Parameter Identification of Competitive Diffusion of Nanoporous Particles Media Using Gradient Method and the Heviside's Operational Method

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Abstract – **The identification of competitive diffusion parameters in heterogeneous nanoporous materials is analyzed. Solutions to the direct and inverse problems are basing on the Heaviside's operational method and gradient method are obtained. New procedures for identification of diffusion coefficients for co-diffusing components (benzene and hexane) in intra- and intercrystallite spaces are implemented using high-speed gradient methods and mathematical diffusion models as well as the NMR spectra of the adsorbed mass distribution of each component in the zeolite bed. The gradient of the residual functional is obtained basing on optimal control theory**. **These diffusion coefficients are obtained as a function of time for different positions along the bed. Benzene and hexane concentrations in the inter- and intracrystallite spaces for every position in the bed and for different adsorption times are calculated.**

Key words: **mathematical model, competitive diffusion, direct end inverse boundary problems, functional identification, gradient method, Heviside's operational method, nanoporous medi**a.

I. INTRODUCTION

New theoretical developments in system analysis and mathematical modeling constitute the basis for information technologies of the control of research experiment and the analysis of the state of complex physical objects. The latter include multicomponent systems of competitive mass transfer in nanoporous media; studying their kinetics is an important problem of the modern nanophysics and nanodiffusion.

Nanoporous media widely used in various branches of industry (medicine, petrochemistry, catalysis, partition of liquids and gases) consist of porous structure particles with different physical and chemical (including diffusion) properties. Nanoporous media is a multilevel system of pores with two most important subsystems (spaces): system of micropores and nanopores with high adsorption capacity and low diffusion penetration rate (intraparticle space) and system of macropores and cavities among particles with low capacity and high penetration rate (interparticle space) [1–4].

The numerous studies in this domain concerned molecular transport of isolated substances in a porous medium, where mass transfer was mainly considered on a macrolevel without significant influence of micro- and nanotransfer in particles [1–8], which is a limiting and governing factor of the general kinetics. The major problems of intermolecular interactions, based on the Langmuir–Hinshelwood principle [4], which take place in real systems of diffusion "competition"(competitive diffusion of two and more substances) are not investigated.

Identifying of kinetic transfer parameters that determine the rate of the process at macro- and microlevels and the conditions of their equilibrium is an important scientific problem, which arises along with determining the concentration and gradient fields for each diffusing substance.

II. THE OBJECTIVE AND INVESTIGATION TASKS

The objective of the work is the development of highly efficient and high-speed parameter identification methods of competitive diffusion of gases in the catalytic media of nanoporous particles taking into account the complex of limiting physical factors of inner transfer kinetics.

The following tasks are stated:

- to stady theoretically the competitive diffusion in media of particles (crystallites) of nanoporous structure, the mechanisms of mass transfer in the system «itercrystallite space-nanoporous particles", intereactions and flow of micro- and macrotransfer, equilibrium conditions,

- basing on the optimal control theory developed for multicomponent distributed systems to state and to interpret the direct and conjugate coefficient identification problems on the basis of functional (residual, error), to implement the gradient procedure of parameter identification;

- to justifay mathematically and to construct analytical solutions of direct and conjugate problems using the Heviside's operational method,

- to implement the technology of transfer parameter identification on the basis of obtaining explicit expressions of gradients residual functional, identification and modeling, to define the distributions of the diffusion kinetic parameters.

III. MATHEMATICAL MODEL OF COMPETITIVE DIFFUSION IN MICROPOROUS SOLIDS

The model presented is similar to the biporous model [6, 7, 15, 16]. We consider a system of complex competitive mass transfers between two diffusing components (benzene and hexane) in a heterogeneous medium (crystallite bed) with crystallites of nanoporous structure. The diffusion process involves two types of mass transfer: diffusion in the macropores (intercrystallite space), and diffusion in the micropores of crystallites (intracrystallite space).

