

# Olefin-Selective Membranes in Gas–Liquid Membrane Contactors for Olefin/Paraffin Separation

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The application of olefin-selective membrane materials in gas–liquid membrane contactors for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid turned out to be very successful, especially with respect to the olefin/paraffin selectivity obtainable. Composite hollow-fiber membranes with a top layer of a highly permeable block copolymer of poly(ethylene oxide) (PEO) and poly(butylene terephthalate) (PBT) are prepared and applied in a gas–liquid membrane contactor for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid. The water present in the absorption liquid swells the hydrophilic polymer sufficiently. This prevents drying out of the layer and enables the partitioning of silver ions into the polymer matrix, making it olefin-selective. Ethylene permeabilities obtained are comparable to the values found for membranes with nonselective, elastomeric top layers (40–50 barrer). Selectivities, however, are more than 20 times higher. Independent of the liquid flow rate, a selectivity of 165 is obtained for PEO/PBT-coated membranes. This makes the application of olefin-selective membranes in a membrane contactor for olefin/paraffin separations very attractive.

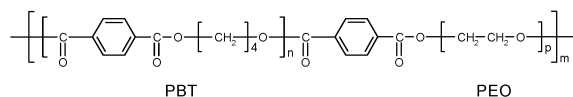
## 1. Introduction

The application of olefin-selective membrane materials in gas–liquid membrane contactors for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid is very promising, especially with respect to the olefin/paraffin selectivity obtainable. Composite hollow fibers with dense olefin-selective top layers of sulfonated poly(ether ether ketone) (SPEEK) give rise to selectivities of at least 2700 when applied in a gas–liquid membrane contactor for olefin/paraffin separation.<sup>1</sup> This is in contrast to the much lower separation factors obtainable when nonselective, elastomeric top layer materials such as ethylene–propylene–diene terpolymer (EPDM) or poly(dimethylsiloxane) (PDMS) are used.<sup>2,3</sup> The olefin selectivity of SPEEK is based on its cation-exchange behavior, which makes it possible to bind silver ions from the absorption liquid both physically and ionically to the sulfonated groups of the polymer chains. The separation of olefins and paraffins is based on the ability of silver ions to reversibly complex unsaturated hydrocarbons.<sup>4,5</sup>

The idea of using olefin-selective membranes in membrane contactor applications for olefin/paraffin separations is based on the theoretical model developed by Shelekhin and Beckman in the early 1990s.<sup>6</sup> According to this model, two limiting cases exist for the olefin/paraffin separation factor obtainable in circulatory membrane absorbers:

(1) At low liquid flow rates, the selectivity is determined by the (high) selectivity of the silver nitrate solution but the total flux is low because of an insufficient supply of the absorption liquid.

(2) At high liquid flow rates, the productivity is high



**Figure 1.** Chemical structure of block copolyether esters based on PBT and PEO.<sup>7–9</sup>

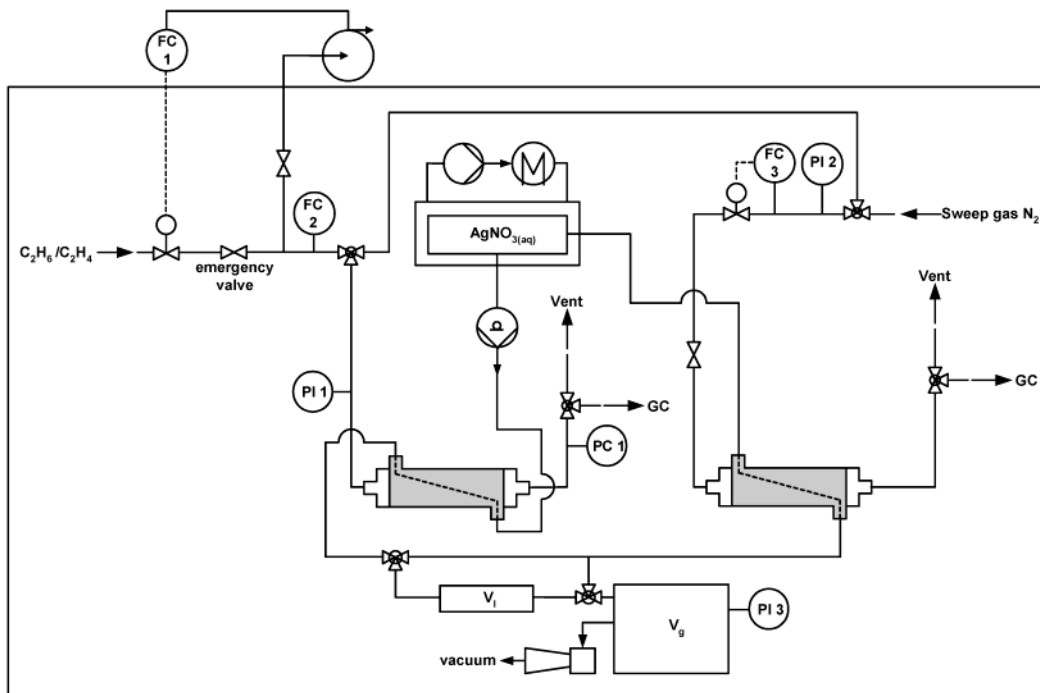
but the selectivity is determined by the (often lower) selectivity of the membrane.

