Generalized Model of Adsorption Equilibria Prediction for CO₂ on Carbonaceous Adsorbents

Kuerbanjiang Nuermaiti, Ming Li*

Department of Chemistry, Tongji University, Shanghai, China

Email address:
khurban@126.com (K. Nuermaiti), limingt@tongji.edu.cn (M. Li)

*Corresponding author

To cite this article:

Received: March 3, 2016; Accepted: April 5, 2016; Published: April 9, 2016

Abstract: The carbon molecular sieve CMS-200 and activated carbon Yigao-A have been adopted as adsorbents for the study of CO₂ adsorption capture. The pore size distributions of both adsorbents were characterized by the modified H-K method. Adsorption isotherms of CO₂ on the carbon molecular sieve CMS-200 and activated carbon Yigao-A were measured by the gravimetric method (Hiden, IGA-001) in the temperature region of 253.15-393.15 K and pressure region of 0-2 MPa. The Henry’s law constants of adsorption equilibria for CO₂ were estimated using the Virial equation. The Ruthven’s generalized model was applied to analyze the experimental data on the basis of the values of the Henry’s law constants. The investigation demonstrates that the Ruthven’s generalized model not only is useful to describe the adsorption equilibria for CO₂ on non-porous homogeneous carbonaceous adsorbents in the subcritical region, but also is reliable to predict the adsorption equilibrium data for CO₂ on carbonaceous adsorbents with the uniform pore size distribution and the wide pore size distribution from the subcritical region to the supercritical region.

Keywords: CO₂, Adsorption, Prediction, Henry’s Law Constant, Generalized Model

1. Introduction

CO₂ capture and storage is becoming a central issue since CO₂ is a predominant anthropogenic greenhouse gas, and the separation technologies of CO₂ from other gases have been practiced extensively to reduce CO₂ emission [1-3]. Among the various CO₂ capture approaches, the adsorption process on different adsorbents (including homogeneous and heterogeneous) proves to be a promising option due to its relatively low operating and capital costs and lower impact on the environment [4, 5]. Therefore, CO₂ adsorption properties on many kinds of solid adsorbents have been widely investigated recently. The prediction of CO₂ adsorption equilibrium has received particular attention because it could conveniently provide fundamental parameters that are important to the design of adsorption processes for CO₂ capture.

Up to now, several methods have been proposed to predict the adsorption equilibria of gas on various adsorbents on the basis of the theories about gas-solid adsorption equilibria. Dubinin and Polanyi developed a predictive method based on the adsorption characteristic curve from their adsorption potential theory [6]. This pioneering work provided a useful tool to the prediction of adsorption equilibria for gas-solid systems in subcritical region. However, it should be mentioned that the main assumption of temperature independence of the characteristic curve may not be accurate enough for some gas-solid systems because there are temperature effects on the adsorbate-adsorbent interactive mechanism and the estimation of adsorbate volume in this theory [7, 8]. In addition, although the adsorption potential theory has been already proved to be predictable for the adsorption of subcritical vapor in wide temperature region, it is not successful enough when the supercritical gas is introduced since no effective method can estimate the pseudo-saturation vapor pressure \( p_0 \) for the supercritical adsorption [9]. Li et al put forward another generalized method on the basis of the relationship between \( n \sim p/p_0 \). The experimental adsorption data of CO₂ and C₂H₆ on the graphitized carbon black STH-2 were checked under subcritical temperature region. The theoretical analysis based on the BET equation approved that this generalized method is reasonable for non-porous adsorbents [10]. Recently Chi \( \chi \) theory may be a kind of predictive method [11]. It used the plot...
n (amount of uptake for gas) versus \(-\ln(-\ln(p/p_0))\) with different temperatures to present a single generalized adsorption isotherm. Since the pseudo-saturation pressure has been also involved in this method, more efforts should be made to estimate \(p_0\) accurately.

