

True and Apparent Oxygen Permeabilities of Contact Lenses

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ABSTRACT

We studied the passage of oxygen through some commercially available contact lenses. Oxygen diffusion coefficients were determined by the time-lag method and a 201T Redher permeometer was used to measure the oxygen permeability and transmissibility by the polarographic method. The measurements were carried out at room temperature with 0.09% sodium chloride physiologic solution. The following types of lenses were tested: (1) 12 lenses of cellulose acetate butyrate (CAB) of a mean thickness of 0.194 mm (observed $Dk \approx 6.3$ barrers) (1 barrer is equivalent to $10^{-11} \text{ cm}^3 \text{ of } O_2 \text{ (STP) } \cdot \text{ cm}^2/\text{cm}^3 \cdot \text{ s} \cdot \text{ mm Hg}$). (2) 13 lenses of a cross-linked polyhydroxyethyl methacrylate (2-HEMA), manufactured by Lenticon and Bausch & Lomb, with 40 and 38.6% water content, respectively. The mean thicknesses were 0.160 and 0.148 mm, respectively (observed $Dk \approx 12$ to 13.5 barrers). (3) Finally 10 lenses of a copolymer of 2 HEMA with N-2-vinylpyrrolidone (2-HEMA/VP), manufactured by Bausch & Lomb under the name Hydrocurve II, with 55% water content and a mean thickness of 0.138 mm (observed $Dk \approx 24.5$ barrers). For a given lens thickness, the transmissibility and permeability of lenses whose main material is 2-HEMA are found to be equivalent. This fact suggests the use of such material as a standard in the study of diffusion processes in contact lenses of low oxygen permeability ($Dk \approx 12$ to 13.5 barrers). We studied the boundary layer effects and found significant discrepancies between true and apparent oxygen permeabilities. The apparent transmissibility decreased with increasing lens thickness, this effect being more apparent for lenses with low water content. Oxygen permeability is found to be exponentially dependent on water content rather than on the chemical composition of the hydrogel.

Key Words: contact lens, oxygen transmissibility, oxygen permeability, gas diffusion

The hydrogels are natural or synthetic hydro-

philic cross-linked polymers that swell up with water and become elastic and soft materials. Such polymers are usually composed of poly-HEMA, a monoester obtained by adding diester and ethylene glycol dimethacrylate in aqueous medium. This can result in homogeneous or heterogeneous gels depending on the water content. Thus, if the content of water is about 40% or more than 50%, homogeneous and heterogeneous gels, respectively,¹ are obtained. Indeed, many gel properties such as permeability, biocompatibility, and surface mechanics change with the equilibrium water content.

Oxygen transport through contact lenses is known to be of great importance for the proper functioning of the cornea. When a contact lens is placed on the eye, the oxygen flux is altered and the normal corneal metabolism can no longer be maintained. Corneal swelling begins when oxygen tension in the precorneal tear film is about 70 to 90 mm Hg and when oxygen flux into the corneal epithelium decreases below the value of $5.5 \cdot 10^{-6} \text{ cm}^3 \text{ of } O_2/\text{cm}^2 \cdot \text{ s}$.^{2,3} Thus, it is important to characterize the lenses on the basis of their oxygen diffusivity in order to know which are the best materials to make contact lenses from a physical viewpoint. Obviously, a physiological study about the suitability of the lenses for the patient would also be required.

Oxygen permeability is a characteristic of the lens which depends on temperature, pressure, water content, and thickness.^{4,5} There are three procedures to measure this lens characteristic. Two of them use the electrode method, in which a Clark polarographic oxygen electrode is covered with the lens during the oxygen flux measurements. They were developed for hydrogel contact lenses, but some minor modifications need to be introduced when they are used with nonhydrogel and rigid lenses. The procedure proposed by Fatt introduces a fine cigarette paper saturated with an aqueous electrolyte solution between the lens and the electrode.⁶⁻⁸ The procedure developed by Refojo introduces a thin Teflon membrane with the aqueous electrolyte gel placed between the electrode and the Teflon membrane.^{9,10} In both methods, oxygen is

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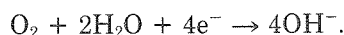
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reduced on the electrode after permeating through the lens and the filter paper or the Teflon membrane. A third procedure uses the 2-chamber method, in which the lens is clamped between the 2 chambers. Oxygen is transported from the chamber of higher to that of lower oxygen concentration, where it is reduced by an oxygen sensor.^{11,12} This method is a variant of the so-called time-lag method.

