Separation of Binary Mixtures of Carbon Dioxide and Methane through Sulfonated Polycarbonate Membranes

S. Sridhar,[1,2] Tejraj M. Aminabhavi,[1] M. Ramakrishna[2]

[1]*Center of Excellence in Polymer Science, Karnatak University, Dharwad, 580 003, India*
[2]*Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India*

ABSTRACT: Polycarbonate (PC) was sulfonated to varying degrees using acetyl sulfate. FTIR and NMR experiments were carried out to confirm sulfonation. The membranes were characterized by DSC and TGA to assess thermal stability. Ion exchange capacity (IEC) and degree of sulfonation (DS) were determined and their effect on permeation of CO_2 and CH_4 gases was investigated. Free volume fractions (FVF) of the membranes were found to decrease from 0.31 to 0.19 as the DS increased from 0 to 39.4%. Single gas permeation studies revealed that sulfonated PC exhibited higher selectivities than unmodified PC at reduced permeability. For a DS of 14.4%, sulfonated PC exhibited a selectivity of 36.1, which was 1.7 times that of unmodified PC, whereas the permeability dropped from 8.4 to 4.7 Barrers. In case of binary CO_2/CH_4 mixture permeation through PC membrane of the same DS, an increase in CO_2 feed concentration from 5 to 40 mol % produced an increase in permeability from 0.24 to 2.0 Barrers and a rise in selectivity from 11.7 to 27.2 at constant feed pressure (20 bar) and temperature (30°C). A rise in the feed pressure from 5 to 30 bar at a constant feed composition of 5% CO_2 resulted in a reduction in permeability from 0.38 to 0.2 Barrers and selectivity from 15.6 to 10.2. Sulfonated PC was found to be a promising candidate for separation of CO_2 from CH_4. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1749–1756, 2007

Key words: gas separation; CO_2/CH_4 mixture; sulfonated polycarbonate; degree of sulfonation; free volume fraction

INTRODUCTION

The world market for natural gas is estimated at approximately 22 billion US dollars annually.[1] Natural gas is a complex mixture containing desirable gaseous hydrocarbons such as CH_4 and nonhydrocarbon components such as CO_2, H_2S, and water vapor, which corrode pipelines and lower calorific value. Separation of CO_2 from the desirable lower hydrocarbons such as methane is an important unit operation. Polymeric membranes that are currently available are able to compete successfully with other technologies.[2] For continued growth in this area, highly permeable and selective membranes must be developed. In membrane-based deacidification of natural gas, permeability ratio of CO_2/CH_4 mixture is a very critical factor, since CO_2 happens to be the slowest gas among the impurities, whereas CH_4 is the fastest among the hydrocarbon components.[3] Cellulosic polymers have been successfully used for natural gas sweetening,[4] but these have been found to suffer drawbacks such as swelling and plasticization, which could be averted through the usage of polymers with rigid aryl backbone.[5] The trend in material development for better gas separation membranes is mainly towards improving the properties of existing polymers. Typically, a trade-off exists between permeability and selectivity in polymer membranes.[6] To achieve good membrane performance, the polymer should ideally possess two characteristics: a high free volume fraction and a narrow free volume distribution. This can be achieved in two ways: (1) by chemical modification during synthesis, using polymer structure–property relationship, and (2) by physical improvement of the membrane structure, such as for example, by ion irradiation.[7]

Glassy polymers with aryl backbone such as polysulfone, polyimide, poly(phenylene oxide) and polycarbonate are known to exhibit good permeability and/or selectivity for CO_2/CH_4 system.[8] Suitable modifications could render some of these polymers commercially viable for CO_2 removal from natural gas. Earlier studies[9–12] have indicated that systematic variations in intersegmental mobility and chain packing can be used to achieve improvement in membrane properties. In a prior article,[13] membrane performance of the mixed matrix composites of polypyrrole with polybisphenol-A carbonate (PC) prepared by the com-

bined *in situ* solution polymerization followed by solvent evaporation was studied. Here, polybisphenol-A carbonate provides the necessary backbone rigidity for good thermal resistance and mechanical strength, while allowing relatively faster gas permeation rates.[14] In a more recent study, Hacarlioglu et al.[15] developed the polycarbonate–polypyrrole mixed matrix membranes for the separation of O_2/N_2, H_2/CH_4 gaseous mixtures and found that incorporation of polypyrrole was helpful in increasing selectivity considerably. However, to the best of our knowledge, no effort has been made on the basic chemical modification of polycarbonate (PC) as a membrane for the separation of CO_2/CH_4 mixtures. This prompted us to undertake the present investigation to modify the structure of polycarbonate by sulfonation and examined its performance for separation of binary mixtures of CO_2 and CH_4. The membranes thus prepared were characterized by FTIR, NMR, DSC, and TGA techniques. The effect of degree of sulfonation (DS) on the permeation characteristics of single gases as well as mixtures of CO_2 and CH_4 was investigated.

