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Impact of surface diffusion on transport through porous materials

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Abstract. The peak parking method was applied to evaluate the surface diffusivity D_s of polystyrenes dissolved in a THF/heptane mixture and transported through porous silica materials with various morphologies. With this method, the overall effective diffusivity D is measured experimentally with coarse-grained models like Maxwell equation allowing one to infer the particle diffusivity D_{pz}. Such particle diffusivity has two main contributions: in-pore diffusivity D_p and surface diffusivity D_s. The diffusion within the pores is determined experimentally using either non-adsorbing conditions or calculated from particle porosity, particle tortuosity, and hydrodynamic hindrance. The surface diffusion coefficient D_s is usually determined using models considering parallel diffusion in the pores and at the surface but this assumption is rather crude. In this paper, to address this problem, another approach is proposed using the Brownian motion of molecules in the pore space. These two approaches lead to similar equations relating the effective diffusion coefficient D, the in-pore diffusion D_p and surface diffusion D_s. The surface diffusion is analyzed as a function of the surface affinity of the probes considered here (polystyrenes of different molecular weights/lengths). Such surface affinity depends both on the probe chain length and surface chemistry of the host solid (the latter being characterized here through the silanol surface density). For short chain lengths, a non-monotonic change in the surface diffusion with affinity (i.e. retention factor) is observed in some cases. Yet, generally, as expected, surface diffusion decreases upon increasing the surface affinity. In contrast to short chain lengths, the longest chain lengths are less sensitive to the silanol surface density.

Keywords: effective self-diffusion, surface diffusion, peak parking method, porous silica

1. Introduction

In chromatography, diffusion is generally estimated from the peak broadening which depends on the contribution of several mass transfer processes occurring inside the column [1]. The mass transfer kinetics in the stationary phase have a significant influence on the column efficiency under high flow rates of the mobile phase (with very important implications for many industrial processes such as catalysis and phase separation). The mass transfer kinetics depends mainly on intraparticle diffusion which has two contributions: diffusion in the porous volume and diffusion at the surface of the porous media (D_s). Hydrophilic interaction liquid chromatography (HILIC) [2] and reversed-phased liquid chromatography (RPLC) [3] are the most widely applied retention modes of liquid chromatography. The retention mechanisms at the heart of these techniques have been explained using molecular simulation in both HILIC and RPLC modes [4,5]. While surface diffusion contributes significantly to intraparticle mass transfer in RPLC, it seems negligible in HILIC [4,6,7]. In chromatography, diffusion can be measured using (1) a dynamic method by considering the response to a pulse solicitation in the framework of the general rate model or (2) a static method through the so-called "stopped flow" or "peak parking" approach. In this context, we note that the peak parking method and pulse method lead to comparable results while being complementary to each other [8]. In general, the peak parking method is preferred for fast particle diffusion as the latter leads to small slopes when plotting the HETP (height equivalent to a theoretical plate) *versus* the mobile phase velocity – the slope being inversely proportional to the particle diffusivity D_{pz} [8].

In 1964, the peak parking method was introduced to determine diffusion coefficient in gas chromatography [9]. Later, this method was applied to liquid chromatography using columns packed with fully porous particles, core-shell particles or monolithic columns [10,11]. In this method, the overall effective diffusivity D – which should be comparable with values obtained using nuclear magnetic resonance experiments because in both experiments gradients of concentration versus time inside the porous medium are analysed– is determined as follows. After very diluted injection in the liquid upstream, the probe molecules are displaced until they reach the middle of the column by using a pump/pressure drop inducing flow. Once the molecules are in the middle of the column, the pump is stopped for a given time during which self-diffusion occurs through the porous medium. The pump is then restarted and the dispersion can be evaluated from the peak spreading increase as compared to the one without parking time. Such self-diffusion has two main contributions: (1) diffusion in the external volume of the

spherical particles or in the interskeleton volume for monoliths and (2) diffusion in the porous zones. Desmet *et al.* (2008) showed using theoretical arguments that the residence-time weighted expressions often used in chromatography to determine *D* are physically inconsistent [12]. Such an important conclusion was also verified experimentally [8,13]. Models such as the effective medium theory (EMT), including the Maxwell model [14], are often used to separate both contributions and to determine the particle diffusion coefficient D_{pz} corresponding to the porous zones. The Maxwell model can also be used to determine the particle tortuosity by means of electrical measurements [15,16]. Higher order models such as Torquato model [17] can also be used but in this model the so-called three-point parameter ζ_2 is unknown. In the present study, the Maxwell model is preferred because it is sufficient to fit correctly the experimental values D_{pz}/D_m where D_m is the bulk self-diffusivity [18]. The particle diffusion coefficient D_{pz} is made up of two contributions: in-pore diffusion D_p and surface diffusion D_s. Our research group has already studied in-pore diffusion of toluene and polystyrenes through bare silica particles and monolithic columns in non-adsorbing conditions [18]. In this previous study, tetrahydrofuran (THF) was used to avoid any adsorption of the solutes on the stationary phase so that no surface diffusion was considered. The in-pore diffusivity was calculated from peak parking experiments by using Maxwell model. Pore diffusion can also be modelled by introducing the friction coefficient as calculated using Renkin equation [19] and the particle tortuosity.

