Strategy for scale-up of SBS pervaporation membranes for ethanol recovery from diluted aqueous solutions

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Abstract

Ethanol is considered a green alternative to fossil fuels. Pervaporation (PV) is claimed to be an economical separation technique for ethanol recovery from fermentation broths.

In this study, styrene-butadiene-styrene (SBS) dense symmetric flat membranes were first prepared by solvent evaporation technique and applied for the pervaporative removal of ethanol from aqueous solutions. The results were compared with the performances of composite membranes made of SBS coated on a highly porous support of Fluoroplast F-42. In this case, an intermediate layer of PDMS (poly dimethyl siloxane) or PU (poly urethane) was used to improve the membrane performances. The results clearly evidenced the role of the intermediate layer (PU or PDMS) in improving the EtOH/H_2O selectivity of the composite flat membranes in comparison to pure flat SBS membrane. Composite membranes were scaled-up in spiral-wound modules configuration and tested for the PV application of interest. A further increase in ethanol selectivity was observed (SF≈8) showing the superior performances of spiral wound modules with respect to their analogous membranes in flat sheet configuration. In all the PV tests carried out, the effect of ethanol concentration and feed temperature was investigated for each type of membrane.

Keywords: SBS membranes; composite membranes; spiral wound modules; pervaporation

Highlights

- SBS symmetric and composite membranes are prepared

- SBS spiral-wound modules are realized

- PV of ethanol/water mixture is carried out

- Experimental conditions and membrane geometry are evaluated

Abbreviations:

A_m: membrane area

C_{ir}: concentration of components i in the retentate

C_{jr}: concentration of components j in the retentate

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D_i : diffusion coefficient of component i

E_D: activation energy of diffusion

E_p: activation energy of permeation

J_i: partial flux of the component *i*

l: the thickness of the membrane

m_{ip}: mass of component i transferred to the permeate

P_i : permeability of the component i

p_{if}: partial pressure of component i in contact with the membrane in the feed side

p_{ip}: partial pressure of component i in contact with the membrane in the perrmate side

p_p: pressure on the downstream side

PDMS: polydimethylsiloxane

p_{SATi}: vapor pressure of the component i

PU: polyurethane

S_i : solubility coefficient of component i

SBS: block co-polymer styrene-butadiene-styrene

SF: separation factor

x_{if} : molar concentration in the feed solution of component i

x_{ip}: molar concentration in the permeate solution of component i

Greek symbols:

α: selectivity

γ: activity coefficient

ΔH_S: change of enthalpy of dissolution

1. Introduction

Increasing demand of energy for transportation, heating and industrial processes is one of the greatest challenges in our society [1]. Fossil fuels such as oil, coal or natural gas will be exhausted in the near future. Thus, renewable sources of energy play a crucial role as alternative

green energy resources. Ethanol produced by biomass fermentation, in comparison to other fuels derived from petroleum, is considered a valid alternative due to its abundance and economy. It has also potential to be "carbon-neutral" on a life cycle basis: all the carbon emitted during the processing and the use of the fuel being is balanced by the absorption from the atmosphere during the fuel crop's growth. For these reasons, the interest for ethanol in transport sector has increased since the 1970's. Nowadays, ethanol has already been introduced on a large scale in Brazil, USA and some European countries and it is expected to become one of the most important renewable biofuels in the transport sector [1].

The fermentation technique is the most widely used for ethanol production, converting the sugars (derived from starches or cellulose) in ethanol by enzymes produced by microorganisms (the most common is Saccharomices cerevisiae). In order to produce fuel grade ethanol, the water concentration should be less than 1.3 wt% [2].

Moreover, at a certain ethanol concentration (around 5-8 wt%), enzymes, responsible of the ethanol production, are inhibited by ethanol itself accumulated in the fermentation broth causing a decrease of the productivity. The fermentation process is generally coupled with a separative process to constantly remove the ethanol produced in order to maintain a higher productivity and to increase the conversion rate. The recovery and purification of ethanol from fermentation broth generally involves distillation, considered an energy intensive and complex separative process [3]. An alternative non-distillation technique for ethanol recovery from water could be represented by pervaporation (PV). Energy saving, cost reduction and low environmental impact are among the main advantages of the PV process. PV is also used for the ethanol dehydration to produce pure ethanol because it allows to break the water-ethanol azeotrope (95.6 wt. % ethanol- 4.4 wt. % water) with hydrophilic membranes [2].

In PV, the membrane acts as a selective barrier between two phases: the liquid feed phase and the permeate vapour phase. The driving force for the transport through the membrane is the chemical potential difference of the permeating components across the membrane. The chemical potential difference can be induced by applying a vacuum on the permeate side of the membrane (laboratory scale), by using an inert sweeping gas in the permeate side or by applying a temperature difference between the feed and the permeate cooling, for example, the permeate vapour (industrial scale) [4].

The separation is achieved by the differences in solvents sorption affinity and diffusion coefficients in the membrane, depending on the chemical-physical interactions between the membrane material and the target components of the feed mixture [5-6]. Usually, polydimethylsiloxane (PDMS) is employed for the preparation of hydrophobic membranes

applied in PV due to its chemical stability, high permeability and hydrophobicity [7]. Nevertheless, efforts have been devoted on the development of mixed matrix membranes based on PDMS or on exploring alternative polymeric materials, such as poly(1-trimethylsilyl-1-propyne) and poly(octylmethyl siloxane), in order to reach higher ethanol–water separation performance [7-9].

In this work, block co-polymer styrene-butadiene-styrene (SBS) was selected as the membrane material for ethanol removal from aqueous solutions. SBS is a hydrophobic thermoplastic elastomer with good properties in terms of mechanical resistance and has been successfully employed in membrane preparation to remove volatile organic compounds (VOCs) from water by PV [10-14]. This polymer was also successfully used, as reported by Dobrak et al. [15], for ethanol removal from water/ethanol mixtures. Gas transport properties have been also studied by Bazzarelli et al. [16] that developed composite membranes with a SBS selective layer supported on an intermediate layer of polydimethyl siloxane (PDMS) or polyurethane (PU) on a microporous support (Fluoroplast F-42) in flat sheet configuration.

