figure 2. The free energy change upon adsorption is taken to be the work done in bringing a molecule from infinite distance to the conditions, especially to the pressure of the surface region. The molecules on the surface are assumed to behave like a compressed liquid, while the pressure in the surface layers is proportional to the potential field strength.

Although Dubinin equations are not thermodynamically consistent at the limit of zero loading (Talu and Myers, 1988), they have been highly successful in correlating vapor adsorption on carbons, especially for hydrocarbons. Similar to the BET model, the major shortcoming for water vapor adsorption is the assumption that the entire surface is wetted. Water being a highly polar species does not wet the carbon basal planes. There is ample evidence in literature (Walker and Janov, 1968) that only the oxygen containing active sites on the carbon surface are responsible for water adsorption.

Recognizing the deficiency of the potential theory, Dubinin and Serpinsky (1981) suggested a kinetic model to describe water adsorption on carbon

$$\frac{P}{P_0} = \frac{N}{c(a_o + N)(1 - k_0 N)} \tag{1}$$

In Eq. 1 a_o is the number of so-called primary adsorption centers, c is a ratio of adsorption and desorption rates, and k_0 is a constant. As the name implies, a_o accounts for the polar/active sites in the carbon structure where the adsorption of water is nucleated. Adsorbed water molecules provide new sites for further adsorption. The original derivation of Eq. 1 is based on kinetic arguments similar to the Langmuir model (1918). This model has been extensively studied to relate the model parameters a_o and c to other physically measurable properties of carbons such as the density of oxygen sites (Bradley and Rand, 1993), the amount of burn-off during carbon activation (Bradley and Rand, 1991; Dubinin, 1980), the heat of immersion (Stoeckli et al., 1983), and so on. It may be the most commonly used model for water adsorption in carbons, which also provides a starting point for the theory developed in this work.

We picture water adsorption in carbons in three different regimes effective at different pressure/loading ranges which constitute the Type 5 isotherm:

(1) At low loading, the behavior is solely controlled by molecule to surface, vertical interactions like all other adsorption systems. The primary adsorption sites are believed to be chemisorbed, oxygen containing functional groups on the surface (Dubinin, 1980) which strongly interact with the polar water molecule. Numerous studies since Pierce et al. (1951) examine and prove that the water adsorption is directly proportional to the number density of these active sites. This effect is most readily displayed in the limiting heats of adsorption at zero coverage, which is solely controlled by the vertical interactions. Unlike the BET theory where nucleation for adsorption is densely and uniformly distributed throughout the surface, here we adapt the Dubinin-Serpinsky approach and stipulate that water molecules are primarily adsorbed on the active sites. The potential theory is not applicable at all in this limiting regime where loading approach zero.

(2) At intermediate loading, the governing adsorption mechanism is still not well understood, although this regime contains the trademark inflection point of Type 5 behavior. It is commonly accepted as readily apparent in the shape of Type 5 isotherms that cooperative molecule to molecule lateral interactions play the major role (Dubinin, 1980). The positive second derivative at the origin also supports this proposition about the importance of cooperative interactions. In this regime, we stipulate that the adsorbed water molecules form large clusters by association via hydrogen bonding in contrast to the uniformly dense regions of the potential theory or tower like structures of the BET model.

(3) At high loading, the finite adsorption volume becomes crowded with molecules resulting in the leveling-off and the plateau region of the isotherm. Water does not usually fill all the micropore volume determined by hydrocarbon or nitrogen adsorption (Bradley and Rand, 1991) probably due to entropic contributions. Nevertheless, there is some correlation between the plateau level (saturation capacity) and the micropore volume as shown by Tsunoda (1990). Here, we will include the effects of finite and limited amount of adsorption volume available for water clusters.

Figure 3 is a representation of the suggested theory. Three features need to be noticed: (1) primary adsorption locations are on and around the active sites; (2) the water molecules form various shape clusters around these sites by association, and (3) adsorption space is limited by micropore volume, regardless of the shape and/or radius of the pores.

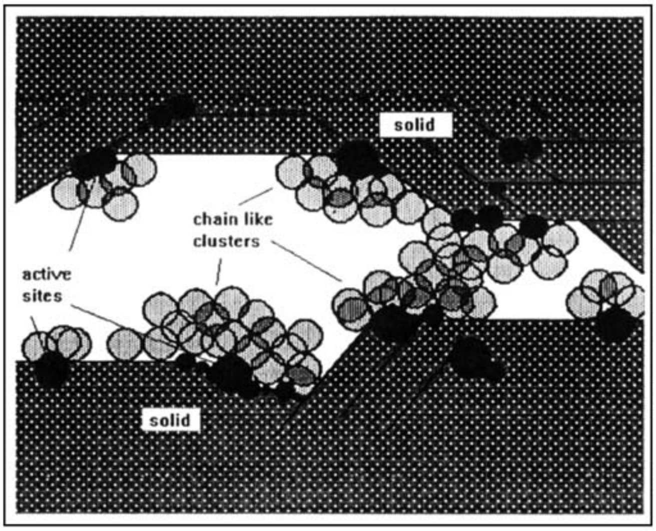

Figure 3. Association theory.

Theory of Association in Micropores

There are three theoretical aspects in the formulations of self-associating molecules contained in micropores: chemical equilibria, equation of state, and phase equilibrium. The first two describe the behavior of the surface phase, and phase equilibrium links the surface phase properties to bulk phase properties which generally, are the only measurable quantities of adsorption systems.

Chemical equilibria of association reactions

It is envisioned that the monomer is involved in sequential chain reactions to form the polymers or the adsorbed clusters

$$\begin{aligned} B + B &= B_2 \\ B_2 + B &= B_3 \\ B_3 + B &= B_4 \\ \cdots \quad & \cdots \quad \cdots \\ B_{k-1} + B &= B_k \end{aligned} \tag{2}$$

B is the building block of the polymer, i.e., a single water molecule of the hydrogen bonded water clusters in the surface phase.

