

## Zeolite-Filled PDMS Membranes. 2. Pervaporation of Halogenated Hydrocarbons

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In order to study in more detail the influence of the filler on pervaporation performance, silicalite, ZSM-5, and zeolite Y were incorporated in poly(dimethylsiloxane) (PDMS) and tested in pervaporation experiments with binary mixtures of chlorinated hydrocarbons (Cl-HC's) in water. The results were compared with unfilled PDMS as a reference. The highest selectivities were obtained with the silicalite-filled membranes. However, these membranes showed a decrease in permeability for voluminous components due to molecular sieving effects. In this respect, the results with zeolite Y were rather disappointing, as its larger pore size was counteracted by its high polarity, whereas ZSM-5-filled membranes showed intermediate selectivities. Therefore, mesoporous silicas were synthesized, silylated to assure their apolarity, and incorporated in PDMS. The resulting membranes showed both improved organic fluxes and selectivities in comparison with all other membranes, even for voluminous organics, proving the absence of molecular sieving effects.

### Introduction

In previous studies,<sup>1–3</sup> we have shown that the incorporation of silicalite in the PDMS polymer phase introduces molecular sieving effects in the membrane. As a consequence, voluminous organics like CCl<sub>4</sub> and t-C<sub>4</sub>H<sub>9</sub>Cl show hardly any permeability in pervaporation experiments with silicalite-filled membranes obtained from GFT–Le Carbone (Neunkirchen-Heinitz, Germany). However, for most of the organics considered, the incorporation of silicalite is beneficial, as it improves the membrane selectivity due to the lower water flux, i.e., approximately 100 g/(m<sup>2</sup> h) for the filled GFT membranes compared to 400 g/(m<sup>2</sup> h) for the unfilled PDMS GFT membranes and this for a comparable permeability of organics. This can be attributed to the apolar character of this zeolite that prevents water molecules from entering the silicalite pores.<sup>4</sup>

In order to study more thoroughly the influence of the molecular sieving effect of the zeolite and to get an idea of the effect of the (a)polarity of the filler on flux and selectivity, PDMS membranes were filled with different zeolites. Silicalite (as a reference), ZSM-5, and zeolite Y were selected as fillers and mutually compared in relation to their performance in the pervaporation of binary water/chlorinated hydrocarbons (Cl-HC's) mixtures. These zeolites were chosen because of their difference in polarity and/or pore size. PDMS was selected for its apolar character and its flexible chains, making the matrix highly permeable for apolar components. Combined with the results in part 1 of this series, the relative importance of sorption and diffusion in the pervaporation process will be evaluated.

All these zeolites have pores smaller than 0.8 nm. It can be expected that further improvement on performance of filled membranes can be realized by incorporating meso- or macroporous inorganic fillers. These fillers not only would offer a large sorption capacity but would also exclude diffusion limitations and molecular sieving effects in the filler, increasing fluxes in all cases and selectivity if sorption in the fillers is selective. Therefore, in some preliminary test runs, silylated

mesoporous structures (amorphous silicas with a pore distribution in the 1–3-nm range) were incorporated in PDMS and their influence on the pervaporation performance was tested. It was shown that these membranes combined high selectivity with high organic fluxes.

### Materials and Methods

**Materials.** PDMS (RTV 615, General Electric) membranes were synthesized, either unfilled or filled with one of the following zeolites: silicalite, ZSM-5, or zeolite Y. As filling degree, the maximum achievable content without introducing pin holes was chosen: 40 vol % for silicalite and zeolite Y, 30 vol % for ZSM-5. The preparation method was already described in detail in part 1 of this series.

**Methods. Silica Filled Membranes.** Amorphous silicas were prepared by acid sol–gel synthesis<sup>5</sup> starting from tetraethoxysilicate (TEOS). Titration with NH<sub>3</sub> to an end pH value of 3 gave a pore distribution mainly in the 1–3-nm range. To make sure that the mesoporous filler had a hydrophobic surface (internal as well as external), it was silylated first with trimethylchlorosilane (TMCS).<sup>6</sup> It was incorporated in PDMS with a filling degree of 20 vol %, following the preparation method described elsewhere.<sup>7</sup> It consisted of a prepolymerization step of 1 h at 70 °C in order to have the PDMS network partially cross-linked in a 10 vol % solution of chloroform. The fillers were added then, and the mixture was stirred for another hour at room temperature, after which it was cast in a Petri dish. After evaporation of the solvent, the membrane was finally cured during 1 h at 150 °C under vacuum. The zeolite-filled membranes were the same as the ones used in part 1 of this series.

