Modelling of Microporous Diffusion of N-Paraffins in Zeolite 5A

Liljana T. Markovska†, Vera D. Meshko and Radmila T. Kiprijanova

Faculty of Technology and Metallurgy, University "St.Cyril and Methodius," Skopje, Republic of Macedonia

Abstract—Sorptive liquid-phase diffusion of two n-paraffins, $C_{10}H_{22}$ and $C_{11}H_{24}$, dissolved in isooctane, onto micropore of 5A zeolite was studied to assess multicomponent diffusion and competitive effects. Diffusion coefficients for adsorbing components are determined from experimental batch reactor data. The experimental data indicate that diffusion through the microporous zeolite crystals is the primary diffusional resistance. A mathematical model of the rate of adsorption of a solute from a liquid by micropore adsorbent in a batch system was developed. The equation describing the mass transport by diffusion in a micropore adsorbent has been solved in order to obtain theoretical uptake curves for systems when the adsorption equilibrium isotherm is the favourable and nonlinear one. A computer simulation of the microporous diffusion is performed by use of the ISIM-Interactive Simulation Language. The effect of main term and cross-term coefficients of micropore diffusion for the system considered is investigated.

Key words : Multicomponent Diffusion, Zeolite, Micropore Diffusion

INTRODUCTION

The first step in developing a mathematical model for description or prediction of adsorption dynamics is to provide a representation of rate phenomena and equilibrium isotherm.

Although extensive research has been conducted on adsorption phenomena, most of the published papers in this field have dealt mainly with equilibrium behaviour, i.e., the interactive and competitive effects of various adsorbates on adsorbents under equilibrium conditions [Hulme et al., 1991; Periasamy and Namasivayam, 1994; Lin and Hsu, 1995]. However, it is well recognized that maximum capacities of adsorbents are seldom fully utilized in most practical applications due to mass-transfer resistances. Therefore, both equilibrium and kinetic studies on adsorption are of importance for processes involving adsorption. Despite its importance, few kinetic studies have been reported on multicomponent liquid phase adsorption processes due to experimental difficulties. Thus, little is known regarding multicomponent diffusion effects for sorptive diffusion of multi-solutes onto adsorbents.

Several versions of the rate equation model have been used to evaluate the available data for adsorption on zeolite to obtain values for diffusion coefficients. These include the homogeneous, heterogeneous, pore, surface, and combined diffusion models.

The homogeneous diffusion model assumes that the particle is a homogeneous solid through which diffusion can be modelled by a solid-phase diffusivity [Ruthven, 1984; Klein, 1983]. The heterogeneous diffusion model assumes that diffusion in the particle occurs by macropore diffusion through the voids of the porous binder and micropore diffusion in the zeolite crystals [Ruthven, 1984]. The micropore diffusion mechanism is assumed to be solid diffusion only because molecular species in zeolite crystals should never be free from force fields associated with the pore walls. For liquid systems, macropore diffusion can be due to molecular diffusion and/or surface diffusion. The frequently used pore diffusion, surface diffusion, and combined diffusion models are special cases of the heterogeneous diffusion model.

Multicomponent models are usually extended from those applied to binary component systems, and the competitive effects are most often accounted for through the multicomponent equilibrium equations.

Such work has been done using the film homogeneous diffusion, film-pore diffusion and film-heterogeneous diffusion models with macropore and micropore diffusion [Moon and Lee, 1983; McKay et al., 1987; Robinson et al., 1994]. Differences between the kinetic behaviour in binary and multicomponent systems have also been interpreted as being due to solute interactions during diffusion. In most cases, binary diffusivities could not be used to directly predict multicomponent data.

In multicomponent diffusion, the flux of one component can be influenced by the concentration gradient of a second component. Such interactions can result in highly coupled mass-transfer phenomena, involving the special characteristics of multicomponent diffusion [Lee et al., 1993].

The competitive adsorption of two adsorbing components in zeolites was theoretically analysed using a Monte-Carlo type of approach [Palenkar and Rajadhyaksha, 1985a, b]. It was found that the multicomponent diffusion effect was significant for the system studied and the contribution of a cross-term diffusivity could not be neglected.

Experiments of competitive adsorption of two dissolved organic compounds onto actived carbon [Fritz et al., 1981] have shown deviations between experimental results with two adsorbing component systems and those calculated from diffusion

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†To whom correspondence should be addressed.
E-mail : lile@ereb.mf.ukim.edu.mk

models using one adsorbing component data. The deviations were especially large for systems with significant internal diffusional resistance, large differences in the mobility of the diffusing molecules or marked displacement of one component by the other. The deviations were caused by diffusional interactions between the two adsorbing components in the adsorbed phase.

