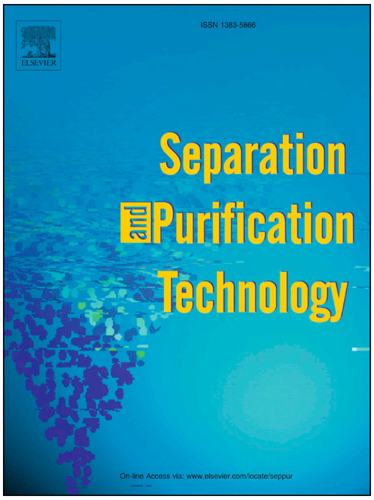

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Polymer inclusion membranes containing ionic liquids for the recovery of n-butanol from ABE solutions by pervaporation

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Abstract

Making economically competitive technologies for using biofuels as alternatives to move towards a low carbon economy has recently increased the interest of researchers and industry. Biobutanol has a good potential due to its attractive physicochemical properties. It can be produced through the ABE process (acetone–butanol–ethanol) by Clostridium bacteria. However, severe product inhibition, leading to low productivity and low final concentration in the broth, the butanol toxicity to the microorganisms and the high energy consumption are still the main challenges. Pervaporation (PV) is proposed as an efficient alternative to the current separation methods. In PV, the properties of the membrane material dictate the separation of the process for the recovery of butanol. Different polymers and additives are being studied for different membrane characteristics. This work focuses on the fabrication of composite membranes with different polymer/ionic liquid (PEBA/HMImFAP) compositions by the temperature-induced phase-inversion technique (TIPS) to be used in a PV unit to recover butanol from ABE synthetic mixtures. Modeling of mass transfer through the membrane using the resistances-in-series approach was used to find the liquid and membrane resistances. It was seen that the overall resistance decreases as the flow rate increases; regarding the liquid side resistance, it becomes important at smaller flow rates and is almost negligible for flowrates above 4.5 L min^{-1}. The resistance that exerted the composite polymeric membrane followed this trend acetone > water > ethanol > butanol. Increasing the IL content favours the selective separation towards butanol because of the smaller membrane resistance. Also, adding IL to the membrane at concentration above 20% leads to a worse separation of the components (in terms of separation factor) because of the formation of defects in the polymeric matrix allowing the water to pass through. Finally, running PV experiments under the same operating conditions allowed the comparison of the PSI of the self-made membranes with a commercial membrane, concluding a better performance of the former membranes.

Keywords: Ionic liquids, membranes, pervaporation, biobutanol separation, biofuels

Highlights

- Novel polymer/ionic liquid membranes were fabricated for the recovery of n-butanol from ABE mixtures
- High IL content in polymer/IL pervaporation membrane shows higher permeate flux
- Overall resistance is strongly influenced by the operating conditions for ABE separation mixtures
- The addition of IL into the polymeric matrix of the membrane improves the selectivity to n-butanol
- Tailored fabricated membranes show improved behavior with respect to commercial membranes

1. Introduction

Making economically competitive technologies for using biofuels as alternatives to move towards a low carbon economy has recently increased the interest of researchers and industry. Raising motivation will continue over the next years as new policies come into effect to increase the share of renewable energy sources in the EU to at least 27% by 2030, and the new sustainability criteria are established for biofuels and bioliquids [1,2]. In this way, the development of the sector opens new options and opportunities to the rising cost of crude oil, the depletion of resources, the CO_2- related environmental challenges, the political instability in oil producing countries, and the reduction of the dependence on imported oil [3]. Biofuels are more biodegradable compared to fossil fuels and despite all their advantages, their use constitute a small percentage especially for the transportation sector due to limitations towards their production [4].

Among others, n-butanol has attracted great attention due its superior advantages such as: higher energy content, lower vapor pressure making it safer to use, less flammability and lower hygroscopicity [5], making it easier to preserve and distribute. In addition, n-butanol is considered an attractive commodity as it can be used as a solvent, in cosmetics, hydraulic fluids, detergent formulations, drugs, antibiotics, hormones and vitamins, as a chemical intermediate in the production of butyl acrylate and methacrylate, and as an extractant in the manufacture of pharmaceuticals [6].

Currently, n-butanol is mainly produced via chemical synthesis, but it can also be produced via ABE fermentation from renewable feedstocks (biobutanol). However, the process has some disadvantages over the petrochemical route as the outcome of the process is very low in final concentration (1-2 % w/w) and low yield due to severe butanol toxicity to microorganisms and the cost intensive butanol recovery technique [3]. In-situ product removal has been suggested to obtain low cost production of biobutanol, making it possible to increase the production rate by a factor of 3-9 as compared with that attained in the conventional batch process [7].

Among different separation processes, pervaporation (PV) is considered to be an economic and safe option for product removal [8,9]. Main PV advantages include high separation efficiency, compact operation space and low energy consumption, flexibility, high selectivity, low operating temperature, reasonable performance to cost ratio, possibility of modular design and the absence of a separating agent that could cause product contamination. Moreover, it does not affect microorganisms and losses of nutrients and substrates are prevented [3]. Nevertheless, PV efficiency might be limited by the membrane performance. Thus, the development of innovative membranes is important for the progress of the biofuel sector.

There are three major types of PV hydrophobic membranes that may be applied to separate biobutanol, namely polymeric, inorganic, and composite membranes [10]. PV membranes are often made with a thin non-porous selective layer (hydrophobic) on a porous substrate that allows the separation of organic compounds from an aqueous solution [11]. Inorganic substrates exhibit the advantages of the chemical, mechanical and thermal stabilities. However, the use of polymeric materials is more desirable for industrial scale because they are easy to fabricate and provide good performance at low cost. Different hydrophobic- organophilic polymeric membranes have been tested for the recovery of n-butanol by PV. Nevertheless, for the recovery of ethanol and n-butanol from fermentation broths and to enhance the fermentation process, PDMS is the most widely used polymer material, which provides a moderate selectivity and high permeability to many organics [12–14].

