Radiation-Induced Graft Copolymerization of Mixtures of Styrene and Acrylamide onto Cellulose Acetate. VI. Permeability of Sodium Chloride and Sodium Sulfate

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Synopsis

Acrylamide, styrene, and mixtures of acrylamide and styrene were grafted onto cellulose acetate film. The permeabilities of sodium chloride and sodium sulfate through the ungrafted and grafted cellulose acetate films were studied. Permeability increases with the increase in the extent of grafting of acrylamide; whereas it decreases with the increase in the extent of grafting of styrene onto cellulose acetate. The same trend in permeability was observed when cellulose acetate was grafted with the binary monomer mixture. Permeability is also found to depend on the nature of the solute dissolved in water. The results were discussed in terms of free volume concept of the water-swollen films.

INTRODUCTION

Various natural and synthetic polymeric membranes play an important role in the diffusion permeability of several solutes. Permeability of water as well as that of salts can be increased by increasing the hydrophilicity of membrane. Again, the hydrophilicity of the membrane can be increased by the introduction of some hydrophilic monomers. Various hydrophilic monomers have been reported to be grafted onto hydrophobic polymeric substrates[1] and tested for the increase of water flux and salt rejection properties. Cellulosic materials[2–4] themselves claim a special interest for their inherent water flux and salt permeation properties. Various monomers[5–11] were grafted onto cellulosics, and the permeabilities of the grafted copolymers toward salts and water were examined in the hope of developing improved membranes. During the preparation of graft copolymers some inherent properties of cellulosics are, however, destroyed. By the judicial choice of the different monomeric mixtures a membrane of versatile character can be prepared. However, permeability of water and salts through the grafted films when multicomponent monomers are grafted are very rarely studied. We have grafted two monomers, e.g., styrene which is hydrophobic and acrylamide which is hydrophilic, onto cellulose acetate film. Attempts have been made to investigate the permeability of NaCl and Na_2SO_4 through such grafted films.

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EXPERIMENTAL

Graft copolymer of styrene and acrylamide on cellulose acetate constitutes the membrane in this study. The preparation of the membrane consists essentially of two parts, e.g., preparation of cellulose acetate film and grafting of the monomer on the film. The film (ca 0.005 cm thick) was prepared by very slow evaporation of an acetone solution of cellulose acetate (acetic acid content 53.5–54.5%) powder (BDH). The monomers were grafted onto these films by taking recourse to the preirradiation grafting technique.[12]

A dialysis cell (Fig. 1) was designed to determine the diffusive permeability of sodium chloride and sodium sulfate. The dialysis cell consists of two removable parallel columns (A) which are connected through a test film (B) near the bottom by a side arm. One column (C_2) of the cell contains an aqueous solution of the solute and the other column (C_1) contains pure water. The cell is set in a thermostat in such a way that two columns can stand vertically on a magnetic stirrer, where D is the stirring bar. Experiments were carried out at a constant speed of the magnet determined by the control (E) of the magnetic stirrer. Before fixing the film between the two liquids in the dialysis cell, the film was first equilibrated with water and later blotted with filter paper, and its thickness was measured. The concentration of the solute that permeated from the solution of higher concentration to the solution of lower concentration was determined by picking up a known volume of solution from the two compartments at regular intervals of time.

The concentration of sodium chloride was determined by measuring the chloride ion using the mercuric thiocyanate method,[13] measurement being made spectrophotometrically at 460 nm. Similarly, concentration of the sodium sulfate was determined by estimating the sulfate ion using barium chloranilate,[14] where measurements were carried out spectrophotometrically at 530 nm.

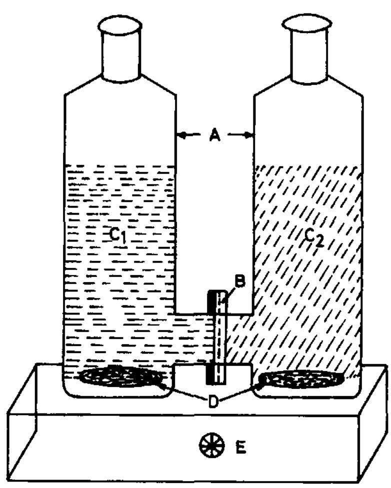

Fig. 1. Dialysis cell. A, vertical column; B, cellulose acetate film; C_1, solution of lower concentration; C_2, solution of higher concentration; D, magnetic stirring bar; E, control of the magnetic stirrer.

The permeability coefficient P (cm^2/min) was calculated using the equation[10]

$$\ln\left(\frac{C_2 - C_1}{C_2 - C_1 - 2C_t}\right) = \frac{2\ PAt}{\delta V} \tag{1}$$

where C_2 is the initial concentration of the solution at higher concentration ($0.1M$), C_1 is the initial concentration of the solution at lower concentration, C_t is the concentration that is permeated at a time (t) from the solution of higher concentration to that of lower concentration, A is the area of the film (ca. 1.5 cm^2), δ is the thickness of the film [$(5.50\text{–}7.5) \times 10^{-3}$ cm], and V is the volume of each of the solutions taken (150 cm^3).

