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Fundamentals of the textural characterization of catalysts

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Fundamental principles involved in the characterization of porous networks are presented through the development of three essential steps: (i) proposition of a convenient model of the porous network, (ii) recognition of the mechanisms governing the processes related to the experiments of textural determination, and (iii) interpretation of the experimental data, taking into account the two preceding steps.

Keywords: Catalyst; determination; porous texture

1. Introduction

Characterization of porous structures must be compulsory preceded by a serious effort to describe such media. A model which considers the porous network as formed by two kinds of alternated elements, sites and bonds (to be defined unequivocally afterwards), seems to be very adequate, having in mind both a perspective of the possible applications as well as a rendering account of the processes undergone by fluids within the pores during a textural determination. Although many authors have conceived the porous medium as an interconnected network, the difficulties and advances provided by such descriptions, have never been fully imagined as will be made apparent throughout this contribution. Here an original treatment, which has been gradually developed during the last ten years, is presented; the particular conception of the porous network allows a natural and direct consideration of phenomena such as adsorption, mercury porosimetry, etc. The concepts of the parameters themselves and which are the most likely to be calculated from a textural determination, are defined with the highest properness.

Section 2 constitutes an abstract presentation of our theory, describing a variety of applications and developed within a much wider context. Section 3 refers to the formal description of the model proposed to simulate the porous network. Section 4 outlines the more important effects accompanying the processes proceeding in the interior of a porous network, during the occurrence of the textural determination experiments and that should be taken very much into account. Specifically, menisci interactions during adsorption phenomena and dynamical effects occurring in mercury porosimetry are pointed out. In section 5, the above concepts are used and this part is in turn, needed in the section immediately following. A classification of porous structures is then proposed in accordance with their statistical structure. Examples of materials corresponding to each type are given and description of the associated hysteresis loop is also undertaken. Section 6 refers to the interpretation of the experimental data, and in particular to the special and important problem of the determination of pore size distribution from the adsorption of vapour in porous solids.

2. Abstract principles of the convoluted description of complex structures

Complex structures will be defined as those statistical entities constituted by units, trees, cycles and networks, which appear to be in a complete disorder but where there exist unexpected morphological laws. Physically these structures correspond to organic and inorganic polymers, formed from aggregation or coagulation processes, irregular particles, fibrous structures, porous media, foams, etc. Such entities are the product either of nature's fancy or of a high technology. Complex structures act as adsorbents, filters, membranes, separators, coalescers, agents for phase change, multiphasic electrodes, reservoirs, etc., as well as catalysts. They allow in their interior the occurrence of unlikely processes such as the incontinent transport of heat, the movement of a fluid contra natura, or accelerated and selective chemical transformations. Most recent science has been focused on such peculiarities. It will be intended to describe the most intricate morphological aspects of such structures that condition many of the observed behaviours.

Since some ten years ago we have developed a theory to describe complex objects, that may be denominated *compound description, convoluted description, dual description, site and bond theory*, etc. Intending to find the application of this theory to the establishment of the model of a porous network to be developed in the next section, in what follows the steps involved in the treatment associated to this particular theory are described in a very abstract fashion:

– To decompose the system into a collection of several kinds of entities, for instance two types of interrelated elements, "sites" and "bonds", each playing a different function in the network that must be clearly recognized.

– To identify a "metric", or a property such as size, number of repetitive units, energy, etc. that characterizes each element. In order to compare this property between the two kinds of elements, the nature of this metrics has to be the same for both sites and bonds.

– To recognize, from the very definitions of "site" and "bond", a *construction principle*: an obvious and constant inequality between the metric of each site and the metric of any of its corresponding bonds. The chains, trees and networks that fulfill the above principle are termed as *self-consistent*.

– To fix a distribution of the metric for each kind of element. The dual distribution should be established on the basis of a number of elements and normalized.