This model thus implies that the use of olefin-selective membrane materials in gas–liquid membrane contactor applications combines high selectivities with high productivities.

Although high selectivities are obtained using SPEEK-coated membranes, ethylene productivities of only  $1 \times 10^{-6}$  cm<sup>3</sup>/s·cm<sup>2</sup>·cmHg are obtained, whereas 10–100 times higher productivities are obtained when elastomeric top layer materials are used.<sup>2,3</sup> To increase the productivity and at the same time keep high selectivity, highly permeable membrane materials, which also carry the potential to bind the silver ion, are required. Poly(ethylene oxide) (PEO) is such a material. This paper focuses on a block copolymer of PEO and poly(butylene terephthalate) (PBT) (Figure 1).

The individual PBT and PEO blocks have some opposite properties.<sup>7–9</sup> At ambient temperatures, PBT is rigid and hydrophobic whereas PEO is flexible and hydrophilic. The crystalline PBT part acts as an impermeable phase, whereas the PEO part has a relatively high permeability due to its high chain mobility. The water present in the absorption liquid swells the polymer sufficiently and enables the partitioning of silver ions into the polymer matrix. Fixation of the silver ions takes place via coordination of the oxygen electron donor groups in the PEO/PBT polymer backbone and improves the stability of the olefin-selective membranes. The high degree of swelling and, consequently, high silver ion uptake guarantee a high gas permeability and,

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**Figure 2.** Process flow diagram of a gas–liquid membrane contactor process for the separation of paraffins and olefins.

at the same time, a high olefin selectivity. The unit phase of PBT gives mechanical strength to the swollen polymer.

In the present work, the application of highly permeable PEO/PBT block copolymers as a stabilizing top layer material in a gas–liquid membrane contactor for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid is investigated as a method to increase productivity and, at the same time, keep high selectivity. The performance of the PEO/PBT-coated membranes is compared to the corresponding results for the same type of membranes having a nonselective, highly permeable, elastomeric EPDM top layer or a highly selective, but low permeable SPEEK top layer (sulfonation degree  $X = 0.85$ ).<sup>1,2</sup>

## 2. Materials and Methods

**2.1. Materials.** PEO/PBT 1000/60/40 (60 wt % PEO, 40 wt % PBT,  $\rho = 1000$ ) was produced by Isotis, Bilthoven, The Netherlands. Chloroform was purchased from Merck, Amsterdam, The Netherlands, and used as received. Ultrapure water (resistivity  $> 18.0 \text{ M}\Omega \cdot \text{cm}$  at  $25^\circ \text{C}$ ) was used. The gas mixture used for membrane contactor experiments [ethane (20%)/ethylene (80%)] was obtained from Praxair, Olen, Belgium. Nitrogen (99.9%) was supplied by Hoekloos, Enschede, The Netherlands.  $\text{AgNO}_3$  (analytical grade) was supplied by Merck and used as received.

**2.2. Film Formation and Characterization.** For characterization purposes, thin PEO/PBT films were prepared by dissolving 8 wt % PEO/PBT in chloroform. The viscous solution was cast on a Teflon plate with a 1.0 mm casting knife. The film was dried under nitrogen to allow chloroform evaporation and to prevent water uptake from the air. After 3–4 h, the film was removed from the Teflon plate and dried in a vacuum oven at  $30^\circ \text{C}$  for 48 h to remove the residual solvent. Films were characterized by means of gas permeability of the dry film and weight increase due to swelling.

**2.3. Composite Membrane and Module Preparation.** Composite hollow-fiber membranes with a PEO/PBT top layer at the outside were prepared with dip coating. Accurel S6/2 polypropylene hollow fibers were used as support material. The fibers had an inner diameter of 1.8 mm and an outer diameter of 2.7 mm. Characteristics of this type of fiber, as supplied by the manufacturer, were presented in a previous work.<sup>1</sup>

Defect-free composite membranes were prepared in two coating steps using an 8 wt % coating solution. Scanning electron microscopy (SEM) was used to investigate the morphology of the prepared composite hollow fibers. Defect-free membranes were used for membrane module preparation. Each module contained 10 fibers. On the basis of the outer diameter, this resulted in an effective membrane area of  $102 \text{ cm}^2$  per module. Modules were characterized by determining the gas permeability for  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{C}_2\text{H}_4$  and the water permeability using a 3.5 M silver nitrate solution as the feed. The exact methods used for composite membrane and module preparation and characterization are described elsewhere.<sup>1</sup>

**2.4. Membrane Contactor Experiments.** Membrane contactor experiments were performed in the bench-scale process presented in Figure 2. A mixture of ethane (20%) and ethylene (80%) was fed to the absorption module, using a pressure controller to apply a feed pressure of 3 bar. The applied feed flow rate was 100 mL/min. Because the outside of the fibers was coated, the gas was fed to the inside of the fibers. The ratio of the amount of absorbed gas and the amount of retentate leaving the absorber module was kept constant at a value of 0.05, indicating that the retentate volume flow rate was 20 times as large as the permeate volume flow rate. The amount and composition of the retentate stream was automatically analyzed by a gas chromatograph [GC; Varian 3300, with a flame ionization detector (FID)]. The composition was constant in

time and equal to the initial feed composition, taking into account the experimental error.

