

## Separation of Liquid Mixtures by Using Polymer Membranes. II. Permeation of Aqueous Alcohol Solutions Through Cellophane and Poly(vinyl Alcohol)

ROBERT Y. M. HUANG and NEIL R. JARVIS,  
*Department of Chemical Engineering, University of Waterloo, Waterloo,  
Ontario, Canada*

### Synopsis

The permeation and separation characteristics of four different alcohol-water systems through cellophane and poly(vinyl alcohol) membranes were investigated. The homologous series of linear alcohols *n*-propanol, ethanol, and methanol as well as isopropanol were studied. A specially designed permeation cell was used to study permeation rates at temperatures ranging from 30° to 50°C. The dependency of both permeation and separation on the molecular size and shape of the permeating species was discussed qualitatively. The temperature dependence of the permeation rate for both pure compounds and binary mixtures was expressed by Arrhenius-type relationships. The rate was found to increase with increasing temperature while the separation decreased. Activation energies of 4-9 kcal/mole were calculated for alcohol-water solutions through cellophane, and of 8-15 kcal/mole through poly(vinyl alcohol). Departure of permeation rates from the ideal rates were discussed in terms of permeation "enhancement" or "depression." These phenomena were explained in terms of both the plasticizing action of water and the "clustering" of water molecules within the polymer network.

### INTRODUCTION

The present series of investigations is concerned with the separation of liquid mixtures using polymer membranes. In the previous paper in this series,<sup>1</sup> the phenomenological basis for membrane permeation and separation was discussed in some detail. Briefly, membrane permeation was said to consist of dissolution of the liquid into the membrane, transport through the membrane by an activated diffusion mechanism, and evaporation from the downstream surface. Separation of liquid mixtures is thus caused by the different solubilities and/or diffusivities of the permeants in the film. In the first paper, studies on the permeation of a series of organic liquids through low-density polyethylene were reported. The liquids were members of the homologous series of liquid aliphatic hydrocarbons between *n*-pentane and *n*-nonane as well as some aromatic and cyclic compounds.

In recent years, considerable interest has been shown in the separation of water-based mixtures, especially in biological, desalination, and water

pollution fields. This paper is an attempt to establish some of the qualitative characteristics of aqueous systems permeating through hydrophilic-type membranes, in particular, cellophane and poly(vinyl alcohol).

Heisler et al.<sup>2</sup> have investigated the selective permeation of water-ethanol solutions through cellophane membranes. Separation factors were reported to increase dramatically when water-soluble, ethanol-insoluble additives were added to the permeating mixture. Schrodt et al.<sup>3</sup> conducted membrane separation experiments for several organic liquid pairs with a number of films, including cellophane and poly(vinyl alcohol). It was shown that close boiling mixtures could be effectively separated by using polymer membranes. Sweeny and Rose<sup>4</sup> studied the effect of molecular size and the chemical nature of the permeant as well as the effect of membrane structure on the permeation of liquid mixtures. They concluded that binary liquid mixtures of different polarity were selectively permeated and that the component whose polarity most closely matched that of the membrane was preferentially permeated. Kuznetsov and Malysov<sup>5,6</sup> reported that pretreatment of cellophane film by boiling in water increased the permeability and decreased the selectivity for a series of water-alcohol solutions. Carter and Jagannadhaswamy<sup>7</sup> investigated the separation of water-alcohol mixtures using a cellophane membrane. They suggested that selective permeation of a liquid mixture involved both preferential absorption at the upstream surface of the membrane and differing rates of transport through the film. They also discussed the effect of film swelling and water-cellophane hydrogen bonding on separation efficiency. Peters<sup>8</sup> postulated the existence of extensive solvated shells around the polymer molecules for the permeation of water-sugar solutions through swollen poly(vinyl alcohol) membranes. Kaufmann and Leonard's investigation<sup>9</sup> of the intramembrane transport properties of sugar-water solutions in cellophane revealed the importance of solute-polymer interactions.

It is the purpose of this study to investigate the permeation and separation characteristics of aqueous alcohol solutions through selected hydrophilic polymer membranes, namely, cellophane and poly(vinyl alcohol). The alcohols that were studied are *n*-propanol, ethanol, methanol, and isopropanol. Factors affecting these characteristics, such as the physicochemical nature of the permeants, polymer morphology, permeant-polymer interactions, and temperature, will be discussed.