The objective of this study is the pervaporative removal of ethanol from water comparing the PV performances of a SBS symmetric dense membrane with composite SBS membranes supported on a porous Fluoroplast F-42 support. In composite membranes, an intermediate layer made of PDMS or PU was used in order to guarantee a good adhesion of SBS coating on Fluoroplast F-42 support and to improve the membrane performance. The effect on the operating conditions, such as ethanol concentration and feed solution temperature, on the performance of the perveporative process was also studied.

In view of possible industrial application, the development of membrane modules for the scale-up of the system is a key issue for the successful application of PV. For this reason, the composite membranes were scaled-up in spiral-wound module configuration with a total area of 0.25 m^2 and tested at lab-scale for the PV of ethanol/aqueous solutions.

2. Experimental

2.1 Materials

The SBS triblock polymer with poly-styrene/poly-butadiene wt/wt ratio 28/72 was purchased from Sigma-Aldrich and used in membranes preparation without further treatments. Toluene was used as the solvent for SBS solubilization.

Ethanol solutions in different concentration (9wt%, 5wt%, 3 wt%) were used to evaluate the performance of the membranes in PV tests.

All solvents (reagent grade) were purchased from Carlo Erba and were used without further purification.

2.2 Membrane preparation

Isotropic dense membranes were prepared by dissolving under magnetic stirring 20 wt% of SBS in toluene. After 24 hours, the solution appeared homogeneous and colorless. The dope solution was then left to degas overnight in order to remove the possible air bubbles.

Membranes were prepared by filming the polymeric solution over a suitable smooth glass plate by means of a hand-casting knife with a slit width of 0.45 mm.

The solvent was evaporated at room temperature for 24 hours and the produced membranes were dried at 40°C for 4 hours in a vacuum oven to remove further traces of solvent.

Both composite membranes (with PDMS and with PU as intermediate layer) and spiral-wound modules were prepared and provided by ZAO STC "Vladipor", Vladimir (Russia).

2.3 Contact Angle Measurement

Contact angle measurements were performed using ultrapure water by the method of the sessile drop using a CAM100 instrument. For each sample, at least ten measurements were taken; the average value and the corresponding standard deviation were calculated for each set.

For dense isotropic membrane, water contact angle measurements were performed both for the air side and the glass side of the membrane.

2.4 SEM Observation

The membrane's morphology was observed by using a scanning electron microscope (SEM) (Cambridge Stereoscan 360). Membrane cross sections were prepared by freeze fracturing the samples in liquid nitrogen to produce a clean brittle fracture using a sharp knif. Sample specimens were sputter–coated with a thin gold film prior to SEM observation.

2.5 Pervaporation tests

The performance of a membrane process can be described in terms of two important parameters: flux and selectivity [6].

The permeant flux J_i of the component i is the absolute mass $mi_{,p}$ [g] of component i transferred to the permeate side through an active membrane area A_m [m^2] and collected in a time t [h]:

$$J_i = \frac{m_{i,p}}{A_m \cdot t} \qquad (1)$$

According to solution-diffusion model, the partial flux can be expressed as:

$$J_i = \frac{P_i(p_{if} - p_{ip})}{l} = \frac{P_i(\gamma_i p_{SATi} x_{if} - p_p x_{ip})}{l} \qquad (2)$$

where l [m] is the thickness of the membrane, p [bar] is the partial pressure of component i in contact with the membrane in the feed side (f) and permeate side (p) and P_i [kg m^{-2} h^{-1} bar^{-1}] is the permeability of the component i in the membrane. The partial pressure of component i in the feed side depends on its vapor pressure (p_{SATi}) [bar], its activity coefficient γ_i and its molar concentration in the feed solution (x_{if}) [-], whereas the partial pressure of component i in the permeate compartment is the product of the pressure on the downstream side (p_p) [bar] multiplied by the molar fraction of the component i (x_{ip}) [-] in the permeant.

The efficacy of the separative process is evaluated using the separation factor:

$$SF = \frac{\left(C_i/C_j\right)_p}{\left(C_i/C_j\right)_r}; \qquad (3)$$

where C represents the concentration of components i and j and subscripts p and r denote respectively the permeate and the retentate or feed side.

The selectivity factor can be expressed as the ratio of the permeabilities P of the two species:

$$\alpha = \frac{P_i}{P_j}. \qquad (4)$$

Eqs. 2 and 3 show that the efficacy of the separation process depends, on the operative conditions, while the selectivity depends exclusively on the materials properties, which, however, may depend indirectly on the operation conditions if, for instance, plasticization or swelling of the polymer occurs.

Two different PV set-ups were used for the evaluation of the performance of SBS membranes in the removal of ethanol from alcohol water solutions.

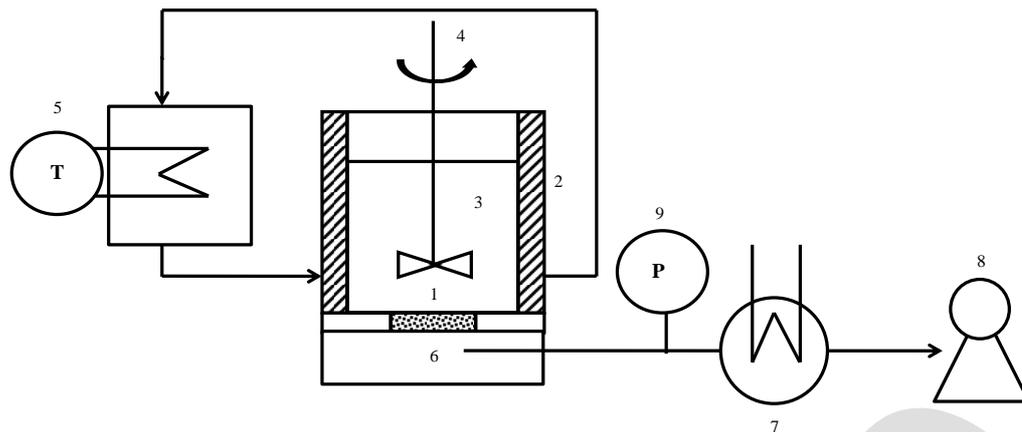The first set-up was used to test flat-sheet membranes and it is schematically presented in Fig.1.

