Pore-blocking and pore-assisting factors during capillary condensation and evaporation

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Abstract

Thirty-four years ago Everett [The Solid–Gas Interface, Vol. 2, Marcel Dekker, New York, 1967, p. 1055] proposed a pore-blocking factor when establishing the foundations of a non-independent domain theory (IDT) of sorption hysteresis. Such pore-blocking factor was defined as the ratio between two desorbed volumes within the same pressure range. The first volume arose from a non-independent pore structure. The second quantity was a virtual one since it represented the volume desorbed if the pores of the substrate had acted as independent domains. In fact, Everett calculated the ratio between pore-blocking factors, while not their absolute values, from experimental data proceeding from sorption results on porous glasses. The astonishing conclusion of all this preliminary work, was that blocking factors depended upon the total amount of condensate at a certain stage of a desorption process rather than on the distribution of it within the porous network. In this way, a unique pore-blocking factor curve ensued from different sorption processes such as boundary and scanning curves. Now, through the aid of simulated heterogeneous 3-D porous networks and the sorption curves thereon developed, an assessment of the above mentioned important assertion has been undertaken. Besides, a pore-assisting factor that may arise during an ascending sorption process has been treated under a similar context.
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1. Introduction

The occurrence of capillary condensation in porous networks usually brings about the incidence of two antagonistic processes [2] with respect to the uptake mechanisms that are developed inside the void entities of the substrate. One effect is a *promoter* or *assister* whilst the other one is an *inhibitor* or *delayer* of the condensation process. Interconnection between pore elements causes: (i) that some voids are invaded by condensate at larger relative pressures than those corresponding to the isolated (non-interconnected) entities; (ii) that other pores are surpassed by liquid–vapour menisci in advance to the expected pressure at which condensation in each of these lonely entities would have taken place. In this work, these ideas will be elucidated in terms of the *dual site-bond model* (DSBM) of porous materials [3]. According to this model, the void structure of porous networks can be visualised in terms of two kinds of pore elements:

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the *sites* (cavities, chambers) and the *bonds* (necks, capillaries, windows). Sites are void cavities surrounded by a number C of narrower necks; in turn, each bond is the link between two sites. C is usually called the *connectivity* or coordination number of the pore arrangement. One simple manner to envisage the structure of a porous body is to think of it as an arrangement made up by hollow spheres (i.e. sites) of varying sizes, each one connected to C neighbouring fellow cavities by means of a corresponding number of open-ended cylinders of diverse sizes (i.e. bonds).

As it has been said, when a phenomenon such as capillary condensation occurs in a porous network, assisting and delaying effects of this process may arise during the uptake of condensate by the void entities [4]. A complete overtake of a pore cavity (site) by condensate will only take place if, prior to the occurrence of this event, a continuous meniscus is already formed round the walls of the site; this process then being a delaying one. In fact, for this phenomenon to happen two conditions are required: (i) the first one is that the radius of curvature of the meniscus that is going to invade the site needs to be larger than (or at least equal to) the radius of the site itself (i.e. the site should be in a saturated or supersaturated state with respect to the formal vapour pressure indicated by the Kelvin equation for liquid filling to occur in the isolated pore); (ii) a second requirement is that either all (i.e. every C) or at least all but one (i.e. $C - 1$) of the bonds attached to the cavity possess condensate in their interiors. Condition (ii) is then associated to the formation of a continuous liquid–vapour meniscus round the site that, at due time, will sweep the whole cavity. If condensation takes place in a site after the merging of $C - 1$ menisci corresponding to surrounding liquid-filled bonds, then the remaining empty neck will be immediately trespassed by condensate; this process constituting an assisting effect. In conclusion, in a porous network subjected to capillary condensation, sites can suffer a delaying liquid replenishment whilst bonds can undergo early or assisted liquid filling; both phenomena originated by the interconnection between pore entities. Everett [1], Aristov et al. [5] and Karnaukhov and Kiselev [6] as well as Morioka et al. [7] have all previously hinted to the appearance of delaying processes during capillary condensation in porous structures.

In turn, the complementary process of capillary evaporation endures an inhibiting mechanism inside a porous medium. When the pore structure is fully occupied by liquid and as the relative vapour pressure is brought down, there is usually a delay for the vapour phase to intruding the void structure. This delay is with respect to the relative vapour pressure at which void entities would have been emptied of condensate if they had been acting as independent (i.e. non-interconnected) pore units. This delaying behaviour is often reflected on the shape of the descending boundary (DB) curve of the sorption isotherm (e.g. a type H2 hysteresis loop) through a plateau along which liquid remains in whole possession of the pores until, at some later stage of decreased vapour pressure, it disappears altogether because of the sudden emptying of the structure. This behaviour has been explained in terms of a *pore-blocking effect*, firstly introduced by Quinn and McIntosh [8]. The inherent reason for the occurrence of this delaying effect is the necessity of a liquid-filled pore entity of having a free vapour path to the outer bulk vapour phase in order to evaporate its condensate, as it was pointed out by Everett [9] and Barker [10]. However, much care has to be exercised in order to realise the real occurrence of this pore-blocking phenomenon, since the mere difference between menisci shapes during condensation and evaporation can explain the existence of a plateau along the DB curve and therefore the real extent of this phenomenon could be overestimated [2]. When the pore-blocking effect is a real one, then a percolation process (i.e. an extensive invasion of the pore structure by vapour) happens at some point of the DB curve of the sorption isotherm.

In this work, a study of both pore-assisting and pore-blocking factors, which arise during the occurrence of capillary condensation and capillary evaporation in an assortment of simulated 3-D porous networks constructed under the framework of the DSBM, will be undertaken. The dependence of these factors, on the total volume of condensate that is present in the void structure at some stage during an adsorption or desorption process, will be especially analysed. A global test, about the validity of assuming blocking and assisting factors essentially as functions of the volume of condensate, will be made when a set of primary ascending curves will be induced from a set of primary descending (PD) curves and then compared with the actual ones obtained directly from simulated sorption on 3-D porous networks.