A cylindrical bed of zeolite crystallites, assumed to be spherical (radius R), is exposed to a constant concentration of adsorbate in the gas phase (Fig. 1). One face of this bed is permeable to the two gases. In this case one can consider that diffusion of the two gases is axial in the macropores of the intercrystallite space (z direction along the height, l, of the bed) and radial in the micropores of the zeolite. We have made the following assumptions: (i) during the evolution of the system towards equilibrium there is a concentration gradient in the macropores and/or in the micropores; (ii) the effect of heat is negligible; (iii) diffusion occurs in the Henry's law region of the adsorption isotherm; (iv) all crystallites are spherical and have the same radius R; (v) the crystallite bed is uniformly packed.
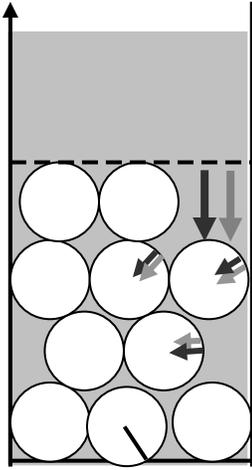

Fig. 1. Schema of diffusion competitive in nanoporous particles media

The coefficients of competitive diffusion in intracrystallite space D_{intra_s} and intercrystallite space D_{intra_s}, $s=\overline{1,2}$ (s = 1 for benzene and s = 2 for hexane) being unknown, the mathematical model of gas diffusion kinetics in the zeolite bed is defined in domains: $\Omega_T = (0,T)\times\Omega$, $\Omega = (0,1)$ by the solutions of the system of differential equations (with dimensionless coordinates defined in the nomenclature) [5, 8]:

$$\frac{\partial C_s(t,Z)}{\partial t} = \frac{D_{inter_s}}{l^2}\frac{\partial^2 C_s}{\partial Z^2} - e_{inter}K_s\frac{D_{intra_s}}{R^2}\left(\frac{\partial Q_s}{\partial X}\right)_{X=1}, \quad (1)$$

$$\frac{\partial Q_s(t,X,Z)}{\partial t} = \frac{D_{intra_s}}{R^2}\left(\frac{\partial^2 Q_s}{\partial X^2} + \frac{2}{X}\frac{\partial Q_s}{\partial X}\right). \quad (2)$$

Initial conditions

$$C_s(t=0,Z)=0; \quad Q_s(t=0,X,Z)=0; \quad X\in(0,1), Z\in\Omega, \quad (3)$$

boundary conditions for coordinate Z:

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

boundary conditions at itch point $(Z,t)\subset\Omega_T$ for concentrations Q_s for particle radius X :

$$\frac{\partial}{\partial X}Q_s(t,X=0,Z)=0 \text{ (symmetry condition)}, \quad (5)$$

$Q_s(t,X=1,Z)=C_s(t,Z)$ (equilibrium condition), $t\in(0,T)$, $Z\in\Omega$; (6)
additional condition (*experimental data*):

$$\left[C_s(t,Z)+\overline{Q}_s(t,Z)\right]\Big|_\gamma = M_s(t,Z)\Big|_\gamma, \quad s=\overline{1,2}; \gamma\in\Omega, \quad t\in(0,T). \quad (7)$$

The problem of the calculation (1)–(7) is: to find unknown functions $D_{intra_s}\in\Omega_T$, $D_{inter_s}\in\Omega_T$ ($D_{intra_s}>0$, $D_{inter_s}>0$, $s=\overline{1,2}$), when absorbed masses $C_s(t,Z)+\overline{Q}_s(t,Z)$ satisfy the condition (7) for every point $\gamma\subset\Omega$ [16, 17].
Here:

$$e_{inter} = \frac{\varepsilon_{inter}c_s}{\varepsilon_{inter}c_s+(1-\varepsilon_{inter})q_s} \gg \frac{\varepsilon_{inter}}{(1-\varepsilon_{inter})K_s}; \quad e_{intra}=1-e_{inter}, \quad K_s = \frac{q_{s_\infty}}{c_{s_\infty}},$$

$\overline{Q}_s(t,Z)=\int_0^1 Q_s(t,X,Z)XdX$ - average concentration of adsorbed component s ($s=\overline{1,2}$) in micropores; $M_s(t,Z)\Big|_\gamma$ - experimental distribution of absorbed mass in macro- and micropores) at $\gamma\subset\Omega$ (results of NMR data) [8].

IV. MATHEMATICAL JUSTIFICATION OF THE IDENTIFICATION PROBLEM SOLVABILITY

The identification of diffusion coefficients D_{intra_s} and D_{inter_s} is a complex mathematical problem. In general, it is not possible to obtain a correct statement of the problem of calculation of diffusion coefficients (1) - (7) and to construct a unique analytical solution, because of the complexity of taking into account all the physical parameters (variation of temperature or pressure, crystallite structures, non-linearity of Langmuir isotherms, etc.), as well as the insufficient number of reliable experimental data, measurement errors and other factors.