The number of independent reactions is important for equilibrium purposes rather than the reaction mechanisms. For example, the third reaction in Eq. 2 can also be written as the product of two dimers without any consequence on equilibrium conditions. The number of independent reactions in the formation of a "k-mer" is $k-1$ regardless of how the reactions are written.

If the largest cluster size is denoted by k, the association reactions introduce $k-1$ new and chemically distinct species in the surface phase. The thermodynamic degrees of freedom is therefore increased by $k-1$. The mole fractions, except one component, are the additional independent intensive properties. On the other hand, there are $k-1$ relations between the activities of the components when reaction equilibria are reached. Therefore, the total degrees of freedom remains unchanged when molecules associate in the surface phase.

The largest cluster size is physically unbounded. The size of all clusters must approach infinity as the saturation pressure is approached. In addition, there is a finite statistical probability for finding very large clusters even below the saturation pressure. Later, k will be set equal to infinity. Here it should be noted that k being infinity does not have any bearing on the number of independent reactions and/or on the thermodynamic degrees of freedom.

Now, we proceed to develop reaction equilibrium relations. Stable equilibrium state of a surface phase is defined by the *minimum* of total Gibbs free energy at constant temperature (T) and spreading pressure (π)

$$d(n\cdot G)_{T,\pi}=0 \tag{3}$$

Equation 3 can be translated into a relation between stoichiometric coefficients (ν) and chemical potentials (μ) of components involved in each independent reaction denoted by j

$$\Sigma_i \nu_{i,j}\cdot\mu_{i,j}=0 \quad \text{(for reactions } j=2,3,\ldots k) \tag{4}$$

Subscript i is used to denote species B_i for notational simplicity. All k-1 relations in Eq. 4 are satisfied when chemical equilibria are reached. Recursively applying Eq. 4 for the reactions k, $k-1$, $k-2$, ...3,2 as shown in Eq. 2 gives

$$\mu_k = k\cdot\mu_1 \tag{5}$$

Equation 5 can also be directly determined from a mechanistically different nevertheless pertinent reaction

$$kB = B_k \tag{6}$$

The chemical potentials must be related to more readily measurable properties in order to make use of Eq. 5. We prefer to use the fugacity which is related to the chemical potential by

$$d\mu_i = RTd\ln f_i \quad \text{(const. } T) \tag{7}$$

where f_i is the fugacity of an i-mer in the adsorbed mixture of various size clusters. Integration of Eq. 7 at constant temperature from a standard state denoted by * to the system conditions gives

$$\mu_i\{T,\pi,x\}=\mu_i^*\{T,\pi^*,x^*\}+RT\ln\frac{f_i\{T,\pi,x\}}{f_i^*\{T,\pi^*,x^*\}} \tag{8}$$

where { } denotes functionality.

A standard state is necessary in order to fix the absolute values of μ_i and f_i in Eq. 8. The choice of standard state is arbitrary except that it must be at system temperature due to the integration path followed for Eq. 7. Normally, a standard state is chosen where the system properties are easily determined. We will adapt the standard state as pure component species in a ideal-gas-like surface phase (following the equation of state given in Eq. 15) at unity value of the spreading pressure. The standard state properties are

$$x_i^*=1;\quad \pi^*=1;\quad f_i^*=\pi^*\cdot x_i^*=1 \tag{9}$$

f_i^* is equal to π^* because ideal-gas-like behavior is used and pure component standard state is chosen. A combination of Eqs. 5, 8 and 9 gives the reaction equilibrium relation in the more familiar form

$$f_i/f_1^i = e^{[-(\mu_i^*-i\cdot\mu_1^*)/RT]} \equiv e^{[-\Delta G_i^*/RT]} \equiv K_i \tag{10}$$

K_i is the equilibrium constant for the reaction producing B_i. It is independent of composition and density. It is only a function of temperature via the standard reaction free energy, ΔG_i^*.

In reality, the chosen conditions refer to a hypothetical standard state since an i-mer cannot exist as a pure component in the surface phase without the company of other polymers and the monomer. The hypothetical nature of the standard state does not have any significant consequence on the thermodynamic formulations except for the calculation of ΔG_i^*. Here, we will relate ΔG_i^* of all reactions to that for the formation of dimer which, in turn, will be determined from data.

The standard free energy of reaction for the addition of one molecule to any size cluster is assumed to be independent of the cluster size. This approximation was first suggested by Florry (1944) for polymer solutions and it was later adapted by others to explain associating systems with the chemical theory of vapor and liquid phases (Dolezalek, 1908), notably by Renon and Prausnitz (1967) and by Redlich and Kister (1947). With this assumption, the chemical potential of an i-mer and the monomer are related at the standard state by

$$\mu_i^* = i\cdot\mu_1^* + (i-1)\cdot\delta G^* \tag{11}$$

where δG^* is the standard reaction free energy for increasing the cluster size by one, or for any one of the reactions in Eq. 2 at the standard state. By Eq. 11, the equilibrium constants of all reactions are related to a single value.

$$K_i = \exp[-(i-1)\cdot\delta G^*/RT] = K_T^{i-1} \tag{12}$$

K_T, which is the equilibrium constant for the dimer formation, is only a function of temperature. Substitution of Eq. 12 into Eq. 10 provides a simple relation between the fugacities of all polymers and the monomer

$$f_i = K_T^{i-1}\cdot f_1^i \tag{13}$$

There are $k+1$ degrees of freedom for a k component homogeneous system according to the Gibbs postulate (Prausnitz et al., 1986). The independent intensive properties of the surface phase may be chosen as T, π, and $k-1$ mole fractions. The mole fractions of individual polymers in the surface phase are not directly measurable. The $k-1$ reaction equilibrium expressions shown in Eq. 13 and the closure equation ($\Sigma x_i = 1$) enable the calculation of all mole fractions. Therefore, T and π remain as the only two externally variable intensive properties of a surface phase when association occurs, as with other adsorption systems where association does not take place.

