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Pervaporation of Multi Component Aromatic/Aliphatic Mixtures through Copolyimide Membranes

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Abstract: Industrial applications of aromatic/aliphatic separations by pervaporation require the investigation of multi component mixtures. In this work a multi component aromatic/aliphatic mixture was applied as feed. The aromatic feed components were not only mononuclear but also di- and trinuclear. Different membranes based on 6FDA-4MPD/DABA copolyimides were investigated. The copolyimide composition was varied concerning the number of cross-linking sites. For the preparation of cross-linked membranes different cross-linking agents were used. Additionally pre-treatment of the membranes was investigated. The pervaporation conditions were varied concerning the permeate as well as feed pressure, feed temperature, and feed composition. Experiments were carried out at 100°C and 150°C, a permeate pressure of 25 mbar and 250 mbar respectively was applied and the feed pressure was 1 bar or rather 12 bar.

In the course of the measurements acceptable fluxes between $1{,}9\,\mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$ and $23{,}6\,\mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$ were found. Enrichment factors for all aromatics over aliphatic components in the range of $\beta_{arom.} = 1{,}3$ and $\beta_{arom.} = 2{,}3$ were reached. That means in some cases a doubling of the aromatics concentration was achieved.

Keywords: Aromatic/aliphatic separation, multi component mixture, copolyimides, pervaporation

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INTRODUCTION

For the separation of aromatic/aliphatic mixtures basically two industrial applications are of great interest, the removal of aromatics from fuels and the reduction of aromatics from naphtha streams. Especially toxic aromatic components as benzene, toluene but also C_{10} derivates have to be removed from fuel as the prescriptive limits are continuously lowered by law. Both applications require the separation of complex feed mixtures of mononuclear but also di-and trinuclear non-substituted as well as alkyl-substituted aromatic components and linear, branched and cyclic aliphatic components of different chain length.

The separation of binary aromatic/aliphatic mixtures has been studied intensively in the past couple of years (1–4). But as the investigation of multi component mixtures requires a huge analytical expenditure, in most cases only binary mixtures with a mononuclear aromatic component have been examined. Whether the results gained from binary mixtures can be transferred to multi component mixtures is still questionable.

THEORETICAL BACKGROUND

The separation performance of a membrane material is characterized by the selectivity and the permeability. The permeability can be measured by the mass flux through the membrane. The flux is normalized on the membrane area, the membrane thickness and the time, so that its unit is $kg \cdot \mu m \cdot m^{-2} \cdot h^{-1}$. The normalized flux J_{norm} can be evaluated from the thickness of the membrane δ_M, the membrane area A and the amount of permeate m_p collected in a defined time period t using Eq. (1).

$$J_{norm} = \frac{m_p \cdot \delta_M}{t \cdot A} \tag{1}$$

In order to compare the selectivities of the single components in multi component pervaporation experiments, the enrichment factor β is used. β is defined by Eq. (2), whereas w_i characterizes the weight percentage of the considered component.

$$\frac{\beta = w_i^{permeate}}{w_i^{feed}} \tag{2}$$

To describe the overall selectivity of the membranes, the enrichment factor for all aromatic components $\beta_{arom.}$ is used. It is defined by Equation (3). $w_{\Sigma arom.}$ characterizes the weight percentage of all aromatic components.

$$\beta_{arom} = \frac{w_{\Sigma arom}^{permeate}}{w_{\Sigma arom}^{feed}} \tag{3}$$

EXPERIMENTAL

Membrane Materials

Pervaporation experiments were performed with 6FDA-4MPD/DABA m:n copolyimide membranes with different ratios of the diamines 4MPD and DABA which lead to different numbers of cross-linking sites. Besides that the membrane material was pre-treated in order to enhance the separation characteristics. The chemical structures of the membrane polymers used are given in Fig. 1. The synthesis of these cross-linkable membrane polymers was already published (5). Cross-linked copolyimide membranes are particularly suitable for the separation of aromatic/aliphatic mixtures as they have an exceeding chemical resistance, are stable against high temperatures due to high glass transition temperatures, have excellent mechanical properties and show good mass transport abilities. Their chemical structures provide several modification possibilities as the ratio of the cross-linkable group can be set up by the ratio of the diamines and different cross-linking agents can be applied.

