

Studies on the Physical Adsorption Equilibria of Gases on Porous Solids over a Wide Temperature Range Spanning the Critical Region—Adsorption on Microporous Activated Carbon

ZHOU, Ya-Ping^a(周亚平) BAI, Shu-Pei^b(白书培) ZHOU, Li*^{·b}(周理) YANG, Bin^a(杨斌)

^a Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China

^b High Pressure Adsorption Laboratory, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

Adsorption equilibria of nitrogen and methane on microporous (<2 nm) activated carbon were measured for a wide temperature range (103—298 K) spanning the critical region. Information relating to Henry constants, the isosteric heat of adsorption, and the amount of limiting adsorption were evaluated. All isotherms show type-I features for both sub- and supercritical temperatures. A new isotherm equation and a consideration for the importance of the effect of the adsorbed phase volume allow this kind of isotherms to be modeled satisfactorily. The model parameter of the saturated amount of absolute adsorption (n^0) equals the limiting adsorption amount (n^{lm}), leaving the physical meaning of the latter clarified, and the exponent parameter (q) proves to be an appropriate index of surface heterogeneity.

Keywords Adsorption equilibrium, supercritical adsorption, absolute adsorption, isotherm modeling, limiting adsorption

Introduction

Activated carbon with microporous structures has been widely used for a variety of practical applications. It is a representative of a class of adsorbents with micropore structure and non-polar surface. Type-I isotherms are usually observed on such adsorbents, however, the adsorption mechanism might not be the same. Studies on the adsorption of methane or nitrogen on activated carbon have been reported,¹⁻⁷ but no intention has been made to compare the adsorption behavior in both sub- and super-

critical regions. This work presents the results of equilibrium measurements for the adsorption of nitrogen and methane on activated carbon over a wide temperature range spanning the critical region. Differences were identified between sub- and supercritical adsorptions through modeling isotherms, all of which belong to type-I.

Details of the experimental set-up were published previously,⁸ and the compressibility factors were calculated by the Lee-Kesler equation. The activated carbon was made from coconut shell by KOH activation. The adsorbent sample possesses 2800 m²/g specific surface area and 1.5 mL/g pore volume (pore size is less than 2.0 nm). Eleven adsorption isotherms were measured for N₂ in the range of 103.2—298.2 K (The critical temperature $T_c = 126.2$ K), and eight isotherms were measured for CH₄ in the range of 158.2—298.2 K ($T_c = 190.6$ K).

Adsorption isotherms

The adsorption isotherms obtained for nitrogen and methane are shown respectively in Fig. 1 and 2, where points show the experimentally measured excess adsorption (n), and curves show the predicted values by the model. All isotherms possess type-I features except the

* E-mail: zhouli@public.tpt.tj.cn

Received February 5, 2001; revised April 20, 2001; accepted May 8, 2001.

Project supported by the Special Funds of Major State Basic Research Projects (G 2000026404) and the National Natural Science Foundation of China (No. 29936100).

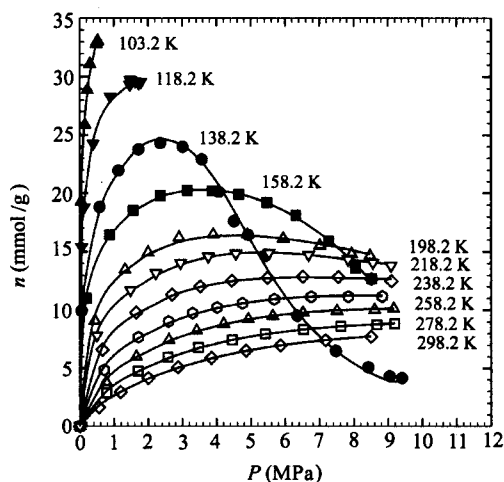


Fig. 1 Adsorption isotherms of N_2 on activated carbon.

