

An Experimental Study on the Adsorption Behavior of Gases Crossing the Critical Temperature*

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Abstract Adsorption equilibria of CH₄ and N₂ on activated carbon and silica gel were measured for a wide temperature range covering the critical point: 158–298 K for CH₄, and 103–298 K for N₂. The determination of the compressibility factor is shown to have considerable effect on isotherm behavior at conditions after the isotherm maximum. A change in adsorption mechanisms on crossing the critical temperature was observed in all cases. The kind of adsorbents and how far the equilibrium temperature to the critical one are major factors affecting the transition of isotherms from sub- to supercritical. All continuous isotherms can be modeled by a unique model for the supercritical region. The satisfactory fitting of the model to the experimental isotherms proved the reliability of the absolute adsorption determined by the proposed method.

Keywords adsorption, supercritical, methane, nitrogen

1 INTRODUCTION

Physical adsorption of supercritical gases on porous solids has found many important applications in practice, for example, in the pressure swing adsorption processes and in the adsorptive storage of natural gas and hydrogen. Because supercritical gases cannot be liquefied under any conditions, the physical state of the adsorbed phase can no longer be regarded as a saturated liquid; therefore, supercritical adsorption must assume a different mechanism than that at subcritical temperatures. Understanding the adsorption mechanism is very important for developing theories to interpret the experimental data and to thermodynamically analyze the equilibrium of adsorption for the supercritical region.

Studies on the adsorption behavior in the critical zone (roughly within 10 K reach from the critical point) have received more interest recently and explanations have been presented from different points of view.^[1–4] However, the special property of fluids in the critical zone can be maintained only in a narrow range of temperature; therefore, any theories applied successfully for the critical zone may not be appropriate for the whole supercritical region. To observe the variation of adsorption phenomena on crossing the critical temperature, a series of adsorption measurements was carried out for nitrogen and methane on activated carbon and silica gel over a wide temperature range covering both the subcritical and supercritical regions. Principal observations and tentative conclusions are presented here.

2 EXPERIMENTAL

A volumetric set-up was used to measure the adsorption equilibrium, the details of which were presented previously^[5]. The temperature was kept constant within ± 0.1 K at higher temperatures, and $\pm (0.2–0.5)$ K at low temperatures. A pressure transmitter model PAA- 23/8465.1-200 manufactured by Keller Druckmesstechnik, Switzerland was used to measure the pressure. The deviation from linearity in the whole range of 20 MPa was less than 0.05%. The purity of N₂, CH₄ and He used in the experiments was higher than 99.99%. The activated carbon used as an adsorbent was made from coconut shell by KOH activation. The sample has 2800 m²·g⁻¹ of specific surface area and 1.5 ml·g⁻¹ of pore volume (pore size is less than 2.0 nm). The silica gel used was mesoporous with 335 m²·g⁻¹ surface area and 0.6 ml·g⁻¹ pore volume (average pore size of 8 nm). Four sets of adsorption isotherms were obtained in the temperature range of 158–298 K for methane and in 103–298 K for nitrogen.

3 RESULTS AND DISCUSSION

3.1 Significance of the compressibility factor for the determination of adsorption near and after the critical zone

The value of the compressibility factor considerably affects the results of adsorption calculations under conditions after the isotherm maximum, as shown in Fig. 1. The abscissa is the relative density of gas phase, and the ordinate is the excess amount of methane adsorbed on activated carbon (AC) at

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198.15 K. Each isotherm corresponds to a source of z -values: the published p - V - T data by IUPAC^[6] and the state equations of real gases including the 3rd virial equation, the Lee-Kesler equation and the Soave-Redlich-Kwong equation^[7]. Different sources of z -values give consistent results of adsorption before the maximum is reached, but divergence appears after the maximum. This might explain, at least partly, the different observations on the behavior of isotherms after the maximum in the literature. A linear section should follow the maximum in the n - ρ ^[8] system, but this is true only when Lee-Kesler equation is used. Proofs from a wider temperature range lead us also to the conclusion that the Lee-Kesler equation is the appropriate source of z -values for methane and nitrogen. However, another source might be better for different gases.

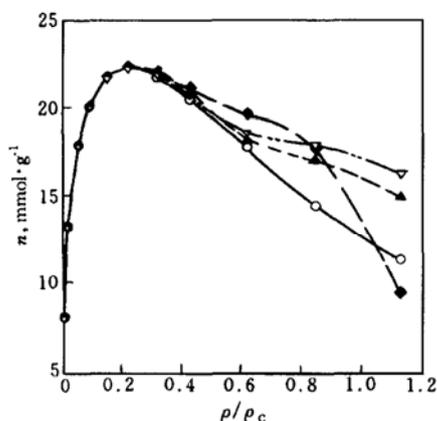


Figure 1 Effect of compressibility factor on isotherm behavior (CH₄ on AC at 198.15 K)

z : —◆— Virial; —▽— SRK; —▲— IUPAC; —○— L-K

3.2 The adsorption isotherms on activated carbon on both sides of the critical temperature can be well modeled by a unique isotherm equation

