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## Competitive diffusion of benzene-hexane mixtures in microporous medium: mathematical modeling and parameters identification

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В статье представлена эффективная процедура идентификации коэффициентов конкурентной диффузии двух газов (бензола и гексана) в пространствах между частицами и в частицах среды, реализована с использованием градиентных методов, разработанной математической модели для процессов конкурентной и моно диффузии и результатов ЯМР-анализа распределений адсорбированной массы каждой из компонент в цеолитной среде. Распределения коэффициентов диффузии получены как функции от времени для различных положений вдоль исследуемой цеолитной среды. Построены модельные профили изменения концентрации бензола и гексана в среде во времени на основе полученных коэффициентов диффузии и разработанной математической модели.

**Ключевые слова:** конкурентная диффузия газов, адсорбция, математическое моделирование, коэффициенты диффузии, микропористая среда, градиентные методы идентификации

В статі представлена ефективна процедура ідентифікації коефіцієнтів конкурентної дифузії двох газів (бензолу та гексану) у міжчастинковому та внутрішньочастинковому просторах, реалізована з використанням градієнтних методів, розробленої математичної моделі для процесів конкурентної та моно дифузії та результатів ЯМР-аналізу розподілів адсорбованої маси кожної з компонент в цеолітному середовищі. Розподіли коефіцієнтів дифузії отримано як функції від часу для різних положень уздовж досліджуваного цеолітного середовища. Побудовано модельні профілі зміни концентрації бензолу та гексану в середовища в часі на основі отриманих коефіцієнтів дифузії та розробленої математичної моделі.

**Ключові слова:** конкурентна дифузія газів, адсорбція, математичне моделювання, коефіцієнти дифузії, мікропористе середовище, градієнтні методи ідентифікації

In the paper we propose new effective identification procedures for competitive diffusion coefficients of two gases (benzene and hexane) in intra- and inter-crystallite space. This procedure is developed using high-speed gradient methods, mathematical models of competitive as well as monodiffusion, and NMR imaging of adsorbed masses distribution for each component in zeolite crystallite bed. Distributions of diffusion coefficients as functions of time were obtained for different positions along the microspores. The benzene and hexane concentration curves as functions of time were built at every level of crystallite bed for inter crystallite space, based on identified coefficients and developed mathematical models.

**Key words:** Competitive diffusion of gases, adsorption, modeling, diffusion coefficient, microporous zeolite bed, intra- and intracrystallites space, gradient methods of identification.

### 1. General problem

Knowledge of the co-diffusion and co-adsorption coefficients of reactants and products is essential when a heterogeneous catalysis reaction is performed by means of gases flowing through a porous catalyst bed. It can be even more important in a

fluidized bed where the contact times between the catalyst pellets and the reactants are very short, which means that one hardly ever knows whether the pellet is used completely or only superficially. Under these experimental conditions the system is never at adsorption equilibrium. The distribution of the various reactants adsorbed on the catalyst is very heterogeneous and, moreover, it varies greatly from one reactant to another. However, calculations on the kinetics are generally performed by assuming the ideal case of a homogeneous assembly, both for the totality of the catalyst and for the distribution of all the reactants, which makes these calculations, even when they are mathematically rigorous, rather approximate as reality regards.

Mass transfer in catalysis is a rather complex process involving several parameters which are seldom defined by a single technique. Nuclear magnetic resonance (NMR) has provided much information about these problems. It can be divided into two parts: conventional NMR and Magnetic Resonance Imaging (MRI) [1]. With the first one, measurements characterize the entire sample without spatial resolution. Its application to the study of the diffusion of an adsorbate most often concerns self-diffusion measurements on species in adsorption equilibrium.

Unlike the known research on diffusion of separate gases for the adsorptions catalysts, this project includes research of kinetics and development of methods of kinetic parameters identification for competitive (compatible) diffusive transfer and adsorption of two hydrocarbon components in macro- and nanoporous of heterogeneous catalysts.

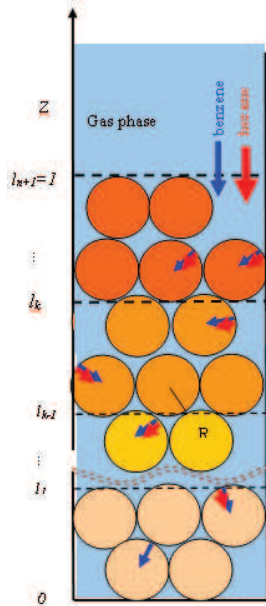
Many researches in this area of problem mainly concerned molecular transport of certain substances in the porous medium and considered mass transfer at the macro level without significantly influence the effects and characteristics of micro- and nanoporous of particles itself. But this kind of mass transfer are limiting and determining factor in overall diffusion kinetics of such type of mediums [2]. Another unexplored aspect is co-diffusion of two or more components in the same time or so-called competitive diffusion [3]. It is therefore essential to clarify mechanisms and factors of competitive diffusion kinetics of microporous mediums and to identify each of interacting components.