Ionic liquids (ILs) have been investigated and are widely used in numerous separation processes [15,16]. They are organic salts with melting points around or below the ambient temperature. Their unique properties make polymer membranes containing ionic liquids (PM-ILs) have many advantages [17–19] such as high fluxes and faster separation because molecular diffusion is much higher in ionic liquids than in polymers and it can be enhanced by a proper choice of IL components. In addition, only small amounts of ILs are necessary to form the membrane making them more viable in terms of cost [20,21]. In this work, ionic liquids are incorporated into the membranes in the form of polymer inclusion membranes (PIMs), where the membrane is usually formed as a thin stable film by casting a viscous mixture solution composed of an ionic liquid and a base polymer. PIMs offer promising results of both permeability and selectivity but their stability mostly depends on the compatibility and partial miscibility between the polymer and the IL, which results in the formation of differentiated regions between them, and the loss of IL from these regions is the main mechanism of degradation of these membranes during PV [22]. Consequently, and given the large number of combinations between polymers and ILs, more studies are needed regarding their interactions to determine their potential compatibility. Nevertheless, a number of studies have begun to examine butanol recovery with IL membranes.

Among all preliminary works, it is noticed that the most preferred combination for this type of membranes is PDMS/IL. For example, Kohoutová et al. [20] made quasi-solidified [BBIm][BF_4] /PDMS membranes for the separation of 1-butanol from 5 wt% aqueous solution showing high stability. The separation factor of 1-butanol raised up to 37 when 30 wt% of [BBIm][BF_4] was introduced in the membrane. A [EEIm][PF_6]/ PDMS membrane was prepared into an TiO_2 ceramic module for the separation of 1-butanol-water mixtures obtaining higher diffusion coefficients than in PDMS only [23]. Also, Izák et al. [24] separated 1-butanol and acetone from water using by a [N3333][$B(CN)_4$]/PDMS membrane with ultrafiltration membrane as support material. The enrichment factors of 1-butanol and acetone increased compared to PDMS membrane only. Mai et al. [25] performed ABE pervaporation separation by using a [Omim][Tf_2N]/PDMS membrane from aqueous solution and Plaza et al. [26] investigated the separation of ABE from aqueous solution using a [BMIm] [PF_6]/PTFE hollow fibers. Marszalek et al. [10] performed a PV separation comparing a commercial membrane PERVAP 4060 and IL ([HMIm][PF_6] and [BMIm][Tf_2N]) /PDMS membranes; as main finding, they reported that the IL-PDMS membrane provides higher butanol selectivity, compared to the commercial membrane, but suffers from low flux caused by the additional layer resistance. Recently, Cabezas et al. [27] have reported the butanol separation from ABE mixtures by pervaporation using silicone-coated IL gel membranes, using different imidazolium-based or phosphonium-based ionic liquids. These authors found that butanol/water selectivity for [$P_{6,6,6,14}$][Tf_2N]-based membranes reached a value equal to 892, which is 150 times higher than the value obtained for a single PDMS layer membrane. Simultaneously, for the same IL, the transmembrane fluxes of butanol and water were 37 % and 99.6 % lower than the values obtained using a single PDMS layer membrane, respectively.

Recent studies by our research group evaluated the combination of various ILs with the polymers Pebax 2533 and PVDF-HFP for the synthesis of membranes in pervaporation. Pebax 2533/ HMImFAP offered the highest selectivities towards n-butanol. However, the ratio in the composition between polymer/IL that provides better results for pervaporation performance must still be optimized [28]. Together, these studies indicate that there is room in the PV separation of n-butanol with polymer/IL membranes to improve the process. In this way, this work focuses on the development of polymeric inclusion membranes, and incorporating different amounts of IL and polymer, for the separation of n-butanol-ethanol-acetone aqueous solutions by PV. Moreover, a methodology for the manufacture of dense membranes with polymeric inclusion using the technique of phase inversion by evaporation of the solvent is used. The influence of the composition of the membranes in the separation of n-butanol-water mixtures is also studied and finally a comparison of the performance of the IL membranes with a commercial membrane is discussed.

2. Experimental Methodology

2.1.Materials

To prepare the polymer inclusion membranes 1-butanol (CAS No. 71-36-3) was used as solvent and the ionic liquid 1-Hexyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate (HMImFAP) (CAS no. 713512-19-7) as membrane additive (Figure 1). Both reagents supplied by Sigma-Aldrich and used as received. Polymer PEBAX 2533 (CAS No. 77402-38-1) was kindly supplied by ARKEMA, France.

On the other hand, an organophilic commercial membrane made of polyether block amide (PEBA) was supplied by PERVATECH and used as benchmark for the synthetic membranes.

The aqueous feed solution for the PV experiments was prepared by mixing: 1-butanol, ethanol and acetone with ultrapure water Milli Q obtained from a MERCK Millipore system. All materials were of analytical grade and were used without further purification.

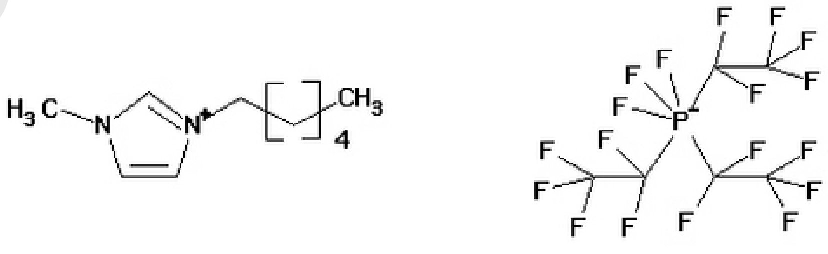

Figure 1: HMImFAP ($C_{16}H_{19}F_{18}N_2$) Ionic liquid structure.

2.2. Membrane preparation

The composite membranes prepared in this work were fabricated by the temperature-induced phase-inversion technique (TIPS). The following polymer/IL composition (%w/w) were used: 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50. Then 6 mL of 1-butanol (solvent) were added into a beaker after the polymer and the IL were weighted and poured in the container. This solution was left in a heating agitator plate for about 4 hours, with a stirring magnet to help the mixture dissolve at a controlled temperature (∽70 ^{o}C). Once a homogenous mixture was obtained, the containers were left to stand for 30 min at room temperature. The mixture was then evenly poured over the surface of a Petri dish, then it wasplaced in a vacuum oven (VO200 supplied by Mermmet) and left over night at 30 ^{o}C at a pressure of 150 mbar. Finally, the dried membranes were peeled off and placed into the PV cell.

2.3. Characterization of membranes

The physico-chemical interactions that may occur between the polymer and the ionic liquid were characterized by a FTIR using a Perkin Elmer spectrum 65 Fourier Transform Infrared Spectrometer.

For the morphological characterization (microscopic structure and distribution of the polymer and the ionic liquid) of the membranes a scanning electron microscopy (SEM), model EVO MA15, supplied by Zeiss was used. All the samples were coated with a thin layer of gold to prevent charging. The structural analysis was carried out for both the transversal and the surface area of the membranes.