Therefore, according to the principle of Tikhonov [12], later developed by Lions [13] and Sergienko and Deineka [17], the same problems of identification of diffusion coefficients require the specification of the model solution with each iteration step, by minimizing the difference between the calculated values and the experimental data.

The method proposed is a generalization of the identification approaches presented in [7, 15, 16]; it allows to reduce the number of iterations to 2-3 of magnitude for each specification cycle. It can also be used to identify parameters for more complicated adsorption systems and to identify three or more parameters simultaneously.

The solution of the problem of calculation of diffusion coefficients (1) - (7) is reduced to the problem of minimizing the functional of the difference (9) between the model solution and the experimental data, the solution being refined incrementally by means of a special regularisation procedure which uses fast, high-performance gradient methods [13, 14, 17].

Gradient methods of diffusion coefficients identification based on a Lagrange functional of residuals (target, error, etc.) have found practical application in the work of Lions [13] (problems of thermoelasticity), later developed by Alifanov (calculation of temperature fields for plane apparatus elements) [14], then by Sergienko, Deineka, Petryk, and Fraissard (problems of hydromechanics, of filtration, of adsorption, etc.) [17, 15, 16].

Gradient method of identification. According to [17, 16] and using the error minimization gradient method for identification of competitive diffusion coefficients for intracrystallite space D_{intra_s} and intercrystallite space D_{inter_s} of the s-th diffusing component, we obtain the iteration expression for the $n+1$-th identification step:

$$D_{intra_s}^{n+1}(t) = D_{intra_s}^n(t) - \nabla J_{D_{intra_s}}^n(t) \frac{\left[E_s^n\left(D_{intra_s}^n, D_{inter_s}^n; t, \gamma\right)\right]^2}{\left\|\nabla J_{D_{intra_s}}^n(t)\right\|^2 + \left\|\nabla J_{D_{inter_s}}^n(t)\right\|^2},$$

$$D_{inter_s}^{n+1}(t) = D_{inter_s}^n(t) - \nabla J_{D_{inter_s}}^n(t) \frac{\left[E_s^n\left(D_{intra_s}^n, D_{inter_s}^n; t, \gamma\right)\right]^2}{\left\|\nabla J_{D_{intra_s}}^n(t)\right\|^2 + \left\|\nabla J_{D_{inter_s}}^n(t)\right\|^2}, \quad (8)$$

where $J(D_{inter_s}, D_{intra_s})$ - the error functional (residual), which describes the deviation of the model solution from the experimental data on $\gamma \in \Omega$ written as:

$$J(D_{inter_s}, D_{intra_s}) = \frac{1}{2}\int_0^T \left[C_s(t,Z,D_{inter_s},D_{intra_s}) + \bar{Q}_s(t,Z,D_{inter_s},D_{intra_s}) - M_s(t)\right]_\gamma^2 dt, \quad (9)$$

where $\nabla J_{D_{intra_s}}^n(t)$, $\nabla J_{D_{intra_s}}^n(t)$ - the gradients of the error functional $J\left(D_{inter_s}, D_{intra_s}\right)$,

$$\left\|\nabla J_{D_{intra_s}}^n(t)\right\|^2 = \int_0^T \left[\nabla J_{D_{intra_s}}^n(t)\right]^2 dt, \quad \left\|\nabla J_{D_{inter_s}}^n(t)\right\|^2 = \int_0^T \left[\nabla J_{D_{inter_s}}^n(t)\right]^2 dt,$$

$$E_s^n(t) = C_s\left(D_{intra_s}^n, D_{inter_s}^n; t, \gamma\right) + \bar{Q}_s\left(D_{intra_s}^n, D_{inter_s}^n; t, \gamma\right) - M_s(t).$$

V. ANALYTICAL SOLUTION OF DIRECT PROBLEM

The solution C_s, Q_s of the direct problem (1)-(6) was obtained by the procedure described in [6] using the Heaviside's operational method:

$$C_s(t,Z) = 1 + 2\pi\left(\frac{R}{1}\right)^2 \frac{D_{inter_s}}{D_{intra_s}} \sum_{n=1}^\infty \sum_{k=1}^\infty \Phi(\beta_{kn},Z)\exp\left(-\frac{D_{intra_{s1}}}{R^2}\beta_{kn}^2 t\right).$$

$$N_s(t,X,Z) = 1 + 2\pi\left(\frac{R}{1}\right)^2 \frac{D_{inter_s}}{D_{intra_s}} \sum_{n=1}^\infty \sum_{k=1}^\infty \Phi(\beta_{kn},Z)\frac{\sin(\beta_{kn}X)}{\sin(\beta_{kn})}\times$$
$$\times\exp\left(-\frac{D_{intra_s}}{R^2}\beta_{kn}^2 t\right), \quad (10)$$

