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New method to determine the true transmissibilities and permeabilities of oxygen in hydrogel membranes

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Abstract

In the present paper, an electrochemical method to obtain the true transmissibilities and permeabilities of hydrogels to oxygen is proposed. The method involves the measurement of the electric current arising from the flow of oxygen through a potentiostat cell integrated by a top water layer, the hydrogel membrane, and a thin water layer between the membrane and the cathode, where the oxygen is reduced. Varying the thickness of the top water layer, the true permeation characteristics of the hydrogels are obtained. A parallel study was carried out in which the transmissibilities and permeation coefficients were obtained from the variation of the steady state current with the thickness of the membranes. The permeation results obtained by the two methods agree very satisfactorily. The method also permits to determine the values of the transmissibility of the water layers of the experimental set-up. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Acrylic and methacrylic polymers are important starting materials for the development of hydrogels that can be further used in the preparation of contact lenses. The usefulness of these materials for these applications arises, in part, from the facilities they present to incorporate hydrophilic groups into their structure, and also from the ease with which they may be copolymerized with a series of comonomers, including multifunctional crosslinking agents. The swelling properties of hydrogels prepared from water-soluble hydrogels are controlled by the amount of crosslinking agent used in their preparation. As the amount of crosslinking agent decreases, the degree of swelling increases, thus facilitating the permeation of oxygen through the hydrogels. Highly swollen hydrogels, however, exhibit very poor mechanical properties. Consequently, in the preparation of hydrogels for soft contact lenses it is necessary to reach a compromise between the diffusivity characteristics and the mechanical properties of the hydrogels by controlling the amount of crosslinking agent incorporated in the copolymerization medium.

It is very important to know the permeability characteristics of hydrogels to oxygen when these materials are used in the preparation of soft contact lenses, but this task may present some difficulties. Electrochemical methods based on the reduction of the permeating oxygen in the cathode of a cell are commonly used [1–15]. However the values of the transmissibilities determined by these procedures may differ significantly from the true ones as a consequence of the effects that both the water layer located above the membrane and the thin layer between the hydrogel and the cathode may have on the measurements [6, 7, 16].

This work addresses the determination of the true transmissibilities of oxygen through membranes of poly(2-hydroxyethyl methacrylate) and poly(2-hydroxyethyl methacrylate-co-*N*,*N*-dimethylacrylamide), two hydrogels which could be used for the preparation of contact lenses. The method developed involves the measurements of the steady-state flow of oxygen in an experimental set up integrated by a top water layer, the membrane hydrogel and a narrow water layer between the membrane and the electrode. Electrochemical measurements obtained varying the thickness of the top water layer allows not only to separate the contribution of each layer, thus obtaining information on the boundary effects, but also to determine the true transmissibility and permeability of oxygen in hydrogel

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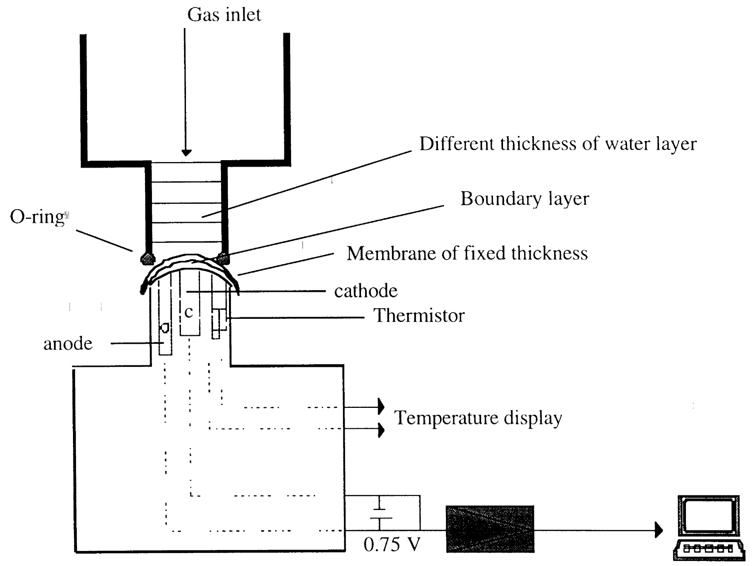

Fig. 1. A schematic view of the experimental assembly used in the determination of oxygen transmissibility.

membranes. These results are compared with those obtained in an experimental set-up in which the thickness of the membranes, rather than the thickness of the top water layer, is varied.

