The pore length, the pore number and the pore anisotropy distributions in porous materials

Philippos Pomonis*, Antigoni Margellou

Department of Chemistry, University of Ioannina, Ioannina, 45110, Greece

ABSTRACT

The differential pore lengths L_i, the differential pore numbers N_i and the differential pore anisotropies B_i in porous materials are estimated in a unified way and presented as a function of pore radius r_i. Those parameters can be determined from the differential specific surface area S_i and the differential specific pore volume V_i calculated via nitrogen porosimetry, assuming cylindrical pores. The differential pore length is estimated from relation $L_i = S_i^2/V_i = N_i l_i$ and corresponds to the total length of N_i pores with similar local length l_i at each pore group of radius r_i estimated at partial pressure (P_i/P_o). This parameter bears similarities with the differential pore anisotropy B_i given by $B_i = S_i^3/V_i^2 = N_i b_i$ where b_i is the local pore anisotropy. Parameter B_i is suitable for the ranking of pore numbers *vs.* pore volumes and, for isotropic cavities with $bi = 1$, leads to the ranking of pores according to the Zipf's law. Parameter L_i is suitable for the ranking of pore lengths as a function of pore radii and reveals some morphometric similarities between the pore networks in solids and the branching of trees described by the so-called allometric relations. In addition these relations may be used for the distinction of pore number evolution via either power law or exponential mechanisms, expressed by corresponding distributions. Such effects, observed previously by volcanologists in the vesicles of volvanic magmas in mm scale, are also observed in the present study for random pores of nm scale in lab made materials.

1. Introduction

The pores in porous solids are usually considered as cylinders and the methods for calculating their pore size distribution (psd) by nitrogen porosimetry are based on such a geometry as described in the standard textbooks [1–3]. By the term 'size' the pore radius r is meant. This parameter actually corresponds to the mean value of two orthogonal radii, r_1 and r_2, describing the curvature of meniscus during the filing of narrow cylindrical capillaries, which is given by the Young-Laplace equation $\Delta P = \gamma(1/r_1 + 1/r_2)$. There are two extreme cases: (i) Cylindrical geometry when one radius becomes very large, almost infinite $r_2 \to \infty$, and as a result $1/r_2 \to 0$ and $\Delta P \approx \gamma (1/r_1)$. (ii) Spherical geometry when the two radii are identical $r_1 = r_2 = r$ and $\Delta P = 2\gamma (1/r)$. Although usually $r_1 \neq r_2$, it is customary considered that the pores exhibit rotational symmetry and their combined value amounts to $(1/r_1 + 1/r_2) = 1/r = 2/D$. It is this value used in the Kelvin equation $r = D/2 = \gamma V_m/RT \ln(P/P_o) + t$ which is the basis of N_2 porosimetry, with the symbols having their customary meaning [1–3].

Nevertheless the complete description of a cylinder necessitates its *length L* too, especially in the case (i) mentioned above. Then if the pore volume V and radius r are known, its length is automatically found, e. g.

$L = V/(\pi r^2)$. So in a first approach there is no need for a separate estimation of pore lengths which are considered easily tractable. This point has been touched briefly in one of the standard textbooks on porous materials by Lowell et al. [2] who suggested that if the string of values of pore volume distribution $dV = f(r)$ is divided by the corresponding cross sectional areas (πr^2) the result will be the pore length distribution function $dL = f(r)$. As far as we know the consequences of this observation have not been pursued.

But in a segment i of N_i similar cylindrical pores, filled at partial pressure $P_i (=P_i/P_o)$ and exhibiting differential specific pore volume V_i, differential specific surface area S_i, pore radius (diameter) $r_i = 2V_i/S_i$ $(D_i = 4V_i/S_i)$ and local (not total) pore length l_i, the thus calculated *differential pore length* L_i corresponds to the *sum* of lengths of all local similar pores, e.g.

$$L_i = N_i \cdot l_i = V_i / \pi r_i^2 = S_i^2/V_i \tag{1}$$

The differential pore length L_i in this approach is the product of the differential pore numbers N_i and the local pore lengths l_i. This in turn poses the question of differential pore numbers. The main purpose of this work is to search for the distribution of pore lengths and pore numbers as a function of pore radius based on N_2 porosimetry data. In

---

addition, since the pore number distribution is interwoven with the pore anisotropy distribution, we shall touch this point too. The pore number distributions are also important in relation to vesicles formed in solidified volcanic magmas, whose growth may follows either power or exponential laws and related to volcanic explosions. Since the approach to all those problems brings together various diverse points of view, we shall review them briefly.

The pore numbers and the pore lengths. The estimation of pore numbers and pore lengths has attracted attention in the 1960–1970′ in relation to the *gasification of carbon particles.* The problem was approached by modeling the heterogeneous non-catalytic reactions between porous carbon particles and gaseous reactants, like oxygen, carbon dioxide, water or hydrogen [4–7]. Those studies were totally unrelated to the field of porosimetry and were more akin to chemical engineering point of view. They deal with the estimation of pore lengths as quantities independent of pore radii based on models of mass transfer in combination with the experimental reaction rates. We shall refer to a selection of them related to specific points of the present work.

In 1973 Hashimoto and Silveston [4] proposed a model describing the gradual development of specific surface area, specific pore volume, porosity, mean pore radii and pore lengths of porous carbon species as a function of the kinetically controlled gasification of carbon. They found that the pore radii develop *differently* than the pore length as a function of coal conversion. Their model introduces the total pore length L and the constant local pore length l assumption, which means that the total number of pores per unit mass is given by $N = L/l$. This point tallies to the above relation (1).

