Diffusive transport of fluids through porous solids observed by neutron transmission

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Abstract

The diffusive transport of water, methanol, ethanol, butene, benzene and toluene through porous bodies of compacted, microcrystalline zeolite of type NaX has been studied by slow neutron transmission at ambient temperature and pressure. The observed moving profiles of density can be understood in terms of solutions of a nonlinear diffusion equation containing a drift term. The experimental data have been interpreted with diffusivities in the order of magnitude of 10^{-10} m^2 s^{-1} and drift velocities of about 10^{-6} m s^{-1}.

Keywords: zeolite; diffusion; neutron spectroscopy; porous media; mass transport

Introduction

The diffusive transport of fluids through porous media has been studied intensively because of its important role in different fields of science and technology [1–6]. There are many experimental methods to look at the distribution of the density $C(x, t)$ of an adsorbate inside of an adsorbens at the position x and time t [7–16]. Sophisticated mathematical models containing various parameters have been developed which yield the function $C(x, t)$ as a solution of coupled, nonlinear differential equations [17–23]. The values of the parameters have to be determined by a comparison of theoretical and experimental data. However, those types of experiments in which $C(x, t)$ is more or less directly observed have rarely been done. Usually one only measures outside of the porous medium the amount of fluid which diffuses through the sample. Often the uptake of the adsorbate is measured volumetrically or gravimetrically.

Slow neutrons are waves suitable to observe the concentration of hydrogenous fluids (H_2O, CH_4, CH_3OH, ...) if the adsorbens contains nuclei (Si, Al, C, O, Na, K, ...) with scattering cross-sections which are small compared to the incoherent scattering cross-section of the proton. The first studies on adsorbed hydrocarbon molecules, measuring the neutron transmission, have been done by Todireanu [24]. At that time phase transformations have been looked for, which are indicated by steps in the intensity of the transmitted neutron beam when the temperature of the sample is slowly changed (the total scattering cross-section of the proton depends on the molecular mobility). Neutron time-of-flight experiments, where the differential scattering cross-section is involved, can yield more detailed information on the molecular motion (diffusion, vibration, rotation). Since the work of Verdan [25] numerous papers concerning the scattering law of adsorbed molecules have been published. For technical aspects of the method see for instance ref. 26. The results – translational and rotational diffusion of adsorbed molecules – refer to systems in thermodynamic equilibrium and do not directly lead to values for the parameters in the macroscopic equation for diffusive transport. In the simplest one-dimensional case – omitting the coupling between mass and heat transport [27] – the diffusion equation, which describes the

motion of a fluid with a liquid/gas phase boundary in the porous solid, is of the form [28–30]

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(C)\frac{\partial C}{\partial x}\right] + \dot{s}(t)\frac{\partial C}{\partial x} \qquad (1)$$

$\dot{s}(t)$ denotes the velocity of the front of a fluid which is moving through the sample driven by capillary forces [29]. We studied the irreversible, macroscopic transport of fluids in porous bodies, the morphology of which was near to that of natural sediments. A powder of zeolite microcrystals has been sintered at ambient temperature in a wet state to achieve nearly the bulk density of a zeolite crystal. Thus, $C(x,t)$ in eqn. (1) denotes the number of nuclei (protons) in an element of volume, the extension of which is large compared to the size of a microcrystal (1 μm) but smaller than the interval $\Delta x = 100$ μm which was used for solving eqn. (1) numerically. In terms of capillary models the travel distance s increases with the square root of the time t,

$$s^2 = D_k t \qquad (2)$$

with a pseudo 'diffusion constant' D_k.

The disordered structure of the channels between the crystals leads – in terms of a capillary model – to a relation between the mean distance of travel, s, and time, t, as if the transport was due to molecular diffusion, but the value of the diffusion constant, D_k, depends on the structure of the porous solid, on the capillary pressure and on the viscosity of the fluid [29].

The diffusivity $D(C)$ has to be determined by comparing the observed profile of the moving boundary of the fluid in the porous solid with solutions of eqn. (1). A physical model used in zeolite science may be quoted to interpret the experimental $D(C)$ if two conditions are fulfilled:

(a) The porous body is homogeneous like an undisturbed single crystal.

(b) The step and the gradient of the density $C(x,t)$ at the start of the transport process is so small that the linear response theory can be applied.

