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Gas permeation and separation properties of sulfonated polyimide membranes

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Abstract

Permeability and selectivity of pure gas H_2, CO_2, O_2, N_2 and CH_4 as well as a mixture of CO_2/N_2 for sulfonated homopolyimides prepared from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoro propane disulfonic acid (BAPHFDS) were measured and compared to those of the non-sulfonated homopolyimide having the same polymer backbone. The polyimide in a proton form (NTDA–BAPHFDS(H)) displayed higher selectivity of H_2 over CH_4 without loss of H_2 permeability. Strong intermolecular interaction induced by sulfonic acid groups decreased diffusivity of the larger molecules. The CO_2/N_2 (19/81) mixed gas permeation was investigated as a function of humidity. With increasing relative humidity from 0% RH to 90% RH, the CO_2 permeability for NTDA–BAPHFDS(H) polyimide increased by more than one order of magnitude, and the selectivity of CO_2/N_2 also increased twice or more. On the other hand, the gas permeability for the non-sulfonated polyimide slightly decreased with increasing humidity. NTDA–BAPHFDS(H) polyimide displayed a CO_2 permeability of 290×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) and a separation factor of CO_2/N_2 of 51 at 96% RH, 50 °C and total pressure of 1 atm.

Keywords: Sulfonated polyimides; Separation of carbon dioxide; Humidity

1. Introduction

Polyimides have been attractive as membrane materials for gas separation because of their excellent thermal, chemical and mechanical properties, as well as excellent film-forming properties. Relationship between the chemical structure of polyimides and their gas permeation and separation properties has been investigated extensively. A large amount of experimental data for polyimides was used to propose a group contribution method to predict gas permeability [1,2]. Recently, novel sulfonated polyimides (SPIs) have been successfully synthesized in several laboratories to develop new proton exchange membrane materials for fuel cell application [3–9]. They are also interesting as membrane materials for gas separation, since they have strong polar groups, sulfonic acid groups. Only a few studies investigated sulfonated polyimides as membrane materials for gas separation. Piroux et al. reported gas permeation and separation properties for sulfonated copolyimides prepared from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) with a commercial sulfonated diamine, 2,2′-diamino-4,4′-biphenyl sulfonic acid (BDSA) and some non-sulfonated diamines such as 9,9′-bis(4-aminophenyl)fluorine [10,11]. They reported that a large range of gas permeability could be obtained varying the nature of the non-sulfonated diamine, the sulfonated diamine content and the sulfonated block length. However, the chemical structures of the non-sulfonated diamines were quite different from the sulfonated diamine. Because the backbone structures also changed with varying sulfonic acid contents of the copolyimides, the effect of introduction of sulfonic acid groups into polyimides on their gas permeation property was not clear.

The effect of introduction of sulfonic acid groups into polymers have been studied for poly(2,6-dimethyl-1,4-phenylene oxide) [12–14], polystyrene [15] and polysulfone [16]. The papers reported the introduction of sulfonic acid groups decreased gas permeability and increased gas selectivity for O_2/N_2 and CO_2/CH_4 separations. It is interesting to investigate the effect of introduction of sulfonic acid groups into polyimides. However, most of the sulfonated polyimides

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developed for fuel cell were not suitable to investigate gas permeation property because they were designed to have lower gas permeability in order to prevent fuel gases (H_2 and O_2) from permeating through the membranes. The NTDA–BDSA polyimide was also a low gas permeable material. It is necessary to design a sulfonated polyimide displaying high gas permeability.

We prepared a new sulfonated polyimide containing hexafluoroisopropylidene linkage ($>C(CF_3)_2$) [17,18], which moiety is well known to enhance gas permeability without loss of selectivity [19–21]. The sulfonated polyimide was prepared from NTDA and the sulfonated diamine (BAPHFDS), which was prepared by sulfonating a fluorinated diamine (BAPHF). The pyrolytic membrane prepared by pyrolyzing NTDA–BAPHFDS polyimide membrane displayed higher selectivity of C_3H_6/C_3H_8 separation [17], or excellent separation performance for O_2/N_2 system [18]. However, the gas permeation and separation properties of the precursor membrane have not been investigated in detail.

Their permeation and separation properties for wet gas are also interesting because sulfonated polyimides generally show high water uptake (>40 g/(100 g dry polymer)) [9,11]. For CO_2/N_2 separation, it was reported that amine-modified polyimide membranes showed both higher permeability and selectivity especially in the presence of water vapor [22]. The sorbed water might enhance the interaction between the amine moiety and CO_2 molecules. This is advantageous for recovery of CO_2 from wet flue gas. For the NTDA–BDSA copolyimide, it was reported that a decrease in CO_2 permeability was observed in relative humidity range 0–70 %RH followed by an increase at higher relative humidity [11]. The CO_2 permeability coefficients at 0 and 100 %RH were reported roughly similar. Pure CO_2 and N_2 permeability coefficients at dry condition were reported to be 2.6 and 0.03 Barrer [1 Barrer $= 10^{-10}$ cm^3 (STP) cm/(cm^2 s cmHg)], respectively [10]. It follows that the ideal separation factor for CO_2/N_2 is as high as 90. However, permselectivity at wet condition was not reported [11].