## THEORY

### Pure Liquid Permeation

The permeation rate of a liquid through a polymer membrane depends on both the solubility and diffusivity of the liquid in the polymer. The steady state permeation rate may be described by Fick's first law of diffusion,

$$q_A = -D_e \frac{dC_A}{dx} \quad (1)$$

where  $q_A$  is the permeation rate of component A,  $D_c$  is a concentration-dependent diffusivity, and  $\frac{dC_A}{dx}$  is the concentration gradient across the membrane.

Integrating with proper conditions gives

$$q_A \int_0^L dx = - \int_{C_{A_1}}^{C_{A_2}} D_c dc \quad (2)$$

where  $L$  is the membrane thickness, and  $C_{A_1}$  and  $C_{A_2}$  are the concentrations of permeant A in the polymer at the upstream and downstream surfaces, respectively. If the downstream side of the membrane is maintained at a high vacuum,  $C_{A_2}$  is essentially zero.  $C_{A_1}$  can be determined by equilibrium sorption of liquid in the polymer, and the steady state permeation rate of component A can be expressed as

$$q_A = \frac{1}{L} \int_0^{C_s} D_c dc \quad (3)$$

where  $C_s$  is the solubility of liquid in the polymer. This equation shows that the permeation rate of a liquid depends not only on its diffusivity but also on its solubility in the membrane.

For the permeation of aqueous solutions through hydrophilic membranes such as cellophane and poly(vinyl alcohol), the diffusion coefficient may become a function of permeant concentration in the polymer. This is due to the plasticizing effect of water as well as the possible formation of water clusters within the polymer structure. Water acts as a plasticizer to loosen and swell the polymer structure, allowing the polymer segments to move more freely about the polymer backbone. As the amorphous portion of the polymer swells, a greater percentage of the total polymer volume becomes available for diffusion. Thus, an increase in water concentration may decrease the activation energy for diffusion and increase the diffusion rate.

In fact, one empirical equation<sup>11</sup> relates the diffusion coefficient to an exponential function of permeant concentration,

$$D_c = D_0 e^{\alpha c} \quad (4)$$

where  $D_0$  is a diffusivity defined for zero permeant concentration in the polymer, and  $\alpha$  is the plasticizing effect of a permeant-polymer pair.

Rouse<sup>11</sup> and Barrer and Barrie<sup>12</sup> have reported that the diffusion coefficient can decrease with increasing concentration. This phenomenon has been ascribed to the mutual association of water molecules to form "clusters." These clusters, once formed, do not appear to take part in the diffusion process.<sup>13</sup> Their immobility is attributed to the relative difficulty in making a diffusive jump as compared to isolated water molecules.<sup>14</sup> Thus, as the water concentration in a polymer increases, a significant number of diffusing molecules will be immobilized in the form of clusters. As a result, the rate of diffusion can be expected to decrease.

Polymer morphology also has a pronounced effect on permeation characteristics. Only the amorphous regions in the polymer take part in the transport process. Therefore, any changes affecting either the degree of crystallinity or the crystalline arrangement within the polymer can be expected to alter the membrane's permeation and separation characteristics.

### Binary Liquid Permeation

The selective permeation of a binary liquid solution A and B can be expressed in terms of a separation factor,  $\alpha_{A/B}$ , which is a measure of the preferential permeation of component A. The factor  $\alpha_{A/B}$  is defined as the concentration ratio A/B in the product (permeate) divided by the concentration ratio A/B in the feed (permeant), as follows:

$$\alpha_{A/B} = \left( \frac{y_A}{y_B} \right) / \left( \frac{x_A}{x_B} \right) \quad (5)$$

where  $y_A$  is the weight fraction of A in the permeate,  $x_A$  is the weight fraction of A in the permeant, etc.

If the permeation rate is ideal, the component rates in the mixture can be expressed in terms of the pure component permeation rates as

$$q_A^0 = x_A q_A \quad (6)$$

$$q_B^0 = x_B q_B \quad (7)$$

where  $q_A$  and  $q_B$  are the pure component permeation rates of A and B, respectively, and the superscript zero refers to the ideal permeation rate. The total ideal permeation rate,  $Q^0$ , is thus given by

$$Q^0 = x_A q_A + x_B q_B \quad (8)$$

Huang and Lin<sup>1</sup> have defined a permeation ratio,  $\theta$ , which is a measure of the departure of the actual permeation rate,  $Q$ , from the ideal rate,  $Q^0$ .

