

## Transfer of Gas to Dissolved Oxygen in Water Via Porous and Nonporous Polymer Membranes

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### Synopsis

The transfer rates of oxygen via polymer membranes in gas-membrane-gas and gas-membrane-water (dissolved oxygen) were investigated with various porous membranes and compared with results of silicone rubber sheet (nonporous, homogeneous polymer membrane). With a nonporous membrane, the permeability constant obtained by gas-membrane-gas represents the true membrane permeability in gas-membrane-water system, and consequently the transport resistance due to boundary layer can be quantitatively estimated. With a porous membrane, the data in gas-membrane-gas system (under applied pressure) merely represent the gas effusion rate of the membrane and are not directly related to the dissolved oxygen transfer rate in gas-membrane-water system. The penetration of liquid water into the pores of porous membrane is the most important controlling factor for the dissolved oxygen transfer rate of a porous membrane. With a porous membrane in which liquid water does not penetrate into the pore, the overall transfer rate of dissolved oxygen reaches the level which corresponds to that of the boundary layer found with silicone rubber membrane.

### INTRODUCTION

Permeabilities of polymer membranes to various gases have been quite extensively studied in past years; however, most evaluations are based on the ideal situation in which both sides of test films are in contact with gas (of different total or partial pressure). Transport of gases through a nonporous polymer membrane proceeds by (1) sorption of gas into polymer at the high pressure side, (2) diffusion of dissolved gas through the film, and (3) desorption of gas at the low pressure side. In these processes, the nearly ideal rapid equilibration is established at the surfaces, and the effect of the boundary layer is negligible.

When a membrane is used in contact with liquid rather than gas on either side, the effect of the boundary layer becomes significant and the actual transport rate of gas through a membrane becomes considerably lower than the value calculated from the permeability constant of the polymer (obtained by the gas-membrane-gas experiment). The transport resistance due to the boundary layer may be a function of many factors such as shape of the interface, wettability of the surface to the liquid, velocity of the liquid at the interface, and so forth. Since the true membrane permeability can be obtained from gas-membrane-gas experiment,<sup>1</sup> the

experiments of gas transfer which involve gas-membrane-liquid and liquid-membrane-liquid provide excellent model cases to investigate the nature of boundary resistance.

Hwang, Tang, and Kammermeyer<sup>2</sup> have studied the transport of dissolved oxygen through silicone rubber membrane to investigate the boundary layer resistance and showed that over 50% of the total membrane resistance of a thin silicone rubber membrane used in water-membrane-water is due to the boundary resistance.

The ideal situation found with gas-membrane-gas experiment to obtain true membrane permeability constant does not apply to porous membranes in which gas transport is characterized by viscous flow or Knudsen flow. In porous membranes, the transport of gas in a gas-membrane-gas system is essentially effusion of gas through small holes, and the permeability coefficients obtained under the conditions are significantly different in many respects from those of nonporous polymer membranes<sup>3</sup> and do not represent the true membrane permeability constants when they are used in other conditions such as gas-membrane-liquid.

Let us consider the oxygen transfer rate of gas-membrane-water system, since this particular combination provides the case of some important applications of polymer membranes such as membrane oxygenators of heart-lung machines and other gas saturation devices.

In nonporous membranes, the transport of oxygen through a membrane proceeds in an ideal manner up to the interface of membrane-water, and nonideal situation occurs only at the downstream side of the membrane. In this case, however, the boundary layer resistance can be accurately estimated from a single measurement since the true membrane permeability can be obtained by gas-membrane-gas system.

In a porous membrane, in principle, the gas phase penetrates through the membrane and contacts with water somewhere within the bulk phase of the membrane. Therefore, how far the liquid water penetrates into the membrane is the most important factor in the overall transport property of a porous membrane. Since liquid water that has penetrated into the pores of the membrane is hardly affected by stirring of the bulk water, it will provide the worst boundary layer resistance, and oxygen transfer rates could drop in orders of magnitude from the effusion rate (gas-membrane-gas) unless the membrane is used as a bubbling device under excessive gas pressure. These situations were examined in the following experiments.

