J. Chem. Eng. Data **2004,** *49,* 73−76

Supercritical Methane Adsorption Equilibrium Data on Activated Carbon with Prediction by the Adsorption Potential Theory

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This work reports experimental adsorption data of supercritical methane on K02 microporous activated carbon. The adsorption isotherms were measured using a volumetric method in the experimental pressure range (0 to 12) MPa and the temperature range (273 to 333) K. Based on the Gibbs equation, the experimental data were changed into the absolute amount and analyzed by the adsorption potential model using the characteristic curve. The adsorption isotherm measured at 303 K was adopted to calculate methane adsorption equilibria over a wide range. A comparison of the predicted results is presented with different methods to estimate the adsorbate density and the quasi-saturated vapor pressure. The study demonstrates the most appropriate approach for predicting supercritical methane adsorption equilibrium data.

Introduction

Adsorption theories have been widely studied due to the recent expansion of adsorption technology into gas separation and purification processes.[1−4] The adsorption potential theory, introduced by Polanyi and later developed by Dubinin et al., has been successfully applied to vapor adsorption equilibrium on microporous adsorbents for nonpolar and weakly polar systems.[5−7] Based on the relationship between the adsorption potential and the adsorbate volume, the theory could transform adsorption isotherms at different temperatures into a single characteristic curve. Then the adsorption equilibria over a wide range of conditions could be readily predicted from one measured adsorption isotherm. This viewpoint has been substantiated by considerable vapor adsorption data on microporous adsorbents. Further development of the adsorption potential theory reveals that the temperature invariance of the characteristic curve remains if the adsorbate compressibility is taken into account, at least sufficiently far from the critical temperature.[8,9] Therefore, the adsorption potential theory provides a great convenience for engineering design and development. In the case of supercritical gas adsorption on microporous adsorbents, the adsorption potential theory is confronted with some difficulties, because the conception of the adsorbate being in the liquid state and the saturated vapor pressure are ambiguous under supercritical conditions. Several efforts have been made to expand the application of the adsorption potential theory to the supercritical range. Assumptions of the supercritical adsorbate state and the quasi-saturated vapor pressure have been put forward, and different empirical methods have been proposed to estimate the two parameters.[10] Unfortunately, no discussion has been provided on which approach is the most accurate to calculate the adsorbate state and the quasi-saturated vapor pressure for utilizing the adsorption potential theory to predict adsorption equilibria.[11]

The present work was undertaken to measure the supercritical methane adsorption data on activated carbon over a wide temperature and pressure range. In addition, the accurate prediction of the adsorption potential theory was explored under the supercritical conditions.

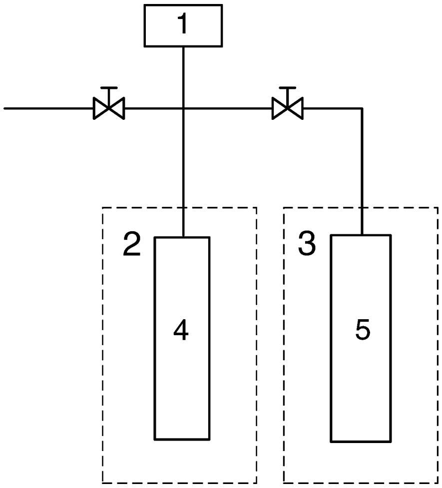

Figure 1. Principle of the volumetric method to measure gas adsorption equilibria: 1, pressure transducer; 2 and 3, thermostats; 4, storage vessel; 5, adsorption vessel.

Experimental Section

A volumetric method was used to measure the supercritical methane adsorption equilibrium data on a commercial activated carbon K02, as shown schematically in Figure 1. Both the storage vessel and the adsorption vessel were contained in thermostats. The temperature of the storage vessel was kept constant at (298 ± 0.1) K, and the temperature of the adsorption vessel was controlled at the required temperature to within ±0.1 K. The free volume of both vessels was (81 ± 0.07) cm^3, respectively. Connecting stainless steel pipes between the storage vessel and the adsorption vessel were designed to be as short as possible. The volume of the pipes connecting to the storage vessel and to the adsorption vessel was (0.34 ± 0.01) cm^3 and (0.38 ± 0.01) cm^3, respectively. In addition, the tubes,

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10.1021/je034074c CCC: $27.50

which were not thermostated, were controlled at a temperature approaching 298 K with fluctuations not exceeding ±0.3 K. The experimental temperature range was (273 to 333) K, and the equilibrium pressure was about (0 to 12) MPa. The pressure was measured using a transducer with precision of ±0.1%. The mean relative uncertainties of the experimental data were 1.2% over the whole range.

