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Gas phase transport, adsorption and surface diffusion in a porous glass membrane

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Abstract

Due to their improved performance and excellent chemical resistance, there is a growing interest in applying inorganic membranes not only for gas separation, but also in combination with heterogeneous-catalysts in membrane reactors. Obviously, a thorough understanding and a quantification of the mass transfer processes are essential for optimal application. The objective of this work is to study the mass transfer through a Vycor glass membrane, which might be applied successfully in membrane reactors. Transient diffusion experiments were carried out and the exchange of two different gases via the membrane was investigated. The observed pressure responses reveal the complicated nature of the transport through Vycor glass. If adsorbable gases are involved there is a strong asymmetry between corresponding exchange experiments. Very complex responses were observed for the exchange experiments with C_4H_{10} and C_3H_8. To understand the observed behavior, the adsorption capacity of Vycor glass was measured for several gases at ambient temperature. In order to analyze the transient diffusion experiments, a transport model was applied, which is based on the Dusty Gas Model for the quantification of gas phase transport and on the generalized Maxwell–Stefan theory for the description of the transport of adsorbed species. The model describes relatively well the exchange experiments performed with the pairs H_2/N_2 and He/CO_2. It was found that the quality of the theoretical results for experiments with adsorbable gases depends strongly on the reliability of the model applied to quantify the adsorption isotherms.

Keywords: Gas phase transport; Adsorption; Surface diffusion; Transient diffusion experiments; Vycor glass

1. Introduction

Currently intensive efforts are devoted to develop improved inorganic membranes. These materials are attractive due to their high thermal and chemical stability in combination with a good mechanical strength. Besides using inorganic membranes for gas separation (e.g. [1,2]) there is currently a growing interest in applying them to various configurations of membrane reactors (e.g. [3–7]). In order to use membrane separations successfully in combination with chemical reactions, the relevant rates of transport and reaction processes must be compatible. Thus, the evaluation of the potential and eventually the design and optimization of membrane reactors require careful determination of the reaction and mass transfer kinetics.

In a previous study, a systematic investigation of the dehydrogenation of cyclohexane to benzene using a supported Pt-catalyst was performed [6,8]. The hydrogen formed in this reversible model reaction was removed using a porous Vycor glass membrane leading to enhanced cyclohexane conversion. In several experiments, the equilibrium conversion was exceeded indicating the potential of such operation. Selected experimental results of this study are summarized in Fig. 1. In this figure, predictions are also shown using a 1D isothermal dispersed plug flow reactor model in combination with the Dusty Gas Model (DGM) in order to quantify the mass transfer through the membrane [6]. As can be seen, the simulations systematically underestimate the performance of

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B_0	permeability constant (m^2)
b_i	parameter in the Langmuir adsorption isotherm (bar^{-1})
D^0_{ij}	binary molecular diffusivity in gas phase ($m^2\ s^{-1}$)
D^s_i	Maxwell–Stefan surface diffusivity ($m^2\ s^{-1}$)
D^s_{ij}	counter-sorption diffusivity ($m^2\ s^{-1}$)
$D^e_{K,i}$	Knudsen diffusivity ($m^2\ s^{-1}$)
K_0	Knudsen coefficient (m)
M_i	molecular weight ($g\ mol^{-1}$)
$N_{tot,i}$,	total diffusive molar flux of a species i ($mol\ m^{-2}\ s^{-1}$)
N^p_i	diffusive molar flux through gas phase of a species i ($mol\ m^{-2}\ s^{-1}$)
N^s_i	diffusive molar flux of surface diffusion of a species i ($mol\ m^{-2}\ s^{-1}$)
n	number of diffusing species
p	total pressure (Pa)
Δp	pressure difference between outer and inner volume $\Delta p(t) = \sum_i^n p_{2,i}(t) - p_1$ (Pa)
p_i	partial pressure of i component (Pa)
q_i	adsorbed phase concentration of i component ($mmol\ m^{-3}$)
q_{sat}	total saturation capacity of adsorbed species ($mmol\ m^{-3}$)
r	radius (m)
R	universal gas constant ($J\ mol^{-1}\ K^{-1}$)
t	time (s)
V	volume (m^3)
$\dot{V}$	volumetric flow rate ($m^3\ s^{-1}$)
x_i	molar fraction of a component i in gas phase
z_i	molar fraction of a component i in adsorbed phase
z	axial coordinate in eqs. (14) and (15) (m)
1,2	referring to inner/outer volume of the cell

