

Review

The use of nitrogen adsorption for the characterisation of porous materials

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Abstract

Problems, which may arise when low-temperature nitrogen adsorption is used for the characterisation of porous materials, are discussed in this review. Continuous or discontinuous manometric techniques can be employed for nitrogen adsorption measurements at 77 K. For pore structure analysis, the nitrogen adsorption–desorption isotherms should be determined over the widest possible range of relative pressure, while allowing for slow equilibration and other operational problems, particularly at very low pressures. In spite of its artificial nature, the Brunauer–Emmett–Teller (BET) method is still used for the determination of surface area. In principle, nitrogen isotherms of Types II and IV are amenable to BET analysis provided that pores of molecular dimensions are absent and that the BET plot is obtained over an appropriate range of the isotherm. An empirical method based on the application of standard adsorption data is useful for checking the validity of the BET-area. All the computational procedures for pore size analysis have limitations of one sort or another. The various assumptions include an ideal pore shape, rigidity of the structure and an oversimplified model (capillary condensation or micropore filling). The derived pore widths and pore volumes should be regarded as effective (or apparent) values with respect to the adsorption of nitrogen at 77 K. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gas adsorption is of major importance for the characterisation of a wide range of porous materials. Of all the many gases and vapours, which are readily available and could be used as adsorptives,

nitrogen has remained universally pre-eminent. With the aid of user-friendly commercial equipment and on-line data processing, it is now possible to use nitrogen adsorption at 77 K for both routine quality control and the investigation of new materials. In view of the importance of the technique, it is of interest to trace its historical development.

The earliest reported studies of the adsorption of nitrogen and other gases at liquid air temperature

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(~ 88 K) appear to have been made by Dewar [1] and Ramsay [2] in the course of their investigations of the composition of the atmosphere and the separation of the noble gases. There followed a number of other low-temperature studies of the adsorption of nitrogen and other gases by charcoal, including an extensive series of measurements over a wide range of temperature by Ida Homfray [3].

Langmuir's monumental work on monolayer adsorption [4] resulted in renewed interest in the interpretation of adsorption data. According to the Langmuir model (now called 'ideal localised monolayer adsorption'), the amount adsorbed at the plateau of a Type I isotherm corresponds to complete monolayer coverage. In the early 1930s, it was realised that multilayer adsorption of nitrogen can occur at liquid nitrogen temperature (77 K). The work of Benton and White [6] prompted Brunauer and Emmett [7] to adopt gas adsorption for the determination of surface area. They found that the adsorption isotherms of nitrogen and several other gases on an iron synthetic ammonia catalyst were all of similar sigmoidal shape (later designated, Type II). Empirical evidence indicated that the changeover from monolayer to multilayer adsorption occurred at the beginning of the middle, nearly linear, section of the isotherm (termed Point B). In 1938, the publication of the Brunauer–Emmett–Teller (BET) theory [8] appeared to provide theoretical support for this proposal since the uptake at Point B was found to be in good agreement with the BET monolayer capacity, n_m .

To obtain the specific surface area, a , from n_m , Brunauer, Emmett and Teller followed Emmett and Brunauer [9] in assuming the completed monolayer to be in a close-packed state. In spite of the perceived theoretical limitations of the BET model, the BET-nitrogen method soon became established as a standard procedure for surface area determination.

The use of nitrogen adsorption for pore size analysis dates from the late 1940s. It is based on the application of the Kelvin equation, with a correction for the multilayer thickness on the pore walls. One of the first computational procedures was proposed by Shull [10] but the method [11]

devised by Barrett, Joyner and Halenda (BJH) in 1951 remains the most popular way of deriving the pore size distribution from an appropriate nitrogen isotherm.

Unfortunately, over a long period many investigators overlooked Langmuir's caveat [4] that the equations he derived for plane surfaces are not applicable to such highly porous adsorbents as charcoal. It was not until much later that it became clear that the plateau of a Type I isotherm is generally associated with the completion of pore filling [5] rather than monolayer coverage. The importance of Langmuir's comments concerning the nature of adsorption in narrow pores was appreciated by Dubinin [12], who argued that very narrow pores (micropores of width < 2 nm) are filled at low relative pressure by a volume-filling process. It is now widely accepted [13] that this micropore filling mechanism is not the same as capillary condensation in mesopores with widths in the range 2–50 nm [5].