All membrane thicknesses were around 150 μm. In order to compare fluxes of different membranes in a proper way, the obtained fluxes were all normalized to a thickness of 150 μm, using the inversely proportional relationship between flux and membrane thickness.

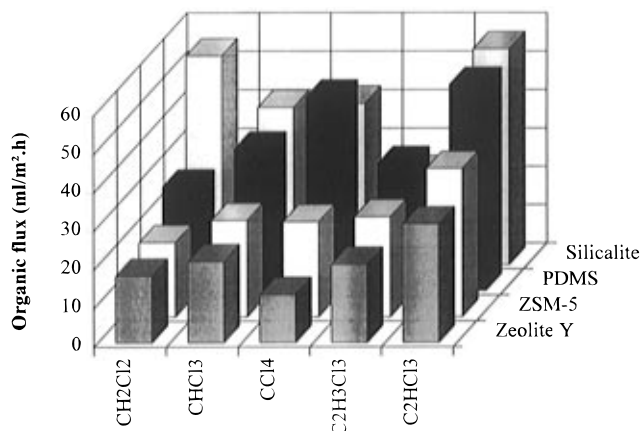
**Pervaporation.** Pervaporation experiments were carried out with the laboratory test cell (Lab Test Cell Unit from GFT–Le Carbone), containing a flat-sheet membrane of 6-in. diameter. Pervaporation experiments were done with different binary

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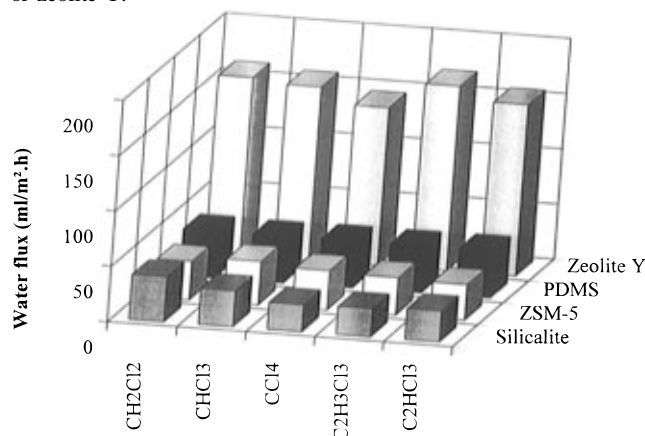
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**Figure 1.** Organic fluxes (600 ppm feed concentration) for PDMS membranes and for PDMS membranes filled with silicalite, ZSM-5, or zeolite Y.



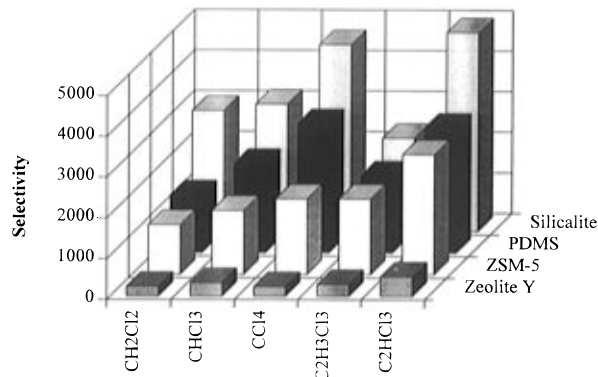
**Figure 2.** Water fluxes for PDMS membranes and for PDMS membranes filled with silicalite, ZSM-5, or zeolite Y.

mixtures (Cl-HC's/water) at 50 °C feed temperature and 10 mbar of permeate pressure. The chloromethane series (C1 series) and trichloroethylene and 1,1,2-trichloroethane (C2 series) were selected as target components. Samples from both retentate and permeate were taken at frequent intervals. The concentration of organics in the retentate was analyzed by gas chromatography (Hewlett-Packard 5890 series II, wideboar column, DB-1 dimethylpolysiloxane), whereas the water concentration for the permeate was determined by Karl Fischer titration (Metrohm 678 EP/KF processor).

