

# Hindered diffusion of proteins and polymethacrylates in controlled-pore glass: An experimental approach

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## Abstract

The diffusion of several proteins and acrylic polymers on controlled pore glass particles has been studied using the chromatographic technique. Effective diffusivities for compounds of several molecular weights and different chemical nature diffusing in solids of different pore size were measured together with the adsorption constants, using the chromatographic technique and the method of Kubin and Kucera. Several empirical, semiempirical and phenomenological models are tested for the description of the experimental values of  $f$  (ratio between the effective and the bulk diffusivities) vs.  $\lambda$  (ratio between the size of the molecule and that of the pore). While the empirical and semiempirical models are exponential and hyperbolic functions of  $\lambda$ , respectively, the phenomenological models are based on the partition coefficient ( $K_{eq}$ ) and the drag coefficient ( $K^{-1}$ ), which include the interaction energies between the diffusing molecules and the pore wall, changing the geometry (sphere–plane or sphere–cylinder) and the nature of the interaction (Lifshitz–van der Waals, electrostatic and acid–base) from model to model. The fit of the proposed models to experimental data as well as the value of the parameters obtained have been compared to data given in the literature. Both a sphere–plane Lifshitz–van der Waals interaction model with linear increase of the Hamaker constant with  $\lambda$  and a sphere–inner cylinder multiple interaction models are chosen for polymethacrylates and proteins. Both are able to fit polyacrylate diffusion data well, while the more complex SEI model including all interaction types is more adequate to describe protein diffusion.  
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## 1. Introduction

The transport of a solute with a size similar to that of the pore through which it is transported is known as hindered diffusion (Shao and Baltus, 2000a,b; Deen, 1987), as this transport is slower compared to that in the bulk phase. This phenomenon is of great importance in devices for controlled release of drugs and pesticides, ultrafiltration and other membrane techniques for reaction and/or separation, in chromatographic and electrophoretic separations, and in heterogeneous catalysis (Shao and Baltus, 2000a,b). Diffusion transport inside porous and polymeric solids have been the subject of extensive work, from studies whose aim was the experimental observation of such phenomenon to others where mathematical models for the description of transport, that is, hydrodynamic treatment of

diffusion, were introduced (Smith and Deen, 1983; Davidson and Deen, 1988; Shao and Baltus, 2000a,b). Deen (1987) wrote an extensive review aimed at both types of studies and mainly focused on the hindered diffusion of neutral spherical particles. Transport of polymers in porous materials is usually described as hindered diffusion. This diffusion is much influenced by the existence of interactions (Davidson and Deen, 1988; Smith and Deen, 1983) and the type of polymer: hard sphere (Smith and Deen, 1983) or random coiled polymer (Cifra and Bleha, 2005). As a random coiled polymer is much more flexible, it can change its shape to the pore where it is diffusing. Thus, values of the effective diffusivity significantly higher than zero are obtained even though the radius of gyration of the polymer is bigger than the pore size (Cifra and Bleha, 2005).

Usually,  $f$ , the ratio between the effective diffusivity and the bulk diffusivity is considered as a function of  $\lambda$  (the ratio between the particle size and that of the pore). Since 1960, an

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Table 1  
Empirical and semiempirical models used in the present work

Reference	Model	Equation(s)
Model 1 (Ternan, 1987)	Exponential model	$f = \frac{D_e}{D_0} = \frac{A_e \varepsilon_{\text{part}}}{\tau} e^{(-B\lambda)}$ (T1-1)
Model 2 (Ternan, 1987)	Hyperbolic model	$f = \frac{D_e}{D_0} = \frac{(1 - \lambda)^2}{1 + P\lambda}$ (T1-2)

empirical model based on an exponential decrease of  $f$  with  $\lambda$  is used (Ternan, 1987). This author also proposed an approach that can be considered intermediate between the phenomenological and empirical models (Ternan, 1987). He considered that the ratio  $f$  depends on two factors: a concentration factor and a viscosity or pore wall effect factor. The first term is also named the steric partitioning factor. The second one takes into account the possible variation of the viscosity of the fluid in the proximity of the wall (which is supposed to increase) and it is, in fact, a hyperbolic function with a unique parameter,  $P$ . Thus, all data can be fitted by a function with only one parameter,  $P$ , assumed to be function of geometric coefficients and viscosities. The increase in viscosity is assumed to be a direct consequence of the hydrogen-bond interactions between the solvent molecules and the pore wall atoms. The exponential model and the Ternan model are shown in Table 1, Eqs. (T1-1) and (T1-2), respectively.

