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A Study on the Adsorption Isotherms in the Vicinity of the Critical Temperature

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Abstract. Adsorption data of nitrogen and methane on micro-porous activated carbon and on meso-porous silica gel were measured near the critical temperature. It was found that the values of the compressibility factor (z) exerted a significant effect on the behavior of isotherms. Selection of reliable z-values is very important for the analysis of experimental results obtained near the critical temperature. The isotherms on activated carbon always show type-I features at sub- and supercritical temperatures, but those on silica gel remarkably show a change from type-II at sub-critical temperatures to type-I at supercritical temperatures. The critical temperature appears to be shifted up in some case.

Keywords: equilibrium, experimental data, measurement techniques, gas phase, supercritical

1. Introduction

Studies on the adsorption of supercritical gases have been encouraged by the important applications that working on the principle of such adsorption. Representative applications include the adsorptive storage of hydrogen (Noh et al., 1987) and natural gas (Matranga et al., 1992), and the pressure swing adsorption process used for gas separation/purification (Tsai et al., 1983). Thermodynamic analysis of the specified task is the first step in engineering a project. However, available knowledge of the supercritical adsorption is too scarce to complete the analysis. Adsorption theory has been well developed for the adsorption of vapors at sub-critical temperatures. However, many fundamentals of the adsorption have not been clear if the equilibrium temperature is higher than the critical temperature of adsorbates. It is quite logical to measure the adsorption isotherms nearby the critical temperature if the transition of adsorption mechanism over the two distinct

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physical regions is studied. A pioneering experiment was contributed by Findenegg (1983), who measured the adsorption isotherms of ethylene on carbon black crossing over the critical temperature. All the isotherms nearby the critical temperature showed a discontinuous peak. Chen and co-workers (1997) measured the adsorption of CO_2 on activated carbon for the temperature range 284–314 K covering the critical temperature (304.2 K) in experiments. Their isotherms seem quite different from those of Finndenegg. Both works did not mention how the compressibility factors of gas were determined. In fact, the compressibility factor of gas exerts a considerable effect on the calculated amount adsorbed, but its reliability of precision is not guaranteed for the critical zone. Therefore, more experiments on different kinds of adsorbents seem necessary. We measured the adsorption data of nitrogen and methane on a meso-porous silica gel as well as on a micro-porous activated carbon nearby the critical temperature. Activated carbon is a representative of adsorbents with non-polar surface, but micro-porous in comparison with carbon black. Silica gel is a representative of adsorbents with polar surface and meso-pores.

The difficulty in measuring adsorption isotherms around the critical temperature of nitrogen and methane lies in two respects. Firstly, a cryostat that maintains a temperature constant for the range $T_c \pm 20$ K is not commercially available. Secondly, the compressibility factor of gases is not as definitely determined for the vicinity of T_c as for the other temperatures. However, its value considerably affects the determination of the amount adsorbed for both volumetric and gravimetric techniques. A special cryostat was designed for studying the supercritical adsorption in our laboratory. It can maintain any temperature in the range from 77 K to room temperature constant. Details of the cryostat have been described previously (Zhou and Zhou, 1996). To select the *correct* values of compressibility factor of N_2 and CH_4, a volumetric set-up used for adsorption measurement was also used to measure the compressibility factor at some temperatures. The in situ measured results were compared with the well-known data, published by IUPAC and in J. Phys. Chem. Ref. Data. Such data usually are authoritative, but they are also calculated values by an equation of state, whose parameters were correlated to experimental p-V-T data of more or less origins. Besides, the tabular data are not as convenient to use as an equation of state for modeling calculations. Therefore, compressibility factor values were also generated by several equations of state of real gases. The alignment of an isotherm can remarkably change if z-values of different origins are applied. Selection of reliable z-values was made basing on a comparison between z-values of different origins. The z-values determined as such are believed to be reasonable to the knowledge available.

