Studies on syntheses and permeabilities of special polymer membranes:
33. Permeation behaviour of aqueous alcohol solution through cellulose membranes

Tadashi Uragami, Yasuhiro Sugitani and Mizuho Sugihara
Department of Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, *Japan*

(*Received* 29 *December* 1980; *revised* 10 *June* 1981)

The permeabilities of various aqueous alcohol solutions through cellulose membranes were investigated by changing the preparation conditions of membranes, the feed concentration, and the feed solute, etc. The permeation rates for aqueous solutions of alcohols, glycols, glycerol, trihydroxyl benzene were greater than for pure water. This permeation phenomenon could be explained by some permeation models considering water cluster, activation of water molecules (second bound water-like) attached weakly to the bound water in cellulose membrane, and the surface of cellulose membrane, and plasticization of cellulose molecules.

Keywords Polymers; membranes; cellulose; permeation; synthesis; alcohol

INTRODUCTION

In general, the permeation rates for aqueous solutions through porous polymeric membranes are mainly governed by the viscosity of the feed solution, molecular size of the feed solute, and the affinity of the feed with the membrane, etc., as the feed solute is not rejected by the membrane. However, we have found that in spite of the fact that the feed viscosities increase, the permeation rates for aqueous solutions become greater, when hydrophilic polymers are used as membrane materials and hydrophilic solutes such as alcohols, amines, and inorganic salts are employed as feed solutes[1,2]. This permeation phenomenon of the aqueous solution is significantly dependent on the hydrophilicity of the polymer membrane. That is, in hydrophilic polymer membranes such as membranes of cellulose acetate, cellulose nitrate, and nylon-12, etc. the above permeation phenomenon is not recognised, but is recognised in extremely hydrophilic polymer membranes such as crosslinked poly(vinyl alcohol) membranes[1] and interpolymer membranes[2] from poly(vinylidene fluoride) and poly(styrene sulphonic acid). To reveal the above permeation behaviour of an aqueous solution containing a hydrophilic solute is important in understanding permeation mechanisms through the polymer membranes.

Here, cellulose is selected as the hydrophilic polymer and the permeation behaviour of aqueous solutions of various alcohols through cellulose membranes are discussed in detail.

EXPERIMENTAL

Materials

Cellulose powder (Cell) (produced by Sanyo Kokusaku Pulp Co. Ltd., W-4) dried under reduced pressure, was employed as membrane material. Pure commercial dimethyl sulphoxide (DMSO) was used as the solvent for the casting solution. Paraformaldehyde (PF) used as the hydroxymethylation reagent of cellulose and triethyl amine (TEA) used as the basic catalyst were pure commercial reagents. Poly(ethylene glycols) used as the solutes of feed solutions were PEG 200, PEG 400, PEG 600, PEG 1000, PEG 2000, and PEG 6000, whose number average molecular weights were 190–210, 380–420, 570–630, 950–1050, 1900–2100, and 7800–9000, respectively. All alcohols and sorbitan monolaurate used as the feed solutes were pure from commercial sources.

Preparation of membranes[3]

Cellulose powder (2 g) immersed in dimethyl sulphoxide (80 g) was stirred in a stream of nitrogen gas for 3 h at 110°C. Paraformaldehyde (5 g) and triethyl amine (0.01 ml) were added to the above heterogeneous solution containing cellulose powder and simultaneously the nitrogen gas stream was removed. When this mixture had been stirred for 90 min at 115°C, the cellulose powder was dissolved. This dissolution of cellulose was dependent on the hydroxymethylation by formaldehyde generated with the decomposition of paraformaldehyde[4]. This solution was filtrated at a desired temperature in an oven with gauze comprising four layers to remove undecomposed paraformaldehyde. The membranes were made by pouring this clear filtrate (casting solution) onto a rimmed glass plate in the oven set at 50°C, to evaporate the solvent for a desired period, and immersing the glass plate together with the solution into water (25°C). During this water treatment, the regenerated cellulose membranes were obtained by hydrolysing the hydroxymethylated cellulose membranes. All cellulose membranes used in this work were pressure treated with water in the normal manner at 8 kg cm^{-2} for more than 10 min in order to obtain stable permeability during permeation experiment.