The particle tortuosities obtained by means of the peak parking method are usually comparable to those determined using electrical measurements. The particle tortuosity can also be calculated using the following equation: $\tau_p = 1 - p \ln \varepsilon_{pz}$ in which *p* is a topological parameter and ε_{pz} the particle porosity. This equation can be established theoretically for freely overlapping spheres (Weissberg equation) [20] and generalized to other systems using *p* as a free parameter [15,16,21,22, 23,24,25]. The *p* values obtained by means of the peak parking method are around 1.4 for silica columns. This model, which was recently used by Desmet *et al*. [26] on reversed C18 columns, led to $p \sim 0.6$-0.9. In the present study, the same columns and solutes are used as in [18] but adsorbing conditions are considered to study the influence of surface diffusion (in practice, a mixture of heptane and THF is used to ensure such adsorbing conditions). The solutes are a series of polystyrenes having different lengths and thus affinities for the surface. The pore diffusion and surface diffusion are often assumed to occur in parallel [1,4,27] but this approximation is rather crude. In the present paper, another model based on

intermittence between adsorption steps and self-diffusion relocation of the molecules in the confining pore network [28] is analysed. For such intermittent dynamics, a comparable equation is obtained while adding a constant factor and taking into account detailed balance conditions between proximal fluid in the adsorption layer and distal fluid in the pore network. The model proposed in this paper is applied to the mesoporous zone as well as to the whole column. The peak parking method is used to evaluate experimentally D for polystyrenes of different molecular weights in heptane/THF mixture through porous silica having different morphologies: fully porous and core-shell particles are considered as well as monolithic columns. The Maxwell model is then used to estimate the particle diffusion coefficient D_{pz}. The surface diffusion D_s is also calculated as a function of the retention factor or equilibrium adsorption constant by using either the classical, commonly used equation or the models presented in this paper.

2. Theory

2.1. Particle diffusion coefficient

Band broadening in a chromatographic column is mainly due to diffusion inside the particles. In the peak parking method diffusion occurred inside and outside the particles during the parking time leading to band broadening. In the peak parking method, the overall effective diffusion coefficient D is directly obtained from the concentration profile at the end of the column. To calculate the diffusion coefficient D_{pz} inside the particles, effective models are needed. As shown in the literature, the effective medium theory (EMT) can be used to calculate particle diffusion coefficients. Those models describe more accurately the experimental results than the parallel zone or residence time weighted model which is usually used in liquid chromatography. Among EMT models, despite its simplicity, the Maxwell model allows efficient separation of the contributions from the porous and interstitial zones [8].

2.1.1 Maxwell model for spherical particles

Fully porous particles. The Maxwell model can be used to relate the effective intraparticle diffusion coefficient D_{pz} to the total diffusion coefficient in the column D or equivalently its value normalized to the bulk self-diffusivity $\gamma = D/D_m$. The Maxwell equation applied to diffusion in a medium with retention writes as [18,26]:

$$\gamma = \frac{D}{D_m} = \frac{1}{\varepsilon(r_m)[1+k']}\frac{1+2\beta[1-\varepsilon_e]}{1-\beta[1-\varepsilon_e]} \quad \text{Eq. (1)}$$

where $\varepsilon(r_m)$ is the total porosity accessible to the diffusing molecule of size r_m, ε_e is the external porosity or the porosity in the macropores, and k' is the retention factor. k' is calculated from the mean retention time as $k' = (t_R - t_0)/t_0$ where t_R and t_0 are the mean retention times of the analyte in adsorbing conditions and non-adsorbing conditions, respectively. In practice, γ is obtained experimentally using the peak parking method as explained in the next section. The parameter β can be expressed by inverting Eq. (1). Upon introducing $\alpha_{pz} = (1 + 2\beta)/(1-\beta)$, the effective intraparticle diffusion coefficient in adsorbing conditions D_{pz} can be expressed as:

$$\frac{D_{pz}}{D_m} = \frac{\alpha_{pz}[1-\varepsilon_e]}{\varepsilon(r_m)\,[1+k'] - \varepsilon_e} \quad \text{Eq. (2)}$$

Core-shell particles. In this case, the porosity in the porous zone is calculated as $\varepsilon_{pz} = \varepsilon_p/(1-\rho^3)$ where ρ is the ratio of the non-porous core radius to the particle radius. To account for the effect of solid core, it is also important to distinguish between D_{pz} and D_p. While D_p is the effective particle diffusion, D_{pz} is the effective diffusion in the mesoporous zone (entire particle in the case of fully porous particles, shell layer in the case of a core-shell particle). For spherical particles, the relation between the two diffusion coefficients is given by [8]: $D_{pz} = (1+\rho^3/2)D_p$.

2.1.2 Maxwell model for monoliths

The Maxwell model has also been established for cylinder packings [17]. It is assumed to provide a reliable representation of the skeleton in monoliths [10]. In this case, Eq. (1) giving the ratio γ is slightly modified:

$$\gamma = \frac{D}{D_m} = \frac{1}{\varepsilon(r_m)[1+k']}\frac{1+\beta[1-\varepsilon_e]}{1-\beta[1-\varepsilon_e]} \quad \text{Eq. (3)}$$

Again, by inverting this last equation, one obtains the following expression for the parameter β. Like for spherical particles, the intraskeleton effective diffusion coefficient D_{pz} for monoliths in adsorbing conditions is given by Eq. (3) but with $\alpha_{pz} = (1+\beta)/(1-\beta)$.

2.2. Surface diffusion coefficient

The intraparticle diffusion coefficient D_{pz} has two contributions: the diffusion in the mesoporous zone $\gamma_{pz}D_m$ and surface diffusion D_s. In the literature, it is often assumed that the two phenomena occur in parallel so that the following model is used [26]:

$$\frac{D_{pz}}{D_m} = \frac{\varepsilon_{pz}(r_m)\gamma_{pz} + \left[1 - \varepsilon_{pz}(r_m)\right]K_a D_s/D_m}{\varepsilon_{pz}(r_m) + \left[1 - \varepsilon_{pz}(r_m)\right]K_a} \qquad \text{Eq. (4)}$$

where the adsorption equilibrium constant $K_a = k'\varepsilon(r_m)/[1 - \varepsilon(r_m)]$ takes into account the volumes of the liquid and solid phases. The term γ_{pz} is the ratio between the intraparticle diffusion coefficient in the porous zone without adsorption and the molecular diffusion coefficient D_m. The diffusion in the mesoporous zone is hindered by the tortuosity τ_{pz} and the friction coefficient $k_f(r_m)$ which is due to the collisions between the diffusing molecule and the pore walls [6]:

$$\varepsilon_{pz}\gamma_{pz} = \varepsilon_{pz}(r_m)\frac{D_{pz}^0}{D_m} = \frac{\varepsilon_{pz}(r_m)\, k_f(r_m)}{\tau_{pz}(r_m)} \qquad \text{Eq. (5)}$$

In some literature [e.g. 10] the value of ${\tau_{pz}}^2$ is used with a factor 2 in the exponent coming from a difference in the definition of the tortuosity which is then considered as a ratio of length, whereas in the present paper the definition used is a ratio of lengths to the square.

