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Utility Study of Conventional Adsorption Equations for Modeling Isotherms in a Wide Range of Temperature and Pressure

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ABSTRACT

The utility of the commonly applied isotherm equations in a wide range of temperatures and pressures was studied using the sorption data of supercritical hydrogen on activated carbon. The equilibrium condition covers 77–298 K and 0–7 MPa. The isotherm models tested include the Langmuir equation, the generalized Freundlich equation, the virial equation, and the Dubinin–Astakhov equation. The fitness is quantitatively expressed by standard deviations at each temperature and general deviation for the whole range. Discussions and inferences are presented on the applicability of the equations and on the state of the adsorbate at supercritical temperatures.

Key Words. Supercritical adsorption; Isotherm modeling; Hydrogen adsorption; Adsorption equation

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INTRODUCTION

Studies on the adsorption of hydrogen on activated carbon have been promoted by its potential application in the large-scale storage of hydrogen (1, 2). Studies on hydrogen adsorption at storage temperatures have been published during the last 10 years (3–5). The authors recently completed a systematic measurement of the adsorption/desorption isotherms over a wide range of temperature (6). Such a set of data is required for an inquiry into the nature of supercritical adsorption and for engineering a project of hydrogen purification by a PSA process. Conventional adsorption equations have been used in the past to model supercritical adsorption isotherms with only minor modifications or assumptions (5, 7, 8). However, the difference in the nature of adsorbates below and above the critical temperature calls for a different theory of supercritical adsorption. Observations of adsorption behavior over a wide temperature range may help to reveal the intrinsic features of this group of adsorptions. Modeling the adsorption behavior in a wide temperature range is also applicable to engineering projects; for example, adsorption storage of hydrogen or a PSA process for the separation/purification of hydrogen.

Adsorption equations applied for type-I isotherms were tested for feasibility in a wide range of temperatures. The equations studied include Langmuir and its modified equations, the virial equation, and the Dubinin–Astakhov equation. There are different points of view (9–11) on how to model isotherms; however, the above equations are the ones most commonly referred to. Researchers can usually acquire some information about the adsorbent structure by using fitting isotherms. Application of these equations to supercritical adsorptions were reported previously. However, the temperature range covered was quite limited, for example, only about 20 K (5, 12). Therefore, the properties of the model parameters, especially those of temperature independence, might not be fully explored.

An abnormal behavior of some of the model parameters was actually observed in the 200 K range. For example, parameter n_0, the saturated amount adsorbed included in some equations, varies with temperature. However, it is not supposed to behave like that since it is related to micropore volume. An extrapolation strategy was used to determine the upper limit of adsorption (13). Applying this strategy for the absolute adsorption, we determined the upper limit of adsorbate density in micropores. By comparing this limit value with the density of liquid hydrogen, we can make a judgment on the physical state of adsorbate under supercritical conditions.

EXPERIMENTAL

About 20 g of activated carbon AX-21 was used as the adsorbent in our study. AX-21 is commercially available and is frequently referred to in the

