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Tortuosity of Porous Particles

M. Barrande, R. Bouchet, and R. Denoyel*

MADIREL, CNRS-Université de Provence, Centre de St Jérôme, 13397 Marseille cedex 20, France

Tortuosity is often used as an adjustable parameter in models of transfer properties through porous media. This parameter, not reducible to classical measured microstructural parameters like specific surface area, porosity, or pore size distribution, reflects the efficiency of percolation paths, which is linked to the topology of the material. The measurement of the effective conductivity of a bed of particles saturated with an electrolyte is a simple way to evaluate tortuosity. Nevertheless, it received only little attention because of the real difficulties in both getting reliable results and interpreting data. Notably, the discrimination between the contribution of interparticle and intraparticle porosities to the tortuosity is not resolved. To our knowledge, there is no model able to fit the experimental data of the tortuosity of a suspension, and a fortiori of a particle bed, in the whole porosity range. Only empirical expressions have been proposed, but they do not allow deriving intratortuosity of a porous particle. For a dilute system, Maxwell's equation predicts the effective conductivity of suspensions of spherical particles as a function of the bulk electrolyte conductivity and of particle conductivity. The intraparticle tortuosity can be derived from the particle conductivity obtained from the Maxwell equation applied to data at infinite dilution of particles. Then, by assuming that the Maxwell equation is a first-order approximation of the conductivity as a function of porosity, we propose an explicit relation of the tortuosity τ of a suspension of porous particles, obtained by conductivity measurement, as $\tau = \tau(\epsilon, \epsilon_p, \tau_p)$, where ϵ is the total porosity of the suspension, τ_p is the intraparticle tortuosity, and ϵ_p is the particle porosity. This relationship fits the experimental data in the whole porosity range and can be used to determine τ_p from an experiment at only one porosity. Finally, the obtained values of τ_p for a set of porous particles used in chromatography are discussed and compared to the data available in the literature.

The understanding of the role of the porosity architecture on the transfer properties of a fluid through a porous medium is one of the key factors of many industrial and environmental processes that cover a very broad range of domains (geology, engineering, chemistry, and physics) with important applications: catalysis, separation and filtration, cement chemistry, oil recovery, and migration of soil pollutants. The principle of these processes is

based on the circulation of a fluid through a porous material with the desired surface properties. Due to the interactions between molecules of the fluid and the surface of the pores, this flow may be accompanied by other phenomena like adsorption, dissolution, or precipitation, depending on the specific aim of the application. For any of these processes there is a need to model or predict the effect of the porosity on the fluid flow. A minimum number of microstructural parameters is necessary. Surface area, porosity, and pore size distributions are the most commonly measured parameters. For that, standard methods such as gas adsorption, mercury porosimetry, or inverse size exclusion chromatography give a reasonable account of surface accessibility, pore size range, and porosity. Nevertheless, these methods are based on rough theoretical simplifications. For example, for pore size calculations, simple models of unconnected cylindrical pores are used, which do not reflect the complexity of most porous networks that consist of labyrinths of interconnected pores with irregular shapes and cross sections. This complexity, which is therefore not reducible to classical microstructural parameters, has direct consequences on the transfer properties through a porous medium. Hence, there is a need to define a limited number of parameters that (i) describe the complexity, (ii) may be introduced in model, and (iii) may be measured in a straightforward manner. In this paper, we want to focus on such a parameter, very naturally called tortuosity τ . This concept was originally introduced by Carman¹ to explain the difference between modeled permeability values and experimental observations. τ is often used in models for chromatographic or membrane separation applications, but rather as an adjustable parameter. Carman proposed the determination of tortuosity from conductivity measurements on porous media filled with an electrolyte of conductivity σ^0 . The liquid-filled cross section available for passage of current will be only a fraction ϵ of the total cross-sectional area. In an isotropic random pore space, ϵ is exactly the porosity of the media. Moreover, it appears experimentally that all the void volumes are not used with the same efficiency for transport. The effective conductivity of a suspension will be inferior to $\sigma^0\epsilon$ by a factor $1/\tau$, with τ larger than 1:

$$\sigma_{\text{eff}} = \sigma^0 \epsilon / \tau \quad (1)$$

where τ is the tortuosity. Hence, $1/\tau$ could be defined as the fraction of void volumes owning the same efficiency for transport as the bulk electrolyte, the complementary fraction being perfectly inefficient. For rocks and sands, characterized generally by a low

* To whom correspondence should be addressed. E-mail: rdenoyel@up.univ-mrs.fr.

