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Is the BET equation applicable to microporous adsorbents?

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1. INTRODUCTION

Although most scientists are aware that the application of the BET method to microporous adsorbents is essentially erroneous, we must also recognize that most of us find it convenient, year after year, to use this popular method even when we know or suspect the existence of micropores. Its success probably has much to do with the fact that it eventually provides us with an "area", which is a quantity easily available to our imagination, especially since it is usually expressed in m^2 , an order of magnitude which we can daily see, touch and imagine. Now, since we all expect science to do something more than to feed imagination, *is it a rigorous and sound way to apply the BET method in the case of microporous materials?* This is the issue we wish to address hereafter. For that purpose, after recapping the basic limitations of the BET method, we propose to examine whether and how it can still provide reproducible, meaningful and useful information about microporous adsorbents.

2. WHY NOT SIMPLY USE THE LANGMUIR EQUATION WHEN THE ADSORBENT IS KNOWN TO BE MICROPOROUS ?

Micropores tend to provide Type I gas adsorption isotherms (in the IUPAC classification for *physisorption* isotherms [1]), similar to the Langmuir isotherm. It therefore looks natural and simple to apply the Langmuir equation to the above isotherms. Now, this is not really suitable for the following reasons:

1/ The Langmuir equation was clearly established for the specific case of *chemisorption in a single layer* in free contact with the gas phase; this is quite different from adsorption in micropores, where adsorption is not necessarily limited to adsorption sites (simple filling can occur) and where most of the adsorbed phase is not in contact with the gas phase.

2/ *If the material is purely microporous*, its isotherm is perfectly Type I. In this case, *the horizontal plateau exactly provides the micropore capacity*. There is no need for any further assumption and therefore no need for applying the Langmuir equation.

3/ *Most often, the isotherms obtained for microporous materials are composite, i.e.* mixing either Types I and II (resulting from micropores and external surface, respectively) or Types I and IV (resulting from micropores and mesopores, respectively). Now, the Langmuir equation does not apply to composite isotherms, simply because the Langmuir theory was established for a single phenomenon (chemisorption in a single layer). It follows that, for composite isotherms, the calculated "Langmuir monolayer" is never completed within the pressure range in which it is calculated (as usual for true Langmuir isotherms), but at a higher pressure, which is a sign of inconsistency.

We therefore conclude that something else than the Langmuir equation is needed to interpret the adsorption isotherms for microporous materials. Is the BET equation the good answer?

2. WHY IS THE BET METHOD ALSO LIMITED IN CASE OF MICROPOROUS MATERIALS?

The BET method can be considered, essentially, as a mathematical means to analyse the adsorption isotherm in order to derive a “monolayer capacity” and then a surface area. This analysis requested a number of assumptions, of which we just remind the main ones [2]:

1/ Adsorption takes place on a *uniform surface* and the energies of adsorption of all molecules in the first layer are identical

2/ *Each molecule adsorbed* in a layer is itself a potential adsorption site for the next layer

3/ There is *no steric limitation to the thickness* of the multilayer

4/ It is *only for the first layer* that the differential energy of physical adsorption E_1 is higher than the energy of liquefaction E_L

5/ *Interactions between molecules adsorbed in the same layer do not play any part* in the adsorption equation

6/ The second and further layers start to build up before the completion of the first one

If the application of the BET equation was to be limited to the type of adsorbent assumed above (an energetically uniform surface and no pores), there would probably not be many people to remember it to-day. In reality, most interesting adsorbents are either heterogeneous from the viewpoint of adsorption energy, or porous, or both. Finally, assumptions 1/ and 2/ are exceptionally fulfilled, if ever, assumption 3/ does not hold for porous adsorbents, assumption 4/ is an acceptable approximation, assumption 5/ is incorrect, and, finally, only assumption 6/ is usually right ... except for those ultra-micropores whose width cannot accommodate more than two molecules. Moreover, at the time of deriving a surface area from the monolayer content, three other assumptions are used:

7/ All molecules in the monolayer cover the same area σ

8/ The arrangement of these molecules is assumed to be a hexagonal close-packing

9/ The molecular cross-sectional area σ can be derived from the density of the adsorptive in the bulk liquid state

The above three assumptions again raise a number of questions, especially when the BET method is applied to adsorbents containing micropores (in the presence or not of larger pores). It follows that the questions we wish to address in this paper are the following:

1/ Irrespective of its meaning, is the BET “monolayer capacity” a *reproducible* quantity?