The particle porosity $\varepsilon_{pz}(r_m)$ accessible to a molecule of a given size r_m can be estimated in non-adsorbing conditions with the same molecule or can be directly calculated with the following equation (which considers a spherical molecule in a cylindrical pore): $\varepsilon_{pz}(r_m) = \varepsilon_{pz}^0(1 - \lambda)^2$ where ε_{pz}^0 is the total particle porosity calculated from the porous volume obtained by classical characterization methods (e.g. nitrogen adsorption or inverse size exclusion chromatography with an analyte molecule very small compared to the pore size). In this equation, $\lambda = r_m/r_p$ is the ratio between the molecule radius r_m and the pore radius r_p. The friction coefficient is usually calculated using Renkin equation [19]: $k_f(r_m) = 1 - 2.10\lambda + 2.09\lambda^3 - 0.95\lambda^5$.

While the particle tortuosity τ_{pz} may be taken as a constant which usually lies between 1.4 and 2, it can also be considered as dependent on the particle porosity accessible to a molecule of a given size r_m. In previous publications [8,18], it was shown that the Weissberg equation could be used to calculate the particle tortuosity. The Weissberg equation writes $\tau_{pz}(r_m) = 1 - p\ln\varepsilon_{pz}(r_m)$ where p is a topological factor that depends on the morphology of the solid. The tortuosity of the silica used here has been measured previously by electrical measurements and

the details are given in [18]. D_{pz}/D_m was calculated from the overall effective diffusion coefficient and the Maxwell model introduced above. By using Eq. (4), the surface diffusion coefficient D_s can be calculated in a second step.

Because the assumption of parallel in-pore diffusion and surface diffusion is rather crude, another approach is proposed here. We consider the molecular trajectory as an intermittent dynamic made of a succession of adsorption steps and relocation steps in the pore network between two adsorption events. Some statistical properties of this rich dynamics type were already analyzed [28,29]. Various statistics can be chosen to describe elementary molecular displacement inside the pore, such as overdamped Langevin dynamics, Pearson statistics [28] or Brownian motions based on Gaussian probability. In any case, the trajectory of a molecule can be decomposed in N steps involving successive displacements inside the pores, $\vec{r}_i$, and displacements at the surface, $\vec{e}_i$, (with i varying between 1 and N). For a sufficiently long path (N very large), the mean square displacement can be written as (e.g. [30]):

$$\langle \vec{r}^2 \rangle = \left\langle \left[\sum_{i=1}^{N} \vec{r}_i\right]^2 \right\rangle + \left\langle \left[\sum_{j=1}^{N} \vec{e}_j\right]^2 \right\rangle \quad \text{Eq. (6)}$$

where complete decorrelation between adsorption and bulk self-diffusion segments is assumed. At long time (large N), the mean square displacement associated to molecular self-diffusion can be written as $\langle \vec{r}^2 \rangle = 6D_{app}N[t_a + t_r]$ where D_{app} is the apparent self-diffusion coefficient in the considered porous system and t_a (resp. t_r) is the mean residence time on the surface (resp. mean duration of a path inside the pore between two contacts with the surface). For non-adsorbing conditions, *i.e.* $t_a = 0$, we get

$$\left\langle \left[\sum_{i=1}^{N} \vec{r}_i\right]^2 \right\rangle = 6D_{app}^0 N t_r = \frac{6D_{m,p}Nt_r}{\tau_r} \quad \text{Eq. (7)}$$

where D_{app}^0 is the self-diffusion coefficient in the porous network without adsorption and τ_r the associated pore network tortuosity. $D_{m,p}$ is the local self-diffusion coefficient inside a pore; it is here considered as different from the bulk diffusion coefficient D_m as local confinement effects might lead to non-negligible departure between these two values. The second right hand side of Eq. (6) reads $\left\langle \left[\sum_{j=1}^{N} \vec{e}_j\right]^2 \right\rangle = 4D_s N t_a$ where the surface self-diffusion D_s is considered bidimensional and independent of pore curvature, which means that the lengths covered by adsorbed molecules on the surface are lower than pore size. This leads to the following equation:

$$D_{app} = \frac{t_r}{t_r+t_a} \times \frac{D_{m,p}}{\tau_r} + \frac{t_a}{t_r+t_a} \times \frac{4}{6} \times D_S \quad \text{Eq. (8)}$$

At this point, it is needed to take into account detailed balance conditions which allow imposing thermodynamic equilibrium between the adsorbed layer and the molecular population in the pore network. This condition reads $t_a/[t_a + t_r] = f_{ads,}$ where f_{ads} is the average molar fraction of molecules that are adsorbed at equilibrium (in this equation, we use assume ergodicity which imposes that the fraction of time spent by a molecule in one of the phases is proportional to its molar fraction in this phase). Using the later condition into Eq. (8), we get $D_{app} = (1 - f_{ads})D^0_{app} + \frac{4}{6} f_{ads}\, D_S$. This equation was proposed to analyse gas diffusion inside porous media [31].

