

Preparation of Porous Membranes

B. G. HARPER

Organic Basic Research Laboratory, The Dow Chemical Co., Freeport, Texas

INTRODUCTION

The fact that one gas will pass through a nonporous plastic membrane more rapidly than another has been known since 1831¹ and has been the foundation for much experimentation. Graham proposed in 1886² that this permeation was due to solution, diffusion, and re-evaporation of the gas. Any separation of gases resulting from passing them through a nonporous membrane is therefore due to a difference in their solubility and diffusion coefficients.

These separations and their industrial importance have been discussed at length by Kammermeyer and Brubaker,³⁻⁵ Barrer^{6,7} and Jost.⁸ Weller and Steiner⁹⁻¹¹ have patented processes based on these principles. This method of gas separation, in its present state of development, is not of industrial importance, at least as far as large scale separation is concerned. The reason for this is that even though the selectivity in many cases is quite high, the permeability of the nonporous membranes is too low. This necessitates the use of high pressure differentials and/or tremendous surface areas to separate appreciable quantities of gases.

Diffusion through porous barriers is also the subject of many studies. If the pore size of a porous barrier is large compared to the molecular diameters of the molecules diffused through it, but small compared to the mean free path of the molecule, then any separation that occurs will be due to the difference in the speed of translation of the molecules. This speed, according to the kinetic theory, is inversely proportional to the square root of the molecular weight of the diffusing materials. The separation that results will be in the ratio of $(M_1/M_2)^{1/2}$, and this seriously limits the use of porous barriers in industrial separations even though their permeability is much greater than the nonporous materials.

Because of the factors limiting the use of known porous and nonporous membranes, it would be desirable to have thin membranes with very small pores such that the molecular weight differences

of the diffusing molecules would not be a controlling limit. It would be more desirable if these pores were of molecular dimensions and the size of the diffusing molecules became a controlling factor, as in the Linde Molecular Sieve.

A method for preparing membranes with finer and more minute pathways for physical transmission is described in this paper. This method involves dissolving two or more polymers in a common solvent, spreading a thin layer of the solution on a smooth surface allowing the solvent to evaporate, and finally extracting one of the polymers with a selective solvent.

EXPERIMENTAL

Nonporous Ethyl Cellulose Film

Shredded ethyl cellulose was added to warm chloroform until a 4.5 wt.-% solution was obtained. The solution was allowed to cool. A thin layer of this solution was spread on a glass plate and the chloroform was allowed to evaporate for several hours, leaving a thin film of ethyl cellulose.

Porous Ethyl Cellulose Film

Shredded ethyl cellulose was added to warm chloroform until a solution containing approximately 4.5 wt.-% ethyl cellulose was obtained. The solution was allowed to cool and to it was added enough Polyglycol E-4000 to make a 4.5 wt.-% solution of both ethyl cellulose and Polyglycol E-4000. A thin layer of the solution was spread on a glass plate and the chloroform was allowed to evaporate for several hours. The resulting film was approximately 50% ethyl cellulose and 50% Polyglycol E-4000. The glass plate with the film on it was then placed in an ice-water bath and the Polyglycol E-4000 extracted from the ethyl cellulose. Thirty-six hours was allowed for this extraction. This time was established by isolating the polyglycol from the water periodically and weighing it. The film was then set aside to dry. Some of the films prepared in this manner were

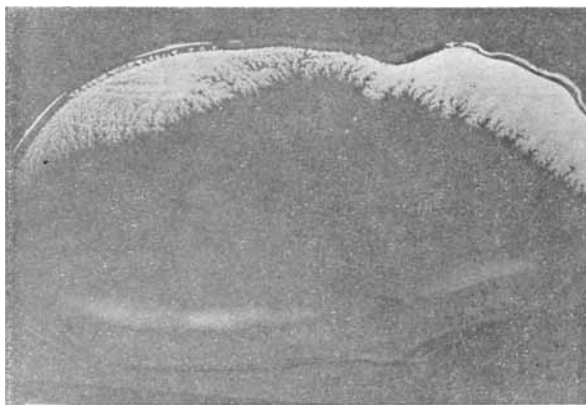


Fig. 2. Polyethylene glycol E-4000 crystallizing in ethyl cellulose as chloroform evaporates, 4X.

