

Novel PVDF-HFP flat sheet membranes prepared by triethyl phosphate (TEP) solvent for direct contact membrane distillation



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ABSTRACT

Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) flat sheet membranes were prepared for aqueous membrane distillation (MD) applications using triethyl phosphate (TEP) as less-toxic solvent via phase inversion. PVDF-HFP concentrations of 10, 12 and 15 wt.% were investigated and it was observed that different polymer concentrations led to membranes with different surface structure and performance; the use of different coagulation bath compositions played a key role in the membrane fabrication and affected the performance in membrane distillation. The results showed that the permeation decreased sharply when the polymer concentration increased from 12 to 15 wt.%. By adding isopropanol as non-solvent to coagulation medium led to interesting results in terms of permeation. However, the use of lithium chloride to the casting solution had also a positive impact on membrane characteristics in price of retrograde membrane mechanical properties. Particularly interesting was the membrane produced from solution containing the 12 wt.% polymer and coagulated in the isopropanol–water mixture, which gave a DCMD permeation of $16.1 \text{ kg h}^{-1} \text{ m}^{-2}$ at feed temperature of 60°C , and a salt rejection of 99.3%.

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1. Introduction

The growth of modern applications by using artificial membranes needs prominent properties of polymers. Polymeric materials need to have high resistance to acids, bases, oxidants or reductants, high pressures and high temperatures, as well as suitable chemical properties in order to enhance the permeation flux with suitable solute separation factor of the membranes for the foreseen applications [1,2].

PVDF-HFP is a copolymer which attracted attention as a possible material for membrane applications [3–6]. In comparison with poly(vinylidene fluoride) (PVDF), PVDF-HFP have lower crystallinity due to the incorporation of the hexafluoropropene comonomer (HFP) into the main backbone which significantly enhances the amorphous phase content. It is also believed that the

presence of HFP groups resulting in an increase of the fluorine content and leads to PVDF-HFP with better hydrophobic chains [3–6]. Therefore, for many applications where the hydrophobicity of membrane material is decisive, PVDF-HFP is a potential candidate [7]. Hence, it is believed that the PVDF-HFP is a good candidate to be used for MD applications. Few works has been done using PVDF-HFP copolymer for producing membranes. Among them, Garcia-Payo et al [7] prepared PVDF-HFP copolymer hollow fiber membranes for MD using dry/wet spinning technique at different copolymer concentrations. They found that there is no significant change of the thickness of all hollow fibers. They showed that at low copolymer concentration, finger-like structure was detected in cross-section membrane. While at high copolymer content, a sponge like structure was observed. They foreseable that permeate flux of MD process would decline with increasing the copolymer composition. Khayet et al. [8] made PVDF-HFP hollow fiber membranes using different polymer concentrations via phase inversion method for direct contact membrane distillation (DCMD). They used a fractional factorial design and a steepest ascent method for possible fabrication of hollow fiber membranes.

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The optimized hollow fiber membranes revealed the highest performance index and the greatest global desirability.

Bottino et al. [9] studied the influence of the type of solvent on the final membrane structure and performance. The obtained results highlighted as the solvent/non-solvent mutual diffusivity plays a relevant role in evaluating the morphology of the membrane.

The 5th principle of Green Chemistry encourages the use of safer solvents and auxiliaries [10]. This comprises any materials that do not directly influence the molecular structure of the reaction product(s) but are still required for the process to occur. Solvents are the most common example of auxiliary compounds for membrane preparation via phase inversion. In fact, they are needed for dissolving the selected polymer and their chemical–physical properties strongly influence the membrane formation and, consequently, its performance. Among the most widely used solvents, *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc) and *N*-methyl pyrrolidone (NMP), represent an excellent choice for dissolving PVDF-HFP. However, they are classified as highly nephrotoxic and developmental harmful [11]. Consequently their use should be avoided whenever possible. Taking into account its low toxicity for human health and worker safety, TEP was proposed as promising solvent for replacing the traditional, highly toxic ones. Although it cannot be defined “green”, it represents a valid choice towards the improvement of membrane preparation in terms of worker safety. Table 1 shows a comparison between the hazard and precautionary phrases of DMF, DMA, NMP and TEP, evidencing as the selected diluent is not classified as carcinogenic, mutagenic and teratogenic, like the traditional used solvents. Its complete miscibility with water and alcohols such as isopropanol, as well as its high boiling point, make it a favorable alternative for dissolving the selected polymer by using water/alcohols as coagulation bath. When TEP was used as solvent, a porous membrane was obtained.

Feng et al. [13] prepared PVDF-HFP flat sheet membranes for DCMD. They found that high value of pore radius of membranes

occurred when ethanol or *n*-butyric acid composition increased in the solidification bath. Also they found that PVDF-HFP membranes presented a stronger hydrophobic nature than PVDF membranes.

Recently, Nejati et al. [14] proposed TEP as less toxic solvent for PVDF homopolymer membrane preparation, obtaining samples with an asymmetric structure (a dense skin layer and highly porous bottom side) suitable for MD applications.

The aim of this research is to discuss a detailed investigation on the production of PVDF-HFP membranes for aqueous membrane distillation application using TEP as alternative, less toxic, solvent. The influence of lithium chloride as pore former agent and different coagulation bath composition, some of which including isopropanol, was studied. Although both the lithium salt and the alcohol used are not safe for human health [15,16] and further investigations are needed to make the entire membrane preparation procedure completely sustainable and harmless, minimizing the toxic effects related to the use of the solvent, represents a first step for the human health protection [17]. Different parameters affecting membrane production including polymer concentration, membrane coagulation medium type and the presence of lithium chloride (LiCl), are studied. The PVDF-HFP membranes were characterized by means of scanning electron microscopy (SEM), capillary flow porometer (PML), thickness, void volume fraction, mechanical properties and contact angle measurements.

2. Experimental

2.1. Materials

PVDF-HFP copolymer (Solef® 21510) was kindly supplied by Solvay Specialty Polymers (Bollate (MI), Italy) and used to prepare the dope solutions. This copolymer possesses a significantly lower melting temperature (130–136 °C) and lower heat of fusion (20–24 J/g) than the corresponding homopolymer with the same molecular weight [18]. Triethyl phosphate (TEP) (Sigma–Aldrich, USA) was used as solvent to dissolve the polymer dope solution.

Table 1

Classification according to Regulation (EC) No 1272/2008 [12] of DMF, DMA, NMP and TEP used as solvents for preparing.