The objective of this work is to investigate the effect of introduction of sulfonic acid groups into a polyimide on its gas permeation and separation property and the effect of coexisting water vapor on mixed CO_2/N_2 gas permeation and separation properties. For this objective, we used the NTDA–BAPHFDS and NTDA–BAPHF polyimides because of the same chemical structure except for sulfonic acid side groups.

2. Experimental

2.1. Materials

Fig. 1 shows the chemical structures of polyimides used in this study. 1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoro propane (BAPHF) were purchased from Tokyo Kasei Co. NTDA was purified by vacuum sublimation before use. 2,2-Bis[4-(4-aminophenoxy)phenyl] hexafluoro propane disulfonic acid (BAPHFDS) was prepared by direct sulfonation of BAPHF, as previously reported [6]. *m*-Cresol was used as received.

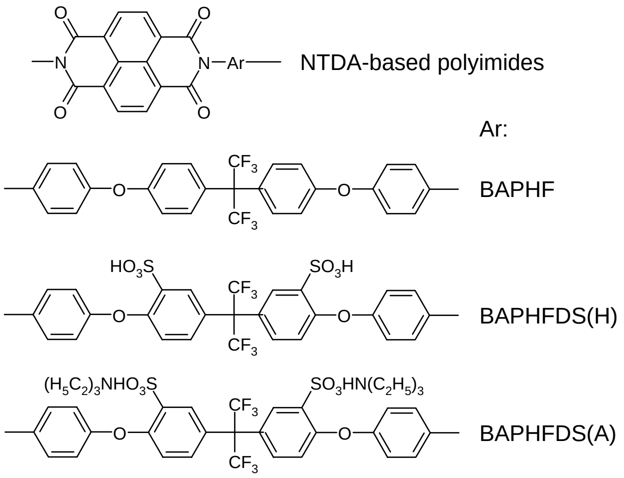

Fig. 1. Chemical structure of polyimides.

2.2. Preparation of sulfonated polyimides

NTDA–BAPHFDS polyimide was prepared by a one-step method as follows [6]. To a 100 ml of completely dried four-neck flask with stirrer was added 2.03 g (3.0 mmol) BAPHFDS, 0.6 ml (6 mmol) triethylamine, and 13 ml *m*-cresol under N_2 flow. After BAPHFDS was completely dissolved, 0.80 g (3.0 mmol) of NTDA and 0.55 g (4.5 mmol) benzoic acid were added into this flask. The mixture was heated at 80 °C for 4 h and 185 °C for 20 h in order to carry out polymerization and thermal imidization. After cooling to room temperature, additional 40 ml of *m*-cresol was added to dilute the highly viscous solution, and the resulting dark-brown polyimide solution was poured into acetone. The fiber-like precipitate was collected by filtration, washed with acetone and dried in vacuo.

NTDA–BAPHF polyimide was prepared by a similar procedure without triethylamine.

2.3. Membrane preparation

The sulfonated polyimide was dissolved in *m*-cresol to prepare a 5 wt% polyimide solution. The solution was cast onto Petri dish and dried at 120 °C for 10 h. The as-cast membrane obtained was soaked in methanol at 60 °C for 1 h to remove the residual solvent and then dried in vacuum at 150 °C for 10 h. The membrane thus obtained was NTDA–BAPHFDS polyimide in triethylammonium salt form. This is denoted by NTDA–BAPHFDS(A) polyimide membrane. Some of these membranes were soaked in 1.0 N hydrochloric acid at room temperature for 24 h successively. The proton-exchanged membranes were washed with de-ionized water, and then dried in vacuum at 150 °C for 10 h. The membrane is denoted by NTDA–BAPHFDS(H) polyimide membrane. NTDA–BAPHF polyimide membrane was obtained in the same procedure as NTDA–BAPHFDS(A) polyimide membrane. The membrane thickness was in the range of 30–50 μm.

2.4. Gas permeation experiments

Pure (single-component) gas permeation experiments were carried out using a vacuum time-lag method to measure the gas permeability coefficient P, which was determined from a steady state permeation flux in a period between 5 and 10 times the time lag θ. The effective membrane area was 18 cm^2. Apparent diffusion coefficient D was calculated from θ and the membrane thickness L:

$$D = \frac{L^2}{6\theta} \qquad (1)$$

The L was measured under an atmospheric condition. Apparent solubility coefficient S was calculated from P and D:

$$S = \frac{P}{D} \qquad (2)$$

Ideal separation factor was calculated as the P ratio of pure gases A and B. It is expressed by the product of the D and S ratios of the pure gases, i.e. diffusivity selectivity and solubility selectivity.

$$\frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \qquad (3)$$

The pure gas permeation measurements were carried out at 35 °C and upstream pressure of 1 atm. The downstream pressure was less than 0.7 cmHg, which was very low compared with the upstream pressure.

