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Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 1: modified Dubinin-Astakhov model

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Abstract Simulations of the thermal effects during adsorption cycles are valuable tools for the design of efficient adsorption-based systems such as gas storage, gas separation and adsorption-based heat pumps. An analytical representation of the measured adsorption data over the wide operating pressure and temperature swing of the system is necessary for the calculation of complete mass and energy conservation equations. In Part 1, the Dubinin-Astakhov (D-A) model is adapted to model hydrogen, nitrogen, and methane adsorption isotherms on activated carbon at high pressures and supercritical temperatures assuming a constant microporous adsorption volume. The five parameter D-A type adsorption model is shown to fit the experimental data for hydrogen (30 to 293 K, up to 6 MPa), nitrogen (93 to 298 K, up to 6 MPa), and for methane (243 to 333 K, up to 9 MPa). The quality of the fit of the multiple experimental adsorption isotherms is excellent over the large temperature and pressure ranges involved. The model's parameters could be determined as well from only the 77 K and 298 K hydrogen isotherms without much reducing the quality of the fit.

Keywords Adsorption · Activated carbon · Dubinin-Astakhov · Supercritical · Hydrogen · Nitrogen · Methane · Modeling

1 Introduction

Physisorption in microporous adsorbents is used in various applications such as gas separation, gas storage, and adsorption heat pumps. In addition to mass transfer, the design of efficient systems must take into account the thermal effects associated with adsorption processes. Simulations of the heat generated during adsorption are a valuable tool for the thermal management of adsorption-based systems (Batos-Neto et al. 2005; Cruz et al. 2003; Mota et al. 1997; Teng et al. 1997). A functional representation of the adsorption data is required to describe the adsorbed phase in the mass and energy balance equations of the system. The parameters of such temperature and pressure dependent functions are determined by fitting a modeled isotherm to experimental adsorption data. Hence, the accuracy of the fit is critical for proper thermodynamic simulation of the absorbent/adsorbate system. As described in details later, the modeling of adsorption in microporous adsorbent at high pressures and over large supercritical temperature ranges brings additional requirements including: calculation of absolute adsorption from excess adsorption data; extension of the Dubinin-Astakhov (D-A) model to the supercritical region and; fitting with only one set of parameters data over a large range of pressure and temperature.

The absolute amount adsorbed (n_a) is defined as the quantity of gas contained in the adsorption volume V_a, the space where the density of the adsorbate is higher than that of the bulk gas. It is given by:

$$n_a = \frac{n_{tot}}{m_s} - \rho_g (V_{v,sys} - V_a). \tag{1}$$

For convenience, the amount adsorbed, n_a, and the volumes are expressed per unit mass of adsorbent. n_{tot} is the total

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amount of adsorbate introduced in the measuring system containing the adsorbent, m_s is the mass of adsorbent, ρ_g is the density of the bulk gas, and $V_{v,sys}$ is the total void volume of the adsorption system per unit mass of adsorbent (including the pore volume of the adsorbent, the interstitial space, and any additional empty space). The total void volume can be measured by helium probing. However V_a cannot be measured separately. Consequently, the absolute adsorption cannot be measured directly. We deduct instead the excess adsorption (n_{ex}) which measures the additional amount of gas present in $V_{v,sys}$ due to adsorption:

$$n_{ex} = \frac{n_{tot}}{m_s} - \rho_g V_{v,sys}. \tag{2}$$

In terms of absolute adsorption variables, the excess adsorption is thus given by:

$$n_{ex} = n_a - \rho_g V_a = n_a \left[1 - \frac{\rho_g}{\rho_a} \right]. \tag{3}$$

If the bulk gas density is negligible compared to the average adsorbed density (ρ_a), the excess adsorption is a good approximation of the total amount adsorbed. However, the excess adsorbed density n_{ex} differs appreciably from n_a at high pressure and low temperature due to the different functional dependence of n_a and ρ_g on pressure (Myers and Monson 2002; Salem et al. 1998; Sircar 1999). The adsorbed density increases with pressure until it levels off as it approaches saturation asymptotically. On the other hand, the density of the bulk supercritical gas increases monotonically with pressure. Because the excess adsorbed density is defined as the difference between the two, a maximum occurs in the excess adsorption isotherm. Close to this maximum, the pressure can no longer be expressed as a single-valued function of the amount absorbed, which results in a singularity in the isosteric heat of adsorption ($-\Delta \bar{h}_a$) (Myers and Monson 2002; Sircar 1999):

$$\Delta \bar{h}_a = -RT^2 \left[\frac{\partial \ln P}{\partial T} \right]_{n_a}. \tag{4}$$

Adsorption models are generally developed for absolute adsorption. They cannot represent this maximum and cannot be adequately fitted to excess adsorption experimental data at high pressures. As discussed later, to be modeled and derived into thermodynamic properties, excess adsorption data is to be first converted into absolute adsorption n_a by estimating the adsorbed phase density or the adsorption volume V_a.