## 2. Mathematical model

The presented mathematical model is similar to biporous model [4, 5], with a system of complex competitive mass transfer between two diffused components (benzene and hexane) in a heterogeneous media (crystallite bed) of porous crystallites. We suppose that diffusion process causes two types of mass transfer: diffusion in the macropore (intracrystallite space) by the space between particles and diffusion in micro- and nanopores of crystallites (intraparticle space).

A cylindrical bed of microporous zeolite crystallites, assumed to be spherical (radius  $R$ ), is exposed to a constant concentration of adsorbate in the gas phase. One face of this bed is permeable to the two gases (benzene and hexane). In this case one can consider that two gases diffusion is axial in the macropores ( $z$  direction along the height,  $l$ , of the bed) and radial in the micropores. We assume that the crystallites zeolite bed consists of a large number  $N$ , of very thin solid layers of thickness  $\Delta l_k = l_k - l_{k-1}$ , perpendicular to the propagation of the gas in the  $z$  direction. In the proposed mathematical model we assume that: (i) during the evolution of the system

towards equilibrium there has to be a concentration gradient in the macropores and/or in the micropores; (ii) the effect of heat is negligible; (iii) diffusion occurs in Henry's law region of the adsorption isotherm; (iv) all solid particles are spherical; (v) all solid particles are of the same size; uniform packing through the crystallite bed is assumed.



*Diffusion in macropores*

Length of the bed:  $l$

Characteristic position of the layer:  $l_k, k = \overline{1, n+1}$

Thickness of layer  $k$ :  $\Delta l_k = l_{k+1} - l_k, k = \overline{1, n+1}$

Intercrystallite diffusion coefficient

in  $k^{\text{th}}$  layer:  $D_{inter,k}$  ;

Corresponding characteristic time:  $\tau_{inter,k}$

*Diffusion in micropores*

Crystallite radius:  $R$

Intracrystallite diffusion coefficient

in  $k^{\text{th}}$  layer:  $D_{intra,k}$

Corresponding characteristic time:  $\tau_{intra,k}$

$l \gg R ; D_{inter,k} \gg D_{intra,k} ; k = \overline{1, n+1}$

Fig. 1 The scheme of diffusion complete in crystallite bed

The mathematical model of gas diffusion kinetics in the crystallite zeolite bed (which we consider to be a heterogeneous and multilayer porous medium) is defined in domains  $\Omega_{m_r}$  by the solutions of the system of differential equations [6]

$$\frac{\partial C_{s_m}(t, Z)}{\partial t} = \frac{D_{inter,s_m}}{l^2} \frac{\partial^2 C_{s_m}}{\partial Z^2} - e_{inter,m} K_{s_m} \frac{D_{intra,s_m}}{R^2} \left( \frac{\partial Q_{s_m}}{\partial X} \right)_{X=l}, \quad (1)$$

$$\frac{\partial Q_{s_m}(t, X, Z)}{\partial t} = \frac{D_{intra,s_m}}{R^2} \frac{\partial^2 Q_{s_m}}{\partial X^2}. \quad (2)$$

Domain:  $\Omega_{m_r} = (0, T) \times \Omega_m, (\Omega_m = (L_{m-1}, L_m), m = \overline{1, N+1}, L_0 = 0 < L_1 < \dots < L_{N+1} = l)$ .

With initial conditions

$$C_{s_m}(t=0, Z) = 0; \quad Q_{s_m}(t=0, X, Z) = 0; \quad X \in (0, R), Z \in \Omega_m, m = \overline{1, N+1}, \quad (3)$$

boundary and interface conditions for  $Z$  coordinate:

$$C_{s_1}(t, L_1) = 1, \quad \frac{\partial C_{s_1}}{\partial Z}(t, Z=0) = 0, \quad t \in (0, T); \quad (4)$$

$$\left[ C_{s_m}(t, Z) - C_{s_m}(t, Z) \right]_{Z=L_m} = 0, \quad m = \overline{1, N}$$

$$\frac{\partial}{\partial Z} \left[ D_{inter_{s_{m-1}}} C_{s_{m-1}}(t, Z) - D_{inter_{s_m}} C_{s_m}(t, Z) \right]_{Z=L_m} = 0, \quad t \in (0, T) \quad (5)$$

and boundary conditions for X coordinate:

$$\frac{\partial}{\partial X} Q_{s_m}(t, X=0, Z) = 0; \quad Q_{s_m}(t, X=L, Z) = C_{s_m}(t, Z), \quad Z \in \Omega_m, \quad m = \overline{1, N+1}. \quad (6)$$