– If the distributions for sites and bonds are inappropriate or the overlap between them is considerable, then the construction principle could be violated. With the aim to preclude this event, two "self-consistency laws" appear: (i) the first law deals with the restrictions imposed to the distributions as a whole in order to find a permitted collection of sites and bonds, and (ii) the second law, of a local character, prevents the reunion of elements that may violate the construction principle.

– A balance of sites and bonds when applying a self-consistent assignation of the metric to elements directly connected, allows an easy determination of the function expressing the correlation of metrics throughout the structure. This function is similar for different types of structures.

– When the randomness in the assignation process is raised to a maximum, being self-consistency the only restriction, the structure is called *verisimilar*, or that one possessing the most likely morphology in the absence of more particular information. Correspondingly, a confrontation between a verisimilar model and experiment leads to the conviction that there are indeed physicochemical restrictions for the formation of chains, trees or networks.

– The use of this function, either in analytical methods (probabilistic) or digital (Monte Carlo), makes evident a *segregation effect* of the metric throughout the whole structure, what means that usually media are not completely random but there exist regions of reunited elements which exhibit extreme values of their metric.

Then the information rendered by the convoluted description, is not only the most detailed with respect to the distribution of the metric, for instance because this is a dual one, but also provides valuable information about the *morphology*, or the sequence of values taken by the metric across the structure, statistically expressed.

The term "dual description" that has been used in previous works is related to the consideration of two kinds of elements, nevertheless the treatment can be multivariate, as in fact occurs in the treatment of arboreous aggregates.

As for the fractal description, for example, the basic idea is the autosimilarity, in our composed description the corresponding concept is the verisimilarity: is not more important this last notion?

The composed description has been used to establish models of porous networks [1–3], capillary processes [4–6], heterogeneous surface adsorbents [7], surface processes [8], aggregates resulting from the sol–gel transition [9], polymers [10], although plausibly all the complex structures mentioned before are object of analysis under this theory.

3. A model for the porous medium

Among the traditional parameters used to describe the porous networks and that are worthy to determine by means of a great variety of techniques, one can mention the porosity, surface area, mean radius of pores, pore size-distribution, connectivity, tortuosity, constriction factor, etc. Every one of these parameters translates a capacity of the porous medium, related to the visualized applications.

There have been pointed out with more or less success relationships between these variables. Because of the great variety of these parameters, a satisfactory model will be that which allows a determination of all these capabilities from a minimal number of basic parameters. This is exactly what can be made in the convoluted description. The basic parameters are the size distributions of the void elements constituting the network and the connectivity, all will be conveniently defined in the next paragraphs, and from them all other properties can be obtained through the momenta of these distributions (first moment: mean radius; second moment: surface area; third moment: porosity; fourth moment: permeability, ...).

A convenient model of the porous structure must be sufficiently general as to embrace all the particularities of a wide variety of porous materials.

The first step consists in recognizing every porous network as constituted by two kinds of elements: *sites* (antrae, cavities) and *bonds* (capillaries, passages), that unavoidable alternate to form the connected network. The connectivity, C, is the number of bonds that meet in the same site. For simplicity, the size of each entity will be expressed using a unique quantity, R, defined in the following way: for sites, considered as hollow spheres, R is the radius of the sphere, while for bonds, idealized as hollow cylinders open at both ends (due to their function of passages), R is the radius of the cylinder.

Instead of only considering the size distribution of voids without regard to the kind of elements they belong to (sites or bonds), it would seem more appropriate to establish a double distribution. $F_S(R)$ and $F_B(R)$ will be, respectively, the normalized size distribution functions, for sites and bonds, on basis of the number of elements, so that the probabilities to find a site or a bond having a size $\boldsymbol{R}$ or smaller are, correspondingly

$$S(\boldsymbol{R}) = \int_0^{\boldsymbol{R}} F_S(R)\,\mathrm{d}R, \quad B(\boldsymbol{R}) = \int_0^{\boldsymbol{R}} F_B(R)\,\mathrm{d}R. \tag{1}$$

