

Computer modelling as a new approach to the description of kinetics of the *n*-hexane sorption in the ZSM-5 zeolite

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A new theoretical attempt to describe the diffusion of *n*-hexane in the ZSM-5 zeolite with the use of the difference quotients was made. While constructing a model of the sorption kinetics, the shape of crystals, dependence of the diffusion coefficient on the sorbate concentration, and anisotropy of the diffusion were taken into account. The theoretical kinetic curves based on the elaborated models were completely fitted to the experimental data. The results of these fittings were compared with those from the standard solution of the diffusion equation. It was found that the corrected diffusivity, included in the Darken equation, strongly rises with the *n*-hexane concentration in the zeolite pores. Contrary to the values of the corrected diffusivity derived with the standard methods, those obtained with the use of the difference quotients are accurate enough to ascertain that this growth is probably exponential.

1. INTRODUCTION

Investigation of the kinetics of sorption is a method for determination of the diffusion coefficient, which has been known for years. It is a comparatively simple technique and it requires no expensive instrumentation. Thus, in spite of many other methods that have been elaborated during that period, it is still utilised by a number of authors [1-7]. For many reasons, however, the sorption methods for the kinetic investigations, especially the gravimetric techniques, have only a limited application. While using these methods, it is necessary to apply relatively large crystals of the studied material on the one hand, and the sample amount is limited by a small mass (or heat capacity) of the weighing bottle on the other. Therefore, the contemporary sorption methods are mostly based on volumetric techniques [1,3] that allow for using relatively large

samples and require just the pressure transducers as the technical equipment. The gravimetric techniques need accurate and automated measurements of the sorbent weight in addition to the pressure measurements. Although instrumentation used in these techniques is more complicated and more expensive as compared to that in the volumetric ones, two quantities (weight and pressure) are obtained instead of one (pressure). This allows for the selection of a higher number of initial experimental parameters and, consequently, for obtaining more options for the experiment.

The data reported in the literature [1,8] show that the values of the diffusion coefficient determined with the sorption techniques differ from one another by several orders of magnitude and the highest of them, e.g., that for the sorption of *n*-hexane in silicalite-1, are still ca. one hundred times lower than those obtained with other methods [9]. So far, the reason for such discrepancies is unclear. Differences in theoretical approaches applied to the particular experimental methods may be one of possible causes of variations between the values of the diffusion coefficient [10]. Approaches to the description of uptake curves, being applied up to the present, may also generate the lowering of the determined values of the diffusion coefficient. All the approaches use the models of the one-dimensional diffusion, in which the diffusion is either unidirectional [11,12] or isotropic [1,4,13,14]. The advantage of such models lies in the fact that they allow for using analytical mathematical methods, which yield relatively simple equations for calculating the diffusion coefficient. Application of these models is justified in the case of, e.g., porous materials with the one-dimensional system of channels. When the channel system is of another type, it is necessary to assume that particles of the studied material are spherical. Though very useful, this assumption is doubtful if the shape of the crystals differs significantly from a sphere or even a cube. In addition, it has been found that the diffusion is often anisotropic, e.g., in the case of some zeolites, including those of the MFI type [15-18]. The course of the sorption process may depend on the crystal structure as well [16].

The analytical methods applied to the problem of the diffusion are attractive but, as mentioned above, they require significant simplifications. One of them is the assumption, although not necessary in some cases [1,8] that the diffusion coefficient is independent of the sorbate concentration in the sorbent. This simplification leads to serious limitations in performing the uptake measurements. In addition, only final sections of the kinetic curves, corresponding to the condition close to the sorption equilibrium, can be used for calculations [13,19,20]. Thus, the discussed assumption may cause a substantial inaccuracy in the determination of the diffusion coefficient.

The above considerations implicate a necessity to replace the analytical approaches with the methods employing the approximation of differential

equations that include the difference quotients. Such methods have effectively been applied for many years to model very complex phenomena while they allow for taking into account many factors influencing the course of these phenomena through consideration of individual fragments of the system and use of experimental data without additional assumptions.