2. Theoretical aspects

2.1. Basic definitions

The concept of pore-blocking factor is due to Everett through his preliminary exposition of sorption hysteresis occurring in interdependent pore domain structures [1]. Everett himself had made before an important study of capillary condensation and evaporation through the establishment of the independent domain theory (IDT) of sorption hysteresis [11–14]. This approach presumes that the porous structure is made by a collection of independent void units or isolated *pore domains*, as for instance a group of non-intersecting cylindrical capillaries or a collection of individual ink-bottle pores. Each pore domain is a region of void space accessible from neighbouring regions through pore constrictions and is characterised by two quantities x_{12} and x_{21}. The first one (x_{12}) is associated to the relative vapour pressure at which a pore becomes filled with condensate, while the second one (x_{21}) refers to the relative pressure at which the same void will be emptied of this liquid. The observed macroscopic irreversible sorption behaviour of a porous material is then the summation of individual pore hysteretic contributions, whose origin rests on the different mechanisms by which each void fills with condensate and empties of it and expressed in the form

$$x_{12} \geq x_{21}, \quad \forall \text{ pore entity} \tag{1}$$

In order to define both the blocking and assisting factors to be calculated in this work from simulated sorption isotherms on 3-D porous networks, it is now necessary to introduce some specific nomenclature regarding the volume of condensate that is present at some stage during the occurrence of a particular sorption phenomenon. For a given sorption path, the adsorbed volume will not be only a function of the current relative pressure x but also of some other pressure values that are attained during the development of this particular process (i.e. the volume of condensate depends on the history of the system). Volume labelling of diverse sorption processes will be as follows:

- The volume of condensate existing at some point of the ascending boundary (AB) curve of the isotherm will be labelled as $V_{AB}(0, x_u)$, this meaning that the vapour uptake during this adsorption process has

started from a relative pressure $x = 0$ up to some specific upper x_u value.

- In the same way, a DB curve will be bound to a volume $V_{DB}(0, 1, x)$. First, total liquid saturation of the porous medium is attained by pursuing the AB curve from $x = 0$ to $x = 1$, the DB process then proceeds subsequently down to a specific pressure x.

- A volume $V_{PD}(0, x_u^*, x)$ can be ascribed to a PD scanning curve since this sorption process is first developed along the AB curve up to a reversal point x_u^*, hereafter the PD process takes place down to a pressure x.

- In the case of a primary ascending (PA) scanning curve, the related volume is $V_{PA}(0, 1, x_1^*, x)$. The reversal point is located at a lower pressure x_1^* on the DB curve, then the ascending scanning process ensues up to some relative pressure x.

Volumes associated to more complicated sorption paths can also be labelled in a similar way.

2.2. Pore-blocking factor for a desorption boundary process

Most real porous bodies are configured as true networks instead of as a collection of independent pore units. These real substrata are recognised to be non-independent pore domains in which the behaviour of a pore entity towards capillary phenomena depends not only on its own characteristics but also on the states of surrounding void bodies. Therefore, it should be expected that pore structure morphology would influence very strongly the development of a capillary phenomenon, in reason of the appreciable size correlation existing between pore entities. The state of a given pore domain (i.e. liquid or vapour filled) will thus depend both on the states of its neighbouring voids as well as on the history of the system as a whole [1].

In order to study quantitatively, the extent of the pore-blocking effect in porous networks that show interdependence of domain processes, Everett suggested, for the case of the DB curve, the introduction of a pore-blocking quantity (P) (that in our case it will be labelled as P_{DB}) defined as the ratio of the following volumetric contributions

$$P_{DB}(1, x, V) = \frac{V_{AB}(0, 1) - V_{DB}(0, 1, x)}{V_{DB}^0(x, 1)} \tag{2}$$

$V_{AB}(0, 1)$ is the total saturation volume that can be attained after following the AB curve completely, $V_{DB}(0, 1, x)$ the current condensate volume existing at pressure x on the DB curve, in turn, $V_{DB}^0(x, 1)$ the amount of condensate that would have been evaporated if no interdependence between pore domains had occurred from $x = 1$ to x along the DB curve (the superscript 0 stands for independent domain behaviour). Thus, the numerator of Eq. (2) corresponds to the volume that has been desorbed from an initially liquid-saturated porous network after reaching a relative pressure x, once the system having been subjected to some capillary evaporation along the DB curve. Independent of the nature of the desorption phenomenon, a value of $P_{DB} = 1$ depicts a descending process free of pore-blocking effects, whilst $P_{DB} = 0$ portrays a situation of total blocking of the structure in which no condensate can evaporate.

Thus P_{DB}, as Everett stated, is the factor by which the potential contribution to the desorbed volume, V_{DB}^0, is reduced by the blocking established between pore entities. It is also important to say that, in general, P_{DB} depends on the current values of x and of V; unity being the maximum value that this parameter can possibly attain.

2.3. Pore-assisting factor for an adsorption boundary process

A pore-assisting factor can be defined for an AB process in terms similar to those involved in the definition of P_{DB}. A quantity Q_{AB} can be established as follows:

$$Q_{AB}(0, x, V) = \frac{V_{AB}(0, x)}{V_{AB}^0(0, x)} \tag{3}$$

$V_{AB}(0, x)$ is the actual volume of condensate that exists in the structure after an adsorption boundary process is carried out up to some pressure x and $V_{AB}^0(0, x)$ is the corresponding adsorbed volume that would have resulted if the pore domains had acted as independent units. Q_{AB} is supposed to be a function of the current pressure x and of the current volume V. In contrast to P_{DB}, Q_{AB} has an assisting character since promoted liquid-filling processes can occur during the development of the AB curve. Comparison between condensation in interdependent

and independent domains through Q_{AB} means that this coefficient should always attain values larger than unity. On the one hand, vapour in an ascending process is ubiquitous at all times in non-filled void entities, so condensation in interdependent domains is not forfeited with respect to the same phenomenon occurring in dependent domains. On the other hand, assisting processes require the cooperativeness of interconnected pore entities and this is possible in interdependent but not in independent pore domains.

Finally, it should be remarked that the assisting character of Q_{AB} is directly linked to bonds since liquid invasion of these necks could take place from condensate arriving from a neighbouring cavity; however, sites can also profit from this bond filling and eventually a percolative behaviour (the overall invasion of the void structure with liquid) may arise in some very correlated porous networks. In this way, we have that $Q_{AB} \geq 1$ and a particular value of $Q_{AB} = 1$ would mean domain independency.

2.4. Blocking and assisting factors related to primary scanning curves

The case of primary scanning curves is also an interesting one because of the appearance of assisting or delaying mechanisms during the upbringing of these processes.

