

Separation of Liquid Mixtures by Using Polymer Membranes. III. Grafted Poly(vinyl Alcohol) Membranes in Vacuum Permeation and Dialysis

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Synopsis

A series of poly(vinyl alcohol) membranes were modified by radiation-induced graft copolymerization with acrylic acid and methacrylic acid monomers. These grafted poly(vinyl alcohol) membranes were then tested for their separation and permeability characteristics in vacuum permeation and dialysis experiments. The permselectivity of the membranes toward methanol and water was studied on a vacuum permeation apparatus at 30, 40, and 50°C. The permeation process was found to be a temperature-activated process. The logarithm of the permeation rate varied linearly with the reciprocal of the absolute temperature. The permeability of the grafted membranes was found to increase with the degree of grafting, with no appreciable selectivity toward water in binary mixtures. The acrylic acid-grafted membranes generally showed greater improvement in permeability than the methacrylic-grafted membranes. The permeability of the grafted membranes toward methanol, sodium chloride, urea, creatinine, and uric acid was studied in a dialyzer. In all cases, the grafted membranes showed an improved permeability toward these solutes over the commercial poly(vinyl alcohol) membranes. The dialysis results were then compared with those obtained for dialysis-grade cellophane membranes. For the case of sodium chloride, urea, and methanol, the permeability of the grafted membranes was comparable to that of cellophane. A comparison of commercial and grafted poly(vinyl alcohol) membranes in their permeability toward ionic solutes exhibited somewhat anomalous behavior in that the permeability of the commercial membranes was higher than that of the grafted membranes. This related to the ionic nature of the modified membrane. The permeability coefficients determined in the dialysis experiments were found to be directly related to the degree of hydration of the grafted membrane. This behavior was attributed to changes in the size and shape of voids within the membrane structure.

INTRODUCTION

There is a growing interest in the use of hydrophilic polymer membranes in biological and medical applications and in water pollution control. The solubility of water in these membranes is inherently quite high, and this makes them particularly useful in the above-mentioned applications. In recent studies conducted in this laboratory, Jarvis¹ investigated the permeability of poly(vinyl alcohol) membranes toward water in binary mixtures of alcohols and water. He found that although the flux was very low, the membrane possessed a high degree of selectivity toward water in the binary mixtures. It is the purpose of this study to improve the permeability characteristics of poly(vinyl alcohol) membranes and yet maintain the selectivity at a level comparable to that cited by Jarvis. This was achieved by grafting the hydrophilic monomers acrylic acid and methacrylic acid onto the polymer backbone poly(vinyl alcohol) by means of

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gamma-ray irradiation. In addition, tests were conducted to determine the permeability of the modified membranes toward sodium chloride, methanol, urea, creatinine, and uric acid in a dialyzer. The results are compared to those obtained for dialysis-grade cellulose membranes to determine if poly(vinyl alcohol) might be considered as a candidate in artificial kidney applications.

Very little information has been published on the permselectivity of poly(vinyl alcohol) membranes. Schrodt et al.² studied the permselectivity of poly(vinyl alcohol) membranes, among others, to organic liquid mixtures under conditions of vacuum permeation. Binning et al.³ patented a process to remove water from organic chemicals by the use of poly(vinyl alcohol) membranes. They described a multistage vacuum permeation process in their patent. It was claimed that if an aqueous solution of ethanol and isopropanol, containing about 5% by weight water, was charged to the cell, the membrane would selectively permeate water yielding 90% water and 10% alcohols in the product.

Peters⁴ studied the permeation of water-sugar solutions through poly(vinyl alcohol) membranes and postulated that water molecules enveloped the polymer chains due to hydrogen bonding. Markle et al.⁵ examined the permeability of several synthetic membranes to urea in dialysis. Poly(vinyl alcohol) was one of the membranes studied, and it was found that by crosslinking the polymer with 10% glutaraldehyde, the permeability to urea was improved over that of cellophane. As the amount of glutaraldehyde, and therefore the degree of crosslinking, was increased, the permeability was found to decrease. Odian and Leonard⁶ simultaneously grafted and crosslinked poly(vinyl alcohol) film by irradiating the polymer with Co-60 gamma rays in the presence of allyl methacrylate in the grafting solution. This changed the permeation characteristics of the membranes toward monodispersed samples of polyethylene glycols of specified molecular weights.

To produce a membrane of improved mechanical strength, Odian et al.⁷ grafted poly(vinyl alcohol) and poly(vinylpyrrolidone) onto polyethylene using gamma irradiation. The resultant membranes were found to be weaker in mechanical strength than commercial dialysis membranes but showed a tenfold increase over the commercial membranes in their permeability toward various solutes. Duncalf and Dunn⁸ and Sakurada and Matsuzawa⁹ have described the process of crosslinking poly(vinyl alcohol) films and fibers. They have attributed the crosslinking mechanism at least partially to the splitting off of water in an intermolecular condensation reaction leaving an ether linkage between the main chains. The effect of ionizing radiation on poly(vinyl alcohol) was found to depend on the medium in which the polymer was irradiated. Alexander and Charlesby¹⁰ and Danno^{11,12} have found that aqueous solutions of the polymer would gel under gamma-ray irradiation if the amount of polymer present was above a certain minimum concentration. Sakurada and Matsuzawa¹³ studied the effect of gamma irradiation on water-swollen poly(vinyl alcohol) film and found the polymer to degrade rather than gel. The grafting of vinyl monomers onto poly(vinyl alcohol) in aqueous solution by chemicals is well documented in the literature. Mino and Kaizerman¹⁴ found ceric ion to be a good initiator for the grafting reaction, and subsequently various researchers have grafted methyl methacrylate,¹⁵ vinyl acetate, acrylonitrile,¹⁶ and acrylic acid¹⁹ onto poly(vinyl alcohol) in aqueous solutions.

Chapiro and Stannett¹⁸ have grafted methyl acrylate and styrene onto poly-

(vinyl alcohol) films, and Sakurada et al.¹⁹ have grafted methyl methacrylate, acrylonitrile, and vinyl acetate onto poly(vinyl alcohol) films by gamma irradiation. They found that the degree of grafting varied with the amount of water present in the film. It was reported that the irradiation of the system resulted in a surface-grafted film, whereas a depth of grafting was attributed to the swelling of the polymer by the water, thereby increasing the rate of diffusion of the monomers to the active sites within the polymer matrix. Bernstein et al.²⁰ have grafted allyl methacrylate onto poly(vinyl alcohol) films. They found the resulting polymer to be insoluble in water. Since the allyl methacrylate is a bifunctional monomer, they concluded that there was a simultaneous grafting and crosslinking reaction taking place.

