건/습기체에 대한 아민화된 폴리설폰막의 투과특성

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한남대학교 화학공학과 (2015년 9월 15일 접수, 2015년 11월 14일 수정, 2015년 11월 18일 채택)

Permeation Characteristics of Aminated Polysulfone Membranes for Dry and Wet Gases

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초록: 폴리설폰에 아미네이션을 통하여 음이온교환능력을 부여해 주기 위하여 클로로메틸 에틸 에테르에 대한 트리 에틸아민의 몰 비율을 변경하며 개질하였다. 아민화된 폴리설폰막을 제조하여 전체적인 투과도에 확산도와 용해도 중 어떤 인자가 더 지배적인가를 알려주는 타임래그 측정법을 이용하여 질소, 산소, 메탄, 이산화탄소 및 이산화황 순 수 기체에 대한 투과도 실험을 수행하였다. 또한 여러 아민화율의 폴리설폰막은 습기체인 질소와 이산화탄소에 대하 여 상대습도 30%로부터 100%까지 투과도 및 이상 선택도를 측정하였다. 대표적으로 아민화율 3:1의 폴리설폰막은 상대습도 100%에서 이산화탄소 투과도 165 barrer와 질소에 대한 이산화탄소의 이상 선택도 294.4 값을 얻었다.

Abstract: Polysulfone (PSf) is modified to give the anion exchange capability through the amination according to the molar ratios of triethylamine against chloromethyl ethyl ether. Upon producing the aminated PSf (APSf) membranes, single gas permeation experiments were performed for N_2 , O_2 , CH_4 , CO_2 , and SO_2 by using the time-lag method to differentiate which factor is more dominant of diffusivity and solubility to overall permeability of the resulting membranes. Then APSf membranes with various amination ratios is tested again for N_2 and CO_2 gases for wet gases of relative humidity from 30 to 100% in terms of permeability and ideal selectivity. The APSf membrane of 3:1 amination ratio indicated 165 barrer of CO_2 permeability and 294.4 of CO_2/N_2 selectivity at 100% relative humidity.

Keywords: facilitated transport, aminated polysulfone, fixed site carrier, relative humidity, carbon dioxide.

Introduction

The first facilitated transport membranes (FTM) for gas separations were introduced by Ward and Robb¹ by filling the pores with a carrier solution of aqueous bicarbonate-carbonate solution resulted in 4100 times more permeable to carbon dioxide than oxygen. Today, we call these membranes the supported liquid membranes (SLMs) which are known to have the serious problem, loss of carrier solution, usually accompanied by the loss of the chemical complexing agent.² To overcome this fatal weakness of SLMs, LeBlanc³ introduced the ions as mobile, membrane-bound carriers and the counter ions in ion-

exchange membranes that are not easily forced out of the membrane. In this type membranes, the ion-exchange membranes act as supports while ions in membranes do as complexing agents which are exchanged into the membrane and then held there by electrostatic forces.² Also this electrostatic force between carrier and ion exchange membrane contributes to the prevention of the carrier loss to some extent, but this prevention is not perfect especially in the presence of other ions leading to the carrier loss.⁴ Therefore, in this article, to exclude the possibility of carrier loss, the FTM composed of a polymer carrier of polyethylenimine (PEI) and the cationized poly(vinyl alcohol) (PVA) by aminoacetalization as ion exchange domain was prepared to separate CO2/N2. The direct inoculation of carriers into polymer membranes was introduced accompanying the use of ion exchange membranes as supports. Like this, the initial stage studies on the fixed site carrier (FSC) membranes

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have been done intensively elsewhere.⁵⁻¹¹ In most cases, first cation exchange membranes were prepared as supports and various amines used as carriers. In this FSC membranes, the carriers are covalently bonded to the functional group having ionic group of polymer backbone, thus the mobility is restricted while the stability could be increased.

