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Experimental Investigation of Pervaporation Membranes for Biobutanol Separation

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Abstract: Biotechnological production of chemical building blocks is one important step towards a more sustainable production. Unfortunately, the products to be separated are often highly diluted. Pervaporation has received increasing attention for the separation of small amounts of organic compounds from aqueous solutions, especially in the separation of butanol from water or from fermentation broth. To evaluate the potential of pervaporation for biobutanol recovery a consistent database is required, describing the dependency of permeate fluxes and selectivities on process variables like temperature, permeate pressure as well as feed concentrations and compositions. Therefore, within this work we investigated the separation behaviour of a commercially available polydimethylsiloxane (PDMS) membrane and membranes based on poly(ether block amide) (PEBA) fabricated in our own laboratory. The membranes were tested under varying operating conditions. Fermentation by-products or impurities may affect the pervaporation separation performance. Therefore, in addition, the permeate fluxes and the influence of acetone, ethanol, acetic and butyric acid and 1,3-propanediol have been investigated in detail as well. Several differences in the permeability and selectivity of PDMS and PEBA were observed during the experimental study. Swelling experiments were applied to further analyse the separation behaviour of PDMS and PEBA more in detail. Finally the influence of the observed separation performances on the overall butanol pervaporation process is discussed. It was found that especially well permeating by-products like acetone can drastically influence the subsequent downstreaming process.

Keywords: Polydimethylsiloxane (PDMS), Pervap^{TM}, poly(ether block amide) (PEBA), swelling, organic acid, Hansen Solubility Parameter.

1. INTRODUCTION

In recent years the biotechnological production of chemicals moved more and more into the focus of research, offering an opportunity to extend the production of bulk chemicals to a sustainable basis. One of those chemicals is *n*-butanol (hereinafter: butanol) which today is mainly applied for the production of acrylates, esters, ethers and acetates [1,2]. Another potential application is the use of butanol as fuel additive similar to ethanol [3,4]. Biobutanol production with the so-called acetone-butanol-ethanol (ABE) fermentation process is the second largest biotechnological process that has ever been realized in terms of capacities [5]. To improve the ABE fermentation efficiency a number of improvements are reported in literature [6-10], one of which is the development of efficient downstream processes for the recovery of butanol [11]. This is important, because butanol is toxic towards the production organisms limiting its concentration in the fermentation broth to values often lower than 2 % [12]. Due to the low concentrations butanol purification by distillation is very energy consuming. The development of efficient downstream processes is necessary to reduce the energy required for purification. An efficient process is accomplished by a continuous (in-situ) product removal from the fermentation. A continuous recovery of butanol allows an extension of the fermentation time and might even facilitate a continuous fermentation process [12,13]. Furthermore the product removal results in a preconcentration that simplifies the subsequent purification of butanol.

In general, pervaporation, extraction, gas-stripping, adsorption, perstraction or reverse osmosis are reported to be able to separate butanol from aqueous solutions [10,11,14]. Amongst these processes pervaporation is reported to be promising [15,16], whereas processes like extraction or gas-stripping are reported to suffer from emulsion formation and the loss of extraction solvent [16,18] or from low condensate concentrations and foam formation [11,15,17], respectively. Therefore pervaporation is in the focus of this paper. The integration of an ABE fermentation and pervaporation was already successfully tested by various research groups [19–21]. A simplified flow scheme for a process with a continuous separation of butanol is given in Figure **1**. Fermentation and pervaporation can be connected by an external cycle. Fermentation broth at the outlet of the pervaporation still contains carbohydrates, nutrients or intermediate products and can be recycled to the fermentation. The permeate enriched in butanol can further be purified, e.g. by distillation [14].

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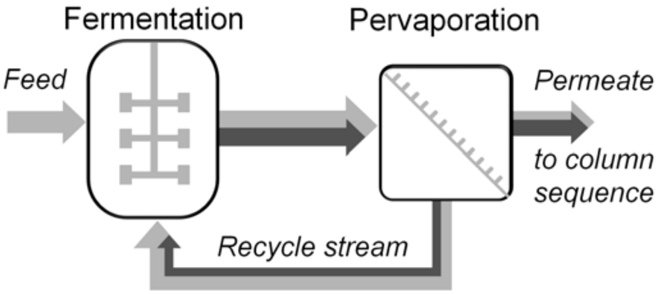

Figure 1: Simplified flow scheme for continuous separation of butanol from a fermentation using pervaporation.

Next to articles reporting on the direct integration of a fermentation process and a pervaporation unit, a number of articles have been published on new membrane materials or on improvement of existing membranes, showing advantageous mass transfer properties or selectivities compared to conventional materials. Articles by Oudshoorn *et al*. [11], Beltran *et al*. [22] and Vane [23] provide good overviews. Despite the number of articles focusing on experimental investigations, economic studies and publications on process design are rarely found [23]. For a reliable process design a consistent database is required, which considers a number of factors heavily influencing a pervaporation process. Especially the feed concentration, the pervaporation temperature, the permeate pressure and the membrane thickness have a decisive impact on performance parameters like the permeate flux and membrane selectivity [24]. Furthermore, factors like reliability and reproducibility of the membrane production and permeate fluxes are important.

Therefore, in this article two different membrane materials are systematically tested with varying feed concentrations, temperatures and permeate pressures. Additionally the effect of the presence of the potential by-products acetone, ethanol, butyric and acetic acid and 1,3-propanediol was investigated. A commercially available poly(dimethyl siloxane) (PDMS) membrane was used for experiments, because PDMS is reported to be suitable for separation of organics from aqueous mixtures (see for instance [14,20,25–27]). Next to PDMS, poly(ether block amide) (PEBA) is investigated within this study, which is another polymer reported for recovery of butanol from mixtures with water [28–30]. PEBA is reported to show high permeate fluxes too, but lower permeate concentrations than obtained with PDMS [28].

The experimental procedures are presented in chapter 2. Pervaporation experiments were used to analyse the membrane performance. Swelling experiments were applied to further examine the different separation characteristics of the membrane. Chapter 3 summarizes the experimental results, which are compared to results published in literature. In chapter 4 the findings of pervaporation experiments are analysed in detail. Next to a direct comparison of fluxes also the influence of the component properties, like e.g. boiling points or the non-ideal behaviour is discussed. Swelling experiments are compared to pervaporation experiments; Hansen Solubility Parameters were investigated to describe the results of our swelling experiments. In addition, the influence of the separation performance of PDMS and PEBA membranes on a pervaporation process is discussed. Within this work, a comprehensive database is obtained, which facilitates extensive process studies and the evaluation of the economic feasibility of an integrated fermentation-pervaporation process. Furthermore, the results obtained for various components over a wide temperature and permeate pressures range may serve as basis for comparison and evaluation of new membrane materials, under simultaneous consideration of the experimental conditions.

2. EXPERIMENTAL BASICS AND PROCEDURES

PDMS and PEBA have been used as membrane material. Next to commercially available PDMS membranes, prototype membranes produced at our laboratory were tested. Information on materials and membrane fabrication is given in sections 2.1 and 2.2. Pervaporation experiments were performed to investigate on the permeation behaviour of butanol, acetone, ethanol, water, acetic and butyric acid and 1,3-propanediol through the different membranes and to examine their influence on the butanol separation (section 2.3). Swelling experiments (section 2.4) were carried out to analyse the permeability behavior of the membranes more in detail. The results of the experiments are presented in chapter 3 and are discussed subsequently (chapter 4).

2.1. Materials

The commercially available PDMS membrane Pervap^{TM} 4060 was provided by Sulzer Chemtech AG, Switzerland. PEBAX® 2533 was supplied by Arkema, France. Room temperature curing, one-component silicone (Momentive TSE 399C) was delivered by KVD Schmidt, Germany. Sepro Membranes, US kindly supplied polysulfone membranes PS 20 on a polypropylene backing that were used as support for membrane production. *n*-Butanol (99.0 %) was purchased from Sigma Aldrich, Germany. Acetic acid (96 %), butyric acid (99 %), acetone (>99.9 %), 1,3-propanediol (>99.9 %), methanol (99.9 %) and acetonitrile (>99.9 %) were obtained from VWR International GmbH, Darmstadt. Ethanol (>99.5 %) and n-heptane (>99 %) were provided by Merck Schuchardt OHG, Hohenbrunn and Merck KGaA, Darmstadt, respectively.

2.2. Membrane Production

Next to commercially available Pervap^{TM} 4060 membranes, silicone and PEBA membranes were tested. These were produced in our own laboratory by coating of the polysulfone membrane with PEBA or silicone. The coating procedures are described in the following.

For coating of the polysulfone membrane with silicone the membrane was fixed on a plane plate. One-component, room temperature curing silicone was mixed with n-heptane in a mass ratio of 1:9 to increase the fluidity of the silicone. This silicone solution was then poured onto the surface of polysulfone membrane; afterwards the membrane was placed in an upright position to let the excess solution drain off. To ensure the silicone is fully cured the membrane was placed in an oven (60 °C) for one day. The silicone applied for manufacture of the Silicone–FVT membranes was used for production of samples used in swelling experiments.

For coating of the polysulfone membrane with PEBA, PEBAX® 2533 pellets were dissolved in acetic acid in a mass ratio of 1:4 at a temperature of 70 °C. Subsequently, the homogeneous PEBA solution was cooled down to room temperature and coated on the polysulfone membrane (fixed on a glass plate) by using a coating knife (gap heights 50 µm, Zehntner Testing Instruments GmbH, Switzerland). Afterwards the membranes were placed in an oven at 70 °C to dry them and additionally to evaporate the remaining acetic acid.