EXPERIMENTAL

Materials

Polycarbonate ($M_n = 64,000$) was purchased from Aldrich Chemical (Milwaukee, WI). The solvents 1,2-dichloroethane, acetic anhydride, and sulfuric acid of A.R. grade, were purchased from S.D. Fine Chem. Ltd., Mumbai, India.

Membrane preparation

Sulfonated polycarbonate (SPC) was synthesized by using acetyl sulfate as the sulfonating agent,[16] which was freshly prepared by mixing 15.3 mL of acetic anhydride with 5.6 mL of sulfuric acid in 79 mL of 1,2-dichloroethane. A desired quantity of acetyl sulfate solution was added to the reaction flask containing a solution of 20.8 g of polycarbonate in 98 mL of 1,2-dichloroethane. The sulfonation reaction was carried out for 1 h at 50°C and was then terminated by adding methanol. The resulting sulfonated polycarbonate was isolated by introducing steam. The polymer thus formed was recovered by filtration.

Membranes synthesized for the study were prepared by solution casting followed by solvent evaporation. Dense PC membrane was prepared by dissolving 20 wt % of PC in 1,2-dichloroethane. The bubble-free solution was cast on a clean glass plate and dried in a vacuum oven at 60°C for about 24 h. In case of SPC, approximately 12 wt % of the polymer was dissolved in 1,4-dioxane and cast per the same procedure described above.

Membrane characterization

Fourier transform infrared spectra

FTIR spectra of the dense and the sulfonated polycarbonate were scanned in the range 4000–400 cm^{-1} using Nicolet-740, Perkin-Elmer 283B FTIR Spectrometer.

Differential scanning calorimetry

DSC runs on PC and SPC membranes were taken on a Perkin–Elmer DSC Model 7. Measurements were performed over the temperature range between 30° and 200°C at a heating rate of 5°C/min in a hermetically sealed aluminum pan. Membrane samples were allowed to attain steady state with the solvents and the sample pan was conditioned in the instrument before running the experiment.

Thermogravimetric analysis

Thermal stability of the PC based membranes was examined using Seiko 220TG/DTA analyzer, from 25 to 700°C at a heating rate of 10°C/min with nitrogen flushing at the rate of 200 mL/min. The membrane was subjected to TGA to determine the thermal stability and decomposition characteristics.

Mechanical properties

The equipment used for evaluating the mechanical strengths of the polymers was the universal testing machine (UTM), model AGS-10kNG of Shimadzu make, Japan, with an operating head load of 5 kN. Cross-sectional area of the sample of known width and thickness was calculated. The membranes were placed between the grips of the testing machine. The grip length was 5 cm, while the speed of testing was set at the rate of 12.5 mm/min. Tensile strength was calculated using the equation:

$$\text{Tensile Strength} = \frac{\text{Max load}}{\text{Cross sectional area}} \text{ N/mm}^2 \quad (1)$$

Ion exchange capacity and degree of sulfonation

The ion exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of the dry polymer. While the degree of sulfonation indicates the average number of sulfonic acid groups present in the sulfonated polymer. To determine the degree of substitution by the acid groups, the sulfonated membranes and the unmodified polymers of similar weights were soaked in 50 mL of 0.01N sodium hydroxide solution for 12 h at ambient temperature. Then, 10 mL of the solution was titrated with 0.01N sulfuric acid.[17] The sample was regenerated with 1M hydrochloric acid,

washed free of acid with water, and dried to constant weight. IEC was calculated as:

$$IEC = \frac{B - P \times 0.01 \times 5}{m} \quad (2)$$

where B is the amount of $0.01N$ sulfuric acid used to neutralize the blank, P is the amount of $0.01N$ sulfuric acid used to neutralize the sulfonated membranes, 0.01 is the factor used to account for normality of sulfuric acid/NaOH, 5 is the factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration, and m is sample mass in g. The empirical relationship between DS and IEC is:

$$DS = \frac{254 \times IEC}{[1000 - (254 \times IEC) - (335 \times IEC)]} \quad (3)$$

Free volume fraction (FVF)