In the light of recent developments in computer simulation, density functional theory and adsorbent design [14], it may seem surprising that the BET and BJH methods are still used for the evaluation of surface area and pore size distribution! It is the aim of this short review to throw some light on this situation.

2. Methodology

Gas adsorption manometry is the method generally used for the determination of adsorption isotherms of nitrogen at the temperature of liquid nitrogen (~ 77 K). This type of approach was known as a 'volumetric determination' (or alternatively as the 'BET volumetric method') since it originally involved the measurement of gas volumes, before and after adsorption. However, it has been pointed out [14] that it is no longer appropriate to use the term 'volumetric' since the amount adsorbed is now generally evaluated by measuring the change of gas pressure, rather than a change in gas volume.

Two different operational procedures can be used for the determination of the adsorption isotherm. The conventional technique makes use

of a discontinuous, point-by-point procedure. Successive amounts of the adsorptive are introduced and at each stage the system is allowed sufficient time to attain equilibrium, which of course corresponds to a series of single points on the adsorption isotherm. The continuous approach is more recent and is dependent on the principle of ‘quasi-equilibrium’ [14,15]. In this case, the introduction of the adsorptive must be slow enough to provide a continuous ‘equilibrium’ isotherm (i.e. with an infinite number of points). If properly used, the continuous manometric procedure has the great advantage that it is possible to reveal inconspicuous features (e.g. sub-steps), which may not be detectable by the discontinuous method [14].

In general, commercial manometric equipment has not been designed for measurements at very low relative pressures. Since the filling of micropores of molecular dimensions (i.e. ultramicropores) takes place at $p/p^0 < 10^{-4}$, it is necessary to undertake high-resolution adsorption (HRADS) measurements [14,16,17] to investigate ‘primary micropore filling’. Inverse gas chromatography is another technique, which can be used to obtain adsorption data at low pressures. The filling of wide mesopores occurs at high p/p^0 and here the control of temperature becomes important [13]. It is necessary to pay particular attention to the choice and calibration of the pressure gauges, the verification of adsorption equilibrium and the conditions of outgassing.

The aims of outgassing are two-fold [14] — (a) to reach a well-defined intermediate state by the removal of physisorbed molecules; (b) to avoid any drastic change as a result of ageing or surface modification. Conventional vacuum outgassing is the generally preferred technique, but with fine powders, there is always a risk of spurting. Spurting can be avoided and changes in the adsorbent minimised by controlling the rate of outgassing by the application of a form of controlled rate thermal analysis, CRTA [15], which is also termed ‘sample controlled thermal analysis’ [17].

3. Surface area determination

3.1. The BET method

As is well known, the BET theory [8] is based on an over-simplified model of physisorption [13]. As in the Langmuir theory, the adsorbent surface is pictured as an array of equivalent sites on which molecules are adsorbed in a random manner. It is assumed that the occupation probability of a site is independent of the occupancy of neighbouring sites and that there are no lateral interactions between the adsorbed molecules (i.e. the ideal localised monolayer). The molecules in the first layer act as sites for molecules in the second layer; these in turn are sites for molecules in the third layer and so on for molecules in the higher layers. Although no lateral interactions are allowed, all layers above the first are assumed to have liquid-like properties.

In view of the artificial nature of the BET theory, it is not surprising to find that the range of applicability of the BET equation is always limited to a part of the nitrogen isotherm. The best fit rarely extends above $p/p^0 \sim 0.30$ and with some adsorbents (e.g. graphitised carbons) the upper limit is at $p/p^0 < 0.1$. It is evident that the location and extent of the linear region of a BET plot is dependent on the adsorption system (both adsorbent and adsorptive) and the operational temperature. In view of this situation, it is strongly recommended [14] that the BET monolayer capacity, n_m , should be derived from the best linear fit for that part of the isotherm which includes Point B.

A high value of the parameter C , which is associated with a sharp Point B, is an indication of strong adsorbent–adsorbate interactions. Typical C values in the range 80–150 for nitrogen at 77 K are consistent with the formation of well-defined monolayers on many non-porous and mesoporous adsorbents [13,14].