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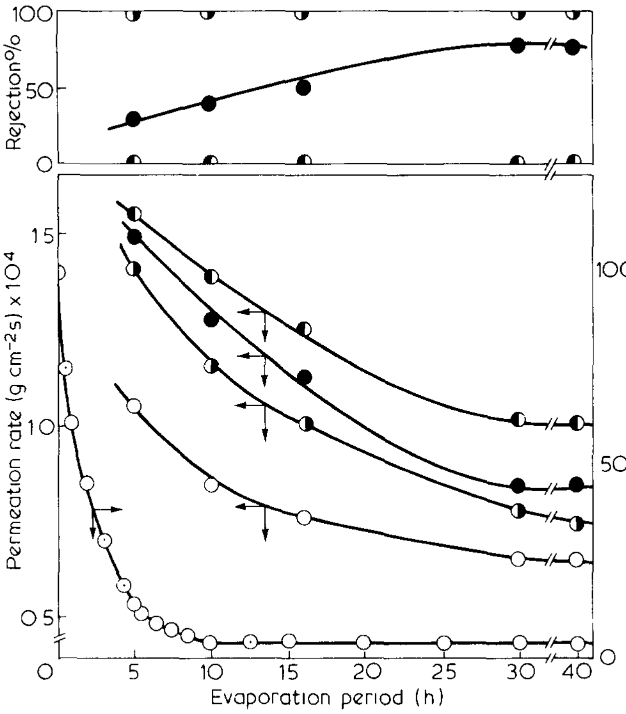

Figure 1 Effect of evaporation period on permeation characteristics. Feed, (○) pure water; (◐) 1% glycerol; (●) 1% PEG 1000; (◑) 1% PEG 6000 aqueous solutions: evaporation temperature, 50° C; operating conditions, 40° C, 4 kg cm^{-2}; (⊙) weight of casting mixture

Apparatus and measurements

The apparatus and the experimental procedure, and the analysis of feed and membrane-permeated liquid have been reported[3,5]. The effective membrane area set in the cell was 11.8 cm^2. All experiments were of the short run type.

The amount of bound water in the cellulose membranes was determined by differential scanning calorimetry (Shimadzu DSC-30M).

RESULTS AND DISCUSSION

Effect of evaporation period

The effect of evaporation period during membrane formation process on the membrane characteristics is shown in *Figure 1*, where the casting solution consists of cellulose hydroxymethylated with paraformaldehyde, tirethyl amine, and dimethyl sulphoxide and the evaporation temperature is 50°C. The rate of pure water permeability, the rates for aqueous solutions of glycerol, PEG 1000, and PEG 6000 decrease markedly up to an evaporation period of 10 h. These decreases are rather small after 10 h. The rejection for PEG increases with an increase in the evaporation period. These permeation characteristics are significantly related to the weight change of casting mixture during evaporation process, W_t/W_0, where W_0 is the starting weight of casting mixture and W_t is the weight of casting mixture after t hours. Up to 10 h the casting solvent still remains in the membranes prior to the gelation in water. Therefore, the resulting membranes may be asymmetric. The skin layer in this asymmetric membrane becomes denser and thicker with the evaporation period. Consequently, the decrease in permeation rate and the increase in rejection appear. However, after 10 h the casting solvent is completely evaporated. Therefore, symmetric dense membranes are formed. With a longer evaporation period, the membranes are shrunk and become symmetric dense membranes which are annealed at the evaporation temperature. The decrease of permeation rate and the increase of rejection are due to these factors.

Permeation model

As can be seen from *Figure 1*, the permeation rates for aqueous solutions of glycerol and PEG are greater than for pure water. Also the difference between the permeation rates for aqueous solution and for pure water becomes smaller with an increase in evaporation period. These phenomena may be explained by the models as shown in *Figure 2*. Model A is the permeation model when the feed is pure water and the evaporation period is short. In this case, water clustering is large and hydrogen bonds are formed between water molecules and free hydroxyl groups of cellulose molecules in the rough sponge layer. These factors result in lower permeability.

