

Application of the Theory to Experimental Results

The kinetic data⁵ for hydrazine-bromine reaction in 7.2M H₂SO₄ are plotted in Figure 1. Simple second-order treatment by Eq. (16) gives gradually decreasing value of k_1 starting from 97 M⁻¹sec⁻¹ at 7.5 sec to 88 at 82.5 sec. However both Eqs. (14) and (16') give fairly good straight lines that are dominated by $\ln B$. The straight line portion of the competitive consecutive second-order plot of Eq. (14) gives 42 M⁻¹sec⁻¹, whereas the plot of Eq. (16') gives 86 M⁻¹sec⁻¹. The fact that the deviation of initial stage is rather small and diminishes rather rapidly can be attributed to a large value of K so that the magnitude of the term A_0z^K becomes negligible at an early stage of the reaction. Since the point corresponding to $z=0.98$ lies on the straight line, the value of K is inferred to be greater than 10.² Unfortunately, a small

portion of B (mainly N₂H₂ in the present example) is consumed by some side reaction so that estimation of the value of K from stoichiometry may not give results of desirable accuracy, in the present example.

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Temperature Dependence of Self-Diffusion of THO in Copolymer Hydrogel Membrane as a Function of Gel Compositions

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The self-diffusion experiment of THO was performed across a series of copolymer hydrogel membranes at different temperatures. Copolymer hydrogel membranes were prepared by copolymerizing 2-hydroxyethyl methacrylate (HEMA) and 2-aminoethyl methacrylate (AEMA) in the presence of the solvent and the crosslinker, ethylene glycol dimethacrylate (EGDMA). By changing the crosslinker content and the ratio of HEMA and AEMA monomer, two series of copolymer hydrogel membranes were synthesized. The tagging material was THO and efflux of THO was counted on a Liquid Scintillation Counter. The experimental data show that the permeability decreases as the amount of EGDMA and the mole fraction of HEMA increase, and the permeability is proportional to the temperature. The partition coefficient shows a parallel trend with permeability. Using the relationship between viscosity and diffusivity, the viscosity of water within the membrane was obtained. According to the result, the viscosity of water within the membrane has the same value with those of supercooling water. And we obtained the activation energy of THO for transport in the membrane by using Arrhenius plotting.

Introduction

The properties of poly(2-hydroxyethyl methacrylate) (HEMA) hydrogel membrane were investigated by many authors. It is the reason that poly(HEMA) have attracted considerable attentions for medical applications because of their low chemical reactivity, high strength, and high permeability, and have been introduced as important biocompatible materials.¹⁻⁶ The experiments for the transport phenomena have been performed by many authors and given many informations about it. Spacek *et al.*⁷ showed that the diffusion coefficient strongly depends on the structure of the hydrogel membrane investigated. Chen⁸ found that water swelling was changed by the crosslinker content in the dehydrated poly (HEMA) hydrogels. Recently, Kim *et al.*⁹ measured the permeability of THO through fully swollen poly (HEMA) hydrogel membrane with varying the cross-

linker content. They found that diffusion coefficients decrease as the crosslinker contents increase. Refojo *et al.*³ measured the swelling contents in hydrogels at the temperature is varied. They found that the minimum in the amount of water in hydrogel is found in the neighborhood of 60°C and the amount of water in the hydrogel increases up to the freezing and boiling temperature, and the minimum found in the curve in the HEMA hydrogel is independent of the temperature at which the polymerization was carried out. Wisniewski¹⁰ measured the temperature effects of permeation of THO across poly (HEMA) membrane. According to the temperature dependence of diffusion coefficient, they performed the Arrhenius plots and found the activation energy of THO for transport through poly (HEMA) membrane.