The investigation of adsorption of n-paraffins dissolved in different solvents onto zeolite 5A used a macroporous controlled diffusion model [Jakimova et al., 1983]. The macropore diffusion coefficients were determined, and they were of order 10^{-9} m^2s^{-1}. M. F. M. Post [1991] presented results for microporous diffusion coefficients of n-paraffins on different zeolites. For zeolite 5A they were of order 10^{-16} m^2s^{-1}. These considerations enabled us to assume a microporous rate controlling mechanism for adsorption study in the frame of this paper.

In this investigation the ternary systems are studied. The effects of main term and cross-term coefficients of micropore diffusion for the system considered are investigated. The mathematical expressions for the kinetics curves will be used to develop a mathematical model of the fixed bed adsorption column which is based on a mass balance on the column and a mass balance on the particles in the column.

THEORETICAL

Rate of adsorption in porous adsorbents is generally controlled by transport within the pore network, rather than by the intrinsic kinetics of adsorption at the surface. So it is convenient to consider intraparticle transport as a diffusive process and to correlate kinetic data in terms of a diffusivity defined in accordance with Fick's first law [Crank, 1975]. Such a definition provides a convenient mathematical representation.

The rate of adsorptive diffusion was determined from the concentration curve of adsorbing component as a function of time. A mathematical model using Langmuir adsorption isotherm was used to find the best fit of an effective diffusivity to the adsorptive diffusion data. Diffusion of one and two adsorbing components dissolved in isooctane on zeolite 5A was modelled by a set of diffusion equations combined with source-sink terms due to adsorption inside adsorbent particles. Since the model of adsorptive diffusion for one adsorbing component can be found elsewhere [Ruthven, 1984; Weber, 1984], only the model for two adsorbing components is presented here. The homogenous diffusion model assumes that the zeolite crystal is a homogenous solid through which diffusion of each individual species can be modelled by a single solid phase diffusivity. To account for the multicomponent diffusion effect, the generalised Fick's law flux equation was used to describe the diffusion process, where the driving force for diffusion of one adsorbing component is dependent not only on its own concentration gradient but also on that of the second adsorbing component [Lee et al., 1993].

Accordingly, for the system with two adsorbing components in isooctane on 5A, the governing equations for adsorptive diffusion assuming spherical micropore in the zeolite crystal, are

$$\frac{\partial q_i}{\partial t} = \sum_{j=1}^{2} D_{ij}\left(\frac{\partial^2 q_j}{\partial r^2} + \frac{2}{r}\frac{\partial q_j}{\partial r}\right), \quad i=1, 2 \tag{1}$$

Subscripts i and j represent the adsorbing components. The diagonal (D_{ij}, j=i) and off-diagonal (D_{ij}, j≠i) terms are called main-term and cross-term diffusion coefficients, respectively [Lee et al., 1993]. The diffusion coefficient D_{ij} may not be equal to D_{ji}. A nonzero value of a cross-term diffusivity indicates the influence of the concentration gradient of one component on the flux of another adsorbing component.

If the uptake of the adsorbing component by the adsorbent is small relative to the total quantity of adsorbing component introduced into the system, the ambient concentration of the adsorbing component will remain essentially constant following the initial step change.

The appropriate initial and boundary conditions are

$$\left.\begin{array}{ll} q_i = 0 & \text{at} \quad t = 0 \\ q_i = q_i^* & \text{at} \quad r = r_c \\ \left(\dfrac{\partial q_i}{\partial r}\right) = 0 & \text{at} \quad r = 0 \end{array}\right\} \quad i = 1, 2 \tag{1a}$$

where q_i^* is in equilibrium with initial fluid concentration c_{0i}. In this case transport within macropores in pellets can be assumed to be very fast, since the concentration of the adsorbing component throughout the pellet is essentially uniform. It means that the adsorbing component concentration at the surface of the microporous crystal is the same as the average adsorbing component concentration in fluid phase.

Eq. (1) represents two coupled partial differential equations which describe two adsorbing component diffusion in adsorbent micropores. In treating dynamic adsorption data, it was shown [Meshko, 1990] that the adsorption rate is much faster than the diffusion rate, and hence local equilibrium can be assumed at the surface of the crystal.

The boundary condition at the surface of the microporous crystal q_i^* depends on the isotherm being used.

Many relationships have been proposed to represent phase distributions governed by adsorption equilibrium including the Gibbs, Freundlich, Langmuir, Dubinin, and Brunauer-Emmet-Teller equations [Yon and Turnock, 1971]. In this investigation the extended Langmuir isotherm equation is used:

$$\frac{q_i^*}{q_{mi}} = \frac{k_i c_i}{1 + \sum_{j=1}^{2} k_j c_j} \qquad i = 1, 2 \tag{2}$$

It has been shown that this expression provides a reasonably good empirical correlation of the equilibrium data for the investigated systems [Meshko, 1990; Poposka et al., 1990].