The mixed CO_2/N_2 gas permeation experiments were carried out using a RGP-1001S (Round Science) gas permeation experimental apparatus under dry and wet conditions. Fig. 2 shows the schematic diagram of the apparatus. The experiments were carried out by a carrier gas method using gas chromatographic analysis of the permeate gases. Water vapor was added to both feed and permeate carrier gas streams at the same relative humidity. The humidity was adjusted by controlling the temperature of humidifiers. The experiments were carried out at 50 °C and total pressure of 1 atm using a CO_2/N_2 (19/81) mixture. The partial pressures of CO_2 and N_2 at the permeate side were less than 1 and 0.1 cmHg, respectively. Permeability coefficient to each gas was determined using the steady state permeation flux of each gas, its partial pressure. Separation factor $\alpha_{A/B}$ was calculated by the following equation.

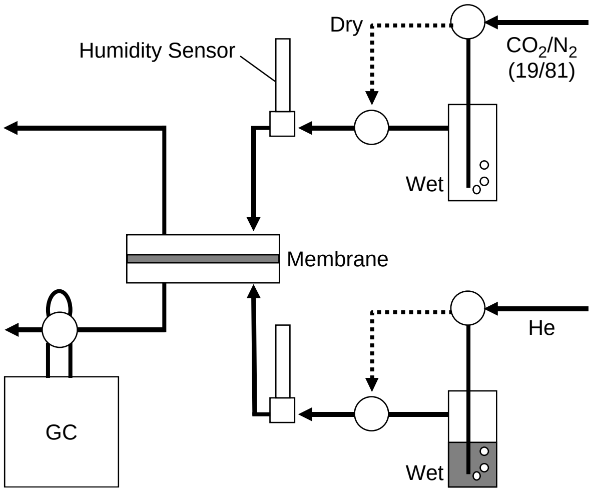

Fig. 2. Schematic diagram of apparatus for mixed gas permeation experiment.

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B} \qquad (4)$$

where x_i and y_i are mole fractions of component i in feed and permeate gases, respectively.

2.5. Other measurements

Water vapor sorption at different water vapor activities was measured at 50 °C using a sorption apparatus (BEL-18SP) by means of a volumetric method. The weight of membrane sample used was about 100 mg [8,9]. The density measurements were carried out in a dry box by the floating method using mixtures of carbon tetrachloride and xylene at a room temperature (20 °C) [9]. Differential scanning calorimetry (DSC) was carried out on a Rigaku DSC-8230 at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Characterization

Table 1 lists characterization results of the polyimides. The non-sulfonated polyimide displayed a glass transition temperature T_g of about 280 °C. The sulfonated polyimides had a small and broad endothermic DSC signal above 300 °C, which may correspond to the decomposition temperature of sulfonic acid groups. NTDA–BAPHFDS(H) polyimide did not show any DSC signal assigned to the glass transition below 300 °C. This polyimide was considered to have T_g above 300 °C because T_g may be increased by strong intermolecular interaction. On the other hand, NTDA–BAPHFDS(A) polyimide displayed a signal assigned to glass transition at 270 °C. Exchange of proton for triethylammonium reduced the intermolecular interaction, resulting in reduction in T_g.

Fractional free volume V_F was calculated from the following equation

$$V_F = \frac{V_T - V_0}{V_T} \qquad (5)$$

Table 1
Density and fractional free volume V_F of polyimides

Polyimide	T_g (°C)	Density (g/cm^3)	V_F
NTDA–BAPHF	ca. 280	1.407	0.183
NTDA–BAPHFDS(H)	(>300)	1.485	0.183[a]
NTDA–BAPHFDS(A)	ca. 270	1.380	0.093[a]

[a] The van der Waals volume of SO_3H is assumed to be the same as the sum of $-SO_2-$ and –OH as used in literature [14].

where V_T is the molar volume at temperature T and V_0 is the volume occupied by the molecules at 0 K per mole of repeat unit of the polymer. V_T is calculated from density data. V_0 is estimated to be 1.3 times [23] the van der Waals volume V_W calculated by the group contribution method of Bondi [24]. Since, the V_W of a sulfonic acid group –SO_3H was not determined so far, the V_W of –SO_2– and –OH group were combined instead, as reported in literature [14]. Most polyimides had the V_F in the range from 0.12 to 0.19 [21]. NTDA–BAPHF polyimide had relatively high V_F value, which was attributed to CF_3 groups. The CF_3 groups tended to disturb efficient packing of polymer chains because of reduced intermolecular interaction and a steric hindrance [21]. NTDA–BAPHFDS(H) polyimide had almost the same V_F as NTDA–BAPHF polyimide. Introduction of sulfonic acid may have two opposite effects on the packing of polymer chains. One is strong intermolecular interaction to reduce V_F [25,26] and another is a steric hindrance to increase it. The two effects seemed to be canceled out. NTDA–BAPHFDS(A) polyimide had lower V_F than the other polyimides, although bulky triethyl groups were introduced. This result may be because the bulky groups increased over all chain mobility and increase the packing of polymer chains. Similar decrease in V_F was observed when side-chain length increased for a polyacetylene [27].

