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PERMEABILITY OF POLYMER MEMBRANES TO DISSOLVED OXYGEN *Chen 1*

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INTRODUCTION

The permeation of dissolved oxygen through membranes is an important phenomenon in many biological systems. However, methods of measuring the permeability of oxygen through polymer membranes such as those which rely upon the pressure-volume relationship of the gas are not applicable to some hydrophilic polymers and biological membranes, since the membranes exist in a highly hydrated state and their morphological or topological structure depends on the degree of hydration.

The polarographic method of measuring oxygen provides a quick and accurate means of measuring the permeability of oxygen through many membranes, both in the gas phase and as dissolved oxygen. Accordingly, the oxygen permeability can be utilized as a means of estimating changes in the structure of hydrated membranes, especially hydrophilic polymer membranes and hydrated polymer gels.

Oxygen has a molecular size somewhat similar to that of water, and their diffusivities are also similar in many cases. For instance, the diffusion constant of oxygen in water at 25°C is 2.5×10^{-5} cm²/sec, and the self-diffusion constant of water is expected to be on the order of $2.3 - 2.4 \times 10^{-5}$ cm²/sec (1). Diffusion constants of oxygen and water in some polymers are also somewhat similar.(2). For this reason, the oxygen permeability may be used as a means of investigating changes in the structure of a hydrated polymer membrane and also as a tool for comparing the ease of water movement through hydrated membranes.

The measurement of oxygen permeability may have advantages over the measurement of water movement, since oxygen flow can be created without causing appreciable change in the water activity and, consequently, it is possible to maintain the conditions of the hydrated

membrane at the point of interest.

In order to compare the oxygen permeability of both hydrated and non-hydrated membranes by the same method, the polarographic method is applied for measurement of permeability both as the gas and as dissolved oxygen.

EXPERIMENT AND RESULTS

A Beckman laboratory oxygen analyzer, model 777, was used in this experiment. The sensor is sealed into a stainless steel permeation cell, which was originally designed by Amicon Inc., Cambridge, Massachusetts, by means of a screw and O-ring. The rough sketch of the cell is presented in Fig. 1.

Experiments were done in the gas phase and dissolved oxygen in water, which are represented schematically in Fig. 2. All experiments were done at room temperature.

A) G/G measurement

Oxygen is supplied in the gas phase and detected in the gas phase. The oxygen in the air was used as the source of oxygen, and the air in the detection side of the cell was replaced by nitrogen by blowing nitrogen gas into the cell until the meter reading dropped to zero. In this type of measurement, the water jacket of the cell was removed and the air above the film was circulated by a fan.

B) W/W measurement

Distilled water in which oxygen is purged by nitrogen gas was allowed to fill the cell and the water was stirred with a magnetic stirrer. The speed of the magnetic stirrer was adjusted prior to the measurement to obtain the required flow rate across the face of the sensor. This was done by filling the cell with oxygen con-

taining water and stirring it until there is no increase in the meter reading with increasing agitation.

The water jacket above the membrane was filled with air-saturated water, of which the oxygen partial pressure was measured by the sensor prior to the measurement. The water in the jacket was stirred with a propeller-type stirrer.

The polarographic oxygen sensor measures only the partial pressure of oxygen and does not measure the actual quantity of oxygen in a solution. Therefore, the meter reading can be treated just as the pressure reading of oxygen in a vacuum method, regardless of whether it is detected as gas or as dissolved oxygen. Prior to each measurement, the meter is calibrated using air as a standard (the partial pressure of oxygen is 159 mmHg at one atmosphere).

In measuring permeability, the meter reading is recorded against time, and the slope ($\Delta \bar{p} / \Delta t$) of the curve is calculated from the tangential line at a certain pressure reading (usually 30 - 40 mmHg). The difference of the partial pressure between the point where the slope is taken and the partial pressure on the high oxygen side is taken as the driving pressure.