Surface phase equation of state

An equation of state (EOS) is necessary to calculate the surface phase fugacities. Exact thermodynamic relations provide the fugacity from an EOS (Van Ness, 1969)

$$RT \ln \frac{f_i}{\pi \cdot x_i} = \int_0^{\pi} \left[\left(\frac{\partial n \cdot \sigma}{\partial n_i} \right)_{T,\pi,n_{j \neq i}} - \frac{RT}{\pi} \right] d\pi \qquad (14)$$

Any equation of state can be adapted to describe the $\pi - \sigma - T$ behavior of the surface phase depending on the desired complexity. The simplest EOS stipulates ideal-gas-like behavior in the surface phase

$$\pi \cdot \sigma = R \cdot T \qquad (15)$$

There are two basic assumptions implicit in Eq. 15: (1) Point or zero size molecules (clusters or polymers in our case); (2) No lateral interactions in between the molecules. Although simplistic, this EOS is theoretically very important since it is asymptotically exact at zero surface density. All thermodynamically rigorous formulations of adsorption must conform to ideal-gas-like behavior at zero loading because

(1) The point molecule assumption is inconsequential since the reduction in adsorption space to give the free space is zero at zero density, even though real molecules have finite sizes.

(2) There cannot be any lateral interaction between molecules at zero density since they are infinitely apart.

The ideal-gas-like EOS also provides the relations in the Henry's law region of the isotherm when coupled with phase equilibrium. The Henry's law behavior is determined solely by the vertical interactions between the molecules and the solid, which may be the single most important aspect of adsorption phenomena. The formulations provided here also comply with the Henry's law limit at zero pressure like all other thermodynamically consistent models. One additional aspect in the Henry's law region for associating systems is that only monomers can exist at zero density, as will be shown later.

The zero-size assumption of ideal-gas-like EOS is somewhat unrealistic for associating systems where large clusters are formed. On the other hand, the assumption of negligible lateral interactions is reasonable since formation of clusters already includes the very strong interaction of chemical association; the interaction between clusters should be negligible compared to the chemical interactions within the clusters. Neglecting the lateral interactions but including the finite size of the clusters, the Volmer EOS (Ross and Olivier, 1964) is chosen to describe the π-σ-T relation for associating surface phases

$$\pi \cdot (\sigma - \beta) = R \cdot T \qquad (16)$$

The size parameter of the mixture β can be determined from sizes of the components β_i by the Lorentz-Berthelot mixing rules (Horry and Prausnitz, 1967)

$$\beta = \Sigma x_i \cdot \beta_i \qquad (17)$$

Furthermore, the size of an i-mer can be approximated from the number of molecules in a cluster

$$\beta_i = i \cdot \beta_1 \qquad (18)$$

Combination of Eqs. 14, 16, 17 and 18 gives the fugacity of a component in the surface mixture with the Volmer EOS as

$$f_i = x_i \cdot \pi \cdot \exp(i \cdot \beta_1 \cdot \pi / RT) \qquad (19)$$

Phase equilibrium

The reaction equilibrium relations and the EOS are sufficient to describe the behavior of the surface phase. Phase equilibrium relation provide the crucial link between the surface phase properties and the bulk phase properties which are the only measurable quantities. In adsorption phenomena, phase equilibrium stipulates the equality of thermal potential (temperature) and chemical potential, but not the mechanical potential (pressure) since the actual surface phase is transformed into a two-dimensional mathematical dividing surface by the Gibbs definition of adsorption. In fact, the lack of mechanical equilibrium is responsible for the additional degree of freedom of adsorption systems.

For simplicity, we will only stipulate phase equilibrium between the monomers in the surface and in the bulk phases. The extension to systems where association also occur in the bulk phase is straightforward following standard procedures as first suggested by Dolezalek (1908) and detailed in Prausnitz et al. (1986). The phase equilibrium relation of the monomer, the adsorbing species, is

$$\mu_1^{\circ}\{T,P\} = \mu_1\{T,\pi,x\} \qquad (20)$$

where pure component bulk phase chemical potential (μ_1°) is a function of T, and P while the chemical potential of the monomer in the surface phase is a function of T, π and x. The chemical potential of the monomer in the surface phase (μ_1) with the pure component standard state (see Eq. 9) is given by

$$\mu_1\{T,\pi,x\} = \mu_1^*\{T,\pi^*\} + RT \ln(f_1/\pi^*) \qquad (21)$$

Utilizing fugacity with ideal gas reference state, the chemical potential in the bulk phase is

$$\mu_1^{\circ}\{T,P\} = \mu_1^{\circ *}\{T,P^*\} + RT \ln(f_1^{\circ}/P^*) \qquad (22)$$

where $\mu_1^{\circ *}$ is the reference state chemical potential.

There is a difference between the reference/standard states used for the bulk and the surface phases. The difference can be consolidated by setting the bulk phase reference pressure to that corresponding to $\pi^* = 1$ in accordance with Eq. 9 and using phase equilibrium under these conditions

$$\mu_1^{\circ *}\{T,P^*(\pi^*)\} = \mu_1^*\{T,\pi^* = 1\} \qquad (23)$$

When Eqs. 20 to 23 are combined and ideal gas phase behavior is assumed for simplicity, i.e., $f_1^{\circ} = P$, the phase relation becomes

$$P = H'\{T\} \cdot f_1 \tag{24}$$

where $H'\{T)$ is a simple ratio of mechanical potentials (respective pressures in the two phases) and it is related to the Henry's law constant

$$H'\{T\} = P^*\{\pi^* = 1\}/\pi^* \tag{25}$$

Although unity spreading pressure value may be quite high for some systems where the Henry's law may not apply, it is rigorously applicable at the standard state conditions since ideal-gas-like surface behavior is stipulated.