First, let us consider a PD scanning path. When this curve starts at some upper reversal point x_u^*, the volume of condensate is $V_{AB}(0, x_u^*)$, then as x decreases along the desorption path some of the liquid-filled entities will be emptied of condensate, so that the volume of liquid that has been evaporated at some point x during the descending scanning course, can be related to a quantity P_{PD} defined as

$$P_{PD}(x_u^*, x, V) = \frac{V_{AB}(0, x_u^*) - V_{PD}(0, x_u^*, x)}{V_{PD}^0(x, x_u^*)} \tag{4}$$

Here again $V_{PD}^0(x, x_u^*)$ represents the volume of liquid that would have been evaporated in an independent domain system. The blocking factor P_{PD} thus depends on the pressure at the reversal point x_u^* as well as on the current values of x and of V.

Consider now a primary ascending scanning curve. At the reversal point x_l^* the volume of adsorbate is

$V_{DB}(0, 1, x_l^*)$ and a pore-assisting factor Q_{PA} is defined as

$$Q_{PA}(x_l^*, x, V) = \frac{V_{PA}(x_l^*, x)}{V_{PA}^0(x_l^*, x)} \qquad (5)$$

where $V_{PA}(x_l^*, x)$ is the volume of condensate that reappears in void entities during the primary ascending process from x_l^* to x, while $V_{PA}^0(x_l^*, x)$ is the increase in condensed volume if the refilling had taken place in an arrangement of independent pore entities. It should also be remarked that Q_{PA} is a function of the current values of x and V as well as of x_l^*.

If a PA and a PD scanning curves have reversal points at x_l, V_{PA}^* and x_u, V_{PD}^*, respectively, the increase in liquid volume $V_{PA}(x_l, x_u)$ along the primary ascending process is

$$\begin{aligned} V_{PA}(x_l, x_u) &= V_{PA}(0, 1, x_l, x_u) - V_{DB}(0, 1, x_l) \\ &= Q_{PA}(x_l, x_u, V_{PA}) P_{DB}(1, x_l, V_{PA}^*) V^0(x_l, x_u) \end{aligned} \qquad (6)$$

where V_{PA} is the actual volume reached by the primary ascending curve at x_u and $V^0(x_l, x_u)$ is the volume of independent pore domains that fill and empty between x_l and x_u. Similarly, the decrease in condensate volume $V_{PD}(x_u, x)$ due to the descending course between x_u and x_l, is given by

$$\begin{aligned} V_{PD}(x_u, x_l) &= V_{PD}(0, x_u, x_l) - V_{AB}(0, x_u) \\ &= P_{PD}(x_u, x_l, V_{PD}) Q_{AB}(0, x_u, V_{PD}^*) V^0(x_l, x_u) \end{aligned} \qquad (7)$$

So that the ratio between the two former volumes becomes

$$\frac{V_{PA}(x_l, x_u)}{V_{PD}(x_u, x_l)} = \frac{Q_{PA}(x_l, x_u, V_{PA}) P_{DB}(1, x_l, V_{PA}^*)}{P_{PD}(x_u, x_l, V_{PD}) Q_{AB}(0, x_u, V_{PD}^*)} \qquad (8)$$

This ratio is a mere relationship between assisting and blocking factors and under the fortunate circumstance of pore-assisting and pore-blocking factors mostly depending on the total amount of condensate rather than on anything else, primary ascending curves can be inferred from PD ones or vice versa; all blocking and assisting factors being calculated from the DB and AB curves at the right volumes, respectively.

3. Results and discussion

3.1. Construction of heterogeneous 3-D porous networks

Heterogeneous 3-D porous networks, endowed of variable pore size and connectivity [15,16] were chosen as suitable substrata to perform the analysis of assisting and blocking factors. The porous networks used in this work ensued from cubic lattices where the maximum connectivity of a site is thus $C_{max} = 6$; therefore bonds were arranged orthogonally around a site and interpenetration between any pair of contiguous capillaries was not allowed. The amounts of sites and bonds were acquired from two-fold Gaussian distribution functions; the parameters of the simulated porous networks used in this work are given in Tables 1 and 2. The *overlap* Ω between the distribution of sites and bonds (i.e. the common area shared by these two kinds of pore elements in the two-fold distribution) is one of the most important parameters that define the topology of porous networks and that can strongly

Table 1
Structural parameters of lowly correlated 3-D porous networks[a] used to calculate pore-blocking factors

$\bar{R}_S$ (Å)	$\bar{R}_B$ (Å)	σ_A, σ_B (Å)	$\bar{C}$	Ω	Network type
80	32	8	2	0	I
80	32	8	4	0	I
80	32	8	6	0	I

[a] Node-to-node distance is taken as 1.1 times the size of the largest site, i.e. 1.1 $(\bar{R}_S + 3\sigma_S)$. $\bar{R}_S$ is the mean site size, $\bar{R}_B$ is the mean bond size and $\sigma_S = \sigma_B$ are the standard deviations of the Gaussian two-fold distribution. $\bar{C}$ is the mean connectivity of the network and Ω the overlap between the site and bond size distributions.

Table 2
Structural parameters of highly correlated 3-D porous networks[a] used to calculate pore-blocking factors

$\bar{R}_S$ (Å)	$\bar{R}_B$ (Å)	σ_S, σ_B (Å)	$\bar{C}$	Ω	Network type
34	32	8	2	0.33	IV
43	32	8	4	0.31	IV
52	32	8	6	0.14	IV

[a] Node-to-node distance is taken as 1.1 times the size of the largest site, i.e. 1.1 $(\bar{R}_S + 3\sigma_S)$.

influence the development of sorption processes taking place in them, as it will be seen in this work. Variable site connectivity in these 3-D networks was allowed by supplying a total amount of bonds lesser than that required to fully connect each cavity (i.e. there exist sites with less than six bonds attached to them). Mean connectivity values $\bar{C} = 2, 4$ and 6 were mostly considered, besides the size ranges of the two-fold distributions were sought to lie within the meso-porous range (i.e. 20–500 Å).

The porous networks shown in Table 1 correspond to type I porous structures [17], thus meaning that bonds in these arrangements are actually very small compared to sites and also that the condensate filling of bonds would occur ahead of the liquid filling of sites; in consequence the adsorption behaviour of all these networks should be expected to be similar to that followed by *independent* pore domains along the AB curve, whilst a pore-blocking phenomenon should occur along the DB curve. Contrastingly, the porous networks reported in Table 2 correspond to type IV structures [17] and a higher degree of size correlation is inherent to bonds and sites forming these arrangements; site and bond sizes are not too dissimilar from each other. In consequence, significant pore-blocking and pore-assisting factors could be arising while being influenced by the morphologies of these correlated porous networks; this time the sorption behaviour should be ascribed to *interdependent* pore domains.