3.2. Diffusion

Fig. 3 shows D the polyimide membranes studied here as a function of the effective diameter d of gas. The effective diameters used are 0.35 nm for CO_2 and the Lennard–Jones collision diameters for other gases. The d value for CO_2 was determined based on a good correlation between logarithm of D and d of the gas for various polyimide membranes [28,29]. With increasing the effective diameter, the D decreased. The D values for H_2 were not accurately determined because of too short time lag. They seemed to be around 10^{-6} cm^2/s, judging from the d of H_2 (0.29 nm).

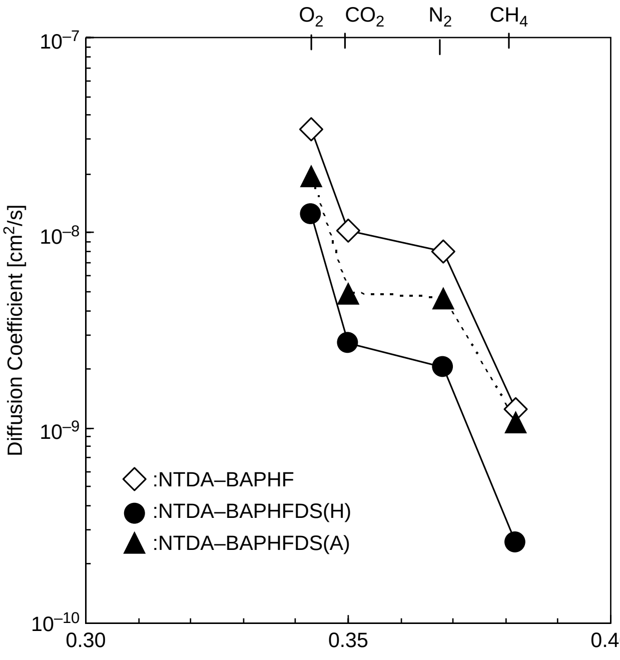

Fig. 3. Plots of D for the polyimide membranes at 35 °C and 1 atm versus effective diameters of gases.

Table 2
Apparent diffusion coefficients D to CO_2, O_2, N_2 and CH_4 and their ratio for CO_2/N_2 and O_2/N_2 separation systems for NTDA–BAPHFDS polyimide membranes in amine salt and proton forms and NTDA–BAPHF polyimide membranes at 1 atm and 35 °C

Diamine of NTDA-based polyimide	D (10^{-8} cm^2/s)				D_{CO_2}/D_{N_2}	D_{O_2}/D_{N_2}
	CO_2	O_2	N_2	CH_4		
BAPHF	1.0	3.4	0.81	0.12	1.3	4.2
BAPHFDS(H)	0.27	1.2	0.20	0.026	1.3	6.1
BAPHFDS(A)	0.49	1.9	0.46	0.11	1.1	4.2

Table 2 lists diffusion coefficients and their ratio. The D value for every gas was in the following order of diamines BAPHF > BAPHFDS(A) > BAPHFDS(H). Introduction of sulfonic acid groups into NTDA–BAPHF polyimide decreased the D by a factor of 3–5, although V_F did not change. The decrease in D was larger for the larger molecules. The decrease may be restricted local segmental mobility caused by strong intermolecular interaction caused by sulfonic acid groups. NTDA–BAPHF polyimide has two ether linkages, which are easily mobile [21]. For the polymer with similar packing density of polymer chains, higher local segmental mobility can momentarily create free volume holes large enough for a large gas molecule to pass through [21]. Strong intermoleculer interactions may make segmental motion difficult. When the sulfonic acid group was changed to sulfonic acid triethylammonium ($SO_3NH(C_2H_5)_3$), the D increased by a factor of 2–4, although V_F decreased. The increase in D was larger for the larger molecules. Reducing of intermolecular interactions and enhanced of local motion of ethyl side groups may provide larger effect on the D than V_F.

Diffusivity selectivity for O_2/N_2 increased with introduction of sulfonic acid groups and decreased with exchange of proton for triethylammonium. On the other hand, diffusivity selectivity for CO_2/N_2 hardly changed. This difference was because the difference in molecular size between CO_2/N_2 is smaller than that between O_2/N_2.