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porosity, which is moreover not homogeneously distributed in the volume, the use of eq 1 asks the question of the flow input section in the porous media,² which is no more exactly ϵ . On the contrary, for a fluidized bed, this condition is always fulfilled, so that eq 1 can be taken as a definition law for tortuosity. The value of tortuosity obtained by conductivity measurement depends not only on the sinuousness of the path in pores as proposed by Carman¹ but also on complex geometric parameters like the connectivity and the constrictivity of pores.³ Several groups have since performed such experiments on porous media in either a packed^{4,5} or fluidized bed.⁶

Other methods to evaluate tortuosity in a direct manner are based on the determination of the ratio of the value of the diffusion coefficient of a probe in bulk to its apparent value in the porous network ($D_{\text{eff}} = \epsilon D^0 / \tau$). The diffusion coefficients may be derived from direct transport data (for example, by analyzing the shape of chromatographic peaks,⁷ by diffusivity measurements with Wicke Kallenbach cells⁸), or from NMR applied to various probes.⁹ In the latter case, it has been shown that tortuosity derived from diffusion coefficient measurements by pulse-field-gradient NMR, at long observation times, where a stationary regime is obtained, converges to that deduced from conductivity measurements.¹⁰ Nevertheless, it is important to quote that tortuosity, understood as a topologic characteristic of the porous network, should be independent of the used probe. Therefore, the tortuosity determined by conductivity measurements is interesting due to the fact that the used probes, i.e., ions, can be considered, for mesoporous or macroporous materials, very small as compared to the pore size.

Though this concept was initially introduced to explain permeability results, tortuosity derivation from such measurements is less direct. It was integrated to permeability equations as the ratio of the effective length L_{eff} of the fluid flow path through the porous media to the apparent length L_{app} . This is a restrictive definition of tortuosity that corresponds to model the pore network as a bundle of unconnected pores with a constant section. Derived from conductivity or from diffusional experiments, tortuosity is viewed as a retardation factor,² which does not need any microstructural description. Electrical and diffusional tortuosity may be related in a rigorous way, notably because both phenomena, electrical conductivity and diffusion, may be formulated by the Laplace equation.² Moreover, conductivity and diffusion coefficient are directly related through the Nernst–Einstein equation. It is also easy to verify that electrical tortuosity is related to $(L_{\text{eff}}/L_{\text{app}})^2$ as is the case for permeability when the system is described as a

bundle of capillaries.¹ Finally, a generic relationship for tortuosity definition may be proposed:

$$\left(\frac{J}{\text{DFG}}\right)_{\text{eff}} = \frac{\epsilon}{\tau} \left(\frac{J}{\text{DFG}}\right)_0 \quad (2)$$

where J/DFG , is the ratio between a parameter J defining the transport (flow of matter, velocity, current) and the driving force gradient. The index “eff” and “0” are reference to a measurement with and without the porous medium, respectively. This definition is not directly applicable to permeability.

Tortuosity measurements carried out on fixed or fluidized beds of porous particles depend both on the porosity of the particles and of the arrangement of these particles in the bed. As shown recently,¹¹ the discrimination between the contribution of interparticle and intraparticle porosities, ϵ_e and ϵ_p , respectively, to the tortuosity is not resolved, and in the case of a fixed bed, the conductivity is apparently only sensitive to the interparticle porosity. For a dilute system, Maxwell's equation¹² predicts the effective conductivity of suspensions of spherical particles as a function of the bulk electrolyte conductivity and of particle conductivity. It is shown here that the intraparticle tortuosity may be derived from the particle conductivity obtained from the Maxwell equation applied to data at an infinite dilution of particles. The Maxwell equation is then used as a starting point to propose an explicit relation of the tortuosity τ of a suspension of porous particles, obtained by conductivity measurement, as a function of total porosity ϵ , intraparticle tortuosity τ_p , and intraparticle porosity ϵ_p . The proposed relationship allows fitting the experimental data in the whole porosity range. Examples of tortuosity measurement of various spherical particles (porous and nonporous) will be shown. Finally, the obtained values of τ_p are discussed and compared to the data available in the literature.