3.2. Simulation of sorption processes in heterogeneous 3-D porous networks

Diverse sorption processes including adsorption and desorption boundary processes as well as primary ascending and PD scanning curves, were all simulated under the premises announced elsewhere [17,18]. The processes discussed here were all related to N_2 sorption at 77 K; the influence of the adsorbed layer was taken into account by means of the Halsey equation [19]. Succinctly, a site can be potentially filled with condensate at a given relative pressure x_c, if its radius R_S is lower than the Kelvin radius of curvature R_C [20] that is associated with x_c. Additionally and if the former condition is being fulfilled, the site should be surrounded by C or at least $C - 1$ bonds already filled with liquid for condensation to occur [4]. Correspondingly, a bond can be filled in two alternative ways: (i) independently, when its radius, R_B, is smaller than $R_C/2$; (ii) cooperatively, when besides of fulfilling that $R_B \leq C$, a liquid–vapour interface invades this throat from either one of its two neighbouring sites. In this latter case, the neighbouring site has just been filled with condensate by the merging of $C - 1$ menisci lodged in its other remaining bonds, before undertaking the condensate invasion of the incumbent bond. In the case of independent filling, condensation in a bond is reached once the thickness of the adsorbed cylindrical layer acquires a critical value that is related to x_c, the interface then going through a series of unstable unduloidal shapes that finally collapse into two hemispherical lenses. These menisci then displace towards the ends of the capillary, filling it completely with condensate [21]. Evaporation from sites or bonds along the DB curve requires: (i) that the radius of the pore entity is smaller than R_C; (ii) that a continuous vapour trajectory is available for the dislodgement of condensate from the pore entity in question to the outer bulk vapour phase. In the case of a PD scanning curve, a liquid-filled bond has also the opportunity of evaporating its condensate if it is linked to an empty site, that in turn needs not necessarily to be connected by a continuous vapour path to the bulk vapour phase [18,22]. Thus, the mechanisms of adsorption and desorption processes intrinsically involve the possibility of pore-blocking or pore-assisting effects.

The set of N_2 sorption isotherms at 77 K (including boundary and primary scanning curves) that will be used to calculate pore-blocking and pore-assisting factors throughout this work are plotted in Figs. 1 and 2. In these figures the relative pressure $x(\equiv p/p^0)$ is plotted versus θ_V (the fractional amount of condensate that is present in the interconnected porous network at different stages of the sorption process).

3.3. Calculation of pore-assisting and pore-blocking factors

The following strategy has been devised for the calculation of pore-assisting and pore-blocking factors. Contrastingly to real media, a simulated porous structure related with a given two-fold distribution of sites and bonds, allows the tracing of two types of sorption processes: (i) one that can be developed between the interconnected void entities of a porous network; (ii) another one that can be pursued in a
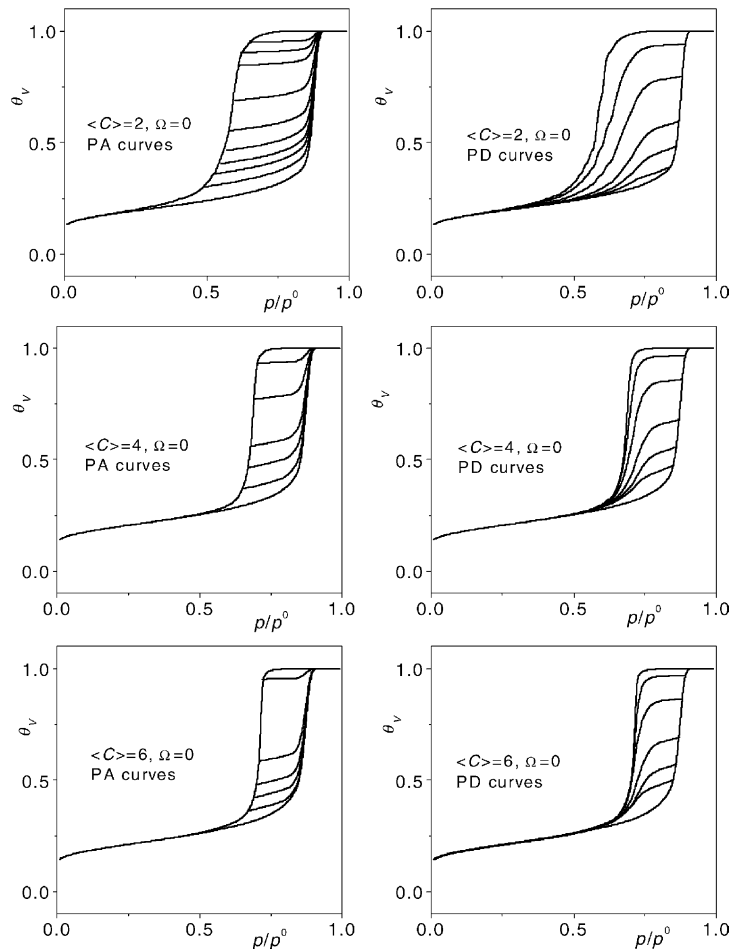
Fig. 1. N_2 sorption isotherms at 77 K on type I, 3-D porous networks. Boundary, primary ascending and primary descending scanning curves are shown. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

collection of separated, independent pore domains. To explain this in more detail, let us imagine that an interconnected porous structure formed by sites and bonds has been already set up. Interdependent pore domains thus make this arrangement; every site is surrounded by a certain number of bonds that allow its interconnection with homologous entities. Now assume that this network is disassembled into a collection of elementary pore domains, each of these units being composed of a site and C half bonds (the concept of half bonds surges because every neck is being shared, in the original interconnected network, by two neighbouring sites). Every one of these pore domains (i.e. a site and its C half bonds) can be also termed as a *multiplex*, given that these pore blocks are

the assembly of several void elements. To have an image collection (with respect to the characteristics of the elementary blocks that conform the precursory interconnected network) of independent pore domains, it is necessary to preserve the original disposition of bonds (half bonds to say this more exactly) around sites all through the disengaging process in order to end with a disassembled set of multiplexes, each formed by a site surrounded by C half bonds.