2.4. PV experiments

The PV performance of the membranes was evaluated by a custom-built lab scale PV unit. A diagram of the experimental set up is shown in Figure 2.

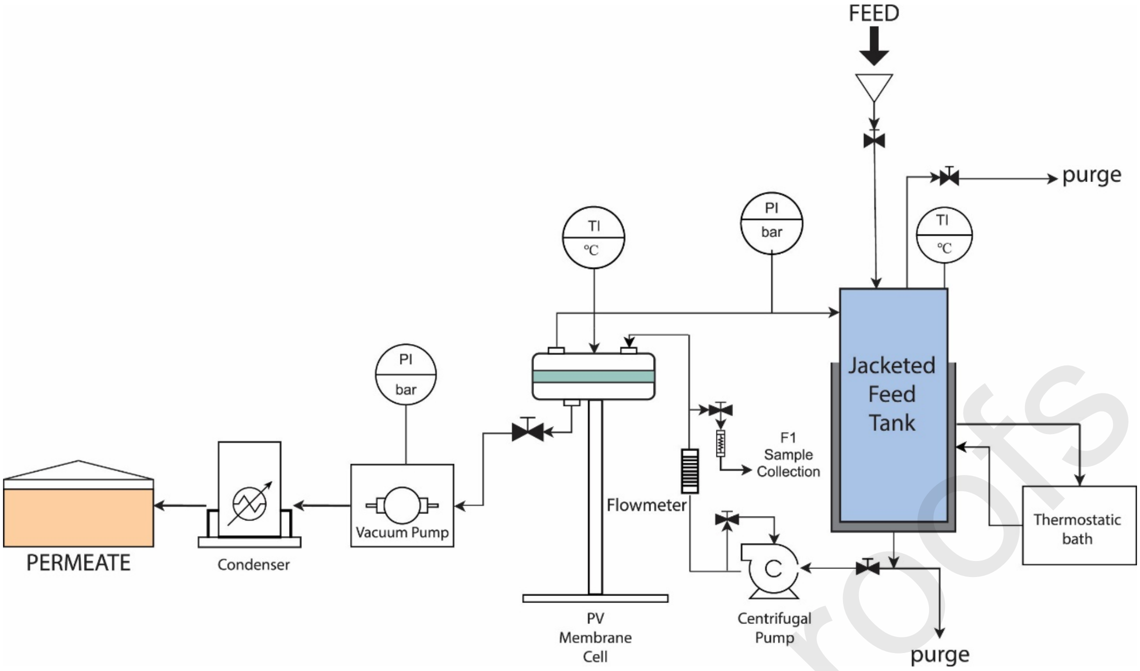

Figure 2: Diagram of the experimental set up for PV experiments.

The flat membrane was placed and sealed in a stainless-steel PV circular cell (radial flow) with an effective area of 0,00546 m^2. A 2 L feed solution (liquid phase), ABE mixture 1:2:1 %w/w, was continuously recirculated from a feed tank to the upstream side of the membrane by a centrifugal pump and maintained at a constant temperature. On the other side of the membrane, vacuum was applied using a vacuum pump (Vacuubrand PC 3004 VARIO) and the permeate was condensed and collected as liquid in the permeate tank. Before starting the experiments, the set point of the vacuum pump was set to 1 mbar However during the experiments the permeate pressure was between 10 and 30 mbar, corresponding to the vapor-liquid equilibrium pressure of the permeate stream at the condensation temperature. Every 30 minutes samples of the feed and permeate were collected, weighed and analyzed in a gas chromatograph equipped with a flame ionization detector (GC-FID) model GC-2010 from Shimadzu. Each PV experiment lasted for about 4 h to be sure that a pseudo-steady state is reached. After each experiment the membrane thickness was measured using a digital micrometer (Mitutoyo model 293-821).

The PV performance of a membrane was evaluated in terms of permeate flux J, separation factor β and pervaporation separation index (PSI). Moreover the mass transfer in the system was also characterized using the resistances in series approach [29,30].

In order to calculate the permeability of each component, their fluxes must first be obtained. For the calculation of the latter, one must first obtain the total permeate flux, which is obtained experimentally by Eq. (1):

$$J = \frac{m}{A_m \cdot \Delta t} \tag{1}$$

Where J represents the total flux across the membrane (kg m^{-2} h^{-1}), A_m the membrane area (m^2), m the mass of permeate collected (g) and Δt (h) the permeate sampling time interval.

Then the flux of each component is calculated from the total flux and the permeate composition obtained by chromatographic analysis (Eq. 2):

$$\mathrm{J_i} = \mathrm{J} \cdot \mathrm{w_{i,p}} \tag{2}$$

Where J_i represents flux of each component across the membrane (kg m^{-2} h^{-1}), and $w_{i,p}$ the concentration of the component *i* in the permeate stream.

In order to characterize the mass transfer in the system the resistances-in-series approach based on the solution-diffusion concept has been applied. According the solution-diffusion model the flux of a component *i* across the membrane can be written as a function of an overall mass transfer coefficient and the driving force [31,32]:

$$\mathrm{J_i} = \mathrm{Q}_{overall,i}\left(\mathrm{P_i^{sat}}\gamma_\mathrm{i}\mathrm{x_i} - P_p y_i\right) \tag{3}$$

where, $Q_{overall}$ is the overall mass transfer coefficient for the component *i*, P_i^{sat} is the vapor pressure of the component *i*, γ_i is the activity coefficient, xi and y_i are the molar fraction of the component *i* in the feed and permeate streams respectively and P_p is the total pressure at the permeate side.

In this case as vacuum is applied in the permeate side the downstream pressure approaches zero and Eq. (3) can be simplified as follows:

$$\mathrm{J_i} = \mathrm{Q}_{overall,i}\left(\mathrm{P_i^{sat}}\gamma_\mathrm{i}\mathrm{x_i}\right) \tag{4}$$

The overall resistance can be written as a function of the individual resistances and following the approach by García et al. [30] where they are related to the pressure-normalized permeation flux across the boundary layers of the liquid $Q_{l,i}$, the membrane $Q_{m,i}$ and the vapour $Q_{v,i}$ (which is assumed negligible), then the total resistance $R_{overall}$ is given as:

$$R_{overall} = \frac{1}{\mathrm{Q_{overall}}} = \frac{1}{\mathrm{Q_{l,i}}} + \frac{1}{Q_{m,i}} + \frac{1}{Q_{v,i}} \tag{5}$$

Each resistance can be more conveniently expressed as a function of process parameters:

$$\frac{1}{\mathrm{Q_{overall,i}}} = \left(\frac{\mathrm{P_i^{sat}\gamma_i}}{\mathrm{k_{L,i}}\,\rho}\right) + \left(\frac{\delta}{\mathrm{P_i}}\right) \tag{6}$$

Where $\mathrm{k}_{\mathrm{L},i}$ is the mass transfer coefficient (m s^{-1}) for the component i in the liquid boundary layer expressed in relation to a concentration gradient and ρ is the density of the liquid feed (kg m^{-3}). The term $\frac{\mathrm{P_i^{sat}\gamma_i}}{\rho_i}$ is the conversion factor from a concentration driving force (kg m^{-3}) to a partial vapor pressure driving force (bar).