The diffusive decay of a small disturbance in the density of particles of a manybody system at thermal equilibrium is related to the long time limit of the velocity–velocity correlation function of a particle. In this sense microscopic equilibrium data (NMR, quasielastic neutron scattering) can be correlated with the real mass-transport phenomena.

We shall use the following expression, which physically means the ideal situation, to rationalize the observed transport of mass:

$$D(C) = D_0(C)\frac{\partial \ln p}{\partial \ln C} \qquad (3)$$

In the above-mentioned ideal case $D_0(C)$ denotes the coefficient of self-diffusion as derived from microscopic equilibrium data. The pressure p in eqn. (3) is meant to be measured in the gas phase above the adsorbents in thermal equilibrium with an adsorbate at the concentration C in the sample. For the intracrystalline diffusion of molecules in zeolites, numerous models and experimental data have been presented [7,31–35]. The eqns. (1)–(3) can be a useful tool to simulate the transport of fluids through zeolite compacts in applications such as storage of hydrocarbons or transformation of low-temperature heat, if it turns out that they fit to the experimental function $C(x,t)$. The choice of this mathematical description is not uniquely determined by the system under study, but it is the simplest possible one with a well-defined physical meaning in a limiting, though unrealistic, situation. The diffusivity $D(C)$ has not yet been determined by measuring $C(x,t)$ on a macroscopic scale and comparing the experimental results with the solution of eqn. (1). In this paper neutron transmission experiments are reported in which compacted bodies of a zeolite NaX sediment are used as the adsorbens. The diffusive transport of water, methanol, ethanol, *cis*-butene-2, toluene and benzene was observed at ambient temperature and pressure.

Experimental

Porous bodies were prepared by pressing a zeolite sediment of type NaX between two metal plates. Sample 1 was kept under mechanical pressure between two plates of aluminum of 15-mm thickness within a teflon frame of length $L=$

200 mm, height $H = 60$ mm, and thickness $T = 6$ mm. A density of $\rho_z = 1.5$ g/ml was achieved under vacuum at 80°C (the NaX framework density is 1.3 g/ml; the mass density of crystals loaded with water is 1.93 g/ml [36]). At both ends of the sample holder, at the distance L, inlet(outlet) tubes served to adsorb(desorb) the fluids, the transport of which through the NaX sample was studied. Similarly, a second sample was prepared with $L = 170$ mm, $H = 50$ mm, $T = 12$ mm. T is the length over which the neutron beam is attenuated when transversing the sample.

After three weeks of vacuum treatment of the sample 1 at 80°C and the sample 2 at 200°C, the leakage of the sample holders was tested by closing the valves for one week. Then the samples were again connected to the vacuum system and mass spectroscopy showed that still water was the dominant residual gas with a partial pressure of 10^{-7} mbar. This extended drying process yielded a mass density which was still larger than that of the pure zeolite NaX framework. An absolute measure of the residual water content cannot be given. In order to have realistic initial conditions for the neutron transmission experiments, after each regeneration period (24 h) the sample was loaded with air (in some cases He). Experiments with water passing through a dried sample kept under vacuum at one side of the sample holder showed a wavy modulation on the density profile. We do not present and discuss this part of the data here but mention it because of the coupling between heat and mass transfer which seems to be important if the molecules at the front of the density profile interact strongly with the NaX framework.

Neutron transmission experiments on fluids passing through porous media (Fig. 1) were carried out on the FMRB reactor at the PTB Braunschweig. The experimental setup as shown in Fig. 2 was used at the end of the neutron guide S7 [37]. The experiment was controlled by a Keithley Series 500 DAS which was connected to a PC. The programs for the data acquisition, the motion of the sample and the data handling were coded in ASYST. The neutron transmission experiments were organized as a sequence of cycles in which the sample was moved forward and back-
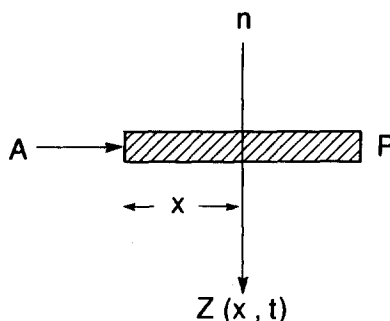

