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Facilitated transport of CO_2 through novel imidazole-containing chitosan derivative/PES membranes

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ABSTRACT

In the present study, anew imidazole alkyl derivative of chitosan (Im-CS) synthesized and characterized by the FT-IR and H-NMR spectroscopy. This derivative was blended in various ratios with polyethersulfone (PES) to fabricate newly integrally skinned PES membranes. Scanning Electron Microscopy (SEM) was used to study the changes in the membrane morphologies. The prepared membranes were used for the separation of CO_2fromCH$_4$. Our findings indicated that by adding a small amount of Im-CS, membrane performance was improved significantly. In addition, effect of feed pressure and feed temperature on the performance of the prepared membranes was investigated at this study.

Key words: Membrane, Polyethersulfone, Fixed facilitated transport, Chitosan, Carbon dioxide, Methane.

1. Introduction

Natural gas sweetening is a well-known process for the separation of the acidic gases like CO_2 and H_2S from methane and ethane as the main components of the natural gas. This process prevents the corrosion of pipelines and equipment and enhances the heat value of transported natural gas. Up to now, several techniques have been reported for the separation of CO_2 from gas mixture. Separation by solvent/sorbent, cryogenic distillation and membranes are three basic methods that have been used for gas separation. Solvent/sorbent process and cryogenic distillation have some drawbacks including high energy and chemical consumption and environmental pollution[1]. Membrane processes in comparison with other methods have some advantages such as less energy consumption, lower capital cost and ease of operation.[2-4]
Various types of membranes including inorganic, metal and polymeric ones are used for gas separation. Mechanical and thermal stability, cheapness and proper chemical strength make PES a proper polymer for preparation of the Integrally-skinned asymmetric membranes that provide high gas permeation because of their thin skin layer[5-13].

Many researches use amine-containing polymers for facilitated transport of CO_2 using thin film composite (TFC) membrane. In these researches, the effect of the concentration of amine containing polymer, feed pressure, feed temperature and relative humidity were investigated[14-19]. Generally, high selectivity and permeability can be achieved using facilitated transport membranes (FTMs). Presence of some CO_2 carriers in FTMs is the reason of their high CO_2/CH_4 selectivity. Amine functional group is a good carrier for CO_2that can transport it via the following reversible reactions. CH_4 cannot contribute in these reactions, so the final result is the enhancement of CO_2 flux across the membrane[11]

$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH^+_3$
$CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH^+_2$
$R_3N + H_2O + CO_2 \leftrightarrow R_3NH^+ + HCO_3^-$

There are many reports about using of amino-containing polymers as fixed site carriersin facilitated transport membranes. Shen et al. prepared composite membranes consisting of poly (2-N, N-dimethyl aminoethyl methacrylate-co-acrylic acid sodium) as selective layer and polysulfone (PS) ultrafiltration membrane as porous non-selective support. By measuring the real and ideal CO_2/CH_4 selectivity of prepared membranes, it was shown that real selectivity was not as good as the ideal selectivity[16]. Hägg et al. used high molecular weight polyvinyl amine (PVAm) casted on polysulfone (PSf) supports for CO_2/N_2 separation. Selectivity up to 197 was obtained by using of these membranes[20]. Poly (N-vinyl-sodium aminobutyrate-co-sodiumacrylate) (VSA–SA)/polysulfone (PS) composite membranes were used by Wang et al. for CO_2/CH_4separation. They found that the ideal selectivity is 10 times higher than real selectivity[21]. Deng et al. prepared some composite membranes consisting of polyvinyl amine (PVAm)/ PVA blend as separation layer and porous polysulfone (PSF) as support for separation of the CO_2/CH_4 mixture. They investigated the effect of feed pressure and relative humidity. They documentedthe CO_2/N_2 separation factor of up to 174 and a CO_2permeanceup to $0.58 m^3(STP)/(m^2\ h\ bar)$[22]. Cai et al. prepared polyallylamine (PAAm)/PVA blend coated on PSF ultrafiltration membrane. The real and ideal performances of the synthesized composite membrane for the separation of CO_2 from CH_4 and N_2were investigated. They found that the membrane performance was improved with an increase in PAAm content followed by an optimum condition[23].

Investigation of the CO_2/N_2 permeation of PVA/poly (ethyleneimine) (PEI)/poly (ethyleneglycol) (PEG) blend membranes at various blend compositions by Hamouda et al. showed that only CO_2 is transported by the facilitated transport mechanism[24].

It has been confirmed that the presence of water increases the CO_2 permeability in facilitated transport mechanism. Therefore, hydrophilic polymers such as PVA and PEG have been widely used as suitable and compatible materials for holding the amino containing polymer in membrane fabrication[14, 15, 22-25].

Chitosan is a linear polyamine polysaccharide produced by deacetylation of chitin. The presence of NH_2group in chitosan backbone, make it soluble in some organic acid diluents, so membranes can be made by casting of these solutions[26]. However, the low solubility isthe main drawback of chitosan, therefore, numerous chemical modifications have been introduced into the chitosan backbone to make it soluble in water or organic solvent systems [27-30].

Nevertheless, in the gas membrane separation field, the application of chitosan is limited and quite a few articles have been published in this field. Ito et al. used water-swollen chitosan for CO_2/N_2 separation. They achieved CO_2 permeability of 2.5×10^{-8} cm^3(STP)cm/Scm^2cmHg and CO_2/N_2 selectivity of 70[31].Feng et al. used trimesoyl chloride crosslinked chitosan membranes for CO_2/N_2 separation. They observed that the membranes with higher degree of crosslinking undergoes higher swelling[32]. Through using a series of chitosan/Pebax blend membranes for CO_2/CH_4 and CO_2/N_2 separation by Jiang et al., it was found that the membranes show high CO_2 permeability and high stability. They observed that highest CO_2 permeability was achieved when chitosanto Pebax mass ratio was 1:1.They related the high permeability of the membranes to the incorporation of Pebax. They justified that high CO_2 permeability of these membranes results from the incorporation of Pebax[33]. El-Azzami et. al prepared swollen chitosan membranes for CO_2 separation from hydrogen and nitrogen. They used prepared membranes at elevated temperatures up to 150°C and low feed pressure of 5 atm[34]. They also used arginine salt–chitosan membranes for separation of CO_2 from H_2/N_2, and found that presence of arginine salts in swollen chitosan membranes enhances the CO_2 permeability because the arginine salts increases the number of amino groups as well as water levels in the membranes [35]. Shen et al. developed miscible carboxymethyl chitosan/polyethyleneimine blend membranes for CO_2/N_2 separation. It was observed that water vapor enhances the membrane performance[36]. As far as we know, in this field, no chemically modified chitosan except carboxymethyl chitosan was used for CO_2 separation. So in the current study, we tried to synthesize a new organic soluble derivative of chitosan and use of it as a fixed carrier for facilitated transport of CO_2 to produce newly integrally-skinned asymmetric membranes based on PES. Here in, the effect of Im-CS concentration on the morphology and the separation performance of fabricated membranes were investigated. Furthermore, the effect of feed temperature and feed pressure on the permeance and selectivity of produced membrane were studied.