EXPERIMENTAL SECTION

Materials. The list of the particles used in this study is given in Table 1 together with their suppliers, their chemical nature, their density, and their mean microstructural properties. All materials selected for this work are made of spherical particles except the Fractosil sample. However, at high porosity, the influence of the shape of the particles is supposed to be negligible.¹³

Pore size and pore volume measurements were carried out using a water desorption method described in a preceding paper¹⁴ and confirmed by mercury porosimetry (Autopore 9920, Micromeritics) or nitrogen adsorption (ASAP 2010, Micromeritics) when possible. Finally, densities of materials were measured by using standard picnometry with deaerated water.

Conductivity Measurements. Particles were fluidized in a solution of sodium chloride using a magnetic stirrer. The chosen concentration was 1 M so that the extension of the electrical double layer from the pore surface into the bulk electrolyte (<1

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Table 1. List of Studied Particles and Their Available Structure Parameters

samples	suppliers	nature	density g·cm ⁻³	particle diameter/ μm	mean pore radius/nm	particle porosity	specific area/m ² ·g ⁻¹
glass beads	Malvern	silica	2.5	30			0.3
X005	BioSeptra	silica	2.2	40–100	100	0.69	20
X030	BioSeptra	silica	2.2	40–100	30	0.69	45
X075	BioSeptra	silica	2.2	100–300	10	0.69	101
Si60	Merck	silica	2.2	12	3	0.66	721
Si100	Merck	silica	2.2	12	6	0.73	380
Fractosil	Merck	silica	2.3	40–100	30	0.60	21
S Ceramic	Ciphergen	silica	2.2	50	19	0.61	
HyperD F		polyacrylic					
Fractoprep	Merck	vinyl polymer	1.7	30–150	10	0.89	
SP Sepharose	Amersham	agarose	1.54	90	37	0.87	
Fast Flow	Bioscience						
MEP	Ciphergen		1.53	80–100	22	0.90	
HyperCel							
Fractogel	Merck		1.35	40–90	25	0.83	
SE Hicap							

nm) is small compared to the pore size. Therefore, the conductivity in pores can be assumed to be equal to that of the bulk electrolyte. Nevertheless, it was experimentally verified (in the case of glass beads and of the sample with the smallest pores, Si60) that the measured tortuosity is independent of salt concentration provided it is higher than 10^{-2} mol·L⁻¹. The cell temperature was controlled within 0.1 K thanks to a circulating thermostated bath. The electrical resistance measurements were carried out by impedance spectroscopy (from 1 kHz to 1 MHz) using a standard two-electrodes conductivity cell integrated in the fluidized bed. The amplitude of the exciting signal was fixed to a small value of 30 mV. Impedance spectroscopy is a very precise tool for measuring electrical properties of materials and fluids.^{15,16} A Solartron 1260 frequency analyzer controlled by a personal computer using Z-Plot software (Scribner) was used. Finally, Z-view software (Scribner) was used to visualize the impedance diagrams and separate suspension resistance from electrode effects. The resolution on the measured resistance is 3 over 10 000.

Variation of the porosity of the fluidized bed was obtained by adding powders by 0.5-g increments to 15 cm³ of electrolyte. At each step, the cumulative volume V_p of particles added to the solution was calculated by dividing the cumulative weight of dried material, m_p (in g), by the density ρ of the material:

$$V_p = m_p / \rho \quad (3)$$

The total porosity ϵ was then deduced by

$$\epsilon = \frac{V_i}{V_i + V_p} \quad (4)$$

where V_i is the initial volume of electrolyte.

Conductivity measurements were also performed in a fixed bed, using a chromatographic column filled with a compacted bed of particles in a 1 M sodium chloride solution. Two porous (10

μm) stainless steel electrodes were placed at the extremities of the column. The column temperature was also controlled within 0.1 K thanks to a circulating thermoregulated bath.

Porosity and tortuosity values were determinate with reproducibility better than 1%.