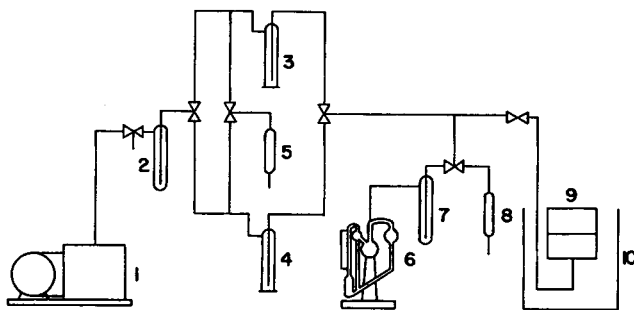
$$\theta = Q/Q^0 \quad (9)$$

Thus, the permeation ratio should be equal to unity when the system exhibits ideal permeation behavior. If the permeation ratio exceeds unity, permeation "enhancement" is said to occur, while a value less than unity indicates a permeation "depression" effect.

## EXPERIMENTAL

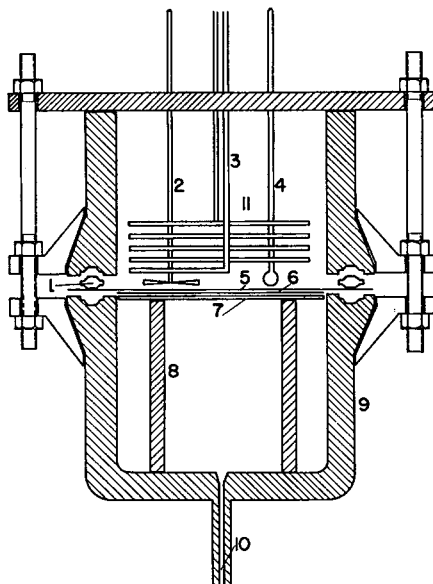
### Apparatus

The permeation equipment consisted of a permeation cell with a temperature control system, a product collection system, and a vacuum pumping system, all connected in a series arrangement. This apparatus has been described in detail in the previous paper in this series,<sup>1</sup> and only a general description will be given here. A schematic diagram of the appa-



PERMEATION APPARATUS.

Fig. 1. Schematic presentation of permeation apparatus: (1) vacuum pump; (2) cold trap; (3,4) collection tubes; (5,8) vents to atmosphere; (6) McLeod-Lippincott vacuum gauge; (7) trap; (9) permeation cell; (10) water bath.



PERMEATION CELL

Fig. 2. Schematic presentation of permeation cell: (1) teflon gasket; (2) stirrer; (3) heating coils; (4) thermometer; (5) membrane; (6) filter paper; (7) sintered brass plate; (8) glass tubing support; (9) permeation cell; (10) outlet to collection system.

atus is shown in Figure 1, and a cross section of the permeation cell is shown in Figure 2.

#### *Permeation Cell and Temperature Control System*

The Pyrex glass permeation cell had a feed solution capacity of approximately 500 ml with a membrane permeation area of 83.3 cm<sup>2</sup>. The cell

was immersed in a water bath, and a 300-watt heater connected to a Fischer Scientific Co. temperature controller maintained the bath temperature at  $\pm 0.1^\circ\text{C}$  of the set point. A variable speed stirrer was fitted through the cover of the cell to eliminate thermal and concentration gradients in the feed solution. A thermometer was placed in the cell to determine the temperature of the liquid feed.

#### *Product Collection System*

The permeating vapor was collected in a system of two collection tubes connected in parallel to the cell. The tubes were inserted in flasks of liquid nitrogen in order to sublime the vapor as it passed into the tubes. A McLeod-Lippincott vacuum gauge capable of measuring vacuums of  $10^{-3}$  mm Hg was connected to the vacuum system upstream from the collection tubes.

#### *Vacuum Pumping System*

The collection system and permeation cell were connected to a Precision Scientific Model 150 vacuum pump having a free air capacity of 150 liters/min.

