Synthetic Membranes Containing Schardinger Cyclodextrin Additives

CHENG H. LEE,* *International Playtex, Inc., Paramus, New Jersey 07652*

Synopsis

The permeation characteristics of the isomers of such aromatics as dichlorobenzenes, nitrochlorobenzenes, xylenes, etc., through a Methocel HG membrane containing various amounts of Schardinger α-cyclodextrin and β-cyclodextrin additives were measured in liquid/liquid dialysis and pervaporation experiments. The results showed that the cyclodextrins are able to selectively mediate molecular transport through the Methocel HG membranes. In general, increased membrane selectivity and a decrease in permeation rates were observed. Permeation rates for some aromatic compounds were decreased several hundred times with only 25% amounts of additive cyclodextrins in the Methocel HG membranes. Concentration electrical potential and bi-ionic electrical potential in membranes containing the Schardinger cyclodextrin have been measured and also show that the cyclodextrins are able to induce ion transport selectively through nonionic membranes. Dynamic mechanical properties of Methocel HG membranes containing cyclodextrins suggest these additives to be antiplasticizing agents. A mechanism for the modification of the intrinsic membrane permeation properties by cyclodextrin additive involving antiplasticizing action by the additives plus induced tortuous diffusion, where the latter is a result of specific interactions between the cyclodextrin additive and the permeating molecules, is proposed.

INTRODUCTION

Molecular transport in a membrane may be classified into two types—mediated and nonmediated processes.[1] The former process needs a third component to mediate the transport. This process in general occurs in biological membranes in which enzymes and other carriers mediate the transport. Specific interactions between the substrate and the carrier constitute this transport process. No major studies of synthetic polymeric membranes containing carriers or additives to mediate the molecular transport properties have been reported. The purpose of this article is to demonstrate the possible use of additives in membranes for mediating molecular transport.

Schardinger α-cyclodextrin[2,3] is a cyclic compound which has six units of glucose while the β-cyclodextrin isomer has seven units of glucose. These cyclic compounds have a 6 Å inner diameter and a 7 Å channel length. Both α- and β-cyclodextrins could form "inclusion complexes" with many organic compounds and ions which are called guest molecules. The formation constants for inclusion complexes depend primarily on the sizes of the guest molecules.[2,3] For example, the inclusion complex formation constants between cyclodextrin and para aromatic isomers are usually larger than those between cyclodextrin and meta or ortho aromatic isomers.[2,3] Thus, Schardinger cyclodextrins appeared to be good candidates as membrane additives for investigating transport-mediating effects.

* Present address: Rohm and Haas Co., Research Laboratories, Norristown and McKean roads, Spring House, PA 19477.

Journal of Applied Polymer Science, Vol. 26, 489–497 (1981)
 CCC 0021-8995/81/0026-0489$01.00

In this study, synthetic polymeric membranes containing Schardinger cyclodextrins were studied for their related transport characteristics. These included pervaporation, liquid/liquid dialysis, solubility, electrical potential, and dynamic properties. From these measurements, it was shown that Schardinger cyclodextrins as additives indeed do mediate molecular transport in membranes.

EXPERIMENTAL

Materials

Methocel HG (hydroxypropylmethyl cellulose) (viscosity = 50 cps) was obtained from Dow Chemical; Schardinger α-cyclodextrin and Schardinger β-cyclodextrin were purchased from Sigma-Aldrich and were kept in a freezer. All aromatic isomers studied were purchased from Fischer Scientific Co. Polyethersulfone (PSF) polymers were purchased from ICI Co. The acrylonitrile copolymers studied were made in this laboratory.

Membrane Preparation

All membranes of Methocel HG containing Schardinger α-cyclodextrin and Schardinger β-cyclodextrin were cast from aqueous polymer solutions and dried at 100°C. Methocel HG aqueous solution was prepared by dispersing the Methocel HG in hot water and then adding the required amount of ice to dissolve the Methocel HG. For membranes of all other type polymers containing cyclodextrin, they were cast from dimethyl formamide solution. All polymers studied appeared to be compatible with cyclodextrins and gave clear, homogeneous films.

