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An Apparatus for the Measurement of Gas Fluxes through Immobilized Liquid Membranes

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Abstract

An automated apparatus to measure gas fluxes through immobilized liquid membranes is described. Specific design features permit safe operation for experimentation with CO, NO, and H_2S. Nitric oxide fluxes through immobilized Fe(II) *solutions have been measured and are presented as a typical equipment application.* Facilitation factors (ratio of total flux to flux without carrier) greater than 5 were observed.

INTRODUCTION

Membrane separation is an area deserving special attention because of its great potential for low capital cost and high energy efficiency relative to distillation or other conventional processes where a change of phase is involved. To date, however, few membrane processes other than desalination and hydrogen recovery have been shown to be industrially feasible, primarily due to problems of speed and selectivity in separation. The diffusion coefficient of most molecules in polymers is so low that exceedingly thin membranes must be constructed to produce industrially acceptable fluxes. These thin polymer membranes often have fabrication and mechanical integrity problems. Selectivity has usually been poor in membrane systems unless the mixture components are radically different, as in desalination.

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The selectivity problems of polymeric membranes can be overcome in a process known as facilitated transport, in which a mobile, nonvolatile carrier is incorporated within a liquid membrane. The carrier reacts reversibly with the transported species to greatly increase the selectivity (ratio of permeabilities) for the component of interest; in the case of CO_2 over O_2 the selectivity is enhanced by as much as a factor of 10^3 (*1*). Studies show potential cost savings of 30–50% over common acid gas scrubbing for CO_2 and possible energy savings up to a factor of 3 (*2*) by using facilitated transport. Increased selectivity by a factor of 2.5 and reduced utilities requirements are advantages of membrane separation of H_2S from gasified coal over traditional hot carbonate scrubbing of H_2S (*3*).

A possible configuration for an industrial-scale acid gas scrubber is a bundle of porous, hollow fibers impregnated with a liquid containing a carrier species such as potassium carbonate or cesium carbonate. Here, the liquid film is the membrane material. The carrier species in the liquid reacts with the acid gases forming a complex which diffuses to the low-pressure side of the membrane. There the reaction is reversed and the acid gases desorb and are swept away. The facilitated transport membrane can be viewed as an absorber on the high-pressure side and an absorbent regenerator on the low-pressure side. Thus, the membrane system is analogous to a conventional scrubbing system, but requires only a single vessel.

Separation is the key area of work for the chemical process industry, because separation processes may consume 30 to 80% of the capital costs of gas processing and approximately 50% of the energy (*4*). Thus, novel separation techniques, such as liquid membranes, could substantially reduce the high cost of separation processes in the CPI.

BACKGROUND

For separating or purifying gases, it is advantageous to immobilize the liquid membrane by impregnating a porous, inert substrate with the solvent containing the facilitating carriers. Maintaining the integrity of the immobilized liquid membrane is a serious experimental difficulty. The liquid membrane is held in the pore structure solely by capillary forces and must be kept within the pore structure. Another experimental difficulty for gas separations with immobilized liquid membranes occurs if the solvent has an appreciable vapor pressure. A supported aqueous liquid membrane can quickly dry out if the humidity of the gas streams in contact with the membrane is not carefully controlled.

Several experimental methods of supporting liquid membranes have been reported in the literature. Ward and Robb (*1*) impregnated a porous cellulose acetate film with a Cs_2CO_3 solution, and then held the saturated film between two semipermeable silicone rubber membranes. The silicone membranes did not contribute to the mass transfer resistance. To increase the available surface area, porous hollow fibers have been used as supports (*5, 6*). This method of supporting liquid membranes has great promise for industrial application.

The most common mass transfer measurement made in liquid membrane research is flux. Several techniques have been reported for flux measurement. Ward (*7*) measured the flux of nitric oxide through a solution of $FeCl_2$ in formamide. The solution was immobilized between two silicone rubber membranes in a vacuum chamber. Nitric oxide was admitted to one side of the liquid membrane chamber while the other side was maintained at a vacuum. The nitric oxide pressure was measured as a function of time and the flux was computed from the measurements. Matson et al. (*3*) employed a flow cell to measure gas fluxes through immobilized liquid membranes. Permeant gas flowed across the membrane on the feed side while an inert gas flowed across the sweep side. Concentration of the permeant gas was determined by gas chromatography, and the molar flux was then calculated by a material balance.

An apparatus to make flux measurements using the flow-cell technique is described in this paper. This technique was chosen because it simulates proposed industrial liquid membrane permeators. The apparatus will permit cocurrent or countercurrent flow across the liquid membrane, and the flow system is not restricted to a planar membrane geometry. The design of the liquid membrane cell has been improved over that reported by Matson et al. (*3*).

