Measuring BET Surface Areas using Organic Probe Molecules

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This paper demonstrates the use of Organic probe molecules in a DVS advantage to measure BET surface area at ambient temperature and pressure.

Introduction

The measurement of the surface properties of powders is of increasing importance to many industries that involve powder processing. One of the most fundamental of these properties is the surface area available for adsorption of gas molecules. Though there are a number of methods in use, by far the most prevalent and successful methods are based on the BET method for gas adsorption onto a solid surface.

The adsorption method of Brunauer, Emmett and Teller (BET) is based on the physical adsorption of a vapour or gas onto the surface of a solid. Historically, this work has been typically undertaken using inert gases such as nitrogen, argon and krypton. For the samples to adsorb at least a monolayer of these inert species, the experimental temperatures must be close to their boiling point (i.e. 77K for nitrogen adsorption). There can be no doubting the universality or importance of the nitrogen BET method at low temperatures, however the rapid development of newer dynamic gravimetric methods for BET analysis offers interesting options compared with the traditional approach. A comparison of the two techniques is given below:

Table 1. *Comparison of volumetric and gravimetric BET surface area determination.*

	Traditional Volumetric BET	**Newer Gravimetric BET**
Adsorbing Species	Nitrogen, Argon, Krypton	Liquid vapours at 300K
Temperature	Always at very low T i.e. 77K	Can be undertaken at ambient T
Sample Size	Typically 1g	Typically 100mg
Surface Area	Gives the surface area seen by small molecules i.e. N_2	Gives the surface area as seen by a 'real world' molecule
Experimental Conditions	Low temperatures and vacuum	Ambient temperature and pressures

Theory

The classical BET equation (1) is given below where x is the partial vapour pressure of vapour above the surface and V is the amount of vapour adsorbed.

$$\frac{1}{V}\frac{x}{1-x} = \frac{c-1}{cV_m}x + \frac{1}{cV_m} \qquad (1)$$

A plot of $(1/V)[x/1-x]$ as the ordinate and x as the abscissa should give a straight line. By determining the slope and the intercept of this line, V_m the amount of gas adsorbed if a monolayer was to form and **C** a constant related

to the adsorbate-adsorbent interaction strength can be determined.

The BET equation assumes a simple physical adsorption mechanism where the surface sites are populated homogeneously and there are no adsorbate-adsorbate interactions. Therefore in principle the equation can be applied to any adsorption system where this holds true. In practice this is most likely to be applicable to alkane molecules with boiling points between 350-400K. Highly polar adsorbates such as water tend to have very strong adsorbate-adsorbate interactions and may adsorb preferentially at specific adsorption sites, therefore in this case the BET equation should be applied with caution, as the physical significance of the calculated surface areas will be highly suspect.

Method

All the vapour sorption experiments were carried out on a DVS automated gravimetric vapour sorption analyser modified for use with organic vapours. The exhaust organic vapours from the system were vented to a fume extraction system for safety considerations. Isotherms were measured on α-Lactose monohydrate in the partial pressure range 0% to 100% using n-octane at 25.0°C.

Table 2 shows a list of typical DVS adsorbates with their molecular size, dispersive component of their surface energy and their chemical character.

Table 2. Properties of DVS adsorbate

	Molecular Size Å²	Dispersive Surface Energy mN/m (at 25°C)	Specific Characteristic
Hexane	51.5	18.4	Neutral
Heptane	57.0	20.3	Neutral
Octane	62.8	21.3	Neutral
Nonane	68.9	22.7	Neutral
Chloroform	44.0	25.0	Acidic
Carbon Tetrachloride	46	26.8	Acidic
Acetone	42.5	16.5	Basic
Ethyl Acetate	48.0	19.6	Basic
Isopropyl alcohol	44**	19.8	Amphoteric
Water	10.4-12.5*	21.8	Amphoteric
Nitrogen	16.2		Neutral

*Depends on strength of interaction and thus surface packing dependent

** Calculated from bulk properties.

Results

Figure 1 shows isotherm data for the adsorption of octane on α-Lactose monohydrate. The data is plotted as percent change in mass referenced to the mass after drying in 'dry' air (<0.1%RH). The isotherm shows typical type II/IV adsorption shape and hysteresis between sorption and desorption is minimal. The fact that the uptake is relatively low (<0.1% at saturation partial pressure) together with fast sorption kinetics indicates a surface-only sorption mechanism. Therefore the BET model may be appropriately applied in this case.
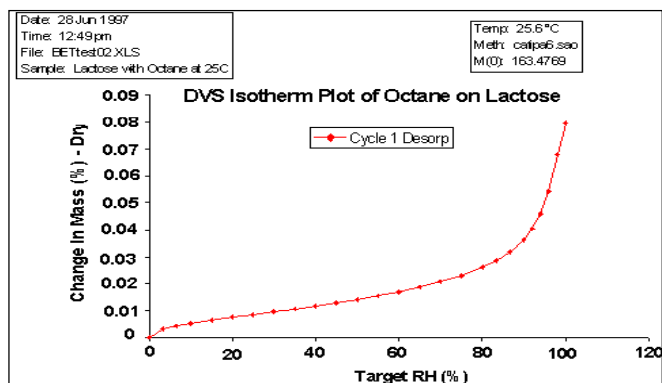
Figure 1. Sorption isotherm plot of octane on lactose.

Analysis of the experimental results using the BET equation gave a good straight line data fit shown in Figure 2, over the partial pressure range 5% to 30%. The surface area obtained of 0.25m^2/g using octane is consistent with published nitrogen surface area values of between 0.2 and 0.8 m^2/g for this material.
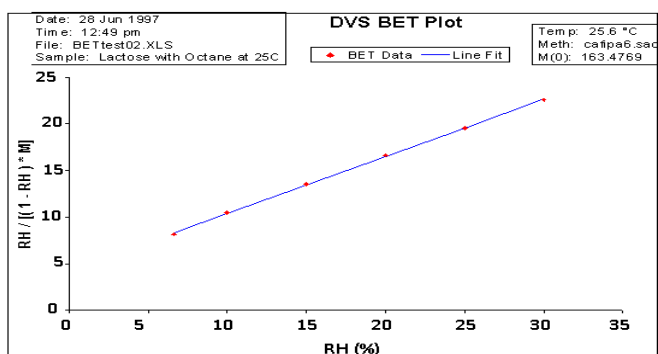

Figure 2. BET analysis for lactose sample.

Figure 3 is a sample output of the BET calculation in the DVS advanced analysis suite used to provide a BET equation fit and surface area determination.

Experimental Parameters

Molecular weight:	114.23 g/mol
Effective molecular area:	62.8 A²
Adsorbate:	Octane
Temperature read from file	

Calculation Options

RH lower limit range:	0.05
RH higher limit range:	0.30
RH type:	Target
Half cycle:	Desorption
Isotherm cycle 1	

Analysis Results

V_m:	0.01526 cm³/g
c:	15.30
Specific surface area:	2576 cm²/g
R-squared of line fit:	99.964 %

Figure 3. Sample BET calculation.

Conclusion

The dynamic gravimetric BET methods offer new opportunities for studying powder and particle surface area properties when combined with traditional nitrogen BET methods. This includes the possibility of studying small sample sizes at ambient temperature and pressure with a wide range of adsorbing vapour species. In addition, the sensitivity of the ultra-microbalance gravimetric technique also allows relatively low surface areas to be measured.

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References

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