2. Experimental

2.1. Materials

Polyethersulfone (PES Ultrason E6020P with MW = 58,000 g/mol) was obtained from BASF (Germany) and poly (vinyl alcohol) (PVA) was purchased from Kuraray. Chitosan (Medium molecular weight), phenyl chloroformate, N-(3-Aminopropyl)-imidazole, phthalic anhydride, and pyridine were obtained from sigma-Aldrich. All other solvents and chemicals were reagent grade and used without further purification.

2.2. Instrumental analysis

^{1}H-NMR spectra were measured by Bruker 400 MHz NMR spectrometer inDMSO-d6 at ambient temperature. FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100FTIR spectrophotometer. Elemental analysis was used to establish the DS-values of chitosan derivative.KYKY-EM3200Scanning Electron Microscope (SEM) was used for investigating the cross-sections of the membranes.

2.3. Synthesis N-phthaloylchitosan (phth-CS)

N-Phthaloylchitosan was prepared according to the procedure reported by Kurita[37]. A 500 mL round-bottom flask was charged with chitosan (5 g, 30.8 mmol of glycosidic units), *N,N*-dimethylformamide (200 mL) and water (10 ml). Then, the reaction flask was heated to 120°C and 13.83 g phthalic anhydride was added. After that, the mixture was stirred for 8 hours at 120°C. Afterward, the reaction mixture was cooled to room temperature and poured into 2 Lit of ice water with stirring, and the precipitate was washed repeatedly with deionized water. The resulting product was then washed with methanol several times and dried at room temperature to give 7.3 g of a light orange solid. The degree of substitution (DS) was 1.0.

2.4. Synthesis of phenylcarbonated-N-phthaloylchitosan(Carbonate-Phth-CS)

A 250 mL flask was charged with 150 mL *N,N*-dimethylacetamide and 6 g of *N*-phthaloyl chitosan and the mixture was stirred at 80°C overnight to swell completely. Then, 8 g lithium chloride was added and the reaction mixture was cooled slowly to room temperature to obtain a brown viscous solution. Then, 10 mL pyridine (126.6 mmol) was added and the reaction flask was cooled in a salt-ice bath (-5-0°C). After that, 4 mL phenyl chloroformate (31.70 mmol) was added dropwise to this solution with stirring. The reaction mixture was stirred at 0 °C for 2 hours. Then, the ice bath was removed and the mixture was stirred for an additional 22 hours at room temperature. Finally, the mixture was poured into a large amount of ice-water with stirring, and the yellow precipitate was washed repeatedly with deionized water. The resulting product was then washed with methanol several times and dried at room temperature to give 7.9 g of a light yellow solid. The degree of carbonate substitution (DS) was 0.85.

2.5. Synthesis of Imidazole containing derivative ofchitosan(Im-CS)

50 mL DMF and 5 g phenylcarbonated-N-phthaloylchitosan were added to a 100 mL flask and the mixture was stirred at room temperature until a solution was obtained. To this 10 mL (83.8mmol) of N-(3-Aminopropyl)-imidazole was added and the solution was stirred for 24 hours at room temperature. The resultant solution was precipitated in THF. The precipitate was filtered and washed repeatedly with THF and then with diethyl ether, and dried at room temperature to give 2.40 g of a yellow powder.

2.6. Membrane preparation

The various amounts of Im-CS were dissolved in NMP. Then, PES was added until the total polymer concentration reach to 29.5 wt.%. The compositions of the solutions of PES:Im-CS were 29.5:0, 29:0.5, 28.5:1, 28:1.5, and 27.5:2. Dry/wet phase inversion technique was used for preparation of the integrally skinned asymmetric membranes. A stainless steel homemade applicator was used to prepare polymeric films with the thickness of 250 µm. The polymer-coated glass plates were kept at ambient temperature for 2 min and then immersed in a non-solvent bath containing water and isopropanol in composition of 75:25. After detaching the membrane from the glass plate in non-solvent bath, it was rinsed with fresh tap water and kept in distilled water overnight and then was dried at ambient temperature for 24 h.

2.7. Gas permeation apparatus

A mixed gas set up as schematically shown in Fig. 1 was used for gas permeation studies. The prepared membranes were cut into rectangular 5 × 3 cm shape and were placed in appropriate stainless steel cell that housed in a temperature-controlled electronic oven. The composition of the feed gas was controlled by mixing the specific mass flow rate of CO_2 and CH_4 using Brooks mass flow controller. Although primary and secondary amines can transport the CO_2 by the facilitated transport mechanism in the absence of water (as discussed before); it is believed that in the presence of the water and carrier (primary and secondary amine), CO_2 can form amine–CO_2–H_2O complexes and small HCO_3^-ion. Bicarbonate ion (HCO_3^-) acts as a mobile carrier that can transport CO_2 across the membrane and enhances the diffusion rate of CO_2 through the membrane significantly. Because of the acceleration of the facilitated transport of CO_2 and higher CO_2 permeability in the presence of water vapor, for the separation of CO_2 from gas streams in facilitated transport membranes[22], the feed gas is saturated with water vapor. Here a bubble humidifier was used for humidifying the feed. Desired feed presser in permeation cell was achieved by using a backpressure regulator. The Argon gas was used to sweep the permeate gas. The permeate was cooled down to ambient temperature and condensed water was removed using water knockout. The composition of the permeate stream was determined using Agilent gas chromatograph equipped by a thermal conductive detector (TCD). When the thickness of the membrane is measurable such as dense polymeric membrane the performance of the membranes is reported using gas permeability. Barrer is most common unit for reporting the permeability of the membrane, which is defined as