After this investigation of FSC membranes retaining electrostatic forces between carriers and supports, FSC membrane material that the supports themselves have carriers was introduced.⁴ In that article, the polyethylenimine containing primary and secondary amino groups which can react with CO₂ to form carbamate was used as a carrier of CO₂ and the aminated PVA acted as support leading to the retainment of carrier in the membrane by the entanglements of PEI and PVA. It is reported that the CO₂ permeability was 8.5×10⁻⁸ (cm³·cm/ (cm²·s·cmHg)) with a selectivity of more than 160 when the PEI wt% is 32.7%. Shen et al.12 have synthesized the copolymer containing tertiary amine and carboxyl groups for CO₂ facilitated transport by radical polymerization of DMAEMA (2-N,N-dimethyl aminoethyl methacrylate)-AA (acrylic acid). The membrane displayed a CO₂ permeance of 6.12×10^{-7} cm³ $(STP)/cm^2 \cdot s \cdot Pa$, and a CH₄ permeance of 2.4×10⁻⁹ cm³ (STP)/ cm²·s·Pa at 299 K, 1.140 kPa of gas pressure. Quinn et al.¹³ developed polyelectrolyte membranes based on poly(vinylbenzyl trimethyl ammonium fluoride) (PVBTAF) which exhibited the exceptional permselectivity properties of CO₂ permeance of 6×10⁻⁶ cm³/cm²·s·cmHg and CO₂/H₂ and CO₂/ CH₄ selectivities of 87 and 1000, respectively at 23 °C and 32 cmHg CO₂. Wang et al.¹⁴ used poly(N-vinyl-sodium aminobutyrate) obtained from the hydrolyzed polyvinylpyrrolidone which contained secondary amine and carboxylate as fixed carriers. Ho et al.15 synthesized novel CO2-selective membranes consisting of both fixed and mobile carriers in crosslinked PVA. At 120 °C, the CO₂ permeability and CO₂/H₂ selectivity reached 8200 barrers (1 barrer=10⁻¹⁰ cm³ (STP) cm/ (cm²·s·cmHg)) and 450, respectively. Nunes et al.¹⁶ synthesized two compounds having one or two quaternary ammonium moieties and polymerized via hydrolysis of the triethoxysilane moiety. High affinity to CO₂ was found for both compounds leading to the CO₂/N₂ solubility selectivity up to 1500. Humid gas measurements showed strong increase of the permeability coefficients for all gases without the selectivity loss compared to the dry gas measurements. CO₂ permeability up to 2×10⁻¹³ kmol mm⁻²·s⁻¹·kPa⁻¹ was measured in humid environment. Recently, Hagg et al.17-28 investigated polyvinylamine (PVAm)/PVA blended membrane for CO2 separation very strongly. This blended membrane showed the typical separation factor for CO_2/N_2 of 130 and the CO_2 permeation of 0.04 m³ (STP)/m²·h·bar was obtained for CO_2/N_2 mixture gas system, suggesting that amino groups in PVAm are not only fixed inside the PVA structures but act as the CO_2 carriers.¹⁸

In this work, the polysulfone (PSf) is aminated according to the molar ratios of triethylamine against chloromethyl ethyl ether. Upon producing the aminated PSf (APSf) membranes, single gas permeation experiments were performed targeting for N₂, O₂, CH₄, CO₂, and SO₂ by using the time-lag method to understand how diffusivity and solubility affect permeability of the resulting membranes. Then APSf membranes with various amination ratio is tested again for N₂ and CO₂ gases under the wet conditions of relative humidity from 30 to 100% in terms of permeability and ideal selectivity.

Experimental

Materials. Polysulfone (PSf) was obtained from Solvay Chemicals. Methanol, dichloroethane (DCE), dimethyl acetamide (DMAc), and chloromethyl ethyl ether (CMEE) were purchased from Sigma-Aldrich Co (Milwaukee, USA). Zinc chloride (ZnCl₂) and trimethylamine (TEA) used in the amination reactions were purchased from Junsei Co., Japan. All reagents and solvents were used without further purification.