Solvent	Classification according to regulation (EC) no 1272/2008	
	Hazard statements	Precautionary statements
DMF	H226 flammable liquid and vapour H312 + H332 harmful in contact with skin or if inhaled H319 causes serious eye irritation. H360D may damage the unborn child Germ cell mutagenicity: mouse, lymphocyte Mutation in mammalian somatic cells	P201 obtain special instructions before use P280 Wear protective gloves/protective clothing P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 IF exposed or concerned: get medical advice/attention
DMA	H312 + H332 harmful in contact with skin or if inhaled H319 causes serious eye irritation H360D may damage the unborn child May cause congenital malformation in the fetus. presumed human reproductive toxicant overexposure may cause reproductive disorder(s) based on tests with laboratory animals	P201 obtain special instructions before use P280 Wear protective gloves/protective clothing P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 if exposed or concerned: get medical advice/attention
NMP	H315 causes skin irritation H319 causes serious eye irritation H335 may cause respiratory irritation H360D may damage the unborn child Damage to fetus possible	P201 obtain special instructions before use P261 Avoid breathing vapors P305 + P351 + P338 if in eyes rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing P308 + P313 if exposed or concerned: get medical advice/attention
TEP	H302 harmful if swallowed H319 causes serious eye irritation Other hazards: this substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic, or very persistent and very bioaccumulative at LEVELS OF 0.1% or higher	P305 + P351 + P338 if in eyes: rinse cautiously with water for several minutes Remove contact lenses, if present and easy to do. Continue rinsing

2-Propanol (IPA) (BDH PROLABO, VWR Italy) and methanol (MeOH) (Fluke, Germany) were used as a non-solvent in the coagulation medium. Lithium chloride (LiCl) (Sigma–Aldrich, USA) was used as a pore former additive in the dope solution. NaCl (Carlo Erba, Italy) was used in preparation of salt solution for performance test. All materials were used as received without further purification.

2.2. Flat sheet membrane preparation

PVDF-HFP powder and lithium chloride (LiCl) were dissolved at different concentrations (see Table 2) in triethyl phosphate (TEP) using magnetic stirrer at room temperature. The mixing process continued till the solution becomes clear and homogeneous. The polymer solution was left for 24 h at 20 °C to remove all air bubbles before casting it on a glass support.

Membranes were cast using knife of 250 µm gap. After that, the membranes were immersed in a precipitation bath (Table 2) at 20 °C until the membranes got separated from glass surface. The produced membranes were moved to another water bath to complete their formation. The membranes remained in the water bath for 24 h at 50 °C to make sure that all residual TEP solvent was removed from the membranes. Thereafter, the membranes were dried in atmospheric air for 24 h. Finally, they were transferred to oven at 50 °C for 24 h to complete the drying process.

2.3. Membrane characterization

2.3.1. Membrane thickness

Membranes thickness was measured using digital micrometer (Carl Mahr, Germany) with a precision of ±0.001 mm. At least five regions of membrane were measured and the average value of membrane thickness was taken into account.

2.3.2. Membrane porosity

Because of the strong relationship between the porosity and the performance of the membrane, the porosity of membranes prepared in this method was determined using the following correlation:

$$\text{Porosity}[\%] = \frac{wt_w - wt_d/\rho_k}{(wt_w - wt_d/\rho_k) + (wt_d/\rho_p)} \times 100 \quad (1)$$

where wt_w is the membrane wet weight, wt_d is the membrane dry weight, ρ_k is the kerosene density and ρ_p is the polymer density.

Three different pieces of membrane were weighted before and after dipping in kerosene liquid for 24 h to determine the porosity.

2.3.3. Contact angle

The hydrophobicity of the membrane can be evaluated by measuring the contact angle of the membranes. Contact angle measurements were performed with Optical Tensiometer (CAM 100, Nordtest Srl, Italy) using the drop method. In this method, a drop of distilled water was deposited on a piece of membrane using micropipette. At least five independent measurements of each piece of membranes were performed.

2.3.4. Pore size and pore size distribution (PDS)

Average pore size and pore size distribution of the membranes were evaluated by liquid–gas displacement process [19] using Porewick as wetting liquid (surface tension 16 dyne/cm) and a capillary flow porometer (PMI, USA).

2.3.5. Mechanical properties

Tensile strength, strains at break and Young's modulus were measured using Zwic/Roell test unit (Germany) to reveal the mechanical properties of the membranes. Five samples of each membrane were tested and the average value was taken into consideration.

2.3.6. Scanning electron microscopy (SEM)

Images of top and bottom surfaces as well as cross sectional area were taken for all of the membranes using a scanning electron microscope (Zeiss-EVO Ma10). For cross section images, membranes were first frozen in liquid nitrogen and then fractured.

2.3.7. Liquid entry pressure (LEP)

Liquid entry pressure (LEP) is an important parameter for evaluating the performance of membranes used in MD. LEP is defined as the pressure difference at which the liquid crosses the hydrophobic membrane. In fact, during MD tests, liquid passage across the membrane should be avoided. LEP has been measured by gradually increasing pressure on the feed side of the membrane until the first feed solution drop reaches the permeate side and estimated by using the following equation [20]:

$$\Delta P = P_f - P_p = -\frac{2b\gamma_i \cos\theta}{r_{\max}} \quad (2)$$

where γ_i is a liquid surface tension, θ is the contact angle and r_{\max} is a maximum pore size and b is a pore shape coefficient. For MD process, the liquid–solid contact angle must be greater than 90° since LEP largely depends on hydrophobicity of membrane.

2.3.8. Membrane performance

The membranes performance was detected in terms of permeation and NaCl rejection (see Eqs. (3) and (4)). The permeation and salt rejection were examined for two hours by using the experimental unit illustrated in Fig. 1.

Salt water was prepared by dissolving 35 g of NaCl into 1 L of double distilled water. The feed and permeate concentration were determined by using conductivity and TDS meter (HANNA, Italy). The Main DCMD process conditions are reported in Table 3.

$$\text{Permeation}[\text{kg h}^{-1} \text{m}^{-2}] = \frac{Wt_p}{A \times t} \quad (3)$$

$$\text{Rejection}[\%] = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where Wt_p is the permeate weight, A is the membrane area, t is the experiment time, C_p is the permeate concentration and C_f is the feed concentration.

Table 2
Dope solution compositions and type of coagulation bath.

Coagulation medium	Polymer and additive content in the dope solution	Membrane name
H ₂ O	10 wt.% PVDF-HFP 3 wt.% LiCl	FS-LiCl
H ₂ O–IPA (50/50 v/v)	12 wt.% PVDF-HFP	FS-IPA
H ₂ O–TEP (50/50 v/v)	12 wt.% PVDF-HFP	FS-TEP
H ₂ O–TEP (50/50 v/v)	15 wt.% PVDF-HFP	FS-15