2/ Is *adsorption calorimetry* on microporous adsorbents helpful to evaluate the BET energetic assumptions (1/, 4/ and 5/)?

3/ Since assumptions 3/, 6/, 7/, 8/ and 9/ do not hold for a microporous adsorbent, what meaning can we then give to the “*BET surface area*”? Should we complement this concept by another one to make it useful for industrial applications of microporous adsorbents?

3. IS THE BET “MONOLAYER CAPACITY” OF A MICROPOROUS MATERIAL A REPRODUCIBLE QUANTITY?

One could think that the problem of reproducibility of the BET “monolayer content” is a simple matter of experimental accuracy. In reality, the problem does not lie there anymore since, with modern gas adsorption equipment and with careful and reproducible outgassing [3,4], one can obtain reliable and satisfactory data. The issue is that once a reliable adsorption isotherm is obtained it may still lead to several values of the BET “monolayer content”. This is due to the fact that the BET equation must be applied to a straight part of the BET plot, but that *various portions of that plot may look linear*, so that, in the absence of any other criteria, their choice can be purely subjective.

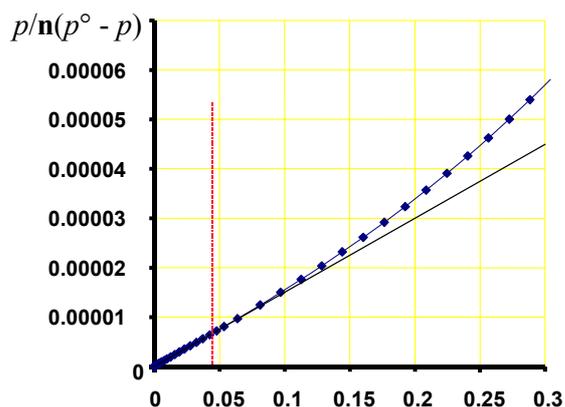


Fig. 1. BET plot for Ar on Zeolite 13 X at 87 K

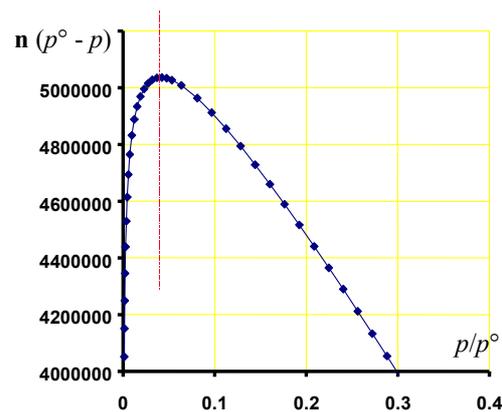


Fig. 2. Plot of the term $n^a(p^\circ - p)$ vs. p/p°

The simplest way to avoid subjectivity could be to decide for ever on a pressure range in which to carry out the calculation. This was proposed by Brunauer with a relative pressure range from to 0.05 to 0.35 [1] which is indeed well suited, in general, in the absence of micropores or of any other type of strongly adsorbing sites, *i.e.* for adsorption isotherms of type II or IV. Now, in the case of materials containing micropores, such a broad pressure range largely exceeds the real range of linearity of the BET plot, as illustrated by the plot given in Fig 1 and obtained for the adsorption of argon on a zeolite 13X at 87 K.