EXPERIMENTAL

Sample Preparation

Samples of poly(vinyl alcohol) were cut into sections 5 in. square, weighed, and placed in 50-ml screw-cap test tubes. The tubes were filled with the appropriate grafting solution consisting of methanol, water, and acrylic or methacrylic acid. The following were the compositions (by volume) of water, methanol, and acrylic or methacrylic acid, respectively: series 1—10% water, 60% methanol, 30% acrylic acid; series 2—10% water, 70% methanol, 20% acrylic acid; series 3—10% water, 80% methanol, 10% acrylic acid; series 4—10% water, 70% methanol, 20% methacrylic acid; series 5—10% water, 80% methanol, 10% methacrylic acid. The samples were allowed to equilibrate in the solution for 24 h and then were irradiated in the Cobalt-60 gamma cell to a total dose of 0.64 Mrad. Samples were removed from the test tubes as required, rinsed with water to remove any surface homopolymer, and placed in distilled water for 24 h prior to use. This was done to remove any homopolymer within the polymer matrix. The samples were then dried and weighed to determine the percent grafting by the equation:

$$\% \text{ grafting} = \frac{w_2 - w_1}{w_1} \times 100$$

where w_1 and w_2 are the initial and final weights of the membrane respectively.

Determination of the Degree of Hydration

Samples of commercial and grafted poly(vinyl alcohol) and cellophane membranes were allowed to soak in beakers of distilled water for 48 h. They were then removed, blotted dry, and weighed. This was recorded as the wet weight of the membrane. The membranes were then placed in a vacuum oven to dry and then reweighed. The degree of hydration was determined by the following equation:

$$\text{degree of hydration} = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 and W_2 are the wet and dry weights of the membranes, respectively.

Vacuum Permeation

The membranes were soaked in distilled water for 24 h prior to use to ensure that all homopolymers and plasticizers were removed. Permeation runs were conducted at 30, 40, and 50°C. The same membranes were used to study the permeation characteristics of methanol, water, and binary mixtures of methanol and water. Details of the experimental apparatus and the operating procedures and methods of calculations have been reported in the previous paper in this series.¹ All the experimental runs were duplicated and were found to vary by not more than 6%.

Dialysis

Prior to use, all the membranes were soaked in distilled water to remove any homopolymers and plasticizers. Details of the dialysis apparatus and the calculation and operating procedures have been described previously.¹ All the runs were duplicated to ensure reproducibility within 10%.

TABLE I
Data for Acrylic Acid-Grafted Membranes: Poly(vinyl Alcohol)-g-Acrylic Acid^a

<i>S</i>	X_A	E_P	<i>T</i>	<i>Q</i>	Y_A	$\alpha A/B$	θ
71.8	1.000	5.4	20.0	1059	1.000		
			30.0	1508	1.000		
			40.0	1918	1.000		
	0.000	9.9	20.0	30.8	0.000		
			30.0	43.6	0.000		
			40.0	92.4	0.000		
	0.485	10.7	20.5	214	0.951	20.7	0.41
			31.0	456	0.953	21.3	0.61
			40.0	673	0.931	14.4	0.69
42.3	1.000	6.6	20.0	782	1.000		
			30.0	1168	1.000		
			40.0	1625	1.000		
	0.000	9.0	20.0	63.3	0.000		
			30.0	110	0.000		
			40.0	171	0.000		
	0.485	8.3	20.0	341	0.905	10.0	0.83
			30.0	550	0.898	9.3	0.88
			40.0	833	0.844	5.7	0.95
18.1	1.000	6.7	20.0	602	1.000		
			30.0	875	1.000		
			40.0	1262	1.000		
	0.000	7.1	20.4	24.0	0.000		
			30.2	36.2	0.000		
			39.7	51.0	0.000		
	0.485	7.9	20.0	282	0.904	10.0	0.93
			30.0	397	0.904	10.0	0.90
			40.0	674	0.879	7.7	1.06

^a *S* = Percent graft of substrate on poly(vinyl alcohol); X_A = weight fraction of water in feed solution; E_P = activation energy for permeation (kcal/mol); *T* = permeation temperature (°C); *Q* = total permeation rate (g/h·m²); Y_A = weight fraction of water in the product; α = separation factor; θ = permeation ratio.

Materials

The poly(vinyl alcohol) membranes used in this study were manufactured in Japan and were supplied by Airco Chemical Division of Cumberland Chemical Corporation. They were biaxially oriented films 1.2 mil thick and contained approximately 4% of a polyol plasticizer. The dialysis-grade cellophane membranes were supplied by Union Carbide Canada Ltd. They were 1.6 mil thick and contained an unspecified amount of glycerine and approximately 0.1% sulfur compounds. The following are the chemicals used in this study and their sources: bacitracin (Nutritional Biochemical Corporation), creatinine (Nutritional Biochemical Corporation), methanol (Fisher Scientific Co. Certified A.C.S. grade), sodium chloride (Baker Chemical Company, ACS grade), urea (Baker Chemical Company, Certified ACS Grade), uric acid (Baker Chemical Company, Baker Grade).

RESULTS

The experimental results consist of three main parts: the grafting of acrylic acid and methacrylic acid monomer onto the poly(vinyl alcohol) membranes; the permeation and separation of solutions of methanol and water in vacuum permeation using the grafted membranes; and the dialysis of methanol, sodium chloride, urea, creatinine, uric acid, and bacitracin through the grafted membranes and through cellophane. The data for the permeation and separation studies as well as the calculated results for the separation factors, permeation rates, and activation energies are found in Tables I-III. The data for the dialysis results and the calculated permeability coefficients are presented in Table IV.

TABLE II
Data for Methacrylic Acid Grafted Membranes: Poly(vinyl Alcohol)-g-Methacrylic Acid^a

<i>S</i>	<i>X_A</i>	<i>E_P</i>	<i>T</i>	<i>Q</i>	<i>Y_A</i>	<i>αA/B</i>	<i>θ</i>
21.9	1.000	6.2	30.0	890.	1.000		
			40.0	1249	1.000		
			50.3	1705	1.000		
	0.000	10.7	30.4	18.3	0.000		
			40.1	31.1	0.000		
			50.0	53.9	0.000		
	0.485	10.6	30.2	266	0.947	18.8	0.60
			40.1	488	0.938	16.1	0.78
			50.2	791	0.911	10.8	0.93
6.7	1.000	7.5	30.0	650	1.000		
			39.7	961	1.000		
			49.3	1380	1.000		
	0.000	10.3	30.1	15.0	0.000		
			40.1	27.0	0.000		
			50.4	44.0	0.000		
	0.496	6.9	30.0	200	0.957	22.6	0.61
			40.1	276	0.935	14.6	0.82
			50.0	410	0.894	8.5	0.98

^a Symbols same as in Table I.

TABLE III
Data for Commercial Poly(vinyl Alcohol) Membranes^a

<i>S</i>	X_A	E_P	<i>T</i>	<i>Q</i>	Y_A	<i>A/B</i>	θ
0	1.000	6.5	30.0	455.	1.000	0.00	
			40.0	640.	1.000	0.00	
			50.0	890.	1.000	0.00	
	0.000	10.9	30.0	22.2	0.000	0.00	
			40.0	39.4	0.000	0.00	
			50.0	68.5	0.000	0.00	
	0.485	11.2	30.0	198.	0.953	15.9	0.85
			40.0	340.	0.917	12.0	1.03
			50.0	631.	0.904	8.2	1.35

^a Symbols same as in Table I.