In this paper, we measured the permeability and partition coefficient of THO in the copolymer hydrogel membranes with varying the ratio of HEMA and AEMA monomer and

the crosslinker content at three different temperatures. From the obtained permeability and partition coefficient, we evaluated the self-diffusion coefficient. Using the relationship between diffusivity and viscosity, the viscosity of water within the membrane was obtained. From the temperature dependence of self-diffusion coefficient, we evaluated the activation energy of THO for transport in copolymer hydrogel membrane by means of Arrhenius plotting. From these results, we predict the change of gel matrix by copolymerizing HEMA and AEMA monomer.

Experimental Method

Materials. Highly pure 2-hydroxyethyl methacrylate (HEMA) and 2-aminoethyl methacrylate (AEMA) monomer of low diester content were obtained from Polyscience Inc. Ethylene glycol dimethacrylate (EGDMA) was also obtained from Polyscience Inc. The tagging material, THO, was supplied by New England Nuclear Company and its specific activity is 25 mCi/mol.

Membrane preparation. Membrane was prepared by copolymerizing the HEMA and AEMA monomer in the presence of water as a solvent. The redox system, ammonium persulfate and sodium metabisulfite (Fisher Scientific Company), was used as an initiator agent for copolymerization. To prepare the copolymer hydrogel membrane, the comonomer solutions were placed between two glass plates for 24 hrs. at room temperature. The recipes of the comonomer solutions are given in Table 1.

Permeability. We obtained the permeability P , using the following relation derived from the mass balance equation;¹¹

$$\ln(1-2C_t/C_0) = -(1/V_1 + 1/V_2) \cdot A \cdot P / d \cdot t \quad (1)$$

where V_1 is the volume of the concentrated compartment, V_2 is the volume of the diluent compartment, A is the membrane area, d is the membrane thickness, C_0 is the count of THO at time 0 in the concentrated compartment, and C_t is the count of THO at time t in the diluent compartment. The plots of $\ln(1-2C_t/C_0)$ versus time yield a straight line with the slope of $-(1/V_1 + 1/V_2) \cdot A \cdot P / d$. Substituting measured values of V_1 , V_2 , A , and d gives the permeability $P(\text{cm}^2/\text{sec})$. A permeation cell was designed in our laboratory.¹² It has two compartments of equal volume, 200 ml. Initially, one compartment was charged with the THO aqueous solution whose concentration was 40 $\mu\text{l/l}$ and the other compartment with triply distilled water. Each compartment stirred at 750 rpm to eliminate the boundary effect. The experiment was performed at 5°, 25° and 50°C respectively. At time t , 50 $\mu\text{l/l}$ of the sample was taken from the diluent compartment and transferred into plastic vials into which scintillation solutions were previously introduced. The samples were analyzed on a Liquid Scintillation Counter.

Partition coefficient. We used two-step sorption and desorption technique to obtain the partition coefficient. Here K_{D_2} is defined as follows;¹³

$$K_{D_2} = \frac{V_s^0}{V^m} \left(\frac{C_{i_2}'}{C_{i_1}' - C_{i_2}'} \right) \quad (2)$$

TABLE 1: Recipe of the Comonomer Solution (Unit: ml)

	1	2	3	4
HEMA	10	11	12	12.5
AEMA	2.5	1.5	0.5	0
EGDMA	0.1	0.1	0.1	0.1
(NH ₄) ₂ S ₂ O ₈ (40g in 100 ml H ₂ O)	2.5	2.5	2.5	2.5
Na ₂ S ₂ O ₅ (15g in 100 ml H ₂ O)	2.5	2.5	2.5	2.5
	I	II	III	IV
HEMA	9	11	11	12.5
AEMA	3.5	1.5	0.5	0
EGDMA	0.25	0.25	0.25	0.25
(NH ₄) ₂ S ₂ O ₈ (40g in 100 ml H ₂ O)	2.5	2.5	2.5	2.5
Na ₂ S ₂ O ₅ (15g in 100 ml H ₂ O)	2.5	2.5	2.5	2.5

where V_s^0 is the volume of the surrounding solution, V^m is the volume of the swollen membrane which is equal in both sorption and desorption experiments, C_{i_1}' is the count of the surrounding solution after sorption, and C_{i_2}' is the count of the surrounding solution after desorption. Presoaked membranes at constant temperature were surface dried between damp filters and placed in the stoppered bottle containing 20 ml of aqueous THO solution of known concentration. The membranes were equilibrated for 48 hrs. at constant temperature, then, removed, surface dried and placed in the bottle containing 20 ml of pure water for 48 hrs. at constant temperature. From the first equilibrium, we obtained C_{i_1}' and from the second equilibrium, C_{i_2}' was obtained. The samples were analyzed on a Liquid Scintillation Counter.