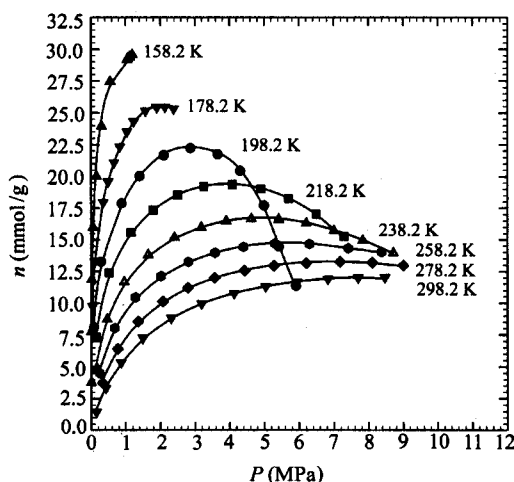


Fig. 2 Adsorption isotherms of CH_4 on activated carbon.

maximum and the negative increments shown at relatively low supercritical temperatures. The information of interest for the adsorption systems was obtained in interpreting these experimental isotherms.

Henry constants and isosteric heat of adsorption

Henry constant (K') is an important property of a gas/solid adsorption system even for thermodynamic analysis,⁹ and can be reliably evaluated by the intercept of the plot of $\ln(P/n)$ versus n ,¹⁰ where P is the equilibrium pressure. The logarithms of the evaluated Henry constants are shown against the reciprocal of temperature (T) forming the so-called van't Hoff plot as shown in Fig. 3 and 4 for N_2 and CH_4 respectively. The slope of

the linear plot is 1555 for nitrogen, and 1966 for methane. The isosteric heat of adsorption (ΔH) is thus evaluated:

$$\Delta H = -8.314 \times 1555/1000 = -12.9 \text{ kJ/mol (for } N_2)$$

$$\Delta H = -8.314 \times 1966/1000 = -16.3 \text{ kJ/mol (for } CH_4)$$

It is noticed that two points for the sub-critical temperatures are not on the straight line in Fig. 3, while perfect linearity is obtained in Fig. 4.

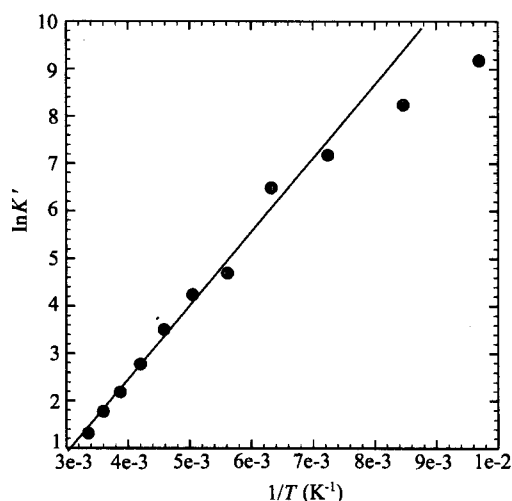


Fig. 3 van't Hoff plot of N_2 on activated carbon.

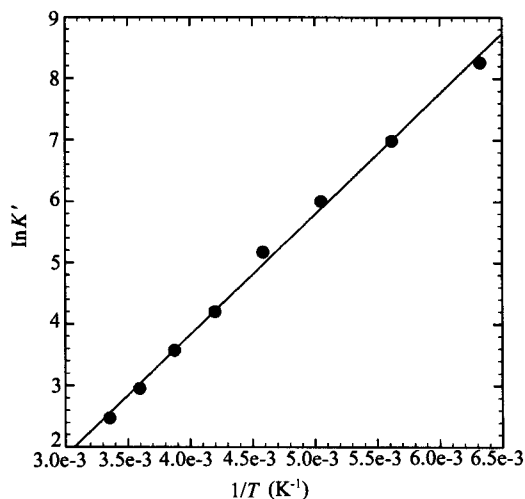


Fig. 4 van't Hoff plot of CH_4 on activated carbon.