From the very definitions of "site" and "bond" emerges, in a natural way, the following *construction principle*: the size of any site is always bigger or at least equal to the size of every one of its bonds. Two self-consistency laws guarantee the fulfillment of the above principle. The first law establishes that bonds must be sufficiently small as to accommodate together with the sites belonging to a given size distribution,

$$\text{FIRST LAW} \qquad B(\boldsymbol{R}) \geqslant S(\boldsymbol{R}) \quad \text{for every } \boldsymbol{R}. \tag{2}$$

A second law is still required since when there is a considerable overlap between the size distributions, there appear topological size correlations between neighbouring elements. Thus, the events of finding a size R_S for a site and a size R_B for a given one of its bonds, are not independent. The probability density for the joint event $R_S \cap R_B$ to occur is

$$F(R_S \cap R_B) = F_S(R_S) F_B(R_B) \phi(R_S, R_B) . \qquad (3)$$

The second law can be expressed as:

$$\text{SECOND LAW} \qquad \phi(R_S, R_B) = 0 \quad \text{for } R_S < R_B . \qquad (4)$$

If the randomness in the topological assignation of sizes is raised to a maximum, while complying the restriction imposed by the construction principle, the most *verisimilar* form of ϕ for the correct case $R_S \geqslant R_B$ [2] is obtained:

$$\phi(R_S, R_B) = \frac{\exp\left[-\int_{S(R_B)}^{S(R_S)} \mathrm{d}S/(B-S)\right]}{B(R_S) - S(R_S)} = \frac{\exp\left[-\int_{B(R_B)}^{B(R_S)} \mathrm{d}B/(B-S)\right]}{B(R_B) - S(R_B)} . \qquad (5)$$

The topological size correlations promote a *size segregation effect*, consisting in that sites and bonds of the biggest size join together to form regions of big elements, while elements of smaller size reunite to constitute alternated regions of small entities. The more important this effect is, the greater is the overlap. The consequences of this effect in the development of capillary processes arising during the determination of porous structures by adsorption of vapours and mercury porosimetry are, without doubt, of huge importance.

Recently [5,11], we have proposed a classification of porous structures based upon the relative position of the size distributions of sites and bonds. Five types have been recognized, each exhibiting a characteristic behaviour during the processes of capillary condensation and evaporation [5,6].

4. Some relevant effects related to textural determinations

The processes taking place in antrae suffer interesting and not well known effects, which should be considered in the interpretation of the experimental results associated with textural determinations. In this section a few of these arising during adsorption of vapours and mercury penetration will be mentioned.

Menisci interaction in capillary condensation. Two antagonistic effects occur within the porous network. One is a promoter while the other one is an inhibitor of the capillary condensation: (i) condensation is impossible in a site if the liquid–vapour meniscus lacks the continuity necessary to reach a curvature smaller than the site itself, i.e. at least $C - 1$ of the delimiting bonds of a site must be previously filled with liquid; (ii) condensation in a site having an empty bond automatically provokes condensation in such a bond. These behaviours can be predicted from the ideas of Everett [12] and Kiselev and Kharnaukhov [13]. Morioka and Kobayashi [14] were the first to treat in quantitative terms the phenomenon using Monte Carlo methods. The analytical treatment is posterior [4,5]. The variety of morphologies for porous networks permits a wide spectrum of responses, as will be appreciated afterwards.

Percolative behaviour in the course of capillary evaporation. This is an inhibiting effect in the evaporation process. Unjustly, this theme is much more popular than the former one. The phenomenon has been overstated and used irrestrictly and uncritically. A desorption curve made of an initial plateau followed by a steep descent, is not proof of the percolative character of the phenomenon. On the contrary, there would be an explanation based exclusively on the geometries of the liquid–vapour menisci, which are different for condensation and evaporation [11]. Moreover, up till now percolation has been studied in completely random media, that do not resemble to most real porous bodies, as these are provided of appreciable size correlationships between neighbouring elements. This has indeed, caused an overestimation of the percolative effect.

