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Use of a Polynomial Equation for Analyzing Low-Concentration Adsorption Measurements of Ethane on Activated Carbons

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Abstract

A polynomial equation is used for analyzing ethane adsorption measurements in the low-concentration region carried out by a dynamic chromatographic method for two microporous activated carbons. For low gas-phase concentrations, this equation reduces to Henry's law. It is shown that this polynomial equation gives a good description of hydrocarbon adsorption on microporous activated carbons.

INTRODUCTION

In the most general representation of the adsorption isotherm equation, the equilibrium pressure p is a function of the adsorbed amount a_t; i.e., $p = f(a_t)$. Theoretical and experimental studies (1-6) showed that an exponential polynomial effectively describes the experimental dependence of p/a_t

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on the adsorbed amount a_t. Everett (*1*) and Sing (*2*) utilized this polynomial for evaluating the monolayer capacity and the specific surface area of nonporous adsorbents. Numerical studies of gas adsorption on graphite (*3*) showed that the first few terms of the exponential polynomial are sufficient to assure an accurate description of the experimental isotherm. Also, a good description of the experimental isotherms was reached for adsorption on zeolites (*4*).

In this work the exponential polynomial equation will be adapted to describe gas adsorption on microporous solids in the low-concentration region. Ethane adsorption isotherms in the low-concentration region for two microporous activated carbons were used to verify the abovementioned equation. It is shown that this equation is useful for characterizing hydrocarbon adsorption on microporous activated carbons.

ADSORPTION ISOTHERM EQUATION

The exponential polynomial used for describing gas–solid adsorption isotherms may be written as follows (*6*):

$$p/\theta = K \exp\left(-\sum_{i=1}^{n} C_i'\theta^i\right) \tag{1}$$

where

$$\theta = a_t/a_0 \tag{2}$$

where θ denotes the relative adsorption defined as the ratio of the adsorbed amount a_t to the adsorption capacity a_0, K is Henry's constant, and the coefficients C_i' for $i = 1, 2, \ldots, n$ are associated with the two-dimensional virial coefficients that appear in the expansion of the spreading pressure with respect to the adsorbed amount a_t. Note that Eq. (1) for $C_i' = 0$ $(i > 1)$ reduces to Henry's law.

Experimental studies of gas adsorption on microporous solids (*7, 8*) showed that the so-called characteristic adsorption curve is often temperature invariant; this curve represents the dependence of the relative adsorption θ on the adsorption potential A defined as follows (*7*):

$$A = RT \ln (p_s/p) \tag{3}$$

where p_s is the saturation vapor pressure, T is the absolute temperature, and R is the universal gas constant. The above discussion indicates that in adsorption on microporous solids, it is convenient to express the adsorption potential A as a function of the relative adsorption θ. Presentation of Eq. (1) in terms of the adsorption potential A gives

$$A = A_s - RT \ln \theta + \sum_{i=1}^{n} C_i\theta^i \tag{4}$$

where

$$A_s = RT \ln (p_s/K) \tag{5}$$

and

$$C_i = RTC_i' \qquad \text{for } i = 1, 2, \ldots, n \tag{6}$$

It follows from Eq. (4) that the function $Z(\theta) \equiv A + RT \ln \theta$ may be represented by the polynomial

$$Z(\theta) \equiv A + RT \ln \theta = A_s + \sum_{i=1}^{n} C_i\theta^i \tag{7}$$

where A_s and C_i for $i = 1, 2, \ldots, n$ are the linear coefficients of this polynomial.

Differentiation of Eq. (4) with respect to θ gives

$$dA/d\theta = -RT/\theta + \sum_{i=1}^{n} iC_i\theta^{i-1} \tag{8}$$

The adsorption potential distribution function $X(A) = -d\theta(A)/dA$ associated with Eq. (4) is expressed as follows:

$$X[A(\theta)] \equiv Y(\theta) = -1/(dA/d\theta) = \theta/(RT - \sum_{i=1}^{n} iC_i\theta^i) \tag{9}$$

where the dependence between θ and A is given by Eq. (4). The adsorption potential distribution $X(A)$ characterizes the energetic heterogeneity of a solid adsorbent.

RESULTS AND DISCUSSION

To illustrate the practical utility of Eq. (4), we used this equation for describing the ethane adsorption isotherms on BPL and PA activated carbons at 273 K. A dynamic chromatographic method, which is described by Huang et al. (*9*), was employed to measure these isotherms in the low-concentration region. The BPL carbon was obtained from the Calgon Carbon Corportion in Pittsburgh, Pennsylvania, whereas the PA carbon was obtained from the Barnebey-Cheney Company in Columbus, Ohio. Both of these carbons were designed for adsorption of gases and vapors.

To convert the measured ethane concentrations in the gas phase and the solid phase to the relative adsorption θ and the adsorption potential A, we need to know the saturation vapor pressure p_s and the adsorption capacity a_0. For the ethane saturation pressure p_s, we assumed the value 13,640 mmHg, which was estimated by Lee et al. (*10*) with the Peng-Robinson equation of state. We evaluated the adsorption capacity a_0 according to the Dubinin-Radushkevich equation, which is commonly used in gas adsorption on microporous activated carbons (*7*, *8*). The values of a_0 for ethane on the BPL and PA activated carbons at 273 K are given in Table 1.