Membrane Preparation

To prepare a membrane of approximately 30 µm thickness and 10 cm diameter 300 mg of the membrane polymer 6FDA-4MPD/DABA m:n, 6 times of the stoichiometric amount of the cross-linking agent referring to the cross-linkable groups of the polymer and 0,6 times of the stoichiometric amount of toluene-4-sulfonic acid monohydrate as catalyst were dissolved in 10 ml freshly distilled dry N,N-dimethylacetamide. The solution is then filtered and effused in a plain glass platter. At 70°C the solvent evaporates within 18 hours. The produced membranes are stored for another 18 hours at 150°C to perform the cross-linking reaction.

Some membranes were pre-treated before they were applied in the separation cell. That means the membrane was exposed to pure toluene over night and dried in the cabinet desiccator at 60°C before application. The exposure to pure toluene causes a swelling of the membrane which is not

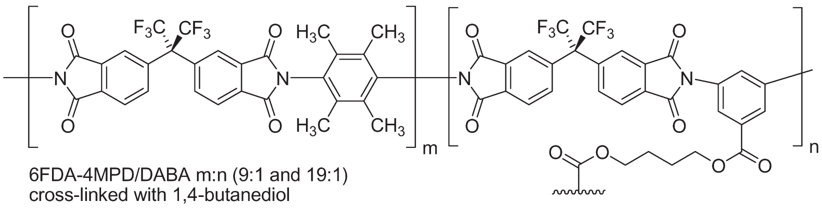


Figure 1. Chemical structure of the cross-linked 6FDA-4MPD/DABA m:n copolyimide used.

completely reversible. The reverse reaction seems to be kinetically inhibited as the enhanced pervaporation results were still found after several weeks (6).

Pervaporation Setup

The experiments were carried out with a special pervaporation setup completely made from stainless steel. The construction is schematically shown in Fig. 2 and ensures that pervaporation experiments can be performed up to a feed temperature of 150°C and up to a feed pressure of 12 bar, which can be generated by nitrogen. The applied feed pressure can be controlled by the pressure measuring device.

Pervaporation Experiments

For the pervaporation experiments different multi component feed mixtures with 5 to 9 components were used. All three feed systems are supposed to represent simplified benzine or diesel fuel mixtures that consist of hundreds of components. The chosen compositions assure that the boiling points of the feed mixtures are comparable to the real fuel mixtures but differ in their number of different components. Feed 1 consists of seven components. The four aromatics account for 39 wt.%, while the three aliphatics account for 61 wt.%. Feed 2 is a nine component system which includes five aromatic (43 wt.%) and four aliphatic (57 wt.%) components. The five component mixture of feed 3 contains of three aromatics with 27,5 wt.% and two aliphatics with 72,5 wt.%. The feed compositions and the chemical structures of the applied components can be found in Table 1 in detail.

The thicknesses of the membranes were measured on several points by a micrometer screw and averaged over all.

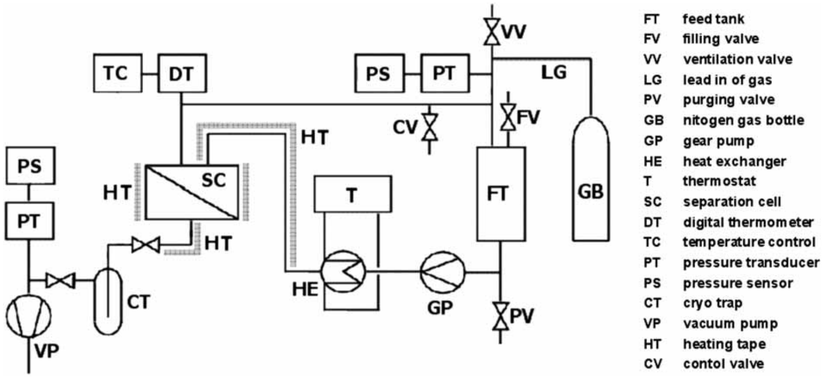
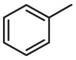
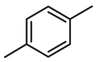
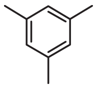
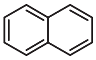
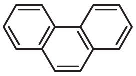
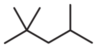
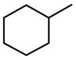
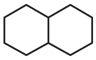


Figure 2. Schematical construction of the pervaporation setup.