Limiting adsorption and adsorbed phase volume

To our understanding, the reason for showing the

maximum and negative increments on supercritical adsorption isotherms originates in the effect of the adsorbed phase volume. Such kind of isotherms can be well modeled if this effect has been properly accounted for. To do so, the value of the so-called *absolute* adsorption (n_t) has to be determined properly. Zhou¹¹ proposed a method to evaluate n_t based on the Gibbs definition of adsorption:

$$n = V_a(\rho_a - \rho_g) = n_t - V_a\rho_g \quad (1)$$

where V_a is the adsorbed phase volume, ρ_a and ρ_g represent the density of the adsorbed phase and the bulk gas phase respectively. It is apparent that $n_t \cong n$ if either ρ_g is far less than ρ_a , as for the case of vapor adsorption, or V_a is not much different from zero, as for the case of supercritical adsorption under conditions of low pressure or high temperature. Therefore, the value of absolute adsorption (n_t) can be formulated using the excess adsorption data of the initial part of isotherms. The

isotherms are linearized in a plot of $\ln[\ln(n)] \sim 1/\ln P^{12}$ to render the formulation reliable. Such plots for the adsorption systems of $N_2/A.C.$ and $CH_4/A.C.$ (A.C.: activated carbon) are shown in Fig. 5 and 6 respectively. To avoid evaluating logarithms of negative numbers, pressure P is in unit of kPa, and n (in mmol/g) is enlarged ten fold. The limiting adsorption, defined by the intersection point of linear isotherms, is 29 mmol/g for both N_2 and CH_4 .

Fig. 5 and 6 depict that the isotherms of sub-critical temperatures or other lower temperatures might not intersect with those of higher temperatures, rather they may indicate a higher limiting adsorption. However, they can all be modeled by a linear equation:

$$\ln \ln(n_t) = \alpha + \frac{\beta}{\ln P} \quad (2)$$

$$\text{or} \quad n_t = \exp \left[\exp \left(\alpha + \frac{\beta}{\ln P} \right) \right] \quad (2-1)$$

where α and β are correlation parameters and are found to be functions of temperature, that is, for nitrogen:

$$\alpha = 2.68934 - 0.0162T + 1.05837 \times 10^{-4}T^2 - 2.61386 \times 10^{-7}T^3 + 2.89034 \times 10^{-10}T^4 \quad (2-2)$$

$$\beta = -1.49387 + 0.02545T - 1.9104 \times 10^{-4}T^2 + 9.22048 \times 10^{-8}T^3 - 2.01562 \times 10^{-10}T^4 \quad (2-3)$$

and for methane:

$$\alpha = 2.19805 - 5.44028 \times 10^{-3}T + 2.08908 \times 10^{-5}T^2 \quad (2-4)$$

$$\beta = -2.20203 + 0.036343T - 1.78031 \times 10^{-4}T^2 \quad (2-5)$$

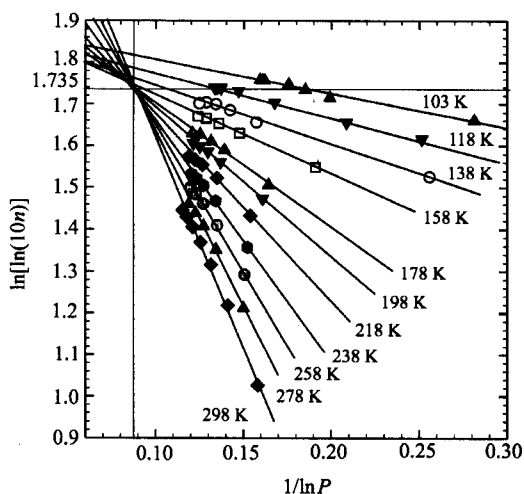


Fig. 5 Linear isotherms of N_2 on activated carbon.