It is well known[6] that when the solutes having hydrophilic groups such as hydroxyl, amine, carboxyl, and aldehyde groups are added to water, 'clusters'[7-9] of water molecules connected by hydrogen bonds are broken and becomes smaller than that in pure water in model A. Therefore, the permeation model is shown by model B. Furthermore, in this case hydrophilic solute brings about an activation of motion of the water molecules (second bound water-like) that are weakly

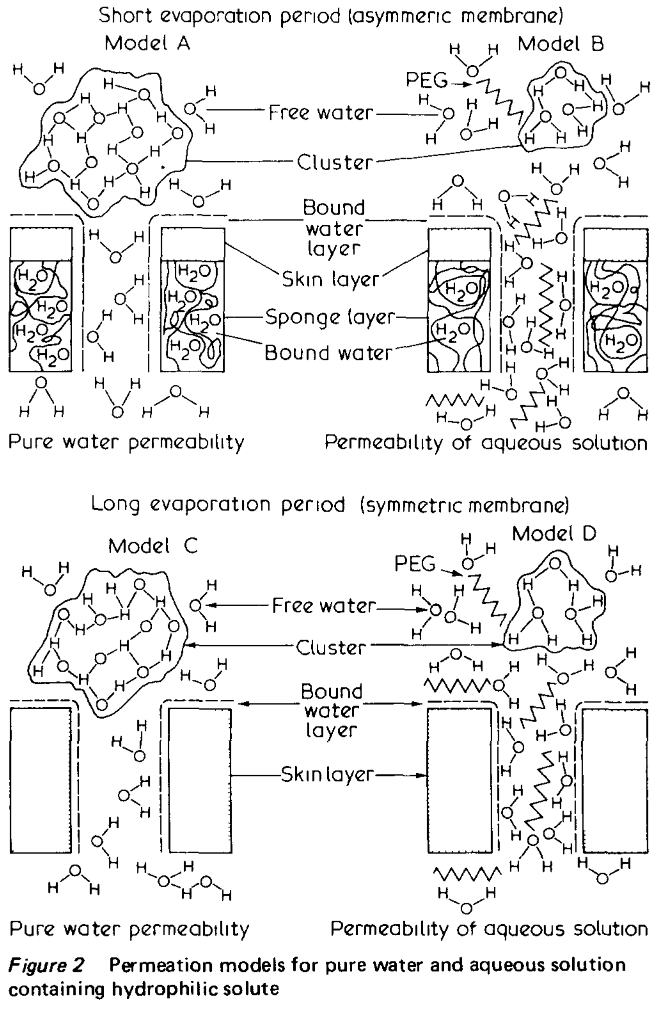

Figure 2 Permeation models for pure water and aqueous solution containing hydrophilic solute

Table 1 Apparent total bound water in cellulose membrane

Evaporation period (h)*	Apparent total bound water (g-water/g-dry membrane)	H_2O/OH
5	0.91	2.7
9	0.65	1.9
18	0.45	1.3

* Evaporation temperature, 50° C

attached to bound water layers on the membrane surface and in the membrane. In addition, hydrophilic solute may act upon the very weak hydrogen bond sites of cellulose molecules, and consequently these sites may be plasticized somewhat. These factors contribute to an extention of the apparent effective pore size in the membrane. Therefore, the permeation rates for aqueous solutions of glycerol and PEG (model B) are greater than for pure water (model A).

