J. Am. Chem. Soc. **1991**, *113*, 742-749

Mechanism for Selective Ammonia Transport through Poly(vinylammonium thiocyanate) Membranes

Abhoyjit Bhown and E. L. Cussler*

Contribution from the Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455. *Received June 11, 1990*

Abstract: Ammonia diffuses selectively through poly(vinylammonium thiocyanate) membranes. This high selectivity occurs because the membranes react with ammonia to produce a solution of poly(vinylamine) and ammonium thiocyanate, a salt in which ammonia is highly soluble. Liquid membranes made of ammonium thiocyanate and membranes of poly(vinyl alcohol) impregnated with ammonium thiocyanate show similar behavior. None of these membranes operate by means of mobile carriers, the mechanisms most often responsible for selective facilitated diffusion.

This paper is concerned with membranes that separate ammonia from gases like nitrogen and hydrogen. The manufacture of ammonia is a major business. Ammonia itself ranks fifth in tonnage of all chemicals produced; when the ammonia used in the manufacture of nitric acid, urea, and ammonium nitrate is included, the total ranks ammonia second, behind only sulfuric acid.[1] The social importance of ammonia is greater still: ammonia-based fertilizers are the key to the increased agricultural production that has prevented famine in the face of growing population.[2]

Almost all ammonia is made from air and natural gas. These gases are burned to produce carbon dioxide, nitrogen and hydrogen. After the carbon dioxide is removed, the nitrogen and hydrogen are combined at high pressure (30 000 kPa) and high temperature (400 °C) to produce ammonia. This reaction, requiring catalysis originally developed by Haber, does not go to completion.[3] Instead, the reactive mixture is cooled to condense ammonia, and the unreacted nitrogen and hydrogen are reheated and recycled. The cooling and reheating are a major expense in ammonia production.

One dream of ammonia manufacture would be a new reactor with one reactor wall made of an ammonia-selective membrane. Ammonia produced in the reactor could pass through this membrane wall, but the hydrogen and nitrogen would be retained. These retained gases would then react further. Such a membrane reactor would circumvent the usual constraint of an equilibrium between nitrogen, hydrogen, and ammonia.

Such a membrane reactor remains a dream. One major step toward realizing this dream has come from membranes developed by Pez and Laciak.[4,5] These membranes, made of poly(vinylammonium thiocyanate), are highly permeable to ammonia but almost impermeable to nitrogen and hydrogen. They are not stable at the high temperatures used in ammonia synthesis, but they do illustrate the high selectivity required for the membrane reactor. Moreover, this selectivity is especially interesting because it is more than 100 times higher than those for membrane separations of other gases, including oxygen and nitrogen.[6-8]

This paper attempts to explain the ammonia selectivity of these poly(vinylammonium thiocyanate) membranes. In the presence of ammonia, the membrane becomes rubbery, so its selectivity must have a different origin than those of the more common gas separations using glassy membranes.[9] The ammonia-selective membrane almost certainly achieves selectivity by means of chemical reaction, but what reaction is unclear. The ammonia-selective membrane has similarities with mobile-carrier assisted diffusion in liquid membranes,[10] but these similarities turn out to be superficial.

This paper begins with a discussion of four possible mechanisms by which this membrane might operate. The predictions of these four mechanisms are then compared with experiment. This comparison is not completely definitive, but it suggests a relatively simple explanation for ammonia selectivity. The paper concludes with implications for ammonia production.

Theory

The most striking feature of membranes of poly(vinylammonium thiocyanate) is their extremely high selectivity for ammonia. Any theory of diffusion in these membranes must have as its chief priority an explanation of this selectivity. Any theory should also explain how the ammonia flux varies with ammonia pressure and how it varies with the concentration of thiocyanate in the membrane.

The simplest explanation is that the flux of ammonia diffusing through the membrane is given by Fick's law

$$j_{\mathrm{NH_3}} = \frac{DH}{l}(p_{\mathrm{NH_3}} - 0) \qquad (1)$$

where $p_{\mathrm{NH_3}}$ and 0 are the ammonia pressures at position $z = 0$ and $z = l$. The diffusion coefficient D and the partition coefficient H are responsible for any membrane selectivity. Obviously, this implies that the flux varies linearly with the feed pressure of ammonia. The flux varies in some unknown way with the concentration of thiocyanate.

How this mechanism could effect highly selective ammonia diffusion is unclear. Some membranes separate gases on the basis of differences in diffusion coefficient.[9] However, these differences are usually much less than the selectivities of 1000 or more that are observed here. In addition, diffusion coefficients of light molecules like hydrogen are usually larger than those of heavier species like ammonia.[11] Finally, differences in diffusion coefficients are most important for glassy membranes, and the membranes used here are not glassy. Thus, differences in D seem unlikely to cause the selectivity observed.

The selectivity might also come from H.[12] However, partition coefficients rarely result in high selectivity. Any selectivity they do engender tends to drop in highly swollen membranes. That

---

(1) *Chem. Eng. News* **1990**, *68*, 12.

(2) Brown, L. R. *The Social Impact of the Green Revolution*; Carnegie Endowment for International Peace: New York, 1971.

(3) LeBlanc, J. R.; Madhaven, S.; Porter, R. E. Ammonia. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1978.

(4) Laciak, D. V.; Pez, G. P. U.S. Patent 4,758,250 July 19, 1988.

(5) Pez, G. P.; Laciak, D. V. U.S. Patent 4,762,535, Aug 9, 1988.

(6) Nishide, H.; Okyanagi, M.; Okadu, O.; Tsuchida, E. *Macromolecules* **1986**, *19*, 494.

(7) Nishide, H.; Okyanagi, M.; Okadu, O.; Tsuchida, E. *Macromolecules* **1986**, *20*, 417.

(8) Delaney, M. S.; Reddy, D.; Wessling, R. A. *J. Membr. Sci.* **1990**, *49*, 15.

(9) Koros, W. J.; Chern, R. J. In *Handbook of Separation Processes Technology*; Rousseau, R. W., Ed.; Wiley: New York, 1987.

(10) Noble, R. D.; Koval, C. A.; Pellegrino, J. T. *Chem. Eng. Prog.* **1989**, *85*, 58.

(11) Henis, J. M. S.; Tripodi, M. K. *Sep. Sci. Tech.* **1980**, *15*, 1059.

(12) Cussler, E. L.; Evans, D. F. *J. Membr. Sci.* **1980**, *6*, 113.