The purpose of this work was to apply the method of the difference quotients [21] to study the diffusion during the sorption of *n*-hexane in the ZSM-5 type zeolite. The zeolite crystal structure and the diffusion anisotropy were taken into account and a new approach to the description of the sorption isotherm was proposed.

2. EXPERIMENTAL

Determination of the *n*-hexane uptake by the ZSM-5 zeolite was done with a gravimetric technique, using a system including a Sartorius balance of the 0.001 mg accuracy (Figure 1).

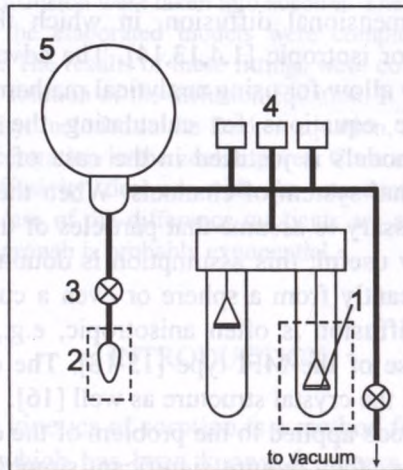


Fig. 1. Scheme for the measuring system used

A 20-mg zeolite sample was placed on a scale pan 1 and was spread into a thin layer so that the heat of sorption to be evolved was minimised. The *n*-hexane vapour was fed to the vacuum line from an ampoule 2 with a metering solenoid valve 3. The vapour pressure was measured with a set of the MKS Baratron transducers 4. A large container 5 was connected to the vacuum line in order to stabilise the pressure. To avoid the excessive resistance to flow, all the connections were made of elements with relatively large diameters.

Consequently, a condition for a rapid propagation of the *n*-hexane vapour was obtained so that a target pressure could be attained within a few seconds. All joints and seals were greaseless since it was found that, under the presence of grease, the rate of sorption decreases, presumably because of blocking the crystal surface by the grease molecules. The measurements and the equipment control were fully automated.

The uptake measurements proceeded similarly to typical adsorption measurements. A zeolite sample was degassed at 423 K for 48 h and then quickly (within 45 min) cooled down to 298.2 K. Next, the *n*-hexane vapour was introduced into the vacuum line to achieve the first target pressure. The vapour was continually added in order to maintain the pressure at a constant level. The growth of the sample weight in time was recorded until the sorption equilibrium was established. Then, the next target pressure was achieved. Thus, a sorption isotherm and a pencil of kinetic curves were obtained.

3. THEORETICAL CONSIDERATIONS

General remarks. To describe the course of the kinetic curves and to determine the diffusion coefficient, there were applied two theoretical models that allow for use of the difference quotients. The results obtained were compared with those from the diffusion rate equation, which is commonly used to describe the data from sorption measurements [8,13,19,20]:

$$\frac{m_t - m_0}{m_\infty - m_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \cdot \pi^2 \cdot D \cdot t}{r^2}\right) \quad (1)$$

Here, m_0 , m_t , and m_∞ are the initial sample weight, the sample weight after a time t , and the final sample weight, respectively, r is the radius of a sphere of the volume equal to that of a single crystal, and D is the diffusion coefficient. Eqn. 1 is a solution of the following differential equation [21]:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r} \right) \quad (2)$$

which is valid under the assumption that the crystal is spherical, the sorbate flow is isotropic, and the diffusion coefficient is independent of the sorbate concentration. Eqn. 2 can be considered as a relationship reflecting a standard model for the sorption kinetics. If a sample weight approaches its maximum value, then the sum in Eqn. 1 reduces to one term and the equation can be expressed in a linear form:

$$\ln\left(1 - \frac{m_t - m_0}{m_\infty - m_0}\right) = -\frac{\pi^2 \cdot D}{r^2} \cdot t + \ln\left(\frac{6}{\pi^2}\right) \quad (3)$$

Eqn. 3 allows for a simple calculation of the diffusion coefficient.