Greek letters

ε	porosity
η	viscosity (Pa s)
μ	chemical potential ($J\ mol^{-1}$)
$\bigtriangledown\mu$	gradient of chemical potential ($J\ mol^{-1}$)
τ	tortuosity
γ_i	activity coefficient of i component in adsorbed phase
Π^*_{mix}	spreading pressure

Superscript

0	pure component

the membrane reactor. Due to the simplicity of the applied model there might be several reasons for these discrepancies. Besides unavoidable thermal effects leading to deviations from isothermal operation and limitations of the independently determined reaction rate model [8], there is strong evidence that the applied transport model is not sufficient to quantify correctly the mass transfer in Vycor glass. In refs. [6,8,9], it was explained that at lower temperatures certain gases can adsorb on this material, and thus there might be a significant additional flux related to gradients occurring in the adsorbed phase.

It is the purpose of this study to present new experimental results related to the diffusion of inert and adsorbable gases under transient conditions through a Vycor glass membrane. These data should lead to a more precise quantification of the complex mass transfer. Thus, they might support a better description of membrane reactors in which such membranes are involved. Since the phenomena of adsorption on membrane surfaces and transport via surface diffusion are more general, the results achieved might be also useful for other membrane types.

2. Mass transfer through porous media and adsorption isotherms

The mass transfer of gases through a porous solid is typically due to viscous flow and molecular diffusion in larger pores and Knudsen diffusion in small pores. In a very small pore (in the subnanometer range), the transport is usually an activated process. Details concerning the different transport mechanisms and useful models are presented, e.g. in ref. [10]. A frequently used model is the Dusty Gas Model [11], which is based on the Maxwell–Stefan diffusion equations. For a gas i in a mixture of n gases, the specific fluxes in the pores can be described using eq. (1).

$$-\frac{p}{RT}\nabla x_i - \frac{x_i}{RT}\left(1 + \frac{B_0}{\eta D^e_{K,i}}p\right)\nabla p = \sum_{j=1, j\neq i}^{n} \frac{x_j N^p_i - x_i N^p_j}{(\varepsilon/\tau)D^0_{ij}} + \frac{N^p_i}{D^e_{K,i}}, \quad i = 1, \ldots, n \tag{1}$$

where N^p_i is the flux of component i, B_0 the permeability constant of the viscous flow, $D^e_{K,i}$ the effective Knudsen diffusion coefficient, D^0_{ij} the binary molecular diffusivity and ε/τ is the ratio of porosity to tortuosity. For $D^e_{K,i}$, it holds:

$$D^e_{K,i} = \left(\frac{4}{3}\right) \times K_0 \sqrt{\frac{8RT}{\pi M_i}}, \quad i = 1, \ldots, n \tag{2}$$

In the above, K_0 is the Knudsen coefficient. Thus, for a homogenous porous structure there are the free parameters B_0, K_0 and ε/τ. In general, for a certain porous material these parameters must be determined experimentally.

Besides the flux through the pores, in case of adsorbable gases, an additional flux due to surface diffusion could contribute significantly to the overall mass transfer. The Generalized Maxwell–Stefan (GMS) equations [12] can describe this phenomenon:

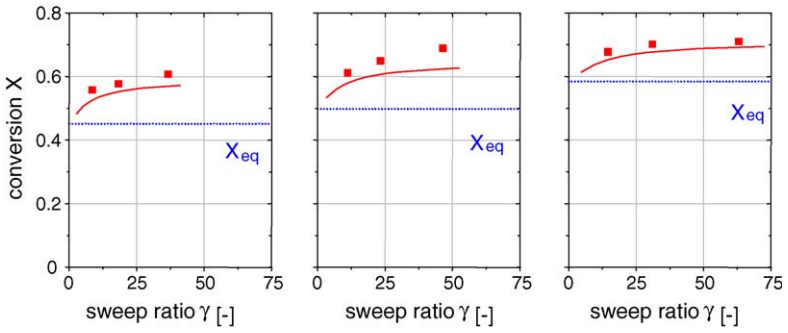

Fig. 1. Comparison between experimentally (symbols) determined and predicted (lines) conversions of cyclohexane in a membrane reactor using a Pt-catalyst and a Vycor glass membrane in order to remove selectively the hydrogen out of the reaction zone [6,8]. The sweep ratio γ is the ratio of the sweep and feed volumetric flow rates. Temperature 473 K. Cyclohexane feed concentrations: 3.7 vol% (left), 4.9 vol% (middle) and 5.8 vol% (right). The corresponding equilibrium conversions X_{eq} are indicated by dashed lines.

