



Research article

Extension of Kelvin equation to CO₂ adsorption in activated carbonGuojun Yin^a, Qingya Liu^b, Zhenyu Liu^{b,*}, Weize Wu^b^a Shandong Provincial Key Lab of Chemical Engineering and Process, Yantai University, Shandong 264009, PR China^b State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Keywords:

Critical pore diameter
Kelvin equation
CO₂ adsorption
Activated carbon
YL parameter

ABSTRACT

CO₂ adsorption in activated carbon (AC) at ambient temperature was found to be mainly accomplished by filling of pores with diameter smaller than 1 nm. Kelvin equation correlates operating conditions with the critical (or maximum) diameter of pores where pore filling occurs, but it is not valid for the micropores due to deviation of the physical parameters of CO₂ from their normal values. This work extends Kelvin equation to CO₂ adsorption in AC by introducing a general dimensionless parameter ($K_{\text{CO}_2\text{-AC}}$, termed YL parameter) to account for the changes in physical parameters of CO₂ in micropores. This approach is similar to the use of fugacity and activity coefficients to modify the ideal gas equation. The work includes measurements of CO₂ adsorption capacity for 3 types of AC, fitting the capacity to the ACs' pores from the smallest one to the larger ones to determine the critical pore diameter at each condition, and fitting the critical pore diameter data to a modified Kelvin equation to obtain $K_{\text{CO}_2\text{-AC}}$. It is found that $K_{\text{CO}_2\text{-AC}}$ varies slightly with the pore diameter but significantly with temperature and can be approximated by an empirical equation. The modified Kelvin equation excellently describes CO₂ adsorption data for ACs reported in the literature and studied in this work.

1. Introduction

Separation of CO₂ from mixed gases over activated carbon (AC) has been widely studied and practiced [1–3]. It is generally recognized that CO₂ physically adsorbs in the pores of AC mainly via condensation or liquefaction in the pores of smaller than 1 nm in diameter, and the chemical properties of AC play a minor role in the adsorption [2,3]. In this regard, it is possible to estimate CO₂ adsorption capacity of an AC under given operating conditions if the AC's pore size distribution (PSD) is available.

The PSD determined by the nonlocal density functional theory (NLDFT) and free energy of an inhomogeneous fluid [4,5] has been recognized to be accurate for AC in recent years [3,6,7]. The theory assumes that at any condition the gaseous adsorbates adsorb in all the pores of an adsorbent but the amounts of the adsorbates in pores of different sizes are different, i.e. the smaller the diameter, the more the adsorbate's amount. Although the assumption of NLDFT is reasonable, the inexplicit relation between adsorption capacity and operating conditions makes it difficult to correlate them directly. Consequently experiments have to be performed to obtain an adsorption isotherm under every condition to determine adsorption capacity.

Kelvin equation, Eq. (1), is the classical theory that directly correlates adsorption conditions (temperature T and pressure P_d) with the critical or maximum diameter of the pores (d) where capillary

condensation or pore filling occurs [8]. In the equation, R is the ideal gas constant and P_0 , γ and V_m are the saturate vapor pressure, the surface tension and the liquid molar volume of the adsorbate at temperature T , respectively. Pore filling does not occur in pores with diameters greater than d under the considered conditions. The value of d allows determination of adsorption capacity if PSD is available.

$$RT \ln \frac{P_d}{P_0} = -\frac{4\gamma V_m}{d} \quad (1)$$

Although this equation has been successfully applied for macropores, it was found to be invalid for pores smaller than 7.5 nm in diameter [9]. Many researchers had modified Kelvin equation to investigate its validity in narrower pores. Barret, Joyner and Halenda (BJH) [10], Pierce [11], Dollimore and Heal (DH) [12] attributed this limitation to the presence of an adsorbed layer that is formed prior to the occurrence of pore filling and proposed equations to determine the thickness of adsorbed layer, consequently made Kelvin equation effective in smaller pores. The BJH and DH methods have been frequently used in the literature but they are capable of extending Kelvin equation only to pores of 2–6.5 nm in diameter. The applicable minimum pore diameter of Pierce method is 2.5 nm [11]. Kruk, Jaroniec and Sayari further modified the BJH method (BJH-KJS) and made it applicable to pores of 2–12 nm in diameters [13]. Rocha et al. established a so called PM method by modifying the Kelvin equation with a correction term

* Corresponding author.