Pervaporation, Dialysis, and Solubility Measurements

Pervaporation, dialysis, and solubility properties of aromatic isomers in polymeric membranes containing cyclodextrin were measured as before.[4a] Composition analysis of aromatic isomers was conducted on a Hewlett–Packard series 5750 gas chromatograph equipped with a thermal conductivity detector.

Bi-Ionic and Concentration Electrical Potential

The measurements of bi-ionic and concentration electrical potential in membranes were as described before.[4b] A Leeds and Northrup potentiometer was used to measure electric potentials.

Dynamic Mechanical Properties

The dynamic mechanical properties of polymeric membranes were measured in air on an automated Rheovibron instrument. The frequency used was 11 Hz and the temperature of the sample was raised at a rate of 1°C/min.

RESULTS

Pervaporation

The results of pervaporation of some aromatic compounds through Methocel HG membranes with various amounts of Schardinger cyclodextrins are shown in Table I. The following trends are indicated.

(1) Both α- and β-cyclodextrin additives in Methocel HG membrane decrease the permeation rates of aromatic compounds. The degree of decrease of the permeation rate depends on the amount of cyclodextrin and the system of permeating molecules. With only 25% α-cyclodextrin additive, permeation rates for benzene and dichlorobenzene are reduced by about 500 and 200 times, respectively. The decrease of permeation rate appears also to be directly related to the amounts of cyclodextrin, and β-cyclodextrin is more effective in reducing permeation rates than α-cyclodextrin.

(2) Both α- and β-cyclodextrin additives increase the membrane selectivity properties for aromatic isomers. In all cases studied, para isomers transport faster than meta isomers, and meta isomers transport faster than ortho isomers. The highest separation factors for para/meta and para/ortho isomers of dichlorobenzene, nitrochlorobenzene, and nitrotoluene are all approximately 3.2 and 2, respectively, for the Methocel HG membrane containing 25% α-cyclodextrin. β-cyclodextrin is slightly less effective in increasing the selectivity properties of membranes than α-cyclodextrin.

TABLE I
Pervaporation of Some Organic Compounds through Hydroxypropyl Methylcellulose Membranes with Various Amounts of Schardinger Cyclodextrin

Feed[a]	% Cyclodextrin[b] in membrane	Temp., °C	Rate[c] (gm/cm² hr)	SF_o^p[d]	SF_m^p[e]
Benzene	0%α	70	1.22×10^{-2}	—	—
Benzene	5%α	70	2.27×10^{-3}	—	—
Benzene	10%α	70	2.7×10^{-4}	—	—
Benzene	25%α	70	5.5×10^{-5}	—	—
DCB(P/M/O = 1:0:1)	0%α	72	6.8×10^{-3}	2.1	—
DCB(P/M/O = 1:0:1)	15%α	72	1.18×10^{-3}	2.2	—
DCB(P/M/O = 1:0:1)	25%α	72	3.6×10^{-5}	3.24	—
DCB(P/M/O = 1:0:1)	30%α	72	3×10^{-5}	3.15	—
DCB(P/M/O = 1:0:1)	30%α	85	1.3×10^{-4}	2.5	—
DCB(P/M/O = 1:0:1)	5.7%β	72	8.8×10^{-4}	2.1	—
DCB(P/M/O = 1:0:1)	16%β	72	1.2×10^{-4}	2.3	—
DCB(P/M/O = 1:0:1)	29%β	72	1×10^{-5}	3.0	—
DCB(P/M/O = 1:1:1)	25%α	62	5.6×10^{-6}	3.23	1.83
DCB(P/M/O = 1:1:1)	25%α	52	4.5×10^{-6}	3.51	2.06
NCB(P/M/O = 1:0:1)	25%α	62	1.5×10^{-5}	3.06	—
NCB(P/M/O = 1:0:1)	25%α	52	3.6×10^{-6}	3.0	—
NCB(P/M/O = 55/40/5)	25%α	72	3.6×10^{-6}	3.66	1.7–1.8
NT(P/M/O = 1:1:1)	25%α	72	4×10^{-6}	2.62	1.5
NT(P/M/O = 1:1:1)	25%α	65	4.8×10^{-6}	3.0	2.0
Xylene(P/M/O = 1:1:1)	25%α	72	2×10^{-4}	1.8–2.0	1.5

[a] DCB = dichlorobenzene, P = para, M = meta, O = ortho, NCB = nitrochlorobenzene, NT = nitrotoluene.

