

Permeation of Water through Some Heterogeneous Hydrophilic Membranes

MIGUEL F. REFOJO, *Corneal Research Unit and the Department of
Retina Research, Institute of Biological and Medical Sciences, Retina Founda-
tion, Boston, Massachusetts*

Synopsis

The permeation of water through glyceryl methacrylate (2,3-dihydroxypropyl methacrylate) and 2-hydroxyethyl methacrylate hydrogels was increased by the incorporation of silica fillers. Both the amount of water at equilibrium and the amount of filler in the gel contribute to increase the permeability of these membranes.

INTRODUCTION

Membranes are porous sheets which, when placed between two phases, may allow the passage of some particles but hinder or prevent the passage of others.¹ There is currently a wide interest in semipermeable membranes for desalination of water by the process of reverse osmosis. Essentially, the requirement is a barrier which will allow, under hydrostatic pressure, the passage of water but will retain the salts dissolved in the solution. To date, membranes of cellulose acetate seem to be the best for this purpose.² Other materials, e.g., polyelectrolyte complexes, have been investigated.³ Graves⁴ discovered that polymer films of 2-hydroxyethyl methacrylate are semipermeable. In addition to permselectivity, for an economical process of reverse osmosis a high permeability to water is required.

Fluid is transferred through a barrier in two different ways:⁵ (a) by viscous flow caused by hydrostatic or osmotic pressure in which a velocity component is imposed on all fluid molecules and (b) by diffusional flux caused by a gradient of the chemical potential of the fluid. The gradient of the chemical potential may arise from differences in the concentration and/or the hydrostatic pressure, in which case the transfer of the fluid arises from the random movement of its molecules. The relative importance of the two processes is dependent on the nature of the barrier. The permeation of water through homogeneous hydrophilic membranes has been reported previously.^{6,7} The transport process was found to be predominantly viscous flow in the membranes which contain more than 75% water at equilibrium, while diffusion seemed to play a more important part in the movement of water through the hydrogels with less water

content. These homogeneous membranes are three-dimensional hydrophilic polymer networks saturated with water or with an aqueous solution. They are synthesized from hydrophilic acrylate and methacrylate esters, such as a glycol monomethacrylate and glyceryl methacrylate (2,3-dihydroxypropyl methacrylate). Hydrogels of this general type have been proposed for certain medical uses by Wichterle and Lim.⁸ Their transparency and softness makes them particularly interesting in the field of ophthalmology.

Since hydrogels, especially those with higher water content, have a low tensile strength, some inorganic fillers were added in an attempt to improve their physical properties. The addition of fillers to hydrogels improved somewhat the tensile strength of the membranes, but what is more remarkable is the finding that the water permeation through the heterogeneous membranes (with fillers) increased considerably in relation to the permeation through a homogeneous membrane (without fillers) of similar water content.

EXPERIMENTS

Membranes

2-Hydroxyethyl methacrylate (HEMA) is a commercially available monomer (The Borden Chemical Co., Philadelphia, Pa.), and it was used without further purification. Glyceryl methacrylate (GMA) monomer was prepared as described elsewhere.⁹

Two types of silica fillers were used: Cab-o-sil M-5 (Cabot Corporation, Boston, Mass.) which is a silicone dioxide of average particle size 0.012μ ., and Min-u-sil (Pennsylvania Glass Sand Corporation, Pittsburgh, Pa.), which is a crystalline silicone dioxide in uniform 5μ sizes.

GMA membranes were prepared from aqueous solutions of the monomer to which were added different amounts of filler. HEMA membranes were made from ethylene glycol-water solutions¹⁰ of the commercial monomer mixed with the filler. The filler was dispersed in the monomer solution with a fast stirrer, and then aliquots of the mixtures were taken out and polymerized. Ammonium persulfate (6% aqueous solution) and sodium metabisulfite (12% aqueous solution) were used as redox initiator in the polymerization. For example, to a solution of GMA (15 ml.) in water (30 ml.) was added gradually increasing amounts of Cab-o-sil. After each successive addition of the filler, 2 ml. of the resulting mixture was taken out and polymerized at 50°C . between two glass plates by adding 0.1 ml. of the persulfate and 0.1 ml. of the bisulfite solution, respectively. Likewise, to a solution of HEMA (10 ml.) in ethylene glycol (10 ml.) and water (5 ml.) was added 5 g. of Min-u-sil and dispersed with a fast stirrer. Each 4 ml. of the above mixture, after addition of 0.2 ml. each of the persulfate and the bisulfite solutions, were polymerized between two glass plates at 60°C . After polymerization, the

heterogeneous hydrogel membranes were allowed to equilibrate in distilled water for several weeks.

