Effect of Different Additives on Separation Performance of Flat Sheet PVDF Membrane Contactor

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(Received: 05/22/2018, Revised: 09/17/2018, Accepted: 10/04/2018)
[DOI: 10.22059/JCHPE.2018.258530.1233]

Abstract

This paper investigates effects of different additives on morphology and subsequently, separation performance of asymmetric flat sheet Polyvinylidene fluoride (PVDF) membranes to separate CO_2 using membrane contractor. Five different additives from different chemical families including Lithium chloride (salt), Polyethylene glycol 400 (polymer), glycerol (weak anti-solvents), methanol (alcohols) and acetic acid (weak secondary solvents) were used for controlling the morphology of the fabricated membranes. The fabricated PVDF membranes were applied to separate CO_2 from a gas mixture of (20/80 wt/wt) CO_2/N_2 by contacting with (20/80 wt/wt) Monoethanolamine/H_2O as absorbent. The investigations revealed that among the all considered additives, glycerol has the most promising effect on the performance of CO_2 separation from the feed gas mixture. Effects of operational parameters such as flow rate and temperature of absorbents on the separation performance were also studied. Investigations showed that the lowest level of temperature (30 ºC) and the highest level of the flow rate of absorbent (500 ml/min) provide better separation performance. Additionally, the presence of glycerol increased absorption performance (η) from 0.63 to 0.78 (at the lowest level of flow rate) and from 0.79 to 0.91 (at the highest level of flow rate) compared to the bare PVDF membranes.

Keywords

Absorption Performance;
Membrane Contactor;
Morphology;
Operating Parameters

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1. Introduction

Membrane contactors are one of the most important membrane technologies with the advantages of both absorption and membrane processes for separation of acid gases like carbon dioxide (CO_2) from light gas streams. In membrane contactors, the liquid phase adjacent to the gas phases using a porous membrane. This is while the gas solute enters the membrane pores after crossing the gas phase boundary layer and is absorbed by the liquid absorbent on the opposite side. Then it enters the liquid stream after passing the liquid phase boundary layer [1]. Since the gas and liquid phases are not in direct contact, the common challenges associated with separation by amine-based columns, such as weeping, flooding, and entrainment are not usually found in membrane contactors [2]. Moreover, liquid and gas flow rates can also be independently adjusted in membrane contactors, which is not possible in conventional amine columns. The diffusivity coefficient of penetrants through the liquid phase is 10^4 times less than that of the gas phase, so the membrane pores should be gas filled for higher performance achievement [3]. Qi and Cussler [4,5] were pioneers for introducing the idea of application of polymeric membranes for CO_2 absorption using porous polypropylene membrane and sodium hydroxide solution as an absorbent.

Afterward, several studies have been carried out on the application of membrane contactors for separation purposes. For instance, Tan et al. [6] prepared asymmetric PVDF membranes by phase separation method and applied it in the ammonia separation from water; Bhaumik et al. [7], examined the separation of gaseous compounds, such as CO_2 and O_2, from treated water through porous polypropylene membranes. Furthermore, different researches have also been conducted on the separation of H_2S from gas streams using membrane contactors [8,9].

CO_2 emission is responsible for global warming and climate change. Also, its existence in natural gas is one of the major sources of the equipment corrosion [10-13]. Hence, different researches have focused on CO_2 separation from natural gas and some other gas streams by membrane contactors. Karoor and Sirkar [14] studied the application of membrane contactors to separate CO_2 and SO_2 from a mixture of CO_2/N_2 and SO_2/air, using water as the absorbent. Kim et al. [15] have examined the separation of CO_2/N_2 mixtures in a membrane contactor. In order to achieve a high separation efficiency in membrane contactor processes, the applied membranes should have high wetting resistance, low porosity and also high permeability [3].