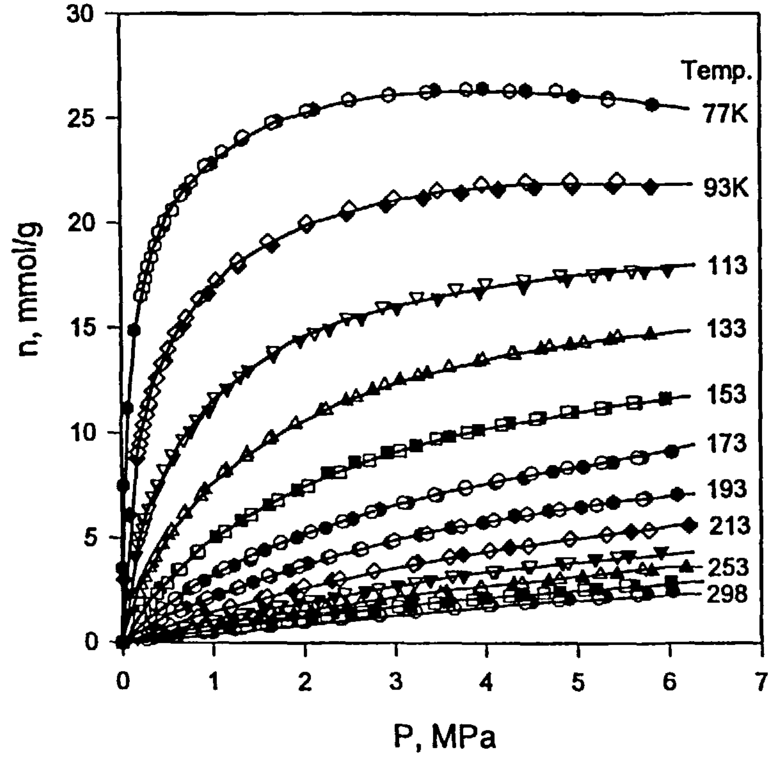

FIG. 1 The experimental sorption isotherms of H_2 on activated carbon AX-21. Filled symbols: Adsorption. Open symbols: Desorption.

literature. It possesses 3000 m^2/g of specific surface area and 1.5 mL/g of pore volume as determined by N_2 and CO_2 adsorption. Hydrogen of ultrahigh purity (99.999%) was used as the adsorptive. A standard volumetric method was used to measure the amount adsorbed and desorbed in the 0 to 7 MPa pressure range. Helium was used to measure the free volume in the adsorption space before the adsorption experiment. The equilibrium temperature was selected from the 77–298 K range with 20 K increments. The readers are referred to Ref. 6 for more details of the experimental procedure. The measured adsorption and desorption isotherms are shown in Fig. 1.

ISOTHERM MODELING

Modeling isotherms is a useful tool in adsorption studies. Pertinent models, especially those with physical backgrounds, can often provide useful information about a adsorptive/adsorbent system (14). Isotherms of pure substances provide a basis for studying the adsorption behavior of gas mixtures. They are usually incorporated into an engineering software package for such separation processes as PSA.

The experimental isotherms shown in Fig. 1 possess the typical features of Type I (21). The most commonly applied equations for Type-I isotherms include Langmuir and its derived equations, the virial equation, and the Dubinin–Astakhov equation. However, the feasibility of these equations for supercritical adsorption, especially in a wide range of temperatures, has never been proved. Therefore, the hydrogen adsorption data over 200 K were fitted to these equations in this work. All the parameters in the equations were determined by a commercially available nonlinear regression program.

The Langmuir equation was derived theoretically for a transitional range of adsorption from dilute to a largely covered surface; however, it can describe most Type-I isotherms satisfactorily. Therefore, this equation was extensively applied to interpret the experimental data. It contains only two parameters and, hence, is very convenient to use. The Langmuir equation is frequently written as

$$n = n_0\left(\frac{bP}{1 + bP}\right) \tag{1}$$

where n is the amount adsorbed, mmol/g; P is the equilibrium pressure, MPa; and b and n_0 are parameters of the equation. Apparently, $n = n_0$ when $P \rightarrow \infty$; therefore, n_0 is the saturated amount adsorbed, mmol/g.

The Langmuir model of experimental data in the whole range of temperatures is presented by correlations of the parameters with respect to temperature:

$$b = \exp\left(-5.4951 + \frac{862.94}{T} - \frac{22245.2}{T^2}\right) \qquad (r^2 = 0.9993) \tag{2}$$

and

$$n_0 = 1.6841 + \frac{2367.9}{T} - \frac{34121}{T^2} \qquad (r^2 = 0.9973) \tag{3}$$

where r^2 is the correlation coefficient of the equation.