The membrane morphology was investigated by scanning electron microscopy (SEM, Laboratory of Biomaterials and Polymer Science, TU Dortmund University). Figure **2** exemplarily shows the cross section of a PEBA pervaporation membrane. As one can see a dense polymer layer is formed that is properly connected to the porous support membrane. No voids or macro pores were observed.

2.3. Pervaporation Experiments

The membranes were characterised in a lab-scale pervaporation plant with a feed vessel volume of 1.5 L and a flat circular membrane module (Helmholtz-Zentrum Geesthacht, Germany) with an effective membrane area of 104 cm^2. The temperature of the feed was controlled by an oil bath; feed pipes and the membrane cell were equipped with heating tape and additionally insulated. The feed flow rate was set to 30 L/h. After passing the membrane cell the retentate was recirculated to the feed vessel. A generalized flow scheme of the lab-scale plant can be found elsewhere [31]. Feed samples (4 mL) were taken at the beginning and at the end of an experiment to determine the mean concentration; because of the small permeate amounts compared to the feed volume a steady feed concentration is assumed during one experiment. Permeate samples were collected in one of two parallel cooling traps, cooled by liquid nitrogen (-196 °C). The cooling traps were weighed before and after the experiments to determine the permeate mass; one

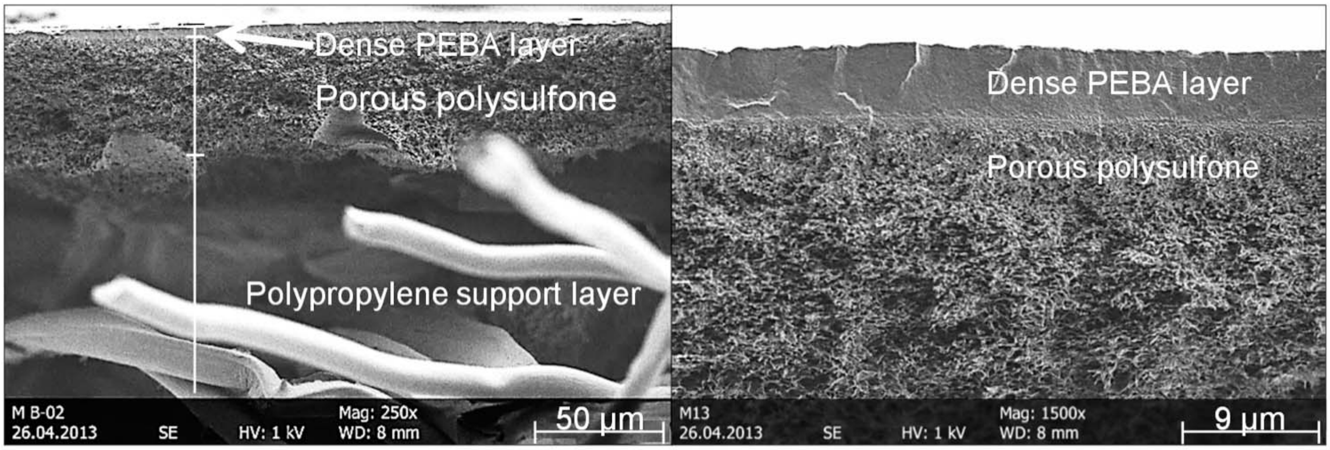

Figure 2: SEM images of the cross section of a PEBA membrane. Pictures were taken with different magnifications.

experiment lasted between 30 and 60 minutes. The permeate pressure was adjusted to the desired value by a vacuum pump (Ilmvac, Germany).

Feed and permeate samples were analysed by Shimadzu gas chromatographs using a sample volume of 10 µL. For detection of butanol, acetone, ethanol and 1,3-propanediol a capillary column (Restek Rrx-5) was used, methanol served as internal standard and helium as mobile carrier phase. Concentrations of butyric acid and acetic acid were analysed with a different capillary column (FFAP Innopeg) and acetonitrile as internal standard. Flame ionization detection was operated at 320 °C and 250 °C respectively. Each sample was analysed threefold.

Based on the permeate mass m_{Perm} that permeated through the membrane area A_M in a certain time t_{exp} the overall flux J_{tot} was calculated. By using the permeate mass fraction of solvents in the permeate $w_{i,Perm}$ the partial fluxes J_i of solvents were estimated.

Pervaporation experiments were carried out in a temperature range from 37 °C to 60 °C to obtain a comprehensive database for the temperature dependency. When applying pervaporation for the continuous separation of solvents from a fermentation the pervaporation temperature is usually defined by the fermentation temperature. However, in this study the temperature was increased up to 60 °C to investigate the influence of the temperature on the permeate fluxes and concentrations. Permeate pressures varied from 10 mbar up to 80 mbar. Butanol concentrations in the feed medium up to 0.04 g/g were investigated to provide a sufficient amount of data to identify the influence of the feed concentration. In tests using multi-component mixtures, an acetone-butanol-ethanol (A:B:E) ratio of 3:6:1 was chosen to consider the product ratio that is formed by the classical ABE strains [12]. Furthermore, varying ratios of butanol to acetone and ethanol were tested to investigate how the components mutually influence the permeation behaviour of each other.

2.4. Swelling Experiments

To investigate the sorption behaviour of solvents into the different polymer materials small polymer blocks were produced that were immersed in 200 g of aqueous solvent mixtures. Solvent concentrations were varied between 0 and 0.05 g/g. Experiments lasted for five days, allowing to reach equilibrium between polymer sample and liquid. The temperature was adjusted to 37 °C. Solvent concentrations in the remaining liquid phase were analysed afterwards by gas chromatography.

Silicone samples with a weight of 3.5 g to 4.5 g were prepared by pouring silicone into small plastic pans, without diluting the silicone by heptane. PEBA samples with a weight of about 3 g to 6 g were prepared by melting PEBAX® pellets at a temperature of 180 °C. The sample weight ranged between 3 and 6 g. Sorption of the components into the polymeric samples was evaluated based on the mass increase of the polymer samples compared to the mass m_0 of the pure polymer.

$$S_w = \frac{m_{eq} - m_0}{m_0} \cdot 100[\%] \qquad (1)$$

Prior to the first experiments all samples were immersed in an aqueous butanol solution to flush out residues and afterwards dried in an oven at 60 °C.

3. CHARACTERISATION OF THE PERVAPORATION MEMBRANES

Results of pervaporation experiments with PDMS and PEBA membranes are presented in this chapter. For each membrane the permeate fluxes and concentrations were determined, dependent on feed concentrations and compositions, temperatures and permeate pressures. The results obtained in this work are compared to results published in literature. Experiments have been reproduced for different membranes sheets, six different sheets of the Pervap^{TM} 4060 membrane as well as five sheets for the PEBA membranes were tested. In addition, the results from swelling experiments with silicone and PEBA samples are presented. The findings presented in sections 3.1 and 3.2 are discussed in detail in the following chapter.

3.1. PDMS-Based Membranes

Figure **3A** shows the partial fluxes of butanol, which linearly increase with the feed concentration (black symbols). The partial fluxes of butanol measured with 6 different membrane sheets are similar to each other. Values higher than 500 g/(m^{2}h) were obtained for a butanol feed concentration of 0.028 g/g. Like the butanol fluxes the permeate mass fractions of butanol measured for the different membrane sheets are similar to each other, resulting in permeate mass fractions higher than 0.4 g/g (Figure **3B**, black symbols). A high reproducibility of the pervaporation experiments was achieved, what confirms the high

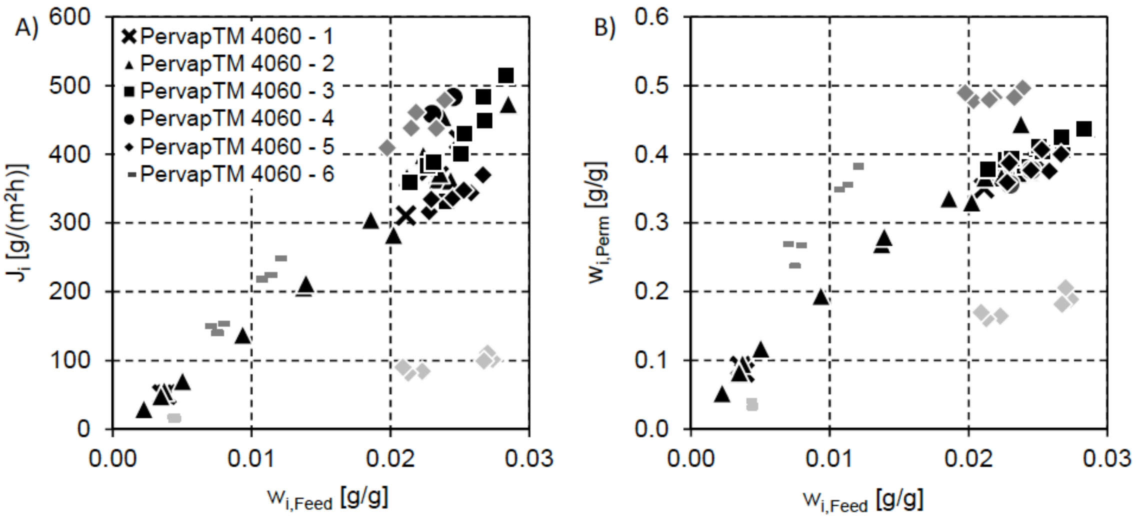

Figure 3: Pervaporation of binary aqueous mixtures of butanol (black), acetone (grey) and ethanol (bright grey) with six different PERVAP^{TM} 4060 membranes (T = 37 °C, p_{Perm} = 10 mbar): Component fluxes (**A**) and permeate mass fractions (**B**).

quality of the Pervap^{TM} 4060 membranes. Generally acetone partial fluxes (grey symbols) are about 30 % higher than butanol fluxes, resulting in permeate concentrations up to 0.5 g/g. In contrast to this fluxes of ethanol (bright grey symbols) are about 70 % lower compared to butanol, resulting in low permeate concentrations of ethanol.