## Results and Discussion

**Silicalite-, ZSM-5-, and Zeolite Y-Filled PDMS Membranes.** Different membranes can only be compared mutually if the concentration effects are eliminated. Therefore, all experimentally determined organic fluxes are converted by interpolation to flux values corresponding to a feed concentration of 600 ppm exactly. The water flux, on the other hand, can be considered to be a constant, and a mean value was derived for each experiment. The organic and water fluxes for each membrane and for each binary mixture are presented in Figures 1 and 2, respectively.

It can be seen from Figure 1 that in comparison with the unfilled and the silicalite-filled membranes, the incorporation of ZSM-5 and zeolite Y occurs with an overall organic flux decrease, most pronounced for zeolite Y. As appeared in earlier publications<sup>1-3</sup> and part 1, two factors govern sorption and diffusion in filled membranes and may thus be expected to govern the pervaporation behavior: polarity and steric hindrance. Both fillers, i.e., ZSM-5 and especially zeolite Y, are



**Figure 3.** Selectivity (at 600 ppm feed concentration) for PDMS membranes and for PDMS membranes filled with silicalite, ZSM-5, or zeolite Y.

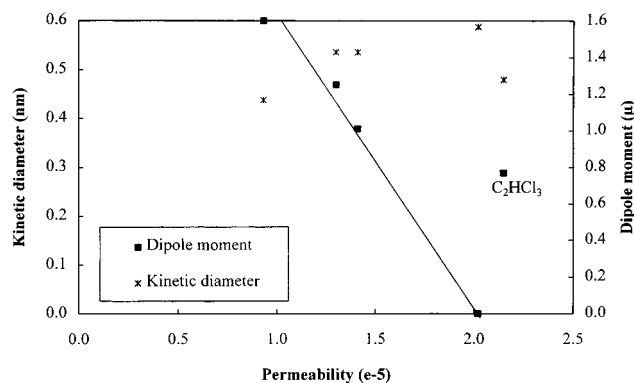
indeed more polar than silicalite, thus reducing the flux of the organic compounds. Furthermore, steric effects will play a part in ZSM-5-filled membranes, as this filler has the same pore size as silicalite. For the zeolite Y-filled membranes, a higher CCl<sub>4</sub> flux was expected as seen by the larger pore size of this filler. Obviously, the positive effect of the larger pore size is counteracted by the increased polarity of this filler so that the apolar CCl<sub>4</sub> molecules are repelled rather than attracted by the filler. In addition, the water molecules can pass unhindered through the wide zeolite Y pores. In other words, the exclusion mechanism of the zeolite is no longer working for water. This is clearly demonstrated by the 4-fold increase of the water flux when incorporating zeolite Y in the PDMS matrix (Figure 2), making these membranes very unattractive for our purposes. For silicalite- and ZSM-5-filled membranes, on the other hand, a reduced water flux is observed which can be attributed to the cross-linking action of the zeolites on the polymer, resulting in a more dense membrane system.

In the C2 series, the beneficial effect of a double bond can be observed for all membranes. It gives the molecule a plane geometry which apparently favors transport in each of the considered zeolites and in the PDMS matrix. Moreover, by comparing the dipole moments of both molecules, one can notice that the introduction of a double bond makes the molecule less polar so that a higher selectivity can also be predicted on the basis of polarity.

For the silicalite-filled membranes, an expected (see part 1) flux decrease of CCl<sub>4</sub> in comparison with the unfilled membranes was observed, whereas for CH<sub>2</sub>Cl<sub>2</sub> a rather unexpected and important flux increase can be noticed. Yet, the latter observation is fully in agreement with the earlier published work of te Hennepe,<sup>4</sup> who also studied the effect of the incorporation of silicalite in PDMS membranes on the pervaporation performance of alcohol/water mixtures. CH<sub>2</sub>Cl<sub>2</sub> in the C1 series can be well compared with CH<sub>3</sub>OH in the linear alcohol series. Both molecules are small and, speaking in relative terms, rather polar so that they fit well in the pores of the zeolite.

From the organic and water flux data, the  $\alpha$  selectivity factor, was calculated and plotted in Figure 3 as a function of the feed mixture and the membrane type. The silicalite-filled membranes show an increased selectivity, whereas the ZSM-5 membranes present a somewhat lower selectivity due to the more polar character of this zeolite. A dramatic decrease in selectivity is observed for the zeolite Y-filled membranes which, of course, is the result of the increased water flux.

