Pore size effects on convective flow and diffusion through nanoporous silica gels

Charlotte Hamngren Blomqvist [a,b], Christoffer Abrahamsson [b,c], Tobias Gebäck [b,d], Annika Altskär [b,e], Anne-Marie Hermansson [b,c], Magnus Nydén [b,f], Stefan Gustafsson [a,b], Niklas Lorén [a,b,e], Eva Olsson [a,b,*]

[a] Applied Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
[b] SuMo Biomaterials, VINN Excellence Centre, Chalmers University of Technology, S-412 96 Göteborg, Sweden
[c] Chemical and Biological Engineering, Chalmers University of Technology, S-412 96 Göteborg, Sweden
[d] Mathematical Sciences, Chalmers University of Technology, S-412 96 Göteborg, Sweden
[e] Structure and Material Design, SP Food and Bioscience, Frans Perssons väg 6, S-402 29 Göteborg, Sweden
[f] Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia

HIGHLIGHTS

- A direct methodology for determining mass transport as a function of pore sizes.
- TEM characterisation of silica NPs of different morphology, before and after gelation.
- A highly adjustable soft model material for the microporous to the mesoporous length scales.
- New insight on the relation between structure and mass transfer properties on the nanometer scale.

GRAPHICAL ABSTRACT

The influence of pore size distributions on flow speed was studied in three colloidal silica gels of equal volume fraction but different primary particle size and morphology.
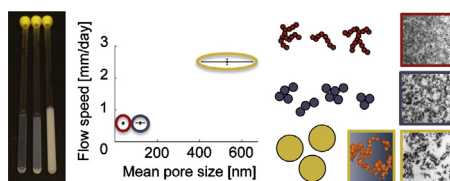
ARTICLE INFO

ABSTRACT

Material structure has great impact on mass transport properties, a relationship that needs to be understood on several length scales. Describing and controlling the properties of flow through soft materials are both challenges concerning the industrial use of gel structures. This paper reports on how the porous structure in nanoporous materials affects the water transport through them. We used three different silica gels with large differences in the pore sizes but of equal silica concentration. Particle morphology and gel structure were studied using high-resolution transmission electron microscopy and image analysis to estimate the pore size distribution and intrinsic surface area of each gel. The mass transport was studied using a flow measurement setup and nuclear magnetic resonance diffusometry. The average pore size ranged from approximately 500 nm down to approximately 40 nm. An acknowledged limit for convective flow to occur is in the pore size range between 100 and 200 nm. The results verified the existence of a non-linear relationship between pore size and liquid flow at length scales below 500 nm, experimentally. A factor of 4.3 in flow speed separated the coarser gel from the other two, which presented almost identical flow speed data despite a factor 3 in pore size difference. In the setup, the mass transport in the gel with the largest pores was flow dominated, while the mass transport in the finer gels was diffusion dominated. Besides providing new insights into mass transport as a function of pore sizes, we conclude that three-dimensional analysis of the structures is needed for a comprehensive understanding of the correlation between structure and mass transport properties.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author at: Applied Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden.
    E-mail address: eva.olsson@chalmers.se (E. Olsson).

Nomenclature

2D	two-dimensional or two dimensions
3D	three-dimensional or three dimensions
AMD	arithmetic mean diameter
BF	bright field
CLAHE	contrast limited adaptive histogram equalisation
FEG	field emission gun
HAADF	high-angular annular dark field
ISA	intrinsic surface area
NMR	nuclear magnetic resonance
Pe	Peclét number
PSD	pore size distribution
Re	Reynolds number
SE	standard error
STEM	scanning transmission electron microscope/y
SVF	solid volume fraction
TEM	transmission electron microscope/y
VWMV	volume-weighted mean volume
wt%	weight percent

1. Introduction

The research topic of soft porous colloidal materials is very current for direct industrial applications as well as basic research [1–3]. These kinds of materials are already abundantly used in everyday applications such as food, pharmaceuticals [4], chromatographic gels [5], catalysts [6,7] and batteries [8]. A common application denominator is the need for controllable mass transport properties within the materials. One important category of soft porous colloidal materials is particle gels. They usually consist of a particle network forming a continuous three-dimensional (3D) network on the macroscopic scale. Formation of this network is usually described by the percolation model [9]. The network is contained in a matrix of a continuous liquid phase. The liquid phase in the gel fills a geometrically isotropic 3D network of pores of varying sizes (i.e. the diameter of a pore at a specific place).