High-purity methane, helium, and carbon dioxide, better than 99.99%, were used without further purification. The K02 activated carbon was provided by Hainan Qiongchi Co. with a mean particle diameter equal to 0.9 mm. It was made of coconut shell with physical activation. The sample of the adsorbent was evacuated at 0.1 Pa and 413 K for more than 24 h before the adsorption measurements. The pore volume of K02 activated carbon was about 0.47 $cm^3 \cdot g^{-1}$, and the specific surface area was 960 $m^2 \cdot g^{-1}$ from CO_2 adsorption equilibrium data at 273 K. Based on the pressure change in the storage vessel and the adsorption vessel after adsorption, the amounts of the adsorbate could be calculated through mass balance. The density of the bulk methane was calculated by the BWRS equation.

Results and Discussion

Figure 2 presents the experimental adsorption isotherms of supercritical methane on K02 activated carbon. The adsorption equilibrium data are given in Tables 1 and 2. For pure gas adsorption equilibria on a microporous adsorbent, the adsorption potential theory is usually adopted, which is expressed by

$$\begin{aligned} v_a &= f(\epsilon) \\ &= f(RT\ln(f_s/f)) \end{aligned} \tag{1}$$

in which v_a is the adsorbate volume ($cm^3 \cdot kg^{-1}$), ϵ is the adsorption potential, T and f are the equilibrium temperature and fugacity, respectively, R is the universal gas constant, and f_s is the fugacity at saturation which can be approximated to the saturated vapor pressure p_s at low pressure under subcritical conditions. In addition, the experimental equilibrium data, defined as the excess adsorption amount n_{exc}, should be changed into the absolute adsorption amount n_{abs} through the Gibbs equation to make the theoretical analysis.[12] The Gibbs equation is given by

$$n_{exc} = n_{abs} - v_a\rho_g \tag{2}$$

in which ρ_g is the density of the bulk phase, and $n_{abs} = v_a\rho_a$. If the adsorbate density ρ_a (mol/cm^3) is considered as a constant at a fixed temperature T, eq 2 is usually transformed to

$$\begin{aligned} n_{exc} &= n_{abs} - v_a\rho_g = v_a\rho_a - v_a\rho_g \\ &= n_{abs}(1 - \rho_g/\rho_a) \end{aligned} \tag{3}$$

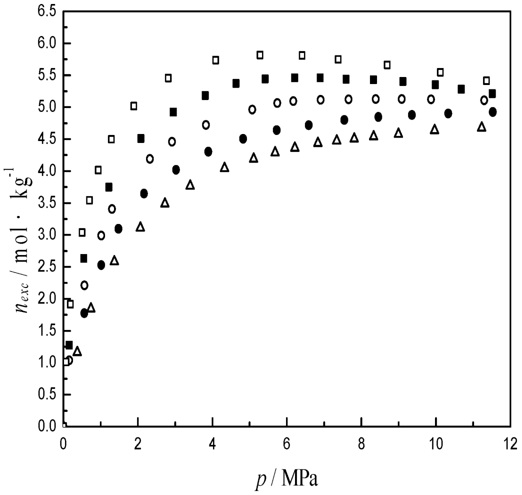

Figure 2. Equilibrium isotherms of methane adsorption on K02 activated carbon: □, 273 K; ■, 288 K; ○, 303 K; ●, 318 K; △, 333 K.