[b] Weight %.

[c] Rate refers to 1-mil thick membrane.

[d] SF_o^p = separation factor between para and ortho isomers.

[e] SF_m^p = separation factor between para and meta isomers.

(3) The effect of temperature on the permeation rates in Methocel HG membranes with or without cyclodextrins in general is similar to other systems reported before.[5,6] Increasing the temperature gives high permeation rates and lower separation factors. The activation energy for transport through Methocel HG with 30% α-cyclodextrin is higher than that without cyclodextrin (35 vs. 12 kcal).

Liquid/Liquid Dialysis

Liquid/liquid dialysis permeation mode is different from liquid/gas permeation.[4a,7] In the case of liquid/liquid dialysis, the membrane is exposed to both dialysis solvent and feed species, while only feed species exist in the membrane in pervaporation. As a result, the permeation properties may be different in dialysis than pervaporation. Table II shows the results for dialysis of dichlorobenzene through Methocel HG membranes with and without dextrin.

The following may be concluded from the data:

(1) Permeation properties in the liquid/liquid dialysis of dichlorobenzene through Methocel HG membranes, with or without α-cyclodextrin additive, depend greatly on the type of solvents employed. Linear hexadecane as dialysis solvent results in higher permeation rates but lower separation factors than the branched (2,2,4,6,6 pentamethyl-heptane) isomer as dialysis solvent. In both cases, permeation rates are higher than those noted in pervaporation.

(2) Where α-cyclodextrin is employed as an additive in the Methocel HG membrane, it decreases permeation rate and increases the time lag in the dialysis of dichlorobenzene. The time lag in liquid/liquid dialysis, in general, is inversely proportioned to the effective diffusion constant.[4a] Thus, the additive α-cyclodextrin in effect decreases the effective diffusion constant for dichlorobenzene as much as ten times.

Effect of α-Cyclodextrin on Solubility of Dichlorobenzene

Table III shows the effects of α-cyclodextrin as an additive on the solubility of para and ortho dichlorobenzenes in the Methocel HG membrane. α-Cyclodextrin is shown to increase the solubility selectivity but decreases the solubility constants for para and ortho dichlorobenzenes in Methocel HG membranes. The highest solubility selectivity for para and ortho dichlorobenzene is the Methocel

TABLE II
Liquid/Liquid Dialysis of Dichlorobenzene Isomers through Methocel HG Membranes with or without α-Cyclodextrin Additive at 72°C

Membrane	Feed	Dialysis solvent	Rate[a] (gm/cm^2 hr)	SF^p_o	SF^p_m	Time lag (hr)
Methocel HG	P/O 1:1	hexadecane	5.4×10^{-3}	1.8	—	1
Methocel HG with 25% α-cyclodextrin		hexadecane	4×10^{-4}	2.3	—	12
Methocel HG	P/O/M 1:1:1	2,2,4,6,6-penta-methyl-heptane	1.7×10^{-4}	3.3	2.0	—

[a] Rate refers to 1-mil thick film.

TABLE III
Solubility of Para/Ortho Dichlorobenzene (50/50 by Weight) in Hydroxypropyl-Methyl Cellulose Membrane with Various Amounts of α-Cyclodextrin

α-Cyclodextrin, %	Solubility,[a] %	K_o^p [b]
0	19	0.86
5	19	0.74
15	15	0.85
25	10	1.15
30	12	1.02

[a] Solubility is obtained from ratio of increased weight of membrane, exposed to dichlorobenzene (50/50 by weight) until equilibrium of solution in membrane is reached, to weight of dry membrane. Thus, units are g/g.

[b] K_o^p is ratio of solubility of para dichlorobenzene relative to that of ortho dichlorobenzene in membrane. Calculated from GC analysis of composition of dichlorobenzene in hexadecane solution, obtained by extracting dichlorobenzene in membranes with hexadecane.