Here

$$Z = \frac{z}{\ell}, \quad X = \frac{r}{R}, \quad C = \frac{c}{c_\infty}, \quad Q = \frac{q}{q_\infty};$$

$$e_{inter_m} = \frac{e_{inter_m} c_{sm}}{e_{inter_m} c_{sm} + (1 - e_{inter_m}) q_{sm}} \approx \frac{e_{inter_m}}{(1 - e_{inter_m}) K_{sm}}; \quad e_{intra_m} = 1 - e_{inter_m}, \quad K_{s_m} = \frac{q_{s_m \infty}}{c_{s_m \infty}}.$$

$$\bar{Q}_s(t, Z) = \int_0^1 Q_s(t, X, Z) dX \quad - \text{average concentration for } s^{\text{th}} \text{ adsorbed component}$$

( $s = \overline{1, 2}$ ) in microporous of crystallite;  $c_s, q_s$  – adsorbent concentration in macro and micro porous (molecule/cm<sup>3</sup>);  $D_{intra_s}, D_{inter_s}$  – diffusion coefficient in micro- and macro porous (m<sup>2</sup>/s);  $K_s$  – adsorption equilibrium constant,  $\varepsilon_{inter}$  – porosity;  $e_{inter}$  – porosity coefficient;  $R$  – partial radius (m);  $\ell$  – thickness of working area of catalytic media (m).

### 3. Analytical solution

To find the analytical solutions of direct problems (1)-(6) we used the Heaviside method according to procedure originally used by Leniuk & Petryk [9]. As result we obtained functions  $C_{sm}$  and  $N_{sm}$  in theform:

$$C_{sm}(t, Z) = 1 + \frac{2\pi}{\Delta L} \frac{R^2}{D_{intra_{sm}}} \frac{D_{inter_{sm}}}{\Delta L^2} \times$$

$$\times \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \exp\left(-\frac{D_{intra_{sm}} \vartheta_{kn_m}^2}{R^2} t\right) \frac{n \left( \theta_{sm} \sin\left[\frac{n\pi}{\Delta L}(Z - L_{m-1})\right] + \theta_{s_{m-1}} \sin\left[\frac{n\pi}{\Delta L}(L_m - Z)\right] \right)}{(-1)^n \vartheta_{kn_m}^2 \left( \frac{3}{e_{inter_m}} \left( \frac{1}{\sin^2(\vartheta_{kn_m})} - \frac{c \operatorname{tg}(\vartheta_{kn_m})}{\vartheta_{kn_m}} \right) + 2 \right)} \quad (7)$$

$$N_{sm}(t, X, Z) = 1 + \frac{2\pi}{\Delta L} \frac{R^2}{D_{intra_{sm}}} \frac{D_{inter_{sm}}}{\Delta L^2} \times$$

$$\times \sum_{n=1}^{\infty} \sum_{k=1}^{\infty} \exp\left(-\frac{D_{intra_{sm}} \vartheta_{kn_m}^2}{R^2} t\right) \frac{n \cdot \sin(\vartheta_{kn_m} X) \left( \theta_{sm} \sin\left[\frac{n\pi}{\Delta L}(Z - L_{m-1})\right] + \theta_{s_{m-1}} \sin\left[\frac{n\pi}{\Delta L}(L_m - Z)\right] \right)}{(-1)^n \vartheta_{kn_m}^2 \sin(\vartheta_{kn_m}) \left( \frac{3}{e_{inter_m}} \left( \frac{1}{\sin^2(\vartheta_{kn_m})} - \frac{c \operatorname{ot}(\vartheta_{kn_m})}{\vartheta_{kn_m}} \right) + 2 \right)} \quad (8)$$

where  $\epsilon_{kn_m}$  are roots of transcendent equations:

$$\varphi_{s1}^2(\beta) \equiv \frac{3}{e_{\text{int}e_{r_1}}} \frac{\Delta L^2}{R^2} \frac{D_{\text{intra}_{s1}}}{D_{\text{int}e_{r_{s1}}}} \left( \frac{e_{\text{int}e_{r_1}}}{3} \frac{R^2}{D_{\text{intra}_{s1}}} \beta^2 - \beta \cot \beta + 1 \right) = \frac{2n-1}{2\Delta L} \pi, \quad n, k = \overline{1, \infty}. \quad (9)$$

**4. Identification of diffusion coefficients.**

Assuming, that coefficients of competitive diffusion in intracrystallite space  $D_{\text{inter}_s}$  and inter crystallite space  $D_{\text{intra}_s}, s = \overline{1, 2}$  ( $s=1$  – corresponded benzene and  $s=2$  corresponded hexane) are unknown.

