



Selective permeation through modified vinylidene fluoride membranes
by Ronanth Zavaleta

A thesis submitted in partial fulfillment of the requirements for the degree DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

A permeation apparatus was developed for determining permeability coefficients of gases and mixtures of gases over a wide range of temperatures and pressures.

Several chemicals were tested as modifiers for vinylidene fluoride based membranes, primarily for the separation of sulfur dioxide from SO₂/N₂ mixtures. Sulfolene was found to be a very selective modifier for the separation of sulfur dioxide. The effect of the sulfolene content in the membrane was investigated, and an 18 wt% sulfolene was found to be a good membrane composition. The permeability coefficients for sulfur dioxide, nitrogen, hydrogen, carbon dioxide, carbon monoxide, oxygen, argon, methane, ethane, ethylene and 1,3 butadiene were determined. The permeability coefficients for SO₂ were found to be 4 orders of magnitude greater than those of N₂, CO, O₂, Ar, CH₄, C₂H₆, C₂H₄ and 1,3 butadiene; about 3 orders of magnitude greater than those for hydrogen, and about 2 orders of magnitude greater than those for carbon dioxide.

The permeability coefficients for SO₂ decrease with increasing temperature. For the other gases studied, except CO₂, the coefficients increase with temperature. CO₂ shows a mixed behavior. The permeabilities were found to be exponential functions of pressure and temperatures, except for N₂, CO and Ar, which are independent of pressure.

Very efficient separations of SO₂ from SO₂/N₂ mixtures were obtained. A permeate containing 95.5 vol. % SO₂ was obtained for an exhaust gas SO₂ concentration of 5.6 vol. %, with permeate flow rates of about 1×10^{-3} cc(STP)/cm².sec, at 0°C and 315 psia upstream pressure. Separation of CO₂ from CO₂/H₂ mixtures was found to be possible. Separation factors of about 2.5 were obtained for CO₂.

When working with mixtures of gases a very strong plasticizing effect by the sorbed gas on the membrane was noticed, which, was stronger at lower temperatures, where the deviations from ideality are greater.

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RONANTH ZAVALETA

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of the requirements for the degree

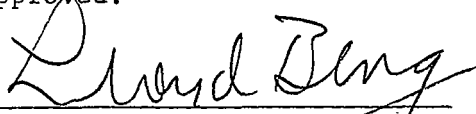
of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

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MONTANA STATE UNIVERSITY

Bozeman, Montana

June, 1975

ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University for their advice, questions and criticisms, which helped guide this investigation.

The author is indebted to Dr. F. P. McCandless, for his advice, assistance and encouragement throughout the course of this project. Thanks goes to James Tillery and Silas Huso who helped in building the apparatus and tracking down various parts and pieces of equipment during the work.

The author gratefully acknowledges financial support, in the form of a scholarship, from the Organization of American States.

The author wishes to thank his mother, whose example and encouragement were fully and unselfishly provided. The author also wishes to thank his wife and son, for their sacrifices and support.

Finally, thanks goes to Sherry Greene for typing this thesis.

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ABSTRACT

A permeation apparatus was developed for determining permeability coefficients of gases and mixtures of gases over a wide range of temperatures and pressures.

Several chemicals were tested as modifiers for vinylidene fluoride based membranes, primarily for the separation of sulfur dioxide from SO_2/N_2 mixtures. Sulfolene was found to be a very selective modifier for the separation of sulfur dioxide. The effect of the sulfolene content in the membrane was investigated, and an 18 wt% sulfolene was found to be a good membrane composition. The permeability coefficients for sulfur dioxide, nitrogen, hydrogen, carbon dioxide, carbon monoxide, oxygen, argon, methane, ethane, ethylene and 1,3 Butadiene were determined. The permeability coefficients for SO_2 were found to be 4 orders of magnitude greater than those of N_2 , CO , O_2 , Ar , CH_4 , C_2H_6 , C_2H_4 and 1,3 butadiene; about 3 orders of magnitude greater than those for hydrogen, and about 2 orders of magnitude greater than those for carbon dioxide.