To calculate FVF, the molar volume of the polymer was first determined by van der Waals method of group contribution. Then the FVF was calculated according to the equation:[18]

$$FVF = \frac{(1 - V_w\rho)}{M} \quad (4)$$

where V_w is van der Waals molar volume of the polymer, M is molecular weight of the polymer and ρ is density of the membrane. The following equations were used to calculate the molecular weight, M, and molar volume, V_M, of the chemically modified PC polymer.[19]

$$V_w = \frac{64,000}{254}\left[V_{w,PC}\left(1 - \frac{DS}{100}\right) + V_{w,SPC}\left(\frac{DS}{100}\right)\right] \quad (5)$$

$$M = \frac{64,000}{254}\left[254\left(1 - \frac{DS}{100}\right) + M_{SPC}\left(\frac{DS}{100}\right)\right] \quad (6)$$

Description of gas separation unit

Schematic diagram of the high-pressure gas separation manifold used in permeability studies is given in Figure 1. A permeability cell of SS 316 was designed and fabricated indigenously and was used in the permeability measurements. Effective area of the membrane in the cell was found to be 10 cm^2. Feed and permeate lines for the manifold were made of 1/4″ SS piping connected together by means of compression fittings. The vacuum line consisted of a network of high vacuum rubber-glass valve connections capable of giving pressure as low as 0.05 mmHg.

Permeability measurements

The continuous flow method was chosen to carry out permeability measurements. In this method, the feed
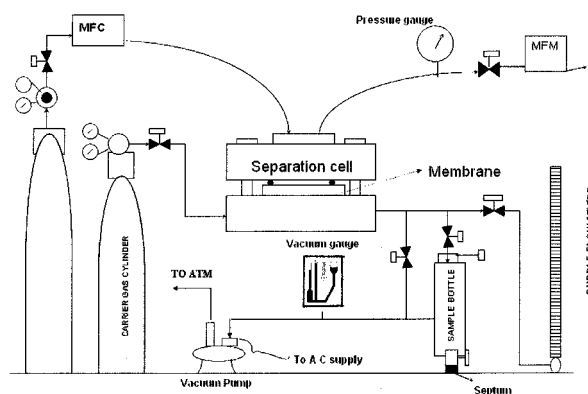

Figure 1 Experimental manifold for gas separation studies.

component permeates through the membrane into a flowing stream of inert gas in the permeate compartment. The stream exiting the permeate side is then analyzed to determine the component concentration, i.e., the product of concentration and stream flow rate gives the permeation rate. The continuous flow method was preferred since the measurement of low as well as high permeation rates could be easily done by varying the carrier gas flow rate accordingly so as to bring the concentration of the penetrant in the permeate stream within the detectable range of the analyzer (gas chromatograph).

Pure gas permeabilities of methane and carbon dioxide were determined using the polymer membranes by maintaining a constant pressure differential of 20 kg/cm^2 across the membrane. All experiments were performed at ambient temperature (30°C). Feed and permeate lines were evacuated using a vacuum pump (Model ED-18, Hind High Vacuum Co, Mumbai, India). The feed gas was introduced slowly into the upper chamber by means of a mass flow controller (MFC), keeping the outlet valve partially closed until the dial gauge indicated the constant desired pressure. Hydrogen was used as the carrier gas to sweep the permeated gas to SS 316 gas sample containers (capacity 100 mL) for subsequent analysis. Samples were collected after steady state was reached. Experiments were repeated in triplicate to check for reproducibility, within a maximum of 3% standard error.

Flow rate of the carrier gas was controlled and kept constant with the help of a needle-valve and measured by means of a soap-bubble meter connected at the end of the permeate line. Permeate stream was collected after 3 h of equilibration of the membrane with the feed gas. The duration of sample collection was 6–8 h and composition of the feed and permeate streams were determined by gas chromatography. Permeability coefficient (K) was calculated using the equation,

$$K = \frac{Q}{tA(P1 - P2)}l \quad (7)$$

where Q is volume of gas permeated [cm^3 (STP)], t is the permeation time (in s), A is the effective membrane area (in cm^2) for gas permeation, l is membrane thickness (in cm); and $P1$ and $P2$ are the feed side and permeate side partial pressures (in cmHg), respectively. Selectivity was then determined as the ratio of permeability coefficients of the two gases (K_{CO2}/K_{CH4}).

Analytical procedure

Feed and permeate compositions were determined using a Nucon gas chromatograph (GC) operated with a thermal conductivity detector (TCD) using a Haysep "Q" column. The oven temperature was maintained at 50°C, while the injector and detector temperatures were set at 150°C. Hydrogen at a pressure of 0.9 bar was used as the carrier gas. Equal volumes (1 μL) of the feed and permeate samples were injected into the GC. The ratio of permeate and feed peak areas at a fixed attenuation gives the quantity of gas permeated. When dealing with the binary and multicomponent mixtures, calibration is necessary. The calibration was carried out by injecting 0.1 mL each of pure CO_2 and CH_4 to determine the peak areas obtained followed by a gradual increase in the sample size in steps of 0.1 mL each up to a maximum of 1.1 mL.

