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Cheng H. Lee[a]
[a] BASIC RESEARCH DEPARTMENT, INTERNATIONAL PLAYTEX, INC., PARAMUS, NEW JERSEY

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Separation of Liquid through Polymer Membrane. Benzene and Cyclohexane System

CHENG H. LEE

BASIC RESEARCH DEPARTMENT
INTERNATIONAL PLAYTEX, INC.
PARAMUS, NEW JERSEY 07652

Abstract

Separation of benzene–cyclohexane liquid mixture by permeation through Methocel HG (hydroxypropyl–methyl cellulose) membranes was studied using the pervaporation mode. The separation factor and permeation rates for benzene in Methocel HG are found to be strongly dependent upon the concentration of benzene in the benzene–cyclohexane mixtures. The separation factor for benzene versus cyclohexane was found to be at least 200 in the case of benzene–cyclohexane liquid mixtures with a 50/50 weight ratio. Addition of Schardinger α-dextrin into the Methocel HG membrane increases the relative solubility for benzene versus cyclohexane, but decreases the permeation rates and separation factor for the benzene–cyclohexane permeation system. Thus the reverse of separation of benzene–cyclohexane in the Methocel HG membrane was found when the Methocel HG membrane contained more than 25% Schardinger α-dextrin. The mechanism of this drastic effect is explained in terms of induced tortuous diffusion and the reduction of the self-plasticizing effect of benzene in the membrane permeation.

INTRODUCTION

The permeation of gases and liquids through polymer membranes has been the subject of extensive research during the past three decades. In recent years there has been considerable interest in the potential uses of polymer films or membranes for separating mixtures of chemical compounds (*1–3*). The basis of a membrane separation process is the selective permeation of the permeating molecule or permeant through the specific selective membrane. This specific selective membrane, in general, is made of specific synthetic polymers. Tailoring of the chemical and physical structures of synthetic polymers is the main way of making a selective membrane.

The mechanism of liquid permeation via the membrane process may be described in terms of solution-diffusion theory (*4*). The strong interaction between the liquid molecules and the polymer membrane led to various types of diffusion mechanisms. They include (*6*) (1) concentration-independent Fickian diffusion, (2) concentration-dependent Fickian diffusion, (3) time-dependent diffusion anomalies, (4) Case V transport, and (5) solvent crazing stress cracking. Depending upon the activities and temperature, the transport of a liquid in any specific membrane can have various types of diffusion. This kind of complex transport mechanism is different from the concentration-independent diffusion of noncondensable gases in a glassy amorphous polymer membrane (*6*). Separation of benzene–cyclohexane via membranes was studied before (*2*, *3*). However, the separation factor found was not high enough to justify any economical and practical uses.

It is the purpose of this study to demonstrate that the separation of liquid benzene–cyclohexane can be achieved through a highly selective membrane in which the separation factor for benzene versus cyclohexane can be as high as 200 to 1000. This highly selective permeation membrane for the benzene–cyclohexane can be decreased or even reversed by the addition of some specific additives to the membranes.

EXPERIMENTAL

Materials

Methocel HG (hydroxypropylmethyl cellulose) (viscosity = 50 cP) was obtained from Dow Chemical; Schardinger α-cyclodextrin and Schardinger β-cyclodextrin were purchased from Sigma-Aldrich and were kept in a freezer. Benzene and cyclohexane were purchased from Fisher Scientific Co.

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.

Pervaporation and Solubility Measurements

Pervaporation and solubility properties of aromatic benzene and cyclohexane in polymer membranes containing cyclodextrin were measured as before (*5*). Composition analysis of aromatic isomers was conducted on a Hewlett Packard Series 5750 Gas Chromatograph equipped with a thermal conductivity detector.

Liquid Permeation Equations

In the case of concentration independent-type diffusion, liquid permeation through membranes using various permeation modes such as pervaporation, reverse osmosis, and liquid/liquid dialysis has been described previously (*4*). In the case of concentration dependent-type diffusions, many expressions have been proposed to relate the relationship between the diffusion constant and concentration of liquid in the membrane. An equation commonly used is

$$D = \frac{D_0 e^{rc}}{\gamma} \quad (1)$$

where D_0 and r are constant at a given temperature for a specific permeation system. The constant r is a measure of the plasticizing action of liquid on the polymer. γ is the tortuous diffusion factor for permeating molecules. The concentration c is the amount of sorption of liquid in the polymer which is determined from the solubility of the liquid in the polymer. Thus, at a steady state, the permeation rate can be expressed as

$$\theta = \frac{D_0}{\gamma r L}(e^{rc_1} - e^{rc_2}) \quad (2)$$

where L is the thickness of membrane.

In the pervaporation mode, the concentration downstream, c_2, approaches zero. Therefore, Eq. (2) becomes

$$\theta = \frac{D_0}{\gamma r L}(e^{rc_s} - 1) \quad (3)$$

where c_s is the solubility of liquid in the polymer (*1*). The permeability constant for the liquid permeation in this case will become (*1*)

$$P = \frac{D_0}{\gamma r c}(e^{rc_s} - 1) \quad (4)$$

where c is the concentration of permeant in the liquid phase. Since (*1*)

$$c_s = sc \quad (5)$$

therefore

$$P = \frac{D_0}{\gamma rc}(e^{rsc} - 1) \tag{6}$$

if $\gamma \rightarrow 0$, then

$$P = sD_0/\gamma \tag{7}$$

This is the same as for concentration independent-type diffusion.

