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Identification problem of interface boundary conditions for diffusive transport between water and silica hydrogel

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Diffusion is the process of transport due to gradient of concentration and random molecular motion. In low permeability materials like clay or gels, diffusion is the most important transport mechanism [1, 2] and therefore identification of an appropriate model and parameters describing the process of diffusion is essential to design e.g. waste containment facilities, controlled drug release or to model contaminants migration in ground water through very low permeability soils. This paper discusses the form of boundary conditions between water and hydrogel appropriate for the diffusion process. The analytical solutions of equilibrium models describing the diffusive transport of solute from porous material to water assuming arbitrary initial concentrations and Dirichlet or mixed boundary conditions are considered. The estimation of the diffusion coefficient, retardation factor, partition or mass transfer coefficients of silica hydrogel were carried out with the Levenberg-Marquardt optimization method, implemented in the Matlab numerical computing environment

Key words: *diffusion; interface boundary condition; estimation*

1. Introduction

The identification of a model of diffusive transport in porous materials is usually focused on the selection of a type of sorption and boundary conditions [1, 3]. The evaluation of parameters depends on the adopted model, particularly the number of parameters and the easiness (or difficulty) of their identification depends on the properties and complexity of the model. This paper deals with the single reservoir method assuming a linear model of diffusive transport and equilibrium model of sorption. In order to formulate the general model of such transport from the viewpoint of initial and boundary conditions, arbitrary uniform in space, initial concentrations in the tested material and reservoir and different conditions at the interface between the res-

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ervoir liquid and the sample are considered. The interfacial conditions are modelled 1) by continuity or jump of concentration represented by the interfacial distribution coefficient or 2) by the flux of mass proportional to the concentration difference through a thin interfacial layer.

The purpose of this paper is to identify the form of boundary condition at the interface between water and hydrogel for diffusive transport. Analytical solutions of equilibrium models of diffusive transport of solute from porous material to water are used, assuming arbitrary initial concentrations and Dirichlet or mixed type of boundary conditions. The solutions and experimental data for silica hydrogel allowed for the estimation of model parameters carried out with the Lavenberg-Marquardt optimization method, implemented in the Matlab numeric computing environment.

2. Experimental

Samples of silica hydrogel were prepared by mixing pure water-glass with hydrochloric acid and distilled water at room temperature. The mixture was poured to PMM cylinder and left for gelation. The measurements were done using the experimental setup shown in Fig. 1, which includes: the diffusion chamber (1), the conductometer (2) made by Elmetron, model CPC – 551, which measures continuously the conductivity and temperature of the reservoir liquid, the controlled adapter (3) which powers the stirrer located in reservoir, and the thermostat (4) which stabilizes temperature during the test.

Fig. 1. Experimental set-up

The concentration of sodium chloride (in g/dm^3) in the reservoir was determined taking into account its linear relationship with conductivity, while the scaling factor for concentrations above 100 mg/dm^3 was assumed to be 0.55 [4]. For each test fresh samples were prepared and reservoir conductivity was sampled every 3 minutes on the average for about 30 hours.

3. Mathematical model of diffusion in a single reservoir test

The mathematical model corresponding to the applied experimental test assumes that the cylindrical sample of gel is isolated at the bottom and remains in contact with a constant amount of liquid in the reservoir, where the concentration is homogeneous due to stirring, Fig. 2.

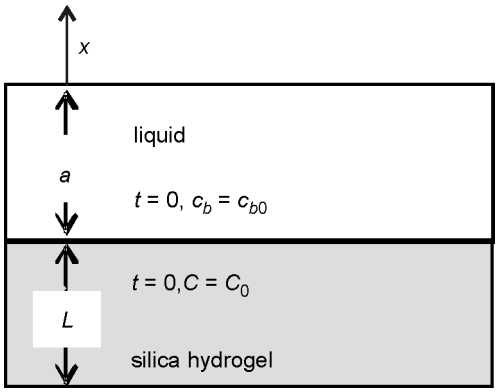

Fig. 2. The schematic diagram of the experiment with boundary conditions

The model of transport is a superposition of models of diffusive migration in gel and mass exchange between the gel and the reservoir liquid. The process of one-dimensional diffusion with equilibrium sorption in hydrogel can be represented by the second Fick's law

$$\frac{\partial}{\partial t}C - \frac{D}{R}\frac{\partial^2}{\partial x^2}C = 0 \tag{1}$$

where C denotes the mass concentration of salt in a gel referred to the elementary volume of the sample, t and x are time and spatial coordinates, D stands for the effective coefficient of diffusion, and R is the retardation factor. The effective diffusion coefficient is smaller than the diffusion coefficient in a free solution because of the tortuous pathways of molecules of solute within a porous medium. The relation of the diffusion coefficient in a free solution D_t to the effective diffusion coefficient D is represented by the tortuosity factor [5]

$$\tau = \frac{D_t}{D}$$

The equation of mass exchange between the sample and the reservoir is obtained from the condition that the change in mass of solute in reservoir liquid c_b must be balanced by the mass flux of the diffusing substance from or to the sample described by the first Fick law. The equation reads:

$$a\frac{dc_b}{dt} = -D\frac{\partial C}{\partial x}\bigg|_{x=L} \tag{2}$$

where a is the height of the liquid in reservoir.