Taking into account mathematical model (1)–(6), the identification problem can be formulated as: to find unknown functions  $D_{\text{intra}_s} \in \Omega_T, D_{\text{inter}_s} \in \Omega_T$  ( $D_{\text{intra}_s} > 0, D_{\text{inter}_s} > 0, s = \overline{1, 2}$ ), when absolute absorbed masses for every point  $\gamma_m \subset \Omega_m$  of  $m$ -th crystallite bed segment satisfy the condition:

$$\left[ C_{s_m}(t, Z) + \bar{Q}_{s_m}(t, Z) \right]_{\gamma_m} = M_{s_m}(t, Z)_{\gamma_m}, \quad s = \overline{1, 2}; \quad \gamma_m \in \Omega_m, \gamma_m = L_m - L_{m-1} \quad (10)$$

According to paper [8] and using errors minimization gradient method for identification of competitive diffusion coefficients as function of time for intracrystallite space  $D_{\text{intra}_{s_m}}$  (mycro level) and intercrystallite space  $D_{\text{inter}_{s_m}}$  (macro level) of  $s$ -th diffused components ( $s=1$  -benzene and  $s=2$  - hexane), we obtain regulation expression for  $(n + 1)^{\text{th}}$  identification step:

$$D_{\text{intra}_{s_m}}^{n+1}(t) = D_{\text{intra}_{s_m}}^n(t) - \nabla J_{D_{\text{intra}_{s_m}}}^n(t) \times \frac{\left[ C_{s_m} \left( D_{\text{inter}_{s_m}}^n, D_{\text{intra}_{s_m}}^n; t, \gamma_m \right) + \left( \frac{1}{X} \right)_{X=\frac{1}{2}} N_{s_m} \left( D_{\text{inter}_{s_m}}^n, D_{\text{intra}_{s_m}}^n; t, \frac{1}{2}, \gamma_m \right) - M_{s_m}(t) \right]^2}{\left\| \nabla J_{D_{\text{intra}_{s_m}}}^n(t) \right\|^2 + \left\| \nabla J_{D_{\text{inter}_{s_m}}}^n(t) \right\|^2}, \quad t \in (0, T) \quad (11)$$

$$D_{\text{inter}_{s_m}}^{n+1}(t) = D_{\text{inter}_{s_m}}^n(t) - \nabla J_{D_{\text{inter}_{s_m}}}^n(t) \times \frac{\left[ C_{s_m} \left( D_{\text{inter}_{s_m}}^n, D_{\text{intra}_{s_m}}^n; t, \gamma_m \right) + \left( \frac{1}{X} \right)_{X=\frac{1}{2}} N_{s_m} \left( D_{\text{inter}_{s_m}}^n, D_{\text{intra}_{s_m}}^n; t, \frac{1}{2}, \gamma_m \right) - M_{s_m}(t) \right]^2}{\left\| \nabla J_{D_{\text{intra}_{s_m}}}^n(t) \right\|^2 + \left\| \nabla J_{D_{\text{inter}_{s_m}}}^n(t) \right\|^2}, \quad t \in (0, T) \quad (12)$$

Where:

$J(D_{inter_s_m}, D_{intra_s_m})$  - error's functional of model solution from experimental data (observation traces) on  $\gamma_m \in \Omega_m$ :

$$J(D_{inter_s_m}, D_{intra_s_m}) = \frac{1}{2} \int_0^T \left[ C_{s_m}(\tau, Z, D_{inter_s_m}, D_{intra_s_m}) + \left( \frac{1}{X} \right)_{X=\frac{1}{2}} N_{s_m} \left( t, Z, D_{inter_s_m}, \frac{1}{2}, D_{intra_s_m} \right) - M_{s_m}(t) \right]^2 d\tau, \quad \gamma_m \in \Omega_m, \quad m=1, N+1. \quad (13)$$

