Выводы. Приведенные модификации классического алгоритма прямого построения привели к резкому снижению вычислительных затрат, необходимых для его работы. Дальнейшая оптимизация алгоритма состоит в определении оптимального критерия выбора "точки-кандидата" из текущего набора точек.

ЛИТЕРАТУРА

1. Делоне Б. Н. О пустоте сферы / Б. Н. Делоне. – М.: ОМЕН, 1934. – С. 793-800.

2. Скворцов А. В. Триангуляция Делоне и ее применение / А. В. Скворцов. – Томск: Томский ун-т, 2002. – 128 с.

3. Романюк А. Алгоритмы триангуляции / А. Романюк, А. Сторчак// Компьютеры + Программы. – М.: Комиздат. – 2001. – № 1.

4. Скворцов А. В. Эффективные алгоритмы построения триангуляции Делоне / А. В. Скворцов, Ю. Л. Костюк // Геоинформатика. Теория и практика / Томский ун-т. – 1998. – № 1. – С. 22–47.

5. Ласло М. Вычислительная геометрия и компьютерная графика на С++ : Пер. с англ. — М. : БИНОМ, 1997. – 304 с.

M. Petryk, D. Mykhalyk

MATHEMATICAL MODELING OF CONCENTRATION PROFILES IN HETEROGENEUS AND NANOPORES MEDIA

Introduction. The transport of molecules in the pore system of zeolites and other solids has been extensively studied by several authors (Barrer 1979, Kдrger and Ruthven 1992, Chen *et al*. 1994). When a bed of zeolite crystallites is considered, it can be assumed that molecular transport involves two important processes: diffusion in the macropores formed by the space between the crystallites (intercrystallite diffusion) and diffusion in the nanopores within the crystallites (intracrystallite diffusion). To determine the contribution of each of these processes to the overall diffusion process, one has to know the values of certain parameters, such as diffusion coefficients, the pressure in the gas phase, the dimensions of the crystallite bed, the adsorption isotherm, etc.

The relationship between these different parameters and the concentration profiles can be established after having chosen a diffusion model and solved the equations which describe it. In a previous article by Magalhres *et al.* 1997, the competitive effects of inter- and intramolecular diffusion were analyzed semi quantitatively on the basis of the concentration profiles obtained by a numerical method. In the present work, analytical solutions of the diffusion equations are presented both for macropores and micropores. In this way the parameter which allows an evaluation of the relative importance of inter- and intracrystalline diffusion is clearly identified.
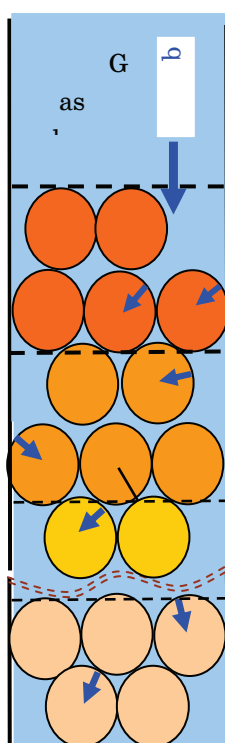
Diffusion in macropores

Characteristic length: ℓ

Diffusion coefficients: $D_{\mathrm{int}er_k}$;

Characteristic times: $\tau_{\mathrm{int}er_k}$

Diffusion in nanopores

Characteristic length: R

Diffusion coefficients: $D_{\mathrm{int}ra_k}$

Characteristic times: . $\tau_{\mathrm{int}ra_k}$

Fig.1 - The scheme of the process of diffusion in the zeolite bed

Mathematical model. The mathematical model of benzene diffusion kinetics in the zeolite bed which we consider to be heterogeneus and multicomposed (n-composed) media constituting the pore system of the zeolite bed is a boundary problem: to find in the area