Contact angle hysteresis in relation to mercury porosimetry. This ability of the meniscus has been pointed out as the cause of hysteresis in the penetration and retraction of mercury. This would not appear to be serious if the criteria for the equilibrium and stability of the mercury menisci within each element of the network and their mutual interaction [15] are not deeply analyzed. The minimal representation of a network, useful for a penetration analysis is a *multiplex*, i.e. a site and the bonds delimiting it. A complementary multiplex for the retraction analysis consists of a bond and its two boundary sites. Two inhibiting effects associated with a lone meniscus, provoked by the phenomenon of *canthotaxis* (a curvature variation of the meniscus while the line of tension separating the solid, liquid and vapour phases remains anchored at the union vertex between a site and a bond) are: (i) penetration of a site from a bond. When the pressure of the external liquid source is risen, there is an increase in the curvature of the meniscus due to canthotaxis. The threshold pressure for penetration of the meniscus into the site corresponds to the maximum allowable curvature, and can be as much as 30% higher than that calculated directly from the size of the bond. This means that the overcoming of the bond is not necessarily the only condition for the invasion of the site to take place. (ii) Meniscus retraction from a bond up to a site. When the pressure of the external source is diminished, the curvature of the meniscus is reduced by canthotaxis. Given a geometry of the bond–site joint, is necessary for the meniscus to acquire a negative curvature to access into the site; this requirement is associated with a state of tension of the mercury. Such a condition is not attainable in a traditional porosimeter, so that this effect is one of the causes of mercury *retention* within the structure (a second cause is the breaking up of the liquid phase during the pressure diminution, which provokes to a certain extent, the impossibility for the mercury to escape due to the lack of continuity up to the external source). Two promoting effects associated with the interaction of several menisci sharing a common site during canthotaxis are (iii) coalescence during penetration, which immediately leads to the invasion of the site and (iv) coalescence in the course of retraction to a site, which causes the immediate displacement of the meniscus. The probability of coalescence becomes greater as the overlap between size distributions grows [15].

Dynamics of mercury penetration. When the equation of movement is solved for the flow of mercury along the axis of pores of variable circular cross-section, a sub dampened regime is found. This means that menisci are induced to cross capillaries that in principle, given their small size and the external pressure of the fluid, should not be penetrated. What happens is that a great part of the kinetic energy gained by the fluid when invading a site, is transformed into a pressure energy at the mouth of the posterior bond, and then the local penetration pressure of a certain capillary is momentarily larger than the pressure of the external source, thus the fluid being able to trespass such bond. Once this obstacle is subdued, the meniscus can accelerate again in ulterior cavities to continue the same behaviour. This *tunnel-like effect* [15] shows very well that the Young–Laplace equation is insufficient to understand the true mechanism of penetration. Conner et al. [16] have found that penetration curves are not affected by the velocity of pressure change of the external source, but this does not mean that inside the porous structure the dynamical behaviour of the menisci is not promoting penetration as well as retraction, thus leading to a reduction of the hysteresis caused by such processes.

Recognition of the complexity associated to these effects and many other ones, for instance of a thermal nature [17], raises an attitude of incredulity before the pretended coincidence with respect to the experimental curves and certain analytical or digital calculations of an ingenuous nature, both in how the porous network is conceived as well as in what the menisci really undergo within the void structure.

5. The five types of porous structures and their hysteresis loops

Recently we have proposed a classification of porous structures in five types [5,11], which is based upon the relative position of the curves representing the size distributions of sites and bonds. This classification has been established having in mind the phenomenon of capillary condensation: each type exhibits a different behaviour with respect to this process, and leads to a particular appearance of the hysteresis loop. In the next paragraphs, the main characteristics of each type are briefly described.