$$\Phi(\beta_{kn},Z) = \frac{(2n-1)\cos\left(\frac{2n-1}{2}\pi Z\right)}{(-1)^n \beta_{kn}^2 \left[\frac{3}{e_{inter}}\left(\frac{1}{\sin^2(\beta_{kn})} - \frac{ctg(\beta_{kn})}{\beta_{kn}}\right) + 2\right]},$$

were β_{kn} - roots of transcendent equations

$$\frac{3}{e_{inter}}\frac{l^2}{R^2}\frac{D_{inttra_s}}{D_{inter_s}}\left(\frac{e_{inter}}{3}\beta^2 - \beta ctg\beta + 1\right) = \frac{2n-1}{2}\pi,$$
$$n,k = \overline{1,\infty}$$

VI. IDENTIFICATION METODS OF COMPETITIVE DIFFUSION IN MICROPOROUS SOLIDS

According to [17] the identification procedure of coefficients diffusion (8) requires a special calculation technology of gradients $\nabla J_{D_{intra_s}}^n(t)$, $\nabla J_{D_{inter_s}}^n(t)$ of functional residual (9), which is a major determinant components of regularization formulas (8). This leads to the problem of unconditional optimization of Lagrange extended functional [13, 17]

$$\Phi\left(D_{inter_s}, D_{intra_s}\right) = J_s + I_{s_1} + I_{s_2}, \quad (11)$$

here I_{s_1}, I_{s_2} - the components, accounted of specificity of basic equations of direct problem (1)-(6):

$$I_{s_1} = \int_0^T\int_0^1 \phi_s(t,Z)\left(\frac{\partial C_s}{\partial t} - \frac{D_{inter_s}}{l^2}\frac{\partial^2 C_s}{\partial Z^2} + e_{inter}K_s\frac{D_{intra_s}}{R^2}\frac{\partial Q_s}{\partial X}\bigg|_{X=1}\right)dZdt,$$

$$I_{s_2} = \int_0^T\int_0^1\int_0^1 \psi_s(t,Z)\left(\frac{\partial Q_s(t,X,Z)}{\partial t} - \frac{D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2} + \frac{2}{X}\frac{\partial}{\partial X}\right)Q_s\right)XdXdZdt,$$

here J_s - residual functional (9), ϕ_s, ψ_s, $s,=\overline{1,2}$ – unknown factors of Lagrange, to be determined from the condition of stationary of the functional $\Phi(D_{inter_s}, D_{intra_s})$ [8, 14]:

$$\Delta\Phi(D_{inter_s}, D_{intra_s}) \equiv \Delta J_s + \Delta I_{s_1} + \Delta I_{s_2} = 0. \quad (12)$$

The calculation of components in eq. (A.4) is carried out assuming that the values D_{inter_s}, D_{intra_s} received increments ΔD_{inter_s}, ΔD_{intra_s}. As a result, the concentration $C_s(t,Z)$ will change into some increment $\Delta C_s(t,Z)$ and the concentration $Q_s(t,X,Z)$ well change into increment $\Delta Q_s(t,X,Z)$, $s=\overline{1,2}$.

VII. Conjugate Problem

The calculation result of functional increments ΔJ_s, ΔJ_{s_1}, ΔJ_{s_2} in (A.4) (using the integration by parts, by the initial and boundary conditions of direct problem (1)-(6), equating outside integral members and the inside integral components with the same increments $\Delta C_s(t,Z)$ and $Q_s(t,X,Z)$ to zero) leads to solving the additional conjugate problem of determining the unknown Lagrange factors ϕ_s, ψ_s of functional (11):

$$\frac{\partial \phi_s(t,Z)}{\partial t}+\frac{D_{inter_s}}{l^2}\frac{\partial^2 \phi_s}{\partial Z^2}+e_{inter}K_s\frac{D_{intra_s}}{R^2}\frac{\partial \psi_s}{\partial X}\Big|_{X=1}=E_s^n(t)\delta(Z-\gamma) \quad (13)$$

$$\frac{\partial \psi_s(t,X,Z)}{\partial t}+\frac{D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right)\psi_s=E_s^n(t)\delta(Z-\gamma). \quad (14)$$

$$\phi_s(t,Z)\big|_{t=T}=0; \ \psi_s(t,X,Z)\big|_{t=T}=0 \ \text{(conditions at } t=T) \quad (15)$$

$$\frac{\partial}{\partial Z}\phi_s(t,0)=0, \ \phi_s(t,1)=0, \quad (16)$$

here $E_s^n(t)=C_s(D_{intra_s}^n,D_{inter_s}^n;t,\gamma)+\overline{Q}_s(D_{intra_s}^n,D_{inter_s}^n;t,\gamma)-M_s(t)$, $\delta(Z-\gamma)$ - function of Dirac [6].