In some cases one more parameter was included in the expression of the isotherm in order to improve the precision of the Langmuir equation. For example, the generalized Freundlich equation (Eq. 4) considerably enlarged the feasibility scope for a given set of data, as is shown later in Fig. 2:

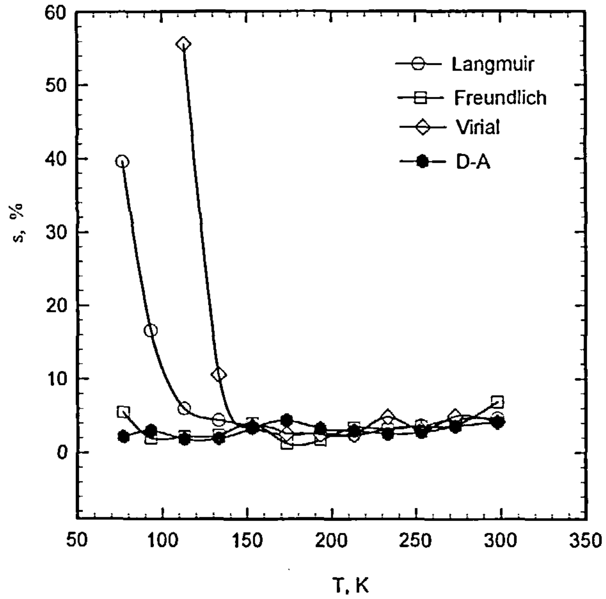

FIG. 2 A comparison of the fitness of the models.

$$n = n_0\left(\frac{bP}{1 + bP}\right)^m \tag{4}$$

The generalized Freundlich model for the present set of sorption data consists of three correlations:

$$n_0 = 0.7132 + \frac{2657.9}{T} - \frac{44720.3}{T^2} \quad (r^2 = 0.9911) \tag{5}$$

$$m = 1.070 + \frac{2.3054}{T} - \frac{4238.9}{T^2} \quad (r^2 = 0.9490) \tag{6}$$

$$b = \exp\left(-5.4062 + \frac{889.01}{T} - \frac{33321}{T^2}\right) \quad (r^2 = 0.9849) \tag{7}$$

The virial equation is an important model for Type-I isotherms since some coefficients of the model have definite physical meaning (15). Jagiello and coworkers used a 3-dimensional virial equation (Eq. 8) to model the adsorption data of H_2 on activated carbon (5):

$$\ln P = (c_0 + c_1 n + c_2 n^2 + c_3 n^3)/T + \ln n \qquad (8)$$

All the coefficients were found temperature independent in the 78–92 K range and, hence, can be conveniently utilized to calculate the isosteric heat of adsorption. However, it was discovered in our preliminary regression study that the fourth term was redundant. Therefore, the 2-dimensional virial equation was used in the present work. The virial model of the sorption data obtained by nonlinear regression analysis is

$$c_0 = 2406 - 53.09T + 0.3658T^2 - 1.0434E - 3T^3 + 1.1074E - 6T^4 \quad (r^2 = 0.9961) \qquad (9)$$

$$c_1 = 57.84 - \frac{8842.3}{T} \quad (r^2 = 0.9335) \qquad (10)$$

$$c_2 = 2.3504 - 3.6302e - 3T - 6.1086E - 5T^2 + 2.6548E - 7T^3 \quad (r^2 = 0.8960) \qquad (11)$$

The Dubinin–Astakhov equation (16) is commonly regarded as the best model for adsorption isotherms of vapors and gases on microporous adsorbents. AX-21 is highly microporous, and hence the D–A equation should be a better fit for our sorption isotherms. One of the expressions of the D–A equation is

$$n = n_0 \exp\left[-\left(\frac{A}{E}\right)^q\right] \qquad (12)$$

where A is the adsorption potential and is expressed as

$$A = RT \ln \frac{P_s}{P} \qquad (13)$$

where P_s is the saturated pressure of the adsorbate. Actually, Eq. (13) was suggested by Polanyi (23) for temperatures in the neighborhood of the boiling point of the adsorbate. He also used the density of the liquid adsorbate to correlate the adsorbed amount with the molar volume of the gas. The isotherms at other temperatures could then be predicted. We did not make predictions based on Polanyi's strategy since the equilibrium temperatures in the present measurement were too far above the boiling point of hydrogen. Polanyi's idea is further developed in the D–A equation which becomes more generous by introducing parameter E, the characteristic energy of adsorption. However, the saturated pressure P_s is not definitely related to the boiling point but is expressed by different empirical correlations (16, 17). Recently Amankwah and Schwarz (12) suggested a new correlation and claimed a better fitting for their sorption data. Their correlation introduced one more