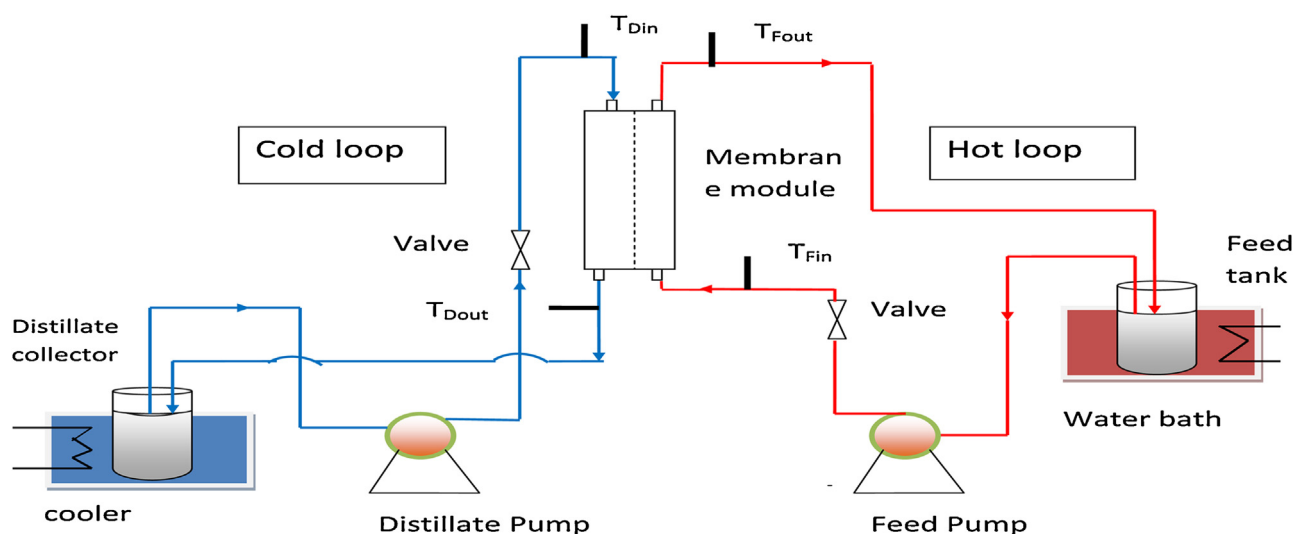


Fig. 1. Schematic drawing of DCMD set up.

Table 3
Direct contact membrane distillation (DCMD) process conditions.

Main DCMD variables	Process condition
Feed temperature	40–60 °C
Feed flow	200 mL/min
Feed velocity	0.033 (m/s)
Permeate temperature	18.5 °C
Permeate flow	200 (mL/min)
permeate velocity	0.033 (m/s)
Reynolds number	173

3. Results and discussion

3.1. The influence of polymer concentration

Fig. 2 illustrates the cross sectional morphology of flat sheet membranes prepared from the dope containing different PVDF-HFP concentrations. All the prepared membranes showed nearly symmetric pattern with sponge like structures across the whole membrane and increasing polymer concentration from 10 to 15 wt. % exerted slight effect on the cross section morphology. By comparing the top surface images in Fig. 2, membranes produced from low polymer concentrations (10 and 12 wt.%) had higher surface porosity than that prepared from high polymer concentration (15 wt.%). This phenomenon can be attributed to increasing polymer concentration at the polymer-solvent-non solvent interface leading to a decrease in membrane surface porosity [21].

Khayet et al. [8] using DMA as solvent for the hollow fiber membrane preparation via phase inversion, observed the formation of asymmetric structure, characterized by a finger-like structure on the top side and a spongy matrix on the internal side.

The formation of more porous structure exhibited by the membranes prepared with TEP as diluent, was probably related to its weak solvent power in comparison to DMA. In other words, TEP seems to be a poorest solvent compared to DMA. Another explanation might be the weaker mutual affinity between TEP and the non-solvent in comparison with DMA, which favored the formation of sponge membrane matrix.

The main characterization results of the membranes prepared with 10, 12 and 15 wt.% and using the mixture H₂O-TEP as coagulation bath are summarized in Table 4.

It can be seen that membrane thickness increased concomitantly with the increase of polymer content. Ortiz de Zarate et al. [22] also found that membrane thickness, with sponge-like structure across the membrane and free of macrovoids, increased with the increasing of polymer content. In contrast, polymer concentration plays a minor effect on membrane porosity as shown in Table 4. Membrane porosity decreased for membrane prepared under high polymer concentration. Pu et al. [23] reported that the difference in porosity may be due to the fact that the more the ratio between water concentration and polymer concentration is, the higher the porosity is. On the other hand, polymer concentration had a distinct effect on membrane contact angle. Contact angle of membrane prepared from high polymer concentration (15 wt.%) was larger than that prepared from low polymer concentrations (10 and 12 wt.%). Contact angle often decreased with high surface porosity as seen in SEM top surface pictures (Fig. 2).

Table 4 reveals also the mechanical properties of membranes against polymer concentration. Mechanical features are always related to porosity and crystallinity of the membrane [24]. The rigidity feature (Emod) increased with increasing polymer concentration from 10% to 15 wt.% since at the same time porosity decreased. Also the elongation at break follows the same trend of the Young's Modulus, increasing for the sample prepared with the highest polymer content.

Fig. 3 reveals the crucial effect of polymer concentration (i.e., 12 and 15 wt.%) on the performance of two sorts of membranes. The permeation of membrane prepared from low polymer concentration was higher than that of the membrane prepared from high polymer concentration, while the salt rejection was 99% for both membranes. This is in agreement with previously reported membrane features, where membrane deriving from dope solutions with low polymer concentration was thinner than that obtained by employing high polymer concentration (0.049 ± 0.008 mm 0.072 ± 0.002 for 12 and 15 wt.%, respectively). Therefore, the resistance to vapor mass transfer would be higher for membrane produced with high polymer concentration. In addition, the sponge like structure was more compact for 15 wt.% membrane compared with that of the membrane prepared from 12 wt.%, as shown in Fig. 2. However, the fluxes obtained at high feed temperature for the two membranes were 13 and 9.5 kg h⁻¹ m⁻² are still in the range reported in the literature and also for commercial PP membrane [25,26].

