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SELECTIVE PERMEATION OF AMMONIA AND CARBON DIOXIDE BY NOVEL MEMBRANES

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ABSTRACT

Experimental results are presented on membranes of novel composition which selectively permeate ammonia and carbon dioxide from mixtures containing hydrogen. The CO_2-selective membrane, which consists of a thin liquid film of the salt hydrate tetramethylammonium fluoride tetrahydrate, exhibits a CO_2 permeance of 4-1 x 10^{-5} $cm^3/cm^2 \cdot s \cdot cmHg$ with selectivity, $\alpha(CO_2/H_2)$, ranging from 360-30. The NH_3-selective membrane, poly(vinylammonium thiocyanate), displays a high NH_3 permeance, 5-20 x 10^{-5} $cm^3/cm^2 \cdot s \cdot cmHg$, with $\alpha(NH_3/N_2)$ as high as 3600 and $\alpha(NH_3/H_2)$ as high as 6000. Such membranes, which retain H_2 at pressure in the feed stream, may offer new opportunities in the design of separation processes.

INTRODUCTION

Polymeric membranes are gaining acceptance as an emerging technology in gas separation processes. For example, cellulose acetate membranes are now being used in large commercial installations for CO_2

separations and polysulfone hollow fiber membranes are used to recover hydrogen in ammonia synthesis purge stream applications. Hydrogen, being the more permeable gas, is almost always recovered at low pressures. There are, however, some applications in which it would be desirable to retain hydrogen at pressure while permeating other components from the stream. For example, in ammonia synthesis plants the converter product stream contains NH_3 and unreacted N_2 and H_2 (and also smaller amounts of CH_4 and Ar). Incorporation of an NH_3-selective membrane, as first suggested by Kammermeyer (1), would be advantageous because the refrigeration loop could be significantly downsized while permitting unconverted H_2 and N_2 to be recycled to the converter with minimum compression energy. In the production of merchant hydrogen, carbon dioxide, which is a by-product of the steam reforming and CO-shift conversion steps, has to be removed from the hydrogen rich product gas. This is currently done using acid-gas scrubbing solvents which require thermal energy for their regeneration. An energy savings could result from using a membrane to selectively permeate a major portion of the CO_2 from the product stream, thus reducing the load on the scrubber. An economic implementation of these technologies requires stable membranes which possess not only high permeability towards NH_3 and CO_2 but also high selectivity over H_2. This goal cannot be realized using known organic polymer membranes because of their low selectivity ,$\alpha(CO_2/H_2)$ and $\alpha(NH_3/H_2)$. The $\alpha(NH_3/H_2)$ of polyethylene membranes is 4 (1); that of a mixed-phase polyethylene glycol/silicone rubber membrane is 300 (2); aromatic polysulfonamide membranes have selectivity of 400 (3). The permselective properties of the latter were observed to degrade at temperatures above ca. 30°C. Membranes consisting of thin films of hydrated polymers can effect a separation of CO_2 from H_2 (4) but with a selectivity, $\alpha(CO_2/H_2) \approx 10$, which is too low to be useful.

We approached the problem of preparing highly permeable NH_3- and CO_2-selective membranes by seeking compositions, both liquid and polymeric, which would reversibly interact with these gases in a way that would enhance their transport through a membrane. In this paper we report preliminary results on such facilitated transport membranes. We describe the preparation of laboratory-scale membranes and demonstrate their effectiveness for separating CO_2 and NH_3 from mixtures with other gases, especially H_2.

MATERIALS

Tetramethylammonium fluoride tetrahydrate ($TMAF \cdot 4H_2O$) was used as supplied by Aldrich Chemical Co. The degree of hydration was checked before use by Karl-Fisher titration. Poly(vinylammonium thiocyanate)

(PVAmSCN) was prepared by ion-exchanging poly(vinylammonium chloride) with excess ammonium thiocyanate (NH_4SCN) (5). This method gave polymer which was approximately 80% in the SCN^- form. PVAmSCN was cast from a 5 wt% aqueous solution. Poly(trimethylsilylpropyne) (PTMSP) was polymerized and cast into films as described by Langsam et al (6).