Figure 1: PV set-up for flat sheet membranes: (1) membrane positioned on a porous stainless steel support; (2) jacketed pervaporation cell; (3) feed/retentate solution; (4) mixer; (5) thermostatic bath; (6) permeate; (7) condenser; (8) vacuum pump, (9) manometer.

The hydro-alcoholic solution (300 mL) containing 3 wt%, 5 wt% and 9 wt% of ethanol in water, was added inside the pervaporation cell. The active membrane area was 2.54 cm^2. The feed solution was kept at constant temperature (30, 40, 50°C) using a thermostatic bath and it was continuously stirred in order to avoid the concentration polarization phenomenon.

The driving force was generated by means of a RVS vacuum pump (Edwards High Vacuum International). Permeate was condensed in a cold trap immersed in liquid nitrogen, collected and weighted periodically to examine the flux variation. The composition was analyzed by a refractometer (Abbe 60 IDR) to determine the membrane selectivity.
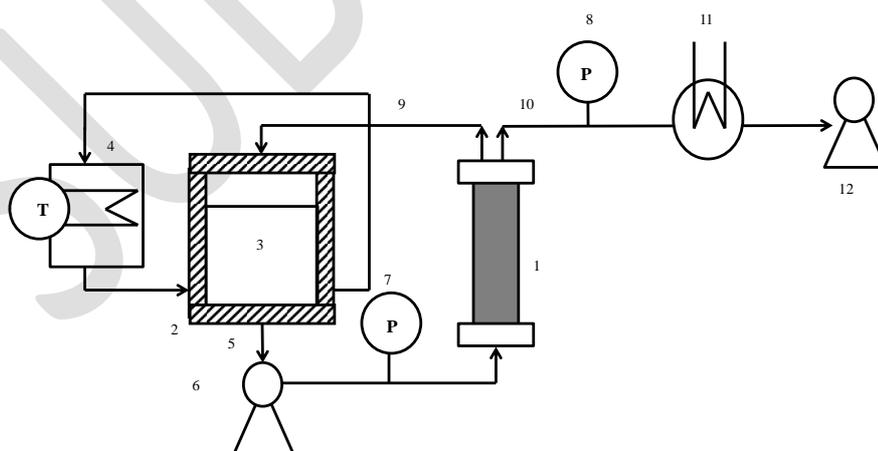

Figure 2: PV set-up for spiral-wound modules: (1) spiral-wound membrane module; (2) feed cell; (3) feed/retentate solution; (4) thermostatic bath; (5) feed; (6) peristaltic pump, (7-8) manometer, (9) retentate stream, (10) permeate stream, (11) condenser, (12) vacuum pump.

The set-up depicted in Fig. 2 was used to test spiral-wound modules. In this case the feed solution was continuously re-circulated through the spiral wound module. The flow rate of the feed solution was kept constant at 910 mL min^{-1} with a pressure of 0.2 bar. The experiments were conducted at different feed temperatures (30, 40 and 50 °C) and ethanol feed concentrations (3, 5 and 9 wt% EtOH in water). The permeate was condensed in a cold trap immersed in liquid nitrogen and analyzed periodically by refractometer analyses in order to evaluate the ethanol concentration in the permeate. Changes in the retentate concentration were determined as well in order to calculate correctly the membrane selectivity.

In all cases, both for flux and selectivity, the relative standard error was about 5%.

3. Results and discussion

3.1 SEM observations

The morphology of dense and composite membranes was studied by SEM analysis.

Figure 3 (a,b) depicts the structure of the dense isotropic SBS membrane, revealing a dense and homogeneous structure with a thickness of about 60 µm, as previously observed for solvent-cast SBS membranes [14].

Figure 3 (c,d) shows the morphology of composite SBS/PU/F-42 membrane. The cross-section shows a dual layer made up of a top dense SBS skin over the PU-impregnated Fluoroplast-F42 ultrafiltration membrane. The thickness of the dense SBS layer was about 6 µm. The surface presented a regular and homogenous structure.

Figure 3 (e,f) shows the structure of composite SBS/PDMS/F-42 membrane. The cross-section clearly shows the SBS coating on the PDMS-impregnated Fluoroplast-F42 membrane on the nonwoven fiber support. Also in this case the surface was dense and homogeneous. The thickness of the active layer was about 7 µm.
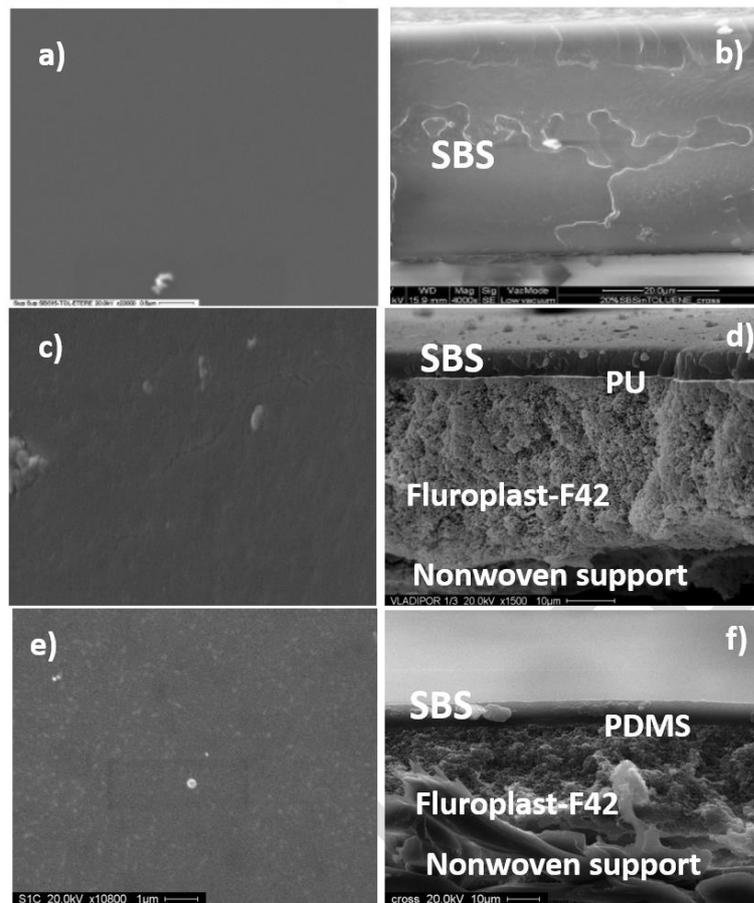
Figure 3: SEM surfaces and cross-sections of tested membranes: SBS isotropic membrane (a,b); composite SBS/PU/F-42 membrane (c,d) ; composite SBS/PDMS/F-42 membrane (e,f). Left: top surface, right: cross section