Table 1. Experimental Data of Methane Adsorption Equilibria on K02 Activated Carbon at 273 K, 288 K, and 303 K

T = 273 K		T = 288 K		T = 303 K	
p/MPa	n_{exc}/mol·kg^{-1}	p/MPa	n_{exc}/mol·kg^{-1}	p/MPa	n_{exc}/mol·kg^{-1}
0.19	1.916	0.54	2.632	0.57	2.209
0.51	3.037	1.22	3.746	1.02	2.991
0.70	3.543	2.08	4.508	1.31	3.404
0.94	4.016	2.95	4.924	2.32	4.189
1.29	4.496	3.81	5.179	2.92	4.459
1.89	5.015	4.64	5.371	3.83	4.721
2.81	5.454	5.42	5.439	5.07	4.963
4.09	5.735	6.21	5.461	5.75	5.063
5.28	5.818	6.89	5.459	6.17	5.094
6.41	5.810	7.59	5.437	6.91	5.113
7.38	5.748	8.33	5.427	7.66	5.122
8.70	5.660	9.12	5.401	8.38	5.126
10.12	5.543	9.99	5.350	9.08	5.126
11.36	5.414	10.68	5.279	9.87	5.121
		11.51	5.211	11.29	5.106

Table 2. Experimental Data of Methane Adsorption Equilibria on K02 Activated Carbon at 318 K and 333 K

T = 318 K		T = 333 K	
p/MPa	n_{exc}/mol·kg^{-1}	p/MPa	n_{exc}/mol·kg^{-1}
0.56	1.774	0.37	1.162
1.02	2.529	0.74	1.844
1.48	3.094	1.37	2.581
2.17	3.647	2.06	3.120
3.03	4.019	2.73	3.487
3.89	4.302	3.41	3.766
4.83	4.504	4.33	4.042
5.73	4.640	5.11	4.191
6.59	4.717	5.69	4.286
7.54	4.799	6.21	4.361
8.46	4.844	6.83	4.433
9.36	4.878	7.34	4.473
10.34	4.901	7.81	4.504
11.53	4.925	8.33	4.539
		9.00	4.578
		9.97	4.636
		11.23	4.677

Once the adsorbate density ρ_a and the saturated vapor pressure p_s have been determined, the relationship between v_a and ϵ can be established from the experimental data based on eqs 1−3. Assuming that the temperature-independent dispersive force is the dominant interaction between the adsorbate molecules and the surface atoms of the micropore, Dubinin suggested that the relationship between v_a and ϵ at different temperatures might be described by one characteristic curve.[13] This has been proved valid by subcritical experimental data. However, if the equilibrium temperature is higher than the critical temperature of the adsorptive, it is difficult to determine ρ_a and p_s directly from the adsorption experiments. There have been different approaches proposed to evaluate ρ_a and