Phenomenological models are known since 1950. This type of models are based on the existence of two phenomena that happen when the molecule is inside the pore: one, of thermodynamic nature and coming from the concentration gradient across the pore is partition; the other is a hydrodynamic transport effect due to the proximity of the solid wall to the particle, the loss of kinetic energy due to movement increases as drag increases. The concentration gradient depends on steric exclusion, due to size, and long- and short-range interactions, due to the chemical nature of both solute and porous solid (Shao and Baltus, 2000a,b; Bhattacharjee and Sharma, 1995, 1997). To describe partition in terms of its influence in the hindered diffusion coefficient, an equilibrium partition coefficient,  $K_{\text{eq}}$ , has to be calculated. This coefficient is the ratio between the average solute concentration in the pore and that of bulk at equilibrium and is shown by the first factor of  $f$  in Eq. (T2-1), Table 2, where  $E(\beta)$  includes all the long- and short-range interactions of the particle with the solid and  $\beta$  is the dimensionless radius (Eq. (T2-2), Table 2). A similar expression (second factor in the same equation) can be used to calculate the drag or transport factor,  $K^{-1}$ , which is the ratio between the friction coefficient in bulk and that inside the pore.

When the solute spherical particles are only subjected to steric exclusion and the drag experienced by all particles is similar to that experienced by particles in the centre of the pore ( $\beta = 0$ ), the relationship between the hindered diffusion coefficient and the diffusion coefficient in bulk is described by

the Renkin equation (Renkin, 1954):

$$\begin{aligned} f &= \frac{D_e}{D_0} \\ &= K_{\text{eq}} K^{-1} \\ &= (1 - \lambda)^2 (1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5). \end{aligned} \quad (1)$$

Moreover, the phenomenological model of Renkin was the first one of several models addressing the situation of a non-interacting spherical particle moving along the centreline of the pore (Deen, 1987). In recent years, much research on macromolecules of hydrophilic nature and in membrane technology has been done. The behaviour of these compounds interacting with membranes of a similar nature is of importance in a number of interesting new separation techniques based on membranes: from ultrafiltration to pervaporation (Casado et al., 2005; Bhattacharjee and Sharma, 1997; Deen, 1987). The development of new models considering repulsive or attractive interactions is leading to the understanding of transport phenomena under these conditions. Shao and Baltus (2000a,b) reported in their studies the enhancement in the diffusional behaviour of dextran and polyethylenglycol compared to a neutral spherical molecule. Thus, calculated values of  $f$  at different values of  $\lambda$  were greater than those expected considering the Renkin equation. Their results encompassed a limited  $\lambda$  range between 0 and 0.2, so a model describing the interaction energy between a sphere and a plane sufficed for the description of such behaviour. These authors (Shao and Baltus, 2000a,b) applied a known long-range interaction: the Lifschitz–van der Waals (LW) force, described mainly by the Hamaker constant with the mentioned geometry, being able to fit their results successfully. Their model is described by Eq. (T2-3) in Table 2, where  $A$  is the Hamaker constant for interactions between materials in a given medium and is obtained from the Hamaker constants for every material in the system in vacuum (estimated from measured  $A_{ii}$  values for each material with Eq. (T2-4), Table 2). Shao and Baltus (2000a) could describe the diffusion for their polymers through pores of track-etched membranes of polycarbonate using a Hamaker constant value of  $5.0 \times 10^{-21}$  J to calculate the partition coefficient by integration of the interaction energy term for each non-dimensional radial position ( $\beta$ ).

The model of Bhattacharjee and Sharma (1995) takes into account the long-range LW interaction of a spherical particle moving inside a cylindrical pore. While the sphere–plane approach is valid when the value of  $\lambda$  is small, it underestimates considerably the interaction energy when the molecule and the pore sizes are similar. Their simple solution approaches with little error the most rigorous numerical calculation of the energy. First, they calculated the energy between the particle and an atom of the pore, followed by the deduction of the energy of interaction of the particle and pore by integrating the previous energy over the wall material, reaching a dimensionless equation of the energy (dimensionless variables in Table 2, Eq. (T2-2)). As the general equation obtained by these authors cannot be solved analytically, they proposed

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