

# Sorption and Pervaporation of Aroma Compounds Using Zeolite-Filled PDMS Membranes

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In view of the pervaporation of aroma compounds from water with PDMS (polydimethylsiloxane) membranes, it was investigated how incorporated zeolites influenced the membrane performance on the level of sorption as well as diffusion. The feasibility of the separation process was coupled to a more fundamental study of the importance of functional groups and molecular chain length of the compounds in the feed mixture. The influence of temperature on sorption and pervaporation is included as well as a comparison with commercial membranes. Sorption of aromas in PDMS could be brought in relation to the Hildebrandt parameters. This sorption decreased when adding zeolites to the polymer due to the cross-linking action of the zeolite. Apart from the expected increase in fluxes, increased temperatures induced higher selectivities as well. For the selective removal of ethanol from the aroma mixture, silicalite-filled PDMS membranes were found to be the best.

## Introduction

The growing use of membranes in biotechnology can be attributed to the absence of thermal or pressure stresses and chemical alterations on the reactor constituents. Among biotechnological processes, the dealcoholization of beverages,<sup>1–3</sup> the concentration of juices,<sup>4,5</sup> and the production of aroma compounds<sup>3,5–21</sup> are areas gaining increasing interest in pervaporation. In most cases, high-value substances are produced<sup>6</sup> and tailor-made membranes are requested.<sup>22</sup> Indeed, applied in biotechnology,<sup>7,23,24</sup> pervaporation discloses some specific advantages, such as operation at physiological temperature, simple equipment, no fouling problems, and no toxic solvents. Traditional methods on the other hand often demand high-energy inputs (vacuum distillation) or lead to polluted water (solvent extraction).

In this work, unfilled PDMS (polydimethylsiloxane) and zeolite-filled PDMS membranes were tested for two purposes: firstly, the removal of aroma compounds as a whole from a model mixture, and secondly the selective removal of ethanol from the same solutions. Nowadays, low-alcohol beverages can be realized by two major processes:<sup>2</sup> biologically by using special yeasts, or technologically by removing the alcohol after the fermentation. In the latter case, distillation is often used, but this leads to a so-called “cooked” taste and the undesired removal of certain flavor substances. More recently, two membrane processes, reverse osmosis and dialysis, were introduced in alcohol removal, but some important flavor compounds are still lost through the membranes. Kimmerle and Guderhatsch<sup>2</sup> proved that combining evaporation and pervaporation is best. According to these authors, further lowering of the retention limit for the pervaporation membrane to a molecular weight of 50 is still a great challenge, since only ethanol (MW = 46) would be removed then.

PDMS was reported already to be an appropriate membrane<sup>3–11,13,14,21,22</sup> for both applications studied in this paper. Upon using silicalite-filled PDMS,<sup>9</sup> selectivity for 1-octen-3-ol was even doubled, while the flux decreased slightly. In this work, the influence of the zeolite on the membrane performance is further investigated, and the prepared membranes are compared with commercially available PDMS membranes

(GFT-Le Carbone, Germany). Sorption measurements and the influence of temperature will be used to explain pervaporation results. A selection was made from the wide variety of aroma compounds. They were chosen so as to contain relevant aromas, representing the four most important functional groups: alcohols, aldehydes, esters, and ketones. For every functional group, two molecules were selected with different numbers of carbon atoms. Consequently, this mixture allowed—apart from its practical application—a more fundamental study of the importance of functional groups and molecular chain length on the pervaporation using zeolite-filled PDMS membranes, in addition to the earlier reported study of alcohol pervaporation with these systems.<sup>25</sup>

## Materials and Methods

**Preparation of the Membranes.** Membranes were prepared from dilute PDMS solutions as described by Vankelecom et al.<sup>26</sup> The self-prepared membranes were all self-supporting, with thicknesses varying between 200 and 250  $\mu\text{m}$ . All self-prepared membranes contained 20 vol % zeolite. Table 1 lists the main characteristics of these zeolites. For USY (ultrastable zeolite Y) and the amorphous fillers, the same density as for zeolite Y was taken. The GFT membranes were asymmetric membranes consisting of a dense top layer with a thickness of 11 or 48  $\mu\text{m}$  for the unfilled and silicalite-filled (60 wt %) PDMS, respectively. They were supported by a polyacrylonitrile asymmetric membrane coated on a polyester nonwoven.