$$-\frac{1-\varepsilon}{RT} q_i \nabla \mu_i^{s} = \sum_{j=1, j\neq i}^{n} \frac{q_j N_i^{s} - q_i N_j^{s}}{q_{sat} D_{ij}^{s}} + \frac{N_i^{s}}{D_i^{s}}, \quad i = 1, \ldots, n \tag{3}$$

where N_i^{s} is the flux of component i due to surface diffusion. In eq. (3), ε is again the porosity, q_i the adsorbed phase concentration, $\nabla \mu_i^{s}$ the chemical surface potential gradient of component i and D_{ij}^{s} is the GMS counter-sorption diffusivities. D_i^{s} is the surface diffusivities of the adsorbed components. If surface diffusion is relevant, these are important additional free parameters. The chemical surface potential gradient of a species is related to the adsorption isotherms

$$q_i = q_i(p_1, p_2, \ldots, p_n), \quad i = 1, \ldots, n \tag{4}$$

In case that for an adsorbable gas both the contributions by gas phase transport and by surface diffusion are relevant, the total molar flux can be described using eq. (5):

$$N_{tot,i} = N_i^{p} + N_i^{s}, \quad i = 1, \ldots, n \tag{5}$$

An equation frequently used to quantify the adsorption isotherms for single components is the Langmuir equation eq. (6).

$$q_i^{0} = \frac{q_{sat,i} b_i p_i^{0}}{1 + b_i p_i^{0}}, \quad i = 1, \ldots, n \tag{6}$$

This equation can be extended in order to quantify the partial adsorption isotherms of several components in ideal mixtures.

$$q_i = \frac{q_{sat,i} b_i p_i}{1 + \sum_{j=1}^{n} b_j p_j}, \quad i = 1, \ldots, n \tag{7}$$

A thermodynamically consistent description requires all saturation capacities $q_{sat,i}$ in eq. (6) to be identical [13].

Besides the competitive Langmuir isotherm equation (eq. (7)), the more flexible Ideal Adsorbed Solution (IAS) theory [13,14] can be applied to describe the partial adsorption isotherms for a mixture. The amounts of each component adsorbed in a mixture can be calculated from the following set of equations:

$$z_i = \frac{q_i}{\sum_j^{N} q_j} \tag{8}$$

$$\sum_{i=1}^{N} \frac{q_i}{q_i^{0}(p_i^{0})} = 1 \tag{9}$$

$$z_i = \frac{p_i}{p_i^{0}} \tag{10}$$

$$\Pi_{mix}^{*} = \Pi_i^{*}(p_i^{0}) = \int_0^{p_i^{0}} \frac{q_i^{0}(p_i^{0})}{p_i^{0}} \, \mathrm{d}\, p_i^{0} \tag{11}$$

where z_i is the fraction of component i in the adsorbed phase and Π^{*} is the modified spreading pressure. The superscripts designate single component adsorption. For the individual isotherms, $q_i^{0}(p_i^{0})$, arbitrary analytical models can be applied, including eq. (6).

In case of non-ideal adsorbed solutions, the amounts adsorbed should better be calculated by the Real Adsorbed Solution (RAS) theory, where activity coefficients characterize the properties of the adsorbed phase. Instead of eq. (10), then eq. (12) has to be used [15–17].

$$\gamma_i z_i = \frac{p_i}{p_i^{0}}, \quad i = 1, \ldots, n \tag{12}$$

3. Experimental

The Vycor glass applied for the measurements was provided by Corning Inc. (USA), equally as for the studies described in refs. [6,8,9]. It consists of 96% silica with the remainder being mainly B_2O_3 (glass code is 7930). The mean pore diameter is 3.8 nm. The glass was supplied in tubular geometry. Compared to refs. [8,9] the tubes had slightly different dimensions: 100 mm (length), 2.85 mm (inner radius) and 4.05 mm (outer radius).

Two sets of experiments were carried out:

(a) the determination of adsorption isotherms for selected gases;
(b) transient diffusion experiments for different gas mixtures.