Most of the adsorption phenomena in microporous adsorbents occur in pores of commensurate size with the adsorbed molecules. The D-A model has been applied to describe pore filling of subcritical gas in microporous adsorbent. The isotherm is given by the following expression (Dubinin 1975):

$$\theta = \frac{n_a}{n_{\max}} = \exp\left[-\left[\frac{A}{\varepsilon} \right]^m \right], \tag{5}$$

where

$$A = RT \ln\left(\frac{P_0}{P} \right). \tag{6}$$

The function A is the differential maximal molar work of adsorption equal, with a minus sign, to the variation in free enthalpy (the reference state is that of the bulk liquid phase in equilibrium with the saturated vapor at temperature T). θ represents the degree of filling of the volume of the micropores, ε is the characteristic free energy of adsorption in J/mol, P is the equilibrium pressure and P_0 is the saturation pressure of the vapour for the temperature T. The distribution parameter m is generally close to a small integer and is equal to 2 for most activated carbons. The variable n_a is the amount adsorbed in mol/kg and the parameter $n_{\max}$ is the limiting adsorption in mol/kg, corresponding to the maximum filling of the entire volume of adsorption space. In Dubinin's approach, $n_{\max}$ is assumed to depend on the temperature according to a thermal expansion factor of the adsorbed vapour. The limiting adsorption density is often approximated using the bulk liquid density at the normal boiling point, but this assumption is not always verified (Dubinin 1975). Also, for high pressures, it is recommended to use fugacity instead of pressure as the independent variable.

The D-A model has been developed to describe subcritical adsorption. Above the critical temperatures, the saturation pressure is undefined; a different standard state has to be chosen. The model can still be used by defining an empirical pseudo-saturation pressure (or pseudo-saturation fugacity) calculated from the critical pressure and temperature, such as (Amankwah and Schwarz 1995):

$$P_0 = P_c \left(\frac{T}{T_c} \right)^k \quad \text{or} \quad f_0 = P_c \left(\frac{T}{T_c} \right)^k, \tag{7}$$

where P_c and T_c are the critical pressure and temperature. The exponent k is a fit parameter. In a previous version of this expression, the exponent k was fixed at 2 (Dubinin 1960). The parameters $n_{\max}$, P_0 and ε have also been determined through a regression fit of the isotherms, sometimes assuming a constant $n_{\max}$ (Czerny et al. 2005).

The object of this paper is the modeling of hydrogen, nitrogen and methane adsorption on activated carbons over a wide temperature and pressure range above the critical point. The model needs to fit the experimental data accurately but also to be simple enough to allow analytical derivation of the terms used to describe the adsorbed phase in the mass and energy balance equations. The approach used to determine V_a and the D-A model parameters for the supercritical region is presented in the next section. The parameterization of the model is obtained from a fit to experimental adsorption data of hydrogen on the activated carbon AX-21™ (30 to 293 K, 0–6 MPa)[1] (Bénard and Chahine 2001), of nitrogen on the activated carbon C034 (93 to 298 K, 0–6 MPa) (Czerny et al. 2005) and of methane on the activated carbon CNS-201™ (243 K−333 K up to 10 MPa) (Bénard and Chahine 1997). The results are then presented and discussed.

2 Modeling approach

2.1 Determination and interpretation of the adsorption volume

Excess adsorption data can be converted into absolute adsorption by determining either the adsorption volume (i.e., the Gibbs volume) or the adsorbed phase density. In the first approach, the adsorption volume V_a is assumed to correspond to the volume of the adsorbent subjected to the potential field of the solid (Myers and Monson 2002; Talu and Myers 2001). The adsorption volume, generally constant, may be temperature dependant (a different volume for each isotherm) (Bae and Bhatia 2006; Murata et al. 2001, 2002) or not (Czerny et al. 2005; Myers and Monson 2002; Salem et al. 1998; Talu and Myers 2001). In the other approach, the adsorbent is assumed to be gradually filled with liquid-like adsorbed phase (Agarwal and Schwarz 1988; Ozawa et al. 1976; Zhang et al. 1991). The adsorbed phase density is often assumed to be similar to the liquid at the boiling point with a thermal expansion factor. A pressure dependant adsorbed phased density has also been used (Dreisbach et al. 2002). The outcome of the density approach is that V_a and the volume of the bulk gas phase in contact with the adsorbed phase (V_g), will vary with the amount adsorbed and temperature. Compared to the temperature independent constant volume approach, this strategy would lead to more complex mass and energy balance equations and, even more importantly, will have to be taken into account during the derivation of the adsorbed phase energy terms (as shown in the companion paper). By defining a constant V_a, we consider that the adsorbed gas occupies the space of the whole adsorption field set up by the solid body and that its average density gradually increases up to an asymptotic value during adsorption.