**Pretreatment of the Membranes.** Membrane desorption, prior to both sorption and pervaporation, occurred in a vacuum oven for at least 12 h at 150 °C. GFT membranes were pretreated at 80 °C under vacuum, as they showed a lower thermostability.

**Sorption.** Sorption experiments were done on pure compounds as described elsewhere<sup>25</sup> at 4 and 57 °C. The temperature dependency was calculated as follows:  $S_2 - S_1/S_1\Delta T$ , with sorption  $S$  expressed in mL/g.

**Pervaporation.** Pervaporation was performed using a GFT-Le Carbone test cell (6 in. membrane diameter). The permeate pressure was kept below 3 mbar, and a feed flow of 50 L/h was installed. A feed temperature of 40 °C was chosen to combine a reasonable flux, realistic temperatures for possible applications, and limited evaporation of the aromatics in the

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TABLE 1: Main Properties of the Zeolites Used

	silicalite (CBV-2802)	ZSM-5 (CBV-3020)	borosilicate	USY (ZF 520)	zeolite Y
company	PQ-zeolites	PQ-zeolites	Amoco	Zeocat	Zeocat
cation form	NH <sub>4</sub>	NH <sub>4</sub>	H	H	Na
SiO <sub>2</sub> /X <sub>2</sub> O <sub>3</sub>	275 <sup>a</sup>	33 <sup>a</sup>	11.82 <sup>b</sup>	40 <sup>a</sup>	2.7 <sup>a</sup>
size (μm)	0.4–0.8	0.1–0.8	0.1–1.0	0.4–0.8	0.5–2.0
BET (m <sup>2</sup> /g)	410	430	304	738 (micro) + 174 (meso+ macro)	672
topology	MFI	MFI	MFI		FAU
density (mL/g)	1.76	1.76	1.76		1.27
void volume (cm <sup>3</sup> /g)					
micro	0.1275	0.1275	0.1275	0.316	0.3156
meso + macro				0.316	0.0922

<sup>a</sup> X = Al. <sup>b</sup> X = B.TABLE 2: Some Important Parameters of the Aroma Compounds<sup>a</sup>

	$\delta_d(\sqrt{\text{J/cm}^3})$	$\delta_p(\sqrt{\text{J/cm}^3})$	$\delta_h(\sqrt{\text{J/cm}^3})$	$\delta_{\text{tot}}(\sqrt{\text{J/cm}^3})$	$\Delta_{\text{PDMS}}(\sqrt{\text{J/cm}^3})$	activity coefficient $\gamma$	partial pressure (mbar)
ethanol	15.8	8.8	19.4	26.5	17.1	4.98	0.035
butanedione	14.9	11.4	6.5	19.9	11.5	5.38	11.10 <sup>-5</sup>
ethyl acetate	15.2	5.3	9.2	18.5	6.9	68.6	0.348
valeraldehyde	18.1	8.5	6.9	21.2	8.9	229	0.460
isoamyl alcohol	17.8	4.5	13.5	22.8	10.0	279	0.068
hexanal	16.4	6.7	6.1	18.7	6.7	963	0.599
hexanone	19.4	7.7	4.5	21.4	8.3	295	0.175
isoamyl acetate	15.3	3.1	7.0	17.1	3.8	3050 <sup>b</sup>	0.844

<sup>a</sup> For the liquids, the Hildebrandt values were taken from refs 27 and 28 and for PDMS from ref 29. <sup>b</sup> The activity coefficients were calculated following the UNIFAC method, except for isoamyl acetate, where this method resulted in an unrealistic number. For this compound, the coefficient was calculated as the mean of the values obtained using the NRTL and the Wilson method.