RESULTS

To our knowledge, there is no model able to fit the experimental data of the tortuosity of a suspension (and, a portiori, of a particle bed) in the whole porosity range. Various phenomenological expressions have been proposed to describe the tortuosity as a function of the porosity.^{17–22} Among these, Comiti and Renaud²² proposed the following equation for nonporous particles:

$$\tau = 1 - p \ln(\epsilon) \quad (5)$$

This equation satisfies the boundary condition $\tau = 1$ for $\epsilon = 1$. p depends on the shape of particles and their mean orientation in the bed. It is important to specify that their experimental results were based on permeability measurements. For beds of spheres, Mauret and Renaud²⁰ gives $p = 0.49$ in agreement with the value 0.5 of Weissberg,²¹ who derived eq 5 from a theoretical derivation of the effective diffusion coefficient in a suspension but with the unrealistic assumption that particles may overlap. This equation is plotted in Figure 1 together with data obtained with spherical glass beads of different mean sizes (20 μm, 30 μm, 130 μm, and 1 mm). The agreement is good in the whole porosity range, which means that this empirical equation is valid for both fluidized and fixed beds. In the literature, some experiments were performed in fixed bed with particles of diameters larger than 1 mm.^{22–24} The value of p obtained for these results varies between 0.39 and 0.46, but in that case, the particle size is perhaps no more negligible as compared to the size of the conductivity cell or the

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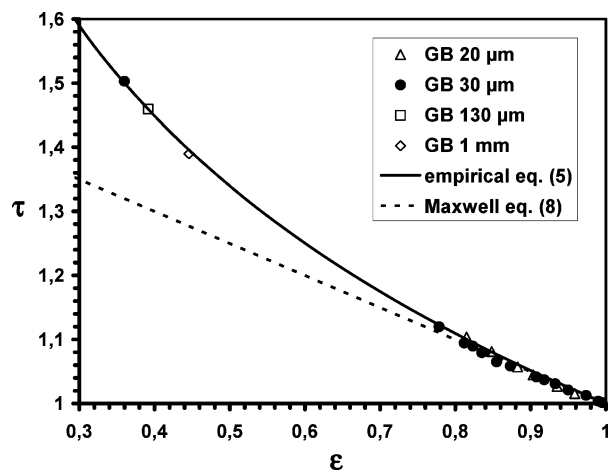


Figure 1. Tortuosity as a function of porosity for glass beads (GB). Empirical eq 5 with $p = 0.49$ (solid line), Maxwell equation for nonporous particles (8) (broken line). The three points at low porosity correspond to fixed beds.

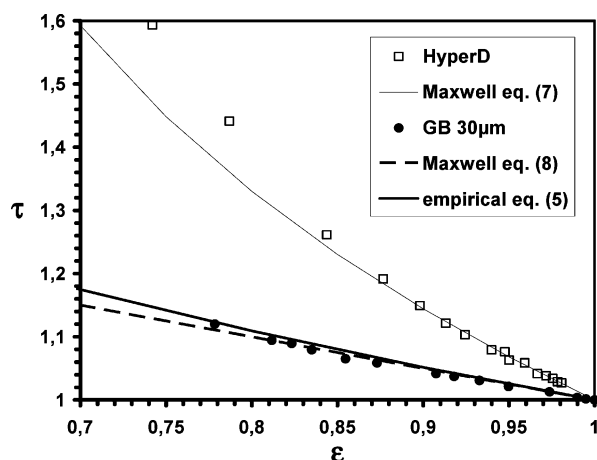


Figure 2. Tortuosity as a function of porosity for spherical porous and nonporous particles. Experimental values for nonporous glass beads in fluidized bed (●), empirical eq 5 with $p = 0.49$ (thick line); Maxwell equation for nonporous particles (8) (broken line); experimental values for porous spheres of HyperD (□). The thin line corresponds to eq 7, the ratio σ_p/σ^0 was varied until experimental and calculated data are tangent at high porosity.

fixed bed is not homogeneous. Commiti and Renaud²² showed that the value of p depends strongly on the shape aspect of particles. It is really surprising that the eq 5 proposed initially to model the tortuosity parameter evolved into the equation that links the dependency of the flux with the applied entry pressure (permeability equation) is in so good agreement with the tortuosity determined by conductivity measurement. It seems that it is the first time to our knowledge that such a correlation is shown; it would mean that $\tau_{\text{permeability}}$ defined by Carman has the same meaning that $\tau_{\text{conductivity}}$.