HG membrane containing 25% α-cyclodextrin. Thus, the additive α-cyclodextrin in the membrane appears to have the same solubility selectivity for isomers dichlorobenzenes as individual free α-cyclodextrin does.

Membrane Electrical Potential

Two types of electrical potential might occur through the permeation of ions across a membrane: concentration potential and bi-ionic electrical potential.[4b,8] Concentration potential is a measure of the relative affinity and mobility for cations and anions, while bi-ionic potential is a measure of those properties for either different anions or for cations. Thus, membrane electrical potential is one of the methods that can be utilized for the characterization of ionic membranes.

Schardinger α-cyclodextrin can form complexes with many cations.[2] As a result, membranes containing Schardinger cyclodextrin may be ionic membranes. For this reason, some electrical potentials were measured for the membranes containing α-cyclodextrin and the results are shown in Table IV. These results indicate that membranes containing α-cyclodextrin, indeed possess ionic membrane characteristics, and have more affinity for K^+ than for Cl^-. Also the negative value of bi-ionic potential for the pair Na^+/K^+ in copoly(acrylonitrile/4-vinyl pyridine) membrane containing additive α-cyclodextrin indicates

TABLE IV
Electrical Potential in Various Membranes Containing 20% Schardinger α-Cyclodextrin at Room Temperature

Membrane[a]	System	Type of electrical potential	Measured value, mV
AN–4VP	0.01*N* KCl/0.1*N* KCl	concentration	−32.8
AN–4VP	0.1*N* NaCl/0.1*N* KCl	bi-ionic	− 8
PSF[b]	0.01*N* KCl/0.1*N* KCl	concentration	−16

[a] AN–4VP = copolymer(acrylonitrile/4-vinyl pyridine).

[b] PSF = polyether sulfone.

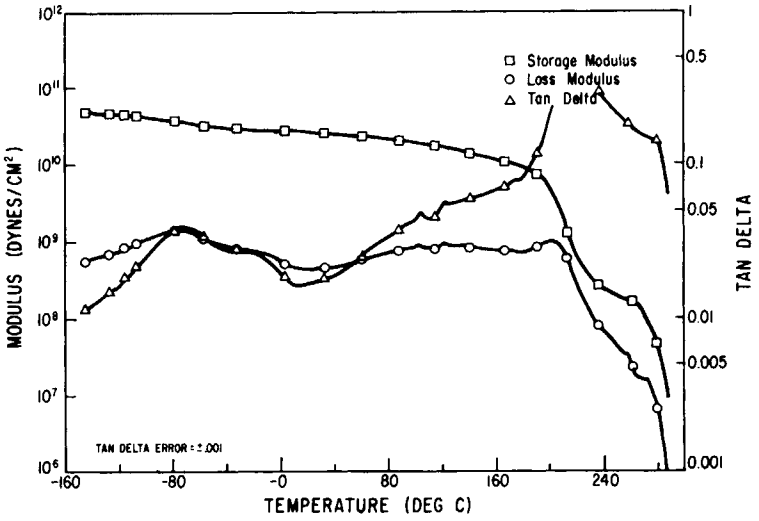

Fig. 1. Plots of Young's storage modulus, loss modulus, and tan Δ vs. temperature for Methocel HG film. □, Storage modulus; ○, loss modulus; △, tan Δ. Tan Δ error ±0.001.

that the additive indeed has induced the membrane to have more affinitive for K^+ than Na^+. These results further indicate that the additive can modify the intrinsic permeation properties of the membrane.

Dynamic Mechanical Properties

The dynamic mechanical properties of Methocel HG membranes with or without cyclodextrines were measured and are presented in Figures 1–3.

