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The Modification of the BET Surface Area by Considering the Excluded Area of Adsorbed Molecules

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The BET method is known as the conventional method for surface area measurements. Surface area is determined using the linearized form of the BET equation to calculate the volume of the adsorbed gas in the monolayer. An adsorbed molecule occupies an area that is inaccessible to other molecules on the surface. Taking this into account, this study reports on a correction factor k', as the ratio of van der Waals constant (b) and the molar volume of the liquid ($\bar{v}$), that corrects the monolayer volume of the adsorbed gas obtained from the BET model. The obtained correction factor will increase as the size of the molecule increases.

Keywords: BET isotherm, Specific surface area, Surface area determination, Monolayer capacity, Excluded volume, Excluded area

INTRODUCTION

Surface area is an important factor in determining the behavior of porous and finely divided solids. It plays an important role in adsorption, reaction on the surface, and catalysis. Many of the properties of a material, such as catalytic activity, dissolution rate, reactivity, and separation, are correlated to that material surface area. Therefore, surface area analysis is of great importance in the characterization of solid materials. Gas adsorption is one of the most widely used methods to measure surface area, and one of the most commonly used methods based on gas adsorption is the Brunauer-Emmett-Teller (BET) method [1,2], developed by Brunauer, Emmett, and Teller for the description of multilayer adsorption. The BET equation is used to obtain the monolayer capacity, which is directly proportional to the surface area.

Despite some drawbacks on its initial assumptions, the classical BET adsorption equation is now generally accepted as the conventional method to evaluate the specific surface area and approved by the International Union of Pure and Applied Chemistry (IUPAC) [3,4]. Some corrections have been made to the BET model and the cross-section area of molecules used in the BET model. A very recent modification of the BET method is presented by Lidia López-Pérez *et al.* [5]. In their study, it is suggested that the conventional cross-section area of N_2 could be 50% higher than the geometrical area.

While the BET analysis has been found to be a useful method in surface area analysis, the area excluded by each molecule is not considered in the BET theory. The specific surface area calculated by the BET method is less than the actual value. This study aimed to introduce a correction factor to correct the monolayer volume of the adsorbed gas obtained by the BET model.

THEORETICAL BASIS

BET Theory

In 1938, Brunauer, Emmett, and Teller developed the multilayer adsorption theory, which was an extension of Langmuir's theory [6,7]. Both theories were originally based on kinetic considerations, and their basic assumptions were the same.

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To derive an equation which describes multilayer adsorption, Brunauer, Emmett, and Teller suggested that the surface be divided into n slabs covered by1, 2,….,i layers of adsorbed molecules. Adsorption and desorption occur at the top of these slabs. While in the BET equation, there is a dynamic equilibrium between each pair of successive layers, the Langmuir equation can be applied only to each layer. The equilibrium between the uncovered surface and the surface with one adsorbed layer can be expressed as follows:

$$a_1 p s_0 = b_1 e^{\frac{-E_1}{RT^{s_1}}} \tag{1}$$

where E_1 is the heat of adsorption of the 1st layer, a_1 and b_1 are adsorption and desorption constants, respectively, R is the gas constant, T is the temperature, and p is the pressure of the gas above the surface. For the successive layers, the equilibrium condition is as follows:

$$a_i p s_{i-1} = b_i e^{\frac{-E_i}{RT^{s_i}}} \tag{2}$$

where S_{i-1} and S_i are the surface area covered by i-1 and i layers, respectively. Some simplified postulates were taken into account, the most important of which were as follows: (a) the heat of adsorption for the first layer is different from that of other layers, and the heat of adsorption for all subsequent layers is equal to the heat of liquefaction E_L; (b) as the pressure approaches the saturation pressure, the number of adsorbed layers tends to infinity on a free surface. The details of the derivation of the BET isotherm can be found in the literature [1,4]. Below, only the resulting equation is presented:

