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Transport through zeolite filled polymeric membranes

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Abstract

In this paper the effect of zeolite particles incorporated in rubbery polymers on the pervaporation properties of membranes made from these polymers is discussed. Pervaporation of methanol/toluene mixtures was carried out with membranes prepared from the toluene selective polymer EPDM and the methanol selective polymers Viton and Estane 5707. From the results of the pervaporation experiments it could be concluded that the addition of the hydrophilic zeolite NaX as well as the hydrophobic zeolite silicalite-1 leads to an increase in methanol flux and a decrease in toluene flux through the membranes. Pervaporation experiments with bi-layer membranes consisting of an unfilled polymer layer and a polymer layer filled with zeolite particles demonstrated that the effect of addition of particles depends on their position in the membrane. Furthermore, the component flux through the membranes as a function of the volume fraction of zeolite is modelled with existing theories describing the permeability of heterogeneous materials. The results show that the apparent permeability of the dispersed phase is lower than the intrinsic permeability of the dispersed phase when the flux through the particle is restricted by the polymer phase. This phenomenon was confirmed by numerical simulation of the transport in the membrane through a plane parallel to the transport direction. The simulations are carried out for an unfilled membrane, a membrane filled with an impermeable particle, a rubber particle and with a particle which shows Langmuir sorption behaviour. The reason for the discrepancy between the apparent permeability and the intrinsic permeability is that the apparent permeability of the zeolite phase is calculated by dividing the flux with the driving force over the entire membrane which is larger than that over the particle. In case of numerical simulation the concentration in every position in the plane is known and therefore the intrinsic permeability of the filler can be calculated on basis of the actual driving force. This treatment results in a permeability which is correct over several orders of magnitude.

Keywords: Transport; Zeolite; Pervaporation

1. Introduction

The effect of zeolite particles incorporated in a polymer on transport properties of membranes made from these polymers has been described in several publications [1–4]. Most of the work described in the literature deals with the pervaporation of aqueous mixtures or with the separation of gases.

In the present paper the separation of two organic solvents, i.e. methanol and toluene by means of pervaporation using rubbery polymers containing zeolite particles will be discussed. The reason for selecting rubbery polymers for this study is that preliminary tests have shown that it is difficult to prepare defect-

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free membranes from glassy polymers with incorporated zeolites due to insufficient adhesion between the polymer and the zeolite particles. From the two solvents used in the feed mixture, methanol is the more polar molecule and it has smaller molecular diameter than toluene [5]. Therefore it can be expected that the incorporation of a hydrophilic zeolite in a polymer will lead to an increase in its methanol selectivity. Thus, the incorporation of such a zeolite into a polymer to improve its methanol selectivity is only useful if the polymer matrix itself is methanol selective. This means that for the preparation of methanol selective membranes a polar polymer should be used. However, most polar polymers have a glassy structure and are thus not very well suited for the preparation of zeolite filled membranes. A polymer screening was carried out in order to find a methanol selective rubber and two polymers were selected, i.e. Viton B, which is a fluorocarbon polymer and Estane 5707 which is a polyurethane.

The effect of the zeolite particles incorporated in a membrane on the selectivity of the membrane depends on the intrinsic properties of the zeolite. Hydrophilic zeolites will be methanol selective while more hydrophobic types will most likely be toluene selective. In this study two different zeolites have been used. One was the hydrophobic zeolite silicalite-1 which is sorption selective for toluene at small toluene concentrations. The other is the zeolite NaX which is methanol selective over the entire concentration range of the feed mixture. This is demonstrated by sorption tests which were carried out with the pure zeolites and a methanol/toluene feed mixture. The results are given in Fig. 1 where the methanol depletion of the solution is shown as a function of the methanol concentration in the solution. The methanol depletion is defined as the initial methanol concentration in the solution minus the equilibrium methanol concentration obtained after addition of 4.35 g silicalite-1 or 3.60 g NaX to 10 g of MeOH/toluene mixture. When the depletion is 0, i.e. the composition of the mixture is identical before and after the addition of the zeolite, there is no selective sorption. When the depletion is positive the zeolite is methanol selective, when it is negative the polymer sorbs toluene preferentially. Fig. 1 shows that the methanol depletion is decreasing with increasing methanol concentration in the initial solution for both zeolites. This behaviour has also been observed by others [6–8]. Because silicalite-1 is toluene selective at high methanol concentrations, incorporation of this zeolite might lead to an increase in toluene flux. Therefore experiments were carried out also with zeolite filled membranes made from the toluene selective EPDM rubber which is a copolymer of ethylene and propylene.

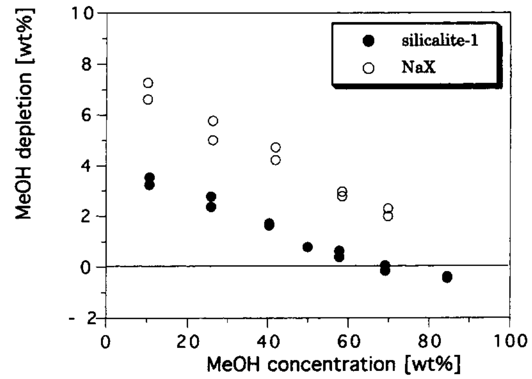

Fig. 1. Results of depletion tests with silicalite-1 and NaX in mixtures of methanol and toluene.

2. Experimental

2.1. Materials

Two zeolites are studied. The hydrophillic zeolite NaX was purchased from Aldrich and had an average particle size of 2.5 μm. It is a Faujasite and has cylindrical pores formed by a 12-membered ring. The pore diameter is 0.74 nm and the Si to Al ratio is 1.2. The hydrophobic zeolite silicalite-1 was supplied by Union Carbide and had comparable dimensions. It has straight rectangular pores of 0.52×0.57 nm in one direction and the ratio of Si to Al was infinite [5]. For gravimetric sorption experiments, large coffin-type silicalite-1 crystals of 50 μm length supplied by Mr. J.P. Verduijn of Exxon Basic Chemical Technology were used. In the case of NaX small crystals (2.5 μm) were used. The zeolites were activated by heat treatment to remove residual contaminants or in the case of silicalite-1, to remove the template compound. Silicalite-1 was activated at 500°C and NaX at 350°C. After activation the zeolites were stored under vacuum at 30°C.

2.2. Membrane preparation and characterization

Pure polymer membranes were prepared by dissolving the polymer in a suitable solvent. EPDM was dissolved in *n*-hexane and Viton and Estane in THF. The solutions were cast on a glass plate and the solvent was evaporated at room temperature by nitrogen flushing. Zeolite filled membranes were prepared in a similar way except that a dispersion of zeolite particles in the solvent was added to the polymer solution. The mixture was stirred over night to obtain a homogeneous casting solution. Scanning Electron Microscopy (SEM) and density measurements were used to check whether the obtained membranes were free of defects. SEM-photographs indicate that there are no macroscopic voids. Comparing the experimentally determined density of the zeolite filled membrane with data calculated from the densities of the polymer and the zeolite and their weight fractions also indicated that the membranes were without voids. For NaX the highest volume fraction which could be reached without introducing defects was 0.47 in the case of EPDM, 0.45 in the case of Viton and 0.55 in the case of Estane. Silicalite-1 was only incorporated in EPDM and the highest achievable volume fraction was 0.54.

2.3. Pervaporation experiments

Pervaporation experiments were carried out at 30°C on a standard pervaporation set-up described elsewhere [9]. The permeate pressure was kept below 1 mbar by means of a vacuum pump. The flux was measured by weighing the permeate collected in a cold trap cooled with liquid nitrogen. The effective membrane area was 50.3 cm^3. All fluxes are normalized to a membrane thickness of 100 μm. A HayeSep Q column in combination with a thermal conductivity detector (TCD) was used to analyse both the feed and permeate compositions by means of gas chromatography with an accuracy better than 0.2 wt%.

2.4. Sorption experiments

Sorption from the liquid phase was determinated by immersing a polymer film in the pure liquid to determine the sorption of the pure components, or in a mixture of methanol and toluene to determine the preferential sorption. The sorption is defined as the weight increase divided by the original sample weight. Furthermore, gravimetric sorption experiments were carried out from the vapour phase in order to determine the sorption in a zeolite or polymer as a function of the activity. The set-up used for these experiments is shown schematically in Fig. 2. Two mass flow controllers are used to control the flow rate of two nitrogen streams (purity >99.99%). One of the streams is saturated with a vapour in a thermostated bath. The two nitrogen streams are mixed and fed in a thermostated electrobalance. The activity of the vapour is a function of the ratio of the two nitrogen streams and the temperatures in the liquid and in the balance, respectively. The activity can be instantaneously altered by changing the two flow rates. The total flow velocity of the gas mixture through the balance is kept constant in order to maintain a constant upward drag force on the sample. The sample weight is monitored continuously and recorded. In the case of sorption of organic components, the sorption of nitrogen in a polymer sample can be neglected [10]. This also applies to the zeolite, since the interaction between zeolite and organic component is much larger than the interaction between zeolite and nitrogen [5]. All sorption measurements were carried out at 30°C.

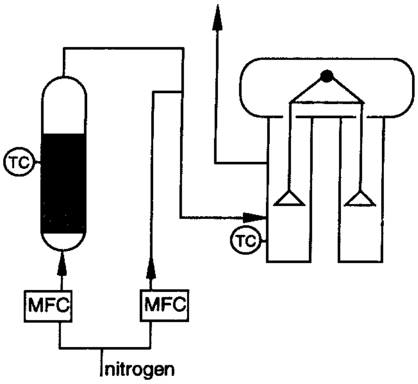

Fig. 2. Schematic diagram illustrating the set-up used for sorption measurements (MFC, mass flow controller; TC, temperature controller).

The sorption isotherm is obtained by a stepwise increase of the activity of the vapour. For polymers and the large silicalite-1 crystals, also the diffusion coefficients were determined using Eq. (1) [11].

$$\frac{\Delta m_t}{\Delta m_\infty} = \frac{2A}{V}\frac{\sqrt{D_c t}}{\pi} \qquad (1)$$

Here m_t and m_∞ are the mass uptake at time t and at equilibrium respectively, A is the surface area and V the volume of the sample, D_c is the diffusion coefficient and t the time. Eq. (1) is only valid for constant diffusion coefficients and for diffusion in infinite media or in finite media for a short period of time [12].