Type I. This situation, unusual indeed, corresponds to the case of zero overlap (sizes of elements are set completely at random), with distributions widely separated from each other: the smallest site is at least twice the size of the biggest bond. This guarantees an absolute independence among the condensation processes in elements. At low vapour pressures there is condensation in bonds, the sites remaining empty. After saturating with condensate all bonds, condensation in sites starts according to the size of each element. The product of the thermal dehydration of gibbsite at 205°C [18] is a rare example of type I. The hysteresis loop is extremely wide. The ascending boundary curve (ABC) starts the ascent only when the relative pressure is close to unity, while the descending boundary curve (DBC), shows an extended plateau before that, at a well defined percolation threshold an abrupt descent takes place.

Type II. This corresponds to the general case of zero overlap, with the distributions somewhat apart. Naturally, these structures are less unusual than the preceding ones. Examples are globular structures with some irregularity but suffering of a low degree of sintering [19], as well as Vycor porous glass [20]. The hysteresis loop, although narrower than before, presents a shape similar to type I, however, the ABC starts the ascent at lower pressures due to the development of an adsorbed layer.

Type III. This type can be ascribed only to very regular porous solids, carefully prepared in the laboratory, because even if the overlap is still zero, the distributions are so close together that the size of the biggest site is less than twice the size of the smallest bond. Again the sizes of elements are distributed fully at random. Examples of these solids are globular and monodisperse aggregates of carbon [21] and silica [22]. The hysteresis loops are too narrow, showing very steep ABC and DBC, as a consequence of the intense cooperative effects arising during the condensation and evaporation processes. The DBC still shows an initial plateau due to the existence of pore blocking effects throughout the evaporation process.

Type IV. This is the most general case of intermediate overlap, surely the most frequent in real porous bodies (although this has not been the most usual of the models proposed by diverse authors). The materials are both natural or synthesized using a conventional technology, such as commercial xerogels of silica [19] and alumina [23]. Sintering promotes overlap. So this is how some products associated to type II are transformed into type IV by virtue of sintering, as for example the silica gels doped with ions and thermally treated [24], or silica–alumina microspheres steam stripped [11]. The hysteresis cycle is somewhat narrow, both ABC and DBC develop gently, and the plateau previous to evaporation is a very shallow one.

Type V. When the overlap reaches plenitude, the segregation introduced by ϕ is a maximum and the network structurates in such a way that there are homogeneous domains in which all elements possess almost the same size. Elements of rather different size are too far apart. Within each domain, condensation in bonds automatically assumes the filling of sites. Evaporation is absolutely free of percolative effects. The domains behave as independent patches. The hysteresis loop associated to type V is extremely narrow.

6. Interpretation of results

As an example of how to interpret experimental results, the technique of vapour adsorption will be dealt with with respect to the exploitation of the hysteresis loops, with the final objective of determining the pore size distribution.

Much effort has been made in the proposition of methods to determine the texture of porous materials. A central point is the determination of the "pore-size distribution". Wheeler [25] proposed an estimation of the structure from a material balance of the capillary condensate which abandons the pores during the evaporation, along the DBC. Many approaches relative to this idea have been implemented, the best known being that of Barrett, Joyner and Halenda [26]. Initially it was thought that the DBC should give better results than the ABC, if only for the reason that the hemispherical menisci present in the development of the DBC are more stable than the cylindrical ones corresponding to the ABC (Foster's delayed meniscus theory [27] and Cohan [28]). However, Cranston and Inkley [29] proved that, in many cases, the ABC provides better results than the DBC, choosing as a consistency criterion the close agreement between the specific surface area determined by the BET method [30] and their own estimation from a condensate balance. By that time it became apparent [31] that a *pore blocking effect* during the evaporation should appreciably distort the results of the pore-size distribution obtained from the DBC, providing a rational support to the election made by Cranston and Inkley. Everett [32] and Barker [33] analyzed in detail the causes of this effect and since then the process of percolation (consisting in vapour invading a structure initially saturated with liquid) has been extensively studied.

