

Mathematical model of diffusion in a layered zeolite medium with spherical symmetry

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Abstract

Based on the methods of integral transformations and in comparison with difference approaches, a mathematical model is constructed that describes the nonequilibrium diffusion process of mass transfer of volatile substances in multilayer media containing microporous inclusions. The effect of various types of interface conditions on the efficiency of adsorption processes has been studied. It has been established that the results obtained using direct analytical methods of mathematical modeling correlate well with the results obtained by using finite difference schemes approximating the diffusion equation boundary conditions compared to it.

Keywords

Mass transfer, Poisson's equation, finite difference method, layered zeolite medium

1. Introduction

A variety of zeolite materials are widely used in various and relevant areas of modern technology [1-5]. In particular, materials such as ZSM-5 zeolite or silica gel have found their application in exhaust gas cleaning systems [6-8]: both in the case of internal combustion engines and in cleaners of chemical and energy industries. This predetermines one of the key roles of zeolites in the protection and purification of the environment. The practical utility of these materials is determined by their physicochemical properties, which consist in the presence of micropores in these materials, which function in the mode of traps for molecules of various hydrocarbons. This effect is directly explained by the emergence of Van Eder Waals forces at the boundary between micropores and the external environment, as a result of which, due to attraction, they are able to capture light gas molecules, such as methane, propane, water vapor, etc.

The problems associated with the use of zeolites and constantly requiring additional research are the need to provide conditions for the effective functioning of traps for gaseous hydrocarbons under various environmental conditions: pressure, temperature, percentage of gases in the adsorbed mixture. Also a poorly studied case is the simultaneous use of several different zeolite media at the same time. The mentioned scientific and technical problems lead to the need for additional rethinking of the existing mathematical models of diffusion in microporous media and their modification. In the proposed work, we propose the implementation of a mathematical model that describes the diffusion of hydrocarbons in a layered zeolite sample with spherical symmetry. Based on the proposed model, the concentration distributions of methane absorption were calculated for a homogeneous zeolite and a medium consisting of different layers of zeolites. The general case is considered when the trapped particles can carry a charge.

2. Statement of the problem. Mathematical model of diffusion in the layered zeolite medium

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The process of diffusion of light hydrocarbons in a layered zeolite medium is considered, the schematic geometric diagram of which is shown in Fig. 1. It is assumed that a stable adsorption process occurs in each of the layers of the test sample, which is described at the macrolevel of the zeolite medium by the following equation:

$$\frac{\partial C_k(t, r, z)}{\partial t} + \frac{\partial a_k(t, r, z)}{\partial t} + \eta_k^2 C_k = D_k \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_k}{\partial r} \right) + \frac{\partial^2 C_k}{\partial z^2} \right] + f_k(t, r, z). \quad (1)$$

where D_k - is the coefficient of diffusion for k-th layer.

At the macrolevel, which corresponds to the micropore-target boundary and the zeolite medium, diffusion is described by the following condition [9, 10]:

$$\frac{\partial a_k}{\partial t} = \beta_k (C_k - \gamma_k a_k). \quad (2)$$

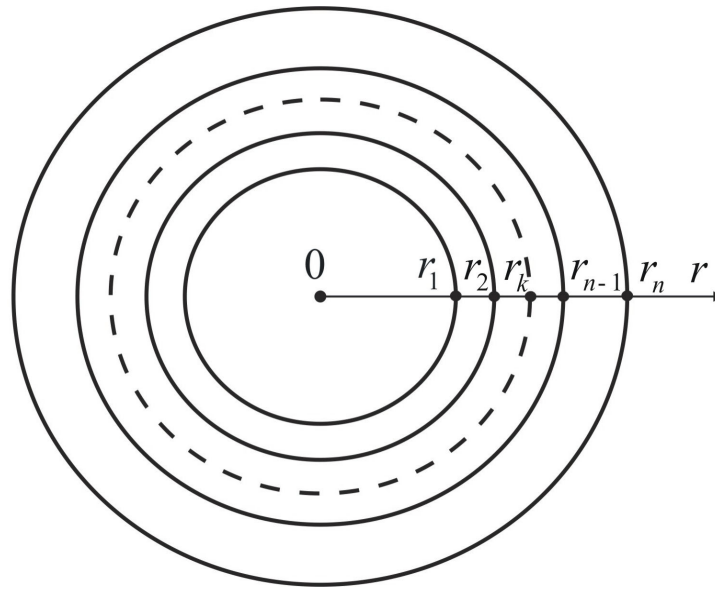


Figure 1: Geometric diagram of cross-section a multilayer sample of zeolite material