$$1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cmHg}$$

In integrally skinned asymmetric membranes, the skin layer is not detectable and measurable correctly. Hence the pressure-normalized fluxes $(P/l)_i$ is more common for determining the gas permeability of the asymmetric membranes which can be presented using the following equation:

$$\left(\frac{P}{l}\right) = \frac{Q_i}{\Delta p_i\, A} \quad (1)$$

where Q_i is the volumetric flow rate of the permeate gas i at STP, Δp_i is the trans membrane pressure and A is the effective surface area of the membrane. Gas permeation unit (GPU) is most common unit for pressure-normalized flux calculated as follows:

$$\text{GPU} = 1 \times 10^{-6} \text{cm}^3\text{(STP)/cm}^2\text{.s.cmHg}$$

The following equation was used to calculate membrane selectivity [38, 39].

$$\alpha_{CO2/CH4}=(P/l)_{CO2}/(P/l)_{CH4}=[x_{CO2-p}/x_{CH4-p}]/[x_{CO2-f}/x_{CH4-f}] \qquad (2)$$

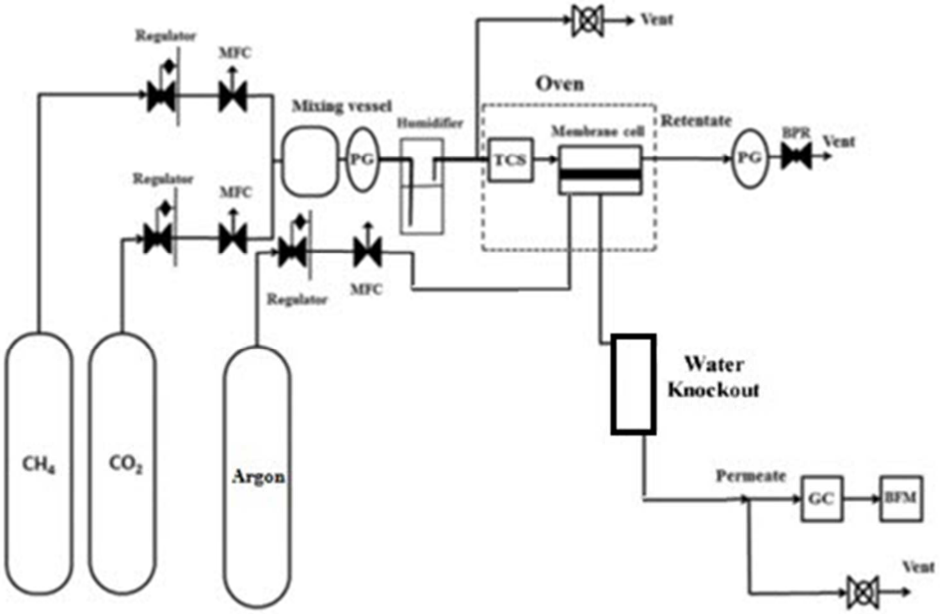
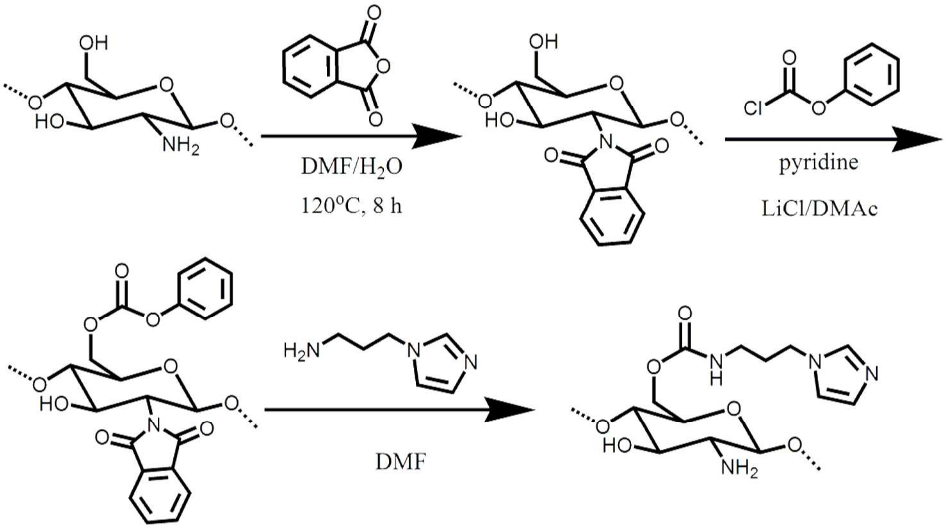


Fig. 1.Schematic diagram of experimental setup for gas permeation test

3. Results and discussion

3.1. Synthesis and characterization of chitosan derivatives

The process for the synthesis of Im-CS in this research is shown in Scheme 1. First, amino groups of chitosan were blocked using phthalic anhydride in DMF/H_2O (95:5) mixture to prevent their participation in the subsequent reaction. In the following step, primary hydroxyl groups of N-phthaloylchitosan were converted to active phenyl carbonate groups. Finally, the carbonate derivative was reacted with N-(3-Aminopropyl)-imidazole, which eliminates phenol as a leaving group. According to the literature[40], phthalimido groups of the glycosidic units also can deprotect by primariy amines.The final derivative has two types of basic groups (i.e. imidazole groups and primary amino groups) which can work as good carriers for CO_2 facilitated transportation.



Scheme 1. Synthetic procedure for the chitosan derivatives.

3.2. Spectral characterization of chitosan derivatives

The chemical structure of the chitosan derivatives were characterized by FT-IR and^{1}H NMR analysis. The FTIR spectra of chitosan (CS) and its derivatives are shown in Figure2. In the spectrum of N-phthaloylchitosan, characteristic peaks of the phthalimido group have appeared at 1775 (imide C=O), 1710 (imide C=O), and 719 cm^{-1} (aromatic). In the spectrum of carbonate derivative, signal at 3070 cm^{-1}is related to the aromatic C-H bonds, and signals at 1600 and 1495 cm^{-1} are related to the aromatic C=C bonds, the peak at 1765 cm^{-1}is related to carbonate group on the chitosan backbone. Furthermore, the intensity of OH band around 3500 cm^{-1}is decreased in the carbonate derivative spectrum. In the spectrum of Im-CS, the characteristic peaks of phenylcarbonate and phthalimido groups are eliminated and a new peak at 1712 cm^{-1} appeared that is related to the carbonyl of carbamate group.