If the ratio m_t/m is plotted as a function of the square root of time, the initial slope will be linear in the case of Fickian diffusion. It can be seen that in the case of a thin polymer film, the term A/V is equal to $2/l$ with l being the membrane thickness. Eq. (1) can be applied to both polymer and zeolite samples. In the case of polymer samples, care should be taken that the activity increase is small enough that the assumption of a constant diffusion coefficient over the small concentration range is valid. In the case of zeolite samples, the sample size should be small enough and the crystal size large enough to avoid transport limitations in the vapour phase [13]. For the large silicalite-1 crystals and for sample weights less than 8 mg, the measured diffusion coefficient appeared to be independent of the sample size. However, for the diffusion of methanol in the small NaX crystals, the calculated diffusion coefficient for a sample of 4.7 mg was a factor 5–8 lower than that obtained with a sample of 2.1 mg, indicating that in this case the conditions of a constant diffusion coefficient were not fulfilled.

3. Results of pervaporation and sorption experiments

Results of pervaporation and sorption experiments were performed with membranes prepared from EPDM, Viton and Estane 5707 filled with different zeolites. The feed solutions were mixtures of methanol and toluene. All experiments are carried out at room temperature unless indicated differently.

3.1. Test results obtained with EPDM membranes

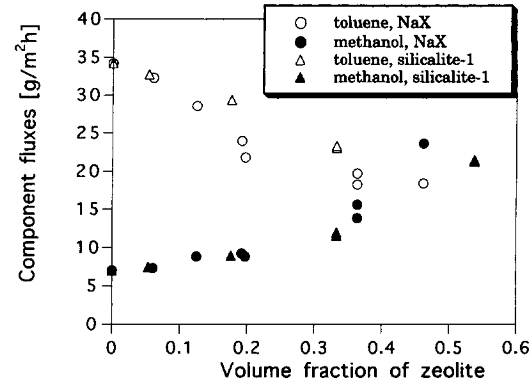

Fig. 3. MeOH and toluene fluxes through EPDM membranes as a function of the volume fraction of zeolite. (Feed 91.6 wt% MeOH in toluene.)

The pervaporation experiments were carried out with a feed mixture of 91.6 wt% of methanol in a mixture with toluene and membranes prepared from the pure polymer and from the polymer filled with particles of the zeolites NaX and silicalite-1 respectively.

3.1.1. Pervaporation results of zeolite filled EPDM-membranes

The component fluxes through the membranes are calculated from the selectivity and the overall flux and are shown in Fig. 3. It can be seen that incorporation of both NaX and silicalite-1 leads to a decrease of the toluene flux and an increase of the methanol fluxes. Therefore a decrease of the toluene selectivity is found. The results are shown in Fig. 4. The sum of the component fluxes varies slightly between 42 and 32 g m^{-2}h^{-1}.

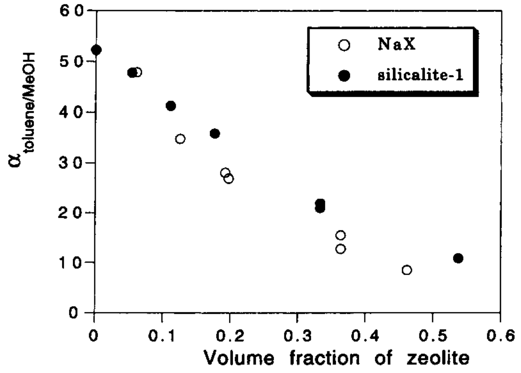

Fig. 4. Selectivities of EPDM membranes as a function of the volume fraction of zeolite. (Feed 91.06 wt% MeOH in toluene.)

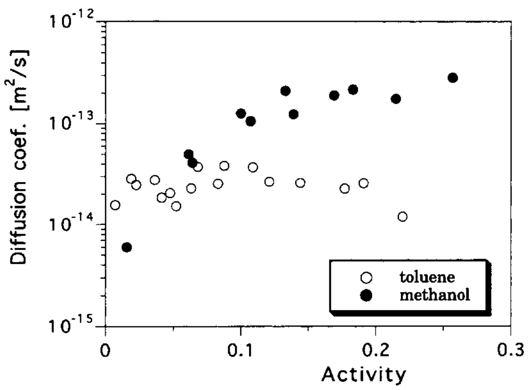

Fig. 5. Diffusion coefficients of methanol and toluene in silicalite-1 as a function of solvent activity. (The experiments were carried out at 40°C.)

Two pervaporation experiments were carried out with pure methanol as feed in pure EPDM and in EPDM filled with 54 vol% of silicalite-1. The flux through the EPDM membrane increases from 13 to 180 g m^{-2} h^{-1} when 54 vol% of silicalite-1 is added. These results confirm the fact that the methanol transport is indeed enhanced by the incorporation of silicalite-1. Similar experiments with toluene could not be performed since the EPDM membrane was not stable in pure toluene.

3.1.2. Sorption and diffusion in zeolites and mixed matrix membranes

To get more information about the transport process in zeolite filed membranes, sorption and diffusion measurements were carried out. Fig. 5 shows the diffusion coefficients of methanol and toluene in silicalite-1 as a function of the activity at 40°C. It can be seen that methanol diffuses much faster in zeolite than toluene. Similar results are found for the zeolite NaX. These latter results, however, are not shown here since they were obtained with very small crystals and therefore the obtained diffusion coefficients might be affected by the transport limitations in the vapour phase.

Sorption experiments using zeolites/polymer composites proved that the equilibrium sorption in the composite is the sum of the sorption in the two phases. Similar effects were found by Kemp et al. [1], Duval et al. [2], and Bartels et al. [3]. This means that for polymers with a low affinity for methanol the sorption in the zeolite filled polymer is generally enhanced. Since these equilibrium sorption measurements are steady state values, no conclusions can be drawn with respect to the sorption under permeation behaviour. However, te Hennepe [4] showed that for the system propanol/water also the propanol sorption under permeation conditions is enhanced by the presence of the zeolite.

3.1.3. Pervaporation with bi-layer EPDM membranes

For a pervaporation membrane, the permeability of the rubber is high at the feed side and low at the permeate side due to swelling of the polymer at the feed side. Duval [4] showed that the zeolite permeability calculated by a model that describes the permeability of heterogeneous media is a function of the polymer permeability. This so-called apparent zeolite permeability can not be regarded as the intrinsic zeolite permeability. However, the flux through the zeolite phase often increases with increasing polymer permeability. This means that for the zeolite filled EPDM membranes studied in this work, the effect of a zeolite particle should be a function of its position in the membrane. In order to investigate whether this is true or not, four bi-layer membranes were prepared. The membranes consisted of a pure rubber layer of about 100 μm and a layer with 40 wt% (28 vol%) NaX filled rubber of about 110 μm. The two layers were pressed together and tested. Two of these bi-layer membranes were tested with the zeolite filled layer at the permeate side and two others with the zeolite filled layer at the feed side. The total flux of these membranes is given in Fig. 6. The selectivities and the component fluxes are listed in Table 1. Because the thickness of the bi-layer membranes could not be determined accurately, one should be critical about the absolute flux values.

From the results shown above, it can be concluded that the zeolite acts more strongly on the methanol selectivity when it is situated at the permeate side. NaX hinders the toluene flux by a tortuosity effect.

3.2. Test results obtained with Viton membranes

From the membrane characterization tests it was concluded that the adhesion between the zeolite and the polymer in the case of silicalite-1 filled Viton

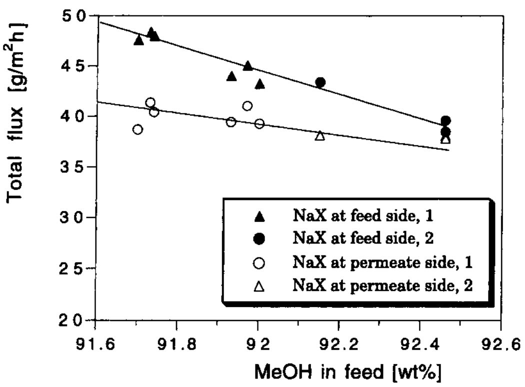

Fig. 6. Total flux of bi-layer membranes as a function of the methanol concentration in the feed mixture. EPDM with 40 wt% NaX.

Table 1
Selectivity and component fluxes of bi-layer membranes

Membrane	$\alpha_{\mathrm{toluene/MeOH}}$ [–]	Toluene flux [g m^{-2} h^{-1}]	Methanol flux [g m^{-2} h^{-1}]
NaX at feed side, membr. 1	43.6±0.5	39.4	9.8
NaX at feed side, membr. 2	40.1±1.7	38.6	10.5
NaX at permeate side, membr. 1	28.4±0.2	29.4	11.2
NaX at permeate side, membr. 2	26.7±1.1	28.8	11.8
Pure EPDM membrane	53.0	34.2	7.0

membranes is insufficient. Therefore no pervaporation experiments were carried out with this membrane. The results of the NaX filled membranes using a feed mixture of 30 wt% methanol in toluene are given in Figs. 7 and 8. The selectivity increases with a factor of about three as a result of the increase in the methanol flux and the decrease in the toluene flux. The total flux slightly increases from 22 to 28 g m^{-2} h^{-1}. The pervaporation results for methanol/toluene mixtures are similar to those of pervaporation experiments using pure components as the feed. The results are given in Table 2.

3.3. Test results obtained with Estane 5707 membranes

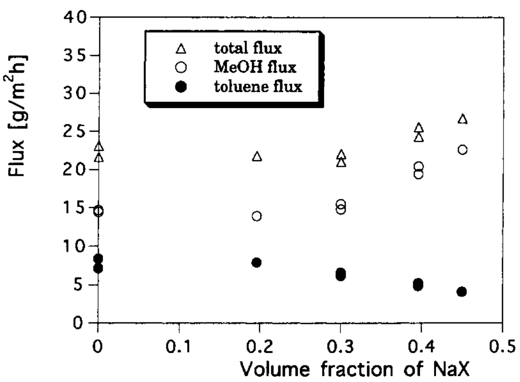

Fig. 7. Total and component fluxes of a MeOH/toluene mixture (30/70 wt% ratio) through Viton membranes as a function of the volume fraction of NaX.

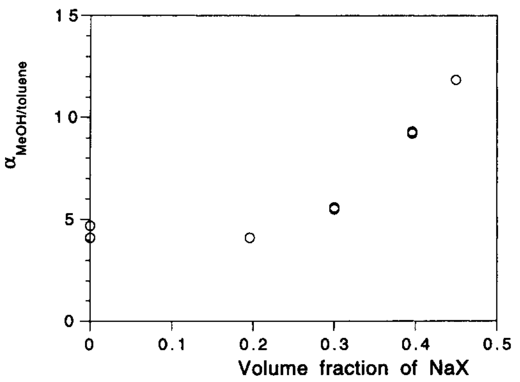

Fig. 8. Selectivity of Viton membranes as a function of volume fraction of NaX. (The feed mixture used is MeOH/toluene, 30/70 wt% ratio.)