Different hydrophobic polymers, such as poly (tetrafluoroethylene) (PTFE) and PVDF, has been applied for CO_2 absorption in membrane contactor with amine absorbents. Studies have shown that the porous structure of the membranes has a great impact on the separation performance of the membrane contactors. Generally, the final porous structure of the applied membranes in membrane contactors is controlled by the rate of the phase inversion process during the membrane fabrication procedure. Incorporation of different additives in polymeric solutions is a simple method to change the rate of the phase inversion process. Some of the most common additives which are used for this aim are poly (vinyl pyrrolidone) (PVP), poly (ethylene glycol) (PEG), organic and inorganic acids (acetic acid, phosphoric acid), weak non-solvents (glycerol, ethylene glycol), co-solvents (ethanol, acetone) and inorganic salts (lithium chloride (LiCl), lithium nitrate). Mansourizadeh et al. [16] investigated the performance of CO_2 absorption using a membrane contactor constructed with PVDF hollow fibers. In that study, the authors used some additives such as phosphoric acid and hydrated lithium chloride to control the morphology of the porous fibers. Shi et al. [17] investigated the effects of LiCl and glycerol on the morphology of PVDF hollow fiber membranes. Naim et al. [18] investigated the PVDF hollow fiber membranes using LiCl as an additive for CO_2 separation by ethanolamine as absorbent. In other work, Bottino et al. [19] studied the effect of LiCl on the morphology of PVDF hollow fiber membranes. Kung and Li [20] observed that the addition of PVP, as a hydrophilic additive, leads to increasing the porosity and average pore size of the PVDF hollow fiber membranes. Furthermore, it has been reported that adding water to the polymer solution, increases the pore size of the PVDF membrane [21].

Application of flat sheet membranes in membrane contactor systems is rarely reported in the literature. Wang et al. [22] theoretically studied CO_2 absorption in a parallel plate membrane contactor. Also, Paul et al. [23] introduced a mathematical model for CO_2 absorption in membrane contactors with flat sheet membrane using single and blended alkanolamine solvents.

To the best of our knowledge, the effect of different additives on the morphology and the performance of the flat sheet membrane contactors has not been investigated up to now. In this study the effect of different additives from different chemical families, such as salts (LiCl), polymers (PEG400), weak anti-solvents (glycerol), alcohols (methanol) and weak secondary solvents (acetic acid) was investigated on the ultimate performance of flat sheet PVDF membranes used in a membrane contactor apparatus. The prepared membranes were characterized by SEM, contact angle, tensile and gas permeation tests. Additionally, for all of the membranes, the effect of operating parameters, such as absorbent flow rate and temperature, on the absorption of CO_2 was investigated.

2. Materials and Methods

2.1. Materials

Polyvinylidene fluoride (PVDF), (Kynar720 grade, ELF Atochem Co., France) and Dimethylacetamide (DMAc) (Merck Co.) were used as polymer and solvent, respectively. Distilled water was used as the non-solvent. LiCl, PEG 400, acetic acid, glycerol, and methanol were used as additives. All chemicals with purity above 99% were purchased from Merck Co., Germany. Monoethanolamine (MEA) with the purity of 99.9%, manufactured by Arak Petrochemicals, was used as an absorbent.

2.2 Preparation of the flat sheet membranes

The PVDF powder was placed in a vacuum oven for 2 hours at 60 °C in order to remove any hydration for further usage. To prepare the polymer solutions, PVDF was dissolved in DMAc at a weight percentage of 20 % at 25 °C to form a homogeneous solution. Then it was put aside for one day to remove all entrapped air bubbles. The prepared polymer solution was placed in an ultrasonic bath for 60 minutes at 40 °C for further homogenization and elimination of potential air bubbles. In order to prepare the membranes, a film applicator (Elcometer Co., UK) was used at a fixed film thickness of 200 microns. After the casting step, the films were quickly transferred to a coagulation bath at a constant temperature of 20 °C, with a 15 sec evaporation time. The prepared membranes were kept in distilled water for two days for the complete solvent removal. To investigate the effect of incorporated additives (LiCl, PEG 400, acetic acid, glycerol, and methanol) on membrane morphology and performance, the membranes were prepared with the aforementioned procedure with 4 wt.% additives in dope solutions.

