Onset of the Henry Constant for Supercritical Adsorption into Carbonaceous Porous Materials

C. Nguyen and D. D. Do*

Department of Chemical Engineering, The University of Queensland, St Lucia 4072, Australia

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The Henry constant is commonly used as a measure of how strong an adsorbate is attracted towards a solid surface and is regarded as one of the fundamental parameters in adsorption studies. Having a sound basis in thermodynamics, the Henry Law is often used as a criterion to evaluate the validity of adsorption isotherm equations. However, the application of the Henry Law for microporous materials, especially microporous activated carbon, remains questionable. It is the aim of this paper to examine the Henry Law behavior of supercritical adsorbates in carbonaceous pores of different sizes, and to define the conditions for the Henry Law to be applicable for carbonaceous adsorbents.

I. Introduction

It is generally acknowledged that adsorption at low pressures can be described by the following Henry Law equation:

$$C = KP \tag{1}$$

with C and P being the amount adsorbed and equilibrium pressure. The Henry constant is usually calculated from the slope of the initial linear portion of the plot of the amount adsorbed versus pressure. When data at low pressure range are not available, the Henry constant is usually found by fitting the Langmuir equation, $C = C_s bP/(1 + bP)$ against the experimental data, and thence the Henry constant is obtained as $K = bC_s$ with b and C_s being Langmuir adsorption affinity and saturation capacity, respectively.

The Henry constant is one of the fundamental parameters used in describing an adsorption system. The Henry constants measured for pure components are commonly used as the basis for multicomponent adsorption studies. The sound theoretical basis of the Henry Law and its successful applications in many systems make it a criterion for assessing adsorption isotherm equations for their thermodynamic consistency. Many isotherm equations such as the Langmuir, BET, etc., comply with such a criterion at sufficiently low pressures.[1] Other equations do not exhibit this feature. DR equation, for example, gives a zero Henry constant at zero loading, and this has aroused much debate about the validity of the equation at very low pressures.

The Henry Law can be easily derived for adsorption on an energetically homogeneous surface using the traditional thermodynamic concepts. The extension of the Henry Law to adsorption onto mesoporous materials is also quite straightforward. On the other hand, its applicability to microporous materials is not so simple. It is known that the Henry Law behavior is not observed for many systems involving microporous materials.

In this paper, we will discuss the applicability of the Henry Law for carbonaceous porous materials using an adsorption model proposed in our earlier paper.[2] The aim is to develop a method of determining the Henry constant on the basis of the knowledge of pore size distribution (PSD) of the solid. The

method will be compared to other traditional methods used in obtaining the Henry constant.

II. Adsorption in Carbonaceous Porous Materials

1. Adsorption in Porous Materials. More often than not, the surfaces of nonporous or mesoporous materials can be considered to be energetically homogeneous, whereas energetic heterogeneity is an intrinsic characteristic for microporous materials. Adsorption in a porous environment is enhanced by the overlapping of the force fields exerted by the opposite pore walls. This enhancement depends on the degree of overlapping and hence it is a function of pore size. The narrower is the pore, the larger is the adsorption enhancement. With a lesser density of the functional groups, the energetic heterogeneity exhibited by carbonaceous microporous materials is commonly assumed to originate from the distribution of pore size.[3] In general, adsorption into micropores is distinctive from that occurring on a surface (and in larger pores) by a strong potential enhancement and a finite adsorption capacity due to the finite volume of the micropores.

Very often, adsorption of supercritical gases onto microporous activated carbon is described using equations derived for surface adsorption, for example the Langmuir equation. Adsorption in micropores can also be treated using the density function theory (DFT), which is developed on the basis of statistical mechanics and is more sophisticated than the other mentioned methods.[3]

2. Our Solution for Supercritical Adsorption in Porous Media. A model for adsorption of supercritical gases has been proposed and presented in a previous paper.[2] The model uses the Langmuir equation as the local isotherm, while the effect of the pore wall proximity on the adsorption process is accounted for by introducing pore enhanced parameters. These parameters are based on the potential energy calculation of the probe molecules. The main features of the model are discussed briefly below.