Grafting Results

Figure 1 shows how the percent grafting of acrylic acid and methacrylic acid increased with monomer content in the grafting solution. Figure 2 illustrates how the degree of hydration of the membranes increased with the degree of grafting for both acrylic acid and methacrylic acid grafted membranes.

Vacuum Permeation

Permeation Results

Figures 3, 4, and 5 present the permeation rates of water, methanol, and a 50% by weight binary mixture of methanol and water as a function of the degree of grafting of acrylic acid and methacrylic acid, while Figures 6 and 7 present the same data on an Arrhenius-type plot. It can be seen that generally the permeation rate increased with the temperature, the degree of grafting, and the concentration of water in the feed solution.

Separation of Binary Mixture

The vacuum permeation product composition data are listed in Tables I–III. It can be seen from these results that water was selectively permeated through the membranes from a binary mixture. The selectivity for water decreased with temperature and degree of grafting. In Figure 8, it is shown that the separation factor increases with the degree of grafting of methacrylic acid and decreases with an increase in the degree of grafting of acrylic acid. The variation of the permeation ratio, θ , which is a measure of the nonideality of permeation of binary mixtures,¹ with the temperature and degree of grafting illustrated in Figure 9.

Activation Energies

The activation energies for permeation through the various membranes are also listed in Tables I–III. For the permeation of pure water the activation energy is seen to have decreased with an increase in the degree of grafting. On the other hand, for the permeation of pure methanol, the activation energy increased with the degree of grafting.

TABLE IV
Tabulated Results for the Permeability Coefficients of the Solutes through the Polyvinyl and Cellophane Membranes

Membrane	Permeability coefficients, cm/min				
	Methanol	Urea	Creatinine	Sodium chloride	Uric acid
Commercial polyvinyl	0.0037	0.0033	0.0015	0.0026	0.00099
Poly(vinyl alcohol)-g-acrylic acid (18% graft)	0.0071	0.0054	0.0017	0.0014	0.00038
Poly(vinyl alcohol)-g-acrylic acid (44% graft)	0.0109	0.0074	0.0020	0.0024	0.00055
Poly(vinyl alcohol)-g-acrylic acid (72% graft)	0.0131	0.0118	0.0020	0.0051	0.00089
Poly(vinyl alcohol)-g-methacrylic Acid (6.5% graft)	0.0051	0.0047	0.0016	0.0013	0.00026
Poly(vinyl alcohol)-g-methacrylic Acid (22% graft)	0.0078	0.0086	0.0017	0.0019	0.00049
Cellophane dialysis membranes	0.0164	0.0130	0.0074	0.0077	0.0046
					0.0027

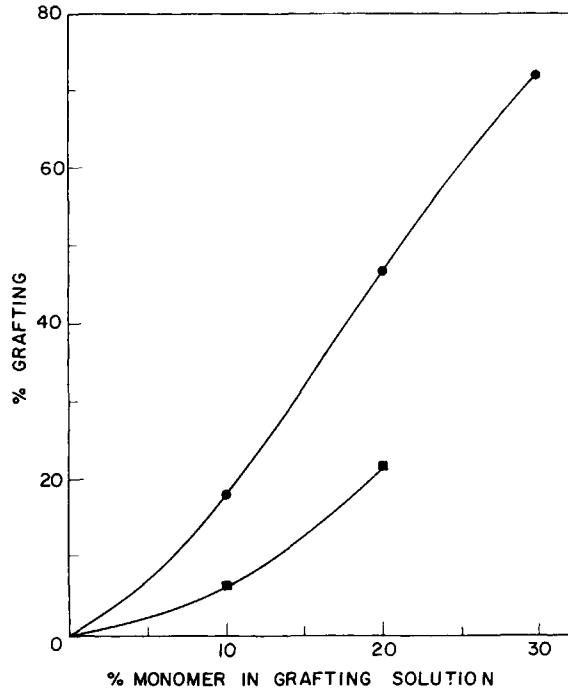


Fig. 1. Effect of monomer concentration on the irradiation grafting of acrylic acid and methacrylic acid on poly(vinyl alcohol). Total dose 0.64 Mrad; Temperature 35°C. (●) Acrylic acid; (■) methacrylic acid.

Dialysis Results

Dialysis Rates through the Modified Membranes

The rates of dialysis of methanol and urea through the acrylic acid membranes are shown in Figures 10 and 11. The dialysis rates of the ionic species sodium chloride and uric acid are presented in Figures 12 and 13. For the nonionic so-

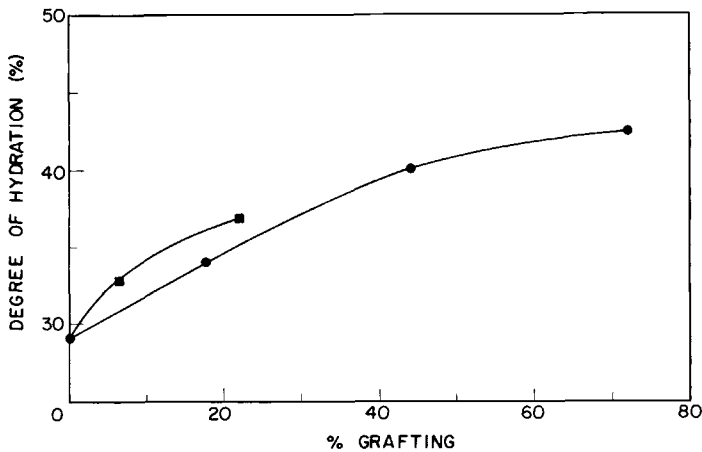


Fig. 2. Effect of degree of grafting on the degree of hydration of the modified membranes. (●) Poly(vinyl alcohol)-g-acrylic acid; (■) Poly(vinyl alcohol)-g-methacrylic acid.