A 3.5 M silver nitrate solution was used as the absorption liquid. Liquid flow rates of 50–350 mL/min were applied, resulting in estimated Reynolds numbers between 19 and 135. Nitrogen with a pressure of 1 bar and a flow rate of 100 mL/min was used as the sweep gas at the desorption side. The ratio of the hydrocarbon permeate and the nitrogen stream was kept constant at a value of 0.05, to assume a constant driving force for hydrocarbon permeation at the desorption. All experiments were performed at room temperature (25 °C).

The overall ethylene or ethane productivity  $Q$  ( $\text{cm}^3/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ ) was calculated as the volume flow rate of the permeate stream  $V$ , multiplied by the volume fraction of ethylene (or ethane) in the permeate stream  $\gamma$ , divided by the effective membrane area  $A$  of one membrane module ( $102 \text{ cm}^2$ ) and the partial pressure difference across the membrane  $\Delta p$  (eq 1).

$$Q = \gamma V / A \Delta p \quad (1)$$

The ideal separation factor  $\alpha_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6}$  was calculated as in eq 2, where  $Y_i$  is the concentration of component  $i$  in

$$\alpha = \frac{Y_{\text{C}_2\text{H}_4} / Y_{\text{C}_2\text{H}_6}}{X_{\text{C}_2\text{H}_4} / X_{\text{C}_2\text{H}_6}} \quad (2)$$

the permeate stream that leaves the desorber and  $X_i$  is the concentration of component  $i$  in the feed.

The bench-scale membrane contactor process used in previous work<sup>1,2</sup> was modified in such a way that the degree of ethylene saturation of the silver nitrate stream that leaves the absorber and enters the desorber could be determined. The ethylene-loaded silver nitrate solution flowed through a bypass ( $V_1 = 15.0 \text{ mL}$ ). At a certain moment, the valves to the main liquid stream were closed and the valve to the expansion vessel ( $V_g = 541.4 \text{ mL}$ ) was opened to allow the ethylene–silver system to expand. After 15 min, the ethylene equilibrium pressure was obtained. The solubility ( $S$ ) of ethylene in the silver nitrate solution after expansion could be calculated using the empirical relation proposed by Cho et al.<sup>10</sup> that gives the relation between this solubility and the ethylene equilibrium pressure ( $P$ ), the temperature ( $T$ ), and the silver nitrate concentration ( $c$ ).

### 3. Results

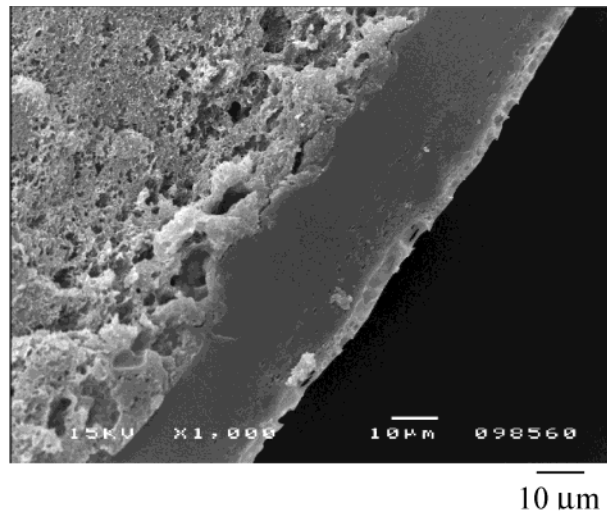
**3.1. Polymer Characterization.** The PEO/PBT films prepared and used for characterization have an average thickness of 100–150  $\mu\text{m}$ . Experimentally determined characteristics of PEO/PBT, EPDM,<sup>2</sup> and SPEEK<sup>1</sup> films are given in Table 1. The ethane and ethylene permeabilities of PEO/PBT films are lower than the corresponding values for EPDM. This is due to unfavorable interactions between the polar, oxygen-containing PEO/PBT polymer and the  $\text{C}_2$  hydrocarbons.<sup>11–13</sup>

The water permeability of potential top layer materials for the separation of paraffins and olefins in a membrane contactor application may be important because it can give an indication of whether undesired humidification of the gas streams in the contactor is likely to occur. The experimentally determined water permeability of PEO/PBT films using a 3.5 M silver nitrate solution as the feed is extremely high compared

**Table 1. Experimentally Determined Characteristics of PEO/PBT, EPDM, and SPEEK Films Used for Membrane Contactor Experiments**

polymer	permeability (barrer <sup>a</sup> )			swelling (wt %)		
	$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_4$	$\text{H}_2\text{O}^b$	$\text{H}_2\text{O}$	3.5 M $\text{AgNO}_3$	$\text{H}_2\text{O real}^c$
PEO/PBT	10.4	16.5	$5.4 \times 10^5$	53.7	84.7	42.5
EPDM	40.2	46.4	$1.5 \times 10^3$	0.3	0.1	na <sup>d</sup>
SPEEK	na <sup>d</sup>	na <sup>d</sup>	$1.2 \times 10^5$	88.0	51.0	11.0

<sup>a</sup> 1 barrer =  $1 \times 10^{-10} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ . <sup>b</sup> Feed: 3.5 M  $\text{AgNO}_3(\text{aq})$ . <sup>c</sup>  $\text{H}_2\text{O real}$  is the real water uptake due to swelling of the film in 3.5 M  $\text{AgNO}_3(\text{aq})$ , calculated as the weight of the swollen film corrected for the weight increase due to the presence of silver nitrate ( $M_{w, \text{AgNO}_3} = 170 \text{ g/mol}$ ). <sup>d</sup> Not analyzed. Permeability is below the detection limit of the gas permeation device.



