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On the Mesoscopic Model of Mass Transfer in Microporous Membranes

Gulmira Sakhmetova, Arnold Brener*, Marat Satayev, Korlan Korabayeva

State University of South Kazakhstan, Tauke Khan, 5, Shymkent, 160012, Kazakhstan
amb_52@mail.ru

The paper deals with the simplified mesoscopic model for describing the membrane purifying process. The problem of working out the reliable models and the appropriate calculating methods is very important both for extracting valuable components and for purifying gases from hazardous substances. The main supposition of the model is that mass transfer through the microporous crystalline films is determined by a superposition of two streams. The first stream is the diffusion stream described by the Fick law, and the second stream is conditioned by the random walk of molecules about active centres of the grid. It is supposed that characteristic time delay of diffusing substance inside the membrane is proportional to the probability of its capturing by active centres into the membrane. On the base of such consideration the asymptotic analysis of the submitted concept has been carried out.

1. Introduction

The complex problem of gas purifying from various toxic or ballast ingredients has always been and remains to this day very relevant (Makaruk et al., 2010). Nowadays this problem gets of particular importance in the connection with the development of alternative energetic. Power and chemical production based on biogas technology becomes nowadays an important and promising component in long-term economic planning (Li Sun et al., 2014). The contribution of biogas energetic into the power production shows steady growth during the last decade (McKendry, 2002). Intensity of biomass production in chemical industry also increases (Di Donato et al., 2009).

Many techniques to solve this problem have been offered (Ryckebosch et al., 2011). At the same time the complete ingredients content for many processes is not given, or it can vary into wide range (Teplyakov et al., 1996). Therefore for optimal designing the power and chemical production devices with allowance for the scaling problem the engineering practise needs the appropriate scientific well-founded methods.

One of the main methods of gas, and of biogas purification especially, is the membrane technology (Esteves et al., 2008). Creation of engineering methods for calculating mass transfer through thin microporous films or membranes is a relevant science problem (Basu et al., 2010). Microscopic approach to calculating the mass transport inside membranes is accompanied however with great computing difficulties (Giacomin & Lebowitz, 1997).

The mesoscopic approach under a correct employment calls for using stochastic integro- differential equations taking into account the nonequilibrium transport phenomena (Katsoulakis & Viachos, 2000). Such equations can be obtained in the long-rage order limit for intermolecular forces (Katsoulakis & Viachos, 2004). Standard practice in permeation modeling has employed the partial equilibrium assumption that enforces fixed boundary loadings. The more rigorous approach entails use of Robin boundary conditions at each side of the membrane. It can be shown that non-linearity of equation leads to the certain delay of concentration wave regarding the initial moment of the process (Viachos & Katsoulakis, 2000). But the known mesoscopic models in strict approach also entail the principal mathematical difficulties (Snyder et al., 2003).

In this paper we try to offer and submit the simplified engineering model for describing that process. Previous results of our computer experiments with models of relaxation transfer cores showed that we can extend the mesoscopic approach for describing heat and mass transfer over less space scales as diffusion or heat

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boundary layers (Brener, 2006).The main supposition of our model is that mass transfer through the microporous crystalline films is determined by a superposition of two streams. The first stream is the diffusion stream described by the usual Fick law, and the second stream is conditioned by the random walk of molecules about active centers of the lattice (Brener et al., 2009). In our opinion such supposition corresponds to the mesoscopic models (Lam et al., 2002).

2. Theoretical details

2.1 Main concept

We submit an approach for accounting molecular hopping drift inside the membrane based on simple stochastic model. Namely, let us suppose that characteristic time delay of diffusing substance inside the membrane is proportional to the probability p of its capturing by active centres into the membrane. Thus, this probability can be supposed as proportional to a product of two probabilities:

$$p = p_1 p_2 \tag{1}$$

The first probability p_1 is proportional to the admixture concentration, since the more concentration the more a probability of molecules capturing (Horntrop, 2010). The second probability p_2 is proportional to the specific number of free active centres inside the membrane. This number is proportional, in turn, to the specific number of active centres except of the number of centres occupied by captured molecules of an admixture.
And the last number can be supposed as proportional to the admixture concentration, but only if this concentration is not so great that it would limit capturing potential of active centres (Figure 1).