In 1979 Simons and Finson [5] put forward another model describing the structure of porous coal char, using data from a previous article by Berger et al. [6]. The pores were assumed to be cylindrical tubes of length l and radius r and the pore length was shown to be *proportional* to the pore radius. The model also suggests that the pore sequence forms a 'pore tree' resembling an ordinary tree or a river system. Finally the authors concluded that there is a statistical linear distribution between $log(1/r^3)$ and the pore number density $log(N)$. This relation is actually an early manifestation of Zipf's law for pore ranking, recognized 38 years later in Refs. [8,9] and reviewed bellow.

In a follow-up article [7], published the same year 1979, Simons described a mechanistic model of pore development which includes the engulfment of the smaller pores by the larger ones leading to depletion of the small pores and enhanced the growth of the large pores. The corresponding pore volume distributions demonstrate qualitative agreement with laboratory measurements. He also mentioned that such effects are responsible the appearance of relation $(N) \alpha (1/r^3)$ observed initially in [5] and much later in Refs. [8,9]. The envisaged sequence of events for the pore development in this model is practically similar to the models proposed much later for the development of vesiculars in volcanic magmas we shall refer next.

More recently in 2004 Rigby and co-workers [10] made a concerted attempt for the simultaneous determination of the pore-length distribution and pore connectivity for porous catalyst supports using integrated nitrogen sorption and mercury porosimetry. They employed the method to determine pore connectivity and lattice size from nitrogen sorption data developed by Seaton and co-workers [11] where it was assumed that the average pore lengths l_i are the same in each pore-size interval. This concept is fundamental in the estimation of relation (1). The authors in Ref. [11] assumed also that the average pore length l_i is a function of the pore diameter d_i in the form $l_i = k. d_i^a$ where k - a normalization factor and a - important constant to be determined. In a striking coincidence, an almost similar power law $l_i = r_i^a$ was proposed practically simultaneously, but totally independently, by this group in Ref. [12] where a method for the estimation of pore anisotropy was initially proposed.

The pore numbers in volcanic magmas and their distributions. Another field of science exhibiting keen interest for the estimation of

pore number distribution as a function of their size is *volcanology.* The aim in this case is to understand the bubble nucleation in volcanic magmas, initiated by the exsolution of dissolved volatile gases like H_2O and CO_2, and the subsequent bubble coalescence and growth which, if extensive and fast, lead to huge and catastrophic volcanic explosions [13–20]. For this purpose the bubble size distributions *(bsd)* and the vesicular growth with time is considered of paramount importance. The vesicles trapped either in solidified volcanic rocks, or in mimic laboratory experiments, are in the range of mm and practically isotropic. So there is no point searching for pore lengths or pore anisotropy. The methods of observation are direct and usually include optical imaging, SEM and X-ray tomography [13–17].

In such cases a crucial point is the mechanism of bubble development in the magma. In the relevant geological literature there are two main approaches [16–19] describing the *bsd* either in the form $N = f(V)$, or $N = f(r)$, where N-the bubble density (mm^{-1}), $V \sim r^3$ - the bubble volume (mm^3) and r-the bubble radius (mm): The exponential distribution [20–22] and the power law distribution [13,23–25].

The *exponential distribution* has the form

$$N = No \ exp \ (-r/G\tau) \tag{2}$$

where $(G\tau)$- a product of the average *unknown* bubble steady growth rate (G), (τ)- the average crystal growth time and (N_o)- the nucleation density for $r{\to}0$. Relationship (2) stems its origin from a model proposed by Randolph and Larson in 1971 in relation to industrial crystallization processes based on the classical balance Creation + Input = Annihilation + Output [20]. The model was adapted by Marsh in 1988 to describe the development of crystal size distribution in rocks [21] and then applied by various authors for the description of bubble size distribution in volcanic magmas or lab mimics [14–18,22]. If this distribution upholds, then plots of the form $log (N) = f(r)$ should provide straight lines with slope $(-1/G\tau)$ and intercept $log(N_0)$.

The second approach is the *power law distribution* which reads

$$N \approx 1/V^{B} \tag{3}$$

where B- an exponent to be define. This theory was introduced in 1996 by Gaonac'h et al. [13,23] and expanded a few years later by Lovejoy et al. [24,25]. Its basic assumption is that small bubbles, generated from the magma, are gradually diffused and jointed each other in a cascading series of events. At each generation two smaller bubbles merge into a single larger one of increase size and so on.

Eventually there will be a percolation limit where an infinite bubble occupies the whole section of the reservoir and, if the sequence of events is fast enough, the system is driven to explosion. The model predicts two regimes: For small bubbles, the rate determining step (rds) is considered the bubble diffusion, and then the exponent $B = 1$. For medium to large bubbles the rds is their coalescence and then $B \neq 1$. If this distribution upholds, then plots $log(N) = f (log(V))$ should provide straight lines with slope $(-B)$.

The above are considered the main mechanisms controlling the pore development. Nevertheless during such processes, multiple vesiculation events may occur simultaneously and overprint each other, like multiple nucleation and growth, coalescence, ripening and collapse [19]. Therefore the relevant results and plots call for 'interpretative prudence' [19] but in any case the two main approaches constitute a good basis for comparison.

The differential pore anisotropy and the pore numbers. A method of estimation of *Differential Pore Anisotropy Distribution* was proposed recently for pores in the size of nm based on N_2 porosimetry [8,9]. This property, which is interwoven with the pore numbers, was symbolized as (b_{diff}) in Refs. [8,9] but will be designated in the next as $B_i (\equiv b_{diff})$ to facilitate symbolization.

Briefly, parameter B_i can be determined from the dimensionless ratio $[S_i^3]/[V_i^2]$ between the cube of differential specific surface area S_i