We measured the oxygen diffusion coefficients, transmissibilities, and permeabilities of 48 contact lenses. We used the time-lag method to obtain the oxygen diffusion coefficients. The permeability measurements were obtained with a potentiostatic cell and following the technique described by Fatt and St. Helen,¹³ which assumes that all the oxygen reaching the cathode is instantly reduced. These permeability measurements are related to the system composed by the lens and the two boundary layers and, therefore, they are called apparent permeabilities. We determined the effect of the boundary layers in order to evaluate the true permeabilities of the lenses. It is worth noting that some authors have not considered the possible effect of the boundary layers on the measurement of the oxygen permeability.^{14,15} But others have studied this effect and determined the thickness of these layers and calculated the true oxygen permeability of contact lenses.^{3,6-10}

FUNDAMENTALS

The oxygen passing through the sample follows the reduction process on the cathode



Oxygen transmissibility is calculated by measuring the electrical current I in the polarographic cell through the equation¹⁶

$$\frac{DK}{L} = \frac{I}{nFA\Delta p} \quad (1)$$

where n is the number of electrons involved in the reduction of 1 molecule of oxygen (in this case, $n = 4$), F is the Faraday constant divided by the molar volume of the gas at standard conditions (22.4 L/mol), A is the cathode surface area, equal to the membrane surface area, and Δp is the oxygen partial pressure difference between the two faces of the lens (in this case, $\Delta p = 155$ mm Hg). Equation 1 assumes that zero oxygen concentration is maintained at the cathode surface.

Fatt and Chaston⁵ included the residual current I_0 , i.e., the electrical current that was observed when no dissolved oxygen was present. Then, equation 1 can be modified to

$$\frac{Dk}{L} = \frac{I - I_0}{nFA\Delta p} \quad (2)$$

where $I - I_0$ is called the diffusion current.

The oxygen transmissibility measured in this way is termed apparent transmissibility because it is

related to the whole cell and not to the lens. The diffusion resistance of the solution layer between the sample and the electrode must also be taken into account. The true transmissibility is related to the apparent one through equation 3¹⁷

$$\left(\frac{L}{Dk}\right)_{\text{app}} = \left(\frac{L}{Dk}\right)_{\text{lens}} + R_{\text{b.l.}} \quad (3)$$

where $R_{\text{b.l.}}$ is the boundary layer resistance. Thus, when several samples of the same hydrogel having different thicknesses are studied, the plot of $(L/Dk)_{\text{app}}$ vs. lens thickness L should give a straight line, $(1/Dk)_{\text{lens}}$ being its slope (i.e., the reciprocal of the true oxygen permeability of the hydrogel), and $R_{\text{b.l.}}$ its intercept. The oxygen permeability can be estimated by multiplying the oxygen transmissibility $(Dk/L)_{\text{lens}}$ obtained in this way by the lens thickness. The dependence of the electric current upon the true permeability and transmissibility can also be found by substituting equation 3 into equation 2. And, finally, the thickness of the boundary layers can be obtained from the value of the solution permeability.¹⁸

On the other hand, oxygen diffusion coefficients can be determined from time-lag measurements and equation 4¹¹

$$D = \frac{L^2}{6\theta} \quad (4)$$

where θ is the time-lag and L is the average membrane thickness. It can also be proved that the time-lag is related to the steady-state electrical current in the potentiostatic cell, I , through equation 5¹⁶

$$\theta = \frac{It_0 - q}{I} \quad (5)$$

where t_0 is the time needed to reach the steady state and q the electrical charge transported during that time.