### **Analysis of Binary Mixtures**

Analysis of binary solutions collected in the cold traps was conducted on a Barber-Colman series 5000 gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector and an integrator-recorder module for data readout.

### **Materials**

#### *Films*

Two different films were used for this study. The first was uncoated, nonmoisture-proofed, 1.1-mil-thick cellophane supplied by TCF of Canada Ltd., Cornwall, Ontario. The film was reported to contain a glycerol or ethylene glycol softening agent.

The second film was a Japanese-manufactured biaxially oriented poly(vinyl alcohol) membrane. It was provided by the Airco Chemical Division of Cumberland Chemical Corp. It was a 1.2-mil-thick film containing approximately 4% of a polyol plasticizer.

#### *Chemicals*

Both pure compounds and binary mixtures were used in this permeation study. The liquids and sources were as follows: *n*-propanol (Fischer Scientific Co., certified ACS), isopropanol (Fischer Scientific Co., certified ACS), ethanol (Consolidated Alcohol Ltd., absolute unmaturred, guaranteed 99% pure), methanol (Fischer Scientific Co., certified ACS).

### Procedure

Both the cellophane and poly(vinyl alcohol) membranes were stored in a humid atmosphere to prevent them from drying and cracking. The membranes, which had been cut to 12 cm diameter circles, were pretreated by soaking in deionized water. In order to ensure that all of the plasticizers were removed, after soaking in water samples of the membranes were dried until constant weight was attained. The soaking time was increased until the change in dry weight was negligible. Soaking for 24 hours at room temperature was found to be sufficient for this purpose. The pretreated membrane was mounted in the permeation cell which was then connected to the collection system and the vacuum pump. Adequate sealing of the system was indicated when a vacuum of 0.1 mm Hg could be maintained. A prepared feed solution of approximately 400 ml was then charged into the feed compartment through the thermometer port to start the permeation run. Samples were also taken with a pipette through the thermometer port.

Permeation experiments were conducted at 30°, 40°, and 50°C, with the same membrane being used for a complete composition range study of a given binary pair. Permeation and separation data were collected for the binary solutions *n*-propanol-water, isopropanol-water, ethanol-water, and methanol-water permeating through both cellophane and poly(vinyl alcohol). Permeating vacuums of 0.1–1.0 mm Hg were maintained for all runs.

Upon reaching steady state flow conditions, product samples were collected for timed intervals, isolated from the vacuum system, warmed to room temperature, and weighed. Meanwhile, permeate collection was continued in the alternate cold trap. When the feed was a binary solution, the feed composition was determined and the sample was returned to the feed compartment to ensure constant feed composition. A small sample was removed from the feed compartment to determine the steady state feed composition.

## RESULTS AND DISCUSSION

Experimental results are presented in Figures 3 to 12. The figures are arranged in the order in which they appear in the discussion. The effect of molecular size and shape are presented first, followed by the effects of temperature on permeation and separation. The effects of plasticization and clustering are presented in the final set of figures.

### Effect of Molecular Size and Shape

Huang and Lin<sup>1</sup> have shown that as the molecular weight of compounds in a given homologous series increases, the permeation rate decreases and the separation increases. The present study shows that the same relationships hold for the homologous series methanol, ethanol, and *n*-propanol for both cellophane and poly(vinyl alcohol). Figure 3 and Table I show

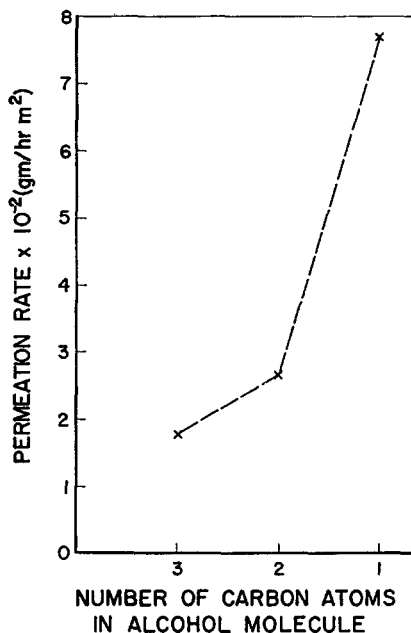


Fig. 3. Effect of chain length on permeation rate of pure alcohols through cellophane at 30°:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (*n*-propanol),  $\text{CH}_3\text{CH}_2\text{OH}$  (ethanol), and  $\text{CH}_3\text{OH}$  (methanol).