If there are two components in the liquid mixture, the separation factor for these two components is the ratio of permeability constants. Therefore the separation factor SF will be

$$SF_B{}^A = \frac{P_A}{P_B} \tag{8}$$

or

$$SF_A{}^B = \frac{D_0{}^B}{D_0{}^A}\frac{c_A}{c_B}\frac{\gamma_A r_A}{\gamma_B r_B}\frac{(e^{r_A s_A c_A} - 1)}{(e^{r_B s_B c_B} - 1)} \tag{9}$$

Thus the separation factor will be dependent upon not only the solubility and diffusion constants, but also upon the concentration of the liquid mixture and the relative plasticization constant.

RESULTS

The results of permeation and solubility studies of benzene–cyclohexane liquid mixtures via the Methocel HG membranes with various amounts of Schardinger α-dextrin are shown in Tables 1 and 2. We may summarize them as follows.

(1) Methocel HG membrane (hydroxypropylmethyl) cellulose may be used for the separation of benzene from cyclohexane. Benzene will preferentially permeate through the membrane. The separation factor for benzene versus cyclohexane in the 50/50 benzene–cyclohexane liquid mixture is at least 200. This separation factor also depends upon the composition of benzene–cyclohexane liquid mixtures. The permeation rates for benzene appear to decrease as the composition of cyclohexane increases. Thus the separation factor is decreased as the concentration increases.

(2) Schardinger α-dextrin additive in Methocel HG membrane decreases the permeation rates for benzene but not for cyclohexane. The permeation rate will be reduced proportionately to the amount of Schardinger α-dextrin in the Methocel HG membrane. Therefore the separation factor for benzene versus cyclohexane may be decreased or even reversed in a Methocel HG membrane containing more than 25% Schardinger α-dextrin additive.

TABLE 1

Permeation Properties of Benzene–Cyclohexane Liquid Mixtures via the Methocel HG Membranes with Various Amounts of Schardinger α-Dextrin

% Additive in mebrane	Feed	$P_{benzene}$[a]	$P_{cyclohexane}$[a]	$SF^{benzene}_{cyclohexane}$[b]
0	Benzene	3.1×10^{-5}	—	—
0	Cyclohexane	—	9.6×10^{-11}	—
0	Benzene–cyclohexane[a]	1.6×10^{-6}	$\sim 10^{-9}$	>200
5	Benzene	4.6×10^{-6}	—	—
5	Benzene–cyclohexane[a]	2×10^{-7}	3×10^{-9}	~60
10	Benzene	7×10^{-7}	—	—
10	Benzene–cyclohexane[a]	1.3×10^{-8}	5×10^{-9}	2.5
25	Benzene	2.5×10^{-7}	—	—
25	Benzene–cyclohexane[a]	1.5×10^{-9}	1.5×10^{-9}	1.0

[a]Benzene/cyclohexane composition is 50/50 by weight. $P_{benzene}$ or $P_{cyclohexane}$ is the permeability constant.

[b]$SF^{benzene}_{cyclohexane}$ is the measured separation factor between benzene and cyclohexane.

TABLE 2

Solubility of Benzene–Cyclohexane (50/50 by wt) in Methocel HG Membrane with Various Amounts of α-Dextrin (at 72°C)

% α-Dextrin	K_C^B	%
0	4.9	13
5	6.0	14
10	7.5	13
25	15.0	13

(3) Schardinger α-dextrin additive in Methocel HG membrane, on the other hand, decreases the solubility in the membrane for cyclohexane but not for benzene. The relative solubility ratio for benzene versus cyclohexane increases with the addition of Schardinger α-dextrin in the membrane.

DISCUSSION

The basis of the separation mechanism for benzene–cyclohexane via the Methocel HG membrane is primarily due to the difference of diffusion constants of benzene and cyclohexane. The large difference of diffusion constants between benzene and cyclohexane cannot be completely due to the difference of sizes of these molecules. It may be due to the difference of plasticization constants as indicated in Eq. (1). This can be further demonstrated by the *dependence* of the benzene permeation equation on the concentration of benzene in the

Permeation rates for benzene increase as the concentrations of benzene in the benzene–cyclohexane mixture increase. Addition of Schardinger α-dextrin may reduce the mobility of the Methocel HG polymer segment. Therefore Schardinger α-dextrin reduces the membrane permeability rates. Further, the additive may block the diffusion of permeant and therefore induce the so-called tortuous diffusion. It is known (*7*, *8*) that Schardinger α-cyclodextrin is a cyclic compound which has 7 Å channel length and 6 Å inner diameter. Any permeating molecules which are less than 6 Å inner diameter might be able to diffuse through the channel of α-cyclodextrin and may diffuse tortuously into the polymeric phase. This "induced tortuous diffusion" results in different tortuous diffusion factors. Thus it is possible that the various tortuous diffusion factors for benzene and cyclohexane may result in a decrease of the separation factor of benzene versus cyclohexane in Methocel HG containing Schardinger dextrin additives.

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Note Added in Proof. The author's present address is Rohm and Haas Co., 727 Norristown Rd., Spring House, Pennsylvania 19477.