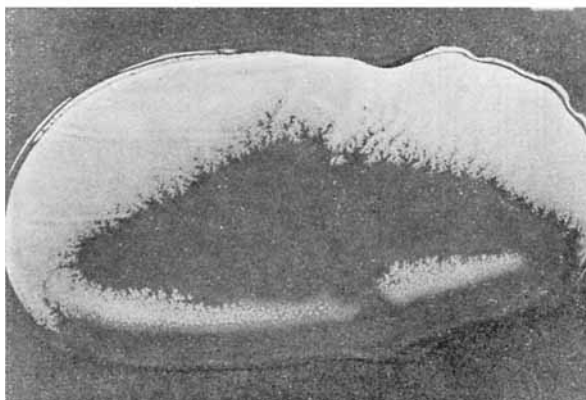


Fig. 3. Polyethylene glycol E-4000 crystallizing in ethyl cellulose as chloroform evaporates, 4X. Fig. 2 + 40 sec.

To check the apparatus, the permeability of polyethylene was measured and found to agree with the literature⁴ as follows: $P = 0.63 \times 10^{-9}$ at 23°C. as compared to $P = 0.79 \times 10^{-9}$ to 1.42×10^{-9} at 25°C. depending on the type polyethylene used.

EXPERIMENTAL MATERIALS

The hydrogen and carbon dioxide gas used were obtained from Matheson and had a purity of 99.8%. Both were designated as anhydrous and neither was further purified before use.

Chloroform: Eastman spectro-grade.

Polyethylene film: The Dow Chemical Company.

Polyglycols: The polyethylene glycol and polypropylene glycol used in this investigation are products of The Dow Chemical Company.

Ethyl cellulose: The Dow Chemical Company.

Tri and Tetranitrocellulose: Mallinckrodt Collodion.

DISCUSSION

Preparation of Porous Membranes

Nitrocellulose films were prepared and investigated briefly. This was done as a preliminary

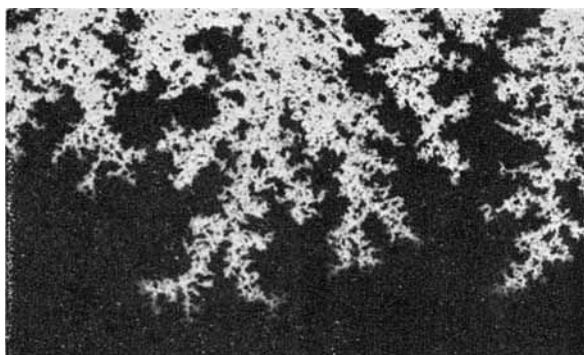


Fig. 4. Polyethylene glycol E-4000 crystallizing in ethyl cellulose as chloroform evaporates, 15X.

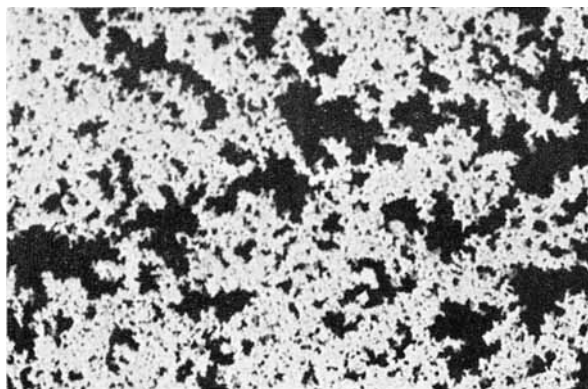


Fig. 5. Polyethylene glycol E-4000 crystallizing in ethyl cellulose as chloroform evaporates, 15X.