The aforementioned disengaging procedure will allow us to induce desorbed or adsorbed volumes in independent pore domain arrangements [1,11–14]. These volumetric values, combined with the appropriate volumes obtained from interconnected porous networks made of non-independent pore domains, will
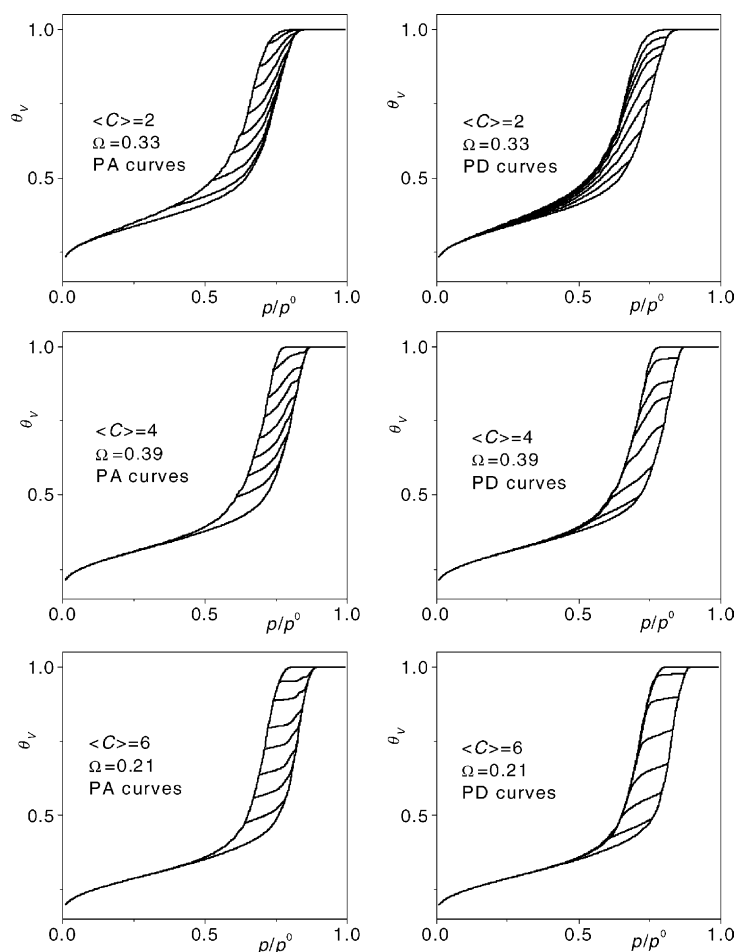
Fig. 2. N_2 sorption isotherms at 77 K on type IV, 3-D porous networks. Boundary, primary ascending and primary descending scanning curves are shown. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

finally lead us to the ascertainment of assisting and blocking factors. More specific details will be given in the following paragraphs concerning the calculation of these factors for both boundary and primary scanning sorption processes.

3.3.1. Pore-blocking factors along a DB curve

To calculate P_{DB}, it is necessary to estimate the pertinent desorbed volumes from both interdependent and independent pore domain arrangements. In the case of interdependent domains, this estimation can be made straightforwardly from data of the simulated isotherm. For independent domains, first it is necessary to separate the network into a collection of

independent multiplexes and afterwards to undertake the desorption process in the whole set of these isolated pore assemblies.

Fig. 3 depicts N_2 sorption isotherms (full lines) found for 3-D porous networks having $\Omega = 0$ (i.e. those whose structural parameters are shown in Table 1), compared with the sorption isotherms obtained from corresponding independent domain collections (symbols) comprising the same structural parameters. For this case of null Ω, we have that (independently of the value of $\bar{C}$): (i) the AB curves of the interconnected porous networks coincide a great deal with the adsorption curves of the multiplex collections; (2) the DB curves of interconnected
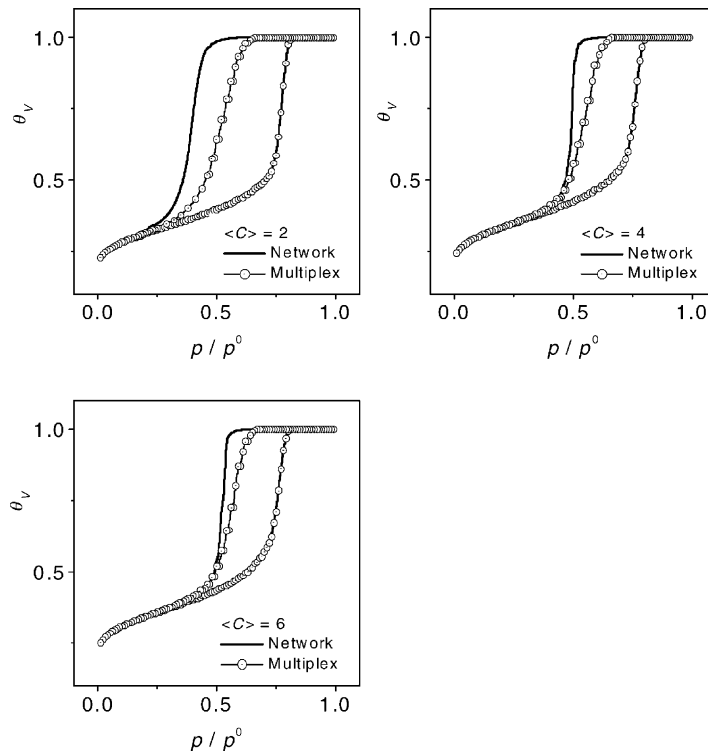
Fig. 3. Comparison between N_2 sorption at 77 K on an interconnected porous network (full lines) and on an independent domain arrangement (symbols) for lowly correlated (type I) 3-D porous networks. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

networks are clearly different from those proceeding from independent domains. The pore-blocking factor, P_{DB}, can then be calculated as function of θ_V from the DB isotherms of Fig. 3, by simply dividing the desorbed volume associated with the interconnected network by the corresponding quantity that is linked to the independent domain set (these two desorbed volumes taken at the same x). Figs. 4 and 5 depict plots of P_{DB} versus θ_V for type I and IV networks calculated in this way. In these figures, there are also included blocking factors associated to PD scanning curves, the calculation of which is similar to desorption boundary paths and that will be described in the next section of this work.

Fig. 4 shows that the curves of P_{DB} versus θ_V obtained here are similar indeed to those obtained by Everett [1], i.e. P_{DB} decreasing steadily with θ_V, thus meaning that a strong pore-blocking effect is taking place at high volume fillings (i.e. $P_{DB} \to 0$ as $\theta_V \to 1$). The intrinsic reason for the occurrence of this blocking phenomenon is the disparity in sizes

between actual sites and bonds in these scarcely correlated networks; bonds remaining liquid-filled not only at high but also at intermediate relative pressures, thus impeding sites to evaporate their condensates. A vapour percolation phenomenon arises in these lowly correlated networks; the percolation threshold depending on the connectivity of the porous network and occurring, approximately, when the relative pressure is such that a fraction of $1/(\bar{C} - 1)$ bonds can be potentially overtaken by vapour [22].