METHODS

The following types of lenses were tested: (1) 12 lenses of CAB of a mean thickness of 0.194 mm; (2) 13 lenses of a cross-linked 2-HEMA, manufactured by Lenticon and Bausch & Lomb, with 40 and 38.6% water content, respectively—the mean thicknesses were 0.160 and 0.148 mm, respectively; and (3) finally 10 lenses of a copolymer of 2-HEMA/VP, manufactured by Bausch & Lomb under the name Hydrocurve II, with 55% water content and a mean thickness of 0.138 mm. The CAB lenses, provided by Danker and Wohlk Co., are not single plastic materials. Instead, they are basically formed by a resin which has about 15% acetyl, 40% butyryl, and 2% unsubstituted hydroxyls.

The central thicknesses of the lenses, L , were measured with a micrometer. The mean value of 10 measurements was obtained. Oxygen transmissibility Dk/L and permeability Dk were measured by means of a Createch Permeometer (model 201 T,

Redher Development Co., USA) designed for the accurate measurement of these quantities. The polarographic cell of the permeometer was a Schema cell (Schema Versatae, Berkeley, CA). The radius of curvature of the electrode tip was made to fit the inner surface of the lens. We used a gold cathode and a silver anode. The measurements were made at room temperature, $(20 \pm 1)^\circ\text{C}$, in a 0.09% NaCl solution with double distilled water and the voltage was set to 0.75 V for all experimental tests. The cathode surface area A was $(14.24 \pm 0.13) \cdot 10^{-2} \text{ cm}^2$. Further details on the potentiostatic cell can be found elsewhere.^{6,19}

The polarographic method described by Fatt and St. Helen¹³ was used. This method is based on the complete reduction of the dissolved oxygen reaching the cathode surface after passing through the lens. All the measurements were conducted according to the following procedure.¹⁹ The electrodes were first moistened with a drop of 0.09% NaCl aqueous solution before adjusting the lens. Then, the lens was removed from a receptacle containing the same NaCl solution and placed on the electrodes. The vertical hollow cylinder was adjusted to the lens after inserting a piece of wet nylon. A calibrated weight was then placed on the cylinder. Next, 0.5 ml of the above-mentioned solution was introduced through the opening of the cylinder. Then, the system was exposed to a nitrogen atmosphere until a negligibly small current was observed. Finally, the system was exposed to the ambient atmosphere and the electric current reached a steady value, I .

RESULTS AND DISCUSSION

The flow of oxygen to the cornea through a contact lens may also be retarded by the resistance due to the tear layers at the anterior and posterior surfaces of the lens.^{17,20} In this sense, we may obtain erroneous values that are particularly enhanced when Dk is determined from equation 2. This effect is more important for rigid than for hydrogel contact lenses.

The polarographic method used can yield values of the oxygen permeability that are lower than the true ones when applied to thin contact lenses. Measurements carried out on a set of lenses of the same material having different thicknesses can be used to obtain the true values. Also, the values of the oxygen permeability obtained from the direct determination of the electrical current may be wrong if the effect of the resistance to oxygen flow due to the boundary layers is not taken into account. Furthermore, Goldenberg et al.²¹ have observed that the Createch Permeometer can lead to wrong results when used for ultrathin and highly oxygen-permeable silicone rubber sheets due to the nonlinear relation between electrical current and oxygen partial pressure difference (see equation 2 above). In our study of a set of commercial contact lenses used widely in Spain, we assessed the linear relation between these two magnitudes and, then,

we took into account the effect of the boundary layers and the discrepancies between true and apparent oxygen permeabilities.