3.2 Contact angle measurements

SBS dense membrane showed a contact angle of $102°\pm 2$ (Figure 4). The difference of contact angles between the two surfaces is below the experimental error confirming the isotropy of dense SBS membrane. The contact angles for both composite membranes resulted similar but slightly higher than that of the SBS pure membrane. The composite SBS/PU/F-42 membrane presented a contact angle of $109°\pm 2°$, while for the composite SBS/PDMS/F-42 membrane the contact angle was $104°\pm 2$. All the membranes showed a high degree of hydrophobicity explaining their potentially higher affinity for ethanol in comparison to water. The slightly higher contact angle of the composite membranes with respect to the neat dense membrane might be due to difference in the surface roughness, or in the microphase separation and the arrangement near the surface of the polybutadiene blocks and the polystyrene blocks of the SBS copolymer.
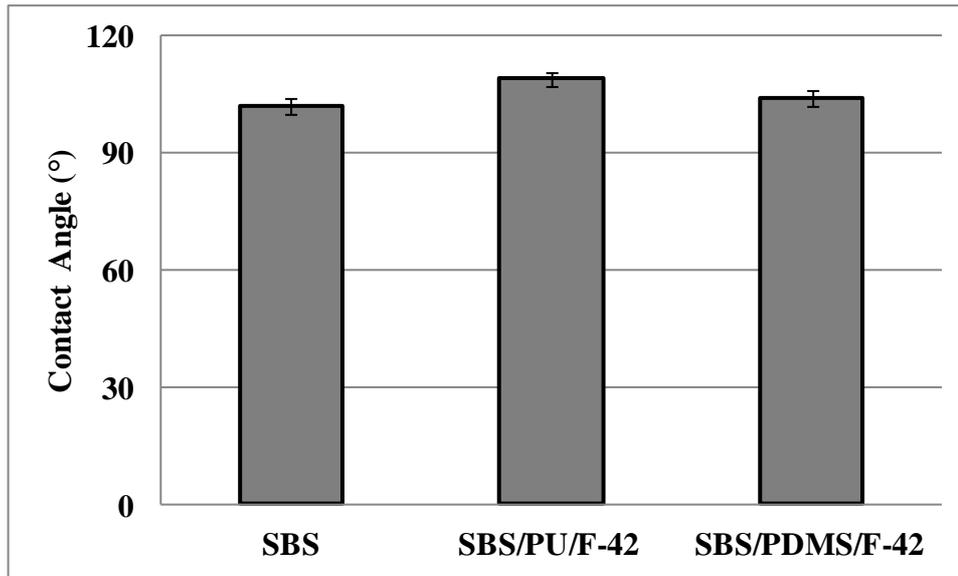
Figure 4: Contact angle of the evaluated SBS membrane types.

3.3 Pervaporation tests

3.3.1 Isotropic dense membrane

The results of PV experiments for SBS dense membrane at different operative conditions are summarized in Table 1.

Table 1: Results of isotropic dense SBS membrane on ethanol removal by PV. Permeate pressure: 6 mbar

Membrane	T (°C)	EtOH (wt%)	J_{TOT} 10^{-3}(kg m^{-2} h^{-1})	J_{EtOH} 10^{-3}(kg m^{-2} h^{-1})	J_{water} 10^{-3}(kg m^{-2} h^{-1})	$SF_{EtOH/water}$
Isotropic SBS	30	3	20.0	1.6	18.4	2.9
	30	5	20.5	2.6	17.9	2.8
	30	9	21.0	4.3	16.7	2.6
	40	3	40.0	3.6	36.4	3.2
	40	5	40.8	5.7	35.0	3.1
	40	9	41.5	9.2	33.0	2.9
	50	3	56.6	6.3	51.0	4.0
	50	5	61.0	10.3	50.7	3.9
	50	9	70.0	17.9	52.1	3.5

The isotropic dense SBS membranes showed to be ethanol-selective in the entire range of ethanol concentrations investigated.

The total flux at the highest EtOH concentration increased from 0.02 to about 0.07 kg m^{-2} h^{-1} by increasing the temperature from 30 to 50°C due to the increase of the driving force.

The enhancement of the separation factor (from 2.6 to 4.0) as a consequence of the increase of the temperature from 30°C to 50°C can be explained by a enrichment of the ethanol vapor phase due to its lower boiling point in comparison to water.

Increasing the ethanol concentration in the feed solution led to an increase of the flux and a decrease of the separation factor. This is probably due to a superior degree of swelling of the membrane material at higher ethanol concentrations. Swelling of the membrane can cause a higher permeation of molecules (both ethanol and water molecules) through the membranes increasing the flux and decreasing consequently the separation factor. There is also a potential coupling effect, which means that swelling by ethanol reduces the hydrophobicity of PDMS, consequently leading to a relatively strong increase of the water vapour permeability, and thus a decrease in separation factor [17].

3.3.2 Composite flat sheet membranes

On the basis of the promising results of the isotropic dense membrane in terms of ethanol/water selectivity, composite flat-sheet membranes were tested in order to evaluate two aspects on the membrane performance:

- the thickness reduction of the selective SBS dense active layer
- the presence of the intermediate layer of PDMS and PU.

