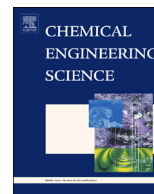




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## Capillary models of solvent diffusion

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### HIGHLIGHTS

- Bosanquet model for the diffusion of fluid/solvent into glassy polymers.
- Explored a connection between the Bosanquet model and 1D correlated random walk.
- The telegraph equation describes concentration profiles of the penetrating fluid.
- Case II diffusion is related to a fluid inertia effect.

### ARTICLE INFO

#### Article history:

Received 23 October 2012

Received in revised form

28 June 2013

Accepted 6 July 2013

Available online 19 July 2013

#### Keywords:

Diffusion

Polymers

Pharmaceuticals

Mathematical modeling

Bosanquet equation

Correlated random walk

### ABSTRACT

Capillary invasion-type models such as molecular sorption theory [Vesely D. Polymer 2001; 42:4417–22] and Bosanquet equation are applied to the diffusion of fluid/solvent into glassy polymers. It is found that both models show close description of the Fickian and Case II diffusion rates in agreement with the available experimental data. The Case II diffusion linear front advance, however, can be interpreted more naturally as inertial effect in the frame of the Bosanquet model. It is also shown that there is a connection between the Bosanquet model and 1D correlated random walk with the probability density described by the telegraph equation. The telegraph equation can be used to estimate the concentration profiles of the penetrating fluid.

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### 1. Introduction

The penetration rate of liquid into polycrystalline or amorphous polymers is an important parameter of interest for practical applications of such materials. In the pharmaceuticals, for instance, water uptake rate of compacted tablets can be a controlling factor in the disintegration process that directly affects the release of the drug (van Kamp et al., 1986; Massimo et al., 2000). It has been observed in earlier studies that the mass transport of small molecules through the polymer matrix often deviates from the classical Fickian description (Crank, 1975), which predicts that the liquid penetration rate is proportional to a square root of time. Instead, the process is best described by linear kinetics with a sharply moving front, which is known as Case II diffusion (Alfrey et al., 1966). Since the fluid concentration gradient behind the front is small (Windle, 1985), the penetration distance (depth) can be naturally defined by the position of the front.

In comparison with the Fickian diffusion, described as a concentration driven random molecular motion, the Case II behavior on the micro-level presents a combination of several physical and chemical processes. This complicates reduction of the Case II diffusion representation to a single model or theory, adequate for practical applications. From a mathematical viewpoint, linear penetrating front motion is not consistent with the solution of the nonlinear diffusion equation, even with the diffusion coefficient being a sharp function of the concentration. One of the first successful non-Fickian penetration theories, developed by Thomas and Windle (1980), recognizes that the kinematics of the penetration is controlled by the rate at which the polymer structure rearranges, or relaxes as a result of liquid entering. The discussion of other ideas and theories that can be used to interpret the experimental penetration data are presented in overviews (Windle, 1985; Vesely, 2008). In particular, Wu and Peppas (1993a) extended the Thomas and Windle theory by introducing a coupling between mass transport, driven by the concentration gradient and deformation in the polymer. They employed the Maxwell viscoelastic stress–strain constitutive relation that defines a polymer's relaxation time. This model can describe a transition

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from Fickian to Case II transport depending on which process – solvent diffusion in a swollen polymer or stress relaxation in the glassy region – advances at a slower rate. It is mathematically formulated as a boundary-value problem for a system of coupled partial differential equations (PDEs) from which the time evolution of the concentration and stress fields can be obtained numerically (Wu and Peppas, 1993b).

However, while the Wu–Peppas and similar models capture the physical mechanisms of the penetration well and are supported by experimental evidence, they are often difficult to apply for practical use. One reason for this is the technical complexity of fitting the PDEs to the experimental penetration data. Also, such models contain several empirical parameters, such as concentration dependent diffusion and viscosity coefficients that are difficult to measure. When interpreting the water uptake of pharmaceutical tablets, for instance, such measurements are feasible only for a small set of tablets. The development of drugs with optimal performance, however, requires processing of a large number of tablets that have different properties/components. Thus, an alternative approach for describing the penetration process and experimental treatment is required.

Vesely (1999, 2001) proposed a new Molecular Sorption model (MSM), which is based upon the following two ideas: (1) the sorption of the penetrant molecules into polymers is the driving force for diffusion; and (2) initial diffusion rate is finite. The main advantage of this model over previously mentioned ones is its simplicity and practical convenience: the MSM is expressed in an algebraic form with only two parameters. Nevertheless, the MSM fits well the experimental data and compares favorably with established models driven by the concentration gradient (Vesely, 2008). A crucial feature of the MSM is that it combines linear Case II behavior for early times, followed by the Fickian penetration at later times. Vesely (1999) especially emphasizes that “... the slow beginning of the diffusion can be wrongly interpreted as a linear time dependence, as used for Case II sorption. This is particularly convincing for thin films, which show deviation from this rule only at the last measured points.” Note, however, that despite practical advantages over existing model, one downside of the MSM is that model parameters interpretation is not straightforward.