EXPERIMENTAL

The test apparatus was similar to that used by Bateman (7). A blended gas mixture was constantly passed over one side of the membrane while the opposite side was continually swept by a helium stream leading into a gas chromatograph. For experiments involving CO_2-selective membranes, the feed gas was presaturated with H_2O by passing it through a bank of bubblers maintained at 10°C. The membrane was sealed in a stainless steel test cell similar to that described by Otto (8) with the added provision for incorporation of a thin stainless steel frit to support the membrane. The membranes used in this work had an effective surface area of 3.8 cm^2. Data gathered over 6 - 24 hours of steady-state operation were used to calculate the permeance of the respective gases.

RESULTS AND DISCUSSION

CO_2-selective Membranes

Carbon dioxide-selective membranes are based on our discovery of a reversible reaction between CO_2 and molten tetramethylammonium fluoride tetrahydrate, $TMAF{\bullet}4H_2O$ (mp 39-42°C) (9). This salt hydrate has an unusually large capacity for CO_2 as shown by the CO_2 absorption/desorption isotherm in Figure 1. The solubility of CO_2 in $TMAF{\bullet}4H_2O$ at 50°C approaches 0.3 mol CO_2/mol $TMAF{\bullet}4H_2O$ at 80 cmHg CO_2 which corresponds to a solution which is approximately 2 molar in the gas. For comparison, the CO_2 concentration in pure H_2O at the same pressure and temperature is 0.02M (10) and 0.01M in a 3.4M aqueous NaCl solution (11). This reversible chemical reactivity arises from the following reactions occurring in the melt (12).

$$2F^- + H_2O = HF_2^- + OH^- \qquad (1)$$

$$OH^- + CO_2 = HCO_3^- \qquad (2)$$

For evaluation purposes a membrane was constructed by supporting a thin layer of molten $TMAF{\bullet}4H_2O$ on a 50 μm thick film of poly(trimethylsilylpropyne), PTMSP. The latter is a highly gas permeable, nonporous polymer which was used to increase the mechanical stability of the liquid membrane without adding any significant mass transfer resistance (6). Gas permeabilities were determined at 50°C with both the feed (CO_2, H_2) and permeate sweep gas (He) humidified to a dew point of 10°C. Results and other test conditions are given in Figure 2. The performance of the membrane is given in terms of gas permeance, P_o/l, in units of cm^3(STP) gas/cm^2 membrane area•sec•cmHg CO_2. At low CO_2 feed partial pressures there is a very effective separation of CO_2 from H_2 with selectivity, $\alpha(CO_2/H_2)$ approaching 370. The decrease in CO_2 permeance (P_o/l) with increasing CO_2 partial pressure is typical of many carrier-mediated facilitated transport systems and indicative of carrier saturation; this behavior is suggested by the Langmuir-like shape of the CO_2 absorption isotherm. The H_2 permeance was found to be independent of pressure indicating that it permeates by a solution-diffusion mechanism. Thus, the decrease in $\alpha(CO_2/H_2)$ is due to the decline in CO_2 permeance at higher CO_2 pressures; however, even at 80 cmHg CO_2, the observed selectivity of 30 represents a significant improvement over the performance of polymeric CO_2/H_2 separation membranes.

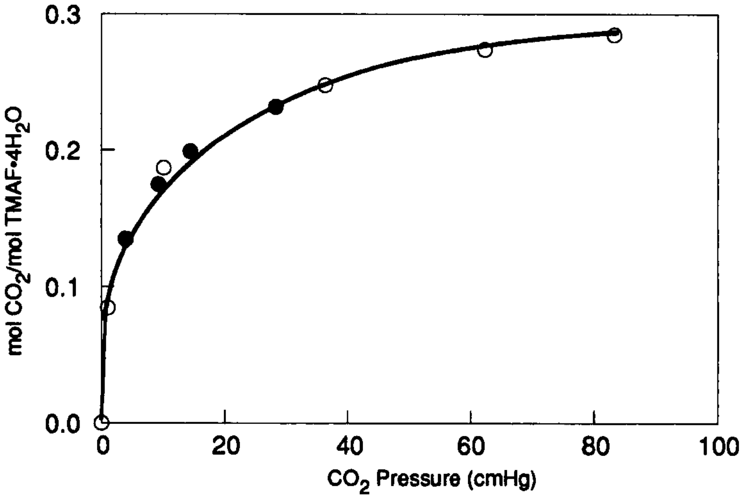

Figure 1. CO_2 Absorption Isotherm of TMAF•$4H_2O$ at 50°C: (○) absorb, (●) desorb.