Membrane Synthesis. The aminated polysulfone (APSf) was prepared by a two-step reaction: (1) chloromethylation of PSf using CMEE in the presence of ZnCl₂, a Friedel-Crafts catalyst, followed by (2) amination by means of TEA.²⁸ The reaction scheme is illustrated in Figure 1. The chloromethylation of PSf was carried out by dissolving PSf in DCE while stirring to form an 8 wt% solution. Then the catalyst, ZnCl₂, was added at 10 wt% of the PSf and an amount of CMEE 4 times that of the PSf was introduced very slowly followed by stirring at 40 °C for 4 h. After the reaction, the solution was washed with methanol several times and dried at 60 °C for 24 h in a forced convection oven. Next, molar ratios of 1:1, 2:1, 3:1 and 5:1 of TEA against CMEE were added into the chloromethylated PSf dissolved in DMAc and kept for more than 12 h at room temperature in order to synthesize APSf. The APSf solution was filtered to get rid of suspended particles through 10 µm microfiltration poly(tetrafluoro ethylene) membrane. Filtered solution was casted on the glass plates with the aid of the Gardner casting knife and then dried in the forced convection oven at 60 °C for 12 h. The thickness of the resulting APSf film was about 20 µm and stored in distilled water



Figure 1. Schematic amination reaction of PSf.

for further use.

Gas Permeability Measurement for Dry Gases. The gas permeation performance of APSf was measured using a single gas permeation technique,²⁹ and the measurement of the gas permeability was carried out using the well-known time-lag method.³⁰ The effective membrane area was 13.5 cm², and the permeation measurement was carried out at 25 °C. The error in the permeation results was less than 3%. Gas permeability coefficients were determined from the slope of a downstream pressure versus time plot when steady-state had been reached:

$$P = \frac{dp}{dt} \left(\frac{VT_0 L}{P_0 T \Delta P A} \right) \tag{1}$$

where *P* is the permeability (barrer= 1×10^{-10} cm³ (STP) cm/ cm²·s·cmHg) represented; the rate of the pressure rise under the steady-state (dp/dt), the downstream volume (*V*, cm³), the membrane thickness (*L*, cm), the pressure difference between the feed side and permeate side (ΔP , cmHg), the measurement temperature (*T*, K), the effective membrane area (*A*, cm²), standard pressure (*P*₀) and temperature (*T*₀), respectively. The timelag device schematic used for the membrane gas permeability experiment is shown in Figure 2. First, the membrane is fixed between the permeable cells, which were centered with the surrounding layers maintained in a vacuum. Then, the gas is inserted into the above layer at 1 atm. Once it fills the layer, the valve is opened so that the gas diffuses to the bottom layer owing to pressure differences. Hence, the gas is able to permeate through the membrane. The device maintains a constant



Figure 2. Gas permeation apparatus for dry gases.

temperature at 25 °C. The ideal separation factor ($\alpha_{A/B}=P_A/P_B$) for component A and B is defined as the ratio of permeability of each component.

Gas Permeability Measurement for Wet Gases. The gas permeability measurement for the wet gases, i.e. single gas in the water vapor environment, was carried out by the following apparatus depicted in Figure 3. The mass controlled gas as 30 cm^3 /s at 5 atm was passed through gas bubblers containing water in upper oven. In the downstream He gas as the sweeping gas was flown with the flow rate of 10 cm^3 /min and the He gas containing the permeated gas from the membrane was passed to the cold trap to remove the water vapor in the permeated gas. Then the permeability was measured by the Gilbrator at least hundred times for the relative humidity of 30, 50, 70 and 100% for N₂ and CO₂ gases only.



1: Mass flow controller, 2: Relative humidity and temperature transmitter 3: Flat type membrane cell, 4: Trap 5: Desiccator, 6: Gas chromatography

Figure 3. Gas permeation apparatus for wet gases.



Figure 4. Gas permeability of the aminated PSf membranes as a function of amination ratio at 25 °C.

Results and Discussion

In general, the permeation properties of a gas are determined by its chemical nature, crystallinity, and morphology of a membrane. Since the introduction of the functional group such as amino groups to the backbone of polymers changes the chemical nature and morphology as well, the gas permeation properties would be varied. As the amination ratio increases, the permeability of each gas except for SO₂ decreases (Figure 4). The downward trend of the permeability of each gas except for SO₂ may be attributed to the free volume decrease through the addition of more amino groups.^{31,32}

However, the permeability of SO_2 gas increases as the amination ratio increases. This may be due to the mutual interaction effect of between the basic and acidic properties of the



Figure 5. Ideal gas selectivity of the aminated PSf membranes as a function of amination ratio at 25 °C.