Results and Discussion

Figure 1 and Figure 2 show that the permeability of THO across the membrane decreases with the increase of crosslinker content and the ratio of HEMA, and it is proportional to the temperature. This is a parallel trend with poly (HEMA). The permeability data obtained from the membrane with different crosslinker content (0.52, 1.3 mole %) exhibit a parallel trend but the membrane with 0.52 mole % crosslinker gives the higher value of permeability than the membrane with 1.3 mole % crosslinker. The partition coefficient of THO obtained from two-step sorption and desorption technique is shown in Figure 3 and Figure 4. The partition coefficient and the permeability exhibit a parallel trend with the crosslinker content and ratio of HEMA, but the partition coefficient is inversely proportional to the temperature. Assuming that the partition coefficient is proportional to the water content, we estimate the temperature dependence of partition coefficient from the temperature dependence of swelling of hydrogels. According to Refojo, a minimum in the amount of water in hydrogels is found in the neighborhood of 60°C and the amount of water in hydrogels increases up to the freezing and boiling temperature. So, the inverse propor-

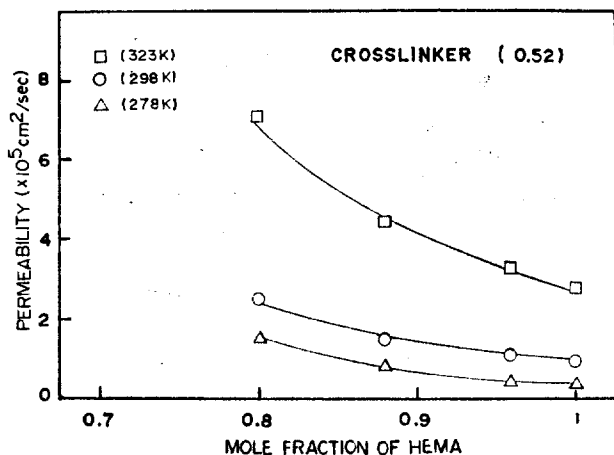


Figure 1. The Permeability of THO through copolymer hydrogel membranes with 0.52 mole % crosslinker as a function gel composition.

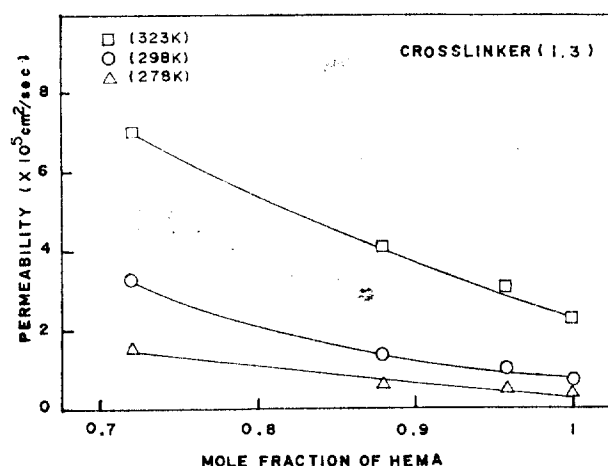


Figure 2. The permeability of THO through copolymer hydrogel membranes with 1.3 mole % crosslinker as a function of gel composition.