2. Experimental Determination of the Compressibility Factor

A set-up based on volumetric method was applied to measure adsorption and the compressibility factor of gases in the study. Principle of the equipment is shown in Fig. 1. Two containers of known volume are connected by tubes and a valve (C). One container, called reference cell of volume V_r, is kept at a constant temperature T_r, which is usually close to the room temperature. The value of V_r includes the volume of tube between the reference cell and valve C. Another container is called adsorption cell, where adsorbent might locate and the equilibrium temperature of adsorption, T_d,is maintained. The volume of the connecting tube between the adsorption cell and valve C was divided into two parts: one part of volume V_t exposures in room and, therefore, of the same temperature as the reference cell. Another part buries in the atmosphere of the cryostat, and is of the temperature T_d and, thus, its volume was added to adsorption cell V_d. The amount adsorbed was determined from the p-V-T data before and after opening valve C. The precision and reliability of the adsorption data relies firstly on how accurate the p, V and T are measured. 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 is less than 0.05%. The volume of the reference cell was determined by a method of titration.

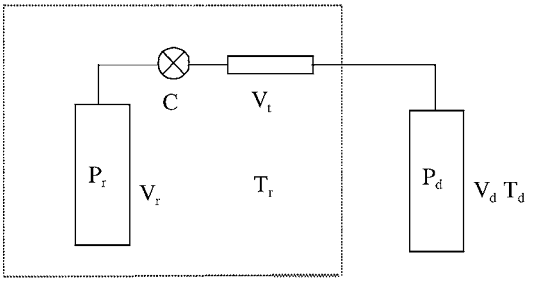

Figure 1. Schematic structure of a volumetric set-up.

Volume V_d was determined by helium at T_r temperature. The amplitude of temperature variation is ±0.1 K for T_r and ±0.2–0.5 K for T_d. This difference comes from the thermal conductivity of water, iso-octane and air. The thermostat is filled with water; the cryostat is filled with iso-octane at 173 K and higher temperatures, but empty at lower temperatures. The purity of N_2, CH_4 and He used in experiments is higher than 99.99%. The activated carbon was made of coconut shells activated by KOH. CHEMBET-3000 was used to analyze the specific surface area and pore volume of adsorbents. The adsorption of nitrogen at 77 K reports that the activated carbon has surface area 2800 m^2/g and pore volume 1.5 ml/g (pore size is less than 2.0 nm), and the silica gel has surface area 300 m^2/g and pore volume 1.9 ml/g (average pore size of 3.3 nm).

The principle of the experimental determination of compressibility factor is simple. Both cells were empty and evacuated before experiments. Then an amount of gas was inlet into V_r to maintain a pressure p_1. The moles of gas confined in V_r was calculated as:

$$n_1 = \frac{p_1 V_r}{z_{r1} R T_r} \tag{1}$$

Since T_r is far from the critical temperature, compressibility factor z_{r1} can be determined reliably by an appropriate equation of state, for example, by the 3-order virial equation. The pressure dropped to p_2 after opening valve C. The amount of gas maintained in V_r, V_t and V_d are:

$$n_2 = \frac{p_2 V_r}{z_{r2} R T_r} \tag{2}$$

$$n_3 = \frac{p_2 V_t}{z_{r2} R T_r} \tag{3}$$

$$n_4 = n_1 + n_3' + n_4' - n_2 - n_3 \tag{4}$$

where n_3 and n_4 are the moles of gas remained in V_t and V_d respectively before opening valve C. Since z_{r2} can be determined as z_{r1}, all the equations can be solved. The compressibility factor at p_2 and T_d was then calculated by

$$z_d = \frac{p_2 V_d}{n_4 R T_d} \tag{5}$$

This method was applied for both nitrogen and methane. The equilibrium temperature selected is 103.15 K, 118.15 K, 126.15 K, 138.15 K and 158.15 K for nitrogen and the critical temperature of T_c = 126.2 K (p_c = 3.35 MPa) is covered. Similar experiments were completed for methane. The equilibrium temperature selected is 158.15, 178.15, 190.15, 198.15 and 218.15 K covering the critical temperature T_c = 190.6 K (p_c = 4.54 MPa).