0002-7863/91/1513-742$02.50/0 © 1991 American Chemical Society

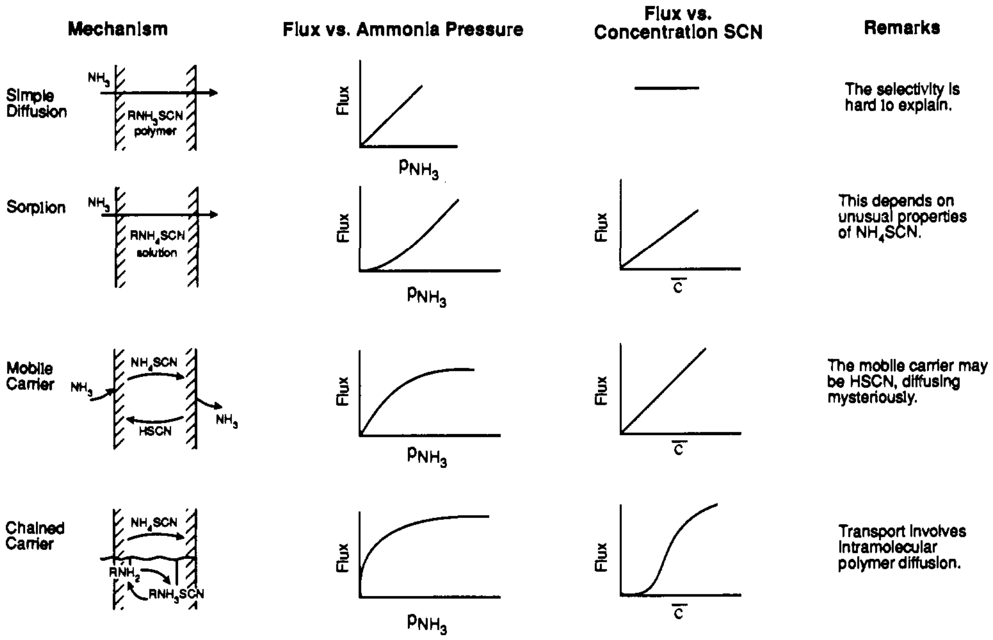

Figure 1. Four possible mechanisms for ammonia transport. The four mechanisms predict different variations with ammonia pressure and thiocyanate concentration.

is not the case here; the membranes retain their selectivity even when highly swollen with ammonia. Partition coefficients seem an unlikely source of high selectivity.

The high selectivity observed here seems most likely to result from chemical reaction. After all, reactions are responsible for many selective separations, including those in liquid membranes.[10,12] In the remainder of this section, we will assume that selective ammonia diffusion involves the reaction

$$NH_3 + RNH_3SCN \rightleftharpoons NH_4SCN + RNH_2 \qquad (2)$$

in which R represents the polyvinyl backbone. This reaction, which is assumed to be fast, produces ammonium thiocyanate, a salt known to have unusual properties.[13,14] The salt is assumed to remain dissolved in the membrane, largely as ion pairs. If the reaction in eq 2 occurs, then we can imagine selective ammonia diffusion occurring by a variety of mechanisms. Three seem especially interesting:

(1) **Sorption**. Ammonia dissolves in the NH_4SCN produced by the reaction and diffuses across the membrane.

(2) **Mobile Carrier**. The acid HSCN facilitates ammonia diffusion, reacting with ammonia, diffusing with it across the membrane, and then diffusing back.

(3) **Chained Carrier**. Ammonium thiocyanate diffuses across the membrane, and the thiocyanate moiety returns by a mechanism including intramolecular polymer diffusion and reaction.

The differences between these three mechanisms are compared schematically with that for simple diffusion in Figure 1. As suggested in the figure, the mechanisms imply that the ammonia flux will vary differently with the ammonia concentration and with the amount of thiocyanate present in the membrane. These implications result from the equations developed in the following paragraphs.

Sorption. The simplest of the three mechanisms based on the reaction in eq 2 reflects the unusual properties of ammonium thiocyanate.[13,14] This salt dissolves huge quantities of ammonia. It dissolves so much ammonia that, at room temperature and at an ammonia pressure above 20 kPa, it forms a homogeneous liquid solution. While this solution might be described as a molten salt, it has a few free ions, as shown in the following text. It seems less analogous to molten NaCl than to a deliquescent nonelectrolyte.

Our analysis should include both the reaction in eq 2 and these unusual properties. The reaction in eq 2 implies the equilibrium

$$[NH_4SCN][RNH_2] = K[NH_3][RNH_3SCN] \qquad (3)$$

Note each concentration, including the value of ammonia, is that within the membrane. Because the total amount of thiocyanate in the membrane $\bar{c}$ is fixed, we expect that

$$\bar{c} = [RNH_3SCN] + [NH_4SCN] = [RNH_3SCN] + [RNH_2] \qquad (4)$$

In addition, we assume that the solubility of ammonia in the membrane is dominated by the concentration of NH_4SCN:

$$[NH_3] = H'[NH_4SCN]p_{NH_3} \qquad (5)$$

Note that the partition constant H' is a rough parallel to the Henry's law constant H in the simple theory of eq 1. Equations 3–5 imply an isotherm for the total ammonia absorbed by poly(vinylammonium thiocyanate) (where NH_{3ta} is total ammonia absorbed):

$$[NH_{3ta}] = [NH_3] + [NH_4SCN] = (H'p_{NH_3} + 1)\left(\frac{KH'\bar{c}p_{NH_3}}{1 + KH'p_{NH_3}}\right) \qquad (6)$$

This suggests that the isotherm may increase quickly (with slope $KH'\bar{c}$) at small p_{NH_3} but may rise more slowly (with slope $H'\bar{c}$) at larger p_{NH_3}. This is consistent with experiment.[13,15] While such a change in slope is reminiscent of dual-mode transport in glassy polymers,[9,16] the chemistry assumed here is more explicit than in the dual-mode case.

To find how much ammonia diffuses, we write continuity equations for both NH_3 and the original polymer

$$0 = D\frac{d^2[NH_3]}{dz^2} - r \qquad (7)$$

$$0 = D'\frac{d^2[RNH_3SCN]}{dz^2} - r \qquad (8)$$

where D and D' are the diffusion coefficients of the ammonia and the polymer, respectively; and r is the rate of the reaction in eq 2. We expect that D' is small, so r is also small; as a result, the

---

(13) Fraser, L. H. D. *Refrig. Eng.* **1932**, *18*, 20.

(14) Nicholls, D. *Inorganic Chemistry in Liquid Ammonia*; Elsevier: Amsterdam, 1979; p 20.

(15) Laciak, D. V., Air Products and Chemicals, private communication. See also a forthcoming issue of *Sep. Sci. Technol.*

(16) Barrer, R. M. *J. Membr. Sci.* **1984**, *18*, 25.

ammonia flux is found by integrating eq 7 and combining the result with eqs 3–5:

$$j_{\mathrm{NH_3}} = \frac{D}{l}([\mathrm{NH_3}]_0 - 0) \qquad (9)$$

$$j_{\mathrm{NH_3}} = \frac{D}{l}\left[\frac{K(H')^2\bar{c}p_{\mathrm{NH_3}}{}^2}{1 + KH'p_{\mathrm{NH_3}}} - 0\right] \qquad (10)$$

This interesting result suggests that the flux varies linearly with ammonia pressure at high ammonia pressure. It varies with the square of ammonia pressure at low ammonia pressure, and it varies linearly with the thiocyanate concentration $\bar{c}$ at all ammonia pressures. This behavior is shown schematically for this sorption mechanism in Figure 1.

Mobile Carrier. The mobile-carrier mechanism is an obvious alternative to the sorption mechanism described previously. In a mobile-carrier mechanism, a solute retained within the membrane—the "mobile carrier"—reacts with ammonia and diffuses with it across the membrane. Such reaction-assisted transport, sometimes called "facilitated diffusion", often yields highly selective separations. One familiar example is blood, where hemoglobin facilitates oxygen diffusion; other examples are the wide variety of liquid membranes.[10]

There are two main reasons why we might suspect this mechanism for poly(vinylammonium thiocyanate) membranes. First, these membranes are dramatically plasticized by ammonia: they go from being a brittle glass to a viscous liquid in the presence of ammonia.[17] Moreover, pure ammonium thiocyanate easily forms liquid solutions with ammonia, as mentioned above.[13,14] Thus, ammonia transport may be analogous to that in liquid membranes. Second there is a strong apparent parallel with membrane-based alkane–olefin separations.[18] A membrane containing fixed sulfate groups and silver or mercurous counterions is permeable to ethylene but not to ethane. The reason is that the metal ion complexes ethylene and diffuses with it across the membrane. The metal ions do not complex ethane and so do not facilitate ethane diffusion.