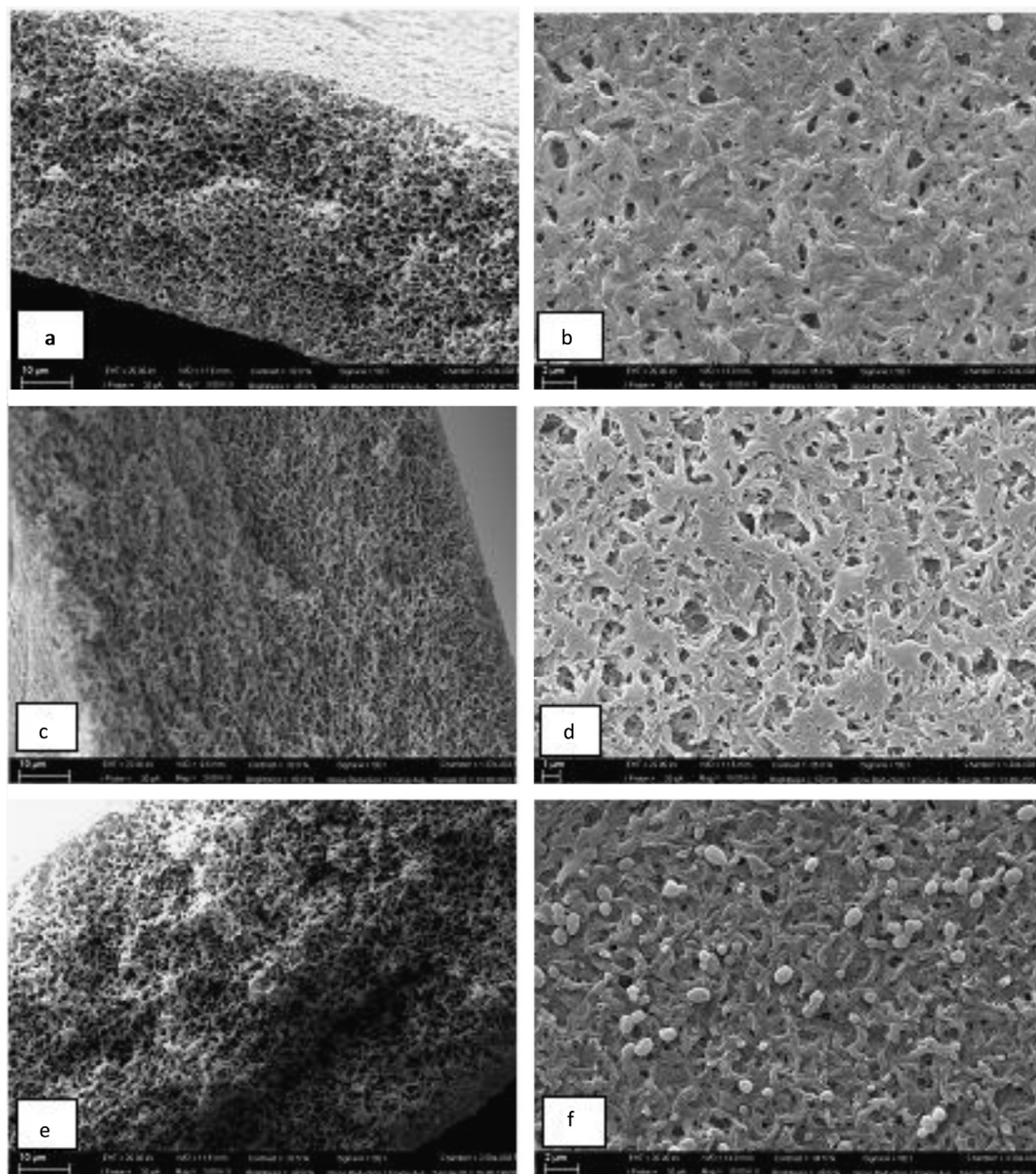


Fig. 2. a, c, e: cross section and b, d, f: top surface pictures of the membranes prepared by using 10 wt.%, 12 wt.% and 15 wt.% of polymer, respectively, and coagulated in the H_2O -TEP bath. Cross section magnification: $3000\times$; top surface magnification: $10,000\times$.

Table 4

Thickness, porosity, contact angle (air side) and mechanical properties of the membranes prepared with 10, 12 and 15 wt.% of polymer and coagulated in H_2O -TEP bath.

Polymer content in the dope solution	Thickness (mm)	Porosity (%)	Contact angle Air side ($^{\circ}$)	Mechanical strength	
				Emod (N/mm 2)	Break (%)
10 wt.%	0.045 ± 0.002	79.0 ± 1.6	94.3	48.7 ± 0.3	170.3 ± 0.8
12 wt.%	0.049 ± 0.008	78.1 ± 1.1	89.25	55.5 ± 2.0	166.3 ± 0.6
15 wt.%	0.072 ± 0.002	77.5 ± 0.7	108.5	86.9 ± 2.0	182.0 ± 5.2

3.2. The influence of coagulation medium

A series of membranes was prepared by casting a solution of PVDF-HFP at 12 wt.% using different coagulation mediums

(Table 5). In all the cases (Fig. 4), the membranes exhibited sponge like structure although they were coagulated in three different coagulation baths. Similar finding was reported in the literature [27,28].

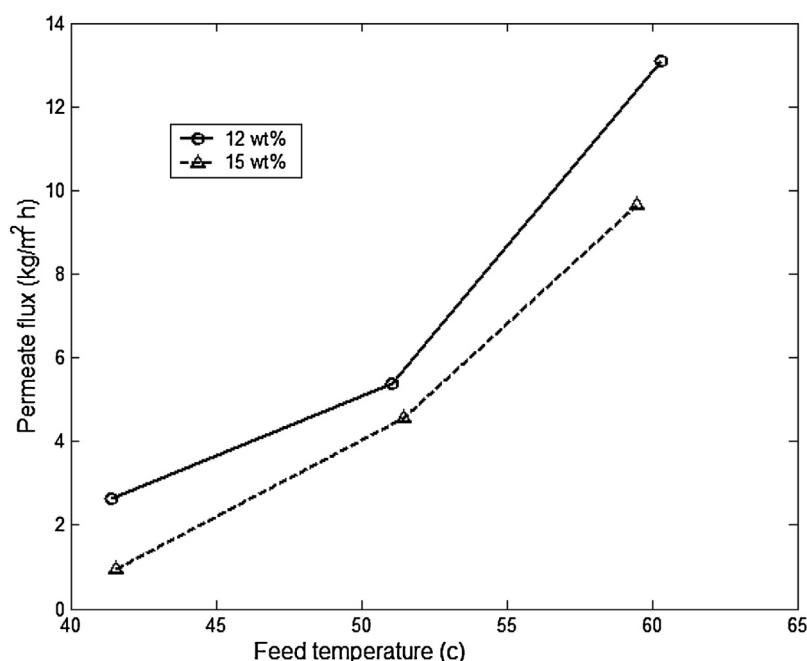


Fig. 3. DCMD Permeate flux versus feed temperature for 12 and 15 wt.% membranes.

Table 5

Solubility parameters of solvent and coagulation mediums.

Solubility parameter difference between coagulant and TEP	Solubility parameter δ_t (MPa ^{1/2})	Coagulation medium
25.46	47.8	Water
–	22.34	TEP (solvent)
12.73	35.07	TEP–H ₂ O (50%)
16.36	38.7	MeOH–H ₂ O (50%)
13.36	35.7	IPA–H ₂ O (50%)

The relative affinity of a solvent and non-solvent can be determined using three dimensional solubility parameter δ_t (Eq. (5)), which include a polar component (δ_p), a dispersion force component (δ_d) and a hydrogen bonding component (δ_h) [29]:

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (5)$$

In the present system, the solvent used is TEP and different types of coagulation medium have been used (Table 5).

According to Table 5, the mixing rate between TEP and TEP–H₂O, MeOH–H₂O and IPA–H₂O are higher than that for TEP and H₂O alone. However, when the inter-diffusivities of TEP and water are taken into account, it can be noticed from Table 6 (D values calculated from Wike and Chang equation [30]) that diffusivity of solvent TEP in different non solvent medium were in the sequence of $D_{\text{TEP–MeOH}} > D_{\text{TEP–water}} > D_{\text{TEP–IPA}}$. This means that the delayed demixing process took place in different rates when the coagulation bath composition changed. This conclusion is consistent with SEM pictures of Fig. 3 where all the membranes revealed a sponge-like structure with different surface appearance. Membranes coagulated in MeOH–H₂O had dense surface while the other two membranes had porous surface with different intensity. As the diffusion coefficient decreased (for IPA), the solvent transfer would be low and the membrane matrix would be more porous.