RESULTS AND DISCUSSION

In the present study, sulfonation was used to modify the structure of the membrane, which could help in inducing polarity to an intrinsically nonpolar/hydrophobic polycarbonate[20] as well as in reducing free volume of the matrix. However, the distribution of substituent sulfonated groups, need not necessarily be uniform throughout the PC backbone as suggested by Chiou and Paul,[21] who reported that sulfonic groups in Nafion membrane, a sulfonated fluorohydrocarbon, form clusters. Similar effects can be observed for SPC membrane. The presence of such clusters would probably induce polar and nonpolar regions in SPC. Chemical structures of polycarbonate and sulfonated polycarbonate are given in Figure 2.

IEC versus solubility in organic solvents

Since sulfonation could modify the chemical character of PC, it helps to reduce the crystallinity and consequently affects its solubility. In the present study, PC was sulfonated to various degrees by varying the amount of acetyl sulfate to give IEC values ranging from 0.25 to 1.19 meq/g, which correspond to the DS values in the range 6.6–39.4%, respectively. However, a judicious selection of the sulfonating agent can provide DS in the range of 1–100% per repeat unit of the
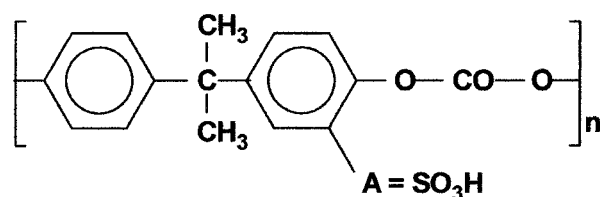
b) Sulfonated polycarbonate
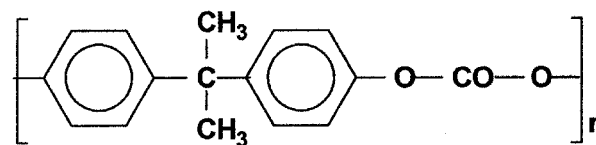
a) Polycarbonate

Figure 2 Structures of (a) polycarbonate and (b) sulfonated polycarbonate.

polymer.[22,23] Note that physical and chemical properties of SPC membrane depend upon the concentration of sulfonic groups and the nature of counter ions. For a DS of 25%, sulfonic groups are attached on approximately every fourth repeating unit of the polymer, but this distribution may not be as expected. The modification of PC has a significant effect on its solubility. For instance, SPC with a DS of 10%, is soluble in dipolar aprotic solvents like dimethyl formamide (DMF), dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO). On the other hand, >40% of sulfonation renders SPC soluble in almost all the common organic solvents. The polymer becomes soluble in hot water above 100% sulfonation and loses its mechanical stability completely.

Fourier transform infrared spectra

Spectra of the sulfonated polycarbonate as shown in Figure 3(b) exhibit sharp peaks at 1160 and 1340 cm^{-1}, and broad peaks around 1150–1220 cm^{-1}, which are not observed in the unmodified polycarbonate. The peak at 1360 cm^{-1} identified in the spectra of SPC is due to asymmetric stretching of S=O bond, whereas symmetric vibration of this bond produces a characteristic split around 1150–1185 cm^{-1}. Thus, FTIR data indicates the presence of —SO_3H groups, which confirms the occurrence of sulfonation.
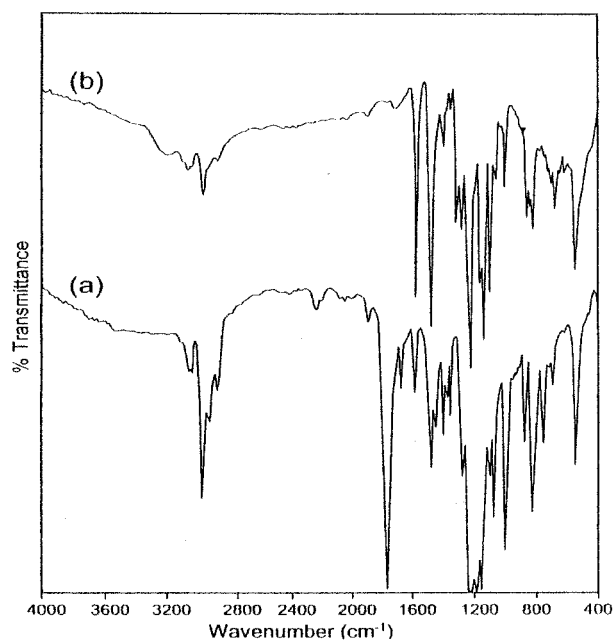
Figure 3 FTIR spectra of (a) polycarbonate and (b) sulfonated polycarbonate.