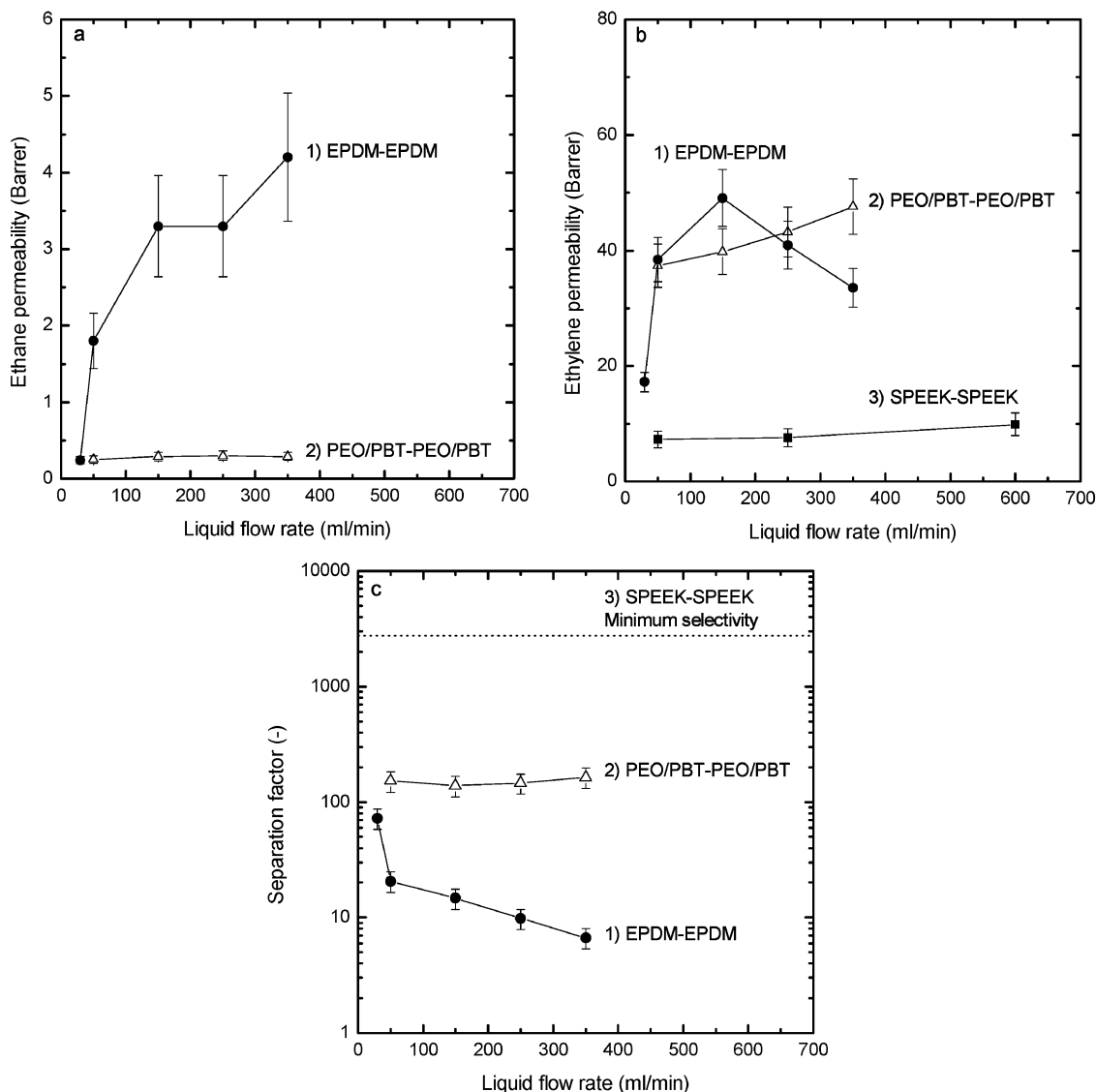
**Figure 3.** SEM picture of the cross section of a composite hollow-fiber membrane with a PEO/PBT top layer. Magnification: 1000 $\times$ .

to the values obtained for EPDM and SPEEK. This is due to the high amount (60 wt %) of hydrophilic PEO in the block copolymer and could be a problem when using PEO/PBT composite hollow fibers in membrane contactor applications.

To allow mass transport of olefins through dense PEO/PBT layers, swelling of these layers and the presence of silver ions in the polymer matrix is required. The weight increase after swelling of PEO/PBT films in a 3.5 M silver nitrate solution is considerably higher than the weight increase after swelling in ultrapure water. However, when the real water uptake after swelling in a 3.5 M silver nitrate solution is calculated, the obtained value is almost equal to the value obtained after swelling in ultrapure water. The difference in weight stems from the silver nitrate.