2.3 Characterization

2.3.1. Scanning electron microscope (SEM)

Morphology of the prepared membranes was observed by a scanning electron microscope (VEGA, TESCAN, Czech Republic). In order to observe the membranes cross sections, they were first put in liquid nitrogen and then were broken through at the same media after a while. Also, in order to induce conductivity, the samples were coated with gold, prior to SEM imaging.

2.3.2. Contact angle measurement

The surface hydrophilicity of the prepared membranes was measured by using the water contact angle measuring instrument (G-10, Kruss Co, Germany). This test was applied to compare the hydrophilicity of the membranes as a result of the addition of different additives. The numerical value of the contact angle was calculated using a sessile drop method and by placing 3 drops on each sample. The reported values for contact angles in Table 1 are the average of three measurements.

2.3.3. Mechanical test

The mechanical properties of the membranes were evaluated using a tensile testing machine (Instron 5566) at 25 °C with a tensile speed of 5 cm/min, an initial length of 10 cm, and a load cell of 1 kN. All of the samples had the same width equal to 2 cm. The averaged thickness of Pristine PVDF, PVDF-PEG, PVDF-Acetic acid, PVDF-LiCl, PVDF-Methanol, and PVDF-Glycerol were 72, 61, 55, 62, 81, and 47 microns, respectively.

2.3.4. Gas permeation test

Membrane pore size and porosity are important factors affecting membrane contactor performance. Higher membrane pore size and porosity facilitate the permeation rate of gas solutes into the membrane, but they also increase the wettability of the membrane which is responsible for the reduction of performance of membrane contactors [24]. Mean pore size and effective surface porosity of the prepared membranes in this study were measured by gas permeation method in triplicate for each sample. According to the literature [25, 26], the total gas permeation rate through the porous membranes can be considered as the combination of Knudsen and Poiseuille flows. In Eq. 1, the first and the second terms are representing the Knudsen and Poiseuille flows, respectively. The membrane average pore size and the effective surface porosity are obtained using Eqs. 1-4. In these equations, it is assumed that the pores are cylindrical in shapes near the surface, which is an accurate assumption regarding the SEM micrographs [24, 26].

Table1. Mechanical properties of the prepared membranes

Samples	contact angle (°)	Ultimate Tensile strength (Mpa)	Young's modulus (Mpa)	Elongation at break (%)
Pristine PVDF	88	6.05	494	15.6
PVDF-PEG	74	2.67	210	9.4
PVDF-Acetic acid	76	5.63	758	14.2
PVDF-LiCl	72	12.06	3788	2.2
PVDF-Methanol	80	6.73	518	4.6
PVDF-Glycerol	78	5.01	628	10.4

$$J = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\left(\frac{r_p}{RT}\right)\left(\frac{\varepsilon}{L_p}\right) + \frac{1}{8\mu}\left(\frac{r_p^{\,2}}{RT}\right)\frac{\varepsilon}{L_p}P_{av} \qquad (1)$$

$$J = A + B \times P_{av} \qquad (2)$$

where J is the gas permeance through the membranes (mol /m^2.s.Pa). r_p and L_p are mean pore size (m) and the effective length of the pores in the membrane structure (m), respectively. Ɛ is the membrane surface porosity, R is the universal gas constant (8.314 J/mol.K), μ is viscosity of the input gas, which is nitrogen here (kg/m.s), M is molecular mass of the input gas (kg/mol), T is input gas temperature (K), and P_{av} is arithmetic mean of the input and output gas stream pressures (Pa). Eq. 1 can be simplified as Eq. 2; while A and B are the intercept and slope of the line crossing the points, respectively.