It should be noted that Eq. 24 can be also derived from an application of the Gibbs adsorption isotherm equation which is based on the differential phase equilibrium relation, or the differential form of Eq. 20. Here, Eq. 20 is used directly; the two approaches are identical.

Isotherm equation

Although all necessary relations (reaction equilibria in Eq. 13, the EOS in Eq. 16, fugacities in Eq. 19, and phase equilibria in Eq. 24) are developed, they are not yet directly useful with the traditional isotherm data consisting of pressure and adsorbed amount at constant temperature. The measured amount adsorbed N is related to the true number of moles per gram in the surface phase n by material balance over different size polymers

$$N = \Sigma i \cdot n_i = n \cdot \Sigma i \cdot x_i \tag{26}$$

The summation over components, different size polymers in this case, extends to infinity as discussed earlier.

First, the infinite sum in Eq. 26 is resolved in terms of π to determine the relations between measured and true amounts adsorbed. The mole fractions of polymers are related to that of the monomer by reaction equilibria (Eq. 13) simplified with the aid of Eq. 19

$$\chi_i = (K_T \cdot \pi)^{i-1} \cdot \chi_1^i \tag{27}$$

The closure equation $\Sigma x_i = 1$ with Eq. 27 gives the relation between x_1 and π

$$x_1 = 1/(1 + K_T \cdot \pi) \tag{28}$$

Equation 26 can be resolved using Eqs. 27 and 28

$$\Sigma i \cdot x_i = 1 + K_T \cdot \pi = <n> \tag{29}$$

The number average cluster size $<n>$ is also defined in the above equation.

Second, the EOS in Eq. 16 is used to relate N to π, or to its more common form $\Psi = \pi A/RT$. Making use of $\sigma = A/n$ and $\beta_1 = A/Nm$ where Nm is the measured saturation amount adsorbed of the monomer, the measured amount adsorbed N is related to Ψ by

$$\Psi \cdot (1 + K \cdot \Psi) = Nm \cdot N/(Nm - N) = \zeta \tag{30}$$

where $K = K_T \cdot RT/A$. This quadratic equation can be solved for Ψ

$$\Psi = \frac{-1 + \sqrt{1 + 4 \cdot K \cdot \zeta}}{2 \cdot K} \tag{31}$$

Finally, the phase equilibrium relation, Eq. 24 is written in terms of Ψ as

$$P = H \cdot \Psi/(1 + K \cdot \Psi) \cdot \exp(\Psi/N_m) \tag{32}$$

where the measured Henry's law constant ($H = H'RT/A$) is defined as usual at the limit N approaches zero

$$H = \mathrm{Lim}\ dP/dN \tag{33}$$

H is only a function of temperature.

The isotherm expression is pressure explicit, as usually is the case when surface EOS is used. The solution procedure is simple; given the measured amount adsorbed (N), Eq. 31 gives Ψ and Eq. 32 is used to calculate the equilibrium pressure P. There are three parameters in the isotherm: (1) the Henry's law constant H; (2) the reaction constant K, (3) the measured saturation capacity Nm. The Henry's law constant scales the pressure axis as with other isotherm equations. The effect of K and Nm on the isotherms is examined next.

Isotherm Behavior by Association Theory

The association theory can show Type 1 to Type 5 isotherm behavior depending on the value of the reaction constant. When $K = 0$, association does not occur. Both the mole fraction of the monomer and the average cluster size are unity, and they become independent of π (Eqs. 28 and 29). The isotherm becomes Type 1 since it simply reduces to the Volmer form

$$P = H \cdot Nm \cdot N/(Nm - N) \cdot \exp[N/(Nm - N)] \tag{34}$$

As K increases from zero, the degree of association increases as indicated in Eq. 29 for $<n>$. An inflection point appears and the isotherm becomes Type 5. The inflection point moves to lower pressure values with increasing K value as can be seen in Figure 4.

The saturation capacity Nm primarily determines the plateau level of the isotherm. It also has a significant effect on the shape of the isotherm since it controls the impact of K on the isotherm shape through the EOS (Eq. 31). At a fixed K, the isotherms become sharper with increasing Nm value as can be seen in Figure 5.

It is instructive to examine how the mole fraction of the monomer and the average cluster size vary with loading since they are unique to the association theory developed here. The mole fraction of the monomer is shown in Figure 6 as a function of loading for various values of K and Nm. For all K and Nm values, the limit of x_1 as loading approaches zero is unity as dictated by the Henry's law; only the monomer can exist at zero loading. The monomer mole fraction decreases with increasing N and becomes zero when $N = Nm$; every-

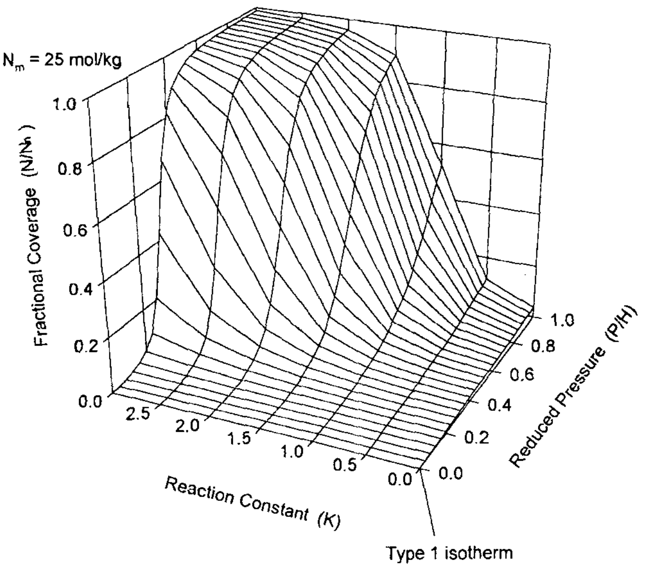

Figure 4. Effect of the reaction constant on isotherms by the association theory.

thing is polymerized at saturation. The drop in x_1 becomes more severe as either K and Nm increases.