The pore potential enhancement affects both molecules in the adsorbed phase and those of the gas phase occluded within the pore. Because of the enhancement on the occluded molecules, the fluid-phase pressure within the pores, p_p, is different from the bulk pressure p, and it can be estimated as follows:

* Corresponding author.

$$p_p(r) = p \exp\left(\frac{-\langle E_p^g(r) \rangle}{RT}\right) \tag{2}$$

with $\langle E_p^g \rangle$ and T being the average potential energy of the occluded molecules and system temperature, respectively. This average potential is a function of pore siz*e* and in this paper it will be approximated by the potential energy at the pore center E_p^g.

Let us consider a slit-like carbonaceous pore. An adsorbate molecule occluded in such a micropore interacts with both pore walls. When the molecule moves from the bulk gas phase to the adsorbed phase, its potential energy decreases and the magnitude of such decrease ΔE_p is a function of pore size. The Langmuir affinity coefficient of adsorption in the pore b_p can be estimated from that on a flat surface having the same surface chemistry, b_s, by the following formula:

$$b_p(r) = b_s \exp\left(\frac{\Delta E_p(r) - \Delta E_s}{RT}\right) \tag{3}$$

ΔE_s is the potential energy change when a molecule is moved from the bulk to the flat surface. A theoretical approach to determine b_s was introduced by Hobson,[4] who derived the expression $b_s = \beta/\sqrt{MT} \exp(\Delta E_s/RT)$ with M being the molecular weight. The parameter β takes a value of 0.426 to give b_s in the unit of 1/MPa. In our earlier paper,[2] we found that a value of 0.021 for β is more appropriate for activated carbon. The calculation is carried out for methane and nitrogen adsorption at 300 K into carbon pores of different sizes. Figure 1 shows, for example, the methane single pore isotherms at 300 K. The isotherms indicate that adsorption takes place mostly in smaller pores, while that in larger pores is not significant even at high pressures.