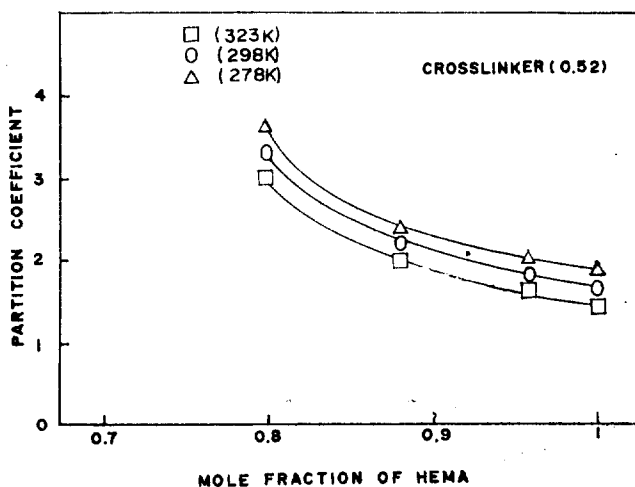


Figure 3. The partition coefficient of THO copolymer hydrogel membranes with 0.52 mole % crosslinker as a function of gel composition.

tionality of partition coefficient to the temperature is reasonable.

The self-diffusion coefficient of THO is obtained from the

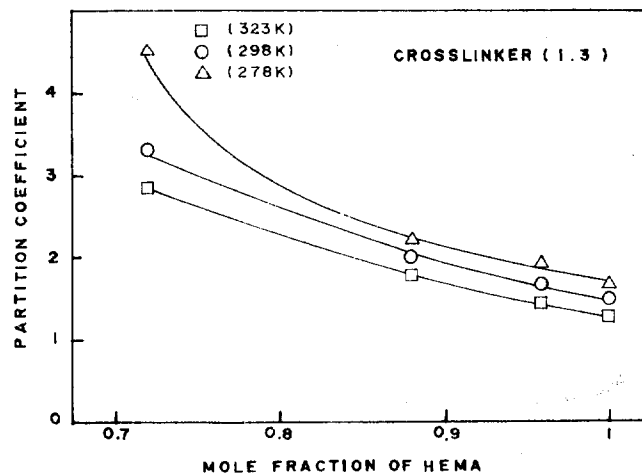


Figure 4. The partition coefficient of THO copolymer hydrogel membranes with 1.3 mole % crosslinker as a function of gel composition.

following relationship;

$$P = K_D \cdot D \quad (3)$$

where P is the permeability and K_D is the partition coefficient. The obtained self-diffusion coefficient data are presented in Table 2 and exhibit a parallel trend with the permeability.

The relationship^{14,15} between the self-diffusion coefficient and viscosity is used to calculate the viscosity of water in the membrane;

$$D = \frac{kT}{6 \left(\frac{\sqrt{2} V_s}{N} \right)^{1/3} \eta} \quad (4)$$

where V_s , N , k , and T are the solid-like volume of water, Avogadro's number, Boltzman constant, and absolute temperature, respectively.

The corresponding temperature to viscosity of water in the membrane phase can be obtained by the following equation;¹⁶

$$\log \frac{\eta_t}{\eta_{20}} = \frac{A(20-t) - B(t-20)^2}{t+C} \quad (5)$$

where η_t is the viscosity of water at temperature t °C, η_{20} is the viscosity of water at 20°C ($\eta_{20} = 1.02$ cp), and the parameter A , B , and C represent 1.1709, 0.001027, and 89.93, respectively.

The calculated viscosity and the corresponding temperature of water in the membrane phase from above equations are presented in Table 3. The results show that the calculated viscosity increases as the ratio of HEMA and the crosslinker content increase, and the corresponding temperature of water in the membrane phase is lowered as the ratio of HEMA and the crosslinker content increase.