3.1. Adsorption isotherms

Due to their importance for a proper understanding of the transport of adsorbable gases adsorption isotherms have been measured at ambient temperature for several gases as single components and in binary mixtures.

To perform the adsorption measurements one tubular glass membrane was crushed into small fragments. Adsorption equilibrium data were determined for CO_2, C_3H_8 and C_4H_{10} as single gases and for C_3H_8/CO_2 and C_3H_8/C_4H_{10} mixtures (1:1) using a volumetric method. The set-up for measurements with mixtures consists of two compartments with well-defined volumes, which are connected by valves and can be evacuated and filled with gases individually. Before the measurement the mixture constituents are introduced into the first compartment, while in the second compartment a known amount of Vycor glass is placed. The pressures and compositions are determined by pressure transducers and a gas chromatograph, respectively. To perform the measurement, the sample compartment is connected with the other compartment. After reaching the adsorption equilibrium, the final pressure and composition of the gas are measured. The adsorbed amounts can then be calculated from the initial and the equilibrium pressures and compositions using material balances.

3.2. Transient diffusion experiments

Transient diffusion experiments were performed using a modified Wicke–Kallenbach arrangement according to [18]. A schematic illustration of the set-up is shown in Fig. 2. This set-up allows to perform transient experiments, which are started, after an initialization period, by substituting an enclosed gas via the membrane by another gas. Before an experiment was started, the cell volume (Fig. 2a–c) was completely swept through with gas 1. At the beginning of the measurement, gas 1 is replaced by gas 2 by switching the four-way valve. The total pressure difference between the closed outer volume c and the open inner volume b, Δp, is recorded as a function of time. After reaching a steady-state, characterized by $\Delta p = 0$, the reverse experiment can be performed by switching back the valve. These experiments were performed at ambient temperature for exchanging two non-adsorbable (inert) gases (He/N_2), an inert and an adsorbable gas (He/CO_2 and N_2/CO_2) and two adsorbable gases (C_3H_8/CO_2 and C_3H_8/C_4H_{10}).

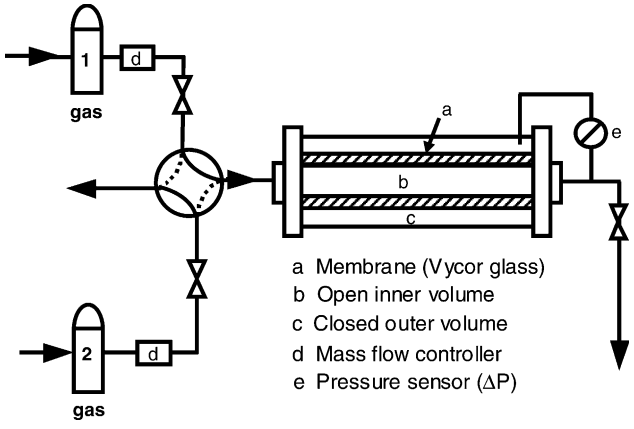

Fig. 2. A schematic diagram of set-up for transient diffusion experiment (according to ref. [18]).

In order to describe the performed transient diffusion experiments quantitatively, the following mass balances for the membrane eq. (13), the outer cell volume (closed, index 2, eq. (14)) and the inner cell volume (open, index 1, eq. (15)) must be solved together [9]:

$$\frac{\varepsilon}{RT}\frac{\partial p_i}{\partial t} + (1-\varepsilon)\frac{\partial q_i}{\partial t} = \nabla N_{\mathrm{tot},i}, \quad i = 1,\ldots,n \tag{13}$$

$$\frac{1}{RT}\frac{\partial p_{2,i}}{\partial t} = \frac{2\pi r_2}{V_2}\int_0^L N_{\mathrm{tot},i}(z, r = r_2)\,\mathrm{d}z, \quad i = 1,\ldots,n \tag{14}$$

$$\frac{1}{RT}\frac{\partial p_{1,i}}{\partial t} = -\frac{1}{RT}\frac{p_1}{A_1}\frac{\partial(x_{1,i}\dot{V}_1)}{\partial z} - \frac{2\pi r_1}{A_1}N_{\mathrm{tot},i}(z, r = r_1), \quad i = 1,\ldots,n \tag{15}$$

These equations can be solved numerically together with the required initial and boundary conditions using the method of lines [8]. Provided the parameter of the transport models and the isotherms (in case of adsorbable gases) are known, eqs. (13)–(15)) allow to predict the development of the pressure difference $\Delta p(t) = \sum_i^n p_{2,i}(t) - p_1$. And by comparing such predictions with experimental observations of $\Delta p(t)$ free model parameters can be estimated as described in ref. [9].