Taking into account the possible different ways in which the interfacial transport between the liquid and the porous sample can occur, the boundary and initial conditions, corresponding to the considered single reservoir configuration were determined by the following set of equations:

$$x = L \quad \Rightarrow \quad c_b = \frac{1}{K'}C_s\,, \qquad C_s = C(x = L, t) \tag{3}$$

or

$$x = L \quad \Rightarrow \quad -D\frac{\partial C}{\partial x} = h(C_s - nc_b) \tag{4}$$

and

$$x = 0 \quad \Rightarrow \quad \frac{\partial C}{\partial x} = 0 \tag{5}$$

$$t = 0 \quad \Rightarrow \quad C(x) = C_0 \tag{6}$$

$$t = 0 \quad \Rightarrow \quad c_b = c_{b0} \tag{7}$$

Equation (3) refers to the model assuming continuity or surge of concentration at the interface and which is further called DKR. The effective partition coefficient K' for continuous concentration is equal to porosity n, i.e. $K' = n$, while for surge of concentration $K' = K_n$, where parameter K denotes the interfacial partition factor. The possibility of occurrence of the latter case is assumed by reference to polymer materials [1, 2]. Equation (4) describes an alternative interfacial condition formulated for the flux of mass which is proportional to the difference between the actual concentration of solute at the boundary of porous material C_s and the concentration in the stirred liquid in the reservoir multiplied by porosity. The constant h is called the mass transfer coefficient in the boundary layer and the model is referred to as DhR. The boundary condition (5) is the consequence of the assumption that there is no mass transport at the bottom of the sample. The initial conditions (6) and (7) assume uniform, and in general non-zero, concentrations in pore fluid and the reservoir. Because of using the equilibrium model of sorption $C_0 = 1/RC_{\text{tot}}$, where C_{tot} comprises the mass of solute in pore liquid and mass adsorbed on the internal surface of the porous material.

The analytical solution of equations describing the evolution of solute in the reservoir liquid with boundary and initial conditions for the DKR model can be found through reformulation of the problem to the form of the Sturm–Liouville problem (see [6]) and can be written as the following

$$c_b(t) = \frac{C_0 + \alpha K' c_{b0}}{K'(1+\alpha)} + \sum_n \frac{2a(K'c_{b0} - C_0)}{K'(1+\alpha+q_n^2\alpha^2)} e^{-\gamma q_n^2 t} \tag{8}$$

where q_n is the root of the transcendental equation $\tan q_n = -\alpha q_n$, and $\alpha = a/K'RL$, $p_n = Dq_n^2/RL^2$, $\gamma = D/RL^2$. Since the porosity of the gel was not determined in the performed tests, instead of distribution coefficient K, the $K' = Kn$ parameter, called the effective coefficient of surface distribution, was introduced.

The analytical solution corresponding to the DhR model, i.e. the model with specified mass flux at the interface and both initial conditions being inhomogeneous, are obtained by the rearrangement of the considered problem and application of the solution given by Carslaw and Jaeger [7] (see discussion in [6]), and the evolution of concentration in the reservoir c_b is :

$$c_b(t) = \frac{1}{n}\left(\frac{nc_{b0} - C_0}{1+k} + 2k\bar{\lambda}^2 (nc_{b0} - C_0) \sum_{i=1}^{\infty} \frac{1}{P_i} \mathrm{e}^{-\alpha_i^2 Tt} + C_0 \right) \tag{9}$$

where:

$$\tan\alpha = \frac{\bar{\lambda}\alpha}{\alpha^2 - k\bar{\lambda}}$$

and

$$\bar{\lambda} = L\frac{hR}{D}, \quad k = \frac{LnR}{a}, \quad T = \frac{D}{RL^2}$$

$$P_i = \alpha_i^4 + (\bar{\lambda}^2 + \bar{\lambda} - 2k\bar{\lambda})\alpha_i^2 + k\bar{\lambda}^2(1+k)$$