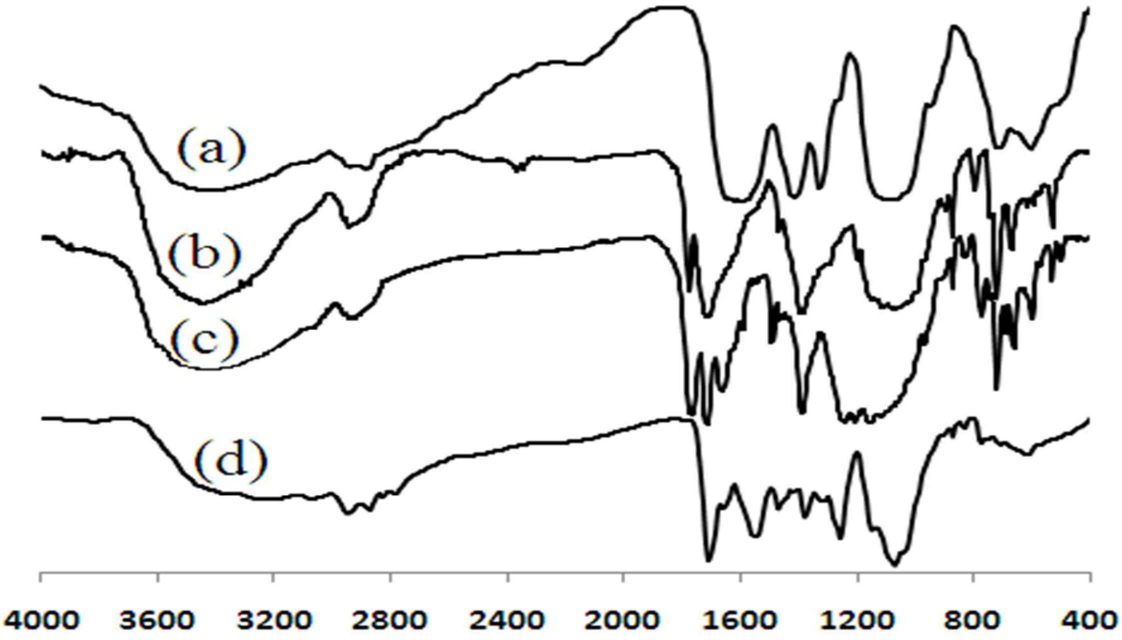


Fig.2.FT-IR spectra of CS (a), Phth-CS (b), Carbonate-Phth-CS(c), and Im-CS (d).

The ^{1}H-NMR spectra of Carbonate-Phth-CS and Im-CS are shown in Figure3. The protons in both structures are assigned completely in the figures. In the spectrum of Carbonate-Phth-CS signals at the range of 6.95–7.35 ppm correspond to the aromatic hydrogens of phenyl group and the signal appeared at 7.78 ppm corresponds to the aromatic hydrogens of phthaloyl group. The signals at the range of 4.9-5.3 ppm are related to the anomeric hydrogen of chitosan backbone, and the other glycosidic protons of chitosan are observed at the range δ 3.20-4.60 ppm. In the ^{1}H-NMR spectrum of Im-CS the characteristic peaks of the phenyl and phthaloylgroups disappeared. Instead, new signals correspond to the propylimidazole group have appeared at ~1.84, 3.18, 6.85, 7.17, and 7.46 ppm.

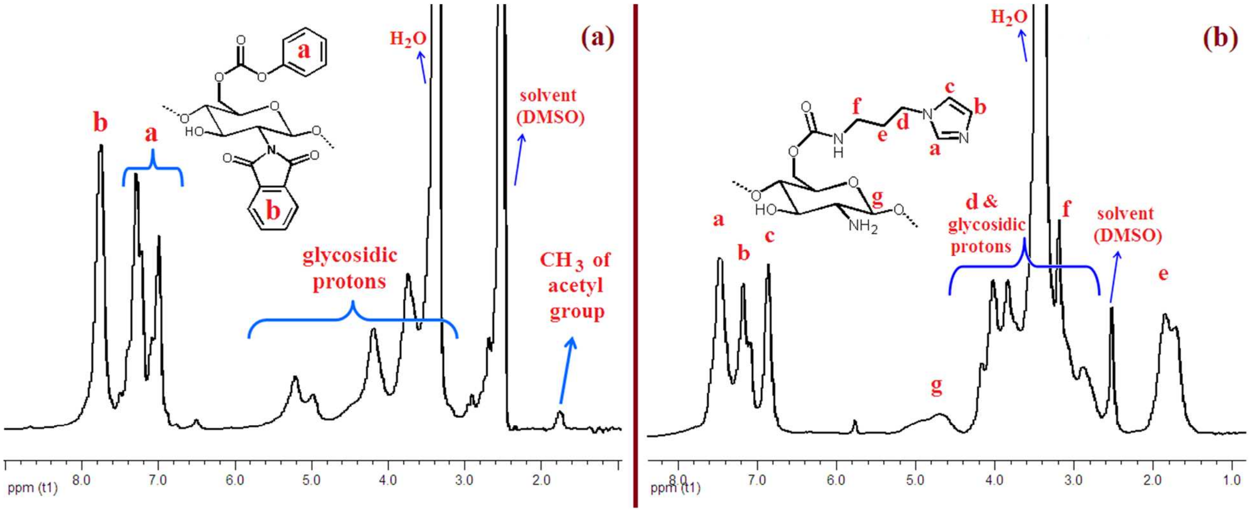


Fig.3.^{1}HNMRspectra of Carbonate-Phth-CS(a) and Im-CS (b).

3.3. Effect of Im-CS on the membrane morphology

According to the literature, morphology and performance of assymetric membranes can be affected by additives[41, 42]; Therefore, the SEM images of the cross section of prepared membranes are taken to investigate the effect of Im-CS on the morphology of PES membranes (Fig. 4).