t_a and t_r can be related directly to the experimental retention times with adsorption t_R and without adsorption t_0. Indeed, the latter can be decomposed into contributions from inside t_0^{pz} and outside t_0^{ext} the mesoporous zone:

$$t_R = t_0^{ext} + t_0^{pz} + t_{ads} = t_0^{ext} + N(t_r + t_a) \qquad \text{Eq. (9)}$$

$$t_0 = t_0^{ext} + t_0^{pz} = t_0^{ext} + Nt_r$$

where $t_0^{pz} = Nt_r$ is the porous zone retention time without adsorption, $t_{ads} = Nt_a$ is the time spent in the adsorption phase, while the external retention time t_0^{ext} can be determined in non-adsorbing conditions of excluded molecules. While N is generally unknown, the effective diffusivity formula for D_{app} allows using experimental data for f_{ads} (see in line equation above). In more detail, the equilibrium adsorption constant K_a can be calculated from chromatographic experiments as $K_a = C_a/C_s = \varepsilon k'/(1 - \varepsilon)$ where C_a is the concentration of adsorbed molecules expressed as moles per volume of solid phase and C_s the bulk solution concentration. ε is the porosity of the considered porous medium and k' the corresponding retention factor. By imposing the mass balance condition, it is easy to verify that: $f_{ads} = (1 - \varepsilon)K_a/[\varepsilon + (1 - \varepsilon)K_a]$.

Coming back to chromatography experiments, one can now consider two cases.

(1) The considered porous medium is the mesoporous zone. In that case $D_{app} = D_{pz}$ (adsorbing conditions) and $D^0_{app} = D^0_{pz}$ (non-adsorbing conditions) are those of the mesoporous zone whose porosity is ε_{pz}. Using the mass balance condition, the equation for D_{app} given above becomes:

$$D_{app} = D_{pz} = \frac{\varepsilon_{pz}(r_m)}{\varepsilon_{pz}(r_m)+[1-\varepsilon_{pz}(r_m)]\,K_a} D^0_{pz} + \frac{4}{6} \times \frac{[1-\varepsilon_{pz}(r_m)]\,K_a}{\varepsilon_{pz}(r_m)+[1-\varepsilon_{pz}(r_m)]\,K_a} D_S \qquad \text{Eq. (10)}$$

(2) The considered porous medium is the column itself. In that case, $D_{app} = D$ and $D_{app}^{0} = D^{0}$ are those of the whole column and correspond to the total diffusion coefficients with and without adsorption, respectively:

$$D = \frac{\varepsilon(r_m)}{\varepsilon(r_m)+[1-\varepsilon(r_m)]\,K_a} D^0 + \frac{4}{6} \times \frac{[1-\varepsilon(r_m)]\,K_a}{\varepsilon(r_m)+[1-\varepsilon(r_m)]\,K_a} D_S \qquad \text{Eq. (11)}$$

Interestingly, starting from a microscopic description based on serial molecular transport, a macroscopic parallel description of the diffusion coefficient is obtained where the surface diffusion is simply multiplied by a factor 4/6 (which is the ratio between surface/bulk dimensions).

3. Material and methods

3.1 Chemicals

The organic solvents used are tetrahydrofuran (THF) purchased from Carlo Erba Reagents (SDS) and n-heptane. Toluene (T) was purchased from Aldrich. A series of twelve polystyrenes (-CH[C_6H_5]-CH_2-)$_n$ with various molecular weights and molecular sizes was provided from Polymer Standards Service (Mainz, Germany). They are named from P01 for the monomer to P12 for the biggest polymer. THF was used for non-adsorbing conditions while a heptane:THF mixture (97:3) was used for adsorbing conditions. Toluene and polystyrenes were dissolved in the mobile phase at a concentration of 1 g/L. Detection of the polymers was done using UV-VIS spectroscopy at a wavelength of 262 nm.

3.2. HPLC system

The experiments were done using the 1200 HPLC system (Agilent Technologies) including a quaternary gradient pump with a multi-diode array UV-VIS detector, an automatic sample injector with a 100µL loop, an autosampler and a thermoregulated column compartment. The injection volume was set at 1 µL and all experiments were conducted at 298 K. The system was controlled using the Chemstation software. The columns used in this study were composed of porous silica with various morphologies: fully porous silica particles (Lichrospher Si100, Merck), core-shell silica particles (Poroshell 120, Agilent) and monolithic silica (Chromolith, Merck). The main characteristics of the columns and their characterization made by means of mercury porosimetry, nitrogen adsorption and ISEC can be found in Ref. [18]. The tortuosities determined by electrical measurements are also given in Ref. [18]. The main characteristics are

summarized in Table I. The silicas were characterized by thermogravimetry (TGA) using the TA Instruments TGA Q500. Around 10 mg of sample are placed in a platinum crucible and lowered into a temperature-controlled oven. The evolution of the sample mass was followed under argon atmosphere as a function of temperature from 25 to 850 °C with a heating rate of 5°C/min. The number of silanol groups (number of OH per nm^2) was determined from the weight loss between 175 and 800°C. All results are given in Table I.