APPARATUS

Design of the apparatus was shaped by considering safety, ease of operation, and automation. Laboratory safety was of maximum importance, followed by the desire for simple operation and automated experimentation. Automation is critical when designing an apparatus to be used in a long-range experimental program over extended periods of time.

Toxicity of the gases used dictated a completely enclosed system. Enclosure pressure was maintained below ambient using an exhaust fan; thus any system leakage could not escape to the laboratory and was exhausted outside. In addition, continuous monitoring of the toxic gas concentration took place both within and external to the enclosure. Solenoid valves were controlled by the toxic gas monitors to stop the gas flow if the concentration exceeded a preset threshold (15 ppm for NO). Figure 1 illustrates the

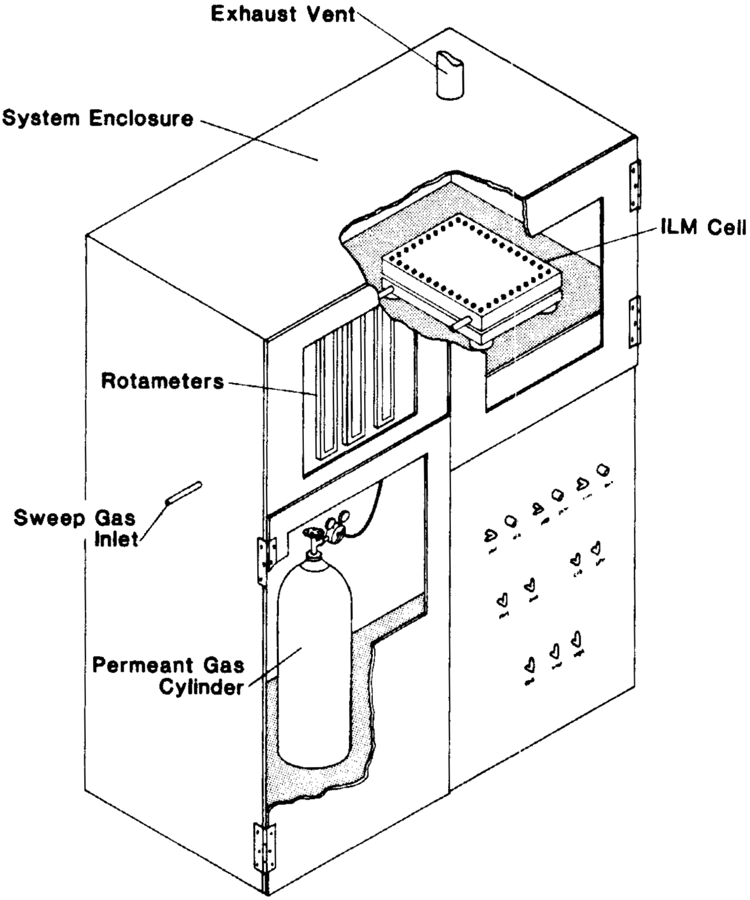

FIG. 1. Experimental system. Location of gas cylinder, control panel, and ILM cell is illustrated. Enclosure pressure is reduced by connecting the vent to an exhaust fan.

important external features of the system and shows positioning of the gas cylinders and membrane permeation cell. All flow switching valves were mounted on a single front panel and were grouped to permit easy recognition of function. Valves were of the stainless steel ball type; two-way valves were used for shut off and three-way valves allowed simple bypass plumbing. All valves were clearly marked as to function and proper position for operation.

Flow control was achieved using all stainless steel electronic mass flow controllers and mass flowmeters. Backup was provided with rotameters and needle valves to allow manual control of the gas flow. The flow metering valves were mounted on the front panel with the switching valves.

All permanent gas connections were made with stainless steel fittings using one piece stainless steel ferrules. Tubing was either stainless steel or thick-walled fluorinated polymer. Cell connections were made with stainless steel, zero-clearance, O-ring fittings on polymer tubing. Conventional practice of hard plumbing with stainless steel tubing requires replacement of components whenever a design change is made. Use of polymer tubing for cell connections allowed ease of cell installation and removal as well as providing valuable flexibility to permit changes in cell configuration without replumbing. Stainless steel ferrules were used with good results on the polymer tubing.