4. Results and discussion

We present the discussion of some numerical results obtained from the above analytical solutions of equilibrium models being interesting from the viewpoint of the reservoir method of identification of transport parameters. The diffusive transport of solute from porous material to reservoir and the two types of the interfacial boundary conditions are considered. Figure 3 shows the results obtained from Eq. (8) and (9) representing the evolution of concentration in the reservoir liquid for the DKR model (a) and DhR model (b). The role of the parameters describing interfacial conditions: the effective partition factor K' and mass transfer coefficient h, was examined. The parameters assumed for simulation are following: the thickness of sample $L = 0.01$ m, the height of liquid in reservoir $a = 0.04$ m, the porosity $n = 0.8$, the effective diffusion coefficient $D = 1.5\times10^{-9}$ m^2/s, the retardation factor $R = 1$, the effective distribution coefficient K' takes the values 0.8, 1 and 1.5, the mass transfer coefficient in the

boundary layer takes the values 6×10^{-7}, 2×10^{-6}, 2×10^{-5} m/s, the initial concentration in the reservoir and the sample are $c_{b0} = 1$, and $C_0 = 2$ g/dm^3, respectively.

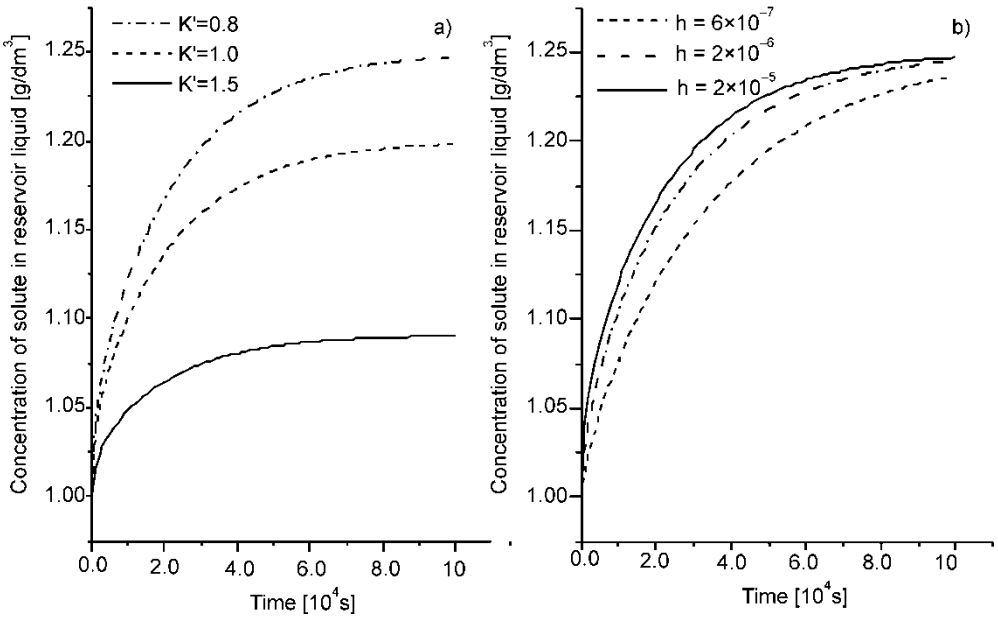

Fig. 3. The evolution of solute concentration in the reservoir liquid from the DKR model (a) and the DhR model (b)

The value of the distribution coefficient influences significantly the intensity of the process of diffusion and the final concentration of solute in the reservoir. The value of h also influences the intensity of mass transfer to the reservoir but unlike in the DKR model, the final value of concentration tends to reach the same level. It is interesting to note that the value of h parameter equal to 2×10^{-6} m/s gives a very close prediction of the DhR model as it results from the DKR model with continuous concentration at the interface (where $K' = 0.8$). This means that for a given coefficient of diffusion, there is a boundary value of the mass transfer coefficient beyond which it ceases to control the mass exchange between the reservoir and the material.

The solution of the inverse problem, aimed at identifying of the interfacial boundary condition and estimation of the appropriate parameters of diffusive transport was performed within the Matlab environment. The least squares error function is defined and its minimum is identified to evaluate the set of parameters D, K', R or D, h, R. The minimization of the error function is performed using optimization toolbox of Matlab, particularly the function lsqnonlin, which uses the Levenberg–Marquardt method. The set of parameters characterizing the experimental configuration of the reservoir test is the following: $L = 10.5$ mm; $a = 43.8$ mm; $c_{b0} = 0$ and $C_0 = 22.4$ g/dm^3. The initial concentration of sodium chloride in silica hydrogel C_0 was determined from the

stoichiometry of chemical reaction between sodium silicate (water glass) and hydrochloric acid. The results of numerical optimization for the data obtained for two temperatures 23 and 26 °C are given in Table 1.