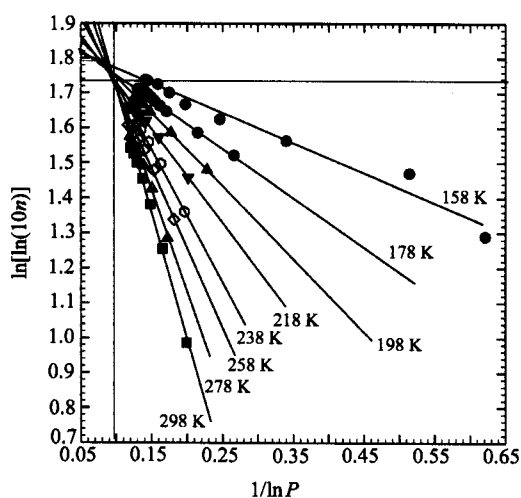


Fig. 6 Linear isotherms of CH_4 on activated carbon.

Since the value of n_t can be generated by Eq. (2), the volume of the adsorbed phase, V_a , can be evaluated:

$$V_a = \frac{(n_t - n)}{\rho_g} \quad (3)$$

The gas phase density, ρ_g , is calculated from P , T and z (compressibility factor) values, and correlated with P for the convenience of modeling:

$$\rho_g = \sum_{i=1} c_i P^i \quad (4)$$

where c_i is correlation coefficient. The calculated V_a values of the adsorbed N_2 and CH_4 are shown in Figs. 7 and 8 respectively. They can also be correlated with pressure for each temperature as the following:

$$V_a = \sum_{j=0} c_j P^j \quad (5)$$

where c_j is correlation coefficient. Instead of V_a , ρ_a can be evaluated also:

$$\rho_a = \frac{n_t}{(n_t - n)} \rho_g \quad (6)$$

Both V_a and ρ_a are not expected to be evaluated reliably at the sub-critical temperatures because the pressure is too low to have a significant difference ($n_t - n$).

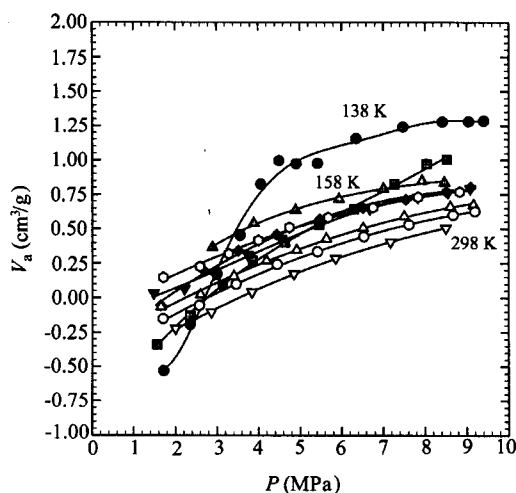


Fig. 7 Volume of the adsorbed N_2 for 138—298 K.

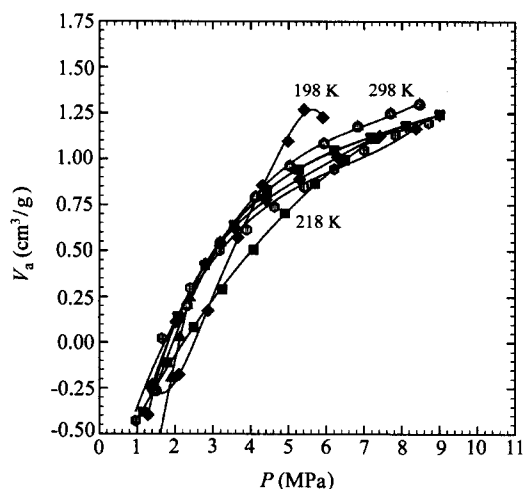


Fig. 8 Volume of the adsorbed CH_4 for 198—298 K.