3. PSD in Terms of Volume and Capacity. It is known that in the case of supercritical adsorption, the adsorbed phase does not occupy the whole pore volume, even at very high pressures. The degree of occupancy at any stage of adsorption differs from pore to pore depending on their dimension. The narrower the pore, the higher this degree of occupancy, but it is always less than 1, except in ultra-micropores. This is different from subcritical adsorption, where in principle all pores are filled by subcritical adsorbate when pressure approaches a critical pore-size-dependent value called the pore filling pressure, which is smaller than the vapor pressure. For subcritical fluids, the PSD for pore volume density in terms of pore size $dW/dr = f(r)$ can be derived from the distribution of maximum capacity $dC_s/dr = g(r)$ by assuming that the adsorbed density is equal to the liquid density. Whereas for supercritical adsorption, the relationship between the pore volume distribution (cc/g/nm) and adsorptive capacity distribution (mmol/g/nm) is not straightforward because of reasons given earlier on occupancy. The relationship between the two requires idealizations regarding the boundary of the adsorbed phase. In a previous work,[2] we proposed a pore-size-dependent factor termed the threshold potential energy E^*, which defines the energy boundary between the adsorbed phase and the occluded gas phase. This threshold potential energy is taken to be the minimum potential energy of a flat surface. This assumption implies that without potential enhancement, adsorption of super-critical fluids is restricted within a monolayer. In a pore system, a critical thickness z^* from the pore wall, where the potential energy of molecules equal to the potential threshold, is used to define the physical phase border between the adsorbed and gas phase. This critical thickness is determined for any pore at any stage of adsorption.
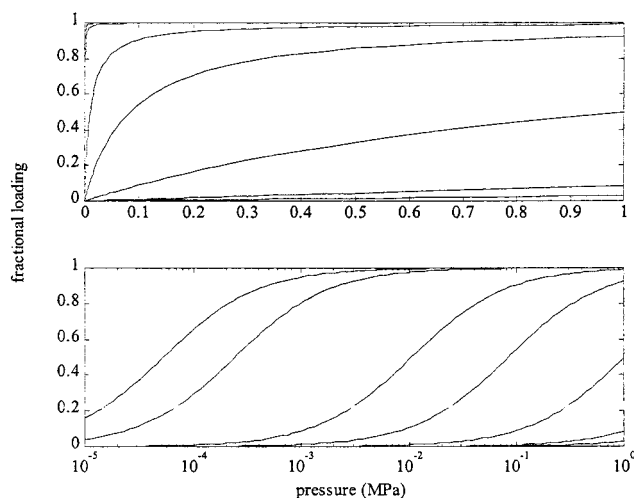
Figure 1. Methane isotherms at 300 K in carbon slit-like pores of different half widths (reading from left to right: 0.36, 0.40, 0.43, 0.47, 0.54, 0.72, and 1.79 nm).
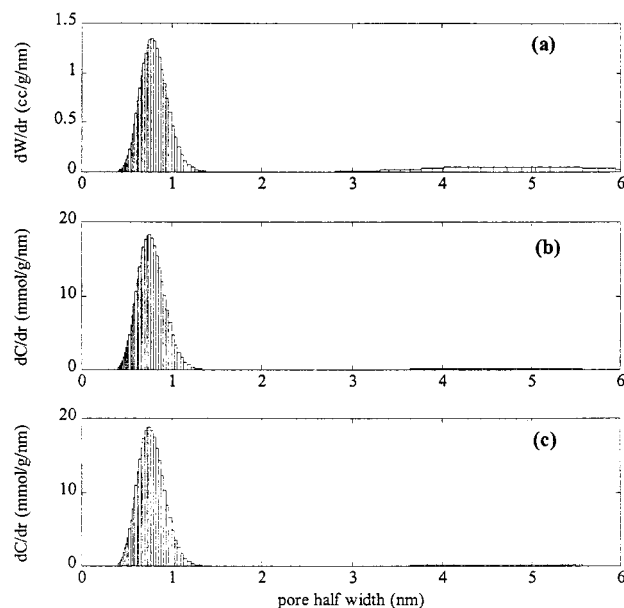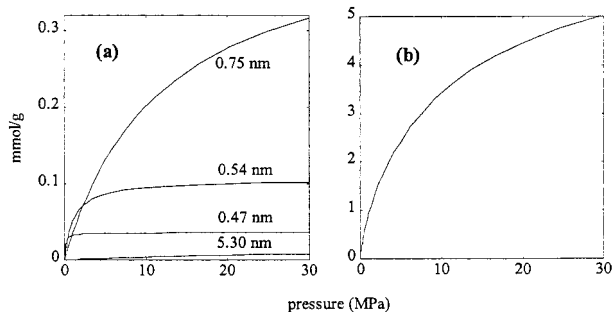

Figure 2. Volume PSD of the conceptual AC sample I (a) and the derived PSD in terms of methane (b) and nitrogen (c) capacity.

TABLE 1: Simulated AC Samples and Their Derived Capacities

sample	distribution function	volume PSD			capacity PSD (mmol/g)	
		mean (nm)	variance (nm)	volume (cc/g)	methane	nitrogen
A	gamma 1	1.6	0.3	0.50	6.73	6.95
	gamma 2	10	2.2	0.15	0.32	0.33
	total			0.65	7.05	7.28
B	gamma	variable	0.3	0.50	variable	

We also use the liquid densities at normal boiling points for the adsorbed phase, which are available in the literature.[5] Since z^* and E^* are probe-molecule-dependent, the same pore volume PSD would yield different mole capacity PSDs for different adsorbates. To illustrate this, we assume two model carbon samples, A and B, the volume PSD of which are generated by either a double Gamma or a single Gamma distribution function (Table 1). Figure 2a shows the volume PSD of the carbon A, described by a double Gamma distribution function. The mean pore widths of the two peaks are 1.6 and 10 nm (cf. Table 1). The total pore volume is 0.65 cm³/g, of which 0.5 cm³/g is