We have obtained solution ϕ_s, ψ_s of conjugate problem (13)-(16) by the procedure described in [6] using the operational method of the Heaviside's.

VIII. Relationship Between Direct And Conjugate Problem

Substituting in the initial direct problem (1) - (6) instead D_{inter_s}, D_{intra_s} and $C_s(t,Z)$, $Q_s(t,X,Z)$ the corresponding values with increments $D_{inter_s}+\Delta D_{inter_s}$, $D_{intra_s}+\Delta D_{intra_s}$ and $C_s(t,Z)+\Delta C_s(t,Z)$, $Q_s(t,X,Z)+\Delta Q_s(t,X,Z)$, and subtracting with the transformed equations and conditions of the problem the relevant components of the equations of problem (1) - (6) and neglecting terms of the second order of smallness, we obtain basic equations of the direct problem (1)-(6) in terms of increments $\Delta C_s(t,Z)$ and $\Delta Q_s(t,X,Z)$, $s=\overline{1,2}$ in the operator form:

$$L w_s(t,X,Z)=X_s, \ w_s\in(0,1)\bigcup\Omega_T, \quad (17)$$

Similarly we record the system of he basic equations of conjugate boundary problem (13)-(16) in operator form:

$$L^*\Psi_s(t,X,Z)=E_s(t)\delta(Z-\gamma), \ \Psi_s\subset(0,1)U\Omega_T, \quad (18)$$

$$= L = \begin{bmatrix} \frac{\partial}{\partial t}-\frac{\partial}{\partial Z}\left(D_{inter_s}\frac{\partial}{\partial Z}\right) & e_{inter}\frac{D_{intra_s}}{R}\frac{\partial}{\partial X}\Big|_{X=1} \\ 0 & \frac{\partial}{\partial t}-\frac{D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right) \end{bmatrix},$$

$$= L^* = \begin{bmatrix} \frac{\partial}{\partial t}+\frac{\partial}{\partial Z}\left(D_{inter_s}\frac{\partial}{\partial Z}\right) & e_{inter}\frac{D_{intra_s}}{R^2}\frac{\partial}{\partial X}\Big|_{X=1} \\ 0 & \frac{\partial}{\partial t}+\frac{D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right) \end{bmatrix}$$

$$w_s(t,X,Z)=\begin{bmatrix}\Delta C_s(t,Z)\\\Delta Q_s(t,X,Z)\end{bmatrix}, \ \Psi_s(t,X,Z)=\begin{bmatrix}\phi_s(t,Z)\\\psi_s(t,X,Z)\end{bmatrix},$$

$$X_s(t,X,Z)=\begin{bmatrix}\frac{\partial}{\partial Z}\left(\Delta D_{inter_s}\frac{\partial}{\partial Z}C_s\right)-e_{inter}\frac{\Delta D_{intra_s}}{R^2}\frac{\partial}{\partial X}Q_s\big|_{X=1}\\\frac{\Delta D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right)Q_s(t,X,Z)\end{bmatrix},$$

$$(19)$$

here L^* - conjugate Lagrange operator to operator L.

IX. Obtaining The Residual Functional Increment Formula

Increment calculated of residual functional (9), neglecting terms of the second order of smallness, has the view

$$\Delta J_s(D_{inter_s},D_{intra_s})=\int_0^T\int_0^1 E_s(t)\Delta C_s\delta(Z-\gamma)dZd\tau+\int_0^T\int_0^1\int_0^1 E_s(t)\delta(Z-\gamma)\Delta Q_s XdXdZdt.$$

Using the change of variable $w_s=L^{-1}X_s$, here L^{-1} - inverse operator to operator L, we obtain

$$\Delta J_s\left(D_{intra_s},D_{inter_s}\right)=\int_0^T\int_0^1 L^{-1}X_{s_1}(t,Z)E_s(t)\delta(Z-\gamma)dZdt+$$
$$+\int_0^T\int_0^1\int_0^1 L^{-1}X_{s_2}(t,X,Z)E_s(t)\delta(Z-\gamma)XdXdZdt \quad (20)$$