This leads us to the selection of an *appropriate pressure range for each adsorbent* with the problem that the above "linearity criterion", which is essential, is unfortunately not self-sufficient, since several portions of the BET plot can fulfil this requirement. One can indeed consider, in Fig 1, several relative pressure ranges in which the plot is reasonably linear: for instance 0.01-0.2, 0.02-0.05 and 0.05-0.15, the latter being the most commonly used. The resulting monolayer contents are **40, 45 and 52** $\mu\text{mol}\cdot\text{g}^{-1}$, respectively, *i.e.* a variation of up to 30%! Hence the need of other *criteria leading to the "objective choice" of a single linear portion of the BET plot*. Those two selected hereafter are aimed to provide such a single choice:

1/ The straight portion selected should have a *positive intercept on the ordinate*, *i.e.* no negative value of "C", which would be meaningless. In Fig 1, one sees that this criterion eliminates the upper half portion of the BET plot represented there

2/ *The term $n^a(p^\circ - p)$ should continuously increase together with p/p°* ; if not, the pressure range should be narrowed. In Fig 2, derived from the same data as Fig 1, one sees that this criterion now eliminates the whole relative pressure range above 0.04. This criterion can be considered as a self-consistency criterion for the modified BET equation proposed by Keii *et al.* [5] and used by Parra *et al.* in the case of microporous carbons [6].

Although the above criteria look sensible and consistent with each other, we don't claim that they allow to reach "the" actual surface area of the sample (which, furthermore is never really accessible by the BET method in the case of microporous materials, as developed later on in this paper). We simply think that these criteria, easy to apply and to introduce in the automatic processing of data (especially in the software of modern adsorption equipment) can make easier and safer the comparison between BET results obtained in different places. We have been using them systematically, for years, and never found any problem in their application [7,8]. Furthermore, the two checks of consistency hereafter were systematically applied and we never saw them failing:

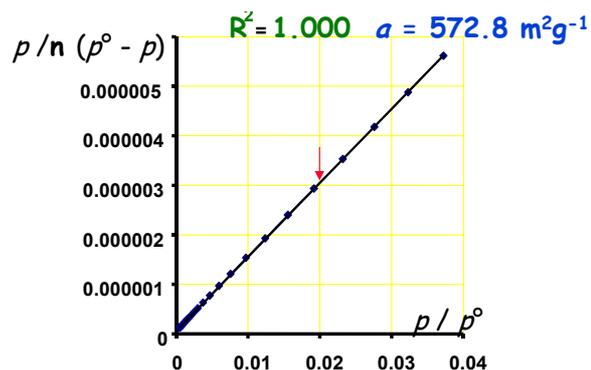


Fig. 3. BET plot in the finally selected pressure range for Ar on Zeolite 13 X at 87 K

a/ The calculated BET monolayer capacity, when reported on the adsorption isotherm, should correspond to a relative pressure p/p_m° located within the pressure range selected for the calculation

b/ Alternatively, the relative pressure p/p_m° for the monolayer capacity can be recalculated from the value of “C”, through the BET equation, after stating $n^a = n_m^a$. The calculated p/p_m° and the experimental one (read on the isotherm, like in the previous check) should not be apart from each other by, say, more than 10%.

Figure 3 shows the portion of the BET plot finally selected with help of these criteria for our Ar/13 X system. The calculated BET monolayer capacity is now **47.6** $\mu\text{mol.g}^{-1}$, whereas it previously ranged between **40 and 52** $\mu\text{mol.g}^{-1}$.

4. IS THE BET APPROACH REASONABLY SUPPORTED BY CALORIMETRY?

For non-porous adsorbents, it was early shown, by adsorption calorimetry, especially by Isirikyan and Kiselev [9] and by Beebe [10] that, on an energetically homogeneous surface like graphitized carbon, the part of adsorbate-adsorbate interactions can hardly be ignored. It was also seen, especially on common oxides like silicas [11] or titanias [12], that the surface of these technological adsorbents is energetically heterogeneous so that they do not lend themselves to the assumption of a constant energy of adsorption on the first layer. Most fortunately, the effects of the adsorbate-adsorbate interactions and of the surface heterogeneities upon the energies of adsorption partly compensate each other, which therefore supports, in some respect, the simultaneous use of these simplifying assumptions in the BET theory.