Table 2
Results of pervaporation experiments with pure components and a mixture of 30 wt% methanol in toluene

Membrane	Methanol flux [g m^{-2} h^{-1}]	Toluene flux [g m^{-2} h^{-1}]
Pure components		
Viton, not filled	12.0±2.0	4.3±0.4
Viton + 40 vol% NaX	16.2±1.2	2.7±0.3
Mixture of 30 wt% methanol in toluene		
Viton, not filled	15	8
Viton + 40 vol% NaX	20	5

Pervaporation tests were carried out with NaX filled Estane 5707 membranes with the pure components and mixtures containing 5, 10 and 15 wt% methanol in toluene. In Fig. 9 the selectivity of Estane 5707 membranes is shown as a function of the volume fraction of zeolite NaX in the membrane. In Fig. 10 the fluxes of the different component and the total flux

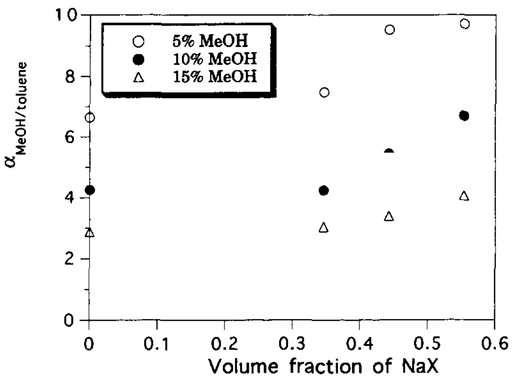

Fig. 9. Selectivity of Estane 5707 membranes as a function of the volume fraction of NaX for various methanol concentrations in the feed.

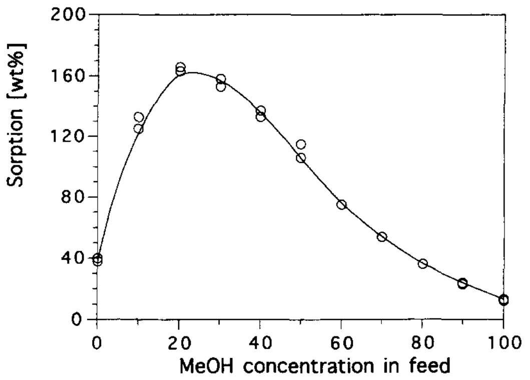

Fig. 11. Equilibrium sorption determined for Estane 5707 as a function of the methanol concentration in the feed.

are shown as a function of feed concentration for various amounts of NaX.

The fluxes through the membranes depend strongly on the methanol/toluene ratio in the feed. In Fig. 11 the equilibrium sorption in Estane 5707 is plotted as a function of the methanol content in the feed. The curve clearly demonstrates that the equilibrium sorption increases with the same trend as the flux does up till methanol concentrations of 20 wt%.

Furthermore, Fig. 10 shows that the methanol flux is not very much dependent on the degree of filling at the feed concentrations measured. This means that the flux through the zeolite phase must be equal to the flux through the polymer phase even when this last one

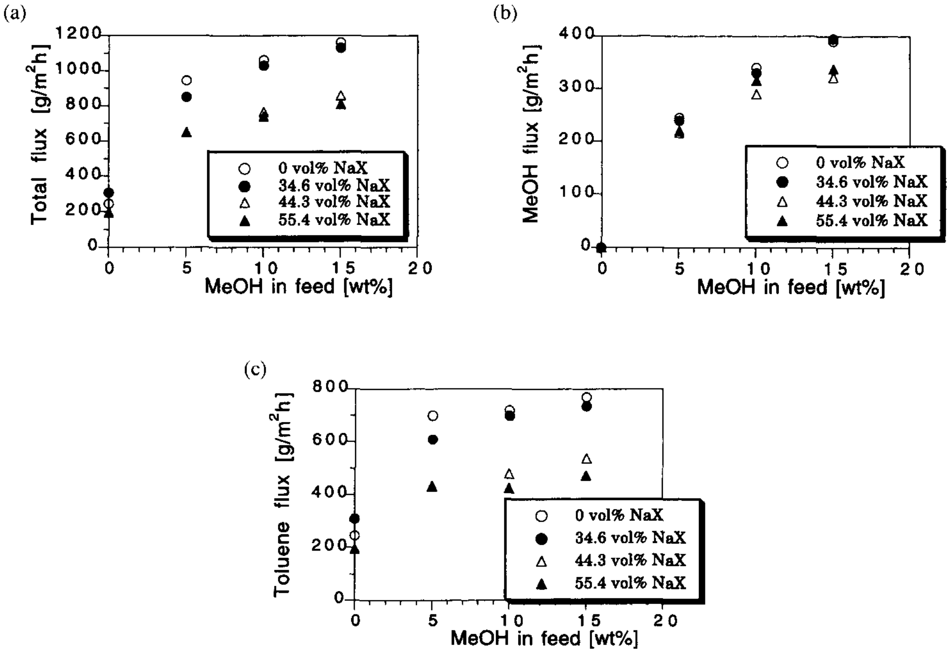

Fig. 10. Fluxes through Estane 5707 membranes as a function of methanol concentration in the feed for various filling degrees with zeolite NaX. Total flux (a), methanol flux (b) and toluene flux (c).

Table 3
Results of pervaporation experiments with bi-layer membranes consisting of a layer of Estane 5707 and Estane 5707 filled with 40 wt% NaX (34 vol%). The feed mixture contains 10 wt% methanol in toluene

Membrane with zeolite at:	$\alpha_{MeOH/Tol}$ [–]	Total flux [g m^{-2} h^{-1}]	Methanol flux [g m^{-2} h^{-1}]	Toluene flux [g m^{-2} h^{-1}]
Feed side	4.35	1020	332	688
Permeate side	5.75	932	363	569
Pure Estane 5707	4.2	1070	340	730

increases. This effect will be discussed extensively in the second part of this paper.

3.3.1. Test results obtained with bi-layer membranes made from Estane 5707

For membranes made from EPDM it was shown that the effect of a zeolite particle depends on its position in the membrane. To study the effect of the position of the zeolite particles in membranes made from Estane 5707 bi-layer membranes were also prepared from this polymer and tested. The results are given in Table 3.

The results are roughly compared to the results obtained with the EPDM membranes. The bilayer membrane becomes more methanol selective when the zeolite is situated at the permeate side due to the strong decrease of the toluene flux in that case.

4. Modelling of the pervaporation results

In the first part of this paper the results of pervaporation experiments with zeolite filled membranes were presented. Experiments with bi-layer membranes show that the effect of incorporation of a zeolite particle on the over-all transport through the membrane depends on its position in the membrane.

In order to get more insight in the transport phenomena in zeolite filled membranes, the pervaporation results can be modelled by equations describing the transport through dispersed systems. Furthermore, the transport through rubber containing filler material will be simulated using a 2-dimensional representation of the membrane.

4.1. Theoretical considerations

There are various models describing mass transport through dispersed systems all of them having their advantages and drawbacks. Two models will be used here. The first one Eq. (2) was originally developed by Maxwell to describe a dispersion of spheres in a continuum if their mutual distance is large enough that flow lines do not interfere with each other.

$$\frac{\mathbb{P}_\mathrm{i}}{\mathbb{P}_\mathrm{r}} = 1 + 3\phi_\mathrm{z}\left(\frac{\alpha+2}{\alpha-1} - \phi_\mathrm{z}\right)^{-1} \quad \text{and} \quad \alpha = \frac{\mathbb{P}_\mathrm{z}}{\mathbb{P}_\mathrm{r}} \tag{2}$$

with $\mathbb{P}_\mathrm{i}$, $\mathbb{P}_\mathrm{z}$, and $\mathbb{P}_\mathrm{r}$ being the permeabilities of the composite, the zeolite and the polymer respectively, while ϕ_z represents the volume fraction of filler in the membrane.

Petropoulos [15] showed that Eq. (2) is also valid for higher volume fractions of dispersed particles.

The second equation that will be used was derived by te Hennepe [4] to describe results of pervaporation experiments using silicone–rubber membranes filled with silicalite-1. This model is represented by Eq. (3).

$$\mathbb{P}_\mathrm{i} = \frac{1}{\left(\frac{(1-\phi_\mathrm{z}^{1/3})}{\mathbb{P}_\mathrm{r}} + \frac{3/2\phi_\mathrm{z,i}^{1/3}}{\mathbb{P}_\mathrm{r}(1-\phi_\mathrm{z})+3/2\mathbb{P}_\mathrm{z}\phi_\mathrm{z}}\right)} \tag{3}$$

Duval [14] used these models to calculate the permeability of CO_2 in silicalite-1, in case the silicalite was incorporated in rubbers having a different permeability for CO_2. He also used the geometrical mean model represented by Eq. (4). His results are repotted in Fig. 12.

$$\ln(\mathbb{P}_\mathrm{i}) = \phi_\mathrm{z}\ln(\mathbb{P}_\mathrm{z}) + 1 - \phi_\mathrm{z}\ln(\mathbb{P}_\mathrm{r}) \tag{4}$$

Since the calculated zeolite permeability is a function of the permeability of the polymer matrix, it can be concluded that the calculated permeability is an 'apparent' permeability and not the intrinsic permeability.

The meaning of the 'apparent' permeability becomes more clear when the fluxes through the composite materials are considered instead of the permeabilities.

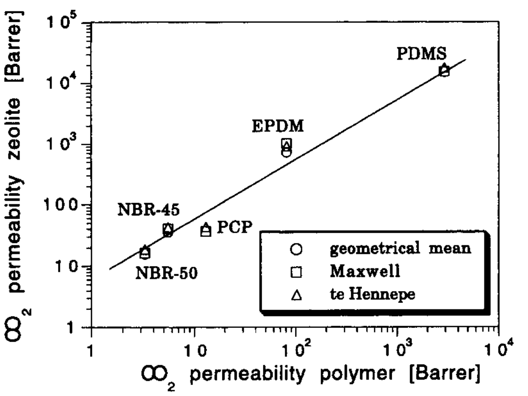

Fig. 12. Calculated CO_2 permeability of the zeolite as a function of the CO_2 permeability of the polymer phase, redrawn from [2]. NBR-50, NBR-45, nitrile butadiene rubber with 50 and 45 nitrile content; PCP, polychloroprene; EPDM, ethylene–propylene rubber; PDMS, polydimethylsiloxane.