We notice that the effective coefficient of diffusion is identical for the two models and does not exceed the coefficient of molecular diffusion in pore fluid which, for temperature of 25 °C, amounts to 1.6×10^{-9} m^2/s [8]. The ratio of the two models, defined as tortuosity of the porous material, is equal to 1.02. The values of the effective coefficient of surface distribution K' and retardation factor R indicate that from the macroscopic viewpoint of the DKR model predicts a significant surge of concentration of sodium chloride at the interface between the reservoir liquid and the pore liquid in the gel and a negligible sorption of sodium chloride in silica hydrogel. The latter effect is in conformity with the prediction of the DhR model.

Table 1. The values of the estimated parameters

Temperature [°C]	Model DKR			Model DhR		
	$D\times10^9$ [m^2/s]	K'	R	D$\times10^9$ [m^2/s]	$h\times10^{-5}$ [m/s]	R
23	1.57	1.88	1.08	1.57	1.04	1.72
26	1.57	1.84	1.00	1.57	1.05	1.56

For further evaluation of the role of the surge of concentration at the interface between the gel and the liquid within the DKR model, the range of values for K' parameter in the optimization procedure was restricted assuming that it must be equal or less than one (because of high porosity of the gel it means that K is approximately continuous). Running the optimization procedure again for both temperatures (Table 2), we obtain the same values of the effective diffusion coefficient as previously (Table 1), and essentially higher values of retardation factors.

Table 2. The values of estimated parameters of the DKR model obtained from optimization for $K'\leq 1$

Temperature [°C]	Model DKR		
	$D\times10^9$ [m^2/s]	K'	R
23	1.57	1.00	1.57
26	1.57	1.00	1.42

Figure 4 shows the comparison of the experimentally measured evolution of concentration for temperature 23 °C and theoretical curves corresponding to the DKR model with continuity (K' = 1) or surge (K' = 1.88) of concentration at the interface and the DhR model assuming parameters from Tables 1 and 2. It can be seen that there is almost perfect agreement between the experimental data and the theoretical curve for the DKR model with the surge of concentration at the interface hydrogel–water.

The two other models give a significant difference between the experimental results and the theoretical predictions.

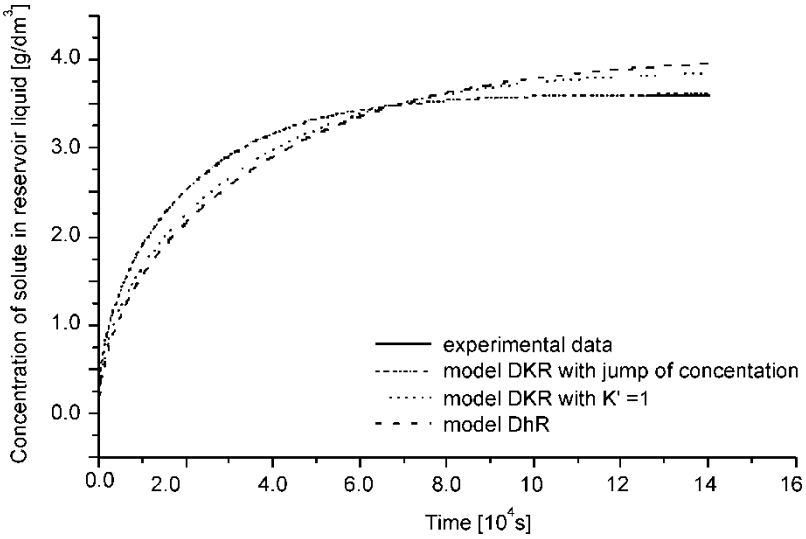

Fig. 4. The comparison of experimental and theoretical curves

5. Conclusions

The main purpose of this paper was to identify the proper form of boundary condition at the interface between water and silica hydrogel for diffusive transport. Analytical solutions of the transport of solute from the porous material to water with equilibrium model of sorption are used, assuming arbitrary homogeneous initial concentrations and boundary conditions represented by 1) the continuity or surge of concentration measured by interfacial distribution coefficient or 2) the flux of mass proportional to the concentration difference through a thin interfacial layer.

First, based on the considered models the role of the effective partition factor K' and mass transfer coefficient in the boundary layer h were studied. The solutions and the experimental data from the single reservoir test were used in estimation of effective diffusion coefficient, retardation factor and partition coefficient or mass transfer coefficient. The results have shown that the values of distribution coefficient and mass transfer coefficient influenced the intensity of the process of diffusion while the final concentration of solute depended only on the former parameter. The estimated values of effective diffusion coefficient were lower than the values of molecular diffusion in free liquid which means that tortuosity factor was greater than unity. From the comparison of the two models and the experimental data it is evident that the model assuming a surge of concentration at the interfacial layer represents a better model describing the diffusive mass transport between silica hydrogel and water.

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