pervaporation reservoir. Before applying the membranes in the pervaporation cell, they were immersed at 40 °C in a solution having the same composition as the feed solution. This pretreatment minimizes the time for the membrane to come to a steady state permeation in the pervaporation cell and avoids the depletion of the aromatics from the feed solution before the measurement actually can be started. This equilibrium time was determined experimentally and fixed at one-eighth of the total pervaporation time. Pervaporation was continued each time until about 1 g of permeate was collected. A mixture of eight aromatic compounds in water, 100 ppm each, was used as feed solution. The compounds contained four of the most important functional groups found in alcoholic beverages: esters (ethyl acetate (C2Ac), isoamyl acetate (iC5Ac)), aldehydes (valeraldehyde (C5al), hexanal (C6al)), alcohols (ethanol (C2ol), isoamyl alcohol (iC5ol)), and ketones (2-hexanone (C6one), 2,3-butanedione (C4dione)). Their main characteristics are listed in Table 2. The activities were calculated using the Uniquac model (Aspen Plus software, release 9.2-1), assuming interaction between each aromatic compound and water. Because of the very low concentrations, no interaction with the other aromatic compounds was taken into account.

The feed and permeate solutions were analyzed using gas chromatography (HP 5890 series II with HP 3396 integrator). The column had a CP-SIL-5 CB packing (column length 25 m, film thickness 1.2 μm, and 0.32 mm internal diameter). The detector was at 300 °C and the injector at 290 °C with a column head pressure of 62 kPa. Analysis was isothermal at 110 °C and cyclohexanol was used as external standard. The standard was added to feed solutions as a 4000 ppm solution and to permeates as a pure compound, after dilution of the permeate with acetone to make one phase. The enrichment factors are expressed as a ratio of wt % aromatic present in the permeate over the wt % present in the feed.

## Results and Discussion

**Sorption in PDMS.** Figure 1 illustrates the sorption in unfilled PDMS for the various aromatic compounds, ordered

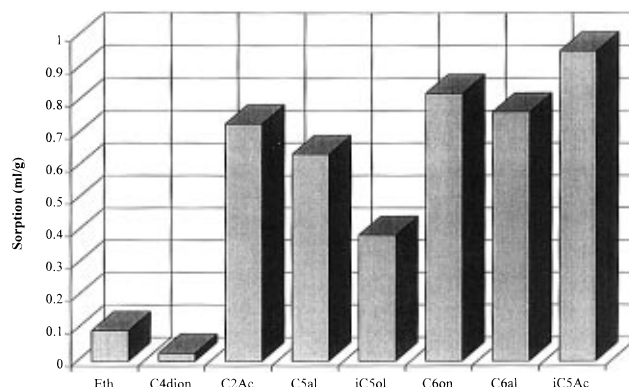
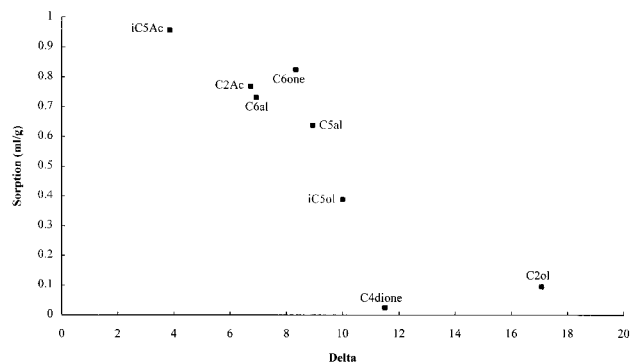


Figure 1. Sorption of aroma compounds in unfilled PDMS ( $T = 57$  °C).

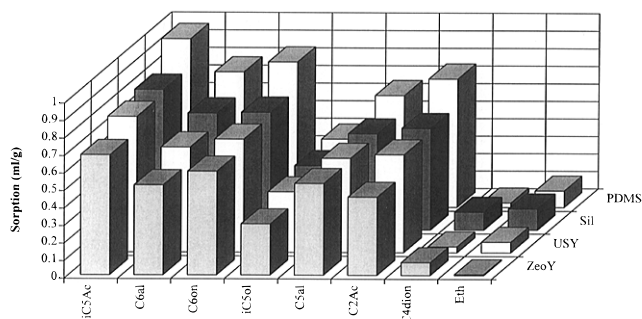
according to the number of carbon atoms present. The graph proves that—for the compounds considered—the functional group of the compound exerts a more important influence than the number of carbon atoms, in agreement with Lamer et al.<sup>19</sup> The low sorption for 2,3-butanedione is striking. Obviously, the presence of the two polar ketone functions strongly reduces the interactions with the PDMS. Similarly, the formation of hydrogen bonds, as introduced by alcohol groups, decreases sorption. Due to their low polarity, the acetates are found to sorb best.