The second stage in the application of the BET method is the calculation of the specific surface area, $a(\text{BET})$, from n_m . The evaluation of $a(\text{BET})$ is, of course, dependent on the average area, σ , occupied by each molecule in the

completed monolayer. In the case of nitrogen at 77 K, $\sigma(\text{N}_2)$ is usually taken as 0.162 nm^2 , this value was originally proposed by Emmett and Brunauer [9] and was based on the assumption that the monolayer had the liquid form of close-packed structure. However, other investigators have proposed various alternative values, extending over the range $\sigma(\text{N}_2) = 0.13 - 0.20 \text{ nm}^2$ [13,14] and we are left with an apparently confused picture.

The following are inherent difficulties of the BET-method — (a) the validity of n_m is questionable; (b) the monolayer structure is not the same on all surfaces; (c) strong adsorption at very low p/p^0 may involve localised monolayer coverage and/or primary micropore filling (i.e. in pores of molecular dimensions). In principle, it is not difficult to establish whether there is a significant micropore filling contribution, but the true value of $\sigma(\text{N}_2)$ is usually unknown, especially when the adsorbent surface is heterogeneous.

3.2. Empirical methods

Since the nitrogen molecule is quadrupolar, it is not surprising to find that the structure of the nitrogen *monolayer* is dependent on the surface chemistry of the adsorbent. However, the *multilayer* structure is rather insensitive to the nature of the adsorbent [13]. Indeed, this ‘universal’ character of the nitrogen multilayer at 77 K is a useful feature [14], which is not shown by other adsorptives such as argon or krypton at 77 K. For example, nitrogen isotherms on uniform surfaces such as graphitised carbon blacks do not exhibit the stepwise character shown by argon or krypton isotherms. For this reason, it is relatively easy to use an empirical approach (e.g. the t or α_s methods) for the analysis of nitrogen isotherms [13,14].

Before the α_s method [18] can be applied, a reduced, α_s -curve must be constructed from adsorption isotherms determined on an appropriate non-porous, reference material. Thus, the adsorption at a pre-selected p/p^0 is used to convert the standard amounts adsorbed into a dimensionless α_s form. For this purpose, it is usually convenient to take $p/p^0 = 0.4$ and then $\alpha_s = n/n_{0.4}$. The reduced isotherm for the non-porous reference adsorbent is, therefore, arrived at empirically without any need

to determine the BET monolayer capacity, unlike the t -method [19]. An isotherm on a porous solid can then be transformed into the α_s -plot — n versus α_s . An unambiguous interpretation of the α_s -plot is obtained if the surface chemistry of the reference adsorbent is the same as that of the porous material under investigation.

Over the past 30 years, α_s -plots have been constructed from nitrogen isotherms determined on a wide range of porous materials [13,14,16,17,20]. The approach has been found to be particularly useful as a means of checking the validity of $a(\text{BET})$. If the initial section of the α_s -plot is linear (i.e. from the lowest measurable p/p^0) and provided that this can be back extrapolated to the origin, we may conclude that monolayer coverage has occurred on the pore walls in the same manner as on the open surface. The validity of BET-area is thereby confirmed, since the isotherm has not been distorted through primary micropore filling [13,14].

The shape of the α_s -plot also gives a useful indication of the type of pore structure [14]. Thus, an upward deviation from linearity at $p/p^0 < 0.4$ is associated with the filling of wide micropores [17] (the supermicropores of width $\sim 1-2 \text{ nm}$); whereas at higher p/p^0 , an upward deviation can be attributed to capillary condensation in mesopores. In favourable cases, it is possible to evaluate the supermicropore wall area and/or the external area [14,17].

Another useful approach is to make use of the Frenkel–Halsey–Hill (FHH) equation [13]. Nitrogen isotherms at 77 K on many non-porous oxides and carbons have been found to give linear FHH plots over a wide range of p/p^0 , corresponding to $\sim 1.5-3$ molecular layers [14]. Furthermore, the slopes of the FHH plots are in remarkably close agreement, which is consistent with the ‘universal’ nature of the nitrogen multilayer.