Models C and D are the permeation models when the evaporation period becomes longer. The greater permeation rate of model D compared with that of model C is due mainly to the decrease in the size of the water cluster with the addition of hydrophilic solute. The cellulose molecules in the surface layer of the membrane densly aggregate. Therefore, it is difficult for the hydrogen bonds between the cellulose molecules and the water molecules to form, and the cellulose molecules are plasticized by the hydrophilic solute. The membranes prepared at longer evaporation periods consist mainly of a dense surface layer. Consequently, the difference between the rate of pure water permeability and the rate for the aqueous solution in the longer evaporation period is caused mainly by water clustering. However, in the rough porous back layer, hydrogen bonds between the cellulose molecules and the water molecules and plasticization of the cellulose molecules by the hydrophilic solute occurs, because many free hydroxyl groups exist in this back layer. Therefore, in the shorter evaporation period the difference between the rates for pure water and for aqueous solution containing hydrophilic solute depends on the above three factors. That is, the first factor is water clustering, the second factor is the activation of attached water molecules, and the third factor is the plasticization of cellulose molecules.

Bound water

In the discussion of permeation mechanisms through the polymer membranes, one important factor is the bound water in the membrane[10,11]. The bound water in the membrane is confirmed by cobalt chloride[12], nuclear magnetic resonance[13], and differential scanning calorimetry[14]. *Table 1* summerizes the amount of the bound water in the cellulose membranes determined by d.s.c. The amount of apparent total bound water in the cellulose membranes decreases with increase in the evaporation period. This result suggests that the dense surface layer in the membrane increases as the evaporation period increases. The number of bound water molecule per one hydroxyl group in the cellulose molecule is ~1 to 3. However, since this number is an average value for the whole of the membrane, each number in the dense surface layer and the rough porous back layer increases and decreases.

Feed concentration

It was found in the above section that the permeability was significantly influenced by the effect of surface-active agent of the feed solute. *Figure 3* shows the effect of feed concentration on the permeation characteristics, using sorbitan monolaurate, which is a nonion surface-active agent, as feed solute. In spite of the fact that relative viscosity of the feed solution increases with an increase in feed concentration, the permeation rate up to 0.5% increases remarkably. This phenomenon depends on a steep decrease in relative surface tension of the feed solution. That is, this result supports a rupture of water cluster with the addition of sorbitan monolaurate which increases the permeation rate. When the feed concentration is greater than 0.5%, the feed solution reaches a critical micelle concentration. Therefore, this implies that the degree of water cluster is almost equal. This is understood because the surface tension is kept constant. The decrease in permeation rate above 0.5% is due mainly to the permeation resistance which is caused by the increase in the feed viscosity with the formation of the micelle of sorbitan monolaurate. Also, higher rejection is related to the micelle formation.

Membrane characteristics

Figure 4 shows the effect of molecular weight of feed solute on the permeation characteristics. As can be seen from *Figure 4*, the cellulose membrane used has a wide pore distribution. Even if PEG molecules are rejected, the permeation rates for PEG aqueous solutions are greater than for pure water. From these results it can be seen that the degree of water cluster significantly affects the permeation rate. When the molecular weight of solute is

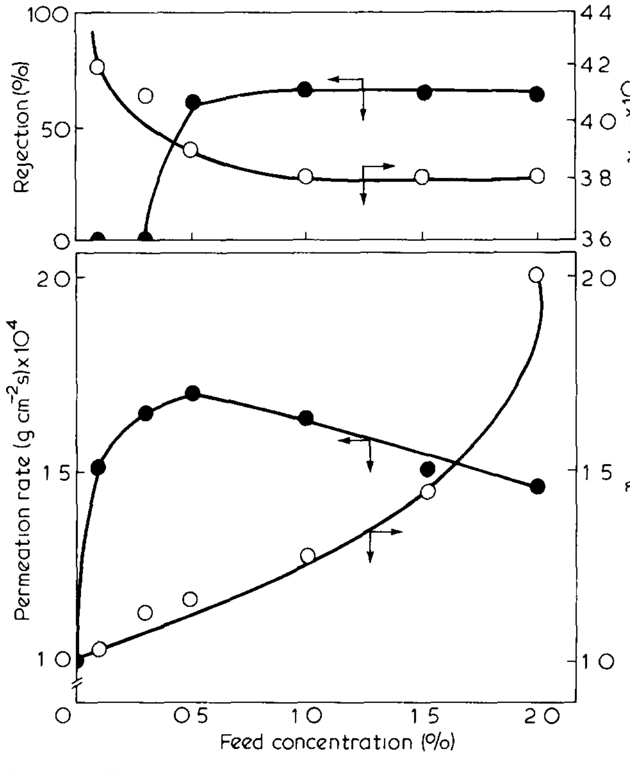

Figure 3 Effect of feed concentration on permeation characteristics. Feed, aqueous solution of sorbitan monolaurate; conditions of membrane preparation, 50° C, 5 h; operating conditions, 40° C, 4 kg cm^{-2}: η_{rel}, relative viscosity for pure water; γ_{rel}, relative surface tension for pure water