However, eq 5 is no longer valid for porous media as shown in Figures 2 and 3. In the other side, Maxwell¹² proposed a theory to predict the effective conductivity of a mixture of two phases: a continuous phase and a disperse phase. This effective medium theory can be applied to the conductivity of a suspension of spherical particles in an electrolyte.²⁵ Maxwell's theory is supposed

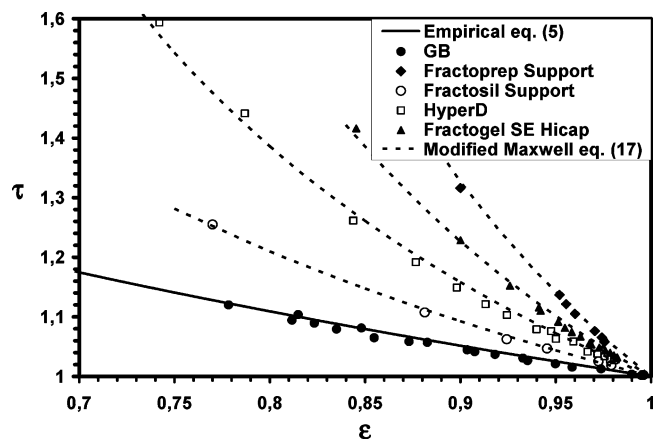


Figure 3. Tortuosity as a function of porosity for spherical porous and nonporous particles. Empirical eq 5 with $p = 0.49$ (solid line) and modified Maxwell eq 17 for porous particles (broken lines) with a fixed value of intraparticle tortuosity τ_p for each type of particles.

to be valid for diluted suspensions where there is no interaction between particles.¹³ This theory leads to the so-called Maxwell equation, in which the effective conductivity σ_{eff} of the suspension is related to the conductivities of particles (σ_p) and of electrolyte (σ^0) by

$$\frac{\sigma_{\text{eff}}}{\sigma^0} = \frac{2\sigma^0 + \sigma_p - 2(1 - \epsilon_{\text{ext}})(\sigma^0 - \sigma_p)}{2\sigma^0 + \sigma_p + (1 - \epsilon_{\text{ext}})(\sigma^0 - \sigma_p)} \quad (6)$$

where ϵ_{ext} is the interparticle porosity. The tortuosity of the bed is obtained by combining eqs 1 and 6:

$$\tau = \epsilon \frac{2 + \frac{\sigma_p}{\sigma^0} + (1 - \epsilon_{\text{ext}})\left(1 - \frac{\sigma_p}{\sigma^0}\right)}{2 + \frac{\sigma_p}{\sigma^0} - 2(1 - \epsilon_{\text{ext}})\left(1 - \frac{\sigma_p}{\sigma^0}\right)} \quad (7)$$

Let us first consider the case where particles are both nonporous and nonconducting, i.e., $\sigma_p = 0$ and $\epsilon_{\text{ext}} = \epsilon$. eq 7 simplifies to

$$\tau = 1 + 0.5(1 - \epsilon) = \frac{3 - \epsilon}{2} \quad (8)$$

The expression of the tortuosity for a suspension obeying the Maxwell theory is then rather simple. It is added in Figure 1 together with the empirical eq 5 and experimental data for spherical glass beads. As expected the Maxwell theory is in agreement with experiment and eq 5 at high porosity where both data are tangent and tends toward 1. It is not surprising since first-order development of eq 5 for ϵ tending to 1 gives

$$\tau = 1 + p(1 - \epsilon) \quad (9)$$

with $p = 0.49$ according to Mauret and Renaud.²⁰ The p value is fixed, in the present case, by the fixed bed data, and the agreement is effectively better with 0.49 than 0.5.

Let us now consider the case of porous particles made of nonconducting walls. These particles are conducting since their

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Table 2. Particle Toruosities Obtained by the Infinite Dilution Method or Eq 17

materials	particle tortuosity	$\tau_p = 1 - 0.49 \ln(\epsilon_p)$	tortuosity of fixed bed	porosity of fixed bed
glass beads			1.50	0.36
X005	1.33	1.18	1.30	0.80
X030	1.35	1.18	1.22	0.83
X075	1.33	1.18	1.26	0.81
Si60	1.42	1.20	1.46	0.77
Si100	1.50	1.15	1.22	0.84
Fractosil	1.43	1.25	1.26	0.77
Fractoprep	1.33	1.06	1.32	0.90
SP Sepharose	1.32	1.07	1.24	0.92
Fast Flow				
S Ceramic	1.97	1.24	1.59	0.74
HyperD F				
MEP	1.30	1.05	1.40	0.91
HyperCel				
Fractogel SE	1.38	1.09	1.42	0.85
Hicap				