4. Pore size analysis

4.1. The classical approach

Capillary condensation is generally responsible for the filling of mesopores and macropores (i.e.

pores of width, $w > 2$ nm). However, capillary condensation is a secondary process since it is always preceded by multilayer adsorption on the pore walls. Thus, the onset of capillary condensation is indicated by an upward deviation from the corresponding *multilayer* (Type II) isotherm and the process is complete if a plateau is attained at higher p/p^0 . Since macropore ($w > 50$ nm) filling occurs only at very high p/p^0 , the characteristic Type IV isotherm shape is generally associated with mesoporous adsorbents. The mesopore capacity is the amount adsorbed at the plateau and the mesopore volume is then obtained by assuming the condensate density to be that of liquid nitrogen (i.e. 0.808 g cm^{-3}).

According to the classical approach [11,13], a corrected form of the Kelvin equation can be used to evaluate the pore width from the pore filling pressure. It is necessarily assumed that the pores are rigid and all of the same simple shape (cylinders or parallel-sided slits) and that the meniscus curvature is dependent on the dimensions of the pores. In the computation of the mesopore size distribution, allowance must be made for the effect of the multilayer thickness in reducing the dimensions of the free pore space available for capillary condensation.

It is generally agreed that the corrected Kelvin equation is not applicable to the filling of micropores [20]. It is not easy to establish the limiting pore size below which the equation is unreliable, but there are some indications that this may be as high as 7.5 nm [21,22]. One reason for its failure is that multilayer thickness correction is dependent on the pore width, as well as on pressure and temperature.

Various empirical procedures have been used to evaluate the micropore capacity from a Type I or a composite (e.g. Types I and II) nitrogen isotherm [13,14]. In practice, caution should be exercised in the application of any particular equation (e.g. a Dubinin–Radushkevich plot). A safer way of obtaining the micropore capacity is by back-extrapolation of the α_s -plot. Indeed, if the conditions are favourable this procedure can be used to evaluate the ultramicropore capacity and/or the supermicropore capacity.

To convert the micropore capacity into the micropore volume, it is usually assumed that the micropores are filled with a liquid-form of the adsorptive (as in mesopore filling). This assumption does not allow for the dependency of the molecular packing on both pore size and pore shape. It is recommended that the term ‘effective micropore volume’ should be used (or alternatively ‘apparent micropore volume’).

The exact shape of a Type I nitrogen isotherm (especially when plotted in the semi-log form of n vs. $\log p/p^0$) can provide a useful first indication of the range of micropores (i.e. the presence of ultramicropores and/or supermicropores) [17]. To obtain a quantitative evaluation of the micropore size distribution, it is advisable to employ a number of probe molecules of different size. The number of adsorptives can be minimised, however, by taking account of the different stages of micropore filling [14].

4.2. Density functional formulation

Over the past few years density functional theory (DFT), which in the refined form of nonlocal density functional theory (NLDF), has become an important tool for the characterisation of porous materials [21–24]. The approach is based on the established principles of statistical mechanics and necessarily assumes a model solid structure and pore topology. The pores of different size are assumed to be all of the same regular shape (e.g. cylinders or slits) and generally each pore is assumed to behave independently. The adsorbate is pictured as an inhomogeneous fluid, which is characterised by its density profile across the pore. According to the DFT theory, the solid–fluid and fluid–fluid interactions control the pore filling, which may take the form of micropore filling or capillary condensation. If the adsorbent surface is assumed to be homogeneous, the derived energetic heterogeneity can be attributed to the pore size distribution. The interpretation is evidently more complicated when the energetic heterogeneity is associated with both the surface chemistry and the pore structure [14,23].

With the availability of commercial software, DFT has become user friendly [21,23]. However, it must be kept in mind that it is of limited value unless the solid and surface structures are known and the pores are all of a similar, well-defined, shape. Much attention has been given so far to assemblies of slits between graphitic slabs, which are taken to represent porous carbons [23,24]. Another favoured structure is an assemblage of non-intersecting tubular pores as in MCM-41 [22].