From the temperature dependence of self-diffusion coefficient, Arrhenius activation energy of THO across the membrane can be obtained by using the following relationship;

$$D = D_0 \exp(-E_a/RT) \quad (6)$$

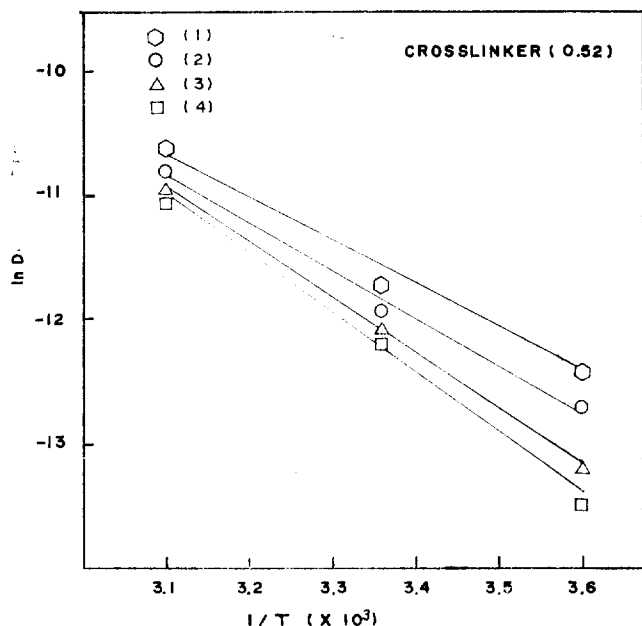
where D is the diffusion coefficient, E_a is the Arrhenius

TABLE 2: Diffusion Coefficient (D) of THO Across the membrane ($\times 10^6$ cm²/sec)

	278 K	298 K	323 K
1	0.42	0.72	2.39
2	0.32	0.65	2.17
3	0.18	0.56	1.73
4	0.13	0.53	1.67
I	0.33	0.91	2.37
II	0.29	0.64	2.12
III	0.24	0.58	1.84
IV	0.11	0.39	1.57

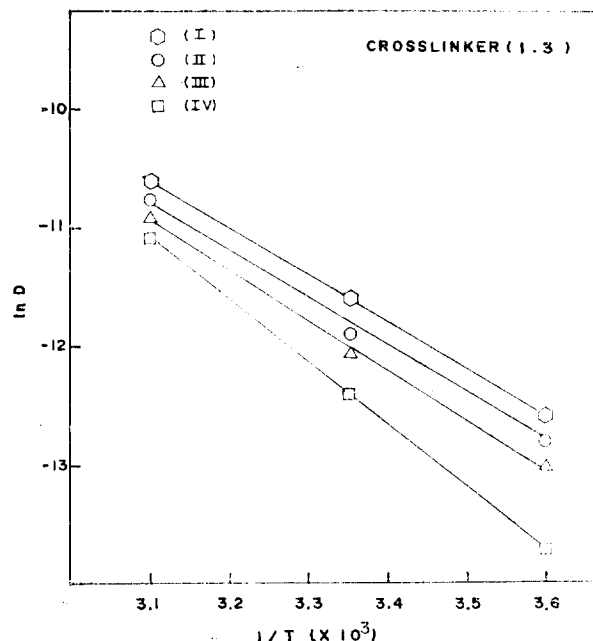
TABLE 3: The Calculated Viscosity and the Corresponding Temperature of Water

	278 K		298 K		323 K	
	η_r	t (°C)	η_r	t (°C)	η_r	t (°C)
1	4.40	-19.53	2.75	-10.15	0.90	25.00
2	5.57	-23.49	3.05	-12.41	0.99	21.23
3	10.26	-31.98	3.54	-15.47	1.24	12.52
4	14.20	-35.70	3.74	-16.53	1.29	11.23
I	5.60	-23.58	2.18	-4.57	0.91	23.84
II	6.37	-25.56	3.09	-12.69	1.01	20.40
III	7.69	-28.25	3.42	-14.78	1.17	14.65
IV	16.78	-37.42	5.08	-22.00	1.41	8.10

**Figure 5.** The plot of $\ln D$ versus $1/T$ for copolymer hydrogel membranes with 0.52 mole % crosslinker.

activation energy of THO across the membrane, R is the gas constant, T is the absolute temperature, and D_0 is the pre-exponential term.