## EXPERIMENTAL

The gas transfer constant, of nonporous polymer membranes and the effusion rates of porous membranes were measured by the conventional vacuum-type apparatus described previously.<sup>4</sup>

The transfer rate of dissolved oxygen was measured by using a polarographic oxygen sensor (Fieldlab Oxygen Analyzer, Beckman). For this pur-

pose, an Amicon ultrafiltration cell Model 50 was modified so that the effluent side of the cell could be maintained in oxygen stream (at 1 atm pressure) and gas could be bubbled into the water above the membrane. The oxygen sensor was placed in the water side using an O-ring seal, approximately 0.5 cm above the magnetic stirrer of the cell. After a membrane was positioned and the cell was tightly sealed, 35 cc of deionized water was poured into the cell through the liquid inlet of the cell, and both sides of the membrane were flushed by N<sub>2</sub> gas with moderate stirring in the water side. (The calibration of the sensor was carried out by saturating the water by flushing O<sub>2</sub> on both sides.) After the O<sub>2</sub> partial pressure in water had dropped to zero, both valves on the gas line for the water side were closed (inlet valve first to eliminate pressure build-up in the cell), and N<sub>2</sub> gas was switched to O<sub>2</sub> on the gas side. The stirring rate was kept as the maximum which did not suck gas into the water. The increase in O<sub>2</sub> partial pressure was recorded as a function of time. It was found that the partial pressure increase in the gas phase above the water was much delayed, despite the stirring of the water, and did not affect the initial stage of O<sub>2</sub> increase in water in cases of the highly permeable membranes investigated in this study. However, for the study of dissolved oxygen permeability of slow membranes, the gas phase above the water should be eliminated.

The increase in partial pressure of oxygen (read by the polarographic oxygen sensor) can be given by

$$\frac{dp}{dt} = \frac{KA}{V} (p_0 - p)$$

where  $p$  is the partial pressure of oxygen at time  $t$ ,  $p_0$  is the partial pressure of oxygen in gas phase,  $K$  is the transfer constant of overall membrane plus boundary layer,  $A$  is the membrane area, and  $V$  is the volume of water in the cell. The integration of the equation with boundary condition of  $p = 0$  at  $t = 0$  leads to

$$\ln \left( 1 - \frac{p}{p_0} \right) = -\frac{KA}{V} t.$$

Hence, the value of  $K$  can be obtained from the slope of the plot  $\log (1 - p/p_0)$  versus time.

The oxygen transfer constant  $Q$ , in cm<sup>3</sup>(S.T.P.)/cm<sup>2</sup>·sec·cm Hg, is calculated by

$$Q = K \frac{\sigma}{76}$$

where  $\sigma$  is the solubility of oxygen in water in units of cm<sup>3</sup>(S.T.P.) O<sub>2</sub> in cm<sup>3</sup> water at 76 cm Hg O<sub>2</sub> partial pressure. Experiments were carried out at room temperature (24°C) and the  $\sigma$  value<sup>5</sup> of  $2.88 \times 10^{-2}$  was used for the calculation.

As nonporous polymer membrane,  $1.5 \times 10^{-2}$ -cm-thick poly(dimethyl siloxane), Silastic sheeting by Dow Corning Corporation, was used (Table I). Porous membranes were prepared in the laboratory by either surface treatment of a porous substrate or by casting-coagulation of polymer solution. Membranes 2-5 are silicone-coated Millipore filter, pore size  $0.01 \mu$  and membranes 7-10 are silicone-coated Tyvek polyolefin paper. Uncoated Millipore Filter could not be used for this purpose, since water leaks through the filter. Tyvek as supplied has a wettable surface and does not hold water, but by treating with gas plasma the surface becomes nonwetable. Tyvek treated by  $H_2$  plasma for 4 min was used as uncoated olefin paper (membrane 6).

Surface treatment was carried out by plasma deposition of triethylsilane from the vapor phase. The deposition rate was approximately  $8 \times 10^{-3}$  mg/cm<sup>2</sup> per minute. The procedure of vapor phase deposition was described before.<sup>6</sup> The plasma deposition was carried out at  $50 \mu$  Hg vapor pressure and 100 watts discharge power. Membranes 11-13 are porous polysulfone membranes.