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Figure 3. Methane adsorption in individual pores (a) and the overall isotherm (b) at 300 K for the sample A.
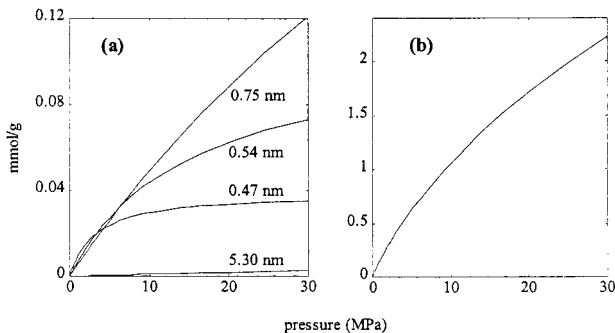
Figure 4. Nitrogen adsorption in individual pores (a) and the overall isotherm (b) at 300 K for the sample A.

contributed by micropores. In the figure, the pore spectrum of half widths from 0.4 to 10 nm is presented by 100 pore subranges. The methane and nitrogen capacity PSDs of the carbon A are calculated using the procedure presented above, and results are presented in Figure 2b,c as plots of dC_s/dr versus r. As seen in Figure 2, the capacity PSDs are different from the volume PSD, and the dominance of the adsorption in narrower pores is evident. For example, while the micropore volume is about 3.3 times greater than the mesopore volume (0.5 cm^3/g compared with 0.15 cm^3/g), the methane capacity in the micropores is 21 times greater than the mesopore capacity (6.73 mmol/g compared with 0.32 mmol/g). It is also noted that the medians of the capacity PSDs are slightly left compared to those of the volume PSD. This is due to the stronger adsorption enhancement in smaller pores.

Knowing the pore capacity, we can calculate the overall adsorption as the sum of adsorption in individual pore ranges. This is shown in Figures 3 and 4, where the methane and nitrogen adsorption at 300 K onto the carbon sample A is presented. The overall isotherms (Figures 3b and 4b) are calculated as the sum of the individual pore isotherms, corresponding to 100 pore sub-ranges shown in Figure 2. The isotherms exhibit a typical shape for carbonaceous materials. For the sake of clarity, the single pore isotherms are shown for only four pore bands (0.47, 0.54, 0.75, and 5.30 nm) in Figures 3a and 4a. As seen, methane and nitrogen adsorption in individual pores is a strong function of the pore size and dependent on the pore volume. At any stage of adsorption, the narrower the pore, the higher the fractional loading and the absolute amount adsorbed depends on the pore maximum capacity.

IV. Onset of the Henry Law

1. Henry Constant Derived from our Technique. In our technique, adsorption is described at a single pore level and the overall adsorption is determined as the summation of

contribution from all pores. In this section, we will show theoretically that our approach is Henry Law-compatible, i.e., at low-pressure region, we can recover a linear relationship between amount adsorbed and pressure. The use of the Langmuir equation to describe adsorption means that for pores of larger dimensions, where the adsorption enhancement is insignificant, the Henry Law behavior is always the case. The question here is about the Henry Law behavior in smaller pores, where the potential energy enhancement is evident.

Let us consider a sample having pores of different sizes. If we divide the pore spectrum into n pore sub-ranges, the volume PSD then can be approximated by n pore volumes and n corresponding nominal pore half widths $r_{i\ =\ 1...n}$. Equation 2 means that the pressure of the gas phase occluded inside pores of size r_i is enhanced by a factor $f_i = \exp(-\langle E_p^g(r_i)\rangle/RT)$. Similarly, the affinity coefficient of adsorption in these pores is also enhanced by a factor of $g_i = \exp(\Delta E_p(r_i)-\Delta E_s/RT)$, which comes from eq 3. If the maximum capacity of all pores of size r_i is denoted as $C_{s,i}$, the overall adsorption can be written as

$$C = \sum C_{s,i} \frac{b_{p,i} P_{p,i}}{1 + b_{p,i} P_{p,i}} = \sum C_{s,i} \frac{b_s g_i f_i P}{1 + b_s g_i f_i P} \quad (4)$$