4. Results and discussion

4.1. Adsorption isotherms of single components and mixtures

Fig. 3a shows measured adsorption equilibrium data for C_3H_8 and C_4H_{10} as single components and 1:1 mixtures. As a single component, C_4H_{10} is adsorbed in larger amounts than C_3H_8. For C_4H_{10}, the amount adsorbed from the mixture is, as expected, smaller than that for the single component. Surprisingly, for the same partial pressure, the amount of C_3H_8 adsorbed from the mixture is almost the same as that for the single component. This indicates almost negligible competition by C_4H_{10} and the presence of severe non-ideality of this system.

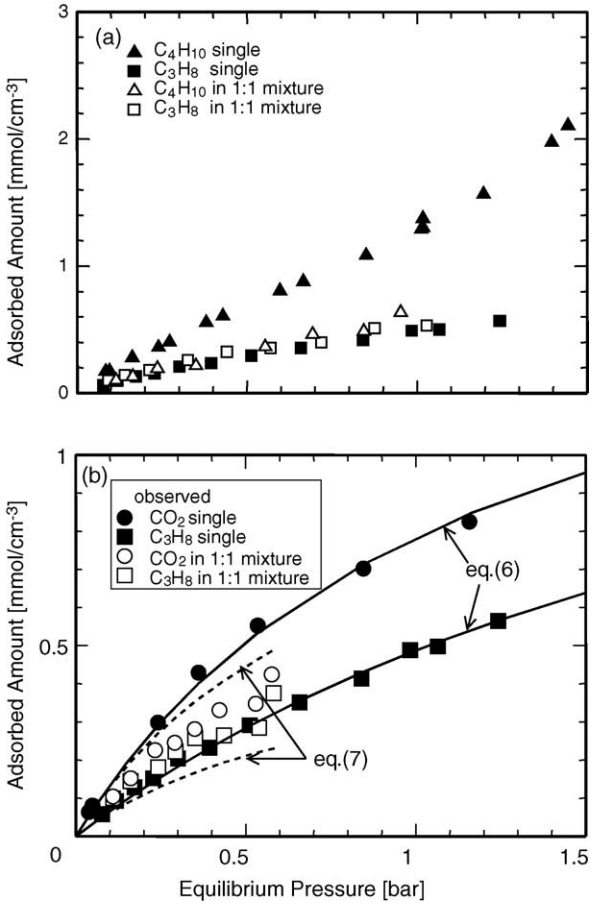

Fig. 3. (a) Observed adsorption isotherms for C_4H_{10} and C_3H_8 single components and for C_3H_8/C_4H_{10} binary mixtures (1:1) at ambient temperature. (b) Observed adsorption isotherms for C_3H_8 and CO_2 single components and for C_3H_8/CO_2 mixtures (1:1) and predicted ones by using eq. (6) (solid line) and eq. (7) (dashed line) and the parameters in Table 1 for $q_{sat,CO_2} \neq q_{sat,C_3H_8}$.

In Fig. 3b, the observed adsorption isotherms for the single components C_3H_8 and CO_2 are shown and competitive isotherms for C_3H_8/CO_2 mixtures with an equilibrium partial pressure ratio of 1:1. CO_2 is more adsorbed on Vycor glass than C_3H_8. However, it is less adsorbed than C_4H_{10} (Fig. 3a). The two single component isotherms can be well described by the Langmuir equation (eq. (6), solid lines). The corresponding parameters are given in Table 1. Again surprisingly, the observed adsorbed amounts of C_3H_8 from the mixture (symbol □) are similar to those for the single component (symbol ■). Thus, they are larger than the values predicted by the competitive Langmuir equation (eq. (7), dashed lines). In contrast, for CO_2 adsorption the observed amounts adsorbed from the mixture