It was classical to accept that cooperative phenomena were absent during capillary condensation. As has been mentioned above, Morioka and Kobayashi [14] were the first to consider and even quantitatively estimate the extent of such phenomena by Monte Carlo methods. Inevitably, cooperative phenomena should be taken into account when the ABC is chosen to estimate the pore-size distribution.

At present the following opinion could stand: either the ABC, the DBC or both, if properly analyzed, i.e. having in mind the geometries of menisci and the cooperative phenomena, should lead to the ascertainment of the pore-size distribution curve.

The central point of this section consists in judging if it is possible to reach such an objective. Moreover, our end is a more ambitious one, since we are deeply interested to ascertain which kind of information (qualitative as well as quantitative) should be considered as the most fundamental in order to characterize mesoporous structures by adsorption methods.

Calculations of the pore-size distribution for the three simplest types are now outlined.

Conditions for phase-transition: the Kelvin equation [34] relates the *mean radius of curvature*, R_C, with the relative vapour pressure, x,

$$R_C = \frac{2\sigma v_L}{R_g T \ln(1/x)}, \qquad (6)$$

where σ and v_L are, respectively, the surface tension and the molar volume of the adsorbate, R_g is the gas constant and T is the absolute temperature. Both R_C and the meniscus shape determine together the critical size of the element for which there would be a phase transition [5,6]: (i) condensation in a site of size R_S occurs, in principle, when $R_S \leqslant R_C$. However, at least $C-1$ of its bonds need to be previously filled with condensate, to guarantee the advancement of the meniscus; (ii) condensation in a bond of size R_B, takes place in an independent way if $R_B \leqslant R_C/2$, (iii) or in an assisted manner, if at least one of the delimiting sites has been already filled with liquid and $R_B \leqslant R_C$; (iv) from a state of complete saturation, the takeover of any element by vapour requires the existence of a continuous path of this fluid from the external vapour phase up to the entrance to such element. For bonds an additional constraint is that $R_B \geqslant R_C$.

Experimental data provide θ_V, the global degree of filling of the network by liquid, in volume, as function of x. $\theta_V(R_C)$ is related to $\theta_S(R)$ and $\theta_B(R)$, the degrees of filling by capillary condensate for sites and bonds of size R, in a number of elements basis,

$$\theta_V = \frac{\int_0^\infty \theta_S(R) V_S(R) F_S(R)\,\mathrm{d}R + \frac{1}{2}C \int_0^\infty \theta_B(R) V_B(R) F_B(R)\,\mathrm{d}R}{\int_0^\infty V_S(R) F_S(R)\,\mathrm{d}R + \frac{1}{2}C \int_0^\infty V_B(R) F_B(R)\,\mathrm{d}R}, \tag{7}$$

where the volume of each element of size R, $V(R)$, has been considered and the fact that in the whole network, for each site there are $C/2$ bonds. The global degrees of filling for sites and bonds are

$$\theta_S = \int_0^\infty \theta_S(R) F_S(R)\,\mathrm{d}R, \quad \theta_B = \int_0^\infty \theta_B(R) F_B(R)\,\mathrm{d}R. \tag{8}$$

The problem of the textural characterization of a porous material consists precisely in determining F_S and F_B as functions of R. Since θ_V is the measured experimental quantity, such estimation can be made through eq. (7). The general solution seems however too complicate. Instead an analysis is presented here of the three simplest cases corresponding to the extreme types of porous structures [3].

Type I. (i) ABC: If $V_B(R)$ is negligible compared to $V_S(R)$ and in the absence of all kinds of cooperative condensation interactions, eq. (7) simplifies to give

$$S(R_C) = \frac{\int_0^{\theta_V(R_C)} \mathrm{d}\theta_V / V_S(R)}{\int_0^1 \mathrm{d}\theta_V / V_S(R)}, \tag{9}$$

an expression which can be used to determine the size distribution for sites from the ABC. (ii) DBC: A classical percolation treatment for completely random structures allows to obtain

$$B(R_C) = \frac{\theta_V^{1/C} - \theta_V^{(C-1)/C}}{1 - \theta_V^{(C-1)/C}}. \tag{10}$$

From this expression the size distribution for bonds can be determined, unless that evaporation proceeds by a mechanical failure of the condensate or by an appreciable nucleation of bubbles.