Our current understanding of the transport mechanism in TMAF•$4H_2O$ membranes is that the CO_2 flux is augmented over that of other salt

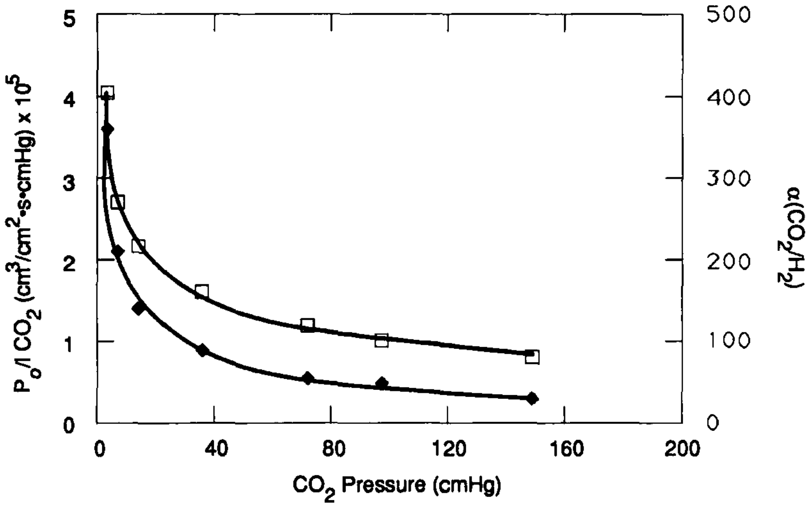

Figure 2. Performance of $TMAF \cdot 4H_2O$ Membrane at 50°C. Feed gas=1:2 $CO_2:H_2$ @ 20 sccm; He sweep gas @76 cmHg, 10 sccm: (□) $P_o/l\ CO_2$, (◆) selectivity, $\alpha(CO_2/H_2)$.

solutions such as NaCl via the reactions shown above. Bicarbonate and bifluoride ions (equations 1 and 2) diffuse in a concentration gradient to the permeate side of the membrane where the reactions are reversed, liberating CO_2. Hydrogen, and to some extent CO_2, permeate by a conventional solution-diffusion mechanism. This carrier-mediated mechanism is similar to that reported for aqueous carbonate/bicarbonate CO_2 facilitated transport membranes (8) which involves the following reactions:

$$CO_3^{2-} + H_2O = HCO_3^- + OH^- \tag{3}$$

$$OH^- + CO_2 = HCO_3^- \tag{4}$$

A quantitative analysis of the HCO_3^-/HF_2^- mediated facilitated transport of CO_2 will be given in a future article (12).

NH_3 - selective Membranes

The ammonia-selective membranes are based on the reversible interaction of $NH_3(g)$ with NH_4SCN and its derivatives (13,14). Crystalline NH_4SCN deliquesces under 80 cmHg NH_3 at 25°C to yield a colorless liquid solution (15-17). We immobilized this solution within a microporous nylon membrane and tested it for the separation of NH_3 from N_2. While good permselectivity was achieved we found the membrane to be unstable at transmembrane pressures greater than about 1 atm. To overcome this problem we synthesized a polymeric analog of NH_4SCN; namely poly(vinylammonium thiocyanate), abbreviated PVAmSCN. The NH_3 absorption for this material at 30°C is shown in Figure 3. It has a high NH_3 absorption capacity, approximately 50 mmol NH_3/g PVAmSCN at 600 cmHg, and is not saturated over the pressure range measured. Whereas NH_4SCN deliquesces in an NH_3-rich atmosphere (17), absorption of NH_3 by PVAmSCN causes the polymer to visibly gel at pressures above ca. 150 cmHg NH_3. The high affinity of NH_4SCN, and hence of PVAmSCN, for NH_3 is postulated to arise from strong hydrogen bonding interactions of NH_3 with the NH_4^+ and SCN^- ions (19). We ascribe the continuous absorption of NH_3 by PVAmSCN to the formation of ammoniates of composition PVAmSCN•xNH_3 where x =1,2,3... mol NH_3/repeat unit of polymer.