3. Determination of *z*-Values for the Vicinity of the Critical Temperature

Aside from the *z*-values measured experimentally, we collected other available information of *z* for the vicinity of the critical temperature. Those published by IUPAC in the *International Thermodynamic Tables of the Fluid State 5 and 6* for methane and nitrogen respectively and those presented by Jacobson et al. (1986) for nitrogen are included. An interpolation method of *local smooth curve* was applied to evaluate the entry for the experimental temperature and pressure. The equations of state tested include the 3-order virial equation, the Soave-Redlich-Kwong (SRK) equation, and the Lee-Kesler (LK) equation (Guo et al., 1983). Remarkable disagreement between different *z*-values was observed in T_c± about 10 K. The *z*-values of different origins are presented in Figs. 2–4 for nitrogen and in Figs. 5–7 for methane respectively for such temperature range.

It is concluded for nitrogen, Lee-Kesler equation generates *z*-values that are most close to the IUPAC data and/or those in situ measured, therefore, is used to calculate *z*-values of nitrogen for the vicinity of

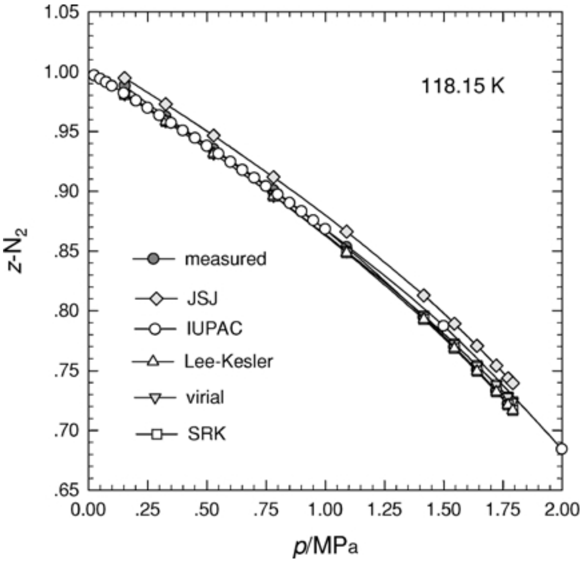

Figure 2. *z*-values of N_2 at 118.15 K.

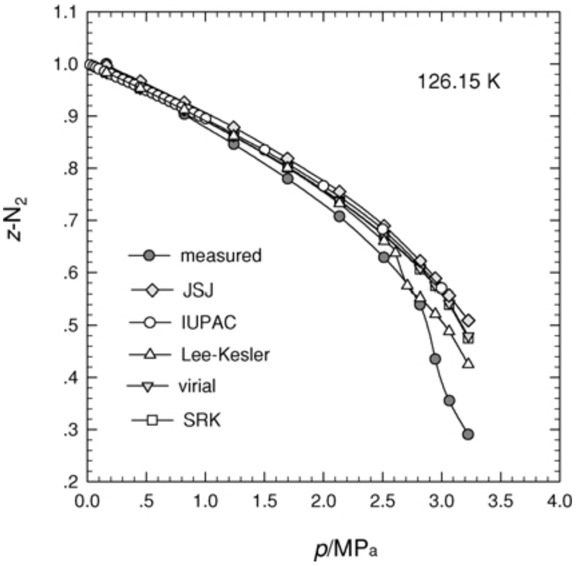

Figure 3. z-values of N_2 at 126.15 K.

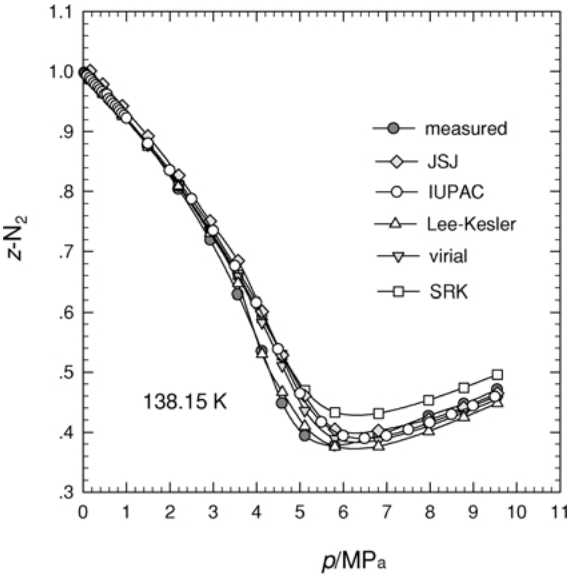

Figure 4. z-values of N_2 at 138.15 K.