In this paper we shall first consider another molecular interactions-type model developed by Bosanquet (1923) in his studies of transient flow in a capillary tube, which allows physical interpretation of the two regimes observed in the MSM, as well as model parameters. In particular, the linear initial part is due to the inertia of fluid, which is taken into account in the Bosanquet model to enforce the finite initial diffusion rate. The Bosanquet model also contains two parameters that can be obtained by fitting the penetration data – thus it combines the simplicity of the MSM with the clear and explicit physical interpretation.

In the second part of the paper we explore other physical situations in which the inertial effects play a similar regularization role, as in the case of the Bosanquet model. Well-known examples include heat and diffusion theories with finite relaxation time, mathematically described by hyperbolic diffusion equations (Joseph and Preziosi, 1989). Our goal here is to analyze how the time-dependent concentration profiles can be obtained from the experimental penetration data. In this respect, however, the correlated random walk diffusion model seems to be most relevant since the Bosanquet equation and the mean square displacement of the correlated random walk have the same mathematical expression with the parameters that can be naturally related. In other words, the position of the front as calculated by correlated random walk is equivalent to the position as calculated by the Bosanquet equation. Since the probability density of such a random process satisfies the telegraph equation, we also use this equation to obtain concentration profiles of the penetrating solvent.

## 2. Capillary penetration models

### 2.1. Molecular Sorption model

The motivation behind developing the MSM was to capture basic mechanisms responsible for experimentally observed features, including finite initial penetration rate, sharp concentration at the diffusion front, filling of cavities or voids, and correlation of diffusion and permeability (Vesely, 1999, 2001). According to these references, most observations can be explained assuming that the diffusion in polymeric materials is driven by the molecular interactions, similar to capillary suction. Such a mechanism is typical for mass transfer in a porous medium, in which solvent and solid interactions are characterized by a surface tension  $\sigma$  and contact angle  $\alpha$ . The pore size in individual polymer particles is on the nanometer scale, but the bulk porosity of polymeric materials, such as compacted tablets, vary and may exceed 20% (Hancock et al., 2003). Porosity can also increase due to swelling, which is often the case when the cohesive bonds between particles relax, and individual particles dissolve or deform. Finally, the diffusion in a such porous medium is typically limited by the resistance of the structure to the flow of the penetrant.

Working from the physical description above, the mathematical formulation of the MSM is derived based on an analogy to capillary flow in a tube. Thus, the penetrant motion is driven by the capillary pressure and opposed by the viscous resistance forces:

$$\frac{8\mu x}{R^2} \dot{x} = \frac{2\sigma \cos \theta}{R}. \quad (1)$$

The right side of (1) is the Laplace equation, and the left side is the viscous Hagen–Poiseuille pressure loss. Here  $x$  refers to the variable diffusion distance,  $R$  to the capillary radius,  $\mu$  to the dynamic viscosity, and  $\theta$  to the contact angle. Integrating Eq. (1) with the initial condition  $x(0) = 0$  leads to the well-known Washburn equation (Washburn, 1921):

$$x^2 = \frac{\sigma R \cos \theta}{2\mu} t. \quad (2)$$

It shows the square-root-of-time dependence of penetration distance, in agreement with the concentration gradient driven Fickian mechanism. This equation, however, fails for short times, since the initial velocity  $\dot{x} \propto 1/\sqrt{t}$  diverges as  $t \rightarrow 0$ . The problem appears in the governing equation (Eq. (1)): it has a positive constant on the right side, which implies that at the initial time the left side should be positive as well. However, because of the initial condition  $x(0) = 0$ , the velocity  $\dot{x}$  cannot be finite at the initial time. To fix the initial penetration rate, Vesely (1999, 2001) makes an assumption that the diffusion starts at some nonzero distance  $B$ ; thus the modified momentum Eq. (1) becomes

$$(x + B) \dot{x} = \frac{\sigma R \cos \theta}{4\mu}. \quad (3)$$

The solution of this equation with the initial condition  $x(0) = 0$  gives the final expression of the molecular sorption theory:

$$x = B(\sqrt{kt + 1} - 1), \quad (4)$$

where  $k = \sigma R \cos \theta / 2\mu B^2$  is a scaling constant. It appears that this equation allows accurate approximation of the penetration distance measurements corresponding to the Fickian, as well as Case II diffusion (Vesely, 1999). The fitting parameters  $B$  and  $k$  here are calculated using the standard least squares technique. Indeed, a Taylor series expansion of the square root term of (4), valid at the initial time when  $kt \ll 1$  gives:

$$x \cong \frac{Bkt}{2}. \quad (5)$$

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