The permeability coefficients for SO_2 decrease with increasing temperature. For the other gases studied, except CO_2 , the coefficients increase with temperature. CO_2 shows a mixed behavior. The permeabilities were found to be exponential functions of pressure and temperatures, except for N_2 , CO and Ar , which are independent of pressure.

Very efficient separations of SO_2 from SO_2/N_2 mixtures were obtained. A permeate containing 95.5 vol. % SO_2 was obtained for an exhaust gas SO_2 concentration of 5.6 vol. %, with permeate flow rates of about 1×10^{-3} cc(STP)/cm².sec, at 0°C and 315 psia upstream pressure. Separation of CO_2 from CO_2/H_2 mixtures was found to be possible. Separation factors of about 2.5 were obtained for CO_2 .

When working with mixtures of gases a very strong plasticizing effect by the sorbed gas on the membrane was noticed, which was stronger at lower temperatures, where the deviations from ideality are greater.

INTRODUCTION AND PURPOSE

The selective permeation of gases through nonporous polymeric membranes is a potentially effective separation technique that has attracted much attention since the early 1950's. This technique has made considerable progress in recent years in areas such as the development of more permeable and selective membranes, as well as of efficient permeation equipment for large scale operations.

The study of selective permeation is generally motivated by the economic necessity of developing more competitive separation methods. The investigation of carbon dioxide control is perhaps an exception, since it has been aimed towards a reduction in the weight and size of separation equipment used in aerospace missions.

In order to determine the potential usefulness of a gas permeation process, whether in terms of process economics or hardware requirements, it is important to determine the membrane area and the number of stages that are necessary to perform the desired separation. The membrane area requirements are of particular interest from an economic point of view because they determine a large fraction of the investment costs of a large permeation plant. Studies indicate that these costs may constitute as much as 95% of the total costs of a gas permeation process (1, 2).

Sulfur oxides are the most common air pollutants, and result mainly from processes burning high sulfur coal (power generation) and some metallurgical operations such as roasting, smelting and refining of

copper and lead ores. An economic way of separating these oxides from gaseous mixtures is not available yet. The alternative of discontinuing the operations that generate these pollutants seems highly unlikely in view of the limited reserves of other traditional sources of energy and raw materials, and the still distant future of some other non-conventional forms of energy.

It is then necessary to search for improved methods of separation of these oxides, and especially of sulfur dioxide, from the most common mixture of gases, that will probably include nitrogen, oxygen, carbon dioxide, carbon monoxide and probably some hydrocarbons and hydrogen. In an attempt to contribute to the realization of these ultimate goals, this work was undertaken with the following specific objectives in mind:

- (1) To design and construct an improved permeation apparatus suitable for the accurate determination of the permeability coefficients of a wide variety of membrane - gaseous mixtures systems, over a broad range of temperatures and pressures.
- (2) To determine a membrane composition and manufacturing technique that gives a high selectivity with respect to SO_2 .
- (3) To investigate over a wide range of temperatures and pressures, the selectivity of the improved membrane with respect to other gases that form mixtures with sulfur dioxide in industrial processes.

- (4) To determine operating conditions that give the best separation over the range of temperatures and pressures studied.
- (5) To investigate the possibility of performing other gas separations that are of practical interest, by using the membranes developed.

REVIEW OF THE LITERATURE

The best results in the separation of acid gases have been obtained using modified polymeric membranes. Among these:

A. LIQUID MEMBRANES

One of the most successful separations of sulfur dioxide from mixtures containing mainly nitrogen, oxygen and carbon dioxide, has been achieved by means of the so called "liquid membranes". The use of these membranes for gas separations has been disclosed in U. S. Patent No. 3,335,545 Robb et al.(3). Basically the process consists of including a highly selective solvent in the membrane, resulting in a considerable increase in the degree of separation of certain gases. Immobilization or support of the solvent in the membrane can be accomplished in different ways. The liquid can be supported in a non-interacting polymer in such a way to insure that the solvent is the controlling factor. Also, a thin film of the solvent can be supported by a porous, unmet backing having such small holes that the liquid cannot flow through it.

