

Preparation of supported-deep eutectic solvent membranes: Effects of bath medium composition on the structure and performance of supported-deep eutectic solvent membrane for CO₂/N₂ gas separation

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Article history

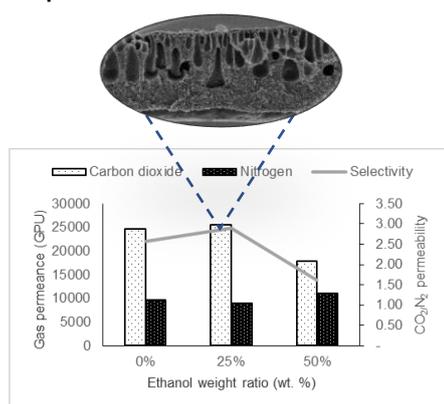
Received 10 Mac 2019

Revised 31 May 2019

Accepted 3 February 2020

Published Online 15 June 2020

Graphical abstract



Abstract

Polyvinylidene fluoride-co-polytetrafluoroethylene, PVDF-co-PTFE polymer was used as a membrane support. The asymmetric membranes were formed by immersion of casted membrane film into the coagulation bath. This work manipulated the coagulant bath medium by mixing ethanol with distilled water at different weight percentages (0, 25 and 50 wt. % of ethanol). The structures of fabricated membranes were observed to have different morphologies. Higher ethanol content altered the membrane structure from finger-like to sponge-like structure, and hence differed in membrane porosity. Vacuum-based technique was chosen to impregnate the deep eutectic solvent (DES) into the pores of membrane support. DES was prepared by mixing choline chloride (ChCl) and ethylene glycol at a ratio of 1:3. Scanning electron microscopy (SEM) was used to study the membrane morphology changes while in order to determine the immobilization of DES, energy dispersive X-ray (EDX) analysis was used. The porosity of fabricated PVDF-co-PTFE membrane was determined by means of gravimetric method. Lastly, the membrane separation performance using CO₂ and N₂ gasses were used to determine the capability of the supported-DES-membrane. The results demonstrated the highest immobilization of DES in supported membrane pores was achieved when combination of 25 wt. % of ethanol and 75 wt. % distilled water was used as a coagulant bath medium. The respective membrane has 74.5% porosity with the most excellent performance of CO₂ separation at 25.5 x 10³ GPU with CO₂/N₂ selectivity of 2.89.

Keywords: PVDF-co-PTFE polymer, coagulant bath medium, gas separation, deep eutectic solvents

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INTRODUCTION

Carbon dioxide (CO₂) is one of the greenhouse gases other than water vapor, methane, nitrous oxide and ozone. Extreme emission of CO₂ to the atmosphere is believed to cause a global warming effect. If the CO₂ gas concentration released to the atmosphere keeps increasing, the gas concentration may reach up to 570 ppm by a year of 2100, as predicted by International Panel on Climate Change (IPCC). This will then lead to increasing of mean sea level by 38 m and increasing of global mean temperature by 1.9 °C, which may cause a negative impact to the ecosystem, biodiversity and human activities [1, 2]. There are few technologies available to capture CO₂ gas such as physical and chemical absorption, adsorption, cryogenic distillation and membrane separation. Up to date, cryogenic distillation and absorption technology using aqueous alkanolamines solutions have been applied in industrial level and used commercially [3]. Nevertheless, both technologies possess few drawbacks such as high possibility of equipment corrosion, high in energy consumption and requirement of larger equipment [4]. In recent years, membrane

separation has become an attractive technology due to its low in both capital and operating cost, simple operation and lower energy requirements. The advantages of membrane technology are believed to overcome most of the traditional method problems.

Polymer based membrane has been widely used in industrial level for CO₂ separation. Cellulose acetate, polyimides, polysulfone, polycarbonate and polyamides are examples of the polymer materials employed as a membrane precursor [5]. However, current polymer membranes possess few disadvantages such as plasticization, aging and also permeability-selectivity trade-off [6]. Thus, supported liquid membrane (SLM) has been introduced and explored in the last 15 years to overcome commercial polymer solid membrane drawbacks [1]. Basically, liquid in SLM is retained in the membrane pores by capillary forces. However, SLM is not yet been applied in high scale due to instability of liquid in membrane supports. The stability of SLM can be affected by few factors such as polymer support chemical natures and morphology properties, type of chosen liquid and method of SLM preparation [7].

The liquid chosen must have a certain criteria to develop a stable SLM such as low volatility, hydrophobic, moderate viscosity and high surface tension [8, 9]. The research using ionic liquids (IL) in SLM has become an attractive solvent since it has been introduced by Blanchard and co-workers for CO₂ separation in 2001 [1]. ILs are molten salts, liquid at room temperature and possess a tuneable physicochemical properties like their viscosity, density, hydrophilicity and solubility. Despite of their advantages, the environmental friendliness of some ILs are still uncertain due to their poor biodegradability, biocompatibility and sustainability. In addition, synthesis of ILs is costly and high energy demand for recycling purposes. [10-12]. Hence, a new solvent named DES has been introduced to overcome the ILs toxicity and cost.