pores are filled by the electrolyte. The original (to our knowledge) proposal of the present paper is to use the Maxwell equation to determine the conductivity of these particles and then their tortuosity. The tortuosity of the suspension is measured as a function of porosity by eq 1 and calculated theoretically by eq 7 where the ratio σ_p/σ^0 is varied until experimental and calculated data are tangent and tends toward 1 at high porosity (infinite dilution of particles) as in Figure 1 for nonporous particles. This is illustrated in Figure 2 for porous silica. The tortuosity τ_p of the particles may then be calculated classically by

$$\tau_p = \sigma^0 \epsilon_p / \sigma_p \quad (10)$$

where ϵ_p is the porosity of the particles. The following relationship holds between the various porosities:

$$\epsilon = \epsilon_{\text{ext}} + \epsilon_p(1 - \epsilon_{\text{ext}}) \quad (11)$$

This approach, designed as the “infinite dilution method” in the following, allows determining the contribution of intraparticle tortuosity. The particle tortuosity results are reported in Table 2. For both porous and nonporous materials, the tortuosity of a fixed bed is also given.

Before discussing the results, a new model for the tortuosity of a suspension of porous particles is proposed with the aim to be able to (i) represent data in the whole porosity range and (ii) derive particle tortuosity from only one measure at one porosity.

MODEL

Following the thought of Mauret and Renaud,²⁰ who showed that p depends on a shape aspect, one may suppose that a general law of the form of eq 5 would be also truth even for porous spherical particle. Therefore, introducing eq 10 in Maxwell eq 7, one obtains

$$\tau = \epsilon \frac{1 + 2 \frac{\tau_p}{\epsilon_p} + (1 - \epsilon_{\text{ext}}) \left(\frac{\tau_p}{\epsilon_p} - 1 \right)}{1 + 2 \frac{\tau_p}{\epsilon_p} - 2(1 - \epsilon_{\text{ext}}) \left(\frac{\tau_p}{\epsilon_p} - 1 \right)} \quad (12)$$

ϵ_{ext} can be skipped using (11):

$$\tau = \epsilon \frac{(\epsilon_p + 2\tau_p)(1 - \epsilon_p) + (1 - \epsilon)(\tau_p - \epsilon_p)}{(\epsilon_p + 2\tau_p)(1 - \epsilon_p) - 2(1 - \epsilon)(\tau_p - \epsilon_p)} \quad (13)$$

After some elementary algebra, τ can be expressed with the same form as that of eq 9:

$$\tau = 1 + \frac{(\tau_p - \epsilon_p)(2 + \epsilon) - (\epsilon_p + 2\tau_p)(1 - \epsilon_p)}{(\epsilon_p + 2\tau_p)(1 - \epsilon_p) - 2(\tau_p - \epsilon_p)(1 - \epsilon)} (1 - \epsilon) = 1 + p(1 - \epsilon) \quad (14)$$

where

$$p = \frac{(\tau_p - \epsilon_p)(2 + \epsilon) - (\epsilon_p + 2\tau_p)(1 - \epsilon_p)}{(\epsilon_p + 2\tau_p)(1 - \epsilon_p) - 2(\tau_p - \epsilon_p)(1 - \epsilon)} \quad (15)$$

At infinite dilution,

$$p = \frac{3(\tau_p - \epsilon_p) - (\epsilon_p + 2\tau_p)(1 - \epsilon_p)}{(\epsilon_p + 2\tau_p)(1 - \epsilon_p)} \quad (16)$$

In first approximation, eq 13 can be considered as a first-order development, which leads us to finally propose the following modified Maxwell equation in analogy with eq 4:

$$\tau = 1 - \frac{(\tau_p - \epsilon_p)(2 + \epsilon) - (\epsilon_p + 2\tau_p)(1 - \epsilon_p)}{(\epsilon_p + 2\tau_p)(1 - \epsilon_p) - 2(\tau_p - \epsilon_p)(1 - \epsilon)} \ln(\epsilon) = 1 - p \ln(\epsilon) \quad (17)$$

Of course, by construction, this equation obeys the boundary conditions, $\tau = 1$ when $\epsilon = 1$. The results of the best fits using this equation are plotted in Figure 2 for some of the studied particles. In the whole range (till fixed bed), there is a very good agreement between experimental data and the modified Maxwell equation. By this fit, the value of the only unknown, which is the intraparticle tortuosity τ_p , may be determined to give the same value as that obtained by the infinite dilution method. The originality of this approach is to give a semiempirical equation, which allows separating the contribution of intraparticle tortuosity from the tortuosity of a random arrangement of particles.