experiment to see if diffusion rates could be changed appreciably by extracting one polymer from another. The first film was prepared by spreading a thin layer of collodion solution on a glass plate and then allowing the solvent to evaporate, leaving a thin film of nitrocellulose. The second film was prepared by dissolving a long chain, water-soluble polymer in the collodion, evaporating the solvent and extracting the second polymer with water. The water soluble polymer was polypropylene glycol P-1200. The permeability of these films was determined and found to differ appreciably. Because collodion is a solution prepared elsewhere and the composition is not accurately known to us, and because the effect of the plasticizer is not known, it was decided to thoroughly investigate another similar system.

The mutual solubility of ethyl cellulose and polyglycols in organic solvents and their vastly different solubilities in water made these polymers seem a good pair to study. Several modified ethyl cellulose films were prepared before deciding to investigate films prepared from a chloroform solution of Polyglycol E-4000 and ethyl cellulose. This decision was made because of the appearance of the

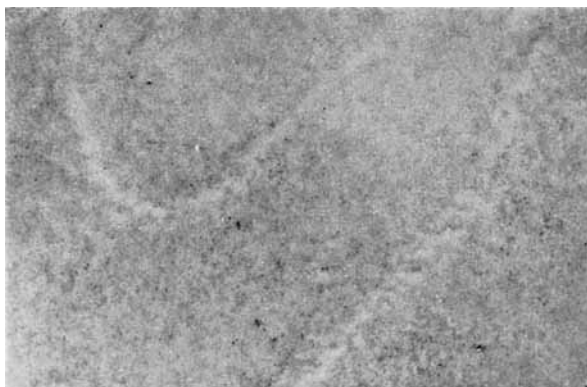


Fig. 6. Polyethylene glycol E-4000 crystallizing in ethyl cellulose as chloroform evaporates, 15 \times .

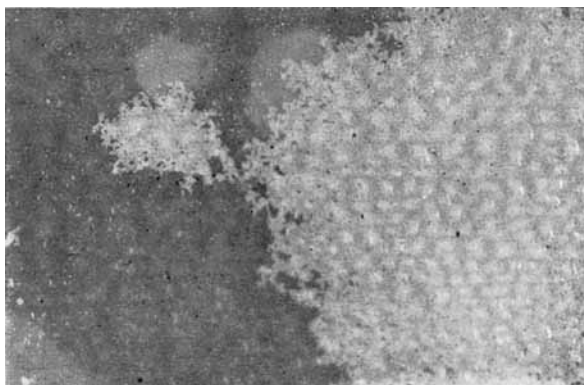


Fig. 7. Formation of small pores as water evaporates from vacancies left by Polyglycol E-4000, 15 \times .

film at the different stages in its preparation. The procedure used was as follows:

1. Ethyl cellulose sheet, with no treatment, was investigated first for the sake of comparison.
2. A film was investigated that was prepared from a chloroform solution of ethyl cellulose alone. This was done to see if the chloroform would affect the permeability of the ethyl cellulose.
3. Films were investigated that had been prepared from chloroform solutions of ethyl cellulose and Polyglycol E-4000; and the results compared with those obtained from 1 and 2. These films were prepared as follows:

Ethyl cellulose and Polyglycol E-4000 was dissolved in chloroform until a 4 $\frac{1}{2}$ wt.-% solution of each was obtained. A thin layer of this solution was spread on a glass plate and the chloroform was allowed to evaporate for several hours, leaving a thin film. During this evaporation tiny white rivulets appeared and ran through the film until it was white. Figures 2 and 3 show consecutive pictures of this occurrence at 4 \times magnification. The time lapse between these two pictures is approximately 40 seconds. Figures 4, 5, and 6 are similar pictures taken at 15 \times magnification. The Polyglycol E-4000 was then extracted in an ice-water bath. Cold water was used since the solubility of polyglycol in water is greater at ice-water temperatures than at room temperature. The film, after the polyglycol had been extracted, was light gray in color. As the film dries in air the tiny white rivulets again appear and run through the film until it is white. Figure 7 shows these tiny rivulets