In the previous paragraph, much attention was given to the effect of the incorporation of different zeolites on flux and selectivity for each individual Cl-HC. Here, in this paragraph, the different Cl-HC's will be mutually compared per zeolite. Therefore, the fluxes at 600 ppm will be converted to perme-



**Figure 4.** Permeability of the Cl-HC's as a function of the corresponding dipole moment and kinetic diameter.

abilities. The obtained permeabilities will be related to some component properties like dipole moment and kinetic diameter. Figure 4 gives the correlation between the permeabilities, the dipole moment, and the kinetic diameter of the Cl-HC's in pure PDMS. At pervaporation conditions (activity  $\ll 1$ ), the plateau value which corresponds to the maximum sorption capacity of the polymer (see part 1) will not be reached, and a linear relationship between the permeability and the dipole moment is observed.  $C_2HCl_3$  is the exception, showing a higher permeability than expected and thus indicating once again that its planar structure favors membrane transport. No relationship between the permeability in PDMS and the kinetic diameter could be found (see Figure 4). Therefore, we can conclude that the permeability in PDMS is determined by polarity aspects. In other words, the less polar the component, the higher its affinity for the polymer and the higher the corresponding permeability through the apolar polymer. It proves the dominating effect exerted by sorption (see part 1) in the pervaporation through unfilled PDMS membranes.

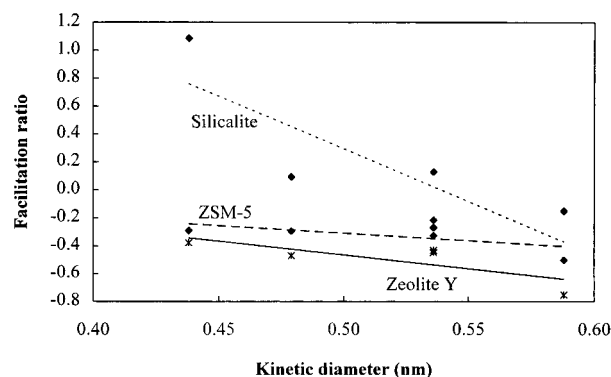
According to Jia et al.,<sup>8</sup> the facilitation ratio,  $F_{r,i}$ , of component  $i$  and zeolite  $r$  is defined as

$$F_{r,i} = \frac{P_{z+p,i} - P_{p,i}}{P_{p,i}}$$

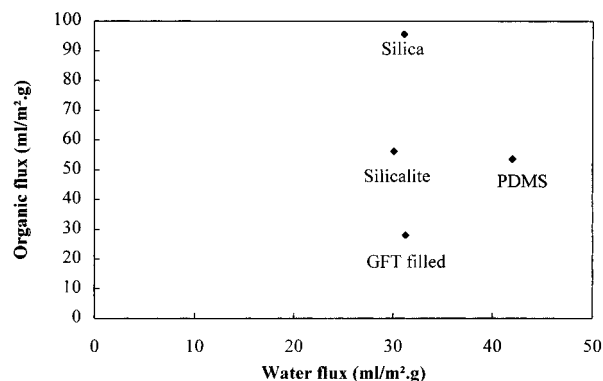
where  $P_{z+p,i}$  is the permeability of component  $i$  in the zeolite-filled membrane and  $P_{p,i}$  is the permeability of component  $i$  in the unfilled membrane. The incorporation of zeolites has a positive effect as long as the facilitation ratio remains larger than zero. A negative value of this parameter means that the incorporation of the zeolite reduces the overall permeability of the organic.

The facilitation ratio for the five Cl-HC's and for the three zeolites was calculated and plotted as a function of the kinetic diameter in Figure 5. A decreasing tendency of the facilitation ratio with the kinetic diameter can be noticed. Moreover, the incorporation of ZSM-5 and zeolite Y results in a negative facilitation ratio for all components considered. Both fillers reduce the organic permeability in comparison with the unfilled PDMS, and the effect is even larger for zeolite Y-filled membranes (40 vol % loading) than for ZSM-5-filled membranes (30 vol %). A pronounced positive effect of the zeolite occurs only for silicalite-filled membranes (40 vol %) in the case of  $CH_2Cl_2$  molecules.