The method by which the membranes were made, the procedure for determining their thickness and the water content at equilibrium in the conditions of the measurements have been described before.⁷ The amount of filler in the heterogeneous hydrogel, which has been equilibrated in water at room temperature, was determined gravimetrically upon calcination of the wet specimen, and it is given as per cent of ashes in the wet hydrogel.

The heterogeneous membranes with Cab-o-sil as the filler are more or less transparent, depending upon the amount of filler in the membrane. On the other hand, membranes with Min-u-sil as the filler, at the level studied, are opaque.

Permeability Measurements

The permeability apparatus was described previously^{11,7} and was similar to that used by White⁶ for determining the permeability of acrylamide polymer gels. Essentially, the apparatus consists of two water chambers separated by the membrane whose permeability was to be determined. Air pressure, measured in a U-tube mercury manometer, was applied to the water in one chamber of the apparatus. Connected to the water chamber on the other side was a calibrated capillary tube for measuring flow rates. The measurements were carried out with the apparatus immersed in a constant-temperature bath at 25°C. The rate of flow was determined by timing the movement of the meniscus along the capillary tube. Four determinations were made at each of four different pressures. A plot of flow rate versus pressure gradient yielded a straight line through the origin. A deviation from linearity indicated a leak in the system and such results were discarded.¹²

RESULTS

The equation^{6,12} used for calculating the permeability coefficient, K , (in square centimeters), was

$$K = VL\eta/tA\Delta P$$

where V is the volume of water (in milliliters), of viscosity η (in poises) flowing through a membrane of thickness L (in centimeters) and area A (in square centimeters), in a time t (in seconds), under a pressure difference ΔP (in dynes/square centimeter).

The permeability coefficients obtained for the heterogeneous hydrophilic membranes are compiled in Tables I and II. For easy comparison, the permeability coefficients of some homogeneous hydrophilic membranes of similar water content obtained previously⁷ are included in the tables. All these results were obtained operating in the same way.

TABLE I
Homogeneous GMA and Heterogeneous GMA-Cab-o-sil Membranes

H ₂ O, %	Ashes, %	$K \times 10^{15}$, cm. ²
80.3	—	4.65 ± 0.06
78.8	7.28	12.25 ± 0.35
83.2	—	6.08 ± 0.06
82.7	1.34	8.73 ± 0.24
84.7	1.44	16.82 ± 0.71
85.1	—	6.09 ± 0.59
87.0	0.78	24.32 ± 0.68
87.6	—	6.55 ± 0.20

TABLE II
HEMA Membranes

Filler	H ₂ O, %	Ashes, %	$K \times 10^{15}$, cm. ²
—	38.7 (clear film)	—	0.075 ± 0.006
Cab-o-sil	40.1	10.53	0.244 ± 0.001
—	53.8 (hazy film)	—	0.09 ± 0.01
Cab-o-sil	45.8	17.5	2.06 ± 0.32
Cab-o-sil	57.8	21.6	122.64 ± 3.11
Min-u-sil	34.5	22.9	0.28 ± 0.02
Min-u-sil	30.9	34.4	0.28 ± 0.002

DISCUSSION

A priori, one would expect that the addition of fillers into a gel would hinder rather than increase their permeability. Barrer et al.^{15,16} found that the diffusional permeability of gases in filled rubbers decreased with increasing amounts of filler in the elastomer. Generally, all polymers exhibiting low diffusional permeability have in common crystallinity as a structural feature.¹³ The permeability of the crystalline phase of a polymer has been regarded as being almost negligible compared to the permeability of the amorphous phase.¹⁴ In filled rubbers and in crystalline polymers the transport process is by a solution mechanism in the amorphous regions, between crystalline portions or between filler particles. On the other hand, the transport process in the hydrogels is undoubtedly predominantly viscous flow^{6,7} through the pores of the membranes.

It has already been shown^{6,7} that the permeation of water through a hydrogel increases with decreasing concentration of polymer in the gel. Taking into account the amount of filler in a filled hydrogel, the density of polymer molecules in the same volume of filled and unfilled hydrogels is lower in the filled gel; hence the amount of water in relation to the amount of polymer chains is higher in the filled membrane than in the unfilled one. Both membranes have equal water content by weight. Since the formation of pores is controlled primarily by the concentration

of polymer chains, it is logical then that filled hydrogels are more permeable than homogeneous hydrogels. Sergeeva and Lipatov,¹⁷ studying the packing density of molecules in films of polystyrene and poly(methyl methacrylate) filled with short glass fibers, concluded that the behavior of polymers containing large amounts of filler corresponds to the behavior of porous bodies. These authors measured the adsorption of vapors on filled films and found that the adsorption becomes higher with increasing filler content, indicating less dense packing of the molecules. These findings are in agreement with ours, in so far as we can also conclude that filled hydrogels behave as very porous bodies, though the order of magnitude of the porosity in both cases is undoubtedly different due to the more compact molecular structure of plastics than gels.