In this test, nitrogen passes through a high-precision regulator and then enters into a dead-end flat sheet membrane cell while the permeate flow side is open to the atmosphere. In the working procedure, the pressure was increased at 0.3 bar intervals from 1 to 4 bar. After each pressure raise cycle, the permeate flow is detected by a bubble flowmeter. By plotting the J values against the mean pressure of the input and output nitrogen, and passing the optimum line through these points, the average pore size and effective surface porosity could be determined using the slope and the intercept of Eq. (2) as are given below:

$$r_p = 5.333\frac{B}{A}\left(\frac{8RT}{\pi M}\right)^{0/5}\mu \qquad (3)$$

$$\frac{\varepsilon}{L_P} = \frac{8\mu RTB}{r_p^{\,2}} \qquad (4)$$

2.3.5. Critical entry pressure of water (CEPw)

To study the wettability resistance of the prepared membranes, critical entry pressure of water was evaluated in triplicate for each sample. This test determines the maximum pore size and the minimum pressure for liquid entry to the membrane. As the pressure increases, the liquid is pushed to enter into the pores of the membrane. After each pressure raise (about 0.3 bar), a 30-minute interval will be considered to check if the fluid egresses or not. Eventually, by pressure raising of the input liquid, at a certain pressure, the liquid crosses the membrane thickness. This certain pressure is called the critical pressure, and the maximum pore size of the membrane is then determined regarding this critical pressure by the following equation [27].

$$\Delta P = \frac{2\delta \cos\theta}{r_p} \tag{5}$$

where δ is the surface tension of water (72.8×10^{-3} N/m), θ is the contact angle between water and the membrane surface (equal to 0 degree for the first drop), r_p is the maximum pore that the water passes through, and ΔP is the critical pressure of the input water to the membrane.

2.4. Gas-liquid membrane contactor test

This test was performed in a gas-liquid membrane contactor apparatus by using a flat membrane module and MEA as the absorbent. The mixtures of (20/80 wt/wt) CO_2/N_2 and (20/80 wt/wt) MEA/H_2O were applied as the feed gas stream and the absorbent, respectively. A schematic of the constructed apparatus in this study has been illustrated in Fig. 1. Different operating parameters such as liquid and gas pressures, gas and liquid flow rates and also the absorbent temperature were controlled as adjustable parameters in the conducted experiments. Eqs. 6 and 7 were used to calculate the absorption performance (η) and the CO_2 flux (J) through the membranes [28, 29].

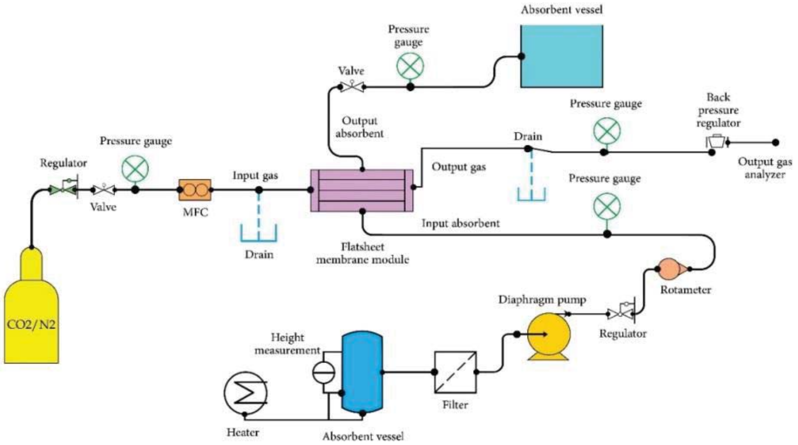

Figure 1. Schematic view of the constructed membrane contactor apparatus

$$\eta = \frac{Q_{G(in)} \times C_{G(in)} - Q_{G(out)} \times C_{G(out)}}{Q_{G(in)} \times C_{G(in)}} \tag{6}$$

$$J = \frac{Q_{G(in)} \times C_{G(in)} - Q_{G(out)} \times C_{G(out)}}{0.0224 \times A} \tag{7}$$

where Q_G and C_G stand for gas flow rate (m^3/s) and CO_2 concentration (mol/m^3), respectively. Subscripts (in) and (out) show input and output gas streams. A is the contact area of the membrane between gas and liquid streams (m^2) CO_2 molecules have three paths to traverse from the gas into the liquid stream. The most important and the greatest amount of resistance within the path (from the gas mixture, then through the membrane pores and finally into the liquid phase) is related to the liquid phase [29]. As a result, the total resistance was determined by the liquid phase.