The plots of $\ln D$ versus $1/T$ yield a straight line with the slope of $-E_a/R$. The results are presented in Figure 5 and Figure 6. The results indicate that the Arrhenius activation energy of THO across the membrane increases as the ratio of HEMA and the crosslinker content increase. The Arrhenius activation energies as a function of gel composition are

**Figure 6.** The plot of $\ln D$ versus $1/T$ for copolymer hydrogel membranes with 1.3 mole % crosslinker.**TABLE 4: Arrhenius Activation Energies of THO Across the Membrane as a Function of Gel Composition**

	E_a (kcal/mole)
1	6.93
2	7.62
3	9.02
4	10.12
I	7.75
II	7.93
III	8.12
IV	10.58

presented in Table 4.

Conclusion

There are many informations about the properties of poly (HEMA) because many experiments in many aspects have been performed. The measurement of permeability, partition coefficient, and diffusivity as a function of gel composition, crosslinker content, and temperature can be one of the examples of above experiments.

In this paper, we applied these experiments to copolymer hydrogel membrane consisting of HEMA and AEMA. These experimental data show that copolymer hydrogel membrane exhibits a parallel trend with poly (HEMA) hydrogel membrane. The permeability, partition coefficient, and diffusion coefficient of THO in the copolymer hydrogel membrane give larger value than those of poly (HEMA) membrane.

From these results, we expect that the transport of THO across the copolymer hydrogel membrane is much faster than the transport across the poly (HEMA) membrane. Assuming that the transport takes place in the water region

within membranes, the faster transport indicates that copolymer hydrogel membrane contains the larger amount of water than poly (HEMA) membrane does. This result is not due to the higher water affinity of AEMA including amino group than that of HEMA including hydroxy group, but due to the lower degree of aggregation of copolymer hydrogel membrane than that of poly (HEMA) membrane. So one may expect that the copolymerizing HEMA and AEMA produce the more porous part in the hydrogel.

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Mechanism of Metal Ion Binding to Chitosan in Solution. Cooperative Inter- and Intramolecular Chelations

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Interactions between metal ions and chitosan in solution were studied by spectroscopic and viscometric measurements. Cu^{++} -chitosan complex exhibited an absorption band at 265 nm, whereas D-glucosamine complex showed one at 245 nm. The difference in λ_{max} was attributed to the different amine to Cu^{2+} ratios of the complexes, that is, 2:1 for chitosan and 1:1 for D-glucosamine. The molar absorptivities and binding constants of the complexes were evaluated. The binding of Cu^{2+} to chitosan was cooperative near pH 5, and both intra- and intermolecular chelations depending on chitosan and Cu^{2+} concentrations were observed. The intermolecular chelation was stabilized by addition of salts. The cooperative intermolecular chelation of Ni^{++} was also observed at pH 6.2. No significant binding of other divalent ions was observed. The reported high adsorption abilities of chitosan particles for these ions were attributed to the deposition of metal hydroxide aggregates in pores of chitosan particles rather than chelation to amine groups.

Introduction

Chitosan is the deacetylated product of chitin, poly-(N-acetyl-D-glucosamine), which is the most abundant naturally occurring polysaccharides containing amino sugars. Recently, chitin and chitosan have drawn a great amount of interests, because of their wide range of applicabilities.¹ The chelation of various metal ions by chitosan has demonstrated the effectiveness of the polymer in inorganic chromatography and in heavy metal removal from polluted water. Muzzarelli

has given excellent summaries of works in this field.^{2,3} The adsorption (chelation) ability of chitosan for various metal ions was reported to be high, but it was shown that the ability depends on the method of preparation of chitosan sample, and is not directly proportional to the degree of deacetylation of chitin.⁴ Masri *et al.*⁵ also have shown that the relative adsorption ability of chitosan for different metal ions is significantly different from that of poly-(p-aminostyrene).

Despite of extensive studies on interaction of metal ions with chitosan, there is a paucity of data as to how they in-