Permeability of Solutes through Cellophanes Grafted with Vinyl Monomers. I. Diffusion of Potassium Chloride, Urea, and Uric Acid

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Synopsis

The diffusive permeability of potassium chloride, urea, and uric acid through cellophanes grafted with acrylamide, acrylic acid, styrene, and N-vinyl-2-pyrrolidone by γ-ray irradiation was studied. The diffusive permeability coefficients of the permeants through the grafted cellophanes were increased with increase in hydration of the grafted membranes, except for the permeation of potassium chloride through cellophanes grafted with acrylic acid. The permeation of potassium chloride, urea, and uric acid through the various grafted cellophanes is explained by the free volume concept of homogeneously water-swollen membranes. However, the behavior of the permeation of potassium chloride through cellophane grafted with acrylic acid deviated from that of nonionic membranes because of the contribution of the electrical interaction between electrolyte and charge of the membrane.

INTRODUCTION

Cellophane and modified cellulosic and synthetic polymer membranes have been extensively investigated with regard to transport of solutes[1–4] and water[5,6] for many years. Presently, regenerated cellulose membranes are used as artifitial kidneys,[7] and cellulose acetate is developed as salt rejection membrane.[8] The diffusive permeability of solutes through water-swollen polymer membranes based on the free volume theory of diffusion was studied by Yasuda et al.[1–4] However, there is little work on permeation of solutes through grafted membranes except for studies on pervaporation[9,10] and reverse osmosis.[11–13]

In this paper the diffusive permeabilities of potassium chloride, urea, and uric acid through cellophanes grafted with various vinyl monomers by γ-ray irradiation were studied and are discussed based on the concept of the free volume theory of diffusion.

EXPERIMENTAL

Materials

Cellophane (3×10^{-3} cm thick) produced by Tokyo Cellophane Co. Ltd. was used. The degree of crystallinity of the cellophane determined by the x-ray method was 32%. The cellophane was used after extraction with boiling water for 48 hr to remove plasticizer (urea and diethylene glycol).

Acrylamide (AM) was purified by recrystallization from benzene a few times. Acrylic acid (AA) and N-vinyl-2-pyrrolidone (NVP) were distilled under reduced pressure. Styrene (St) was passed through a column of activated alumina to

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remove inhibitors of polymerization before use. Potassium chloride, urea, uric acid, and other chemicals were reagent grade and were used without further purification.

Irradiation

After the purified cellophane was dried under vacuum at 50°C for 20 hr, it was irradiated under nitrogen atmosphere for 1 hr by ^{60}Co γ-rays with an exposure rate of 1.0×10^6 R/hr.

Graft Copolymerization

Graft copolymerization of AM, AA, and St onto the irradiated cellophanes was carried out in a reaction systems of AM–dioxane–water, AA–water, and St–methanol, respectively, under nitrogen atmophere at 30°C. Liquor-to-material ratio was maintained at 200:1. In the case of NVP, cellophane was grafted by the mutual irradiation method[14,15] as follows. The cellophane was put into the glass tube with NVP, water, and buffer solution (ammonium hydroxide–ammonium chloride, pH 9.1). The tube was subjected to several freeze–thaw cycles under reduced pressure and then irradiated with ^{60}Co γ-rays at an exposure rate of 1.0×10^6 R/hr for 1 hr at room temperature. After graft copolymerization, the samples grafted with AM, AA, and NVP were washed with distilled water and extracted with boiling water to remove homopolymers. After St-grafted cellophanes were washed with methanol and distilled water, the samples were extracted with hot benzene to remove homopolymer prior to drying under vacuum. Extent of grafting was expressed as weight percent increase based on the original weight of the sample.

Diffusive Permeability

The diffusive permeability of potassium chloride, urea, and uric acid was measured by the use of a dialysis cell,[16] as shown in Figure 1. The upper and lower compartments were filled with aqueous solution of concentrations C' and C'' (in moles/l. $C' < C''$), respectively. The membrane was equilibrated in the solution of permeant which had the same concentration as the solution filled in the upper compartment of the cell, and was blotted between sheets of filter paper and attached to the upper compartment of the cell. The cell was set in a thermostat at 30 ± 0.1°C, and the solution in both compartments were magnetically stirred at 50 rpm. The concentration of solute that permeated from the lower compartment to the upper one was determined by picking up the little amount of solution from the upper compartment at regular time intervals. Permeability coefficient P (in cm^2/min) was calculated according to the equation

$$\ln \frac{C'' - C'}{C'' - C' - 2C_t} = \frac{2PAt}{\delta V} \tag{1}$$

where C' is the initial concentration of the solution in the upper compartment, C'' is the initial concentration of the solution in the lower compartment, C_t is the concentration of the solute that is transported from the lower compartment to the upper one at time t (in min), A is the membrane area (20 cm^2), δ is the