$$I_n = \left\{ t > 0, r \in (0, R), z \in \bigcup_{k=1}^{n+1} (\zeta_{k-1}, \zeta_k); \zeta_0 = 0; \zeta_{n+1} \equiv l < \infty \right\}$$

the bounded solution of the partial differential equations system:

$$\varepsilon_{inter_k} \frac{\partial c_k}{\partial t} = D_{inter_k} \cdot \varepsilon_{inter_k} \frac{\partial^2 c_k}{\partial z^2} - \frac{3\left(1 - \varepsilon_{inter_k}\right)}{R} \cdot \left(D_{intra_k} \frac{\partial q_k}{\partial r}\right)\Big|_{r=R} \;;$$

(1)

$$\frac{\partial q_k}{\partial t} = D_{intra_k} \left(\frac{\partial^2 q_k}{\partial r^2} + \frac{2}{r} \frac{\partial q_k}{\partial r}\right)$$

(2)

with the initial conditions :

$$c_k\left(t = 0, z\right) = 0, \qquad\qquad q_k\left(t = 0, r, z\right) = 0\;;$$

(3)

the boundary conditions:

$$c_{n+1}\left(t, z = l\right) = c_{\infty\, n+1}, \qquad q_k\left(t, r = R, z\right) = K_k \cdot c_k\left(z, t\right);$$

(4)

$$\frac{\partial c_1}{\partial z}\left(t, z = 0\right) = 0, \qquad \frac{\partial q_k\left(t, r = 0, z\right)}{\partial r} = 0$$

(5)

and interface conditions:

$$\left[c_k\left(t, z\right) - c_{k+1}\left(t, z\right)\right]\Big|_{z=\zeta_k} = 0\;; \quad \left[\frac{\partial}{\partial z}c_k\left(t, z\right) - \frac{\partial}{\partial z}c_{k+1}\left(t, z\right)\right]\Big|_{z=\zeta_k} = 0\,, \quad k = \overline{1, n}.$$

(6)

here $\quad K_k = \dfrac{q_{\infty_k}}{c_{\infty_k}}; k = \overline{1, n+1}$ ·

Analytical solution: concentration profiles. Applying the *Laplace* integral transformation for the system boundary problems, we finally obtain the analytical solution of this problem in such form:

$$C_k(t,Z) = 1 + \sum_{j=1}^{\infty} \frac{\exp\left(-\beta_j^2 \cdot t\right)}{\beta_j^2 \cdot d\delta\left(\beta_j\right)} \begin{cases} \prod\limits_{j=1}^{n}\varphi_{j+1}(\beta) \cdot \cos\left[\varphi_l(\beta)Z\right] & ;k=1 \\[2mm] \prod\limits_{j=k}^{n}\varphi_{j+1}(\beta) \cdot \left[\Phi_{22}^{k-1}(\varphi_k(\beta)l_{k-1}, \varphi_k(\beta)Z) \cdot \delta_{\overline{1,2k-1}}(\beta) - \Phi_{12}^{k-1}(\varphi_k(\beta)l_{k-1}, \varphi_k(\beta)Z) \cdot \delta_{\overline{1,2k-1}}(\beta)\right] & ;k=\overline{1,n} \\[2mm] \left[\Phi_{22}^n(\varphi_{n+1}(\beta)Z, \varphi_{n+1}(\beta)l_{n+1}) \cdot \delta_{\overline{1,2n-1}}(\beta) - \Phi_{12}^n(\varphi_{n+1}(\beta)Z, \varphi_{n+1}(\beta)l_{n+1}) \cdot \delta_{\overline{1,2n-1}}(\beta)\right] & ;k=n+1 \end{cases}$$