In order to obtain the values of the true and apparent oxygen permeability, we first register the time evolution of the diffusion current. Typical registers are presented in Fig. 1. The steady-state values of the electrical current are obtained from these plots and the apparent oxygen transmissibilities are calculated by means of equation 2. Then, the average central thickness of the lenses is measured and the apparent oxygen permeabilities are calculated as the product of the apparent oxygen transmissibility and the lens thickness. Next, the reciprocal of the apparent oxygen transmissibilities are plotted against the lens thicknesses. These plots can be seen in Fig. 2 and the corresponding linear regression parameters are shown in Table 1. According to equation 3, the true oxygen permeability is given by the reciprocal of the slope of this plot and the contribution of the boundary layers to the resistance to oxygen diffusion is related to the intercept. Finally, by assuming that the oxygen permeability of these layers is that of water, $(Dk)_{b,1}$.

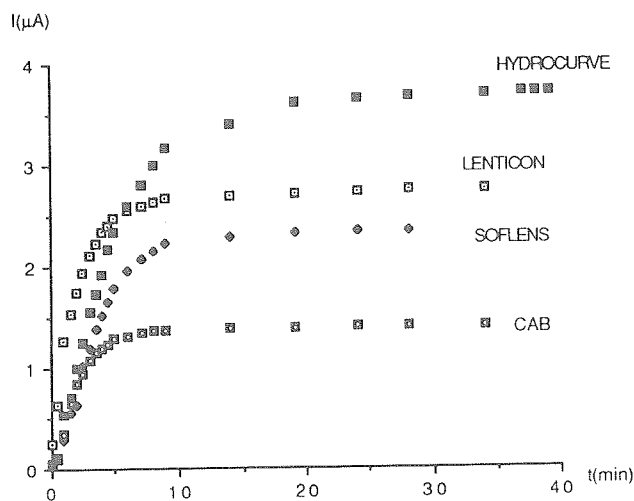


Figure 1. Diffusion current vs. time.

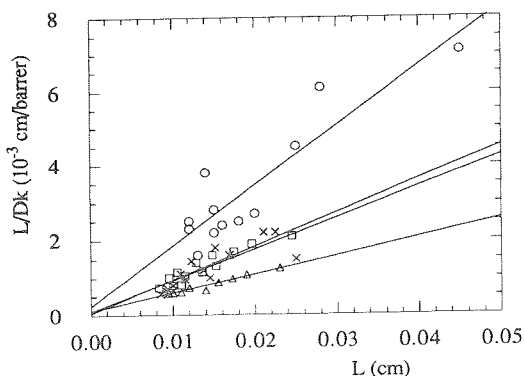


Figure 2. Reciprocal of apparent oxygen transmissibility vs. lens thickness for CAB (O), Lenticon (X), Soflens (□) and Hydrocurve II (Δ) lenses.

TABLE 1. Parameters of the linear regressions shown in Fig. 1.

Lens	Slope (barrer ⁻¹)	Intercept (10 ⁻⁴ cm/barrer)	Correlation Coefficient
CAB	0.164 ± 0.025	2 ± 4	0.90
Soflens	0.089 ± 0.010	0.6 ± 1.4	0.94
Lenticon	0.083 ± 0.018	1 ± 3	0.81
Hydrocurve II	0.049 ± 0.004	1.1 ± 0.6	0.97

≈ (Dk)_w = 79 barrers,^{18,20} the thicknesses of the boundary layers are computed.

Table 2 shows the results obtained for the true and apparent oxygen permeability and the thickness of the boundary layers. In this table it can be observed that lenses with high water content also show high oxygen permeability. Furthermore, the relative differences between true and apparent oxygen permeabilities also seem to be related to the water content, being greater for thin lenses with a high water content. Then, we can deduce that the effect of the boundary layers on the experimentally observed oxygen permeability is important for lenses with high water content, small thickness, and high oxygen permeability. The thickness of the boundary layers in the lenses evaluated are thicker than the tear film. Thus, a given contact lens placed in the eye will transmit somewhat more oxygen to the cornea than the amount determined in our experimental set-up, in which the boundary layer resistances are larger than the ones due to the tear film, even though we assume that the tear film is constituted like bulk water, which it certainly is not.

