

SOME REMARKS ON THE DETERMINATION OF SPECIFIC SURFACE AREAS OF SOLIDS FROM ADSORPTION ISOTHERMS OF VAPOURS

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The reliability of the well-known method for computing specific surface areas of solid adsorbents from adsorption isotherms of vapours by the BET equation has been repeatedly questioned mainly on the ground that the derivation of this equation is based on the assumption that the surface is energetically homogeneous, whereas experimental evidence shows that this is seldom, if ever true. It is also a well-known fact, already stressed by the authors of the method that the customary transformation of the experimental adsorption data does not ordinarily give the expected linear plot from the beginning, but only in the interval of about 0.05 to 0.35 of the values of the relative pressure. The departures at higher relative pressures are usually ascribed to disturbances caused by capillary condensation or by the filling up of narrow capillaries (Type I isotherms), whereas those at the lower pressures are attributed to the inhomogeneities of real surfaces. Though there is no doubt this latter explanation is right in principle, it is by no means evident a priori that a linear plot can result under such conditions at the higher relative pressures, and if so, whether the unimolecular coverage as computed from the linear section is the true value. No detailed discussion of these latter questions is to be found in current literature, so it may be of interest to examine them here.

Let us for this purpose consider the following model: the surface of the adsorbent may be divided into a part 1 and a part 2, both of uniform activity, but the former one is active. Adsorption activity is characterized by the constant c of the BET equation, and the higher activity of part 1 may be expressed by $c_1 = a c_2$, with $a > 1$. In view of the definition of the constant c , this means that the net heat of adsorption on the more active part of the surface is higher by $2.3 RT \lg a$. This more active part may be a fraction β of the total surface. This certainly radically simplified model was chosen in order to avoid mathematical complications, but nevertheless it seems apt to give instructive informations.

Adsorbed amounts may be denoted by a and unimolecular coverage by a_u . For the two parts of the surface the pertaining BET isotherm equations

may be valid separately but simultaneously:

$$a_1 = \frac{a_{u1} c_1 x}{(1-x)[1+(c_2-1)x]} = \frac{a\beta a_u c_2 x}{(1-x)[1+(ac_2-1)x]}$$

$$a_2 = \frac{a_{u2} c_2 x}{(1-x)[1+(c_2-1)x]} = \frac{(1-\beta) a_u c_2 x}{(1-x)[1+(c_2-1)x]}$$

where we have denoted the relative pressure of the vapour by x and have taken into account the relations following from our model:

$$a_{u1} = \beta a_u, \quad a_{u2} = (1-\beta)a_u$$

The resulting overall isotherm is then:

$$\frac{a_1 + a_2}{a_u} = \frac{a}{a_u} = \Theta = \frac{c_2 x}{1-x} \left[\frac{a\beta}{1-(ac_2-1)x} + \frac{1-\beta}{1+(c_2-1)x} \right] =$$

$$= \frac{c_2 x}{1-x} (Q_1 + Q_2) = \frac{c_2 x}{1-x} Q$$

Θ being the adsorbed amount expressed in fractions of the unimolecular coverage, Q_1 and Q_2 the respective terms in the foregoing brackets and $Q = Q_1 + Q_2$. In the "linearized" form:

$$\frac{x}{(1-x)\Theta} = \frac{1}{c_2 Q}$$

According to our program, this latter expression has to be tested as to whether it gives a linear plot. This test was carried out numerically for a median value $c_2 = 50$, for three different assumed inhomogeneities. The results are summarized in Table I, containing the figures resulting for Q_1 , Q_2 , Q , $1/50 Q$ and in the fifth row of each group the differences between neighbouring values of the last expression (under Δ), from which the constancy or variability of the slope of the curve can be estimated.

As may be seen from the table, with $a = 10$ and $\beta = 0.05$, the slope is quite constant between $x = 0.15$ and 0.35 , but in view of the experimental uncertainties, we might get a practically constant slope from $x = 0.05$, and certainly from 0.10 on. By increasing the assumed inhomogeneity either by taking a higher value for a (20) or for β (0.10), the situation remains essentially the same, though a slight drift of the slope appears throughout, more markedly in the latter case, when not the difference in the net heats of adsorption but the fraction of the more active surface has been increased. Below $x = 0.05$ the slope is decidedly greater.