The coagulation medium had a relevant effect on membrane thickness, porosity and average pore size, as shown in Table 7. Membrane coagulated in IPA–H₂O medium was thicker and more porous than that coagulated in MeOH–H₂O medium. Molar volume

of non-solvent IPA was higher than that for MeOH (Table 8). Therefore, the inter diffusion rate between solvent and non-solvent would decrease in IPA–H₂O medium and gave thicker and more porous membrane. The same trend was detected by Buonomenna et al. [31] where they mentioned that high molar volume and also the increase in compatibility with polymer (decreases the interaction parameter) would cause finally swelling of the membrane and resulted in more porous and thicker membrane. On the other hand, the membrane coagulated in H₂O medium was the thinner, due to the fast exchange rate between the solvent and the non-solvent which promoted a rapid solvent mass transfer and a decreasing in the coagulation rate. Moreover, the addition of non-solvent to the coagulation bath affected significantly the contact angle values of membranes. The contact angle increased when IPA and MeOH were added to the coagulation bath since the contact angle is related to the surface porosity which also increased with non-solvent addition. Li et al. [32] reported that hydrophobicity is related with the surface porosity for PVDF membrane which increased when ethanol was added to coagulation medium.

Fig. 5 reveals the cumulative filter flow percentage versus pore diameter of 12 wt.% membranes coagulated in four different coagulation mediums. This graph defines the percentage of flow through the filter membrane for a specific pore size. It could be noted that for all the samples it was finally reached a value above 90% cumulative filter flow.

The addition of TEP (50 wt.% of the total coagulation bath composition) to the coagulation medium led to a mean flow pore

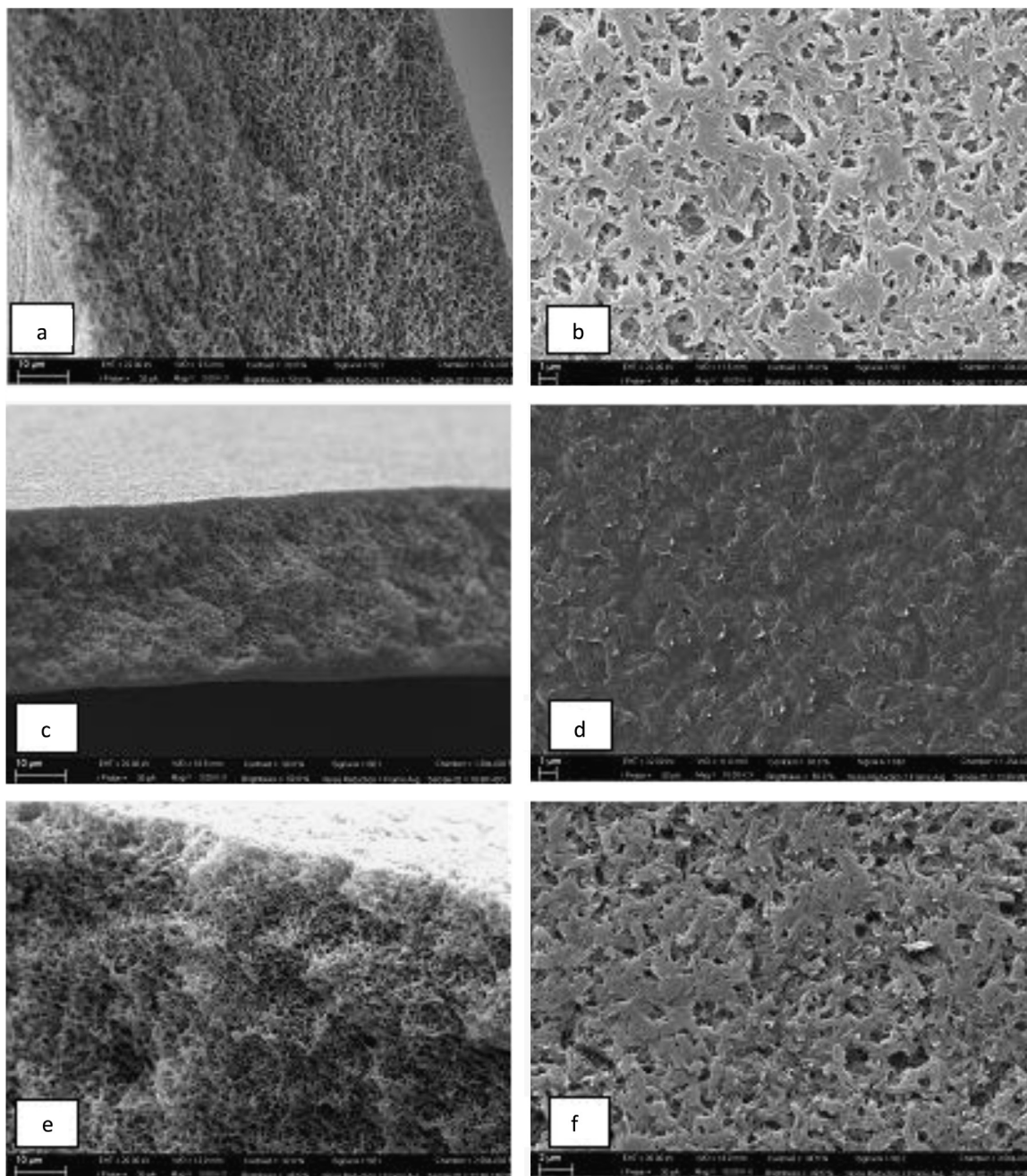


Fig. 4. a, c, e: cross section and b, d, f: top surface pictures of the membranes prepared by using 12 wt.% polymer and coagulated in the TEP–H₂O, MeOH–H₂O and IPA–H₂O bath, respectively. Cross section magnification: 3000 \times ; top surface magnification: 10,000 \times .

Table 6
Diffusion coefficient of TEP in different mediums.

Value $\times 10^{-10}$ (m ² /s)	Diffusion coefficient type
6.6	$D_{\text{water-TEP}}$
5.6	$D_{\text{TEP-water}}$
2.6	$D_{\text{TEP-IPA}}$
9.1	$D_{\text{TEP-MeOH}}$

size of ~ 0.06 m which means that $\sim 74\%$ of the flow is occurring through pores larger than this pore size (Fig. 5). This result was in agreement with previous discussion that slow solvent mass transfer was in favor when solvent was added to the coagulation medium. Nevertheless, the addition of non-solvent (IPA and

MeOH) to the coagulation medium allowed to obtain a mean flow pore diameter of ~ 0.05 and ~ 0.08 m, which corresponded to ~ 51 and $\sim 46\%$ of the filter flow, by using IPA and MeOH, respectively. These results reflected the solvent/non-solvent exchange rate as reported in Table 7. For the IPA–H₂O system, the mutual diffusion of TEP in the alcohol–water mixture was the lowest. Therefore, the polymer precipitation would be very slow and big pores would be formed.