Permeability coefficient, P, is calculated by the following relation (3).

$$P = \frac{(\Delta p)}{(\Delta t)} \frac{(273)}{(273 + T)} \frac{(V)}{(A)} \frac{(\ell)}{(p)} \frac{(1)}{(760)}$$

where ℓ is the thickness, A the area of the membrane, V the volume of the cell, p the driving pressure and T the temperature in degree centigrade.

The results of the measurement are summarized in Table 1.

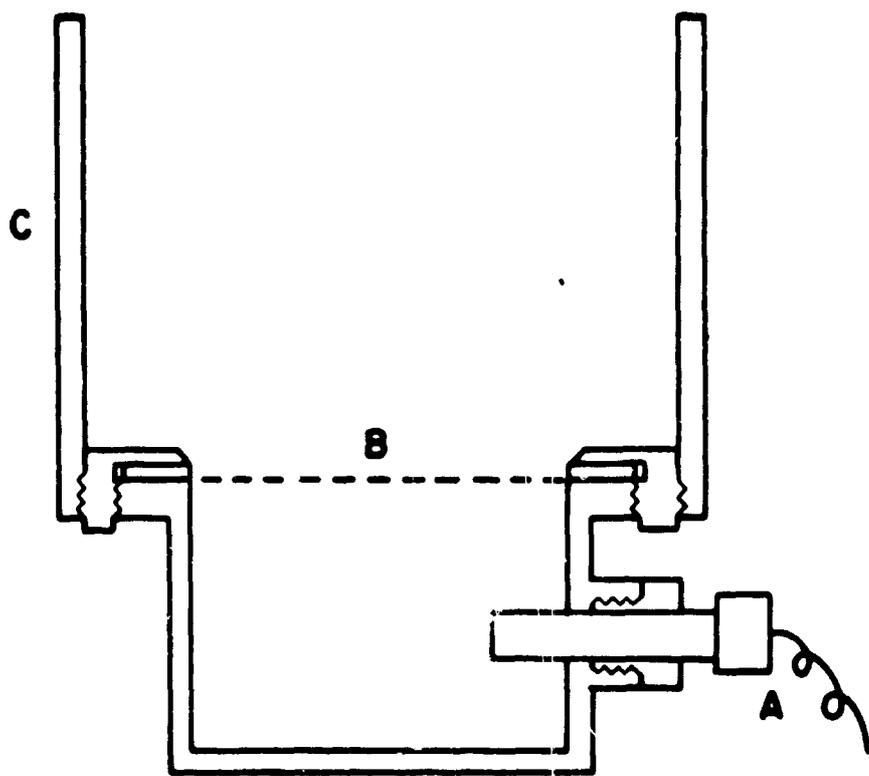
The results indicate that higher oxygen permeability is usually observed with dissolved oxygen even for highly hydrophobic polymer membranes. This may be due to the fact that the solubilities of water in many polymers (including hydrophobic polymers) are much higher than those of oxygen in the same polymers, and also that the solubility of oxygen in water is much greater than in polymers. Consequently, oxygen may permeate through the preexisting water in the polymer matrix, which may exist as uniformly distributed single molecules and also as clusters of water in existing voids.

The results also indicate that the permeability of oxygen (and possibly some other gases) in some hydrated membranes which can only be measured accurately (without altering the structure of the membrane) with dissolved gas can not be compared directly with the reported permeability values of many polymers, which are mostly obtained by measurements in G/G condition. Factors of 4 to 30 found in polymers presented here for permeability of dissolved oxygen over the gas phase oxygen must be taken into account for proper comparison.