3.1.1. Influence of Temperature and Permeate Pressure on Butanol Fluxes

Temperature and permeate pressure have a large impact on the permeate fluxes of all components as one can see in Figure **4**. The pervaporation temperatures were varied from 37 °C to 60 °C, at the same time the permeate pressure was fixed to values between 10 mbar and 80 mbar. All experiments were carried out with quaternary mixtures and A:B:E ratios of 3:6:1. Figure **4A** shows the permeate fluxes of butanol. The highest flux is obtained for temperatures of 60 °C (bright grey circles, O). An increase of the temperature from 37 °C to 60 °C at a permeate pressure of 30 mbar results in an increase of permeate fluxes from 250 g/(m^{2}h) up to 1600 g/(m^{2}h) (black circles O and bright grey circles O). At the same time the partial flux of water increases up to 2000 g/(m^{2}h) (Figure **4D**), the butanol permeate concentration is 0.33 g/g. Experiments at higher temperatures (open symbols in Figure **4**, Pervap^{TM} 4060 - 4) were conducted with another sheet of the Pervap^{TM} membrane, which showed slightly higher butanol fluxes compared the other Pervap^{TM} membranes (filled symbols). However, the use of a membrane with a slightly different performance does not change the trends observed in Figure **4**. The same temperature dependency that is found for butanol is monitored for all components, also for water (Figure **4B-D**). Therefore, the permeate concentration of butanol changes only slightly with an increasing temperature.

When increasing the permeate pressure from 10 mbar to 70 mbar at 37 °C the butanol flux decreases by more than 80 % (black squares ■□ and asterisks Ж). At a temperature of 60 °C a pressure increase from 30 mbar to 80 mbar results in an drop in fluxes by about 55 % (bright grey circles O and crosses x). However, in contrast to the temperature, the permeate pressure not only influences the permeate fluxes but also the permeate concentrations at lower temperatures. For a temperature of 37 °C the maximum permeate concentration measured at 70 mbar is 0.23 g/g, compared to 0.33 g/g at 10 mbar (supplementary material, Figure **A3**).

Pervap^{TM} 4060 membranes were also tested by Claes *et al*. [32] and Marszałek *et al*. [33]. Claes *et al*. [32] carried out pervaporation experiments with binary aqueous solutions containing 0.05 g/g butanol resulting in butanol partial fluxes of about 2290 g/(m^{2}h) and permeate concentrations of 0.67 g/g. These fluxes are somewhat higher than fluxes observed during our studies, what might be a result of the lower permeate pressure applied during their studies, which is stated to be 0.04 mbar. For a feed concentration of 0.02 g/g Marszałek *et al*. [33] reported butanol fluxes of about 360 g/(m^{2}h) measured at a permeate pressure of 30 mbar. Although the temperature in their experiments was 60 °C these fluxes seem to be somewhat lower compared to the results obtained in our studies.

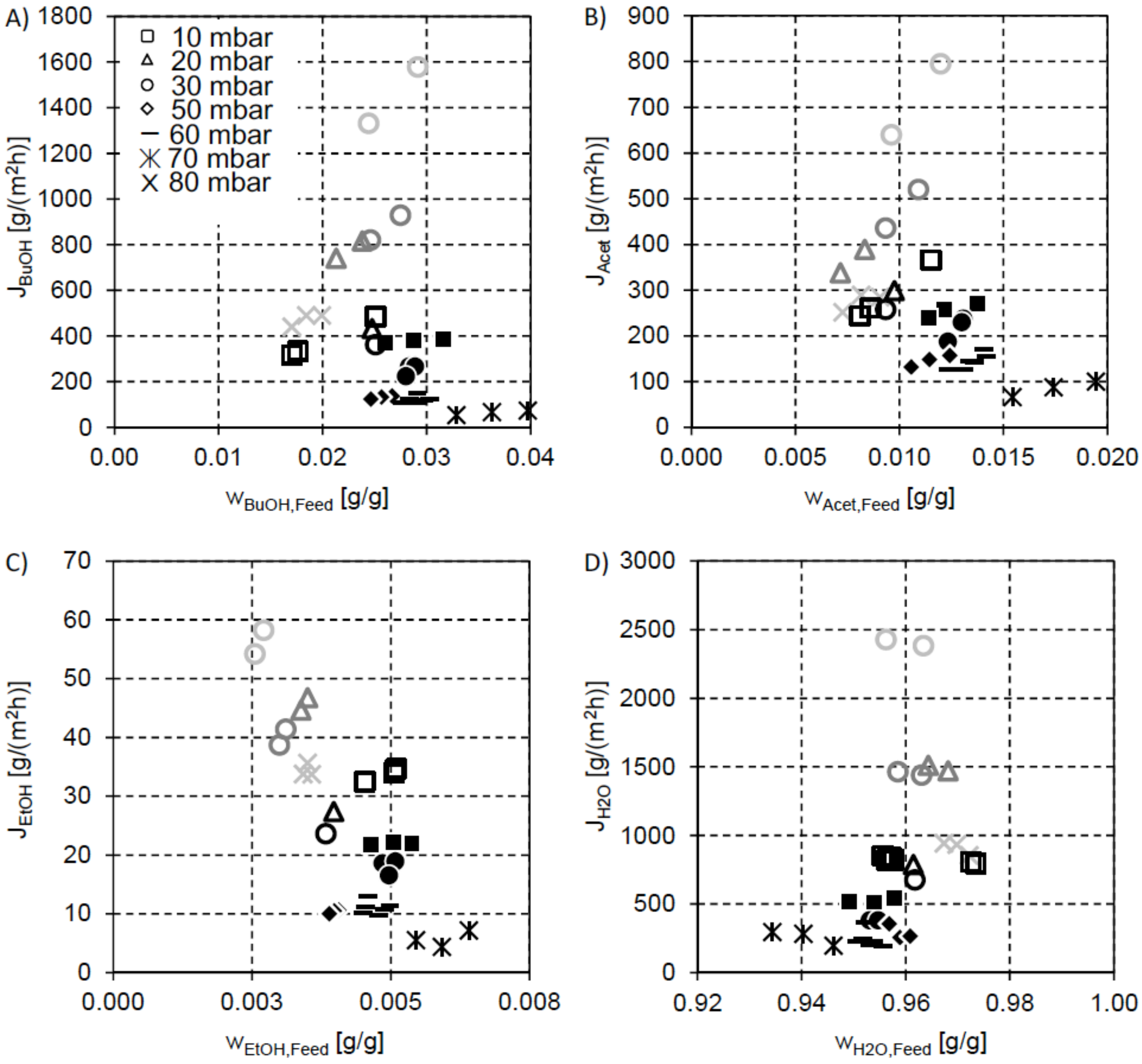

Figure 4: Component fluxes through Pervap™ 4060 membranes determined at different temperatures (black = 37 °C; grey = 50 °C; bright grey = 60 °C) and permeate pressures (10 mbar to 80 mbar). Feed mixtures contained acetone, butanol and ethanol in a 3:6:1 concentration ratio.

3.1.2. Permeation of by-Products

The temperature and permeate pressure dependent permeation of the main by-products acetone and ethanol is shown in Figure **4B** and **C**. A similar temperature dependency that was found for butanol is observed for all components. The highest fluxes are obtained for temperatures of 60 °C, acetone fluxes of 800 g/(m^{2}h) and ethanol fluxes of 58 g/(m^{2}h) were measured (bright grey circles ○). Lower pervaporation temperatures and higher permeate pressures let the fluxes drop to values lower than 100 g/(m^{2}h) and 10 g/(m^{2}h), respectively (black asterisks Ж).

To analyse the mutual influence of acetone (A), butanol (B) and ethanol (E) on each other, further pervaporation experiments were carried out with quaternary mixtures. A:B:E ratios were varied from 3:12:1 to 3:3:1. No influence of the presence of butanol on the acetone or ethanol flux was observed (supplementary material, Figure **A2**). Niemistö *et al*. [25] also tested commercially available PDMS membranes obtained from Pervatech, NL. In accordance with our results they have not observed a mutual influence of the different components.

In contrast to this an influence of the butanol concentration on the permeate flux of water can be observed during all experiments. Especially for experiments with binary mixtures of water and butanol this effect is seen. Whereas water fluxes vary between 400 and 500 g/(m^{2}h) in the absence of butanol, water fluxes of up to 800 g/(m^{2}h) are observed in the presence of butanol (supplementary material, Figure **A1**). This effect has also been observed before [14]. Because the feed concentration of water and therefore the driving force for the mass transport of water through the membrane changes only slightly with changing solvent concentrations one would expect the water permeate fluxes not to change drastically. Probably the flux increase is caused by an enhanced swelling of the membrane. An effect of acetone and ethanol on the partial fluxes of water is not observed at low concentrations.