Nuclear magnetic resonance

NMR characterization (Fig. 4) revealed that the aromatic segment of proton HNMR spectra of the modified polycarbonate is diminished because of sulfonation as depicted by the replacement of aromatic protons with sulfonic acid groups. New signals at 3.2 ppm, 3.4 ppm, and 3.6 ppm display the changes in field strength around protons pertaining to the methyl groups.

Tensile strength and elongation

Tensile strengths at break for polycarbonate before and after sulfonation were found to be 182.3 N/mm^2 and 157.2 N/mm^2, respectively. The decrease in the tensile strength post sulfonation, probably occurs because of the expansion of polymer chain matrix upon reaction. This type of expansion could increase the free volume, thereby increasing the chain movements, which makes the polymeric material softer and flexible. Such increased chain segmental movement implies that polymer could probably change partially from a glassy state (hard and brittle) to a rubbery state (flexible and soft), thus, causing a reduction in tensile strength at break as well as elongation.

Differential scanning calorimetry

DSC thermo grams shown in Figure 5, indicate that after sulfonation of polycarbonate, its T_g has shifted from 147°C to 120°C. However, the unneutralized free acid form (—SO_3H) of the sulfonated PC
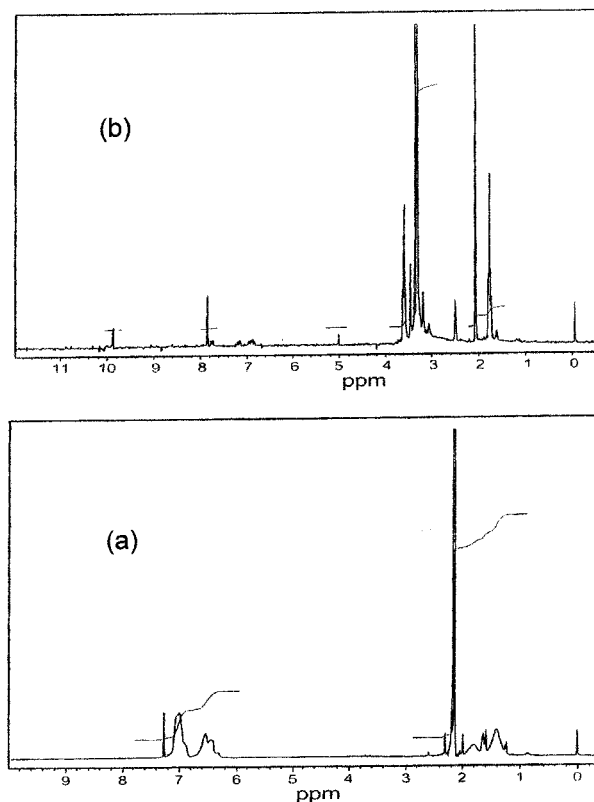

Figure 4 NMR spectra of (a) polycarbonate and (b) sulfonated polycarbonate.

showed significantly lower T_g than the unmodified PC, because of the structural changes occurring on account of sulfonation. The higher the degree of sulfonation, greater will be the free volume of the sulfonated
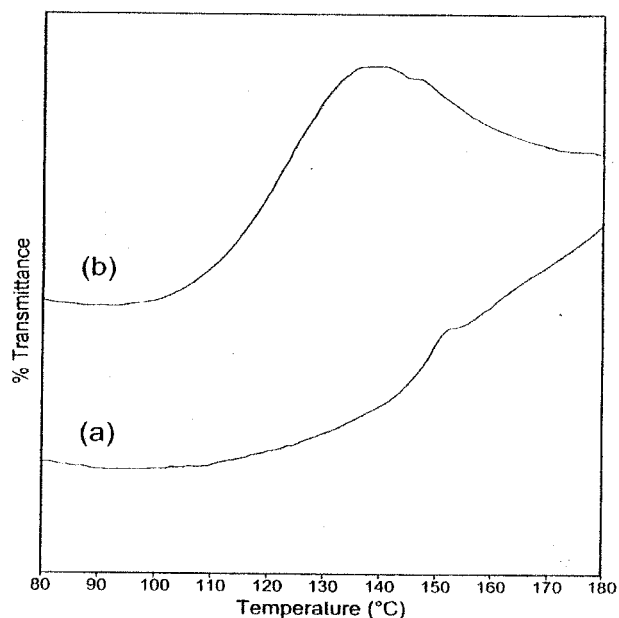