The pore volume of the adsorbent (micropores and mesopores) (V_p) is usually taken as a reasonable approximation of the space lying within the potential field of the solid and is used to convert absolute to excess variables (Myers and Monson 2002; Salem et al. 1998; Talu and Myers 2001). To classify porous material, the microporous and mesoporous volumes are generally estimated by nitrogen adsorption and desorption at 77 K. These values depend on the adsorbate and on the model chosen, and do not constitute a direct measurement of adsorption volume. Talu et al. determined the pore volume in silicate using molecular simulations of helium adsorption (Talu and Myers 2001). Czerny et al. estimated the pore volume of activated carbon by considering it as a parameter in model fits to experimental adsorption isotherms and by averaging the values obtained from various isotherms. This empirical volume was attributed to V_v, the void volume of the adsorbent (micro, meso-, and macropores as well as interstitial space). However, the value calculated by this method was lower than the void volume measured with helium (Czerny et al. 2005).

Since the adsorption in microporous activated carbon take place mostly in the micropores and not in the interstitial space, the adsorption volume V_a should be different from V_v. In this work, since the accurate representation of the experimental data with the model is the main objective, the constant V_a is determined by fitting the experimental data to the modeled excess isotherms using:

$$n_{ex} = n_a - \rho_g V_a, \tag{8}$$

where the expression for n_a is the chosen adsorption model. Instead of being an average of individual isotherms fit, the parameter V_a is determined by fitting all the experimental isotherms of an adsordent/adsorbate pairs in the same regression. The adsorption volume is interpreted as the microporous volume of the adsorbent and not the void volume (V_v) of the adsorbent. Even if a physical significance is attributed to V_a, it can be seen as a control volume defined by a Gibbs dividing surface. The part of the V_v where negligible adsorption takes place and where the density of the gas is the same than the bulk is defined as:

$$V_g = V_v - V_a, \tag{9}$$

where V_v is experimentally measured by helium probing or calculated from the bulk and the skeletal density of the adsorbent. The determination of the value of V_g is necessary for the gas bulk phase mass and energy calculation in adsorption system simulations.

2.2 Modified Dubinin-Astakhov approach

The Dubinin-Astakhov (D-A) micropore volume-filling adsorption model is particularly adapted to describe adsorption in activated carbons. Using the D-A model, the absolute adsorption is:

$$n_a = n_{\max} \exp\left[-\left[\frac{RT}{\varepsilon}\right]^m \ln^m\left(\frac{P_0}{P}\right)\right], \tag{10}$$

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[1] Michelsen, J., Chahine R.: Private communication (2005). These experiments where conducted with the same carbon than (Bénard and Chahine 2001).

Table 1 Sets of experimental adsorption excess isotherms data

		Set 1	Set 2	Set 3
Reference		(Bénard and Chahine 2001)[a]	(Czerny et al. 2005)	(Bénard and Chahine 1997)
Adsorbate		H_2	N_2	CH_4
Adsorbent	Carbon	AX-21™	C034	CNS-201™
	Specific Surface Area (m^2/g)	2800	2000	1150
	Bulk density (g/cm^3)	0.30	0.34	0.48
	Void volume (cm^3/g)	2.9[b]	2.5[c]	1.6[b]
Temperature range (K)		30–77[a] and 77–298	93–298	243–333
Pressure range (MPa)		0–6	0–6	0–10

[a] Michelsen, J., Chahine, R.: Private communication (2005). These experiments where conducted with the same carbon than (Bénard and Chahine 2001)

[b] Measured with helium

[c] Calculated from the bulk activated carbon density and the density of graphite

where $n_{\max}$, ε, and P_0 have to be determined for the supercritical region.