2. Theoretical basis of the model

As shown in Fig. 1, the experimental assembly used in the determination of flow through hydrogels is made up by a layer of water on the top of the membrane, the membrane, and a thin layer of water between the membrane and the cathode. Flow of oxygen, at pressure p on the surface of the top layer, to the gold cathode is monitored by the following reduction reaction

$$O_2\ \text{(dissolved)} + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Once steady-state conditions are reached, combination of Fick's first law and Henry's law gives

$$J = -\frac{Dk}{L}\Delta p \qquad (1)$$

where $\Delta p/L \cong p/L$ is the gradient of pressure of oxygen across the experimental assembly. The term Dk/L, called the instrument oxygen transmissibility (IOT) coefficient [3,4], involves both the diffusion coefficient D and the solubility coefficient k of the gas in the assembly water layer/membrane/thin water layer. Because the steady electric current I flowing through the membrane is given by

$$I = -n{\cdot}A{\cdot}F{\cdot}J \qquad (2)$$

where n is the number of electrons exchanged in the electrodes for each molecule of oxygen ($n = 4$), and A is the active area of the membrane, i.e. the area of the gold cathode and F is the Faraday constant, the IOT coefficient can be written in terms of the steady-state current by means of the following expression [8–10]

$$\frac{Dk}{L} = \frac{I}{n{\cdot}F{\cdot}A{\cdot}\Delta p} = B{\cdot}I \qquad (3)$$

where $B = (nFA\Delta p)^{-1}$. Since in the experimental device used in this work $\Delta p = 15.5$ cmHg, and taking into account that $n = 4$, $F = 96480$ C/mol and $A = (14.24 \pm 0.13) \times 10^{-2}$ cm^2, the value of B is 0.02629 cm^3 of oxygen (STP)/cm^2 s cmHg if I is given in μA.

The instrument apparent permeability is the value of the instrument oxygen transmissibility (IOT) (given by Eq. (3)) times the harmonic mean thickness of the assembly (L_{av}):

$$Dk = \frac{I{\cdot}L_{av}}{n{\cdot}F{\cdot}A{\cdot}\Delta p} \qquad (4)$$

Usually, Dk is given in barrers

$$1\ \text{barrer} = 10^{-10}\,\frac{\text{cm}^3\ \text{of gas.cm}^2}{\text{cm}^3\ \text{of polymer.s.cmHg}}$$

As indicated above, the oxygen transmissibility (OIT) determined by means of Eq. (3) is 'apparent' because it is related to the whole cell and not solely to the membrane. The reciprocal of the IOT transmissibility may be viewed as the resistance of the assembly of Fig. 1 to the flow of oxygen and, consequently, it may be considered as the sum of the resistances of the components of the assemble, that is [14–17],

$$\left(\frac{L_{av}}{Dk}\right)_{app} = \left(\frac{L_{sl}}{D_{sl}k_{sl}}\right)_{app} + \left(\frac{L_{av}}{Dk}\right)_{memb} + \left(\frac{L_{bl}}{D_{sl}k_{sl}}\right) \qquad (5)$$

where the first, second and third terms on the right hand side of this equation are, respectively, the resistance of the top water layer, the resistance of the membrane, and the resistance of the boundary layer between the membrane and the cathode. The subindices 'sl' and 'bl' mean sandwich and boundary layers, respectively. Sandwich layers are the layers of solution between two membrane, whereas the boundary layer is the layer between the membrane and the cathode + the solution layer on the top of the membrane.

Two methods can be devised to obtain $(L_{av}/Dk)_{memb}$ from Eq. (5). The first method involves an experimental set-up in which the oxygen flux is determined through swollen samples of different thickness. In this method, called method (a), the true value of the permeability coefficient (Dk) can be obtained by plotting the results for the reciprocal of the apparent transmissibility corresponding to each thickness against L_w. According to Eq. (5), $(1/Dk)_{memb}$ corresponds to the slope of the straight line obtained, while the combined resistance of the two water layers flanking the membrane is determined from the intercept.