Figure 2 shows the sorptions for the aromatic compounds in PDMS and indicates the correlation that exists between the sorbed amounts and the Hildebrandt  $\Delta_{\text{PDMS}}$  parameter.<sup>27–29</sup> It demonstrates that sorption in PDMS can be explained fairly well by the difference between the three interaction parameters of the aromatic compound and the polymer, just as found before for alcohols.<sup>25</sup> Only the introduction of two functional groups, as in 2,3-butanedione, seems to result in a deviant behavior.

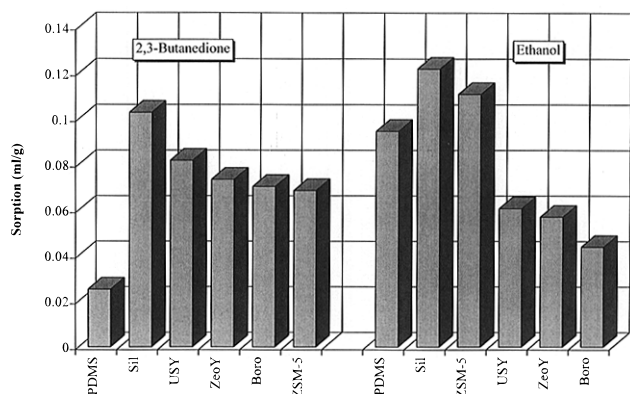
**Influence of the Inorganic Filler on Sorption.** For the compounds interacting strongly with the PDMS, it is clear in Figure 3 that the nature of the zeolite is of no importance for the membrane sorption. The incorporation of 20 vol % zeolite



**Figure 2.** Relation between the membrane sorption capacity and the  $\Delta$  Hildebrandt parameter between the aroma compound and PDMS.



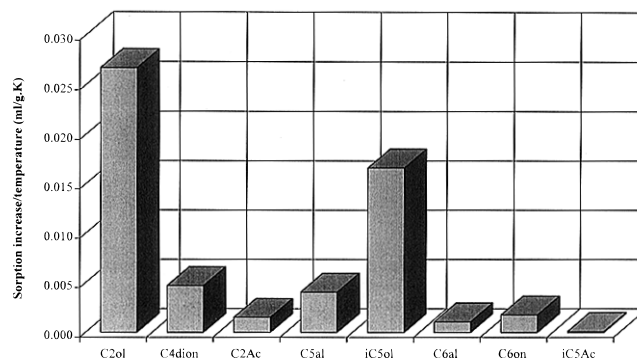
**Figure 3.** Influence of the zeolite incorporated on the sorption of the aroma compounds.



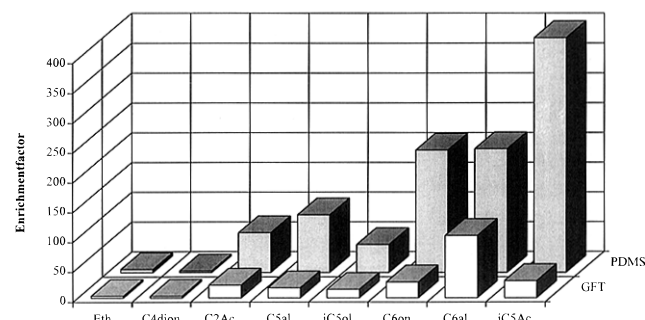
**Figure 4.** Ethanol and 2,3-butanedione sorption as a function of the zeolite incorporated.

always results in the same decreased sorption, as a consequence of the cross-linking of the zeolite on the polymer.<sup>30</sup> In these cases, the sorption capacity available in the rigid zeolite structures is indeed negligible compared to the amount sorbed in the strongly swollen PDMS matrix. As the three zeolites—borosilicate, ZSM-5 and silicalite—showed the same sorptions, only one of them is shown in Figure 3. It proves that the chemical composition of these zeolites and consequently their hydrophobic/hydrophilic properties are of minor importance.