3.3. Molecular diffusion coefficients

The molecular diffusion coefficients of toluene and of the smallest polymers (P01-P03) in the mixture heptane:THF 97:3 were determined by Taylor Dispersion Analysis (TDA). Such TDA experiments were done three times with a stainless-steel tube (0.876 mm internal diameter, length 1.20 m) at three different flow rates. The molecular diffusion coefficient D_m was calculated using the following equation:

$$D_m = R_C^2(t_R - t_i)/24(\sigma_R^2 - \sigma_i^2) \quad \text{Eq. (12)}$$

were R_C is the capillary internal radius, t_R and σ_R^2 are the mean retention time and variance of the peak with the stainless-steel tube, and t_i and σ_i^2 correspond to the retention time and the variance obtained without the stainless-steel tube. Eq. (12) is valid as long as the two following conditions are fulfilled: (1) The dimensionless residence time $t' = D_m t_R R_c^2$ should be $t' > 1.4$ and (2) and the Peclet number should be Pe > 70. Those conditions are verified here. The hydrodynamic radius of the polymers r_m in the mixture is then calculated by using Stokes-Einstein equation. D_m and r_m for T, P01, P02 and P03 in the mixture 97:3 (heptane:THF) at 298 K are given in Table II. The molecular diffusion coefficients and size of polystyrenes in non-adsorbing conditions, i.e. using pure THF as solvent, can be found in Ref. [18].

3.4. Peak parking experiments

The peak parking method was used to measure the apparent effective diffusion coefficient of molecules through the different porous media under study. In these experiments, 1 µL of a dilute sample solution was injected at a rate of 0.5 mL min^{-1}. The columns were eluted during the time needed for the liquid sample to arrive about half length of the column. Then, the flow was stopped and the molecules left to diffuse freely during a given time called the parking time t_p. The flow was then started again to the same flow rate and the peak variance of the solute band σ_t^2 was measured. In more detail, the peak variance is measured by fitting the chromatograms with a Gauss function. To correct for other band broadening effects (injector,

connecting tubing), the peak variances obtained without parking were subtracted from the peak variance values obtained with parking. The variance in time unit was then plotted versus the parking time to infer from the slope the effective diffusion in the column:

$$D = \frac{1}{2}\frac{\Delta\sigma_t^2}{t_p}\left(\frac{\varepsilon_e}{\varepsilon(r_m)[1+k']}\right)^2 u^2 \qquad \text{Eq. (13)}$$

where the porosities ε_e and ε are obtained by ISEC, u is the interstitial linear velocity and k' is the retention factor. k' is given by $k' = [t_R - t_0]/t_0$ where t_R and t_0 are the mean retention times of the analyte in adsorbing and non-adsorbing conditions, respectively.

4. Results and discussion

4.1. Peak identification and polydispersity index

The analyte molecules used in this study are toluene and a set of polystyrenes having different sizes. While P01 is the monomer used for the polystyrene synthesis, the polystyrenes ranging from P02 to P12 are polydisperse with a polydispersity index PDI > 1.0. In practice, this means that each polystyrene is a mixture of polymers having a different number of units. In adsorbing conditions, toluene and P01 have only one peak but for the other polystyrenes many peaks are observed in the chromatograms. The heptane/THF mixture (97/3) was chosen to ensure a good separation of the fractions contained in each polystyrene. It was shown that adsorption increases usually with the molecular weight of the polymer, therefore leading to a significant polymer separation according to their affinity for the silica surface [32]. For the polymerisation of polystyrene, n-butyllithium (C_4H_9Li) is added to styrene monomer to react with another styrene radical in the next step and so on. At the end of this stage, the terminating agent proton H^+ is added to remove lithium at a given time. At end, the molecular weight of the polystyrenes is given by $M_w = 104P + 58$ where P is the number of units.

The PDIs given by the supplier are 1.09 and 1.05 for P02 and P03, respectively. Such PDI, which corresponds to the width of the molecular weight distribution, is defined as the ratio of the average molecular weight M_w to the number average molecular weight M_n, i.e. PDI = M_w/M_n. M_w is calculated from the weight fraction distribution of molecules of different size, $M_w = \sum_{i=1}^{n} M_i$ where n is the degree of polymerization while w_i and M_i are the mass fraction and molecular weight of each fraction. M_n is the total weight of all polymer molecules in the sample divided by the total number of polymer molecules: $M_n = \sum_{i=1}^{n} N_i M_i \,/\, \sum_{i=1}^{n} N_i$ where N_i is the number of molecules of size i: $N_i = N_A m_i / M_i$ (in this equation, m_i is the total mass for each

fraction while N_A is Avogadro's number). From the chromatograms shown in figure 1 for the column filled with fully porous silica particles, one can obtain the mass fraction of each peak. When doing so, the number of units for each peak must be assumed. For the polymer P02, the first peak has been assumed to correspond to 3 units, 4 units for the second peak, and so on. Then, the highest peaks for P02 and P03 are assumed to correspond to 6 and 13 units, respectively. By using the equations above, the PDI for P02 and P03 are found to be 1.07 and 1.08, respectively. These values are close to those provided by the supplier. Similar chromatograms were obtained with Poroshell and Chromolith columns.

4.2. Porosities and diffusivities in non-adsorbing conditions

To calculate the surface diffusion coefficients, it is necessary to estimate or measure experimentally a number of parameters such as the mean retention time t_0, the porosities ($\varepsilon(r_m)$ the total porosity of the column accessible to a probe of size r_m, ε_e the external porosity) the molecular diffusion coefficients D_m, the total diffusion coefficient in the column D^0 and the effective diffusion in the mesoporous zone D_{pz}^0 in non-adsorbing conditions for each polymer length. Those parameters have been published previously in non-adsorbing conditions for the three columns and polystyrenes under study (by using THF instead of the mixture heptane/THF as solvent [18]). The parameters were estimated by taking the mean values of the molecular weights for the polystyrenes. In adsorbing conditions, each polystyrene is divided in fractions having different unit numbers and thus different molecular weights. To calculate each fraction contribution, it is necessary to rely on a simple mathematical equation. In practice, a second order equation can be used for the retention time and porosity ($y = a + bM_w + cM_w{}^2$) while a power law can be used for the diffusion coefficients ($y = aM_w{}^b$). These equations were used to calculate the following parameters for each fraction in non-adsorbing conditions (THF): t_0, ε, D_m, $\frac{D^0}{D_m}$,$\frac{D_{pz}^0}{D_m}$. Typical illustrative fits are provided in figure 2 for the retention time t_0 in non-adsorbing conditions for the three columns (the regression coefficient *R* is such that $R^2 > 0.95$ for all parameters and columns under study).

