



Modifying the BET model for accurately determining specific surface area and surface energy components of aggregates

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HIGHLIGHTS

- Develop a modified BET model in the light of multilayer adsorption theory.
- Separate SSA of non-zero adsorption site from total SSA for calculating spreading pressure.
- Perform vapor adsorption tests of three probe vapors on selected aggregates.
- Compare calculation results between two BET models.
- Identify significance of application of M-BET model as well as separation of SSA of non-zero adsorption site.

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ABSTRACT

When adopting the vapor adsorption method to measure the surface energy components of aggregates, a critical step is to determine the specific surface area (SSA) using the traditionally-used BET (T-BET) model. However, this model is demonstrated to be valid only for a limited relative pressure range of 0.05–0.40. Furthermore, the determined total SSA from this model is arbitrarily utilized to calculate the spreading pressure of probe vapors on aggregates, which does not comply with the multilayer adsorption theory. All these would definitely lead to the erroneous values of SSA and surface energy components of aggregates.

To overcome these deficiencies, this study develops a modified BET (M-BET) model in the light of the multilayer adsorption theory, based on which five steps are designed to determine the SSA and the surface energy components for aggregates. The vapor adsorption tests of three probe vapors are performed on four types of aggregates. The SSA, spreading pressure and surface energy components are then separately calculated using the two BET models. It is observed that the linear fit of M-BET model applies satisfactorily to the entire adsorption isotherm with the R^2 value larger than 0.98. The adsorption heat of the probe vapor in the second to the i th layer is demonstrated to be less than the heat of liquefaction, which accounts for the derivations of the data points of the T-BET model from linearity over the limited pressure range. The accompanying calculation results of the M-BET model reveal significant differences from those of the T-BET model, while the separation of SSA of the non-zero adsorption site from the total SSA also produces a non-negligible effect on the calculated surface energy components, identifying the significance of accurate measuring the SSA. Thus, in the vapor adsorption method it is imperative to employ the M-BET model to determine the SSA of the non-zero adsorption site so as to obtain the accurate surface energy components for aggregates.

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1. Introduction

The vapor adsorption method has been most widely recommended to measure the surface energy components of aggregates

because it provides insights into irregular shape, size, mineralogy, and surface roughness for aggregates [1–4]. When adopting this method, a critical step is to determine the specific surface area (SSA) of aggregates because in principle this parameter is served as an input for calculating the spreading pressure π_e , which is directly associated with the determination of aggregates surface energy components, as shown in Eq. (1) and (2), respectively [5–7].

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$$\pi_e = \frac{RT}{MA} \int_0^{p_0} \frac{n(p)}{p} dp \tag{1}$$

$$\pi_e + 2\gamma_L = 2 \left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^+} + \sqrt{\gamma_S^- \gamma_L^-} \right) \tag{2}$$

where $\gamma_L, \gamma_L^{LW}, \gamma_L^+, \gamma_L^-$ = total surface energy, nonpolar component, polar acid component and polar base component of probe liquid, respectively; $\gamma_S, \gamma_S^{LW}, \gamma_S^+, \gamma_S^-$ = total surface energy, nonpolar component, polar acid component and polar base component of aggregates, respectively; R = universal gas constant; T = test temperature; M = molar mass of probe liquid; A = SSA of aggregates; p = vapor pressure of probe liquid; p_0 = saturated vapor pressure of probe liquid at test temperature; and $n(p)$ = total capacity per unit aggregate mass of adsorbed probe vapor molecules, as a function of vapor pressure. For aggregates, $n(p)$ is demonstrated to be modeled using the Dubinin-Astakhov (DA) model (Eq. (3)) [8].

$$n(p) = n_D \exp \left\{ -B \left[\ln \left(\frac{p_0}{p} \right) \right]^{k_D} \right\} \tag{3}$$

where n_D, B and k_D = fitting parameters.

To determine the SSA of aggregates, the traditionally-used Brunauer-Emmett-Teller (T-BET) model is generally employed [9–13], which is developed on the basis of the multilayer adsorption theory. As shown in Fig. 1, to characterize the energetic surface heterogeneity, this model assumes that various adsorption sites with different binding energy are distributed on the adsorbent, resulting in that 0, 1, 2, 3, ... i , ... ∞ layers of adsorbate molecules are adsorbed at different sites. Let $S_0, S_1, S_2, S_3, \dots, S_i, \dots, S_\infty$ represent the SSA that is covered by these different layers, the total SSA of the adsorbent is then given by a summation expressed in Eq. (4). Herein, S_0 is defined as the SSA of the zero adsorption site, while the rest are defined as the SSA of the non-zero adsorption site.