However, this relationship is not valid for the two aroma compounds that hardly sorb in the PDMS: ethanol and 2,3-butanedione. In these cases, the sorption capacity available in the zeolite sometimes even exceeds that available in the polymer. Consequently, unfilled PDMS is no longer the membrane with the highest sorption. Figure 4 describes in detail the influence of the respective zeolites. For the very polar 2,3-butanedione—hardly sorbing in PDMS, as shown in Figure 1—the incorporation of any zeolite in PDMS results in an increased sorption. For ethanol, increased sorptions are found in the case of silicalite and ZSM-5.



**Figure 5.** Increase of sorption in PDMS per kelvin.



**Figure 6.** Enrichment factors compared for the two PDMS membranes.

**Influence of Temperature on Sorption.** It is remarkable how the change in sorption per kelvin, as depicted in Figure 5, reverses the sequence found for total sorptions. Indeed, the least sorbing molecules undergo the largest influence of temperature. The compounds having strong interactions with the polymer make the polymer swell so much that an increase in temperature can hardly expand more the strongly swollen polymer. Sorption for both alcohols is extremely temperature dependent. This can be ascribed to the limited amount of heat dissipated when a molecule sorbs in the polymer, as given by the high  $\Delta$ <sup>PDMS</sup> values (Table 2). Since this is the only exothermic step in the overall endothermic sorption process—being a combination of three steps: desorption from the bulk liquid, increase in free volume of the polymer, and sorption in the membrane—it makes the overall sorption process more endothermic and consequently more temperature dependent.

**Pervaporation Using PDMS.** Figure 6 reflects how the hydrophobic aroma compounds are much more enriched when using the self-prepared PDMS. This result can be explained by considering the chemical nature of the PDMS. The acrylate groups present in the GFT membrane make the membrane much more polar and, consequently, increase water sorption and permeation. It should be taken into account that the commercial GFT membranes are built up by a thin top layer adhered on a support material consisting of a polyacrylonitrile layer on a polyester nonwoven. The effective thickness of the top layers was measured by SEM, and 11  $\mu$ m was taken for the GFT-PDMS. The possible effect of the support layer on the overall membrane performance was thus not considered.

Our results confirm the observations made by Bengtsson et al.<sup>4</sup> and Lamer et al.,<sup>19</sup> where the alcohols are called “slow permeating” molecules and the esters “fast permeating”. The aldehydes and ketones show an intermediate behavior. The two ketone functions on 2,3-butanedione reduce the permeation of the molecule to a large extent, as explained directly by the sorption measurements mentioned before. Figure 6 clearly indicates that in pervaporation the importance of the functional group is—in contrast to sorption—overshadowed by the more decisive molecule chain length, with isoamyl alcohol as the only

**TABLE 3: Influence of the Filler on the Fluxes and Overall Enrichment Factors**

filler	organic flux (g/m <sup>2</sup> ·h)	water flux (g/m <sup>2</sup> ·h)	total flux (g/m <sup>2</sup> ·h)	overall enrichment factor
PDMS	7.34	66.35	73.69	125
USY	5.80	46.24	52.04	139
zeo Y	5.77	722.00	727.77	10
sil	5.52	49.45	54.17	126

**TABLE 4: Aroma Enrichment Factors**

	GFT	GFT Sil	PDMS	20 vol % silicalite	40 vol % silicalite
eth	3	10	5	3	28
C4dion	3	9	3	4	12
C2Ac	21	46	67	56	126
C5al	17	47	97	113	17
iC5ol	14	31	47	64	157
C6on	27	77	206	34	110
C6al	104	66	208	151	120
iC5Ac	29	89	394	313	104

exception, probably because of a combined effect of low sorption and steric hindrance from the iso group.