Fig. 1. In the neutron transmission experiment, the neutron transverses the sample P at a distance x from the surface, where the adsorbate A started to travel through the sample at the time $t = 0$. The neutron flux $Z(x, t)$ behind the sample is measured while stepwise moving the sample through the neutron beam. The counts measured before (Z_0) and after (Z_m) the start of adsorption are evaluated to yield a function which is proportional to the adsorbate density distribution $C(x, t)$ (or pore filling Θ in zeolites): $(\ln Z_0 - \ln Z_m)/\ln Z_0 \sim C(x, t)$.
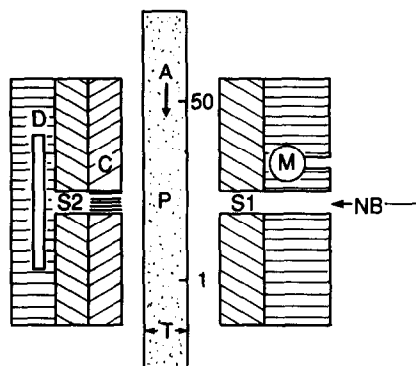

Fig. 2. The neutron beam NB passes the slot S1, the sample P of thickness T, the collimator C, the slot S2 and is recorded by the detector D, which consists of 5 He³ tubes with a diameter of 6 mm. The height of the beam was limited to 40 mm and the width of the beam was reduced to 2.5 mm by the variable slots S1 and S2. The sample holder was moved stepwise through the neutron beam in cycles of back-and-forth motions over a distance of 80 mm. When the sample is at the position, which is denoted by the position index $v = 1$ in the data sets, then the neutron beam hits the position which is marked by 1, at a distance of 60 mm from the end of the sample 1.

ward over a distance of 80 mm perpendicular to the neutron beam with 100 steps of motion. The neutron counts, $Z(x, t)$, from the detector behind the sample were accumulated at each step during an interval of time $\Delta t = 30$ s. In each experiment, first some cycles with the degassed sample (200°C,

$t=24$ h) have been run, yielding neutron data Z_0. Then the inlet valve to the adsorbate was opened and neutron data Z_m measured. The pressure conditions for the mass transport through the sample were varied. The pressure over the storage level of the fluid to be adsorbed was either given by the ambient atmosphere ($p_i=1$ bar) or by the vapor pressure of the fluid ($p_i=0$ bar). The gas pressure in the sample was either that achieved after the regeneration of the zeolite ($p_0=0$ bar), with the outlet valve kept open to the vacuum pump, or the sample was loaded with helium (or air, $p_0=1$ bar) before starting the neutron transmission experiment. Experiments were carried out with water, methanol, ethanol, cis-butene-2, benzene and toluene and the motion of a liquid/gas phase boundary in the sample was observed during about 10 h. The resolution of the neutron transmission experiment is shown in Fig. 3. A sample consisting of foils of polyethylene and a sheet of cadmium was moved through the beam. The first step at position number $n=8$, from zero to 7% beam attenuation, indicates that the first foil with an effective thickness of 0.12 g cm^{-2} has reached the beam, the width of which is limited to $x=2.5$ mm by the slots S1 and S2 (Fig. 2). The next

increase of the beam attenuation by 3% corresponds to an increase of mass by 0.06 g cm^{-2}. The large step at $n=35$ is due to the edge of the Cd-sheet which enters the beam. The drawn curve in Fig. 3 is the solution of the linear diffusion equation with $D_0=10^{-11}$ m^2 s^{-1} and an assumed velocity of a fluid/gas phase boundary $v=3\cdot10^{-6}$ m s^{-1}. The comparison of the points in Fig. 3 and the drawn curve shows that with this experimental setup the rounding of a passing concentration profile can be seen if the diffusivity is larger than 10^{-11} m^2 s^{-1} [$D(C)=$const. is assumed for an analytical solution of eqn. (1)].