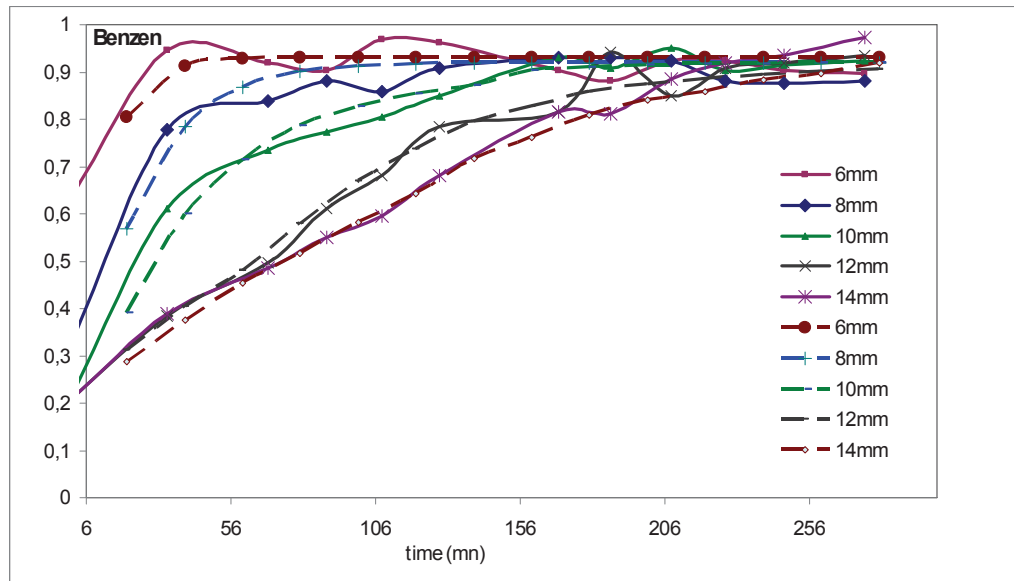
Here:

$\nabla J_{D_{intra_s_m}}^n(t), \nabla J_{D_{inter_s_m}}^n(t)$  are errors's functional gradients  $J(D_{inter_s_m}, D_{intra_s_m})$ ;

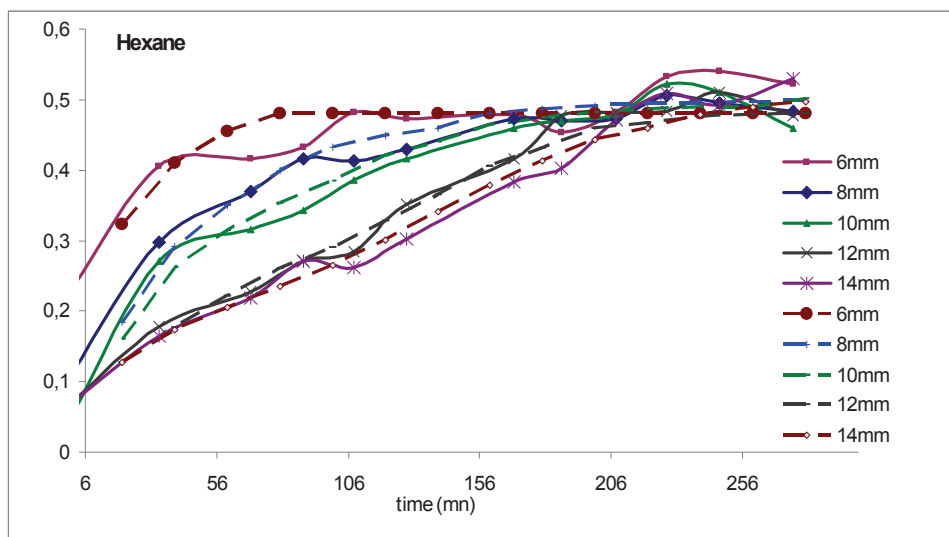
$\|\nabla J_{D_{intra_s_m}}^n(t)\|^2 = \int_0^T [\nabla J_{D_{intra_s_m}}^n(t)]^2 dt, \|\nabla J_{D_{inter_s_m}}^n(t)\|^2 = \int_0^T [\nabla J_{D_{inter_s_m}}^n(t)]^2 dt$  - norms of functional gradient;

$M_s(t, Z)|_{\gamma_m}$  - data vector of experimental distribution (observational trace) of absorbed mass in macro- and micro porous on surface area  $\gamma_m \subset \Omega_m$  as results of NMR-analysis (Fig. 2a – experimental data for benzene, Fig. 2b – experimental data for hexane).