The average concentration for each adsorbing component throughout the zeolite crystal is defined as:

$$\bar{q}_i(t) = \frac{3}{r_c^3}\int_0^{r_c} q_i(r, t) r^2 dr \qquad i = 1, 2 \tag{3}$$

The mathematical model cannot be solved analytically because of its non-linearity and the complicated boundary condition on the surface of the microporous crystal.

EXPERIMENTAL

Adsorption equilibrium and kinetics studies were carried out in a thermostated batch reactor [Meshko, 1990] with mixing

device and volume 1.5 dm³.

All the experiments were carried out using n-paraffins ($C_{10}H_{22}$, $C_{11}H_{24}$, $C_{12}H_{26}$, $C_{13}H_{28}$, $C_{14}H_{30}$) and a mixture of two adsorbing components ($C_{10}H_{22}$ and $C_{11}H_{24}$) dissolved in isooctane. Each experiment was repeated three times. For the one adsorbing component diffusion study, the initial concentration of each n-paraffin in isooctane was 5-150 mmol dm⁻³. For the two adsorbing component diffusion studies, the initial concentration of n-$C_{11}H_{24}$ was two times the initial concentration of n-$C_{10}H_{22}$. In this study the total initial concentrations were 30 mmol dm⁻³ and 76 mmol dm⁻³. Isooctane with purity of 99.3 % was used as solvent. The adsorbent used in this investigation was zeolite 5A (Union Carbide product) with average particle diameter, 1.6 mm. The amount of adsorbent employed per run varied in the range from 50 g to 150 g. Prior to an experiment the sieve was regenerated at 673 K for a period of 24 hours in order to remove any traces of moisture or other contaminants. The sieve was cooled to room temperature, still under a nitrogen purge, and then transferred to the batch reactor which was filled with a known amount of pure solvent. It is necessary to perform the experiment immediately after the regeneration in order to minimise the possibility of picking up moisture from the air. Usually a period of one hour was allowed for the non-adsorbable solvent to saturate the macropores of the sieve. At time zero a known amount of n-paraffin was introduced into the system.

To maintain a uniform composition throughout the system the stirrer was operated at a fairly high speed (1,000 rpm). Preliminary experiments showed that above this speed, there was very little change in the experimental uptake curves. Under these conditions the film mass-transfer was assumed to be insignificant.

The temperature in the batch reactor was held constant at 295 K. The volume of the solution was 1 dm³. The measurements were made by taking small samples (0.5 cm³) from the solution at planned intervals. This means that it is possible to assume that the solution composition was constant during the runs. The concentrations of n-paraffins were measured using Perkin-Elmer gas chromatograph 3920 B. For this purpose a glass capillary column type WCOT-0.25 mm with OV-101 as stationary phase and FID detector were used.

RESULTS AND DISCUSSION

1. Details of Computation

The computer simulation of the mathematical model described by Eqs. (1) to (3), was performed using ISIM-Simulation Language [ISIM, 1986]. This language is capable of solving ordinary and partial differential equations and provides a choice of four different integration routines. In this investigation the coupled partial differential equations were transformed into a set of first order ordinary differential equations using finite difference method [Crank, 1975]. The Sarafyan fifth order variable-step explicit integration algorithm was used [ISIM, 1986].

The effect of main term and cross-term coefficients of micropore diffusion on the kinetic curves was investigated.

2. Results of Simulation

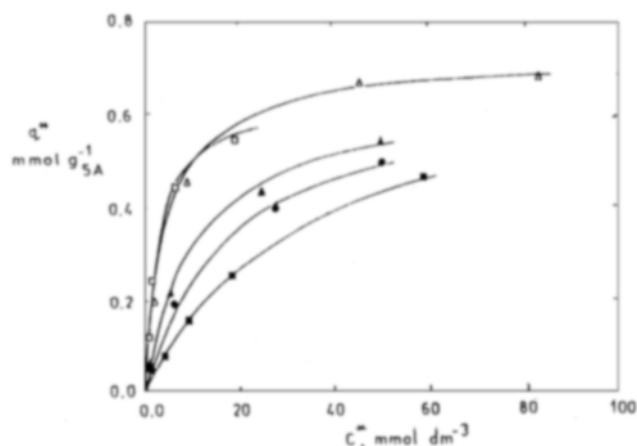The investigation of adsorption equilibrium and kinetics of n-

Fig. 1. Equilibrium adsorption isotherms of n-paraffins dissolved in isooctane with zeolite 5A as adsorbent, T=295 K, experimental points.
• : $C_{10}H_{22}$, △ : $C_{11}H_{24}$, • : $C_{12}H_{26}$, • : $C_{13}H_{28}$, + : $C_{14}H_{30}$ — : Langmuir isotherm

paraffins in isooctane on zeolite 5A was carried out with one adsorbing component ($C_{10}H_{22}$, $C_{11}H_{24}$, $C_{12}H_{26}$, $C_{13}H_{28}$, and $C_{14}H_{30}$) and two adsorbing components ($C_{10}H_{22}$-$C_{11}H_{24}$).