Defining the scalar product

$$\left(L w_s(t,X,Z),\Psi_s(t,X,Z)\right)=\begin{bmatrix}\iint_{\Omega_T}L\Delta C_s(t,Z)\phi_s(t,Z)dZdt\\\iiint_{(0,R)\cup\Omega_T}L\Delta Q_s(t,X,Z)(t,X,Z)\psi_s(t,X,Z)XdXdZdt\end{bmatrix}, \quad (21)$$

and taking into account (A.20) the identity of Lagrange [13, 17]

$$\left(L w_s(t,X,Z),\Psi_s(t,X,Z)\right)=\left(w_s(t,X,Z),L^*\Psi_s(t,X,Z)\right) \quad (22)$$

and the equality $L^{-1*}\left[E_s(t)\delta(Z-\gamma)\right]=\Psi_s$, we obtain the increment of residual functional expressed by the solution of conjugate

problem and the vector of right parts of equations system (19):

$$\Delta J_s(D_{inter_s}, D_{intra_s}) = (\Psi_s(t,X,Z),\ X_s(t,X,Z)),\qquad (23)$$

here $\phi_s(t,Z)$ and $\psi_s(t,X,Z)$ belong to $\bar{\Omega}_T$ and $[0,1]\cup\bar{\Omega}_T$ respectively, L^{-1*} - conjugate operator to inverse operator L^{-1}, Ψ_s - solution vector of conjugate problem (13)-(16).

Revealing in equation (23) the components $X_s(t,X,Z)$ taking in account the equality (19), we come to the important formula, which establishes the relationship between the direct problem (1) - (6) and the conjugate problem (13) - (16) and which makes it possible to obtain explicit analytical expressions of components of the residual functional gradient

$$\Delta J_s(D_{intra_s}, D_{inter_s}) = \left(\phi_s, \frac{\partial}{\partial Z}\left(\Delta D_{inter_s}\frac{\partial}{\partial Z}C_s\right) - e_{inter}\frac{\Delta D_{intra_s}}{R^2}\frac{\partial}{\partial X}Q_s\big|_{X=1}\right) + \\ + \left(\psi_s, \frac{\Delta D_{intra_s}}{R^2}\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right)Q_s\right). \tag{24}$$

Analytical expressions of the gradients of the residual functional. Differentiating expression (24), by ΔD_{intra_s} and ΔD_{inter_s} respectively, and the opening of scalar products according to (21), we obtain the required analytical expressions for the gradient of the residual functional respectively to the components necessary of diffusion coefficients as functions for time in intracrystalite space and intercrystalite space respectively:

$$\nabla J_{D_{intra_s}}(t) = -\frac{e_{inter}}{R^2}\int_0^1\frac{\partial}{\partial X}Q_s(t,X,Z)\phi_s(t,Z)dZ + \\ + \frac{1}{R^2}\int_0^1\int_0^1\left(\frac{\partial^2}{\partial X^2}+\frac{2}{X}\frac{\partial}{\partial X}\right)Q_s(t,X,Z)\psi_s(t,X,Z)XdXdZ \tag{25}$$

$$\nabla J_{D_{inter_s}}(t) = \int_0^1\frac{\partial^2 C_s(t,Z)}{\partial Z^2}\phi_s(t,Z)dZ . \tag{26}$$

The formulas of gradients $\nabla J^n_{D_{intra_s}}(t)$, $\nabla J^n_{D_{intra_s}}(t)$ include analytical expressions of direct problem solutions (1) - (6). It provides high performance of computing process, avoiding a large number of inner loop iterations by using exact analytical methods.

Another advantage of the formulas (8) is that it is possible to identify the unknown kinetic parameters as a function of time $(D_{intra_s}(t), D_{inter_s}(t))$ and other coordinates. It provides the possibility of internal diffusion kinetics in intracrystallite space and intercrystallite space and get an overall vision of the whole process.