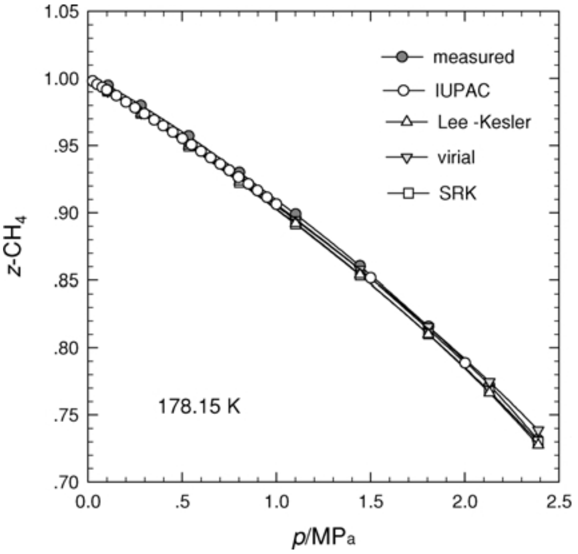

Figure 5. z-values of CH_4 at 178.15 K.

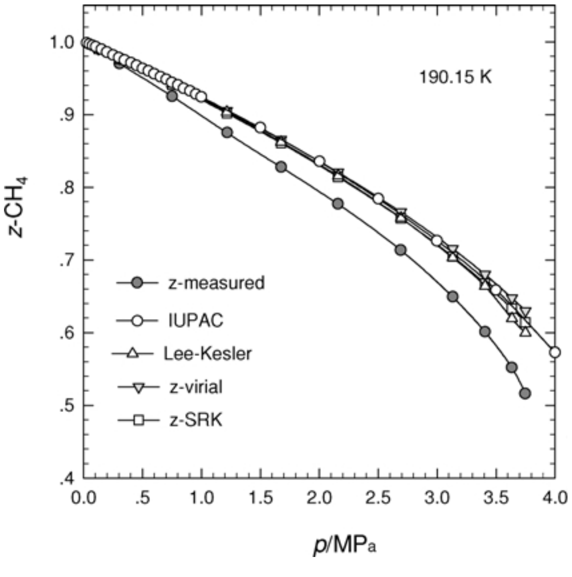

Figure 6. z-values of CH_4 at 190.15 K.

the critical temperature. This equation is also pertinent for methane. The in situ measured z-values are in good agreement with the others except at 190.15 K, the critical temperature of methane. It founds difficult for the compressibility behavior of gases to reach a stable state in the critical zone. However, the other z-values are in good agreement, therefore, the in situ measured z-values of methane at 190.15 K are considered unreliable and discarded. All equations of state tested generate quite close z-values for temperatures more than 10 K away from the critical.

According to the Lee-Kesler model, compressibility factor, z, is calculated as:

$$z = z^{(0)} + \frac{\omega}{\omega^{(r)}}\left(z^{(r)} - z^{(0)}\right) \qquad (6)$$

where the superscript (0) denotes "simple fluid" ($\omega = 0$) while (r) denotes the reference fluid (octane); ω and $\omega^{(r)}$ are the eccentric factors of the real fluid of interest