Figure 5 DSC curves of (a) polycarbonate and (b) sulfonated polycarbonate.
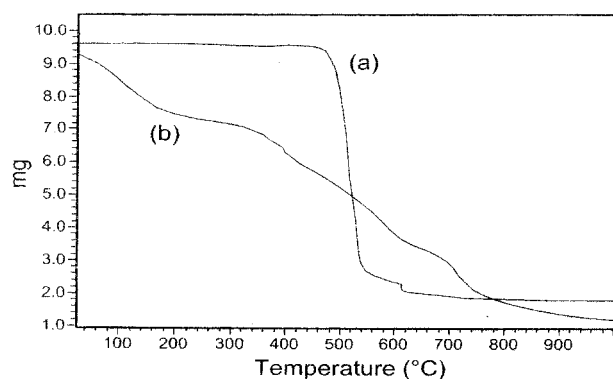
Figure 6 TGA curves of (a) polycarbonate and (b) sulfonated polycarbonate.

PC membrane, thereby enabling a change of polymer state from amorphous to crystalline.

Thermogravimetric analysis

The TGA data of the SPC shown in Figure 6(b) has three weight loss stages occurring in the regions 70–140°C, 260–410°C, and 470–500°C with the final decomposition occurring at 510°C. The locations of weight loss stages observed are quite identical to the those reported by Gilbert.[24] For those membranes that were exposed to air before subjecting to TGA, weight loss in the first, second, and third stages could be attributed to the loss of moisture absorbed from air, the decomposition of sulfonic groups as well as splitting of the main chains respectively, prior to the final decomposition of the polymer.

Free volume fraction

The structure of PC is shown in Figure 1(a). The group A in Figure 1(b) represents an atom or a substituent group attached to the aromatic carbon. In case of SPC, A is sulfonic acid (—SO₃H) group. Table I lists van der Waals volumes of different groups constituting the repeat units of the sulfonated PC. For the unmodi-

TABLE II
van der Waals Molar Volume, Molecular Weight and Fractional Free Volume of the Membranes

DS (%)	ρ (g/cm^3)	V_w (cm^3/mol)	M (g/mol)	FVF (cm^3)
0	1.20	36,787	64,000	0.310
6.6	1.246	37,291	65,347	0.289
14.4	1.288	37,887	66,939	0.271
19.8	1.326	38,299	68,041	0.254
25	1.383	38,696	69,102	0.226
39.4	1.452	39,795	72,123	0.199

fied PC, molecular weight of the repeat unit structure is 254 g/mol, whereas the weight average molecular weight of the unmodified PC is 64,000 g/mol. Table II summarizes the results of free volume fraction for the unmodified and the sulfonated PC membranes. It is evident that as the DS increases from 0 to 39.4%, the FVF reduced from 0.31 to 0.199 for SPC of 39.4% DS. This reduction in FVF gives an indication of the compaction of the polymer segments leading to enhancement in chain packing density.

Gas permeation results

Single gas permeation behavior of CO₂ and CH₄

Table III compiles single gas permeability and ideal selectivity data for PC and SPC membranes at a feed pressure of 20 bar. It is evident that an increase in DS from 0 to 39.4% caused a reduction in CO_2 permeability from 8.4 to 1.5 Barrers, but an enhancement in selectivity from 21.0 to 74.8. The decrease in free volume element size upon sulfonation could lead to a much greater steric hindrance for the diffusing species,[19] as depicted in Table II and Figure 7. A reduction in diffusivity for both gases would be expected and therefore a reduction in permeability would occur. However, a greater reduction would be expected for methane whose molecular size (Lennard–Jones kinetic diameter) is 3.8 Å than for carbon dioxide whose molecular size is approximately 3.3 Å. Therefore an increase in

TABLE I
Molecular Weight and van der Waals Molar Volume of Chemical Groups Forming the Repeat Units of PC and SPC Membranes

Sl. No.	Chemical group	V_w (cm^3/mol)	M_w (g/mol)
1	—C	4.76	12.0
2	—H	3.44	1.0
3	—SO₂⁻	20.03	64.1
4	—OH	8	17.0
5	—O	5.5	16.6
6	—C₆H₄—	42.32	76
7	—CH₃	15.08	15
8	—CO—	10.26	28
9[a]	—SO₃H	28.03	81

[a] —SO₃H = —SO₂⁻ + —OH⁻.