Table 2 also shows the oxygen diffusion coefficient obtained from time-lag measurements and equation 4. The time-lag has been determined from the diffusion current registers (Fig. 1).²² This time is characteristic of the lens and is only slightly different from one lens to another. The results in Table 2 show that the value of the oxygen diffusion coefficient is high for lenses with a high water content. As compared with the other lenses, Hydrocurve II lenses (distributed by Bausch & Lomb) offer the minimum resistance to the transit of oxygen. Their diffusion coefficient is 36% higher than those of Lenticon and Soflens lenses. On the other hand, we see that the contact lenses of the same material but from different manufacturers present slightly different values for the oxygen permeability and the oxygen diffusion coefficient. Finally, CAB lenses, although substantially more oxygen-permeable than the conventional hard lenses, show lower

oxygen permeability than hydrogel lenses because of their lower water content.

In view of the relatively high uncertainties of the L_{b.l.} values in Table 2, we should consider them as rough estimates showing the characteristic order of magnitude. The analysis of a larger number of lenses could certainly improve these results, but this paper emphasizes the measurement of the permeabilities, and the latter shows reasonable uncertainties.

From the above results, we can consider 2-HEMA as a standard material for the determination of the oxygen transmissibility and permeability of hydrogel contact lenses. However, it could not be considered as a general standard material because of the problems in comparing the permeability of a soft contact lens material with a rigid gas permeable material (e.g., boundary layer effects, etc.). The relative differences between true and apparent oxygen permeabilities never exceed 10% for this material and they may be due to the thickness of the boundary layer. This thickness may vary from one experiment to another because of slight changes in pressure, temperature, and lens humectability. Other factors that are thought to contribute to experimental errors in the determination of the material permeability include sorption and desorption effects and unstirred boundary layers on the surface of the lens.²³

The resistance to oxygen flow due to the boundary layers is found to be smaller for membranes treated by N-(1,1-dimethyl-3-oxobutyl) acrylamide (also known as diacetone acrylamide) and 2-ethyl-2(hydroxymethyl)-1,3 propanediol than for nontreated membranes (2-HEMA). The results obtained here for the boundary layers' thicknesses (Table 2) are not very different from those by Yang et al.²⁴

In order to study which is the control mechanism of the oxygen diffusion through the lens-dissolution system, we have introduced a generalization of the criterion given by Helfferich²⁵ to find whether the control of the diffusion process is exerted by the lens or the boundary layers. The procedure is based on an estimation of the ratio

$$\frac{(Dk)_{b.l.}p^0L}{(Dk)_{lens}p_{lens}\delta} \quad (6)$$

where (Dk)_{lens} is the oxygen permeabilities of the lens, (Dk)_{b.l.} that of the boundary layers, p⁰ the average oxygen partial pressure in the air in equilibrium with the sodium chloride solution, p_{lens} the

TABLE 2. True and apparent permeabilities and their relative difference of some hydrogel contact lenses.^a

Brand Name	Main Material	Water Content (%)	(Dk) _{app} (barrers)	(Dk) _{true} (barrers)	Difference (%)	L _{b.l.} (μm)	D (10 ⁻⁷ cm ² /s)
CAB	CAB	30	6.3 ± 0.6	6.7 ± 0.9	7	200 ± 300	2.30 ± 0.11
Soflens	2-HEMA	38.6	11.2 ± 1.6	12.1 ± 1.4	7	50 ± 100	2.71 ± 0.12
Lenticon	2-HEMA	40	12.1 ± 1.8	13.1 ± 1.2	8	80 ± 200	2.52 ± 0.14
Hydrocurve II	2-HEMA/VP	55	20.5 ± 2.0	24.5 ± 2.5	20	90 ± 50	3.97 ± 0.20

^a Oxygen diffusion coefficients and lens thicknesses are also included. Standard deviations from average values are shown.

oxygen partial pressure in the boundary layers, and L and δ the lens and boundary layers' thicknesses, respectively. If the ratio (6) is much greater than 1, the pressure gradient is mostly maintained by the lens.