3.3.2. Pore-blocking factors during the development of a primary descending scanning path

The pore-blocking factor P_{PD} that can be induced from a PD scanning curve is also the ratio between two desorbed volumes. The first desorbed volume is obtained from the pertinent simulated sorption curve (arising from the interconnected porous network) in the range of relative pressures between x_u^* and x, the quantity x_u^* corresponding to the pressure value at the reversal point. Its counterpart, the desorbed volume
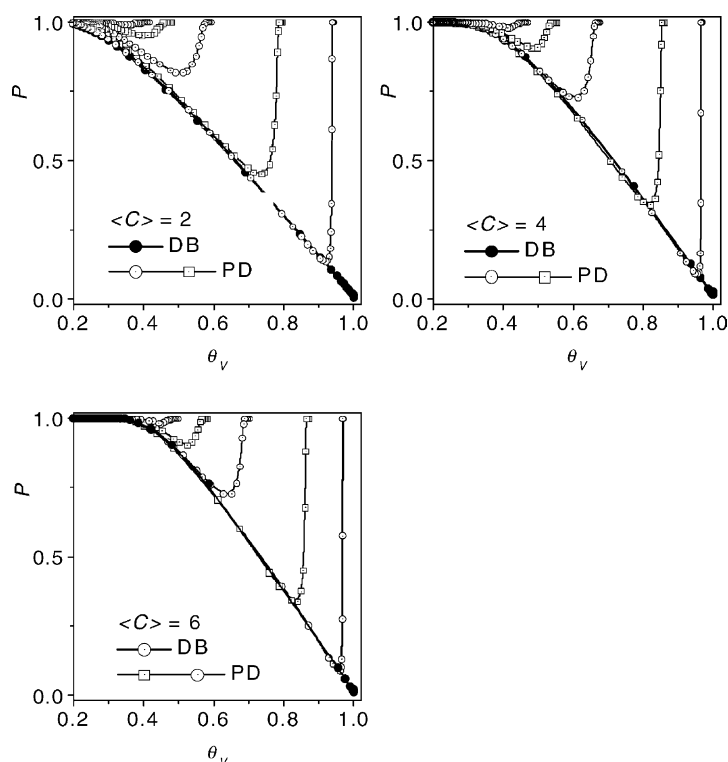
Fig. 4. Pore-blocking factors for descending boundary (DB) and primary desorption (PD) scanning processes on heterogeneous type I ($\Omega = 0$) networks. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

related to independent pore domains, can be calculated by disengaging, from the original interconnected network, the multiplexes that are completely or partially filled with condensate; the emptying of these isolated pore assemblies then being simulated from x_u^* down to x. It is pertinent to mention that pore domain arrays that are partially liquid-filled at the point of reversal, involve empty sites surrounded by a certain amount of bonds that can contain condensate or an adsorbed film and whose number ranges from 1 to C.

Fig. 4 portrays plots of P_{PD} versus θ_V obtained from a collection of primary desorption curves initiated at diverse x_u^* values and considering networks of different $\bar{C}$, all of them having $\Omega = 0$ (networks of Table 1). Plots of P_{PD} corresponding to PD scanning curves show very interesting characteristics. These curves involve, first, an initial decline (from $P_{PD} = 1$ downwards) at high θ_V values (this decrease becoming steeper the larger the value of x_u^*), afterwards the curves tending to join the path established by the

DB isotherm (P_{DB}). The finding of Everett concerning the invariance of P irrespectively of the kind of sorption process involved in the determination of this factor, proves to be reasonably *valid* for the case of lowly correlated type I networks when these are appreciably filled with condensate and when the sorption measurements involved in the determination of P are made not too close to the reversal point of the PD curves.

The shape of P_{PD} plots resulting from the analysis of scanning curves related to networks with $\Omega = 0$, can be understood after considering the following premises. First, it should be said that P_{PD} curves have several characteristics: (i) P_{PD} is always smaller than or at most equal to 1; (ii) after the point of reversal, P_{PD} decreases sharply from 1 down to the curve defined by P_{DB}; (iii) P_{PD} closely follows P_{DB} after these two curves meet together; (iv) the higher the point of reversal (in terms of θ_V) of the scanning curve, the sharpest is the approximation of P_{PD} towards P_{DB}
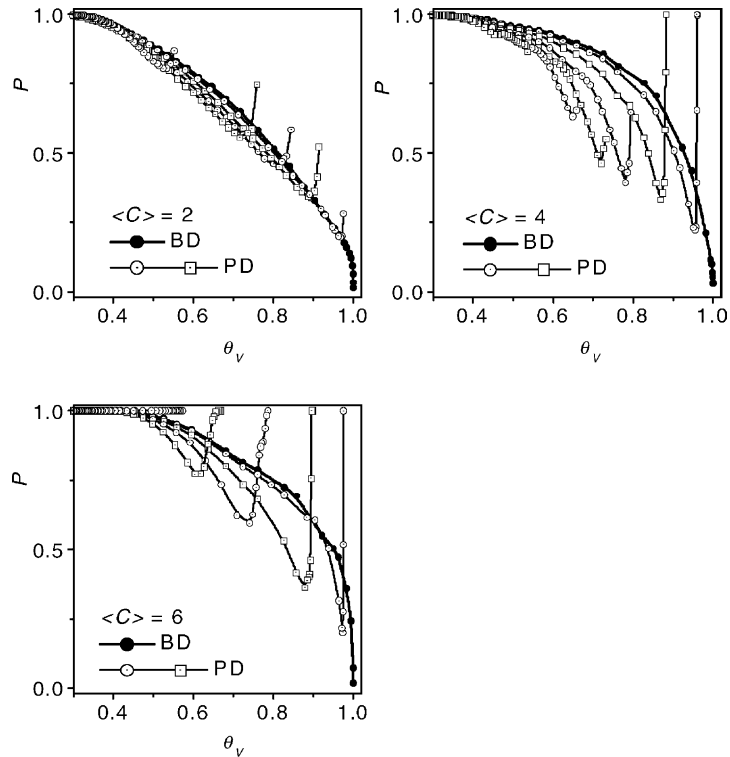
Fig. 5. Pore-blocking factors for descending boundary (DB) and primary desorption (PD) scanning processes carried out on heterogeneous type IV ($\Omega > 0$) networks. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