A subsequent improvement over the Robb et al. immobilized liquid membrane was that of Ward et al. U. S. Patent 3,396,510 (4), embodying the phenomenon described as "facilitated transport", applied to the transfer of carbon dioxide, sulfur dioxide and oxygen across liquid membranes. In the case of sulfur dioxide, a large concentration difference of ions HSO_3^- and $\text{SO}_3^{=}$ was used in the immobilized liquid

film. These ions are termed "carrier species" and must be non-volatile and reversible chemically reactive with the gaseous component, the transport of which is being facilitated.

The next step was to look for better solvents for given separations. The U. S. Patent 3,506,186, Ward (5), was issued in the preparation of liquid membranes for sulfur dioxide extraction. Advantage is taken of the high solubility of SO_2 in tetraethylene glycol-dimethyl ether (TEG-DME). The separation is accomplished using a liquid film of this solvent. A suitable film construction employs a thin porous cellulose layer impregnated with the solvent. First a porous membrane of modified cellulose derivation is prepared, hydrolyzed to cellulose, the hydrolyzing agent is leached out and the newly formed cellulose film is impregnated with the liquid glycol.

Preliminary permeability measurements of the immobilized film of TEG-DME have indicated permeability coefficients of about $10,000 \times 10^{-9}$ cc(STP). cm/sq cm.sec.cm Hg for SO_2 , 3.2×10^{-9} cc(STP). cm/sq cm.sec.cm Hg for N_2 and $105. \times 10^{-9}$ cc(STP).cm/sq cm.sec.cmHg for CO_2 at 25°C . The ratio of permeability coefficients is of about 3100 for the SO_2/N_2 system and of about 95 for the SO_2/CO_2 system. Thus, this membrane is highly selective for SO_2 and has the advantage of being essentially non volatile at room temperature, and with the potential use of glycols of higher molecular weight for higher temperature separations. Ward (5), claims that a permeate of more than 95% SO_2 could be obtained

out of a 10% feed gas, provided the downstream of the liquid membrane be subjected to vacuum or to sweep gas.

B. MODIFIED NON-LIQUID POLYMERIC MEMBRANES

Seibel and McCandless (6) used vinylidene fluoride membranes modified with sulfolane (tetrahydrothiophene 1, 1-dioxide) to separate SO_2 from SO_2/N_2 mixtures. These membranes were made by dissolving vinylidene fluoride and sulfolane in dimethyl formamide. The films were cast on glass plates between thicknesses of masking tape. The solvent was evaporated placing the plates in an electrically heated oven. The membrane was found to be quite selective to SO_2 . Maximum separation was achieved with 8% sulfolane in the membrane at 400 psi. The selectivity decreased with increasing temperature. Permeation rate increased with increasing pressure and with increasing amount of sulfolane in the membrane. The greatest separation achieved was with a feed of 12.5% SO_2 at 400 psi and 23°C . The permeate at these conditions was 93.5% SO_2 and the flux, $1.86 \text{ ft}^3(\text{STP})/\text{ft}^2 \text{ day}$.

Tajar and Miller (7) studied the permeation of CO_2 , O_2 and N_2 through a four component membrane system, polyethylenimine-polyvinylbutyral-epoxy-water, using a variable pressure technique. To make the membrane the ingredients were dissolved in a compatible mixed solvent system. The films were cast on glass plates, dried in oven and removed from the casting surface by soaking in water. The membrane was found

to be quite selective to CO_2 over O_2 and N_2 . The permeability coefficient ratios were of the order of 30:1 or greater, compared to typical ratios for inert membrane systems of the order of 4:1 or 5:1.

In general for all the systems reviewed, it appears that the high selectivity with respect to acid gases is a result of reversible chemical reactions that increase greatly the solubility of these gases in the active ingredient of the membrane (7, 5).