Next to butanol, acetone, ethanol and water also the pervaporation behaviour of acetic acid and butyric acid was analysed. These organic acids are precursor for the formation of acetone, butanol and ethanol by clostridia strains. Their concentrations in fermentation broths are generally lower than the butanol concentrations and vary around 0.005 g/g [13]. Table **1** shows the permeate fluxes and concentrations of these acids. As one can see the acids hardly permeate through the Pervap^{TM} 4060 membrane, whereas butyric acid permeates three times better than acetic acid. The permeate concentration of acetic acid is even slightly lower than the feed concentration. Therefore, enrichment factors for acetic acid, calculated according to eq. 2, are lower than 1, whereas butyric acid is enriched by a factor of 2.8.

$$\beta_i = \frac{w_{i,perm}}{w_{i,Feed}} \tag{2}$$

These experiments were carried out by using unbuffered aqueous solutions. The initial pH of these solutions was therefore comparatively low (pH = 2.5), but did not affect the permeation characteristics of the membrane. The better separation of butanol compared to the organic acids is preferable, because acids should remain in the fermentation broth, as they are precursor for butanol formation. Pervaporation experiments were also carried out using 1,3-propanediol, which is reported to be another by-product in biobutanol fermentations [34]. However, when using the Silicone–FVT membranes, during pervaporation of an aqueous feed containing butanol and 1,3-propanediol, no 1,3-propanediol was found in the permeate samples, whereas butanol permeated as expected. Enrichment factors for butanol are higher than 10 and therefore much higher than for the organic acids (determined with the Pervap^{TM} 4060 membrane).

3.1.3. Swelling of Silicone

To further analyse the separation behaviour of the membrane, swelling experiments were conducted within this study. These experiments will be compared to the pervaporation experiments in chapter 4. For this, small polymer blocks were produced from a room temperature vulcanizing silicone. Furthermore, membranes were produced from the silicone and tested with quaternary mixtures of acetone, butanol, ethanol and water (A:B:E ratio = 3:6:1). These silicone membranes produced at our laboratory (Silicone-FVT, unfilled symbols in Figure **5**) showed similar permeate fluxes of acetone, butanol and ethanol, when compared to the Pervap^{TM} 4060 membrane (filled symbols). Similar permeate compositions have been measured (supplementary material, Figure **A4**).

Swelling experiments were conducted at 37 °C using binary aqueous mixtures of solvents and small polymer block made from silicone. As shown in Figure **6**, an increasing concentration of the organic components in the liquid resulted in an increased swelling. Sorption of butanol into PDMS causes a weight increase by up to 2.5 %. Immersion in acetone solutions of 0.05 g/g increases the PDMS sample weight by about 1 %. In contrast to this, butyric acid and acetic acid, which permeate much worse through the Pervap^{TM} 4060 membrane (which show a

Table 1: Permeation of organic acids through Pervap^{TM} 4060 and permeation of 1,3-propanediol through the Silicone-FVT membrane (T = 37 °C, p_{Perm} = 10 mbar). Experiments were carried out with ternary mixtures of butyric acid (BuAc), acetic acid (AcAc) and water or butanol (BuOH), 1,3-propanediol (1,3-PDO) and water

	$w_{i,Feed}$ [g/g]		J_i [g/(m^{2}h)]		$w_{i,Perm}$ [g/g]		β_i [-]	
Pervap^{TM} 4060-6	***BuAc***	***AcAc***	***BuAc***	***AcAc***	***BuAc***	***AcAc***	***BuAc***	***AcAc***
	0.0041	0.0043	4.65	1.60	0.0117	0.0040	2.85	0.93
	0.0040	0.0043	4.36	1.56	0.0109	0.0039	2.73	0.90
Silicone -FVT	***BuOH***	***1,3-PDO***	***BuOH***	***1,3-PDO***	***BuOH***	***1,3-PDO***	***BuOH***	***1,3-PDO***
	0.0486	0.0229	637.2	0	0.5367	0	11.04	0
	0.0455	0.0238	599.4	0	0.5383	0	11.83	0

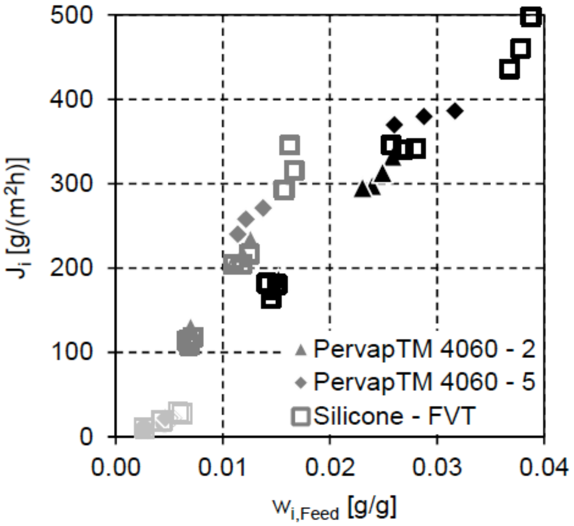

Figure 5: Comparison of component fluxes of butanol (black), acetone (grey) and ethanol (bright grey) obtained with the PERVAP^{TM} 4060 (2 and 5) and Silicone-FVT membranes (T = 37 °C, p_{Perm} = 10 mbar).

separation behaviour similar to the Silicone-FVT membrane), cause a swelling up to 5.1 % and 1.5 %, respectively. Noteworthy is also that 1,3-propanediol, which was not detected in any permeate sample during pervaporation experiments, does not swell the PDMS polymer. Swelling that is observed in the presence of 1,3-propanediol is similar to swelling of pure water, as the mass did not perceptibly increase.

Swelling of PDMS membranes has also been analysed by Niemistö *et al*. [25] by immersing pure PDMS into pure acetone, butanol or ethanol. The trends for sorption of acetone, butanol and ethanol were similar to trends found during our swelling experiments. However, sorption of butanol into PDMS was found to be 25 wt.-% and therefore much higher than observed during our studies, which is a result of the use of pure solvents instead of aqueous solutions. A similar value for sorption in PDMS has also been published by Favre *et al*. [35].

3.2. PEBA Membranes

PEBA membranes were produced in our own laboratory because commercially available PEBA membranes are not available. Figure **7** shows partial fluxes of butanol (black symbols) as function of the feed concentration, determined by using five different sheets of PEBA membranes. As one can see the partial fluxes of butanol seem to linearly increase with the feed concentration and are similar for all the different membrane sheets. The maximum butanol flux was 413 g/(m^{2}h), the maximum butanol concentration in the permeate was 0.33 g/g. Furthermore the fluxes of acetone and ethanol are displayed. The partial flux of acetone is lower than the butanol flux when using a PEBA membrane. The highest flux measured is 130 g/(m^{2}h) (grey squares ■). The maximum permeate concentration is 0.17 g/g for binary mixtures of acetone and water. Ethanol permeates worse through the membrane, permeate fluxes and concentrations are 39 g/(m^{2}h) and 0.06 g/g (bright grey squares ■). Liu *et al*. [36] tested PEBAX® 2533 membranes with mixtures containing butanol, acetone and ethanol and observed the same permeation trends that we found for permeation of the three components.

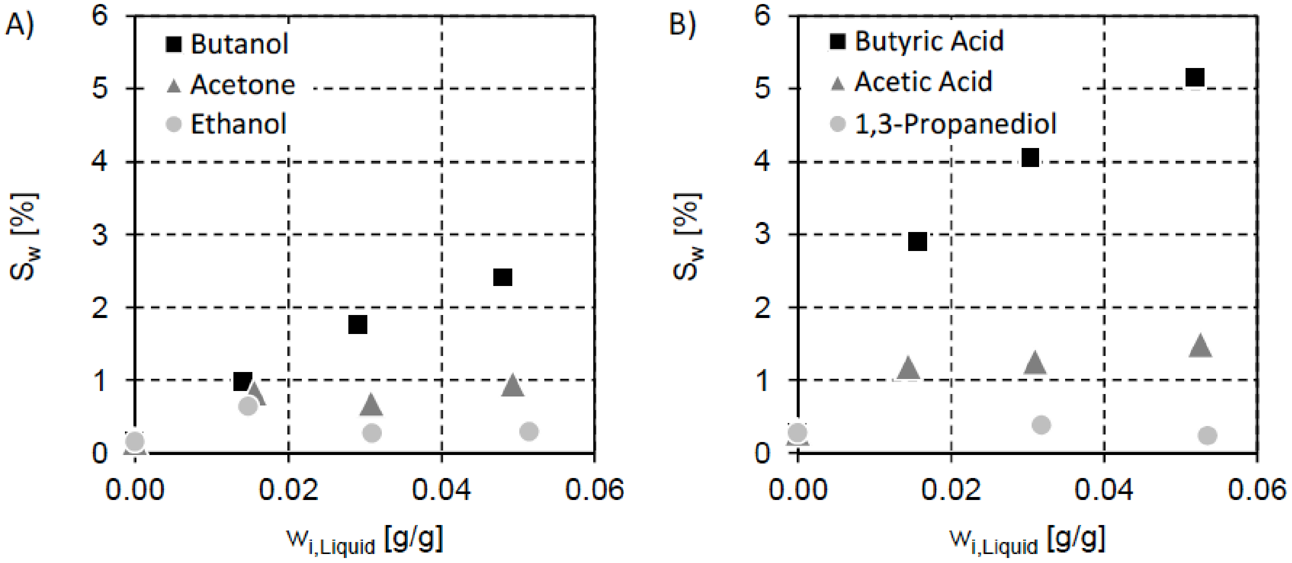

Figure 6: Swelling of silicone samples (representing the Silicone-FVT membranes) immersed in binary aqueous solutions of solvents; measurements were carried out at 37 °C.