The first model of the two applied to the description of the course of the kinetic curves with use of the difference quotients is similar to the standard model (Eqns. 1-3). Likewise, it was assumed here that the crystal is spherical and the sorbate flow is isotropic. Unlike in the standard model, the diffusion coefficient was assumed to depend on the sorbate concentration. The differential equation of the mass balance is then of the following form:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial c}{\partial r}\right) + \frac{\partial D}{\partial r} \cdot \frac{\partial c}{\partial r} \quad (4)$$

Eqn. 4 differs from Eqn. 3 by the term that determines the dependence of the diffusion coefficient on the concentration. It is a limit form of the following equation that includes the difference quotients:

$$\frac{\Delta c}{\Delta t} = D(r)\left(\frac{c(r+\Delta r) - 2c(r) + c(r-\Delta r)}{(\Delta r)^2} + \frac{2}{r} \cdot \frac{c(r+\Delta r) - c(r-\Delta r)}{2\Delta r}\right) + \frac{D(r+\Delta r) - D(r-\Delta r)}{2\Delta r} \cdot \frac{c(r+\Delta r) - c(r-\Delta r)}{2\Delta r} \quad (5)$$

In the other model, the assumption that the crystal is spherical and the sorbate flow is isotropic has not been included. Thus, the equation of the mass balance is of the following form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D \frac{\partial c}{\partial z}\right) \quad (6)$$

The right-hand side of Eqn. 6 is a sum of the terms that are of the same form. This means that three flow processes independent of one another proceed in the system. Each of these terms is a limit form of the following difference quotient:

$$\left[\frac{D(u+\Delta u) + D(u)}{2} \cdot \frac{c(u+\Delta u) - c(u)}{\Delta u} - \frac{D(u) + D(u-\Delta u)}{2} \cdot \frac{c(u) - c(u-\Delta u)}{\Delta u}\right] \frac{1}{\Delta u} \quad (7)$$

where $u = x, y, z$.

Model 1 for the sorption kinetics. It is assumed that the crystal is spherical and the radius of such a sphere can be expressed as:

$$R = \sqrt[3]{(X_0 \cdot Y_0 \cdot Z_0) \cdot \frac{3}{4} \cdot \frac{1}{\pi}} \quad (8)$$

where X_0 , Y_0 , and Z_0 are average sizes of a zeolite crystal along the crystallographic axes, equal to 0.0408, 0.0441, and 0.1099, respectively. This sphere is then divided into n parts of the same thickness, Δr (Figure 2):

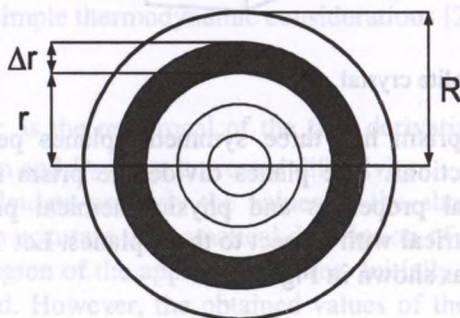


Fig. 2. Scheme for calculations in Model 1

The difference form of the mass balance equation, derived from Eqn. 5, can be written for the i th part of the sphere as follows:

$$\Delta c_i = \left[D_i \left(\frac{c_{i+1} - 2c_i + c_{i-1}}{(\Delta r)^2} + \frac{2}{r_i} \cdot \frac{c_{i+1} - c_{i-1}}{2\Delta r} \right) + \frac{D_{i+1} - D_{i-1}}{2\Delta r} \cdot \frac{c_{i+1} - c_{i-1}}{2\Delta r} \right] \cdot \Delta t \quad (9)$$

The change in the crystal weight due to the sorption in time Δt is then equal to:

$$\Delta m = \sum_i (\Delta v_i \cdot \Delta c_i) \quad (10)$$

where Δv_i is the volume of the i th element.