There is a simple inverse relation between the average cluster size $<n>$ and mole fraction of the monomer x_1 by Eqs. 28 and 29

$$<n> = 1/x_1 \tag{35}$$

$<n>$ is also unity at zero loading indicating all monomers. At saturation where $x_1 = 0$, $<n>$ becomes infinity indicative of condensation as the size of all clusters go to infinity. Although the limit of $<n>$ is infinity at $N = Nm$, it has physically reasonable finite values even at very high loadings as should be the case for adsorption in micropores. Figure 7 shows $<n>$ at 99% loading for different K and Nm values. $<n>$ is in the order of hundreds even for very strong association with large K values.

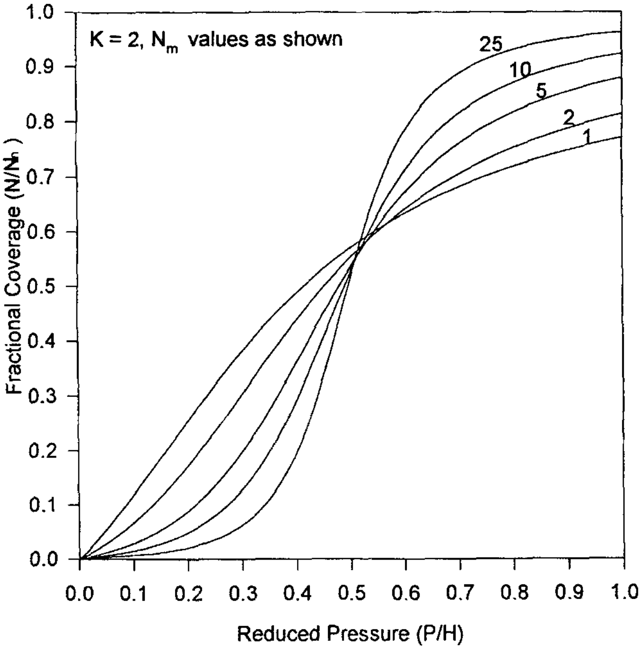

Figure 5. Effect of the saturation capacity on isotherms by the association theory.

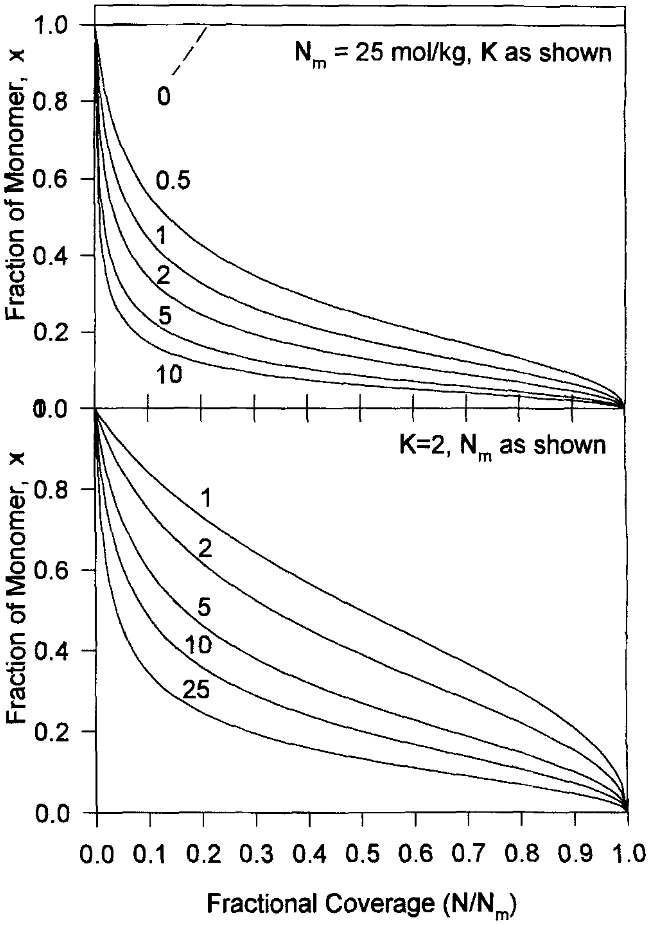

Figure 6. Effect of the saturation capacity and the reaction constant on the "monomer" mole fraction by the association theory.

Application to Isotherm Data

The association theory is applicable to any Type 5 isotherm displaying an inflection point. Water adsorption in activated carbons is the most common Type 5 isotherm data in literature. There are many water/carbon data in literature displaying widely varying characteristics such as the steepness of the isotherm, the location of the inflection point, the saturation level, and so on. A representative group of four data sets are chosen to demonstrate the theory with isotherm data. Figure 8 shows the water isotherms around room temperature.

(1) The very high surface area AX21 is produced from petroleum pitch by hot KOH activation. Water isotherm data taken from Barton et al. (1991) shows a steep rise at fairly high, rather delayed relative pressures indicating the highly uniform microporous nature of AX21. The saturation capacity is high due to the very large surface area; apparent surface area of about 3,500 m^2/g.

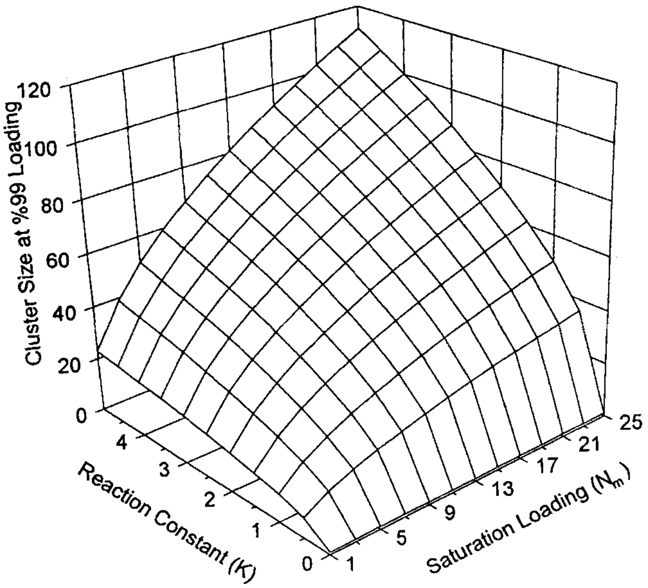

Figure 7. Effect of the saturation capacity and the reaction constant on the number average cluster size by the association theory.