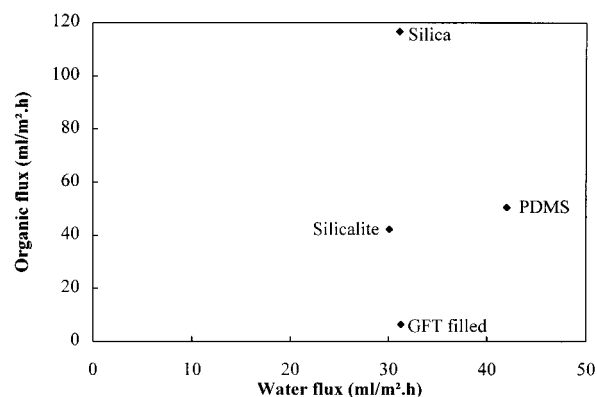
One can conclude that zeolite Y and ZSM-5 are unsuitable fillers for an application such as the removal of organics from water, as their selectivity is too low. As these zeolites are more polar than silicalite, they give higher water fluxes than the silicalite-filled membranes and, thus, lower selectivities. On the other hand, silicalite introduces molecular sieving effects



**Figure 5.** Facilitation ratio as a function of the kinetic diameter of the considered molecules and for several zeolites.



**Figure 6.**  $C_2HCl_3$  and  $H_2O$  fluxes for PDMS membranes synthesized by us (unfilled or filled with silicalite or silylated silicas) and for commercial silicalite-filled GFT membranes.



**Figure 7.**  $CCl_4$  and  $H_2O$  fluxes for PDMS membranes synthesized by us (unfilled or filled with silicalite or silylated silicas) and for commercial silicalite-filled GFT membranes.

into the polymer matrix, resulting in a membrane with low fluxes for voluminous organics. Zeolite Y has larger pores, but it is also the most polar of the considered zeolites and therefore shows rather disappointing organic fluxes.

In the next paragraph, a new filler will be used which combines the low polarity of silicalite (exclusion mechanism) with the large pore size of zeolite Y. We expected silylated mesoporous silicas to fulfill these requirements.

**PDMS Membranes Filled with Amorphous Silicas.** Amorphous silicas possess meso- and macropores, and to be sure of the apolar character of this filler, it was primarily silylated by TMCS. The PDMS membrane containing this filler was tested for two binary mixtures:  $H_2O/C_2HCl_3$  and  $H_2O/CCl_4$ . The obtained organic fluxes are presented as a function of the water fluxes in Figures 6 and 7, respectively. Both figures also include the corresponding data for the PDMS (unfilled) and silicalite-

filled PDMS membranes synthesized by us (see previous paragraph), as well as the results for the commercial silicalite-filled PDMS membranes (the so-called GFT membranes). All fluxes were normalized to flux values corresponding to a feed concentration of 600 ppm and a membrane thickness of 150  $\mu\text{m}$ .

The PDMS membranes filled with amorphous silicas combine high organic fluxes with low water flux (high selectivities). The  $\text{CCl}_4$  flux is even larger than the  $\text{C}_2\text{HCl}_3$  flux, which proves our hypothesis of the molecular sieving effect observed for zeolites. Moreover, the results also prove that the silylation was successful, since the water flux of the membranes filled with amorphous silicas is as low as the water fluxes of the silicalite-filled membranes, indicating that despite the larger pore size, the water exclusion mechanism is still working. The unfilled PDMS membranes showed, of course, an enhanced water flux in comparison with the filled membranes. The lowest organic fluxes were reported for the commercial silicalite-filled GFT membranes. It must be emphasized though that the commercial membranes are real composite membranes consisting of three different layers (polyester, poly(acrylonitrile), filled PDMS top layer with a thickness of 35  $\mu\text{m}$ ), while the other membranes taken in consideration here are one layer only. Therefore, the results for the GFT membranes can be compared with the results of the membranes synthesized by us, but only with great care.

## Conclusions

Zeolite Y and ZSM-5 are not suitable as fillers in PDMS when the removal of organics from water is envisaged.

Especially the zeolite Y-filled membranes are unattractive because of their high water permeability. ZSM-5, on the other hand, has the same pore size as silicalite; in other words, molecular sieving effects will occur. This filler is more polar than silicalite, so the water fluxes are higher than for the silicalite-filled membranes. In addition, due to the polar character of ZSM-5, the filler even causes a decreased organic flux.

We have clearly demonstrated that PDMS membranes filled with amorphous silicas combine the best of both worlds: i.e., a large pore size with apolarity. In this case, the  $\text{CCl}_4$  flux is even larger than the  $\text{C}_2\text{HCl}_3$  flux. The water flux is as small as for the silicalite-filled membranes and proves that the exclusion mechanism prevents water molecules from entering the silylated pores.

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