Model 2 for the sorption kinetics. Let a zeolite crystal be of the form of a rectangular prism with the sizes equal to X_0 , Y_0 , and Z_0 , i.e., to the average values determined with use of a microscope (Figure 3).



Fig. 3. Scheme for a zeolite crystal

The rectangular prism has three symmetry planes perpendicular to the crystallographic directions. The planes divide the prism into eight identical parts. All the crystal properties and physicochemical processes, including diffusion, are symmetrical with respect to these planes. Let 1/8 of the crystal be divided into n^3 parts as shown in Figure 4.

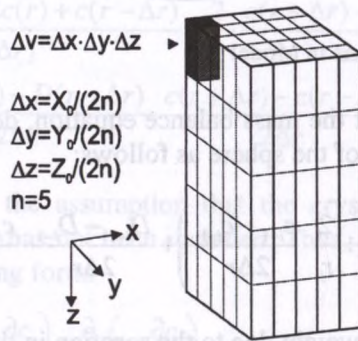


Fig. 4. Scheme for calculations in Model 2

For each i,j,k th part, the difference form of each of the differential functions appearing in Eqn. 6 is expressed according to Eqn. 7 by the following relationship:

$$B_{i,j,k}^u = \left(\frac{D_{i+1,j,k} + D_{i,j,k}}{2} \cdot \frac{c_{i+1,j,k} - c_{i,j,k}}{\Delta u} - \frac{D_{i,j,k} + D_{i-1,j,k}}{2} \cdot \frac{c_{i,j,k} - c_{i-1,j,k}}{\Delta u} \right) \frac{1}{\Delta u} \quad (11)$$

The change in the concentration is then equal to:

$$\Delta c_{ijk} = (B_{ijk}^x + B_{ijk}^y + B_{ijk}^z) \cdot \Delta t \quad (12)$$

The total change in the crystal weight due to the sorption in time Δt is as follows:

$$\Delta m = 8 \cdot \sum_{ijk} (\Delta v_{ijk} \cdot \Delta c_{ijk}) \quad (13)$$

Equation of the sorption isotherm. The two assumed models for the sorption kinetics include the assumption that the diffusion coefficient depends on concentration. In general, this relationship can be described with the Darken equation based on simple thermodynamic considerations [22]:

$$D = D_0 \cdot \frac{\partial \ln p}{\partial \ln c} \quad (14)$$

where $\partial \ln p / \partial \ln c$ is the reciprocal of the first derivative of the logarithmic form of the isotherm and D_0 is the corrected diffusivity.

In order to calculate properly the values of the above derivative, it was necessary to find an accurate mathematical description of the sorption isotherm within the whole region of the applied pressures. Initially, different polynomial functions were used. However, the obtained values of the derivative were too sensitive to changes of the parameters included in the used equations. Next, equations based on common theories of the adsorption were tried. Simple equations derived from the Polanyi-Dubinin potential theory appeared to be useful because if an isotherm of the *n*-hexane sorption is plotted in the co-ordinate system of $(x, y) = ([\ln(133.2/p)]^2, c)$, where c is the concentration and p the *n*-hexane vapour pressure, then the course of the isotherm within the range of low pressures is described very well with the following formula:

$$f_b = b_1 - b_2 \cdot x^{b_3} \quad (15)$$

Eqn. 15 is a form of a 3-parameter Dubinin-Astakhov equation with a real exponent. The course of the isotherm within the range of high pressures can be described with the formula being a form of a 2-parameter Dubinin-Radushkevich equation:

$$f_e = e_1 - e_2 \cdot x \quad (16)$$

A 2-parameter sigmoid function was applied to secure continuity between both pressure ranges:

$$f_g = 1 / (1 + 10^z) \quad (17)$$

with $z = 2 \cdot \frac{x - g_1}{g_2 - g_1} - 1$.