As can be seen in Figure 3, all of the prepared membranes show a thin skin layer at the top surface and a tear like and finger like pores at the porous sublayer. This structure is a classical asymmetric structure for integrally skinned assymetric membranes[5, 13]. For itegrally-skkined asymmetric membranes and in a solustion-diffusion mechanism, membranes properties including skin layer'sthickness[13, 43], overall porosity of membrane[7] and surface micro defect [43]significantly affect gas permeability of membranes. Higher membrane porosity, thinner skin layer and presence of micro defects lead to higher gas permeability across the membrane[7].As is evident from Figure 4, PES:Im-CS membranes in comparison to pure PES membranes have larger finger like pores. Also small pores near the skin laye are disappeared in PES:Im-CS membranes.

Higher porosity of sub layer in integrally-skkined assymetric membrane is resulted from higher phase inversion rate throughout membrane formation from polymeric film[42]. Presence of an additive can affect phase inversion rate significantly[44].The presence of a hydrophile additvie in casting solution enhances phase inversion rate and results in higher porous sublayer[45, 46].The used non-solvent was a mixture of 75 V.% of water and 25 V.% of isopropyl alchol, therfore Im-CS as a hydrophilic polymer enhances the phase inversion rate significantly. Higher phase inversion rate leads to higher porosity of sub layer and an enhancement of the size of finger like pores of sub layer.

Skin layer thickness is the another membrane properties that is determind by the phase inversion process[47]. In integraly skinned asymmetric membranes usually skin layer has different thickness at diffrenent point of membranes.Also measureing the skin layer thickness of these type of membranes using SEM images are not easy as thin film composite membranes, because the boundary between the real skin layer and transition layer is not detectable appropriately.

Therfore for integrally skinned asymmetric membranes, apparent skin layer thikness is defined and can be calculated using following equation;

$$l = \frac{P_i}{\left(\frac{P}{l}\right)_i} \qquad (3)$$

Where P_i is the interinsic permeability of dense membrane for gas i and $(P/l)_i$ is the pressure-normalized flux of membrane for gas i[13]. Interinsic permeability of a dense membrane for a specific gas is a constant value. Hence an increase in pressure-normalized flux of membrane for a non-reactive gas implies that the apparent skin layer thickness is decreased. As can be seen in Fig.5 generally by increasing Im-CS conentration the pressure-normalized flux of CH_4 (as non-reactive gas in contrast with CO_2) enhances that implies the thickness of skin layer (l) in eq. is decreased.

As described by the Kawakami et al[48] in a ternary polymer/solvent/coagulant system, skin layer thickness is determinedby liquid–liquid demixing as well as polymer–liquid demixing in the phase separationprocess. In an instantaneous demixing between solvent and no-solvent, an ultrathin skin layer supported by a poroussubstrate is formed. In contrast, in a delayed demixing proccess between solvent and no-solvent a dense and thick skin layer is formed.

In other words by increasing Im-CS concentration the apparent skin layer thikness of integrally skinned asymmetric membranes decreases. Because high phase inversion rate results in a hurried formation of skin layer and subsequently thinner skin layer.

As mentioned before another intersting observationis the decrease of the small tear like pore near the top surface of membranes. These tearlike pores at the near of the skin layer results in the creation of micro defects and decreasing the membrane selectivity. Leroux and Van Schalkwyk [49]reported that gas permeability as well as gas pair selectivity of polysulfone halow fiber membrane were enhanced by the surfactant additive. They reasoned that the surface tension of spinning solution is affected by the additive and this leads to decrease of defects during phase inversion rate. Therefore, same justification can be used for the smaller tear like pores of the membranes at the presence of Im-CS that may affect the surface defects of membranes.

