IMMOBILIZED LIQUID MEMBRANES FOR CO_2 SEPARATION

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Introduction

Gas separation using facilitated transport membranes (FTM) has been extensively investigated. Major advantages of FTM over conventional polymeric membranes include higher permeabilities for reacting species like CO_2 and the resultant high selectivities over nonreacting species like N_2. This is due to the facilitating reaction mechanism in FTMs compared to the solution-diffusion mechanism in polymeric membranes. FTMs are particularly attractive at low reacting species concentrations where the driving force is very low. This is especially advantageous for removal and sequestration of carbon dioxide when it is present in low concentrations. Facilitated transport membranes include immobilized liquid membranes (ILMs) where the carrier in a solvent, usually water, is immobilized in the pores of the membrane.

Despite the obvious advantages offered by the ILMs, commercialization of these membranes is restricted because of the inherent limitation of stability of the liquid membrane. The reasons for the ILM instability are: (a) absence of any chemical bonding to the support matrix; (b) evaporation of the solvent liquid into gas phases during operation; (c) lower breakthrough pressures. To improve the ILM stability, the feed and sweep sides are completely humidified minimizing solvent loss by evaporation. Another alternative is to use low-volatile and hygroscopic solvents for the ILM preparation.

We have been studying replacement of water by glycerol in the ILMs for separating CO_2 from N_2 streams (Chen et al., 1999, 2000). Since glycerol is very viscous when dry and has higher viscosity than polyethylene glycol (PEG) 400 at ambient temperatures, we can expect lower permeabilities for the non-reacting species like N_2 and higher selectivity for the reacting species like CO_2. The general objective of this work is to investigate CO_2 permeation characteristics through glycerol-based ILMs using different carriers like sodium carbonate and sodium salt of glycine.

Both carriers mentioned above require a solvent, either water or glycerol, to dissolve them. The use of novel carrier liquids/oligomers which do not require any additional solvent was also explored. These carrier liquids are non-volatile and have high densities of reactive functional groups for CO_2 separation. Such carrier liquids eliminate the necessity of a solvent; the liquid membranes formed can be inherently stable.

Experimental Details

Hydrophilized polyvinylidenefluoride (PVDF) and hydrophilized polypropylene Celgard 2500 were used as flat membrane substrates; hydrophilized polysulfone was used as the hollow fiber substrate.ILMs were prepared by immersion or coating techniques. After immersing the substrate in the solution for a pre-determined period of time, it was removed from the solution: the extra liquid on the substrate surface was wiped away. If the immersion time is long enough, the ILMs prepared can be assumed to fill the entire pore length of the substrate. For hollow fibers, immobilization was carried out on the shell side before the fibers were placed in a shell casing.

The CO_2/N_2 permeances were measured by the flow cell technique which involved passing an inert sweep gas on the permeate side whose flow rate and compositions were continuously monitored. The feed gas stream was humidified with water before passing into the cell. For feed gas relative humidities (RHs) less than 100%, dry and humidified gases were blended to achieve the required RH. Sweep gas used was dry helium. The experimental procedure consisted of setting the feed gas flow rate such that the partial pressure of CO_2 remained essentially constant along the feed side of the membrane which had a small area. The sweep flow rate was set to keep the partial pressure of CO_2 in the permeate relatively small, yet high enough for accurate measurement. The permeation rates of CO_2 and N_2 were determined from their concentrations in the sweep gas and sweep gas flow rate.

Results and Discussion

Glycerol-based ILMs having average thicknesses ranging from 15 to 100 microns were studied. The concentrations of carriers examined were: 0 to 4.0 mol/dm^3 for sodium carbonate, 0.3-5 mol/dm3 for glycine-Na. While 1M sodium carbonate solution was clear and stable, higher carbonate concentrations in glycerol led to turbid solutions at room temperature. Most of the glycine-Na based ILMs were prepared using less than 3M solutions; higher concentration solutions tend to be turbid. An oligomer providing high liquid density of reactive functional groups was also studied with and without the presence of glycerol as solvent in the ILM.

Table 1 compares the effect of carrier concentration of sodium carbonate and glycine-Na in glycerol systems in hydrophilized PVDF membranes. The entering feed gas was completely humidified with water. For a sodium carbonate concentration of 0.1M, the CO_2 permeability through the ILM increased by a factor of nearly 100 compared with that through pure glycerol. In the higher carrier concentration range, the permeability of carbon dioxide did not increase proportional to the carrier concentration, but there was an increase in the selectivity of ILM for CO_2, possibly due to increase in solution viscosity and ionic strength and the resultant decrease in solubility and diffusivity of N_2 in the ILM. Similar behavior was observed for glycine-Na-glycerol based ILMs also. Some data were obtained for membranes having both carriers, glycine-Na and sodium carbonate. The mixed carriers-based ILMs gave CO_2/N_2 permeation performances close to the glycine-Na based ILMs of corresponding concentration.