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- A OXYGEN SENSOR
- B MEMBRANE
- C WATER JACKET

Fig.1. Permeability Cell

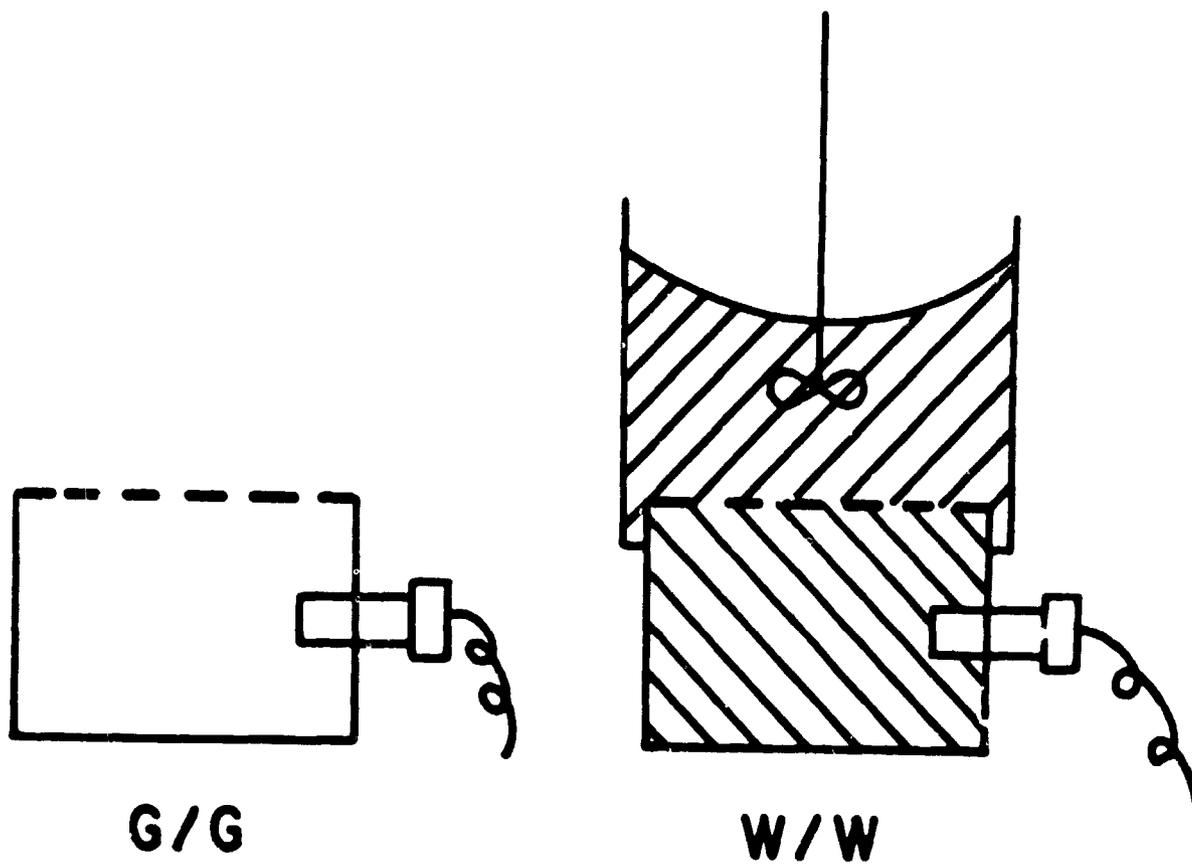


Fig. 2. Schematic representation of gas phase and dissolved oxygen in the permeability measurements.

TABLE I

Permeability of Gas and Dissolved Oxygen in Polymers

Polymer	$P \times 10^{10}$, (cc STP) (cm)/(cm ²) (sec) (cmHg)	
	G/G	W/W
Poly(dimethyl siloxane)*	665	4000
Polyethylene (low density)	2.34	50.0
Poly(fluorinated ethylene-propylene), (Teflon FEP)	3.86	105
Poly(tetrafluoroethylene)	23.7	91.0
(HEMA) Hydrogel**	-	180
Polyelectrolyte Complex***	-	270

* Dow Corning "Medical Silastic", with SiO₂ fillers.

** Cross-linked poly(hydroxyethyl methacrylate); water content 38%.

*** Poly(vinyl trimethylammonium)-poly(styrene sulfonate); water content 35%, (Amicon Inc., Cambridge, Massachusetts)