THEORETICAL BACKGROUND

A. THE NATURE OF THE TRANSPORT PROCESS

The permeation of a gaseous mixture through a solid polymeric material includes three different transport stages:

- (1) Transport from the gas mixture to the surface of the membrane.
- (2) Transport through the membrane.
- (3) Transport from the membrane to the stream of permeate.

B. TRANSPORT THROUGH A GASEOUS FILM

The steady state transport of gas A from the bulk stream in the high pressure side of the cell to the surface of the membrane may be treated as the sum of a diffusional contribution and a bulk flow contribution:

$$N_A = c D_{AB} \frac{dx_A}{dz} + x_A (N_A + N_B) \quad \text{III-1}$$

The diffusional contribution is proportional to the concentration gradient at the interface, therefore should be roughly proportional to some characteristic composition difference Δx_A between the surface of the membrane and the main stream. The bulk flow contribution on the other hand, is independent of any concentration difference (8). It seems adequate to define a local high mass transfer coefficient

$k_{x,loc}^*$ in terms of the diffusion of species A normal to the interface:

$$J_{A_z}^* \Big|_{z=0} = k_{x,loc}^* \Delta x_A$$

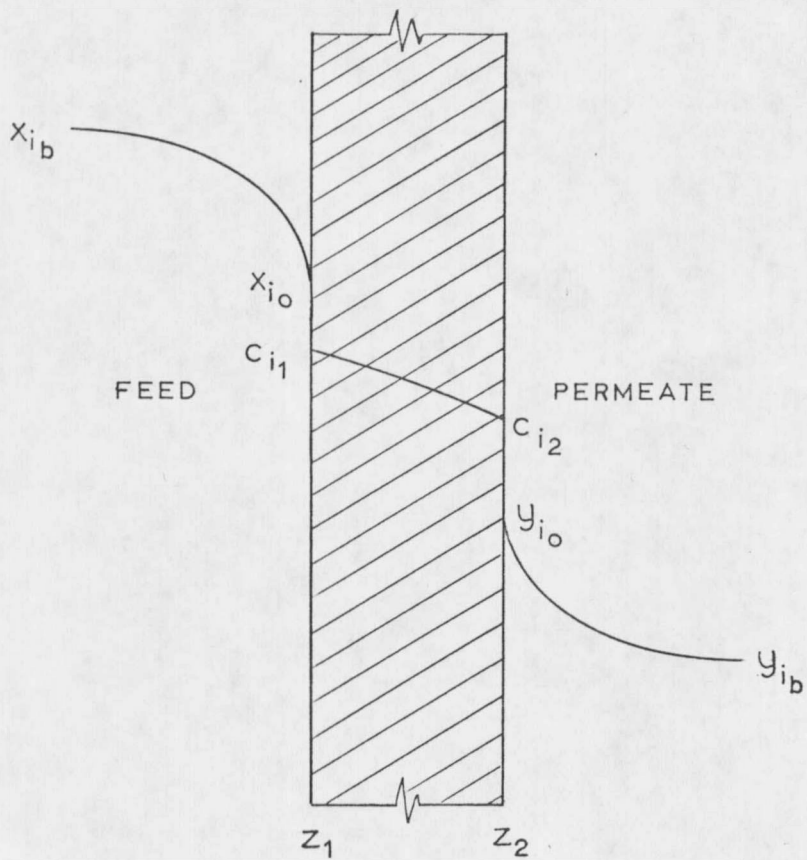


FIGURE III-1. CONCENTRATION PROFILES OF i IN THE MEMBRANE AND ITS NEIGHBORHOOD

Or in terms of the rate of diffusion of species A normal to the interface:

$$N_{A_o} - x_{A_o} (N_{A_o} + N_{B_o}) = k_{x,loc}^* \Delta x_A \quad \text{III-2}$$