TABLE III
Variation of Single Gas Permeability and Ideal Selectivity with Degree of Sulfonation of Polycarbonate Membranes (Feed Pressure = 20 bar)

Degree of sulfonation (%)	IEC (meq/g)	Permeability (Barrers[a]) CO₂	Permeability (Barrers[a]) CH₄	Selectivity K_{CO2}/K_{CH4}
0	0	8.4	0.4	21.0
6.6	0.47	6.3	0.23	27.4
14.4	1.04	4.7	0.13	36.1
19.8	1.42	3.2	0.07	45.7
25.0	1.80	2.6	0.046	56.5
39.4	2.84	1.5	0.02	74.8

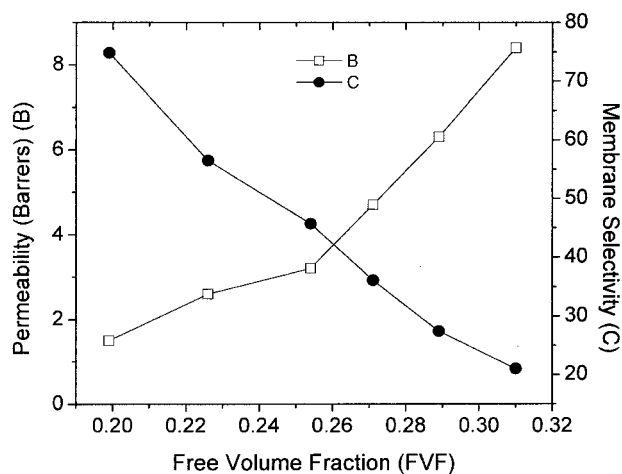[a] 1 Barrer = 10^{-10} cc(STP) cm/cm^2 sec cmHg.

Figure 7 Effect of FVF in sulfonated PC on CO_2 permeability and selectivity.

CO_2/CH_4 selectivity, coupled with decreasing permeability for both, would be expected with reduction in free volume element size.

Single gas studies give a clear indication of behavior of the membranes with respect to individual gases. As evident, membranes with high degree of sulfonation (e.g. 39.4%) render them more selective to CO_2, but yield poor permeabilities, thereby prohibiting their use in separating CO_2 and CH_4 mixtures. To strike a balance between permeability and selectivity, PC needs to be sulfonated to the extent of 5–20% so as to obtain a membrane that could offer a marginally good permeability with a relatively high selectivity without sacrificing much of its mechanical strength.

Permeation of binary mixtures

Effect of feed CO_2 concentration. PC membranes having DS values of 14.4 and 25% were chosen for studying the effect of varying feed compositions and their performance was compared with that of the unmodified PC membrane. This study was conducted at ambient temperature (30°C), at a feed pressure of 20 bar. Figure 8 shows the variation of permeability with increasing CO_2 concentration in feed from 5 to 40 mol %. A corresponding increase in permeability of the unmodified PC from 0.47 to 3.5 Barrers was observed. SPC membranes also showed similar trends, albeit at lower permeabilities, by exhibiting values in the range 0.24–2.0 Barrers at 14.4% DS and 0.17–1.1 Barrers at 25% DS. At increasing feed concentration, carbon dioxide can enhance sorption and hence change the permeability of a polymer through plasticization.[25] Corresponding increments in CO_2 selectivities were observed for all the membranes and found to fall in the range 6.8–15.7 for PC, 11.7–27.2 for SPC with 14.4% DS, and 18.4–40.7 for a DS of 25%. These results
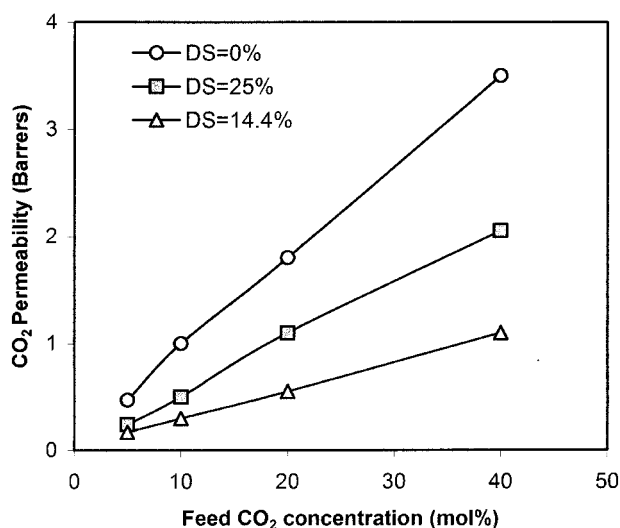