When we try to apply this mechanism to poly(vinylammonium thiocyanate), we are nonplussed by the choice of a solute as a mobile carrier. No obvious choice exists. Still, to illustrate the mechanism, we will assume that the polymer implausibly dissociates to produce HSCN, which then plausibly reacts with ammonia to diffuse as $\mathrm{NH_4SCN}$. This implies continuity equations like the following

$$0 = D\frac{\mathrm{d}^2[\mathrm{NH_4SCN}]}{\mathrm{d}z^2} \qquad (11)$$

$$0 = D\frac{\mathrm{d}^2[\mathrm{HSCN}]}{\mathrm{d}z^2} + r \qquad (12)$$

$$0 = D'\frac{\mathrm{d}^2[\mathrm{RNH_3SCN}]}{\mathrm{d}z^2} - r \qquad (13)$$

in which D is a diffusion coefficient, taken as the same for both $\mathrm{NH_4SCN}$ and HSCN; D' is the polymer's diffusion coefficient, expected to be much smaller than D; and r is the rate of formation of HSCN. These continuity equations are subject to the constraints

$$z = 0 \qquad [\mathrm{NH_4SCN}] = H''[\mathrm{HSCN}]p_{\mathrm{NH_3}} \qquad (14)$$

$$z = l \qquad [\mathrm{NH_4SCN}] = 0 \qquad (15)$$

$$z = 0, l \qquad j_{\mathrm{RNH_3SCN}} + j_{\mathrm{HSCN}} + j_{\mathrm{NH_4SCN}} = 0 \qquad (16)$$

and

$$\bar{c} = \frac{1}{l}\int_0^l([\mathrm{RNH_3SCN}] + [\mathrm{HSCN}] + [\mathrm{NH_4SCN}])\mathrm{d}z \qquad (17)$$

By adding eqs 11–13, integrating once, using eq 16, integrating again, and using eq 17 and our expectation that $D' \ll D$, we find

$$\bar{c} = [\mathrm{HSCN}] + [\mathrm{NH_4SCN}] \qquad (18)$$

By integrating eq 11 and combining with eqs 14, 15, and 18, we find the ammonia flux

$$j_{\mathrm{NH_3}} = \frac{D}{l}\,\frac{H''\bar{c}p_{\mathrm{NH_3}}}{1 + H''p_{\mathrm{NH_3}}} \qquad (19)$$

The flux varies linearly with thiocyanate concentration $\bar{c}$ and linearly with low ammonia pressure; it reaches a maximum value at high ammonia pressure. This behavior, characteristic of many mobile-carrier mechanisms, is also shown in Figure 1.

The chief problem with this mobile-carrier analysis is the unwarranted assumption of the occurrence and unfettered movement of HSCN. There is little chemical basis for this. One way to make the analysis more realistic is to assume that HSCN is formed by dissociation of the polymer, followed by near-instantaneous association with $\mathrm{NH_3}$. When we consider this possibility, we quickly encounter a new problem: how does the HSCN released at $z = l$ get back to $z = 0$?

There are two limiting possibilities. First, it can diffuse back as polymer with a diffusion coefficient as large as those of the other solutes (i.e., $D = D'$). This unlikely limit, detailed elsewhere,[17] leads to predictions much like those in eq 19, but with less than linear variations at low $p_{\mathrm{NH_3}}$. The second limit depends on the additional assumption that the HSCN returns by some combination of diffusion and reaction. This second limit is the chained-carrier case described text.

Chained Carrier. The concept of chained carriers is an effort to rationalize highly selective diffusion in solid polymer films.[19] Such highly selective diffusion, common in thin liquid films,[20,21] often depends on mobile-carrier mechanisms like that described previously. While these mechanisms are often postulated in solid polymer films, they rarely resist careful chemical scrutiny; they usually turn out to be artifacts like Donnan equilibria or membrane conditioning.[17,22] Still, in a few cases, the results seem most easily explained by chained carriers.[6,7]

In the case considered here, we again assume that ammonia reacts at $z = 0$ with poly(vinylammonium thiocyanate) to produce ammonium thiocyanate and poly(vinylamine). This ammonium salt then diffuses across the membrane. At $z = l$, the reaction is reversed, releasing ammonia and locally generating poly(vinylammonium thiocyanate). The thiocyanate then returns across the membrane by means of the reaction:

$$\mathrm{RNH_2}|_z + \mathrm{RNH_3SCN}|_{z+\Delta z} \rightleftharpoons \mathrm{RNH_3SCN}|_z + \mathrm{RNH_2}|_{z+\Delta z} \qquad (20)$$

In terms of one vivid analogy, the thiocyanate is like a solute Tarzan, swinging from one poly(vinylamine) vine to the next.[19]

The ammonia flux by such a mechanism involves the coupled transport of $\mathrm{NH_4SCN}$ and $\mathrm{RNH_3SCN}$. The ammonia flux is equal to that of the salt:

$$j_{\mathrm{NH_3}} = j_{\mathrm{NH_4SCN}} = \frac{D}{l}([\mathrm{NH_4SCN}]_0 - [\mathrm{NH_4SCN}]_l) \qquad (21)$$

These concentrations can be rewritten by use of boundary conditions:

$$z = 0 \qquad [\mathrm{NH_4SCN}]_0[\mathrm{RNH_2}]_0 = K'[\mathrm{RNH_3SCN}]_0 p_{\mathrm{NH_3}} \qquad (22)$$

$$z = l \qquad [\mathrm{NH_4SCN}]_l = 0 \qquad (23)$$

The equilibrium constant K' in eq 22 combines a chemical equilibrium constant like that in eq 3 with a partition coefficient like that in eq 1. The other salt concentrations in these equations can be found from a mass balance on thiocyanate at $z = 0$

---

(17) Bhown, A. S. Ph.D. Thesis, University of Minnesota, 1990.

(18) LeBlanc, J. R.; Ward, W. J.; Matson, S. L.; Kimura, S. G. *J. Membr. Sci.* **1980**, *6*, 339.

(19) Cussler, E. L.; Aris, R.; Bhown, A. *J. Membr. Sci.* **1989**, *43*, 149.

(20) Yoshikawa, M.; Shudo, S.; Sanui, K.; Ogata, N. *J. Membr. Sci.* **1986**, *26*, 51.

(21) Yoshikawa, M.; Imashiro, Y.; Samuri, K.; Ogata, N. *J. Membr. Sci.* **1984**, *20*, 139.