These figures indicate that the glass transition temperature for Methocel HG membrane increases from 218.6 to 228 and 231°C, respectively, with the addition

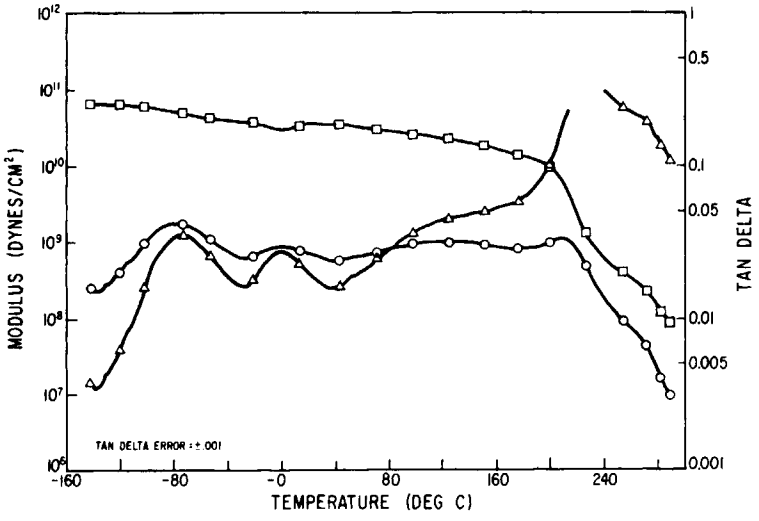

Fig. 2. Plots of Young's storage modulus, loss modulus, and tan Δ vs. temperature for Methocel HG with 25% α-cyclodextrin film. □, Storage modulus; ○, loss modulus; △, tan Δ. Tan Δ error ±0.001.

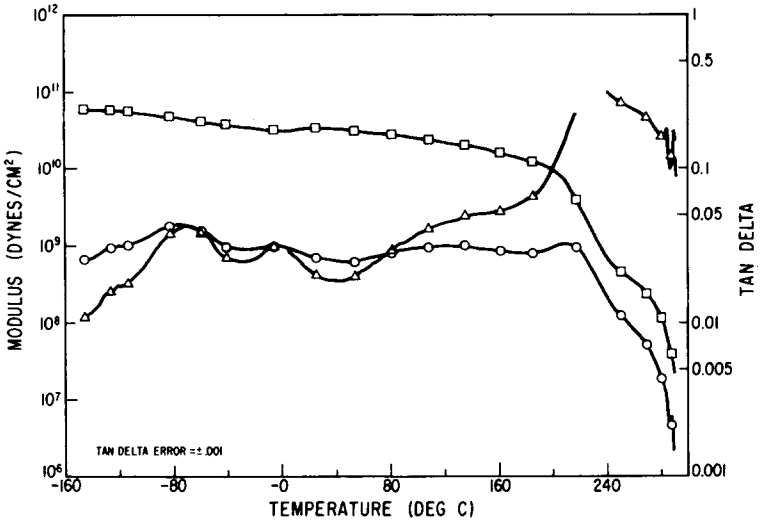

Fig. 3. Plots of Young's storage modulus, loss modulus, and tan Δ vs. temperature for Methocel HG with 25% β-cyclodextrin film. □, Storage modulus; ○, loss modulus; △, tan Δ. Tan Δ error ±0.001.

of 25% of α- and β-cyclodextrin in the membranes. The glassy Young's modulus is slightly increased upon dilution with α- and β-cyclodextrin additives. There is also an enhancement of the secondary transition for Methocel HG at 0°C with the cyclodextrin additives. Thus, both α- and β-cyclodextrin additives are antiplasticizing agents. The enhancement of secondary transition for Methocel HG at 0°C with additives may be the result of hydrogen bonding between Methocel HG and cyclodextrin.

DISCUSSION

Polymeric membranes modified with additives may be homogeneous or heterogeneous depending on the compatibility between the additive and the polymeric membrane. Diffusion and permeation in heterogeneous membranes are well described by Barrer.[10] The major difference between homogeneous membranes and heterogeneous membranes containing additives is that the interaction between the polymer and the additive in homogeneous membranes comes from both individual molecules of the additive and the polymer in the membrane, while in heterogeneous membranes it comes from surface interaction between the additive phase and the polymeric phase. This surface interaction overall is much smaller than it is between individual additive molecules and polymers.