Experimental results from one adsorbing component equilibrium adsorption study of n-paraffins in isooctane on zeolite 5A are shown in Fig. 1. The temperature of the solutions was held constant at 295 K in these tests. All adsorption isotherms display a nonlinear dependence on equilibrium concentration c* [Poposka et al., 1990]. The same shape of the adsorption isotherms was obtained at other temperatures. The adsorption data for all five n-paraffins were fitted by Langmuir isotherm. Values of model parameters q_m and k for each adsorbate-adsorbent pair, determined from the experimental data by nonlinear regression program REPROCHE [1992], are given in Table 1 and they are estimated from experimental data which do not cover the concentration range till attaining plateau state. The goodness of fit is shown by the curves of Fig. 1 and is also indicated by the magnitude of the mean residual square in the Table 1.

It is expected that the values of q_m have to decrease with increasing the chain length because the molecular mobility increases in the cavities of molecular sieves and their bonds with cavity surface become weaker. But in this study the values of model parameter q_m given in Table 1 and the experimental data

Table 1. Langmuir model parameters q_m and k for investigated systems, T=295 K

System	q_m, mmol g_{5A}^{-1}	k, dm³mmol⁻¹	Mean residual square, σ^{2}*
$C_{10}H_{22}$-isooctane-5A	0.625	0.434	0.2328×10⁻²
$C_{11}H_{24}$-isooctane-5A	0.710	0.261	0.1275×10⁻²
$C_{12}H_{26}$-isooctane-5A	0.636	0.103	0.1150×10⁻³
$C_{13}H_{28}$-isooctane-5A	0.643	0.064	0.1235×10⁻³
$C_{14}H_{30}$-isooctane-5A	0.688	0.034	0.2653×10⁻⁴

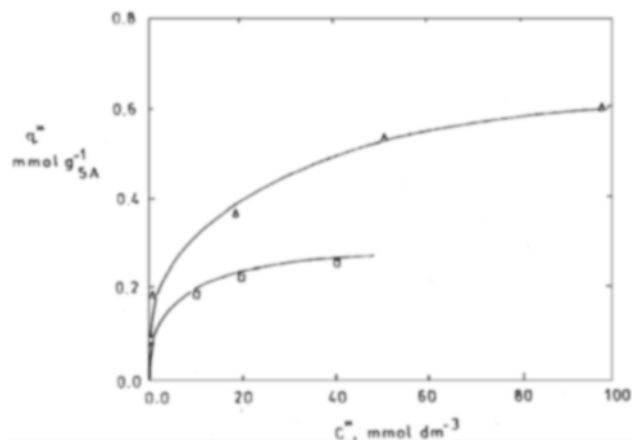$$*\sigma^2 = \frac{\sum_{1}^{N}(q^*_{exp\,i} - q^*_{calc})^2}{f}$$

Fig. 2. Equilibrium adsorption isotherms of adsorbing components in system.
$C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$ dissolved in isooctane with zeolite 5A as adsorbent, T=295 K, experimental points : • : $C_{10}H_{22}$, $\triangle$: $C_{11}H_{24}$, − : Langmuir isotherm Eq. (2)

presented in Fig. 1 do not show this effect.

The two adsorbing component equilibrium adsorption studies of n-paraffins in isooctane on zeolite 5A are performed by use of the extended Langmuir isotherm equation [Eq. (2)] which appeared to be suitable for fitting the experimental data. This equation, which assumes that all adsorbing components compete for the same adsorption sites, has been widely used due mainly to its simplicity and predictive ability within an acceptable accuracy for engineering purposes. It has been found to correlate binary adsorption uptakes if the adsorbing components are similar in nature and follow the Langmuir isotherm relation.

The adsorption isotherms of two adsorbing components in the system $C_{10}H_{22}$-$C_{11}H_{24}$ dissolved in isooctane on zeolite 5A are consistently lower than those of the corresponding single adsorbing component as can be seen from Fig. 1 and Fig. 2.

