Modeling of adsorption isotherms of probe vapors on aggregates for accurate determination of aggregate surface energy components

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HIGHLIGHTS

- Measured adsorption-desorption isotherms of nitrogen on selected aggregates.
- Identified micropore filling and mono-multilayer adsorption at aggregate surface.
- Performed adsorption tests of three known probe vapors on selected aggregates.
- Compared isotherm models in terms of physical significance & goodness of model fit.
- Proved DA model the best for modeling adsorption isotherms of vapors on aggregates.

ARTICLE INFO

ABSTRACT

The vapor adsorption method is a commonly-used method to determine the surface energy components of aggregates for paving asphalt mixtures. It is crucial to appropriately model the adsorption isotherms of the probe vapors on the aggregates. However, the traditionally-used five-parameter modified Toth model was limited to monolayer adsorption and its fitting parameters were highly dependent of seed values.

This study performed the adsorption and desorption of nitrogen on four types of aggregates to characterize the surface pores of the selected aggregates. Micropores, mesopores and macropores in a wide size range were identified at the aggregate surface. Adsorption tests of three probe vapors were then performed on the selected aggregates using the Gravimetric Sorption Analyzer. The measured adsorption isotherms were modeled using multiple isotherm models, including the five-parameter modified Toth model, Dubinin-Astakhov (DA) model and the modified Brunauer-Emmett-Teller (BET) model, for the purpose of comparison. The DA model was identified to be the most appropriate option for modeling the adsorption isotherms of the probe vapors on the aggregates in terms of both physical significance and goodness of model fit. The DA model was able to address the volume filling of micropores and the adsorption in mesopores and macropores; this model also provided the best model fit while its model parameters were independent of the seed values.

It was proved that the appropriate modeling of the adsorption isotherms was critical for the accurate determination of the equilibrium spreading pressure of the probe vapor on the aggregate surface, which then directly affected the accuracy of the calculated surface energy components of the aggregates. A deviation in the determined spreading pressure would cause significantly larger variations in the calculated surface energy components. This fact further demonstrated the importance of the accurate modeling of the adsorption isotherms of the probe vapors on the aggregates.

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1. Introduction

The surface energy components of aggregates have been widely used to evaluate the fracture, healing and moisture damage of paving asphalt mixtures [1–19]. The vapor adsorption method is a major test method for the determination of the surface energy components of aggregates. The principal advantage of this method is its capability of accommodating the irregular shape, size, mineralogy, surface texture and other peculiarities of aggregates. The vapor adsorption method is composed of four major steps [16–22].

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Step 1: Perform vapor adsorption tests on aggregate samples

In a typical vapor adsorption test, the aggregate samples are usually placed in a container in a vacuumed chamber with a constant temperature. A probe vapor with known surface energy then passes into the chamber to achieve a series of steady vapor pressures in sequence. The weight of the aggregate samples is continuously measured using a magnetic suspension balance to determine the mass of probe molecules adsorbed on the surface of the aggregates. Fig. 1 illustrates the configuration of the vapor adsorption tests.

Step 2: Calculate specific surface area of aggregates

Based on the adsorption test data, the Brunauer-Emmett-Teller (BET) model shown in Eq. (1) is employed to fit the adsorption isotherm in the relative pressure range from 0.05 up to 0.40 [20–26]. This model fitting is to determine the monolayer capacity per unit aggregate mass of the adsorbed probe molecules, which is then used to calculate the specific surface area of the aggregates using Eq. (2).

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

where p = vapor pressure, mbar; p_0 = saturated vapor pressure, mbar; p/p_0 = relative pressure, dimensionless; n = total capacity per unit aggregate mass of the adsorbed probe molecules at vapor pressure p, g/g; n_m = monolayer capacity per unit aggregate mass of the adsorbed probe molecules, g/g; and c = fitting parameter.

$$A = \left(\frac{n_m N_A}{M}\right)\alpha \tag{2}$$

where A = specific surface area of the aggregates, m^2/g; N_A = Avogadro constant, 6.0221×10^{23} mol^{-1}; M = molar mass of the probe vapor, g/mol; and α = projected area of a single molecule, which is calculated based on the hexagonal close-packing model as follows [27–31]:

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

where ρ = density of the probe molecules in liquid at the same temperature as the adsorption tests [32,33], g/m^3.