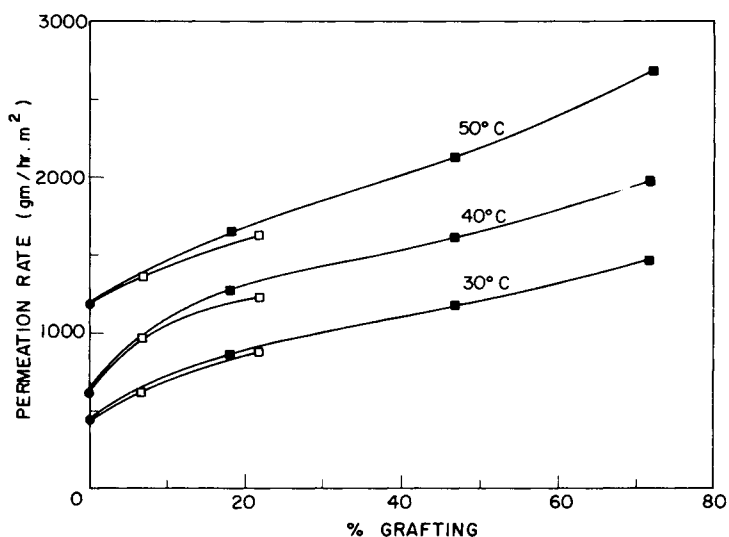


Fig. 3. Effect of degree of grafting on the permeation rate of pure water through poly(vinyl alcohol) membranes: (●) Poly(vinyl alcohol) membrane; (■) poly(vinyl alcohol)-g-acrylic acid membranes; (□) poly(vinyl alcohol)-g-methacrylic acid membranes.

lutes, the permeability coefficients are observed to increase monotonously with the degree of grafting as shown in Figure 14. However, for the ionic solutes (Fig. 15), there is a decrease from the ungrafted membrane to the 18% grafted membrane, followed by an increase as the degree of grafting is further increased. Bacitracin is another substance which was tested under dialysis with the modified membranes. It can be seen in the tabulated data that there was no change in the concentration of bacitracin during the course of the dialysis run.

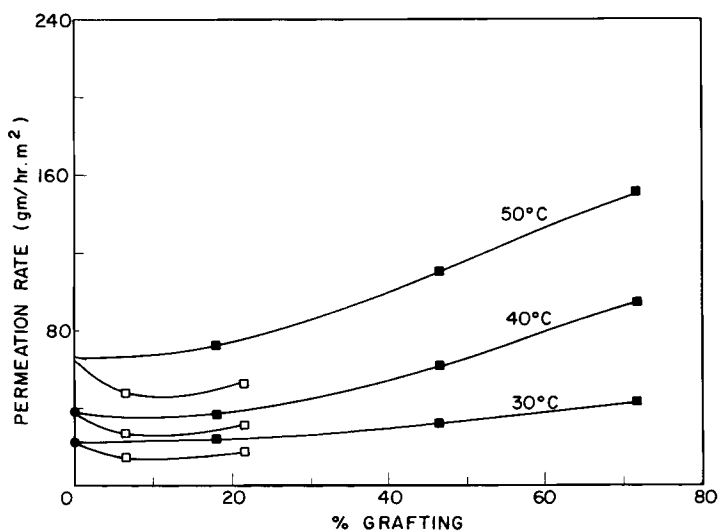


Fig. 4. Effect of degree of grafting on permeation of pure methanol through poly(vinyl alcohol) membranes. (●) poly(vinyl alcohol) membranes; (■) poly(vinyl alcohol)-g-acrylic acid membranes; (□) poly(vinyl alcohol)-g-methacrylic acid membranes.

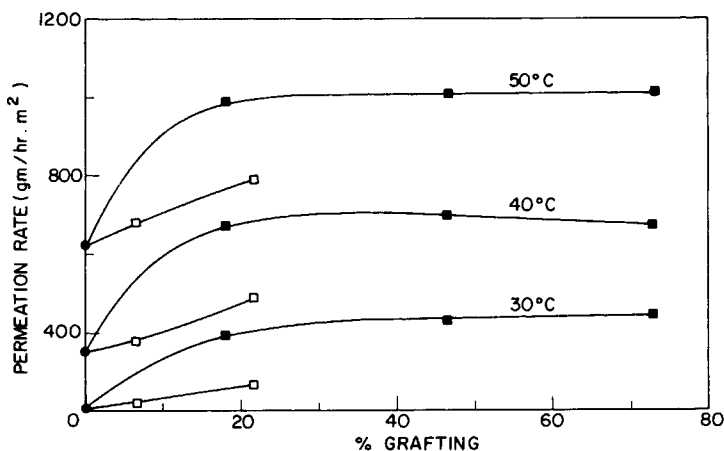


Fig. 5. Effect of degree of grafting on the permeation of a 50% by weight mixture of methanol and water through poly(vinyl alcohol) membranes: (●) poly(vinyl alcohol) membrane; (■) poly(vinyl alcohol)-g-acrylic acid membranes; (□) poly(vinyl alcohol)-g-methacrylic acid membranes.

Dialysis Rates through Cellophane

The permeability coefficients of methanol, urea, creatinine, bacitracin, sodium chloride, and uric acid through cellophane and through modified poly(vinyl alcohol) membranes are compared in Table IV.

Degree of Hydration

The change in the logarithm of the permeability coefficients with the reciprocal of hydration is illustrated for the modified poly(vinyl alcohol) membranes in Figure 16. It is seen that in all cases a linear relationship existed between the two parameters.

DISCUSSION OF RESULTS

Vacuum Permeation and Separation

Effect of Temperature

As shown in Figures 3, 4, and 5, the permeation rates of water and methanol and binary mixtures of the two increased with temperature. It was found that the temperature dependence of the permeation of water and methanol could be represented by an Arrhenius-type temperature relationship as is shown in Figures 6 and 7. The activation energies for permeation were calculated from these plots and are tabulated in Tables I-III. There were two trends established for the variation of the activation energy with the degree of grafting. First, for the permeation of pure water, the activation energy decreased with an increase in the degree of grafting. Secondly, for the permeation of pure methanol, the activation energy increased with the degree of grafting. The decrease in the activation energy for the permeation of pure water can be interpreted in the following manner. The activation energy is the energy required to form a diffusional hole between polymer chains. This serves to decrease the intermolecular forces between the chains yielding a looser polymer network with a corre-

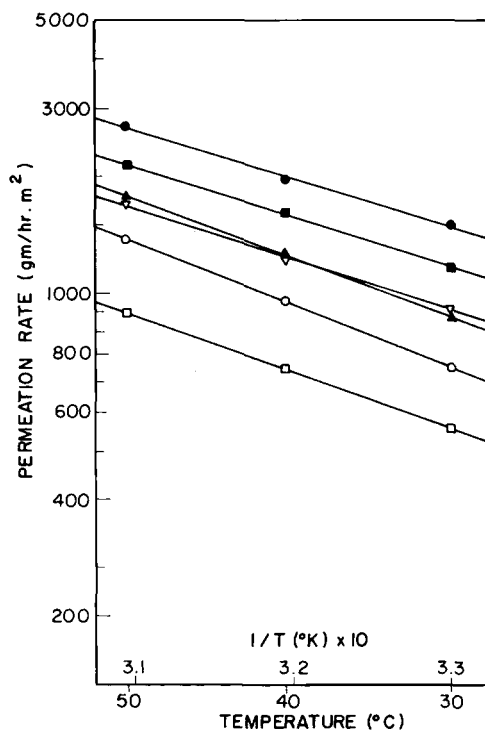


Fig. 6. Arrhenius plot of the permeation of pure water through grafted poly(vinyl alcohol) membranes: (□) poly(vinyl alcohol) membrane; (●) poly(vinyl alcohol)-g-acrylic acid (71.8% graft); (■) poly(vinyl alcohol)-g-acrylic acid (46.5% graft); (▲) poly(vinyl alcohol)-g-acrylic acid (18.0% graft); (▽) poly(vinyl alcohol)-g-acrylic acid (21.9% graft); (○) poly(vinyl alcohol)-g-acrylic acid (6.5% graft).

spondingly lower activation energy. Fels²⁴⁻²⁶ has observed similar trends for the permeation of organic liquids through polyethylene-g-styrene membranes.