The g_1 and g_2 parameters determine the transition pressure range. To make the

approximation within this range more accurate, there was applied a function being the first derivative of f_g , which contains two additional parameters d_1 and d_2 :

$$Df_g = 1 + d_2 \left(\frac{2 \cdot \ln(10 \cdot d_1) \cdot (10 \cdot d_1)^z}{(g_2 - g_1) \cdot [1 + (10 \cdot d_1)^z]^2} \right) \tag{18}$$

Thus, the final 9-parameter equation of the sorption isotherm is of the following form:

$$\ln(c) = [f_b \cdot f_g + f_e \cdot (1 - f_g)] \cdot Df_g \tag{19}$$

In the above considerations, a physical meaning of the obtained equation of the sorption isotherm is not discussed. The objective was to obtain the best possible fit of this equation and of the derivative included in the Darken equation to the experimental isotherm. A comparison of the theoretical isotherm with the experimental points is shown in Figure 5. The dependence of the derivative appearing in the Darken equation (Eqn. 14) on concentration is presented in Figure 6.

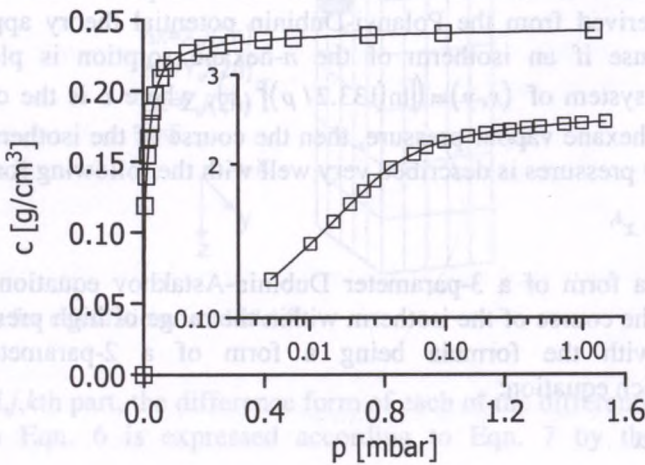


Fig. 5. Comparison of the theoretical isotherm (Eqn. 19) with the experimental points

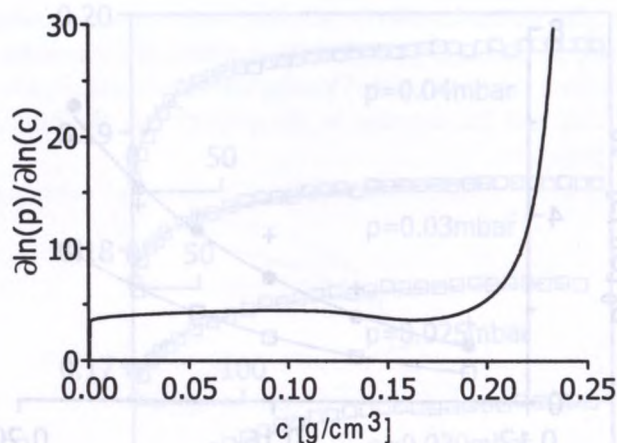


Fig. 6. Dependence of the derivative appearing in the Darken equation on concentration

4. RESULTS AND DISCUSSION

The obtained kinetic curves indicate a significant increase in the equilibration rate with the pressure of the *n*-hexane vapour. Under the pressures above 0.04 mbar, the rate of sorption was already comparable with the vapour-feeding rate and the equilibrium state was attained practically after ca. 20 s. Such a strong increase in the sorption rate is higher than that resulting from the course of the derivative (Figure 6), assuming that the Darken equation is valid and the corrected diffusivity is constant. This leads to the conclusion that the value of D_0 grows with the adsorptive pressure and, thereby, with the concentration of the adsorbed *n*-hexane.