The second procedure, or method (b), proposed in this paper, involves the variation of the thickness of the water layer, L_w, located on the top of the membrane. By plotting the values of the reciprocal of the apparent transmissibility against L_w, the permeability of the top water layer is obtained from the slope of the straight line, whereas the transmissibility of the sample can be determined from the reciprocal of the intercept if the resistance of the layer between the hydrogel and the cathode is neglected. A comparison of the values obtained by the two methods is given below.

3. Experimental part

3.1. Materials

Commercial 2-hydroxyethyl methacrylate (Fluka 95%) was dissolved in water and its dimethylacrylamide and ethylene glycol impurities were extracted with *n*-hexane. The monomer was further separated from the solution mixture by the ‘salting out’ method with an aqueous sodium chloride solution, and the process was repeated several times. Finally the monomer was dried with anhydrous calcium chloride and distilled under high vacuum. *N*,*N*-Dimethylacrylamide (Fluka 98%) was purified by distillation under reduced pressure. Solvents (dioxane and absolute ethanol) and the initiator (2,2′-azobisisobutyronitrile) were purified by conventional methods. The purity degree of the monomers as checked by ^{13}C and ^{1}H n.m.r. spectroscopy and by h.p.l.c. was higher than 99.5%.

3.2. Preparation and characterization of the membranes

Membranes were prepared from PHEMA and a copolymer of 2-hydroxyethyl methacrylate-*N*,*N*-dimethylacrylamide (PHNDA). The synthesis of the membranes was carried out at 50°C by radical polymerization of 2-hydroxyethyl methacrylate and 2-hydroxyethyl methacrylate/*N*,*N*-dimethylacrylamide, respectively, using 0.1% of ethyleneglycol dimethacrylate as crosslinking agent and 2,2′-azobisisobutyronitrile as initiator. The polymerizations were carried out to completion in a teflon mould under nitrogen atmosphere. The membrane was kept in water for 1 week at room temperature to remove any water-soluble uncrosslinked material. The composition of the PHNDA membrane was determined by elemental analysis of carbon and nitrogen, and the molar fraction of *N*,*N*-dimethylacrylamide was 0.48. The values of the glass transition temperature of the dry membranes, determined calorimetrically with a Perkin-Elmer DSC8 calorimeter at a heating rate of 10°C/min, are shown in Table 1. The water uptake at equilibrium of the PHEMA and PHNDA membranes was 55% and 70%, respectively.

Table 1
Characteristics of the polymer networks

Membranes	T_g (°C)	% cross-linking agent	Water content (%)
PHEMA	120	0.1	55
PHNDA	90	0.1	70

Following the procedure described above, five membranes of PHEMA of thickness 0.112, 0.210, 0.261, 0.308 and 0.398 mm and five membranes of PHNDA of thickness 0.108, 0.209, 0.254, 0.311 and 0.406 mm, were prepared for this study.

The thickness of the membranes (L_{av}) was measured with a micrometer. It is the harmonic average of the membrane thickness found by an integration of $1/L$ over five concentric rings with the same thickness L, Fatt [3]. In order to test the reproducibility of these measurements, parallel values of the thickness of the membranes were obtained by means of density measurements, determined from their weight and surfaces assuming additivity of the densities of the dried membrane and water. Good agreement between the two kinds of measurements was obtained.

3.3. Electrochemical measurements: experimental procedure

The current intensity at the cathode was measured with a potentiostat coupled to a permeometer model 201T (Rheder Development Company). The potentiostat is set to a voltage equal to 0.75 V (below the decomposition voltage for water). The area of the gold-plated cathode in contact with the membrane is $(14.24 \pm 0.13) \times 10^{-2}\ cm^2$. The anode is of silver and is positioned concentrically with the cathode (on the same spherical cap), and the two electrodes are electrically isolated by a spherical belt of epoxy resin. The system was kept at (35 ± 1°C) in all the measurements. To avoid dehydration of the samples during the experiments, air and nitrogen saturated with water vapour were introduced into the cell.

The experimental technique for the measurement of the diffusion current was earlier described by Fatt and Helen [12]. However, we have developed two different procedures to determine the steady-state current to which we have referred above. In the first method, the electrodes were wetted with a drop of distilled water before the membrane was placed on the cathode. The swollen membrane equilibrated in a buffer solution of borax was fixed gently by pressing a hollow cylinder with a tightening O-ring towards the membrane and the electrodes, and about 0.1 cm^3 of water solution (water + drop of borax to keep the pH in the interval 5.0–12.0) was poured on the top of the membrane.