DISCUSSION

An interesting result is to consider that the tortuosity obtained here is a topological characteristic of the materials. This is clearly shown by the results with nonporous spheres that obey a similar law for fluidized and fixed bed. It means that tortuosity depends only on porosity for a random system of spheres. As a consequence, if a particle is itself made of spheres with a random space

repartition, then eq 5 should be also verified if applied to internal porosity ϵ_p and internal tortuosity τ_p :

$$\tau_p = 1 - 0.49 \ln(\epsilon_p) \quad (18)$$

The τ_p values are reported in Table 2. For silica beads that are often made by agglomeration of small particles, one may observe that the measured tortuosities are always larger than those calculated by eq 5. It means that the internal structure of these particles cannot be considered as a random distribution of dense spheres. This could be explained by assuming that particles are themselves composed of agglomerated porous particles or simply because the porosity inside particles is not homogeneously distributed. However, our results show that porous particles with the same porosity will not have the same tortuosity and hence the same efficiency for fluid transport. The comparison between the tortuosity calculated by eq 18 and that determined by the proposed methods is a way to assess if the pore structure has the one expected from the synthesis protocol. A disagreement may show two things: (i) either the structure of particles cannot be considered as a homogeneous assembly of spheres, fibers, or any other shape (knowing that the factor p depends on this shape²²), (ii) or the porosity is not homogeneously distributed through the particles. The advantage of the proposed method is to quantify the quality of the sample whereas its disadvantage is that, for the moment, it cannot discriminate between the two possibilities. Finally, independently of microstructural details, this intraparticle tortuosity could give some help for diffusion models, especially in liquid chromatography^{26,27} in order to choose, a priori, the best material.

The three Spherosil materials (X005, X030, X075) have the same intraparticle tortuosity. As their pore sizes are different, but their architectures are equivalent, it is confirmed that the tortuosity of a porous particle does not depend on its pore size, which is in agreement with the results obtained for different sized glass beads. Also, it shows explicitly the interest of the electrical tortuosity due to the fact that the probes are small so that they are supposed to describe the entire porosity: it is really a topological characteristic of the porous medium. The tortuosity of the S Ceramic HyperD F is particularly high especially for silica. In fact, this material is not only silica, there is a hydrogel polymerized within the large pores of the rigid ceramic bead: the pores network obtained is then much more complex than the original ceramic beads. Finally, polymers have large porosities, so they are not very tortuous. In this latter case, to use eq 5 with $p = 0.49$ is not really valid since the structure of such a sample is rather that of entangled fibers than that of agglomerated spheres.

In the literature, many results of tortuosity values derived from electrical resistivity measurements can be found for a fixed bed of porous materials. Garrouch et al.⁴ estimated the tortuosity of a variety of sandstone rock samples. Tortuosities obtained with eq 1 range between 2 and 4, and the porosity of beds is ~ 0.2 . With the same definition of tortuosity, Attia²⁸ obtained values between 1.3 and 2 for petrophysical rocks of porosity between 0.2 and 0.3. One can notice that by applying eq 5 for $\epsilon = 0.2$ one obtained a

tortuosity value of 2, which is in agreement with the result generally obtained for sands at this porosity. Choudhary and Horwath⁵ measured the ratio of σ_{eff} to σ_0 using a capillary electrochromatography column packed with various siliceous and polymeric supports. For a porosity of 0.5, tortuosities range between 1 and 1.3. The tortuosity of a fixed bed packed with porous materials depends on particle shape and packing but also, as we have shown, on the specific architecture of the pore network inside particles. In the papers cited previously, which indicate values in agreement with those we obtained for fixed beds, the contribution of the intraparticle tortuosity is not evidenced.

On the other side, tortuosity measurements on monoliths or membranes give directly the value for the material and there is no reason to distinguish between inter- and intraparticle contributions. For example, Gohil et al.²⁹ worked on the electrochemical characterization of polymeric membranes with very low porosities (between 0.1 and 0.25). They found tortuosity values between 3 and 5. These values can be compared to intraparticle tortuosities. As the porosity of these membranes is very low, their pores are probably not well connected and do not all percolate, so their tortuosities are very high. In the case of monoliths, intraskeleton and interskeleton porosities can be distinguished, and it could be useful to determine the tortuosity contribution of each domain.³⁰ The applicability of eq 17 for this kind of material will be evaluated in the future.