The technology of calculation of each component in case of monodiffusion based on the works optimal control theory [7] and is described in paper [8] in details.



a)



b)

Fig. 2. Distribution of the benzene and hexane concentrations in time for different sample layers (experimental curves and approximations).

### 5. Numerical simulation and analysis.

According to proposed methodology of parameter identification based on optimal control theory [7] and using experimental data approximations (fig.2) the distributions of diffusion coefficients were obtained. The identified benzene diffusion coefficients  $D_{intra_{1,k}}$  and  $D_{inter_{1,k}}$  are presented as functions of time for the five coordinates thickness positions: 6, 8, 10, 12, 14 mm in fig. 3, 4.

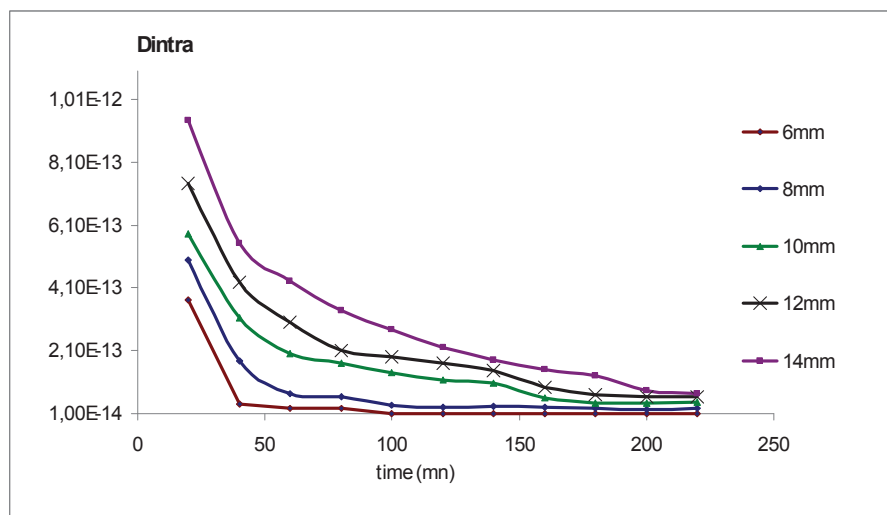


Fig. 3. Diffusion coefficients profiles  $D_{intra_{1,k}}$  in intraparticle space for benzene in time for different positions in catalytic bed

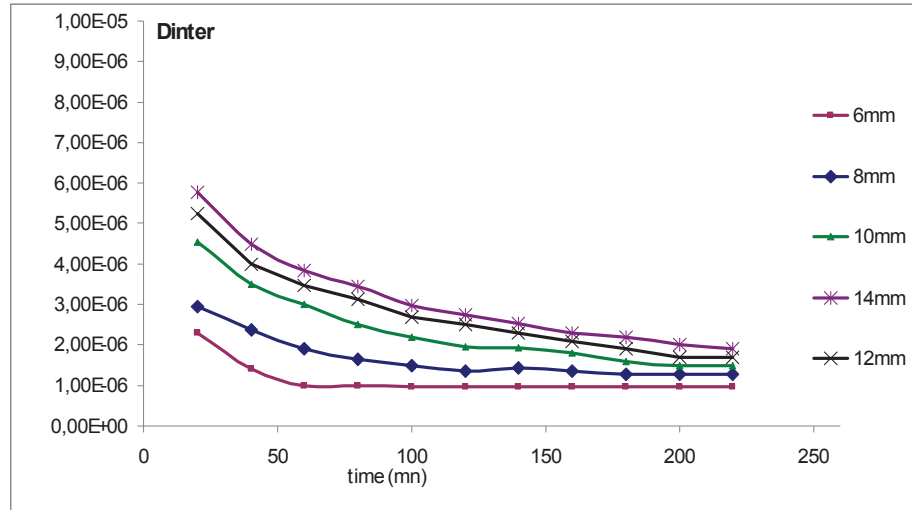


Fig. 4. Diffusion coefficients profiles  $D_{inter,k}$  in interparticles space for benzene in time for different positions in catalytic bed

Competitive diffusion coefficient curves for the intraparticle space are of the pseudo exponential nature and in a case of benzene varying in the range from  $1.0 \text{ e-}12$  till  $5.0 \text{ e-}13$ . Since the diffusion time  $t = 80\text{-}100\text{mn}$  relatively gentle picture of changes in their values is observed testifying the diffusion approximation toward the equilibrium level.