and the closest is the agreement between these two factors during most of the θ_V range. The fact that $P_{PD} \leq 1$ can be explained as follows. When the network is disassembled in a collection of independent multiplexes, desorption starts when R_C (the critical radius of curvature for vapour invasion into a bond) attains a value corresponding to the size of the largest bond. In turn, desorption from an interconnected network only can happen when the percolation threshold for vapour invasion is reached. This means that desorption in an interconnected network will be always delayed with respect to the same phenomenon occurring in independent pore domains. Thus, when the independent domain system is already in the process of being emptied of condensate, the interdependent pore system still requires the relative pressure to attain a lower value for percolation to take place. The initial coincidence between P_{DB} and P_{PD} (i.e. $P_{DB} \approx P_{PD} \approx 1$) around the point of reversal and the sharp decrease of P_{PD} towards the P_{DB} curve occurs

since, before any capillary evaporation can take place from either the interdependent or multiplex arrangement, the only desorption that can arise is due to the thinning of the adsorbed layer on the walls of the pores that were not filled with condensate along the AB curve. Therefore the thinning of the adsorbed layer in both the multiplex system and connected network will be identical during the first stages of the desorption process. Thereafter, as the pressure is further lowered, the multiplex collection will be the first to start evaporating its condensate in reason of the pore blocking existing in the interconnected network so that a drastic drop of P_{PD} will be observed. It is not until capillary evaporation is occurring in both interdependent and multiplex systems, that P_{PD} will start closely following P_{DB}.

Fig. 5 represents the pore-blocking factors calculated from boundary and primary desorption isotherms related to correlated (type IV) porous networks ($\Omega > 0$, Table 2). The characteristics of P_{DB} versus

θ_V curves are similar to the results obtained from type I structures; however, mean values of P_{DB} are higher than in the former substrata, especially around the region where $\theta_V \rightarrow 1$, since around this value the blocking factor increases significantly for correlated structures, this fact becoming more evident the larger is $\bar{C}$. This means that the overall pore-blocking phenomenon in type IV structures can be expected to be less acute than in type I networks. Another noticeable difference concerns the aspect of the P_{PD} curves. In type I structures, P_{PD} is seldom lower than P_{DB}, whilst in type IV arrangements this happens during most of the θ_V range (see Fig. 5). This attribute can be explained in terms of the porous network morphologies involved with type IV structures and also considering the mechanistic aspects of both condensation and evaporation processes, as it will be explained in the next paragraphs.

When the size distributions of sites and bonds are very close to each other, the sizes of neighbouring sites and bonds are not too different from each other. In fact, two concomitant phenomena can occur [16]: (i) a size-segregation effect; (ii) a connectivity segregation effect. The first effect means that, in general, large sites prefer big bonds as neighbours, while small cavities are more likely to be joined to minute bonds. This phenomenon is especially virulent when the porous network has a constant connectivity and Ω is large. The connectivity segregation effect means that, in general, bigger sites will have a larger number of neighbouring bonds than smaller sites. For 3-D cubic networks, one can expect the following morphological features. For regularly connected networks, e.g. when $C = 6$, each site of the porous network has six bonds as neighbours, therefore (if Ω is considerable) one can have a large size-segregation effect. If one now considers an irregular network of varying connectivity, e.g. when $\bar{C} = 2$ and Ω is large, the porous network is mostly a tubular system made by the merging of a site and two bonds of about the same sizes and connected at opposite extremes of the cavity; the porous network is then made of long tubes that meet at some intersection points. For an irregular network with $\bar{C} = 4$ and high Ω, the structure is made of tubes ($C = 2$) and highly connected sites ($C = 6$) in about the same proportions; in this case the system structuralises in zones of highly connected cavities and zones of poorly connected ones.

Now let us think the case of a highly correlated type IV porous network of intermediate connectivity, e.g. $\bar{C} = 4$. Due to the significant cooperative filling that takes place along the AB isotherm of such a network, sites of the lowest connectivity (i.e. those with $C \approx 2$) will be *relatively* more condensate filled than sites of higher C (i.e. those with $C \approx 6$) [4]. Therefore, a descending scanning curve at the point of reversal (x^*) will have a relative larger proportion of lowly connected sites if compared to the DB curve at the same x^*. Since the percolation threshold is inversely related to $\bar{C}$, then one can expect that the blocking conditions for a liquid-filled site chosen at random would be harsher along a scanning process than throughout a boundary one. This explanation holds for networks displaying variable connectivity, such as those for which $\bar{C} < 6$.

For structures of constant connectivity and high Ω, the size-segregation effect together with the cooperative mechanisms of filling and emptying, should still explain the behaviour of P_{PD} depicted in Fig. 5a for $C = 6$. Let us consider again the state of pore entities at the point of reversal. For a PD curve at this point there is again a larger proportion of small sites (and therefore of small bonds) already filled with condensate than in the DB process at the same x_u^*. This is due to the intensive cooperative (early) filling that takes place in type IV structures, causing that the *relative* amount of smaller bonds that are still filled with condensate at a certain x to be greater in the scanning situation than in the DB one. Therefore, P_{PD} values are lower than P_{DB} ones during most of the desorption path for networks displaying a constant C.

Finally, with respect to Everett's presumption on the invariability of P regardless of the nature of the sorption process involved, the following remarks can be said for the case of highly correlated (type IV) structures. For sparsely connected structures (i.e. when $\bar{C} = 2$) the agreement between P_{DB} and P_{PD} is fairly satisfactory, see Fig. 5a. However, when $\bar{C}$ becomes larger (i.e. $\bar{C} \geq 4$), P_{PD} is dependent on θ_V, the agreement developing somewhat better as the point of reversal arises at higher θ_V values.