TABLE 1
The Dubinin–Astakhov Model of the H_2 Sorption Data

	T (K)			
Parameters	298–233		213–77	
q	1.5		2	
n_0	$2.578 + 2315.4/T$,	$r^2 = 0.991$	$-4.288 + 3407/T - 79982/T^2$,	$r^2 = 0.998$
E	$6254.6 - 25.884T + 0.079T^2$,	$r^2 = 0.999$	$3028.5 - 2.1463T + 0.0576T^2$,	$r^2 = 0.999$

parameter in the D–A equation because the exponent k in the expression of P_s needs to be determined by regression:

$$P_s = P_c\left(\frac{T}{T_c}\right)^k \tag{14}$$

However, we found that the fourth parameter seems to be redundant for our experimental data, just like that observed in fitting the data to the 3-dimensional virial equation. The nonlinear regression process was very sensitive to the initial values assumed if four parameters were determined. A consistent model for the whole set of data was not obtained, although two out of the four parameters showed a reasonable function of temperature. Therefore, we only included three parameters in the D–A model. Compared to q, which is related to the pore sizes of the adsorbent (18), the physical meaning of parameter k in Eq. (14) has not been clarified. Therefore we set $k = 2$, as was done previously (6). The D–A model yielded the values listed in Table 1.

FEASIBILITY OF THE MODELS IN A WIDE RANGE OF TEMPERATURES

The feasibility of a model was evaluated according to the standard deviation (Eq. 15) in the whole range of temperatures (19):

$$s = \sqrt{\sum_{i=1}^{v} s_i^2/(v - f)} \tag{15}$$

where s_i is the difference between the ith measurement and that predicted by the model, v is the number of measurements at a given temperature, and f is the number of parameters in the equation. The standard deviations of all the models tested are listed in Table 2. The general deviation of a model is the arithmetic mean of all the standard deviations at each temperature.

It is seen from the table that the Langmuir equation gives a good fit to the sorption data before the temperature decreases to 113 K. However, the stan-

TABLE 2
The Standard Deviation of the Models

Mean error of the fitting, % at temperature (K)	Models			
	Langmuir	Freundlich	Virial	Dubinin–Astakhov
298	4.7	6.9	4.2	4.2
273	4.6	3.8	5.0	3.6
253	3.7	3.6	3.1	2.8
233	3.3	3.2	4.9	2.6
213	2.4	3.4	2.5	3.0
193	2.7	1.8	2.5	3.3
173	2.4	1.3	2.6	4.4
153	3.4	4.0	3.6	3.4
133	4.4	2.4	10.6	2.0
113	6.0	2.2	55.6	1.9
93	16.6	2.0	656	3.0
77	39.6	5.5	21,350	2.2
General deviation, %	3.8[a]	3.3	3.6[b]	3.0

[a] The average in the 298–113 K range.
[b] The average in the 298–153 K range.

dard deviation goes up rapidly as the temperature is further decreased. A similar situation was also observed for the virial equation. It is not appropriate for isotherms of 133 K and lower temperatures. This observation shows there must be a transition in the adsorbate state around 133–113 K since the Langmuir equation is related to sparse occupation of the adsorbent surface.

Improvement was achieved by using the generalized Freundlich equation, especially for low temperatures. The standard deviation did not increase at low temperatures. The general standard deviation also decreased. However, the parameters of the Freundlich equation are totally empirical in nature. The improvement of fitting comes from the mathematical success of the equation. The Dubinin–Astakhov equation seems even better than the Freundlich equation as it has the least general standard deviation. Variations of model feasibility with temperature are clearly shown in Fig. 2.

ABNORMAL BEHAVIOR OBSERVED IN MODELING STUDIES

Compared to previous publications on adsorption, abnormal behavior was observed in the present study. First of all, parameter n_0, the saturated amount adsorbed in the Langmuir or the D–A equation, is no longer constant. As an example, the variation of n_0 in the D–A model with temperature is shown in Fig. 3. AX-21 is a highly microporous adsorbent and, hence, the volume-filling mechanism should prevail over the adsorption process. If the adsorbate is in the liquid state as Polanyi assumed (23), parameter n_0 is limited by the micropore volume of the adsorbent and almost independent of temperature. All observations below the critical temperature of the adsorptive showed this kind of behavior. However, if the adsorbate cannot be in the liquid state, as the above-critical equilibrium temperatures claimed, there will be no definite relation between parameter n_0 and the micropore volume. The considerable variation of the parameter with temperature is no longer irrational. This variation of n_0 with temperature cannot be observed if the equilibrium temperature covers too narrow a range, as is the case in Jagiello's study (5).