Owing to the fact that the solution and the membrane already contain a considerable amount of dissolved oxygen, it was necessary to remove it so that each experiment could start with a 'residual current' close to zero. With the potential difference of 0.75 V applied, nitrogen saturated with water vapour was bubbled through the liquid in the hollow cylinder, and the current was seen to decrease towards zero. When practically all oxygen was eliminated (after approximately 5 min of nitrogen bubbling), moist air, at 1 atm, was introduced into the chamber in contact with the top water layer, and the increase of the electric current with time was monitored. The values of I in the steady-state condition were thus measured for swollen membranes with different thicknesses.

In the second method, small layers of water (0.2, 0.4, 0.6, 0.8, 1.0 cm) were poured on the top of the membrane and the apparent transmissibility in each case was measured.

4. Results and discussion

In Figs 2 and 3 the current intensity versus time is plotted for different heights of water layer (1.0, 0.8, 0.6, 0.4, 0.2 and 0.1 cm, respectively) on the top of the membrane. From these figures we can observe that the values of the steady-state current intensity are quite similar in both cases, and the transient time is smaller when the layer of water is thinner. Moreover, the values of $I(t \to \infty)$ decrease as the thickness of the top layer increases. The values of the stationary electric current obtained were substituted into Eq. (3), from which the results for the apparent transmissibility (IOT) of the PHEMA and PHNDA membranes were calculated.

In Fig. 4, the values of the reciprocal of the apparent transmissibility are plotted against the thickness of the water layer for PHEMA and PHNDA membranes. The plots give perfect straight lines with correlation coefficients equal to 0.9946 and 0.9932, respectively. From the slopes of these plots, values of 1.2×10^{-8} cm^3 of O_2/cm^2 s cmHg, and 1.16×10^{-8} cm^3 of O_2/cm^2 s cmHg were obtained for the permeability coefficient of water, at 25°C, in rather good agreement with the results reported by other authors [18].

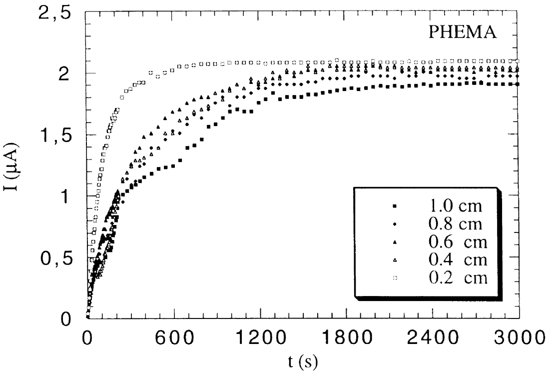

Fig. 2. Current intensity versus time for sample A (PHEMA), with different water layers on the top of the membrane.

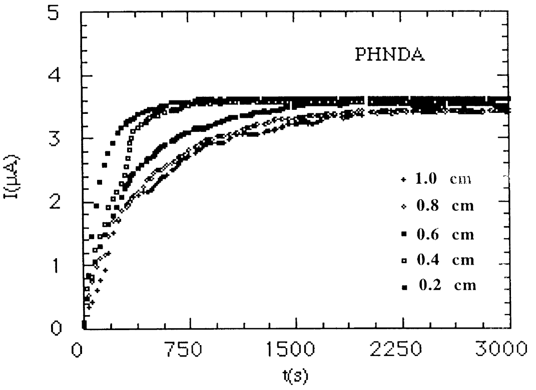

Fig. 3. Current intensity versus time for sample B (PHNDA), with different water layers on the top of the membrane.

The intercepts of the straight lines plotted in Fig. 4 are equal to the sum of the inverse of the transmissibilities of the membrane and the electrode–water boundary layer for PHEMA and PHNDA, respectively. These values are ca. 1.36×10^7 and 7.15×10^6 cm^2 s $cmHg/cm^3$ of O_2 for the samples A and B, respectively. If the thickness of the boundary layer is assumed equal to 100 µm (see Refs. [6,7]), the values of the transmissibility coefficient shown in Table 2 for PHEMA and PHNDA membranes are obtained. In this table the values of the permeability coefficient calculated from the true transmissibility are also given.