Compared to the hydrophilic PEO/PBT films, EPDM films have a much lower weight increase due to swelling because of the strong hydrophobic character of the hydrocarbon polymer chains.<sup>13</sup>

**3.2. Composite Membrane and Module Preparation.** Composite hollow-fiber membranes are prepared by dip coating. Defect-free fibers are obtained in two coating steps using an 8 wt % solution of PEO/PBT 1000/60/40 in chloroform. Based on  $\text{CO}_2$  permeation experiments, the top layer has an effective thickness of 24.3  $\mu\text{m}$ . This is in good agreement with the top layer thickness determined from SEM (Figure 3), indicating that hardly any pore penetration of the coating solution into the porous support occurs. The adhesion between the support and coating layer is good, and peeling off of the coating layer is not observed.



**Figure 4.** Ethane permeability (a), ethylene permeability (b), and ethylene over ethane separation factor (c) as a function of the liquid flow rate for PEO/PBT-, EPDM-, and SPEEK-coated membranes as the absorber and desorber in a membrane contactor. Experiments performed at  $T = 25\text{ }^{\circ}\text{C}$  at a total feed pressure of 3 bar [ethane (20%)/ethylene (80%)]. Ethane permeability results for SPEEK-coated membranes are not shown because the values are below the detection limit of the GC. The minimum selectivity in this case is given by the lower detection limit of the analytical method to quantify the ethane concentration in the sweep gas: (1) Absorber: EPDM. Desorber: EPDM. (2) Absorber: PEO/PBT. Desorber: PEO/PBT. (3) Absorber: SPEEK. Desorber: SPEEK.

**Table 2. Characteristics of the Composite PEO/PBT Membranes Used for Membrane Contactor Experiments**

$\text{C}_2\text{H}_4$ permeability (barrer <sup>a</sup> )	8.5
$\alpha_{\text{CO}_2/\text{N}_2}$	80
$d_{\text{eff, CO}_2}$ ( $\mu\text{m}$ )	24.3
$\text{H}_2\text{O}$ permeability [feed: $\text{AgNO}_3(\text{aq})$ ] (barrer <sup>a</sup> )	$8.7 \times 10^3$

<sup>a</sup> 1 barrer =  $1 \times 10^{-10}$   $\text{cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ .

Only defect-free composite hollow-fiber membranes are used for module preparation. The experimentally determined module characteristics are given in Table 2. The effective membrane thickness ( $d_{\text{eff, CO}_2}$ ) is calculated from the  $\text{CO}_2$  permeation experiments of the module and the intrinsic  $\text{CO}_2$  permeability of PEO/PBT. The  $\text{C}_2\text{H}_4$  permeability is calculated from the  $\text{C}_2\text{H}_4$  permeation experiments and based on this effective thickness ( $d_{\text{eff, CO}_2}$ ).

**3.3. Membrane Contactor Experiments.** Composite hollow-fiber PEO/PBT membrane modules are used in a membrane contactor bench-scale process as absorption and desorption modules during a period of 4 weeks.

The membrane performance was constant during this period and the color and concentration of the silver nitrate solution did not change, indicating that reduction of silver ions did not occur. Water permeation from the absorption liquid into the gas side has not been observed.

Parts a and b of Figure 4 give the ethane and ethylene permeability as a function of the liquid flow rate for PEO/PBT membranes, whereas Figure 4c shows the corresponding separation factors. The results for membranes with nonselective layers of EPDM and olefin-selective layers of SPEEK are presented for comparison.

PEO/PBT composite membranes were applied in a membrane contactor process for olefin/paraffin separation as a method to obtain both high olefin productivity and, at the same time, high separation factors. Figure 4 clearly shows that we indeed succeeded in the development of a highly selective membrane process with corresponding high olefin permeabilities. The permeability of PEO/PBT-coated membranes is consider-

ably higher than the value for SPEEK-coated membranes. It has the same order of magnitude as the permeability of nonselective, EPDM-coated membranes, and at high liquid flow rates (>250 mL/min), it may even exceed this permeability (Figure 4b). Another advantage of PEO/PBT is that these high selectivities are also obtainable at high liquid flow rates, where the membrane determines the overall selectivity of the process (Figure 4c). This makes the application of PEO/PBT-coated membranes in a membrane contactor for olefin/paraffin separations very attractive, especially at higher liquid flow rates (>250 mL/min), where the ethylene permeability for PEO/PBT-coated membranes may even exceed the permeability for membranes coated with a nonselective layer.

#### 4. Discussion

**4.1. Transport Mechanism.** The presence of a silver salt solution in dense polymer top layers such as PEO/PBT can have several effects:<sup>10,14–19</sup>

(1) It reduces the physical solubility of the gases (ethane and ethylene) into the film due to the salting-out effect.

(2) It may affect the diffusivity of ethane through the swollen polymer film.

(3) It can enhance and facilitate the transport of ethylene through the swollen polymer film.

As presented in Table 1, the gas permeability of PEO/PBT in the dry state for ethane is 10.4 barrer and that for ethylene 16.5 barrer. If these values are compared to the permeabilities found in membrane contactor experiments (Figure 4a,b), it is obvious that the ethane permeability in membrane contactor experiments is much lower (approximately 40 times), because of the salting-out effect and the different pathway for ethane transport. The ethylene permeability obtained in contactor experiments, however, is higher (approximately 2.5 times) than the value from gas permeation. The same effect was observed by Shukla and Peinemann<sup>14</sup> for the separation of 1-butene/*n*-butane using fixed silver carrier membranes of Nafion. Because of the salting-out effect, the physical ethylene solubility has decreased and the pathway for permeation has changed. However, the silver ions can enhance the reaction and the lower physical solubility is compensated by the enhancing effect of the silver ions on the ethylene transport, giving an overall ethylene permeability that is 2.5 times higher than the ethylene permeability in the dry state. Without the enhancing effect of silver ions, we expect the ethylene productivity to have almost the same value as the ethane permeability.