To model the kinetics of the sorption according to the two above-presented approaches, a pencil of the curves recorded within the pressure range of 0.005-0.04 mbar was utilised. It was initially assumed that the value of the corrected diffusivity included in the Darken equation is independent of concentration. However, when the same D_0 value was used to calculate all the kinetic curves, these curves hardly fitted the experimental points. Thus, the calculation procedure had to be modified while adjusting the corrected diffusivity to the individual experimental curves. Consequently, two pencils of the theoretical curves and two sets of the D_0 values were obtained. The dependences of D_0 vs. c , based on the Models 1 and 2 and on the standard model (eqns. 3 and 14), are presented in Figure 7.

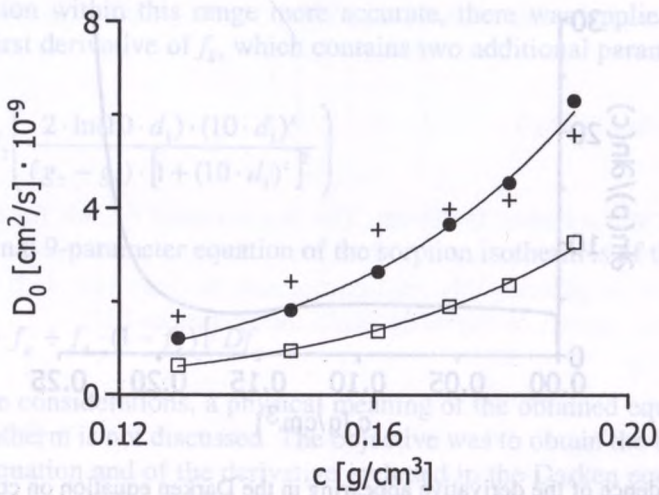


Fig. 7. Plots of the corrected diffusivity vs. concentration, obtained according to Model 1 (circles), Model 2 (squares), and the standard model (crosses)

In each case, the corrected diffusivity increases significantly with the concentration. For the standard model, a clear scatter of the data is observed. It results presumably from the assumptions that were made in this model and from the fact that the approximation could be performed only for the final sections of the kinetic curves, i.e., for the values of the sample weight close to the asymptotic value. In the case of the Models 1 and 2, the plots of D_0 vs. c can be described with the following equation:

$$D_0 = e^{a \cdot c - b} \quad (20)$$

The values of D_0 calculated from Model 1 are almost twice as much as those obtained from Model 2. This is most probably a consequence of the assumptions on the shapes of the zeolite crystals. In the case of a rectangular prism, the flow of n -hexane occurs mostly along x and y axes (Figure 4) while for a spherical shape, the flow is isotropic. Therefore, the diffusion coefficient in the former case should be lower than that in the latter case.

The plots of the pencil of the experimental kinetic curves and of the model kinetic curves calculated from Eqns. 5 and 7 are shown in Figure 8. The theoretical curves agree very well with the experimental points, as shown for the range of concentrations above 0.12 g/cm³. Only the kinetic curve corresponding to the first target pressure declines distinctly from the experimental points, which is illustrated in Figure 9. In this case, the concentration grows almost linearly with time up to ca 1000 s. Such a kinetic behaviour is commonly observed when the sorption is limited by the vapour-feeding rate (or the valve effect) and not by the diffusion rate.