The coefficient $k_{x,loc}^*$ is a function also of the rate of mass transfer. This effect arises from the distortion of the velocity and concentration profiles by the flow of A and B through the interface (9). For the case of small mass-transfer rates N_{A_o} and N_{B_o} , these effects may be neglected. Thus, a local mass transfer coefficient for this limiting condition is defined by:

$$\lim_{\substack{N_{A_o} \rightarrow 0 \\ N_{B_o} \rightarrow 0}} \frac{N_{A_o} - x_{A_o} (N_{A_o} + N_{B_o})}{\Delta x_A} = k_{x,loc}^* \quad \text{III-3}$$

It has been shown that this coefficient can be used for moderate mass transfer rates instead of $k_{x,loc}^*$ (9). For a finite surface A, III-2 can be rewritten:

$$W_A - x_A (W_A + W_B) = k_x^* A \Delta x_A$$

or for small mass transfer rates,

$$W_A - x_A (W_A + W_B) = k_x A \Delta x_A \quad \text{III-4}$$

where, $\Delta x_A = (x_{A_o} - x_{A_b})$

For the case of slow mass transfer in a closed conduit, with known composition, it is convenient to employ a local one phase mass transfer coefficient:

$$dW_A = k_{x,loc} (x_{Ab} - x_{A_o}) + x_{A_o} (dW_A + dW_B) \quad \text{III-5}$$

or

$$N_{A_o} = k_{x,loc} (x_{Ab} - x_{A_o}) + x_{A_o} (N_{A_o} + N_{B_o}) \quad \text{III-6}$$

Defining $r = N_{B_o} / N_{A_o}$, equation III-6 can be rewritten:

$$N_{A_o} = \frac{k_{x,loc} (x_{Ab} - x_{A_o})}{1 - x_{A_o} (1 + r)} \quad \text{III-7}$$

A similar expression can be derived for the gaseous film resistance associated with the permeate, based on the local mass transfer coefficient $k_{y,loc}$:

$$N_{A_o} = \frac{k_{y,loc} (y_{A_o} - y_{Ab})}{1 - y_{A_o} (1 + r)} \quad \text{III-8}$$

C. TRANSPORT THROUGH A POLYMERIC MEMBRANE

The passage of gas through a polymeric non porous membrane is usually considered to involve three independent physical phenomena: (13)

- (1) Solution or sorption of the gas or vapor at one side of the membrane.

- (2) Diffusion of the dissolved gas through the membrane.
- (3) Re-evaporation or desorption.

The gases are transported through the polymeric nonporous membrane by means of activated diffusion, that is a process that exhibits a large positive activation energy and is quite specific, depending on the solubility of the penetrant in the membrane, as well as the ease of mobility of the penetrant molecule inside the polymer matrix. At any given instant, a penetrant molecule can be visualized as occupying a vacant site existing between adjacent polymer chains. In amorphous polymers above their glass transition temperature, such vacant sites are constantly created and eliminated as a result of the segmental motion of the polymer chains. A penetrant may thus proceed, under the influence of a concentration gradient and the cooperative motion of the chains, from one position to another, thus achieving a finite jump in the direction imposed by the concentration gradient. The overall travel of the particle consists then of a series of steps or diffusional jumps. Thus, the energy of activation for diffusion can be associated with the energy required for vacant site formation against the cohesive forces interacting among the chains, in addition to the energy required to force the diffusing molecule through the surrounding chain network.

The motion of the penetrant molecule inside the polymer matrix is strongly affected by the way in which the molecule is held inside the solid and by the molecular environment in which diffusion takes

place. These two factors are associated with the solubility of the penetrating substance in the polymer.

The solubility of a penetrant in a polymeric material can be ascribed to the tendency of the penetrant to distribute itself between two phases. Due to interactions between the penetrant and the polymer, some mixing of the polymer and the penetrant phases will normally occur, with a subsequent increase in the entropy of the system (10). The solutions of penetrants by a solid polymer is referred as "sorption" in the permeation literature, to include both, absorption and adsorption mechanisms. Adsorption includes only the surfaces of the solid, both external and internal. The internal surface would include not only regions comprising pores and pinholes, but also regions on groups of molecules, or even single macromolecules. The total internal surface available for adsorption for a penetrant with a given molecular size and shape would then depend upon the configuration of the macromolecules to form sites of the proper magnitude and shape. The adsorption of a penetrant into these sites is further characterized by the magnitude of the forces interacting between the penetrant and substrate. If these forces are weak and non specific, such as van der Waals forces the process is defined as "physical adsorption". On the contrary, if the forces of interaction are strong and specific, the process may exhibit heats of sorption comparable to those of chemical bond formation and is referred as "chemisorption". The penetrant is

attached firmly to the site and is not readily removable on desorption, leading to hysteresis effects.