Results

We present the experimental data in a reduced form. Firstly, the count rates have been normalized to a constant incident flux. Secondly, the data from the 5 He^3 tubes, stacked on each other behind the sample, showed that the density of the adsorbate indeed depends on the coordinate x only. So we consider only data from the He^3 tube in the middle of the beam. The result of a run is presented by
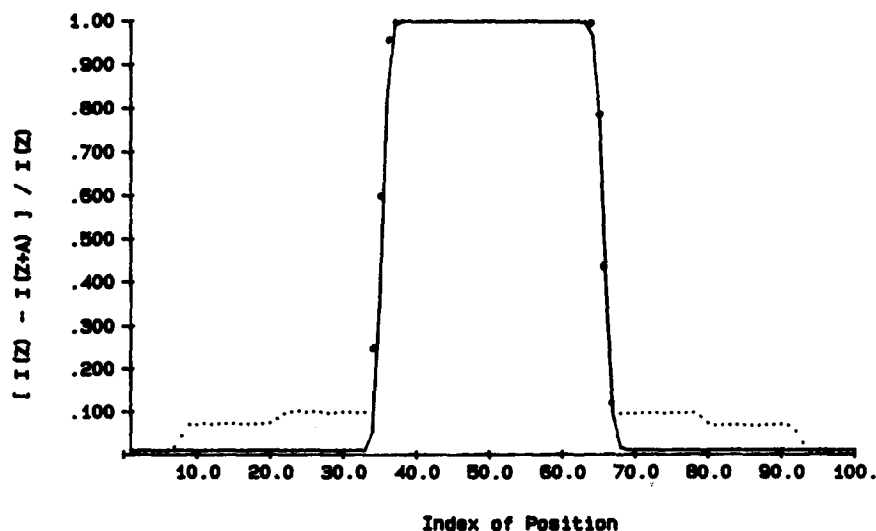

Fig. 3. The points represent the attenuation of the neutron beam which was measured using a sample which is composed of several stripes with a mass density of 0–0.12–0.18 g cm^{-2} of polyethylene and a sheet of cadmium, by which a sharp boundary of an adsorbate was simulated. The drawn curve is the solution of the linear diffusion equation with $D=10^{-11}$ m^2 s^{-1} and a constant drift velocity $v=3\cdot10^{-6}$ m s^{-1}.

the function

$$C(n) = [\ln Z_0(n) - \ln Z_m(n)]/\ln Z_0(n) \qquad (4)$$

The Z_0 data were measured before the start of adsorption, the Z_m data were measured after the start of adsorption. The position index is $n = 1, 2, \ldots 100$ within a cycle. The corresponding time for the N-th cycle after the start of adsorption is

$$t(N, n) = (N-1) \cdot 100 \cdot \Delta t + n \cdot \delta t \qquad (5)$$

The corresponding travel distance is

$$x(n) = x_0 + n \cdot 1.6 \text{ mm} \qquad (6)$$

The observation of the neutron transmission begins at a distance $x_0 = 60$ mm from the outlet side of the sample 1 ($x_0 = 45$ mm for sample 2) and for $n = 50$ the point of measurement is at a distance x_0 from the inlet of the adsorbate.

The points in Fig. 4 represent the results obtained for hydrogenous fluids passing through the samples of compacted zeolite NaX. The density front appears in the x-range of the transmission spectrometer about 2 h after starting the adsorption process. The experimental data can roughly

be characterized by comparison with solutions of eqn. (1) for the initial condition $C(x, 0) = 0$ and the boundary condition $C(0, t) = C_0$ [30,38]

$$C(x, t) = \frac{C_0}{2}[1 + \text{erf}(z)] \qquad (7)$$

$$z = \left[x - \int_0^t \dot{s}(t')dt' \right] / 2 \cdot \sqrt{\int_0^t D(t')dt'}$$