A simple and practical method has been put forward by Ruthven for the prediction of adsorption systems. On the basis of the statistical thermodynamics, the plots of \(\ln(n)\) versus \(\ln(kp)\) (\(k\) is the Henry's law constant, \(p\) is the adsorption equilibrium pressure) under a wide temperature region could approximately give a unique generalized curve. Ruthven presented an example as n-heptane vapor adsorption on 13X molecular sieve CMS-200 and activated carbon Yigao-A, both of which have the wide pore size distribution. The temperature range was selected from the subcritical region extending to the supercritical region. The Henry’s law constants were calculated from the Virial equation to investigate further feasibility of the Ruthven’s generalized model for the prediction of adsorption equilibria of \(\text{CO}_2\), including the subcritical temperature region and the supercritical region.

2. Experimental

2.1. Experimental Process

The microporous carbon molecular sieve CMS-200 (from Dalian Haixin Chemical Company) and the porous activated carbon Yigao-A (provided by Shanxi Yigao Coal-Bed-Methane Company) were used to measure \(\text{CO}_2\) adsorption equilibrium data. Adsorbent samples were outgassed at 423.15 K for at least 24 hours in the vacuum condition of by a vacuum drying oven (DZF-6021, Shanghai Yiheng). The pure gas of \(\text{CO}_2\) was provided from Shanghai Weichuang Industrial Gases Company. It is with the purity better than 99.99%.

The adsorption isotherms of \(\text{CO}_2\) on the carbon molecular sieve CMS-200 and activated carbon Yigao-A were measured by an intelligent gravimetric analyzer (Hiden, IGA-001). The sensitivity of the adsorption amount is about ±1 µg. The temperature range is 253.15-393.15 K with a 20 K interval. The pressure range is 0-2 MPa. The experimental temperatures of \(\text{CO}_2\) adsorption have been held at constant by a thermostat (TF50/3/12/F, Severn Thermal Solutions) within the fluctuation of ± 0.1 K. Before each \(\text{CO}_2\) adsorption experiment, the IGA-001 adsorption system was vacuumed by a molecular pump and the adsorbents were treated at 473 K more than 8 hours.

2.2. Characterizations of Adsorbents

The pore size distributions (PSD) of the carbon molecular sieve CMS-200 and the activated carbon Yigao-A were characterized by the adsorption data of \(\text{CO}_2\) at 273.15 K since \(\text{CO}_2\) is more effective for ultramicropores, which could not be easily approached by \(\text{N}_2\) adsorption at 77 K [15]. The pore size distributions of the two adsorbents were calculated with the corrected Horvath and Kowazoe equation for the slit shaped pore by the programs based on the Matlab codes [16]. The plot of obtained PSD for the carbon molecular sieve CMS-200 and activated carbon Yigao-A are illustrated in Figure 1 and Figure 2. The calculated mean radius of pore for the carbon molecular sieve CMS-200 and for the activated carbon Yigao-A is about 0.61 nm and 1.01 nm respectively. From these figures, the pore size distribution of the carbon molecular sieve CMS-200 is obviously much narrower than that of the activated carbon Yigao-A. Thus the carbon molecular sieve CMS-200 could be regarded as a homogeneous adsorbent with the uniform pore structure. Some related other physical properties of the adsorbents are listed in Table 1.
3. Prediction of Adsorption Equilibria

3.1. Adsorption Isotherms

Experimental isotherms of CO\textsubscript{2} adsorption expressed in the excess gravimetric amount \cite{17} on the carbon molecular sieve CMS-200 and activated carbon Yigao-A are shown in Figure 3 and Figure 4. It could be seen that the CO\textsubscript{2} adsorption on the carbon molecular sieve CMS-200 and the activated carbon Yigao-A appears as type I isotherm in the subcritical region (\(T < T_c\)), where \(T_c\) represents the adsorption equilibrium temperature of CO\textsubscript{2}, \(T_c\) represents the critical temperature of CO\textsubscript{2}, the critical temperature of CO\textsubscript{2} is 304.41 K \(\) and the critical region (\(T_c \leq T < 1.2T_c\)), because the adsorbate could be in the liquid or liquid-like state in this region \cite{18}. In the supercritical region (\(T \geq 1.2T_c\)), the CO\textsubscript{2} adsorption isotherms on the carbon molecular sieve CMS-200 and activated carbon Yigao-A also appear as type I isotherm, however, the mono-layer adsorption mechanism, which is different from the micropore filling or condensation model, may be introduced to these supercritical isotherms \cite{19}.