A similar abnormal behavior was also observed in parameter E of the Dubinin–Astakhov equation. As shown in Fig. 4, it also varies considerably with temperature. However, it is supposed to be independent of temperature

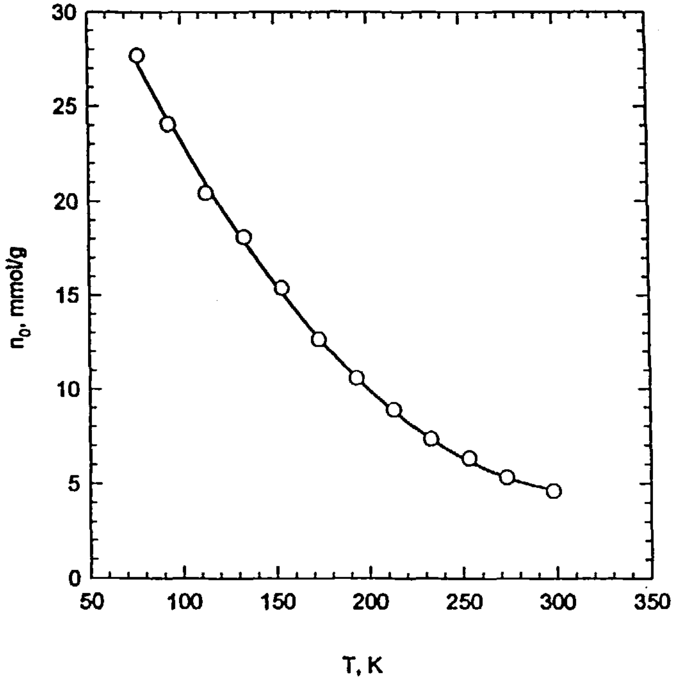

FIG. 3 Variation of parameter n_0 of the D–A model with temperature.

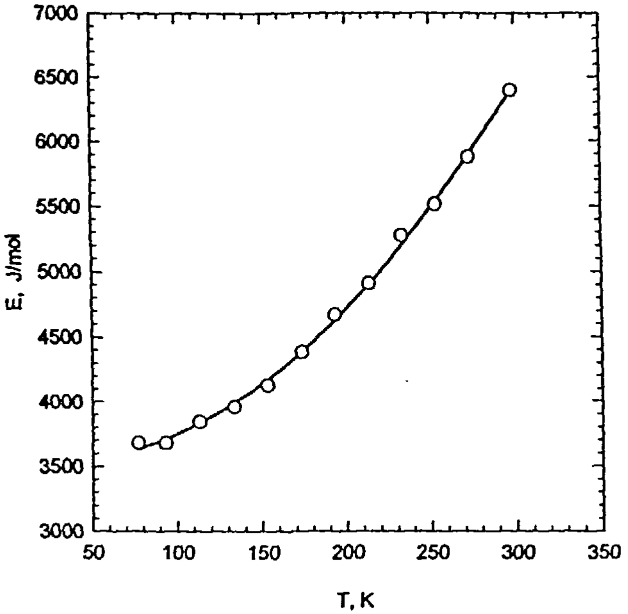

FIG. 4 Variation of parameter E of the D–A model with temperature.

according to a potential theory (23). The origin of the abnormal behavior of parameter E is actually the same as that of parameter n_0. Logically, one of the two parameters cannot be kept constant if the other varies considerably with temperature. Therefore, any parameters extracted from isotherm fitting can hardly reflect the real properties of an adsorbate in supercritical adsorption as in subcritical temperatures.