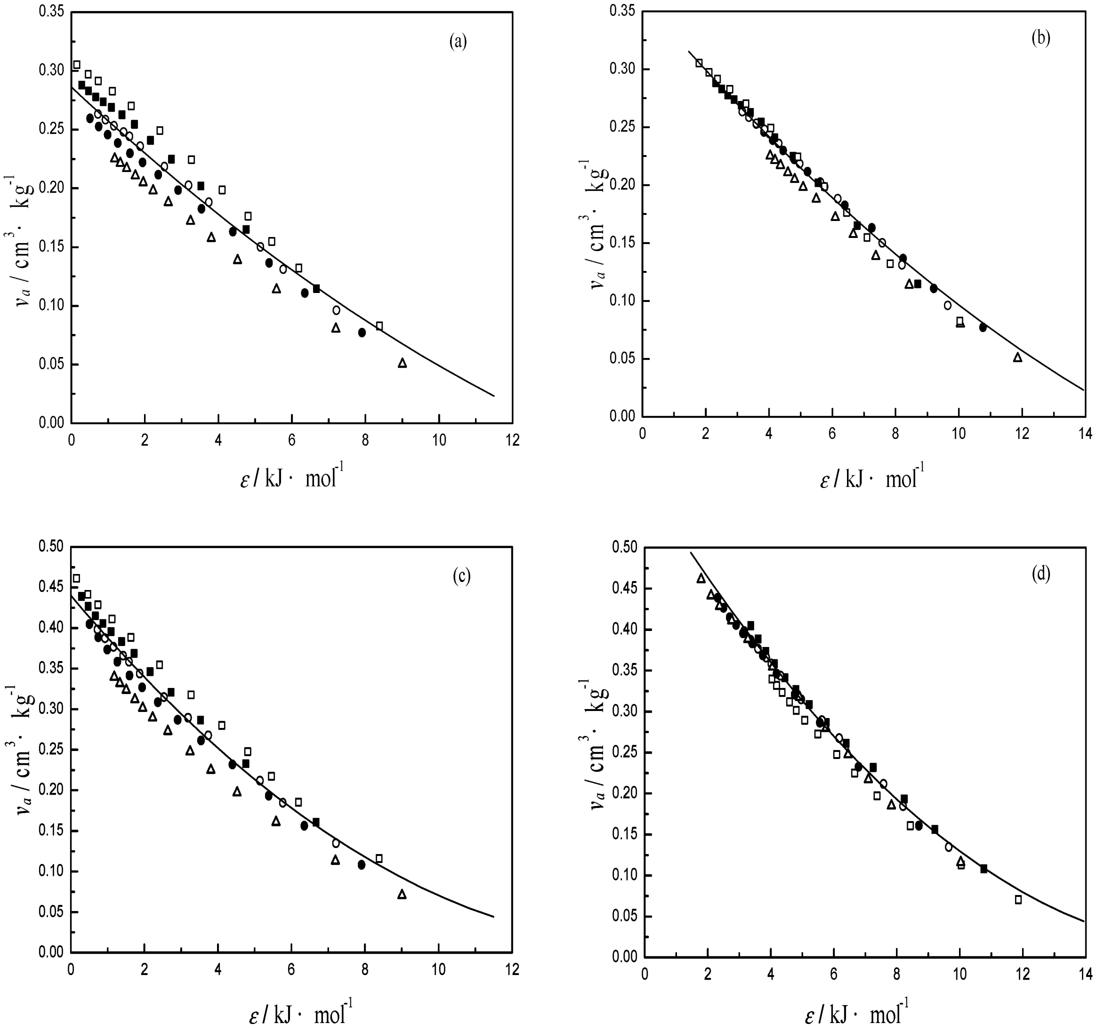

Figure 3. The character curves of methane adsorption on K02 activated carbon: □, 273 K; ■, 288 K; ○, 303 K; ●, 318 K; △, 333 K. (a) ρ_a and p_s calculated by method 1; (b) ρ_a and p_s calculated by method 2; (c) ρ_a and p_s calculated by method 3; (d) ρ_a and p_s calculated by method 4.

p_s, and the simple methods used in the previous literature are listed below:

For ρ_a:

$$\text{Dubinin:}^{13}\ \rho_a = 8p_c/(RT_c) \tag{4}$$

$$\text{Ozawa et al.:}^{14}\ \rho_a = \rho_b \exp(-0.0025(T - T_b)) \tag{5}$$

For p_s:

$$\text{Dubinin:}^{13}\ p_s = p_c(T/T_c)^2 \tag{6}$$

$$\text{Reich et al.:}^{15}\ p_s = p_c \exp[h(1 - T_c/T)] \tag{7}$$

where $h = T_b/T_c[\ln p_c/(1 - T_b/T_c)]$.

In the above equations, ρ_b and T_b are the liquid density and boiling temperature at ambient pressure, and p_c and T_c are the critical properties of methane.[16] Although all those methods have been applied respectively to some supercritical adsorption systems, little research has been made to evaluate the most suitable method to calculate ρ_a and p_s for supercritical gas adsorption equilibria. In this work, an attempt is made to determine the most suitable method to calculate ρ_a and p_s for predicting the supercritical methane adsorption equilibria on activated carbon. The estimating approaches for ρ_a and p_s are presented in Table 3. Combining eqs 1−7, relationships between the adsorption potential ϵ and the adsorbate volume v_a are illustrated in Figure 3a−d calculated from methods 1−4.