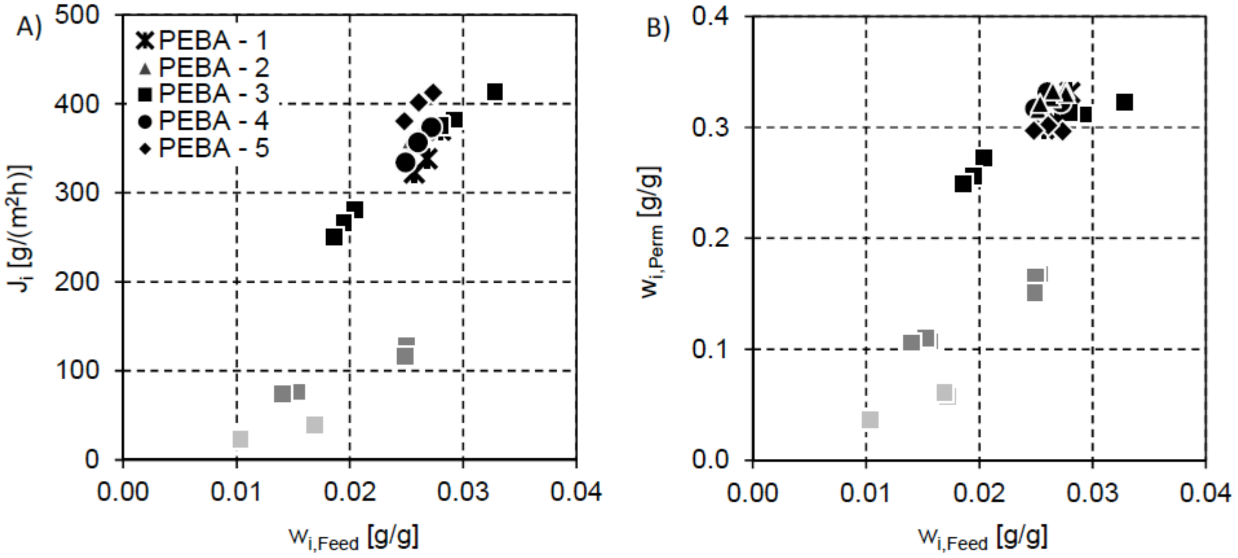

Figure 7: Pervaporation of binary aqueous mixtures of butanol (black), acetone (grey) and ethanol (bright grey) with PEBA membranes: Component fluxes (**A**) and permeate mass fractions (**B**).

3.2.1. Influence of Temperature and Permeate Pressure on Butanol Fluxes

Similar to the experiments with PDMS membranes the influence of process parameters like concentration, temperature or permeate pressure on the butanol separation *via* PEBA membranes was investigated. All experiments were carried out with quaternary mixtures of acetone, butanol, ethanol and water and A:B:E ratios of 3:6:1. Figure **8A** shows the permeate fluxes of butanol. The highest butanol flux measured at a temperature of 37 °C is 550 g/(m^{2}h) for a feed concentration of 0.038 g/g (black bars ━). High fluxes up to 526 g/(m^{2}h) are also obtained at a feed temperature of 60 °C and a permeate pressure of 16 mbar (bright grey crosses ✚). The butanol fluxes at this temperature are generally lower than the fluxes measured with PDMS membranes, which is a consequence of the lower butanol feed concentrations.

Temperature and permeate pressure have a remarkable effect on the permeate fluxes. A temperature increase from 50 °C to 60 °C at a permeate pressure of 16 mbar results in permeate fluxes of butanol which are 40 % higher (grey and bright grey crosses ✚✚). An increase in the permeate pressure from 10 mbar to 50 mbar at a temperature of 37 °C (black squares ■ and rhombi ◆) causes a decrease of the fluxes by 38 %. An influence of temperature and permeate pressure on the permeate concentration of butanol is hardly observed. The butanol permeate mass fraction ranges in between 0.1 g/g and 0.32 g/g for feed mass fractions of 0.07 g/g and 0.32 g/g, respectively. Butanol permeate compositions for all experiments can be found in the supplementary material.

PEBA membranes have also been examined by Boddeker *et al*. [28], Fouad *et al*. [29] or Liu *et al*. [36]. For membranes produced from PEBA 40 Boddeker *et al*. [28] report on butanol fluxes and permeate concentrations somewhat lower than observed in this study. PEBAX® 2533 was used by Fouad *et al*. [29] in experiments with up to 0.004 g/g butanol. Fluxes determined for temperatures between 29 °C and 60 °C seem to be lower than fluxes that were observed in this study. This can possibly be explained by a higher membrane thickness as their membranes were mentioned to be 30 µm thick [29]. Scanning electron microscopy images reveal a thickness of our PEBA membranes varying between 3 µm and 5 µm, for comparison see Figure **2**.

3.2.2. Permeation of by-Products

The temperature and permeate pressure dependent permeation of the main by-products acetone and ethanol through PEBA membranes is shown in Figure **8B** and **C**. Acetone fluxes are lower than 148 g/(m^{2}h) and thus smaller than the butanol fluxes (black bars ━, Figure **8B**). Maximum acetone concentrations in the permeate of 0.13 g/g were determined for experiments at 37 °C with a permeate pressure of 50 mbar and for an acetone feed concentration of 0.014 g/g. The highest ethanol flux measured is 27 g/(m^{2}h) (bright grey crosses ✚, Figure **8C**). In Figure **8D** the permeate fluxes of water are shown as function of the water concentration in the feed. One can see clearly that

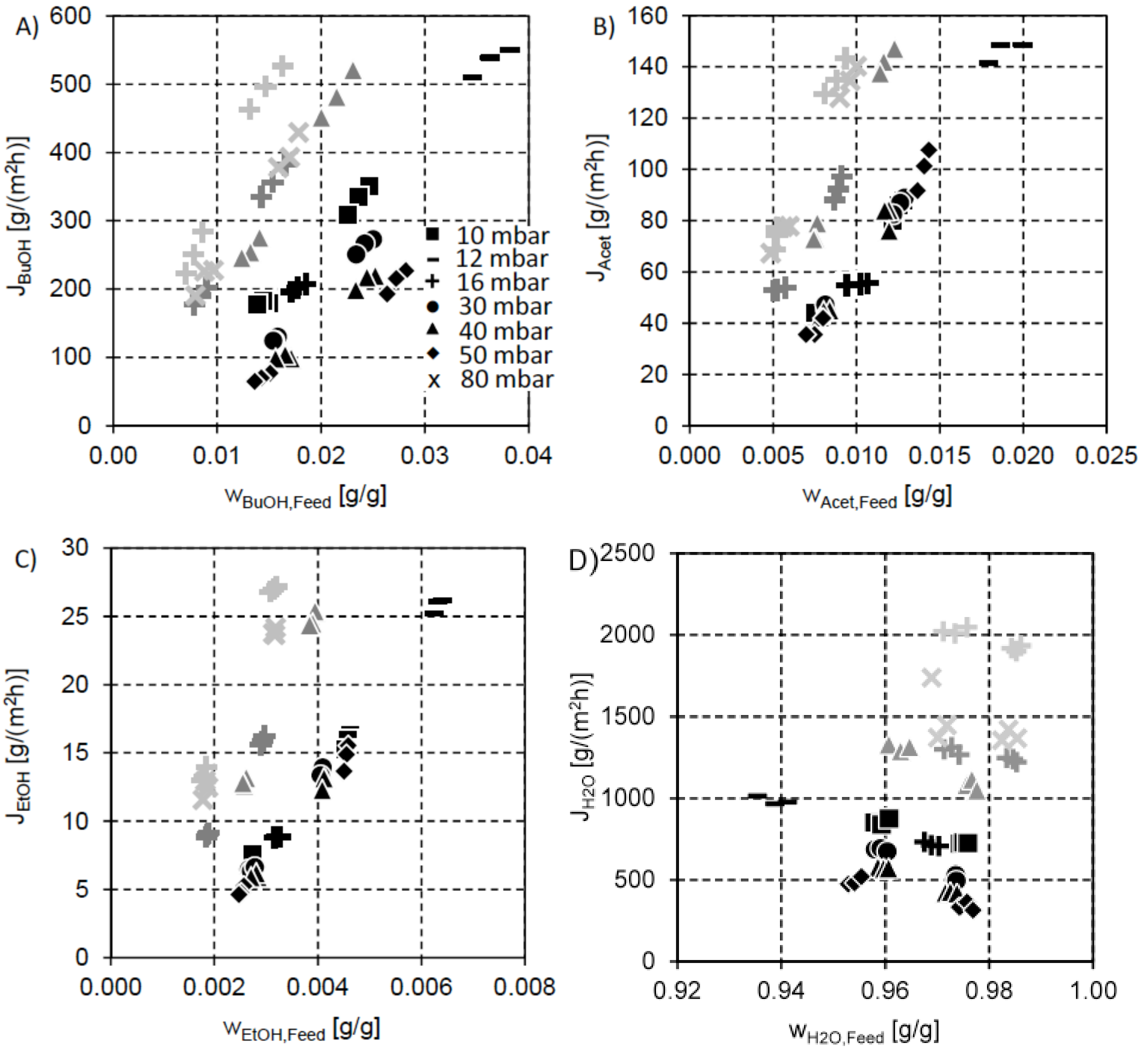

Figure 8: Component fluxes through a PEBA membrane (PEBA - 3) determined for varying temperatures (black = 37 °C; grey = 50 °C; bright grey = 60 °C) and permeate pressures (10 mbar to 80 mbar). Feed mixtures contained acetone, butanol and ethanol in a 3:6:1 concentration ratio.

permeate fluxes of water increase with decreasing water concentrations; decreased water concentrations in the feed are a result from increased solvent feed concentrations. The same dependency is shown in Figure **9A** for varying A:B:E ratios. When the butanol concentration in the feed changes from 0.02 g/g to 0.05 g/g the water permeate flux rises from 800 g/(m^{2}h) to about 1200 g/(m^{2}h). Additionally an influence of a changing A:B:E ratio on the permeate fluxes of acetone and ethanol is seen (Figure **9B**). While the acetone and ethanol concentration was kept constant the butanol concentration in the feed was changed. An increased B:A ratio or an increased B:E ratio enhances the permeate fluxes of both acetone or ethanol. With A:B:E ratios raising from 3:3:1 to 3:9:1 at constant acetone and ethanol concentrations in the feed, the permeate flux of acetone increases by more than 40 % up to 181 g/(m^{2}h) (grey triangles ▲ and rhombi ◆). For a high B:E ratio (bright grey rhombi ◆) the partial flux of ethanol is 39 g/(m^{2}h) and therefore more than 90 % higher compared to the low B:E ratio (bright grey triangles ▲). In contrast to this, the butanol flux is nearly independent of lower acetone and butanol concentrations as was found during further experiments.