The flux through a plane in the mixed matrix membrane perpendicular to the transport direction is the sum of the flux through the zeolite phase and the polymer phase. If the dispersed phase has a different permeability than the polymer matrix, there will be a flux towards or around the filler particle. These kinds of geometrical considerations are taken into account in the derivation of the following Eqs. (5) and (6), which describe the apparent component flux through the zeolite phase.

$$\frac{J_\mathrm{i}}{J_\mathrm{r}} = 1 + 3\phi_\mathrm{z}\left(\frac{\alpha+2}{\alpha-1} - \phi_\mathrm{z}\right)^{-1} \text{and}\, \alpha = \frac{J_\mathrm{z}}{J_\mathrm{r}} \tag{5}$$

$$J_\mathrm{i} = \frac{1}{\left(\frac{(1-\phi_\mathrm{z}^{1/3})}{J_\mathrm{r}} + \frac{3/2\phi_\mathrm{z,i}^{1/3}}{J_\mathrm{r}(1-\phi_\mathrm{z})+3/2J_\mathrm{z}\phi_\mathrm{z}}\right)} \tag{6}$$

Here J_i, J_p and J_z are the fluxes through the composite, the polymer phase and the zeolite phase respectively and ϕ_z is the volume fraction of zeolite. The two equations are similar to Eqs. (2) and (3) except that the permeability has been replaced by the flux. However, this does not mean that the two equations are identical. This would only be the case if the driving force expressed as concentration gradient, over the membrane is constant and the same as the driving force over the zeolite and polymer phase. This is, in general, not the case.

4.2. Results of modelling

For the polymers discussed in Section 3 of this paper, i.e. EPDM, Viton and Estane, the apparent fluxes through the zeolite phase in the membranes were calculated using Eqs. (5) and (6) and listed in Table 4. It should be realized that the results were obtained for different polymers and feed mixtures. In order to compare the results, the fluxes were normalized for an activity gradient of 1 over the membrane.

The data in Table 4 demonstrate the difference between silicalite-1 and NaX. NaX is methanol selective when incorporated in EPDM, while according to Eq. (6), silicalite-1 is toluene selective and according to Eq. (5) only slightly methanol selective.

Table 4

Experimental total flux through the pure polymer membrane and calculated fluxes through the zeolite phase for different polymer matrices. Fluxes are normalized to a thickness of 100 μm and an activity gradient 1

Feed mixture	Polymer	Zeolite	Experimental total flux through polymer [g m^{-2} h^{-1}]	Calculated MeOH flux [g m^{-2} h^{-1}]	Calculated toluene flux [g m^{-2} h^{-1}]	Selectivity[a]
Eq. (5):						
MeOH/tol. (91.4/8.6)	EPDM	NaX	42	121	4.9	24.7
MeOH/tol. (91.4/8.6)	EPDM	Silic.1	42	58	40	1.45
MeOH/tol. (30/70)	Viton	NaX	22	38	2.8	13.6
Eq. (6):						
MeOH/tol. (91.4/8.6)	EPDM	NaX	42	84	26	3.23
MeOH/tol. (91.4/8.6)	EPDM	Silic. 1	42	58	72	0.81
MeOH/tol. (30/70)	Viton	NaX	22	53	4.4	12.0
MeOH/tol. (5/95)	Estane	NaX	950	420	393	1.07
MeOH/tol. (10/90)	Estane	NaX	1050	501	448	1.12

[a] Selectivity is defined as the calculated MeOH flux divided by the calculated toluene flux

Furthermore, from Table 4 it can be concluded that the values of the flux through the zeolite phase vary over two orders of magnitude, despite the fact that the values are corrected for the differences in driving force over the membranes. The results indicate that the flux through the zeolite phase increases with increasing polymer permeability. It seems that the flux through the zeolite phase is limited by the flux through the polymer phase. This is in agreement with the aforementioned results of duval. This will be elucidated by numerical simulation discussed in the Section 5.

5. Numerical simulation of mass transport through membranes containing fillers; model description

5.1. Introduction

The mass transport through heterogeneous membranes containing particles with different mass transfer properties is discussed. Some results of calculations in homogeneous membranes which were carried out to check the validity of the model will be presented. Finally, mass transport through rubbery membranes filled with impermeable particles, rubber particles and zeolite particles respectively is discussed. The reason to incorporate calculations with rubber particles as well, is that transport through these particles is easy to calculate, contrary to the transport through a zeolite particle. Various parameters like volume fraction, permeability of the matrix polymer and the position of the particle(s) in the membrane are varied.

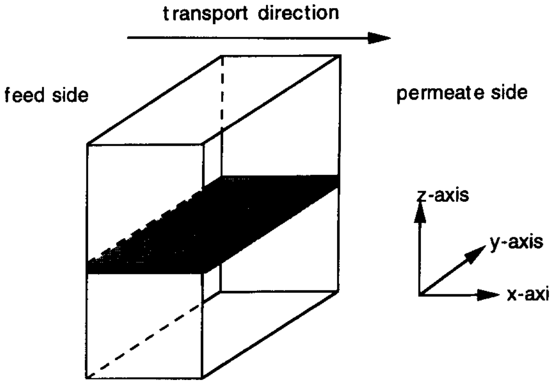

Fig. 13. Cross section of the membrane showing the *X*–*Y*-plane in which transport is taking place and in which the calculations are performed.

5.2. Development of the model

The model that is used in this chapter describes the transport in one plane in the membrane as shown in Fig. 13.

The plane is parallel to the overall transport direction i.e. the *X*-direction. The model describes transport *in* this plane and not *through* this plane, i.e. in two dimensions. The transport in the *z*-direction is not regarded.

The plane can then be divided into small cells between which transport can take place. The cells of the plane correspond with the cells of a spreadsheet as shown in Fig. 14. Each cell contains a numerical value which represents the concentration of a permeating component. The upper row in the spreadsheet (i.e. the *X*-coordinate equal to 1) corresponds with the feed

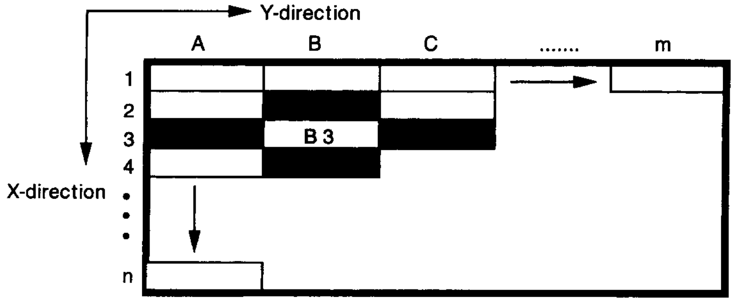

Fig. 14. Spreadsheet which represents the *X*–*Y*-plane in Fig. 2. The *X*-direction is the transport direction.

side of the membrane. Because equilibrium is assumed at the feed side, the concentration in the upper row is kept constant and is normalized to a value of 1. In the same way the lower row (i.e. $X=n$) will be kept at a constant value 0. Therefore a concentration gradient in the X-direction exists and transport will take place in this direction. In case of a homogeneous polymeric membrane there will be no concentration gradient in the Y-direction. So the concentration in cell B3 is only affected by the in-flux from cell B2 and the out-flux towards cell B4. However, for a polymeric membrane in which particles are dispersed which have a different permeability coefficient for the permeating component, this will not be the case.

Of course, the sum of the fluxes in the Y-direction should be zero. In order to fulfil this boundary condition and to avoid undesirable side effects at the edges of the plane (i.e. $Y=0$ or $Y=m$) these edges are coupled. This means that the concentration in cell A3 is not only affected by the in- and out-flow from cells A2 and A4, but also by the in- and out flow from cells B3 and m3. In fact the plane in the membrane has now become the outer shell of a cylinder. This is schematically shown in Fig. 15. It is assumed that the plane has a thickness dz and there exists no concentration gradient in the z-direction.

In case of a homogeneous membrane this assumption is valid. However, in case of a rubber matrix in which particles are incorporated which have different permeabilities, there will be a flow around the particle or towards the particle in case the particle is less or more permeable than the matrix. This means that mass transport will take place in all the three directions. This 3-dimensional problem can be simulated as well, simply by defining a 3-dimensional matrix. There are two disadvantages of this approach. First of all it is difficult to visualize the result. In case of calculations in a 2-dimensional plane, one extra axis is available to plot the concentration, concentration gradient or the flux as a function of the position in the plane. A second disadvantage of the 3-dimensional matrix is the larger number of cells that has to be calculated. This will lead to longer computation time which is needed to reach steady state conditions. Nevertheless, the two-dimensional model can describe the experimentally observed phenomena qualitatively and therefore can lead to a better understanding of transport in zeolite filled membranes.

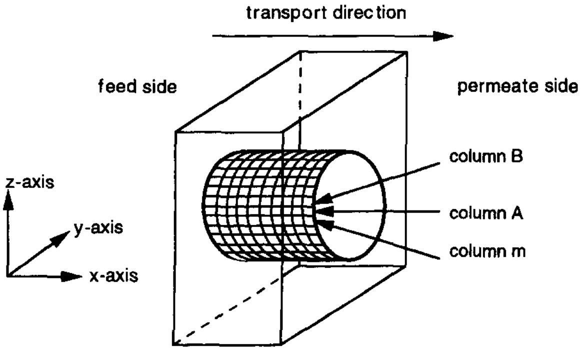

Fig. 15. Cross section of the membrane and the plane for which the calculations are carried out.

5.3. Transport equations

Fick's first law is used to describe mass transport between the cells in the plane [11]. First the equations that are used for calculations in homogeneous polymeric membranes are derived. Then, a rubbery particle is positioned in the plane which has different properties with respect to solubility and diffusivity of the permeating component. Therefore, equations which describe transport through the interface between the particle and the surrounding polymer matrix are derived as well. Finally, similar equations are derived to describe the transport into, through and out of a zeolite particle embedded in a polymer matrix.

5.3.1. Transport in homogeneous membranes

To start calculations, all cells will be given the concentration value 0, except for the first row ($X=0$). This row is assumed to be in equilibrium with the feed side. The concentration in this first row is defined as 1 in arbitrary units. Because of the concentration difference between the first and second row, mass transfer will take place between these two rows and the concentration in the second row will increase from 0 to a certain concentration value. This will then result in mass transfer from the second to the third row etc. In this way a new concentration profile throughout the membrane is calculated. Once the row before the last one has been calculated, one iteration step is finished. After a sufficient number of iterations, the concentration in the cells will remain constant and the steady state concentrations are reached.

The flux between two cells is described by Fick's first law, Eq. (7).

$$J = -D\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right) \tag{7}$$

in which J is the flux, D the diffusion coefficient and $\mathrm{d}c/\mathrm{d}x$ the concentration gradient.