The empirical equations used to determine the limiting adsorption, $n_{\max}$, and the pseudo-saturation pressure, P_0 lose their physical justification as the temperature and the pressure gets significantly above the critical point. Furthermore, the model has to be simple enough to allow analytical derivation of the adsorbed phase terms of the mass rate and energy rate balance equations. Hence, we prefer a simple treatment of the parameters and to keep them constant as much as possible from one isotherm to the other so the resulting analytical expression can then be derived easily with temperature or with pressure. Therefore, the treatment of P_0 and $n_{\max}$ as constant fitting parameters is also evaluated. The exponent m was preferentially set to 2. This special case corresponds to the Dubinin-Radushkevich equation.

The assumption of temperature invariance of the D-A distribution function for the filling of the micropores leads to a temperature independent characteristic free energy of adsorption (ε). This allows the determination of the model parameters with one isotherm only. However, temperature invariance is not mandatory to the theory of adsorption in micropores (Dubinin 1975). For very large temperature and pressure ranges, the assumption of temperature invariance may not be valid. Czerny et al. observed that the fitted characteristic free energy of adsorption, ε, tends to vary linearly with temperature (Czerny et al. 2005). Therefore, the following form of the characteristic free energy of adsorption was tested:

$$\varepsilon = \alpha + \beta T. \qquad (11)$$

Thermodynamically, the characteristic free energy of adsorption, as expressed by (11), can be understood as the sum of two contributions: the enthalpic factor (α) and the entropic factor ($-\beta$). This is explained in details in the companion paper. The contribution of enthalpic and entropic factors was also observed on the Langmuir model (Myers and Monson 2002).

The experimental excess isotherms are fitted using the following equation:

$$n_{ex} = n_{\max} \exp\left[-\left[\frac{RT}{\varepsilon}\right]^m \ln^m\left(\frac{P_0}{P}\right)\right] - \rho_g V_a. \qquad (12)$$

The gas phase density ρ_g is determined using the NIST12 software package (Lemmon et al. 2000). The parameters are obtained by a regression fit of the excess adsorption experimental points to (12). All the experimental adsorption isotherms of an adsorbate/adsorbent pair are fitted simultaneously. The quality of the fit is analyzed using the standard error of the estimate.

2.3 Experimental data

The modified D-A model was fitted to the three different sets of excess adsorption isotherms presented in Table 1.

3 Results and discussion

The standard errors of estimate (σ_{est}) of the models for the different interpretations of the D-A parameters are presented in Table 2. It also includes a more severe test of the parameters: the case where the parameterisation is performed with only the 77 K and 298 K isotherms from the hydrogen adsorption couple but σ_{est} being calculated using the whole range of experimental data. A reliable model that could be parameterised with only 77 K and 298 K isotherms would be of high practical interest for engineering applications. It is not only less time consuming with lesser required experimental data but also the measuring systems at these two

Table 2 Standard error of estimate of the fit to experimental data with various model parameter definitions

	Model parameters[a]	Standard error of estimate (σ_{est}) (mol/kg)			
		H_2	H_2[b]	N_2	CH_4
1	P_0 and $n_{\max}$ are fitted parameters, $m=2$, $\varepsilon=\alpha+\beta T$	0.79	1.19	0.58	0.11
2	ε is a fitted parameter	2.34	5.64	1.02	0.12
3	m is a fitted parameter	0.69	3.46	0.57	0.08
4	m and ε are fitted parameters	1.00	6.46	0.81	0.12
5	$n_{\max}=\rho_l V_a$	3.86	5.05	0.61	0.12
6	$P_0=P_c(T/T_c)^k$	1.59	5.88	0.98	0.10
7	$P_0=P_c(T/T_c)^k$, ε is a fitted parameter	4.25	7.87	1.90	0.27
8	Langmuir model[c]	3.33	6.72	1.38	0.35
9	$\bar{\rho}_a=\frac{V_a}{n_a}=C_{ste}$ (for n_{ex} to n_a conversion)	0.98	4.78	0.64	0.16
Using fugacity as the independent variable instead of pressure					
10	Same as case 1	0.82	1.38	0.53	0.11
11	Same as case 2	2.32	5.67	1.00	0.13
12	Same as case 7	4.22	7.89	1.86	0.26

[a] Unless otherwise specified, the parameters are treated the same way as in case 1 (i.e. P_0 and $n_{\max}$ are fitted parameters, $m=2$, $\varepsilon=\alpha+\beta T$)

[b] Only the 77 K and 298 K isotherms are fitted but the standard error of estimate is calculated using the whole range of experimental data

[c] Myers and Monson (2002)

wide temperatures are easily accessible and it is not necessarily so for the temperatures in between.