With the given value for $(Dk)_{b,l}$ and the thicknesses and permeabilities corresponding to the lenses studied (Table 1), we see that the ratio (6) takes values from 5 to 25 times p^0/p_{lens} . On the other hand, $p^0 \approx 155 \text{ mm Hg} \geq p_{lens}$ and then this ratio is always much greater than one. Nevertheless, the ratio takes very different values from one lens to another. It is therefore clear that boundary layer effects must be taken into account in some lenses. In this work, the ratio was lower for the Hydrocurve lenses than for the others.

Finally, we also studied the relation between the permeability and the water content of the lenses. Our results shown in Fig. 3 suggest an exponential dependence of the permeability (Dk in barrers) on the water content w (in percent).

$$Dk = 1.62e^{0.0504w} \quad (r = 0.993) \quad (7)$$

It is worth noting that we have not studied lenses with very high water content²¹ and, consequently, the range of values of the water content in Fig. 3 is so small that both linear and exponential relations could be suggested. However, we decided to use the exponential dependence because it has already been observed by other researchers.⁵ In any case, our results and those previously reported by different authors^{5-10,15,23} (summarized in Table 3) show that the water content of the lens is a key parameter.

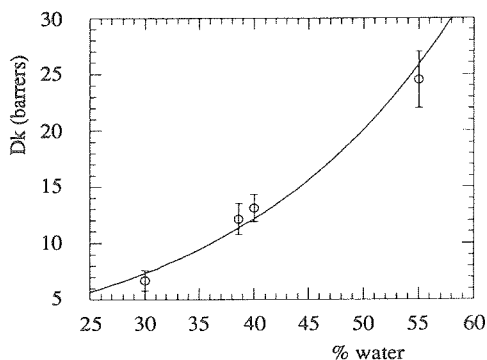


Figure 3. True or intrinsic permeability vs. water content.

TABLE 3. Comparison of apparent permeability values (in barrers) obtained by different authors.^a

Main Material	CAB	2-HEMA	2-HEMA/VP	Reference
$(Dk)_{app}$ (barrers)	6	12-13	20-24	This paper
	5-8	9-11	16-19	4, 6, 12
	5-6	8-10	6-13*	8, 9
	—	10	16-17	15

^a Value marked with * refers to the same main material but with a different water content (45% instead of 55%).

CONCLUSIONS

The oxygen permeability and diffusion coefficient increase with the water content and the thickness of the lens, although the effect of the boundary layers is also more important for thick lenses. This dependence on water content can be used to obtain a first approximation for the permeability of new materials. However, the well-known differences in bound to free water as total water content changes make it impossible to have a reliable estimate for the oxygen permeability.

It would be quite interesting to have a standard method for the determination of the oxygen permeability of hydrogel contact lenses. We think that such a method should use 2-HEMA as a reference material because these lenses give a very reproducible value for the oxygen permeability. Furthermore, lenses based on 2-HEMA from different manufacturers show similar oxygen permeabilities. From the point of view of measurements, hydrogel contact lenses are also very convenient because there is no need to introduce any cigarette paper or Teflon membrane between the lens and the electrode.

Materials containing VP show a very high oxygen permeability thanks to their thickness and water content, the effect of the boundary layers being much less important for them than for the other materials studied. Therefore, they should be considered preferentially. Nevertheless the physiological response of the patient will certainly influence the choice of one lens or another.

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UPCOMING EVENTS

The 15th Annual Wilmer Institute Current Concepts in Ophthalmology will be held on February 7 to 12, 1993 at the Hyatt Regency Cerromar Beach Hotel, Dorado, Puerto Rico.

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The 10th Annual Wilmer Institute Current Concepts in Ophthalmology will be held on March 14 to 19, 1993 at the Manor Vail Lodge, Vail, Colorado.

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