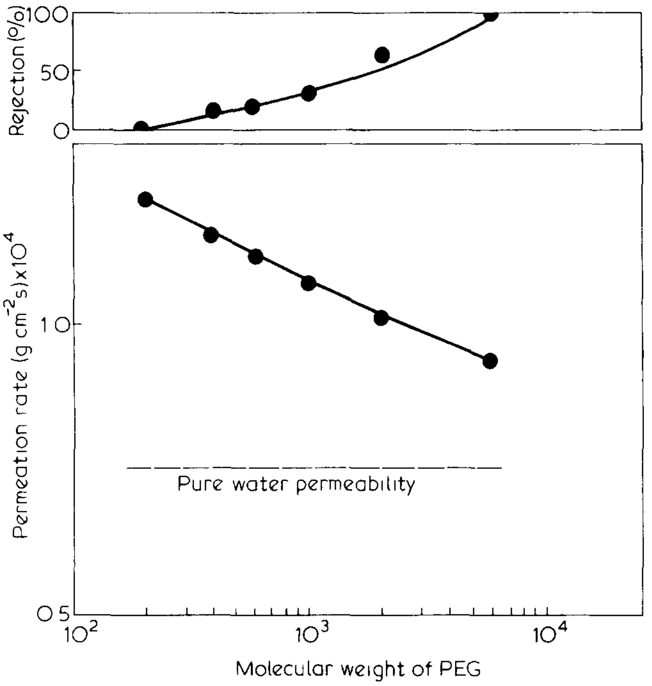

Figure 4 Effect of molecular weight of feed solute on permeation characteristics. Feed, 1% aqueous solutions of PEG; conditions of membrane preparation, 50°C, 18 h; operating conditions, 40°C, 4 kg cm^{-2}

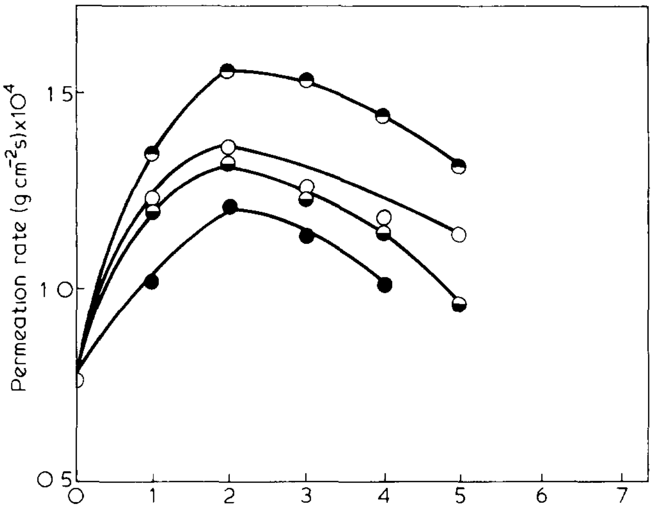

Figure 5 Relationship among number of carbon atoms in linear monoalcohol molecule, concentration, and permeation rate of their aqueous solution. Feed, (●) 0.5, (◒) 0.1, (◓) 0.01, (○) 0.001 M aqueous solutions of mono-alcohols; conditions of membrane preparation, 50°C, 18 h; operating conditions, 40°C, 4 kg cm^{-2}

less than 200, the solute is not rejected. Therefore, the permeation resistance, based on a concentration polarization and blocking of the pores in the membrane, is negligible. The solutes below a molecular weight of 200 are used for all the latter work. Also, in order to neglect the permeation resistance caused by the feed viscosity, very dilute aqueous solutions are employed as the feed solution for all latter work.