The increase in the activation energy with the degree of grafting for the permeation of pure methanol can be interpreted as follows. The methanol does not swell the poly(vinyl alcohol) membrane to the same degree as the water. Thus, the intermolecular forces between the polymer chains are not decreased by any significant degree, the grafted chains hinder the diffusion of the larger molecule, and the activation energy for permeation is increased. The change in the separation factor with the temperature and degree of grafting is illustrated in Figure 8. A separation factor greater than unity indicates an enrichment of the water in the product. The separation factor decreased as the temperature was increased. This can be attributed to an increase in the thermal motion of the polymer chains with the result that larger diffusional holes were formed which could accommodate either of the diffusing species more readily.

Effect of Grafting

It is seen in Figures 3, 4, and 5 that, in all cases except one, the permeation rate increased with the degree of grafting of acrylic acid and methacrylic acid. The exception is the permeation rate of methanol through methacrylic acid-grafted

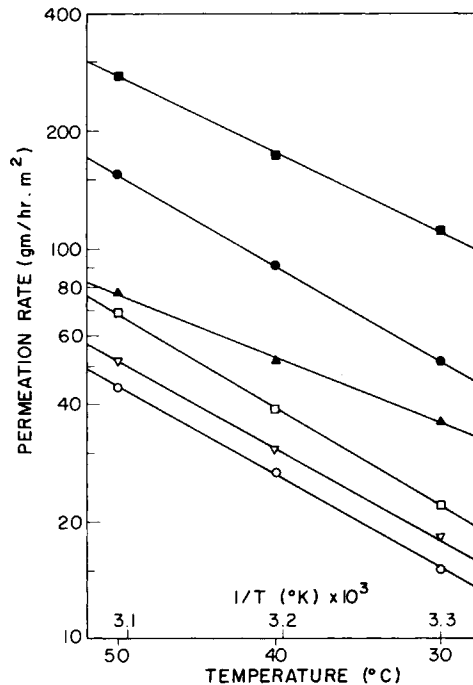


Fig. 7. Arrhenius plot of the permeation of pure methanol through grafted poly(vinyl alcohol) membranes: (O) commercial poly(vinyl alcohol) membranes; (■) polyvinyl-g-acrylic acid (71.8% graft); (●) polyvinyl-g-acrylic acid (46.5% graft); (▲) polyvinyl-g-acrylic acid (18.0% graft); (□) poly(vinyl alcohol)-g-methacrylic acid (21.9% graft); (▽) poly(vinyl alcohol)-g-methacrylic acid (6.5% graft).

membranes where the permeant rate was seen to decrease. The permeation process is a function of the diffusion and solubility of the species under consideration in the membrane. Thus, the enhanced permeability exhibited by the membranes in this study must be interpreted on the basis of solubility and diffusion effects. It is also necessary to explain, at least qualitatively, the grafting increase. Prior to grafting, the polymer is soaked in the appropriate solution of water, methanol, and monomer, and the solution is absorbed into the amorphous region of the polymer. On exposure to gamma-ray irradiation, the graft copolymer is formed in these amorphous regions and the mobility of the polymer chains is reduced. The magnitude of the diffusion coefficient is a function of the mobility of the polymer chains. Therefore, if the solubility of the penetrant in the polymer does not change significantly with the degree of grafting, the permeation rate will decrease. In this study, methanol is readily soluble in poly(acrylic acid) and only slightly soluble in poly(methacrylic acid). Therefore, as is shown in Figure 4, the permeation rate of methanol decreased with increasing degree of grafting through poly(vinyl alcohol)-g-methacrylic acid membranes. On the other hand, water is very soluble in both poly(acrylic acid) and poly(methacrylic acid). Therefore, the presence of these two substances as grafted substrates enhanced the plasticization effect of the water on the membranes with a resulting increase in the permeation rate, as shown in Figure 5. The separation factor is a measure of the relative rates of permeation on the two liquids through the polymer membrane. Therefore, it is also a function of

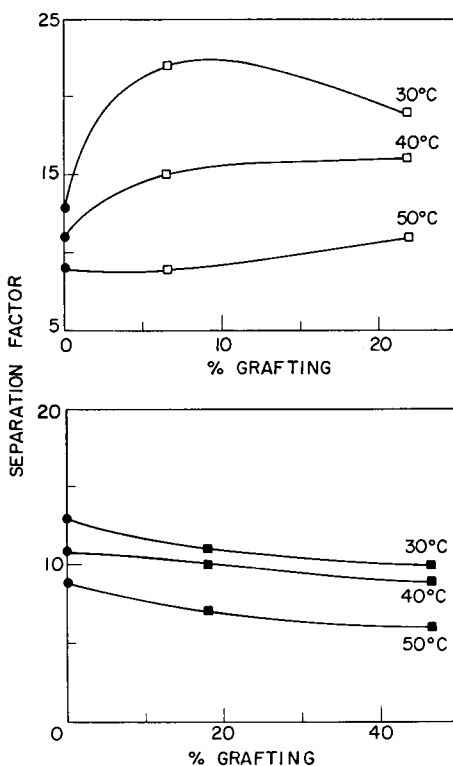


Fig. 8. Effect of grafting on the separation factors: (●) commercial poly(vinyl alcohol) membrane; (■) poly(vinyl alcohol)-g-acrylic acid membranes; (□) poly(vinyl alcohol)-g-methacrylic acid membranes.

the solubility and diffusion of the species in the membrane. As seen in Figure 8, the separation factors increased with the degree of grafting of methacrylic acid and decreased with increasing acrylic acid content. Since the permeation of pure methanol decreased with the methacrylic acid content of the membrane while the permeation of pure water increased, the relative permeation rate of water with respect to methanol in a binary mixture increased. Thus, the separation factor increased accordingly. Since the separation factor for the acrylic acid-grafted membranes decreased, the relative rate of permeation of water with respect to methanol decreased. This suggests that the acrylic acid graft content increased the solubility and therefore the permeation rate of methanol in the membrane to a greater degree than that of water.