Table I

$x =$	0,025	0,05	0,10	0,15	0,20	0,25	0,30	0,35	0,40
$c_2 = 50 ; a = 10 ; \beta = 0,05$									
	2								
$Q_1 =$	0,037106	0,019268	0,009823	0,006592	0,004960	0,003976	0,003317	0,002846	0,002493
$Q_2 =$	0,426966	0,275362	0,161016	0,113772	0,087963	0,071698	0,060509	0,052341	0,046116
$Q =$	0,464072	0,294630	0,170839	0,120364	0,092923	0,075674	0,063826	0,055187	0,048609
$1/50Q =$	0,043096	0,067881	0,117069	0,166177	0,215234	0,264291	0,313348	0,362404	0,411454
$A =$	0,024785	0,049188	0,049108	0,049057	0,049057	0,049057	0,049056	0,049050	
	$\bar{B} = 0,98114; \bar{A} = 0,01901; 1/q = \bar{A} + \bar{B} = 1,00015; c_{\text{eff.}} = 52,61$								
$c_2 = 50 ; a = 20 ; \beta = 0,05$									
$Q_1 =$	0,038498	0,019627	0,009910	0,006629	0,004980	0,003987	0,003325	0,002851	0,002496
$Q_2 =$	0,426966	0,275362	0,161016	0,113772	0,087963	0,071698	0,060509	0,052341	0,046116
$Q =$	0,465464	0,294989	0,170926	0,120401	0,092943	0,075685	0,063834	0,055192	0,048612
$1/50Q =$	0,042967	0,067799	0,117009	0,166111	0,215187	0,264253	0,313312	0,362371	0,411431
$A =$	0,024832	0,049210	0,049102	0,049076	0,049066	0,049059	0,049059	0,049050	
	$\bar{B} = 0,98130; \bar{A} = 0,01893; 1/q = \bar{A} + \bar{B} = 1,00023; c_{\text{eff.}} = (\bar{A} + \bar{B})/\bar{A} = 52,84$								
$c_2 = 50 ; a = 10 ; \beta = 0,10$									
$Q_1 =$	0,038498	0,019627	0,009910	0,006629	0,004980	0,003987	0,003325	0,002851	0,002496
$Q_2 =$	0,404494	0,260869	0,152542	0,107784	0,008333	0,067925	0,057324	0,049586	0,043689
$Q =$	0,442992	0,280496	0,162452	0,114413	0,088313	0,071912	0,060649	0,052437	0,046185
$1/50Q =$	0,045247	0,071302	0,123113	0,174805	0,226467	0,278118	0,329766	0,381410	0,433041
$A =$	0,026155	0,051811	0,051692	0,051662	0,051651	0,051648	0,051644	0,051631	
	$\bar{B} = 1,03302; \bar{A} = 0,01986; 1/q = \bar{A} + \bar{B} = 1,05288; c_{\text{eff.}} = (\bar{A} + \bar{B})/\bar{A} = 53,02$								

After having ascertained that a certain but not too great inhomogeneity of the surface does not materially disturb the linearity of the BET plot in the usually used region of relative pressures, we have next to examine whether the unimolecular coverage computed from the practically linear section is equal to the true value, and how the apparent constant $c_{\text{eff.}}$ is related to c_2 . For the true values we have, with the average intercept \bar{A} and slope \bar{B} pertaining to the practically linear section:

$$\frac{xa_u}{(1-x)a} = \bar{A} + \bar{B}x$$

and for the apparent values:

$$\frac{xa'_u}{(1-x)a} = \frac{1}{c_{\text{eff.}}} [1 + (c_{\text{eff.}} - 1)x]$$

By dividing the respective sides of these equations with one another and putting $q = a'_u/a_u$, the following relation is obtained:

$$\frac{1}{qc_{\text{eff.}}} + \frac{c_{\text{eff.}} - 1}{qc_{\text{eff.}}} x = \bar{A} + \bar{B}x$$

and the values of q and $c_{\text{eff.}}$ can be computed according to the standard procedure followed in the evaluation of BET plots, by the relations:

$$1/q = \bar{A} + \bar{B}; \quad c_{\text{eff.}} = \frac{\bar{A} + \bar{B}}{\bar{A}}$$

The results obtained in this way are also included in Table I. The values of $c_{\text{eff.}}$ are throughout somewhat higher than c_2 , and this is exactly what one would expect. More surprising are the values for q . As may be seen, in the first two cases ($a = 10$ resp. 20 ; $\beta = 0.05$), this ratio is almost exactly 1, which means that such an extent and sort of inhomogeneity does not affect surface area determinations. In the third case, however, the apparent unimolecular coverage is by about 5 per cent less than the true one, but as mentioned already, the section of the plot, which may be regarded as being practically linear, is decidedly shorter and beginning at higher relative pressures.

Though the model treated here is oversimplified, it seems safe enough to draw the general conclusion that the BET method yields reliable results for the surface area when the surface of the solid is not too inhomogeneous. The experimental criterion for this is a reasonable length of the practically linear section of the usual BET plot, and mainly its beginning at $x = 0.05$ or 0.1 to the worst.

We hope to have contributed with these considerations to strengthen the confidence put in the reliability of the BET method when applied with the necessary care. Incidentally, it may be pointed out that this confidence is sustained also by the fact that another independent method, devised by the author and his collaborators has yielded practically identical surface areas whenever a direct comparison of the two methods was made [1].

Summary

By numerical calculations made on a simplified model of the real adsorbent surface (but two distinct values of surface activity) it is shown that inhomogeneity up to a certain extent does not affect the reliability of the BET method for computing specific surface areas.

References

1. SCHAY, G.—NAGY, L., *Journ. Chimie Physique*, **58**, 149 (1961); *this journ.*, **4**, 95 (1960); *Magyar Kémikusok Lapja*, 173 (1964).

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