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Influence of the structure of mesoporous adsorbents on transport properties

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ABSTRACT

The transport of caffeine through columns filled with mesoporous silica was studied by liquid chromatography. The mass transfer parameters were measured by modelling the band broadening of the chromatograms. The experimental height equivalent to a theoretical plate (HETP) data were analysed using the general rate model (GRM) in order to determine the effective diffusion coefficient of caffeine in porous particles. Samples are characterized by gas adsorption for pore size determination, whereas the topological tortuosity of the porous particles was determined by electrical measurements. The effective pore diffusion coefficient through porous particles was modelled with a good accuracy by taking into account that both porosity and tortuosity depend on the ratio between the size of the molecule probe and the pore size. This model has been used to estimate the contribution of the surface diffusion coefficients of caffeine which appears to be small for this system.

1. Introduction

The comprehension of the transport properties of fluids through porous media is critical for the successful design, preparation, and application of adsorbents and membranes in separation science and catalysis. The global performances are directly related to the kinetics of mass transfer through the pore network which is essentially determined by its architecture which could be described by microstructural and topological parameters. In most cases these transfer steps occur in complex porous media that make the prediction rather difficult. The microstructural parameters such as specific surface area, specific pore volume, porosity and pore size distribution (PSD) may be determined, in a standard manner, by techniques like gas adsorption or mercury porosimetry [1,2]. Pore size distribution can also be obtained by inverse size exclusion chromatography (ISEC) [3,4]. This technique uses a set of molecular probes with different sizes to determine pore dimensions in non-adsorbing conditions. Operating conditions such as high pressure, low temperature and drying conditions which are involved in gas sorption or mercury intrusion are not imposed in ISEC. Nevertheless, beyond the fact that very simple model of parallel pores are generally used to calculate the pore size distribution, these basic parameters cannot alone predict transport properties for which other parameters like pore connectivity or tortuosity play a crucial role.

One of the critical parameters used to model the mass transport is the effective diffusion coefficient of the molecules in the porous network. For a given molecule, the effective diffusion coefficient depends on (i) accessible porosity, (ii) pores organisation, (iii) friction with the pore wall and (iv) adsorption kinetics. These four points have been largely analysed in the literature excepted point (ii) which is often seen through the concept of tortuosity, giving a unique value to this parameter independently of the size of the probe whose transfer is studied. Tortuosity is a generic concept used to describe the delay effect on the transport that arises from the complex topology of the sample [5–11]. Tortuosity can be measured experimentally by conductivity [7,10], NMR [12–14], gas chromatography [15] or liquid chromatography using the stop and flow method [16,17]. In a recent study [18] we proposed to evaluate the transfer properties of molecules in non-adsorbing conditions to highlight the effect of porous network organisation and probe size. The mass transfer kinetics of toluene and polystyrenes in a tetrahydrofuran mobile phase through columns filled with silica porous spheres were studied in non-adsorbing conditions. The mass transfer parameters in those columns were measured by modelling the band broadening of the chromatograms. These data were analysed using the General Rate Model (GRM) [19–21] in order to determine the effective pore diffusion coefficient in porous particles as a function of molecular size. The intra- and extra-particle tortuosities were determined by a method based on electrical measurements [10] and were supposed to reflect the topology of the porous network. The accessible porosity was directly determined from chromatographic measurements whereas the probe friction with the wall was modelled by the Renkin equation [22] which relates the diffusion coefficient of a molecule in a cylindrical pore to the molecule/pore size ratio (r_m/r_p). A phenomenological law was proposed to evaluate the evolution of tortuosity

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Table 1
Properties of silica Lichrospher Si60 (Merck) and silica Lichrospher Si300 (Merck) obtained by gas adsorption and conductivity measurements.

Samples	Density ($g\,cm^{-3}$)	Specific surface area ($m^2\,g^{-1}$)	Particle diameter d'_p (μm)	Particle porosity ε_p (BJH)	Mean pore radius r_p(BJH) (nm)	Particle tortuosity [a] τ_p
Lichrospher Si60	2.2	721	12	0.66	2.5	2.1
Lichrospher Si300	2.2	83	10	0.68	22	1.9

[a] Determined experimentally by electrical measurements [10].

Table 2
Porosities and pore radius of silica Lichrospher Si60 (Merck) and silica Lichrospher Si300 (Merck) obtained by ISEC measurements.

Samples	Total porosity of fixed bed (toluene) ε_t,	Extra-particle porosity ε_e,	Particle porosity (toluene) ε_p	Pore radius (ISEC) r_p/nm
Lichrospher Si60	0.63	0.38	0.41	1.95
Lichrospher Si300	0.77	0.38	0.64	17.5

Table 3
Bulk diffusion coefficient D_m obtained by TDA for caffeine in different solvents, viscosity of the solvents and hydrodynamic radii r_m calculated with the Stokes Einstein equation.