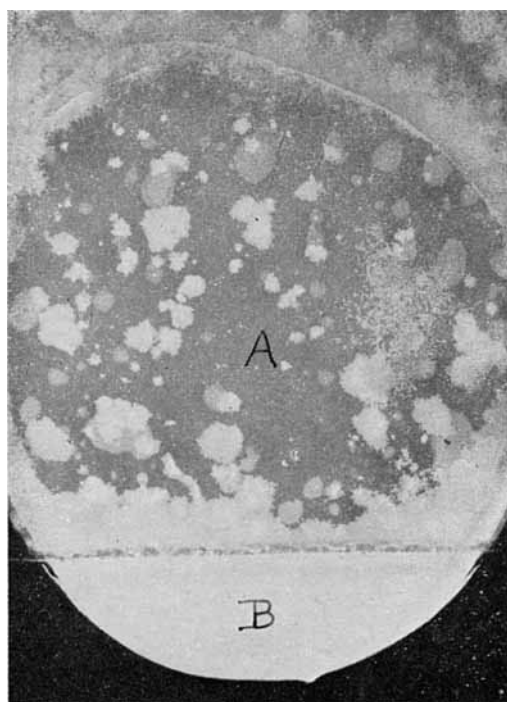


Fig. 8. Photograph illustrating how evaporation of water from small pores can be stopped with a glass plate.

as they are forming at 15 \times magnification. This process may be stopped by covering the film with a glass plate. The glass plate will not allow the water to evaporate from the tiny pores. This is illustrated in Figure 8. The evaporation was stopped in area A and allowed to continue in area B. Some of the films were stretched over an embroidery hoop to dry to see if this would change the pores.

EXPERIMENTAL RESULTS

The permeability results are reported in terms of the permeability constant which is defined as the number of standard cubic centimeters (0°C., one atmosphere pressure) of gas passing through one square centimeter of film, one centimeter thick, per second, per centimeter of mercury partial pressure difference across the film.

The permeability constant of each film was determined several times at approximately 10 cm. Hg pressure differential. These were found to agree to $\pm 10\%$ and their average is given in Table I. Errors resulting from pressure and temperature variations, inaccurate measurements of film area and film thickness, and leaks in the apparatus are believed to be at a minimum.

Electron micrographs of representative films are shown in Figures 9 and 10. Figure 9 shows the surface of untreated ethyl cellulose film. Figure 10 shows the surface of a film that has been treated as described. Both were taken at 30,812 diameters and both are oblique SiO replicas.

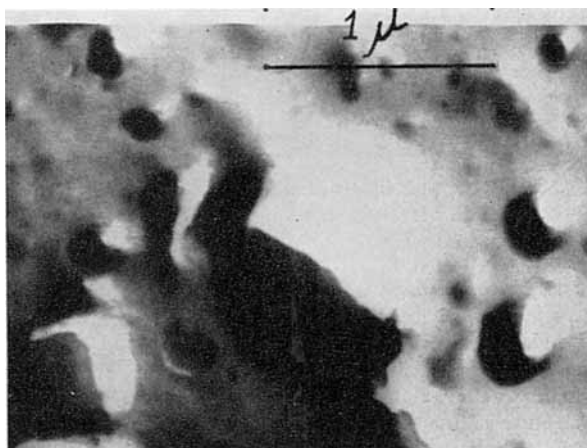


Fig. 9. Electron micrograph of untreated ethyl cellulose film.