Table 2:Results of composite SBS/intermediate layer/F-42 membranes on ethanol removal by PV. Permeate pressure: 6 mbar

Membrane	T (°C)	EtOH (wt%)	J_{TOT} 10^{-3}(kg m^{-2} h^{-1})	J_{EtOH} 10^{-3}(kg m^{-2} h^{-1})	J_{water} 10^{-3}(kg m^{-2} h^{-1})	$SF_{EtOH/water}$
	30	3	156.0	17.8	138.2	4.2
	30	5	164.0	24.6	139.4	3.4
	30	9	183.0	25.0	158.0	3.4
SBS/PU/F-42	40	3	273.0	32.5	240.5	4.4
	40	5	274.5	45.6	228.9	3.7
	40	9	296.5	73.6	222.9	3.4
	50	3	390.0	47.2	342.8	4.7
	50	5	385.0	66.6	318.4	4.0

	50	9	410.0	122.1	287.9	3.3
	30	3	70.3	8.9	61.4	5.0
	30	5	74.0	12.0	61.0	4.9
	30	9	85.0	26.0	59.0	4.9
	40	3	116.1	19.1	97.0	6.2
SBS/PDMS/F-42	40	5	151.2	35.2	115.5	5.7
	40	9	178.8	61.7	117.1	5.5
	50	3	161.8	29.3	132.6	7.5
	50	5	228.4	58.4	170.0	6.5
	50	9	272.6	97.3	175.3	6.1

As reported in Table 2, composite SBS/intermediate layer/F-42 flat-sheet membranes showed similar tends in comparison with isotropic SBS membrane: in all cases, the best performances in terms of separation factor were observed at higher temperature (50°C) and lower concentration of ethanol in the feed solution (3wt%), whereas in terms of the ethanol flux the best results were obtained at higher EtOH concentration.

Composite flat-sheet membranes showed higher fluxes as a consequence of the lower thickness of the dense SBS layer. Regarding the selectivity, similar values were obtained for dense SBS isotropic membranes and the composite SBS/PU/F-42 membrane, while a positive effect was observed by using PDMS as intermediate layer. SBS/PU/F-42 showed higher flux than SBS/PDMS/F-42; but lower selectivity.

The effect of the intermediate PU or PDMS layer of the composite membranes on the PV performance is related to its morphological and chemical characteristics. Although the porous structures of the supports do not present any resistance to vapor transport, the constriction resistance (the resistance encountered by the permeating species in traveling in a radial direction to find a pore of the support to diffuse through) strongly affects the global performance of the pervaporative process [18]. For this reason, the composite membranes often are based on the use of a gutter layer of a highly permeable polymer to promote the transport of the diffusing species from the dense skin into the underlying pores. In this case, best results, in terms of selectivity, were obtained with SBS/PDMS/F-42 membranes considering that PDMS has an important selective effect on ethanol/water separation as very well documented in literature [19-21]. On the other hand, PU is somewhat less hydrophobic and tends to swell in contact with the hydro-alcoholic solutions [22] offering lower resistance to the transport and, as a consequence, favoring higher fluxes as shown in the case of SBS/PU/F-42.

3.3.2 Spiral-wound modules

SBS membranes can successfully be employed on ethanol recovery from aqueous solution, as demonstrated by the tests on laboratory scale. In particular, the composite membranes showed an improved performances in terms of higher flux and separation factor in comparison to isotropic SBS membrane. The optimized procedure to prepare multilayer membranes was scaled-up to prepare spiral-wound modules with an active area of 0.25 m^2. The spiral-wound modules were tested in a different set-up because their geometry imposed the use of a cross-flow system, as is usual in practical separation systems.

Table 3: Results of composite SBS/intermediate layer/F-42 spiral-wounds on ethanol removal by PV. Permeate pressure: 6 mbar; feed flow rate 910ml/min and pressure 0.2bar.

Membrane	T (°C)	EtOH (wt%)	J_{TOT} 10^{-3}(kg m^{-2} h^{-1})	J_{EtOH} 10^{-3}(kg m^{-2} h^{-1})	J_{water} 10^{-3}(kg m^{-2} h^{-1})	$SF_{EtOH/water}$
SBS/PU/F-42	30	3	143.4	18.2	125.2	4.7
	30	5	131.9	26.9	105.0	4.7
	30	9	155.0	43.0	112.0	4.0
	40	3	198.9	41.5	164.0	5.1
	40	5	205.8	45.2	160.5	5.0
	40	9	225.8	52.9	166.4	4.1
	50	3	242.8	39.9	202.8	5.5
	50	5	279.6	63.5	216.1	5.3
	50	9	308.3	87.5	220.8	4.2
SBS/PDMS/F-42	30	3	61.2	12.5	48.7	8.3
	30	5	65.8	18.5	47.3	7.1
	30	9	92.4	23.7	68.7	3.8
	40	3	105.2	20.9	84.3	8.1
	40	5	122.9	36.7	86.2	7.5
	40	9	147.5	49.2	98.3	4.9
	50	3	149.2	29.3	119.9	8.0
	50	5	180.0	54.8	125.2	8.0
	50	9	202.6	74.8	127.8	6.0

As for flat composite membranes, the selectivity was higher for composite SBS/PDMS/F-42 membrane than the SBS/PU/F-42 one due to the contribution of the PDMS layer in ethanol/water separation.. On the other hand, SBS/PU/F-42 membranes showed a higher flux. An increase in the temperature and in the ethanol concentration in the feed positively affects the total flux. The separation factor reached the maximum (SF= 5,5 for SBS/PU/F-42 membrane; SF= 8 for SBS/PDMS/F-42 membrane) at higher temperature (50°C) and lower ethanol concentration (3wt%). Better performances in terms of separation factor for spiral

wound modules in comparison to their analogues membranes in flat configuration, can lie in their different geometry and better hydrodynamics of the system.