X. NUMERICAL SIMULATION AND ANALYSIS: COMPETITIVE DIFFUSION COEFFICIENTS, CONCENTRATION PROFILES IN ITERCRYSTALLITE SPACE AND INTRACRYSTALIYTE SPACE

The benzene and hexane intracrystallite diffusion coefficients D_{intra_1} and D_{intra_2} are presented in Figure 2 as functions of time for the five coordinates positions: 6, 8, 10, 12, 14 mm, defined now from the top of the bed. The curves for benzene D_{intra_1} (Fig. 2a) are pseudo exponentials. D_{intra_1} decreases from 9.0 E-12 to about 1.0 E-14 (equilibrium) depending on the position of the crystallite and the time, as well as on the amount of adsorbed gas. The shapes of the variations of D_{intra_2} for hexane are roughly the same, but the diffusion coefficients are higher, from about 9.0 E-11 to 2.0 E-12 (Fig. 2b).
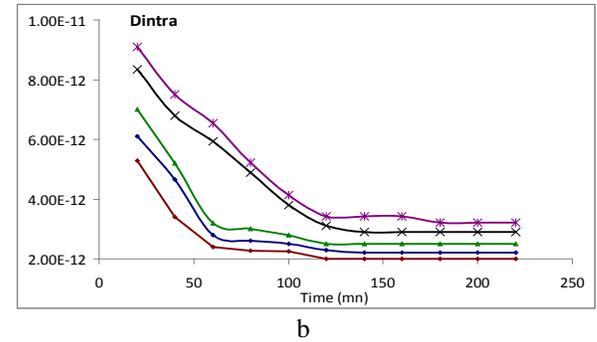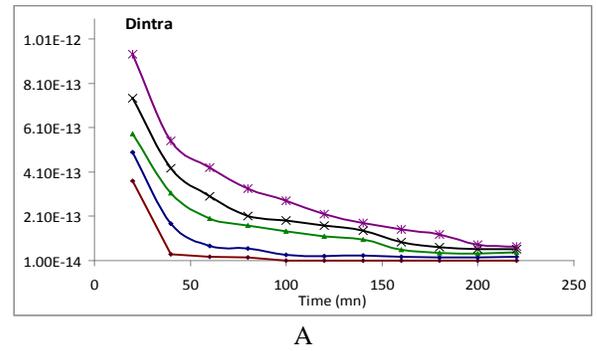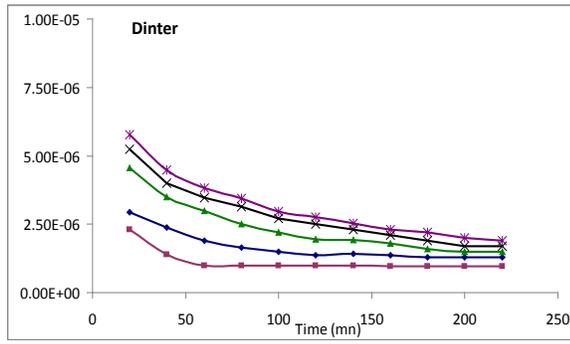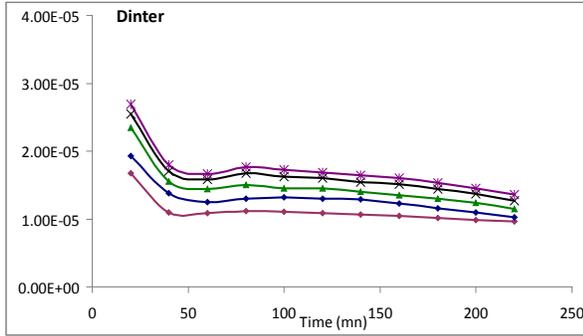

A

b

Fig. 2. Variation of intracrystallite diffusion coefficients for (a) benzene D_{intra_1} and (b) hexane D_{intra_2} against time at different positions of the bed