Figure 6. CO₂ and N₂ permeabilities and ideal selectivity according to the relative humidity and amination ratio.

	Ratio	Diffusivity ^a					Diffusivity selectivity [-]				
		N_2	O_2	CH_4	CO_2	SO_2	O_2/N_2	CO ₂ /CH ₄	CO_2/N_2	SO ₂ /CO ₂	
Amination ratio	1	2.56	3.67	2.55	1.73	4.27	1.434	0.678	0.676	2.468	
	2	2.23	2.97	2.46	1.44	6.19	1.332	0.585	0.646	4.299	
	3	2.11	2.76	2.00	1.35	7.09	1.308	0.675	0.640	5.252	
	5	2.08	2.42	1.89	1.02	10.5	1.163	0.540	0.490	10.29	

Table 1. Diffusivity and Diffusivity Selectivity for Aminated PSf Membranes

^{*a*}unit: 10^{-9} cm²/s.

Table 2. Solubility and Solubility Selectivity for Aminated PSf Membranes

	Ratio -	Solubility ^{<i>a</i>}					Solubility selectivity [-]				
		$\mathbf{N_2}^b$	$\mathbf{O}_2{}^b$	$CH_4^{\ b}$	CO_2	SO_2	O_2/N_2	$\rm CO_2/\rm CH_4$	CO_2/N_2	SO ₂ /CO ₂	
Amination ratio	1	3.52	12.3	3.14	0.137	1.202	3.480	43.6	38.9	8.77	
	2	1.79	10.1	1.22	0.111	1.354	5.648	90.8	61.9	12.22	
	3	0.94	7.25	0.50	0.089	1.537	7.713	177.5	94.4	17.32	
	5	0.48	4.13	0.11	0.067	1.726	8.604	606.1	138.9	25.9	

^aunit: 10⁻⁹ cm²/s. ^bcm³/(STP)/cm³cmHg×10⁻³.

APSf membrane and SO₂ gas, respectively. From these results, it appears that gas transports would be mainly governed by Fickian diffusion; however, from the Figure 4, it is difficult to differentiate what is more dominant for flux enhancement and a more detailed discussion is provided below in terms of diffusivity and solubility measured by the time-lag method. Next the ideal selectivity in relation to the interesting gas pairs is described (Figure 5). In most cases, the selectivity of O_2/N_2 , CO_2/CH_4 , CO_2/N_2 indicate enhancement trends as the amination ratio increases. At amination ratio of 3, the ideal selectivity obtained for O_2/N_2 , CO_2/CH_4 , CO_2/N_2 , and SO_2/CO_2 was 120, 90.8, 60 and 10, respectively.

From a comparison of the diffusivity and diffusivity selectivity of the gases in relation to amination ratio (Table 1), it is shown that diffusivity decreases as the amination ratio increases for all gases except for SO_2 gas. Nevertheless, the diffusivity selectivity for all gas pairs except for SO_2/CO_2 decreases while the selectivity of SO_2/CO_2 increases only.

From observation of solubility and solubility selectivity shown in the same manner as diffusivity (Table 2), both solubility and solubility selectivity decrease as the amination ratio increase except for SO₂ gas. In the dry membranes, it can be considered that the relation of CO_2 and membrane is based on the weak acid-base interaction between CO_2 and amine moiety.¹⁷ Therefore, it is expected that the solubility of CO_2 increases as the amination ratio increase but the solubility decreases in reality, i.e., the kinetic effect (diffusivity) is more dominant than the thermodynamic (solubility) effect. For other gases, O_2 , N_2 and CH_4 , the decrease of solubility may be due to the reduction of free volume since it seems that there are no any particular relations between amino group and the permeating gases. For SO_2 gas, its solubility increases as the amination ratio increases. Since it is known that the diffusivity is a function of the concentration (solubility), the increase of solubility leads to the enhancement of diffusivity (Table 1).