Modeling the experimental isotherms for a wide temperature range

As mentioned above, the effect of adsorbed phase volume must be accounted for to explain the experimental measurements of adsorption at supercritical temperatures. The Gibbs definition of adsorption, Eq. (1) is, thus, taken as a framework of modeling. Zhou presented a simple isotherm equation for the adsorption of gases on porous solids.¹³ This equation is used to describe the absolute adsorption, n_t . Eq. (4) and (5) are substituted into Eq. (1) for ρ_g and V_a . Thus, the model for experimentally measured isotherms can be obtained:

$$n = n_t^0 [1 - \exp(-bp^q)] - \left(\sum_{i=1} c_i P^i \right) \cdot \left(\sum_{j=0} c_j P^j \right) \quad (7)$$

where n_t^0 is the saturated absolute adsorption parameter, b is a parameter related to the adsorption enthalpy change, and q is a parameter related to the surface heterogeneity. All parameters were evaluated using non-linear regression to fit the model to the experimental data. The isotherms predicted by the model are shown by curves in Fig. 1 and 2 for N_2 and CH_4 respectively. The average relative deviation of the model to experimental isotherms is less than 1%. The model parameters are shown as functions of temperature in Fig. 9—11.

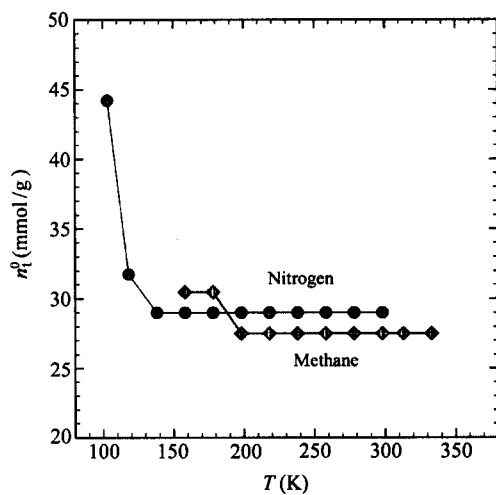


Fig. 9 Variation of parameter n_t^0 with temperature.

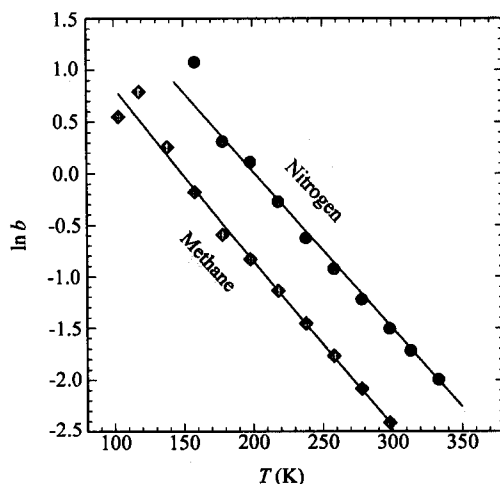


Fig. 10 Variation of parameter b with temperature.

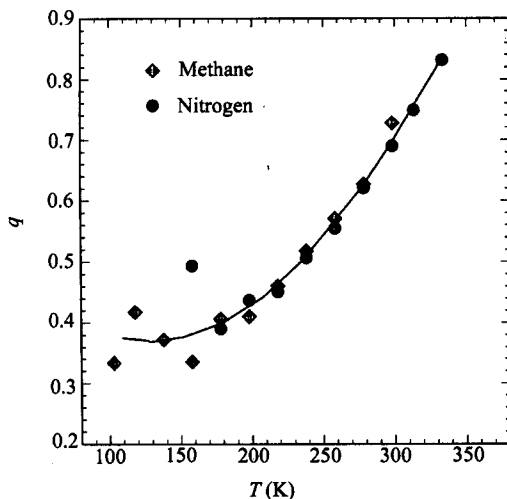


Fig. 11 Variation of parameter q with temperature.