Table 1. Compositions of the different feed mixtures

Component	Chemical structure	Feed 1 wt.%	Feed 2 wt.%	Feed 3 wt.%
Benzene		—	0,9	—
Toluene		13,0	15,9	—
p-Xylene		17,7	17,7	—
Trimethylbenzene		6,7	6,9	18,4
Naphthalene		1,4	1,4	5,6
Phenanthrene		—	—	3,4
n-Heptane		40,6	38,1	—
Isooctane		17,8	17,1	—
n-Hexadecane		—	—	40,1
Cyclohexane		—	0,4	—
Methylcyclohexane		2,8	1,6	—
Decalin		—	—	32,5
Total aromatics		38,8	42,8	27,4
Total aliphatics		61,2	57,2	72,6

To access the flux, the permeate was recondensed in a cryo trap for a defined period of time at steady state conditions. The average flux is evaluated from three to four measured fluxes.

The permeate was analyzed by gas chromatography.

RESULTS AND DISCUSSION

Effect of Permeate Pressure

In order to investigate the effect of different permeate pressures on the separation performance pervaporation experiments were carried out at 25 mbar and 250 mbar permeate pressure. In both experiments a 6FDA-

4MPD/DABA 9:1 membrane cross-linked with 1,4-butanediol was applied at 100°C feed temperature. As feed mixture a seven component mixture with 39 wt.% aromatics (feed 1) was used. The measured data are shown in Fig. 3.

As the driving force of the permeation through the membrane is correlated to the pressure difference between permeate and feed side it was expected that an increase of permeate pressure results in a reduced flux. The experimental results indeed showed that as a consequence of the higher permeate pressure the flux decreases from $12{,}3\ \mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$ to $8{,}2\ \mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$. The total enrichment factor nearly remains constant ($\beta_{arom.} = 1{,}6$ at 25 mbar and $\beta_{arom} = 1{,}5$ at 250 mbar).

Similar results were reached with the same membrane type with a nine component mixture with 43 wt.% aromatics (feed 2) and permeate pressures of 25 and 250 mbar at 100°C feed temperature as shown in Fig. 4. The total enrichment factor decreases from $\beta_{arom} = 1{,}6$ to $\beta_{arom} = 1{,}3$ whereas the flux decreases from $23{,}6\ \mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$ to $15{,}8\ \mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$ due to the reduced driving force. In both cases it has been found that the fluxes as well as the enrichment factors for the single aromatic components are reduced with increasing permeate pressure as shown in Figs. 3 and *4*. This affects naphthalene more than the other aromatics as it is no longer concentrated in the permeate at a higher permeate pressure.

Effect of Feed Pressure

For all following pervaporation experiments a five component mixture (feed 3) with an aromatics amount of 27,5 wt.% was applied. The results of a feed