For a short presentation of the results in the form of a table we have calculated the function (7) for a constant diffusivity D and with a velocity of migration $v = \langle \dot{s} \rangle$ or with D_k according to eqn. (2). The ratio $C(x, t)/C_0$ should be proportional to the experimental values $C(n)$. So we adjusted the maximum of the calculated curves to the measured value $C(50)$ and fitted the parameters D and v (or D_k). This fit does not mean a 'result' in the usual sense of fitting procedures, but is a short notation for the original, measured data. Table 1 reviews the neutron transmission experiments with the compacted zeolite NaX sample 1 in the upper part and with sample 2 data in the lower part of the
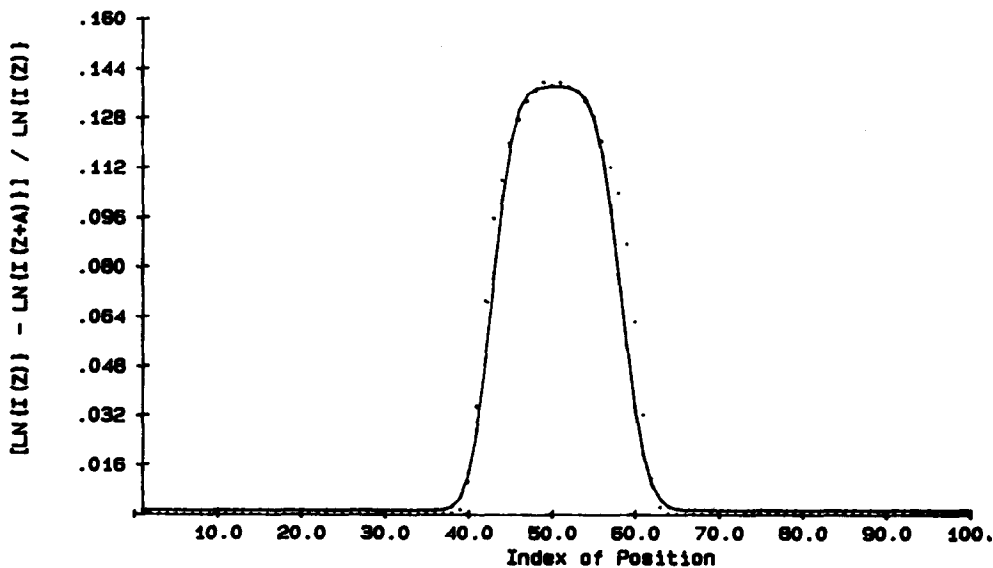
Fig. 4. The points are the neutron transmission data from methanol passing through sample 1, evaluated in a form which is proportional to the density, $C(X(n),t(n))$. The cycles of measurement shown in this figure comprises the interval of time 1.6 h $< t(n) <$ 2.6 h. At an index of position n the distance of the point of observation from the inlet side of the sample holder is $x(n) = 140$ mm $- n \cdot 1.6$ mm for $1 \leqslant n \leqslant 50$ and $x(n) = 60$ mm $+ (n - 50) \cdot 1.6$ mm for $51 \leqslant n \leqslant 100$. The drawn curve is the solution of the linear diffusion equation with $D = 3 \cdot 10^{-10}$ m^2 s^{-1} and a constant drift velocity $v = 3 \cdot 10^{-6}$ m s^{-1}.

TABLE 1

Transport of fluids in zeolite NaX

Fluid	Conditions of experiments		Characterization of the data		
	p_i (bar)	p_0 (bar)	D ($m^2 s^{-1}$)	D_k ($m^2 s^{-1}$)	v ($m s^{-1}$)
sample 1, air					
water	1	0	$5 \cdot 10^{-10}$	$3 \cdot 10^{-7}$	$4 \cdot 10^{-6}$
	1	1	$3 \cdot 10^{-10}$	$2 \cdot 10^{-7}$	
methanol	1	1	$3 \cdot 10^{-10}$	$3 \cdot 10^{-7}$	$3 \cdot 10^{-6}$
ethanol	1	0	$3 \cdot 10^{-9}$	$8 \cdot 10^{-7}$	$6 \cdot 10^{-6}$
	1	1	$3 \cdot 10^{-10}$	$4 \cdot 10^{-7}$	$2 \cdot 10^{-6}$
benzene	0	0	$7 \cdot 10^{-10}$	$8 \cdot 10^{-7}$	$5 \cdot 10^{-6}$
	1	1	$8 \cdot 10^{-10}$	$6 \cdot 10^{-7}$	
toluene	1	1	$1 \cdot 10^{-10}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-5}$
	1	0	$5 \cdot 10^{-10}$	$4 \cdot 10^{-7}$	
sample 2					
ethanol	1	1 (air)	$2 \cdot 10^{-10}$	$1 \cdot 10^{-7}$	
cis-butene-2	1.1	1 (He)	$5 \cdot 10^{-10}$	$3 \cdot 10^{-6}$	
	1	1 (air)	$6 \cdot 10^{-11}$	$4 \cdot 10^{-8}$	

table. The numbers in the first column indicate the pressure on the stored adsorbate which is connected to the inlet tube of the sample holder. The second column shows whether the outlet side of the zeolite body was kept at vacuum conditions after the preceding regeneration of the sample. The parameter D represents the form of $C(x, t)$ at the edges of the moving liquid/gas phase boundary in the intervals $1 < t < 4$ h and $60(45) < x < 100$ mm. D_k characterizes the time-dependent velocity of the front of the adsorbed liquid as given in eqn. (2). In addition, the fit was also done with a constant velocity v in some cases.

Discussion

The experimental data show that the simple neutron transmission apparatus is sufficient to visualize the diffusive rounding of the upper and of the lower edge of the moving adsorbate density profile. The asymmetry of the profile – the upper edge is more broadened than the lower one – indicates that a nonlinear diffusion takes place.