(22) Koros, W. J.; Hellums, M. W. Paper presented at the *Fifth International Conference on Fluid Properties and Phase Equilibria*; May 1989.

$$\bar{c} = [\mathrm{NH_4SCN}]_0 + [\mathrm{RNH_3SCN}]_0 = [\mathrm{RNH_2}]_0 + [\mathrm{RNH_3SCN}]_0 \quad (24)$$

and from a flux equation on the thiocyanate

$$\begin{aligned} -j_{\mathrm{NH_3}} &= j_{\mathrm{RNH_3SCN}} \\ &= \frac{D''}{l}([\mathrm{RNH_3SCN}]_0 - [\mathrm{RNH_3SCN}]_l) \\ &= \frac{D''}{l}([\mathrm{RNH_3SCN}]_0 - \bar{c}) \end{aligned} \quad (25)$$

While the transport coefficient D'' in eq 25 has the dimensions of a diffusion coefficient, it is actually a complex function of diffusion, chemical kinetics, and membrane geometry.[19] When the reaction in eq 20 is fast, D'' is an intramolecular polymer diffusion coefficient. When the reaction in eq 20 is slow, D'' is proportional to the rate constant of the reaction in eq 20. Details are given elsewhere.[17]

The ammonia flux is now easily calculated from eqs 21–25:

$$j_{\mathrm{NH_3}} = \frac{D}{l}\,\frac{K'p_{\mathrm{NH_3}}}{2}\left(\left(1 + \left\{\frac{4D'\bar{c}}{DK'p_{\mathrm{NH_3}}}\right\}\right)^{1/2} - 1\right) \quad (26)$$

There are three important limits of this result. First, when [$\mathrm{RNH_3SCN}$] is less than an unknown critical value, D'' is zero and the ammonia flux is zero. In other words, the membrane shows a percolation threshold. The two other limits occur when [$\mathrm{RNH_3SCN}$] is above this threshold. When the quantity in braces is large, as, for example, at low ammonia pressure, the flux varies with the square root of [$\bar{c}p_{\mathrm{NH_3}}$]. When the quantity in braces is small, as, for example, at high ammonia pressure, the flux varies linearly with $\bar{c}$ and is independent of $p_{\mathrm{NH_3}}$. These results are shown schematically in Figure 1. Both they and the other results in that figure will be tested against experiment in the sections that follow.

Experimental Section

Materials. Poly(vinylammonium thiocyanate) and poly(vinylammonium chloride) were supplied as aqueous solutions by D. V. Laciak, Air Products and Chemicals (Allentown, PA). These were subsequently diluted to 1 wt % with water. The thiocyanate polymer, made by adding excess $\mathrm{NH_4SCN}$ to the chloride, actually contains about 80 mol % SCN groups and 20 mol % Cl groups. Poly(vinyl alcohol) was also supplied by Air Products (Airvol 205 Lot No. 02071618, molecular weight of 11 000–31 000). Ammonium thiocyanate and ammonium chloride were purchased from Aldrich. Ammonia, nitrogen, and helium were purchased from Linde (Union Carbide, Somerset, NJ), either as pure, oil-free gases or as mixtures of known concentration. $\mathrm{ND_3}$ was purchased from Isotec (Miamisburg, OH). Other chemicals were reagent grade and were used as received.

Methods. Two types of membranes were prepared: polymer membranes and salt membranes. For the polymer membranes, ~5 cm^3 of a 1 wt % solution of the appropriate polymer was diluted with ethanol to 10 cm^3 and poured into a 4.4-cm-diameter Teflon Petri dish. The dish was placed in a vacuum oven at 5 psi for 5 min to remove gases dissolved in the solution. The dish was then dried overnight at room temperature and pressure. The polymer film remaining in the dish was exposed to fumes from concentrated $\mathrm{NH_4OH}$ for 3 min. The film, now flexible, was then installed in the flow cell described in the following text. Salt membranes, the second type, were made by first exposing $\mathrm{NH_4SCN}$ crystals to $\mathrm{NH_3}$ to make a viscous solution. A piece of microporous polypropylene (Celgard 3501; Hoechst-Celanese, Charlotte, NC) was soaked in the solution for 5 min, allowed to dry for 2 min, and installed in the flow cell.

The flow cell used with both types of membranes was a modified stainless steel Millipore ultrafiltration unit that accepts a disk-shaped membrane 2.5 cm in diameter. The membrane separates two chambers. The feed chamber, of 5-cm^3 volume, is fed with gas mixtures at total pressures from 100 to 1000 kPa. Samples of this feed can be diverted through a six-port sampling valve for analysis. Because the feed flow was at least 5 L/min, its composition while in the cell was nearly constant. The permeate chamber, also of 5-cm^3 volume, was swept with helium at 100 kPa and a flow of 40 cm^3/min. Lower helium flow rates had no effect on the flux of ammonia or of other gases. The permeate concentration was sampled with the same six-port valve. Fluxes were found from

$$j_{\mathrm{NH_3}} = \frac{Q}{A}[\mathrm{NH_3}] \quad (27)$$

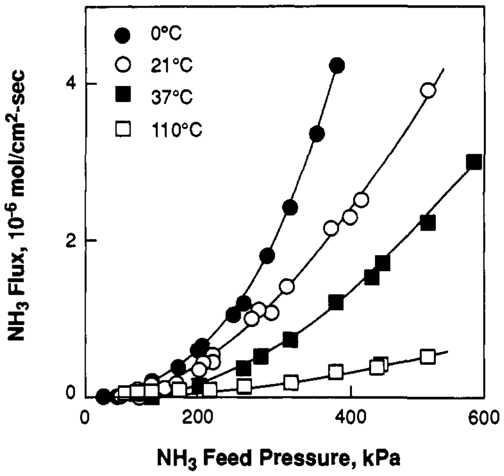

Figure 2. Ammonia flux across membranes of poly(vinylammonium thiocyanate). Nitrogen and hydrogen fluxes are at least 3000 times smaller.

in which Q is the total flow rate exiting the permeate chamber, [$\mathrm{NH_3}$] is its ammonia concentration, and A is the membrane area. The mole fraction was analyzed with a gas chromatograph (Hewlett-Packard Model 5890A) equipped with a thermal conductivity detector. A 5-ft Porapack QS column (Alltech, Deerfield, IL) operating at 120 °C could easily separate the gases. The chromatograph was calibrated by filling the sample loop with gas mixtures of known composition.

Both polymer membranes and salt membranes must be mechanically stabilized in this flow cell. The polymer membranes were stabilized by sandwiching them between two pieces of microporous polypropylene (Celgard 3501) and then between two Teflon-coated, porous metal disks. The Teflon-coated disks have 250-μm pores and a void fraction of 0.20. The polypropylene-supported salt membranes were stabilized by the Teflon disks only. Ammonia fluxes were unchanged by stabilization with disks of different properties.

We based our flux measurements across polymer membranes on the total polymer area. However, we wanted to correct our flux measurements across the supported ammonium thiocyanate membranes for the porosity and the tortuosity of the microporous support itself. To make these corrections, we measured the diffusion of 0.1 M HCl and of 1.0 M urea across 4.23 cm^2 of the microporous polypropylene support, clamped in a Stokes diaphragm cell.[23] For both solutes, we found that the open membrane area per projected area per tortuosity was 0.046, consistent with other measurements on these water-wet supports.[24]

We also made impedance and spectral measurements on these membranes. For the impedance measurements, the membrane was clamped between two stainless steel electrodes and the impedance was measured from 1 Hz to 10 MHz with a Schlumberger impedance analyzer (Model 1260).[25] For infrared studies, the membrane was clamped between two KBr windows, exposed to 370-kPa $\mathrm{NH_3}$ pressure and placed in an IBM FTIR (Model IR/44). For mass spectroscopy, polymer or salt samples were placed in 0.6-cm^3 stainless steel tubes fitted with a septum and exposed to varying pressures of $\mathrm{NH_3}$ or $\mathrm{ND_3}$. Gas samples withdrawn from the tubes were analyzed in an VG Analytical 7070 mass spectrometer.

Results

In this section, we will first report the ammonia flux across thin membranes of poly(vinylammonium thiocyanate). We then compare these with supported membranes made of ammonium thiocyanate. These membrane data seem to support the sorption mechanism more than the alternative mechanisms developed previously. We next describe impedance and spectral measurements, both of the polymer and of the salt, that provide additional information about the chemistry within the membranes.

