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Dendrimer Membranes: A CO_2-Selective Molecular Gate

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Separation of CO_2 from other gases and vapors is vitally important for many industrial and space travel applications as well as for controlling greenhouse gas emissions. Nonporous and glassy polymeric membranes possess rather low CO_2/CH_4 and CO_2/N_2 selectivities around 15−35.[1−3] The problem becomes particularly acute at lower CO_2 feed partial pressures; the CO_2 flux becomes quite low. Facilitated transport membranes (FTMs) have been therefore investigated[4,5] wherein reactive carriers increase the CO_2 permeability drastically and CO_2 permeance significantly at low CO_2 partial pressures. We report here stable and novel FTMs with extraordinary selectivity for CO_2 over N_2. The membrane functions as a CO_2-selective molecular gate at low CO_2 partial pressures and high feed relative humidities.

FTMs are often in the form of an appropriately immobilized thin liquid layer[4,5] (containing species reversibly reactive with CO_2) in the pores of a porous polymer film (the immobilized liquid membrane (ILM)) or between hollow fibers on the shell side to develop the contained liquid membrane.[6,7] The ILMs investigated employ generally an aqueous solution containing a carrier species (e.g., K_2CO_3, diethanolamine, ethylenediamine (EDA)) which reacts reversibly with CO_2. Salts/salt hydrates which are molten at low temperature have also been used.[8] Evaporative loss of water and carriers, slow reaction kinetics, poisoning of carriers, low CO_2 permeances, not-high-enough selectivity for CO_2 have plagued past efforts.

We have used Starburst polyamidoamine (PAMAM) generation 0 dendrimers[9,10] having EDA as the core as the membrane liquid which will strongly facilitate CO_2 transport and efficiently block the transport of other gaseous species. Although dendrimers have been used for a variety of applications,[11−13] there are no studies of dendrimers as membranes. The dendrimers are nonvolatile, can be used with or without polar solvents such as glycerol,[14] water etc. Pure PAMAM dendrimer liquid provides a high concentration of primary and tertiary amine functional groups such as $-NH_2$, $\equiv N$. The primary amine group $-NH_2$ is known to react strongly with CO_2 to produce a carbamate ion and a protonated base. Although the tertiary amine group $\equiv N$ is not supposed to react directly with CO_2 like a primary or a secondary amine because they lack the proton needed in the deprotonation step, experimental results[15] indicate that tertiary amines show considerable reactivity toward CO_2; apparently water is essential for this reaction:

$$CO_2 + NR_3 + H_2O \leftrightarrow NR_3H^+ + HCO_3^- \qquad (1)$$

PAMAM dendrimer has a secondary amine, $=NH$; however, it is present as an amide and not expected to react with CO_2.

Our experiments have been performed using porous hydrophilized polyvinylidene fluoride (PVDF) flat membrane films (porosity 0.7; pore size 0.1 μm; thickness 100 μm; tortuosity 2.58; Millipore) in the pores of which PAMAM dendrimers of generation zero were immobilized. The total permeation rate of species i through a film of area A_m and thickness t_m is

$$W_i = J_i \times A_m = (Q_i/t_m)_{\text{eff}}\, A_m\, (p_{\text{if}} - p_{\text{ip}}) = (Q_i/t_m)_{\text{true}}\, (\epsilon/\tau_m) A_m\, (p_{\text{if}} - p_{\text{ip}}) \qquad (2)$$

where J_i is the flux, Q_i is the species i permeability, Q_i/t_m is the species i permeance (std.cc/cm^2·s·cmHg), τ_m is the membrane tortuosity, and p_{if} and p_{ip} are the partial pressures of species i in the feed side and the permeate side, respectively. The membrane selectivity between species i and j, α_{ij}, is

$$\alpha_{ij} = (Q_i/Q_j) = (Q_i/t_m)|_{\text{true}}/(Q_j/t_m)|_{\text{true}} = (Q_i/t_m)|_{\text{eff}}/(Q_j/t_m)|_{\text{eff}} \qquad (3)$$