The sample of polysulfone was supplied by courtesy of Union Carbide (Polysulfone P-3500). The porous polysulfone membranes were prepared by using the method and recipe reported by Rozel et al.,<sup>7</sup> with minor modification in solvent composition. The coagulated membranes were dried and stored before testing.

TABLE I  
Description of Membranes

Membrane No.	Material	Thickness, cm	Remarks
1	silicone rubber	$1.5 \times 10^{-2}$	nonporous film, Silastic sheet
2	silicone-coated Millipore filter (MF)	$1.4 \times 10^{-2}$	$0.01 \mu$ MF, treatment time 0.5 min
3	silicone-coated Millipore filter	$1.4 \times 10^{-2}$	$0.01 \mu$ MF, treatment time 2 min
4	silicone-coated Millipore filter	$1.4 \times 10^{-2}$	$0.01 \mu$ MF, treatment time 5 min
5	silicone-coated Millipore filter	$1.4 \times 10^{-2}$	$0.01 \mu$ MF, treatment time 8 min
6	Tyvek	$1.4 \times 10^{-2}$	uncoated, $H_2$ plasma treated 5 min
7	silicone-coated Tyvek	$1.4 \times 10^{-2}$	treatment time 3 min
8	silicone-coated Tyvek	$1.4 \times 10^{-2}$	treatment time 4 min
9	silicone-coated Tyvek	$1.4 \times 10^{-2}$	treatment time 5 min
10	silicone-coated Tyvek	$1.4 \times 10^{-2}$	treatment time 6 min
11	polysulfone	$3.0 \times 10^{-3}$	DMF/Ethyl Cellosolve, 5 mil casting
12	polysulfone	$3.2 \times 10^{-3}$	DMF/Ethyl Cellosolve, 2.5 mil casting
13	polysulfone	$4.0 \times 10^{-3}$	DMF, 5 mil casting

## RESULTS AND DISCUSSION

For proper understanding of the oxygen transfer rates via membranes, it must be recognized that we are dealing with actual transfer rate  $Q$  in  $\text{cm}^3(\text{S.T.P.})/\text{cm}^2\cdot\text{sec}\cdot\text{cm Hg}$ , but not the permeability constant generally given by  $P$  in  $\text{cm}^3(\text{S.T.P.})\cdot\text{cm}/\text{cm}^2\cdot\text{sec}\cdot\text{cm Hg}$ . The latter has the significance of material constant for homogeneous polymer membranes; however,  $P$  cannot be used to compare oxygen transfer rates of heterogeneous and homogeneous-heterogeneous composite membranes which have different overall thickness, since the  $P$  values of such membranes are no longer material constants and the inclusion of the actual thickness of the membrane in the constant leads to numbers meaningless for this purpose.

All porous membranes examined in this study have oxygen effusion rates of roughly  $10^{-2} \text{ cm}^3(\text{S.T.P.})/\text{cm}^2\cdot\text{sec}\cdot\text{cm Hg}$ , and above. These effusion rates are higher in orders of magnitude than the permeation rate of the silicone rubber sheet (i.e.,  $3.9 \times 10^{-6}$  for membrane 1). However, these effusion rates are in no way related to the dissolved oxygen transfer rates of the porous membranes in gas-membrane-water system. Examples are shown in Table II. The dissolved oxygen transfer rates of porous membranes, which have 2,000 to 20,000-fold higher gas effusion rates than the permeation rate of the silicone rubber, all dropped to an order of magnitude similar to that of the silicone rubber. The magnitude of the decrease in oxygen transfer rates from gas-membrane-gas system to gas-membrane-water system is  $3 \times 10^{-4}$  to  $2 \times 10^{-6}$  for porous membranes compared to 0.46 for the silicone rubber. Furthermore, the dissolved oxygen transfer rates of porous membranes have no direct correlation to the effusion rates of the membrane.