The diffusion coefficient distributions (fig. 4) are of more gentle nature and changed in the range of  $6.0 \text{ e-}6$  till  $1.0 \text{ e-}6$ . Since the diffusion time  $t = 130\text{-}140 \text{ mn}$  also relatively gentle picture of changes in their values is observed testifying the process of convergence to equilibrium.

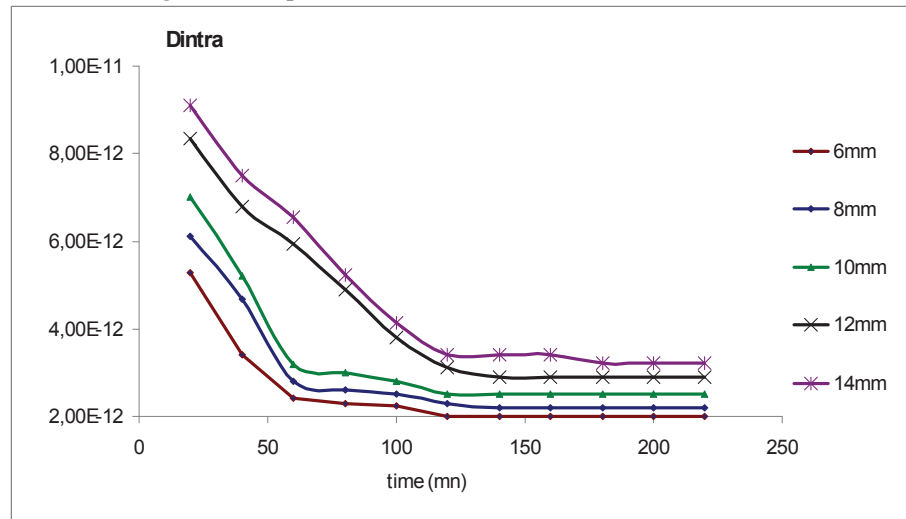


Fig. 5. Diffusion coefficients profiles  $D_{intra,k}$  in intraparticles space for hexane in time for different positions in catalytic bed



Fig. 5 and 6 show similar results but for hexane. Identified competitive diffusion coefficients distributions as functions of time for the same positions of coordinates thickness (6, 8, 10, 12, 14 mm) change in time in the range of  $1.0 \times 10^{-11}$  till  $1.0 \times 10^{-12}$ . Since the diffusion time  $t = 75-90$  mn a slight decrease in their values of time is observed.

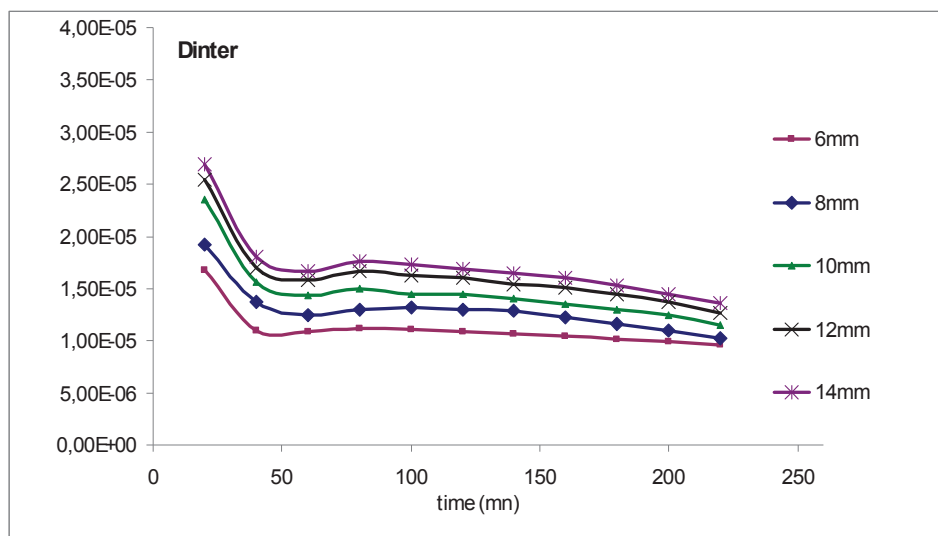


Fig. 6 Diffusion coefficients profiles  $D_{inter2,k}$  in interparticles space for hexane in time for different positions in catalytic bed