The effect of coagulation medium on mechanical properties is presented in Table 7. The addition of non-solvent decreased significantly the Young's Modulus. The presence of non-solvent in the coagulation medium slowed down the solvent–non solvent inter-diffusion and more porous structure would be obtained. On the other hand, adding TEP solvent to coagulation bath enhanced the elongation break. This might be attributed to very thin

Table 7

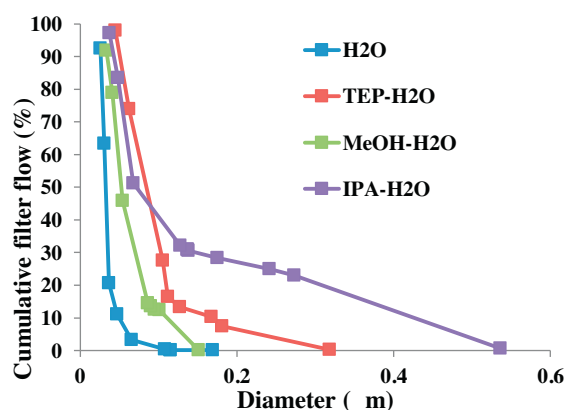
Membrane characteristics versus coagulation medium type for the membrane prepared using 12 wt.% PVDF-HFP.

Coagulation bath type	Membrane thickness (mm)	Porosity (%)	Average Pore size (μm)	Contact angle (air side) ($^\circ$)	Emod (N/mm^2)	Break ε (%)
H ₂ O	0.032 ± 0.002	81.5 ± 1.7	0.03 ± 0.01	83.0 ± 1.5	105.5 ± 0.1	165.3 ± 10.9
TEP-H ₂ O	0.046 ± 0.009	78.1 ± 1.1	0.06 ± 0.01	88.7 ± 1.3	55.5 ± 2.0	166.3 ± 0.6
MeOH-H ₂ O	0.055 ± 0.003	81.1 ± 0.8	0.05 ± 0.01	90.6 ± 0.8	32.7 ± 3.5	15.4 ± 2.6
IPA-H ₂ O	0.065 ± 0.004	82.8 ± 1.0	0.08 ± 0.01	115.2 ± 2.0	31.0 ± 4.1	88.2 ± 5.0

Table 8

Characteristics of non-solvent added to coagulation medium.

Non-solvent	Solubility parameter ($\text{MPa}^{1/2}$)	Molar volume (cm^3/mol)
MeOH	29.6	40.4
IPA	23.6	76.5

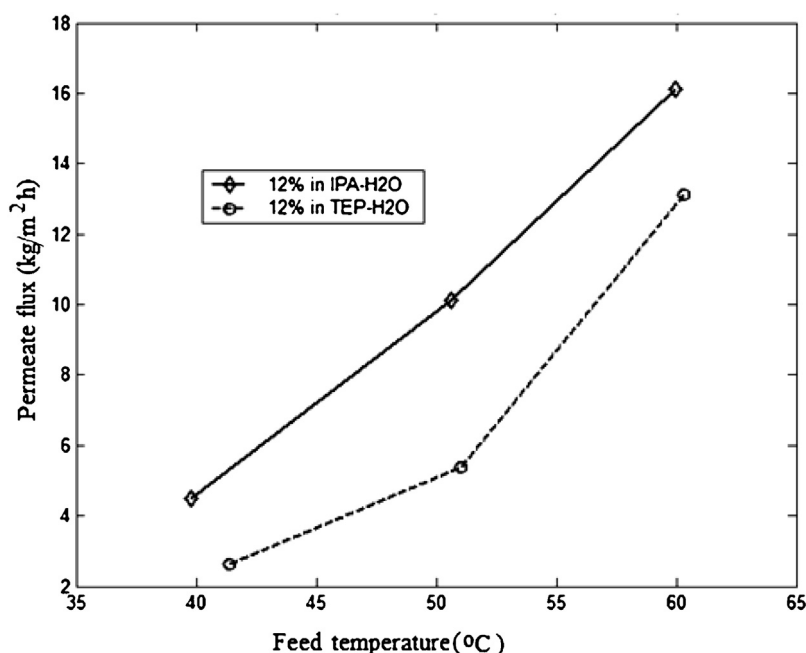
**Fig. 5.** Cumulative filter flow percentage versus pore diameter of the membranes coagulated in (a) H₂O; (b) TEP-H₂O; (c) MeOH-H₂O (d) IPA-H₂O baths.

membrane (0.046 ± 0.009 mm) and low porosity which strengthened the membrane compared to others.

It can be conclude that the addition of non-solvent to coagulation medium deteriorated significantly the mechanical properties of membranes while enhanced the porosity and pore size of membrane. Furthermore, solvent addition to coagulation medium strengthened the membrane with very good characteristics properties.

The clear effect of coagulation medium on permeation can be seen in Fig. 6. FS-IPA, membrane coagulated in IPA-H₂O medium, had a permeation higher than FS-TEP, membrane coagulated in TEP-H₂O medium, while both membranes revealed high salt rejection. Depending on the results reported above, the differences in terms of performance could be related to porosity and pore size differences. Membrane FS-IPA presented a structure with a pore size of $0.08 \mu\text{m}$ and porosity of 82.8% whereas membrane FS-TEP presented a structure with a pore size of $0.06 \mu\text{m}$ and porosity of 78.1%. In Membrane distillation process, a pore size of $0.2\text{--}0.5 \mu\text{m}$ is preferred with porosity of 85% to gain much vapor molecules transfer from high feed temperature to cold side [20,33].

From above discussion, the non-solvent additive (IPA) to coagulation medium had a positive effect on permeate flux while mechanical properties have been worsen. Therefore, to select a membrane for MD application, a trade-off between mechanical properties and permeation should be applied.