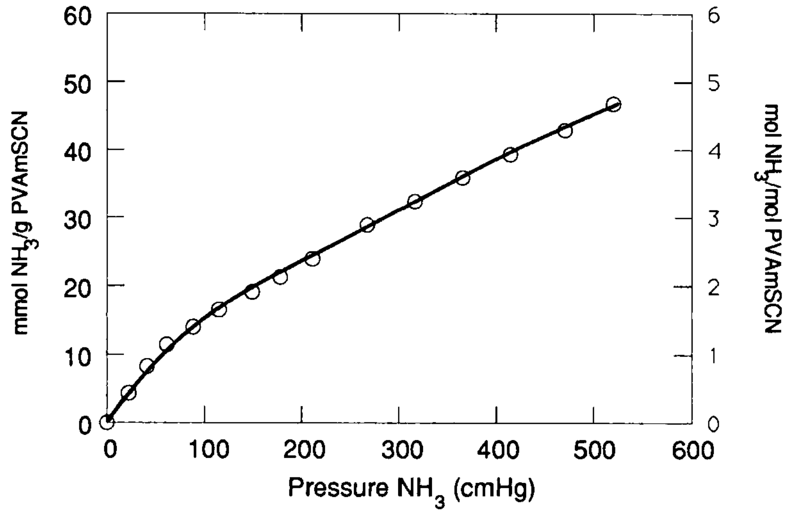

Figure 3. NH_3 Absorption Isotherm of PVAmSCN at 30°C.

A multilayer membrane consisting of a film of PVAmSCN (10 μm thick) sandwiched between two 20 μm thick films of PTMSP was prepared for testing. Again, the PTMSP films add no significant mass transfer resistance but were employed to add mechanical stability to the PVAmSCN as it gelled under the high NH_3 pressures of the test conditions. This membrane was evaluated at 30°C for the separation of NH_3 from a feed stream containing a 1:1 mixture of NH_3 and H_2. Results and other test conditions are given in

Table 1. It is evident that the composite membrane effectively permeates NH_3 from the mixture. Under the test conditions there is a high NH_3 permeance (P_o/l) and a favorable selectivity, $\alpha(NH_3/H_2)$, which ranges from approximately 1250 to 500. At 200 cmHg NH_3, for example, the standard NH_3 permeability is 2420 x 10^{-10} cm^3•cm/cm^2.•s•cmHg while the H_2 permeability is only 5 x 10^{-10} cm^3•cm/cm^2.•s•cmHg (20).

Table 1. Performance of PTMSP/PVAmSCN/PTMSP Multilayer Composite Membrane at 30°C.

FEED GAS†		PERMEATE GAS††		
$P(NH_3)^*$	$P(H_2)^*$	$P_o/l^{**}(NH_3)$	$P_o/l^{**}(H_2)$	$\alpha(NH_3/H_2)$
78	78	5.54	nd	-----
117	117	16.21	0.013	1245
155	155	22.27	0.027	825
194	194	24.21	0.046	525

† feed gas flow 30 sccm; †† He sweep gas @ 10sccm, 76cmHg; * cmHg; ** cm^3/cm^2•s•cmHg x 10^5; nd=not detected.

An Arrhenius plot of the NH_3, N_2 and H_2 permeances is shown in Figure 4. Ammonia permeance decreases with increasing temperature due to its lower solubility in the membrane at higher temperatures (17). The N_2 and H_2 permeances exhibit only a small temperature effect and increase in accord with a solution-diffusion mechanism.

Unlike traditional facilitated transport membranes, the NH_3 permeability PVAmSCN does not diminish with increasing NH_3 pressure, but rather increases. The NH_3 permeability remains high presumably because of the multiplicity of NH_3 coordination to the polymer (Figure 3). The apparent increase in both NH_3 and H_2 permeance with increasing NH_3 pressure (Table 1) may be due to gellation of the polymer which results in an increased mobility of both gases. At this time we do not have a definitive mechanism which explains the rapid permeation of NH_3. Qualitatively, however, PVAmSCN may be viewed as a very good "solvent" for NH_3 which permeates via a solution-diffusion mechanism. Yet, based, on the strong interaction of NH_3 with the polymer (Figure 3 and ref 18), a carrier-mediated or other facilitated transport mechanism cannot be ruled out.