DETERMINATION OF THE POSSIBLE MAXIMUM ADSORPTION

Determination of the physical state of the adsorbate under supercritical conditions is of interest because it provides the starting point for developing thermodynamic relations. It was put forward in the previous section that an adsorbate might not be in the liquid state, which caused abnormal behavior of the parameters in the isotherm equations. The physical state of the adsorbate under supercritical condition has never been experimentally confirmed. Therefore, it was reasonable to assume a quasi-liquid or overheated state for the adsorbate in previous studies. The present paper is intended to estimate the upper limit of the adsorbate density. If the upper limit density is lower than the density of liquid, then the adsorbate must not be liquid.

The real density of the adsorbate is estimated on an absolute adsorption basis. The amount adsorbed as measured in our experiment is actually an excess value according to the definition of adsorption by Gibbs:

$$n = n_{\mathrm{abs}} - V_a\rho_g \tag{16}$$

where n is the measured amount adsorbed (mmol/g), n_{abs} is the so-called absolute adsorption (mmol/g), V_a is the volume of adsorbed phase (mL/g), and ρ_g is the density of bulk gas at the equilibrium temperature and pressure (mmol/mL). The highest value of V_a is apparently the same as the micropore volume of the adsorbent. Replacing V_a by the micropore volume of adsorbent V_p in Eq. (16) gives maximum values of the absolute adsorption corresponding to each of the measured adsorptions:

$$n_{\mathrm{abs}}^{\mathrm{H}} = n + \rho_g V_P \tag{17}$$

The micropore volume of activated carbon AX-21 was determined by N_2 and CO_2 adsorption and yielded a value of 1.5 mL/g. The gas phase density ρ_g in Eq. (17) is determined from the equilibrium state of hydrogen (20). Within the conditions of our experiment, the density of hydrogen can be calculated satisfactorily by the following correlation:

$$\ln \rho_g = a(T) + b(T) \ln P \tag{18}$$

The values of coefficients a and b are listed in Table 3 where ρ_g is in g/mL and P in kPa. Therefore, we can calculate the absolute adsorption from the

TABLE 3
The Coefficients of Eq. (19)

T (K)	a	b
298	−13.97	0.9905
273	−13.87	0.9891
253	−13.80	0.9899
233	−13.71	0.9893
213	−13.64	0.9906
193	−13.55	0.9921
173	−13.42	0.9891
153	−13.28	0.9877
133	−13.12	0.9848
113	−13.01	0.9928
93	−12.85	0.9990
77	−12.73	1.0112

measured adsorption data according to Eqs. (17) and (18). We can, of course, model absolute adsorption by a method similar to the one used above. However, the saturated absolute adsorption cannot be determined through the parameter of the model, as was explained in the previous section. To determine the upper limit of absolute adsorption, we transformed the Dubinin–Radushkevich equation (21) as follows:

$$\begin{aligned} n_{\mathrm{abs}}^{\mathrm{H}} &= n_{\mathrm{abs}_0}^{\mathrm{H}} \exp\left[-\left(\frac{RT}{E}\right)^2 \left(\ln\frac{P_s}{P}\right)^2\right] \\ \ln n_{\mathrm{abs}}^{\mathrm{H}} &= \ln n_{\mathrm{abs}_0}^{\mathrm{H}} - \left(\frac{R}{E}\right)^2 \left(\ln\frac{P_s}{P}\right)^2 T^2 \end{aligned} \tag{19}$$

It follows that the intercept of the $\ln n_{\mathrm{abs}}^{\mathrm{H}}$ vs T^2 plot will give an estimate for the upper limit of saturated absolute adsorption. $P = P_c = 1.297$ MPa and $P = 4$ MPa were selected for such estimates. Both pressures are representative because when $P = P_c$ the adsorption should be saturated, while $P = 4$ MPa is roughly the location of the maximum of the sorption isotherms. Two extrapolation curves are shown in Fig. 5. The intercepts are about 3.83 and 3.92 for $P = 1.293$ and 4 MPa, respectively. The corresponding upper limits