Poly(vinylammonium thiocyanate) Membranes. The flux of ammonia across 35-μm membranes of this polymer is shown as a function of ammonia pressure in Figure 2. The flux is small until the ammonia pressure is above 100 kPa. It then rises, roughly linearly. At the same time, the fluxes of nitrogen and hydrogen,

---

(23) Cussler, E. L. *Diffusion*; Cambridge University Press: London, 1984.

(24) Prasad, R.; Hoechst Celanese; Sirkar, K. K., Stevens Institute of Technology, private communications.

(25) Bard, A. J.; Faulkner, L. E. *Electrochem. Methods* **1980**.

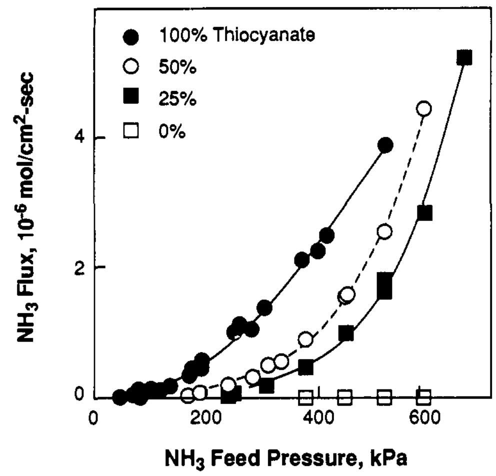

Figure 3. Ammonia flux across membranes of mixed poly(vinylammonium thiocyanate) and poly(vinyl alcohol). Fluxes interpolated at fixed ammonia pressure vary linearly with the fraction of thiocyanate in the membranes.

which are small at low ammonia pressure, remain too small to measure at higher ammonia pressures. From the sensitivity of our concentration measurements, we estimate that the nitrogen and hydrogen fluxes are at least 3000 times smaller than the ammonia flux. In other words, these membranes are at least 3000 times more selective for ammonia than for nitrogen and hydrogen, consistent with earlier work.[5]

The diffusion coefficient in these polymer membranes can be calculated from the high-pressure partition coefficients and from diffusion fluxes in Figure 2. The high-pressure partition coefficients can be found from data by Laciak[4]

$$[\mathrm{NH_3}]/p_{\mathrm{NH_3}} = 6.2 \times 10^{-5} \text{ mol of } \mathrm{NH_3}/(\mathrm{cm^3\ kPa}) \quad (28)$$

The diffusion coefficient can now be estimated from this value and the data in Figure 2. For example, at 400 kPa and 21 °C, the result from eq 9 is

$$j_{\mathrm{NH_3}} = \frac{D}{l}(H'\bar{c})p_{\mathrm{NH_3}}$$

$$\frac{2.4 \times 10^{-6}\ \mathrm{mol}}{\mathrm{cm^2\ s}} = \frac{D}{35 \times 10^{-4}\ \mathrm{cm}}\left(\frac{6.2 \times 10^{-5}\ \mathrm{mol}}{\mathrm{cm^3\ kPa}}\right) 400\ \mathrm{kPa}$$

$$D = 3.4 \times 10^{-7}\ \mathrm{cm^2/s} \quad (29)$$

This value is typical of a liquid in a rubbery polymer and is much greater than the value expected in a glassy polymer.[23] Similar estimates can also be obtained from the simple mechanism implied by eq 1.

The ammonia flux and the threshold pressure both depend on the concentration of thiocyanate in the membrane, as shown in Figure 3. The membranes in these experiments, made at 20 °C, are mixtures of poly(vinylammonium thiocyanate) and poly(vinyl alcohol), prepared as described previously. The fluxes for 100% poly(vinylammonium thiocyanate) are similar to those in Figure 2; the fluxes for 0% thiocyanate (i.e., 100% poly(vinyl alcohol)) are very small. We can interpolate between the data in Figure 3 to find fluxes at constant ammonia pressure vs the concentration of thiocyanate $\bar{c}$. This variation is approximately linear, with a zero intercept. Parenthetically, the flux also depends on the counterion; that through poly(vinylammonium thiocyanate) is faster than that through poly(vinylammonium chloride), as shown at 20 °C in Figure 4. Mixtures of these polymers not surprisingly give fluxes between those of the pure polymers.

The results in Figures 2–4 support the sorption mechanism for membrane transport, as suggested by Figure 1. As predicted, the flux vs ammonia pressure does show an apparent threshold and then varies more linearly with ammonia pressure. This threshold pressure occurs simultaneously with other physical changes: the membrane goes from being brittle and opaque to being soft and transparent. As predicted by the sorption mechanism, the flux at high ammonia pressure extrapolates to zero at finite ammonia pressures. As predicted, the flux varies linearly with the poly(vinylammonium thiocyanate) concentration.

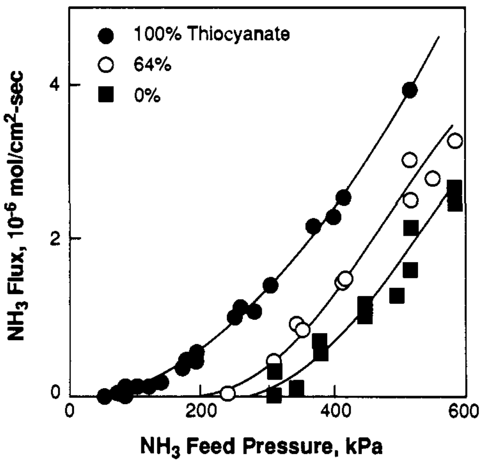

Figure 4. Ammonia flux across membranes of mixed counterions. Replacing thiocyanate with chloride reduces the flux.

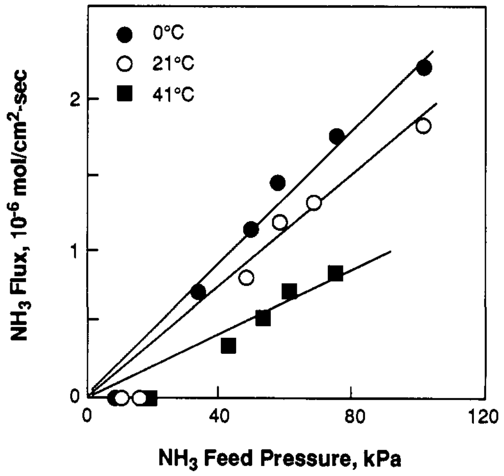

Figure 5. Ammonia flux across supported membranes of ammonium thiocyanate. The membranes appear to melt at ammonia pressures above 20 kPa.

At the same time, the results in Figures 2–4 appear inconsistent with the simple diffusion mechanism, with the predictions of mobile carriers, and with the expectations for chained carriers, as summarized in Figure 1. The simple diffusion mechanism does not predict a threshold pressure. The carrier-assisted mechanisms do not predict the observed threshold pressure for ammonia flux, although the chained-carrier mechanism does predict a threshold concentration for the carrier, presumably poly(vinylammonium thiocyanate). At high ammonia pressures, the flux does not reach the constant "saturation" values predicted by both mobile-carrier and chained-carrier mechanisms.[10,12,19]

Ammonium Thiocyanate Membranes. If this sorption mechanism is correct, then we expect that membranes made of ammonium thiocyanate should show fluxes similar to those across poly(vinylammonium thiocyanate). This expectation comes from the sorption mechanism postulated for the polymer membranes in eqs 2 and 5. This postulated mechanism centers on the reaction of the polymer and ammonia to make an ammonium thiocyanate solution. Ammonia then diffuses through this solution.