Next to acetone, butanol and ethanol also the permeation of acetic acid, butyric acid and 1,3-propanediol was checked. Table **2** shows the permeate fluxes of these components through PEBA membranes. The fluxes of the butyric acid and acetic acid are lower than 7.6 and 3.1 g/(m^{2}h) and thus very low compared to fluxes of butanol, acetone and ethanol. The permeate concentration does not exceed 0.01 g/g, the enrichment factors therefore are lower than 2.8 and 1.4, respectively. In pervaporation

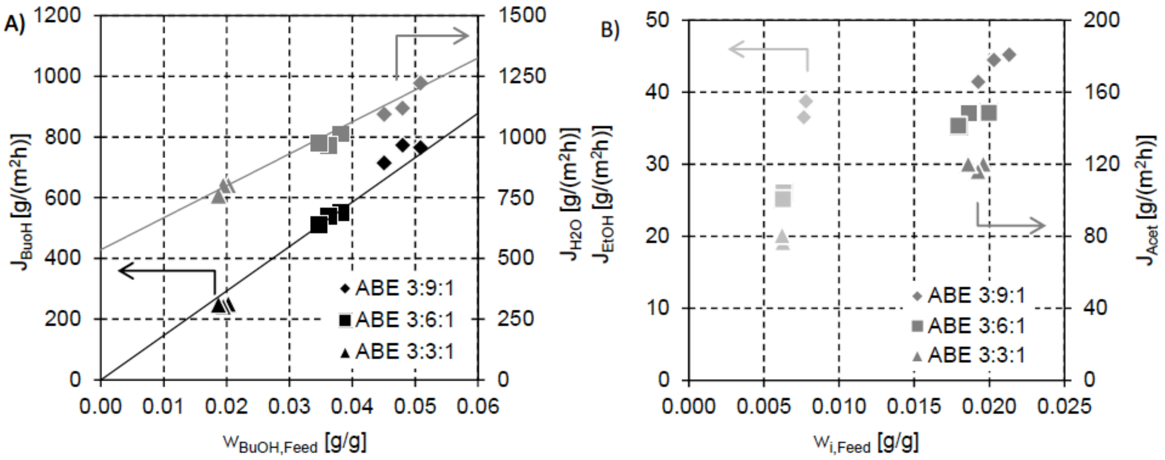

Figure 9: Permeate fluxes of (**A**) butanol (black) and water (grey) or (**B**) acetone (grey) and ethanol (light grey) in pervaporation of feeds with varying A:B:E ratios with PEBA membranes (T = 37 °C, p_{Perm} = 10 mbar).

Table 2: Permeation of organic acids and 1,3-propanediol through PEBA membranes (T = 37 °C, p_{Perm} = 10 mbar). Experiments carried out with ternary mixtures of butyric acid (BuAc), acetic acid (AcAc) and water or butanol (BuOH), 1,3-propanediol (1,3-PDO) and water

$w_{i,Feed}$ [g/g]		J_i [g/(m²h)]		$w_{i,Perm}$ [g/g]		β_i [-]	
BuAc	***AcAc***	***BuAc***	***AcAc***	***BuAc***	***AcAc***	***BuAc***	***AcAc***
0.0037	0.0031	6.98	3.08	0.0100	0.0044	2.70	1.42
0.0037	0.0030	7.63	2.97	0.0105	0.0041	2.84	1.36
BuOH	***1,3-PDO***	***BuOH***	***1,3-PDO***	***BuOH***	***1,3-PDO***	***BuOH***	***1,3-PDO***
0.0234	0.0312	296.7	0	0.2708	0	11.57	0
0.0490	0.0245	673.5	0	0.3952	0	8.07	0

experiments with ternary mixtures of butanol and 1,3-propanediol butanol permeates through the membrane well, whereas no 1,3-propanediol can be detected in the permeate samples.

3.2.3. Swelling of PEBA

As shown in Figure **10A** PEBA sample weight increases by 27 % when immersed in aqueous solutions containing 0.05 g/g butanol. In contrast to this, sorption of acetone and ethanol can only hardly be observed. Interestingly, butyric acid, which permeates through PEBA much worse than butanol, results in a swelling of the membrane by 27 % (Figure **10B**). Sorption of acetic acid is much smaller than sorption of butyric acid, a swelling of 3.6 % is observed. Immersion of the PEBA samples into mixtures with 1,3-propanediol does not result in a weight increase of the PEBA samples. Boddeker *et al*. [28] performed swelling experiments with PEBA 40. For an aqueous solution containing 0.03 g/g butanol a lower sorption of 7.6 % was determined. The difference is likely a result of the differences in the PEBA compositions.

4. DISCUSSION OF THE RESULTS

Several differences in the permeability, selectivity and in the swelling of PDMS and PEBA were observed during the experimental study. The main differences will be discussed in the following. Next to a direct comparison of the fluxes, the permeances and driving forces for mass transfer were calculated to consider component properties like e.g. boiling points or the non-ideal behaviour of the components (section 4.1). In section 4.2 polymer swelling is discussed as a possible explanation for the pervaporation characteristics measured. Because Hansen solubility parameters are reported to be able to describe the interactions between polymers and solvents, they are compared with our swelling experiments. Afterwards the suitability of the different membrane materials for butanol pervaporation is discussed with regard to a pervaporation process design.

4.1. Comparison of the Separation Performance

As presented before the partial fluxes of butanol linearly increase with the feed concentration for both

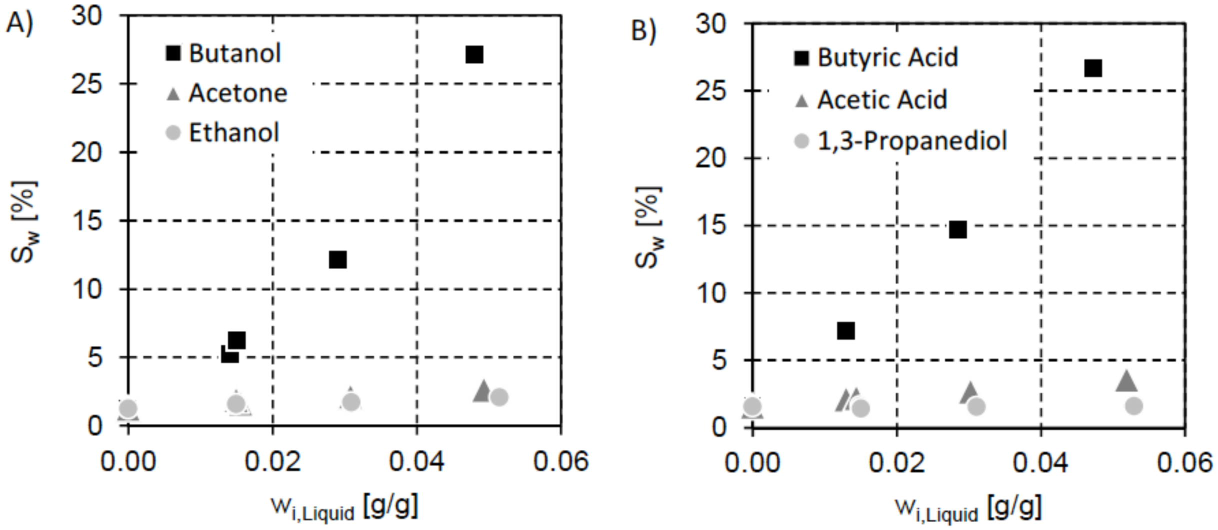

Figure 10: Swelling of and PEBA samples immersed in binary aqueous solutions of solvents; measurements were carried out at 37 °C.

membrane materials. Butanol permeate fluxes measured for the PDMS membranes were only slightly higher than butanol fluxes of the PEBA membrane. A main difference between PDMS and PEBA is seen for the partial fluxes of water, acetone and ethanol. Water fluxes are higher for PEBA membranes resulting in permeate concentrations of butanol decreased by about 25 %. This finding suggests that PEBA is more hydrophilic. However, this assumption would be contradicting to the lowered permeate fluxes of acetone, which were about 75 % lower for PEBA than for PDMS. As acetone is more polar/hydrophilic than butanol [37] one would firstly expect that acetone – similar to water – permeates better through PEBA membranes than through PDMS membranes. Also the fluxes of ethanol are 45 % lower compared to the PDMS membrane. In general, PDMS membranes show a higher selectivity for butanol over water, which is preferable for a pervaporation process to simplify the subsequent downstreaming. Nevertheless, the higher selectivity of the PEBA membrane for butanol over acetone might also contribute to the further downstreaming of the permeate.

Permeate fluxes of acetic and butyric acid are higher for the PEBA membranes, however, due to the increased water flux the permeate concentration of the acids is in a comparable range for both membranes materials. Enrichment factors for butanol are much higher than enrichment factors of the organic acids for both membrane materials. The better separation of butanol compared to the organic acids is beneficial, because acids should remain in the fermentation broth because they are precursor for butanol formation.