Table 3. Different Methods to Calculate the Adsorbate Density ρ_a and the Quasi-Saturated Vapor Pressure p_s

	method 1	method 2	method 3	method 4
ρ_a/mol·kg^{-1}	eq 4	eq 4	eq 5	eq 5
p_s/MPa	eq 6	eq 7	eq 6	eq 7

The relationships between ϵ and v_a at different temperatures in panels b and d of Figure 3 almost fall on the same adsorption potential plot. On the contrary, the calculated data exhibit relative divergence in panels a and c of Figure 3. We selected 303 K as the reference temperature and used the corresponding adsorption equilibrium data to predict the adsorption equilibria at other temperatures. The Dubinin−Astakhov (D−A) equation was adopted to correlate the adsorption isotherm at 303 K, which is given by

$$v_a = \frac{n_0}{\rho_a} \exp(-(\epsilon/E)^t) \tag{8}$$

where n_0 represents the adsorption capacity, E is the characteristic adsorption energy, and t is an exponent factor related to the adsorption energy distribution. The methane adsorption on K02 activated carbon at other temperatures could be predicted with the obtained rela-

Table 4. Parameters of Equation 8 by Fitting Methane Adsorption Equilibrium Data at 303 K and the Mean Relative Deviations of Prediction through Methods 1−4

	method 1	method 2	method 3	method 4
n_0/mol·kg^{-1}	6.422	7.093	7.258	8.888
E/kJ·mol^{-1}	7.138	9.006	6.625	7.862
t	1.3991	1.858	1.141	1.379
δ	0.0922	0.0433	0.0804	0.0385
δ^a	0.0918	0.0327	0.0934	0.0268
δ^b	0.1341	0.0821	0.1210	0.0703

[a] Methane adsorption equilibrium data of Payne et al. in the range of (283 to 323) K and (0 to 14) MPa with the reference temperature 303 K. [b] Methane adsorption equilibrium data of Zhou et al. in the range of (233 to 333) K and (0 to 10) MPa with the reference temperature 293 K.

tionship between ϵ and v_a. The prediction uncertainty was determined by the mean relative deviation δ:

$$\delta = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{n_{\text{exc,i}} - n_{\text{cal,i}}}{n_{\text{exc,i}}}\right)^2} \qquad (T = \text{const}) \qquad (9)$$

The predicted results are listed in Table 4. From Figure 3 and Table 4, it is shown that the most successful approach for ρ_a and p_s is method 4. The mean relative deviation δ of the predicted values is about 3.8%. In addition, there is little difference between the values of δ of method 1 and method 3. The values of δ of method 2 and method 4 are also similar. This indicates the prediction of the adsorption potential theory is not sensitive to the method of estimating the adsorbate density ρ_a if the calculation for p_s has been identified. Therefore, in this case the prediction uncertainties by the different approaches to calculate ρ_a are very approximate.

The predictions of method 2 and method 4 are better than those of method 1 and method 3. The mean relative deviations are about 4% and 9%, respectively. This demonstrates the method chosen for evaluating p_s has a great effect on the predicted results of the adsorption potential theory. The reasonable method to estimate p_s would considerably benefit the prediction of the adsorption potential theory. In this work, eq 7 is more advantageous than eq 6 in the prediction of supercritical methane adsorption equilibrium data.

Furthermore, the published data of supercritical methane adsorption on activated carbon have been analyzed by our proposed process.[17,18] The predicted results are listed in the last part of Table 4. It is observed that these presentations are in agreement with our conclusions. Under these supercritical conditions, the use of different methods for evaluating the quasi-saturated vapor pressure would make the prediction results differ greatly. Hence it is critical to determine how to calculate p_s in application of the adsorption potential theory.

Conclusions

Methane adsorption equilibrium data on K02 activated carbon were measured by a volumetric apparatus in the temperature range of 273 to 333 K and the pressure range up to 12 MPa. The adsorption potential theory was applied to predicting the supercritical methane adsorption equilibria. Approaches for calculating the adsorbate density and the quasi-saturated vapor pressure were investigated in detail. Method 4, using eq 5 and eq 7 to estimate ρ_a and p_s, respectively, is preferable in the range studied for predicting methane adsorption equilibria on activated carbon. The proper method to evaluate the quasi-saturated vapor pressure p_s leads to a satisfactory prediction of supercritical methane adsorption equilibria. The suggestion of Reich et al. to calculate p_s, shown by eq 7, appears more accurate in this work. However, the selection for estimating the adsorbate density ρ_a has little influence on the predicted results of the adsorption potential theory.

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Received for review April 18, 2003. Accepted November 5, 2003. This project is supported by the Shanghai Science and Technology Development Fund (No. 0116nm044).

JE034074C