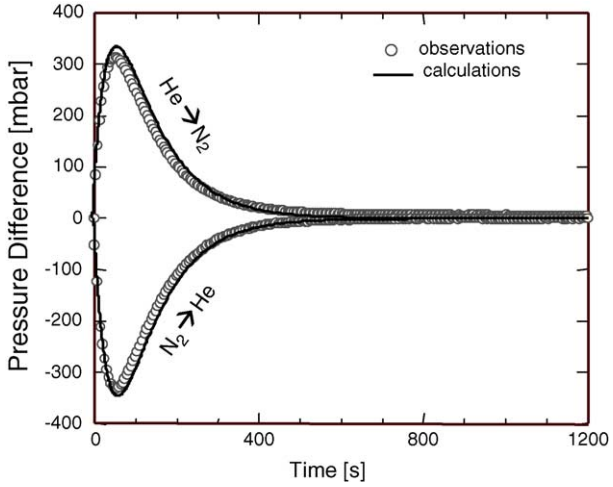

Fig. 4. Observed and calculated (eqs. (13)–(15)) transient of the pressure differences between the two chambers of the cell after exchanging the inert gases He and N_2.

are significantly smaller than those for the single component. This indicates the expected competition in mixtures compared to single component systems. The multi-component Langmuir model (eq. (7)) underestimates the extent of this effect and cannot properly describe the adsorption behavior of C_3H_8 and CO_2 in the 1:1 mixture. This holds for both cases assuming different or identical saturation capacities (Table 1). Additional calculations not presented here in detail revealed that also the IAS theory using the single component Langmuir equation in eqs. (9) and (11) is not capable of quantifying the observed mixture behavior correctly. An alternative approach based on a more complicated description of the single component isotherms using a dual site adsorption model, as suggested in ref. [14], might offer a solution. Also the introduction of concentration-dependent activity coefficients γ_i (eq. (12)) describing non-ideal adsorbed phases, could offer a possibility to correlate the observed adsorption equilibrium data. However, the correct determination of such activity coefficients is complicated [17] and was not considered at the stage of this project.

4.2. Transient diffusion experiments with inert and adsorbable gases

At first, transient experiments were performed for the two non-adsorbable (inert) gases He and N_2. There is a clear symmetry between two consecutive reverse exchange experiments as illustrated in Fig. 4. Analyzing these and

Table 1
Estimated parameters of the adsorption isotherm eq. (6) for CO_2 and C_3H_8 on Vycor at 20 °C (from single component data)

	$10^5 q_{sat,CO_2}$ (mol cm^{-3})	b_{CO_2} (bar^{-1})	$10^5 q_{sat,C_3H_8}$ (mol cm^{-3})	$b_{C_3H_8}$ (bar^{-1})
$q_{sat,CO_2} \neq q_{sat,C_3H_8}$	158.7	0.961	199.1	0.327
$q_{sat,CO_2} = q_{sat,C_3H_8}$	170.0	0.854	170.0	0.401

Table 2
DGM parameters (eqs. (1) and (2)) of Vycor glass determined from experiments with inert gases

$10^{18} \times B_0$ (m^2)	1.748
$10^{11} \times K_0$ (m)	6.346
ε/τ (−)	0.039

other experiments with inert gases, the three structural parameters of the DGM, K_0, B_0 and ε/τ, could be determined by matching experimental and theoretical (eqs. (13)–(15)) transients. The results are summarized in Table 2. The obtained estimates for K_0 and ε/τ agree quite well with the values determined in the previous study [8]. A larger difference was found for the permeability constant B_0. This might be due to the fact that the contribution of viscous flux to the overall mass transfer is very small and the sensitivity of the total flux to B_0 is low. A further reason might be the fact that a different batch of membranes was used for the present investigations. With the parameters obtained, the predicted transients (the solid curves in Fig. 4) are in a good agreement with the observations. This supports the validity of the model applied as well as the parameter estimates.

For the exchange of the inert gas He and the adsorbable gas CO_2, a pronounced asymmetry between two subsequent exchange experiments was observed as illustrated in Fig. 5 (note the difference in the maxima). In order to describe these curves, it was found necessary to include contributions of surface diffusion to the overall flux (eq. (5)). This is in agreement with results presented in ref. [8]. Using the parameters of the DGM and the single component Langmuir isotherm equation only the surface diffusivity $D^s_{CO_2}$ was determined from the observed transients. The obtained values $D^s_{CO_2} = 1.71 \times 10^{-9}\ m^2\ s^{-1}$ is again in good agreement with results obtained earlier [8]. Using this value leads to relatively good agreement between the calculated and observed transients (Fig. 5). Based on a more detailed analysis of the profiles of gas phase and surface diffusion fluxes using eqs. (13)–(15), it can be concluded that during these experiments both gas phase and surface diffusion contributed to the overall flux.