When the pressure is low enough, such that $b_s g_i f_i P \ll 1$, this equation reduces to the following Henry Law equation:

$$C = \sum C_{s,i} b_s g_i f_i P = b_s \sum C_{s,i} g_i f_i P \quad (5)$$

from which the Henry constant is

$$K = \sum C_{s,i} b_s g_i f_i \quad (6)$$

Compared to that of a flat surface (i.e., $b_s P \ll 1$), the condition for Henry Law to be applicable in a pore (i.e., $b_s g_i f_i P \ll 1$) involves two extra factors g_i and f_i, which reflect the effects of adsorption enhancement. Since these factors can be quite large for smaller pores, the conditional inequality means that the Henry Law works for porous materials at much lower pressures than for nonporous materials as one would physically expect. The smaller the pore, the larger the enhancing factors, and the lower the pressure range for the Henry Law to be applicable. Furthermore, eq 6 means that the Henry constant for microporous materials is significantly larger than that of a flat surface. This equation, for example, gives a Henry constant of 8.16 mmol/g/MPa for methane adsorption on carbon A at 300 K. The enhancing effect of the microporosity is quite significant if we note that the Henry constant calculated for methane adsorption onto flat graphite surface at the same temperature is less than 0.03 mmol/g/MPa. This Henry constant is quite comparable, for example, with the experimental value for methane adsorption at 300 K onto AC-40, CECA (8.05 mmol/g/MPa).[6] The methane Henry constant of 8.16 mmol/g/MPa is also comparable to those of many other microporous materials discussed in the work of Mersmann et al.[7]

It is important to point out here that the condition $b_s g_i f_i P \ll 1$ (for all i) for the Henry Law be valid is more than sufficient. It is clear that this factor is greatest for small pores, and if we apply this to determine the critical pressure below which the Henry Law is valid we may obtain far too low value for this critical pressure. We note that the smallest pores have the largest $b_s g_i f_i$, but adsorption in those pores can be negligible if their maximum capacity $C_{s,i}$ are very small. The condition $b_s g_i f_i P \ll 1$, thus, does not need to be considered for those pores.
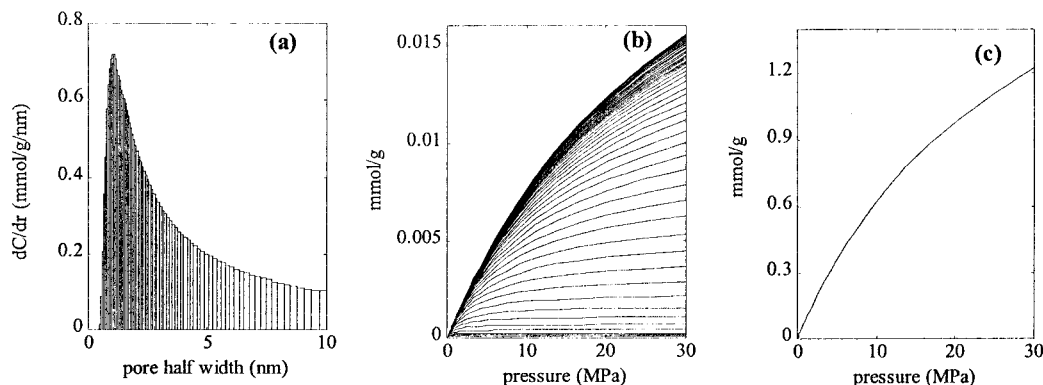
Figure 5. Capacity PSD (a), methane single pore (b), and overall isotherms (c) at 300 K of a simulated carbon sample.
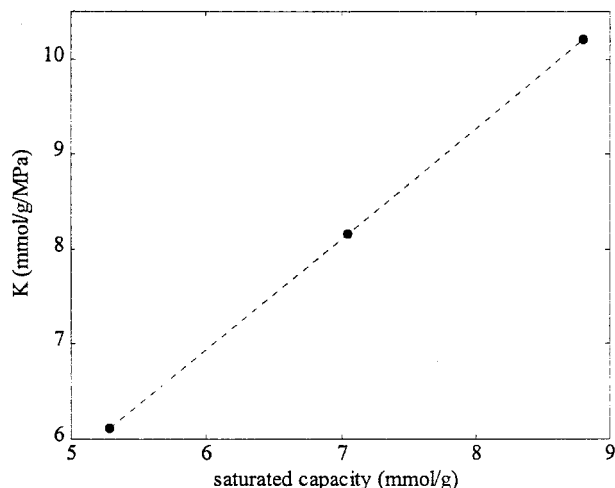