Comparison of cases 1 and 2 shows that taking into account enthalpic and entropic contributions for the characteristic free energy of adsorption ($\varepsilon=\alpha+\beta T$) provides a significantly better fit for hydrogen and nitrogen than when it is considered temperature independent. This is particularly true when it is determined from only two isotherms. This can also be seen by comparing 3 with 4 or 6 with 7. However, for methane, the temperature invariance assumption is acceptable. This is probably due to the narrower temperature range of the experimental data. Setting $m=2$, as originally recommended for most adsorbents, is found to be sufficient. The exponent m does not provide significantly more precision when it is taken as a regression parameter and even hinders the fit when only two hydrogen isotherms are used. Comparison of case 1 and 5 proves that when the limiting adsorption $n_{\max}$ is taken as a fitting parameter provides a significantly better fit for hydrogen than when the density at the limiting adsorption is approximated with the density of the boiling liquid. As shown in cases 6 and 7, treating P_0 as a fitted parameter produces also a better fit and is a simpler approximation than the pseudo-saturation pressure correlation presented in (7) with the same number of parameters. The cases 10, 11 and 12 clearly show that for the data range tested there is no noticeable difference in the fit when fugacity is used as the dependant variable. Not surprisingly, the modified D-A model is shown to offers better precision than the Langmuir model (with 3 fitting parameters and V_a). Finally, in case 9, the excess adsorption is converted into absolute adsorption using the constant adsorbed phase density assumption (with the same parameters of case 1). This assumption does not allow modelling with only two isotherms. We conclude that case 1 provides the best model for adsorption on activated carbon over a large pressure and temperature ranges above the critical point. Its capacity to model hydrogen adsorption with only the 77 K and 298 K isotherms without affecting significantly the quality of the fit makes it even more interesting. Therefore, the absolute adsorption can be calculated using:

$$n_{ex}=n_{\max}\exp\left[-\left[\frac{RT}{\alpha+\beta T}\right]^2\ln^2\left(\frac{P_0}{P}\right)\right]-\rho_g V_a. \qquad (13)$$

The parameters resulting from fitting (13) to the experimental data are listed in Table 3 and the resulting fits are shown in Fig. 1.[2] The model fits the experimental data for hydrogen, nitrogen and methane over the whole measured temperature and pressure range with a σ_{est} of 0.79 mol/kg, of 0.58 mol/kg, and of 0.11 mol/kg respectively. Since no abrupt transition is observed from the adsorption of vapor to the adsorption of supercritical gas, subcritical isotherms (30 K for hydrogen and 93 and 113 K for nitrogen) were also adequately fitted with the supercritical model.

The overall quality of the fit is very good given the large temperature and pressure ranges. For example, for data at a