Pure generation 0 dendrimer liquid was prepared by removing methanol from the methanol solution as received (Sigma) by subjecting it to vacuum for several hours. To prepare the ILM, the porous polymer film was immersed in the pure dendrimer liquid for at least 8 h until the membrane appeared translucent. In some instances, any moisture absorbed by the liquid was removed by applying vacuum during the wetting process. A similar procedure was used for 1 M solution of dendrimer in glycerol. The film was placed between two stainless steel half-cells and supported by a porous stainless steel screen in the bottom cell wall. The feed gas mixture flowed through the top half of the cell. A dry helium sweep stream flowed on the bottom side of the membrane. The outlet composition of the sweep stream containing the permeants yielded $(Q_i/t_m)_{\text{eff}}$ from eq 2. The feed mixture was humidified with water prior to cell entry. The feed inlet relative humidity (RH) could be adjusted by blending the humidified feed stream with the dry feed stream.

The measured room-temperature effective permeance of CO_2 and CO_2-N_2 selectivity obtained for a generation 0 dendrimer ILM in the hydrophilized PVDF substrate are shown in Figure 1 as a function of the CO_2 partial pressure difference, Δp_{CO_2}, between the feed CO_2-N_2 mixture and the permeate. For selectivity, the separation factor, $\alpha_{CO_2-N_2}$, (eq 3) was used. The feed gas mixture at a total pressure of 121.6 kPa was completely humidified with water. The N_2 permeances were so low that a total of up to four test cells were used in series ($A_m = 47$ cm^2). The separation factor $\alpha_{CO_2-N_2}$ could go very close to 19000 at a low Δp_{CO_2} of 0.36 cm Hg. The value of the $(Q_{CO_2}/t_m)_{\text{true}}$ will change with Δp_{CO_2}; at 0.26 cm Hg it was found to be 4.1×10^{-5} cc/cm^2·s·cmHg. The corresponding CO_2 permeability (Q_{CO_2}) is 4100 Barrers (1 Barrer = 1×10^{-10} scc·cm/cm^2·s·cmHg). The true N_2 permeance in the presence of small amounts of CO_2 in

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(1) Ho, W. S. Sirkar, K. K., Eds. *Membrane Handbook*; Chapman and Hall: New York, 1992.

(2) Stern, S. A. *J. Membr. Sci*. **1994**, *94*, 1−65.

(3) Koros, W. J.; Fleming, G. K. *J. Membr. Sci*. **1993**, *83*, 1−80.

(4) Ward, W. J.; Robb, W. L. *Science* **1967**, 156, 1481−1483.

(5) Bartsch, R. A., Way, J. D., Eds. *ACS Symp. Ser*. **1996**, 642.

(6) Majumdar, S.; Guha, A. K.; Sirkar, K. K. *AIChE J*. **1988**, *34*, 1135−1145.

(7) Papadopoulos, T.; Sirkar, K. K. *J. Membr. Sci*. **1994**, *94*, 163−184.

(8) Quinn, R.; Appleby, J. B.; Pez, G. P *J. Am. Chem. Soc*. **1995**, *117*, 329−335; Quinn, R.; Laciak, D. V. *J. Membr. Sci*. **1997**, *131*, 49−60.

(9) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138−175.

(10) Uppuluri, S.; Keinath, S. E.; Tomalia, D. A.; Dvornic, P. R. *Macromolecules* **1998**, *31*, 4498−4510.

(11) Jansen, J. F. G. A.; Meijer, E. W. *J. Am. Chem. Soc.* **1995**, *117*, 4417−4418.

(12) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659−663.

(13) Bolm, C.; Derrien, N.; Seger, A. *Synlett* **April 1996**, 387−388.

(14) Chen, H.; Kovvali, A. S.; Majumdar, S.; Sirkar, K. K. *Ind. Eng. Chem. Res.* **1999**, *38*, 3489−3498.

(15) Versteeg, G. F.; van Swaaij, W. P. M. *Chem. Eng. Sci*. **1988**, *43*, 587−591.