Figure 6. Henry constant for methane at 300 K as a function of saturated pore capacity.

On the basis of the formulas for b_s, g_i, and f_i, a near linear relationship between the logarithm of the Henry constant and temperature can be expected. This is in compliance with the Van Holf's equation used in determining the heat of adsorption.

2. PSD and the Henry Constant. The dependence of the Henry constant on the PSD is investigated in this section in light of eq 6.

a. A Special PSD. The expression $\sum C_{s,i} b_s g_i f_i$ and the pore size dependence of $C_{s,i}$, g_i, and f_i means that the Henry constant is a very strong function of the PSD. It is interesting to consider a case of a hypothetical sample, which has a maximum capacity PSD such that $C_{\mu s,i} = \nu / b_s g_i f_i$ with ν being a constant, which is basically the Henry constant in each pore. According to eq 6, the Henry constant can be calculated as

$$K = \sum C_{s,i} b_s g_i f_i = \sum \frac{\nu}{b_s g_i f_i} b_s g_i f_i = \sum \nu = n\nu \qquad (7)$$

The PSD of such a sample and its methane isotherm spectrum are shown in Figure 5. In this case, the PSD is divided into $n = 100$ ranges and all individual pore isotherms have an identical slope $\nu = 0.001$ mmol/g/MPa at zero loading. The resulting overall Henry constant is $K = n\nu = 0.1$ mmol/g/MPa, and the total adsorption capacity is also calculated to be 2.54 mmol/g.

b. Pore Volume. The effect of the pore capacity on the Henry constant is also clear in eq 6. This equation means that samples with similar PSDs have Henry constants proportional to their adsorption capacities. This linear relationship is demonstrated in Figure 6, where the Henry constants are plotted for samples
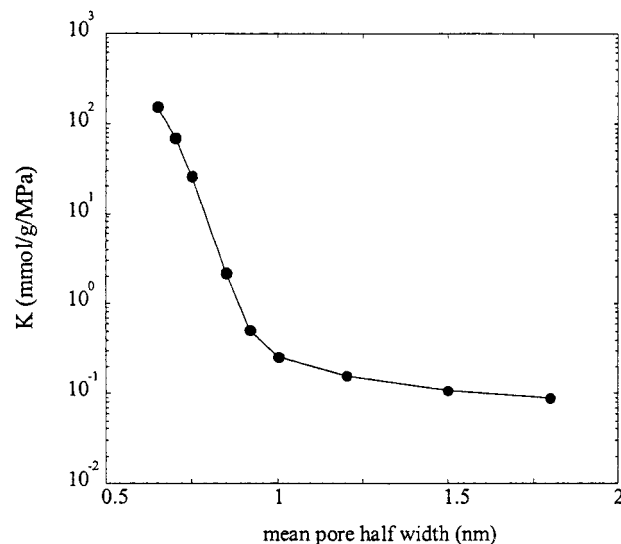

Figure 7. Henry constant of methane as a function of mean pore half width (fixed variance and pore volume).

having different total maximum capacity, but having the same PSD shape as that of carbon A.