Membranes of NH_4SCN were made by forming a solution of this salt with 100 kPa of ammonia, dipping an inert microporous membrane of polypropylene in this solution, and drying it in air. The resulting membrane has a reproducible thickness; at room temperature, it becomes transparent at ammonia pressures above 30 kPa. Above these pressures it is superficially similar to a supported liquid membrane.

Ammonia fluxes across membranes of ammonium thiocyanate are shown in Figure 5. Ammonia fluxes below 30 kPa are small; ammonia fluxes at higher pressures vary linearly with ammonia pressure. Selectivities appear similar to those observed for poly(vinylammonium thiocyanate).[5,17] The temperature variation of the flux also seems similar.

Significantly, the ammonium flux thorough NH_4SCN membranes appears to extrapolate to zero at zero ammonia pressure. This suggests that at high ammonia pressure diffusion occurs by normal diffusion. It is large and selective because ammonia is extremely soluble in NH_4SCN.[13,14] Other gases are much less soluble. The data in Figure 5 also suggest that at low ammonia pressure the membrane becomes glassy, dramatically reducing the diffusion coefficient.

In contrast, the ammonia flux through poly(vinylammonium thiocyanate) membranes shown in Figure 2 extrapolates to zero at a finite ammonia pressure. This is consistent with the hypothesis that ammonia reacts to produce a NH_4SCN–polymer solution. Ammonia dissolving in this polymer solution then diffuses by normal diffusion, just as if it were dissolved in NH_4SCN. Thus, in this picture, membranes of poly(vinylammonium thiocyanate) are essentially a convenient storehouse for NH_4SCN.

If this picture is true, the diffusion coefficient in the NH_4SCN membranes of Figure 5 should be similar to the diffusion coefficient in the polymer membranes in Figure 2. To make this estimate from Figure 5, we need the partition coefficient for NH_3 in NH_4SCN and the void fraction per tortuosity for the microporous support. This partition coefficient at 20 °C is[17,26]

$$H = \left\{\frac{[\mathrm{NH_3}]}{p_{\mathrm{NH_3}}}\right\} = 2.0 \times 10^{-4}\ \mathrm{mol/(cm^3\ kPa)} \qquad (30)$$

The effective area per tortuosity factor ϵ/τ is measured as described above. The diffusion coefficient can then be found from eq 1. For example, at 21 °C and 100 kPa

$$j_{\mathrm{NH_3}} = \frac{DH}{l}\left(\frac{\epsilon}{\tau}\right)p_{\mathrm{NH_3}}$$

$$1.9 \times 10^{-6}\ \mathrm{mol/(cm^2\ s)} = \frac{D}{25 \times 10^{-4}\ \mathrm{cm}}\{2.0 \times 10^{-4}\ \mathrm{mol/(cm^3\ kPa)}\}(0.046)100\ \mathrm{kPa}$$

$$D = 5.2 \times 10^{-6}\ \mathrm{cm^2/s} \qquad (31)$$

This value is in a liquid of ammonia and thiocyanate that under these conditions has a viscosity of 3.0 cP.[17] It seems completely consistent with the value of 1.6×10^{-5} cm^2/s found in water,[23] which obviously has a viscosity of 1.0 cP. Direct measurements with NMR give a value of 8×10^{-6} cm^2/s at 100 kPa and 25 °C.[15] The diffusion coefficient in eq 31 is ~10 times larger than the value in poly(vinylammonium thiocyanate), a difference that may easily be caused by the higher local viscosity or the reduced salt concentration present in the polymer.

Because these values seemed so similar, we made one membrane by physically blending 2 wt % NH_4SCN with poly(vinyl alcohol). The ammonia flux through this composite film was selective over hydrogen and nitrogen. Its values were very close to those of the blend of 25 wt % poly(vinylammonium thiocyanate) and 75% poly(vinyl alcohol), shown in Figure 3. Blends of polymers and salts like NH_4SCN merit additional study.

Impedance Measurements. To probe the nature of these membranes, we also measured their impedance as a function of frequency and ammonia pressure. The results, plotted as the imaginary vs the real part of impedance, are given in Figures 6 and 7. Data for poly(vinylammonium chloride) are qualitatively similar to the thiocyanate polymer in Figure 6, but show more scatter.[17] The values for the supported salt membranes, shown in Figure 7, are *not* corrected for either void fraction or tortuosity.

The values in Figures 6 and 7 show characteristics expected for weak ionic conductors.[25] At low frequencies below those shown, the membranes behave as capacitors, with a limiting real contribution to the impedance but an ever-increasing imaginary part. At larger frequencies, which are shown, the real and imaginary parts often vary linearly, with a slope near 45°. This is characteristic of an impedance controlled by ion transport and is the region of greatest interest here, since it is related to the diffusion fluxes reported above. Still higher frequencies, also shown in

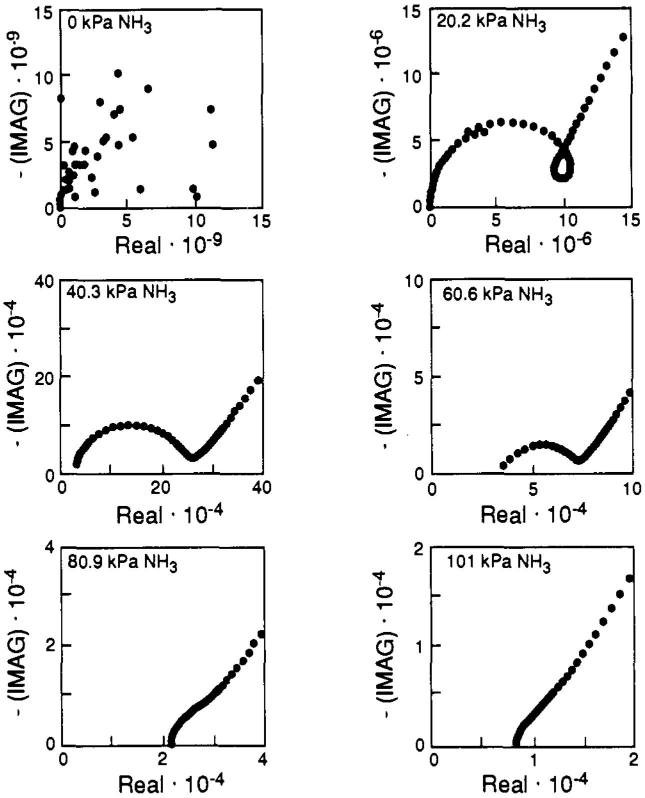

Figure 6. Impedance of poly(vinylammonium thiocyanate) vs ammonia pressure. The dramatic drop indicates the start of ionic conduction.