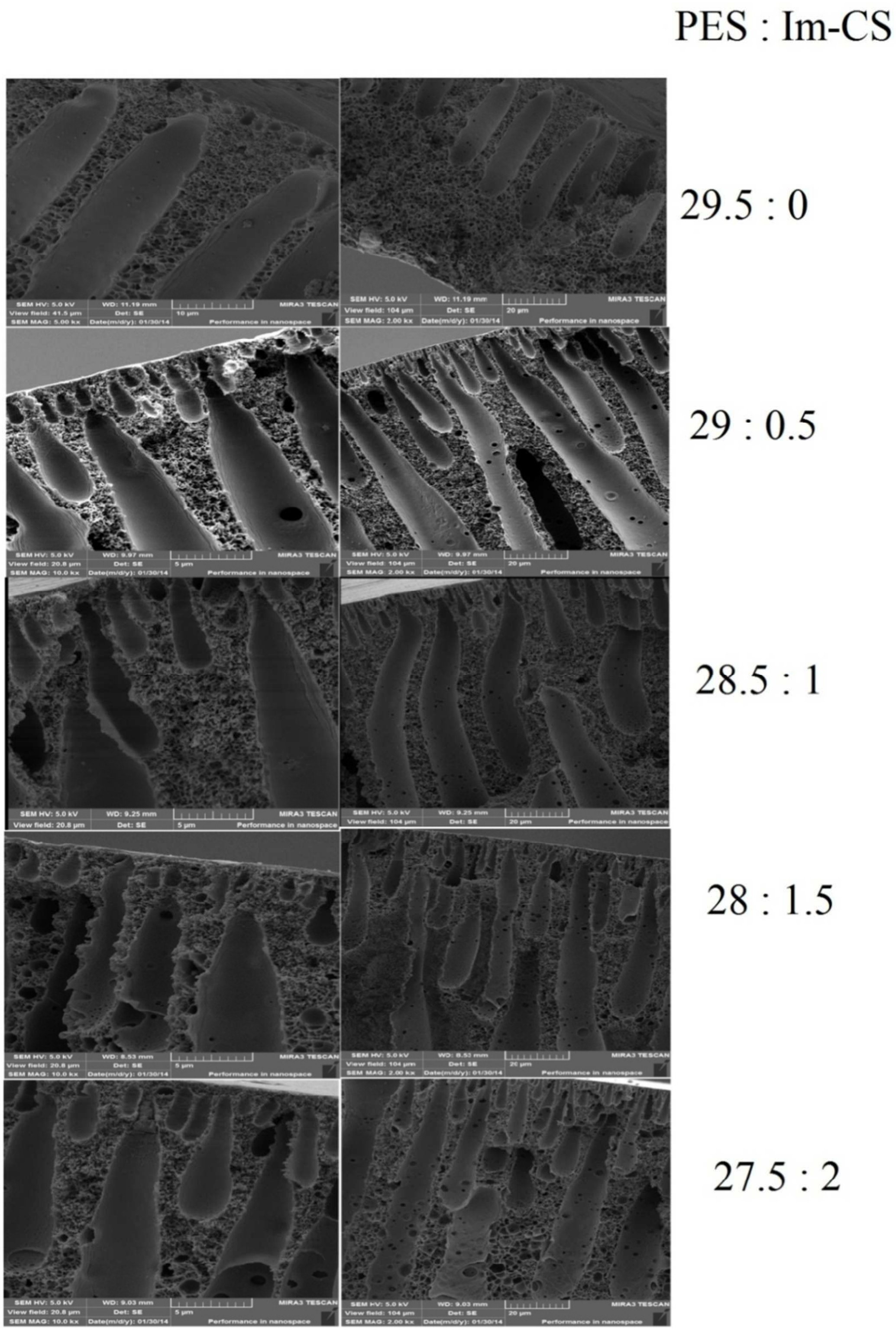


Fig.4. Effect of Im-CS concentration on the morphology of PES integrally skinned asymmetric membranes

The SEM images of the top surface of uncoated pure PES membrane (a), PES:Im-CS with the blend composition of 28.5:1 (b) PES:Im-CS with the blend composition of 27.5:2 are shown in Fig.5.

As can be seenfrom these figures uncoated pure PES membranes has a dark point on the top surface. This dark point is a pinole or defect of the membrane surface that is dissapeared in PES:Im-CS membranes. This observation can cofirm our previous discussion about the disappearance of tearlike pores at the near of the skin layer and surface defect at the presence of Im-CS additive.

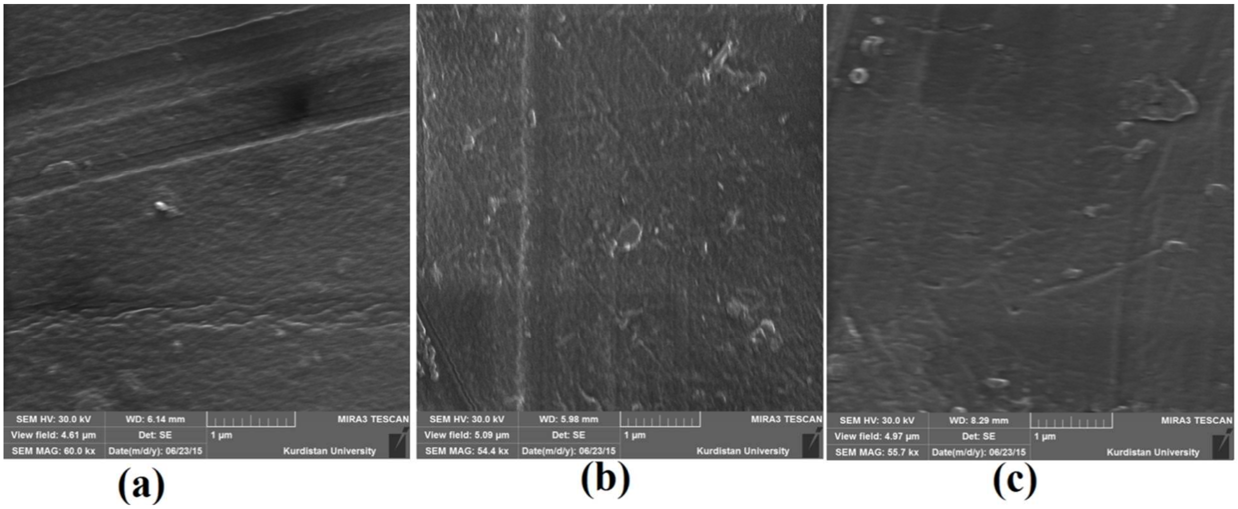


Fig. 5 SEM image of the top surface of uncoated prepared membranes; (a) pure PES, (b) PES:Im-CS with the blend composition of 28.5:1 and (c) PES:Im-CS with the blend composition of 27.5:2

3.5. Effect of Im-CS concentration and feed pressure on membrane performance

The effects of the Im-CS content and feed pressure on the CO_2 and CH_4 permeance and CO_2/CH_4 selectivity of prepared membranes are shown in Figures 6-8, respectively. From these figures, it is obvious that higher quantities of Im-CS enhance the $CO_2$and CH_4permeance, and also increases the CO_2/CH_4 selectivity. As shown in the previous section, the presence of Im-CS enhances the porosity of the sub layer of membranes, so the permeance of CO_2 as well as the permeance of CH_4 has been raised. For PES:Im-CS membranes beside the solution-diffusion mechanism, there is facilitated transport mechanism for the transportation of CO_2.As the concentration of Im-CS increases, more facilitated transport sites are provided. Therefore, total transportation of CO_2 enhances significantly and results in higher CO_2/CH_4 selectivity. In other words, in Im-CS/PES membranes, total CO_2 permeance is determined by the CO_2 transportation via the solution-diffusion mechanism and the facilitated transport mechanism. The higher amount of Im-CS can create more active sites for CO_2 facilitated transportation across the membrane, which in turns results in improved CO_2 permeance[14, 24, 39].

As it is obvious from the Figs. 6-8 for pure PES membrane as well as PES:Im-CS membranes, by increasing the feed pressure, CH_4 permeance decreases while, CO_2 permeance decreases slightly, and so it is reasonable to obtain higher CO_2/CH_4 selectivity when feed pressure increases. Generally, for glassy membranes like PES as the feed pressure increases under plasticization pressure; compaction of the membrane is dominant effect. In other words, despite the fact that the gas sorption and plasticization by CO_2 increase the membrane permeance at higher feed pressure; an obvious decline of gas permeances observed. As can be seen,PES:Im-CS membranes show a normal trend of a glassy membrane[8, 50-53].