(2) The coal based carbon BPL is commonly used for vapor phase adsorption especially in solvent recovery processes. The pore distribution is fairly large and ash content is high compared to the other carbons resulting in flatter shape of the water isotherm. Data is taken from Rudisill et al. (1992). The surface area of BPL is approximately 1,200 m^2/g.

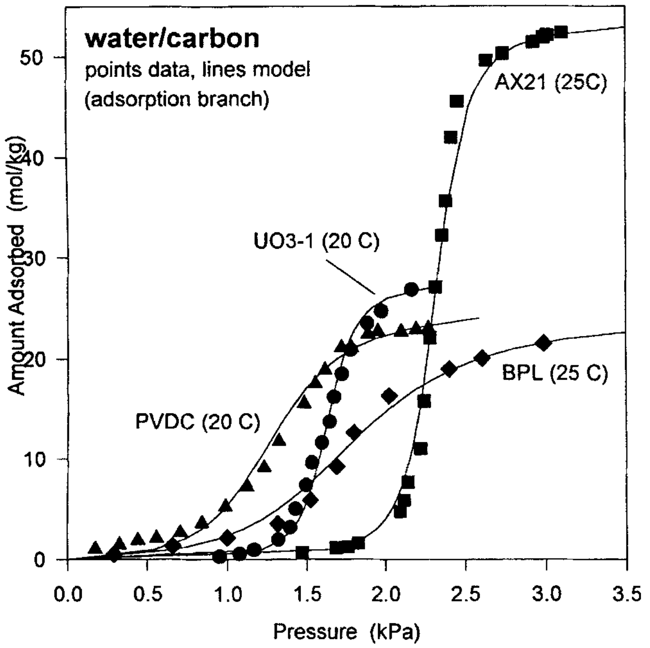

Figure 8. Comparison of the association theory to data of water adsorption on different carbons.

Parameter values are given in Table 1; data are taken from Barton et al. (1991), Rudisill et al. (1992), Bradley and Rand (1993), and Kraehenbuehl et al. (1986).

(3) The PVDC (Bradley and Rand, 1993) is derived from synthetic raw materials which possess well-defined characteristics. Its surface area is somewhat higher than the BPL carbon. Nevertheless, the saturation water capacities are comparable indicating that some of the pore space is not available for water adsorption in the PVDC.

(4) The U03-1 is an experimental carbon especially treated to introduce carboxylic groups on the surface to measure the impact on water adsorption (Kraehenbuehl et al., 1986). The shape of water isotherm is similar to that on AX21 except the inflection is at lower pressure indicating larger pores and the plateau is lower indicating larger amount of solid matrix.

The theory described by Eqs. 31 and 32 is fitted to the isotherm data of these four carbons by nonlinear regression. The objective function was simply written as the difference in experimental and predicted pressure values. A wide range of initial estimates were used which ensured that global minimum of the objective function was located. The correlations were very satisfactory, as can be seen by solid curves in Figure 8.

The regressed parameter values are listed in Table 1. In general, the parameter values are in agreement with the characteristics of the carbons. For AX21 and UO3-1, the K value is high indicating rapid association of water molecules once the primary sites are occupied. On the other hand, the H values are also high (inverse of the common Henry's law constant) indicating that the steep rise in water isotherm is delayed; the active sites are in locations which are not easily accesible by water. In contrast , the K values for PVDC and BPL carbons are low indicating that the primary sites are in widely varying pore environments resulting in a smeared step in the isotherm starting at lower-pressure values. H values are lower (high Henry's constant) meaning that these carbons have a higher average affinity for water molecules. The differences between the Nm values on different carbons simply correspond to the available adsorption space. The adsorption in AX21 at saturation is about twice that of other carbons indicating the very highly porous nature of this super carbon.

It should be noted that the theory developed here is not strictly a homogeneous surface model even though a single equation of state is used. In the theory, the surface provides primary adsorption sites where the vertical interaction is a single value appearing in the Henry's law constant similar to homogeneous models in contrast to heterogeneous systems

Table 1. Parameter Values for Water Adsorption Around Ambient Temperature

Data	H	K	Nm	F	R^2
U03-1	16.64 (±1.27)	10.16 (±0.82)	27.83 (±0.22)	14,874	1.0
AX-21	21.50 (±1.58)	9.28 (±0.70)	53.48 (±0.14)	1,045	0.991
PVDC	1.424 (±0.13)	1.069 (±0.12)	25.63 (±2.29)	285.4	0.971
BPL	1.475 (±0.29)	0.782 (±0.18)	24.97 (±1.01)	249.6	0.984

R^2 = R square, F = regression F value, ± = parameter standard devaition; pressure in kPa, amount adsorbed in mol/kg.

where the adsorption potential is a Boltzman weighted statistical average. On the other hand, the clustering mechanism in the association theory also provides an infinite number of different energy sites for guest molecules. The energy released by adsorption of a molecule is the sum of two contributions: (1) The single vertical interaction value divided by the cluster size, and (2) The energy of reaction. Since different size clusters each occupy a single site, the adsorption potential can take infinite values from the Henry's law value to zero. This is not only a semantic difference attributing the lateral interaction between molecules to vertical interactions, there is no lateral energy contribution in the theory. The variation in the adsorption potential by cluster size is the reason why the theory can mimic the highly heterogeneous behavior of water adsorption in carbon. The effect of heterogeneity is more readily apparent when the heats of adsorption are examined.