(7)

and

$$Q_k(t,X,Z) = \frac{2\pi}{\tau_{m_k}} \sum_{j_l=0}^{\infty} j_l(-1)^{j_l+1} \frac{\sin(j_l\pi \cdot X)}{X \cdot \mu_{j_l}^2} \cdot$$

$$\cdot \left(1 - \exp\left(-\mu_{j_l}^2 \cdot t\right) \cdot \left[1 - \sum_{j=1}^{\infty}\frac{\varepsilon_{j_l j}(t)}{\beta_j^2 \cdot d\delta\left(\beta_j\right)}\right] \begin{cases} \prod\limits_{j=1}^{n}\varphi_{j+1}(\beta) \cdot \cos\left[\varphi_l(\beta)Z\right] & ;k=1 \\[2mm] \prod\limits_{j=k}^{n}\varphi_{j+1}(\beta) \cdot \begin{bmatrix} \Phi_{22}^{k-1}(\varphi_k(\beta)l_{k-1}, \varphi_k(\beta)Z) \cdot \delta_{\overline{1,2k-1}}(\beta) - \\ -\Phi_{12}^{k-1}(\varphi_k(\beta)l_{k-1}, \varphi_k(\beta)Z) \cdot \delta_{\overline{1,2k-1}}(\beta) \end{bmatrix} & ;k=\overline{1,n} \\[2mm] \begin{bmatrix} \Phi_{22}^n(\varphi_{n+1}(\beta)Z, \varphi_{n+1}(\beta)l_{n+1}) \cdot \delta_{\overline{1,2n-1}}(\beta) - \\ -\Phi_{12}^n(\varphi_{n+1}(\beta)Z, \varphi_{n+1}(\beta)l_{n+1}) \cdot \delta_{\overline{1,2n-1}}(\beta) \end{bmatrix} & ;k=n+1 \end{cases}\right).$$

where: $\beta_j, j = \overline{1, \infty}$ are roots of transcendental equation:

$$\delta(\beta) \equiv \delta_{12}(\varphi_{n+1}(\beta)l_n, \varphi_{n+1}(\beta)l_{n+1}) \cdot \delta'_{\overline{1,2n-1}}(\beta) - \delta_{22}(\varphi_{n+1}(\beta)l_n, \varphi_{n+1}(\beta) \cdot \delta_{\overline{1,2n-1}}(\beta) = 0 \,. \quad \textbf{(9)}$$

Symbols. C - dimensionless benzene concentration in macropores; Q - dimensionless benzene concentration in nanopores; M − dimensionless benzene mass integral; $X=r/\mathrm{R}$ - dimensionless distance from crystallite centre; $Z=z/\ell$ - dimensionless distance from bottom of the crystallites bed; ε - bed porosity; **Numerical Simulation and Discussion.** Modeling on the basis of specially developed programs gives the solution of the two problems: inverse problem and direct problem.

Solution of the inverse problem. For numerical modeling we are using the experimental data profiles which were determined with method RMN (Prof. J. Fraissard) for benzene adsorptions in zeolite bed. Using experimental benzene absorbed mass profiles for micro- and nanopores of zeolites bed and modeling absorbant concentration profiles in microspores Q, according to eq. **(8)**, we compute the diffusion coefficients profiles for benzene D_{inter} and D_{intra} by solving the inverse problem.

Solution of the direct problem. Using the obtained value of the benzene diffusion coefficients profiles for macropores in intercrystallite space D_{inter} and intracrystallite space D_{intra} for heterogeneous catalitical zeolite bed, we can compute the concentration distributions $C(t,z)$, $Q(t,X,z)$ and mass integral $M(t,z)$. The other parameters, for example, the function of diffusion velocitys and diffusion gradients in macropores and nanopores also can be calculated. The concentration and mass integral distribution curves are presented in function of time and geometrical coordinates: distances from the zeolite-bed bottom z and dimensionless distance from crystallite centre $X=r/R$.