3.2. Henry’s Law Constant

The Henry’s law constant \(k\) could be calculated from the Virial function of the adsorption isotherm [equation-(1)] in this work.

\[
\frac{ap}{n} = \exp\left(2c_1n + \frac{3}{2}c_2n^2 + \cdots\right)
\]

Where, \(n\) is the uptake amount of CO\textsubscript{2} on the adsorbent, \(p\) is the adsorption pressure for CO\textsubscript{2}, \(a\), \(c_1\), \(c_2\)… are the coefficients of the Virial function. If the higher terms in the high order could be removed when the surface of adsorbent tends to zero coverage for any temperature, plotting \(\ln(p/n)\) to \(n\) would give a linear relationship like the Henry’s laws. Hence, equation-(1) turns into equation-(2) at low pressure without consideration of temperature of CO\textsubscript{2}.

\[
n = ap
\]
Taking the Henry’s law constant \( k=\alpha \) as equation-(3), if \( \xi \) is set as the interception on the ordinate of the Virial plot [see equation-(4)], the Henry’s law constant is calculated from equation-(5) [14]. The Virial plots of CO\(_2\) adsorption on the carbon molecular sieve CMS-200 and on the activated carbon Yigao-A are shown in Figure 5 and Figure 6.

\[
\ln \left( \frac{p}{n} \right) = \ln \left( \frac{1}{\alpha} \right) = \ln \left( \frac{1}{k} \right) \tag{3}
\]

\[
\ln (1/\alpha) = \ln (1/k) = \xi \tag{4}
\]

\[
k = \exp (-\xi) \tag{5}
\]

It could be seen that, at different temperatures, the treated experimental data between \( \ln(p/n) \) and \( n \) in low coverage region are almost in linear relationship. Therefore, these two plots could easily make the extrapolation of the linear relationship to the zero-adsorbed coverage, which provides a simple method of determining the Henry’s law constants. The corresponding values of the Henry’s law constant \( k \) are listed in Table 2. Since it is in assurance to guarantee that the value of the Henry’s law constant \( k \) is greater than zero in Equation-(5), the values of Henry’s law constants \( k \) acquired by this way should be reliable.

From the viewpoint of thermodynamics, the Henry’s law constants must satisfy the van’t Hoff equation [equation-(6)] [12]

\[
\frac{\Delta H}{RT^2} = \frac{d \ln k}{dT} \tag{6}
\]

where \( \Delta H \) is the difference in molar enthalpy between the gaseous state and the adsorbed state, and \( R \) is the universal gas constant. The \( \Delta H \) is always referred as the limit heat of adsorption \( \Delta H_0 \) if the adsorption coverage approached zero. To make sure the accuracy of the calculated Henry’s law constants, the van’t Hoff plots for CO\(_2\) adsorption, plotting \( \ln k \) to \( (-1/T) \), is depicted in Figure 7. It seems that two linear relationships could be obtained for carbon molecular sieve CMS-200 and activated carbon Yigao-A respectively, which means the calculation process of \( k \) is reasonable.