**Fig. 6.** DCMD Permeate flux versus feed temperature for 12 wt.% membranes coagulated in different coagulation baths.

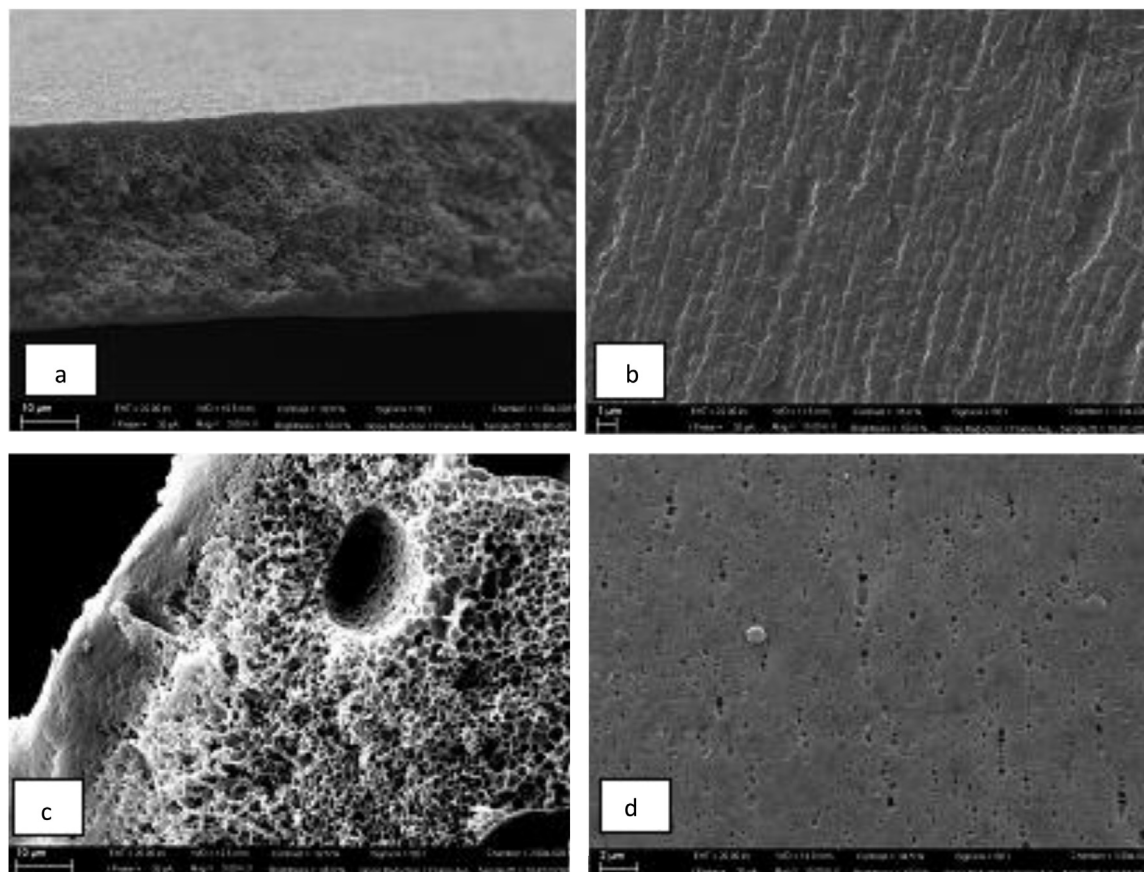


Fig. 7. a, c: cross section and b, d: top surface pictures of the membranes prepared by using 10 wt.% polymer, without or with (3 wt.%) LiCl, respectively, both coagulated in H₂O. Cross section magnification: 3000 \times ; top surface magnification: 10,000 \times .

Table 9

Characteristics of membranes with and without additive.

Polymer and additive content in the dope solution	Coagulation bath	Thickness (mm)	Porosity (%)	Average Pore size (μm)	Contact angle air side ($^{\circ}$)	Emod (N/mm ²)	Break ϵ (%)
10 wt.%	H ₂ O	0.032 \pm 0.002	81.5 \pm 1.7	0.04 \pm 0.01	83.0 \pm 1.5	111.2 \pm 1.3	406.0 \pm 7.6
10 wt.% + 3 wt.% LiCl	H ₂ O	0.072 \pm 0.003	87.5 \pm 1.5	0.05 \pm 0.01	92.0 \pm 1.0	30.9 \pm 1.8	41.8 \pm 5.4

3.3. The influence of lithium chloride (LiCl)

Fig. 7 depicts the cross-section and outer surface morphologies of flat membranes prepared with/without addition of LiCl to casting solution of 10 wt.% of PVDF-HFP. Similar cross-section structure was observed. Basically, sponge-like structure was developed below the outer surface layer. However, with addition of 3 wt.% of LiCl, a big pore size diameter ($\sim 0.5 \mu\text{m}$) and big macrovoids were developed near the edge of the membrane. It also may be noted that membrane prepared without additive shows dense surface (Fig. 7b), while membrane prepared with additive led to a membrane with porous surface (Fig. 7d).

The addition of LiCl as pore former in the dope solution, hindered the exchange between the solvent and the non-solvent during the phase inversion, delaying the precipitation rate and thus favoring the formation of a more porous structure [34]

Table 9 illustrates the effect of LiCl on membrane thickness, porosity, pore size and contact angle. The presence of LiCl in the dope solution led to a bigger pore size in the final membrane, due to the hydrophilic character of the additive. It is clear from Table 9 that LiCl had a minor influence on contact angle of membrane.

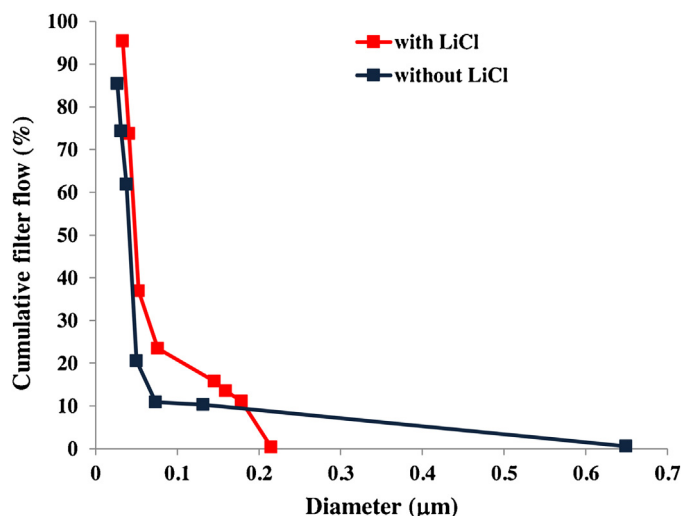


Fig. 8. Cumulative filter flow percentage versus pore diameter of the membranes prepared by using (a) 10 wt.% LiCl and (b) without LiCl in the dope solution.

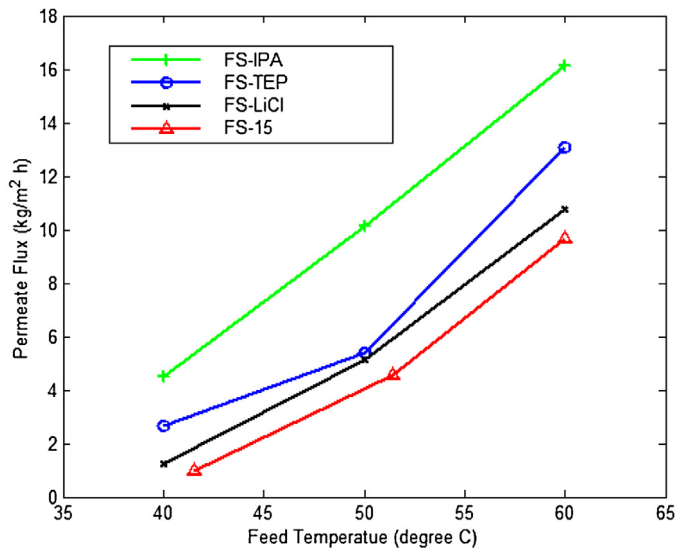


Fig. 9. DCMD Permeate flux of different types of membranes for sea-water as feed solution.