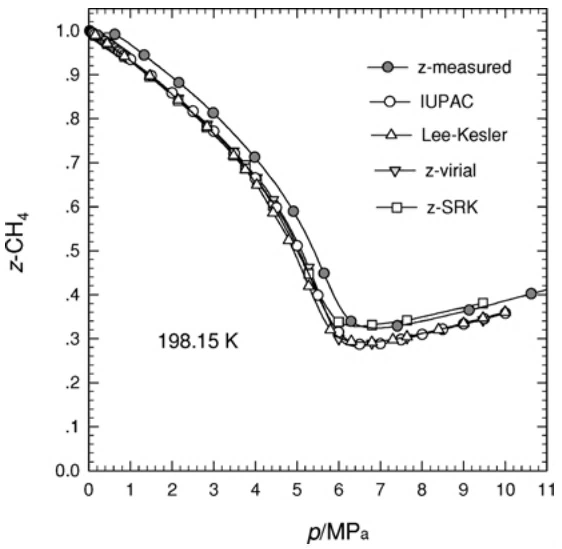

Figure 7. z-values of CH_4 at 198.15 K.

and the reference fluid ($\omega^{(r)}$ was taken as 0.3978). $z^{(0)}$ and $z^{(r)}$ are calculated by the modified BWR equation that in the reduced form:

$$\frac{p_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \tag{7}$$

where

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \tag{8}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \tag{9}$$

$$D = d_1 + \frac{d_2}{T_r} \tag{10}$$

$$V_r = \frac{p_c V}{R T_c} \tag{11}$$

Parameter values for the simple and the reference fluids (octane) are listed in Table 1. There is only one variable in Eq. (7), V_r. A convergence strategy, for example, the secant method, can be used to search for the solution of V_r^0 for simple fluid first, and then V_r^r for the reference fluid afterward. The values of $z^{(0)}$ and $z^{(r)}$ can thus be determined:

$$z^{(0)} = \frac{p_r V_r^0}{T_r} \tag{12}$$

$$z^{(r)} = \frac{p_r V_r^{(r)}}{T_r} \tag{13}$$

Table 1. Parameter values used in the Lee-Kesler model.

Parameter	Simple fluid ($\omega = 0$)	Reference fluid (octane)
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

The effect of the precision of z-values on the determination of the amount adsorbed is significant because an adsorption isotherm is measured by an accumulative manner in the course of pressure increment. In other words, we can only measure the increment of the amount adsorbed for a given increment of pressure. The equilibrium amount adsorbed n at a pressure p is the sum of all the adsorption increments untill pressure p. Therefore, the effect of the precision of z-values is not local, but accumulative for an isotherm. Besides, a stable state was very difficult to recognize in the critical zone. Some periodic slow variation in pressure readings added more uncertainty to the measurement. This might be the cause of different results reported in literature.

4. Adsorption Isotherms Measured Near the Critical Temperature

Four sets of isotherms, five isotherms of each, were measured nearby the critical temperature for the adsorption of N_2 and CH_4 on activated carbon and silica gel (Yang, 2000) as shown in Figs. 8–11. According to the isotherm behavior on crossing over the critical temperature, two classes of adsorption are identified:

4.1. *Class A: Adsorption on Activated Carbon*

No change of isotherm types was observed on crossing over the critical temperature. All isotherms are always showing type-I feature below or above the

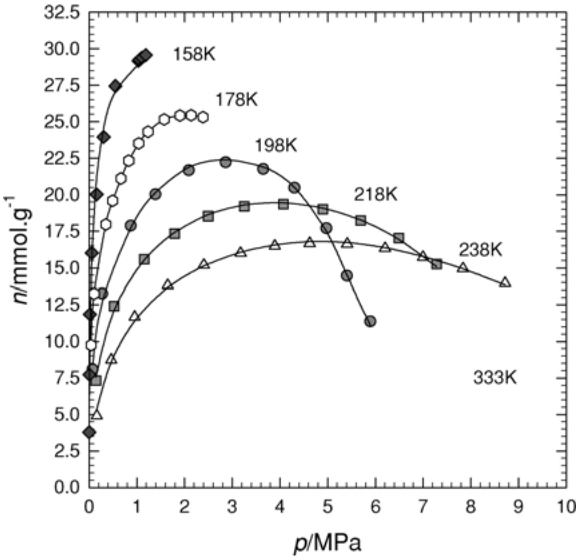

Figure 8. Adsorption isotherm of CH_4 on activated carbon around the critical temperature points: experimental; curves: predicted by model.