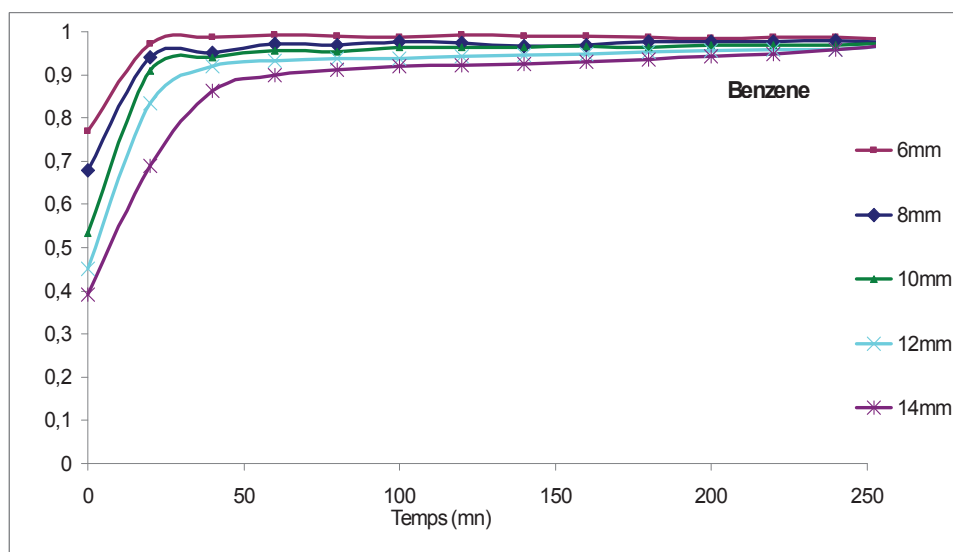


Fig. 7. Diffusion concentration distributions in the intercrystalites space in time at different positions of the catalytic bed for benzene

The hexane diffusion coefficient distributions in the macropore (fig. 6) vary in the range from  $2.7 \text{ E-6}$  till  $1.0 \text{ E5}$ . Since the diffusion time  $t = 70\text{-}80 \text{ mn}$  also relatively gentle pattern changing of their values and slightly higher at the end of diffusion is observed.

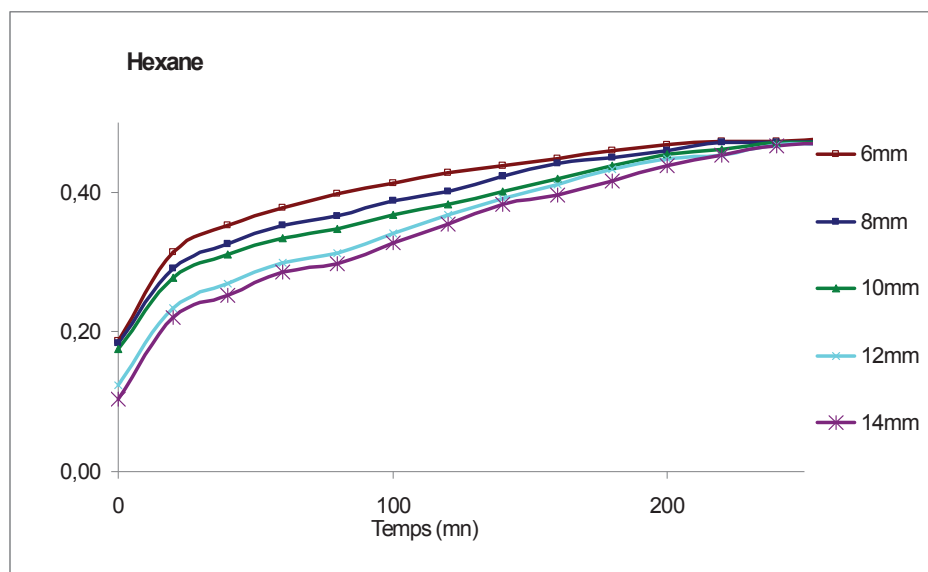


Fig. 8. Diffusion concentration distributions in the intercrystalites space in time at different positions of the catalytic bed for hexane

Fig. 7, 8 shows concentration curves calculated for benzene and hexane in intercrystalites space with taking into account identified diffusion coefficients both for intra- and inter particles spaces. It is easily noticed that model distributions are very similar to experimental data approximations.

## 7. Conclusions

In this paper we propose the new effective identification procedures of diffusion coefficients for both diffused components (benzene and hexane) in intra- and inter crystallites spaces. Procedure implementation are achieved with using of gradient methods of the complex multi-component systems state control, mathematical models of competitive diffusion and mono diffusion in porous zeolite mediums and NMR imaging of the adsorbed masses distribution for each component in the zeolite crystallite bed. As result we obtain distributions of diffusion coefficients as a function of time for different positions along the microspores medium.

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