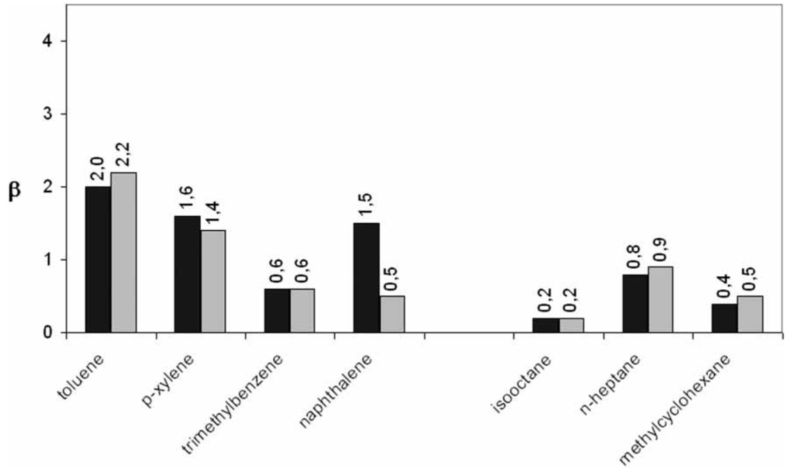


Figure 3. Variation of permeate pressure: 25 mbar (■) and 250 mbar (▨), 6FDA-4MPD/DABA 9:1 membrane, cross-linked with 1,4-butanediol, 100°C, 1 bar feed pressure, feed 1.

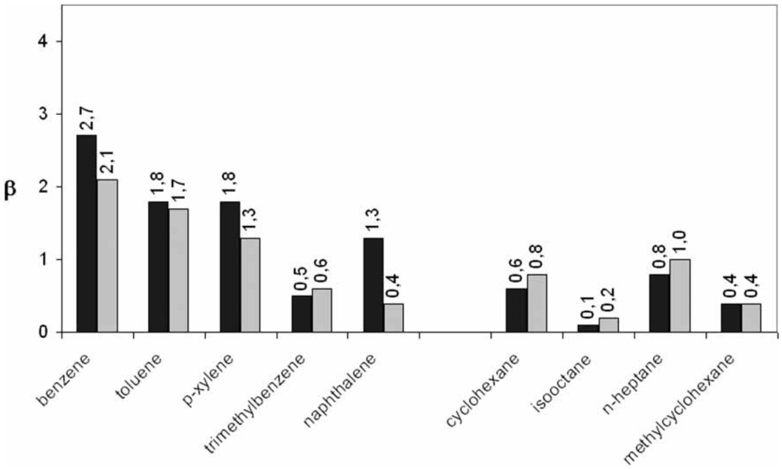


Figure 4. Variation of permeate pressure: 25 mbar (■) and 250 mbar (▨), 6FDA-4MPD/DABA 9:1 membrane, cross-linked with 1,4-butanediol, 100°C, 1 bar feed pressure, feed 2.

pressure increase from 1 to 12 bar with a 6FDA-4MPD/DABA 9:1 membrane cross-linked with 1,4-butanediol are shown in Fig. 5. As expected the feed pressure increase leads to an enhanced flux (1,9 kg · μm · m^{-2} · h^{-1} in comparison to 2,8 kg · μm · m^{-2} · h^{-1}). The reason for this is again the higher driving force of the permeation. The enrichment factor remains nearly

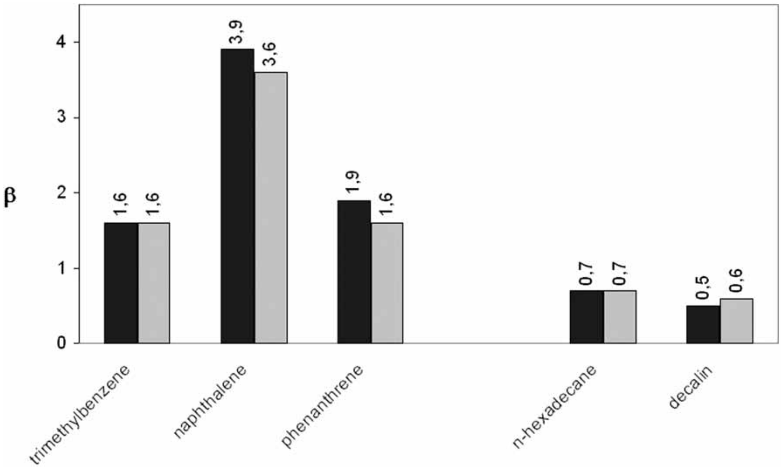


Figure 5. Variation of feed pressure: 1 bar (■) and 12 bar (▨), 6FDA-4MPD/DABA 9:1 membrane, cross-linked with 1,4-butanediol, 150°C, 20–25 mbar permeate pressure, feed 3.

constant, $\beta_{arom.} = 2{,}1$ at 1 bar feed pressure in comparison to $\beta_{arom.} = 2{,}0$ at 12 bar feed pressure. Similar effects have been observed in various pervaporation experiments. From the experimental results presented in Figs. 3–5 it can be concluded that the variation of permeate pressure influences the separation characteristics much more than the change of feed pressure.