The separation factor $\beta_{i\,/\,j}$ is calculated as the ratio between the molar concentrations of the components in the permeate ($y_{i\,/\,j}$) and the feed ($x_{i\,/\,j}$) (equation 7):

$$\beta_{\mathrm{i,j}} = \frac{\mathrm{y_i/y_j}}{\mathrm{x_i/x_j}} = \frac{\dfrac{\mathrm{y_i}}{(1-\mathrm{y_i})}}{\dfrac{\mathrm{x_i}}{(1-\mathrm{x_i})}} \tag{7}$$

The membrane selectivity $\alpha_{\mathrm{i/j}}$ and the pervaporation separation index (PSI) are defined according to Eq. (8) and Eq. (9):

$$\alpha_{\mathrm{i,j}} = \frac{P_i}{P_j} \tag{8}$$

where P_i is the permeability of butanol and P_j is the permeability of water.

$$\mathrm{PSI} = \mathrm{J} \cdot (\alpha_{\mathrm{i,j}} - 1) \tag{9}$$

3. Results

The morphology characterization of the membranes was first performed by Scanning electron microscopy. Figure 3 presents a SEM image of the surface of PEBAX/ HMImFAP polymer inclusion membranes with different compositions studied in this work. In general, the membranes are dense and without defects. As it can be seen from the SEM micrographs the addition of small amounts of IL results in a morphological change in the membrane surface. The granular aspect of the pristine membrane is modified to a smoother appearance when small amounts of IL are added. Unfortunately, authors do not have an explanation for this evidence. On the other hand, although the selected IL have shown a good compatibility with the polymeric matrix, they are only partially miscible in the range 0-30% w/w % IL. Above this threshold value of 30% IL content phase separation starts to occur and small droplets of IL entrapped within the polymeric matric start to be visible. This anisotropic distribution of the IL results in zones with a different membrane composition that can be considered as microdefects that may compromise the separation performance of the membrane.

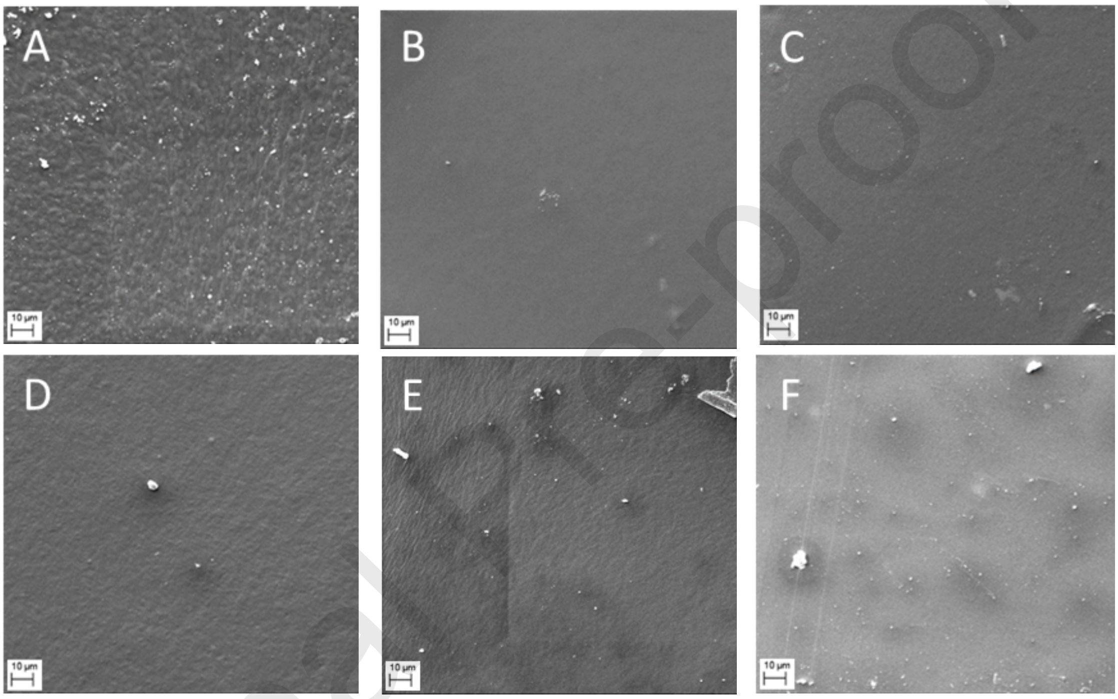

Figure 3: SEM analysis of the surface of the membranes with different polymer/IL ratio: a) 100/0, B) 90/10, C) 80/20, d) 70/30, e) 60/40, a) 50/50.

3.1.Mass transfer resistance characterization of the PV process

3.1.1. Influence of the flow rate on the mass transfer rate in the liquid phase

In order to evaluate the importance of individual mass transfer resistances, first, a polymeric membrane was tested at 40 ºC flowing (1:2:1) ABE solutions at different liquid flow rates. The overall mass transfer coefficient for each component was obtained from Eq.(4). The saturation pressure (P^{sat}) was computed from the Antoine's equation and the activity coefficient (γ) was calculated with the ASPEN PLUS simulation tool using the thermodynamic method UNIQUAC.