In addition, the corresponding values of \( \Delta H \) for the carbon molecular sieve CMS-200 and for activated carbon Yigao-A could be evaluated from the values of slopes of the van’t Hoff plots in Figure 7. The values of \( \Delta H \) for CO\(_2\) adsorption are 24.94 kJ/mol (CMS-200) and 16.14 kJ/mol (Yigao-A) on the carbon molecular sieve CMS-200 and on activated carbon Yigao-A respectively. This proves that the atomic interaction between the adsorbate of CO\(_2\) and the surface of carbon molecular sieve CMS-200 is much greater than that between the adsorbate of CO\(_2\) and the surface of activated carbon Yigao-A. The result is in agreement with the pore size distributions of the carbon
molecular sieve CMS-200 and activated carbon Yigao-A shown already in Figure 1 and Figure 2. Evidently, since the atomic interaction in narrow pore is larger than that in a wide pore because of the much larger enhanced adsorption potential provided from the dispersion forces by the narrower walls of micropore, especially when the walls of micropore are in proximity to each other to make the pore size approaching the diameter of the adsorbate molecule [20,21]. Thus, it is easy to understand that the limit heat of CO$_2$ adsorption on the carbon molecular sieve CMS-200 with narrow pores is larger than that on the activated carbon Yigao-A with wider pores.

3.3. Generalized Curve of CO$_2$ Adsorption Equilibria

Based on the Henry’s law constants listed in Table 2, the Ruthven’s generalized model, plotting lg($n$) versus lg($kp$), was applied to adsorption equilibrium data of CO$_2$ on the carbon molecular sieve CMS-200 and activated carbon Yigao-A at different temperatures and pressures. The results are shown in Figure 8 and Figure 9 respectively. The equilibrium temperature is from 253.15 K to 393.15 K, including the subcritical region and the supercritical region.

$$\ln n_{exc} = \lambda \cdot \frac{b \cdot \ln (kp) - f}{1 + \ln (kp) - f}$$

Since the generalized model, lg(n) versus lg(kp), has been proved with the feasibility and validity for heterogeneous carbonaceous adsorbents in different regions, it should be able to predict the CO$_2$ adsorption equilibria on carbonaceous adsorbents. What is only needed is a temperature-dependent parameter $k$, the Henry’s law constant. It could be determined from the extrapolation of the van’t Hoff plot using the limited experimental data at reference temperatures, or from the theoretical analysis of molecular interaction and the pore size distribution as suggested by Do [7].

It should be especially noticed that, the isotherms of CO$_2$ adsorption on the two heterogeneous carbonaceous adsorbents included the sub- and super-critical region, which means the Ruthven’s generalized model could be used to predict adsorption equilibria in a wide condition across the critical region. The Ruthven’s generalized curve has been proven useful for the adsorption equilibria of gases on homogeneous graphitized carbon black [14]. As a consequence, the relationship between the lg($n$)~lg($kp$) could be effective for the description of CO$_2$ adsorption on different carbonaceous adsorbents including homogenous and heterogeneous materials in the subcritical and supercritical region of temperature.

4. Conclusion

In this work, the adsorption equilibrium data of CO$_2$ on the carbon molecular sieve CMS-200 and activated carbon Yigao-A have been obtained by the gravimetric method. The carbon molecular sieve CMS-200 could be approximate structure uniform and the activated carbon Yigao-A is with a wide pore size distribution. The experimental temperature includes the subcritical and supercritical regions. The Henry’s law constants of CO$_2$ adsorption were calculated from the Virial Plots. The Ruthven’s generalized model on the basis of the relationship between lg($n$)-lg($kp$) has been adopted to express the adsorption equilibria of CO$_2$. It could be concluded that the Ruthven’s generalized model is applicable not only for the prediction of adsorption equilibria of CO$_2$ on homogeneous carbonaceous adsorbents, but also for the prediction of adsorption equilibria of CO$_2$ on heterogeneous carbonaceous adsorbents with different pore size distributions. In addition, this generalized model could be reliable across from the subcritical temperature region to the supercritical temperature region. If the Ruthven’s generalized curve for the CO$_2$-adsorbent system is determined from limited adsorption isotherms, other equilibrium data at different
temperature and pressure can be derived from the generalized curve. This predictive model is more convenient and simpler than the Dubinin-Polanyi’s method of the characteristic curve, because it doesn’t require the estimation of the adsorbate volume and the pseudo-saturation vapor pressure, which are dependent on temperature in some degree, in the supercritical region.

Acknowledgements

Support from the National Natural Science Foundation of China (Grant No. 20506019) and the Fundamental Research Fund for Central Universities of China for this work are acknowledged.

References