10.1021/ja0013071 CCC: $19.00

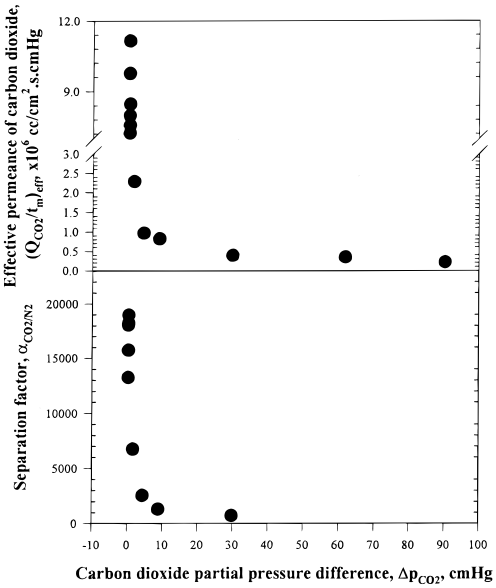

Figure 1. Variation of effective permeance of carbon dioxide ($Q_{CO_2}/t_m)_{eff}$ and separation factor (α_{CO_2/N_2}) with partial pressure difference of carbon dioxide (Δp_{CO_2}) in hydrophilic PVDF membrane. ILM: pure dendrimer (generation 0).

the feed gas was around 1.47 to 1.9 $\times 10^{-9}$ cc/cm^2·s·cmHg. This value was increased to around 3.0 $\times 10^{-9}$ cc/cm^2·s·cmHg for pure N_2. The separation factors are not reported for $p_{CO_2,f}$ exceeding 30 cmHg since no N_2 peaks were detected in the GC. At the highest Δp_{CO_2} of 90 cmHg, $(Q_{CO_2}/t_m)_{eff}$ is 2.2 $\times 10^{-7}$ cc/cm^2·s·cmHg. At the higher $\Delta p_{CO_2} - s$ (∼30 cmHg), $\alpha_{CO_2-N_2}$ is around 700. This behavior reflects carrier saturation in FTMs.

All data were obtained using the same set of membranes which were used continuously for more than 35 days without any visible signs of any membrane leaks or instability. At the lowest Δp_{CO_2}, $\alpha_{CO_2-N_2}$ is at least 5 times higher than the highest reported value.[14] At higher $\Delta p_{CO_2} - s$, $\alpha_{CO_2-N_2}$ is comparable to the highest values reported.[8] In literature,[16,17] gating membranes show very high selectivity for a particular ion or species vis-à-vis other species. In this sense, the dendrimer membranes appear to function almost as a molecular gate for CO_2 vis-à-vis other inert gases, N_2, O_2, etc. in a humid environment. On a comparative basis, the pure dendrimer liquid provides a functional group density of 9.12 M for $-NH_2$ and 4.56 M for $\equiv N$; a conventional aqueous 2 M EDA solution provides only 4 M for $-NH_2$. Thus, pure dendrimer liquid possesses a very high concentration of facilitating species which will simultaneously decrease the gas solubilities drastically via salting-out. Since the primary amine groups in the dendrimer are attached to methylenes, they are unlikely to behave as sterically hindered.[18] The effect of a dense packing of such groups in a pure liquid is, however, unknown.

If the feed gas is dry, (Q_{N_2}/t_m) increased drastically, and $\alpha_{CO_2-N_2}$ was reduced to around 5. However, as the feed gas humidification was started again, the ILM performance returned to its original high $\alpha_{CO_2-N_2}$ and very low Q_{N_2}. For a completely humidified feed inlet stream, the feed exit RHs were usually around 70%. The CO_2 permeability was also affected considerably by the absence of humidity. There appears to be a sharp transition around an average feed RH ($RH_{f,avg}$) of 82% (feed exit RH of 64%) below which the CO_2-N_2 selectivity decreases continuously as the N_2 permeance shoots up; the CO_2 permeance decreases first and then rises slightly. As the RH decreases, the amount of sorbed water in the dendrimer liquid decreases. The ionic concentrations of carbamates and other species decrease just as the local aqueous ionic envelopes around the reactive functional groups shrink. These lead to increased N_2 permeance through the intermolecular and intramolecular space with a decrease in RH. However, for CO_2, initially the permeance is reduced due to reduced facilitation; without moisture, CO_2 does not react with amine functional groups. When, however, the RH is reduced considerably, the inherent high mobility through a low molecular weight liquid (the dendrimer) becomes dominant resulting in a higher Q_{CO_2}.