3.3.3. Pore-assisting factors along an AB curve

Computation of Q_{AB} can be made once more from the determination of adsorbed volumes from interdependent and independent pore domain structures.
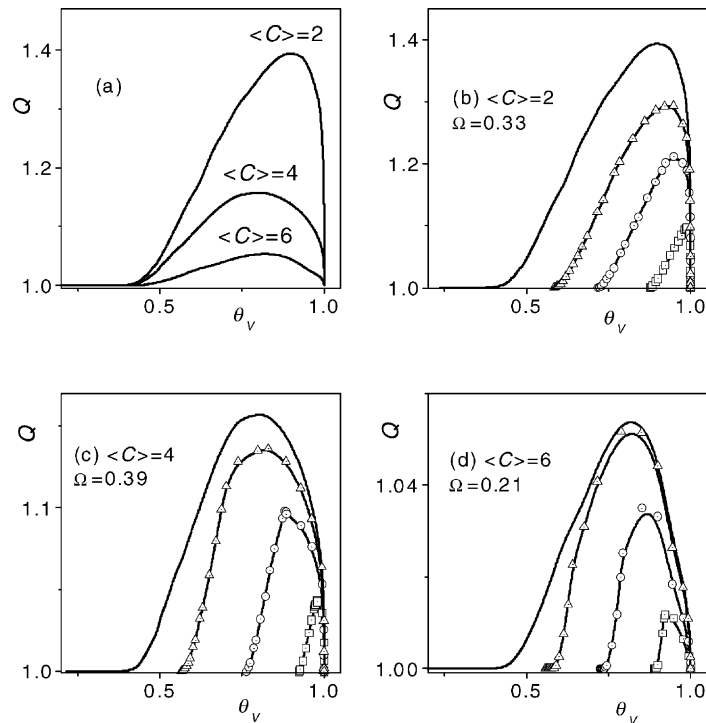
Fig. 6. Pore-assisting factors (Q) calculated for ascending boundary (AB) and primary ascending (PA) scanning curves for type IV porous networks. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots.

The adsorbed volume in interdependent domains is taken directly from the adsorption branch of the simulated isotherm. The adsorbed volume that corresponds to independent pore blocks is computed from the filling of empty pore domains that have been previously detached from the interconnected network. The same filling criteria are employed for both types of pore domains.

For type I substrata the values of Q_{AB} or Q_{PA} are very close to unity, this reflecting the independent domain behaviour of these structures during adsorption processes; therefore the case of type IV networks is the only one to be analysed. Fig. 6 portrays plots of Q_{AB} versus θ_V obtained from AB and PA curves. Fig. 6a shows that the intensity of assisted pore filling is greater in porous networks of the lowest C, for the obvious reason that, at the proper x, e.g. a site with $C = 2$, requires the filling of only one of its attached bonds to become filled itself, while on the other hand, a site with $C = 6$, would need at least five of its bonds to be full of condensate in order to be completely occupied by liquid.

3.3.4. Pore-assisting factors during the development of a primary ascending scanning path

Fig. 6b–d show plots of Q_{PA} versus θ_V, for a collection of primary adsorption curves initiated at different x^* values in type IV structures. Here, all Q_{PA} values are lower than the corresponding Q_{AB} ones at the same θ_V. Therefore, there is no much evidence of a universal behaviour in the sense of pore-assisting (Q) factors mostly depending on θ_V rather than on anything else, nevertheless the magnitudes of Q for cubic lattices are only significant if $\bar{C} < 6$.

3.3.5. Induction of PD curves from PA curves or vice versa

A very interesting result arises when PA curves are induced from PD ones or vice versa. In principle, this can be done by taking a pair of scanning curves and measuring their volumetric ratio as indicated by Eq. (8). Now, if it is assumed that $Q_{PA} = Q_{AB} = Q$ and that $P_{PD} = P_{DB} = P$, one can calculate the presumptive path that it will be followed by a primary scanning curve. To do this, it is necessary to consider a
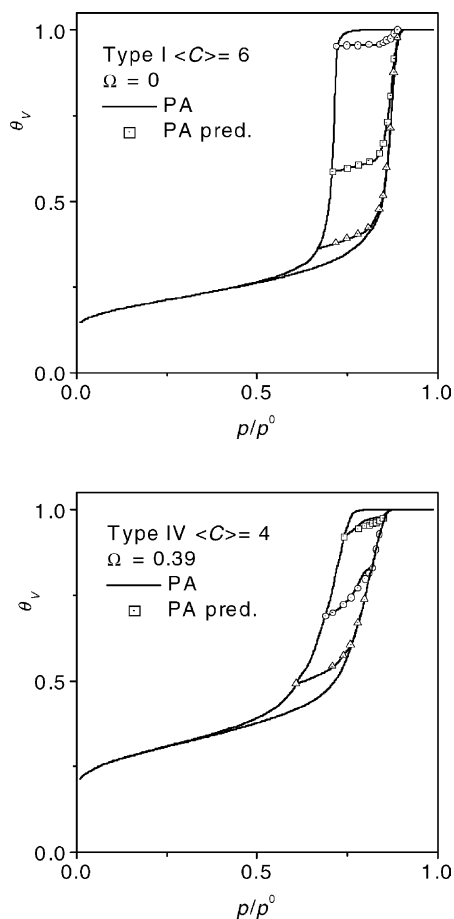
Fig. 7. Calculation of PA curves from PD data. Full lines represent actual PA curves while symbols represent predicted PA data. $\bar{C}$ is labelled as $\langle C \rangle$ in the plots

since in this case the incidence of Q is almost negligible (i.e. $Q \approx 1$).

4. Conclusions

The concepts of P and Q factors can be associated to the extent of cooperative processes occurring in porous media. In porous structures made of large cavities surrounded by narrow necks (type I), one can observe that P mostly depends on the volume of condensate that is present at some stage of a desorption process, rather than on the nature of the process itself. When throats and cavities are size alike (type IV structures), P is not quite complying with the former characteristic; however, when the connectivity of the porous network is low enough the former behaviour is still feasible. On the other hand, Q is almost invariable for type I networks ($Q = 1$), but it differs appreciable from this value for the case of type IV substrata, especially those endowed of low connectivity, thus meaning that cooperative adsorption of pore entities is taking place in this kind of structures. A link between experimental results and the quantities provided in this work still needs to be developed in order to realise which is the type of porous network that is under examination and which would be the best way to perform an appropriate pore structural analysis of the substrate.

particular PA (with an inversion point at x_l^*) curve and a set of PD paths whose points of reversal x_u^* are larger than x_l^*. A similar procedure can be established for the reciprocal calculation of PD data from a set of PA curves. The kind of agreement that can be obtained taking P and Q from the ascending and (DB) isotherms, respectively, is shown in Fig. 7. The agreement is very satisfactory for both type I and IV structures, despite the fact that P and Q for type IV porous specimens would depend somewhat on the kind of sorption process involved. The latter agreement may be also considered as a global proof of the correctness of considering P mainly as a function of θ_V for the case of lowly correlated porous networks,

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