To investigate the effect of absorbent flow rate, the input gas flow rate, consisted of 20% CO_2 in nitrogen, was fixed at 1000 (ml/min); then, different flow rates of the input absorbent (100, 200, 400 and 500 (ml/min)) were investigated. Subsequently, the absorption flux and the related efficiency were calculated using the aforementioned equations. It is noteworthy to mention that it took about 100 minutes to fix the experiment conditions and the data were recorded thereafter. The effect of the input absorbent temperature was studied at constant gas and absorbent flow rates. The absorbent and the gas feed flow rates were fixed at 400 and 1000 (ml/min), respectively. The temperature of the absorbent was fixed at 30, 40, 60 and 70 ºC, by turning on the heating elements inside the feed chamber. It should be stated that the pressure difference between the gas and liquid inside the module was fixed and controlled at 0.5 bar.

3. Results and Discussion

3.1. Membranes morphology

Addition of nonsolvent additives into the polymer solution has a significant effect on the dope thermodynamic stability as well as solvent-nonsolvent exchange rate in the phase-inversion process and results in different morphologies. Non-solvent additives can reduce miscibility of the system, improve the precipitation rate of the solution and cause macrovoid formation in the membrane structure, thermodynamic effect. Contrary, solvent-nonsolvent exchange rate decreases by increasing viscosity of the dope solution in presence of some additives and forms sponge-like structure membranes, kinetic effect [3]. In fact, the competition of the thermodynamic and kinetic effects using different additives determines the final membrane morphology. Morphology of the pristine PVDF membrane is shown in Fig. 2. The membrane had a finger-like structure with a spongy layer beneath it. Addition of PEG and LiCl decreased the miscibility, and thermodynamic stability of the system results in macrovoid formation [19]. On the other hand, LiCl possessed strong interaction with the polymer (electron donor group of PVDF) and solvent, tending to delay the dope precipitation, which partially weakened the thermodynamic impact of LiCl and reduced the size of macrovoids [17, 19, 27]. Addition of acetic acid and methanol suppressed large finger-like pores to thinner pores and formed more sponge-like structure beneath [3]. This could be attributed to the increase of dope viscosity which resulted in a reduction of solvent and nonsolvent exchange rate that delayed the phase inversion process [27, 28]. Glycerol increased the viscosity of the solution and altered the finger-like structure in the upper part to the tear-like structure. Increase in viscosity by adding glycerol has been also reported for PVDF-HFP [17,30]. It is due to the formation of bridge complexes between glycerol, polymer fluorine and solvent, which deteriorated the polymer chains flexibility and caused a decrease in distributive freedom of the polymer in the dope solution [2]. Furthermore, drop shape pores can be observed in membrane bottom because of slow precipitation that impeded the formation of a wall between droplets that caused small droplet combining and forming larger droplets that generated drop shape cavities [27, 31].

3.2. Membranes mechanical properties

The effect of additives on the mechanical properties of the prepared membranes was evaluated and presented in Table 1. The obtained results revealed that adding the additives generally increase Young's modulus of the prepared membranes. The only exception was observed in the case of PEG as an additive. Presence of PEG increased the bulk porosity of the membranes and dramatically drops Young's modulus from 494 to 210 MPa, compared to the Pristine PVDF. The highest value of Young's modulus, 3788 MPa, was observed for the prepared membranes with LiCl. In addition, PVDF-LiCl membranes had the lowest elongation at break, 2.2%, and the highest ultimate tensile strength, 12.06 MPa. However, this observation was somewhat unexpected. As mentioned above, LiCl has a strong interaction with the polymer and solvent tending to delay the dope precipitation and reduces the size of macrovoids. Therefore, this reduction in the size of the macro-voids in PVDF-LiCl membranes may be a reason for the observed surprising mechanical properties. However, higher Young's modulus of PVDF-Acetic acid, PVDF-Methanol, and PVDF-Glycerol membranes compared to that of Pristine PVDF is related to their lower bulk porosity. In another work, Naim et al. have also reported that the mechanical strength of membranes increased by using the additives in the polymer solution [31]. In addition, the tensile analysis showed that the pristine PVDF membranes had the highest elongation at break.