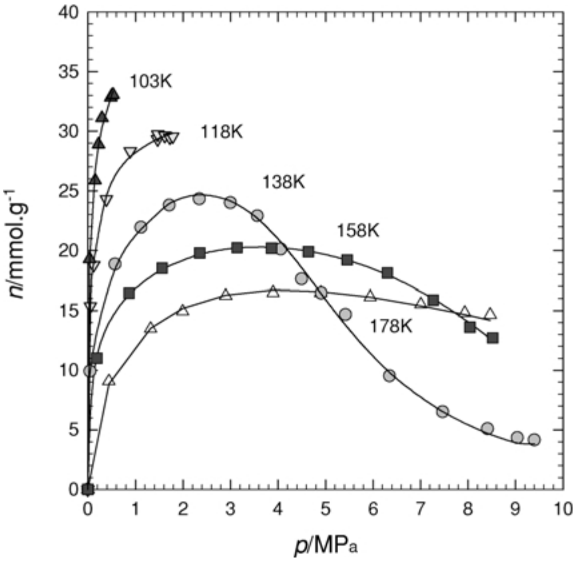

Figure 9. Adsorption isotherm of N_2 on activated carbon around the critical temperature points: experimental; curves: predicted by model.

critical temperature for both N_2 and CH_4. This class of isotherms can be satisfactorily modeled by the following (Zhou et al., 2001):

$$n = n_t^0[1-\exp(-bp^q)] - \left(\sum_{i=1} c_i p^i\right)\cdot\left(\sum_{j=0} c_j p^j\right) \tag{14}$$

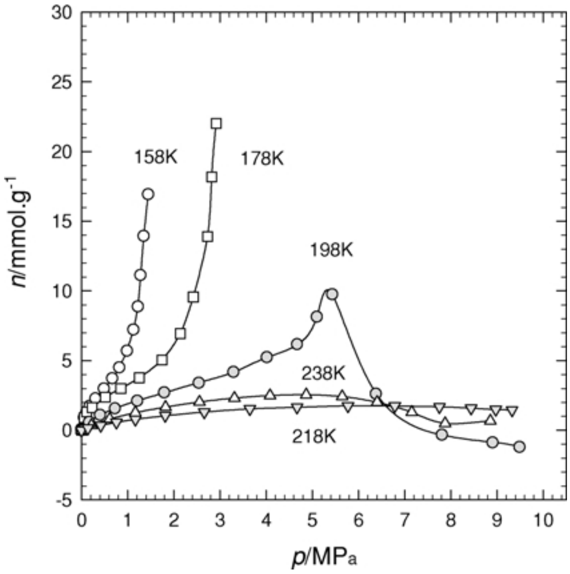

Figure 10. Adsorption isotherm of CH_4 on meso-porous silica gel around the critical temperature.

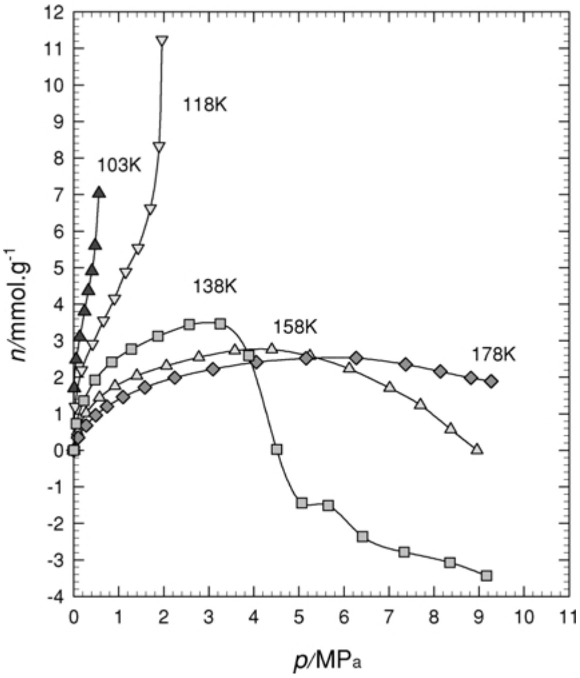

Figure 11. Adsorption isotherm of N_2 on meso-porous silica gel around the critical temperature.