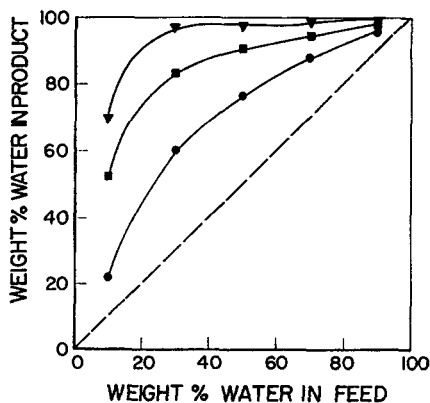


Fig. 4. Effect of feed composition on product composition for an alcohol homologous series in water solutions at 30°C. Cellophane membrane: (▼) *n*-propanol-water; (■) ethanol-water; (●) methanol-water.

that the permeation rate increased as the molecular length,  $\bar{L}$ , decreased for alcohols of similar cross section. Membrane selectivity was also found to depend on the molecular length for this series of linear alcohols. Separation of water-alcohol solutions at given water contents increased as the molecular length of the alcohols increased. This relationship is shown for cellophane in Figure 4.



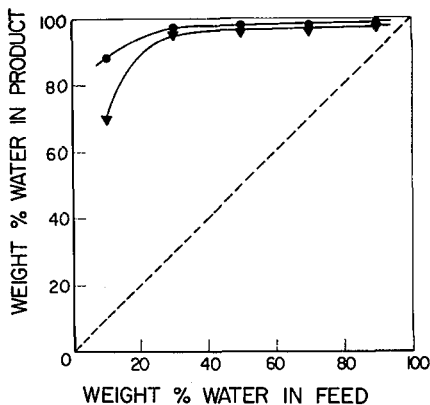


Fig. 5. Effect of feed composition and molecular shape on product composition for alcohol-water solutions at 30°C. Cellophane membrane: (▼) *n*-propanol-water; (●) isopropanol-water.

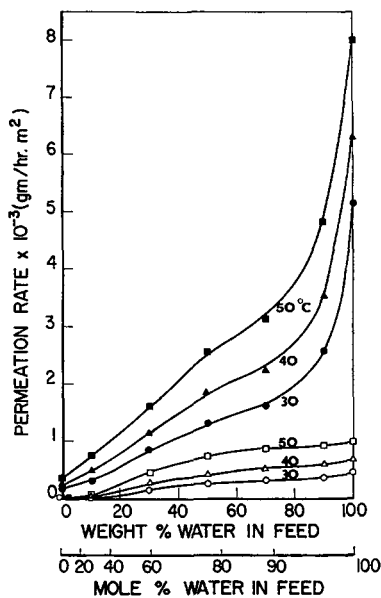


Fig. 6. Effect of feed composition and temperature on permeation rate of *n*-propanol-water solutions. Cellophane membrane: (●) 30°C; (▲) 40°C; (■) 50°C, Poly(vinyl alcohol) membrane: (○) 30°C; (△) 40°C; (□) 50°C.

Both the permeation rate and selectivity are related to the linearity of the permeating molecules. When molecules of similar chemical nature, such as *n*-propanol and isopropanol, were compared (see Table I), the permeation rates were observed to increase as the diffusive cross section decreased. The diffusive cross section,  $\bar{V}/\bar{L}$ , of a molecule is defined as the ratio of the molecular volume,  $\bar{V}$ , and the maximum molecular length,  $\bar{L}$ .

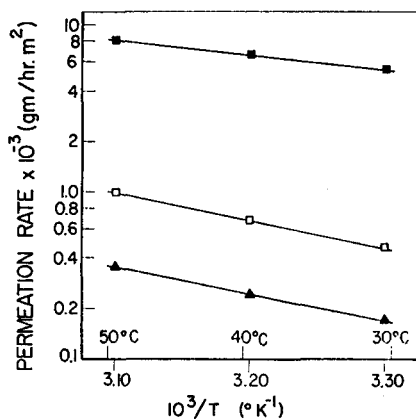


Fig. 7. Arrhenius plots for the permeation of pure water and pure *n*-propanol. Cellophane membrane: (■) water; (▲) *n*-propanol. Poly(vinyl alcohol): (□) water.