3.3. Gas permeation results

The effective surface porosity, the average pore size, and nitrogen permeance were determined using the gas permeation test as described in section 2.4.5. The obtained results are presented in Table 2. However, it should be noted that the determined mean pore sizes by gas permeation test, like other methods i.e. AFM and solute transport test, does not have a physical meaning especially for membranes prepared by phase inversion method. It could be used quantitatively to compare different membranes with different preparation conditions [16].

Regarding the obtained results, it was revealed that the pristine PVDF membrane had the highest N_2 permeance; while, PVDF-glycerol had the lowest due to the sponge-like structure and a higher degree of tortuosity.

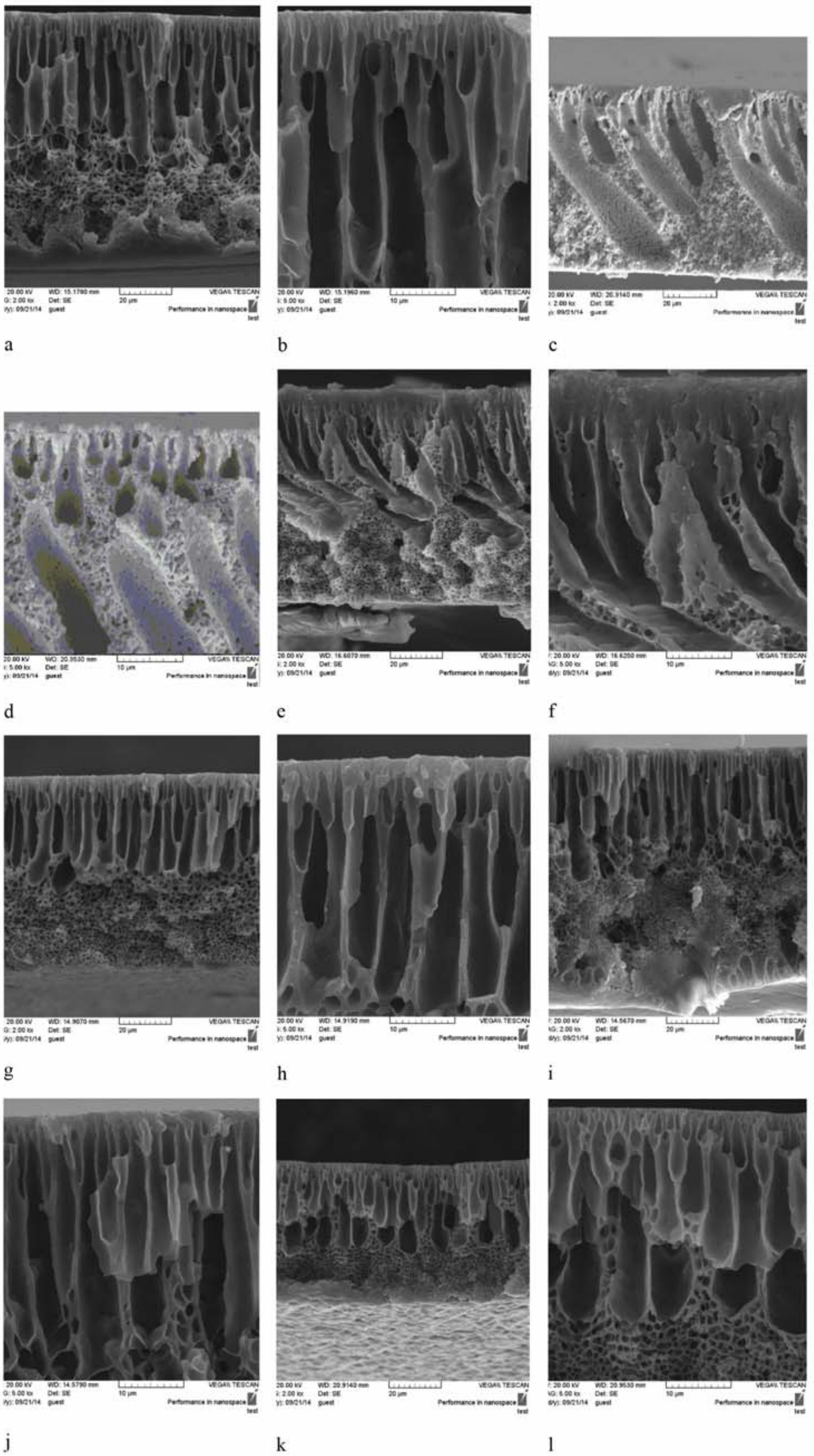

Figure 2. SEM photographs of the cross-section of the prepared membranes pristine PVDF (a,b), PVDF-PEG (c,d), PVDF-LiCl (e,f), PVDF-acetic acid (g,h), PVDF-methanol (i,j), PVDF-glycerol (k,l)

3.4. Resistance against wettability

In order to have a long-term stable membrane contactor operation, it is crucial that the membrane pores be completely gas filled. Therefore, high resistance against wettability is a necessary characteristic for gas-liquid the membrane contactors. In this study, the wetting resistance of the prepared membranes was characterized regarding the contact angle and the critical entry pressure as presented in Table 2. The contact angles of the prepared membranes decreased by the addition of the additive to the polymer solution, which is due to the increase in porosity that enhances water dispersion within the structure [31, 32]. Since the additives had low molecular weight and high solubility in water, they were completely washed out from the membranes during phase inversion process that causes higher membrane surface porosity. The critical entry pressure experiments were performed to evaluate membrane the wetting resistance by presenting the pressure that the liquid starts to fill up the membrane pores [31]. All the prepared membranes had a higher CEPw compared to pristine PVDF. The higher amount of CEPw is related to the sponge-like structure of the membranes and also their lower mean pore size. For instance, the PVDF-glycerol membrane had the highest CEPw due to its sponge-like structure and smaller pore size. In general, the addition of additives caused the suppression of macro-voids and subsequently influenced the CEPw of the membranes [33].

3.5. CO_2 absorption performance of the membranes

CO_2 separation performance of the prepared membranes was evaluated by using the constructed membrane contactor apparatus. The obtained results are shown in Figs. 3 and 4. As mentioned above, the presence of the additives into the dope solution helped to prepare membranes with lower mean pore size and higher effective surface porosity. It should be considered that the higher surface porosity and simultaneously the lower pore size could increase the CO_2 separation.