3.3. Sorption

Fig. 4 shows S as a function of Lennard–Jones potential force constant ε/k of gas. The S increased with increasing ε/k in a similar manner to that for common polymeric membranes. Table 3 lists solubility coefficients and their ratio. The S value for every gas was in the following order of diamines: BAPHF = BAPHFDS(A) < BAPHFDS(H). Introduction of sulfonic acid groups increased the S by a factor of 1.5–2.2, and exchange of proton for triethylammonium decreased the S by similar factors. These changes in S may be due to the changes in T_g. It was reported that glassy polymers with higher T_g

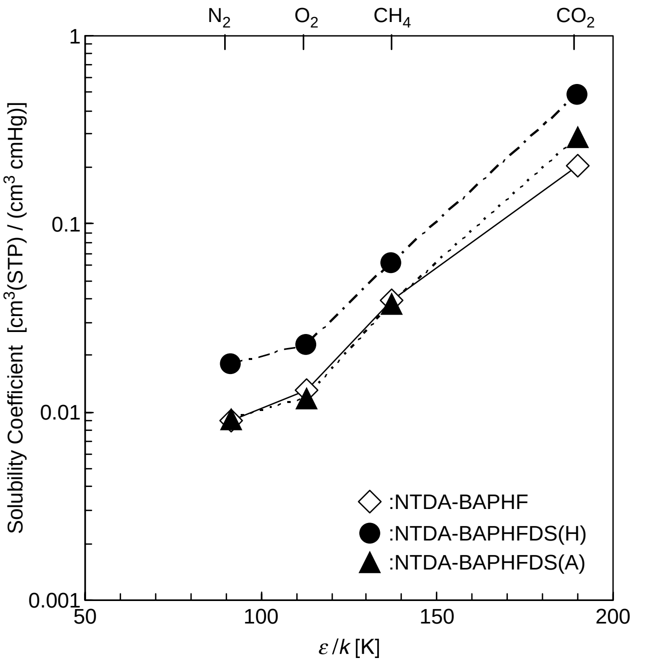

Fig. 4. Plots of S for NTDA–BAPHF, NTDA–BAPHFDS polyimide membranes at 35 °C and 1 atm versus Lennard–Jones potential force constants ε/k of gases.

Table 3
Apparent solubility coefficients S to CO_2, O_2, N_2 and CH_4 and their ratio for CO_2/N_2 and O_2/N_2 separation systems for NTDA–BAPHFDS polyimide membranes in amine salt and proton forms and NTDA–BAPHF polyimide membranes at 1 atm and 35 °C

Diamine of NTDA-based polyimide	S (10^{-2} cm^3 (STP)/(cm^3 cmHg))				S_{CO_2}/S_{N_2}	S_{O_2}/S_{N_2}
	CO_2	O_2	N_2	CH_4		
BAPHF	21	1.3	0.89	3.9	23	1.5
BAPHFDS(H)	49	2.3	1.8	6.2	27	1.3
BAPHFDS(A)	29	1.2	0.91	3.8	32	1.3

tended to display larger solubility [30]. This was explained by the dual mode sorption model [31,32]. According to the model, the sorption amount C of gas in a glassy polymer is expressed by the following equation

$$C = C_D + C_H = k_D p + \frac{C'_H bp}{1 + bp} \tag{6}$$

where k_D is Henry's law solubility constant, C'_H Langmuir capacity constant, b Langmuir affinity constant and p partial pressure of gas. The amount of sorption C_H in Langmuir site is generally much larger than Henry's law sorption amount C_D. It is well known that the parameter C'_H correlate T_g [33]. As a result, over all sorption amount C also correlated to T_g [30]. Although T_g of NTDA–BAPHFDS(H) polyimide was not observed below the onset of decomposition of sulfonic acid groups, it should be higher than T_g of NTDA–BAPHF polyimide and it may be in the temperature range of the decomposition. The difference in solubility selectivity among three polyimides was little. This is possible because the change in C'_H should be similar to every gas.

3.4. Pure gas permeability

Table 4 lists permeability coefficients and their ratio. The P value was in the following order of diamines: BAPHF > BAPHFDS(A) > BAPHFDS(H). Introduction of sulfonic acid groups into NTDA–BAPHF polyimide decreased the P by a factor of 1.6–3 because of a decrease in D, which exceed an increase in S. Exchange of proton for triethylammonium increased the P for CO_2, N_2 and CH_4 by a factor of 1.1–2.5. This was attributed to an increase in D, which exceed a decrease in S. For the smaller molecules such as H_2 and O_2, the increase in D did not exceed the decrease in S. As a result, the P for H_2 and O_2 decreased.

A difference in O_2/N_2 selectivity among the membranes was attributed to the difference in diffusivity selectivity. The difference in H_2/CH_4 selectivity may also be due to diffusivity selectivity. On the other hand, the difference in CO_2/N_2 selectivity was little because of smaller difference in molecular size and little change in solubility selectivity with T_g.

Fig. 5(a) and (b) show plots of P ratios versus P of highly permeable gases for H_2/CH_4 and O_2/N_2 systems for NTDA-based polyimide membranes investigated here together with the data for other polyimides [21,25,26]. NTDA–BAPHF polyimide displayed lower selectivity for H_2/CH_4 system. This was attributed to higher local segmental mobility around two ether linkages in a repeat unit, as observed for the BAPHF-based polyimide membranes prepared from other acid anhydrides [21]. Introduction of sulfonic acid groups increased the selectivity without significant loss of H_2 permeability. This indicated introduction of strong intermolecular interaction was suitable for separation of gas pair with a large difference in molecular size. NTDA–BAPHFDS(A) polyimide displayed lower selectivity than NTDA–BAPHFDS(H) polyimide because of enhanced local motion of the ethyl side groups, as observed for the polyimide with and without mobile side groups [21,28].