The permeation ratio is a measure of the ideality of permeation of binary mixtures. A permeation ratio of unity indicates ideal behavior, while values above and below unity represent a permeation enhancement and depression effect, respectively. As shown in Figure 9, the membrane in this study exhibited a permeation depression effect which became more pronounced as the degree of grafting increased. Huang and Jarvis¹ have attributed this depression effect to the formation of clusters of water molecules within the membrane. It is believed^{29,30} that these clusters form in the swollen interstitial spaces of the membrane due to hydrogen bonding between the water molecules and the polymer chains. They then impede the diffusion of single molecules through

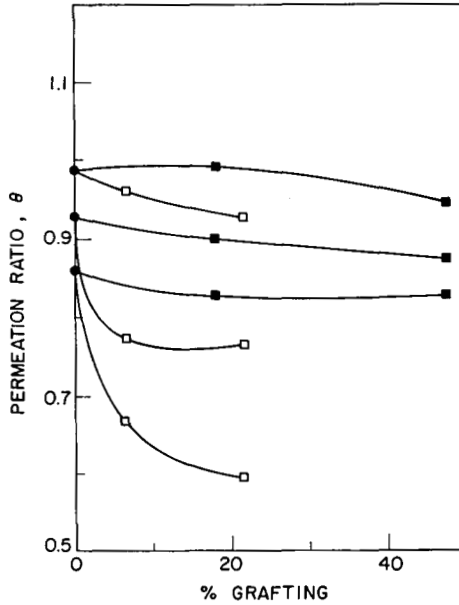


Fig. 9. Effect of the degree of grafting on the permeation ratio: (●) commercial poly(vinyl alcohol) membrane; (■) poly(vinyl alcohol)-g-acrylic acid membrane; (□) poly(vinyl alcohol)-g-methacrylic acid membrane.

the membrane with the result that the permeation rate is also depressed. Since the permeation ratio decreases with increasing graft content, this would suggest that the hydrophilic graft copolymer aids in the formation of these clusters. It can be seen from the above discussion that the grafting of hydrophilic monomers onto the poly(vinyl alcohol) backbone has resulted in an improved permeability

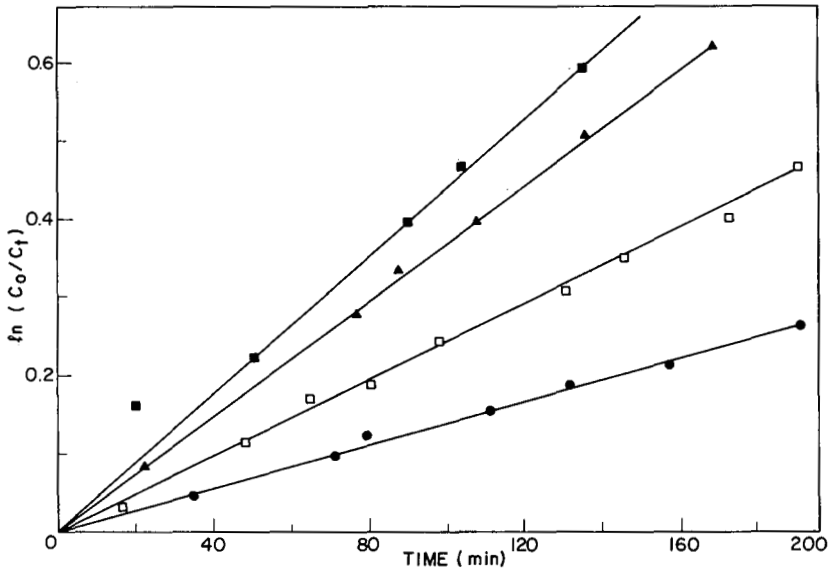


Fig. 10. Effect of acrylic acid grafting on the dialysis of methanol through poly(vinyl alcohol) membrane: (■) 72% graft; (▲) 44% graft; (□) 18% graft; (●) commercial membranes.

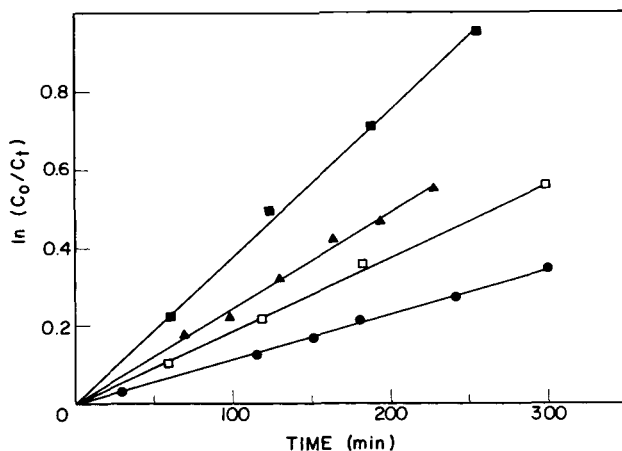


Fig. 11. Effect of acrylic acid grafting on the dialysis of urea through poly(vinyl alcohol) membranes: (■) 72% graft; (▲) 44% graft; (□) 18% graft; (●) commercial membranes.

with maintained selectivity. Although semiempirical in nature, the separation factor and permeation ratio have contributed to the understanding of the very complex nature of the interactions of the permeating species with the polymer membrane.

Dialysis

Effect of Grafting

Poly(vinyl alcohol) is a very "tight" membrane. This can be attributed to its high degree of inter- and intramolecular hydrogen bonding which is caused by the very polar hydroxyl groups. The result is that the diffusion of solutes through the membrane is inherently quite low. The grafting of substrates onto the polymer backbone has the effect of breaking down these secondary bonds and increasing the amorphous content of the membrane to yield a "looser" membrane which exhibits enhanced permeability toward various solutes. The effect of

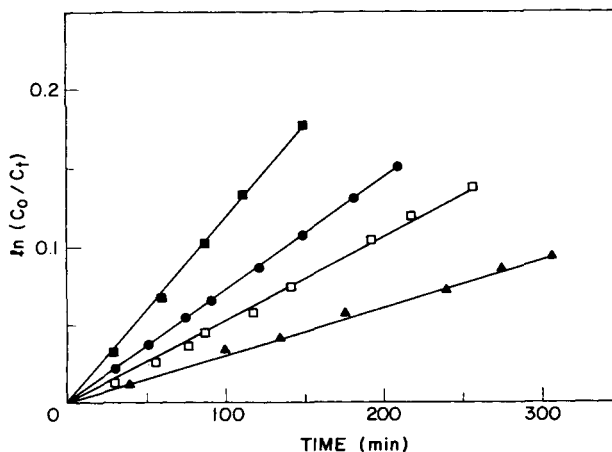


Fig. 12. Effect of acrylic acid grafting on the dialysis of sodium chloride through poly(vinyl alcohol) membranes: (■) 72% graft; (□) 44% graft; (▲) 18% graft; (●) commercial membranes.