The values of the transmissibility determined following method (a), i.e. by measuring the steady-state current through membranes with different thickness, were obtained by the same procedure described above. Plots of the reciprocal of the apparent transmissibility are plotted against the

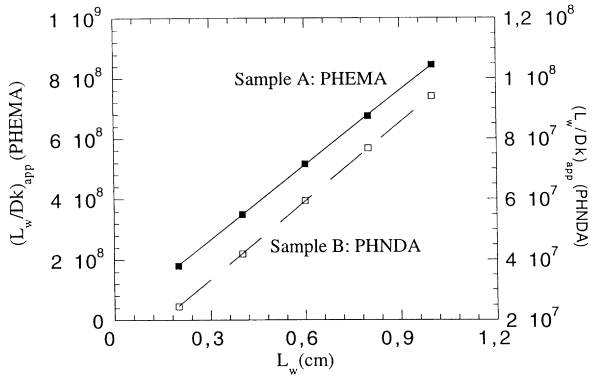

Fig. 4. Reciprocal of apparent transmissibility versus water layer thickness in combination with: a membrane of $L = 0.0210$ cm of sample A (PHEMA) represented by (■); and a membrane of $L = 0.0209$ cm of sample B (PHNDA) represented by (□).

Table 2
True values of transmissibility and permeability obtained following the two procedures described before: (a) with water layers and (b) different thicknesses

Membranes	$(Dk/L_{av})_{true}$		$(Dk)_{true}$ (barrers)		L_w (μm)
	Method (b)	Method (a)	Method (b)	Method (a)	
PHEMA	7.8×10^{-8}	8.2×10^{-8}	16.4	17.2	560
PHNDA	15.9×10^{-8}	15.02×10^{-8}	33.2	31.3	450

In the last column we show the boundary layer thcknesses. The units of transmissibility are cm^3 of O_2/cm^2 s cmHg

thickness of the PHEMA and PHNDA membranes are shown in Fig. 5. From the intercept, the transmissibility of water layer plus the interval layer between the cathode and the membrane were calculated. From these results, and taking into account the value of the water permeability calculated before, the thickness of the two boundary layers could be estimated. From the slopes of the straight lines plotted in Fig. 5, the values of the true permeability coefficient for the oxygen through swollen PHEMA and PHNDA membranes are calculated. These values are given in Table 2. The mean values of the true permeability coefficient determined by the two methods for the two membranes, PHEMA and PHNDA, are $(Dk)_A = (16.8 \pm 0.4)$ and $(Dk)_B = (32.3 \pm 0.9)$ barrers, respectively.

The good agreement found for the permeation characteristics of the membranes by the two methods, lead to the conclusion that either of the two methods gives a good account of the permeation properties of the hydrogels to oxygen. The second method, described by the first time in this work, has the advantage that with a single membrane one can obtain a very reliable description of the permeation characteristics of oxygen in hydrogels.

It is worth noting that PHNDA membranes present a permeability coefficient for oxygen which is nearly two times larger than the value of this parameter for PHEMA membranes. The same applies for the oxygen transmissibility. This behaviour arises from the fact that the water-uptake of the PHNDA membrane is comparatively much larger than that of the other for the same thickness.

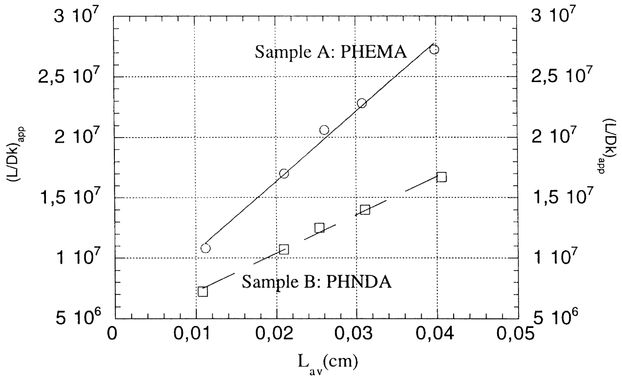

Fig. 5. Reciprocal of transmissibility versus: harmonic average thickness of sample A (PHEMA) and sample B (PHNDA) represented by (○) and (□), respectively.

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