The Langmuir model parameters (Table 1) obtained from single adsorbing component equilibrium adsorption studies of n-paraffins in isooctane on zeolite 5A were used for simulation of the uptake curves. In this investigation microporous diffusivities were estimated by matching the predictions of the adopted theoretical model to the experimental results for n-paraffins ($C_{10}H_{22}$, $C_{11}H_{24}$, $C_{12}H_{26}$, $C_{13}H_{28}$, and $C_{14}H_{30}$). The theoretical model used in this investigation was defined by the equation for diffusion of one adsorbing component [Ruthven, 1984; Crank, 1975]. This equation can also be derived from Eq. (1) by setting i=j=1. The simulation studies were performed in order to obtain the microporous diffusivities for single adsorbing component system. The initial range for varying the diffusivities was estimated by the standard procedure [Ruthven, 1984]. By plotting the experimental values of $\bar{q}$ against $\sqrt{t}$, the diffusional time constant D_{11}/r_c^2 or diffusivity D_{11} (provided that r_c is known) can be directly evaluated from the slope. The simulation of the theoretical uptake curves based on assumed microporous controlled diffusion with Langmuir isotherm indicates satisfactory agreement with experimental data especially in the range of low initial concentrations of n-paraffins (Fig. 5) and for n-paraffins with smaller chain length (Fig. 3 and Fig. 4). The obtained diffusivities of n-paraffins in 5A zeolite decrease with increasing chain length
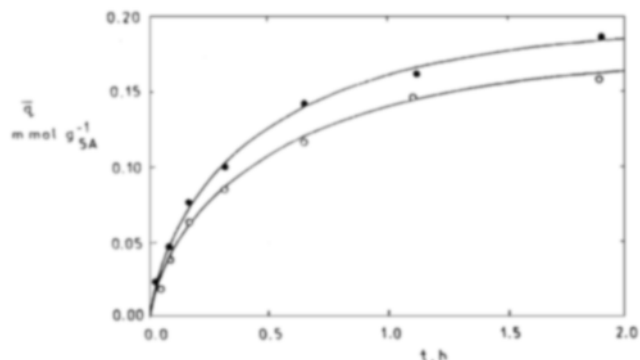
Fig. 3. Calculated and experimental data of the uptake curves for the systems.
$C_{10}H_{22}$-isooctane-5A, T=295 K, c_0=10 mmol dm^{-3}, D_{11}=1.9× 10^{-16} m^2 s^{-1}
$C_{11}H_{24}$-isooctane-5A, T=295 K, c_0=20 mmol dm^{-3}, D_{22}=2.6× 10^{-16} m^2 s^{-1}
• : experimental points for $C_{10}H_{22}$, − : calculated curve Eq. (3) for i=1
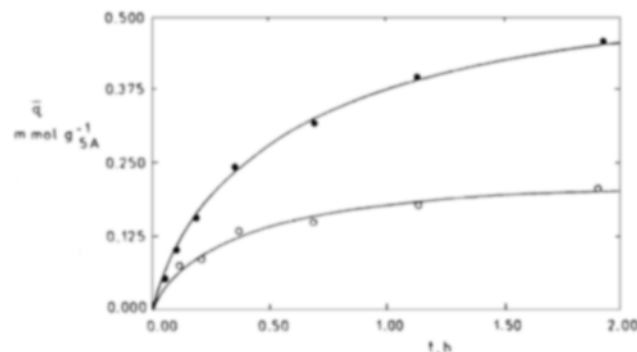• : experimental points for $C_{11}H_{24}$, − : calculated curve Eq. (3) for i=2

Fig. 4. Calculated and experimental data of the uptake curves for the systems.
$C_{10}H_{22}$-isooctane-5A, T=295 K, c_0=25.35 mmol dm^{-3}, D_{11}= 1.7×10^{-16} m^2 s^{-1}
$C_{11}H_{24}$-isooctane-5A, T=295 K, c_0=50.7 mmol dm^{-3}, D_{22}= 2.4×10^{-16} m^2 s^{-1}
• : experimental points for $C_{10}H_{22}$, − : calculated curve Eq. (3) for i=1
• : experimental points for $C_{11}H_{24}$, − : calculated curve Eq. (3) for i=2

and their magnitudes are in agreement with M. F. M. Post [1991].

The procedure of determining the microporous diffusivities of two adsorbing components in system $C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$ dissolved in isooctane on zeolite 5A is accomplished by an appropriate simulation program.