The data of silicone rubber present an interesting calculation for the extent of transport resistance due to the boundary layer, since the overall transport resistance of membrane  $1/Q$  is given by the sum of membrane resistance  $1/Q_M$  and transport resistance of boundary layer  $1/Q_B$  (neglecting the boundary layer in gas-membrane interface), i.e.,

$$1/Q = 1/Q_M + 1/Q_B.$$

TABLE II  
Comparison of Oxygen Transfer Rate of Porous and Nonporous Polymer Membranes in Gas-Membrane-Gas and Gas-Membrane-Water Systems

Membrane		$Q$ , $\text{cm}^3(\text{S.T.P.})/\text{cm}^2\cdot\text{sec}\cdot\text{cm Hg}$	
		Gas-Membrane-Gas	Gas-Membrane-Water
No.	Type		
1	silicone rubber (nonporous)	$3.90 \times 10^{-6}$	$1.81 \times 10^{-6}$
5	silicone-coated Millipore filter	$2.51 \times 10^{-2}$	$1.35 \times 10^{-7}$
6	olefin paper	$7.60 \times 10^{-2}$	$1.97 \times 10^{-7}$
8	silicone-coated olefin paper	$6.46 \times 10^{-2}$	$1.95 \times 10^{-6}$
13	porous polysulfone membrane	$9.16 \times 10^{-3}$	$2.97 \times 10^{-6}$

Since  $Q_M$  is best estimated by the permeability constant measured by gas-membrane-gas experiments,<sup>1</sup>  $Q_B$  for silicone rubber-water boundary layer under the experimental conditions is estimated as  $3.3 \times 10^{-6}$  cm<sup>3</sup>(S.T.P.) / cm<sup>2</sup>·sec·cm Hg.

If such a boundary layer is independent of the nature of the surface, it will set the maximum dissolved oxygen transfer rate obtainable with any membrane, i.e.,  $1/Q_M = 0$ . This seems to be also the limiting case obtainable with an ideal porous membrane in which water and oxygen gas contact at the surface of the bulk membrane.

Results obtained with porous membranes are summarized in Table III. It is interesting to note that the highest dissolved oxygen transfer rate obtained is indeed in the vicinity of the calculated value of the transfer constant for the boundary layer observed with silicone rubber sheet. It seems to be rather unrealistic, however, to consider that the case of  $1/Q_M = 0$  is obtained, and it may be more appropriate to consider that the boundary

TABLE III  
Dissolved Oxygen Transfer Rate  $Q$  and Time to Reach Oxygen  
Concentration of Air-Saturated Water,  $\tau^a$

Membrane no.	$Q \times 10^5$ , cm <sup>3</sup> (S.T.P.) / cm <sup>2</sup> ·sec·cm Hg	$\tau$ , sec
1 S.R.	18.1	152
2 coated M.F.	0.606	4560
3 coated M.F.	0.902	3060
4 coated M.F.	1.49	1860
5 coated M.F.	1.35	2040
6 Tyvek	1.97	1400
7 coated Tyvek	13.2	208
8 coated Tyvek	19.5	142
9 coated Tyvek	14.1	196
10 coated Tyvek	15.7	176
11 Polysulfone	31.2	89
12 Polysulfone	20.0	138
13 Polysulfone	30.0	93

<sup>a</sup>With 1 atm pressure, 100% oxygen, 35 cc oxygen-free water at 24°C, membrane area 11.3 cm<sup>2</sup>.

layer resistance is dependent on the nature of the surface, including the depth of water penetration into the pores of the membranes. The data with silicone-treated porous substrates tend to show this effect. With longer treatment (with more material on the surface), the dissolved oxygen transfer rate increased. This is perhaps due to decreased depth of water penetration because of the hydrophobic surface deposition and hence decreased boundary layer.

The hydrophilicity of the substrate itself seems to play an important role. The similar deposition onto more hydrophobic polyolefin substrate gave consistently higher dissolved oxygen transfer rates than with the hydrophilic Millipore filter. Variations in the values for Tyvek membranes

may be greatly due to the variation of the substrate, since Tyvek membranes are not as uniform (in porosity, thickness, and formation) as Millipore filters.

The surface of porous polysulfone membranes is wettable by water, unlike silicone rubber and silicone-treated membranes, but water does not penetrate until relatively high hydraulic pressure is applied (approximately 20 psi). These two factors seem to favorably contribute to the very high dissolved oxygen transfer rate of the membranes. Membrane 11 gave 1.7 times as fast a dissolved oxygen transfer rate as that of silicone rubber under the same experimental conditions, which seems to be a significant improvement, especially with consideration of the limit due to boundary layer resistance.

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