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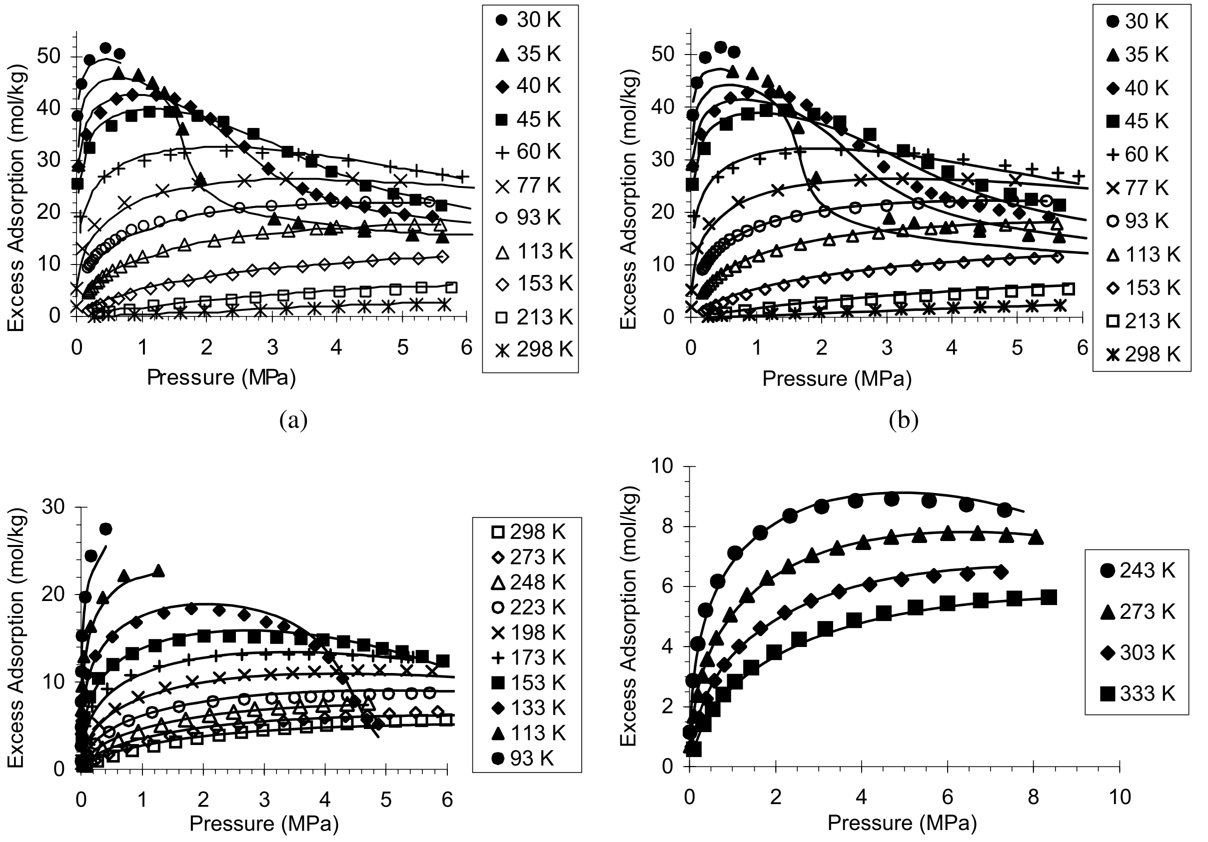
[2] In the case of methane, for the purpose of visual clarity, only isotherms at the extreme and at intermediate temperature are shown.

Table 3 Modified Dubinin-Astakhov model parameters and adsorption volume

Parameters	H_2	H_2[a]	N_2	CH_4
$n_{\max}$ (mol/kg)	71.6	65.4	63.7	25.4
P_0 (MPa)	1470	1090	11320	1850
α (J/mol)	3080	3310	6160	11850
β (J/mol K)	18.9	16.8	24.9	7.05
V_a (m^3/kg)	0.00143	0.00138	0.00183	0.00085

[a] Only the 77 K and 298 K isotherms are fitted but the standard error of estimate is calculated using the whole range of experimental data



(a) (b)

(c) (d)

Fig. 1 Modified D-A model fit (*solid lines*) to experimental excess adsorption isotherms of gases on activated carbon: hydrogen/AX-21™ (Bénard and Chahine 2001) (see footnote 1) (**a**), hydrogen/AX-21™ fit with only the 77 K and 298 K isotherms (**b**), nitrogen/C034 (Czerny et al. 2005) (**c**) and methane/CNS-201™ (Bénard and Chahine 1997) (**d**)

pressure higher than 0.1 MPa, the average relative deviation of the fit to hydrogen adsorption data is 2.2% at 77 K and 8.8% at 153 K. For nitrogen, the average relative deviation is 3.0% at 153 K and 9.8% at 298 K. For methane, the average relative deviation is 2.3% at 243 K and 1.9% at 303 K. Subtracting the adsorption volume from the void volume of the adsorbents, the compression volumes V_g are found to be $7 \times 10^{-4}\ m^3/kg$, $15 \times 10^{-4}\ m^3/kg$ and $9 \times 10^{-4}\ m^3/kg$ for nitrogen, hydrogen and methane respectively.

The characteristic energies calculated using (11) are qualitatively in good agreement with the constant characteristic energy published for hydrogen (Amankwah and Schwarz 1995; Poirier et al. 2006) and nitrogen (Dastgheib and Karanfil 2005) and methane (Himeno et al. 2005). In the case of methane, the small magnitude of the parameter β supports the assumption of invariance of ε in temperature in the data range studied. The density of the adsorbed gas at the limit of complete filling of the adsorbent is calculated by dividing $n_{\max}$ with V_a. The limiting densities of the adsorbed hydrogen, nitrogen and methane are 50.2 mol/L, 34.8 mol/L and 30.0 mol/L respectively, somewhat larger than their normal liquid density (35.1 mol/L, 28.8 mol/L and 26.3 mol/L respectively). It is closer to the density of the solid form (43.7 mol/L, 36.6 mol/L and 28.1 mol/L respectively). These values are not completely surprising considering that the limiting adsorption corresponds to a point where the adsorbed phase density is at its maximum and becomes incompressible. The fact that $n_{\max}$ is temperature independent is equivalent to assuming that at this point, the adsorbed phase thermal expansion factor is negligible. The empirical value of P_0 is two orders of magnitude higher, when fitted as in case 1, than when calculated using the empirical (7), as in case 6 and 7 (Amankwah and Schwarz 1995). Although the very high values of P_0 may seem at first to be "unphysical", they are coherent with the high adsorbed phase density limit. We may draw a parallel between the adsorbate and gas in the supercritical region that would have to be compressed at several hundreds MPa in order to reach liquid or solid density. One should keep in mind the empirical nature of the model. These parameters were fixed while trying to keep the model simple and to fit well adsorption data. We cannot discard the possibility that they do not all have a clear physical significance.