The high selectivities obtained for PEO/PBT in membrane contactor experiments (Figure 4c), therefore, stem from a strong decrease in the ethane solubility and diffusivity as well as an increase in the ethylene permeation due to the large enhancing effect of silver ions.

We hypothesize the same mechanism to hold for the extremely high separation factors obtained in membrane contactor experiments with olefin-selective SPEEK-coated membranes. However, the ethane and ethylene permeabilities of dry SPEEK films are too low to be determined accurately. This makes it currently impossible to accurately quantify a potential decrease in the ethane permeability and a potential increase in the ethylene permeability.

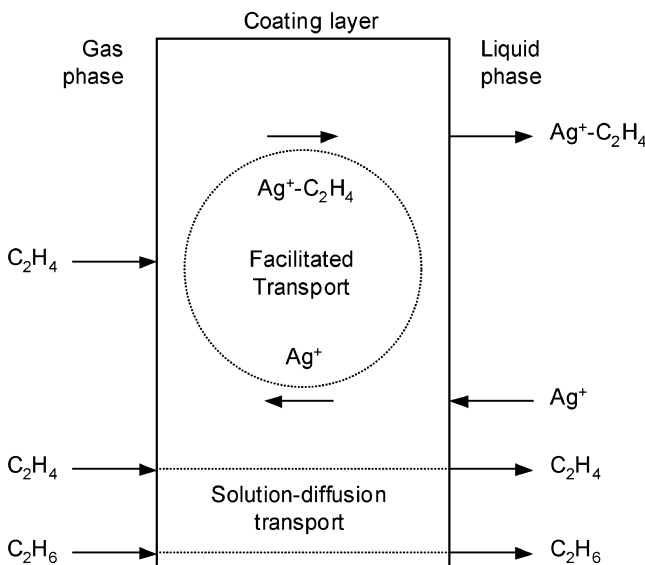
If membranes with nonselective elastomeric EPDM top layers are applied in a membrane contactor for olefin/paraffin separation, the desorption step limits the overall process as a result of the less efficient degassing process in the desorber.<sup>2,3</sup> To determine if this step also limits the ethylene transport when using olefin-selective membranes, we experimentally determined the degree of ethylene saturation of the silver nitrate solution leaving the absorber and entering the desorber. A value of approximately 19% is obtained. This is far below the maximum obtainable degree of saturation at the current temperature and pressure (approximately 40%<sup>10</sup>) and indicates that in this case the transport of ethylene is determined not only by the desorber but also by the absorber.

If olefin-selective membrane materials are used, two different transport mechanisms through the polymer top layer can play a role.<sup>14–19</sup> In the first place, transport of ethylene can occur via mobile silver ions, moving freely in the swollen film (Figure 5a<sup>17</sup>) and enhancement of ethylene transport only takes place at the gas–top layer interface in the absorber. The desorber limits the overall process as a result of the less efficient degassing process in the desorber. This situation is comparable to the situation obtained with EPDM-coated membranes.

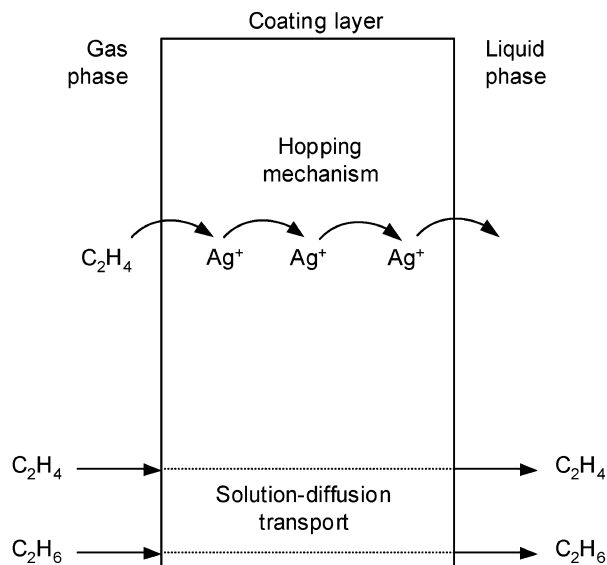
In the second place, ethylene transport can take place via fixed-site carrier molecules<sup>15,16</sup> (Figure 5b). In this mechanism, the silver carrier ions are not mobile but are fixed at certain sites in the polymer matrix. Ethylene transport occurs via the so-called hopping mechanism, in which the ethylene molecules hop from Ag<sup>+</sup> site to Ag<sup>+</sup> site using the motion of the polymer side to which the silver ions are “attached”.<sup>15</sup> Cussler et al.<sup>18</sup> developed a model to describe transport across fixed-site carrier membranes and assumed that the reacting permeate can only be transported by the complexing agent if two complexing agents are close enough to exchange the reacting permeate between the two. Swelling of the polymer layer in water may result in greater mobility of the polymer chains and hence enable easier movement of olefins.<sup>16</sup> The ethylene–silver ion complex is believed to be sufficiently labile to allow this type of transport.<sup>17</sup> In that case, both absorption and desorption are a continuous process of complexation and decomplexation, and the net result is a “symmetric” system in which the only difference between the absorber and desorber will be the driving force for ethylene transport. At a certain moment, the actual degree of ethylene saturation of the silver nitrate solution flowing from absorber to desorber has reached a value that results in an equilibrium situation with equal ethylene fluxes in both the absorber and desorber, and in this situation, the solution is only partly saturated with ethylene. We therefore hypothesize that, in olefin-selective top layers, hopping of ethylene from one fixed silver carrier ion to the next one is the dominant mechanism for ethylene transport and the mechanism of complexation and subsequent diffusion of the complex is of minor importance.