Now, what happens for microporous adsorbents? We shall illustrate the state of affairs by four examples. For each of them, we report a figure providing simultaneously the adsorption isotherm and the curve of adsorption enthalpy, both determined during the same experiment.

Fig. 4 gives the results for methane on Silicalite at 77 K. Like in the figures to follow, the adsorption isotherm starts from the bottom left, with its initial and steep portion merging within the ordinate axis. The calorimetric curve starts from the bottom right and makes use of the same ordinate, which provides the amount adsorbed, whereas the differential enthalpy of adsorption is indicated in the scale on top of the figure. One should first notice the high and constant value of the enthalpy of adsorption over most of the experiment : -17 kJ.mol^{-1} , more than twice higher than the enthalpy of liquefaction. In spite of the appearance, this does not support the BET assumption of a constant adsorption energy on the first layer: we know indeed Silicalite to be microporous, so that what occurs is not the completion of a monolayer but the filling of micropores in volume. Since most of the filling (up to 4 mmol.g^{-1}) takes

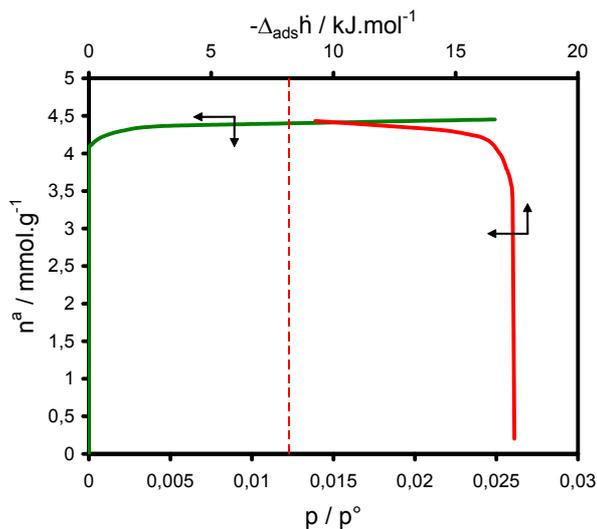


Fig.4. Methane on Silicalite at 77 K: adsorption isotherm (left) and calorimetric curve (right)

place under a pressure lower than 10^{-2} mbar, it should also be pointed out that only direct calorimetric experiments are able to assess the adsorption enthalpies, whereas the isosteric method would not be here reliable at all (because it is too sensitive to small errors in pressure or to small amounts of less adsorbed impurities like nitrogen or oxygen). Finally, one is struck by the symmetrical shape of the two curves, which shows that the enthalpy of adsorption drops just once the plateau is reached on the Type I isotherm, *i.e.* once the micropores are filled. Applying the BET equation with the criteria given in section 3 leads here to an apparent monolayer content of 4.2 mmol.g^{-1} , corresponding, as usual, to the “knee” of the isotherm. The calorimetric curve shows that *this apparent BET monolayer content exactly corresponds to the most strongly adsorbed portion of the adsorbate.*

Fig. 5 also reports results obtained with methane adsorption at 77 K on a micron-sized ZSM-48 sample whose external surface is approximately $50 \text{ m}^2 \text{ g}^{-1}$ and whose pore width is 5-6 nm. In spite of the still ordered porous structure, the picture is quite different from above, both for the isotherm and for the calorimetric curve. The adsorption isotherm is clearly composite (Type I + Type II), which is easily explained by the existence of an appreciable external