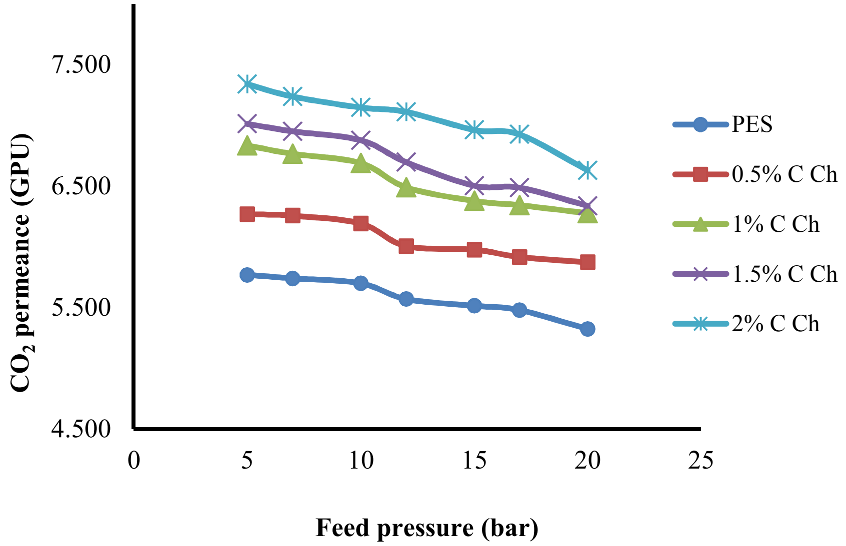


Fig.6. Effect of Im-CS concentration and feed pressure on the CO_2 permeance

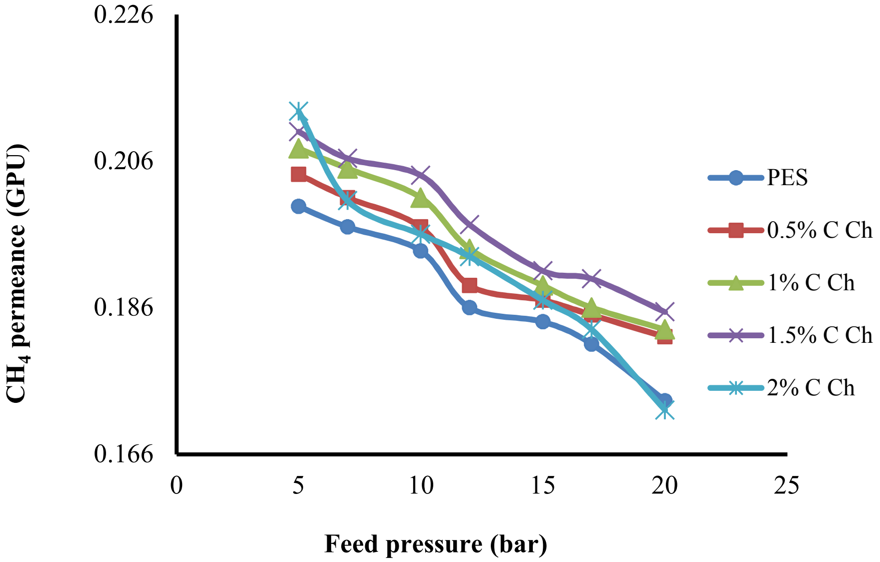


Fig.7. Effect of Im-CS concentration and feed pressure on the CH_4 permeance

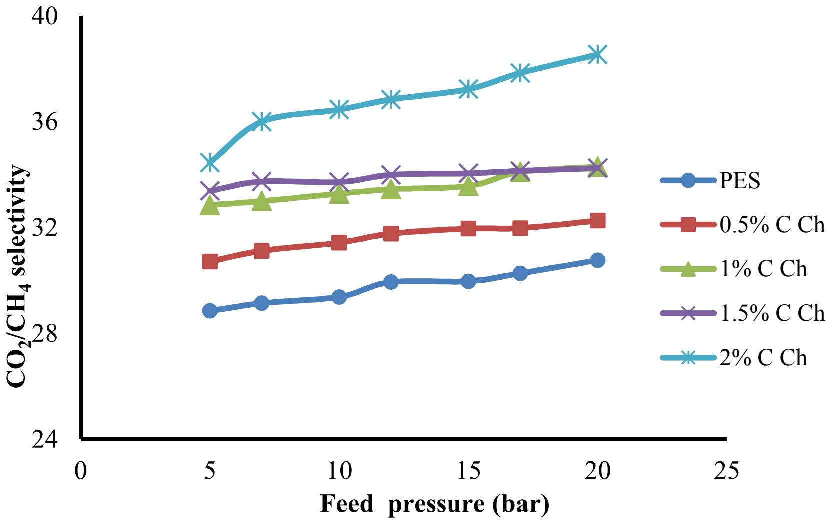


Fig.8. Effect of Im-CS concentration and feed pressure on the CO_2/CH_4 selectivity.

3.7. Effect of feed temperature on the membrane performance

In a dense membrane, that gas permeability is described by solution-diffusion model, Arrhenius equation describes temperature dependency of gas permeability.

$P = P_0\exp(-E_p/RT)$ (4)

where P is the permeability coefficient [Barrer = 10^{-10} cm^3(STP) cm/cm^2cmHgs], P_0 is the pre-exponential factor [Barrer], and the temperature independent constant, E_p is the apparent activation energy of the permeation [kJ/mol], R is the universal gas constant [8.314 × 10^{-3}kJ/mol K] and T is the absolute feed temperature [K][50, 54].