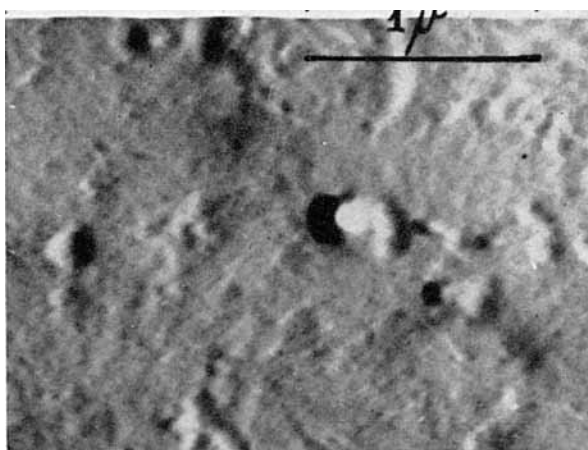


Fig. 10. Electron micrograph of ethyl cellulose film after Polyglycol E-4000 has been extracted with water and the film has been allowed to dry.

These experiments show that CO_2 will pass through ethyl cellulose approximately 1.5 times as fast as hydrogen if the ethyl cellulose is untreated. They further show that film from which Polyglycol E-4000 has been extracted allows hydrogen to pass

TABLE I

Film	Gas	Permeability constant $\times 10^8$
A. Ethyl cellulose	H_2	1.06
B. Ethyl cellulose film prepared from chloroform solution as described in Example 2	CO_2	1.78
C. Ethyl cellulose film from which polyglycol has been extracted. Prepared as described in Example 3	H_2	1.27
	CO_2	2.30
D. Ethyl cellulose film prepared as described in Example 3, but stretched while drying	H_2	1.47
	CO_2	2.83

more rapidly than the untreated ethyl cellulose by a factor of approximately 5, but will allow CO_2 to pass at only a slightly increased rate. It is evident from the data that this is true for the films that are not stretched while drying. Films that were stretched show much less change in permeability.

CONCLUSIONS

The data in Table I, along with the electron micrographs, indicate that a film with extremely small pores was prepared by this process. A summary of the evidence supporting this idea is as follows:

1. When films are prepared from a solution of ethyl cellulose and Polyglycol E-4000 in chloroform, small white dots appear and send out fine runners or rivulets as the solvent evaporates. This would indicate that one of the polymers is crystallizing in the other. Since Polyglycol E-4000 will crystallize, it is believed to be crystallizing in ethyl cellulose. This crystallization continues until the film is entirely white.

2. When this white film is placed in water it becomes grey and much more transparent. This is probably due to the E-4000 being dissolved in water.

Before water extraction the films cannot be taken from the glass plate in one piece if they contain more than 30 wt.-% E-4000. After extraction they come loose of their own accord. The water solution (after extraction) when evaporated to dryness leaves Polyglycol E-4000 in quantities approximately equal to the amount added.

3. When films are taken from the water the excess water is wiped from their surface. They are still gray but within minutes the white points and runners again appear and continue until the film is again white. This would indicate that water is evaporating from the tiny pores left by the extracted Polyglycol E-4000. This happens whether or not the film is stretched while drying.

4. The selectivity of the ethyl cellulose is reversed and the permeability is increased by this treatment. This would be expected if holes or pores were present, because now the relative rates of diffusion are due to a difference in molecular weight, whereas before they were due to a difference in solubility and diffusion coefficients. Of course the differences in solubility and diffusion coefficients will still affect the process to a certain degree since the materials will be in the film by solution as well as in the pores.

The electron micrograph in Figure 10 shows the pores at the surface of the film to be up to about

0.75 microns. The fact that the rate of hydrogen diffusion increased so much while the CO₂ diffusion rate increased only slightly with the treatment indicates that the pores within the film are much smaller.

The fact that the diffusion through the stretched film is changed only slightly over the untreated film would suggest that these tiny pores are closed by the stretching.

This work shows that the permeability and selectivity can be appreciably influenced by this treatment. This influence can likely be varied by correctly choosing the base polymer, polymer to be extracted, the common solvent, and the selective solvent. For instance, the pore size could possibly be varied so that the resulting films would be tailor-made for a given separation.