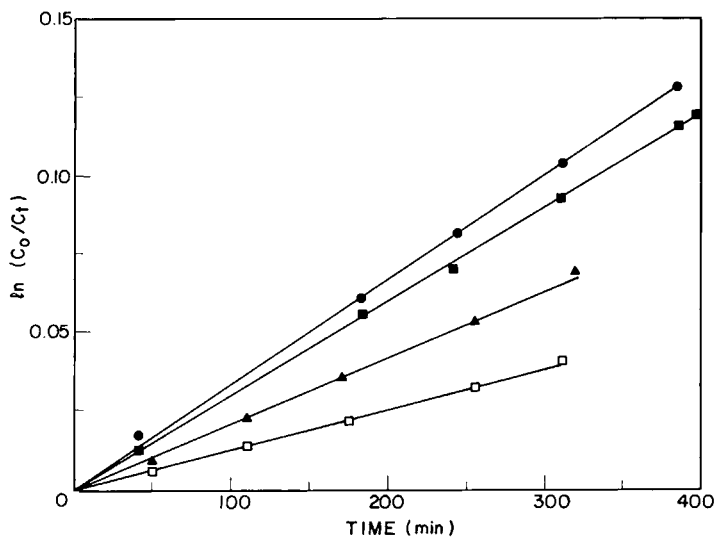


Fig. 13. Effect of acrylic acid grafting on the dialysis of uric acid through poly(vinyl alcohol) membranes: (■) 72% graft; (▲) 44% graft; (□) 18% graft; (●) commercial membranes.

grafting on the permeability coefficients of methanol, urea, and creatinine is shown in Table IV. It can be seen that the commercial membrane exhibited the lowest permeability toward these solutes. Then as the degree of grafting was

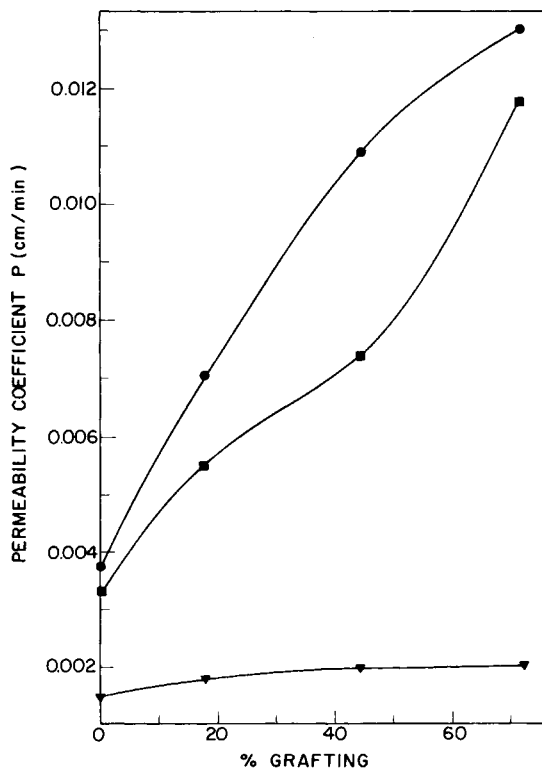


Fig. 14. Effect of acrylic acid grafting on the permeability coefficients of nonionic solutes: (●) methanol; (■) urea; (▲) creatinine.

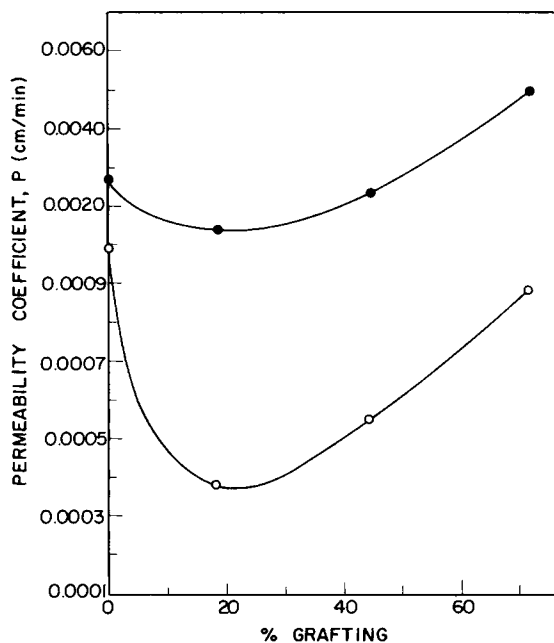


Fig. 15. Effect of acrylic acid grafting on the permeability coefficients of ionic solutes: (●) sodium chloride; (□) uric acid.

increased, the membrane structure was more loosely bound and the permeability increased.

Effect of Degree of Hydration

Ikenberry et al.²² and Yasuda et al.²³ have postulated that the volume of a membrane can be subdivided into many submicroscopic voids of varying size and shape by the segmental motion of the polymer chains. On contact with aqueous systems, these voids become filled with water, and the mechanism of dialysis is then a diffusion process where the solute moves through the water in the voids. The resistance to diffusion is caused by the segmental motion of the polymer chains. As was mentioned previously, water is soluble in both poly(acrylic acid) and poly(methacrylic acid). Therefore, as the graft copolymer content of the membrane increased, the water was able to swell and plasticize the membrane to a greater degree. The solute was then able to diffuse through these larger and more numerous subvolumes at a faster rate with less resistance from the polymer chains. Ikenberry et al.²² and Yasuda et al.²³ have postulated a relationship between the permeability coefficient and the degree of hydration of the following form:

$$\ln P \propto -\frac{1}{H}$$

A plot of the logarithm of the permeability coefficient vs. the reciprocal of the degree of hydration was made for the solutes tested in this study and is shown in Figure 16. It can be seen that a straight-line relationship exists between the two parameters. Thus, the water content of the membrane is the controlling

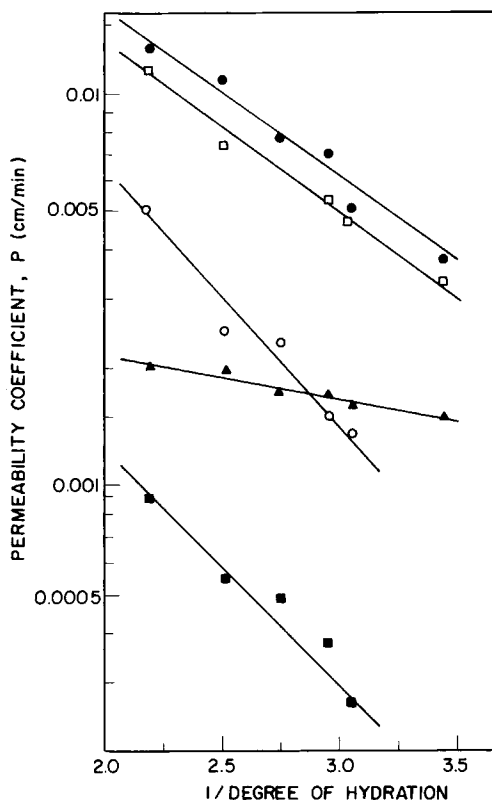


Fig. 16. Effect of the degree of hydration on the permeability coefficient: (●) methanol; (□) urea; (Δ) creatinine; (○) sodium chloride; (■) uric acid.

factor in the rate of dialysis of both ionic and nonionic solutes through the modified poly(vinyl alcohol) membranes.