When the mesopore volume distribution varies and the micropore volume remains the same, the Henry constant does not vary to any extent. This is understandable as the contribution of mesopore capacity toward the Henry constant is very insignificant.

c. Mean Pore Size. Let us consider a carbon B, which has a single modal PSD having a variance and pore volume of 0.3 nm and 0.5 cm³/g, respectively (Table 1). We aim to study the effect of the pore size on the Henry constant by varying the mean half width of the PSD as shown in Figure 7. There, the Henry constant of methane is a strong function of the pore size when the majority of pores is in the micropore range. It does not change significantly when the pore half width gets larger than 1.3 nm. This is because the potential energy enhancement becomes less significant in pores having half width greater than 1.3 nm.

d. Henry Constant of Different Adsorbates. The dependence of the Henry constant on adsorbate is evident by comparing Figures 3 and 4. The nitrogen and methane isotherms are different despite a similarity between their mole capacity PSDs (Figure 2). The Henry constants calculated for methane and nitrogen adsorption at 300 K using eq 6 are 8.16 and 0.25 mmol/g/MPa, respectively. That is, for this sample, the methane Henry constant is more than 30 times larger than that of nitrogen while that figure is about 5 for a flat graphite surface. This means

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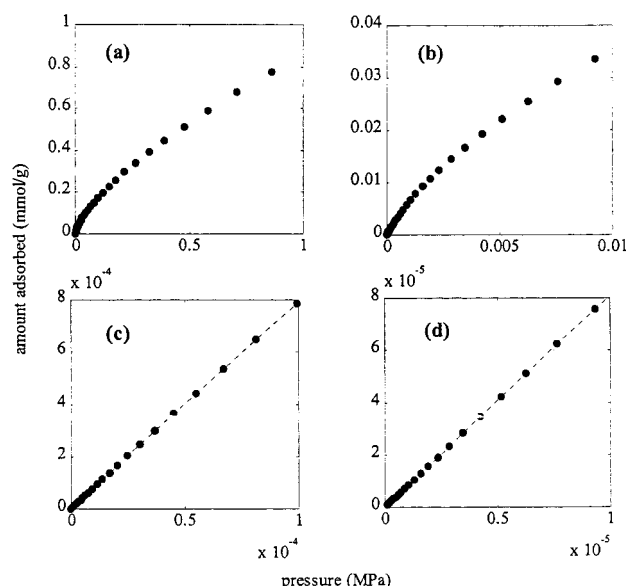
Figure 8. Initial section of the methane isotherm plotted on different scales (sample A at 300 K).

TABLE 2: Henry Constant Derived by Linear Relationship Method (Figures 3 and 9)

upper pressure (MPa)	10^{-5}	10^{-4}	1×10^{-3}	1	30
K (mmol/g/MPa)	8.16	8.14	N/A	N/A	N/A

TABLE 3: Optimized Henry Constant from Langmuir Equation Fitting Using Different Data Ranges

pressure	from:	10^{-7}	10^{-7}	10^{-7}	10^{-7}	10^{-3}	1
range(MPa)	to:	10^{-3}	1	10	30	30	30
C_s (mmol/g)		2.633	1.418	4.610	5.891	5.891	6.023
b (1/MPa)		2.626	1.270	0.218	0.141	0.141	0.131
K (mmol/g/MPa)		6.91	1.80	1.01	0.83	0.83	0.79

that adsorption in porous materials is more selective than that occurring on a flat surface of the same surface chemistry.

3. Traditional Methods of Obtaining the Henry Constant. Having calculated the Henry constants using our method, we now compare the results with those obtained using the traditional methods. There are two practical methods of obtaining the Henry constant:

When adsorption data at low pressures are available, the plot of loading versus pressure is magnified at the lower pressure end to determine a region where a straight line can be drawn over the experimental points. The slope of such a straight line is taken as the Henry constant.