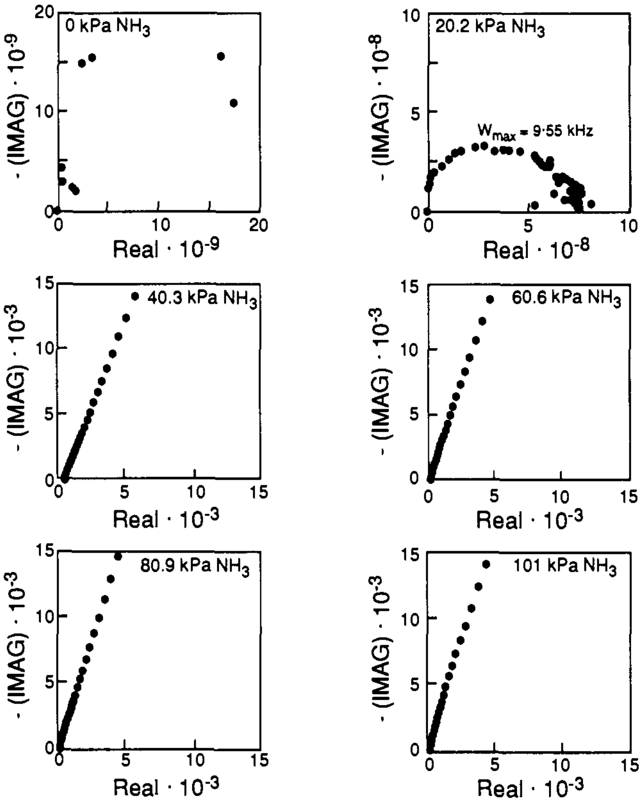

Figure 7. Impedance of ammonia thiocyanate vs ammonia pressure. Ionic conduction starts when films of the salt become liquid.

---

(26) Sipos-Nagy, G.; Horvath, I.; Burger, K. *Inorg. Chim. Acta* **1987**, *130* (1), 75.

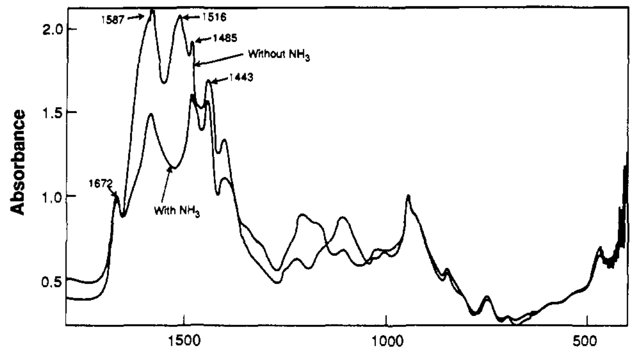

Figure 8. Infrared spectra of poly(vinylammonium thiocyanate). Exposing films of this polymer to *100* kPa of ammonia shifts the spectra as shown.

Figures 6 and 7, produce a semicircular variation characteristic of charge-transfer reactions at the electrodes. These reactions, of unknown chemistry, are of less interest here.

The results in Figures 6 and 7 show that ammonia pressure has a tremendous effect on the electrical properties of the membranes. At zero ammonia pressure, the data scatter with a very high impedance. At ammonia pressures around 20 kPa, the data show evidence of charge-transfer reactions. At ammonia pressures above 40 kPa, they show evidence of ionic transport. This onset of ionic transport occurs simultaneously with the start of the ammonia flux shown in Figures 2 and 5.

The start of ionic transport in Figures 6 and 7 includes a dramatic decrease in membrane resistivity ρ. For example, for poly(vinylammonium thiocyanate) we find

$$\rho = [3.4 \times 10^7\ \Omega\ \mathrm{cm}]^{e^{-(0.81/\mathrm{kPa})p_{\mathrm{NH3}}}} \qquad (32)$$

Thus, the resistivity drops from $\sim 10^7$ Ω cm at a pressure of 14 kPA to 10^4 Ω cm at 100 kPa. This is strong evidence for the formation of partly ionized NH_4SCN within the membranes, the molten salt suggested by earlier studies.[4,14]

We can use this change of resistivity and the diffusion coefficients inferred previously to estimate the fraction of the salt that is ionized. To do so, we assume that the equivalent conductance Λ is proportional to twice the diffusion coefficient estimated from flux experiments.[23] At an ammonia pressure of 100 kPa, this gives values for Λ of 2.6 and 39 $cm^2/(mol\ \Omega)$ in poly(vinylammonium thiocyanate) and ammonium thiocyanate, respectively. When we combine these with resistivities for both systems, we find a concentration of ions of 2×10^{-7} M in both the polymer and the molten salt. This is $\sim 1\%$ of the ions available in the system and is consistent with direct measurements of ammonium thiocyanate dissociation.[26]

Spectra. We sought further evidence of reactions within the membrane from Fourier-transform infrared spectroscopy and mass spectroscopy. The FTIR spectra for poly(vinylammonium thiocyanate) films are shown in Figure 8. The peak at 1516 cm^{-1} disappears after ammonia exposure, characteristic of the conversion from an ammonium side chain to an amine.[27] However, a peak at 800 cm^{-1}, characteristic of amine side-chain bending,[2]18 does not appear on ammonia exposure. This may indicate close association between the amine side chain and NH_4SCN.

We also equilibriated poly(vinylammonium thiocyanate) and ammonium thiocyanate with ND_3 and then analyzed the gases released by placing the membrane under vacuum. The results, shown in Figure 9, show that NH_2D and NHD_2 are both produced. Similar results are obtained for the corresponding chlorides.[17] These results and the FTIR experiments appear to support the reaction postulated in eq 2. The implications of this reaction are explored next.

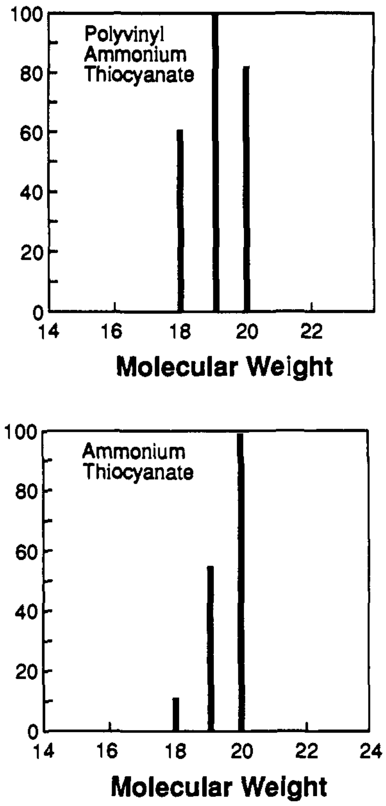

Figure 9. Mass spectrometry of poly(vinylammonium thiocyanate) and ammonium thiocyanate after exposure to ND_3. The results support the reaction postulated in eq 2.

Discussion

Membranes of poly(vinylammonium thiocyanate) can be over 3000 times more permeable to ammonia than to hydrogen and nitrogen. Such membranes suggest two obvious questions. First, what is responsible for the membranes' selectivity? Second, can membranes like these facilitate industrial production of ammonia? While we can answer neither of these questions completely, we want to review the best answers possible now.

Mechanism Causing Selectivity. The results of this paper support the sorption mechanism for ammonia transport across poly(vinylammonium thiocyanate) membranes. In this mechanism, ammonia reacts with the polymer to yield a solution of poly(vinylamine) and ammonium thiocyanate; more ammonia dissolves in the ammonium thiocyanate and diffuses across the membrane.

A variety of experiments support this mechanism. Most importantly, the flux of ammonia across the membrane is small at low ammonia pressures and becomes large and proportional to ammonia pressure above a threshold pressure. The diffusion coefficient inferred from this large flux region is typical of a polymer solution. It is at least 2 orders of magnitude larger than diffusion coefficients typical of glassy polymers.

The ammonia flux across poly(vinylammonium thiocyanate) membranes forms an interesting contrast with that across supported ammonium thiocyanate membranes. In both cases, the fluxes are selective. The flux across the supported salt membranes extrapolates to zero flux at zero pressure, but the flux across the polymer extrapolates to zero at a finite threshold ammonia pressure. The inference is that the supported salt membranes operate by simple diffusion, but the polymer membranes first require reaction to produce NH_4SCN and then operate by diffusion. This initial reaction plus subsequent diffusion is responsible for the polymer membranes' threshold pressure.