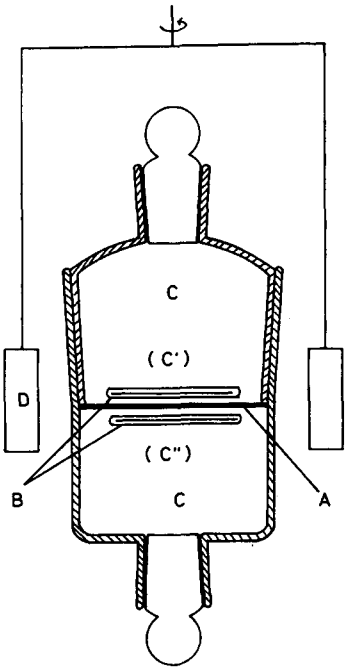

Fig. 1. Dialysis cell: A, membrane; B, stirrer; C, cell; D, magnet; C', concentration of solution in upper compartment of cell (mole/liter), C'', concentration of solution in lower compartment of cell (mole/liter).

membrane thickness (in cm), and V is the volume of each compartment of the cell (100 cm^3). The concentration of potassium chloride was determined by the Mohr method. In the case of urea, *p*-dimethylaminobenzaldehyde was added to the urea solution, and the concentration was analyzed[17] colorimetrically (440 nm). The concentration of uric acid was determined spectrophotometrically (286 nm).

Membrane Thickness

The sample was immersed in the solution with the same concentration as the solution that filled the upper compartment of the cell. After equilibrium, the membrane thickness was measured by microscope.

Density

Density of the grafted sample was measured by use of a density gradient column consisting of carbon tetrachloride and *n*-hexane at 25 ± 0.1°C.

Hydration

The weighed sample was immersed in solution which had the same concentration (C') as the solution in the upper compartment. After equilibrium, the sample was placed between sheets of filter paper and rolled to remove the solution on the membrane surface prior to weighing. This process was repeated several

times to plot the weight of the swollen sample against the times of repeated rolling. By extrapolation of the linear part of the curve to zero time, the weight of the swollen sample at zero time was determined and was subsequently converted into the volume of the swollen sample by using the density of the grafted membrane. Hydration of the sample, H, was calculated according to the following equation:

$$H = \frac{\text{volume of the solution in swollen membrane}}{\text{volume of the swollen membrane}} \quad (2)$$

Partition Coefficient

The weighed samples was equilibrated in the solution of the same concentration as the solution in the upper compartment of the cell; and after picking up the sample, the extra solution on the surface of the membrane was removed by filter paper. The sample was kept in distilled water with stirring for 5 hr, and then the amount of solute extracted from the swollen sample was determined by analyzing the solute. Partition coefficient K_2 was calculated according to the following equation:

$$K_2 = \frac{\text{grams solute per 1 cm}^3\text{ swollen membrane}}{\text{grams solute per 1 cm}^3\text{ solution}} \quad (3)$$

RESULTS AND DISCUSSION

Diffusive permeability of potassium chloride, urea, and uric acid was determined for AM-, AA-, St-, and NVP-grafted cellophanes. The permeability of potassium chloride and urea was measured when r ($= C''/C'$) was 16; however, in the case of uric acid, distilled water without uric acid was charged in the upper compartment. The relation between $\ln (C'' - C')/(C'' - C' - 2C_t)$ and t for potassium chloride is shown in Figure 2 on the various grafted cellophanes. The values of $\ln (C'' - C')/(C'' - C' - 2C_t)$ increased linearly with increase in t for all the grafted membranes. The diffusive permeability coefficients were calculated from the slope of each straight line. Linearity between $\ln (C'' - C')/(C'' - C' - 2C_t)$ and t was similarly obtained when urea and uric acid were used in place of potassium chloride, and the permeability coefficients were calculated. These results are shown in Tables I and II together with the hydration, partition, and diffusion coefficients. As shown in Table I, the permeability coefficients of potassium chloride for untreated and NVP-grafted cellophanes were little changed by variation in C''. Similar results are presumed on cellophanes grafted with St and AM because they are nonionic grafted membranes. However, permeability coefficients of potassium chloride for the cellophanes grafted with AA were dependent on the concentration of C''. This may be due to the diffusive permeation of potassium chloride through AA-grafted cellophane which is polyelectrolyte. Details on the potassium chloride permeation through cellophanes grafted with AA will be reported in our next paper.