Interesting results for feed pressure variation have been obtained with pre-treated 6FDA-4MPD/DABA 19:1 membranes cross-linked with 1,4-butanediol examined under different feed pressures at 150°C. Information about pre-treatment can be found in 4.4. In contrast to the results in Fig. 5., in Fig. 6 it can be seen that the pre-treated membrane does not show an increase but a decrease of flux from $19{,}2\,\mathrm{kg} \cdot \mu\mathrm{m} \cdot \mathrm{m}^{-2} \cdot \mathrm{h}^{-1}$ to $9{,}7\,\mathrm{kg} \cdot \mu\mathrm{m} \cdot \mathrm{m}^{-2} \cdot \mathrm{h}^{-1}$. This could be ascribed to the pre-treatment because this leads to a swollen polymer structure, which is much more versatile against compression due to high feed pressure. It was also observed in this experiment that with higher feed pressure the enrichment factor almost remains constant ($\beta_{arom.} = 2{,}1$ in comparison to $\beta_{arom.} = 2{,}0$).

Effect of Polymer Composition

In Fig. 7 the separation characteristics of a 6FDA-4MPD/DABA 9:1 membrane is compared with these of a 6FDA-4MPD/DABA 19:1 membrane, both were cross-linked with 1,4-butanediol. The pervaporation was performed at 150°C with a five component mixture with 27,8 wt.%

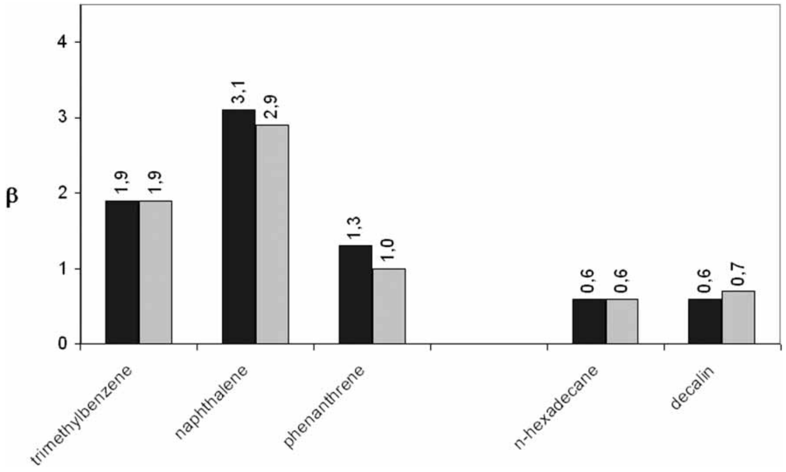


Figure 6. Variation of feed pressure: 1 bar (■) and 12 bar (□), 6FDA-4MPD/DABA 19:1 membrane, cross-linked with 1,4-butanediol, pre-treated with toluene, 20–25 mbar permeate pressure, 150°C, feed 3.