DES is prepared by mixing two or three safe components that interact via hydrogen bonding to form an eutectic mixture. The properties of DES are similar to ILs in such DES contains mostly of ionic species, which favour high dissolution of CO₂ [13]. This characteristic is believed can be a good potential in chemical processes specifically in CO₂ gas separation and purification. DES was firstly synthesized by mixing choline chloride as a hydrogen bond acceptor and urea as a hydrogen bond donor [14]. Impregnation of DES into the pores of the polymer membrane is still new and not yet been reported. Thus, it is crucial to understand the behaviour of DES in the membrane support.

The aim of this work was to investigate the effect of coagulant bath medium on DES loading in the membrane pores and the SLM performance for CO₂/N₂ gas separation. Thus, this work was carried out by preparing PVDF-co-PTFE membrane supports via phase inversion method. The coagulant bath medium was manipulated at different weight ratios of ethanol and distilled water. DES was synthesized by mixing of ethylene glycol and choline chloride, before being impregnated into the membrane pores using vacuum method.

EXPERIMENTAL

Materials

PVDF-co-PTFE polymer was obtained from Arkema Pte Ltd, Singapore. Ethylene glycol and N,N-dimethylacetamide (DMAc) were bought from Merck Milipore Corporation. Meanwhile, polyethylene glycol (PEG) with an average MW 10,000 was supplied by Sigma Aldrich. Lastly, ethanol (EtOH) was purchased from HmbG® Chemicals. All chemicals used were ≥ 99.0% purity.

Preparation of membrane support

A 77 wt. % of DMAc solvent was used to dissolve 20 wt. % of PVDF-co-PTFE polymer in a closed conical flask under continuous rotation for 2 hour using an overhead stirrer. Later, PEG at 3 wt. % was added and the stirring was continued until a homogenous solution was obtained. The temperature of the solution was preserved at 50 °C. Then, the final polymer solution was aerated to remove the air bubbles in an oven with a setting of 45 ± 5 °C for 24 hours. After aeration, the polymer solution was hand-casted using a hand-casting knife on a glass plate. The gap of casting knife was set at 400±10 µm. Next, the casted film was exposed to the surrounding air for 30 seconds before submerging into a coagulation bath for 24 hours to allow the phase inversion process [15]. Table 1 lists the ratio of ethanol and distilled water used in coagulant bath medium. Lastly, the solidified membrane was removed from the coagulation bath and dried for 24 hours at ambient temperature.

Table 1 Conditions of coagulant bath medium.

Membrane	Coagulant bath medium (wt. %)	
	Ethanol	Distilled water
M-0E	0	100
M-25E	25	75
M-50E	50	50

Supported-DES-membranes preparation

Ethylene glycol and choline chloride (ChCl) with a ratio of 3:1 were mixed together to synthesize DES. At 200 rpm, the mixture was stirred continuously at room temperature until the solution became clear and homogenous.

Vacuum immobilization technique was applied to prepare the supported membranes in this study. The synthesized membrane was totally immersed into DES in a petri dish and then placed in a desiccator at room temperature. The pressure of desiccator was set at -10 mbar using a vacuum pump for 3 hours. In order to ensure all the membrane pores were filled up with the solvent, the desiccator was aerated for every hour. Then, by using a filter paper, the excess DES on the membrane surface was wiped off.

Finally, the membrane was coated with 3 wt. % PDMS/n-hexane solution to seal the pinholes and maintain the solvent in the membrane pores. Coating procedure was accomplished by totally immersing the membrane in PDMS solution for 10 minutes at room temperature before being dried for 24 hours at room temperature.

Membrane characterization

Scanning electron microscope (SEM) with model of JSM 6260 LE JEOL was used to investigate the morphologies of synthesized membrane top surface and the membrane cross sectional area. The membrane pore sizes were measured from the SEM images by using ImageJ software. Meanwhile, the overall chemical composition and chemical elements distribution in the membrane pores were analysed by additional of energy-dispersive X-ray (EDX).

The membrane porosity was determined by using gravimetric method. The sample was immersed in octanol for 30 seconds. Then, the sample was dried using a filter paper. Sample mass of before and after soaking procedure were recorded. The membrane porosity was calculated by using Equation (1).

$$\omega = \frac{m_n/\rho_n}{m_n/\rho_n + m_p/\rho_p} \quad (1)$$

Where ω is the membrane porosity, m_n is the mass of absorbed octanol, ρ_n is the density of octanol, m_p is the mass of dry membrane, and ρ_p is the density of the membrane. This method was used to estimate the porosity by determining the weight of liquid that contained in the membrane pores.