Mathematical simulations have demonstrated that the permeate-side pressure of spiral-wound modules exhibits large variations in the *y-direction* since the permeant molecules have to flow all the way through the layer between the two membrane sheets to the centre of the module [23]. For this reason the pressure in the permeate side inside the spiral wound module is certainly higher than the pressure imposed by the pump and detected in the vacuum line. At higher total permeate pressure, the ethanol driving force remains relatively high, but the water driving force strongly reduces by increasing the permeate pressure. Therefore, the water flux in the thin spiral-wounds could be significantly lower than in the small flat sheet membrane, and thus the separation factor is higher. Moreover, it is known that the feed flow velocity in spiral wound modules induces improvements both in permeation flux and separation factor [24]. The increase in feed flow velocity can generate a higher shear stress at membrane surface reducing the phenomenon of concentration polarization. Consequently, the mass transport from the feed and the membrane surface is improved, resulting in a higher ethanol permeation through the membrane. It as demonstrated, that in PV the mass transfer from the bulk liquid feed to the boundary layer is predominant in comparison to the mass transfer exhibited by the membrane itself [25].

Since water molecules are more abundant in the feed, they are not affected by the mass transfer resistance in the bulk liquid feed. On the other hand, the decrease of concentration polarization, due to the high speed velocity, is a benefit for the less concentrated target ethanol molecules which are highly promoted to permeate the membrane favoring the increase of the overall selectivity [26].

As for composite membranes, in the spiral-wound modules the same trends in selectivity (higher for SBS/PDMS/F-42 membranes) and total flux (higher for SBS/PU/F-42) were observed proving the pivotal role that the intermediate layer (PDMS or PU) can play on the performances of the pervaporative process, as already described above.

1.3.1   Comparative study

Effect of feed concentration

Total flux as a function of ethanol concentration in the feed for isotropic membrane, flat composite membranes and spiral wound composite membranes at 40°C and 6 mbar is presented in figure 5.C. All tested membranes followed the same trend: an increase of total flux with increasing ethanol concentration in the feed from 3 wt% to 9 wt% was observed. This is due to

the fact that the increasing of the alcohol concentration in the feed solution enhances the ethanol partial flux as a consequence of the increasing of the driving force due to the higher ethanol partial pressure in the feed compartment, as predicted by Eq. (2). Nevertheless, alcohol sorption into the membrane increases by increasing the concentration of ethanol in the feed solution and, as a result, the membrane swells [27]. SBS/PU/F-42 and SBS/PDMS/F-42 flat composite membranes showed higher values (about 20 %) of total flux in comparison to their corresponding modules. Operating the modules at a certain feed flow velocity, led to an improvement of the membrane ethanol selectivity and a simultaneous pressure drop in the feed channel responsible of the lower total flux [28]. Due to a swelling effect, the total flux for membranes containing PU as an intermediate layer (both composite and spiral wound ones) was higher. The lowest flux occurs in the isotropic SBS membrane because of its higher thickness.

Ethanol flux increases with EtOH concentration due to higher driving force (Figure 5.A). Nearly proportional for the dense film, slightly less than proportional for the asymmetric membrane and even less for the spiral wound module. On the other hand, the water flux depicted in Figure 5.B is constant for dense film and is nearly constant for the asymmetric film or module because the mirror reduction of driving force for water (in all the cases water content>90% in the feed) due to the increment of ethanol concentration in the feed was compensated by the improvement of diffusion of molecules trough the membrane favored by membrane swelling . Therefore total flux increases only slightly with increasing ethanol concentration, probably as a result of a coupling effect.

As a result, the selectivity is strongly affected by the ethanol concentration for the module, much less for the flat films and almost not for the dense film (Figure 5.D).

This behavior can be explained considering that hydrophobic PV is governed by the sorption-diffusion mechanism, where sorption is the first step of the permeation determining the separation performance of the membrane process. A higher concentration of ethanol in the feed leads to a higher equilibrium concentration in the membrane, and thus a higher driving force and EtOH flux. On the contrary, the increase of ethanol concentration in the feed did not affect the water flux which was constant for all the examined membranes (Figure 5.A).

Figure 5.D shows the SF of the membranes. In all cases the separation factor decreased when the ethanol concentration increased in the evaluated interval (from 3 wt% to 9 wt%).

Also for separation factor, an evident role of the intermediate layer was observed in PV experiments: composite multilayer membranes presented higher selectivity than isotropic SBS membranes. Particularly, SBS/PDMS/F-42 material showed better results than SBS/PU/F-42,