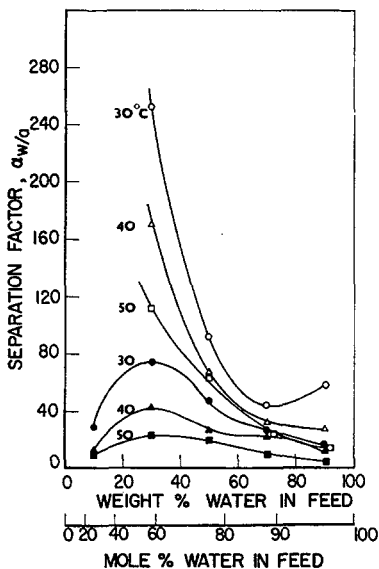


Fig. 8. Effect of feed composition and temperature on the separation factor for the permeation of *n*-propanol-Water solutions. Cellophane: (●) 30°C; (▲) 40°C; (■) 50°C. Poly(vinyl alcohol): (○) 30°C; (△) 40°C; (□) 50°C.

The present results show that for *n*-propanol-water and isopropanol-water solutions the separation is directly proportional to the diffusive cross section of the alcohol. As is shown in Figure 5, isopropanol, with the larger cross section, was separated from water solutions better than *n*-propanol.

The effect of molecular size and shape can be summarized as follows:

1. For pure liquid permeation, members of a given homologous series with lower molecular weights permeate faster than higher molecular weight members. In binary permeation, for members of a homologous series in a

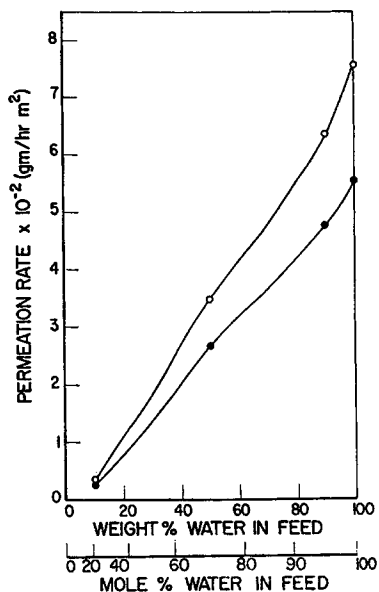


Fig. 9. Effect of feed composition and temperature on the separation factor for the permeation of *n*-propanol-water solutions. Cellophane membrane: (●) 30°C; (▲) 40°C; (■) 50°C. Poly(vinyl alcohol): (○) 30°C; (△) 40°C; (□) 50°C.

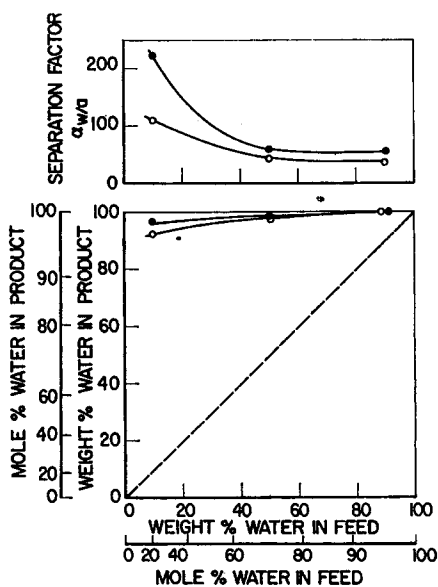


Fig. 10. Effect of pretreatment on the permeation rate of ethanol-water solutions through poly(vinyl alcohol) at 40°C: (○) film presoaked in water at room temperature for 24 hr; (●) no pretreatment.