Heat of Adsorption and Effect of Temperature

Adsorption is an exothermic process. The heat of adsorption carries important information about the primary interactions involved in moving a molecule from the vapor phase to the surface. Isosteric heat of adsorption can be easily calculated from experimental isotherms and from theories which include temperature functionality. The isosteric heat of adsorption with the association theory is given by

$$\frac{Q}{R} = -\left.\frac{\delta \ln P}{\delta 1/T}\right|_N = -\frac{d \ln H}{d 1/T} + K\Psi \frac{2+\Psi/N_m}{2K\Psi+1}\frac{d \ln K}{d 1/T} \qquad (36)$$

The first term on righthand side is the limit of isosteric heat at zero coverage from the Henry's constant, and the second term is the contribution by clustering. Note that the differential is at constant measured amount adsorbed N rather than the true number of moles per weight of adsorbent n. Thus, Q is the measurable heat of adsorption. The Henry's law constant is exponentially related to inverse temperature.

$$H = \exp\left(H_0 + \frac{H_1}{T}\right) \qquad (37)$$

Similarly, K can be expanded as

$$K = \exp\left(K_0 + \frac{K_1}{T}\right) \qquad (38)$$

where K_0 and K_1 are related to reaction entropy and enthalpy. Although K is actually related to the reaction constant for dimer formation K_T by $K = K_T \cdot RT/A$, it is not possible to include the preexponential T in Eq. 38. The exponential temperature dependency overwhelms the preexponential term especially for the limited temperature range of typical adsorption isotherm measurements. It is also common to drop the preexponential T dependency of the Henry's law constant due to the same reason.

The isosteric heat of adsorption with the association theory is a strong function of coverage via the clustering contribution. The coefficient of the second term in Eq. 36 is always positive and the reaction enthalpy for cluster formation is normally negative. The result is a decrease in the heat of adsorption as observed for heterogeneous systems. Figure 9 shows the effect of K_1, the reaction enthalpy, on the variation of isosteric heat shown as the difference from the value at zero coverage. The isosteric heat of adsorption is constant only when the heat of reaction is zero.

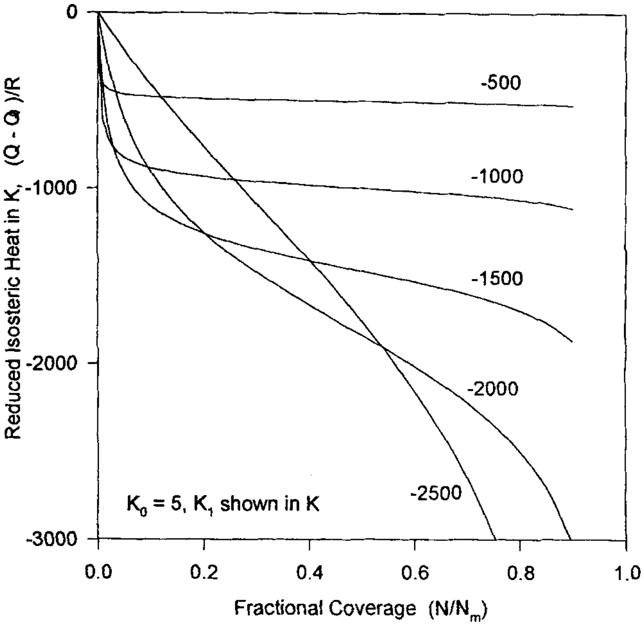

Figure 9. Effect of reaction enthalpy on the variation of isosteric heat of adsorption by the association theory.

There is also an important effect of the reaction entropy on the isosteric heat as can be seen in Figure 10. At low K_0

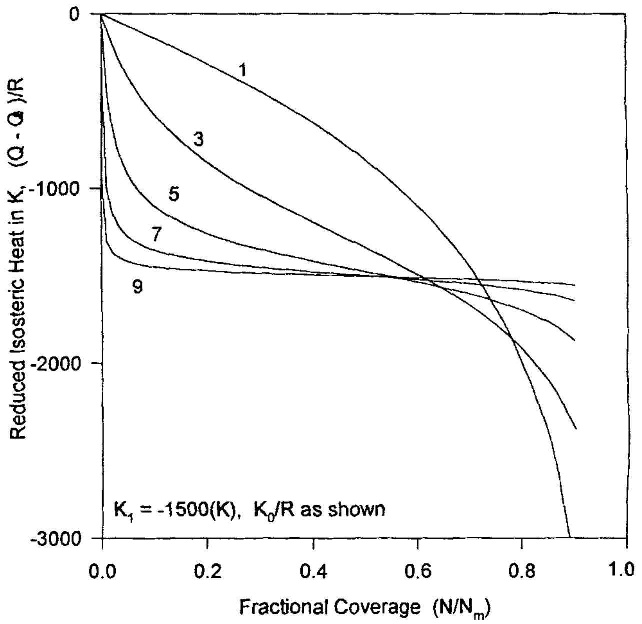

Figure 10. Effect of reaction entropy on the variation of isosteric heat of adsorption by the association theory.

values where the entropy decrease by cluster formation is low, the enthalpic contributions control the system. Thus, the variation in the isostheric heat of adsorption is high. As K_0 increases, the entropy penalty for the formation of larger clusters becomes significant although energetically they are favored. The heat of adsorption stays fairly constant after a sharp drop at low coverage.

Although the saturation capacity Nm appears in Eq. 36 and in the transformation of Ψ to N, its effect on the isosteric heat of adsorption is negligible once its value is above 5 mol/kg which is lower than expected values for associating systems.

Application to data

The association theory can be used for isotherms at different temperatures when Eqs. 37 and 38 are used for H and K with the isotherm expression, Eqs. 31 and 32. The saturation capacity Nm is temperature-independent. Only five temperature-independent parameters are necessary to describe adsorption at any temperature: H_0, H_1, K_0, K_1 and Nm.