The nature and the structure of the gel, and not only its water content, also have a strong influence on its permeability. For example, it has been found⁷ that a polyelectrolyte complex membrane has a higher permeability to water than acrylic hydrogels with the same water content. The effects of fillers in any polymer are complex, and the number of variables involved in each case is multiple. It is evident that SiO₂ fillers affect the structure of the hydrogels in such a way as to increase their permeability. In a heterogeneous hydrogel, both its water content as well as the amount of filler contribute to increased water permeation. Higher water content combined with higher amount of filler would produce a membrane with the highest permeability. Hence, manipulation of water content and amount and kind of filler should yield membranes with the desired properties.

Whether silica fillers other than the types used in these experiments, as well as any other inorganic or organic fillers, would produce similar results in the hydrophilic membranes is not known. Whether similar effects would be found with other kinds of membranes or other fluids is not known. These are questions which should be answered after further experimentation. Particle size and shape, the condition of particle surface, and the way the polymer is prepared are only some of the many variables involved in the preparation of these heterogeneous membranes.

The author gratefully acknowledges the comments made by Dr. Claes H. Dohlman and Miss Jeannette Rose upon reading the manuscript.

This work was supported in part by U. S. Public Health Service Grants B-2220 and B-3489 from the National Institute of Neurological Diseases and Blindness of the National Institutes of Health, and by the Massachusetts Lions Eye Research Fund, Inc.

References

1. Carnell, P. H., and H. G. Cassidy, *J. Polymer Sci.*, **55**, 233 (1961).
2. Loeb, S., and J. W. McCutchan, *Ind. Eng. Chem., Proc. Res. Develop.*, **4**, No. 2, 114 (1965).
3. Michaels, A. S., *Ind. Eng. Chem.*, **57**, 32 (1965).
4. Graves, D. J., "Water and Ion Flux Through Modified Poly(Ethylene Glycol Monomethacrylate)," M. S. Thesis, Massachusetts Institute of Technology, 1965. See in *Preprints of Papers; J. Colloid Sci.*; papers presented to ACS, Div. of Colloid and Surface Chem.; 39th National Colloid Symposium, Potsdam, N. Y., June, 1965; R. F. Baddour, D. J. Graves, and W. R. Vieth, p. 527.

5. Mauro, A., *Science*, **126**, 252 (1957).
6. White, M. L., *J. Phys. Chem.*, **64**, 1563 (1960).
7. Refojo, M. F., *J. Appl. Polymer Sci.*, **9**, 3417 (1965).
8. Wichterle, O., and D. Lim, *Nature*, **185**, 117 (1960).
9. Refojo, M. F., *J. Appl. Polymer Sci.*, **9**, 3161 (1965).
10. Refojo, M. F., and H. Yasuda, *J. Appl. Polymer Sci.*, **9**, 2425 (1965).
11. Hedbys, B. O., and S. Mishima, *Exptl. Eye Res.*, **1**, 262 (1962).
12. Madras, S., R. L. McIntosh, and S. G. Mason, *Can. J. Res.*, **27B**, 764 (1949).
13. Lasoski, S. W., Jr., and W. H. Cobbs, Jr., *J. Polymer Sci.*, **36**, 21 (1959).
14. Klute, C. H., and P. J. Franklin, *J. Polymer Sci.*, **32**, 161 (1958).
15. Barrer, R. M., J. A. Barrie, and M. G. Rogers, *J. Polymer Sci.*, **A1**, 2565 (1963).
16. Barrer, R. M., J. A. Barrie, and N. K. Raman, *Polymer*, **3**, 605 (1962).
17. Sergeeva, L. M., and Y. S. Lipatov, *Kolloid. Zh.*, **27**, 435 (1965).

Résumé

La perméation de l'eau à travers du méthacrylate de glycéryle (le méthacrylate de 2,3-dihydroxypropyle) et le méthacrylate de 2-hydroxyéthyle sous forme d'hydrogel est accrue par l'incorporation de charges à base de silice. La quantité d'eau à l'équilibre et la quantité de charge au sein du gel contribuent toutes deux à accroître la perméabilité de ces membranes.

Zusammenfassung

Die Permeation von Wasser durch Glycerylmethacrylat-(2,3-Dihydroxypropylmethacrylat) und 2-Hydroxyäthylmethacrylathydrogele wurde durch den Einbau von Kieselsäurefüllstoffen erhöht. Sowohl die Wassermenge beim Gleichgewicht, als auch die Füllstoffmenge im Gel tragen zur Erhöhung der Permeabilität dieser Membrane bei.

Received September 29, 1965

Prod. No. 1298