Figure 2 is a schematic diagram of the flow system. The permeant gas passes through a shut-off valve, fine metering valve, rotameter, and an electronic flow controller before mixing with the diluent gas stream. The permeant gas may be diluted with helium to obtain mole fractions of the permeant gas between 0 and 1. Helium diluent gas follows a path analogous to that of the permeant gas to reach the mixing point, and the mixture then flows to the feed side of the membrane. Helium is directed to the sweep side of the membrane, and both feed and sweep exit streams are sent to a gas chromatograph. The gas streams are alternately sampled with an automatic sampling 10-port valve on the chromatograph. A preset program in the chromatograph firmware controlled operation of the valve.

Output from the chromatograph was set to a time-programmable integrator where the permeant gas peaks were integrated. The chromatograph utilized a thermal conductivity detector (TCD) and was capable of determining permeant gas mole fractions as low as 10^{-4}. Integrated peak values were sent directly to a microcomputer where analysis programs computed mass balances as required. Data from an experiment were stored on magnetic disks by the computer.

The central part of the gas flow system is the immobilized liquid membrane (ILM) cell. Figure 3 shows an exploded view of the cell. The

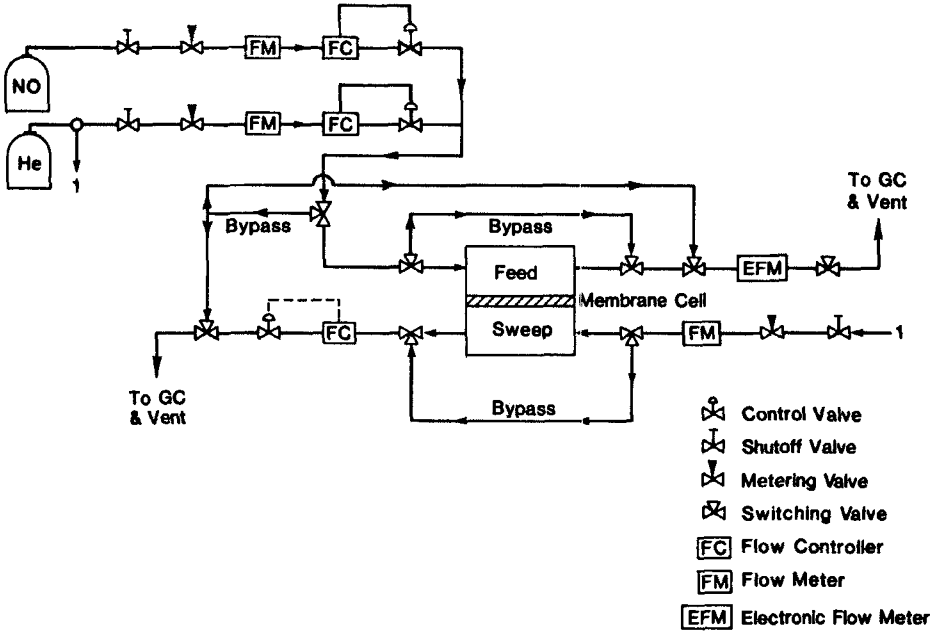

FIG. 2. Flow system schematic indicating the membrane cell, flow controllers, flow meters, and associated valves.

purpose of the cell was to hold a liquid-impregnated membrane in place and allow gas streams to contact it on both sides. Screens were placed in the header areas to support the membrane and provide some turbulence to minimize concentration boundary layers at the liquid membrane/gas interfaces. An O-ring was provided between the spacer plates to prevent leaks in the axial direction. The cell housing was fabricated of clear acrylic for experiments at pressures of 100–500 kPa and ambient temperature. A stainless steel cell was used for higher pressures and elevated temperature experiments. Overall cell dimensions are 17.8 cm × 22.9 cm with 198 cm^2 of exposed membrane area.

Humidifiers were constructed and placed upstream of the cell in both feed and sweep streams when membrane drying was a problem. For the nitric oxide experiments described below, a low vapor pressure solvent was used and humidification was not required.