The solutions of the transport eqn. (1) with a constant value D do not properly represent the measured functions $C(n)$. In comparing calculated

and measured data over a wide range of x and t one sees that D must increase strongly when C approaches C_0. Following a recipe given by Boltzmann, one can derive $D(C)$ from the experimental data applying the transformation

$$y = x/\sqrt{t}$$

$$D(C) = \frac{1}{2} \frac{dy}{dC} \int_C^{C_0} y dC \qquad (8)$$

In practice this procedure appeared to be unrealistic because for $C \to C_0$ a small number must be divided by another small number in expression (8). The experimental interval Δx and the statistical error of the neutron counts (at low transmission of the sample) must be much smaller to overcome this numerical difficulty. We avoided this problem by looking for solutions of the nonlinear, one-dimensional diffusion equation which depend on the assumed form of $D(C)$.

Analytical solutions are available for special cases only [38–40]. Eqn. (1) has been solved therefore numerically and the models for $D(C)$ discussed in ref. 31 have been tested. The reference to models for molecular diffusion in zeolite crystals is meant to be a numerical equivalence to the above-mentioned procedure with a physical background

in the limit of vanishing voids between the crystals and a sufficiently small gradient of concentration. A 'van der Waals'-type of model appeared to be most suitable:

$$D(C) = D_0 \left[\frac{1}{1 - C + \varepsilon} - \alpha \cdot C \cdot (1 - C + \varepsilon) \right] \qquad (9)$$

where D_0 is the value of the diffusivity in the limit of small values of C (but $\mathrm{grad} C \neq 0$). α is the 'van der Waals' number which should be of the order 1. $\varepsilon = 0.1$ has been put into eqn. (9) in order to avoid long computer times when running the program which evolves the initial and boundary conditions for C in small steps of x and t in accordance to eqn. (1). The capillary model for the drift velocity (2) has been adopted by using the expression

$$\dot{s} = v_0 + 0.5 \sqrt{D_k} / \sqrt{t_0 + t} \qquad (10)$$

with a constant velocity v_0 and a small delay time of $t_0 = 10$ s. From a set of numerical solutions of eqn. (1), $C(x_i, t_j)$, on a dense grid of coordinates, x_i and t_j, the functions $C(x(n), t(n))$ have been interpolated which are shown as drawn curves in Fig. 5. These should fit to the experimental data from methanol (symbols in Fig. 5) if the values for the parameters in eqn. (9) and eqn. (10) have been chosen properly. In Fig. 5 the index of position $n = 1, \ldots 50$ refers to the positions $6 < x(n) < 14$ cm and the diffusion times are in the interval $1.7 < t(n) < 6$ h. The mass transport is characterized by the values $D_0 = 3 \cdot 10^{-10}$ m^2 s^{-1}, $\alpha = 0.5$, $D_k = 5.7 \cdot 10^{-7}$ m^2 s^{-1} and a constant velocity $v_0 = 1 \cdot 10^{-8}$ m s^{-1}, which is numerically unimportant for the passing of methanol through the porous solid.

In Table 2 the results are collected of fitting numerical solutions of the nonlinear differential equation to the neutron transmission data from fluids in a compacted zeolite NaX sample at ambient temperature. The parameters describe the diffusive transport in a sample which has been degassed under vacuum and then filled with air. The liquid is driven through the porous solid by capillary forces, not by an external pressure difference. The asymmetric smoothing of the density at the moving liquid/gas boundary cannot be fitted
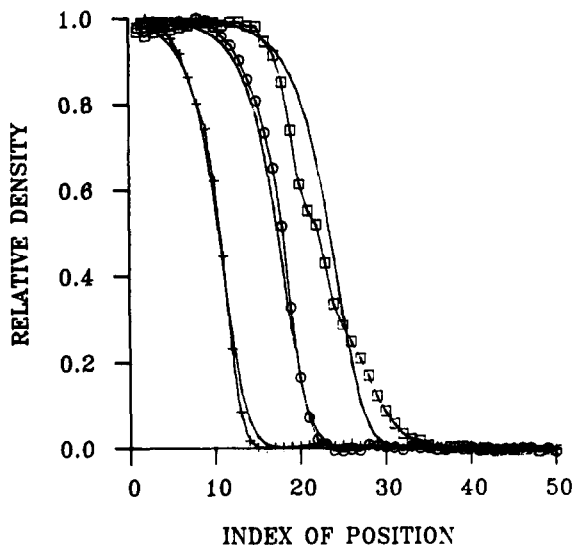