The overall mass transfer resistance for each component was calculated as the reciprocal of the mass transfer coefficient assuming negligible resistance in the vapor phase. Then the overall mass transfer resistance was plotted against the reciprocal of the liquid flow rate fitted to best exponent ($F^{0.6}$) related to the Wilson plot in the radial flow membrane cell used. From the y-intercept the membrane mass transfer resistance was obtained, and therefore, the liquid mass transfer resistance can be calculated from the difference with the total resistance in the system:

$$R_{overall} = R_m + R_L = R_m + \frac{C}{F^{0.6}} \tag{10}$$

Figure 4 shows a positive slope for n-butanol, ethanol and acetone indicating that the larger the flowrate value, the lower the resistance. Among them, acetone is the component with larger overall resistance mainly due to its low affinity for the membrane. On the other hand, n-butanol shows the lowest overall resistance of all and as a consequence the resistance in the liquid phase becomes more important. As it could be previously expected, the water mass transfer resistance does not depend on the flow rate of the feed phase. This is because for water the controlling resistance for mass transfer is located in the membrane (with a contribution higher than 95% to the overall mass transfer resistance) due to the hydrophobic character of PEBA that limits water solubility into the membrane. This is because water is the major component in the liquid feed mixture and also the component with the least affinity towards the membrane so no diffusional resistance in the liquid boundary layer or concentration polarization phenomena takes place.

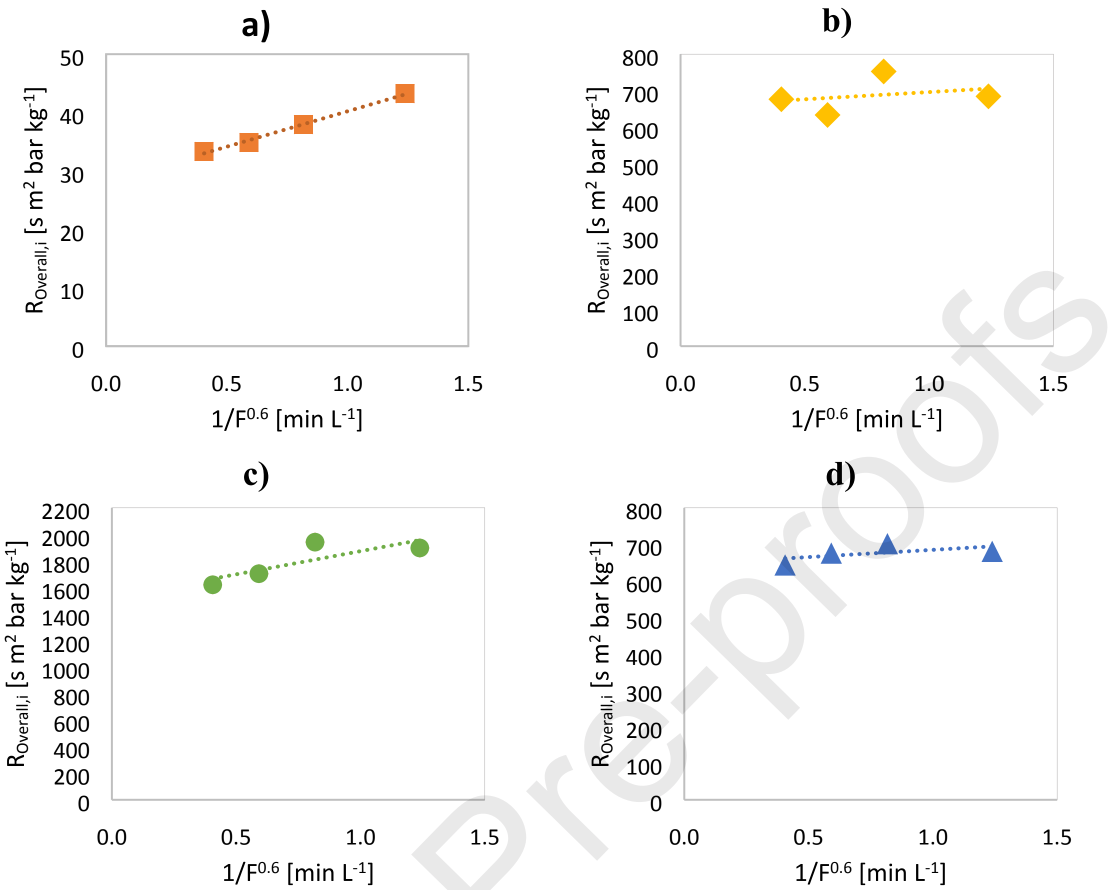

Figure 4: Overall mass transfer resistance for each component for a 100% polymeric (PEBAX) membrane: a) butanol, b) ethanol, c) acetone, d) water.

Table 1 shows the resistances values for a polymeric membrane at different flow rates under the same operating conditions and their percentage contribution to the overall resistance of the system. From this comparison it is observed that the liquid phase resistance becomes smaller as the flow rate increases and it becomes more important for n-butanol and ethanol at smaller flow rates affecting about 35% and 65%, respectively, of the overall resistance. However, the membrane resistance is the one contributing most to the total resistance and that is higher for the water 93-98%, the ethanol 93-98%, the acetone 77-97% and the n-butanol 65-85%, as shown in Figure 5. Therefore, if n-butanol or acetone separation is desired then the liquid phase resistance must be considered especially at low flowrates for an ABE process. For higher liquid flow rates (above 4.5 L min^{-1}) the mass transfer resistance in the liquid phase is negligible and thus, the mass transfer resistance is mostly located in the membrane (Eq. 6).

Table 1: Resistance data and contribution to the overall resistance for each component of an ABE mixture

Component	**F [L min^{-1}]**	**$R_{Overall}$ [s m^2 bar kg^{-1}]**	**R_{Liquid} [s m^2 bar kg^{-1}]**	**$R_{Membrane}$ [s m^2 bar kg^{-1}]**
Butanol	0.7	43.2	15.0	28.1
	1.4	37.9	9.9	
	2.4	34.9	7.2	
	4.5	33.3	4.9	
Ethanol	0.7	684.4	49.0	656.6
	1.4	752.7	32.3	
	2.4	633.4	23.4	
	4.5	676.6	16.0	
Acetone	0.7	1897	432.5	1524
	1.4	1941	285.3	
	2.4	1704	206.5	
	4.5	1620	141.6	
Water	0.7	680.7	49.1	645.2
	1.4	701.7	32.4	
	2.4	675.9	23.4	
	4.5	643.4	16.1	

As can be seen in Table 1, the intrinsic membrane resistance for organic permeants increases in the following order: n-butanol <ethanol <acetone. It is well known that in a non-glassy polymer membrane the permeation selectivity depends primarily on the sorption selectivity; thus, molecules with higher solubility should more readily permeate the membrane [33]. In the case of PEBAX 2533 membranes, the preferential sorption of n-butanol is supported by the results reported by Liu and Feng [34], who carried out sorption experiments at 23ºC, which showed that the solvent uptake in the polymer (in g solvent/g polymer) is 6.83, 0.71 and 0.56 for butanol, acetone and ethanol, respectively. The higher solubility of n-butanol in PEBAX with respect to ethanol and acetone was later confirmed in the work by Heitmann et al. [35].