E-mail address: liuzy@mail.buct.edu.cn (Z. Liu).

(f_c), which improved its accuracy for pores larger than 2 nm in diameter [14]. Clearly, all these modifications to Kelvin equation do not apply to pores smaller than 2 nm in diameter.

It has been recognized that in a domain of a few molecules in size such as in the range of less than 1 nm, physical parameters of a condensed or liquefied adsorbate deviate significantly from their normal values. The surface tension was reported to be greater in micropores than in macropores due to the stronger interaction between the adsorbed molecules and the adsorbent wall [15,16]. It was also reported that the density (ρ or $1/V_m$) of adsorbates is smaller than its normal value and fluctuates which changes in pore size, especially in a range around two molecular diameter [5,17,18]. These observations seem to indicate that Kelvin equation may be extended further to pores smaller than 2 nm by modifying the physical parameters involved. In principle, the changes in γ and V_m in the pores of around 1 nm in diameter are not linear with pore size and the operating conditions and their effects on Kelvin equation are complex. To avoid complicated modification of every physical parameter in the equation, a general non-dimensional parameter may be used to account for the changes in all the physical parameters. This approach is similar to the fugacity and activity coefficients used in modification of the ideal gas equation.

Following the above idea, this work analyzes adsorption behavior of CO_2 on 3 types of AC in a dynamic adsorption unit at conditions suitable for pressure swing adsorption (PSA) and determines a general non-dimensional parameter for Kelvin equation based on PSD given by NLDFT. The parameter extends Kelvin equation to pores of 0.4 nm in diameter and well fits the CO_2 adsorption data of many types of AC, including these studied in this work and those reported in the literature.

2. Experimental

Five types of AC were used in this work, among them 4 are commercial products from Jibe Yanshan Activated Carbon Co., Ltd., China. The commercial ACs were derived from an anthracite (termed AC1), coconut shell (termed AC2), date stones (termed AC3) and apricot stones (AC4). The fifth AC (AC5) was prepared in our laboratory by pyrolysis of a bituminous coal.

CO_2 adsorption experiments were performed on a dynamic adsorption reactor ($\Phi 6 \times 80$ mm), shown in Fig. S1. Before the experiment, the AC was dried at 150°C for 2 h. In each experiment, 0.40 g AC of 20–40 mesh and 10% CO_2/N_2 at a flow rate of 50 ml/min were used and the effluent gas was analyzed on-line by a mass spectrometer. The amounts of CO_2 cumulated in the dead space of the system and in the void space between the AC granules were determined and used to determine the excess adsorption capacity (q_{excess}) from the apparent adsorption capacity. In short, the q_{excess} is the real adsorption capacity of the AC excluding the amounts of CO_2 in the void space in the reactor. The detailed experimental procedure and the method for determination of q_{excess} can be found in the literature [19]. The experimental error, determined by duplication of 20 data points, is smaller than 3%. Fig. S2 presents q_{excess} of the ACs at various conditions.

PSD of the ACs was determined by adsorption of pure CO_2 on a NOVA 4200E (Quantachrome, USA) unit at 273.0 K and NLDFT regression. Prior to the measurement, the ACs were degassed under vacuum at 150°C for 10 h. The results are shown in Fig. S3.