Permeabilities of various aqueous alcohol solutions

The effects of molecular size, hydrophobicity, and feed concentration of linear mono-alcohols on the permeation rates of their aqueous solutions are shown in *Figure 5*. The permeation rates for aqueous solutions of all linear mono-alcohols and all feed concentrations in the range of this work are greater than for pure water. In all feed concentrations, the permeation rate for aqueous solution of ethyl alcohol has a maximum. The permeation rates for 0.01 M aqueous solution are the highest for all the linear mono-alcohols. Higher permeation rates of aqueous alcohol solutions are due to the above three factors; the rupture of water cluster, the activation of attached water molecules, and the plasticization of the cellulose molecules. The decrease in the permeation rate for the higher aqueous alcohol solution, which is greater for n-propyl alcohol is attributed to an increase in permeation resistance based on the increase in molecular size of feed solute and a decrease in the effective degree of the above three factors caused by the increase in the hydrophobicity of the feed solute. When the feed concentration is increased up to 0.01 M, the permeation rate is increased with the enhancement of three factors. Above 0.01 M, the decrease of permeation rate is caused mainly by the increase in the feed viscosity.

Figure 6 shows the effect of the number of carbon atoms in glycol molecules on the permeation rates of their aqueous solutions. The permeation rates for all aqueous glycol solutions are greater than for pure water. This difference is due to the above three factors. The permeation rates of glycols from ethylene glycol to hexylene glycol are found to decrease with an increase in number of carbon atoms in glycol molecule. This decrease depends on the following two factors. (i) The increase of hydrophobicity with the increase in number of methylene groups. (ii) The increase in permeation resistance with increase in molecular size.

The relation between the number of hydroxyl groups in the alcohol molecule and the permeation rate of their aqueous solutions is shown in *Figure 7*. When the number of hydroxyl groups in alcohol molecule increases, the permeation rate increases. This increase in permeation rate is due to an enlargement in the above three factors.

Table 2 summarizes the permeation rate for an aqueous solution of the alcohol isomer. The permeation rate for aqueous solution of tert-butyl alcohol is greatest with the butyl alcohol isomer. It is presumed that if the shape of solute molecule is more spherical, its permeability is great.

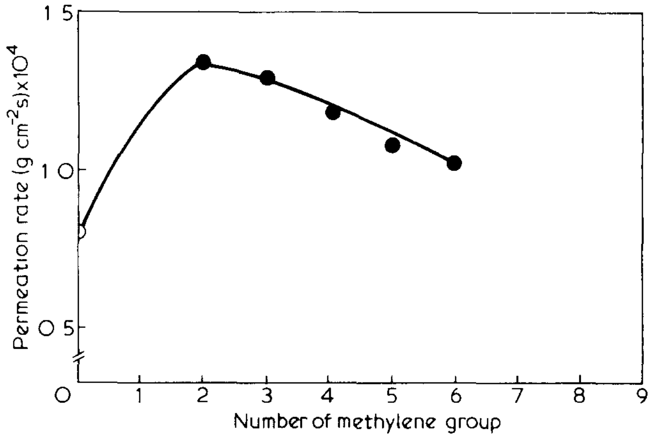

Figure 6 Relationship between number of methylene bonds in glycol molecule and permeation rate for their aqueous solution. Feed: (○) pure water; (●) 1.1 x 10^{-2} M aqueous solutions of glycols; conditions of membrane preparation, 50°C, 18 h; operating conditions, 40°C, 4 kg cm^{-2}