The permeation of urea and uric acid through the various grafted membranes was determined at C'' of 0.16 mole/liter and 0.38×10^{-4} mole/liter, respectively (Table II). Since urea and uric acid are nonelectrolytes, the permeation of the

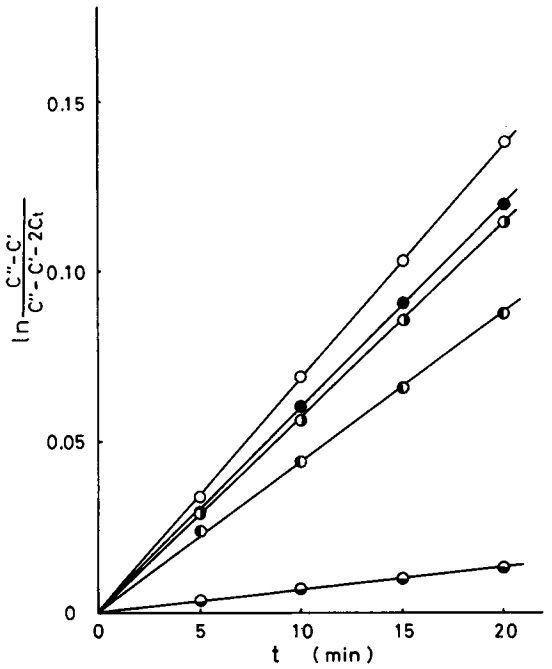

Fig. 2. Relation between ln $[(C'' - C')/(C'' - C' - 2C_t)]$ and measurement time t for potassium chloride: (○) control cellophane; (●) NVP-grafted cellophane with 25% grafting; (◑) AM-grafted cellophane with 60% grafting; (◐) AA-grafted cellophane with 60% grafting; (◒) St-grafted cellophane with 30% grafting.

TABLE I
Hydration H, Permeability $P_{2,13}$, Partition Coefficient K_2, and Diffusion Coefficient $D_{2,13}$ of Potassium Chloride for Various Grafted Cellophanes

Sample	H	$P_{2,13}$, 10^{-5} cm²/min			K_2	$D_{2,13}$, 10^{-5} cm²/min
		C'' = 1.6 mole/liter	0.16 mole/liter	0.016 mole/liter		
Untreated	0.586	7.06	6.80	6.80	0.345	20.46
15% St	0.491	2.76	—	—	0.351	7.86
30% St	0.406	0.84	—	—	0.242	3.47
25% NVP	0.580	6.20	6.20	5.83	0.407	15.23
15% AM	0.574	6.39	—	—	0.331	19.31
60% AM	0.635	10.70	—	—	0.421	25.42
8% AA	0.547	6.78	5.76	4.92	—	—
25% AA	0.555	6.41	4.33	2.24	—	—
60% AA	0.601	6.70	5.46	3.57	—	—

solutes through the grafted cellophanes might be almost independent on concentration C'' as inferred from the result of the permeation of potassium chloride through NVP-grafted membrane, which is a nonionic membrane as shown in Table I.

The diffusional transport of solute in aqueous solution through water-swollen membranes based on the concept of the free volume theory has been reported by Yasuda et al.[1-4] The permeability coefficient $P_{2,13}$ of solute through homogeneously swollen membrane is expressed in the following equation:

$$P_{2,13}/D_{2,1} = K_2 \varphi(q_2) \exp [-B(q_2/V_{f,1})(1/H - 1)] \quad (4)$$

TABLE II
Hydration H, Permeability $P_{2,13}$, Partition Coefficient K_2, and Diffusion Coefficient $D_{2,13}$ of Urea and Uric Acid for Various Grafted Cellophanes

	Urea (0.16 mole/liter)				Uric acid (0.38×10^{-4} mole/liter)	
Sample	H	$P_{2,13}$, 10^{-5} cm^2/min	K_2	$D_{2,13}$, 10^{-5} cm^2/min	H	$P_{2,13}$, 10^{-5} cm^2/min
Untreated	0.579					
Untreated	0.579	5.05	0.324	15.59	0.556	1.93
15% St	0.472	1.31	0.202	6.49	0.492	0.69
30% St	0.383	0.41	0.129	3.18	0.445	0.32
25% NVP	0.609	5.41	0.305	17.74	0.582	1.80
15% AM	0.566	4.90	0.345	14.20	0.542	1.56
60% AM	0.610	7.43	0.311	23.89	0.646	2.76
8% AA	0.547	—	—	—	—	—
25% AA	0.553	4.80	0.367	13.08	0.558	2.21
60% AA	0.583	7.23	0.322	22.45	0.617	2.17

where $D_{2,1}$ is the diffusion coefficient of the solute in pure water, K_2 is the partition coefficient, $\varphi(q_2)$ describes the sieve mechanism by which small molecules are permitted to diffuse and larger molecules are rejected because the macromolecular network has no hole of appropriated size, $V_{f,1}$ is the free volume of pure water, q_2 is the cross-sectional area of the diffusing molecule, and B is a proportionality factor. Suffixes 1, 2, 3, and 13 mean water, solute, polymer, and water-swollen polymer, respectively.