Figure 2 shows the comparison of the computed (model) and experimental kinetic curves of dimensionless mass integral $M(t,z)$ versus time t for four's different values of coordinate of distance in crystallite zeolite-bed z: *z=1mm, z=5mm, z=7mm, z=15mm*. As is seen from fig.2, the model distributions (type 2 curves - Model) agrees satisfactory with experimental kinetic curves (type 1 curves - Experimental) of dimensionless mass integral $M(t,z)$. This is assured by solution of the inverse problem: the obtained profiles of D_{inter} and D_{intra}. The relative error value does not exceed 3-5% for upper part of bed (a) *z=1mm; b) z=5mm; c) z=7mm*).
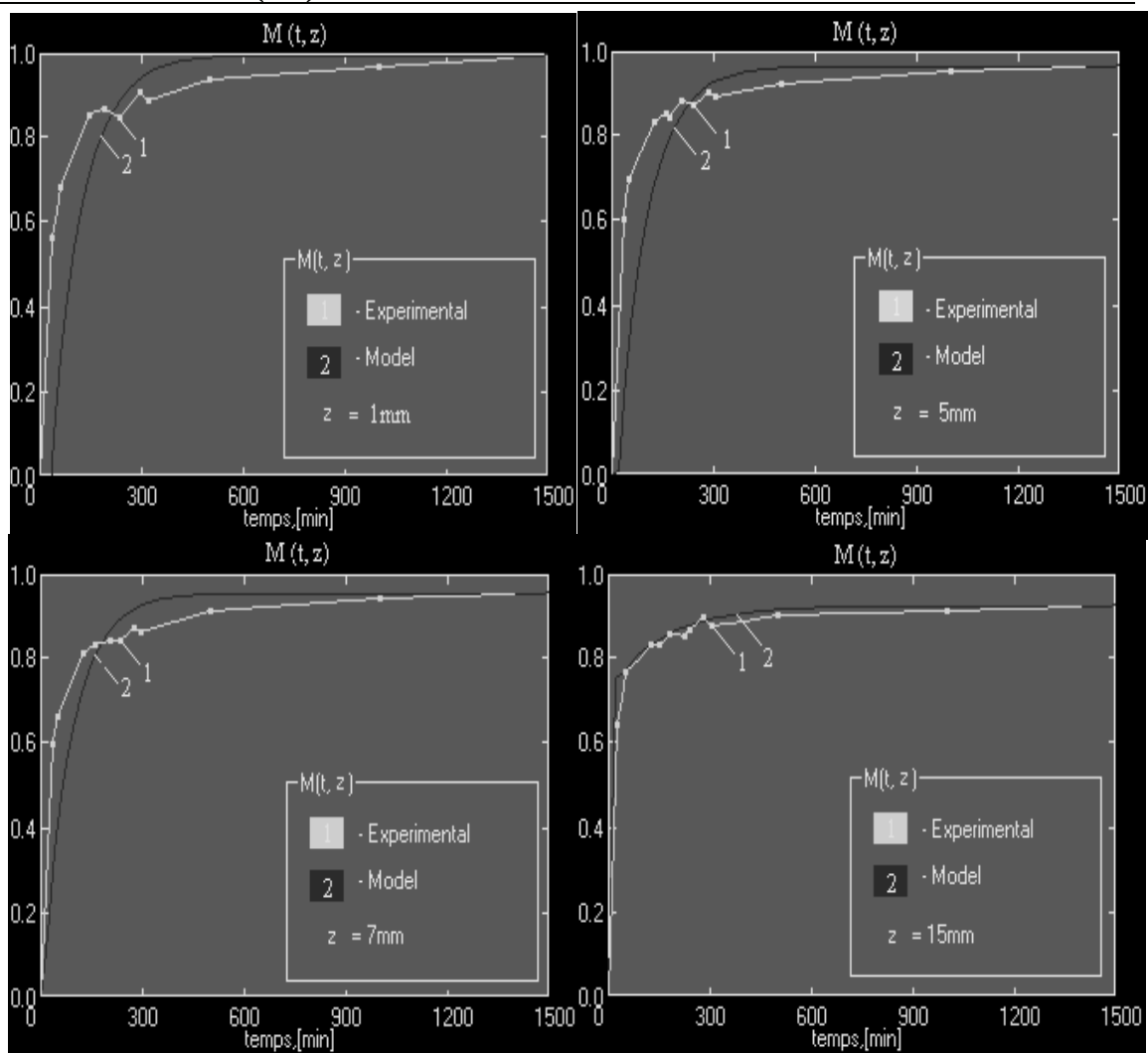
Fig. 2 - Model and experimental kinetic curves of dimensionless mass integral versus time t [min] for different value of distance of the crystallite zeolite-bed z