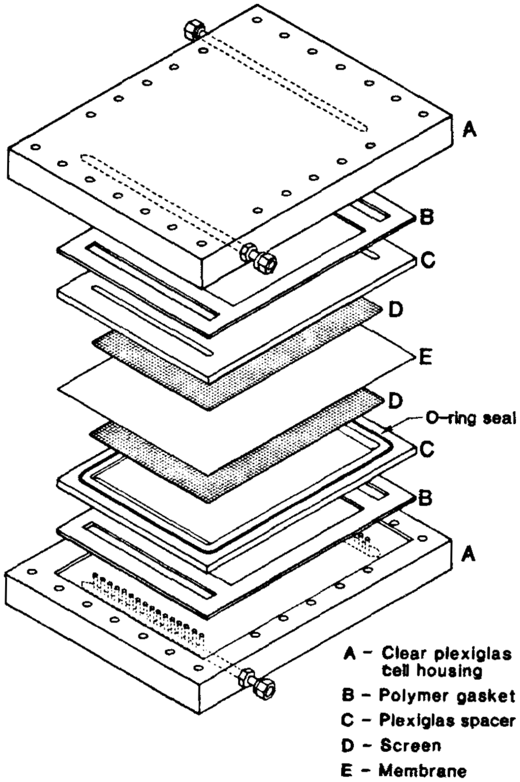

FIG. 3. ILM cell. Fittings are zero-clearance O-ring type for good sealing and ease of cell removal. O-ring seal around membrane prevents leaks in axial direction and eliminates bypass of the membrane.

PROCEDURE

Solutions of $FeCl_2$ in fresh, vacuum-distilled formamide were prepared under a nitrogen blanket to prevent oxidation of Fe(II). The supporting substrate was saturated with the solution under vacuum in order to fill the pore structure. The liquid-impregnated substrate was placed in the cell which was then assembled and installed in the apparatus. The cell was purged and the experiment begun.

Flux measurements consisted of sampling the feed and sweep gas streams leaving the membrane cell and measuring the permeant gas concentrations by gas chromatography. Chromatograph peaks were integrated with a time-programmable integrator. A computer received the integrated peak values and material balances were calculated using analysis programs. Experimental data were stored on magnetic disks. Output of flux versus time was available on a hard-copy plotter.

REAGENTS AND MATERIALS

Formamide was a reagent-grade product further purified by vacuum distillation. Reagent grade $FeCl_2$ was dissolved in formamide to provide the Fe(II) carrier. Helium carrier gas (UHP grade, 99.999%) was purified by passage through an oxygen getter. Nitric oxide (CP grade, 99.9%) was used without further purification. Microporous polypropylene, microporous track-etched polycarbonate, and macroporous cellulosic membranes were used as supporting substrates of the liquid membrane. The microporous polypropylene was treated with a surfactant to be wet by formamide. Use of the macroporous cellulosic filter paper allowed variations in membrane thickness. Track-etched membranes were used because they had uniform, cylindrical pores. Table 1 compares the various properties of the substrate materials.

RESULTS

Flux data were taken for NO permeation through various substrates impregnated with formamide containing no carrier species. If there is no hindered diffusion effect, then the steady-state diffusive flux of NO through a supported liquid membrane is given by

TABLE 1
Membrane Characteristics

Substrate material	Thickness (cm)	Mean pore size (μm)	Porosity	Tortuosity[a]
Polypropylene	2.5×10^{-3}	0.04	0.45	2.0
Cellulosic	1.8×10^{-2}	N/A	0.65	1.5
Polycarbonate	9.5×10^{-4}	0.40	0.126	1.0

[a] Tortuosity is a correction to the physical thickness to account for nonuniform pore geometry.

$$N_{NO} = D_{NO} \frac{\Delta C_{NO}}{\Delta L} \frac{P}{\tau} \tag{1}$$

where N_{NO} is the steady-state flux of nitric oxide (mol/cm^2·s) based on the bulk membrane area, D_{NO} is the diffusivity of nitric oxide (cm^2/s) in the solvent, ΔC_{NO} is the liquid phase concentration difference of NO (mol/cm^3), ΔL is the membrane thickness (cm), P is the porosity of the substrate, and τ is the tortuosity of the substrate. D_{NO} is taken to be independent of concentration and τ corrects for the tortuous path length.

Experiments were performed with feed and sweep streams passing countercurrently on either side of the membrane. In addition, the sweep gas flow rate was set such that the sweep side gas-phase concentration of permeant gas was much less than that on the feed side. Thus, the concentration on the sweep side in the liquid phase could be taken as zero without introducing significant error. This condition was not necessary but simplified data analysis.

We computed N_{NO} from chromatographic data and calculated ΔC_{NO} using Henry's law assuming $C_{NO} = 0$ on the sweep side. The Henry's law constant was 2.98×10^{-8} mol/cm^3·kPa and was determined independently from solubility measurements of NO in formamide.

The diffusion coefficient of NO in formamide-impregnated polymer substrates was found to be 5.76×10^{-6} and 6.79×10^{-6} cm^2/s for the polypropylene and polycarbonate substrates, respectively. These results are in excellent agreement given that the polypropylene material has pore sizes an order of magnitude smaller than the polycarbonate material (4×10^{-6} vs 4×10^{-5} cm). The agreement indicates that a hindered diffusion effect is not present for these systems and that Fick's law may be applied.