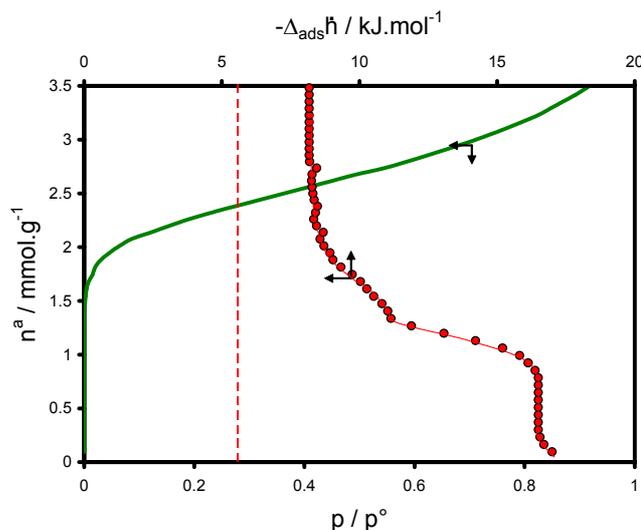


Fig.5. Methane on Zeolite ZSM-48 at 77 K: adsorption isotherm (left) and calorimetric curve (right)

surface, adding its effect to that of micropores.

The calorimetric curve is also more complicated than previously, since now three steps can be distinguished:

- step 1 (the initial vertical part, in the bottom right) corresponds to the filling of the micropores with the same high enthalpy of adsorption as for Silicalite. The small “tail” just before reveals the existence of a small amount of defects or heterogeneities which were not visible (and probably did not exist) in the case of Silicalite
- step 2 (starting around 12 kJ.mol^{-1} and continuing close to the enthalpy of liquefaction) corresponds to the formation of the statistical monolayer (*i.e.* simultaneous formation of first and upper layers) on the external surface
- step 3 (final vertical part, at the level of the enthalpy of liquefaction) exclusively corresponds to the formation of the upper layers (the “multilayer”)

Here again, the apparent BET monolayer content (1.9 mmol.g^{-1}) exactly corresponds to the most strongly adsorbed portion of the adsorbate.

Fig. 6 reports results for the adsorption of nitrogen on a microporous carbon (charcoal 26, from Sutcliffe Speakman, obtained from NPL) at 77K. We see some features in common with the previous example: composite Type I + Type II isotherm and at least two steps in the calorimetric curve. Now, the initial decay of the adsorption enthalpy is much stronger and longer than on the previous example, in part because of the higher heterogeneity of the activated carbon and in part because the permanent quadrupole moment of the nitrogen molecule makes it more sensitive to heterogeneities than the methane molecule.

Fig. 7 shows the results obtained for the adsorption of argon on a microporous silica at 77 K. We get again a composite isotherm, whereas the steadily decreasing enthalpy of adsorption indicates a broad range of micropores, starting with ultramicropores (as it was the case for the activated carbon).

5. FINALLY, IN THE PRESENCE OF MICROPORES, CAN THE BET EQUATION BE MEANINGFUL AND USEFUL?

Everybody agrees on the fact that *the sole concept of “BET monolayer content” is inadequate* in the presence of micropores where a monolayer has no clear physical or theoretical meaning. Now, if we do not want to lose, in the case of microporous materials, the benefits of the BET equation (recapped in the introduction and in section 3), we need to introduce another concept.

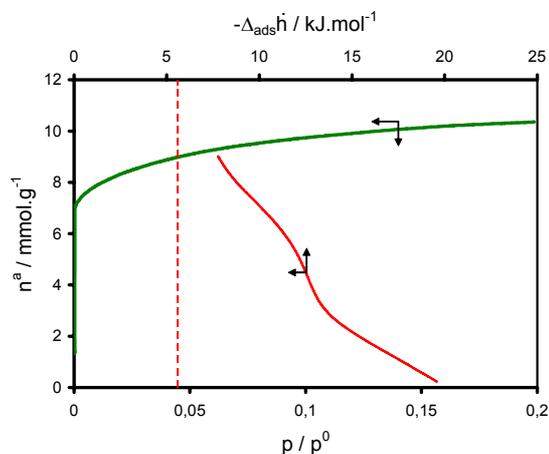


Fig.6. Nitrogen on microporous carbon at 77 K: adsorption isotherm (left) and calorimetric curve (right)