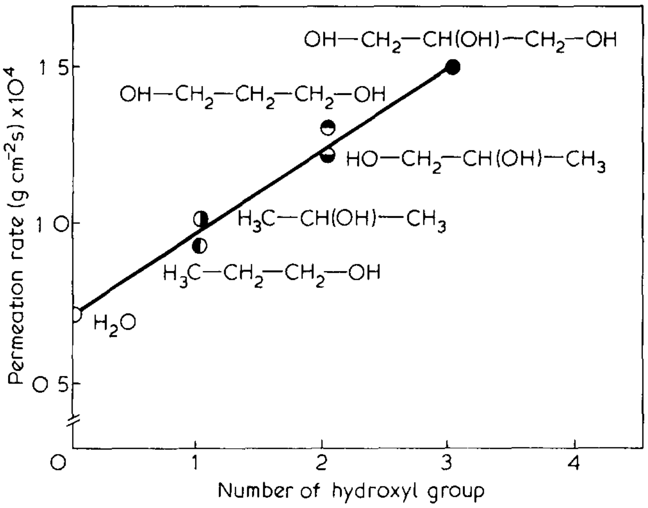

Figure 7 Relationship between number of hydroxyl groups in alcohol molecule and permeation rate for their aqueous solutions. Feed: (○) pure water; (◐) n-propyl alcohol; (◑) iso-propyl alcohol; (◓) trimethylene glycol; (◒) propylene glycol; (●) glycerol aqueous solutions (1.1 x 10^{-2} M); conditions of membrane preparation, 50°C, 18 h; operating conditions, 40°C, 4 kg cm^{-2}

In the trihydroxyl benzene isomer, the permeation rate for 1,2,3-trihydroxyl benzene is the smallest. This result may be attributed to a micelle formation of 1,2,3-trihydroxyl benzene molecule, because the hydroxyl groups localize in this molecule. However, these three isomers are not truly rejected. Therefore, it is presumed that an aggregate of 1,2,3-trihydroxyl benzene is formed with two to three molecules.

Table 2 Permeation rates for aqueous solutions of butyl alcohol and trihydroxyl benzene isomers

Feed solution*	Permeation rate (g cm^{-2} s) x 10^4
Pure water	0.75
n-Butyl alcohol	1.00
sec-Butyl alcohol	0.92
iso-Butyl alcohol	1.20
tert-Butyl alcohol	1.56
1,2,3-Trihydroxyl benzene	0.97
1,2,4-Trihydroxyl benzene	1.42
1,3,5-Trihydroxyl benzene	1.55

* Feed concentration, 1.1 x 10^{-2} M aqueous solution. Conditions of membrane preparation, 50°C, 18 h; operating conditions, 40°C, 4 kg cm^{-2}

REFERENCES

1 Uragami, T., Furukawa, T. and Sugihara, M. *Tech. Rept. Kansai Univ.* 1981, **22**, 99
2 Uragami, T., Fujimoto, M. and Sugihara, M. *Desalination* 1980, **34**, 311
3 Uragami, T., Sugitani, Y. and Sugihara, M. *Makromol. Chem.* in press
4 Johson, D. C., Nicholson, M. D. and Haigh, F. C. *Appl. Polym. Symp.* 1976, **28**, 931
5 Uragami, T., Fujino, K. and Sugihara, M. *Makromol. Chem.* 1976, **55**, 29
6 Nakajima, A. in 'Polymer Membranes' (Eds. M. Nagasawa and A. Takizawa), Chijin Shokan, Japan, 1974, Ch 5
7 Reuse, P. E. *J. Am. Chem. Soc.* 1974, **69**, 1068
8 Barrer, R. M. and Barrie, J. A. *J. Polym. Sci.* 1958, **28**, 377
9 Wellons, J. D. and Stannet, V. *J. Polym. Sci. A-1* 1966, **4**, 593
10 Reid, C. E. and Breton, E. J. *J. Appl. Polym. Sci.* 1959, **1**, 133
11 Sourirajan, S. *Ind. Eng. Chem., Fundam.* 1963, **2**, 51
12 Viencent, A., Barsh, M. and Kesting, R E. *J. Appl. Polym. Sci.* 1965, **9**, 2363
13 Frommer, M. A. and Lancer, D. *J. Appl. Polym. Sci.* 1972, **16**, 1295
14 Nelson, R. A. *J. Appl. Polym. Sci.* 1977, **21**, 645