In the presence of water vapor, the permeability of CO_2 and N_2 was measured in accordance with the amination ratio. As a hydrogel with sufficient primary amino groups, the APSf may exhibit high CO_2 selective absorbability. In highly water-swollen FSC membranes, CO_2 is mediated based on the similar reactions as in mobile carrier membranes although the amino groups are fixed to the membrane matrix.²³ Water can play a role in the CO_2 transport when the membrane is highly swollen in water. It is suggested that CO_2 reacts with the primary amino groups (carriers) and water to produce amine- CO_2 -H₂O complexes, e.g. RNHCOO⁻ and HCO⁻₃ within the membrane,^{15,23} diffusing in the form of HCO⁻₃ ions, as shown in eq. (1). This mechanism may make it possible to obtain the high CO_2 permeability and selectivity which is comparable to those of mobile carrier membranes.

$$2CO_2 + 2RNH_2 + H_2O \leftrightarrow RHNCOOH + RNH_3^+ + HCO_3^-$$
 (1)

In current work, APSf considered as a facilitated transport

membrane, i.e. a polymer with a carrier component incorporated in the polymer structure itself contains the amino groups depending on the amination reaction ratio which contributes to the transport of CO_2 through the membrane as a bicarbonate ion (HCO_3^-) when the membrane is swollen with water. Considering that amino groups are not consumed during the reversible reactions, they are taking the role of catalysts for the reversible CO_2 hydration reactions as finally demonstrated with eq. (2)¹⁵:

$$H_2O + CO_2 \stackrel{* NH_2}{\Leftrightarrow} H^+ + HCO_3^-$$
⁽²⁾

Therefore, CO_2 can be passed the APSf membrane by the facilitated transport mechanism from the feed side to the sweep side in a reduced pressure environment while other gases like non-reacting gases of H_2 , N_2 , etc permeated only by the Fick-ian diffusion.

As the relative humidity increases, CO_2 permeability increases depending on the amination ratio while N₂ permeability increases minutely toward the relative humidity because N₂ solubility in water governed by Henry's law increases with the humidity (Figure 6). At saturated vapor pressure, CO_2 permeability was shown the maximum values for each amination ratio. The APSf membrane of 3:1 amination ratio indicated 165 barrer of CO_2 permeability and 294.4 of CO_2/N_2 selectivity at 100% relative humidity.

Conclusions

Polysulfone (PSf) was modified to endow the anion exchange capability through amination reaction according to the molar ratios of triethylamine against chloromethyl ethyl ether. Upon producing the aminated PSf (APSf) membranes, single gas permeation experiments were carried out targeting for N₂, O₂, CH₄, CO₂, and SO₂ by using the time-lag method to understand how diffusivity and solubility affect permeability of the resulting membranes. Then APSf membranes with various amination ratio were tested again for N₂ and CO₂ gases under the humidified environment with the relative humidity from 30 to 100% by the facilitated transport mechanism. From this study, the following important conclusions can be drawn:

(1) As the amination ratio increases, the permeability of each gas except for SO_2 decreases. The downward trend of the permeability of each gas may be attributed to of a free volume decrease through the addition of more amino groups. However, the permeability increase of SO_2 gas according to the ami-

nation ratio may be due to the mutual interaction effect of between the basic and acidic properties in the membrane and permeate gas, respectively.

(2) For O_2 , N_2 and CH_4 , both the diffusivity and solubility decrease due to the free volume decrease by the more introduction of amino groups. It is expected that the solubility of CO_2 increases as the amination ratio increase but the solubility decreases in reality, i.e., the kinetic effect (diffusivity) is more dominant than the thermodynamic (solubility) effect. For several times increase of SO_2 permeability, not only solubility increases as the amination ratio increases but the diffusivity also increases by a function of the concentration (solubility).

(3) Under the humidified environment, CO_2 permeability increases as the humidity and amination ratio increase. Typically at 30% humidity CO_2 permeability and selectivity toward N₂ was shown 15 barrer and 38.8 with 1:1 APSf membrane, respectively whereas at 100% humidity CO_2 permeability and selectivity were observed 165 barrer and 294.6, respectively with 1:3 APSf membrane.

(4) After the investigation of durability and preparation of composite membranes onto the proper support porous membrane, it may be considered that it is applied to the several removal processes of CO_2 .

Acknowledgement: This research was supported financially by the Ministry of Education (MOE) and National Research Foundation of Korea (NRF) through the Human Resources Training Project for Regional Innovation (Grant No. 2013H1B8A2032261).

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