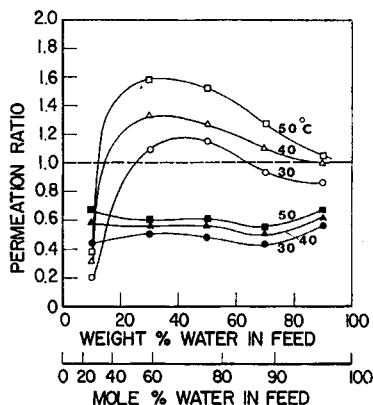


Fig. 11. Effect of pretreatment on separation of ethanol-water solutions through poly(vinyl alcohol) at 40°C: (O) film presoaked in water at room temperature for 24 hr; (●) no pretreatment.

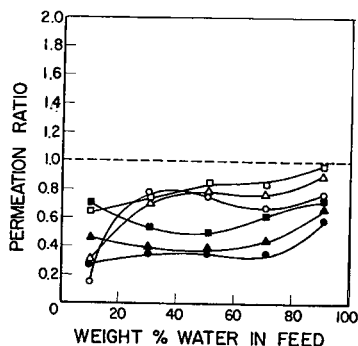


Fig. 12. Effect of feed composition on the permeation ratio for *n*-propanol-water solutions. Cellophane membrane: (●) 30°C; (▲) 40°C; (■) 50°C. Poly(vinyl alcohol): (○) 30°C; (△) 40°C; (□) 50°C.

TABLE I  
Effect of Molecular Length and Shape on Permeation Rates\*

Permeant	$\bar{L}$ , Å	$\bar{V}/\bar{L}$ , Å <sup>2</sup>	Permeation rate (at 30°C), g/hr-m <sup>2</sup>
Isopropanol	4.3	29.6	96
<i>n</i> -Propanol	5.4	23.0	179
Ethanol	4.2	23.1	268
Methanol	2.9	23.2	772

\* The molecular volume  $\bar{V}$  was calculated by dividing the molecular weight by the density and the Avogadro number to yield the volume per molecule. The molecular length  $\bar{L}$  denotes the maximum zig zag length calculated using data from "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London (1958)

common solvent, higher degrees of separation are achieved for the higher molecular weight members.

2. For pure liquid permeation of molecules of similar molecular weight and chemical nature, molecules with a smaller cross section permeate faster. For binary permeation, better separation from a common solvent is achieved with molecules of larger cross section.

### Effect of Temperature

Permeation runs of water, alcohols, and water-alcohol mixtures were conducted at 30°, 40°, and 50°C. Temperature increments of 10°C increased the permeation rates by 1.5 to 2 times for poly(vinyl alcohol) and approximately 1.5 times for cellophane (Fig. 6). Arrhenius-type plots were used to calculate permeation activation energies for pure components (Fig. 7). The activation energies of pure water permeating through cellophane and poly(vinyl alcohol) were calculated to be 4.4 kcal/mole and 8.8 kcal/mole, respectively. *n*-Propanol permeating through cellophane had an activation energy of 6.9 kcal/mole.

The effect of temperature on membrane selectivity is shown in Figure 8 for *n*-propanol-water solutions. The separation factor generally decreased throughout the composition range as the temperature increased. According to Eyring's hole theory of diffusion, the thermal motion of polymer chains randomly produces "holes" through which the permeating molecules can diffuse. As the temperature is increased, the thermal agitation increases and the diffusive "holes" become larger. More alcohol molecules can therefore diffuse through the membrane, and the separation factor is decreased.

### Effect of Permeant-Polymer Interactions

It is well known that the molecular structure of a permselective membrane has a strong influence on the permeation and separation of binary liquid solutions. This is especially true when one of the liquids is a plasticizing agent for the polymer, as is the case of water in hydrophilic membranes.

As the water concentration in a binary solution is increased, the amorphous regions of the polymer are swollen, and the polymer chain segments become more mobile thus decreasing the energy required for diffusive transport through the membrane. These effects are reflected in increasing permeation rates and decreasing separation as the water content of water-alcohol solutions are increased (as shown in Figs. 6 and 8). Figures 9 and 10 show the plasticizing effect of water on the permeability of poly(vinyl alcohol). When the membrane was pretreated by soaking in deionized water at room temperature for 24 hours, the permeation rate increased by 30%–35% above the untreated membrane rates. Pretreatment, however, did not appreciably reduce the membrane selectivity below untreated levels. This is shown in Figure 10.