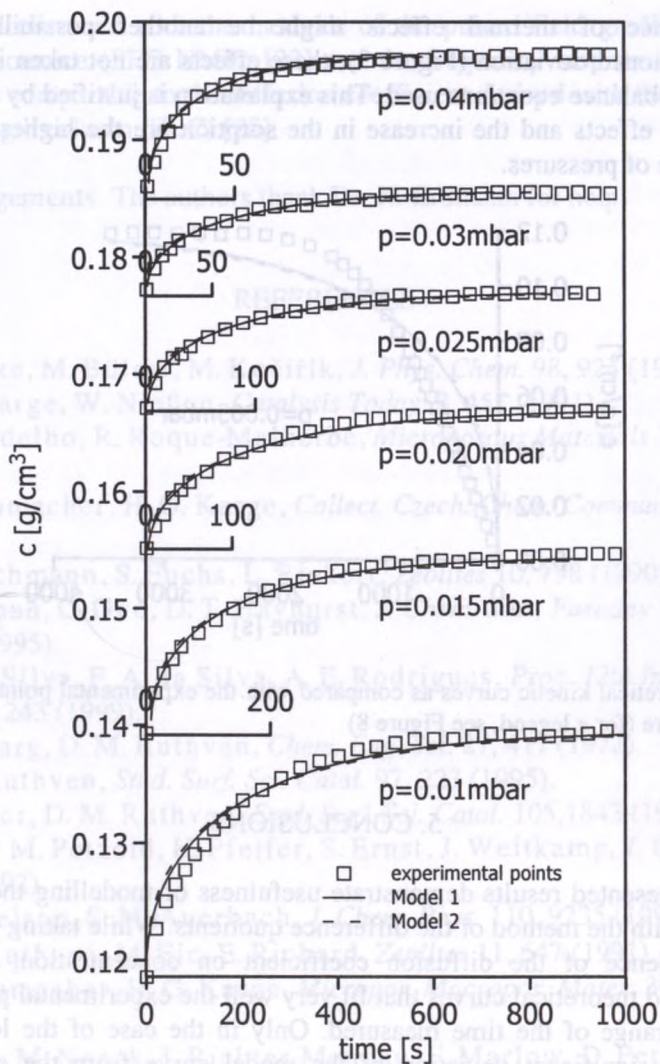


Fig. 8. Theoretical kinetic curves as compared with the experimental points for the target pressures indicated

To verify such a possibility, the feeding ability of the system was estimated while taking into account the construction parameters and the kinetic theory of gases. It was found that ca. 0.5 mg of the adsorptive per second and per cm^2 of the surface of the scale pan can be delivered under the lowest pressure applied (0.005 mbar). This means that the adsorptive vapour pressure at the crystal surface is practically constant during the sorption process, considering that the total sorption equals ca. 3 mg. Thus, there is no valve effect.

Occurrence of thermal effects might be another possibility for the above-mentioned deviation (Figure 9); these effects are not taken into account in the mass balance equations used. This explanation is justified by the fact that the thermal effects and the increase in the sorption are the highest within the initial range of pressures.

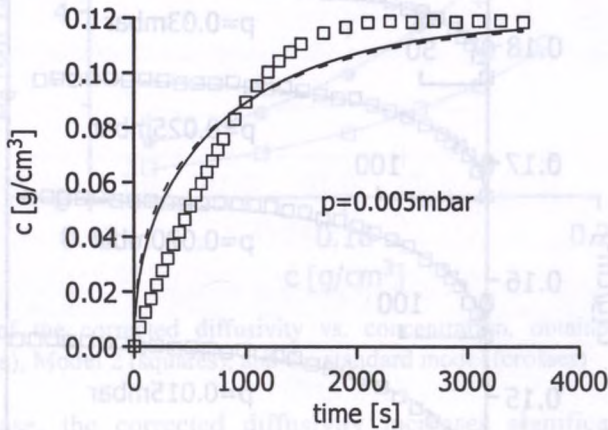


Fig. 9. Theoretical kinetic curves as compared with the experimental points for the first target pressure (for a legend, see Figure 8)

5. CONCLUSIONS

The presented results demonstrate usefulness of modelling the process of diffusion with the method of the difference quotients. While taking into account the dependence of the diffusion coefficient on concentration, the applied models yield theoretical curves that fit very well the experimental points within the whole range of the time measured. Only in the case of the lowest target pressure, a significant deviation of the model curve from the experimental points was observed, which is caused probably by an increase in the sample temperature due to evolution of the sorption heat.