To a first approximation, the data for the two adsorbing components were treated by assuming that each adsorbing component diffuses independently with the same diffusivity as in the case of single adsorbing component diffusion. Under such assumption the obtained diffusivities were in the range 1.0×10^{-16} $m^2 s^{-1}$ to 3.0×10^{-16} $m^2 s^{-1}$ for both adsorbing components and for different initial concentrations. No cross-term coefficients in Eq. (1) were considered and the competitive effect was taken into account only through the extended Langmuir isotherm, Eq. (2). In this case the deviations between the experimental data
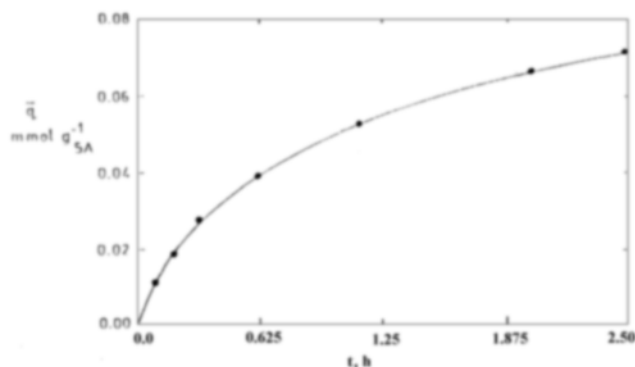
Fig. 5. Calculated and experimental data of the uptake curve for the system.

$C_{14}H_{30}$-isooctane-5A, T=295 K, c_0=8 mmol dm^{-3}, D_{11}=0.58×10^{-16} m^{2}s^{-1}

• : experimental points, — :calculated curve Eq. (3) for i=1

and the estimated data using the model was unacceptable.

In order to achieve better agreement of the experimental data with the model, multicomponent diffusion effects were further investigated. The main-term diffusivities of $C_{10}H_{22}$ and $C_{11}H_{24}$ in the system with two adsorbing components were assumed to be the same as those in the system with one adsorbing component. Then, non-zero cross-term diffusivities were incorporated into the mathematical model [Eq. (1)] to fit the experimental data of $C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$. First the values of the cross-term coefficients were assumed to be equal (D_{12}=D_{21}) due to the principles of irreversible thermodynamics, less than main-term coefficients and they had a negative sign. Lee et al. [1993] indicated that the negative sign implies that the diffusion rate of one adsorbing component is proportional to the reverse of the concentration gradient of the second component, signifying that the diffusion flux of the second adsorbing component has a retarding effect on the diffusion of the first component. The agreement between the experimental data and model was still unacceptable.

For a system with two adsorbing components the lower diffusivity values compared to those obtained for the system with one adsorbing component were expected. So in the further investigation the values of the main-term coefficients and their ranges of varying were assumed to be smaller. Two main-term and two cross-term diffusion coefficients were varied simultaneously. The methodology of experimental planning was used [Kiprijanova and Markovska, 1993]. The full factorial design with four independent variables (D_{11}, D_{22}, D_{12}, D_{21}) was applied and sixteen simulations were carried out in the first step. The diffusion coefficients had their lower and upper levels in the following ranges :

D_{11}×10^{16} ∈ (1.3 to 1.8) m^{2}s^{-1}
D_{12}×10^{16} ∈ (−0.1 to −0.02) m^{2}s^{-1}
D_{21}×10^{16} ∈ (−1.0 to −0.5) m^{2}s^{-1}
D_{22}×10^{16} ∈ (2.0 to 2.5) m^{2}s^{-1}

The values of the cross-term coefficients were not considered to be equal because the initial concentrations of two adsorbing components in the investigated system were not identical. The initial concentration of n-$C_{11}H_{24}$ was two times the initial concentration of n-$C_{10}H_{22}$.

The agreement between the experimental data and the model was better for $C_{10}H_{22}$ than for $C_{11}H_{24}$. So further simulations were accomplished and both diffusion coefficients for the first adsorbing component were held constant (D_{11}=1.7×10^{-16}m^{2}s^{-1} and D_{12}=−1.0×10^{-18} m^{2}s^{-1}). In order to obtain information about sensitivity for various values of the both diffusion coefficients for the second adsorbing component a few simulations were carried out. The simulations for D_{22}=2.0×10^{-16} m^{2}s^{-1}, D_{22}=3.0×10^{-16} m^{2}s^{-1} and different ranges for D_{21} (−1.0 to −0.1)×10^{-16} m^{2}s^{-1} and D_{21} (−2.5 to −1.7)×10^{-16} m^{2}s^{-1}, respectively, were performed. The results are presented in Fig. 6 and Fig. 7. The varying of the cross-term diffusion coefficient D_{21} did not show sensitivity on the uptake curves. The goodness of fit is indicated by the mag-nitudes of mean residual square as is shown in Table 2. As can be seen in Figs. 6 and 7 and Table 2 for the system with two adsorbing components, $C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$, for different total initial concentrations of both adsorbing components the agreement between the experimental results and the calcu-
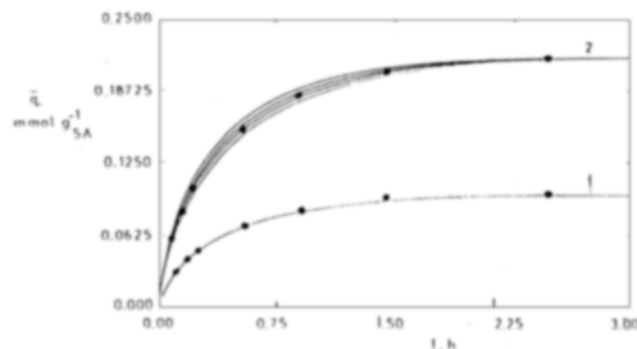

Fig. 6a. Calculated and experimental data of the uptake curves for the system.