The structural parameters of pore size distribution (PSD) and connectivity (ranging over a wide span of length scales) are important factors determining the mass transport through porous materials. It is therefore of utmost importance to determine the relationship between structure and properties in order to design new materials and devices with tailored properties [4]. Previous works have shown a strong correlation between mass transport and structure [4,10–12]. Earlier studies on the transport properties for water of different protein gels as a function of pH, temperature and ionic strength suggests that materials with pore widths in the range from approximately 200 nm and up to 2 μm are more predisposed to lose moisture compared to materials with pores on an even smaller length scale [13–16]. The mass transport through silica gels [3,17] and other porous soft materials [1,2,18] have been recently and previously studied. However, nanoscale correlation between pore sizes and water transport has not earlier been visualised and quantified experimentally, on a length scale less than 100 nm. We do it here using electron microscopy.

The PSD can be determined using indirect methods [19], e.g. mercury intrusion porosimetry [20,21] or other liquid porosimetry [22], N₂ or other gas adsorption/desorption [23,24] calorimetric methods [19,20,25,26] or X-ray scattering techniques [19]. On the nanoscale, however, the gel liquid is firmly kept within the gel by capillary forces, and any attempts to extract a liquid by force would result in gel breakage [16], making said liquid porosimetry techniques inapplicable. Gas adsorption methods are also not applicable here, since the necessary drying of the samples would affect the material structure severely [27]. Studies have shown that the abovementioned methods differ both in the position of the PSD peak, and with respect to which size category of pores that is numerically over- or underestimated [20,24]. A more direct method of determining material structure is transmission electron microscopy (TEM) in combination with image analysis. This approach enables quantification of gel PSD, down to a few nanometres and facilitates analysis of the immediate connection between nanostructure and mass transport properties.

The interaction of water with the structure is very rapid and the diffusion properties depend on both the intrinsic surface area and the accessible volume fraction [28,29]. The reason for characterising the intrinsic surface area is its particular importance for diffusion, especially when there are strong interactions between the solute and the surface [3,30,31]. Another situation arises if the probe molecule or particle size is significant with respect to the size of the microstructure details. Then the diffusion rate will depend on micro structural details in addition to the intrinsic surface area. Silica gels can be produced with small or large PSDs, and with pores ranging from a few nanometres up to several micrometres. Hence, the pore size could be chosen to be typically in the region of the transition between flow and diffusion dominated mass transport [16]. Since silica provides a distinctive contrast compared to the embedding resin both using TEM and scanning TEM (STEM), without the need of staining in order to further enhance the contrast between the particles and the surrounding medium. From these perspectives, the silica gel is well suited for electron microscopy studies.

In this work, we have investigated the direct connection between pore size and mass transport for three different nanoporous silica gels. The diffusion coefficients of water in the different structures were determined using NMR diffusometry and the pressure driven steady state flow speed was determined using a previously described setup [3]. The gels were characterised with respect to the size and shape of the primary particles or primary aggregates, as well as the PSD. Bright field (BF) TEM and high-angle annular dark field STEM (HAADF STEM) were used for the imaging of pores, particles and aggregates. Stereological image analysis was used for the pore size determination. Here, quantitative microscopy is a key element for structural material characterisation, and for understanding the correlation between structure and mass transport properties on different length scales.

2. Theory

The Hagen-Poiseuille relationship,

$$Q = \frac{\pi R^4}{8L\eta} p, \tag{1}$$

is used for determining how well a pipe transports fluid. Here, Q denotes the flow rate. R and L denote the radius and length of the pipe, respectively. η denotes the fluid viscosity, and p is the pressure drop, driving the flow [32]. In Eq. (1), the pores are assumed straight, and the flow is steady and laminar. The flow rate is proportional to the pipe radius to the power of four, and inversely proportional to the pipe length. As a consequence, for a specific pressure, the flow rate through larger pores will be much higher than for smaller pores. Thus, the importance of flow as the dominating mass transport mechanism is expected to decrease with decreasing pore radius.

The hydraulic diameter, d_h^2, of the gel pores is calculated from the permeability, κ, which can be determined using the flow speed values, U. Darcy's law,

$$U = -\frac{\kappa}{\mu} \frac{\Delta p}{L}, \tag{2}$$