$$\frac{\upsilon}{v_m} = \frac{\frac{Cp}{p^0}}{\left(1 - \frac{p}{p^0}\right)\left(1 + \frac{(C-1)p}{p^0}\right)} \tag{3}$$

where v is the total volume of the adsorbed gas, v_m is the volume of gas necessary to cover the surface with a complete monolayer, p^0 is the saturation pressure, and C is the so-called BET constant, which reflects the difference in the adsorption heat of the first layer compared with the heat of liquefaction of subsequent layers and can be written as follows:

$$C \approx \exp \frac{(E_1 - E_L)}{RT} \tag{4}$$

To determine the surface area, Eq. (3) is rearranged into the following linear form:

$$\frac{\frac{p}{p^0}}{v\left(1 - \frac{p}{p^0}\right)} = \frac{1}{Cv_m} + \frac{(C-1)p}{CV_m p^0} \tag{5}$$

A plot of $\frac{p/p^0}{v(1 - p/p^0)}$ on the y-axis as a function of p/p^0 on the x-axis, according to the experimental data, yields a straight line called the BET plot. The value of the slope and its y-intercept are used to calculate the monolayer capacity v_m and the BET constant C.

Total surface area and the specific surface area S_{BET} can then be calculated by the following equations:

$$S_{total} = \frac{v_m}{22414} N_A \delta_m \tag{6}$$

$$S_{BET} = \frac{S_{total}}{a} \tag{7}$$

where v_m is the monolayer capacity in terms of volume (L), N_A is Avogadro's number, a is the mass of adsorbent, and δ_m (Å^2) is the area occupied by a single molecule of adsorbate in a complete monolayer that can be determined from the density of the liquefied adsorbate at the adsorption temperature [8]. For example, the area occupied by a nitrogen molecule at 77 K, by assuming that the molecules are spherical and closely packed in the liquid, is estimated to be 16.2 Å^2.

Van der Waals Volume

The concept of the excluded volume of molecules is well known among chemists. The origin of this useful and successful concept goes back to van der Waals who presented this concept in his PhD thesis in 1837 [9]. Van der Waals believed that molecules were real entities with their own volumes that were inaccessible to other molecules in the system. This idea also formed the basis of his famous equation of state, for which he was awarded the Nobel Prize in Physics in 1910. Van der Waals considered gas molecules to be hard spheres and suggested that the excluded volume for a two-molecule system be eight times higher than that of the molecular volume. This value is then divided by two to obtain the excluded volume per molecule, which is four times as much as the volume of a single molecule $b = 4v_0$, where b has a specific value for each gas [10].

For adsorption on a surface, the excluded area of a molecule determines the distance of the closest approach, and this point should be considered in surface area analysis by the BET method. Each adsorbed molecule has an excluded area that is inaccessible to other molecules on the surface; thus, the number of moles of adsorbate corresponding to the monolayer is expected to be less than the maximum number estimated for the actual amount of the surface area. The purpose of this work was to introduce a correction factor into Eq. (6). The introduced correction factor was intended to correct the number of adsorbed molecules in the monolayer due to the excluded area of the absorbed molecules, improve the value of the surface area calculated from Eq. (6), and bring it much closer to the actual surface area of the solid.

$$v_{m,correct} = \frac{b}{\bar{v}} v_{m,BET} \tag{8}$$

where b is the excluded volume for one mole of the gas and $\bar{v}$ is the molar volume of the liquid. Accordingly, the surface area value is modified as follows:

$$S_{BET,correct.} = \frac{b v_{m,BET}}{\bar{v}\, 2214} N_A \delta_m \tag{9}$$

By applying this correction factor to the monolayer capacity obtained from the BET plot, the $S_{BET,correct}$ is multiplied by a correction factor that is greater than one.

$$\frac{S_{BET,correct.}}{S_{BET}} = \frac{b}{\bar{v}} = k' > 1 \tag{10}$$

RESULTS AND DISCUSSION

The van der Waals constant b volume is available for different gases. The molar volume $\bar{v}$ is calculated from the density of the liquid and the adsorbate molecular weight. The correction factor for the adsorption of different gases can be calculated using Eq. (10). Table 1 summarizes the results of the calculations for some probe gases. The modified occupied area by a single molecule is shown in the last column in Table 1. It can be seen that the obtained values for δ_m are greater than the values obtained previously. In addition, it was found that the obtained correction factor had a higher value for larger molecules.