Type III. (i) ABC: The outstanding characteristic of condensation in this type of structures, is the enhanced cooperative character and the homogeneous filling of sites along the ABC. This is due to the fact that from the onset of condensation all sites (no matter the size) are already in a supersaturated state ($R_S < R_C$), so that size plays no role in this process. If it is also supposed that $V_B(R)$ is negligible, i.e. bonds are like volumeless windows without volume, a great simplification is obtained,

$$\theta_V = \theta_S \,. \tag{11}$$

Using the particular expressions for condensation in this type of solids [5], we have

$$\theta_S = \theta_B^C + C\theta_B^{C-1}(1 - \theta_B)\,, \tag{12}$$

$$\theta_B = B(R_C/2) + [1 - B(R_C/2)][1 - (1 - \theta_B^{C-1})^2]\,. \tag{13}$$

With the three former expressions, $B(R_C/2)$ is obtained in terms of θ_V, so that the bond-size distribution can be calculated from the ABC. Noticeably F_S is absent in the above equations, so that there is no way to determine the bond-size distribution from the ABC for type III materials. (ii) DBC: The strategy to follow is exactly the same as for type I, and the result is again the bond-size distribution.

Type V. In this case $F_S(R) = F_B(R) = F(R)$ and $\theta_S(R) = \theta_B(R) = \theta(R)$ both for condensation as for evaporation [5,6]. These relationships, together with a treatment very similar as that outlined for the ABC for type I, can lead to the following results:

(i) ABC:

$$S(R_C/2) = B(R_C/2) = \frac{\int_0^{\theta_V(R_C/2)} \mathrm{d}\theta_V / V(R)}{\int_0^1 \mathrm{d}\theta_V / V(R)}\,; \tag{14}$$

(ii) DBC:

$$S(R_C) = B(R_C) = \frac{\int_0^{\theta_V(R_C)} \mathrm{d}\theta_V / V(R)}{\int_0^1 \mathrm{d}\theta_V / V(R)}\,. \tag{15}$$

Consequently, both ABC and DBC lead to the same size distribution, indeed remarking the fact that for type V there is only a unique distribution.

7. Discussion

Being centered in the theme of the preceding section, and having in mind what has been mentioned in the remaining sections, we are now in a position to answer the questions raised before. In order to visualize the morphology of the porous networks in a more satisfactory way, one must unavoidably consider a double pore-size distribution. Instead of a unique treatment which involves ϕ and that seems to be very complex, three particular cases can be solved out. For type I and knowing that the volume of bonds is negligible, hemispherical menisci must be considered for both ABC and DBC. There is no reason to look for a coincidence between both results, since these render respectively the site- and the bond-size distributions.

For type III, both curves lead to the ascertainment of the bond-size distribution, and an agreement of results is due. The site-size distribution is not obtainable from the boundary curves, it could possibly be estimated from the scanning curves, that are more selective with respect to the size of the sites (cf. ref. [6], fig. 2(c)).

The method of Barrett, Joyner and Halenda is only valid for materials of type V.

Let me now provide an advice to experimentalists. The general adsorption data analysis to determine the textural characteristics of a given solid, is so difficult to undertake that, from a practical point of view, the following procedure is recommended. First, it is necessary to decide, according to the shape of the hysteresis loop and some other valuable information, e.g. electron microscopy, to which type of porous structure the solid resembles better. Afterwards the analysis should be undertaken using the particular equations corresponding to such type. The appropriate value of C and some other qualitative inferences can be obtained from additional information provided by other methods.

8. Conclusions

Up to date interpretation of adsorption data and mercury porosimetry in order to obtain textural information, has been very uncritical. The present review is a clarifying outline. However, the theoretical results advanced here require of a long confrontation with the experiment.

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