The assumption that hopping of ethylene molecules is the dominant mechanism for ethylene transport in swollen olefin-selective top layers of SPEEK and PEO/PBT is supported by the work of Rabago et al.<sup>15,16</sup> and Cussler et al.<sup>18</sup> Rabago et al.<sup>15</sup> investigated the effect on the facilitated transport of olefins of the incorporation of the sodium form of a perfluoro-1-octanesulfonic acid

a) Mobile carrier



b) Fixed carrier

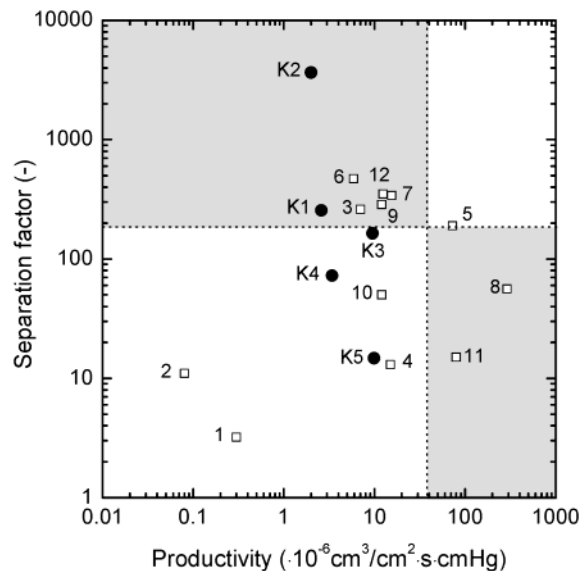


**Figure 5.** Schematic representation of ethylene and ethane transport in the coating layer of a gas-liquid membrane contactor using (a) a mobile silver salt carrier<sup>17</sup> and (b) a fixed carrier that reacts reversibly with ethylene but not with ethane.

surfactant into Nafion membranes. The addition of the surfactant to the  $\text{Ag}^+$ -form Nafion films had a large effect on the olefin flux: because of the addition of surfactant, the ion-exchange capacity increases and consequently the concentration of the silver ion carrier in the films increases. According to the predictions of the model of Cussler et al.,<sup>18</sup> this increase in the carrier concentration should result in a flux enhancement for facilitated species that is directly proportional to the increase in the carrier concentration. However, the results of Rabago et al.<sup>15</sup> show that the facilitated flux through silver-exchanged, surfactant-containing films highly exceeds the predicted improvements based on carrier capacity. With the addition of surfactants, the passing distance between complexation sites is reduced and less movement of the side chains is required to allow hopping of olefins. Furthermore, the surfactant-silver complex can also act as a highly mobile shuttle to transport olefins between ion-paired silver sites. This confirms the idea that facilitated olefin transport is mainly caused by a hopping mechanism and that transport via an  $\text{Ag}^+$ -olefin complex freely diffusing through the membrane is unlikely to be the dominant mechanism.

**4.2. Performance Benchmarking.** Much work has been carried out over the past 15 years by other research groups. Figure 6 aims to compare the results published in the literature and the results described in the present work for ethane/ethylene separations. The ethylene productivity is plotted against the corresponding separation factor. The dotted horizontal and vertical lines give the averaged values for the separation factor and the productivity obtained from the literature data. The dense membranes described in the literature and plotted in Figure 6 have an effective top layer thickness of less than 5  $\mu\text{m}$ . The membranes described in the present work have top layers varying from 8 to 10  $\mu\text{m}$  (EPDM and SPEEK) up to 24.3  $\mu\text{m}$  (PEO/PBT). The productivities obtained in the present work are, therefore, recalculated for an effective membrane thickness of 5  $\mu\text{m}$ .

The results presented in Figure 6 show that it is extremely difficult to obtain membranes with both high



**Figure 6.** Overview of the results published in the literature and described in the present work for ethane/ethylene separations: (1) Staudt-Bickel and Koros;<sup>20</sup> (2) Sungpet et al.;<sup>21</sup> (3) Pinnau and Toy;<sup>17</sup> (4) Morisato et al.;<sup>22</sup> (5) Muller et al.;<sup>23</sup> (6) Eriksen et al.;<sup>24</sup> (7) Tsou et al.;<sup>25</sup> (8) Bessarabov et al.;<sup>3</sup> (9) Teramoto et al.;<sup>26</sup> (10) Teramoto et al.;<sup>27</sup> (11) Creusen et al.;<sup>28</sup> (12) Sungpet et al.;<sup>29</sup> (K1) Nymeijer et al.;<sup>1</sup> (K2) Nymeijer et al.;<sup>1</sup> (K3) this work; (K4) Nymeijer et al.;<sup>2</sup> (K5) Nymeijer et al.<sup>2</sup>

productivity and high selectivity, which is confirmed by the values obtained for nonselective, EPDM-coated membranes (K4 and K5).<sup>2</sup> More attractive with respect to the olefin/paraffin selectivity obtainable is the application of SPEEK-coated membranes (K1 and K2).<sup>1</sup> we obtained previously unknown high selectivities in combination with reasonable productivities. To further improve the productivity, we applied PEO/PBT-coated membranes (K3). This indeed results in an increase in the productivity, however combined with a decrease in the selectivity.