According to the discussed models of the sorption kinetics, the corrected diffusivity (D_0) strongly increases with the sorbate concentration. However, only the equations including the difference quotients give the values of D_0 precise enough to state that this dependence is probably exponential. The value of the corrected diffusivity in the case of the spherical crystal is nearly twice as high as that for the cuboid crystal, the latter resembling better the real crystal than the former one. The maximum value of D_0 , calculated by extrapolation to the maximum concentration, is only ten times lower than the diffusion

coefficient determined with the methods of the pulsed field gradient nuclear magnetic resonance (PFG NMR) [23] and the frequency response (FR) [24], whereas it is comparable to the diffusion coefficient derived with the technique of a zero-length column (ZLC) [25].

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CURRICULA VITAE



Jerzy Włoch was born in 1960 in Kołobrzeg, Poland. He graduated in 1985 from the Nicholas Copernicus University in Toruń, receiving an M.Sc. degree in chemistry. In 1996 he obtained a Ph. D. degree.

While working in the field of zeolites and zeolite-like materials, he published 24 papers and registered 1 patent. He was a member of local organising committees of three Polish German-Zeolite Colloquia (1992, 1995, 1997) and of the Third International Symposium on "Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids"

(1998). For his scientific accomplishments he was awarded by the Polish Ministry of Education.

Main scientific interests: Investigations of adsorption properties of (i) zeolites and zeolite-like materials, including synthesis of the materials of different crystal morphology, measurements of sorption kinetics, and a theoretical description of kinetic curves with use of various calculation methods and (ii) mesoporous materials of the M41S type, covering synthesis, adsorption measurements, and simulation of the course of adsorption isotherms with the method of Molecular Dynamics.

Michał Rozwadowski was born in 1936 at Lidzbark, Poland. He graduated in 1959 from the Nicholas Copernicus University in Toruń, receiving an M.Sc. degree in chemistry. In 1968, he obtained a Ph.D. degree and in 1977, a D.Sc. degree, both from the university in Toruń. He became associate professor in 1985 and professor in 1991. From 1984 to 1990, he was the Deputy Dean of the Faculty of Mathematics, Physics, and Chemistry and then to 1993, the Dean of that faculty. From 1993 to 1996, he was the Vice-Rector for Research and International Affairs, of the Nicholas Copernicus University. Since 1999, he is the Head of the Department of Fundamentals of Chemistry.

While working in the field of novel zeolitic materials, he published over 120



papers and registered 28 patents (26 in Poland and 2 abroad). He organised several symposia: three Polish German-Zeolite Colloquia (1992, 1995, 1997) and the Third International Symposium on "Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids" (1998). For his scientific accomplishments, he was awarded five times by the Polish Ministry of Education and many times by the Rector of the Nicholas Copernicus University. Besides many short visits to European universities in 1974-1975, he was a scholar of the Alexander von Humboldt Foundation at the Karlsruhe University, Germany.

Main scientific interests: Preparation of new zeolitic materials of controlled morphology by both direct synthesis and modification through isomorphous substitution. Investigation of zeolitic materials of the MFI and AFI types with incorporated heteroatoms and of mesoporous molecular sieves of the M41S structure. Full characterisation of physicochemical properties of these materials, including especially sorption and catalytic properties.

Selected publications:

1. *Sorption of benzene on AlPO₄-5 containing various heteroatoms and analytical description of the system*, Langmuir, **15**, 5857-5862 (1999).
2. *Compositional heterogeneity of CrAPO-5 with neutral framework: effect on sorption properties in comparison to other MeAPO-5 with charged frameworks and analytical evaluation of adsorption potentials*, Langmuir, **15**, 5863-5869 (1999).
3. *Electron paramagnetic resonance spectroscopy of chromium in CrAPO-5 molecular sieves*, J. Phys. Chem. A, **104**, 11837-11843 (2000).
4. *Al-MCM-41 modified with carbonaceous deposits – characterisation of surface and structural properties from nitrogen adsorption measurements*, Phys. Chem. Chem. Phys., **2**, 5510-5516 (2000).
5. *Mechanism of adsorption of water, benzene and nitrogen on Al-MCM-41 and effect of coking on the adsorption*, Langmuir, **17**, 2112-2119 (2001).