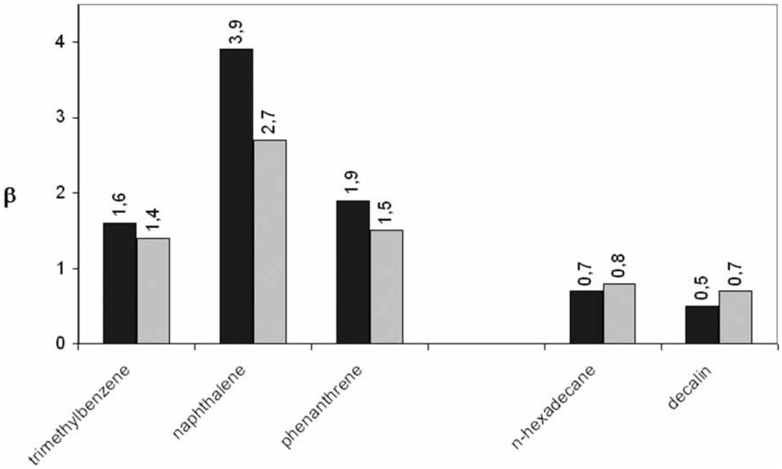


Figure 7. Variation of the diamine ratio in the polymer structure: 6FDA-4MPD/DABA 9:1 (■) and 19:1 (▨) membrane, both cross-linked with 1,4-butanediol, 150°C, 1 bar feed pressure, 20–25 mbar permeate pressure, feed 3.

aromatics (feed 3). By changing the diamine ratio of the polymer structure from 9:1 to 19:1 the number of cross-linkable sites is reduced. The 9:1 polymer has cross-linkable groups statistically in every tenth repeat unit whereas the 19:1 polymer has only one in every twentieth repeat unit which leads to a larger free volume and a higher flexibility of the cross-linked polymer. In consequence the mass-transport through the membrane is enhanced with reduced cross-linking sites which might be the reason for the lower enrichment factor. While the enrichment factor decreases from $\beta_{arom.} = 2{,}1$ to $\beta_{arom.} = 1{,}7$ the flux increases from $1{,}9\ \mathrm{kg \cdot \mu m \cdot m^{-2} \cdot h^{-1}}$ to $11\ \mathrm{kg \cdot \mu m \cdot m^{-2} \cdot h^{-1}}$ by changing the polymer structure from 9:1 to 19:1. Noticeable is that the change in polymer composition influences the permeation of naphthalene more than the other aromatics.

Effect of Pre-treatment

As shown in earlier studies pre-treatment of a membrane is an appropriate method to enhance the flux whereas the selectivity remains constant or even an increase of selectivity can be reached. For example Ren et al. accomplished pervaporation experiments with a benzene/cyclohexane (50:50) mixture at 60°C and 15 mbar permeate pressure and found that the flux of a pre-treated 6FDA-4MPD/DABA 4:1 membrane cross-linked with ethylene glycol is 40% higher than the flux of the untreated membrane (5). Pithan even found higher fluxes and higher selectivities for a 6FDA-4MPD/DABA 4:1 membrane cross-linked with 1,8-octanediol with a toluene/cyclohexane mixture at 60°C and 25 mbar permeate pressure(6).

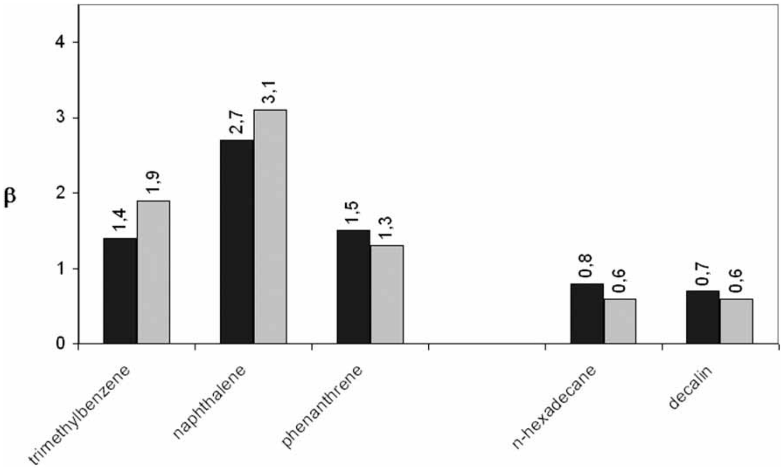


Figure 8. Variation of pre-treatment: without pre-treatment (■) and with pre-treatment (▨), 6FDA-4MPD/DABA 19:1 membrane cross-linked with 1,4-butanediol, 150°C, 1 bar feed pressure, 20–25 mbar permeate pressure, feed 3(7).