For lower part of crystallite bed (*d*) *z=15mm*), relative error value does not exceed 2%. For long diffusion time in intracrystallite space (more then 300 min) we can observe an equilibrium condition for all curves $M(t,z)$. For distance equal *z=1mm*, value of equilibrium dimensionless integral mass in nanopores of crystallites equal to 0.98. For lower layers of bed, we can observe natural reducing of equilibrium dimensionless mass as result of C_6H_6 current concentration reducing in macropores of intercrystallite space $C_k(t,z)$.

In fig.3 shows concentration profiles of C_6H_6 in intercrystallite space $C_k(t,z)$. As is seen in fig.3, concentration curves for each distance *z* are going to equilibrium values.
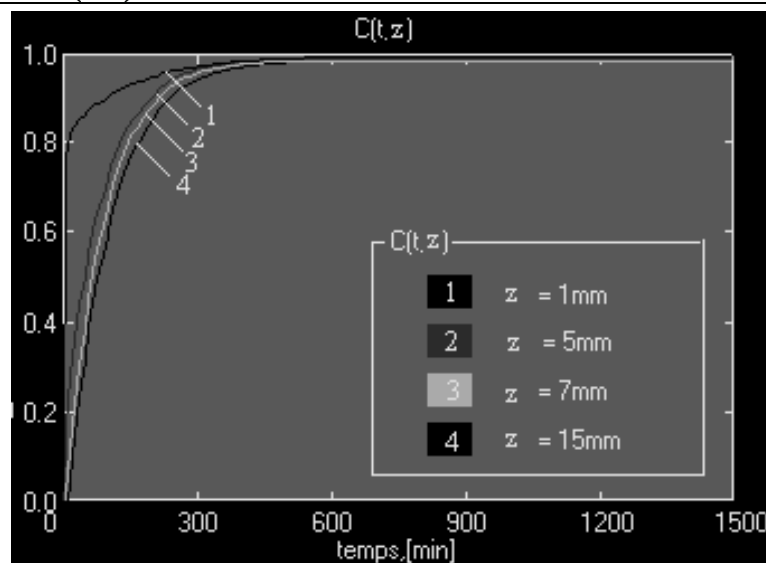
Fig. 3 - C_6H_6 concentration profiles $C_k(t,z)$ versus time t[min] for different values of the distance from the bottom of the crystallite zeolite–bed

z

Figure 4 presents the model concentrations profiles of C_6H_6 in crystallites $Q(t,X,z)$ as a function of dimensionless distance from crystallite centre X for different time values t [min] and four's layers of the crystallite bed z [mm]. As can be seen from fig.4, the concentration in intracrystallite space $Q(t,X,z)$ is more decreased in centre of crystallites (X=0) and elevated towards to crystallite surface (X=1.0).

Conclusion. The solution of proposed mathematical model of benzene diffusion in heterogeneous zeolite bed is based on the *Laplace* integral transformation and *Couchy* methods. The analytical solution of this model permits to analyse the benzene fluid transport in macropores and nanopores of crystallite zeolite beds.

The solution of the inverse problem on the base of experimental data permitted the calculation of D_{inter} and D_{intra} diffusion coefficients distributions as function of time and crystallite dimensionless position.