Table 1. ILM performance in hydrophilized PVDF membranes: effect of carrier concentration

Carrier concentration (M)	CO_2 partial pressure (cm Hg)	CO_2 permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
Na_2CO_3				
0	0.55	14	3.83	3.7
0.1	0.55	1420	3.98	359
1	0.55	2880	3.34	850
4	0.55	2540	1.75	1460
Glycine-Na				
0.3	0.44	4280	1.98	2210
2.25	0.41	9730	1.89	5140
3.5	0.42	8510	1.16	7310
5.0	0.38	7370	1.27	5780
1.0 M Na_2CO_3+ 1.0 M Glycine-Na	0.48	4980	2.22	2240

The partial pressure of carbon dioxide affected the CO_2 permeance according to the expected facilitated transport behavior. At lower CO_2 partial pressures, the CO_2 permeance of sodium carbonate-glycerol ILM or glycine-Na-glycerol ILM is greater than those of DEA-PEG 400 ILM (Saha and Chakma, 1995), but lower than MEA-water ILM (Teramoto et al., 1996). At higher CO_2 partial pressures, fixed-carrier membranes (Quinn and Laciak, 1997) achieve higher CO_2 permeances than these ILMs.

The glycine Na-glycerol ILMs were operated for more than 600 hours with no change in performance. The mechanical stability of the glycerol-based ILMs was studied by subjecting the ILMs to different feed inlet relative humidities. In one such experiment, a 0.6 M sodium carbonate-glycerol ILM was subjected to feed inlet relative humidity varying with time to observe any deterioration in performance. The feed stream was 10.6% CO_2-balance N_2 gas mixture. The feed RH was 100% for the first 48 hrs. Then it was decreased to 13% and maintained at that level for 100 hours. Finally, the feed RH was increased to 100% again. The ILM was not at all damaged during the 100 hour flow of very low RH feed stream: the ILM performance could be restored to normal levels when the feed RH was increased to 100% again. The low volatility and highly hygroscopic nature of glycerol are responsible for the observed stability, which is a marked improvement over water-based ILMs. Glycine-Na- glycerol based ILMs also demonstrated similar behavior.

Table 2 shows the performances for glycerol based ILMs in hydrophilized Celgard 2500 membranes. The permeabilities obtained in the Celgard-based ILMs were lower than those obtained in PVDF membrane based ILMs. The Celgard-based membranes in general showed lower selectivities which may be attributed to imperfect hydrophilization.

Table 3 presents the results for hollow fiber based ILMs. The effective CO_2 permeance for a 0.53% CO_2-balance N_2 feed gas mixture can be as high as 3.13 x 10-5 cc/cm2.s.cmHg with CO_2/N_2 separation factors in the range of 2000-2700. These data represent so far the highest carbon dioxide permeances observed in this study for hollow fiber membranes. Further, they compare very well with the highest CO_2 permeances obtained with flat film ILMs in our studies. The stability of these ILMs was excellent over the period studied, namenly, 300 hours with no apparent deterioration in CO_2 permeance or CO_2/N_2 selectivity.

Table 2. Effect of carrier concentration on the ILM performance in hydrophilized Celgard 2500 membranes

Carrier concentration	CO_2 partial pressure (cm Hg)	CO_2 permeability (Barrer)	N_2 Permeability (Barrer)	CO_2/N_2 Selectivity
1 M Na_2CO_3	0.52	863	1.24	698
2.25M Glycine-Na	0.46	3920	2.23	1770

Table 3. Performance of hydrophilic polysulfone fiber modules for 3.0 M glycine-Na-glycerol solution.

Δp_{CO2} cmHg	Feed in/out RH %	$(Q/t)_{eff,N2}$ cc/cm^2.s.cmHg	$(Q/t)_{eff,CO2}$ cc/cm^2.s.cmHg	CO_2/N_2 selectivity
0.335	91.7/n.a.	1.34e-8	3.13e-5	2330
0.390	100/n.a.	2.54e-8	2.93e-5	1150
0.410	87.6/50.0	1.54e-8	2.98e-5	1930
0.410	93.0/66.0	1.36e-8	3.08e-5	2260
0.410	92.3/32.4	1.14e-8	2.81e-5	2460

The novel use of non-volatile highly functionalized oligomers for selective CO_2 separation was also studied. Pure oligomer was used as the ILM. The results were remarkable. The CO_2-N_2 separation factor could go very close to 19,000 at a low CO_2 partial pressure of 0.36 cm Hg. The corresponding CO_2 permeability was 4100 Barrers. At higher CO_2 partial pressures of about 30 cmHg, the CO_2-N_2 separation factor was around 700. This behavior reflects the classical carrier saturation behavior of facilitated transport membranes. This particular ILM was used continuously for more than 35 days without any visible signs of any membrane leaks or instability. During this period, the ILM was subjected to different carbon dioxide partial pressures, transmembrane pressures, and feed inlet relative humidities. The oligomer-based ILMs appear to function almost as a molecular gate for CO_2 vis-à-vis other inert gases, N_2, O_2 ete at low partial pressures and high feed RHs. Addition of glycerol to the oligomer in forming the ILM tends to reduce the CO_2-N_2 selectivity because of higher N_2 solubility in glycerol.

Conclusions

1) Glycerol-based immobilized liquid membranes provide mechanically stable performance even when exposed to low humidity feed gases. The performance of the ILM can be restored to the normal levels once higher feed humidity is reintroduced. This is a radical improvement over conventional water-based ILMs.
2) ILMs were operated for more than 600 hrs continuously without any deterioration in performance.
3) Increase in partial pressure of CO_2 reduces the CO_2 permeability and its selectivity as expected for the facilitated transport mechanism.
4) Novel non-volatile oligomeric liquids having high density of reactive functional groups appear to function as a CO_2-selective molecular gate, yielding very high CO_2-N_2 selectivities at low CO_2 partial pressures and high feed side RHs.

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