4.3. Hysteresis

Hysteresis loops, which appear in the multilayer range of physisorption isotherms, are generally associated with the filling and emptying of mesopores. For many years, the desorption branch was favoured for mesopore size analysis, but this practice is now considered to be questionable since the *desorption* path may be dependent on network-percolation effects [25] or a variation of pore diameter along single channels [26]. On the other hand, the persistence of a metastable multilayer is likely to delay the condensation process on the *adsorption* branch [22], especially if the pores tend to be slit-shaped [14]. A related problem is the instability of the condensate below a critical p/p^0 , which is dependent on the nature of the adsorptive and the temperature. In the case of nitrogen at 77 K, the hysteresis closure point is never below $p/p^0 \sim 0.4$, which, therefore, corresponds to the lower limit of capillary condensation hysteresis [13].

A completely different source of hysteresis was proposed many years ago — it was postulated that swelling of the adsorbent could lead to opening up of internal areas during the course of the adsorption [27]. Very recently, Reichenauer and Scherer [28] have obtained new experimental evidence that adsorption hysteresis at high p/p^0 may be due to the contraction and slow re-expansion of the adsorbent. Their work on silica aerogels has indicated that the filling and emptying of mesopores may result in a volumetric contraction of up to 50%.

In view of the complexity of the condensation–evaporation mechanisms, one should not expect to be able to derive a reliable mesopore size

distribution unless certain conditions are met. It is recommended that the shape and location of the hysteresis loop should always be taken into account before any computation (classical or DFT) is attempted [14].

Hysteresis *loops* are rarely encountered over the monolayer–micropore filling range (i.e. in an apparently ‘forbidden’ region). One important exception is the reproducible loop at $p/p^0 < 0.2$ given by nitrogen on Silicalite I at 77 K [29], this is a well-defined loop with lower and upper boundaries. The explanation for this interesting phenomenon is still not entirely clear. It appears to be associated with a first-order phase transformation of the adsorbate within the interconnected micropore structure [14].

There are many examples in the literature of another type of low-pressure hysteresis, which does not have upper and lower boundaries. This ill-defined hysteresis is due to either the slow penetration of the adsorbate molecules into very narrow pores or a slow expansion of the pore structure [13,27]. It is, therefore, unlikely that thermodynamic equilibration has been established on any part of the adsorption–desorption isotherm.

5. Conclusions

No other adsorptive has been proposed as a suitable alternative to nitrogen for the characterisation of porous solids. With the commercial equipment now available it is relatively easy to determine nitrogen adsorption–desorption isotherms at 77 K over a wide range of p/p^0 . It is more difficult, however, to undertake measurements at very low or high p/p^0 .

The BET model is strictly incompatible with the energetic heterogeneity shown by most adsorbents. Generally, nitrogen appears to exhibit sufficient (but not excessive) specificity of adsorption to give a well-defined monolayer capacity, which can be evaluated by the BET method. For routine work, it can be assumed that the nitrogen molecules are in a close-packed ‘liquid’ state at 77 K. Caution must be exercised, however, if the C value is low (say, $C < 50$) or high ($C > 150$).

The use of an empirical method of isotherm analysis (e.g. the α_s -method) is recommended for checking the validity of the BET-area and for detecting the onset of pore filling (in ultramicropores, supermicropores or mesopores). If the conditions are favourable, it then becomes possible to evaluate the internal and/or external areas and in some cases also the effective pore volumes. Recent work [30–32] has shown that it is still possible to refine the use of standard nitrogen adsorption data and the application of the FHH equation.

In the computation of the mesopore size distribution, by application of either the modified Kelvin equation or DFT, it is necessarily assumed that the pores are rigid and of well-defined shape. The range of validity of the Kelvin equation and the interpretation of hysteresis loops remain unresolved problems. The DFT approach has much to offer if the adsorbent structure and pore shape are already known, but its value is questionable in the case of poorly ordered materials.

Nitrogen adsorption can be regarded as the first stage in the characterisation of microporous and mesoporous solids. In particular, it should not be expected to give more than a semi-quantitative evaluation of micropore pore size distribution. However, the isotherm itself is always a useful ‘fingerprint’ and derived values of BET-area and effective pore size are of value for patent specification or product control.

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