The relationship between the permeability coefficient $P_{2,13}$ and hydration H given in Tables I and II on various grafted membranes is shown in Figure 3. The plot of log $P_{2,13}$ against $(1/H) - 1$ gives a straight line for all the permeants, and $P_{2,13}$ increases with increase in H. The permeability coefficient was largest for potassium chloride and smallest for uric acid. The slope $Bq_2/V_{f,1}$ calculated from each straight line was 0.48, 0.47, and 0.60 for potassium chloride, urea, and uric acid, respectively. The results on the grafted cellophanes are based on the free volume concept of permeation of solute through homogeneous polymer membrane. In general, the diffusion coefficient $D_{2,13}$ of the solute in a swollen membrane can be related to permeability coefficient $P_{2,13}$ in the following equation[4]:

$$D_{2,13} = P_{2,13}K_2 \tag{5}$$

From eqs. (4) and (5), the diffusion coefficient $D_{2,13}$ can be written as

$$D_{2,13}/D_{2,1} = \varphi(q_2) \exp [- B(q_2/V_{f,1})(1/H - 1)] \tag{6}$$

In this study, the partition coefficient K_2 was measured, and then the diffusion coefficient $D_{2,13}$ was determined according to eq. (6). The values are given in Tables I and II for potassium chloride and urea, respectively. However, it was difficult to determine the diffusion coefficient of uric acid, since the solubility of uric acid in water was so poor that the partition coefficient was not measured for all the grafted membranes. Therefore, the relationship between $D_{2,13}$ and H for potassium chloride and urea is shown in Figure 4.

The plot of log $D_{2,13}$ against $(1/H) - 1$ gave a straight line as did the dependence of log $P_{2,13}$ on $(1/H) - 1$ for both solutes. The intercepts $\varphi(q_2)D_{2,1}$ at H

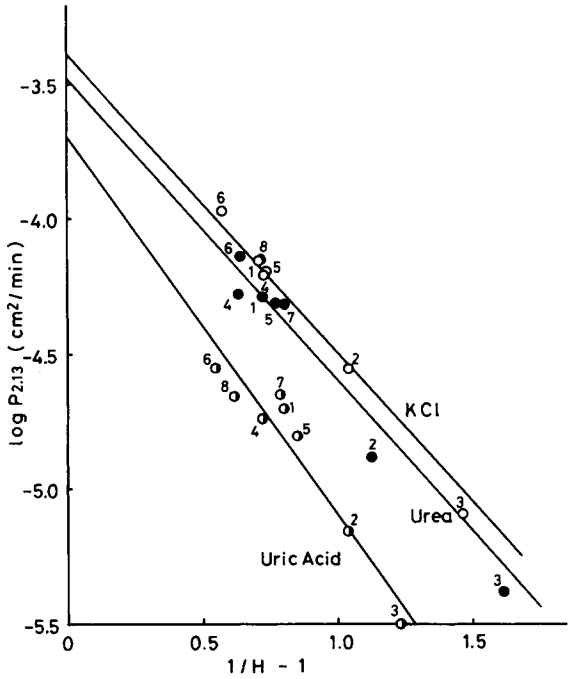

Fig. 3. Relation between log $P_{2,13}$ and $(1/H) - 1$ for various grafted cellophanes: (○) potassium chloride; (●) urea; (◑) uric acid; 1, control cellophane; 2, St-grafted cellophane with 15% grafting; 3, St-grafted cellophane with 30% grafting; 4, NVP-grafted cellophane with 25% grafting; 5, AM-grafted cellophane with 15% grafting; 6, AM-grafted cellophane with 60% grafting; 7, AA-grafted cellophane with 25% grafting; 8, AA-grafted cellophane with 60% grafting.