**Influence of the Zeolite on Pervaporation.** In Table 3, an overall enrichment factor is calculated, expressing the enrichment of the organics as a whole. It is calculated as the wt % of organics in the permeate over the wt % of organics in the feed solution. When considering the potential application of the membranes in pervaporation of aromas, this is actually the most useful parameter.

Zeolite Y clearly shows the most extreme results: an exceptionally high total flux, completely due to the transport of water, leading to an extremely low enrichment factor. It agrees with the results reported for alcohols before.<sup>25</sup> Among all other membranes, unfilled PDMS is one of the best, especially when merely considering the organic fluxes. Given the cross-linking effect of the zeolites on the polymer, it is not surprising to see that all organic fluxes in the composite membranes are lowered by the incorporation of zeolites and that reduced water permeation occurs. For the more hydrophobic fillers—USY and silicalite—the enrichment factors are high, due to the exclusion of water from the pores. The diffusion of the organics is faster in the case of USY, in which mesopores are available. The organic transport through the pores is slightly enhanced, while the water exclusion seems to be maintained.

**Influence of Temperature.** For the various aroma compounds, pervaporation using a 20 vol % silicalite PDMS membrane reveals that the water permeation is less diffusion limited than the permeation of organics. Indeed, the water flux increases by a factor 1.6 with increasing temperature from 40 °C to 58 °C, while the organic flux and the total flux increase by a factor 4.8 and 1.9, respectively. Just as before,<sup>25</sup> this demonstrates the role of diffusion in pervaporation. The influence of temperature is even stronger for higher zeolite loadings in the membrane. For a membrane loaded with 40 wt % silicalite, water, organic, and total fluxes increase by a factor 1.8, 5.9, and 2.2, respectively. Increasing temperatures increase not only fluxes but selectivities as well (from 127 to 325 for the 20 vol % silicalite PDMS), just as proven for alcohols.<sup>25</sup> This is in contrast to the results of Dettwiler et al. (1991), who found constant selectivities, and te Hennepe (1988), reporting decreasing alcohol selectivities with increasing temperature.

**Selective Removal of Ethanol.** Keeping in mind the application of these membranes in the preparation of low-alcohol beverages or in the production of biofermentation products, the removal of ethanol is of prime importance with a high retention

of both water and all the other aromas. As seen from Table 4, the PDMS filled with 40 vol % silicalite would be the best membrane for this purpose. The very small ethanol molecules can pass easily through the composite membrane, while the larger aroma compounds are retained better than in the other self-prepared membranes. Due to the hydrophobic nature of silicalite, water is excluded and no energy is wasted in condensing unnecessary water fluxes. This membrane almost fulfills the challenge mentioned by Kimmerle and Gudernatsch<sup>2</sup> to prepare pervaporation membranes with a low retention limit.

## Conclusions

Sorption of aroma compounds in PDMS can be explained by the Hildebrandt parameters, with a deviation if two functional groups are present on one molecule. Ketone and alcohol functions reduce sorption, while esters show a high affinity for PDMS. Adding any zeolite to the membrane reduces sorption for the compounds with high affinity for PDMS, while the type of zeolite affects only the sorption of those compounds having a limited sorption in unfilled PDMS. Compounds sorbing least show the strongest temperature dependency. In contrast to sorption, where the functional groups determine the behavior, the number of carbon atoms in the molecules determines the rate of pervaporation. The presence of an iso group on a compound seems to induce steric hindrance. Extremely high water fluxes resulted from the incorporation of zeolite Y. All other zeolites induced a cross-linking in the membrane, lowering fluxes through the polymer phase. The influence of temperature revealed the importance of diffusion limitations on the transport of organics through the membranes. This effect was stronger when more zeolite was incorporated. A rise in temperature introduced higher enrichment factors, apart from the expected increase in flux. As transport of aromas through zeolite pore systems reduces the overall membrane transport—regardless the selectivity increase—the incorporation of mesoporous hydrophobic structures seems to be desired for the removal of the aromatics as a whole. Considering the preparation of alcohol-free beverages or the removal of ethanol from biofermentations, high silicalite loadings are recommended, removing ethanol selectively and retaining water as well as most of the aroma compounds.

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