Extensive water adsorption data on BPL carbons by Rudisill et al. (1992) at 25, 50, 75, 100 and 125°C are used to demonstrate the theory. Four data points at high relative pressure corresponding to the onset of capillary condensation were not included in the regression. These points were easily identified by the increase in the slope of the isotherm. This data reduction was necessary since the theory does not account for condensation in meso- and macropores. The remaining data at various temperatures were used in a single nonlinear regression procedure to determine the parameter values listed in Table 2.

The correlations with the association theory and data are shown in Figure 11 where the abscissa (relative pressure) is shifted by 0.1 for each isotherm for clarity. As can be seen in the figure, the association theory is very effective in describing the entire system which includes a fairly large temperature and pressure range. The discrepancy between data and theory is probably within the experimental error given the difficulty in measuring water isotherms on carbon. The standard deviations and t-statistics of the parameters are given in Table 2. All t-values are higher than 2 indicating that all parameters are statistically significant. In addition, the regression F value is 2,907 indicating a high statistical efficiency and a very good fit as also visually apparent in Figure 11.

It is interesting to compare the reaction enthalpy for water association in the micropores of carbon to that in the vapor phase. By the so-called chemical theory, which is similar to the theory presented here, Lambert (1953) determined the reaction constants for water vapor dimerization from the vapor phase second Virial coefficients. He deduced the association enthalpy in the vapor phase as −23.9 kJ/mol. Our results here for the surface phase from the constant K_1 is −12.4 kJ/mol. The enthalpy of reaction is lower in the surface phase, because the molecules cannot approach each other as closely as they can in the vapor phase. The existence of solid walls impose restrictions on the relative orientations and positions of the water molecules and on the shape of the clusters. That results in a lower enthalpy of cluster formation compared to the vapor phase. Although this is a physically plausible explanation, it would be premature to derive any firm general conclusions based on regression results of a single data set. The results can only be generalized by analyzing many accurate data sets, which simply do not exist in current literature.

Table 2. Regression Results for Water Adsorption on BPL Carbon at Several Temperatures

	Parameter	Std. Dev.	t-Statistics
H0	24.04	±1.874	12.83
H1	−6,873.7	±741	−9.28
K0	5.39	±1.84	2.93
K1	−1,489.4	±729	−2.04
Nm	22.21	±0.33	−66.84

Regression F-statistics = 2,907; R-square = 0.997.
Pressure in kPa, amount adsorbed in mol/kg, temperature in K.

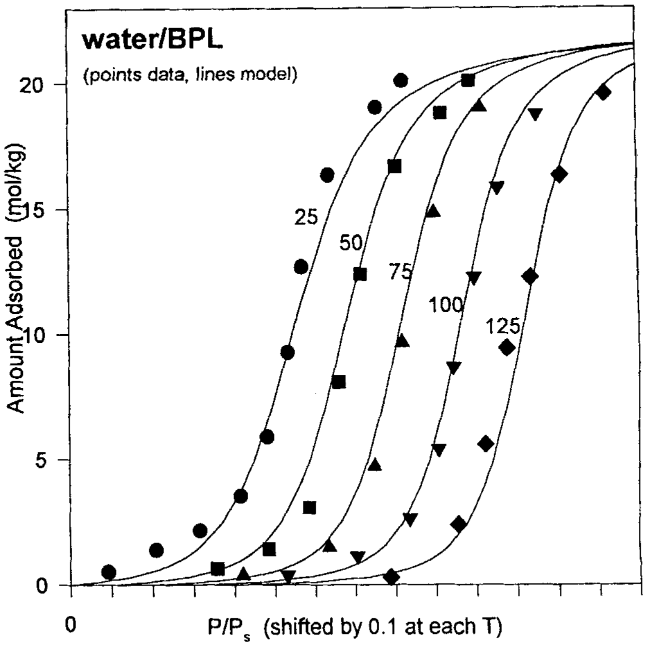

Figure 11. Performance of the association theory with temperature-independent constants for water vapor adsorption on BPL carbon.

Data taken from Rudisill et al. (1992); parameter values are given in Table 2. Relative pressure axis is shifted by 0.1 for each isotherm for clarity.

Conclusion

The chemical theory was applied to vapor and liquid systems to explain nonidealities several decades ago. This idea is applied to adsorption systems for the first time in this work as a thermodynamically rigorous classical model; molecular simulation of similar phenomena has been very recently reported (Vega et al., 1994). The association theory detailed here is fairly straightforward althought the derivations are mathematically complicated. The physical interpretation is extremely simple involving three major features: (1) Guest molecules interact more strongly with each other than they do with the surface; (2) The surface, nevertheless, provides certain hot-spots to nucleate adsorption; (3) The micropore volume available for adsorption is finite. Numerous versions, extensions, and improvements are possible within the outlined theoretical framework; only one complete formulation is provided here. Although the theory is only tested with water on carbon data, it is applicable to all Type 5 isotherms. The preliminary results based on experimental data of several systems are very encouraging to further pursue the development of the association theory which will require more abundant and accurate data.

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Notation

B = guest molecule, monomer
G = molar Gibbs free energy
ΔG_i^* = reaction free energy for the formation of i-mer
δG^* = free energy change for increasing cluster size by one or for the dimerization reaction
k = cluster size
P_o = saturation pressure
Q = isosteric heat of adsorption
R = gas constant
x_i = surface mole fraction of i-mer

Greek letters

β = molecular size parameter
ζ = parameter = $N \cdot Nm/(Nm - N)$
σ = molar area
Ψ = spreading pressure group = $\pi A/RT$

Subscripts

i = ith component in surface phase, i-mer
1 = adsorbing molecule, monomer
T = property function of temperature only

Superscript

$^\circ$ = vapor phase property

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