The direct problem solution permitted the estimation of the concentration profiles, concentration gradients profiles and other parameters profiles inside of nano- and macropores of heterogeneous crystallite bed of zeolite. The comparison of experimental and model kinetic curves of dimensionless mass integral for different layer thickness shows their reasonable adequacy.

REFERENCES

1. Leniuk M.P., Petryk M.R. Fourier, Bessel integral transformations methods with spectral parameter in mathematical modelling problems of mass transfer in heterogenous multilayer medias. - Ќyiv (UA): Naukova Dumka (Academic Publishing), 2000. - 372 p.

2. Leniuk M.P., Petryk M.R. The mathematical modeling of mass transfer with spectral parametr for heterogeneous n − interface limited micro porous medias // Volyn Mathematical Bulletin (UA). - 2003.- № 10. − P. 161-185.
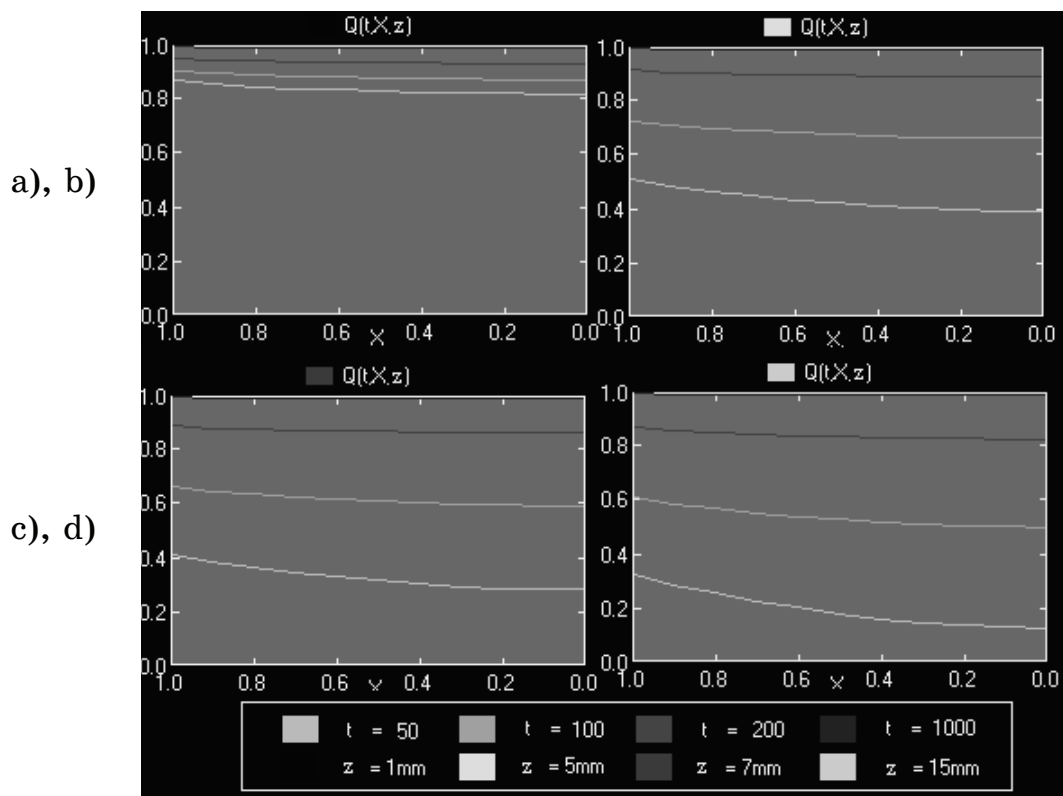
Fig. 4. C_6H_6 - concentration profiles in nanopores of intracrystallite space $Q(t,X,z)$ versus dimensionless distance from crystallite centre X for different distance from bottom of the crystallites bed z and time t [min] : a) $z=1mm$; b) $z=5mm$; c) $z=7mm$; d) $z=15mm$