Gas permeation test

The supported-DES-membrane performance was tested using pure gas permeation procedure. The pure gas permeance was determined by a constant volume. The membrane was placed in a permeation cell and exposed to pure CO₂ or N₂ individually. The effective area of permeation cell was 11.34 cm². Both transmembrane pressure and temperature were constant throughout the testing at 3.5 psi and 27 °C, respectively.

The permeance (pressure-normalized flux) of individual gas was calculated as follows :

$$\left(\frac{P_i}{l}\right) = \frac{1}{A\Delta p} \times \frac{dV_i}{dt} \quad (2)$$

Where i represents the gas penetrant, V_i is the volume of the gas permeated through the membrane (cm³, STP), A is the effective membrane area (cm²), t is the permeation time (s) and Δp is the transmembrane pressure drop (cmHg). The permeance is expressed in gas permeation unit, GPU, as

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

Meanwhile, the selectivity was obtained by

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (3)$$

Where $\alpha_{(i/j)}$ is the selectivity of gas i over gas j. Both $(P/I)_i$ and $(P/I)_j$ are the permeance of gas i and j, respectively.

RESULTS AND DISCUSSION

Effects of coagulant bath medium on membrane morphologies

Fig. 1 shows the SEM micrographs of (a) the membrane top surface and (b) the cross sectional area with a magnification of 5,000x and 500x, respectively. From Fig 1(a), all three membranes showed clear pores or pinholes which were developed due to the existence of PEG (3 wt. %) as a pore former. However, the pores quantities and sizes were differed from each other due to different ethanol contents in the coagulation bath medium. Highest pore formation could be seen from M-0E membrane top surface, whereas both M-25E and M-50E membranes possessed almost the same quantity of pores but variety in size. Among all three membranes, M-50E membrane had a larger pore size on the surface with 50 wt % ethanol in the coagulant bath medium.

Cross sectional area of M-0E membrane synthesized without ethanol in a coagulant bath medium displayed a dominant of macrovoid finger-like structures as shown in Fig 1(b). On the other hand, additional of ethanol by 25 and 50 wt. % diminished the macrovoid and developed a sponge-like structure as shown by M-25E and M-50E membranes, respectively. Formation of larger finger-like macrovoids structure was due to fast precipitation rate in coagulant bath medium. Meanwhile, sponge-like structure was resulted from slower precipitation rate. In short, the polymer precipitation rate in a coagulant bath medium reduced by the presence of ethanol. Similar observation was obtained by Deshmukh and Li (1998) where the additional of ethanol changed the long finger-like to sponge-like structure of PVDF hollow fiber membranes [16].

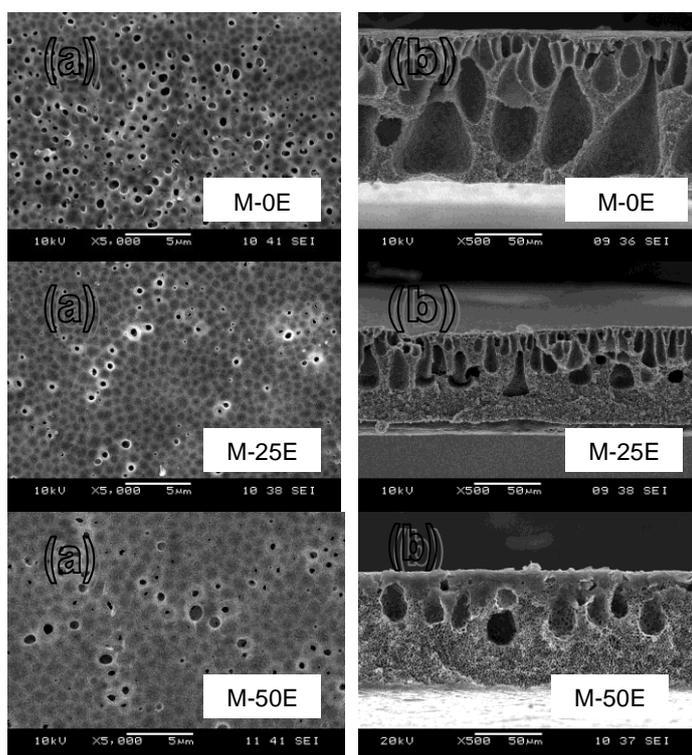


Fig. 1 Micrographs of empty PVDF-co-PTFE membrane (a) membrane top surface and (b) cross sectional view.