The same effect was found in this work by investigating two membrane samples of the 6FDA-4MPD/DABA 19:1 cross-linked with 1,4-butanediol one pre-treated with toluene over night (Fig. 8) (7). The pre-treated membrane shows a higher flux than the untreated one, $11\,\mathrm{kg}\cdot\mu\mathrm{m}\cdot\mathrm{m}^{-2}\cdot\mathrm{h}^{-1}$

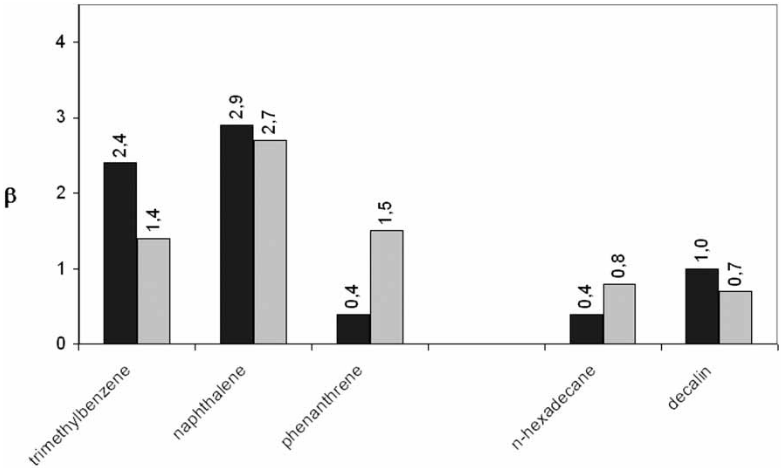


Figure 9. Variation of feed temperature: 100°C (■) and 150 °C (▨), 6FDA-4MPD/DABA 9:1 membrane cross-linked with 1,4-butanediol, 1 bar feed pressure, 20–25 mbar permeate pressure, feed 3 (7).

compared to 19,2 kg $\cdot$ µm $\cdot$ m^{-2} $\cdot$ h^{-1}. Also the enrichment factor increases from $\beta_{arom.} = 1{,}7$ to $\beta_{arom.} = 2{,}1$ after the pre-treatment.

Effect of Feed Temperature

Finally a 6FDA-4MPD/DABA 9:1 membrane cross-linked with 1,4-butanediol was investigated at 100°C and 150°C feed temperature (Fig. 9)(7). Due to the higher temperature the chain mobility of the polymer is increased so that a higher flux was found, 5,8 kg $\cdot$ µm $\cdot$ m^{-2} $\cdot$ h^{-1} at 100°C compared to 12,4 kg $\cdot$ µm $\cdot$ m^{-2} $\cdot$ h^{-1} at 150°C, whereas the enrichment factor decreases from $\beta_{arom.} = 2{,}3$ to $\beta_{arom.} = 1{,}6$.

CONCLUSIONS

An increase of permeate pressure from 25 to 250 mbar results in a lower flux and a lower enrichment factor for the different experiments performed. The lower flux can be ascribed to the reduction of the driving force. The increase of feed pressure provoked an enhanced driving force for the permeation. This results in an increase of flux and a decrease of enrichment factor for the 9:1 membrane cross-linked with 1,4-butanediol but the effects observed were much lower compared to the variation of permeate pressure. The pre-treated membrane shows a reduced flux as well as a reduced selectivity. The reduction of cross-linking sites in the polymer from 9:1 to 19:1 implicates an increase of flux and a decrease of the enrichment factor. Pre-treatment of the membrane results in an increase of flux and enrichment factor. The enhanced feed temperature results in a higher flux and a lower enrichment factor. But it is remarkable that at 150°C all three aromatic components are enriched in the permeate. The aromatic component naphthalene showed a different behaviour than the other aromatics in some pervaporation experiments which will be investigated in further studies.

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