**4.3. Process Optimization.** Although highly olefin-selective composite membranes are prepared in this contribution, one still desires to improve the corre-

sponding ethylene productivities. Methods to further improve the process performance can be found in the fields of (i) membrane performance, (ii) hydrodynamics on the liquid side of the process, and (iii) difference in operating temperature for absorption and desorption.

To obtain better membrane performances, we propose the use of PEO/PBT block copolymers with a higher amount of the hydrophilic PEO block as the top layer material or a SPEEK-coating layer having a higher ion-exchange capacity. In contact with the aqueous absorption liquid, the water and silver ion uptake of the film will increase, leading to increased ethylene transport.

To further increase productivity and selectivity, optimization of module design is inevitable. Because of the small size of the modules, the overall effect of the liquid inlet and outlet on the liquid flow profile is high and development of a smooth liquid flow profile is not possible. Only low liquid flow rates [laminar flow regime ( $11 < Re < 224$ )] can be applied to prevent mechanical damage of the fibers. The membrane surface area is small ( $102 \text{ cm}^2$ ), and liquid holdup in the modules is large. These restrictions result in a system with very poor hydrodynamics and low liquid-side mass-transfer coefficients. An optimized module design offers the possibility to apply higher liquid flow rates, with the latter being important to increase the mass-transfer coefficient of the liquid-phase boundary layer and to reduce the resistance against ethylene transport in this layer.

Because both diffusion and complexation and decomplexation are strongly influenced by the temperature, the application of a temperature difference between absorption and desorption will also affect the overall process performance. In fact, the separate control of the complexation and decomplexation reaction is a significant advantage over pressure-driven solution-diffusion membrane processes. The effect of the temperature on the performance of membranes with an olefin-selective top layer is 2-fold: on the one hand, it influences the diffusion process of the components because diffusion is an activated process, and, on the other hand, it can shift the complexation reaction more to the ethylene (high-temperature) or complex formation (low-temperature) side. The influence of the temperature on the gas separation performance of dry, olefin-selective membranes of  $\text{Ag}^+$  Nafion for the separation of ethane and ethylene is visualized in the work of Sungpet et al.<sup>21</sup> The ethane permeabilities obtained with the silver form membranes are basically the same as those observed with proton-form membranes and increase significantly with increasing temperature, as a result of the increase in diffusivity. The ethylene permeabilities obtained with the silver-form membrane are 4–5 times higher than the ones obtained with proton-form Nafion membranes because of the facilitating effect of the silver ions. Productivity, however, only slightly increases with increasing temperature because of the opposing effect of increased diffusivity and, at the same time, decreased complex formation. The net result is a small increase in the ethylene permeability but an overall decrease in the ethylene of ethane separation factor with increasing temperature. In membrane contactor applications, however, where absorption could be performed at low temperature and desorption at higher temperature, these effects will result in an overall increase in productivity and selectivity.

## 5. Conclusions

The application of olefin-selective membrane materials in gas–liquid membrane contactors for the separation of paraffins and olefins using a silver nitrate solution as the absorption liquid turned out to be very successful, especially with respect to the olefin/paraffin selectivity obtainable. Composite hollow-fiber membranes with an olefin-selective stabilizing layer of a highly permeable block copolymer of PEO and PBT are prepared, and when applied in a gas–liquid membrane contactor for the separation of paraffins and olefins, the water present in the absorption liquid swells the polymer sufficiently and prevents drying out of the membrane. Solution uptake due to swelling and mutual interaction due to coordination of the oxygen electron donor groups in the PEO/PBT polymer backbone with the  $\text{Ag}^+$  ions make the top layer olefin selective. The membrane performance in a membrane contactor is constant for a period of 4 weeks. We hypothesize that hopping of ethylene molecules is the most dominant mechanism for ethylene transport in swollen olefin-selective top layers of SPEEK and PEO/PBT. Ethylene permeabilities obtained are comparable to the values found for membranes with nonselective elastomeric top layers of EPDM (40–50 barrer). Selectivities, however, are more than 20 times higher for PEO/PBT and almost independent of the liquid flow rate. This makes the application of PEO/PBT-coated membranes in a membrane contactor for olefin/paraffin separations very attractive, especially at higher liquid flow rates ( $>250 \text{ mL/min}$ ), where the ethylene permeability for PEO/PBT may exceed the value for EPDM.

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## List of Symbols

- $A$  = effective membrane area ( $\text{cm}^2$ )
- $p$  = partial pressure
- $Q$  = productivity ( $\text{cm}^3/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ )
- $V$  = volume flow rate of the permeate stream ( $\text{cm}^3/\text{s}$ )
- $X_i$  = amount of component  $i$  in the feed stream (%)
- $Y_i$  = amount of component  $i$  in the permeate stream (%)
- $\alpha$  = separation factor
- $\gamma$  = volume fraction of a component

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