4.3. Retention factor k_i' as a function of number of polysterene unit

Each chromatogram peak corresponding to a given fraction *i* was fitted with a Gauss function to determine the peak width and mean retention time $t_{R,i}$. Finally, the retention factor for each fraction in the *n*-heptane/THF mixture can be calculated by applying for each fraction *i* the following equation: $k_i' = \left[t_{R,i} - t_{0,i}\right]/t_{0,i}$. The mean retention time $t_{0,i}$ is obtained from the

equations given in Section 4.2. The evolution of retention factor of the different fractions for P01, P02 and P03 through the Lichrospher Si 100, Poroshell and Chromolith columns at a flow rate of 0.5 ml.min^{-1} is shown in figure 3. As expected, the retention factor increases with increasing the number of units. Such behaviour has also been observed in high-performance liquid chromatography of polystyrene oligomer on the bare silica column in the THF/*n*-hexane mixture. Mass spectrometry was further used to recognize the degree of polymerization for the oligomer peaks in this case [33]. For the three columns, the retention times for the P02 fractions agree with that of the P03 fractions with the same numbers of units. This indicates that the P02 and P03 fraction affinity for the silica surface in the column with the same numbers of units is comparable: there is apparently no competition between these fractions of a given polymer sample. Moreover, this result confirms that our peak assignment to a given polymer chain length is correct. Figure 3 also shows that the retention factors for P02 and P03 in the Si 100 column are larger than for the other columns. This suggests that the surface chemistry in these two materials differ: for silica-based materials, it is often related to the surface density of silanol groups. The number of OH per nm^2 determined by TGA for the three columns are given in Table I. The number of OH per nm^2 is 3.1 for Lichrospher Si100, 2.4 for Poroshell and 1.1 for the Chromolith columns. The retention factor k' increases with the number of OH per nm^2 as seen in figure 3; the largest and smallest k' are obtained for Lichrospher Si100 and Chromolithic columns, respectively.

4.5. Effective diffusion coefficient by peak parking method

Typical chromatograms are given in figure 4 for the monomer P01 and the polystyrene P02 with the column Lichrospher Si100. The peaks are symmetrical and broaden with increasing parking time due to diffusion. For P02 and P03, each polymer fraction was fitted with a Gaussian function. The variance of each peak was evaluated for each parking time to determine the effective diffusion coefficient from the Gauss fit. The peak variance is plotted as a function of the parking time in figure 5 for P01 and some fractions of P02 for the Lichrospher column. Similar results were obtained for the two other columns (they are not shown here for the sake of brevity). It should be noticed that all the curves are straight lines. The slope decreases as the molecular size increases due to the expected decrease in effective diffusion. By applying Eq. (13), the effective diffusion coefficient D for each probe can be determined. The total accessible porosity $\varepsilon(r_m)$, retention factor k' and molecular diffusivity D_m were estimated for each fraction using fits against a second order or power law equation as explained in Section 4.2. The ratios D/D_m as a function of the adsorption equilibrium constant K_a is shown in figure 6.

The relative error in the determination of D/D_m is ± 10% (±5% error for the determination of D_m by TDA measurements and ±5% for the determination of the slope of the peak variance *versus* peak parking time). As expected, for all columns, D/D_m decreases significantly upon increasing the adsorption constant K_a. The effective diffusion D is larger in the monolithic column compared to fully porous and core-shell particle columns. This result may be explained by the fact that the monolithic column possesses a much more open structure than packed columns [34]. In fact, the external porosity of the monolithic column is around 70% against 40% for packed columns while the total porosity is around 90% for monolithic columns against 80 % for fully porous particles and 70% for core-shell particles columns. The values for $K_a = 0$ were published previously [18] and were obtained with P01 and P02 in non-adsorbing conditions with the same columns in pure THF. For small K_a, a maximum is observed for the Lichrospher Si100 and Poroshell columns, which could be explained by diffusion in the mesoporous zone and at the surface of the solid as discussed in the next part.

4.4. Diffusion in the mesoporous zone and surface diffusion

Experimentally, $D_{pz}/D_m$was derived from the experimental values D/D_m using the Maxwell model as explained in Section 2.1. D_{pz}/D_m is plotted in figure 7 as a function of the adsorption equilibrium constant K_a for the three columns (the relative error over D_{pz}/D_m is about ±10%). D_{pz}/D_m values for the fully porous and core-shell particle columns go through a maximum for low K_a values and then continuously decrease. A different behaviour is observed for the monolithic column where D_{pz}/D_m decreases monotonously with K_a. The occurrence of this maximum which indicates that diffusion may be higher in the presence of adsorption than in its absence is of course interpreted by the contribution of surface diffusion which is now calculated.

Surface diffusivity D_s was determined from (i) the equations proposed in this paper by considering the mesoporous zone [Eq. (10)] or the whole column [Eq. (11)] and (ii) the equation which is usually employed when considering parallel diffusion [Eq. (4)]. Figure 8 shows D_s/D_m as a function of the adsorption constant K_a for the three columns. These data show that D_s/D_m obtained by considering the mesoporous zone or the whole column are similar except for the monolithic column for which D_s/D_m are slightly higher when considering the whole column. The Maxwell model is used for the determination of D_{pz} and D_{pz}^0 in eq. 10, but for eq. 11 no model is necessary for the determination of the total diffusion coefficient, all the parameters being determined experimentally. These results indicate that the Maxwell model