The change in concentration for one iteration step in one cell can be described by Eq. (8)

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = c_{i+1} - c_i = D^* \sum_{i=1}^{4} \Delta c_i \tag{8}$$

in which $c_{i+1} - c_i$ is the concentration difference in a cell between iteration step $i+1$ and i. Applying these two equations to the spreadsheet and assuming a constant diffusion coefficient results in Eq. (9) for cell B3

$$\begin{aligned} \mathrm{B3}_{i+1} = \mathrm{B3}_i + D_{\mathrm{rubber}}[(\mathrm{A3}_i - \mathrm{B3}_i) + (\mathrm{B2}_i - \mathrm{B3}_i) \\ + (\mathrm{B4}_i - \mathrm{B3}_i) + (\mathrm{C3}_i - \mathrm{B3}_i)] \end{aligned} \tag{9}$$

in which $\mathrm{B3}_{i+1}$ is the concentration after iteration step $i+1$. In Eq. (9) the infinitely small time interval $\mathrm{d}t$ in Eq. (8) has been replaced by one iteration step and $\mathrm{d}x$ is replaced by the distance between two cells which is assumed to have the value 1 in arbitrary length units.

In case of steady state flux, the concentration in a cell does not change with time. This means that $\mathrm{B3}_{i+1}$ equals $\mathrm{B3}_i$, and therefore the steady state condition is defined by Eq. (10)

$$\mathrm{B3}_{i+1} = (\mathrm{A3}_i + \mathrm{B2}_i + \mathrm{B4}_i + \mathrm{C3}_i)/4 \tag{10}$$

Both Eqs. (9) and (10) will result in exactly the same concentration profile. The only difference is that by applying Eq. (10) less iterations are needed to reach steady state. From Eq. (10) it can be seen that the final concentration profile is independent of the diffusion coefficient. Therefore, the result of the iteration procedure which makes use of Eq. (9) should be independent of the diffusion coefficient results in a faster convergence towards the final concentration profile. However values for the diffusion coefficient of 0.5 and higher result in a strong oscillation of the numerical values in the spreadsheet.

Eqs. (9) and (10) are only valid for a constant diffusion coefficient. It is possible however to incorporate a diffusion coefficient which is dependent on the concentration.

5.3.2. Transport in rubbery membranes containing impermeable particles

If an impermeable particle is incorporated in the membrane, the concentration in the particle is assumed to be zero throughout the iteration process. Furthermore there is no transport from the polymer matrix towards the particle or vice versa. Eq. (9) can be used to calculate the concentration in a large part of the rubber matrix. However, if it concerns a cell in the polymer matrix next to the impermeable particle, mass transfer can be described by an equation which contains three terms since the cell of the impermeable particle does not contribute to mass transfer.

5.3.3. Transport in rubbery membranes containing rubbery particles

Eq. (9) is also valid for transport inside a polymeric particle which is incorporated in a rubber matrix. However, at the interface between matrix and particle there exists a discontinuity in concentration. This is caused by the fact that the Henry coefficient, which describes the sorption in a polymer as a function of activity or pressure, is different for the two polymers. If Henry sorption in both materials is assumed and if the activity or pressure of the permeating species in the cells between which the interface is situated is assumed to be equal, the difference in sorption in the particle and the surrounding matrix is given by a constant k. This constant k is the ratio of the two Henry coefficients of the two polymers. Fig. 16 gives an example of a spreadsheet in which a particle is incorporated. The shaded area represents the rubbery particle. The concentration of cell B4 can be calculated using Eq. (11)

$$\mathrm{B4}_{i+1} = \mathrm{B4}_i + D_{\mathrm{matrix}}\left[\mathrm{A4}_i + \mathrm{B3}_i + \mathrm{B5}_i + \frac{\mathrm{C4}_i}{k} - 4\mathrm{B4}_i\right] \tag{11}$$

The value k represents the jump in concentrations at the interface between particle and matrix. In case of steady state flux, there is another boundary condition that must be fulfilled. The flow from cell B4 towards the interface with cell C4 is equal to the flow from the interface towards cell C4. This boundary condition is met when Eq. (12) is used to calculate the concentration in cell C4.

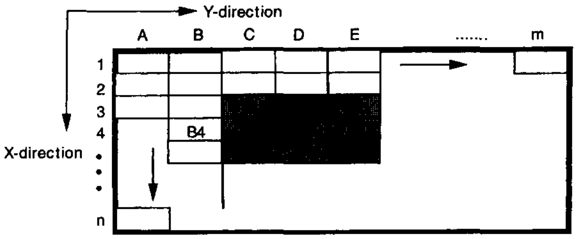

Fig. 16. Spreadsheet in which a rubbery particle is incorporated, which is represented by the shaded area.

$$\mathrm{C4}_{i+1} = \mathrm{C4}_i + D_{\mathrm{matrix}}\left[\mathrm{B4}_i - \frac{\mathrm{C4}_i}{k}\right] + D_{\mathrm{particle}}[\mathrm{C3}_i + \mathrm{C5}_i + \mathrm{D4}_i - 3\mathrm{C4}_i] \quad (12)$$

5.3.4. *Transport in rubbery membranes containing zeolite particles*

When a zeolite particle is incorporated there exists an equilibrium between the concentration in the polymer and the zeolite phase. In case of a rubber particle this equilibrium could easily be described by means of a constant because the sorption in both phases is assumed to be Henry mode sorption. However, in case of a zeolite particle the sorption in the particle may be properly described by a Langmuir equation. This results in more complex equations needed to calculate the concentration in the cells next to the interface. Nevertheless, the same principle is used as for the derivation of Eqs. (11) and (12). For cell B4 the concentration in cell C4 is not important but the activity is. The activity in cell C4 can be calculated from the concentration in cell C4, by assuming a Langmuir isotherm. Then this activity is multiplied by the Henry coefficient of the polymer matrix to calculate the concentration in cell C4 if it were a cell which is positioned in the matrix. Eqs. (13) and (14) can be derived from the calculation of the concentration in cells B4 and C4 in Fig. 16.

$$\mathrm{B4}_{i+1} = \mathrm{B4}_i + D_{\mathrm{matrix}}\left[\mathrm{A4}_i + \mathrm{B3}_i + \mathrm{B5}_i + \mathrm{C4}_i\left(\frac{K_{\mathrm{m}}}{K_{\mathrm{p}}b_{\mathrm{i}} - b_{\mathrm{i}}\mathrm{C4}_i}\right) - 4\mathrm{B4}_i\right] \quad (13)$$

$$\mathrm{C4}_{i+1} = \mathrm{C4}_i + D_{\mathrm{matrix}}\left[\mathrm{B4}_i - \mathrm{C4}_i\left(\frac{K_{\mathrm{m}}}{K_{\mathrm{p}}b_{\mathrm{i}} - b_{\mathrm{i}}\mathrm{C4}_i}\right)\right] + D_{\mathrm{particle}}[\mathrm{C3}_i + \mathrm{C5}_i + \mathrm{D4}_i - 3\mathrm{C4}_i] \quad (14)$$

In these equations K_{p} is the sorption in the zeolite particle at activity 1, K_{m} the sorption in the rubber matrix at activity 1 and b_{i} is the affinity constant from the Langmuir equation.

5.3.5. *Flux equations*

Once the concentration profile inside the membrane is known, it is possible to calculate the flux through the membrane. In case of homogeneous membranes this can be done easily because there is a concentration gradient in only one direction, i.e. the *X*-direction. The difference in concentration between two adjacent cells in the *X*-direction multiplied by the diffusion coefficient gives the transport rate. If these values are summed over the *Y*-coordinate, the total flux between two rows in the plane (and hence the flux through the membrane) is obtained.

In case of membranes in which particles are dispersed, there exists a concentration gradient in both *X*- and *Y*-direction. Therefore the flux in the two directions will be plotted in two separate graphs.

5.4. *Validity of the model*

The results of the model calculations should fulfil three conditions. First, in case of steady state, the flux through the membrane has to be independent of location on the *X*-coordinate. This means that the flux from row 1 towards row 2 in the spreadsheet is equal to the flux from row $n-1$ towards row n. If this is not the case this means that there is accumulation or depletion of mass in the membrane.

A second condition is that there is no net flux in the *Y*-direction of the plane. As mentioned before there exists mass transfer in the *Y*-direction but integration of these fluxes over the whole *Y*-axis should result in a total flux which is equal to zero.

Finally, if a particle is incorporated in the matrix with the same diffusion coefficient and Henry coefficient as the surrounding matrix, the result of the calculation should be the same as the result of an unfilled membrane.

6. Numerical simulation of mass transport through membranes containing fillers; results

6.1. Introduction

The results were obtained using a spreadsheet of 42×41 ($X\times Y$) cells in where in case of filled membranes a particle of 25×25 cells is incorporated. If the dimensions of the spreadsheet and the particle are increased, the total flux through the membrane remains constant. A smaller spreadsheet, e.g. 21×20 resulted in an over all flux which is significantly lower.

The iterative calculation was performed using Excel 4.0 since this program offers nice graphics which can be used to visualize the results. At least 1500 iterations were performed. Steady state is assumed when the flux as a function of the X-coordinate varies not more than 1 percent.

The results of the calculations will be divided in two parts. First the concentration profile and the flux profile in the plane in both X- and Y-direction will be presented and discussed in a qualitative way for various membranes with an without filler. Then the effect of particle size (i.e. volume fraction of filler), matrix permeability, permeability of the particle and position of the particle in the membrane on the total flux through the membrane will be investigated by varying these parameters.

6.2. Concentration profiles and flux profiles

For the unfilled membranes the excepted linear or convex profiles were obtained in case of a constant respectively exponential diffusion coefficient.

The flux through these membranes can be calculated by multiplying the concentration difference between two adjacent cells with the diffusion coefficient. Calculations confirmed that the flux is independent on the position in the plane. This is in agreement with the limiting condition that in the steady state there is no accumulation or depletion of mass in the membrane.

6.2.1. Rubbery membrane containing an impermeable particle

Fig. 17 shows the concentration profile of a rubbery membrane in which an impermeable particle is incorporated. The concentration in the particle is zero.

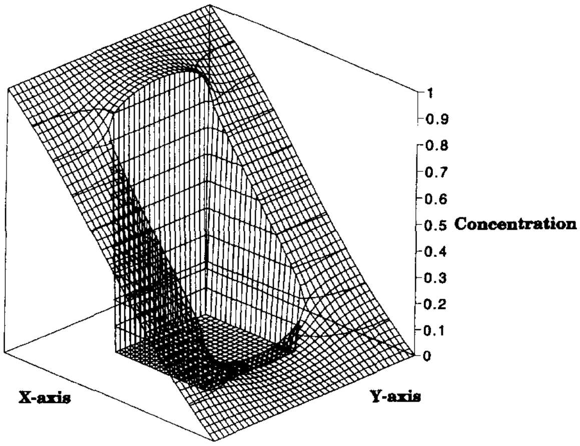

Fig. 17. Concentration profile in a rubbery membrane with an impermeable particle, $D_{\mathrm{matrix}}=0.1$.