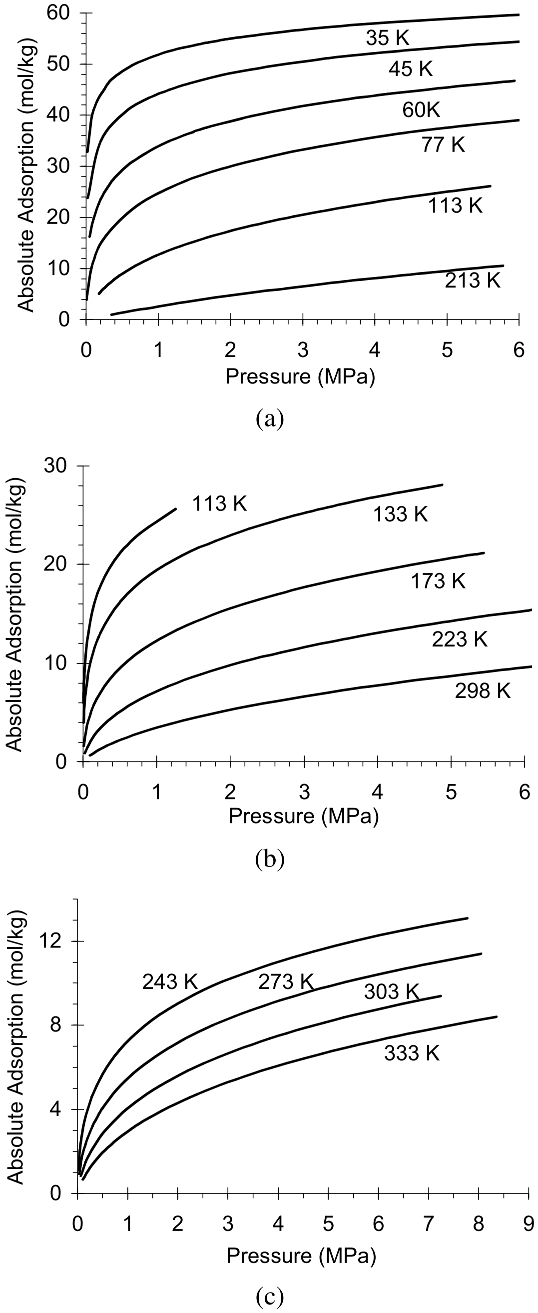
The absolute nitrogen, hydrogen and methane adsorption isotherms calculated from the modified D-A model (cf., first term on the right-hand side of (13)) are shown in Fig. 2. The isotherms obtained are type I isotherms, and absolute adsorption is a single-valued function of pressure as expected.

4 Summary and conclusions

In this paper, the Dubinin-Astakhov (D-A) micropore volume-filling adsorption model is adapted to model nitrogen, hydrogen and methane adsorption on activated carbon over large pressure and temperature ranges in the supercritical region. The model is developed while keeping in mind the two following objectives:

1. The model has to fit the experimental data accurately over the whole temperature and pressure ranges.
2. It has to be simple enough to allow analytical derivation of the adsorbed phase terms in adsorption based system simulations.

The use of excess adsorption becomes problematic at high pressure and low temperature where a maximum in the isotherms is prevalent. Hence, the experimental excess adsorption is converted to absolute adsorption by defining a constant adsorption volume. This adsorption volume (V_a) is obtained as a parameter during the adsorption model parameterization. Well known empirical expressions and assumptions to adapt the D-A model parameter for the supercritical region are compared. A simple treatment of the parameters is found to procure the best fit. Hence, the D-A model is adapted by using fitting parameters for the saturation pressure (P_0) and the limiting adsorption ($n_{\max}$). The distribution parameter (m) was set equal to 2. The assumption of temperature independence of the characteristic free energy (ε) is not verified for the large temperature range studied with hydrogen and nitrogen sets; however, the addition of an entropic factor ($\varepsilon = \alpha + \beta T$) is found to procure good results.