For the absorption process of hydrocarbons, there are also input initial conditions that set the input concentrations in the zeolite medium and micropores:

$$C_k(t, z)_{t=0} = C_{0_k}(z); a_k(t, z)_{t=0} = a_{0_k}(z). \quad (3)$$

The interface boundary conditions of the third kind, describing the vertical transport of hydrocarbons in the diffusion process, are as follows:

$$\left\{ \begin{array}{l} [(\alpha_{11}^0 + \delta_{11}^0 \frac{\partial}{\partial t}) \frac{\partial}{\partial z} + (\beta_{11}^0 + \gamma_{11}^0 \frac{\partial}{\partial t})] C_1(t, z) \Big|_{z=l_0} = \omega_0(t); \\ [(\alpha_{22}^{n+1} + \delta_{22}^{n+1} \frac{\partial}{\partial t}) \frac{\partial}{\partial z} + (\beta_{22}^{n+1} + \gamma_{22}^{n+1} \frac{\partial}{\partial t})] C_{n+1}(t, z) \Big|_{z=l_{n+1}} = \omega_{n+1}(t); \\ \left[[(\alpha_{j1}^k + \delta_{j1}^k \frac{\partial}{\partial t}) \frac{\partial}{\partial z} + (\beta_{j1}^k + \gamma_{j1}^k \frac{\partial}{\partial t})] C_k(t, z) - [(\alpha_{j2}^k + \delta_{j2}^k \frac{\partial}{\partial t}) \frac{\partial}{\partial z} + (\beta_{j2}^k + \gamma_{j2}^k \frac{\partial}{\partial t})] C_{k+1}(t, z) \right] \Big|_{z=l_k} \\ = 0; k = \overline{1, n}; j = \overline{1, 2} \end{array} \right. \quad (4)$$

Accounting for the radial symmetry of the sample also leads to boundary conditions at the boundaries of each of the layers, as well as at the boundaries of the sample with the environment.

These boundary conditions recognize the homogeneity of the flow $I_k = -D_k \frac{dC_k}{dr} - \beta_k \gamma_k \frac{da_k}{dr}$ within the sample and look like as follows:

$$C_k|_{r=r_k+0} = C_{k+1}|_{r=r_k+0};$$

$$\left(D_k \frac{dC_k}{dr} + \beta_k \gamma_k \frac{da_k}{dr} \right) \Big|_{r=r_k} = \left(D_{k+1} \frac{dC_{k+1}}{dr} + \beta_{k+1} \gamma_{k+1} \frac{da_{k+1}}{dr} \right) \Big|_{r=r_k}. \quad (5)$$

In the case when particles trapped by micropores have a charge, then in the mean field model, the potential $\varphi(r, z, t)$ created by them is a continuous function of coordinates, its explicit form is obtained by finding solutions to the Poisson equation:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \varphi}{\partial r} \right) = -\frac{\rho}{4\pi\epsilon_0\epsilon(r)}, \quad (6)$$

where the permittivity of the sample is:

$$\epsilon(r) = \sum_{k=1}^N \epsilon_k [\theta(z - z_k) - \theta(z - z_{k+1})]. \quad (7)$$

The density of charges distributed over the entire volume of the studied sample is expressed as follows:

$$\rho = \frac{1}{V} \int_0^\pi \int_0^{2\pi} [C_k(r, r \cos \theta) - a_k(r, r \cos \theta)] \sin \theta d\theta d\varphi =$$

$$= \frac{3}{2R^3} \int_0^\pi \int_0^{2\pi} [C_k(r, r \cos \theta) - a_k(r, r \cos \theta)] \sin \theta d\theta. \quad (8)$$