If the concentration profile in the rubber matrix is compared to the profile in an unfilled membrane (not shown), it can be seen that at the feed side of the particle accumulation of mass takes place while at the permeate side of the particle depletion of mass takes place. Furthermore the plot shows that for the cells just beside the particle depletion of mass takes place. Furthermore the plot shows that for the cells just beside the particle the concentration gradient is steeper than anywhere else. Because the diffusion coefficient is constant this means that the flux through the cells next to the particle is the highest. This is confirmed by the flux profile in the X-direction as a function of the position in the plane which is given in Fig. 18 and the flux profile in the Y-direction given in Fig. 19. Positive values represent transport in the positive Y-direction.

The peaks at the corners of the particles show that at these positions the flux (and hence the concentration gradient) is maximal.

From Fig. 18 it can be seen that indeed the flux next to the particle is the highest. This is a direct result of the limiting condition that for every X-coordinate, the total flux, i.e. the flux integrated over all columns in the spreadsheet, should be the same. At the place where the impermeable particle is positioned, the area for permeation is much lower than at the feed or permeate side of the membrane.

From Fig. 19 it can be concluded that the flux in the positive Y-direction is equal to the flux in the negative

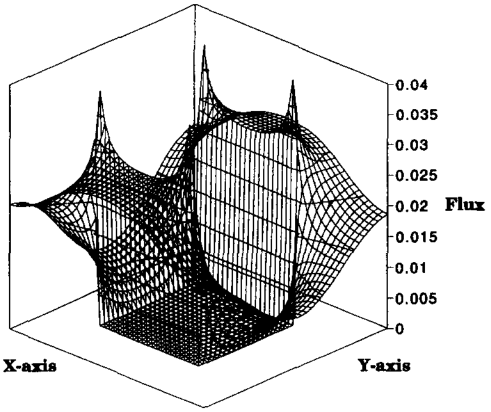

Fig. 18. Flux profile in X-direction in a rubbery membrane with an impermeable particle.

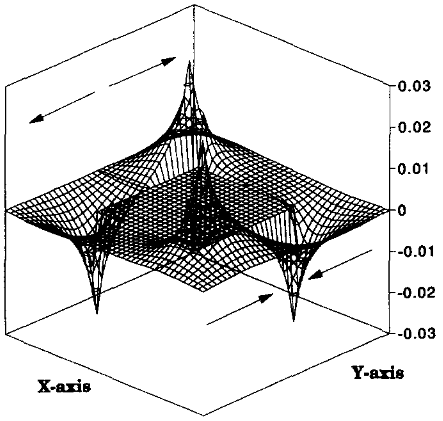

Fig. 19. Flux profile in Y-direction in a rubbery membrane in which an impermeable particle is incorporated. The arrows indicate actual flux directions in front of and behind the particle.

Y-direction since the integral over the plane is zero. This is in agreement with the limiting condition that there should be neither negative nor positive net mass transport in the Y-direction.

6.2.2. *Rubbery membrane containing a rubber particle.*

If a rubber particle is incorporated in the rubber matrix the overall flux through the membrane is determined by the permeability of both phases. Fig. 20 gives the concentration profile in a membrane consisting of a rubber matrix having the same properties as in the case which was discussed above. However, the incorporated particle has a Henry coefficient which is a factor 10 larger than the Henry coefficient in the rubber matrix, while the diffusion coefficients in both phases are kept equal at a value of 0.1.

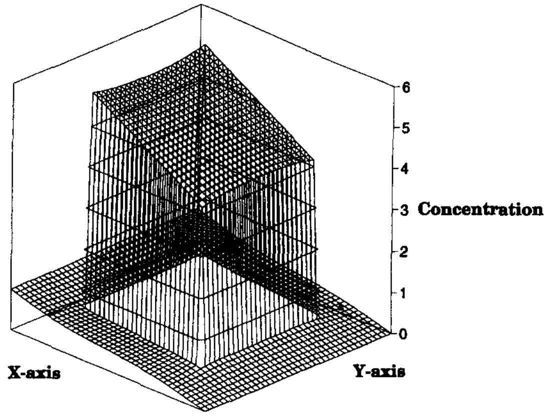

Fig. 20. Concentration profile in a rubber membrane containing a rubber particle, $D_m=D_p=0.1$, $k=K_p/K_m=10$.

Fig. 20 clearly shows the increase in sorption due to the incorporation of a rubber particle which has a higher solubility than the surrounding polymer matrix. In order to make the effect of incorporating this particle on the concentration in the rubber matrix more clear, Fig. 20 has been replotted after dividing the concentration in the particle by the factor $k=10$. The result is given in Fig. 21.

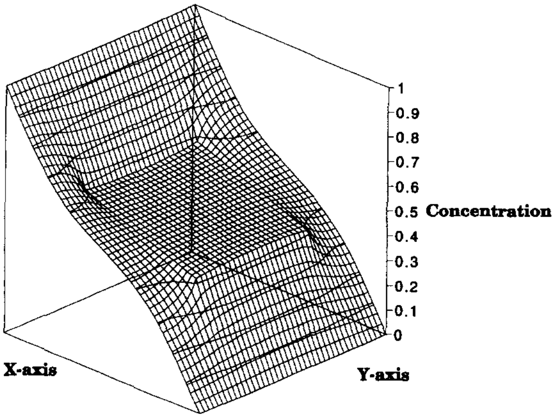

Fig. 21. Concentration profile in a rubber membrane containing a rubber particle in which the concentration in the particle has been divided by k, $D_m=D_p=0.1$, $k=K_p/K_m=10$.

Fig. 21 shows no discontinuity at the interface between the polymer matrix and the polymer particle. This indicates that there exists equilibrium between both phases. This equilibrium is a consequence of the way the concentrations in cells adjacent to the interface are calculated. Whether this equilibrium at the interface exists in case of membranes which contain a filler is difficult to determine experimentally, because then the concentration in both polymer phase and zeolite phase must be known as a function of the X-coordinate. Te Hennepe [4] determined concentration profiles of propanol and water in silicone rubber membranes filled with silicalite-1 under pervaporation conditions. Although the results are somewhat scattered, the results indicate that the propanol sorption in the zeolite phase at the feed side is at its plateau value. This indicates that the assumption that sorption equilibrium exists at the interface is valid.

In Fig. 21 the concentration in the particle has been divided by $k=10$ and therefore the concentration gradient in the particle also decreases by a factor of 10. For both matrix and particle the same diffusion coefficient was used for the calculations, which means that the concentration gradient for both phases is related in the same way to the flux. Fig. 21 shows that the concentration gradient in the rubber particle is less steeper than in the sorrounding matrix. Therefore it can be concluded that the flux through the particle is less than a factor 10 larger than the flux through the surrounding matrix. Because the permeability of the particle, which is the product of diffusivity and solubility, is 10 times larger than the permeability of the matrix and taken into account that the flux through the particle is less than 10 times larger than the matrix, it must be concluded that the flux through the particle is limited by the matrix.

The effect described above is the reason that the permeability of the dispersed phase in these heterogeneous systems which is calculated with the models described in part 1, is dependent on the permeability of the continuous phase. In this case the filler permeability is only ten times higher than the permeability of the polymer matrix. In the next paragraph this effect will be treated in a more quantitative way where the ratio of filler permeability over matrix permeability will be varied over 5 orders of magnitude.

Figs. 22 and 23 show the flux profiles in the membrane in X- and Y-direction respectively. Both graphs seem to be the inverse of the graphs in Figs. 18 and 19 which gave the flux profile in a membrane with an impermeable particle. In that case, mass transport takes place around the particle while in case of the polymer particle for which the permeability is larger than the matrix permeability, there is mass transport towards and through the particle. Fig. 23 demonstrates that there is no net transport in the Y-direction.

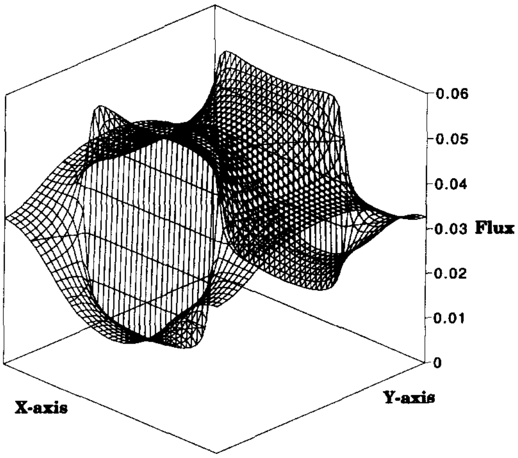

Fig. 22. Flux profile in X-direction in a rubber membrane containing a rubber particle, $D_m=D_p=0.1$, $k=K_p/K_m=10$.

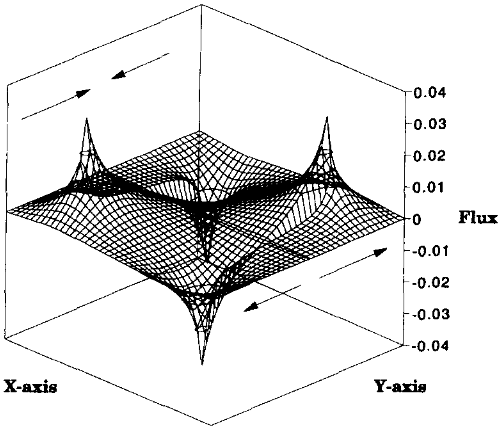

Fig. 23. Flux profile in Y-direction in a rubbery membrane in which a rubbery particle is incorporated. The arrows indicate actual flux directions in front of and behind the particle. $D_m=D_p=0.1$, $k=K_p/K_m=10$.

6.2.3. Rubbery membrane containing a zeolite particle

Eq. (15) was used to described the sorption in the zeolite.

$$c_{\mathrm{i}} = \frac{K_{\mathrm{p}}ba}{(1+ba)} \tag{15}$$

Here c_{i} is the concentration in the zeolite, a the activity, b the affinity parameter and K_{p} the sorption capacity. For b an arbitrary value of 30 was chosen while for K_{p} the value 10 was chosen which means that at activity 1 the sorption in the zeolite is 10 times higher than the sorption in the polymer matrix.