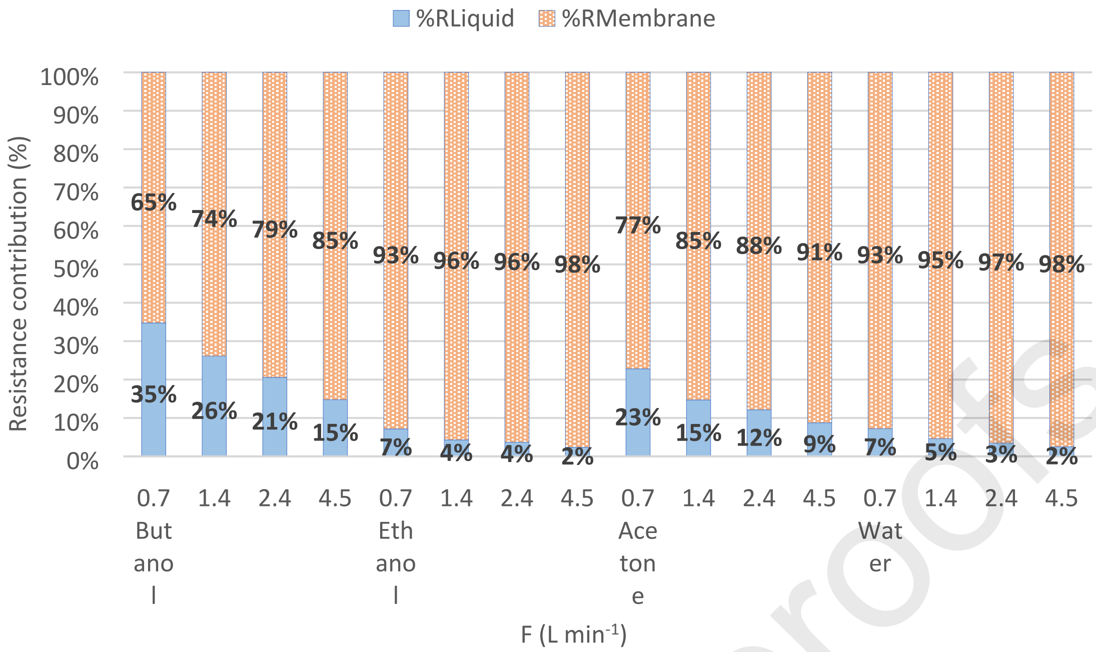

Figure 5: Contribution of the liquid phase and the membrane resistances to the overall mass transport resistance in the pervaporation of ABE mixtures.

3.1.2. Effect of the IL content in the membrane

Once the mass transfer in the system has been characterized, all experiments were carried out at 40 ºC with (1:2:1) ABE solutions at a flow rate of 4.5 L min^{-1} in order to minimize the contribution of the liquid phase resistance to the mass transfer. Membranes with different polymer /IL composition were synthesized to evaluate the influence of the addition of the IL on the membrane performance. Our choice of HMImFAP as the ionic liquid to be added to the polymer matrix has been based on the concept of introducing a membrane modifier that has high affinity for the target compound, that is, n-butanol. Recently, Sun et al. [36] reported a study on the ionic liquid screening by using COSMO-RS for the extraction of n-butanol from ABE mixtures. As a result, HMImFAP was selected as the optimal extractant in that study.

Experimental results show that membranes offer the highest resistance to acetone with a decreasing trend followed by the water and, ethanol and butanol. This translates into butanol facing a faster pass through the membrane and therefore having better separation. When looking at the membrane resistance values individually (butanol, ethanol, acetone and water) as in Figure 6 it is seen that as the % of IL is increased the membrane resistance decreases. For butanol the membrane resistance follows a slight decrease that could probably be due to the high affinity of the IL towards butanol and the higher mobility of the polymeric chains. Which is in accordance to what it was found by Simoni et al. [37] working in liquid-liquid extraction, where HMImFAP provided the highest selectivity among different IL's used to separate butanol. Ha et al. [38] also reported how the butanol distribution between ILs and water strongly depends on the hydrophobicity of anions of ILs, and the butanol extraction efficiency and selectivity depend on the polarity of ILs (in terms of dielectric constant). Nonetheless, for water, increasing the % IL from 0 to 20% increases the resistance of the membrane from about 600 to 900 s·m^2·bar kg^{-1} and this may be due to the high hydrophobicity of the IL, thus, making this IL holds promise for butanol separation. However, concentrations above 20% of IL may translate into defect formation in the polymer matrix allowing the water to pass through. Therefore, 20% IL seems the optimal concentration of IL to be used for a more effective separation.