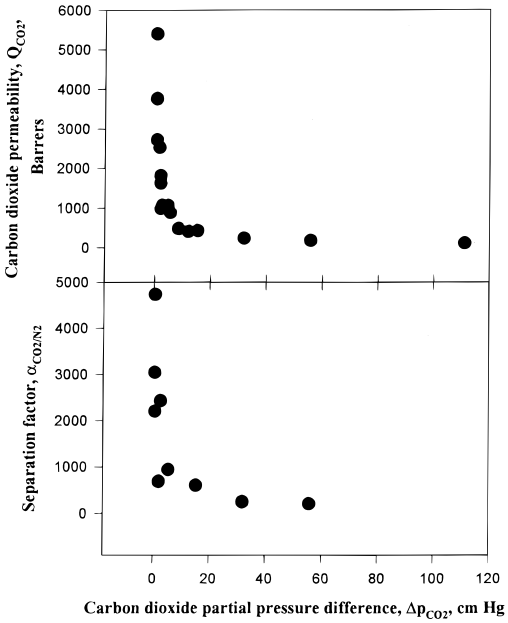

Figure 2. Variation of permeability of carbon dioxide and separation factor with partial pressure difference of carbon dioxide in hydrophilic PVDF membranes. ILM: 1 M dendrimer (generation 0) in glycerol.

The selective CO_2 transport aided by the activation of primary and tertiary amine groups in the presence of water and by a reduction of N_2 transport can be maintained over a broader RH range if an extremely viscous polar low molecular weight hygroscopic liquid like glycerol is incorporated in the pure dendrimer ILM. Under absolutely dry conditions, glycerol present in the intramolecular and intermolecular space could reduce gas transport rates by orders of magnitude and drastically reduce any membrane leakage.[14] At lower RH levels, glycerol will hold much more sorbed water than pure dendrimer (e.g. at an ambient RH of 35.6% and 22.8 °C, glycerol sorbs 0.062 gm H_2O/gm glycerol whereas the dendrimer sorbs 0.013 gm H_2O/gm dendrimer); this will allow considerable CO_2 facilitation and rejection of N_2.

Figure 2 illustrates these results for an ILM of 1 M generation 0 dendrimer in a glycerol solution. The hydrophilized PVDF substrate was soaked in the 1 M dendrimer solution for 8 h; vacuum was applied for about 5 h to remove any absorbed moisture. When the ILM based on 1 M dendrimer solution in glycerol was formed without removing any ambient moisture that was absorbed by the solution/support membrane, the ILM tended to perform poorly under dry feed gas conditions: Q_{N_2} was 1260 Barrers. However when the ILM was formed by vacuuming for about 5 h, Q_{N_2} dropped to about 8 Barrers. Once feed side humidification was started, Q_{N_2} dropped to about 1 Barrer and Q_{CO_2} increased drastically. The highest Q_{CO_2} observed was about 5400 Barrers for a 0.5% CO_2 feed gas.

Thinner dendrimer membranes, smaller pore sizes, hollow fiber support structures, lower glycerol content, and higher-generation dendrimer-based membranes are of great interest.

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[16] Yamaguchi, T.; Ito, T.; Sato, T.; Shinbo, T.; Nakao, S. *J. Am. Chem. Soc.* **1999**, *121*, 4078−4079.

[17] Armstrong, C. *Science*, **1998**, *280*, 56−57.

[18] Sartori, G.; Ho, W. S.; Savage, D. W.; Chludzinski, G. R.; Wiechert, S. *Sep. Purif. Methods* **1987**, *16*, 171.