Solvents	Viscosity of the solvent [a]/cP	Molecular diffusion coefficient D_m/$10^9\,m^2\,s^{-1}$	Probe radius Eq. (5) r_m/nm
Water	0.89	0.63	0.39
Methanol:water (30:70)	1.5	0.43	0.34
Methanol	0.55	1.19	0.33

[a] Data given in Ref. [29].

with probe size, i. e. with accessible porosity, which gives a reasonable prediction of the evolution of effective diffusion coefficient with r_m/r_p. The aim of the work presented here is to validate the proposed model to determine the pore diffusion coefficient in adsorbing conditions. Thus, the transport of caffeine through the same mesoporous silicas has been studied by liquid chromatography in weak adsorbing conditions.

2. Materials and methods

2.1. Stationary phases

The columns used in this work were Lichrospher Si60 and Lichrospher Si300 graciously supplied by the manufacturer (Merck, Germany).

2.2. Characterization of the mesoporous silicas

Nitrogen sorption isotherms at 77 K where determined with an ASAP 2010 apparatus from Micromeritics. The BET equation was applied to determine the surface area of the silicas. Average pore diameters and pore volume have been evaluated from the nitrogen adsorption–desorption isotherms by applying the BJH model [23]. The BJH method is based on the Kelvin equation which defines the equilibrium pressure for capillary condensation. The particle porosities are derived from the pore volume assuming a density of 2.2 for silica. Densities of materials were measured by using standard picnometry with outgassed water.

Pore size distributions were also evaluated by inverse size exclusion chromatography (ISEC) using a HPLC 1200 Agilent system: polystyrene standards (purchased from PSS Standards, Mainz, Germany) of various molecular weights were dissolved in tetrahydrofuran (HPLC grade) at a concentration of 1 g/L. The size of toluene and of the polystyrenes in THF is given in Table 1 of Ref. [18].

The particle tortuosities are determined by conductivity measurements as described in Barrande et al. [10]. Briefly, the effective conductivity of a homogeneous suspension of porous particles in high concentrated electrolyte is measured as a function of the total porosity. The average effective conductivity of one particle is obtained by fitting the experimental data with the Maxwell equation [24] (effective medium theory) in the diluted parts corresponding to the infinite dilution condition. Then the particle tortuosity was calculated by using the general definition law, $\tau_p = \frac{\varepsilon_p \sigma_o}{\sigma_{eff}}$, where ε_p is the particle porosity and σ_o the bulk electrolyte conductivity. The main properties of the porous silica powders are summarised in Tables 1 and 2.

2.3. Liquid chromatography

The experiments were performed using an Agilent 1200 Series HPLC. The chromatographic columns (125 mm × 4 mm) were Lichrospher Si60 and Lichrospher Si300 (Merck). All experiments were carried out at 25 °C, fixed by a column thermostat. Caffeine (purity >99%) was purchased from Aldrich. Methanol was a HPLC grade (Carlo Erba Reagents, SDS, 99.9% purity) and used as the mobile phase with varying ratio in order to adjust the retention factors. Both the column and module were first equilibrated with the mobile phase. Experiments were performed at various volumetric flow rates, f, ranging from 0.04 to 2 ml. min^{-1} which corresponds to interstitial velocities, u, ranging from 0.01 to 0.7 cm. s^{-1}. Caffeine was prepared at a concentration of 1 mM. 2.5 μl was injected and the concentration at the outlet was measured at 273 nm. The pH ranged between 5 and 6.

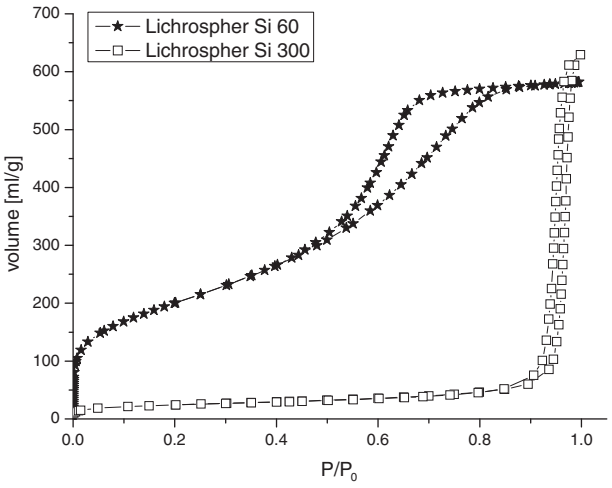

Fig. 1. Nitrogen adsorption–desorption isotherms at 77 K on Lichrospher Si60 and Lichrospher Si300.