In Fig. 1 the experimental functions $Z(\theta)$ for ethane on BPL (open circles) and PA (closed circles) activated carbons are compared with the theoretical lines calculated according to the polynomial Eq. (7). Numerical analysis showed that the third-degree polynomial (viz., Eq. 7 with n = 3) gives a good representation of the experimental isotherms studied; the

TABLE 1
Adsorption Parameters for Ethane on BPL and PA Activated Carbons at 273 K

Quantity	Unit	BPL Carbon	PA Carbon
Adsorption capacity, a_0	mmol/cm^3	4.1	4.7
Coefficient A_s	kJ/mol	16.11	17.02
Coefficient C_1	kJ/mol	−35.29	−33.40
Coefficient C_2	kJ/mol	75.44	64.40
Coefficient C_3	kJ/mol	−64.40	−61.13
Square root of the determination coefficient r_c	—	0.997	1.000

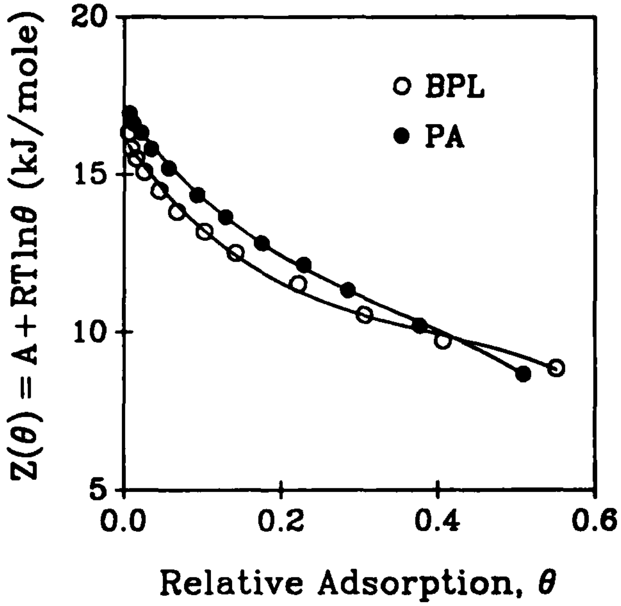

FIG. 1. Comparison of the experimental functions $Z(\theta)$ (circles) with the theoretical curves calculated according to the polynomial Eq. (7) with $n = 3$ for ethane adsorbed on activated carbons at 273 K.

square root of the determination coefficient r_c is greater than 0.997 (cf. Table 1). The determination coefficient r_c is defined as follows:

$$r_c = [S(n) - M\bar{Z}^2]/[\sum_{m=1}^{M} Z_m^2 - M\bar{Z}^2] \tag{10}$$

where

$$S(n) - A_s \sum_{m=1}^{M} Z_m + C_1 \sum_{m=1}^{M} \theta_m Z_m + C_2 \sum_{m=1}^{M} \theta_m^2 Z_m + \cdots + \sum_{m=1}^{M} \theta_m^n Z_m \tag{11}$$

where the quantity Z is defined by Eq. (7), Z_m denotes the Z value for the mth experimental point $\theta = \theta_m$, $\bar{Z}$ is the average value of Z, and M is the number of experimental points. The adsorption potential distributions are plotted in Fig. 2 for ethane-BPL carbon and ethane-PA carbon systems. A comparison of these distribution curves shows that both activated

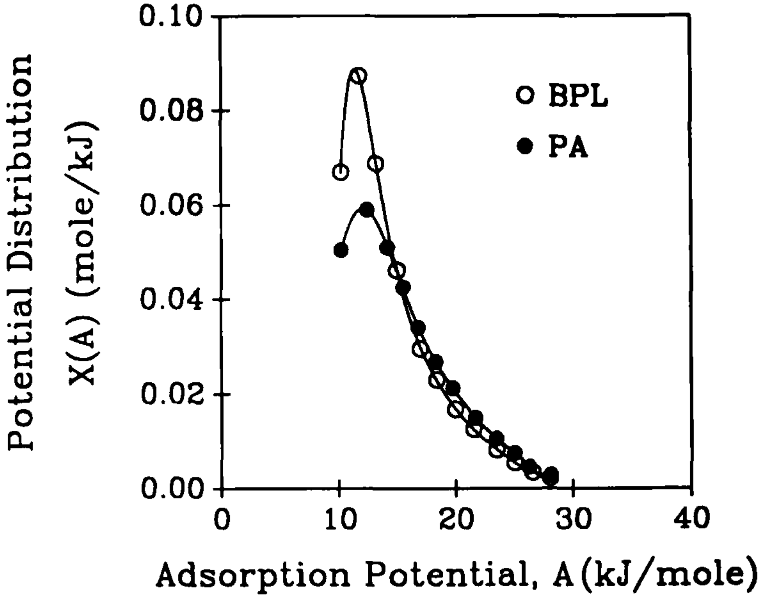

FIG. 2. Adsorption potential distributions calculated according to Eqs. (9) and (4) for ethane on activated carbons.

carbons possess a similar energetic heterogeneity; there is an indication that the PA carbon is a little more heterogeneous than the BPL carbon.

CONCLUSIONS

It is shown that the polynomial Eq. (7) assures an effective approximation of the experimental adsorption isotherms of hydrocarbons on microporous activated carbons. These isotherms in the low-concentration region may be measured quickly and accurately by a dynamic method described elsewhere *(9)*. This low-concentration part of the adsorption isotherm permits evaluation of the adsorption potential distribution function, which characterizes the energetic heterogeneity of microporous solids.

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