both in the flat film and in the spiral wound configuration due to the contribution of the PDMS layer in ethanol permeation. A separation factor of about 8 was reached at 40°C, 3 wt% ethanol and permeate pressure 6 mbar (Figure 5.D) for SBS/PDMS module.
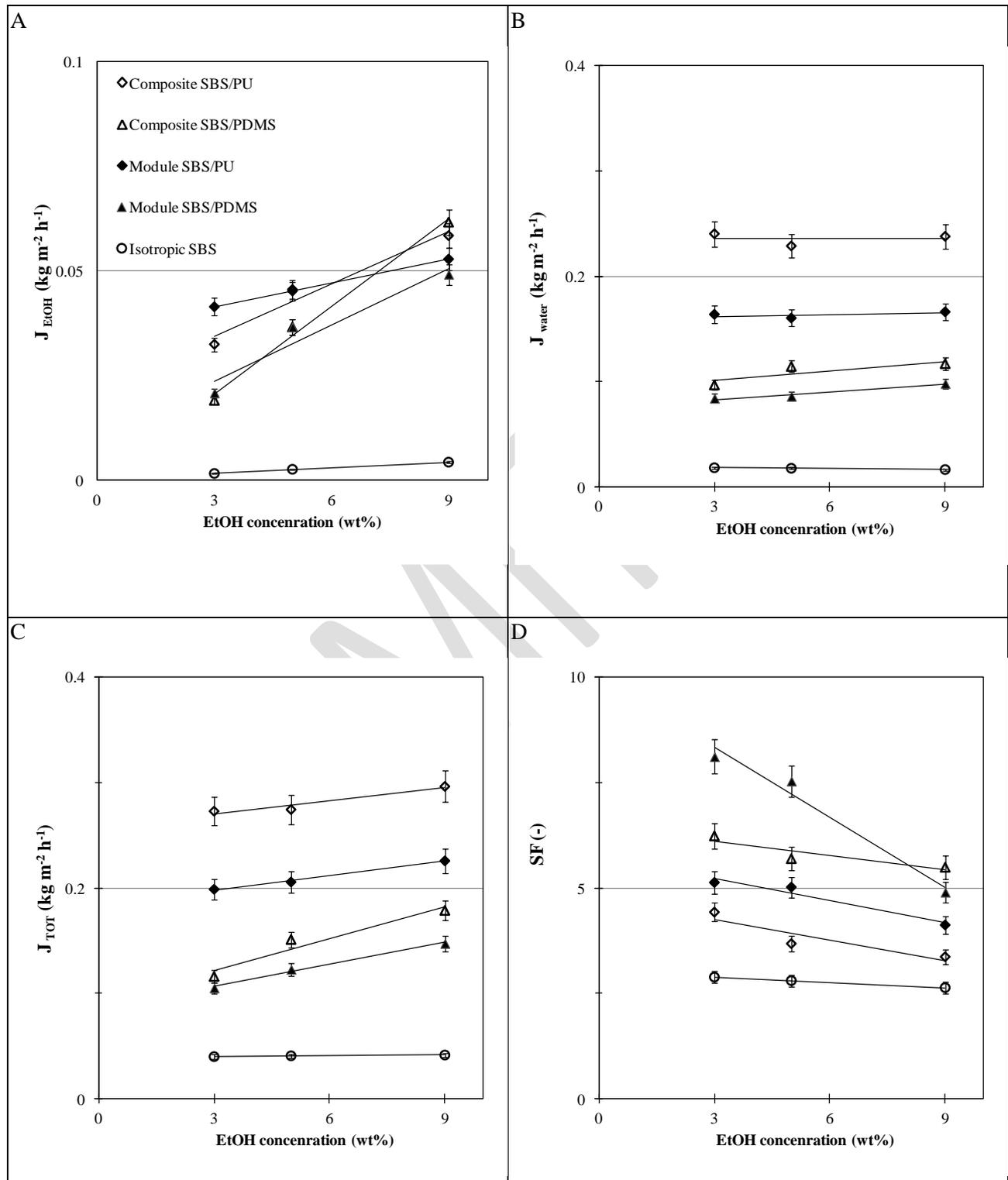

Figure 5. Effect of the feed concentration on the flux and selectivity with tests performed at fixed operating conditions of 40°C and 6 mbar. A) Ethanol flux; B) Water flux; C) Total flux; D) Separation Factor

The highest values of selectivity were found for spiral-wound modules thanks to their geometry and to the decrease of the concentration polarization phenomenon derived.

The overall trend, in terms of total flux and selectivity, exhibited by the evaluated membranes by varying the ethanol feed concentration, can be explained as a consequence of the increase of the free volume in the membrane matrix with a synergetic effect of the driving force. The increase in membrane free-volume caused an increase in carbon chain mobility allowing an easier permeation of ethanol and water molecules leading to an increase of the total flux.

On the other hand, since the molecular size of water molecules is lower than ethanol, its permeation through the membrane was preferred causing a decrease of the selectivity.

Effect of temperature

The effect of the temperature on total, water and ethanol fluxes is reported in Figure 6. The graphs show an increase of total and partial (water and ethanol) fluxes.

Generally, the experimental data of the permeation flux show an increase of the flux with increasing temperature and exhibits an Arrhenius-type relation [29]:

$$J = J_0 \exp(-E_P / RT); \quad (5)$$

where E_p is the activation energy of permeation.

The permeability of the membrane P_i is related to the solubility coefficient (S_i) and diffusivity coefficient (D_i):

$$P_i = S_i D_i. \quad (6)$$

The solubility S_i and diffusion D_i coefficients depends on temperature and can be expressed as:

$$D_i = D_0 \exp(-E_D / RT); \quad (7)$$

$$S_i = S_0 \exp(-\Delta H_S / RT). \quad (8)$$

Thus, the following relation holds for the permeability:

$$P_i = P_0 \exp(-E_P / RT); \quad (9)$$

where the activation energy of permeation $E_P = E_D + \Delta H_S$ is a combination of the activation energy of diffusion (E_D) and the enthalpy of dissolution (ΔH_S) and the pre-exponential factor P_0 is equal to D_0 multiplied by S_0. Eq. (9) shows the positive effect of temperature on permeability as a consequence of the increase of the solubility and diffusion coefficients, as reported in Eqs (7-8).
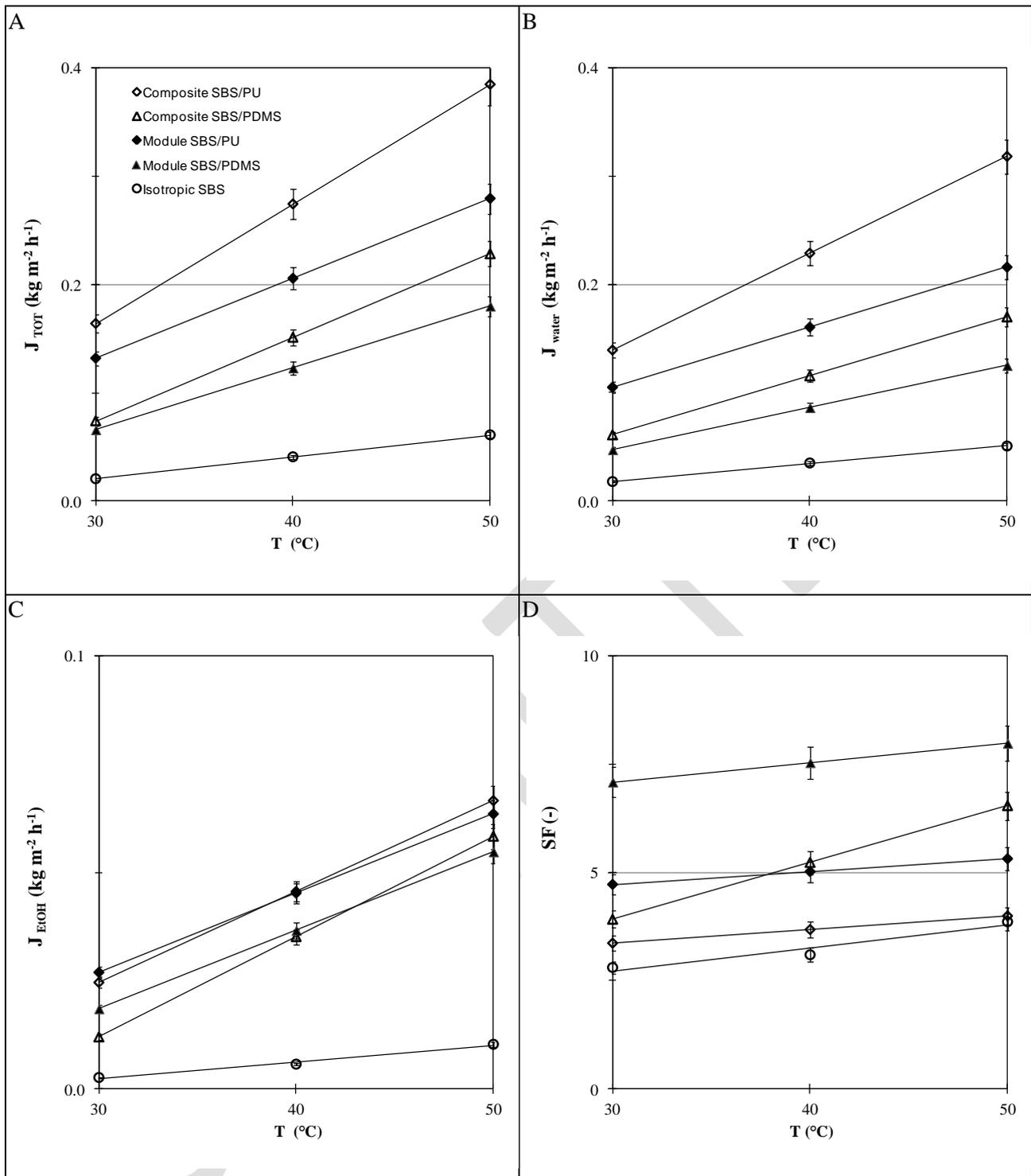
Figure 6. Effect of the temperature on the total flux at 5wt% ethanol concentration and 6 mbar for all tested membranes. A) Total flux; B) Water flux; C) Ethanol flux; D) Selectivity