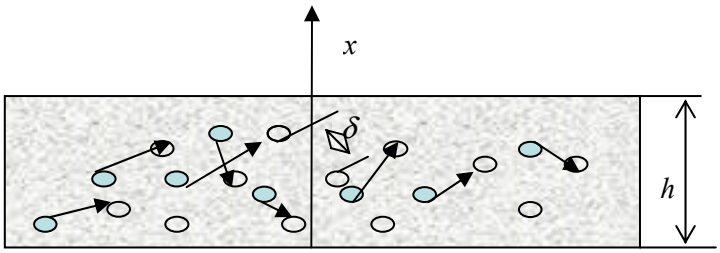

Figure 1: Molecular hopping drift inside the membranes

Thus, the probability p can be written as follows

$$p = k_1 c(n - k_2 c) \tag{2}$$

Here c is the admixture concentration, k_1, k_2 are the coefficients of proportionality, n is the complete specific number of active centres inside the membrane.
Using the well-known Einstein's formula for the random walk diffusivity we obtain

$$J_m = -p\frac{\delta^2}{\tau}\frac{\partial c}{\partial x} \tag{3}$$

Here J_m is the substance flux induced by the molecular hopping drift inside the membrane (Horntrop & Majda, 1994), δ is the typical lattice space scale, τ is the typical relaxation time, x is the coordinate along the diffusion direction.
Thus, the approximation reflecting the qualitative peculiarities of the offered model can be written as follows

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} - D_m c(1 - \chi c)\right] = 0\,, \tag{4}$$

where D is the usual diffusion coefficient, $\chi = k_2/n$ and D_m is a kind of diffusion coefficient describing the random walk about the adjacent active centres of the lattice.
The appropriate expression for D_m reads

$$D_m = k_1 n \frac{\delta^2}{\tau}. \tag{5}$$

In the case of sufficiently large concentration of the admixture, i.e. when the condition noted before deriving formula (2) may be not correct and the parameter $\chi \to 1$, Eq(4) acquires a look of (Brener et al., 2009)

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial x}\left[D\frac{\partial c}{\partial x} - D_m c(1-c) \right] = 0 \tag{6}$$

The further analysis of Eq(4) will be carried out on the likely approximation of

$$D = const\,,\ D_m = D\gamma\,,\quad \gamma << 1\,, \tag{7}$$

where γ is a special migration factor.

2.2 Asymptotic analysis

From Eqs (5) and (7) it follows

$$\frac{\partial c}{\partial t} - D\frac{\partial^2 c}{\partial x^2} = \gamma D \frac{\partial}{\partial x}\left[c(1-\chi c) \right] \tag{8}$$

Let us look for the solution of Eq(8) in the form of asymptotic series

$$c = \sum_{j=0}^{\infty} \gamma^j c_j \tag{9}$$

Under the homogeneous boundary conditions the zero-order term can be represented in the form of Fourier series

$$c_0 = \sum_{i=1}^{\infty} A_{0i} \sin\left(\frac{i\pi x}{h} \right) \exp\left(-\frac{i^2\pi^2}{h^2} Dt \right) \tag{10}$$

Here A_{0i} is the amplitude of the $i-$mode, and h is the typical depth.

However, in reality the boundary conditions can be inhomogeneous:

$$\begin{aligned} &c_0 = f(x) \text{ at } t = 0\,; \\ &c_0 = g(t) \text{ at } x = 0\,; \\ &c_0 = u(t) \text{ at } x = h\,; \end{aligned} \tag{11}$$

In that case the first-order solution can be obtained on the base of special methods (Horntrop et al., 2001) as following

$$c_0 = \frac{2}{h}\sum_{i=1}^{\infty} M_i(t) \exp\left(-\frac{Di^2\pi^2 t}{h^2} \right) \sin\left(\frac{i\pi x}{h} \right) \tag{12}$$

Here

$$\begin{aligned} M_i(t) = &\int_0^h f(x) \sin\left(\frac{i\pi x}{h} \right) dx + \frac{Di\pi}{h} \int_0^t \exp\left(\frac{Di^2\pi^2 t}{h^2} \right) g(t) dt \\ &- (-1)^i \frac{Di\pi}{h} \int_0^t \exp\left(\frac{Di^2\pi^2 t}{h^2} \right) u(t) dt \end{aligned} \tag{13}$$

Both under the homogeneous and under the inhomogeneous conditions the subsequent approximations will be linearized step by step.