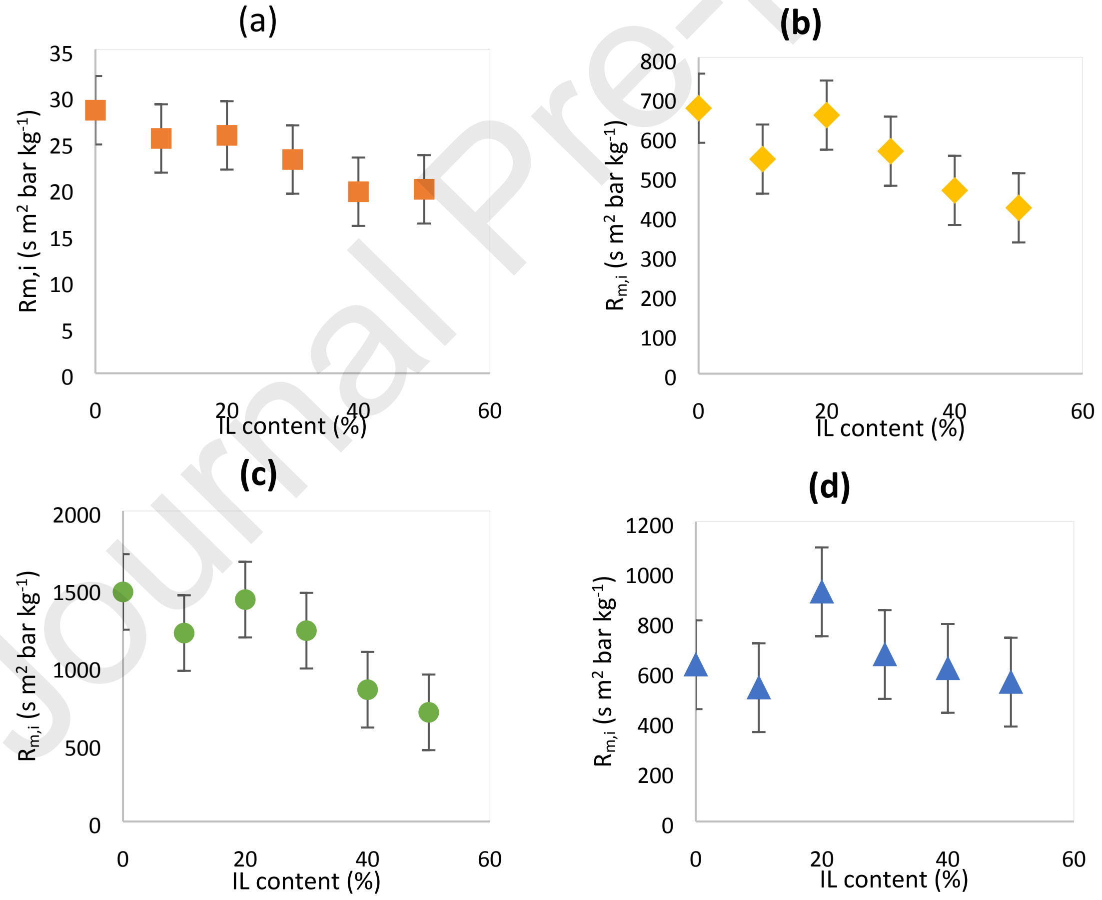

Figure 6: Membrane resistance for individual permeants: a) butanol, b) ethanol, c) acetone, d) water.

3.2. Performance of the membrane

3.2.1. The permeate

Different membranes were tested with different compositions (0-50% w/w of IL). Figure 7 shows the individual content for each component (butanol, ethanol, acetone and water) in the permeate stream. It is seen that water and butanol are present in larger amounts compared to ethanol and acetone making the separation of the stream evident. In general, little variation is seen for ethanol and acetone as the % IL increases; however, for butanol this changes at around 20% of IL. At this point the concentration of butanol starts decreasing showing that the separation needs to be improved; although the overall permeation flux increases with IL content the separation of the components does not necessarily provide more butanol after this point. It is also seen the improvement on the separation of the components of the ABE mixture when adding IL to the membranes compared to the commercial membrane PEBA, especially for butanol.

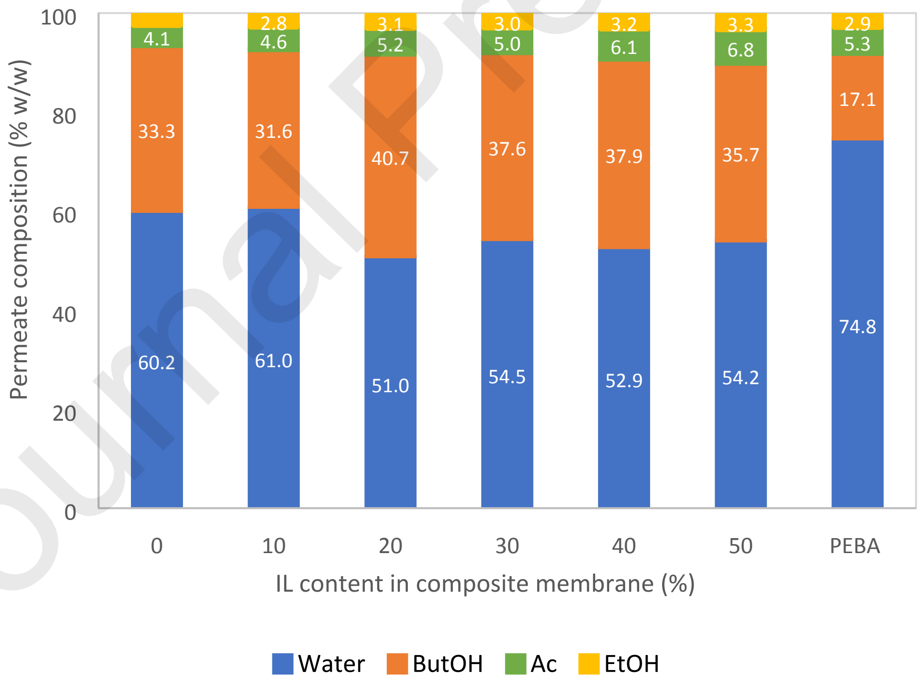

Figure 7: Permeate composition as a function of polymer/IL ratio.

Figure 8 shows how the amount of IL (%) added to the membranes affects the separation factor ($\beta_{i/j}$) of butanol. It increases as the %IL increases up to 20%. Membranes with higher content of IL present lower separation factors. These results, together with the fact that more economical membranes are obtained using less IL, could be used suggest that the optimal concentration of IL in the membrane is located around 20% w/w.