Equation (1) is also useful to determine substrate properties. Using Eq. (1) and an independent measurement of the porosity, we characterized the tortuosity of the filter paper substrate as 1.50. Thus, the effective path length for diffusion in this material is 1.5 times the film thickness. This value may be compared to a tortuosity of 2 for the polypropylene substrate and 1 for the track-etched polycarbonate material.

Experiments were conducted to measure the facilitated flux of NO when the liquid membrane contained a carrier species. Variations in thickness, carrier concentration, and permeant gas partial pressure were studied. Figure 4 shows transient flux data for permeation of NO through liquid-impregnated polypropylene at various carrier concentrations. Facilitation factors (the ratio of facilitated flux to diffusive flux) of up to 5.4 were observed. Thus, a flux 5.4 times the purely diffusive flux was obtained at a carrier concentration of 3.0×10^{-4} mol/cm^3.

Figure 5 shows facilitation versus feed side partial pressure of NO. It is interesting that facilitation increases as the permeant gas becomes more dilute. This trend indicates that the selectivity of such a membrane would improve for dilute feedstocks over enriched feedstocks.

CONCLUSIONS

The design and operation of an automated apparatus for measurement of gas permeation rates through immobilized liquid membranes was described. The diffusion coefficient of NO in formamide was determined and the nitric oxide flux through immobilized liquid membranes containing an Fe(II) ion carrier was measured. The diffusion coefficient of NO in formamide at 25°C was calculated to be 6.27×10^{-6} cm^2/s. Facilitation factors (ratio of total flux to diffusive flux) of up to 5.4 were observed.

Several experimental techniques for flux measurement were presented. The flow cell technique was chosen as the best suited to obtain data necessary for application to industrial practice.

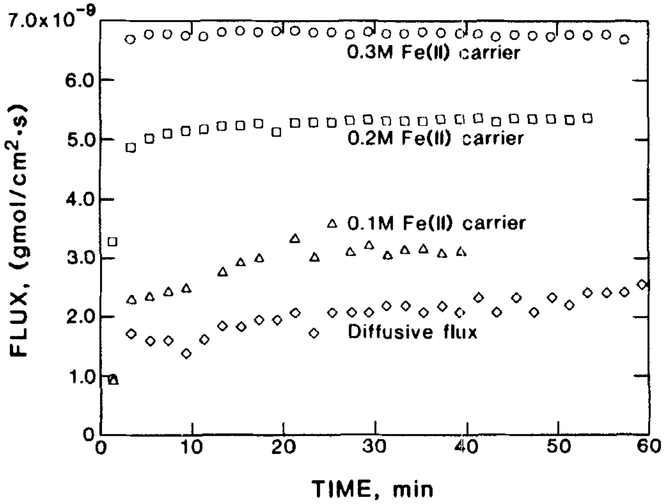

FIG. 4. Flux of nitric oxide vs time for impregnated polypropylene substrates where the liquid phase contained varying concentrations of the Fe(II) carrier.

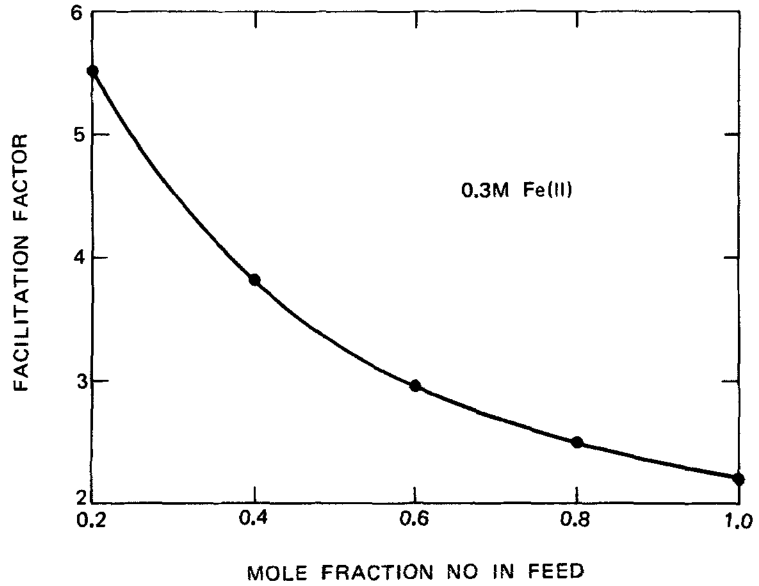

FIG. 5. Observed facilitation factor vs mole fraction nitric oxide in feed. Substrate was filter paper; mole fraction was varied by dilution with He.

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