To further investigate on the permeation of the various organics through the PDMS and PEBA membranes, it is important to consider their component properties, like e.g boiling points or the non-ideal behaviour. In general the permeate flux of a component *i* can be described as product of permeances Q_i, the reciprocal molar volume V_m^{-1} and a driving force ΔDF_i for mass transfer (see eq. 3). In case of pervaporation often the difference in chemical potentials $\Delta\mu_i$ between feed side and permeate side can be used as replacement for the driving force [24,38].

$$J_i = Q_i \cdot V_m^{-1} \cdot \Delta DF_i \tag{3}$$

$$\Delta DF_i = \mu_{i,Feed} - \mu_{i,perm} = R \cdot T \cdot ln\left(\frac{x_i \cdot \gamma_i(T) \cdot p_{s,i}(T)}{y_i \cdot p_{perm}}\right) \tag{4}$$

According to eq. 4, next to concentrations x_i and the permeate pressure p_{Perm}, especially the saturated vapour pressure $p_{S,i}$ (for comparison see boiling points in Table **3**) and the non-ideal behaviour of the components in the form of activity coefficients γ_i have a large impact on the driving force for mass transport through the membrane. Activity coefficients were calculated using the Non-Random-Two-Liquid (NRTL) model [39]. The NRTL parameter sets that were aligned with literature data are given in the supplementary material. After calculation of the driving forces, the permeances of a membrane for a component i can be calculated according to eq. 3 for each experiment. It was found that permeances calculated are linearly dependent on the feed concentrations. This was observed for all membranes tested in this work and suggests that the membrane properties change with an increasing feed concentration, probably induced by an enhanced swelling of the membrane in the presence of higher feed concentrations of the various components. Because the increase of the permeances with the feed mass fractions is linear, a specific permeance Q_i^* is defined (eq. 5).

$$Q_i = Q_i^* \cdot w_{i,Feed} \tag{5}$$

The specific permeances calculated for all components are shown in Table **3**. Since the specific permeance Q_i^* is also temperature and permeate pressure dependent, exemplarily only experiments performed at a temperature of 37 °C and a permeate pressure of 10 mbar were considered, which were carried out with binary aqueous solutions. For illustration also the driving forces of the components were calculated.

As butanol fluxes were lower and water fluxes were higher for PEBA membranes when compared to PDMS membranes the specific permeances listed in Table **3** are somewhat higher or lower. The specific permeance for acetone is always lower than the permeances for butanol. This is also true for the PDMS membranes although the permeate fluxes for acetone were found to be higher. That is a consequence of the low volatility of acetone and the resulting high driving force between feed and permeate side. The difference in chemical potential for mass transfer of ethanol is similar to the difference calculated for acetone although ethanol is less volatile. This results from the low permeate concentrations of ethanol because the fluxes and thus the permeances for ethanol are much lower. Because 1,3-propanediol was not found in the permeate samples the permeances are assumed to be zero, the according difference in the chemical potentials cannot be calculated because the permeate mass fraction $w_{1,3\text{-}PDO,Perm}$ is infinitely small. In accordance with the experimental results the permeances for butyric acid and acetic acid are smaller than the permeances for butanol. The differences in chemical potentials in contrast are similar for acids and solvents. As shown by the experiments, acid permeances are bigger for PEBA than for PDMS. In experiments water showed high fluxes but has the lowest permeance. This is because the feed concentration of water is much higher than the concentration of acids and solvents. With changing solvent concentrations in the feed, the water concentration changes only slightly. Thus the impact onto the permeance is rather small; the influence of butanol on the permeate flux of water was not considered in Table **3**.

For PEBA membranes additionally an influence of the butanol concentration on the permeate fluxes of acetone and ethanol was observed, which was not found for PDMS membranes. In contrast to PDMS the PEBA monomers are not crosslinked covalently. Polymer chains in the PEBA polymer consist of polyether blocks responsible for polymer flexibility, and semicrystalline polyamide blocks determining the polymer rigidity [40]. One can suppose that because of missing covalent bonds the PEBA membrane is swollen by butanol to a greater extend. This might result in higher permeances for acetone, ethanol and also water. Because swelling of the membranes might be an explanation for the effects observed in this study, it will be further discussed in the next section.

Table 3: Comparison of specific permeances and differences in chemical potentials (Determined for experiments with binary mixtures at T = 37 °, p_{Perm} = 10 mbar and a solvent feed mass fractions of $w_{i,Feed}$ = 0.005 g/g, except for water)

	T_{Boil}	Pervap™ 4060^a *or* Silicone-FVT^b		PEBA	
	[°C]	Q_i^* [g/(m^2·h·bar)]	$\Delta\mu_i$ [bar·m^3/mol]	Q_i^* [g/(m^2·h·bar)]	$\Delta\mu_i$ [bar·m^3/mol]
Acetone	56.2	24.5^a	0.053	3.76	0.095
Butanol	117.5	32.5^a	0.038	24.4	0.045
Ethanol	78.4	4.05^a	0.053	1.65	0.077
1,3-Propanediol	213.9	0^b	-	0	-
Butyric acid	162.9	2.30^a	0.043	4.12	0.043
Acetic acid	118.1	0.32^a	0.065	1.06	0.053
Water	100.0	0.16^a	0.048	0.23	0.048

4.2. Influence of the Swelling Behaviour on the Permeate Fluxes

Swelling experiments were conducted to further investigate the permeation behaviour of the membranes. In the previous section is shown that butanol influences the fluxes of acetone and ethanol in case of PEBA, but not when using PDMS membranes. Furthermore one can observe that butanol, in contrast to acetone or ethanol, affects the partial fluxes of water for both membrane materials. When comparing Figures **6** and **10** one can see that the mass increase of PEBA samples during swelling experiments is much higher than for PDMS samples. PEBA membranes are swollen up to 10 times stronger than PDMS. This is a result of the covalent crosslinking of the PDMS-molecules, whereas PEBA molecules are not covalently crosslinked. An influence of the degree of polymer crosslinking on the permeability and selectivity was already observed by other authors e.g. by Holtbrügge *et al*. [41] for vapour permeation processes with polyvinyl alcohol membrane Pervap^{TM} 1255 membranes.

During pervaporation experiments it was further observed that the presence of butanol enhances the permeate fluxes of acetone and ethanol when using PEBA membranes but not when using PDMS membranes. Therefore, we concluded that an enhanced swelling of the membranes at high butanol concentrations is responsible for the dependency of the acetone fluxes through PEBA on the butanol concentration. Due to the covalent crosslinking of PDMS, swelling of PDMS in the presence of butanol is much smaller. Thus higher butanol concentrations in the feed do not change the polymer permeance for acetone of ethanol as largely as observed for PEBA. Because the swelling of the polymers by acetone, ethanol or water is much smaller than swelling by butanol, a mutual effect of acetone, ethanol or water on butanol permeation was not observed. An apparent effect of the butanol induced swelling on the permeate fluxes for both membrane materials can only be seen for water. Water, however, is present in a much higher feed concentration and is a remarkably smaller molecule when compared to the other organic molecules.

PDMS and PEBA polymer samples submerged in aqueous solutions of acetone, butanol or ethanol show the same trend in weight increases that was found during estimation of the permeances: butanol > acetone > ethanol. Immersion in acetone solutions of 0.05 g/g increases the PDMS sample weight by about 1 %, the PEBA sample weight by about 2.5 %. Relatively to butanol PDMS shows a better solubility for acetone than PEBA, what is in accordance with the permeances calculated. 1,3-Propanediol which was not detected in any permeate sample during pervaporation experiments, does not swell the PEBA or PDMS polymer. Swelling that is observed in the presence of 1,3-propanediol is similar to swelling of pure water, the mass of the polymer samples does not perceptibly increase. Interestingly, both membrane materials, PDMS as well as PEBA, show a high solubility for butyric acid, which is similar to butanol. In contrast to this the permeate fluxes and permeances of butyric acid were several times lower than fluxes of butanol. A comparison of permeances and results of the swelling experiments for butanol, acetone and butyric acid shows that a high permeability of butanol cannot be explained by the good sorption in the polymer alone. Whereas butyric acid dissolves in both polymer samples very well, its permeances are much lower compared to butanol. Acetone in contrast dissolves much worse in the polymers but permeates better than butyric acid. One possible reason that might explain the permeation behaviour is a difference in diffusion coefficients of the various components in the polymers. In general, the permeance Q_i is equal to a product of diffusion coefficient D_i and a sorption coefficient S_i [24]. As permeances for butanol and butyric acid are strongly differing from each other (see Table **3**), but similar sorption behaviour for both components was observed, differing diffusion coefficients might be an explanation for the findings of this study. However, to prove this assumption further investigation is necessary in future.

Hansen solubility parameters are reported to be able to describe the interactions between polymers and solvents considering the share of dispersion forces δ_d, dipolar forces δ_p and hydrogen bonding forces δ_h between polymer and solvent [43]. These three force contributions represent a vector of a component in a three-dimensional diagram. The miscibility between polymer and solvent can be described by the length of a connecting vector $D_{S\text{-}P}$ between the two component vectors. For a solvent S and a polymer P the length is a measure for the mutual miscibility of these components and can be calculated according to eq. 6 [43]:

$$D_{S-P} = \sqrt{4 \cdot (\delta_{d,s} - \delta_{d,p})^2 + (\delta_{p,s} - \delta_{p,P})^2 + (\delta_{h,s} - \delta_{h,P})^2} \qquad (6)$$

The different Hansen solubility parameters are listed in Table **4**. Because parameters for PEBA were not

Table 4: Hansen solubility parameters [$MPa^{0,5}$] for polymers and solvents.