(a)

(b)

(c)

Fig. 2 Absolute adsorption isotherms from the modified Dubinin-Astakhov model of hydrogen/AX-21™ (**a**), nitrogen/C034 (**b**), and methane/CNS-201™ (**c**)

The five parameters ($P_0, n_{\max}, \alpha, \beta$ and V_a) of the resulting model are obtained by a simultaneous regression fit to all the experimental adsorption isotherm of an adsorbate/adsorbent pair. The parameterization is presented for the experimental data of hydrogen adsorption on the activated carbon AX-21™ (30 to 293 K, 0–6 MPa) (Bénard and Chahine 2001) (see footnote 1), of nitrogen adsorption on the activated carbon C034 (93 to 298 K, 0–6 MPa) (Czerny et al. 2005) and of methane on activated carbon CNS-201™ (243 K to 333 K, up to 9 MPa) (Bénard and Chahine 1997). The modified D-A adsorption model is shown to fit the experimental data over the whole experimental data range with a very good overall quality, given the large temperature and pressure ranges. The model specific excess adsorption standard error of estimate is 0.79 mol/kg, 0.58 mol/kg and 0.11 mol/kg for hydrogen, nitrogen and methane, respectively. The quality of the fit with hydrogen adsorption is not significantly affected (standard error of estimate of 1.19 mol/kg) when the parameters are fitted using only the 77 K and 298 K hydrogen adsorption isotherms. This property is of high practical interest for engineering applications. It is not only less time consuming with lesser required experimental data but also the measuring systems at these two wide temperatures are easily accessible and it is not necessarily so for the temperatures in between.

The density of the adsorbed gas at the limit when complete filling of the adsorbent is achieved is somewhat larger than their normal liquid density and P_0 is of the order of several hundreds of MPa. This could be understood in the context of supercritical adsorption with a limiting adsorption that would correspond to a point where the adsorbed phase is incompressible and where its density is at its maximum. With constant parameters and adsorption volume, the modified Dubinin-Astakhov model can be easily derived with respect to temperature and pressure, a requirement for its use in the simulations of adsorption based systems. This is the subject of the companion paper (Richard et al. 2009).

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Nomenclature

A	Differential molar work of adsorption (D-A model) (J/mol)
$-\Delta\bar{h}_a$	Isosteric heat of adsorption (J/mol)
k	Fit parameter (pseudo-pressure empirical equation)
m	Distribution parameter (D-A model), generally close to a small integer, equal to 2 for most activated carbons
n_a	Absolute adsorption (per unit mass of adsorbent) (mol/kg)
n_{ex}	Excess adsorption (per unit mass of adsorbent) (mol/kg)
$n_{\max}$	Limiting adsorption (per unit mass of adsorbent), corresponding to the maximum filling of the entire volume of adsorption space (D-A model) (mol/kg)
n_{tot}	Total amount of adsorbate introduced in the measuring system (mol)
P	Equilibrium pressure (Pa)
P_0	Saturation pressure of the vapour at temperature T or pseudo-saturation pressure (D-A model) (Pa)
R	Universal gas constant (8.314 J/mol K)
T	Equilibrium temperature (K)
V_a	Adsorption volume (per unit mass of adsorbent) (m^3/kg)
V_g	Volume of the bulk gas phase (per unit mass of adsorbent) (m^3/kg)
V_p	Pore volume of the adsorbent (micropores and mesopores) (m^3/kg)
V_v	Void volume of the adsorbent (including the pore volume of the adsorbent and the interstitial space) (m^3/kg)
$V_{v,sys}$	Total void volume of the adsorption system (including the pore volume of the adsorbent, the interstitial space, and any additional empty space) (m^3/kg)
α	Enthalpic contribution to the characteristic free energy of adsorption ($\varepsilon = \alpha + \beta T$; modified D-A model), (J/mol)
β	Entropic contribution to the characteristic free energy of adsorption ($\varepsilon = \alpha + \beta T$; modified D-A model), (J/mol K)
ε	Characteristic free energy of adsorption (D-A model) (J/mol)
θ	Degree of filling of the volume of the micropores (D-A model)
ρ_a	Average density of the adsorbed phase (mol/m^3)
ρ_g	Density of the bulk gas (mol/m^3)
σ_{est}	Standard errors of estimate (mol/kg)

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