3. Results

3.1. CO_2 adsorption in ACs

The cumulative pore volumes of the ACs determined from the PSD data (Fig. S3) are displayed in Fig. 1. The volumes of pores smaller than 1 nm in diameter are 0.1682, 0.2131, 0.1626, 0.1703 and 0.0786 ml/g for AC1, AC2, AC3, AC4 and AC5, respectively. In term of the volume, the largest is AC2, the smallest is AC5, while the rest are similar ($\text{AC4} > \text{AC1} < \text{AC3}$). The trend in volume of pores of smaller than

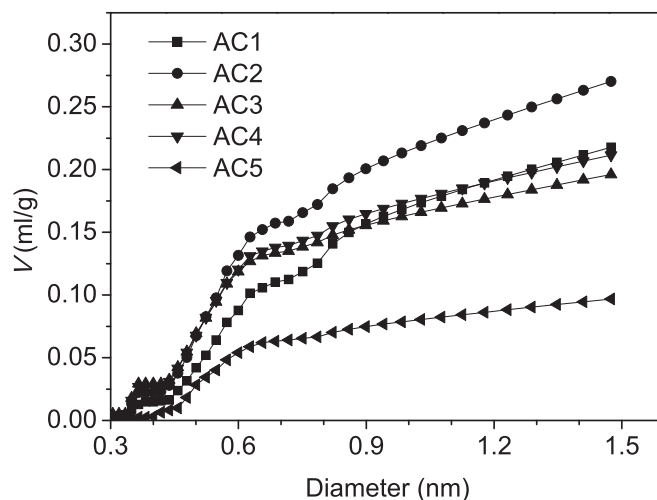


Fig. 1. Cumulative pore volume determined by NLDFT based on CO_2 adsorption.

0.6 nm in diameter, however, is slightly different from that of the pores of smaller than 1 nm, although AC2 is still the largest (0.0693 ml/g) and AC5 is still the smallest (0.0541 ml/g), because AC4 (0.1203 ml/g) $>$ AC3 (0.1186 ml/g) $>$ AC1 (0.0878 ml/g). AC1, AC2 and AC3 are selected to study the adsorption behavior, while AC4 and AC5 are used to test the results.

Fig. 2 shows volumetric excess adsorption capacities (termed V_{excess}) of the AC1–AC3 calculated from q_{excess} in Fig. S2 using the liquid density data in Table S1. Clearly, these V_{excess} increase with an increase in pressure or in temperature, suggesting that the CO_2 adsorption mechanism in ACs is physical adsorption at the adsorption conditions used. In general, the V_{excess} of the AC2 is the largest among the three types of AC. The V_{excess} of AC3 is significantly larger than that of AC1 at pressures of smaller than 0.10 MPa while the V_{excess} of AC3 is similar to that of AC1 at pressures of 0.10–0.20 MPa.

3.2. Critical diameter of Kelvin equation at various conditions

Table S1 shows the physical parameters of CO_2 at 263.0, 268.0, 273.0, 283.0, 288.0 and 293.0 K. They are saturate vapor pressure P_0 , surface tension γ , liquid molar volume V_m and liquid density ρ . Assuming that CO_2 adsorption on the ACs follows the pore filling mechanism suggested by Kelvin equation, i.e. CO_2 fills the ACs' pores gradually from the smallest one to the larger ones with increasing CO_2 pressure, the critical pore diameter at each CO_2 pressure can be determined from the values of V_{excess} in Fig. 2 and the cumulative pore volume of the ACs in Fig. 1 (the procedure is shown in Fig. S4).

The results in Fig. 3 indicate that the critical diameters for the 3 ACs are almost the same at the same adsorption conditions, in a range of 0.45 to 1.07 nm under the adsorption conditions used in this work. This indicates that the micropore filling mechanism can be used for CO_2 adsorption in the ACs and the CO_2 adsorption in the mesopores and on the surface is negligible. This further indicates that Kelvin equation may be adopted reasonably to interpret CO_2 adsorption in the ACs.

It is noted, however, that the critical diameters predicted by Kelvin equation based on the physical parameters of liquid CO_2 in Table S1, the dash lines in Fig. 3, are much smaller than the experimental data in the same figure. They are even smaller than the kinetic diameter of CO_2 , 0.33 nm, indicating that Kelvin equation cannot describe the CO_2 adsorption behavior without modification, agreeing with that reported in the literature [9,10,20] and discussed in the introduction.

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