For the potential created by distributed charges inside the sample, within each of the zeolite layers, the following limiting conditions are met:

$$\varphi_k(r)|_{r=r_k} = \varphi_{k+1}(r)|_{r=r_k};$$

$$\epsilon_k \frac{\partial \varphi_k(r)}{\partial r} \Big|_{r=r_k} = \epsilon_{k+1} \frac{\partial \varphi_{k+1}(r)}{\partial r} \Big|_{r=r_k}. \quad (9)$$

3. Implementation of the mathematical model of diffusion in a multilayer medium

For the direct implementation of the mathematical model given by equations (1)-(5) and additional conditions (6), (7) and (9), the finite difference method is used. To this end, we will replace the area of the sample $D_n = \left\{ (t, r, r \cos \theta) : t > 0, r \in \bigcup_{k=1}^n (r_k, r_{k+1}), l_1 \geq 0, l_{n+1} < \infty, 0 \leq \theta \leq \pi \right\}$ with a discrete spatial grid that looks like as follows:

$$D_{mkl} = \left\{ (t, r, z) : t_m = m\Delta t_m, r_k = k\Delta r_k, z_l = l\Delta z_l, k, l, m \in Z \right\}. \quad (10)$$

Performing now the approximation of the derivatives of the first and second orders according to the relations:

$$\frac{df}{dr} \rightarrow \frac{f_{k+1} - f_k}{h};$$

$$\frac{d^2 f}{dr^2} \rightarrow \frac{f_{k-1} - 2f_k + f_{k+1}}{h^2}; \quad h \approx \Delta r \quad (11)$$

we obtain a difference scheme, which is the implementation of the proposed mathematical model in a form accessible to direct modeling:

$$\begin{aligned}
& \left[\frac{C_{k,l,m+1} - C_{k,l,m}}{\Delta t_m} + \frac{a_{k,l,m+1} - a_{k,l,m}}{\Delta t_m} + \eta_k^2 C_{k,l,m} = \right. \\
& = D_k \left[\frac{C_{k-1,l,m} - 2C_{k,l,m} + C_{k+1,l,m}}{(\Delta r_k)^2} + \frac{C_{k,l,m} - C_{k-1,l,m}}{r_k \Delta r_k} + \frac{C_{k,l-1,m} - 2C_{k,l,m} + C_{k,l+1,m}}{(\Delta z_l)^2} \right] + f_{k,l,m}; \\
& a_{k,l,m+1} - a_{k,l,m} - \beta_k (C_{k,l,m} - \gamma_k a_{k,l,m}) \Delta t_m = 0; \\
& (\alpha_{11}^0 + \beta_{11}^0) C_{k,l,m} + \delta_{11}^0 \frac{C_{k,l,m} - C_{k,l-1,m-1}}{\Delta z_l \Delta t_m} + \gamma_{11}^0 \frac{C_{k,l,m} - C_{k,l,m-1}}{\Delta t_m} = \omega_l \\
& C_{k,l,m} - C_{k+1,l,m} = 0; \\
& D_k C_{k-1,l,m} - (D_k + D_{k+1}) C_{k,l,m} + D_{k+1} C_{k+1,l,m} + \beta_k \gamma_k a_{k-1,l,m} - \\
& - (\beta_k \gamma_k + \beta_{k+1} \gamma_{k+1}) a_{k,l,m} + \beta_{k+1} \gamma_{k+1} a_{k+1,l,m} = 0; \\
& \varphi_{k,l,m} - \varphi_{k+1,l,m} = 0; \varphi_{0,l,m} = \varphi_{N+1,l,m} = 0; \\
& \frac{2\varphi_{k,l,m} - \varphi_{k+1,l,m}}{\Delta r_k} + \frac{\varphi_{k,l-1,m} - 2\varphi_{k,l,m} + \varphi_{k,l+1,m}}{(\Delta z_l)^2} + \frac{\rho_{k,l,m}}{4\pi\epsilon_0\epsilon_k} = 0; \\
& \epsilon_k \varphi_{k-1,l,m} - (\epsilon_k + \epsilon_{k+1}) \varphi_{k,l,m} + \epsilon_{k+1} \varphi_{k+1,l,m} = 0.
\end{aligned} \tag{12}$$