Some attempts to distinguish between inter- and intraparticle tortuosities can be found in the literature. Gustavsson et al.³¹ measured two-dimensional tortuosities in a packed bed of superporous agarose, by following the movement of yeast cells, dyed with a coloring agent, using a microscope/video camera. In this case, the tortuosity is defined as the ratio of the actual length of the flow path to the shortest distance between the beginning and the end of the flow path. Using this technique, Gustavsson et al. were able to differentiate the interstitial tortuosity from the tortuosity of the superpores. The interstitial porosity is 0.4, the superpores diameter is 30 μm and the superpores' porosity is 0.4. For a packed column of agarose beads with a particle size of 300–500 μm , the interstitial two-dimensional tortuosity is 1.08 and the simulated (random walk) three-dimensional tortuosity is 1.15. However, as the agarose beads are spherical, the tortuosity should be 1.44, according to eq 4 with $p = 0.49$. For superpores, the two-dimensional tortuosity is 1.15, and the simulated three-dimensional tortuosity is 1.28. The porosity of superpores is 0.4, which is a very low porosity for porous materials, so the expected tortuosity should be much higher. For instance, the internal tortuosity of the SP Sepharose Fast Flow, a cross-linked agarose, is 1.32 for a porosity of 0.87. Yeast cells used in the work of Gustavsson et al. are probably quite big because they have to be clearly seen under the microscope. So perhaps, these probes do not explore all the pores of the superporous agarose bed. Their path through the column is then less long, and the apparent tortuosity is lower than that obtained by conductivity experiment. This remark can be generalized to diffusion experiments. Indeed, when probe size increases, the flow decreases because of the growing interaction

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between probe and particle walls. Even in nonadsorbing conditions, the ratio of diffusion coefficients D_{eff}/D° depends on the ratio of pore size to probe size.³² So diffusive tortuosity results are not directly comparable to electrical tortuosity if probe size is not negligible compared to pore size. The determination of intraparticle diffusion coefficients for small probes (for example, by analyzing the shape of chromatographic peaks³³) could provide tortuosity values comparable to ours, but data are lacking to calculate them. Another interesting attempt is that proposed of Tallarek et al.³⁴ by pulse field gradient nuclear magnetic resonance, who were able to determine intraparticle tortuosity directly in a chromatographic column for three samples. Their values, as well as others they quote³⁵ are of the same order of magnitude as ours (between 1.4 and 2.3) for spherical porous particles similar to ours. This is expected since their probe is the solvent (water, acetone) whose molecular size is small as compared to the pore size. Many values determined by analyzing gas diffusion processes are also quoted in the book by Yang.³⁵ Despite the difficulty of extracting directly from these data the intraparticle values, it is clear that their data are in agreement with ours when the probe size criterion is fulfilled, whereas very high values of tortuosity are obtained in the case of microporous samples.

CONCLUSION

The original (to our knowledge) proposal of the present paper is to show that the intraparticle tortuosity can be derived from

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the particle conductivity obtained from the Maxwell equation applied to conductivity data at infinite dilution of particles in a suspension. Then, by assuming that the Maxwell equation is a first-order approximation of the conductivity as a function of porosity, we propose an explicit relationship of the tortuosity of a suspension or a fixed bed of porous particles, obtained by conductivity measurement, which fits the experimental data in the whole porosity range and can be used to determine the intraparticle tortuosity from an experiment at only one porosity. The order of magnitude of the values obtained here are in agreement with data obtained by other methods when available. This equation may be notably useful for technologies, like chromatography, that used such type of stationary phases, but also in analysis of cements or petrophysical rocks (oil recovery). This is a first attempt to determine tortuosity at several scales. Comparing the measured particle tortuosity to that determined by applying the empirical eq 18 to particle porosity is a way to assess if the pore structure has the one expected from the synthesis protocol. A disagreement may show that either the structure of particles cannot be considered as a random assembly of primary particles or the porosity is not homogeneously distributed through the particles. The advantage of the proposed method is to quantify the quality of the sample whereas its disadvantage is that, for the moment, it cannot discriminate between the two possibilities.

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