	δ_{total}	δ_d	δ_p	δ_h		$D_{S\text{-}P,PDMS}$	$D_{S\text{-}P,PEBA}$
PDMS	16.6	15.9	0.1	4.7	[45]		
PEBA	20.3	17.6	7.6	6.8	*		
Acetone	19.9	15.5	10.4	7.0	[43]	10.6	5.0
Butanol	23.2	16.0	5.7	15.8	[43]	12.4	9.7
Ethanol	26.5	15.8	8.8	19.4	[43]	17.1	13.2
1,3-Propanediol	31.7	16.8	13.5	23.2	[43]	22.9	17.5
Butyric acid	18.7	14.9	4.1	10.6	[43]	7.4	7.4
Acetic acid	21.4	14.5	8.0	13.5	[43]	12.2	9.1
Water	47.8	15.5	16.0	42.3	[43]	40.8	36.7

*Calculated based on [40,43,44].

available in literature the parameter set was calculated based on parameters for poly(tetramethylene oxide) (a polyether) [44] and polyamide PA12 [43] which are reported to be the building blocks for PEBA production [40].

The length of the connection vector $D_{S\text{-}P}$ between PDMS or PEBA and acetone is smaller than the distance between the polymers and butanol. This trend does not suit the results found during the swelling experiments, as the polymers were swollen to a much larger extend by butanol than acetone. A similar finding was already reported by Niemistö *et al*. [25]. Furthermore it can be seen that the distances between butyric acid and polymers are smaller than the butanol-polymer distances, meaning that butyric acid should dissolve much better in the polymers than butanol. This is true for swelling experiments with PDMS but not for PEBA. The uptake of water induced a swelling lower than 0.3 % or 1.6 % for PDMS and PEBA, despite the high water concentrations compared to the other solvents. This is in good accordance with the calculated distances $D_{S\text{-}P}$. Next to water the longest distances between polymers and solvents were calculated for ethanol, and 1,3-propanediol, for these components no sorption into the polymer was measured. Acetic acid caused a slight swelling of the polymer; however, the length of the connection vector is similar to the length of butanol.

To sum up one can say that Hansen solubility parameters can be used to roughly evaluate whether a component is absorbed by a polymer material or not, however, a detailed prediction of the sorption behaviour is not possible. The use of Hansen solubility parameters is further made difficult as the properties of the polymer used for parameter estimation and the polymer used for membrane production might slightly differ. One must further keep in mind that other factors might influence permeation and sorption. E.g. the rate of solvent evaporation in membrane production has an influence on the formation of macro pores and micro pores and the micro pore tortuosity. The applied solvent can also affect the arrangement of the polymer chains. Nevertheless, Kujawski and Ostrowska-Gumkowska [42] have shown that the preparation conditions (polymer concentration in the casting solution; amount of curing agent in silicone) have only a minor effect on the properties of PEBA and PDMS membranes.

4.3. Process Consideration

For the PDMS and PEBA membranes tested within this study different permeation behaviours were observed. At first glance the use of a PDMS membrane seems to better suited for separation of butanol-water mixtures because of higher butanol permeate fluxes and higher selectivities for butanol over water. However, acetone permeated very well through the PDMS membrane, permeation rates through the PEBA membrane were much lower. High partial fluxes of acetone and ethanol result in a dilution of the permeate. Therefore, the butanol permeate concentrations are lower in the presence of acetone and ethanol when compared to pervaporation experiments with binary butanol-water mixtures. Binary mixtures of butanol and water form a miscibility gap which can simplify the subsequent downstreaming of butanol [14]. If – dependent on the separation characteristics of the pervaporation membrane – the concentration of acetone in the permeate is too high, this miscibility gap closes as one can see in Figure **11**. Pervaporation experiments were carried out using the

Silicone-FVT membrane as well as the PEBA membranes with aqueous feed solutions containing acetone and butanol in varying ratios ($w_{BuOH,Feed}$ = 0.014 to 0.026 g/g; $w_{BuOH,Feed}/w_{Acet,Feed}$ = 0.93 to 2.16 g/g). Permeate samples obtained with PDMS membranes were always single-phasic, whereas permeate samples of PEBA membranes always split up into an organic and an aqueous phase. Because the acetone and ethanol fluxes through the PEBA membrane are lower than the fluxes through PDMS membranes, the dilution of the permeate by the additional acetone fluxes is smaller for PEBA membranes. In this context one should keep in mind that the acetone concentration in the permeate is also dependent on the feed concentration and thus on the butanol-to-acetone ratio that is formed by the production organisms. Dependent on microorganism and the amount of butanol produced, the use of one or the other membrane is advisable. Furthermore one needs to consider that organic acids permeated better through PEBA membranes than through PDMS membranes. This fact is important to be considered, because acids should remain in the fermentation broth as they are precursor for butanol formation. The permeation of acid as well as the influence of the product/by-product ratio show that a membrane should not be selected only because of high permeate fluxes or selectivities for the desired main product. A number of factors need to be considered for finding the best suited membrane material to facilitate an efficient separation process.

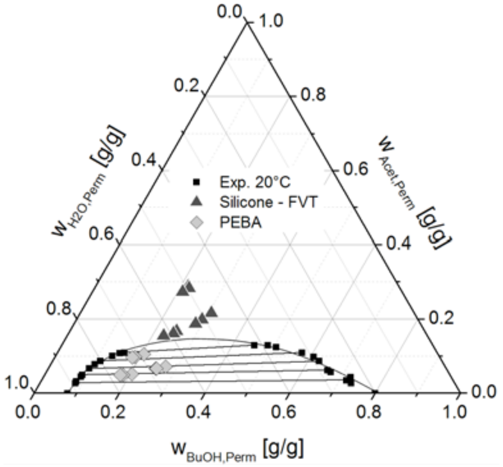

Figure 11: Permeate compositions for pervaporation experiments (T = 37 °C, p_{Perm} = 10 mbar) with ternary butanol-acetone-water mixtures and varying acetone-butanol ratios. Experimental data describing of the miscibility gap at 20 °C were taken from Stephen and Stephen and Santos *et al*. [46,47].

The acetone concentration in the permeate not only influences the miscibility gap, but also the condensation temperature that is required to condense the permeate. Higher condensation temperatures enable the use of a cheaper cooling medium, e.g. by using process cooling water instead of refrigerated water or a low-temperature refrigerant [18]. However, if a sufficient amount of acetone is present in the permeate, due to the low boiling point of acetone the condenser temperature must be noteworthy lowered to maintain a certain permeate pressure. Figure **12** displays the condensation temperature required at different permeate pressures, to condense a permeate containing 0.2 g/g butanol, water and varying amounts of acetone. The condensation temperatures were calculated using Aspen Properties®; NRTL parameter sets are given in the supplementary material. At a certain pressure, in presence of 0.2 g/g acetone in the permeate, the required condensation temperature is lowered by about 15 °C, compared to a permeate that does not contain any acetone. If a cheaper cooling medium shall be employed the condensation temperature must be increase by simultaneously increasing the permeate pressure. Obviously this would lead to decreased permeate fluxes. It needs to be calculated, if savings in the permeate condensation can compensate the additional costs for the membrane area that arise from the lowered fluxes [18].

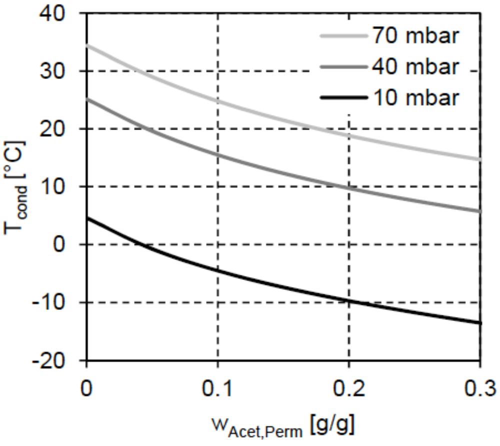

Figure 12: Condensation temperatures for ternary permeate compositions containing varying acetone concentrations, butanol ($w_{BuOH,Perm}$ =0.2 g/g) and water.

5. CONCLUSION

In this study hydrophobic PDMS and PEBA polymer membranes were examined for the separation of organic components from aqueous solutions. A large number of pervaporation experiments were carried out with feeds of varying concentrations and compositions and over a wide temperature and permeate pressure range. A comprehensive and consistent database for two important membrane polymers applied for organic pervaporation is obtained. These data lay the foundation for later process studies which are currently only rarely found in literature.

During experiments it was observed that fluxes of butanol through Pervap^{TM} 4060 membranes and the silicone membrane produced in our own laboratory were slightly higher than for PEBA membranes. The butanol permeate concentration were lower for PEBA membranes. However, the selectivity of the PEBA membranes for butanol over acetone was much higher than for PDMS which is an important advantage of the PEBA membranes. The permeate concentration of acetone has a remarkable influence on the subsequent downstreaming of butanol, because it influences the miscibility gap of the permeate and the permeate condensation temperature. In contrast to butanol and acetone 1,3-propanediol and organic acids permeated not or to a much smaller extent.

To analyse how the solubility of the organic components in the membrane polymers influences the permeation characteristics, swelling experiments were conducted. A detailed prediction of the swelling by Hansen Solubility Parameters was not possible. Furthermore, the comparison of pervaporation experiments and swelling experiments suggests that the solubility of a component in a polymer alone is not sufficient to evaluate the separation behaviour of the component. Butyric acid and butanol both were found to have a similar solubility in the membrane polymers, whereas butanol permeates much better than the acid.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY DATA

The supplementary Figures and Tables can be downloaded from the journal website with the article.

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