Effect of Molecular Size and Chemical Nature of the Solutes

Huang and Lin²⁷ and Jarvis¹ have demonstrated the importance of size and shape of penetrant molecules in vacuum permeation studies. They concluded that as the size of the molecule increased, the permeability decreased, and this was attributed to the fact that the segmental motion of the polymer chains was more likely to produce small diffusional holes than large ones. Table V shows

TABLE V
Tabulated Results for the Permeability Coefficients of the Solutes through Poly(vinyl Alcohol)-*g*-acrylic Acid Membranes

Solute	Molecular weight	Molecular volume, Å ³	Permeability coefficient (× 10 ³) for poly(vinyl alcohol)- <i>g</i> -acrylic acid (72% graft) membrane, cm/s
Methanol	32.04	67.3	13.1
Sodium chloride	58.45	44.9	5.1
Urea	60.06	76.4	11.8
Creatinine	113.12	126.9	1.50
Uric acid	168.1	147.7	0.89

the molecular weights and molecular volumes of the solutes studied in the dialysis. The molecular volume \bar{V} was determined by dividing the molecular weight of the solute by its density and Avogadro's number. By comparing the molecular volumes of the nonionic solutes methanol, urea, and creatinine with the respective permeability coefficients, it can be observed that, as the molecular volume increased, the permeability coefficient and thus the dialysis rate decreased. This can be attributed to the decreased mobility of the larger solute in the membrane.

Because sodium chloride ions have a smaller molecular volume than methanol, it might be expected that the permeability coefficient of sodium chloride would be larger than that of methanol. However, as can be seen in Table V, its permeability coefficient is much smaller. The carboxyl groups on the acrylic acid and methacrylic acid are ionic in nature, and the grafting of these monomers onto poly(vinyl alcohol) imparts an ionic character to the membrane. Thus, the decreased permeability of sodium chloride can be attributed to the interaction between the ionic membrane and the salt. Carr²⁸ has reported that a similar ionic interaction between salts and negatively charged collodion membranes has resulted in a decreased permeability coefficient. The effect of ionic interactions between the membrane and the solute can be further illustrated by comparing the permeability coefficient of sodium chloride through the commercial membrane, which is nonionic in nature, with that through the poly(vinyl alcohol)-g-acrylic acid (18% graft) membrane. The permeability coefficient is seen to drop from 0.0026 cm/s for the commercial membrane to 0.0014 cm/s for the grafted membrane. Thus, as an ionic character was imparted to the membrane, the permeability of the membrane to ionic solutes decreased. Uric acid was another ionic solute tested in this study, and a similar ionic interaction between the solute and the membrane was found to occur.

Comparison of Modified Poly(vinyl Alcohol) and Cellophane Membranes in Dialysis

It was observed (Table IV) that the dialysis rates of methanol and urea through the grafted poly(vinyl alcohol) membranes are quite similar to those for the cellophane membranes. However, the dialysis rates of the larger molecules creatinine and uric acid are considerably lower through the grafted membranes, and bacitracin would not pass through the grafted membranes at all. This suggests that the degree of grafting of acrylic acid and methacrylic acid on poly(vinyl alcohol) has not altered the polymer structure sufficiently to accommodate these larger solutes and a higher degree of grafting is necessary. This is further substantiated by the fact that the degree of hydration of cellophane as seen in Table VI is 58% as compared with 45% for the poly(vinyl alcohol)-g-acrylic acid (72%) membrane. Thus, an increase in the degree of grafting would serve not only to alter the structure of the polymer but also to increase the degree of hydration to a value comparable to that of cellophane. The results obtained in this study indicate that the degree of hydration of the membrane is the important factor in determining the rate of transport of solutes through the membrane. The grafting of hydrophilic monomers onto the poly(vinyl alcohol) backbone has resulted in an increase in the degree of hydration with a corresponding increase in the dialysis rate of various solutes. Thus, it seems evident

TABLE VI
Tabulated Results for the Degree of Hydration of the Poly(vinyl Alcohol) and Cellophane Membranes

Membrane	Degree of hydration H, %	1/H
Commercial poly(vinyl alcohol)	29	0.034
Poly(vinyl alcohol)-g-acrylic acid (18% graft)	34	0.029
Poly(vinyl alcohol)-g-acrylic acid (44% graft)	40	0.025
Poly(vinyl alcohol)-g-acrylic acid (72% graft)	45	0.022
Poly(vinyl alcohol)-g-methacrylic acid (6.5% graft)	33	0.030
Poly(vinyl alcohol)-g-methacrylic acid (21.9% graft)	37	0.027
Cellophane dialysis membranes	58.4	0.017

that with a further increase in the degree of grafting on the membrane, the dialysis rate of these solutes would surpass that of cellophane, and these membranes might be useful in artificial kidney applications. However, it remains to be determined whether these grafted membranes are compatible with blood.

CONCLUSIONS

In this study, it was found that acrylic acid and methacrylic acid monomers could be readily grafted onto poly(vinyl alcohol) membranes from a grafting solution containing water, methanol, and monomer when exposed to gamma-ray irradiation. The grafting of acrylic acid and methacrylic acid onto poly(vinyl alcohol) has resulted in the following changes in the vacuum permeation and separation of methanol, water, and methanol-water mixtures:

(1) The permeation rate of water and methanol through the grafted membranes was found to obey an Arrhenius-type temperature relationship and is therefore an activated diffusion process. The activation energy for the permeation of pure water decreased as the graft content of the membrane increased. This was attributed to the increase in the plasticizing effect of the water on the membrane as the degree of grafting increased. The activation energy for the permeation of methanol increased with the degree of grafting. This was attributed to the resistance to diffusion caused by the grafted segments within the polymer matrix.

(2) The permeation rate of water increased considerably with the degree of grafting. The poly(vinyl alcohol)-g-acrylic acid membrane showed a fourfold increase in the permeation rate over the commercial membrane.

(3) The permeation rate of methanol through the methacrylic acid-grafted membranes decreased as the degree of grafting increased. As a result, the separation factor increased with the degree of grafting.

(4) Water was selectively permeated from binary mixtures of methanol and water, and the selectivity was not affected by the degree of grafting.

(5) The permeation ratio decreased as the degree of grafting in the membrane increased. This was attributed to the formation of water clusters in the polymer network which reduced the diffusion rate through the membrane.

The dialysis of methanol, sodium chloride, urea, creatinine, uric acid, and bacitracin through commercial poly(vinyl alcohol) membranes and through poly(vinyl alcohol)-g-acrylic acid and poly(vinyl alcohol)-g-methacrylic acid

membranes shows that the grafting of these hydrophilic monomers resulted in the following changes: (1) The degree of hydration of the membranes increased with the degree of grafting; this was attributed to the solubility of the water in the grafted substrate. (2) A direct relationship of the permeability coefficients of the solutes and the degree of hydration of the membranes was observed. (3) There was a marked difference between the permeability of the grafted and ungrafted membranes toward ionic solutes; this was attributed to the ionic character of the grafted membranes. (4) The modified poly(vinyl alcohol) membranes compared favorably with cellophane dialysis membranes in their permeability toward methanol and urea. However, the permeability of the higher-molecular-weight species, creatinine and uric acid, was significantly lower than that of cellophane.

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