Membrane pore size and porosity are among the crucial factors that affect the DES immobilization. The membrane pore sizes were measured from SEM micrographs using ImageJ software. Meanwhile, the membrane porosity was calculated by using gravimetric method. Approximately, 10 readings were repeatedly measured to get the final result. Table 2 lists the synthesized membranes pore size and porosity. The larger pore size between 0.6 to 35.0 μm was observed by M-0E

membrane which used purely distilled water as a coagulant bath. As the ethanol ratio was increased, the minimum pore sizes were decreased with a trend; M-50E had the smallest minimum pore size, followed by M-25E and M-0E membrane, respectively. M-25E membrane possessed the highest porosity which was 73 %. This could be explained by the lowest range between minimum and maximum pore size of the membrane. Among all three membranes, finger-like structure of M-25E showed almost uniformity in size.

Table 2 Membranes pore size and porosity

Sample	Pore size (μm)		Porosity, %
	Minimum	Maximum	
M-0E	0.6	35.0	70.5
M-25E	0.6	18.3	73.0
M-50E	0.4	21.0	61.9

Further information on the elemental composition of the samples could be provided by EDX analysis. The elemental composition of supported-DES-membranes is summarized in Table 3. The EDX results confirmed the presence of chlorine, nitrogen and oxygen elements in the samples which corresponded to DES. Both carbon and fluorine elements represented PVDF-co-PTFE membrane support, while PDMS coating could be detected by silicone element. M-25E membrane demonstrated the highest DES loading in the membrane pores for about 55% DES elements. Meanwhile, M-50E showed the lowest DES loading with only 13%. This could be related with membrane porosity. As the membrane porosity was increased, DES loading in the membrane pores was also increased with a sequence of M-50E < M-0E < M-25E.

Table 3 Elemental analysis by EDX for supported-DES-membranes.

Component	Mass %		
	M-0E	M-25E	M-50E
Chlorine	21.30	19.11	8.44
Nitrogen	20.63	30.64	5.12
Oxygen	10.35	5.01	-
Carbon	30.52	20.94	39.37
Fluorine	18.49	33.40	45.93
Silicone	0.71	0.90	1.15

Evaluation of supported-DES-membrane performance

Supported-DES-membrane performance was tested by applying single gas permeation using pure CO_2 and N_2 at 1 bar pressure and ambient temperature. The permeance and selectivity for M-0E, M-25E and M-50E membranes are displayed in Fig. 2. As presented in Fig. 2, M-25E has a superior performance compared to the other membranes. The permeance of CO_2 and N_2 recorded for a membrane without presence of ethanol in the coagulant bath was 24.6×10^3 GPU and 9.6×10^3 GPU, respectively. The permeance of CO_2 gas was increased when 25 wt. % ethanol was added with a value of 25.5×10^3 GPU while N_2 was decreased (8.8×10^3 GPU). However, when the weight ratio of ethanol was further increased to 50%, the CO_2 permeance showed a decrement about 40%. The CO_2/N_2 selectivity for M-25E membrane was the highest with 2.89 compared to M-0E and M-50E membranes.

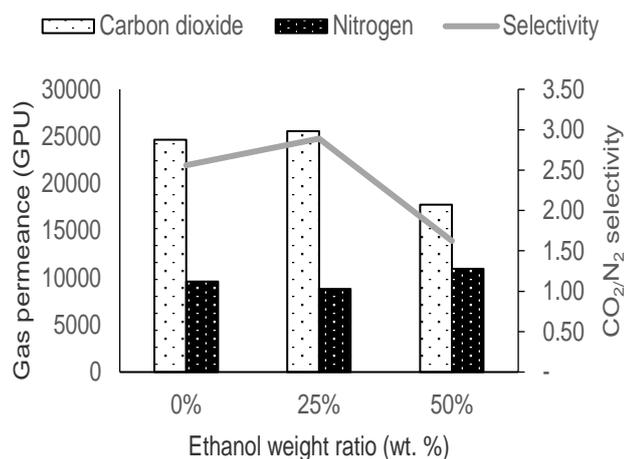


Fig. 2 The permeance and selectivity of supported-DES-membranes.

CONCLUSION

Supported DES in PVDF-co-PTFE flat sheet membrane using different coagulant bath medium has been successfully synthesized. Presence of ethanol in the bath medium altered the membrane microstructure which proven by SEM micrograph. Moreover, EDX analysis confirmed that combination of finger and sponge-like structures that gave the highest porosity and was able to hold DES in higher quantity. Finally, the performance of supported-DES-membrane was tested via gas permeation test. The results of CO₂ permeance and CO₂/N₂ selectivity demonstrated that better performance could be achieved when higher DES immobilized in the membrane pore support.

ACKNOWLEDGEMENT

This work was financially supported by the Universiti Malaysia Perlis (UniMAP) under the Shortterm Grant (9001-00547) and Ministry of Higher Education Malaysia (MOHE).

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