Particularly, the first-order approximation reads

$$\frac{\partial c_1}{\partial t} - D\frac{\partial^2 c_1}{\partial x^2} = \gamma D\frac{\partial}{\partial x}\left[c_0\left(1-\chi c_0\right)\right] \tag{14}$$

As it was above noted the case of the small concentration of an admixture is more interesting. So let us consider this case more detail:

$$c = \varepsilon C\,,\ \ \varepsilon << 1 \tag{15}$$

Eq(8) transforms to the following form

$$\frac{\partial C}{\partial t} - D\frac{\partial^2 C}{\partial x^2} + \gamma D\frac{\partial C}{\partial x} = \varepsilon\chi\gamma D\frac{\partial (C^2)}{\partial x} \tag{16}$$

By using asymptotic approximation methods regarding the small parameter ε the asymptotic series and the zero-order equation read

$$C = \sum_{j=0}^{\infty} C_j \varepsilon^j \tag{17}$$

$$\frac{\partial C_0}{\partial t} - D\frac{\partial^2 C_0}{\partial x^2} + \gamma D\frac{\partial C_0}{\partial x} = 0 \tag{18}$$

Let us look for the solution of Eq(18) in the form of running waves:

$$C_0 = \tilde{C}_0 \exp\left(K\left(x - \frac{\gamma D}{2}t\right)\right)\,. \tag{19}$$

$$\frac{\partial \tilde{C}_0}{\partial t} = D\frac{\partial^2 \tilde{C}_0}{\partial x^2} + D\left(2K-\gamma\right)\frac{\partial \tilde{C}_0}{\partial x} + D\left(K^2 - \frac{K\gamma}{2}\right)\tilde{C}_0 \tag{20}$$

From Eq(20) it immediately follows that at some conditions, for example at $K = \gamma/2$, the concentration running waves along the membrane depth can be arisen.
The appropriate concentrate wave velocity and length are

$$W = \frac{\gamma D}{2} = \frac{D_m}{2} \tag{21}$$

$$\Lambda = \frac{2}{\gamma} = \frac{2D}{D_m} \tag{22}$$

The equations for the first-order reads

$$\frac{\partial C_1}{\partial t} - D\frac{\partial^2 C_1}{\partial x^2} + \gamma D\frac{\partial C_1}{\partial x} = \gamma D\frac{\partial (\chi C_0^2)}{\partial x} \tag{23}$$

Since while solving Eq(23) the homogeneous boundary conditions can be used the solution looks as the Duhamel form

$$C_1 = \int_0^t Z\left(x, t-s; s\right)ds \tag{24}$$

The function Z can be found from the following auxiliary problem

$$\frac{\partial Z}{\partial t} - D\frac{\partial^2 Z}{\partial x^2} - \gamma D\frac{\partial Z}{\partial x} = 0 \tag{25}$$

Moreover, it can be used the homogeneous boundary conditions and the obvious initial condition

$$Z = -\gamma\chi D\frac{\partial\left(C_0^2\right)}{\partial x} \quad \text{at} \quad t = 0 \tag{26}$$

The main interesting conclusion which follows from condition (26) is that the non-linearity of diffusion equation with allowance for the migration factor leads to the non-locality of perturbations propagation. It is manifested as the delay of concentration waves relative to the initial moment:

$$\Delta t \approx \varepsilon\frac{4D}{\chi D_m^2} \tag{27}$$

At the low migration factor the small parameter ε can be evaluated as

$$\varepsilon \approx \frac{h}{\Lambda} \tag{28}$$

The small parameter ε begin compete with the parameter χ that can deform the concentration wave shape at zero order.
The appropriate zero-order solution after some rearrangements can be written as following

$$C_0 = \frac{DA}{\nu}\exp\left(\frac{\chi D_m}{2D}\left(x - \frac{\chi D_m}{2}t\right) - \frac{\nu}{D}\left(x - \nu t\right)\right), \tag{29}$$

where ν is the phase velocity.
The expression for the deformed concentration wave shape with account to the migration diffusion factor reads

$$C_0 = \frac{DA}{\nu}\exp\left(\frac{x}{\lambda^*} - \omega^* t\right) \tag{30}$$

Here the typical wave length is

$$\lambda^* = \frac{D}{\chi D_m - 2\nu} \tag{31}$$

The typical wave frequency reads

$$\omega^* = \frac{D_m^2 - 4\nu^2}{4D} \tag{32}$$

3. Conclusions

The mesoscopic approach can be applied to describing heat and mass transfer in microporous membranes over less space scales as diffusion or heat boundary layers. As it follows from the analysis of submitted mesoscopic model the role of migration diffusion can be appreciable, and this phenomenon with appropriate amendments should be accounted while engineering calculations of the effectiveness of the membrane gas purification process. It is also shown that non-linearity of the master equation leads to the phase delay of the concentration wave relative the initial moment.
As the result it can be concluded that submitted approach allows describing intricate phenomena accompanying the admixture diffusion through the microporous membranes. It is likely to be useful for engineering practice in design of processes and apparatuses for membrane technology with allowance for the scaling phenomena.

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