The first term of the right hand side is used to describe the so-called *absolute* adsorption. It includes a parameter, n_t^0, whose meaning is physically agreeable with the fictitious limiting adsorption n^{lim} (Zhou, 1998). The second term of the right hand side is the product of gas phase density and the volume of the adsorbed phase, which can be evaluated by the *isotherm space transformation* strategy (Zhou, 2000). As shown in Figs. 8 and 9, excellent fit of the model to the experimental excess adsorption isotherms is achieved for both the sub- and the supercritical region. However, this paper will not go further on the details of isotherm modeling. The density of the adsorbed phase can be evaluated similarly as for its volume. It is 0.6–0.7 g/cm^3 for nitrogen ($\rho_c = 0.31$ g/cm^3) within 50 K above the critical temperature, and 0.3–0.35 g/cm^3 for methane ($\rho_c = 0.16$ g/cm^3) in the same range. These values are about double the critical density, and about 80% of liquid density at the normal boiling point.

4.2. *Class B: Adsorption on Meso-Porous Silica Gel*

The isotherms remarkably changed their type from type-II at sub-critical temperatures to type-I after crossing the critical temperature. The isotherm change happened at the temperature closest to T_c is of interest. Although 198.15 K is higher than the critical temperature of methane (190.6 K), the isotherm still shows the feature of type-II at lower pressures; however, it suddenly drops down at a pressure, as observed by Finndenegg (1983) previously. It proves that multilayer adsorption mechanism can still function for a short span of temperature above the critical. In other words, the critical temperature of adsorbate can move up to an extent under the interaction with pore surfaces. Such discontinuous change of isotherm was not shown on the isotherm of nitrogen at 138.15 K, the temperature closest to the T_c of nitrogen (126.15 K). It is possibly because 12 K is too large to observe the phenomenon.

Because the amount adsorbed increases with the decreasing temperature for physical adsorption, isotherms at temperatures close to the critical may show typical feature of supercritical adsorption at relatively low pressures. The same feature can be observed for relatively high temperatures only at very high pressures (Malbrunot et al., 1992). The possible structure change of adsorbents, especially the reliability of the so-called "helium volume" make problems more complicated at very high pressures (Menon, 1968). Such uncertainties, however, are not important and can be neglected for the experiments under conditions of low temperature and relatively low pressures.

5. Conclusions

1. A stable state was very difficult to recognize in the critical zone. Some periodic slow variation in pressure readings added more uncertainty to the measurement of compressibility factor. Therefore, uncertainty in z-values is inevitable for the critical region, which must cause considerable consequences in the isotherms reported.
2. The compressibility factor of gases exerts a considerable effect on isotherm alignment near the critical temperature. Comparisons are given for z-values of different origins including those in situ measured for the vicinity of the critical temperature of nitrogen and methane. Reasonable values of compressibility factors are determined based on comparison.
3. Isotherms will not change their type on crossing over the critical temperature for the adsorption on microporous activated carbon; however, isotherms of type-II changed to type-I for the adsorption on mesoporous silica gel on crossing the critical temperature.
4. A shift up of the critical temperature for about 8 K is observed at the adsorption of methane on silica gel indicated by the abrupt change of isotherm from type-II at a pressure. However, such shift was not observed at the adsorption of nitrogen on silica gel, because the temperature measured may be too far to the critical (12 K).

Nomenclature

n	Excess adsorption (mmol·g^{-1})
p	Pressure (MPa)
R	Gas constant
T	Temperature (K)
V	Volume (ml)
z	Compressibility factor
ρ	Density

Subscripts

a	Adsorbate	*c*	Critical
Cal	Calculated	*d*	Adsorption
Exp	Experimental	*g*	Gas phase
m	Molar	*t*	Absolute

Superscripts

lim	Limiting

Acknowledgments

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