Permeation in heterogeneous membranes can be predicted from the permeation properties in each individual phase.[10] Additives may reduce the free volume and increase the glassy transition temperature and glassy modulus upon dilution; they are commonly referred to as antiplasticizing agents.[10,11] They may also, in the case of homogeneous membranes, interact so strongly with the polymer that the mobility of the polymer may be restricted or enhanced depending on the properties of the additive. These additives tend to have the opposite effect and are called plasticizing agents. On the other hand, permeation

in homogeneous membranes can not be predicted from the permeation properties in each component of the membrane. The additive in the case of homogeneous membranes may interact so strongly with the polymer that the mobility of the polymer may be restricted or enhanced. Additive in the polymeric membrane may induce a barrier for permeation. The barrier may come from individual additive molecules or through cooperative effects of two or more additive molecules aggregating together. Furthermore, the barrier may also come from the induced barrier of those polymer segments near to the additive as a result of reduced segment mobilities due to the strong interactions between additive and polymer. Diffusion in those barriers might be tortuous or nontortuous depending upon the diffusion constants for permeating molecules in additive and polymers. Thus, diffusion and permeation in homogeneous membranes with additives are more difficult to predict than those in heterogeneous membranes.

In the case of Methocel HG membranes containing cyclodextrins, both α- and β-cyclodextrins have been shown to increase the glass transition temperature and glassy modulus upon addition to Methocel HG membranes. Therefore, cyclodextrins act indeed as antiplasticizing agents. However, this antiplasticizing effect cannot fully describe the several-hundred-times decrease in permeation rates for aromatic compounds and the increase in separation properties of the membranes. In fact, Schardinger α-cyclodextrin is a cyclic compound which contains 7Å channel length and 6Å inner diameter. Any permeating molecules which are less than 6Å might be able to diffuse through the channel which is called nontortuous diffusion. On the other hand, molecules which are larger than 6Å may not diffuse through the channels and may diffuse tortuously into the polymeric phase. This "induced tortuous diffusion" results in different "tortuosity diffusion factors" and different transport rates for permeating molecules of different sizes in the membrane. In other words, the increase in separation factor and the decrease in permeation rates for aromatic isomers may be partially due to the mechanism of "induced tortuous diffusion" by the additive cyclodextrins. This mechanism may explain the reasons why we observe the higher separation factor in the dialysis of para and ortho dichlorobenzene using branched hydrocarbons instead of linear hydrocarbons as dialysis solvents, where α-cyclodextrins can complex with linear hydrocarbons, but not with branched hydrocarbons.

Also the different binding constants[2] between various cations and α-cyclodextrin may explain the different values of bi-ionic potentials for various cations.

Thus, the mechanism of modification of membrane permeation properties by the cyclodextrin additives may be the antiplasticizing effect of the additive and various induced tortuous diffusion factors for aromatic isomers and other permeating molecules where the tortuous diffusion is a result of various specific interactions between the additive cyclodextrin and the permeating molecules.

The author's special thanks are due to Eli Perry, Corporate Research Department, Monsanto Co., St. Louis, Missouri, for his guidance. Dr. Erwin Stedronsky is acknowledged for his helpful suggestions. Dr. Allen Kenyon and McClinton Rayford are also acknowledged for their measurements of dynamic mechanical properties of the membranes.

References

1. A. Kotyk, *Biochim. Biophys. Acta,* **300,** 183 (1973).
2. L. Mandelcorn, *Non-Stoichiometric Compounds,* Academic, London, New York, 1964.
3. H. Schlenk and D. M. Sand, *J. Am. Chem. Soc.,* **77,** 3587 (1955).
4. (a) C. H. Lee, *J. Appl. Polym. Sci.,* **19,** 3087 (1975); (b) **21,** 851 (1977).
5. R. E. Kesting, *Synthetic Polymeric Membranes,* McGraw Hill, New York, 1971.
6. S-T Hwang and K. Kammermeyer, *Membranes—In Separations,* Wiley, New York, 1975.
7. C. H. Lee, *J. Appl. Polym. Sci.,* **19,** 83 (1975).
8. F. Helfferich, *Ion Exchange,* McGraw Hill, New York, 1962.
9. R. M. Barrer, *Diffusion in Polymer,* J. Crank and G. S. Park, Eds., Academic, London, New York, 1968.
10. N. Hata, R. Yamauchi, and J. Kumanotau, *J. Appl. Polym. Sci.,* **17,** 2173 (1973).

Received May 22, 1980
Accepted July 25, 1980