$C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$-isooctane-5A, T=295 K, c_0=30 mmol dm^{-3} (c_{01}=10 mmol dm^{-3}, c_{02}=20 mmol dm^{-3})

Diffusion coefficients : D_{11}=1.7×10^{-16} m^{2}s^{-1},D_{12}=−1.0×10^{-18} m^{2}s^{-1}, D_{22}=2.0×10^{-16} m^{2}s^{-1}, D_{21}=(−1.0, −0.1, 0.3)×10^{-16} m^{2}s^{-1}

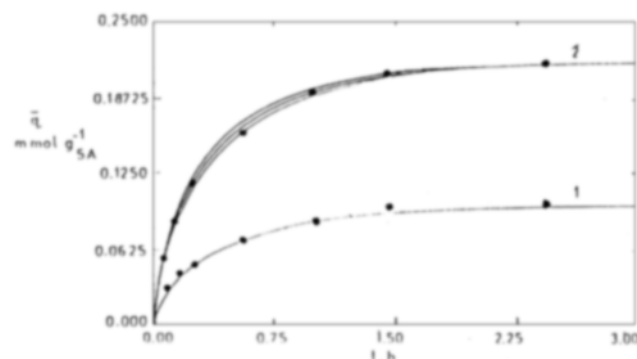• : experimental points, — : calculated curves Eq. (3)

Fig. 6b. Calculated and experimental data of the uptake curves for the system.

$C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$-isooctane-5A, T=295 K, c_0=30 mmol dm^{-3} (c_{01}=10 mmol dm^{-3}, c_{02}=20 mmol dm^{-3})

Diffusion coefficients : D_{11}=1.7×10^{-16} m^{2}s^{-1}, D_{12}=−1.0×10^{-18} m^{2}s^{-1}, D_{22}=3.0×10^{-16} m^{2}s^{-1}, D_{21}=(−2.5, −1.7, 0.4)×10^{-16} m^{2}s^{-1}

• : experimental points, — : calculated curves Eq. (3)

Fig. 7a. Calculated and experimental data of the uptake curves for the system.
$C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$-isooctane-5A, T=295 K, c_0=76 mmol dm^{-3} (c_{01}=25.3 mmol dm^{-3}, c_{02}=50.7 mmol dm^{-3})
Diffusion coefficients : D_{11}=1.7×10^{-16} m^{2}s^{-1}, D_{12}=−1.0×10^{-18} m^{2}s^{-1}, D_{22}=2.0×10^{-16} m^{2}s^{-1}, D_{21}=(−1.0, −0.1, 0.3)×10^{-16} m^{2}s^{-1}
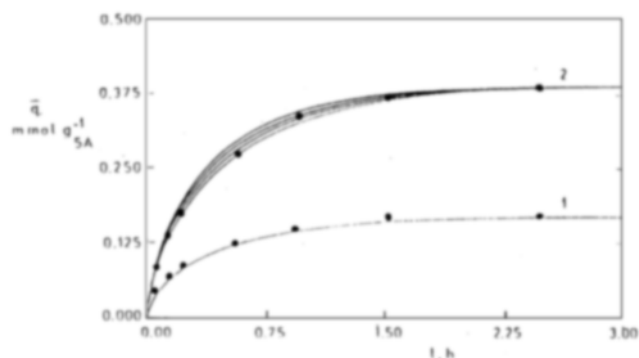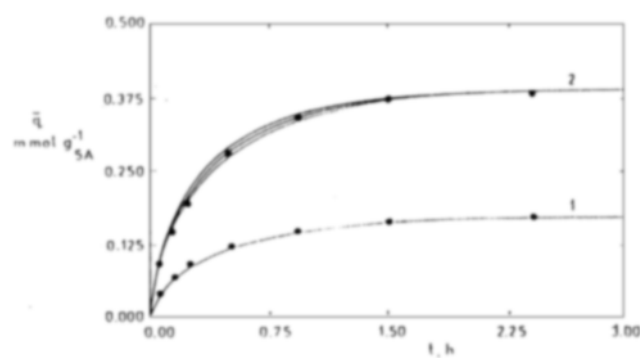• : experimental points, − : calculated curves Eq. (3)