To speculate a little, films might be prepared which have functional groups exposed along their pore walls. These would possibly attract one type of molecule considerably more than another. It is not unreasonable to conclude that films with these properties could become useful in osmosis or dialysis. They might also be useful in chromatography and ion exclusion.

Thanks are due to J. H. Brown, Jr., and J. C. Moore for their many helpful suggestions and advice.

References

1. Mitchell, J. W., *J. Roy. Inst.*, **2**, 101, 307 (1831).
2. Graham, T., *Phil. Mag.*, **32**, 401 (1866).
3. Brubaker, D. W., and Kammermeyer, Karl, *Ind. Eng. Chem.*, **44**, 1465 (1952).
4. Brubaker, D. W., and Kammermeyer, Karl, *Ind. Eng. Chem.*, **45**, 1148 (1953).
5. Brubaker, D. W., and Kammermeyer, Karl, *Chem. Eng. Prog.*, **50**, 560 (1954).
6. Barrer, R. M., *Diffusion in and Through Solids*, Cambridge Press, London, 1951.
7. Barrer, R. M., *Trans. Faraday Soc.*, **35**, 628, 644 (1939).
8. Jost, W., *Diffusion in Solids, Liquids, and Gases*, Academic Press, New York, 1952.
9. Steiner, W. A., and Weller, S. W., U. S. Patent 2,597,907.
10. Steiner, W. A., and Weller, S. W., U. S. Patent 2,540,151.
11. Steiner, W. A., and Weller, S. W., U. S. Patent 2,540,152.

Synopsis

A new method for preparing plastic membranes with very small pores is described. The method involves dissolving two or more film-forming polymers in a common solvent. A thin layer of the resulting solution is spread on a smooth surface and the solvent is allowed to evaporate. One of the polymers is then extracted from the resulting film with a selective solvent. The selective permeability of ethyl cellulose was altered considerably using polyethylene glycol as the second polymer. The apparatus for determining the permeability of these films is described. Pictures of the membranes at different stages in their preparation are shown. Electron micrographs demonstrating the effect of this treatment on ethyl cellulose are presented.

Résumé

Une nouvelle méthode de préparation de membranes plastiques avec de très petites pores est décrite. La méthode comprend la dissolution de deux films de polymères ou plus dans un solvant commun. Une mince pellicule de la solution résultante est étendue sur une surface lisse et le solvant est évaporé. Un des polymères est alors extrait de ce film avec un solvant sélectif. La perméabilité sélective de l'éthylcellulose est considérablement altérée en utilisant du polyéthylène glycol comme second polymère. L'appareil pour déterminer la perméabilité de ces films est décrit. Des photos de membranes à différentes étapes de préparation sont montrées. Des micrographies électroniques démontrant l'effet de ce traitement sur l'éthylcellulose sont présentées.

Zusammenfassung

Es wird eine neue Methode zur Erzeugung von Membranen aus plastischem Material mit sehr kleinen Poren beschrieben. Zunächst werden zwei oder mehr filmbildende Polymere in einem gemeinsamen Lösungsmittel gelöst. Eine dünne Schicht dieser Lösung wird auf eine glatte Oberfläche aufgebracht, wo die Verdampfung des Lösungsmittels erfolgt. Eines der Polymeren wird dann aus dem entstandenen Film mit einem selektiven Lösungsmittel herausgelöst. Die selektive Durchlässigkeit von Äthylcellulose konnte durch Verwendung von Polyäthylenglykol als zweites Polymeres stark verändert werden. Der Apparat zur Bestimmung der Permeabilität der Filme wird beschrieben. Es werden Bilder der Membranen in verschiedenen Stadien ihrer Darstellung gezeigt. Elektronenmikroskopische Aufnahmen die die Wirkung der Behandlung auf Äthylcellulose anschaulich machen, werden vorgelegt.

Received September 2, 1958