The excess adsorption isotherms of methane and nitrogen on activated carbon are shown respectively in Figs. 2 and 3. All isotherms show features of type-I, except the maximum and negative increments^[9] shown on some isotherms in the supercritical region. They all can be satisfactorily modeled by

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

where n is the experimentally measured excess adsorption, and the first term on the right hand side (rhs) is the isotherm equation for the absolute adsorption, which was proposed by the authors recently for the adsorption on porous solids at supercritical temperature^[10]. The second rhs term is the product of

the gas phase density, $\left(\sum_{i=1} c_i p^i \right)$, and the volume of the adsorbed phase, $\left(\sum_{j=0} c_j p^j \right)$. The former was determined by an equation of state and correlated with pressure for each temperature; the latter was calculated by

$$V_a = \frac{n_t - n}{\rho_g} \quad (2)$$

where V_a is the volume of the adsorbed phase, ρ_g is the gas phase density, and n_t is the absolute adsorption, which is determined by the following equation^[11]

$$n_t = \frac{1}{\delta} \exp \left[\exp \left(\alpha + \frac{\beta}{\ln p} \right) \right] \quad (3)$$

where δ is used to avoid evaluating the logarithm of a negative number, and $\delta = 10$ for the sets of adsorption data on activated carbon; α and β are parameters, and are functions of temperature. Details of the isotherm modeling were presented elsewhere^[12,13]. The model fits the experimental isotherms (shown by dots) very well, as shown by curves in Figs. 2 and 3. The three parameters in the model were evaluated by fitting the model to the experimental data through nonlinear regression analysis. The variations of parameters, n_t^0 , q and b , with temperature are shown respectively in Figs. 4—6. Parameter n_t^0 , the saturated absolute mass of adsorbate in the adsorbed phase, remains constant for the supercritical region, while it increases to a higher value on approaching the critical temperature, thus revealing a different adsorption mechanism for the subcritical region. Methane and nitrogen share the same curve of q vs. T because the carbon adsorbent is the same, revealing parameter q as a qualified index of surface heterogeneity. The difference in adsorption potentials between methane and nitrogen is seen in parameter b , as shown in Fig. 6, two nearly parallel plots of $\ln b$ vs. T are obtained.

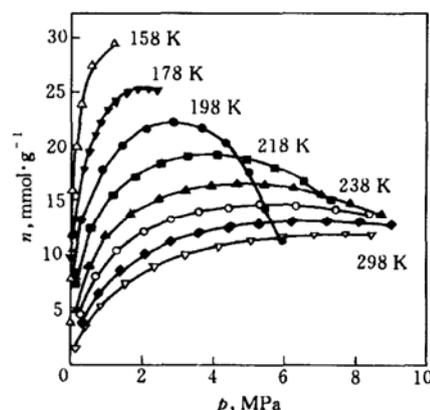


Figure 2 Adsorption isotherms of CH₄ on activated carbon

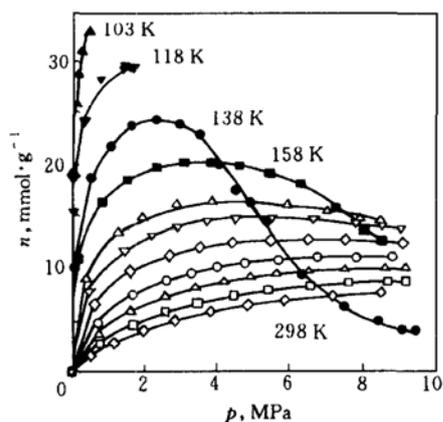


Figure 3 Adsorption isotherms of N_2 on activated carbon

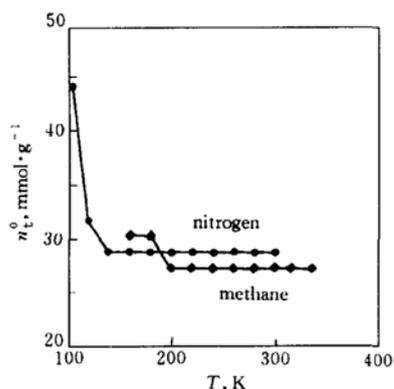


Figure 4 Variation of n_s^0 with temperature

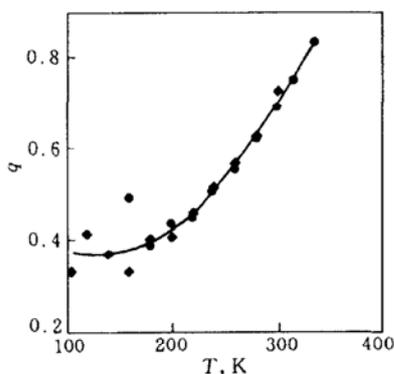


Figure 5 Variation of q with temperature
◆ methane; ● nitrogen

3.3 Transition of isotherm types observed in the adsorption on silica gel

The adsorption isotherms of CH_4 and N_2 on silica gel belong to type-II in the subcritical region, but they switch to typical supercritical isotherms in the supercritical region, as shown in Figs. 7 and 8 respectively. The transition of isotherms is not continuous at temperatures close to the critical point, as shown by the isotherm of methane at 198.15 K ($T_c=190.6$ K), but continuous transition is observed at the 138.15 K isotherm of N_2 ($T_c=126.2$ K). All continuous isotherms in the supercritical region can be modeled in the same