Eqs.(5,6) shows that the increase of temperature positively acts on the flux, because of:

- The increase of permeability through the membrane due to the effect on solubility and diffusion coefficients
- The increase of driving force due to the higher part of feed that change from liquid to vapour phase as predicted by Eq. (2).

The productivity of the PV process can be enhanced increasing the temperature but the economical aspects have to be considered because of the increase of the process costs.

In fact, the increasing of the temperature induces the improvement of the free volumes in the membranes due to a higher motion of polymeric backbone. In addition, the temperature increases the feed vapor pressure and the mobility of permeating molecules. The combination of these effects brings to a rapid increase in permeation fluxes [30]. As reported in Figure 6.D, also the selectivity is significantly influenced by the temperature. For all the tested membranes, the selectivity was superior by enhancing the temperature from 30°C to 50°C.

The vapour pressure of ethanol increased faster than that of water because of its lower boiling point and, as a consequence, an increase in the driving force and in the partial ethanol flux was observed, as explained by Eq.2. Thus, ethanol partial flux was more significantly influenced by the increase of temperature, causing an increase of the selectivity.

Table 4 summarized the apparent activation energies of ethanol and water permeation (ethanol concentration in the feed= 5wt%) estimated from the linear dependence of logarithm the individual fluxes on the inverse temperature.

The activation energy of permeation (Ep) lies from 64 kJ mol^{-1} to 35 kJ mol^{-1} in the case of ethanol and from 42 kJ mol^{-1} to 29 kJ mol^{-1} for water as a consequence of the membrane and spiral-wound employed (Table 4). The positive activation energy implies that permeation flux increases with increasing temperature, as confirmed from the results shown in Figures 6. Moreover, the apparent activation energies for the fluxes of ethanol and water are similar for each membrane tested, but it is slightly higher for ethanol than for water. This implies a more sensitive behavior of ethanol flux towards temperature changes, which reflects the slight increase in the ethanol/water separation factor as the temperature is increased.

Activation energy of ethanol and water permeation (ethanol concentration in the feed= 5wt%).

	Membrane	$E_{p\ EtOH}$ (kJ mol^{-1})	$E_{p\ water}$ (kJ mol^{-1})
Membrane	Isotropic SBS	55	43
Composite Membrane	SBS/PU/F-42	41	34
	SBS/PDMS/F-42	64	42
Spiral-Wound	SBS/PU/F-42	45	40
	SBS/PDMS/F-42	35	29

Conclusion

Isotropic dense SBS membranes were prepared by solvent evaporation and tested for ethanol removal from hydro-alcoholic solutions by varying the temperature and the ethanol concentration in the feed. SBS was found to be ethanol selective. On the basis of the promising performance of the material, new composite flat-sheet membranes with a dense SBS top-layer, coated on Fluoroplast F-42 support with an intermediate layer of PDMS and PU layer, have been developed. The composite membranes showed a strong increase in flux as a result of the lower film thickness in comparison to the isotropic SBS membranes. In general, in terms of selectivity, the membranes with PDMS as intermediate layer showed better results than the PU-containing membranes.

Following these promising results, a spiral-wound modules were prepared and studied as a model for a realistic separation process. In this configuration better results in terms of ethanol/water separation factor were obtained with a maximum of SF= 8,3 at 3 wt% ethanol and at 30°C. Also in this case, membranes with PDMS as the intermediate layer gave better results in terms of selectivity than those with PU.

Overall, the composite SBS films proved promising candidates for ethanol pervaporation as an alternative to the more commonly used PDMS membranes (SF=7), but a separation factor of ca. 20 is required in order to make the process of production of bio-ethanol coupled with PV competitive and economical viable. In this sense, the preparation of mixed matrix membranes SBS-based could be of interest in order to enhance the separation factor. Nevertheless this work has demonstrated as the employment on an adequate strategy allowed the improvement of the performance and the scale-up of the membranes developed in lab.

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