provides a good estimate of the porous zone diffusion coefficient. Higher order models like the Torquato model could also be used but the Maxwell model despite its simplicity gives a good estimation of surface diffusion as also concluded in [10]. D_s/D_m obtained by considering the classical parallel diffusion model are slightly lower than the values obtained by using Eqs. (10) or (11) because of the factor 4/6. Eq. (11) is simpler to use because D_s is directly determined from D_0/D_m and D/D_m obtained by the peak parking method in non-adsorbing and adsorbing conditions, respectively. Regardless of the model used, D_s significantly decreases upon increasing adsorption strength. For $K_a > 3$, D_s/D_m are around 0.1-0.3 for the Lichrospher and Poroshell columns and around 0.3-0.6 for the monolithic column. Upon increasing K_a, surface diffusion is faster in the monolithic column compared to the Lichrospher and Poroshell columns, therefore indicating that the interactions of molecules with surface are probably different. For low $K_a < 2$, D_s/D_m reaches values larger than 1 whatever the model in the case of packed columns. $D_s/D_m > 1$ indicated that surface diffusion of the solutes is faster than bulk diffusion in the mobile phase. In other words, for such D_s/D_m, the solutes are more mobile near the surface which lowers their mass transport resistance. Fast surface diffusion was also observed in reversed-phase liquid chromatography [4]. For the monolithic column, even at low K_a, $D_s/D_m < 1$ regardless of the model used. The three columns are made of pure silica with surface silanol groups which have a polar character due to the polarity of the covalent bond between hydrogen and oxygen atoms. In this study, a heptane/THF mixture is used; those solvents can interact with the silanol surface groups due to non-specific interactions (van der Waals forces). In particular, THF may exhibit polar interactions with silanol groups. A part of the silanol groups is probably covered with THF molecules. In pure THF, the polystyrene molecules are not adsorbed on the silica surface so that polystyrene is not able to displace the THF molecule from the silica surface. The adsorption of polystyrene molecules on silica, which can be due to the interaction of benzene ring with silanols, is enhanced in the presence of heptane which contributes to the displacement of THF. At low K_a, the surface diffusion D_s is close or even larger than D_m for Lichrospher and Poroshell columns. A different behavior is observed for the monolithic column where $D_s/D_m < 1$ even at low K_a (regardless of the model used). These results indicate that, at low K_a, the behaviour with the three silica columns is different; this could be explained by the silanol surface density which differs between these three columns (see Table I). D_s/D_m as obtained from the three proposed equations are plotted in figure 9 as a function of the number of OH groups per nm^2. These data are shown for the three silica columns upon transport of the monomer P01 and the fraction of P02 having 6 units.

For a small molecule such as P01, D_s/D_m increases with increasing the number of OH groups per nm^2. For larger molecules (e.g. P02, P = 6), the effect of the number of OH groups per nm^2 is less pronounced; this indicates that the surface diffusion mechanisms depend strongly on the number of OH groups per nm^2 but also on the size of the molecule. Zhang et al. [35] studied by means of simulation the diffusion of polystyrene on silica surfaces grafted with different densities of hydroxyl groups. These authors showed that, at low or full grafting, diffusion is facilitated compared to moderate grafting density because the activation energy required to induce diffusion is smaller and polystyrene chain prefer a shrinking configuration leading to faster diffusion. For the three columns, $\frac{D_s}{D_m}$ decreases strongly upon increasing K_a and/or the polymer length. Our results are compared hereafter with theory and simulation of polymer surface diffusion previously published by assuming a two-dimensional model for displacement. Such modeling predicts that surface diffusion should scale as $D_s \sim P^{-\alpha}$ with α ranging between 0.75 and 1.5 (we recall that P is the number of units of monomer) [36]. While α = 1 for the Rouse model (free lateral motion of the polymer chain) [37], α = 1.5 for a reptation-type model (hindered lateral motion of the polymer chain) [38, 39]. The difference between these two mechanisms generally depends on surface roughness at the nanoscale. Generally, the Rouse model is verified on smooth surfaces while α becomes larger than 1 on rougher surfaces [38, 39]. Skaug et al. [36], who found α ~ 0.6±0.2, proposed an intermittent-hopping mechanism dominated by a desorption-mediated mechanism; in this model, polymers desorb from the interface, diffuse in the bulk liquid, and adsorb again on another surface site. The log of the surface diffusion coefficient obtained with Eq. (13) is plotted as a function of log P in figure 10 for the three columns. These data are shown for P ranging between 1 and 10 corresponding to the monomer (P = 1) and the different fractions of the polymer P02 (P = 3-10). Similar plots were obtained for the two other models used to infer D_s. As expected by the models proposed in the literature, a linear relation is obtained between log D_s and log P (which is, in particular, consistent with the fact that D_s was found to scale as $1/n$ where n is the hydrocarbon chain length in [40]. α is given in Table 3 for the different models and columns used. For the Lichrospher column, α is close to unity (0.9-1.1 depending on the model used) for the smallest polymers (P = 1-5). For the poroshell column, α is around 0.9 for P ranging between 1 and 10. For the Lichrospher column, the results for P = 5-10 are not shown because D_s/D_m is very close to zero and the error bar becomes very large. Surface diffusion for those columns seems to follow the Rouse model. For the Chromolith column, α is around 0.5 and 0.7 according to the model used (P = 1-10). Such α-values are close to that obtained by Skaug et al. [36] who

proposed an intermittent hopping mechanism. It is finally logical that the transition from a mechanism to the other depends on silanol surface density. For example, the Rouse mechanism can be associated with high silanol density whereas hopping mechanism are observed when distance between sites is large, *i.e.* low silanol density. It means that the activation energy to jump between two adjacent sites increases when distance increases. All in all, these data show that the surface diffusion mechanisms differ between the three columns.