━━◆━━ 6 mm, ━━◆━━ 8 mm, ━━▲━━ 10 mm, ━━✕━━ 12 mm, ━━✳━━ 14 mm

Figure 3 presents the benzene and hexane diffusion coefficient distributions in intercrystallite space D_{inter_1} and D_{inter_2} as functions of time and for coordinate positions from 6 to 14 mm. These coefficients decrease with time from 6.0 E-6 to 1.0 E-6 (equilibrium) for benzene and from 2.7 E-6 to 1.0 E-5 for hexane, depending on the position in the bed and the increase in the adsorbed concentrations.
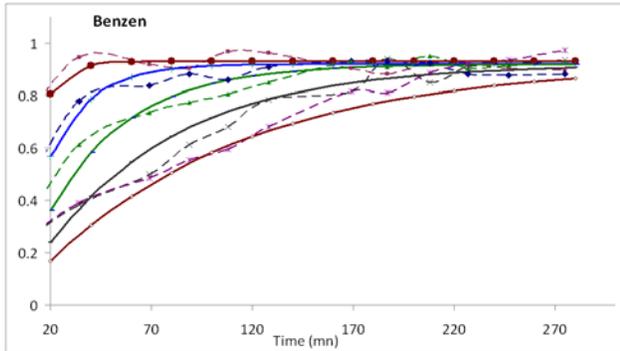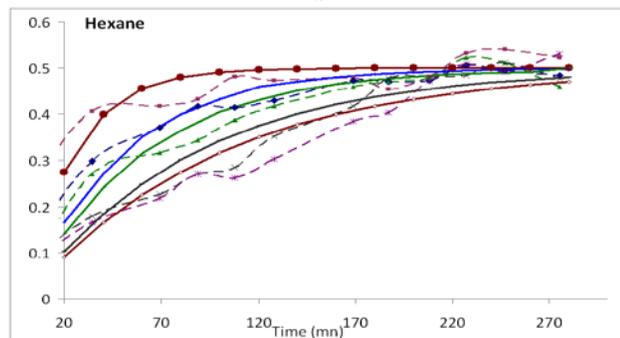
Fig. 3. Variation of intercrystallite diffusion coefficients for (a) benzene D_{inter_1} and (b) hexane D_{inter_2}, against time at different positions of the bed

◆ 6 mm, ◆ 8 mm, ▲ 10 mm, ✕ 12 mm, ✳ 14 mm

Figure 4 compares calculated and experimental curves for the total mass of benzene and hexane in the catalytic bed.

a

b

Fig. 4. Concentration of (a) benzene and (b) hexane *versus* time at different positions of the catalytic bed: *dotted* - experimental curves, *continuous* – model curves

◆ 6 mm, ◆ 8 mm, ▲ 10 mm, ✕ 12 mm, ✳ 14 mm

As it can be seen from the graphs (Fig. 4a), the distributions of the total adsorbed mass of benzene are in good agreement with the experimental distributions for each measurement position. The maximum deviation is generally less than 5%. A similar pattern is observed for hexane (Fig. 4b). Here the greatest differences (6-7%) are for the curves corresponding to positions 6 and 8 mm.

XI. CONCLUSION

As a result for the first time in a single physical experiment it was possible to probe at every moment the concomitant distribution of several gases co-diffusing in a porous solid and to identify their diffusion parameters.

Scientific novelty. For the first time high-speed efficient methods of diffusion parameters identification have been developed taking advantage of low-consuming high-speed solution of the direct and conjugate problem. The analytic solutions of the direct and conjugate problem, using the Heviside's operational methods have been stated and interpreted. Basing on the theory of the multicomponent systems state control, explicit expressions of residual functional gradient have been obtained, which made possible to implement the efficient identification algorithms, to determine diffusion coefficients distributions.

Practical importance. Application of the developed identification methods makes possible to obtain the diffusion coefficients for both components as the functions of time for different positions along the catalytic bed, which allows to specify the main diffusion flows in intercrystallite space (macro level) and in intracrystallite space (micro level) of nanoporous media and to realize the high-speeds procedures of such dependencies creation.

The prospects of investigation are: generalization of the obtained results on the two-components and multi-components catalytic medias of different configuration; obtaining of the methods and identification algorithms of three and more parameters; development of these methods as to their implementation and application to non-linear models of competitive diffusion, when the diffusion coefficients are considered as the functions of concentrations of the diffused components, and other parameters.

Nomenclature:

c : adsorbate concentration in macropores.

c_∞ : adsorbate equilibrium concentration in macropores.

$C = c/c_\infty$: dimensionless adsorbate concentration in macropores.

D_{inter} : macropore diffusion coefficient, m^2/s

D_{intra} : micropore diffusion coefficient, m^2/s

K : adsorption equilibrium constant

l : bed length, mm.

L: dimensionless bed length (L=1)

M : total uptake at time t.

M_T : total uptake at equilibrium.

q : adsorbate concentration in micropores.

q_∞ : equilibrium adsorbate concentration in micropores.

$Q = q/q_\infty$: dimensionless adsorbate concentration in micropores.

x : distance from crystallite center, mm.

R : mean crystallite radius, mm (we assume that the crystallites are spherical).

$X = x/R$: dimensionless distance from crystallite center.

z : distance from the bottom of the bed for mathematical simulation, mm.

$Z = z/l$: dimensionless distance from the bottom of the bed.

e_{inter} – porosity,

T – total duration of diffusion, min.

n - iteration number of identification,

Greek letters

ε_{inter} : bed porosity.

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