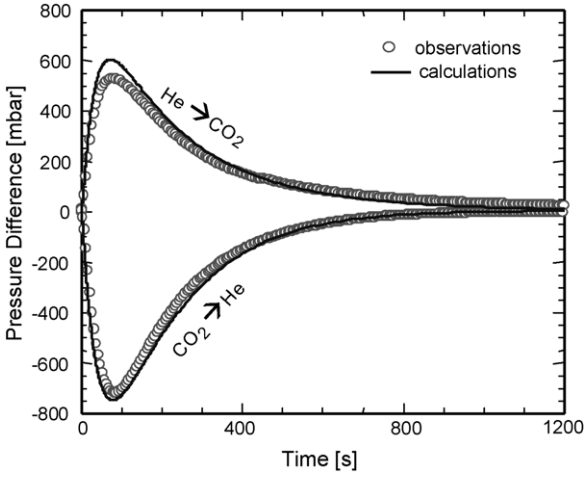

Fig. 5. Observed and calculated (eqs. (13)–(15)) results for the exchange of an inert gas (He) and an adsorbable gas (CO_2).

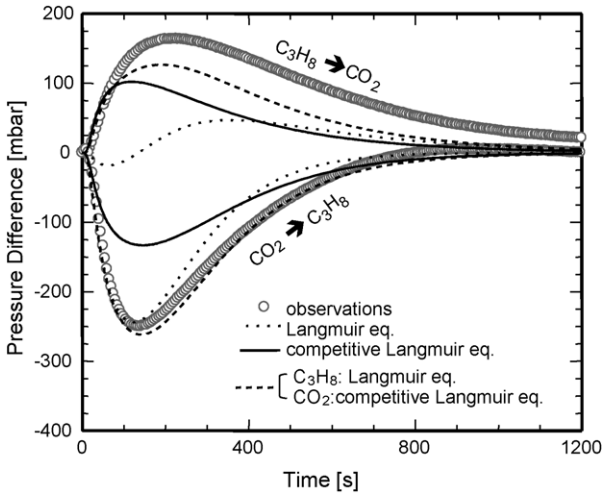

Fig. 6. Observed and calculated (eqs. (13)–(15)) results for the exchange of the two adsorbable gases C_3H_8 and CO_2. (symbol: (○) observations; dotted lines, Langmuir eq. (6) for both components; solid lines, competitive Langmuir eq. (7) for both components; dashed lines, single component Langmuir eq. (6) for C_3H_8 and competitive Langmuir eq. (7) for CO_2).

For the exchange of the two adsorbable gases C_3H_8 and CO_2 an even more pronounced asymmetry between two corresponding reverse experiments was observed, as shown in Fig. 6. Using the DGM and the GMS model, it was attempted to describe these measurements. For this the surface diffusivity of $D^s_{C_3H_8}$ as determined in ref. [8] was used as an additional parameter. The calculations were performed for different combinations of the adsorption isotherms with eqs. (6) and (7). As revealed in Fig. 6, all these calculations show a systematic disagreement compared to the observations. The dotted curves were obtained using the single component Langmuir adsorption isotherm (eq. (6)) for both components. In this case, the overestimation of the amount of adsorbed CO_2 (Fig. 3b) results in an underestimation of the pressure difference for substitution of CO_2 by C_3H_8 and in an overestimation for the reverse experiment. The solid curves were calculated using the competitive Langmuir model (eq. (7)) for both components. As could be seen in Fig. 3b, also this adsorption model does not lead to satisfying results. For the third case, where the single component Langmuir equation is used to describe C_3H_8 adsorption and the competitive Langmuir equation for CO_2 adsorption, a better agreement is achieved between predicted pressure responses (dashed curve) and the observations (open circles).

As can be concluded from the results presented in Fig. 6, the adsorption equilibrium functions have a pronounced effect on the course of the pressure responses in such transient diffusion experiments if they are performed with adsorbable gases. A better quantitative description of the results apparently requires a more accurate isotherm models than provided by eqs. (6) and (7).