The variations of parameter behavior show that the new isotherm equation is physically reasonable. Parameter n_t^0 , the saturated amount of absolute adsorption, is constant for the range of supercritical temperatures, but raises to a higher level as temperature moves toward the critical and sub-critical direction showing a change in the mechanism of adsorption. The constant values of n_t^0 are 29.0 and 27.5 mmol/g for N_2 and CH_4 respectively, which quite agree with n^{lim} , 29 mmol/g, as evaluated previously. It proves that the limiting adsorption, defined previously by the authors,¹² is really a limit of adsorption for the supercritical region. Parameter b relates to the enthalpy changes of adsorption, and decreases with the increasing temperature. The two semi-logarithmic plots are parallel showing clearly the difference in the enthalpy change of adsorption between N_2 and CH_4 . Parameter q is an index of the surface heterogeneity. It increases with the increasing temperature, but shows a minimum around the critical temperature. The heterogeneity of adsorbent surface is exposed to the adsorbate molecules to a different extent at different temperatures depending on the dynamic behavior of the adsorptive molecules. The special property of fluids in the critical zone rendered the largest heterogeneity of surface be discovered and yielded the minimum value of q . Moreover, q -values of N_2 and CH_4 are consistently forming a single curve showing the same heterogeneity property of adsorbent, which is certainly true because both sets of adsorption data were measured on the same activated carbon.

Conclusion

1. The adsorption of N_2 and CH_4 on activated carbon shows similar behavior of type-I isotherm for a wide range of temperatures including the critical region.

2. The amount of limiting adsorption, defined by the intersection of linear isotherms, is about 29 mmol/g for both N_2 and CH_4 on activated carbon. The isosteric heats of adsorption determined by the van't Hoff plot are -12.9 kJ/mol for nitrogen and -16.3 kJ/mol for methane.

3. All the isotherms can be satisfactorily modeled by the new isotherm equation while the effect of the adsorbed phase is properly accounted for. Parameter n_t^0 is equal to the limiting adsorption n^{lim} , which allows the physical meaning of the latter to be clarified for the first

time. The value of n_i^0 increases to a higher level approaching the critical or sub-critical temperatures in accordance with the change of adsorption mechanisms.

4. Parameter q has values only in the range of 0—1, and the adsorptive N_2 and CH_4 give the same value for the same adsorbent. Therefore, q is an appropriate index of surface heterogeneity.

References

- 1 Wakasugi, Y.; Ozawa, S.; Ogino, Y. *J. Colloid Interface Sci.* **1981**, *79*, 399.
- 2 Aukett, P. N.; Quirke, N.; Riddiford, S.; Tennison, S. R. *Carbon* **1992**, *30*, 913.
- 3 Jagiello, J.; Sanghani, P.; Bandosz, T. J.; Schwarz, J. A. *Carbon* **1992**, *30*, 507.
- 4 Kaneko, K.; Shimizu, K.; Suzuki, T. *J. Chem. Phys.* **1992**, *97*, 8705.
- 5 Malbrunot, P.; Vidal, D.; Vermesse, J.; Chahine, R.; Bose, T. K. *Langmuir* **1992**, *8*, 577.
- 6 Mahle, J. J. *Ind. Eng. Chem. Res.* **1994**, *33*, 346.
- 7 Jiang, S. H.; Zollweg, J. A.; Gubbins, K. E. *J. Phys. Chem.* **1994**, *98*, 5709.
- 8 Zhou, Y.; Zhou, L. *Sci. China (Ser. B)*. **1996**, *39*, 598.
- 9 Salem, M. M. K.; Braeuer, P.; Szombathely, M. V.; Heuchel, M.; Harting, P.; Quitzsch, K.; Jaroniec, M. *Langmuir* **1998**, *14*, 3376.
- 10 Zhou, Y.; Zhou, L. *Acta Phys.-Chim. Sin.* **1997**, *13*, 119 (in Chinese).
- 11 Zhou, L.; Zhou, Y. *Chin. J. Chem. Eng.* **2001**, *9*, 110.
- 12 Zhou, L.; Zhou, Y. *Chem. Eng. Sci.* **1998**, *53*, 2531.
- 13 Zhou, L.; Zhang, J.; Zhou, Y. *Langmuir* **2001**, in press.

(E0102051 SONG, J.P.; LING, J.)