As can be seen, when E_p>0, increasing the feed temperature leads to the enhancement of gas permeability. Summation of activation energy of diffusion (E_D) and the enthalpy of sorption (ΔH_S) as tow independent factors results in E_P

$E_P = E_D + \Delta H_S$ (5)

In a general manner, in a glassy membrane E_p>0 because usually in glassy polymers E_D> 0 and $|\Delta H_S| < E_D$. Hence, as a predictable result by increasing feed temperature, gas permeability of all gas species enhances. As the size of the penetrant increases, E_p becomes greater, which means that the feed temperature affect the permeability of larger penetrant more effectively. Therefore, the feed temperature decreases the selectivity of glassy membranes. As a qualitative description, the increased motion of polymer chains at higher temperatures, results in increasing of the fractional free volume. Therefore, since temperature improves the permeation rate of less diffusive gases like CH_4 more than CO_2, at higher temperatures permeance for all components enhances and subsequently the selectivity of membrane decreases[16, 55, 56]. The effect of feed temperature on the membranes performance was investigated in the range of 303-343 K while the feed pressure was remaining constant at 5 bars. The behaviors of the membrane against feed temperature are illustrated at Figures 9-11. As it is evident from these figures, in the general case, all of the membrane including pure PES and PES:Im-CS show a normal glassy membrane behavior. Although some of PES:Im-CS membranes show a slight decline in CO_2 permeance with increasing feed temperature and generally the rate of CO_2 increase in PES:Im-CS membranes is less than pure PES. For PES:Im-CS membranes a higher feed temperature enhances the kinetic of facilitated transport reaction of CO_2 but declines the equilibrium constant of this reversible reaction[16]. It has been observed that the later effect of feed temperature is dominant and higher feed temperature decreases the facilitated transport of CO_2[16, 38, 39, 57]. So our results can be justified by this fact that in PES:Im-CS membranes lower facilitated transport of CO_2 at higher temperatures offsets the effect of feed temperature on solution-diffusion mechanism. Therefore, we observe the lower increasing rate for CO_2permeance at higher feed temperature in PES:Im-CS membranes.

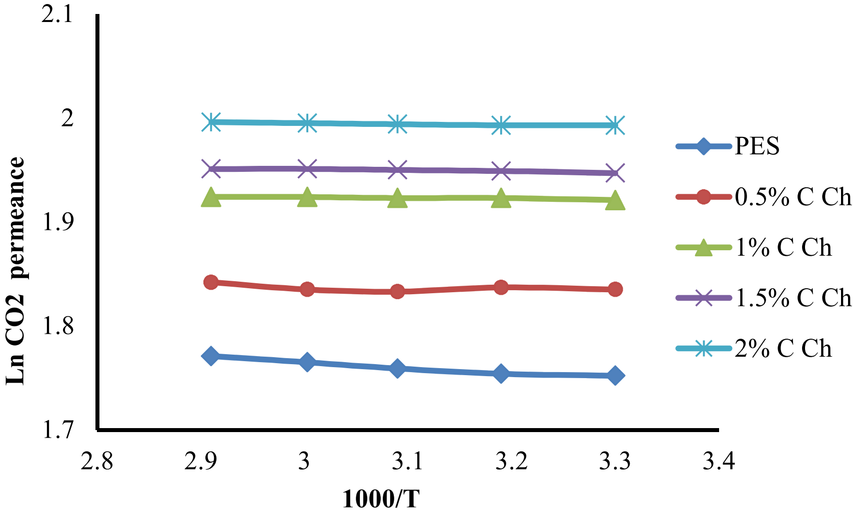


Fig.9. Effect of feed temperature on CO_2permeance

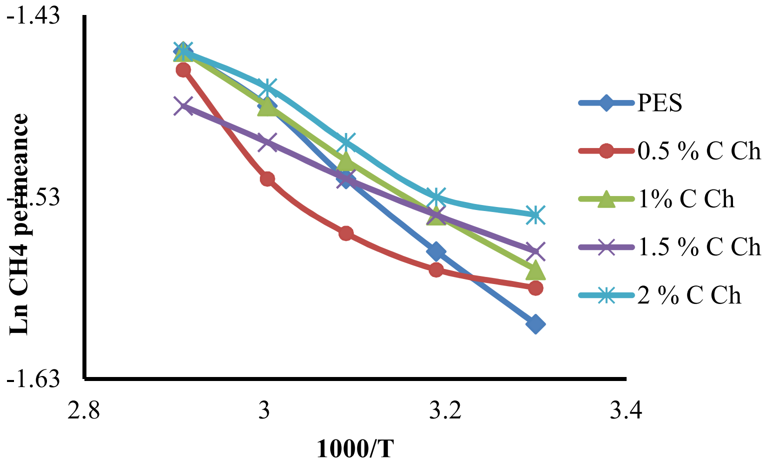


Fig.10. Effect of feed temperature on CH_4permeance

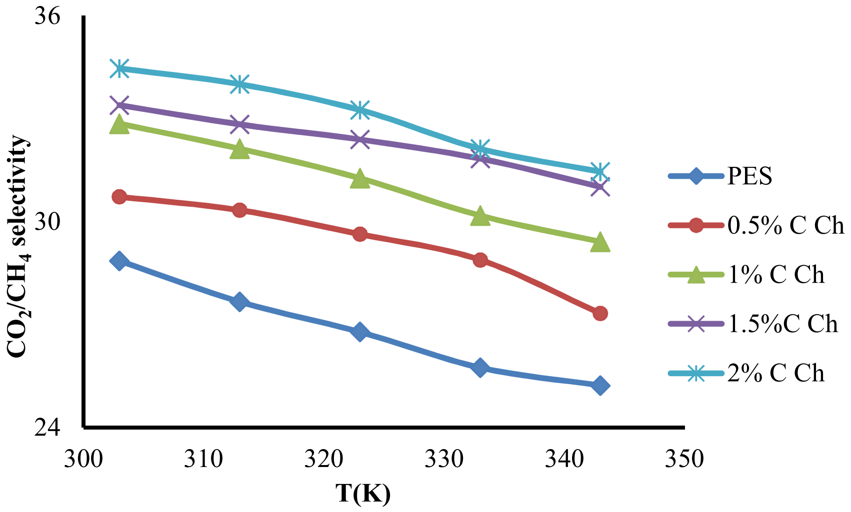


Fig.11. Effect of feed temperature on CO_2/CH_4selectivity.

Conclusion

A new derivative of chitosan containing imizadole group (Im-CS) was synthesized successfully. Integrally skinned membranes from Im-CS/PES were prepared in various ratios and utilized for CO_2/CH_4 separation. Our results showed that the addition of Im-CS as a hydrophilic additive to the PES casting solution enhances the porosity and CO_2permeance of the resulting integrally skinned membranes. Our findings also exhibited that the overall performance of the PES membranes was improved meaningfully. In contrast to pure PES the behavior of Im-CS/PES membranes against feed temperature was different slightly because of the facilitated transport mechanism of CO_2. In addition, the feed pressure affected similarly both pure PES and Im-CS/PES membrane.

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