Hydration of the ungrafted and grafted films was determined by immersing the samples in water. After equilibrium, the excess liquid adhered to the surface of the film was removed by soaking with filter paper and then reweighed immediately. Soaking and weighing were repeated for different time intervals. The weight of the swollen film at zero time of soaking was calculated by a graphical method. Then the volume of the swollen film was determined by considering the density of the film. The density of the film was measured by taking recourse to a flotation technique using carbon tetrachloride and benzene at 25°C. The hydration (H) was calculated[10] as

$$H = \frac{\text{volume of the liquid in swollen film}}{\text{volume of the swollen film}} \tag{2}$$

RESULTS AND DISCUSSION

The permeability of sodium chloride and sodium sulfate for the ungrafted cellulose acetate film and that grafted with different amounts of acrylamide, styrene, or a mixture of acrylamide and styrene were determined. According to eq. (1), $\ln(C_2 - C_1)/(C_2 - C_1 - 2C_t)$ was plotted against t (min). Typical plots, e.g., one for sodium chloride and another for sodium sulfate, are shown in Figure 2. From the initial slope the permeability coefficients P (cm^2/min) were calculated and shown in Table I. It should, however, be noted that the permeability pattern (Fig. 2) of sodium chloride does not always follow eq. (1). This might arise from the fact that diffusion of NaCl is initially larger, but decreases with the decrease of concentration gradient of the solute on the two sides of the membrane. From the table it is evident that the permeability of both sodium chloride and sodium sulfate through the acrylamide-grafted films increases with the increase in the extent of grafting of acrylamide, but decreases with the increase in the extent of grafting of styrene. Permeability also increases with the increase of acrylamide content when two monomers are simultaneously grafted onto cellulose acetate film. It is worthwhile to mention that the tensile strength of the grafted films increases when styrene is grafted to a certain limit[15] (ca. 3%). This is useful in so far as the strength of the graft material is concerned. Keeping the concentration of styrene the same, if acrylamide is grafted along with it, permeability also increases more than when styrene is grafted alone.

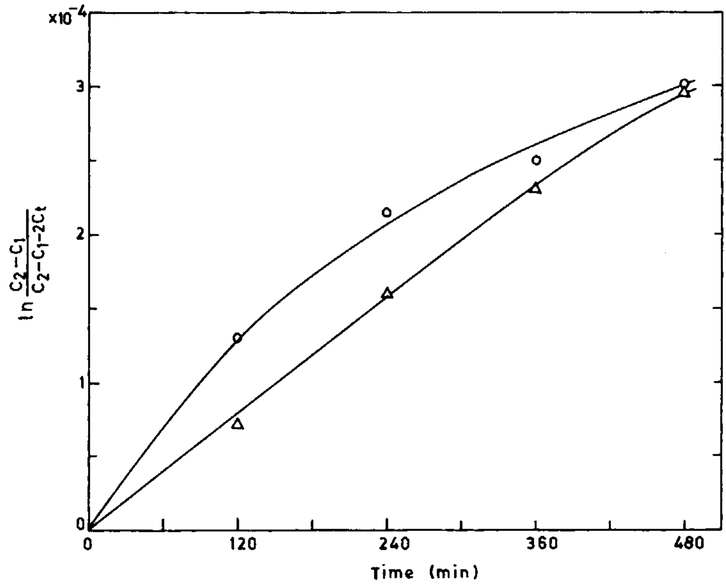

Fig. 2. Typical plot of $\ln(C_2 - C_1)/(C_2 - C_1 - 2C_t)$ against transport time t of inorganic salts through cellulose acetate film when styrene is grafted to the extent of 4.6%: (○) sodium chloride, (△) sodium sulfate.

Thus, a condition may be discovered where strength of material is appreciable and at the same time permeability is also significant. From the table it is evident that the permeability of sodium chloride is higher than that of the corresponding permeability of sodium sulfate.

Since acrylamide is a polar molecule, it increases the hydrophilic behavior of cellulose acetate. Because of the increase of hydrophilic properties of the film with the increase in the extent of grafting of acrylamide, the diffusion of the inorganic salts increases. On the other hand, styrene is hydrophobic in nature and so it decreases the hydrophilicity of cellulose acetate with the increase in the extent of its grafting. Because of the increase of the hydrophobic property of the film, the diffusion of the salts through the film is hindered. The hydrophilic and hydrophobic behaviors of the films were also justified by measuring the hydration (H) of the films. The hydration of ungrafted and grafted films was calculated and shown in Table I. From the table it is evident that hydration increases with the increase in the extent of grafting of a polar monomer, e.g., acrylamide, whereas it decreases with the increase in the extent of grafting of a nonpolar monomer, e.g., styrene. Again, hydration also increases with the increase of content of the polar monomer, e.g., acrylamide, in the mixed graft. Incidentally, Takigami, Maeda, and Nakamura[10] investigated the diffusion of potassium chloride, urea, and uric acid through a cellophane membrane grafted with a single monomer, e.g., styrene, acrylamide, acrylic acid, etc., and reported that hydration of the membranes is an important controlling factor for the permeation of solutes through the membranes. They also reported that greater permeability of solutes through acrylamide-grafted membranes compared with others is due to the greater hydration of acrylamide. In the present system, it is observed that the permeability of the salts through