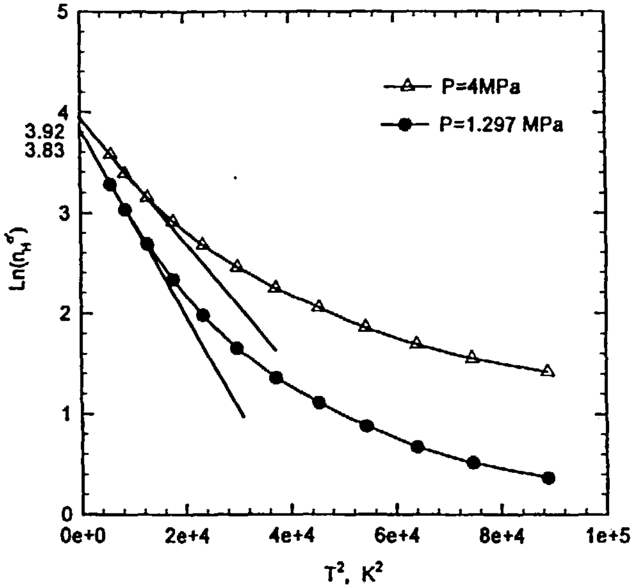

FIG. 5 The extrapolated upper limit of the saturated absolute adsorption.

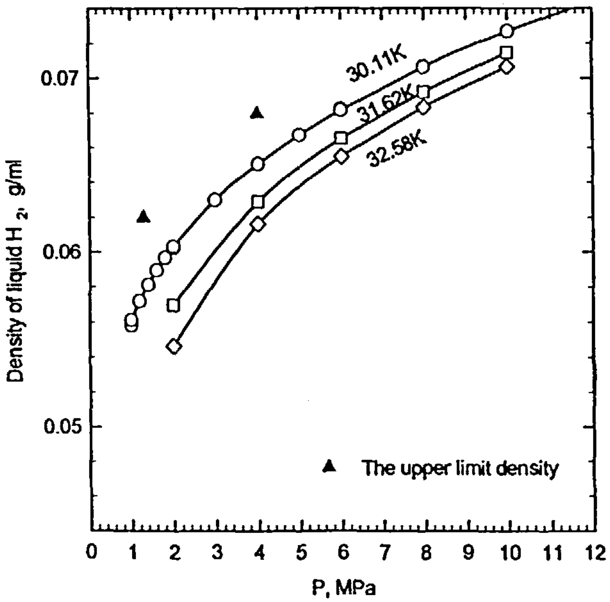

FIG. 6 The location of the upper limit density.

of saturated absolute adsorption are exp(3.83) = 46.1 and exp(3.92) = 50.4 mmol/g or 0.093 and 0.102 g/g. Since the micropore volume is about 1.5 mL/g, the possible maximum density of the adsorbate is 0.093/1.5 = 0.062 g/mL at 1.293 MPa and 0.102/1.5 = 0.068 g/mL at 4 MPa. These densities are compared with the density of liquid hydrogen in Fig. 6. The density of liquid hydrogen was obtained from the literature (20, 22). As is shown in the figure, the upper limit density of the adsorbate has almost reached the liquid state. However, the upper limit condition defined above for adsorbate corresponds to 0 K; therefore, the adsorbate only takes liquid as its limiting state, but it can never reach it at any real temperatures:

DISCUSSION AND CONCLUSIONS

1. The widely applied adsorption equations, including Langmuir, generalized Freundlich, virial, and D–A, were tested to describe the measured adsorption/desorption data of hydrogen in the 77–298 K and 0–7 MPa range. The fitness of each equation to the experimental isotherm was evaluated as standard deviations.

2. Langmuir and/or virial equations specifically relate to the adsorption mechanism. For example, the Langmuir equation relies on the state of an adsorbate which is sparsely distributed on the adsorbent surface. The fact that the Langmuir equation cannot describe isotherms below 113 K shows the transition of the adsorbate state at that temperature.
3. The generalized Freundlich equation and the Dubinin–Astakhov equation describe the isotherms satisfactorily throughout the whole range of the experiment. However, neither equation can provide physical information for the adsorption system. The Freundlich equation is empirical in nature, and the D–A equation shows abnormal behavior in its parameters.
4. The abnormal behavior of parameters in the D–A equation stems from the nonliquid state of the adsorbed phase. This is indirectly confirmed by an extrapolated value of limiting adsorption in supercritical temperatures.

ACKNOWLEDGMENT

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