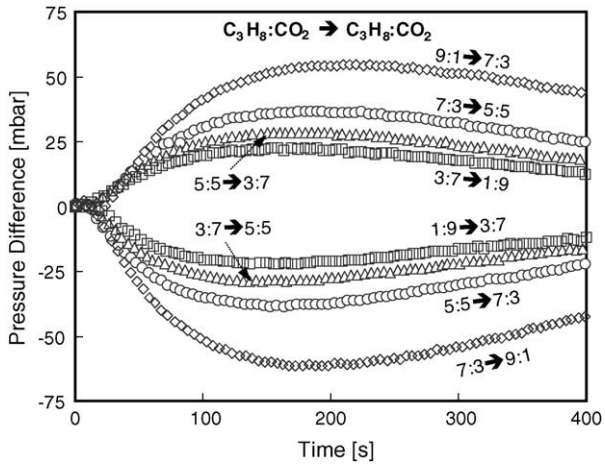

Fig. 7. Observed transients for the exchange of C_3H_8 and CO_2 (various composition ratios).

In Figs. 7 and 8, two more experimental results are depicted. As shown in Fig. 7, it was observed that the shape of the pressure responses depend strongly on the composition of gases 1 and 2 before and after introducing the initial perturbation. This is exemplified for experiments with different C_3H_8/CO_2 mixtures. During the exchange experiments performed, the partial pressure was always changed in steps of 0.2 bar. Thus, the initial partial pressure differences of C_3H_8 or CO_2 realized were always the same. Fig. 7 reveals that there is a strong effect of the gas phase composition on the shape of the transients. This is clearly related to the complicated shape of the competitive adsorption isotherms, which must be known in order to simulate precisely the observed behavior. In contrast, such measured responses seem to contain enough information in order to solve inverse problems and to determine adsorption equilibrium data.

Finally, in Fig. 8, responses of exchange experiments with the two adsorbable gases C_3H_8 and C_4H_{10} are shown.

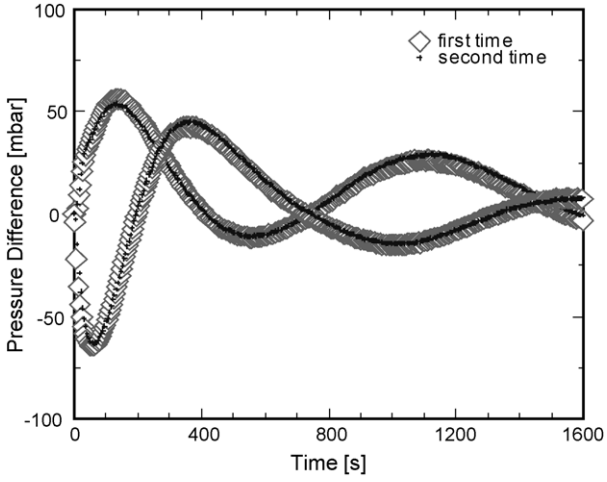

Fig. 8. Observed transients for the exchange of the two adsorbable gases C_3H_8 and C_4H_{10} (measured twice to demonstrate the reproducibility).

These transients possess moments where the pressure difference becomes zero. Obviously distinct fronts travel through the membrane and break through at characteristic times. A more quantitative analysis is currently underway. It should be mentioned that the results could be reproduced very well, as shown in Fig. 8 for the $C_4H_{10} \leftrightarrow C_3H_8$ transients. They confirm again the fact that the dynamics of membrane processes might be quite complex if adsorbable components are involved.

5. Conclusions

Transient diffusion experiments were conducted with a Vycor glass membrane for different inert and adsorbable gases. In addition, adsorption equilibrium data were determined experimentally. The attempt to quantify the observed competitive adsorption isotherms gives strong indication of non-idealities in the adsorbed phases. The observed pressure responses become asymmetrical if adsorbable gases are present. The shapes of the responses depend strongly on concentration and might be quite complex. The Dusty Gas Model and the Generalized Maxwell–Stefan equations appear to be capable of quantifying the observed dynamic behavior for the non-adsorbable and inert-adsorbable systems. However, a successful application requires more reliable knowledge regarding the mixture adsorption equilibria. The results reveal the significant contribution that surface diffusion might add to overall mass transfer. They are considered as another example demonstrating the difficulty of an adequate description of mass transfer through porous media. In general, care should be taken when evaluating the kinetic compatibility of reaction and mass transport required to develop membrane reactors.

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