Table 4
Permeability coefficients to H_2, CO_2, O_2, N_2 and CH_4 and ideal separation factors for H_2/CH_4, CO_2/N_2 and O_2/N_2 separation systems for NTDA–BAPHFDS polyimide membranes in amine salt and proton forms and NTDA–BAPHF polyimide membranes at 1 atm and 35 °C

Diamine of NTDA-based polyimide	P (10^{-10} cm^3 (STP) cm/(cm^2 s cmHg))					P_{H_2}/P_{CH_4}	P_{CO_2}/P_{N_2}	P_{O_2}/P_{N_2}
	H_2	CO_2	O_2	N_2	CH_4			
BAPHF	50	21	4.4	0.72	0.48	100	29	6.1
BAPHFDS(H)	52	13	2.8	0.37	0.16	330	36	7.8
BAPHFDS(A)	29	14	2.3	0.42	0.40	72	34	5.5

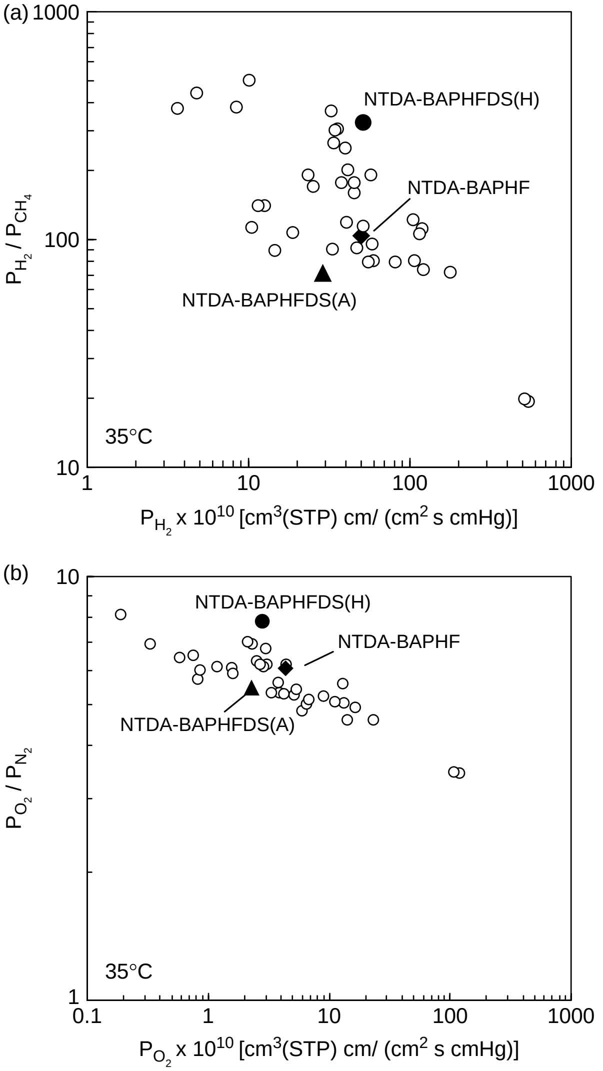

Fig. 5. Plots of *P* ratios versus *P* of highly permeable gases for (a) H_2/CH_4 and (b) O_2/N_2 separation systems for NTDA–BAPHFDS polyimide membranes in amine salt and proton forms and NTDA–BAPHF polyimide membranes (1 atm) together with the data for other polyimides(10 atm for H_2/CH_4 and 2 atm for O_2/N_2) [20,23,24].

NTDA–BAPHFDS(H) polyimide also displayed better performance for O_2/N_2 separation. This indicated strong intermolecular interaction was also effective for O_2/N_2 separation.

3.5. Water vapor sorption

Fig. 6 shows sorption isotherms of water vapor for NTDA-based polyimides used here. The amount of sorbed water at an activity was in the following order: BAPHF ≪ BAPHFDS(A) < BAPHFDS(H). The isotherm for NTDA–BAPHF polyimide was similar to those for other polyimides [34] and interpreted by means of the dual sorption model. On the other hand, the isotherms for NTDA–BAPHFDS(H) and NTDA–BAPHFDS(A) polyimides were sigmoidal and similar to type II BET adsorption. This type isotherm has been observed for hydrophilic polymers having polar groups such as hydroxyl, carboxyl and amide groups [34], and recently observed for some SPIs [8,9]. Sulfonic acid groups interacted strongly with water molecules and acted as water sorption sites, resulting in a Langmuir-type isotherm at lower activity. With increasing activity above 0.7, the amount of sorbed water increased significantly. This was attributed to the plasticization effect of sorbed water [8,9].