4. Results and discussion

In order to verify the developed mathematical model of diffusion in layered samples, the concentrations of adsorbed hydrocarbons were calculated. For this, the following geometric parameters of the sample under study were chosen: the number of layers were taken 100, and the thickness of an individual layer was taken to be 10 μm . In this case, three different cases were considered: the sample layers were created only from silica gel; sample layers are made of ZSM-5 zeolite only; the sample layers are formed by alternating these materials. For each of these cases of the structure of the studied sample, the concentration curves of methane and propane were calculated. The results of these calculations are shown in Fig. 2a, b. The temperature value was chosen as typical for technological processes of hydrocarbon adsorption and equal to 380 K. The arrow in both figures marks the moment of time corresponding to the desorption process.

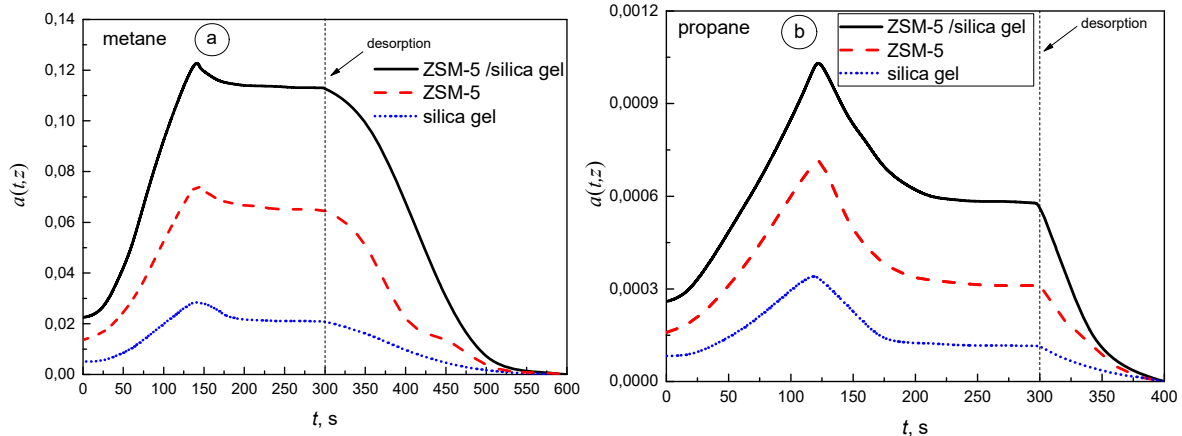


Figure 2: The dependence of the concentration of methane (a) and propane (b) in the process of adsorption-desorption using different types of materials in the test sample.

As can be seen from the dependencies shown in Fig. 2a, 2b, the adsorption-desorption process of methane proceeds somewhat faster than the analogous process for propane. This is due to the fact that micropores in the used zeolite materials have a characteristic size closer to the effective diameter of propane molecules, which entails large Van der Waals forces. As can be seen from Fig. 2a, in the case

of methane adsorption in the range from 150 to 300 s, a "plateau" is formed with an almost constant concentration close to the maximum. In the case of propane, this effect also takes place, but for such a "plateau" the concentration value is almost two times less than the maximum.

As can be seen from Fig. 2a, b, in cases where methane and propane are used, the dependences of the concentrations of the trapped substance on time have qualitatively similar dependences, the maximum values of which are actually formed in the same time interval. However, it should be noted that the use of only silica gel (blue dotted lines) in the sample demonstrates a weak adsorption efficiency of hydrocarbon molecules, which is very low in the case of methane and slightly higher in the case of propane. It should be noted that, as can be seen from the calculated dependences, the use of only ZSM-5 zeolite (red dashed line) in the test sample has advantages over the case of using only silica gel, since the concentration of adsorbed hydrocarbons is almost four times higher in the cases of both gases. It should be noted that the highest adsorption efficiency is achieved when using a sample in which layers of ZSM-5 zeolite and silica gel alternate.

5. Conclusions

A mathematical model is constructed that describes diffusion processes in layered zeolite samples with spherical symmetry. It has been established by direct calculations that the highest adsorption efficiency is achieved for a sample formed by alternating layers of ZSM-5 zeolite and silica gel. The results obtained can be applied in further studies of the processes of hydrocarbon adsorption by microporous materials.

6. References

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