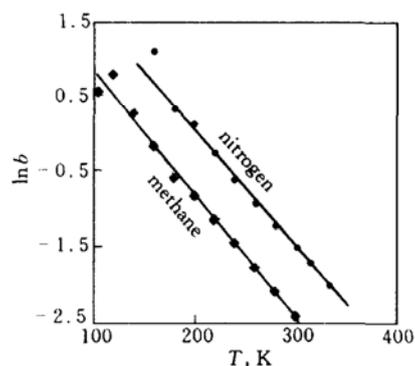


Figure 6 Variation of b with temperature

way as those for the adsorption on activated carbon. This transition of isotherm types is certainly caused by the change of adsorption mechanism on crossing the critical temperature. Both the experimental adsorption isotherms on activated carbon and silica gel substantiate the idea that a unique adsorption mechanism dominates the adsorption behavior at above-critical temperatures no matter what kind of adsorbents is dealt with. This unique mechanism of adsorption is the monolayer coverage. All other mechanisms are impossible for supercritical adsorption because the interaction among the adsorbate molecules becomes unimportant when comparing to the adsorbate-adsorbent interaction at supercritical temperatures^[9]. A model relying on a monolayer adsorption mechanism fits the experimental isotherms of methane on activated carbon very well^[14]. If this argument holds true, then capillary condensation is impossible even for the adsorption of hydrogen on carbon nanotubes so long as the adsorption is physical.

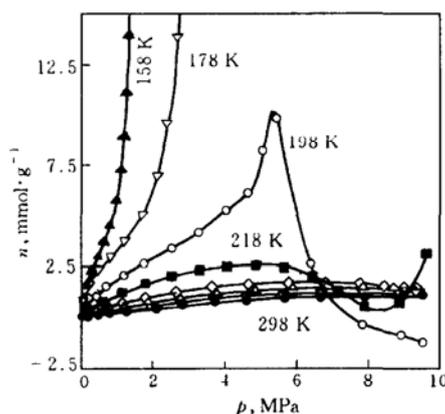


Figure 7 Adsorption isotherms of CH_4 on silica gel

4 CONCLUSIONS

(1) To study the adsorption behavior near the critical region, attention must be paid to the determination of compressibility factor of the gas phase, and

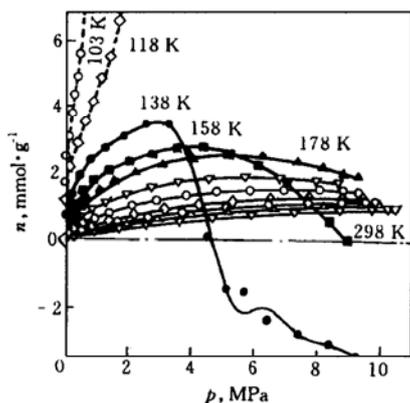


Figure 8 Adsorption isotherms of N_2 on silica gel
Dots: experimental; Solid curves: model predicted

Lee-Kesler equation was proposed for such purpose especially for N_2 and CH_4 .

(2) Two kinds of isotherm transformations were observed on crossing over the critical temperature. Type-II isotherms changed to type-I on silica gel, but the continuity of the transitional isotherm depends on how far the temperature from the critical one: non-continuous isotherm was recorded at a temperature less than 10 K from the critical. No change in isotherm types was shown for the adsorption on activated carbon, however, a transition of adsorption mechanisms was still confirmed by the change in the value of model parameter.

(3) The adsorption isotherms in the supercritical region all show the same feature irrespective of the adsorbents revealing a unique adsorption mechanism functioning. Such isotherms can be satisfactorily modeled by unique model. The satisfactory fit of the model to the experimental isotherms proved the reliability of the absolute adsorption determined by the proposed method.

NOMENCLATURE

b	a parameter of the isotherm equation
c_i, c_j	correlation coefficients
n	amount adsorbed, $\text{mmol}\cdot\text{g}^{-1}$
n_t^0	saturated amount of the absolute adsorption, $\text{mmol}\cdot\text{g}^{-1}$, a parameter of the isotherm equation
p	equilibrium pressure, MPa
q	a parameter of the isotherm equation
T	equilibrium temperature, K
V	volume, cm^3
z	compressibility factor
α, β, δ	correlation coefficients

ρ density, $\text{mmol}\cdot\text{cm}^{-3}$

Subscripts

a	adsorbed phase
c	critical
g	gas phase
t	absolute

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