The permeation ratio,  $\theta$ , defined as the ratio of the actual permeation rate to the ideal rate, assuming additivity of rates, was used to describe the non-ideal behavior of aqueous permeants. The presence of a plasticizing component such as water in the binary permeating mixture was expected to result in permeation enhancement, i.e.,  $\theta$  greater than unity. On the contrary, as shown in the permeation ratio data of Figures 11 and 12, there was a significant permeation depression effect for all alcohol-water solutions except for the case of *n*-propanol-water permeation through poly(vinyl alcohol). The depression of permeation rates below the ideal rates in a plasticized system suggests that other phenomena are masking the initial plasticizing action of water.

It has been postulated by several workers that the permeation of water through polymer membranes can be hindered by the formation of water "clusters."<sup>11-14</sup> The significant permeation depression observed for water-alcohol solutions permeating through cellophane strongly suggests that the mutual association of water molecules and/or alcohol molecules plays an important role in the permeation behavior of this system. It is postulated that the clustering of water molecules occurs to such an extent that it predominates over the effect of plasticization. This would result in a depression of the permeation rate from the ideal rate.

Alcohol-water systems permeating through poly(vinyl alcohol) exhibited less permeation depression than for cellophane. This can possibly be explained in terms of the morphology of poly(vinyl alcohol). It is thought to have significantly smaller interchain spaces than cellophane, thus hindering the formation of water clusters. Unlike cellophane permeation, the permeation ratios for *n*-propanol-water solutions in poly(vinyl alcohol) were observed to pass through a maximum, where permeation enhancement occurred. The ratio then decreased as the water composition of the feed increased to higher levels. At low water concentrations, the clustering phenomenon is thought to predominate over the plasticizing effect of water, and the permeation rate is depressed. As the water concentration in the feed increases, the polymer becomes more swollen and the volume of polymer available for diffusion increases significantly. At approximately 20 wt-% water in the feed, the plasticizing effect predominates and permeation enhancement occurs. At higher water concentrations, membrane plasticizing reaches a maximum, while the probability of cluster formation as well as cluster size continues to increase. This is reflected in decreasing permeation ratios, and finally the permeation rate is again depressed below the ideal rate.

From the above discussion it can be seen that there are complex interactions between permeating molecules and the polymer membrane which may significantly alter permeation and separation characteristics. The concepts of clustering and plasticization, while semiempirical in nature, do provide some insight into the permeation behavior of aqueous solutions in hydrophilic membranes.

### Comparison of Cellophane and Poly(vinyl Alcohol) as Permselective Membranes

In this study the permeation rate of alcohol-water solutions through poly(vinyl alcohol) membranes was observed to be significantly less than that for cellophane. For example, the permeation rate of pure water through 1.1-mil-thick cellophane was 5280 g/hr-m<sup>2</sup> at 30°C, while the rate for 1.2-mil-thick poly(vinyl alcohol) was 446 g/hr-m<sup>2</sup>. This difference can be attributed to differences in both polymer morphology and the extent of polymer plasticization. At the same conditions, the permeation rates of pure *n*-propanol through cellophane and poly(vinyl alcohol) were 179 g/hr-m<sup>2</sup> and 1 g/hr-m<sup>2</sup>, respectively. This difference is attributed to differences in the "tightness" of the molecular structures of the two films as well as possible differences in the relative amounts of amorphous and crystalline regions.

Because of the small size, regular spacing, and polar nature of its hydroxyl side groups, poly(vinyl alcohol) is a polymer wherein chain-to-chain interactions are probably quite large. The poly(vinyl alcohol) used in this study was reported to have been biaxially oriented. This process tends to orient both crystalline and amorphous regions in a more ordered array. Therefore, poly(vinyl alcohol) is thought to consist of a highly ordered, compact structure with some degree of interchain bonding. Cellophane, however, is thought to be much more amorphous in nature, with less interaction between polymer chains. The remarkably good separations achieved with poly(vinyl alcohol) membranes again indicate the existence of a tightly bound, compact structure where both the size and number of diffusive "holes" are limited. As can be seen from Figures 11 and 12, the formation of clusters and subsequent permeation depression was more pronounced in cellophane than in poly(vinyl alcohol). It is felt that the compact nature of the poly(vinyl alcohol) chains inhibited the formation of water clusters, and thus poly(vinyl alcohol) exhibited less permeation depression than the more swollen cellophane membranes.

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