Absorption, on the other hand, occurs when the penetrant-polymer system forms a random mixture, similar to an actual solution. This random mixture may be evenly distributed throughout the solid phase, or may exist only in the amorphous regions of a semi-crystalline polymer (11).

Addition of plasticizers or modifiers to a polymer increases the diffusivity of a given gas or vapor. This increase is attributed to the increase in polymer segmental mobility as a result of lower cohesive forces between chains (12). The solubility may also be greatly increased by the addition of modifiers. This increase is sometimes attributed to reversible chemical reactions taking place between the modifier and the penetrant (7, 5). The combined effect is a marked increase in the permeation rate.

The presence of crystalline regions in a semi-crystalline polymer has a strong negative effect on the rate of diffusion of penetrants through the polymer. The principal effects are: a reduction in the available volume for diffusion; the tortuosity involved in by-passing crystallites; the decrease in the mobility of amorphous chain segments as a result of the presence of crystalline regions which may act as crosslinks.

The permeation process is generally slow. Thus, the use of an

equilibrium relationship between the concentrations of sorbed gas and the partial pressures at the interfaces appears to be justified.

Henry's law can then be assumed to apply,

$$c_A = m p_A \quad \text{III-9}$$

The diffusion process is described by Fick's law:

$$N_A = -D_A \frac{d c_A}{d z} \quad \text{III-10}$$

If an average value of the diffusivity D_A is considered, equation III-10 can be integrated subject to the following boundary conditions:

$$\begin{aligned} z = z_1 & \quad c_A = c_{A1} \\ z = z_2 & \quad c_A = c_{A2} \end{aligned} \quad \text{III-11}$$

to give,

$$N_A = \frac{D_A}{\Delta z} (c_{A1} - c_{A2}) \quad \text{III-12}$$

From equation III-9 and III-12:

$$N_A = \frac{D_A}{\Delta z} (m_1 (p_{A1})_o - m_2 (p_{A2})_o) \quad \text{III-13}$$

If the Henry's law constant is assumed to be a function only of temperature and both membrane surfaces are at the same temperature, then

$$m_1 = m_2 = m$$

and:

$$N_A = \frac{D_A m}{\Delta z} [(p_{A_1})_o - (p_{A_2})_o] \quad \text{III-14}$$

The permeability coefficient P is defined as

$$P_A = D_A m = \frac{N_A \Delta z}{(p_{A_1})_o - (p_{A_2})_o} \quad \text{III-15}$$

$$\text{But } (p_{A_1})_o = P_1 x_{A_o} \quad (p_{A_2})_o = P_2 y_{A_o} \quad \text{III-16}$$

From III-14 and III-16,

$$N_A = \frac{D_A m}{\Delta z} (P_1 x_{A_o} - P_2 y_{A_o}) \quad \text{III-17}$$

D. DEFINITION OF THE OVERALL MASS TRANSFER COEFFICIENT

At steady state the molar fluxes defined by equations III-7, III-8 and III-14 have to be the same. Thus:

$$N_A = \frac{k_{x,loc} (x_{A_b} - x_{A_o})}{1 - x_{A_o} (1 + r)} = \frac{k_{y,loc} (y_{A_o} - y_{A_b})}{1 - y_{A_o} (1 + \bar{r})} = \frac{D_A m}{\Delta z} (P_1 x_{A_o} - P_2 y_{A_o}) \quad \text{III-18}$$

That can be expressed as;

$$N_A = K [(p_{A_1})_b - (p_{A_2})_b] \quad \text{III-19}$$