Recently Bousige et al. [41] proposed a novel strategy by mapping molecular dynamics simulations onto intermittent Brownian motion to describe fluid diffusion in disordered nanoporous media. These authors showed that surface diffusion decreases linearly E/k_BT where E is the adsorption energy of an adsorbed molecule (see Supplementary Fig. S7 in Ref. [41]). In this study, the adsorption constant K_A is such that it can be written as $\ln K_A = E/k_BT$. D_s is plotted as a function of $\ln K_A$ in figure 11; a linear relation is obtained for the three columns as expected from the multiscale approach proposed in [41]. The slope is different from a sample to another as this reflects an expected impact of the surface chemistry at play. The largest slope is obtained for Si100, which clearly shows a higher affinity for the molecules studied here (as already shown in figure 3). The behaviours observed in figure 8 and figure 11 are intriguing; at low affinity, the surface diffusion is higher on Si100 whereas it is lower than for the other samples at high affinity. This apparent behaviour is somewhat qualitatively comparable to the simulation data obtained in Ref. [41]; surface affinity is increased by increasing the polymer chain length in the present work while the adsorption energy is directly increased in the simulation part at constant molecule size. This expected behaviour is confirmed, for example, by calorimetry experiments which indicate that, at low equilibrium concentration, molecules are adsorbed in a rather flat conformation (making the adsorption energy proportional to the chain length) [32]. When the solid is varied, the affinity changes despite an overall identical chemical nature. As already discussed, the difference may arise from the density of silanol groups on the surface. Moreover, the activation energy for a molecule to jump between adjacent surface groups may depend both on the surface group distance and molecule size. As shown above, figure 9 shows that surface diffusion is less affected by OH density when molecules are larger.

5. Conclusion

In this paper, an approach based on the intermittent dynamics of molecules in pore space is proposed. It appears that this approach leads to a simple equation that relates the apparent

diffusion coefficient, the pore diffusivity and surface diffusivity like in similar, classical approximations based on parallel transport between pore fluid and surface fluid. The evolution of surface diffusion is analyzed in the present work as a function of the affinity of the probe for the surface. This affinity is found to depend both on the probe chain length and surface chemistry – the latter being characterized here by the OH silanol density at the silica surface. For short chain lengths, a non-monotonic evolution of the surface diffusion with affinity (or retention factor) may be observed in some cases. However, generally, the surface diffusion decreases upon increasing the surface affinity. Interestingly, the longest chain lengths are less sensitive to the OH silanol surface density. Further investigation including calorimetric studies is needed to evaluate polymer/surface interactions; this would help understand the mechanisms of surface diffusion by looking for complementary correlations between these parameters and the measured surface diffusion coefficients.

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Glossary

D	Overall effective Diffusion coefficient (adsorbing conditions)	$m^2.s^{-1}$
$D°$	Overall effective Diffusion coefficient (non-adsorbing conditions)	$m^2.s^{-1}$
D_{app}	Apparent self-diffusion coefficient in the porous network under adsorbing conditions	$m^2.s^{-1}$
D_{app}^{0}	self-diffusion coefficient in the porous network (non-adsorbing conditions)	$m^2.s^{-1}$
D_m	Bulk self diffusivity	$m^2.s^{-1}$
$D_{m,p}$	local self-diffusion coefficient inside a pore	$m^2.s^{-1}$
D_p	In-pore diffusion coefficient	$m^2.s^{-1}$
D_{part}	Effective particle diffusion coefficient	$m^2.s^{-1}$
D_{pz}^{0}	Particle diffusion coefficient in the mesoporous zone (non-adsorbing conditions)	$m^2.s^{-1}$
D_{pz}	Particle diffusion coefficient in the mesoporous zone (adsorbing conditions)	$m^2.s^{-1}$
D_s	Surface diffusion coefficient	$m^2.s^{-1}$
$\vec{e}_i$	Displacement at the surface	m
f_{ads}	Average molar fraction of molecules adsorbed at equilibrium	
k'	Retention factor	
Ka	Constant of adsorption	
k_B	Boltzmann Constant	$m^2.kg.s^{-2}.K^{-1}$
k_f	Friction factor	
Mn	Number average molecular weight of the sample	$g.moL^{-1}$
Mw	Molecular weight of the sample	$g.moL^{-1}$
N_a	Avogadro's number	mol^{-1}
N	Number of steps in Brownian motion	
P	Number of units in the polystyrene molecule	
p	Topological factor	
Rc	Capillary internal radius (TDA)	m
$\vec{r}_i$	Displacement inside the pores	m
r_m	Molecule hydrodynamic radius	m
r_p	Pore radius	m
t_a	Mean residence time on the surface	s
t_{ads}	time spent in the adsorption phase	s
t_0	Experimental mean retention time (non-adsorbing conditions)	s
t_0^{ext}	Time spent outside the mesoporous zone (external porosity) (non-adsorbing conditions)	s
t_{oint}	Internal retention time without adsorption	s
t_0^{pz}	Time spent inside the mesoporous zone (non-adsorbing conditions)	s
t_p	Parking time	s

t_r	Mean duration of a path inside the pore between two contacts with the surface	s
t_R	Experimental mean retention time (adsorbing conditions)	s
u	Interstitial linear velocity	$m.s^{-1}$
α_{pz}	Parameter in the Maxwell equation	
β	Parameter in the Maxwell equation	
ε	Total porosity	
ε_e	external porosity or porosity in the macropores	
ε_{pz}^{0}	Total particle porosity in the mesoporous zone	
$\varepsilon_{pz}(r_m)$	Particle porosity in the mesoporous zone accessible to a molecule of size r_m	
γ	Ratio between D and D_m	
λ	Ratio of molecule to pore radius	
ρ	Ratio of the non porous core radius and the particle radius	
σ_t^2	Peak variance of the solute in time units	s^2
τ_p	Particle tortuosity	
τ_r	Pore network tortuosity	
τ_{pz}	Tortuosity in the mesoporous zone	