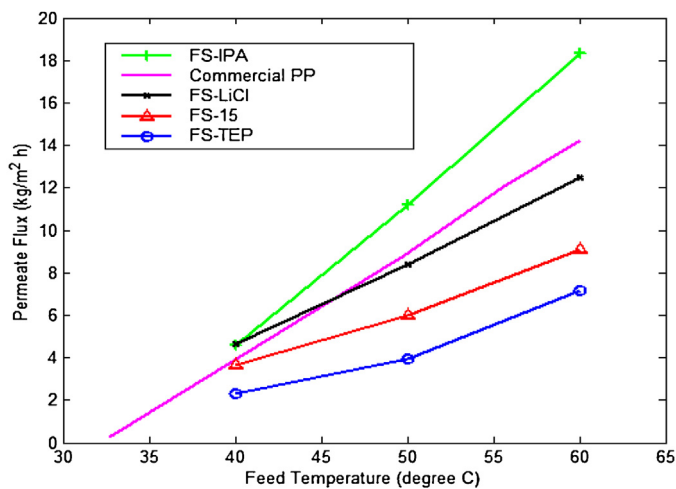


Fig. 10. DCMD Permeate flux of different types of membrane for pure water as a feed.

Similar results were reported also in the literature and were connected to the good LiCl solubility in water and its low molecular weight [35]. Furthermore, the hydrophilic nature of LiCl would offset the effect of big pores on the hydrophobicity of the membrane.

It is quite evident the additive influence on the pore size of the membrane produced from solution containing LiCl (Table 9). This might be explained by supposing a high interaction between LiCl, the polymer and the solvent, which made the dope solution thermodynamically unstable. Moreover, the addition of LiCl

increased the viscosity of dope solution significantly (as observed directly from the appearance of dope solution) and hereby delayed demixing occurred, leading to a thick membrane. Furthermore, high solubility of LiCl in water medium facilitated its removal and resulted in larger pore.

Fig. 8 shows the effect of LiCl on the filter flow expressed as percentage distribution versus pore diameter of the flat sheet membrane produced with 10 wt.% PVDF-HFP copolymer.

The mean pore size diameter for the membrane prepared with LiCl was $\sim 0.05 \mu\text{m}$ which corresponded to a $\sim 62\%$ filter flow through pores larger than that pore size, while in the case of the membrane prepared without any additive, and having a mean pore diameter of $\sim 0.04 \mu\text{m}$, this value decreased to $\sim 37\%$. However, the pore size is still in the range recommended for MD application which is essentially to prevent membrane wetting.

Table 9 shows the massive impact of LiCl on mechanical features of PVDF-HFP membrane. All mechanical properties sharply decreased when LiCl 3 wt.% was added to the dope solution. This influence can be explained in terms of porosity and pore size which increased significantly with adding LiCl as mentioned above. Therefore, mechanical features deteriorated significantly as it was strongly influenced by the membrane structure. Other researchers also found that adding a high concentration of LiCl into PVDF solution can improve the performance of the membrane, but it was gained at a price of decreasing the strength of the mechanical properties [36,37].

3.4. Comparison of membrane performance

The permeation and the salt rejection of the membranes listed in Table 2 were determined in salt and pure water feeds. It is clear that salty feed solution decreases the permeation by 10% due to decrease in vapor pressure difference between the two sides of the membrane (Figs. 9 and 10). It can also be seen that the permeation value for membrane FS-IPA was much higher than permeation values for commercial and other prepared membranes. Moreover, FS-IPA presented the highest salt rejection percentage with a value around 99.3% while other membranes exhibited a low degree of membrane wetting (Table 10). As mentioned early, FS-IPA had very good characteristics with large pore size ($\sim 0.08 \mu\text{m}$) and high porosity ($\sim 82\%$) in comparison to the other produced membranes. In addition, the membrane had high LEP (greater than atmospheric pressure) which is necessary to prevent membrane wetting.

Khayet et al. [8] reported a salt rejection of 99.5% by using a sample prepared under the optimal operational conditions previously identified by means of Lagrange multipliers method agreeing with the factorial models [8]. Morphological analysis evidenced as this hollow fiber presented fingers in the top layer, a spongy bottom side and an intermediate section with larger fingers in comparison to those of the top side. Both macrovoids and fingers exhibited porous opened skin. The DCMD permeate flux, as reported by the authors [8], was probably improved by these morphological characteristics.

The results presented by Khayet et al. are very similar to the experimental data reported in our work, which evidenced the possibility to obtain membranes with a promising performance for DCMD tests by using TEP as less toxic solvent.

Table 10
LEP and NaCl rejection of four different membranes.

Membrane name	Dope solution composition	Coagulation medium	LEP (bar)	NaCl Rejection (%)
FS-IPA	12 wt.% PVDF-HFP	H ₂ O-IPA (50/50 v/v)	2.8	99.3
FS-TEP	12 wt.% PVDF-HFP	H ₂ O-TEP (50/50 v/v)	0.24	98.9
FS-LiCl	10 wt.% PVDF-HFP +3 wt.% LiCl	H ₂ O 100 vol.%	0.99	96.8
FS-15	15 wt.% PVDF-HFP	H ₂ O-TEP (50/50 v/v)	4.85	98.2

Accordingly, we chose this membrane for further investigation and particularly to explore the interaction effects between the operating parameters and therefore, find the optimum operating conditions of DCMD performance.

4. Conclusions

Flat sheet PVDF-HFP membranes were prepared via non-solvent induced phase separation technique (NIPS) for membrane distillation applications.

TEP was employed as solvent during the phase inversion procedure, leading to the fabrication of flat sheet membranes suitable for MD applications. TEP was selected for its lower toxicity compared to that of traditionally used, highly toxic, diluents, such as DMF, DMA and NMP. The influence of PVDF-HFP and LiCl concentration in the dope solution and the type of coagulation medium on the morphology and the performance of the membranes were investigated.

Membranes prepared from different PVDF-HFP concentrations exhibited similar sponge like structure across the membrane and various surface porosities. Increasing PVDF-HFP concentration from 12 to 15 wt.% leads to decrease in permeation and salt rejection as a result of increasing membrane thickness and decreasing surface pore size. Adding IPA, MeOH and TEP to coagulation medium had a slight effect on membrane cross sectional structures, while largely affected surface pore sizes. Moreover, Adding LiCl to the dope solution improved the characteristics of the membrane such as porosity and pore size in price of deteriorating membrane mechanical properties and salt rejection. Also, the addition of IPA to the coagulation medium resulted in higher membrane porosity, larger pore size, higher contact angle and consequently higher membrane DCMD permeation ($16 \text{ kg h}^{-1} \text{ m}^{-2}$) and salt rejection (99.3%).

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