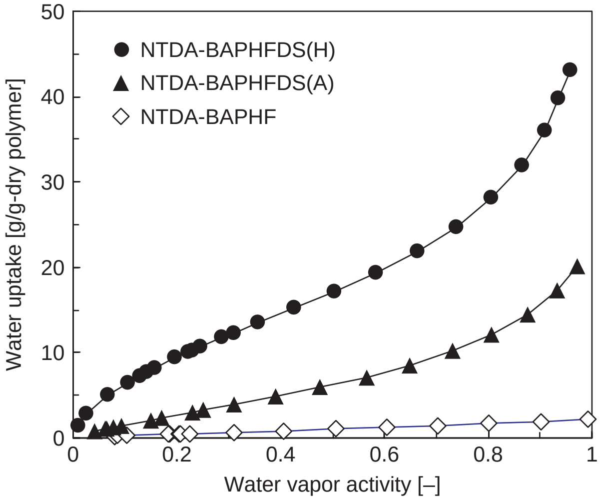

Fig. 6. Water vapor sorption isotherms for NTDA–BAPHF, NTDA–BAPHFDS(H) and NTDA–BAPHFDS(A) polyimides at 50 °C.

3.6. Permeability and selectivity to wet CO_2/N_2 mixture

Fig. 7 shows permeability coefficients to CO_2 and N_2 and the separation factor for a CO_2/N_2 (19/81) mixture at 50 °C and total pressure of 1 atm as a function of relative humidity for the polyimides investigated here. CO_2 permeability coefficients to the mixture at dry condition for three NTDA-based polyimides were about 10% higher than their permeability coefficients to pure CO_2 at 35 °C. On the other hand, N_2 permeability coefficients to the mixture at dry condition were 10, 90 and 70% higher than their permeability coefficient to pure N_2 at 35 °C. The higher values for a mixture were attributed to higher temperature and lower partial pressure (1 atm for pure gas and 0.19 atm for CO_2 and 0.81 atm for N_2 in the mixture).

The effect of coexisting water vapor on gas permeability was quite different for each polyimide. With increasing humidity both CO_2 and N_2 permeability for NTDA–BAPHF polyimide decreased by 50% and the separation factor was around 28. On the other hand, CO_2 and N_2 permeability coefficients for NTDA–BAPHFDS(H) polyimide slightly decreased at low humidity, and then increased by factors of 24 and 12, respectively. CO_2 and N_2 permeability coefficients for NTDA–BAPHFDS(A) polyimide also decreased, but more, at low humidity and turned to increase by factors of 12 and 5, respectively. The separation factors for both sulfonated polyimides are around 21 below 20% RH. However, they increased up to 52 for NTDA–BAPHFDS(H) and up to 40 for NTDA–BAPHFDS(A) polyimides, respectively.

The decrease in gas permeability for NTDA–BAPHF polyimide in the entire range and that for the sulfonated

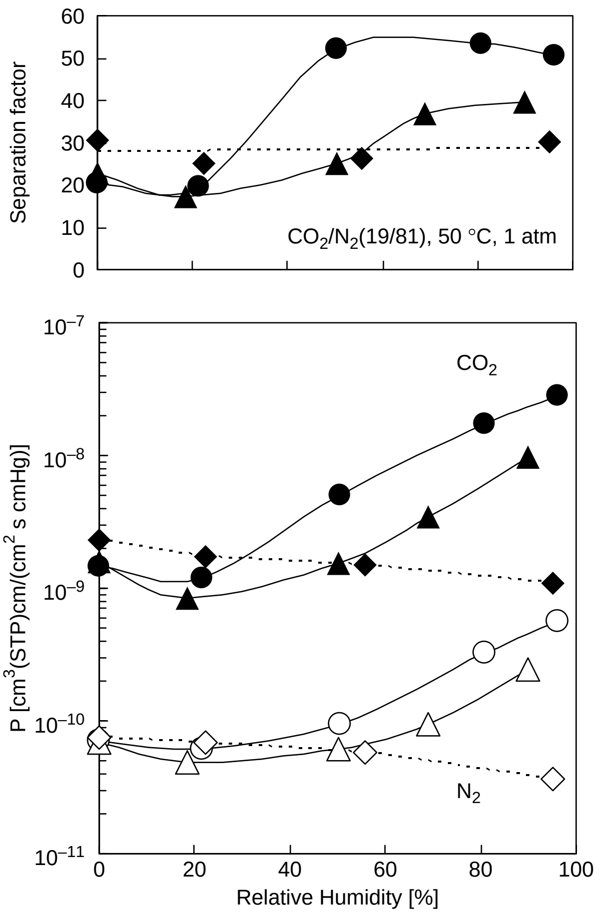

Fig. 7. Plots of permeability coefficients to CO_2 and N_2 and the separation factor for a CO_2/N_2 mixture versus relative humidity. NTDA–BAPHF: ◇, ◆; NTDA–BAPHFDS(H): ○, ●; NTDA–BAPHFDS(A): △, ▲.

polyimides at low humidity was explained by the dual-mode sorption and transport model [31,32]. According to the model, the permeability coefficient of a gas A for a mixture consisting of gases A and B, and water vapor W, is expressed by the following equation:

$$P_A = k_{D,A}D_{D,A} + \frac{C'_{H,A} b_A D_H}{1 + b_A p_A + b_B p_B + b_W p_W} \qquad (7)$$

where $k_{D,A}$ is Henry's law solubility constant, $C'_{H,A}$ Langmuir capacity constant, $D_{D,A}$ and $D_{H,A}$ diffusion coefficients of Henry's law population and Langmuir population, respectively, of component A, and b_i and p_i are Langmuir affinity constant and partial pressure of component i. Water has a much higher affinity constant than gases, that is, $b_W \gg b_A$, especially for sulfonated polyimides having sulfonic acid groups. The equation predicts the presence of water reduces the gas permeability due to competition between water and gases on Langmuir sorption sites.