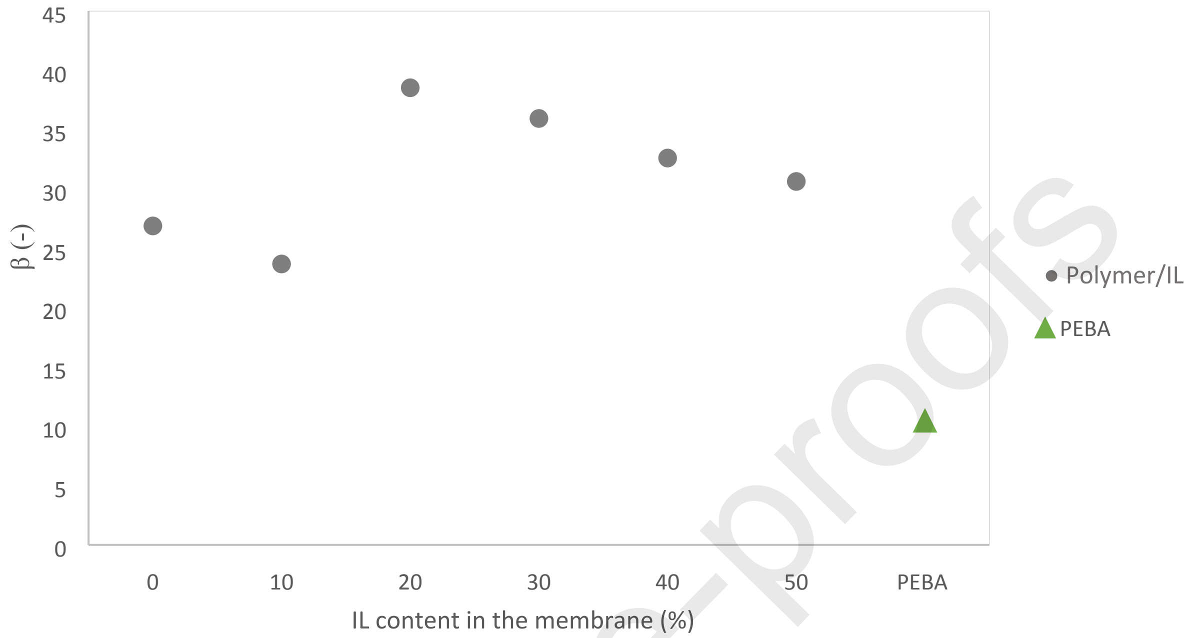

Figure 8: Butanol separation factor (β) of fabricated polymer/IL membranes. PEBA commercial membrane is included as reference.

Finally, the performance of the different membranes prepared in this work has been compared in terms of the pervaporation separation index (PSI) and benchmarked with a commercial membrane based on the same polymer (PEBA). PSI was selected as a factor for the comparison among the different membranes since it accounts for the membrane productivity and the quality of the separation together. Table 2 shows the addition of IL results in membranes with a greatly increase of the PSI. However, this increase is due to an improve quality of the separation performance (better separation factors) when small amounts of the ionic liquid are included into the polymeric matrix. However, at ionic liquids above 20% w/w the PSI is increased due to an increase in the permeate flux at the expense of an important decrease in the separation factor. Considering that doping the polymeric matrix with higher amounts of ionic liquid results in more expensive membranes, a composition between 20 and 30 % seems the optimal concentration of IL in the formulation of the composite membranes.

Table 2: Comparative performance of the polymer/IL membranes at 40ºC.

Membrane Polymer/IL % composition	**Thickness (10^{-6} m)**	**$J_{permeate}$ (kg m^{-2} h^{-1})**	**Butanol permeability (kg s^{-1} m^{-1} bar^{-1})**	**Butanol separation factor (β)**	**Butanol selectivity $\alpha=P_i/P_j$**	**PSI (kg m^2 h^{-1})**
Commercial (Pervatech) PEBA	-----	1.50	-----	10.5	9.0	12.0
Polymeric	16.2	0.68	5.70E-07	26.9	22.1	14.3
10	10.2	0.78	4.02E-07	23.7	21.1	15.6
20	20.6	0.57	8.01E-07	38.5	35.8	19.9
30	21.6	0.70	9.35E-07	35.9	28.9	19.7
40	16.0	0.81	8.08E-07	32.6	31.1	24.3
50	13.2	0.84	6.64E-07	30.6	28.1	22.8

4. Conclusions

The performance of different membranes prepared with different polymer/IL compositions for the separation of butanol from ABE mixtures was evaluated in terms of permeate flux J, separation factor β and pervaporation separation index (PSI). Moreover, the mass transfer in the system was characterized using the resistances in series approach. It was observed that the membrane exerted the lowest overall resistance to butanol, which is motivated by the high affinity of n-butanol with the materials that make up the membrane. Besides, the resistance in the liquid phase becomes more important showing an increasing value as the flowrate decreases. However, for liquid flow rates above 4.5 L min^{-1} the mas transfer resistance in the liquid phase becomes negligible for all components and thus, the mass transfer resistance was mainly located in the membrane. Finally, adding the HMImFAP ionic liquid to the polymer membranes made of PEBA does provide a better separation of butanol even compared to the separation provided by a commercial membrane.

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List of symbols

Nomenclature

A_m	membrane area (m^2)
F	liquid flow rate (L min^{-1})
FTIR	infrared spectroscopy
IL	ionic liquid
J	total flux (kg m^{-2} s^{-1})
J_i	flux of each component (kg $m^{-2}s^{-1}$)
$k_{L,i}$	mass transfer coefficient of the liquid phase for component (i) (m s^{-1})
m	mass of permeate collected (g)
MW	molecular weight
PDMS	polydimethylsiloxane
PEBA	polyether block amide
P_i	permeability of the membrane for component (i) (kg s^{-1} m^{-1} bar^{-1})
P_p	total pressure at the permeate side
P_i^{sat}	vapor pressure of component (i) (bar)
PIMs	polymeric inclusion membranes
POMS	polyoctylmethyl siloxane
PSI	pervaporation separation index (kg m^{-2} s^{-1})
PV	pervaporation
$Q_{overall,i}$	pressure-normalized flux of (i) observed in pervaporation experiments (kg m^{-2} s^{-1} bar^{-1})
$Q_{L,i}$	pressure-normalized permeation flux across the liquid boundary layer for component (i) (kg m^{-2} s^{-1} bar^{-1})
$Q_{m,i}$	pressure-normalized flux (permeance) of component (i) through membrane (kg m^{-2} s^{-1} bar^{-1})
$Q_{v,i}$	pressure-normalized permeation flux across the gas boundary layer for component (i) (kg m^{-2} s^{-1} bar^{-1})
R	mass transfer resistance (s m^2 bar kg^{-1})
SLMs	supported liquid membranes
t	time (s)
x_i	molar fraction of component (i) in the feed stream
y_i	molar fraction of component (i) in the permeate stream

Greek Letters

$\alpha_{i,j}$	membrane selectivity (-)
β	separation factor (-)
γ_i	activity coefficient (-)
δ	thickness of the membrane (m)
ρ_i	density of feed liquid (kg m^{-3})

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Highlights

- Novel polymer/ionic liquid membranes were fabricated for the recovery of butanol from ABE mixtures
- High IL content in polymer/IL pervaporation membrane shows higher permeate flux
- Overall resistance is strongly influenced by the operating conditions for ABE separation mixtures
- The addition of IL into the polymeric matrix membrane improves the selectivity to butanol
- Tailored fabricated membranes show improved behavior with respect to commercial membranes

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Carla Arregoitia-Sarabia: Conceptualization, Investigation, Writing - original draft.

Daniel González-Revuelta: Investigation

Marcos Fallanza: Writing - review & editing, Methodology, Supervision.

Daniel Gorri: Writing - review & editing, Supervision, Funding acquisition

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