Figure 8 Influence of feed composition on CO_2 permeability through PC and SPC membranes (feed pressure 20 bar).

are provided in Figure 9. Under the same operating conditions, permeability data obtained during single gas studies were higher than those observed for binary mixtures because of greater partial pressure gradients in case of the former.[3]

Effect of pressure on gas transport properties. Figure 10 presents the relationship between gas permeability and feed pressure for SPC membrane of 14.4% DS at 30°C and 5 mol % feed CO_2 concentration. It is observed that an increase in feed pressure from 5 to 30 kg/cm^2 resulted in a drop in permeability from 0.38 to 0.2 Barrers as well as selectivity from 15.6 to 10.2. This could be attributed to dual mode sorption, which is a typical phenomenon in most glassy polymers.[26,27] The presence of secondary components
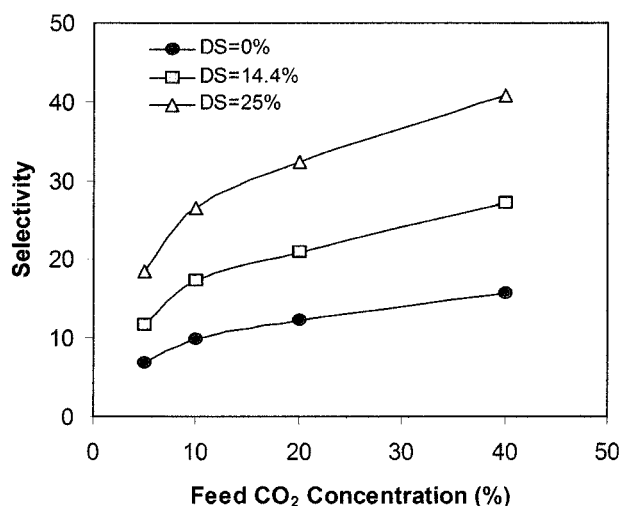

Figure 9 Effect of feed composition on selectivity of PC and SPC membranes (feed pressure 20 bar).
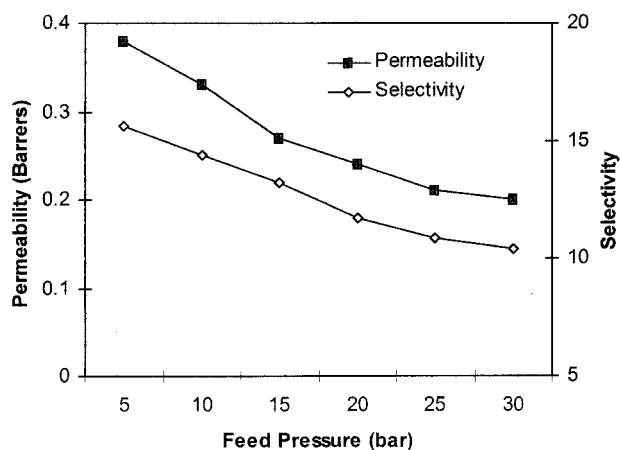
Figure 10 Variation of permeability and selectivity of SPC membrane (DS = 14.4%) with feed pressure [feed concentration = 5% CO_2, temp = 30°C].

such as methane in the feed mixture can have a profound effect on the transport rate of CO_2 due to competitive permeation of the former. The total sorption level for CO_2 is depressed by the second component CH_4, which gets increasingly sorbed in the Langmuir sites (microvoids) at higher pressures leading to exclusion of CO_2 molecules and reduced selectivity.[8]

CONCLUSIONS

In the present study, the applicability of free acid form of SPC for CO_2/CH_4 separation was investigated. Chemical modification of polycarbonate by sulfonation could produce a membrane with strong potential to effectively separate CO_2/CH_4 mixtures as a result of reduction of free volume fraction in the membrane. Sulfonation was confirmed by FTIR and NMR studies and the membranes showed adequate thermal and mechanical stability. Among the sulfonated membranes, PC sulfonated to 14.4% showed optimum permeability and selectivity at varying feed compositions without compromising mechanical strength.

Sulfonated membranes showed higher selectivity but lower permeability compared with their unmodified counterparts. The drawback of low permeability could be overcome by preparation of thin film composite membranes with the sulfonated polymer comprising the nonporous selective skin layer supported on a porous substrate. For binary gas mixtures, an increase in feed concentration enhanced the permea-

tion properties because of greater CO_2 sorption. On the other hand, a rise in feed pressure resulted in a fall membrane performance due to competitive CH_4 sorption and permeation.

The behavior of the neutralized form of sulfonated PC appears interesting and will be investigated in the near future.

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