The increase in gas permeability for both sulfonated polyimides above 20% RH was explained by plasticization caused by a large amount of sorbed water. Plasticization increases diffusion coefficients to gases and permeability coefficients. The plasticization effect was more for NTDA–BAPHFDS(H) polyimide than NTDA–BAPHFDS(A) polyimide because of higher water uptake. Plasticization normally reduce diffusivity selectivity because an increase in D should be larger for a larger gas. However, the difference in molecular size between CO_2 and N_2 is smaller and diffusivity selectivity was around one even at a dry state, as shown in Table 2. Consequently, plasticization did not change diffusivity selectivity virtually. On the contrary, an increase in selectivity with humidity was observed as shown in Fig. 7. It should be concluded that the increase in separation factor observed for both sulfonated polyimides should be attributed to enhance solubility selectivity. The matrix of sulfonated polyimides may become much more polar with increasing the amount of sorbed water, resulting in an increase in solubility selectivity. For NTDA–BAPHF polyimide, plasticization effect was not observed because water uptake was too low even at high humidity.

Fig. 8 shows plots of separation factor for CO_2/N_2 versus CO_2 permeability in mixed gas permeation for the NTDA-based polyimides used here at 50 °C together with the data for the amine-modified polyimides and the other polyimides at 35 °C [22]. It should be noted that the CO_2/N_2 separation performance significantly depends on temperature; it is better at lower temperature, because the selectivity decreases sharply with increasing temperature. The amined-modifed polyimides displayed high selectivity even under a dry condition because of acid–base interaction. On the other hand, the sulfonated polyimides used here displayed low selectivity under a dry condition but displayed relatively high selectivity under wet conditions. The sulfonated polyimides needed water to display high selectivity. This is advantageous in practical application for recovery of CO_2 from flue gas. NTDA–BAPHFDS(H)

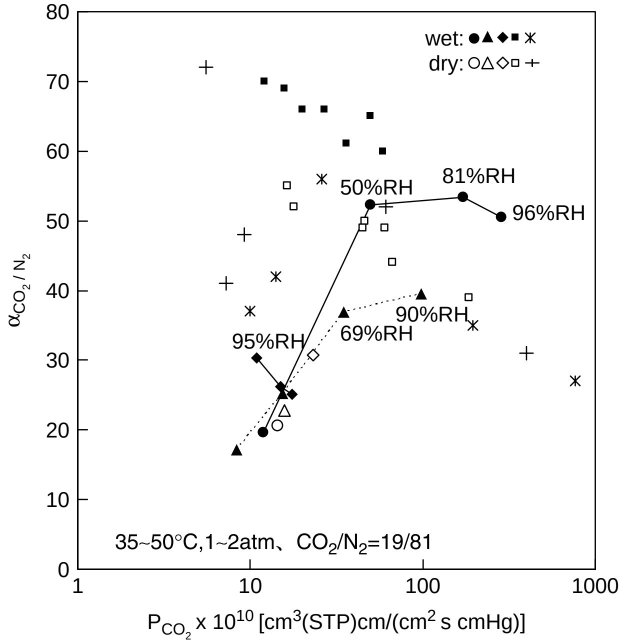

Fig. 8. Plots of separation factor for CO_2/N_2 versus CO_2 permeability in mixed gas permeation for NTDA-based polyimide membranes at 50 °C and 1 atm (NTDA–BAPHF: ◇, ◆; NTDA–BAPHFDS(H): ○, ●; NTDA–BAPHFDS(A)) together with the data in literature at 35 °C and 2 atm (□, ■; amined-modified polyimides: +, ⚹; the other polyimides) [17].

polyimide also displayed high CO_2 permeability compared to the amine-modified polyimides. The performance of NTDA–BAPHFDS(A) polyimide under wet conditions was not as high as NTDA–BAPHFDS(H) polyimide because of lower water uptake. The sulfonated polyimide membranes after the wet gas permeation measurements at 50 °C for 20 h or longer were as tough as before.

4. Conclusion

Gas permeation properties were investigated under dry and wet conditions for sulfonated and non-sulfonated polyimides, which had the same polymer backbone with or without sulfonic acid groups. Introduction of sulfonic acid groups gave the membrane displaying high selectivity for H_2/CH_4 separation under dry condition.

Under wet conditions, the sulfonated polyimide membranes displayed relatively high selectivity with high gas permeability for CO_2/N_2 separation.

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