We also measured membrane performance at conditions closer to those of an actual industrial application; that is, at higher NH_3 partial pressures

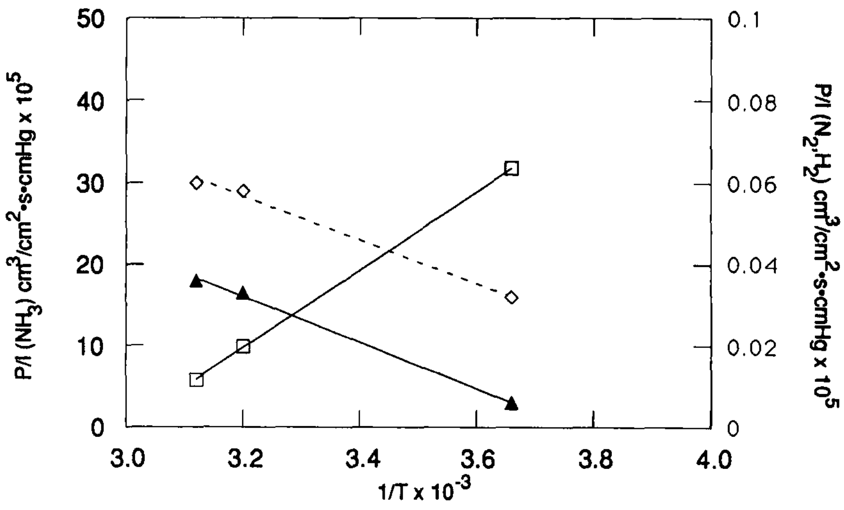

Figure 4. Arrenhius Plot for PTMSP/PVAmSCN/PTMSP Membrane. Feed gas = 1:1:1 NH_3:N_2:H_2 @ 390 cmHg, 45 sccm; He sweep gas @ 76 cmHg, 10sccm: (□)NH_3, (▲)N_2, (◇) H_2

and much higher total system pressure. For this experiment a PTMSP/PVAmSCN/PTMSP multilayer membrane was prepared as described above, however, for this evaluation the PVAmSCN layer was much thicker. The PTMSP films were each approximately 50 μm thick. The composite membrane was evaluated at 30°C for the separation of NH_3 from H_2 and also N_2 under a constant NH_3 feed pressure of 595 cmHg and increasing pressures of N_2 and H_2. Results are shown in Table 2. Even at very high pressures the membrane still functions effectively. Ammonia permeance is ca. 5 x 10^{-5} $cm^3/cm^2 \cdot s \cdot cmHg$ with selectivity $\alpha(NH_3/N_2)$ and $\alpha(NH_3/H_2)$ of 3600 and 6000, respectively. The decrease in permeance of all NH_3 and N_2 with increasing feed pressure may result from densification of the PVAmSCN layer under transmembrane pressures of 2562 to 4239 cmHg (495 to 820 psi). Finally, when the membrane temperature is raised to 60°C the NH_3 permeance decreases as expected. This is accompanied by a small increase in the N_2 and H_2 permeances, most likely as a results of increased diffusion. None the less, an excellent separation is achieved.

CONCLUSIONS

We have shown that the separation of CO_2 from mixtures with H_2 and of NH_3 from mixtures with H_2 and N_2 can be achieved by employing

Table 2. Performance of PTMSP/PVAmSCN/PTMSP Multilayer Composite Membrane at High Transmembrane Pressures. Feed gas @ 60 sccm; He sweep gas @ 76 cmHg, 10 sccm.

	FEED GAS			PERMEATE GAS				
TEMP (^{o}C)	$P^{*}(NH_3)$	$P^{*}(H_2)$	$P^{*}(N_2)$	$P_o/l^{**}(NH_3)$	$P_o/l^{**}(H_2)$	$P_o/l^{**}(N_2)$	$\alpha(NH_3/H_2)$	$\alpha(NH_3/N_2)$
24	595	612	1431	9.2	nd	0.0029	-----	3170
24	595	960	2241	6.0	nd	0.0020	-----	3000
24	595	1116	2604	5.4	0.0009	0.0015	6000	3600
60	595	1116	2604	3.2	0.0023	0.0016	1390	2000

*cmHg; ** $cm^3 / cm^2 \cdot s \cdot cmHg \times 10^5$; nd = not detected membranes comprising TMAF•$4H_2O$ and PVAmSCN as the active separation media. These membranes functions by virtue of a high, reversible affinity for CO_2 and NH_3, respectively. Transport in the CO_2-TMAF•$4H_2O$ system appears to involve a carrier-mediated facilitated mechanism. We have demonstrated that a multilayer PTMSP/PVAmSCN/PTMSP membrane is effective for the recovery of NH_3, even at high pressures. The membranes are unique in that H_2, usually the most permeable gas, is retained in the feed stream with high selectivity, a feature which may offer opportunities not possible with conventional polymeric membranes.

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20. Permeance (Po/l) was converted to permeability (Po) using a membrane thickness determined by scanning electron microscopy of the composite membrane before permeation testing.