$$A = S_0 + S_1 + S_2 + S_3 + \dots + S_i + \dots + S_\infty = \sum_{i=0}^{\infty} S_i \tag{4}$$

In carrying out the derivation of the T-BET model, dynamic equilibrium that the rate of condensation on top of i th layer equals the rate of evaporation from the $i + 1$ st layer is first established. Then for simplification, this model assumes the heat of adsorption except the first layer is equal to the heat of liquefaction. After a series of substitution and rearrangement, the final formulation of this model is derived, as given in Eq. (5). More details about the derivation of the T-BET model are well-documented in [9].

$$\frac{p}{n(p_0 - p)} = \frac{1}{n_m c} + \frac{c - 1}{n_m c} \frac{p}{p_0} \tag{5}$$

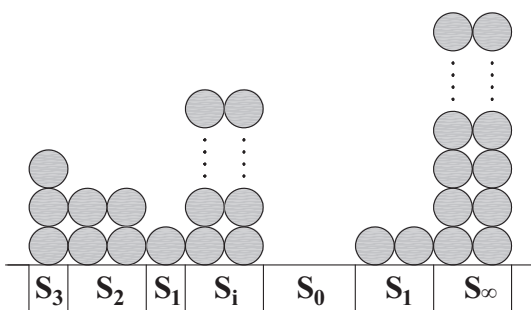


Fig. 1. Multilayer adsorption of adsorbate molecules on adsorbent.

where n = total capacity per unit adsorbent mass of the adsorbed molecules at vapor pressure p ; c = thermodynamic parameter; and n_m = monolayer capacity of the adsorbed molecules on the adsorbent.

When utilizing the T-BET model (Eq. (5)) to determine the SSA of aggregates, the following three steps are included:

- (1) Linearly fit $p/[n(p_0-p)]$ versus p/p_0 plots in the relative pressure range of [0.05, 0.40] [9–14];
- (2) With the known slope K and intercept I of the fitting line, use Eq. (6) to calculate the monolayer capacity of the adsorbed vapor molecules on aggregates;
- (3) Assume vapor molecules on aggregates are hexagonal closest packing, then use Eq. (7) to calculate the SSA of aggregates.

$$n_m = \frac{1}{K + I} \tag{6}$$

$$A = \sum_0^{\infty} S_i = \alpha \cdot \left(\frac{n_m N_A}{M} \right) \tag{7}$$

where N_A = Avogadro constant; and α = project area of a single vapor molecule, which is calculated based on the hexagonal close-packing model [15–19]:

$$\alpha = 1.091 \cdot \left(\frac{M}{N_A \rho_L} \right)^{\frac{2}{3}} \tag{8}$$

where ρ_L = liquid density of the probe molecules at test temperature.

Repeating the above steps with at least three probe vapors, the SSA of aggregates corresponding to each probe vapor is thereafter determined. π_e of each probe vapor can be then calculated by substituting Eq. (7) into Eq. (1). With the known π_e and surface energy components of each probe vapor, a set of at least three equations is established through Eq. (2), based on which the three surface energy components of aggregates are finally solved. Apparently, accurate determination of the SSA is significantly important because it is directly associated with the calculation of aggregate surface energy components. However, the following two major deficiencies existing in the T-BET model make it impossible to achieve adequate accuracy in measuring the SSA for aggregates:

- (1) The T-BET model holds only for a limited relative pressure range of 0.05 to 0.40, which is caused by the arbitrary assumption that the adsorption heat except the first layer is identical to the liquefaction heat [9,20–21]. The SSA of aggregates obtained from this limited range may be incorrect because the molecular arrangement will be continuously changing when p/p_0 exceeds 0.40, as shown in Fig. 2. This change would reversely influence the calculated SSA because the total SSA shown in Eq. (4) is determined by a summation of the individual SSA (i.e. $S_0, S_1, S_2, S_3, \dots, S_i, \dots, S_\infty$) corresponding to each adsorption site.
- (2) It is irrational to use the total SSA containing S_0 to calculate π_e and then to determine the surface energy components for aggregates. This is because, π_e is theoretically defined as the decrease of the total surface energy of adsorbent due to the adsorption of adsorbate [5,6], and the adsorption is a consequence of surface energy interactions [22]. In other words, π_e refers only to the surface energy interactions between the adsorbate molecules and the adsorbent adsorption sites, which therefore accounts only for the non-zero adsorption site. Thus, exclusion of SSA of the zero adsorption site (i.e.

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