= 1 and the slope $Bq_2/V_{f,1}$ calculated from Figure 4 are shown in Table III. $\varphi(q_2)$ is a parameter for the sieve mechanism and depends on the conditions of a membrane in aqueous solution and the size of the permeant. However, since the plot of log $D_{2,13}$ against $(1/H) - 1$ showed a straight line for both solutes, it may be deduced that the value of $\varphi(q_2)$ is a constant for both solutes regardless of the kind of grafted membrane. On the other hand, it was reported that the diffusion coefficient $D_{2,1}$ of potassium chloride and urea, as shown in Table III, is 1.94×10^{-5} and 1.37×10^{-5} cm²/sec, respectively. Taking into account the differences in the measurement conditions, the values are almost the same as the values of $\varphi(q_2)D_{2,1}$ found at $H = 1$. Therefore, it is estimated that $\varphi(q_2)$ is unity for both solutes without dependence on the range of hydration for the various grafted membranes.

From the above results, it is not considered that the sieve effect interferes with the permeation of potassium chloride and urea through the grafted cellophanes. The slope $Bq_2/V_{f,1}$ which is proportional to the effective cross section of the permeant is shown in Table III. The $Bq_2/V_{f,1}$ value of potassium chloride was almost the same as that of urea, but smaller than that of uric acid. These results may be attributed to the fact that the effective cross section of potassium chloride hydrated with water is almost similar to that of urea with hydration but is somewhat smaller than that of hydrated uric acid.

In conclusion, the diffusive permeability coefficients of potassium chloride, urea, and uric acid through cellophanes grafted with AM, AA, St, and NVP, ex-

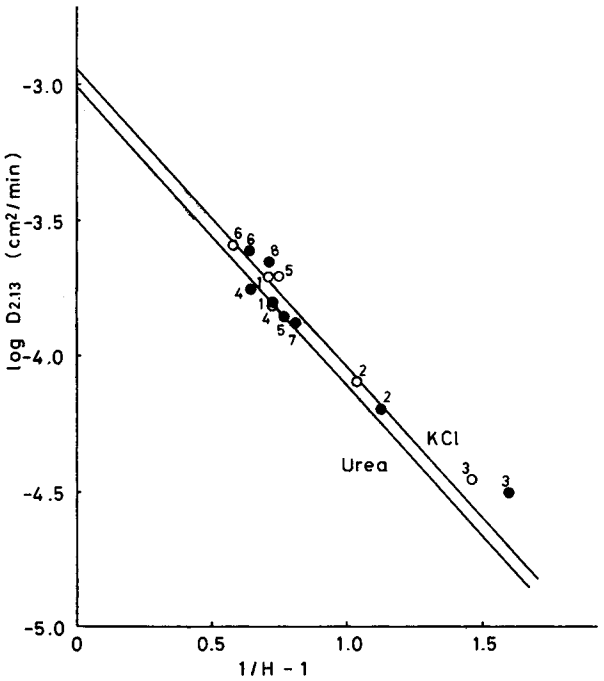

Fig. 4. Relation between log $D_{2,13}$ and $1/H - 1$ for various grafted cellophanes: (○) potassium chloride; (●) urea; 1, control cellophane; 2, St-grafted cellophane with 15% grafting; 3, St-grafted cellophane with 30% grafting; 4, NVP-grafted cellophane with 25% grafting; 5, AM-grafted cellophane with 15% grafting; 6, AM-grafted cellophane with 60% grafting; 7, AA-grafted cellophane with 25% grafting; 8, AA-grafted cellophane with 60% grafting.

TABLE III
Values of Intercept $\varphi(q_2)D_{2,1}$ and Slope $Bq_2/V_{f,1}$ Calculated from Figures 3 and 4

Solute	Difference in concentration ($\Delta C = C'' - C'$), mole/liter	$\varphi(q_2)D_{2,1}$ at $H = 1$, 10^{-5} cm²/sec[a]	$Bq_2/V_{f,1}$
KCl	1.5	1.91	0.48
Urea	0.15	1.63	0.47
Uric acid	3.81×10^{-4}	—	0.60

[a] Difference in concentration C (for KCl is 1.44 mole/liter) with $D_{2,1}$ (of 1.94×10^{-5} cm²/sec at 25°C); ΔC for urea is 0.16 with $D_{2,1}$ of 1.37×10^{-5} cm²/sec at 25°C.

cept for the permeation of potassium chloride through cellophanes grafted with AA, increased with increase in hydration of the grafted cellophanes. The permeation of potassium chloride, urea, and uric acid through the various grafted cellophanes, except for the permeation of potassium chloride through cellophanes grafted with AA, can be well explained by the free volume concept of diffusion for homogeneously water-swollen membrane. Such a deviation on the permeation of ionic solutes through ionic membranes may be due to the contribution of the electrical interaction between electrolyte and charge of the membrane.

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