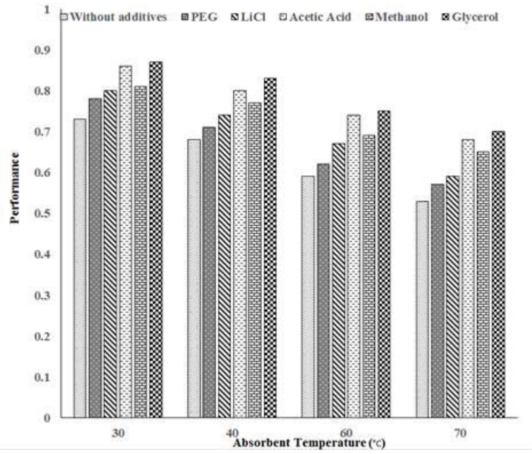

Figure 3. Effect of absorbent flowrate on the CO_2 absorption efficiency

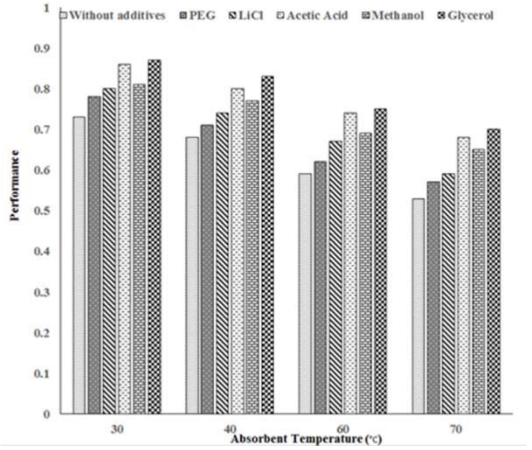

Figure 4. Effect of absorbent temperature on the CO_2 absorption efficiency

Table 2. Gas permeation and water critical entry pressure test results for prepared membranes

Samples	N_2 Permeance at 10^5 Pa ($\frac{10^{-6}cm^3}{cmHg.s.cm^2}$)	Effective surface porosity (m^{-1})	Mean pore size (nm)	CEPw (bar)	Maximum pore size (nm)
Pristine PVDF	142.5	543.84	86	5.1	98
PVDF-PEG	128.7	851.45	59	5.7	69
PVDF-Acetic acid	91.4	1384.20	32	7.8	44
PVDF-LiCl	114.9	1047.62	65	6.3	71
PVDF-Methanol	109.2	1160.73	28	6.9	36
PVDF-Glycerol	86.5	986.91	21	9.3	32

The obtained results showed that all the prepared membranes with additives (PEG, LiCl, acetic acid, methanol, and glycerol) had higher separation performance toward the pristine PVDF membrane. This general behavior could be attributed to the positive effect of the applied additives on surface porosity, pore size and hydrophobicity of the prepared membranes. As expected, the highest CO_2 separation performance was observed for PVDF-glycerol membrane. For instance, separation performance of CO_2 at an absorbent flow rate of 500 (ml/min) and absorbent temperature 70 °C is respectively equal to 0.91 and 0.7. It is worthy to be noted that regarding the gas permeance analysis, this membrane had the lowest mean pore size, 21 nm, and also the lowest maximum pore size, 32 nm. Therefore, it could be expected that the PVDF-glycerol had a higher wetting resistance compared to the other prepared membranes. Similar to the conventional amine columns, with increasing the absorbent flow rate the separation performance enhances for all of the prepared membranes. For example, separation performance increased from 0.67 to 0.82 by increasing the absorbent flow rate increased from 100 to 500 (ml/min) in PVDF-LiCl membrane. In fact, increasing the absorbent flow rate eliminated the concentration polarization effects (preventing CO_2 saturation) and consequently enhanced the separation performance of CO_2. Additionally, at higher absorbent flow rates the concentration driving force was kept up and mass transfer was improved.

According to Fig. 4, the separation performance of CO_2 enhanced with decreasing the absorbent temperature. For instance, with raising the absorbent temperature from 30 to 70 ˚C the separation performance of CO_2 dropped from 0.86 to 0.68 in the case of the PVDF-acetic acid membrane. In fact, by increasing the temperature the MEA absorption capacity reduced and the reaction between CO_2 and amine moved in the opposite direction due to its exothermic nature.

4. Conclusions

In this study, the effect of incorporation of different additives including LiCl, PEG400, glycerol, methanol and acetic acid on the separation performance of flat sheet PVDF in a membrane contactor setup was investigated. The membranes were evaluated by physical, structural, tensile and membrane contactor tests. Incorporating the additives in the dope solution yields to the preparation of membranes with higher effective surface porosity and also lower mean pore size. The membranes prepared with introduced additives in this study have higher CO_2 separation performance compared to the pristine PVDF. Separation performance of CO_2 improved with the absorbent flow rate increase due to high mass transfer driving force. Also, the exothermic nature of the reaction between absorbent and CO_2 caused a reduction in absorption performance with temperature increase. Regarding the obtained results, the prepared PVDF-glycerol membrane was found as distinguished one for performing in a membrane contractor due to its low pore size.

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