The implication that both polymer and supported salt membranes depend on NH_4SCN is supported by measurements of electrical impedance and of spectra. Such measurements support the description of both membranes as molten salts that are only weakly ionized. While molten NaCl shows a high electrical

---

(27) Sadtler. Grating Spectra, Sadtler Research Labs, Philadelphia, 1970; 17699K, 18468K.

(28) Calthrup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic: New York, 1975.

conductivity because the melt contains large numbers of Na^+ and Cl^- ions, NH_4SCN and NH_3 form solutions of lower electrical conductivity, indicating few NH_4^+ and SCN^- ions.

The sorption mechanism developed here can be easily extended in two ways. First, the linear isotherm assumed in eq 5 can be replaced by an experimentally determined Freundlich isotherm.[17] Second, the simple diffusion of ammonia in eq 7 can be modified to include complex formation between ammonia and ammonium thiocyanate.[14] While these improvements give a somewhat better fit of the data, they also obscure rather than clarify the chemistry involved. As a result, we detail these extensions elsewhere.[17]

The current evidence supporting diffusion through sorption does not completely rule out the alternatives of mobile-carrier and chained-carrier mechanisms. These carrier-assisted mechanisms, often lumped together as "facilitated diffusion", produce highly selective separations, like that observed here. They often achieve this high selectivity in liquid membranes, like those used here. As a result, we and others working on these membranes had sensibly suspected that a mobile carrier was responsible for selective ammonia transport. The alternative, that NH_4SCN solutions possessed special, near-magical properties, seemed farfetched. Mobile carriers looked like an excellent possibility.

However, the predictions of mobile-carrier mechanisms in Figure 1 are not supported by the previous results. The results in Figure 3 do show a roughly linear variation of flux and carrier concentration, as predicted by eq 19 and by one limit of eq 26. The results in Figure 2, however, are not predicted by these equations. Both eq 19 and eq 26 predict that the ammonia flux will reach a constant value at high ammonia pressure. The experiments show no trace of such a constant value. Altering the stoichiometry of the ammonia carrier reaction may change the predicted slope of the flux vs ammonia pressure; but any assumed stoichiometry predicts negative curvature. The data show positive curvature. While reports from another group[15] show slight evidence of reduced flux at very high ammonia pressure ($>$10 000 kPa), these might also be caused by fugacity corrections in the gas phase.

The significant fluxes above a threshold pressure of ammonia are not predicted by any carrier-assisted mechanism. In particular, the mobile-carrier mechanism in eq 19 predicts the ammonia flux should vary linearly with ammonia pressure, without any suggestion of a threshold. The chained-carrier mechanism in eq 26 does predict a threshold, but in carrier concentration, not in ammonia pressure. To be sure, such a threshold might be hidden in the correction factors of the chained-carrier theory, but such hidden predictions seem to us unlikely.

But the most serious failing of all theories of carrier-assisted diffusion is the lack of a chemically well-defined mobile carrier. The analogy with the Ag^+-facilitated separation of ethylene and ethane[18] suggests SCN^- as a carrier, but we know of no evidence for large concentrations of NH_3SCN^-. Analogies of acid gas treatment with liquid membranes of amines[29] suggest HSCN as a mobile carrier, and Raman spectra[30] suggest NH_3SCN^- as a carrier. All these possibilities, chemically similar to the sorption mechanism we are urging, fail to explain the lack of saturation, the existence of a threshold pressure of ammonia, and the diffusion of free HSCN back across the membrane. Analogies with oxygen transport in Schiff-base containing films[6,7] suggest transport of HSCN via intramolecular motion of polymer side chains, perhaps by a chained-carrier mechanism. While this mechanism cannot be completely disproved by our experiments, it seems more complex than the sorption arguments outlined above. These sorption arguments are consistent with the experiments to date and so remain our preference.

Industrial Implications. Finally, we turn from the mechanism responsible for membranes' selectivity to their practical value. At the start of the paper, we suggested one application for such a membrane would be in an ammonia synthesis reactor. The membrane would continuously and selectively remove ammonia from the reaction mixture, both facilitating the ammonia separation and overcoming the constraint of equilibrium conversion. We can imagine the membrane either operating hot, as a reactor wall, or operating cool, as a distinct separator.

At the hot reactor conditions, poly(vinylammonium thiocyanate) membranes are a bad choice. We believe that with carefully designed supports they could stand the pressures of such a reactor. They could not stand the temperatures. Moreover, even if the polymer backbone were modified so that it remained stable at higher temperatures, ammonium thiocyanate produced in the sorption mechanism will decompose above 170 °C, well short of the 400 °C in a current ammonia synthesis reactor. Membranes based on NH_4Cl could remain stable to above 300 °C, which was our rationale for the experiments in Figure 4. However, the ammonia flux through all these membranes drops sharply as the temperature rises, as exemplified by the data in Figure 2. Consequently, we are pessimistic about directly using this type of membrane in ammonia synthesis.

At lower temperatures, we are more optimistic. A gas mixture produced in an ammonia synthesis reactor could be cooled and easily separated; the unreacted nitrogen and hydrogen could then be recycled to the reactor. Such a separation would not require reducing the total pressure and might effectively complete with the ammonia condensation method often used now. In addition, we can imagine many cases other than a synthesis reactor where an ammonia selective membrane has value; one obvious application is in a selective electrode. We look forward to the development of these cool applications.

Still, we dream about a membrane capable of separating ammonia during synthesis at high temperature. Such a membrane might well be a molten salt, supported either by a microporous ceramic film or in a ceramic solution.[31] Lithium nitrate might be one candidate for such a salt; it melts at 264 °C, is stable to about 600 °C, and in aqueous solution absorbs large quantities of ammonia.[13,14] We suspect, however, that our dream membrane will need to complex ammonia strongly at high temperatures. We currently have no great ideas for dramatic breakthroughs, but we believe that the chances of developing such a high-temperature, ammonia-selective membrane are good.

Acknowledgment. We are grateful to D. V. Laciak for synthesizing the poly(vinylammonium thiocyanate and chloride) used in these experiments. We benefited from discussions with Dr. Laciak and Dr. Guido Pez, both of Air Products. The work was principally supported by the National Science Foundation (Grant CTS 8912634); other support came from the Graduate School of the University of Minnesota and from the Hoechst-Celanese Corp.

Notation

A	membrane area
$\bar{c}$	total thiocyanate concentration
D,D'	diffusion coefficients
D''	transport coefficient (eq 25)
H,H',H''	partition coefficients defined by eqs 1, 5, and 14, respectively
j_i	flux of species "i"
K,K'	equilibrium constants defined by eqs 3 and 22, respectively
l	membrane thickness
p_i	pressure of species i
Q	gas flow (eq 27)
r	reaction rate per volume, variously defined
z	distance across the membrane
ϵ/τ	fraction membrane area per tortuosity
Λ	equivalent conductance
ρ	resistivity

Registry No. NH_3, 7664-41-7; NH_4SCN, 1762-95-4; poly(vinylammonium thiocyanate), 116829-18-6.

---

(29) Astarita, G.; Savage, D. W.; Bisio, A. *Gas Treating with Chemical Solvents*; Wiley: New York, 1983.

(30) Lemley, A. T.; Lagowski, J. J. *J. Phys. Chem.* **1974**, *78*, 708.

(31) Pez, G. P.; Carlin, R. T.; Laciak, D. V.; Sorensen, J. C.; U.S. Patent 4,761,164. Aug 2, 1988.