Step 3: Determine spreading pressure at saturated vapor pressure

The calculated specific surface area of aggregates is subsequently used in Eq. (4) to determine the equilibrium spread-

ing pressure of the probe vapor on the aggregate surface, π_e [34,35]:

$$\pi_e = \frac{RT}{MA} \int_0^{p_0} \frac{n}{p} dp \tag{4}$$

where R = universal gas constant, 8.3145 J/(K·mol); T = temperature, K; and n = total capacity per unit aggregate mass of the adsorbed probe molecules, as a function of the vapor pressure p, g/g. The most commonly used model for n is a five-parameter model modified from the Toth model [1–22]:

$$n = \frac{mp}{(b + p^t)^{\frac{1}{t}}} + ap^f \tag{5}$$

where a, b, f, m and t = fitting parameters.

Step 4: Compute surface energy components

The above three steps are repeated with at least three probe vapors in sequence. According to the relationship between π_e and the surface energy components (see Eq. (6)) [36], a set of linear equations are established and are presented in the matrix form as shown in Eq. (7). Solving this system of equations, the three surface energy components of the aggregates are therefore obtained.

$$\pi_e + 2\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right) \tag{6}$$

where γ_S^{LW} = Lifshitz-van der Waals component of the aggregates; γ_S^+ = Lewis acid component of the aggregates; γ_S^- = Lewis base component of the aggregates; γ_L^{LW} = Lifshitz-van der Waals component of the probe vapor; γ_L^+ = Lewis acid component of the probe vapor; γ_L^- = Lewis base component of the probe vapor; and γ_L = the total surface energy of the probe vapor, $= \gamma_L^{LW} + 2\sqrt{\gamma_L^+\gamma_L^-}$.

$$\begin{pmatrix} \frac{\pi_{e1}}{2} + \gamma_{L1} \\ \frac{\pi_{e2}}{2} + \gamma_{L2} \\ \vdots \\ \frac{\pi_{ek}}{2} + \gamma_{Lk} \end{pmatrix} = \begin{pmatrix} \sqrt{\gamma_{L1}^{LW}} & \sqrt{\gamma_{L1}^-} & \sqrt{\gamma_{L1}^+} \\ \sqrt{\gamma_{L2}^{LW}} & \sqrt{\gamma_{L2}^-} & \sqrt{\gamma_{L2}^+} \\ \vdots & \vdots & \vdots \\ \sqrt{\gamma_{Lk}^{LW}} & \sqrt{\gamma_{Lk}^-} & \sqrt{\gamma_{Lk}^+} \end{pmatrix} \begin{pmatrix} \sqrt{\gamma_S^{LW}} \\ \sqrt{\gamma_S^+} \\ \sqrt{\gamma_S^-} \end{pmatrix} \tag{7}$$

where π_{e1}, π_{e2}, $\ldots$, π_{ek} = spreading pressure at the saturated vapor pressure of the *1st*, *2nd*, $\ldots$, *kth* probe vapor, respectively; k = number of probe vapors used in the adsorption tests, $k \geqslant 3$; and the subscript L1 denotes the *1st* probe vapor, L2 denotes the *2nd* probe vapor, and Lk denotes the *kth* probe vapor.

In order to obtain the accurate surface energy components of aggregates, it is crucial to accurately determine π_e of each probe vapor on the aggregate surface. The accurate determination of π_e essentially depends on the appropriate modeling of n. However, the traditionally-used five-parameter modified Toth model has the following major deficiencies that may lead to an incorrect determination of π_e:

(1) This model is an empirical model that was originally modified from the Langmuir adsorption model with the assumption of monolayer adsorption [37–40], which may not be in agreement with the actual characteristics of vapor adsorption on aggregates [24,41,42]; and

(2) The modifications by adding more parameters result in multiple solutions, which highly rely on the seed values, although the initial intentions of the modifications were to improve the model fitting of the adsorption experiment data [20,21].
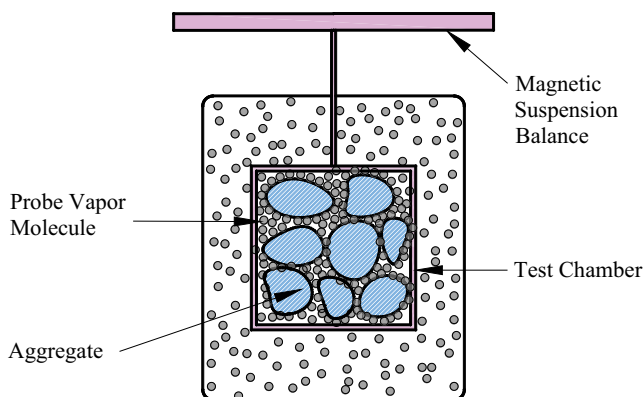

Fig. 1. Configuration of vapor adsorption tests.

Probe Vapor Molecule

Magnetic Suspension Balance

Test Chamber

Aggregate