Fig. 5. The symbols are data from methanol passing through the air-filled sample 1 as shown in the right half of Fig. 4, but from 3 experimental runs taken at times $1.7 < t < 6$ h after the start of adsorption. From the numerical solutions of the nonlinear diffusion equation with a drift term, those triples of numbers (C_n, X_n, t_n), $n = 1, \ldots 50$ are shown as drawn curves over the index of position n which correspond to the experimental values of the coordinate x and time t. The computation has been done with the parameters $D_0 = 3 \cdot 10^{-10}$ m^2 s^{-1}, $\alpha = 0.5$, which describe the softening of the initial step of concentration, and $D_k = 5.7 \cdot 10^{-7}$ m^2 s^{-1}, which stands for the time-dependent drift velocity.

TABLE 2

Parameters of the nonlinear model for mass transport

Liquid	D_0 (m^2 s^{-1})	D_k (m^2 s^{-1})	v_0 (m s^{-1})
water	$1 \cdot 10^{-10}$	$5 \cdot 10^{-7}$	$10 10^{-7}$
methanol	$3 \cdot 10^{-10}$	$6 \cdot 10^{-7}$	$1 \cdot 10^{-8}$
ethanol	$1 \cdot 10^{-10}$	$4 \cdot 10^{-7}$	$1 \cdot 10^{-8}$
benzene	$4 \cdot 10^{-10}$	$9 \cdot 10^{-7}$	$1 \cdot 10^{-6}$
toluene	$5 \cdot 10^{-10}$	$1 \cdot 10^{-7}$	$7 \cdot 10^{-4}$

with functions of type (7) but can be reproduced with a concentration-dependent diffusivity. The constant D_0 is necessarily somewhat larger than measured inside of the microcrystals with other methods because part of the mass transfer is occurring in the free space between the microcrystals. The measured bulk density of the degassed sample, $\rho_z = 1.5$ g/ml, indicates that the free volume in the compacted zeolite is small. An exact figure cannot

be given because the residual content of water has not been measured. The velocity of the migrating liquid/gas boundary, expressed by the values of D_k and v_0, is mainly determined by D_k in the case of the polar liquids water, methanol, and ethanol – in the considered range of time $t < 5$ h. A comparison of the values of D_k, which depend on the disordered structure of the solid, on the capillary pressure and on the viscosity of the fluid, with values from the literature cannot be made because experiments such as presented in this paper have not been done so far. The values found for D_0 (the molecular diffusion coefficient averaged over a proper volume and extrapolated to zero concentration) are of an order of magnitude which is compatible with values for diffusion inside zeolite crystals and in fluids. The solutions of eqns. (1), (9) and (10) cannot explain some features which become important with increasing time of observation.

(1) There appear wave-like modulations of the adsorbate, especially with water in an evacuated sample. This feature can be reproduced by introducing a corresponding modulation of $D(C)$ but this seems to be unrealistic. A coupling between mass- and heat-transfer as considered in ref. 27 may perhaps explain the phenomena.

(2) A retention time must be introduced *ad hoc* into the current model in order to account for the strong smoothing of the upper edge of the front of adsorption. The exchange of molecules between the intercrystalline and the intracrystalline liquid and the residence time in the microcrystals has not been taken into account.

Conclusions

Density variations $\Delta C < 1\%$ of hydrogenous fluids in samples of compacted zeolite sediment can easily be observed by means of slow neutron transmission within a resolution of about 3 mm in space and 10 s in time using a beam from a 1 MW type of steady state neutron source. So far the relative intensities and corresponding relative changes of densities have been measured only. The method will be extended to measure absolute values of the density of the adsorbate.

The transport of fluids through porous solids can be roughly predicted on the basis of error functions which are solutions of the one-dimensional, linear diffusion equation, including a drift term. The knowledge of the transport parameter may be useful for applications of zeolite bodies, for instance, in the field of conversion and storage of energy. Computer simulations of a nonlinear diffusive mass transport yield a better agreement between theory and experiment, although some systematic deficiencies of the model are apparent.

The neutron transmission results encourage to study two further, connected problems:

(a) the reverse mass transport, when the fluid is pumped off from the sample;

(b) the conditions of the stability and the times of steps of density and phase boundaries of fluids in porous solids.

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