Fig. 7b. Calculated and experimental data of the uptake curves for the system.
$C_{10}H_{22}(1)$-$C_{11}H_{24}(2)$-isooctane-5A, T=295 K, c_0=76 mmol dm^{-3} (c_{01}=25.3 mmol dm^{-3}, c_{02}=50.7 mmol dm^{-3})
Diffusion coefficients : D_{11}=1.7×10^{-16} m^{2}s^{-1}, D_{12}=−1.0×10^{-18} m^{2}s^{-1}, D_{22}=3.0×10^{-16} m^{2}s^{-1}, D_{21}=(−2.5, −1.7, 0.4)×10^{-16} m^{2}s^{-1}
• : experimental points, − : calculated curves Eq. (3)

Table 2. Goodness of fit of uptake curves for system $C_{10}H_{22}$-$C_{11}H_{24}$-isooctane-5A

C_0 (mmol dm^{-3})	$D_{11}×10^{16}$ (m^2 s^{-1})	$D_{12}×10^{18}$ (m^2 s^{-1})	$D_{22}×10^{16}$ (m^2 s^{-1})	$D_{21}×10^{16}$ (m^2 s^{-1})	$\sigma^2×10^4$ ($C_{10}H_{22}$)	$\sigma^2×10^4$ ($C_{11}H_{24}$)
30	1.7	−1.0	2.0	−1.0	0.463	0.462
				−0.7		0.623
				−0.4		0.866
				−0.1		0.766
76	1.7	−1.0	2.0	−1.0	1.03	10.3
				−0.7		12.3
				−0.4		14.0
				−0.1		13.0
30	1.7	−1.0	3.0	−2.5	0.46	0.86
				−2.1		0.57
				−1.7		2.20
76	1.7	−1.0	3.0	−2.5	1.03	8.2
				−2.1		9.8
				−1.7		20.3

lated kinetic curves is satisfactory for the set of diffusion coefficients used.

CONCLUSIONS

The study of diffusion of two n-paraffins, $C_{10}H_{22}$ and $C_{11}H_{24}$, dissolved in isooctane, onto micropore of 5A zeolite showed that the adsorption rate of one adsorbing component was slowed down by the presence of the second adsorbing component in the system.

The results obtained during this work revealed that for the system with two adsorbing components, two main-term and two cross-term diffusion coefficients might be obtained by fitting the experimental data to the mathematical model. Based on our results it appeared that introducing the cross-term diffusion coefficients led to better agreement between the experimental data and those calculated from the model. However, the goodness of fit was better if the values of the cross-term diffusion coef-

ficients were not equal, which is contradictory to the principles of irreversible thermodynamics. In such a case the possibility of including another diffusion resistance in the mathematical model has to be considered. For a system with five adsorbing components ($C_{10}H_{22}$-$C_{11}H_{24}$-$C_{12}H_{26}$-$C_{13}H_{28}$-$C_{14}H_{30}$) the number of diffusion coefficients is very high and this leads to the appearance of many difficulties in procedure of their determination. For such systems determining only the main-diffusivities using the proposed simulation technique is recommended.

The mathematical expressions for the uptake curves for the system with two adsorbing components will be used to develop a mathematical model of the fixed bed adsorption column which is based on a mass balance on the column and a mass balance on the particles inside the column. In this case the choice of the best kinetic curves will be a very tedious and time consuming procedure.

It is hoped that this work provides an incentive for further research on multicomponent diffusion.

NOMENCLATURE

c   : concentration of n-paraffins in the liquid phase [mmol dm^{-3}]

c_0 : initial concentration of n-paraffins in the liquid phase [mmol dm^{-3}]

c^* : equilibrium concentration of n-paraffins in liquid phase [mmol dm^{-3}]

D_{ij} : micropore diffusivity $[m^2 s^{-1}]$

f   : number of degree of freedom

k   : parameter in Langmuir equation Eq. (2) $[dm^3 mmol^{-1}]$

q   : adsorbed phase concentration of n-paraffin [mmol g_{5A}^{-1}]

q^* : equilibrium adsorbed phase concentration [mmol g_{5A}^{-1}]

$\bar{q}$: average adsorbed phase concentration [mmol g_{5A}^{-1}]

q_m : parameter in Langmuir isotherm Eq. (2) [mmol g_{5A}^{-1}]

r   : radial coordinate of zeolite crystal [m]

r_c : radius of zeolite crystal [m]

t   : time [s]

T   : temperature [K]

σ^2 : mean residual square

Subscript

i, j   : adsorbing components i and j

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