TABLE I
Permeability of Inorganic Salts through Cellulose Acetate-Grafted Films

Nature of the film	Grafting (%)	Permeability coefficient (*P*) (cm² per min × 10⁷)		Hydration *H*	Slope (*Bq*/*V*) of the plot of log *P* vs. [(1/*H*) − 1]	
		NaCl	Na_2SO_4		NaCl	Na_2SO_4
Original film	—	5.7	4.0	0.183		
Acrylamide grafted	1.8	9.8	5.1	0.196		
	5.8	42.4	10.2	0.221		
	14.8	492.2	254.3	0.341	0.130	0.159
Styrene grafted	1.6	4.3	2.1	0.127		
	4.7	3.8	1.9	0.103		
	17.1	1.9	—	0.093		
Acrylamide: Styrene ratio in the graft copolymer						
1:2.2	1.7	4.1	3.0	0.113		
1:4.8	7.4	3.8	2.7	0.103		
1:4.3	16.1	4.7	3.4	0.137		
3:1.0	10.8	8.6	7.6	0.195		

the films when a single monomer or a mixture of two monomers are grafted, increases with the increase of hydration of the grafted films.

When permeability of two salts are compared, the chloride ion is more efficient than the sulfate ion for permeation through the films. This can be explained by the fact that larger ions like SO_4^{2-} are hindered in penetrating through the films more than the smaller ions like Cl^-, because the

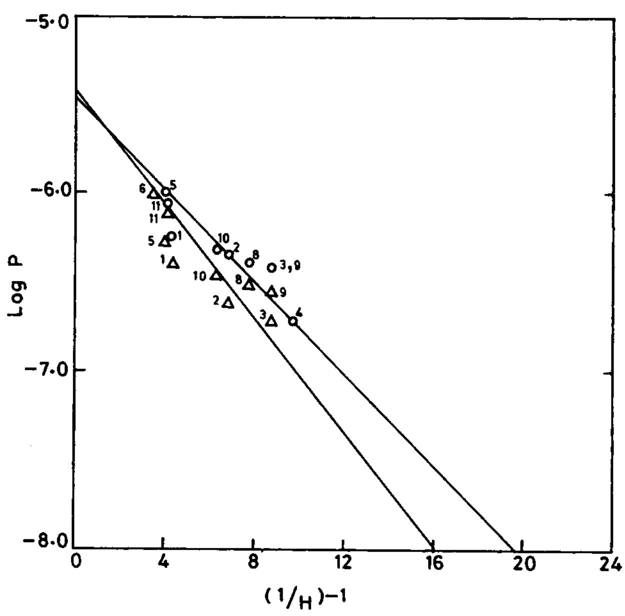

Fig. 3. Plot of log*P* vs. [(1/*H*) − 1] for various grafted cellulose acetate films: (○) sodium chloride, (△) sodium sulfate, (1) ungrafted cellulose acetate film, (2) 1.6% styrene grafted, (3) 4.7% styrene grafted, (4) 17.1% styrene grafted, (5) 1.8% acrylamide grafted, (6) 5.8% acrylamide grafted, (7) 14.8% acrylamide grafted, (8) 1.7% acrylamide + styrene grafted, (9) 7.4% acrylamide + styrene grafted, (10) 16.1% acrylamide and styrene grafted, (11) 10.8% acrylamide and styrene grafted.

macromolecular network is not sufficiently accommodative to allow such large ions[9,10] to pass through. Yasuda et al.[16-19] reported the free volume theory for the diffusional permeability of solute through water-swollen polymer membranes. The permeability coefficient (P) in such cases can be expressed[10] as

$$P/D = K\psi(q)\exp[-B(q/V)(1/H - 1)] \quad (3)$$

where D is the diffusional coefficient of the solute in pure water, K is the partition coefficient of the solute between swollen film and in solution, $\psi(q)$ indicates the sieve mechanism by which small molecules are permitted to diffuse and larger molecules are rejected, B is the proportionality factor, q is the cross-section area of the diffusing molecules, V is the free volume of pure water, and H is the hydration. Log$P$ when plotted against $[(1/H) - 1]$ gives a straight line in cases of either sodium chloride or sodium sulfate as shown in Figure 3. Slopes of such straight lines in Figure 3, i.e., Bq/V, were calculated for sodium chloride and sodium sulfate as 0.130 and 0.159, respectively. The greater permeability of sodium chloride compared with that of sodium sulfate can therefore be explained with the help of the free volume concept of solute through homogeneous polymer films.

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