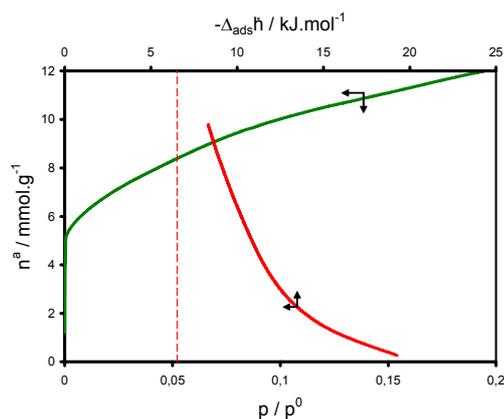


Fig.7. Argon on microporous silica (Davison 950) at 77 K: adsorption isotherm (left) and calorimetric curve (right)

This is fortunately offered by the calorimetric experiments which suggest that the “BET monolayer content” physically corresponds to an energetically strong retention. This quantity, provided by the BET equation, could therefore be called safely the “*BET strong retention capacity*”. This quantity includes two parts, which are the “*micropore capacity*” and the “*monolayer content*” on the non-microporous portions of the surface. The latter, which provides the “external (*i.e.* non-microporous) surface area” is easily assessed by means of the α_S or t methods, without even requesting the very low part of the adsorption isotherm. The α_S method is to be preferred when one wishes to carry out a more detailed analysis of the micropores and when the low pressure range of the adsorption isotherm is available. Conversely, if one only wishes to assess a reliable external surface area, he will probably find it simpler to use the t method: this can indeed easily be done in a software, after introducing the appropriate multilayer equation, like the Harkins and Jura t -curve equation [13]. The recommended succession of calculations is therefore:

1/ Calculation of the “*BET strong retention capacity*”, $n_{m(BET)}^a$, with help of the BET equation and of the criteria given in section 3

2/ Calculation of the “*external surface area*”, a_{ext} , with help of the α_S or t methods, and of the corresponding external monolayer content, $n_{m(ext)}^a$

3/ Derivation of the “*micropore capacity*”, by subtracting $n_{m(ext)}^a$ from $n_{m(BET)}^a$

(It may be worth pointing out that the micropore *capacity* (for a given adsorbative) is highly meaningful and close to physical reality, which is not the case for the micropore *volume* whose calculation relies on the unknown packing of the adsorbate in the micropores)

4/ Along the same lines and always for a given adsorbative, determination of the “*saturation capacity*” from the amount adsorbed at saturation (*i.e.* on the final plateau, usually beyond $p/p^0 = 0.9$)

The four quantities above can be determined systematically and automatically by a software, whatever the adsorbent: in the presence of micropores, they should all be meaningful, whereas in their absence the derived “*micropore capacity*” should simply be negligible. It is only in the latter case that the concept of “BET monolayer content” can be restored and used without ambiguity.

Conclusions

1. Because it was not devised for that, the BET method *should not be applied blindly* to adsorbents containing micropores (and the Langmuir equation even less).

2. Beyond the "linearity criterion" of the BET plot, two other criteria are found necessary, especially in the presence of micropores, to draw the specific advantage of the BET equation, *i.e.* to reach a single and reproducible value for the so-called "monolayer content".

3. Calorimetric data for adsorption on microporous adsorbents confirm the fact that the BET monolayer content, calculated with the above criteria, mostly corresponds to the adsorbate in energetical interaction with the surface.

3. For adsorbents containing micropores, the concept of "BET monolayer content" is misleading and could well be replaced by that of "*BET strong retention capacity*". This concept includes the adsorbate present in the micropores together with the content of the statistical monolayer on the non-microporous portion of the surface.

4 Finally, we suggest that instead of the "absolute" concepts of BET surface area (inadequate for micropores) or microporous volume (which is never correctly assessed, because of the unknown packing of the adsorbate), one should more safely use the concepts of "*BET strong retention capacity*", "*external surface area*", "*micropore capacity*" and "*saturation capacity*" which are close to physical reality and therefore suitable for sound interpretation and practical application.

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