The concentration profile in the membrane is similar to that for a polymer particle in a rubber matrix. Incorporation of the zeolite particles results in a large increase in sorption. The flux profile in the X-direction is given in Fig. 24. The diffusion coefficient which was used to calculate transport between the cells is a constant $D_{\mathrm{p,0}}$ multiplied by the Darken factor dln$a$/dln$c$. Calculations with a constant diffusion coefficient D_0 resulted in a decrease in flux through the membrane.

Fig. 24 shows that due to non-linear sorption in the zeolite phase the flow is not symmetrically distributed through the membrane.

For a polymer particle it can be seen that the flux at both sides in the particle is not zero (see Fig. 22). This means that mass transfer takes place through these sides as well. In case of a polymer particle this is not difficult to imagine since all sides of the particle are accessible for transport. In case of a zeolite particle this might be not realistic because transport takes place via a well defined and directioned pore system. In some zeolites this pore system might be one or two-directional or the pores in the Y-direction have a different size and/or geometry compared to the pores in the X-direction. The model discussed here does not take these effects into account. It was already pointed out by Duval et al. [2] that zeolites with a uni-directional pore system might be not so effective in improving membrane properties because only a fraction of all particles have the right orientation to contribute to mass transfer through the membrane.

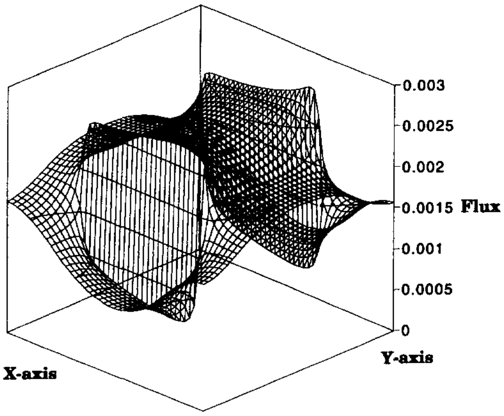

Fig. 24. Flux profile in X-direction in a rubber membrane containing a zeolite particle, D_{m}=$D_{\mathrm{p,0}}$=0.1, K_{m}=1, K_{p}=10.

6.3. Parameters influencing transport in zeolite filled membranes

In this paragraph an analysis is given of the influence of several parameters on the flux which is calculated as described above. As mentioned above it is difficult to relate the outcome of the model calculations directly to fluxes which can be determined experimentally. One problem is that in the model a particle is defined as a square in the plane. Therefore it is difficult to 'transform' this area fraction into a volume fraction. The spreadsheet consists of 42×41 cells and the particle is 25×25 cells and therefore the area fraction is equal to 0.363. In this paper the are fraction will be used as the volume fraction in the models which describe transport through heterogeneous membranes.

6.3.1. Impermeable particles: influence of the degree of filling

It is possible to vary the 'degree of filling in the plane' by varying the size and/or number of particles in the plane. The results of calculations in case the filler is not permeable are listed in Table 5.

From Table 5 it can be seen that by increasing volume fraction of impermeable filler the flux through the membrane decreases as expected. Furthermore if the results are fitted with the model of te Hennepe the calculated flux through the particle is −0.0114 which means that the model describes composites consisting of an impermeable particle embedded in a polymer matrix quite well.

Table 5
Numerical values for the fluxes calculated with the model. Impermeable particles: variation of degree of filling. $D_{\mathrm{matrix}}=0.1$, $K_{\mathrm{matrix}}=1$, particle is positioned in the centre of the plane

Particle size	Area fraction	Overall flux
–	0	0.098
11×11	0.072	0.084
21×21	0.26	0.056
25×25	0.37	0.044
31×31	0.57	0.026

Table 7
Numerical results for fluxes in case of a rubber particle which is embedded in the polymer matrix. The particle occupies 25×25 cells (0.363 volume fraction), $D_{\mathrm{particle}}=0.1$, $K_{\mathrm{particle}}=1$

D_{matrix}	K_{matrix}	P_{matrix} ($=D\times K$)	Overall flux
0.1	1e-4	1e-5	2.041e-5
0.1	1e-3	1e-4	2.030e-4
0.1	0.01	1e-3	2.003e-3
0.1	0.1	0.01	0.0176
0.2	0.1	0.02	0.0313
0.1	1.0	0.1	0.0976
0.1	2.0	0.2	0.1540
0.2	2.0	0.4	0.2509
0.2	4.0	0.8	0.4321
0.1	8.0	0.8	0.4322

6.3.2. Incorporation of a polymer particle: influence of particle properties

If a polymer particle is incorporated in a rubber membrane, the properties of the membrane also will be influenced by the properties of the particle. In case the particle has the same properties as the matrix material, the flux through the membrane should be equal to the flux of an unfilled membrane. That this limiting condition is fulfilled indeed, is shown in Table 6.

The flux through a membrane in which a particle is incorporated which has the same properties as the matrix is equal to the flux of an unfilled membrane. In this respect the model appears to be correct. Furthermore the flux through the membrane increases with increasing permeability of the dispersed phase which is to be expected. Finally the permeabilities calculated by the model of te Hennepe are in reasonable agreement with the theoretical values.

6.3.3. Incorporation of a polymer particle: influence of matrix properties

As mentioned before, the apparent permeability of the zeolite phase which was calculated by means of permeation models for heterogeneous membranes, increases with increasing permeability of the matrix polymer. Table 7 shows that this behaviour is obtained for the two-dimensional model as well.

The influence of the increasing matrix permeability is clear. The last two calculations clearly show that it does not make any difference whether the high permeability of the matrix polymer is due to a high diffusion coefficient of high solubility.

Table 7 shows that the permeability and therefore the flux of the polymer matrix is varied over 5 orders of magnitude. Consequently, the flux through the membrane with the polymer particle also varies strongly. In order to discriminate between the flux through the particle and through the polymer matrix, the models for transport through heterogeneous materials were used. In the equations of the models the permeabilities are replaced by the fluxes. From the calculated fluxes through the unfilled membrane and

Table 6
Numerical results for fluxes in case of a rubber particle which is embedded in the polymer matrix. The particle occupies 25×25 cells (0.363 volume fraction). Theoretical polymer permeability =0.1

D_{matrix}	D_{particle}	K_{matrix}	K_{particle}	Overall flux	Permeability of particle[a]	Theoretical permeability[b]
0.1	–	1.0	–	0.0976	–	–
0.1	0.1	1.0	1.0	0.976	0.155	0.1
0.1	0.1	1.0	5.0	0.157	0.458	0.5
0.1	0.1	1.0	10.0	0.176	0.602	1.0
0.1	0.02	1.0	10.0	0.123	0.264	0.2

[a] Calculated with the model of te Hennepe.

[b] Based on permeability= $K_{\mathrm{particle}}\times D_{\mathrm{particle}}$.

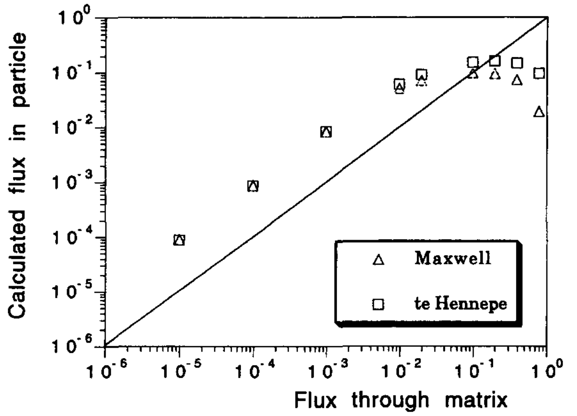

Fig. 25. The flux through the particle as a function of the flux through the unfilled polymer matrix. The flux through the particle is calculated by means of various models from the data listed in Table 7.

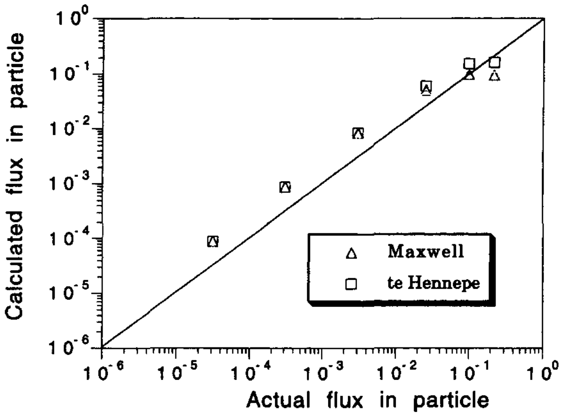

Fig. 26. Calculated model flux through the particle as a function of the actual (simulated) flux though the particle.

the membrane with the rubber particle, the flux through the particle can be calculated. Fig. 25 gives this calculated particle flux as a function of the flux through the unfilled polymer. This figure looks very similar to the graph obtained by Duval (Fig. 12) in which he plots the permeability of CO_2 in silicalite-1 as a function of the permeability of the polymer in which the zeolite is embedded. It is unlikely that the permeability of a zeolite varies over 4 orders of magnitude but for the flux this might be quite well possible because the flux through the particle is limited by the supply of mass towards the particle. Because of this limitation of the flux, the apparent permeability which is calculated becomes very low as well since the global driving force is used to calculate this permeability.

Fig. 25 gives, although in a longwinded manner, a method to estimate the zeolite permeability experimentally by incorporating the zeolite in various rubbers having a higher or lower permeability than the zeolite permeability. This will result in a higher or lower permeability of the composite compared with the unfilled polymer.

Because in the spreadsheet all concentrations are known, it is possible to calculate the actual flux through the particle as well. In Fig. 26 for some of the points in Fig. 25 this actual flux is compared to the flux which was calculated by the various models.

It can be seen that for the two-dimensional model the flux through the particle, which is calculated by means of transport models for heterogeneous materials, deviates not more than a factor of three from the actual flux. If the actual (simulated) flux is divided by the concentration gradient over the particle which can be obtained from the spreadsheet, the permeability of the particle is obtained. This permeability varies from 0.3102 in case of the lowest permeable matrix to a value of 0.2105 in case of the highly permeable polymer matrix. Also this is in reasonable agreement with the given value of 0.1 for the permeability of the particle.

6.4. Discussion of the numerical simulation

The results of the numerical simulations show that the two-dimensional model can describe the phenomena mentioned in the introduction of this chapter adequately. It was clearly shown that the flux through a particle is limited by the flux through the surrounding matrix. However, it is not possible to use the two-dimensional model to calculate the intrinsic permeability of the particle from overall parameters like the flux through the composite and volume fraction of filler without making use of the exact concentrations in the spreadsheet.