If low-pressure data are not available, or no "straight" section of the loading versus pressure plot is observed, an equation such as the Langmuir or Toth can be used to fit the data to extract maximum capacity and the affinity coefficient, from which Henry constant can be calculated.

The reliability of these methods depends primarily on the accuracy of the experimental data, which are always subject to errors, especially those at low pressures.

a. The Method of Linear Relationship. Besides the errors inherent in all experimental data, this method requires the fitting of the experimental points into a straight line. The judgment of a goodness of fit by the residual value could be subjective. The combined effect of those uncertainties is that a linear relationship may seem to be plausible while in fact it is not the case. There is a need to determine the range over which the Henry Law is valid, i.e., to estimate the limit equilibrium pressure, under which a practical linear relationship between *C* and *P* can be assumed.

To illustrate this, we use the methane data of the carbon A at 300 K. The methane isotherm in Figure 3 covers a pressure range up to 30 MPa. The initial section of this isotherm is redrawn in several scales as shown in Figure 8. The plots in the figure show that apparently the equilibrium points at pressures below 1×10^{-4} MPa (Figure 8c) fit into a straight line. The Henry constant derived from this straight line is 8.14 mmol/g/MPa. When we consider equilibrium points within an even lower pressure range (Figure 8d), a slightly higher Henry constant 8.16 mmol/g/MPa is obtained. This value for the Henry constant is comparable to that calculated before using eq 6. It is clear that the inclusion of data above 1×10^{-4} MPa will

result in underestimated Henry constants. Thus, we can see that to obtain a good estimate of the Henry constant for methane adsorption onto carbon A, we need experimental data at pressures below 1×10^{-4} MPa. It is possible to prove that at pressures below 1×10^{-4} MPa, the inequality $b_s g_i f_i P \ll 1$ holds. Results on the obtained Henry constant are summarized in Table 2. Using a similar analogue, the pressure limit for nitrogen is found to be of the order of 0.1 MPa, which is significantly higher than that of methane. This is simply due to the fact that nitrogen is much less adsorbing than methane.

b. The Isotherm Fitting Method. Very often, experimental data are not collected at pressures low enough for the direct application of the Henry Law. In such instances, a practical approach is used by assuming the adsorption isotherm follows the Langmuir or Toth equation isotherm so that the Henry constant can be estimated as the product of b and C_s, which are derived from fitting the equation against the data. This approach is often used for supercritical adsorption in microporous materials. We will demonstrate that despite its widespread use, the use of this method may incur significant errors. The fitting process is carried out against data at different pressure ranges, and the resulting Henry constants are summarized in Table 3. The table shows that the Henry constant is very sensitive to data at the higher pressure end. This is because the optimization is carried out in the "least-squares" sense, which does not "weigh" experimental data. It is observed that the more contribution of data at low pressures, the larger the Henry constant. However, it is also anticipated that this method underestimates the Henry constant and that the value calculated using eq 6 (8.16 mmol/g/MPa) cannot be achieved. The reasons are as follows. First, it is because an overall Langmuirian behavior cannot properly describe adsorption in microporous materials. Second, for the success of the optimization, data at higher pressures are included to take account for the isotherm curvature and saturation capacity. The Henry constant obtained in this manner is "indirect" via the optimally extracted b and C_s. The Henry constant obtained using this optimization method (Table 3) can be several times smaller than that obtained by using the method of linear relationship. Furthermore, it is stressed that a satisfactory goodness of fit when fitting the Langmuir or Toth equation to the data is not always achievable.

V. Conclusions

Using the proposed method for supercritical adsorption, we are able to prove the existence of a Henry Law region for adsorption in porous carbonaceous materials. It is found that the Henry constant is a function of the pore structure of the adsorbent, and it can be calculated from the PSD. Generally speaking, for a microporous adsorbent, the narrower the pores, the greater the Henry constant and the lower the pressure range where the Henry Law is valid. The Henry constant calculated

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using this method could be more appropriate than those of the linear relationship and isotherm fitting methods in assessing adsorption systems.

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