Most surface area determination tests were carried out

Table 1. The Values of Van der Waals Constant (b), Molar Volume (v_m), Calculated from the Density of Liquefied Adsorbate (ρ_L), the Molecular Weight of Adsorbate (M_w), the Cross-Sectional Area of a Single Molecule of Adsorbate (δ_m), and the Calculated Correction Factors(k') for N_2 (77 K), Ar (87 K), O_2 (90 K), CH_4 (83 K), and n-C_4H_{10} (273 K)

Vapor	Temperature (K)	b (M)	$v_m=M_w/\rho_L$ (M^{-1})	Correction factor (k')	δ_m (Å^2)	Occupied area after correction (Å^2)
N_2	77	0.0387	0.0347	1.115	16.2	18.063
Ar	87	0.03201	0.02859	1.12	14.2	15.904
O_2	90	0.03186	0.02804	1.136	14.6	16.018
n-C_4H_{10}	273	0.1226	0.1004	1.219	44	53.636
CH_4	83	0.04278	0.0377	1.137	18.1	20.579

Note: The values of b and ρ_L were taken from Lide [11], and the values of δ_m were taken from Gregg and Sing [4] and Webb [12].

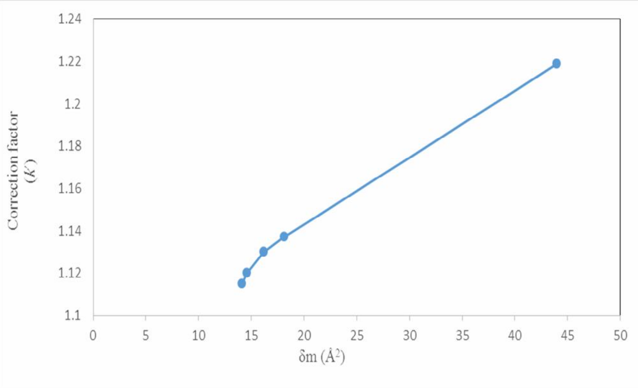

Fig 1. The value of the correction factor (k') *versus* the area occupied by a single molecule of adsorbate in a complete monolayer (δ_m).

using nitrogen, as adsorbate, at liquid nitrogen conditions (77 K). The insertion of ρ_L = 0.808 g cm^{-3} yielded a value of 1.115 for the correction factor for N_2 adsorption at 77 K. This means that to determine the actual solid surface area, the surface area obtained from the BET plot should be multiplied by 1.115. In addition to nitrogen, the surface areas of numerous other gases have been determined by the BET method. The calculations related to the k′ values for some of these gases, including Ar and O_2, are given in Table 1. Argon is frequently used for surface area measurement, usually at 87 K [13,14]. The ratio of the corrected surface area, calculated from Eq. (10), to the BET surface area was equal to 1.12 for Argon. For O_2 at 90 K, the calculated value of k' was 1.136. The correction factor values were also calculated for CH_4 at 83 K and n-C_4H_{10} at 273 K. The obtained values were 1.137 and 1.219, respectively.

These results are also shown in Fig. 1. The correction factor was found to be higher for larger molecules.

CONCLUSIONS

The monolayer volume obtained from the BET plot was modified by taking into account the excluded area of the adsorbed molecules. The obtained results showed that the monolayer volume should be multiplied by a correction factor k', which was the ratio of van der Waals constant b to the molar volume of the liquefied adsorbate. Therefore, the surface area calculated using the correction factor k' had a higher value than that obtained by the BET equation. Finally, the value of the correction factor increased with the increase in the size of the probe molecule.

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