The reason that models like the one of Maxwell and te Hennepe predict a permeability which is orders of magnitude lower than the intrinsic value is caused by

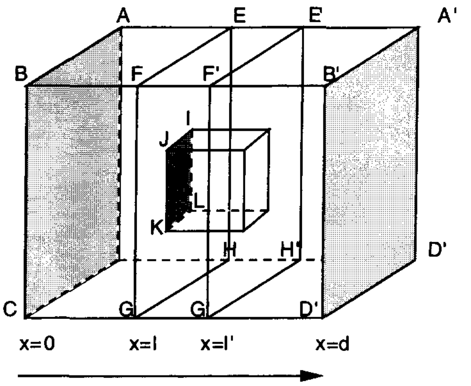

Fig. 27. Basic element consisting of a cube of filler material which is incorporated in the middle of a polymer cube.

the fact that mass transport from the matrix towards the particle and from the particle towards the matrix is limited by the polymer matrix surrounding it. Therefore the flux through the particle increase with increasing permeability of the matrix. However, the driving force which is used to calculate the (apparent) permeability of the particle, the driving force over the membrane, remains constant.

Now the question arises whether it is possible in principle to calculate the intrinsic permeability of the zeolite from permeation experiments with zeolite–polymer composites. This question will be answered using a basic element, which consists of a small cube representing the filler. This filler is incorporated in a larger polymer cube. This is shown in Fig. 27.

It is assumed that the element is representative for the membrane.

In case of steady state, the flux through plane ABCD is equal to the flux through plane A′B′C′D′ or the two planes in between. If the area of these planes is assumed to be equal to 1 in arbitrary area units, the flux through plane ABCD can be described by Eq. (16)

$$J_{\mathrm{overall}} = -P_{\mathrm{r}}\left(\frac{\mathrm{d}p}{\mathrm{d}x}\right)_{x=0} \tag{16}$$

where J_{overall} is the overall flux through the basic element, P_{r} is the rubber permeability and $(\mathrm{d}p/\mathrm{d}x)_{x=0}$ the pressure gradient at $x=0$. The overall flux through the basic element is assumed to be proportional to the flux through filled membrane. Furthermore P_{r} can be determined experimentally and therefore $(\mathrm{d}p/\mathrm{d}x)_{x=0}$ can be calculated with Eq. (16). It is obvious that $(\mathrm{d}p/\mathrm{d}x)_{x=0}$ is averaged over the entire plane. From the simulation results presented earlier it could be concluded that the actual pressure gradient is a function of the position in the plane. Furthermore $(\mathrm{d}p/\mathrm{d}x)_{x=0}$ must be equal to $(\mathrm{d}p/\mathrm{d}x)_{x=\mathrm{d}}$ since the flux through the planes are equal and the polymer permeability is assumed to be constant over the membrane thickness.

In the basic element there are two other planes present, i.e plane EFGH and plane E′F′G′H′. The first plane at $x=1$ is positioned just in front of the filler particle, while the second plane at $x=1'$ is positioned just behind the filler particle. The flux through these planes, which are positioned in the polymer phase, is equal to the flux through the two planes at the outside of the basic element. Because the planes are positioned in the polymer phase the permeability at $x=1$ or $x=1'$ is the known polymer permeability. This means that at these two positions the mean pressure gradient is equal to $(\mathrm{d}p/\mathrm{d}x)_{x=0}$.

Two areas in the planes EFGH and E′F′G′H′ can be distinguished, i.e. the area in front of the particle, IJKL and the residual area. It seems reasonable to assume that when the plane EFGH is close enough to the zeolite particle, molecules which pass the plane EFGH through the small square IJKL, will enter the zeolite and all other molecules will pass by the particle. The flux through the zeolite particle can be described by Eq. (17).

$$J_{\mathrm{zeolite}} = -P_{\mathrm{z}}A_{\mathrm{z}}\left(\frac{\mathrm{d}p_{\mathrm{z}}}{\mathrm{d}x}\right)_{x=\frac{1}{2}d} \tag{17}$$

in which P_{z} is the filler permeability, A_{z} is the area of the small square IJKL and $\mathrm{d}p_{\mathrm{z}}/\mathrm{d}x$ the mean pressure gradient in the zeolite particle at position $x=0.5\times d$, i.e. the plane through the middle of both cubes. A similar equation can be derived for transport through the polymer phase, Eq. (18):

$$J_{\mathrm{polymer}} = -P_{\mathrm{r}}(1-A_{\mathrm{z}})\left(\frac{\mathrm{d}p_{\mathrm{p}}}{\mathrm{d}x}\right)_{x=\frac{1}{2}d} \tag{18}$$

The assumption that mass transport through plane IJKL is equal to the mass transport through the zeolite leads to Eq. (19).

$$P_{\mathrm{r}} * \left(\frac{\mathrm{d}p_{\mathrm{P}}}{\mathrm{d}x}\right)_{x=1,\mathrm{IJKL}} = P_{\mathrm{z}}^{*}\left(\frac{\mathrm{d}p_{\mathrm{z}}}{\mathrm{d}x}\right)_{x=\frac{1}{2}d} \tag{19}$$

In Eqs. (16)–(19) several variables are unknown, i.e. the zeolite permeability P_z, the pressure gradient in the zeolite $(\mathrm{d}p_z/\mathrm{d}x)_{x=0.5\mathrm{d}}$, the pressure gradient in the polymer phase in plane IJKL $(\mathrm{d}p_p/\mathrm{d}x)_{\mathrm{IJKL}}$ and the pressure gradient in the polymer phase at $x=0.5d$ $(\mathrm{d}p_p/\mathrm{d}x)_{x=0.5\mathrm{d}}$. In order to calculate the zeolite permeability, four independent equations must be available which is not the case. Therefore it seems impossible to calculate analytically the zeolite permeability from permeation results obtained using composites.

As mentioned before, the permeability models for heterogeneous media are not able to predict the intrinsic permeability of the dispersed phase but they seem to predict the flux per unit area through the filler in the right order of magnitude. If the flux through the zeolite can be estimated by means of the three models and it is possible to estimate the driving force over the particle the permeability of the dispersed phase can be calculated more accurately. To do so, the basic element will be used again to derive the equations which are needed.

As stated before the pressure gradient at $x=0$ is equal to the overall flux through the filled membrane divided by the matrix permeability according to Eq. (16). The mean pressure gradient in plane IJKL is assumed to be equal to the flux through the zeolite divided by the permeability of the matrix. An approximation of the average pressure gradient between $x=0$ and $x=1$ is then given by Eq. (20)

$$\left(\frac{\mathrm{d}p}{\mathrm{d}x}\right)_{x=0,x=1} = \frac{P_\mathrm{f} + P_\mathrm{z}A_\mathrm{z}}{2P_\mathrm{r}} \tag{20}$$

in which P_f is the permeability of the filled membrane, P_r the permeability of the rubber matrix and P_z the apparent permeability of the dispersed phase which is calculated using the aforementioned permeation models.

If the pressure at $x=0$ is normalized to a value of 1, the pressure in the polymer at $x=1$ can be estimated. In a similar way the pressure in the polymer at $x=1'$ can be estimated. The difference between the pressure at $x=1$ and $x=1'$ is the driving force over the filler particle. By relating A_z and the various distances to the volume fraction of filler, Eq. (21) is obtained.

$$P_\mathrm{z}^* = \frac{2^* P_\mathrm{z} P_\mathrm{r}}{2P_\mathrm{r} - \left(P_\mathrm{f} + P_\mathrm{z}\phi_\mathrm{z}^{\frac{2}{3}}\right)\left(1 - \phi_\mathrm{z}^{\frac{1}{3}}\right)} \tag{21}$$

where P_z^* is the approximated intrinsic permeability.

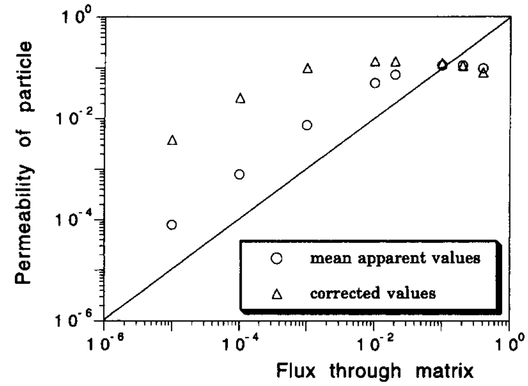

Fig. 28. Apparent values for the permeability of a filler particle embedded in a polymer matrix. Mean apparent values were calculated by means of the three permeation models discussed before. The corrected values were obtained taking a concentration gradient into account which was calculated by Eq. (20). Intrinsic permeability of the particle is 0.1.

This correction can be applied to the calculated results given in Fig. 14. In this figure the calculated apparent permeability is plotted as a function of the permeability of the matrix polymer. Fig. 28 gives the mean values for apparent permeability of the filler obtained for various models together with the corrected values P_z^*.

It can be seen that the corrected apparent permeability is more or less equal to the intrinsic permeability of the particle over three orders of magnitude. Still at low matrix permeabilities, the calculated value differs a factor of 25 from the intrinsic permeability.

7. Conclusions

The experimental results discussed in this paper show that in pervaporation of methanol and toluene feed mixtures with membranes prepared from rubbery polymers the performance is influenced by incorporation of zeolite particles. In case of the toluene selective rubber EPDM, addition of silicalite-1 or NaX leads to a decrease in toluene selectivity due to a decrease in the toluene flux and an increase in the methanol flux. From sorption measurements with pure zeolites it can be concluded that NaX is methanol selective and silicate-1 is only toluene selective at toluene concentrations less than 30 wt%. Furthermore, from diffusion measurements it can be concluded that methanol diffuses faster in the zeolite than toluene.

Therefore it can be expected that incorporation of these zeolites in a toluene selective polymer results in a decrease in the intrinsic selectivity of the polymer for toluene. The methanol selectivity Viton and Estane 5707 membranes is enhanced due to the incorporation of NaX. In the case of the polymer Viton which has a low intrinsic permeability for both components also the total flux through the membrane is increased, contrary to the effect for the highly permeable Estane membranes for which a decrease in total flux is observed with an increase in zeolite content.

From experiments with double layer membranes it can be concluded that the effect of adding zeolite particles to a polymeric membrane of selectivity of the membrane depends on the position of the zeolite particles in the membrane. It seems that the effect of the zeolite on the over-all selectivity is larger when the zeolite is situated at the less permeable permeate side.

This behaviour is illustrated by numerical simulations which also show that conventional models which are used to describe permeabilities of heterogeneous materials are inadequate in case there is a large difference between the permeability of the matrix and that of the filler. Furthermore it was shown that the failure of these models is caused by the fact that they do not incorporate local driving, which is not correct

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