Studies on syntheses and permeabilities of special polymer membranes: 24. Permeation characteristics of poly(vinylidene fluoride) membranes

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The permeation characteristics of poly(vinylidene fluoride) membranes were investigated by changing the preparation conditions of the membranes, the composition of the casting solution, membrane thickness, time of heat treatment and temperature, etc.; and by changing the permeation conditions, operating temperature, the feed concentration, and the feed solute, etc. Aqueous solutions of poly(vinyl alcohol) and poly(ethylene glycol) were used as feed. The permeation characteristics were influenced significantly by the change of the above conditions and were dependent on the structure of resulting membrane, the viscosity of feed, the form of polymer molecules in aqueous solution, and the concentration polarization of polymer solute molecules onto the membrane surface. The permeation through very swollen membranes (ca. 85% in water content) followed the viscous flow.

INTRODUCTION

The membranes most commonly used at present in the reverse osmosis and ultrafiltration are cellulose acetate and cellulose nitrate. However, these membranes are not always stable to change of pH and temperature, and in resistance against chemical agents. Recently, it is reported that the aromatic polyamide membrane[1] and cross linked poly(ethylene imine) membranes[2] are very stable in the range of pH 2–12.

In this work, poly(vinylidene fluoride), having better resistance against acid and organic solvent, was selected as the membrane substance. This paper deals with the permeation characteristics of poly(vinylidene fluoride) membranes with change of the preparation conditions, (the casting solution composition, the heat treatment time and temperature, etc.) and of the permeation conditions, (the operating temperature, the feed concentration, and the feed solute) to obtain the fundamental data.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVF_2) produced by Kureha Chemical Co. Ltd., average degree of polymerization 1000 was employed throughout this study. Pure commericeal dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF) were used as solvents for the casting solutions. The three kinds of poly(vinyl alcohol) (supplied by Kurary Co. Ltd.) used as the solutes of feed solutions were PVA 205, PVA 210, and PVA 217, whose average degrees of polymerization were 550 ± 50, 1250 ± 50, and 1725 ± 25, respectively. Poly(ethylene glycol) (PEG 20000) produced by Sanyo Kasei Co. Ltd., was also used as feed solute having an average degree of polymerization of 330 ± 50.

Preparation of membranes

The casting solutions consisted of poly(vinylidene fluoride), tetrahydrofuran and dimethyl sulphoxide. These were stirred at the casting temperature (23–25°C) for 48 h until the polymer was dissolved completely. The membranes were made by pouring these casting solutions onto a rimmed glass plate, allowing the solvent to evaporate at 23–25°C for a desired period, and immersing the glass plate into water together with the casting mixtures (23–25°C). After 24 h in water, the membranes were removed from the glass plate and treated in hot water.

Apparatus and measurements

The apparatus, the experimental procedure, and the analysis of feed and membrane-permeated liquid have been reported[3]. The effective membrane area set in the cell was 11.2 cm^2. All experiments were of the short run type. The rejection (R) is defined as:

$$R(\%) = (1 - C_t/C_f) \times 100$$

where C_f is the starting feed concentration and C_t is the concentration of permeated solution after t h.

RESULTS AND DISCUSSION

Effect of casting solution composition

The effect of casting solution composition on the permeation characteristics is shown in *Figure* 1 where during the membrane formation process, the concentration of poly(vinylidene fluoride) and the exposure period of casting solution under casting conditions (temperature 25°C, humidity 60%) are kept constant at 7 wt% and 2 h, respectively. The rate of pure water permeability and the permeation rate for an aqueous solution of PVA 205 decrease, and the rejection for PVA 205 increases with an

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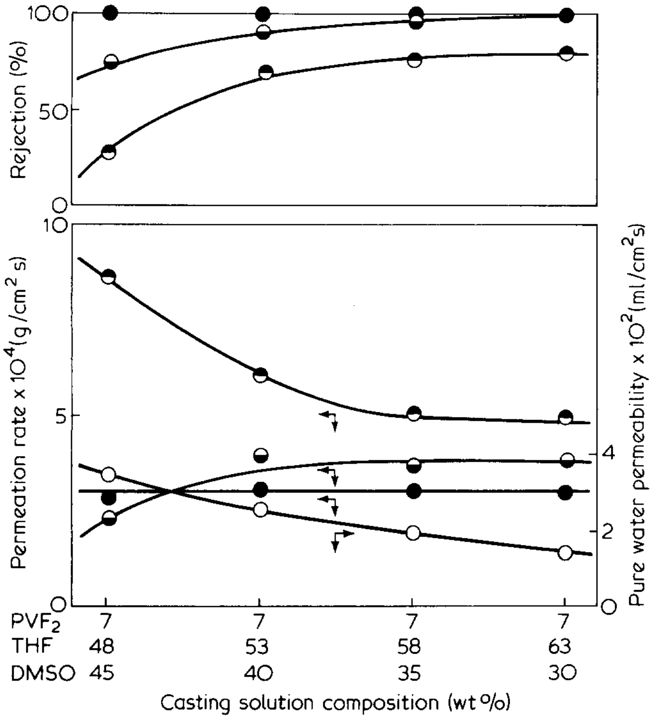

Figure 1 Effect of casting solution composition on permeation characteristics at 2 h in exposure period. Heat treatment, 40° C, 20 min; feed, (○) pure water, (◓) 1% PVA 205, (◒) 1% PVA 210, (●) 1% PVA 217 aqueous solutions; operating conditions, 40° C, 2 kg cm^{-2}

increase in tetrahydrofuran content which is a low boiling point solvent in the casting solution. Considering that the burst strength of the resulting membranes increases with an increase in content of tetrahydrofuran in the casting solution, this phenonenon may be attributed to two factors: (1) an increase in thickness of surface dense layer with evaporation of tetrahydrofuran during an exposure process; (2) the difference of microporous structure of the resulting membranes based on a difference of dissolving form of poly(vinylidene fluoride) molecules in the casting solution because the poly(vinylidene fluoride) molecules cannot be dissolved in only tetrahydrofuran or dimethyl sulfoxide. In spite of the fact that the rejection for PVA 210 is higher than that for PVA 205, the permeation rate tends to increase as the content of tetrahydrofuran increases. Both increase of the permeation rate and the rejection for PVA 210 are desirable. This may be due to complex interactions between PVA 210 molecules and pore size. In the case of PVA 217, the permeation rates are approximately constant regardless of the casting solution composition. This phenomenon is attributed to the concentration polarization[3-5] of PVA 217 molecules onto the poly(vinylidene fluoride) membrane surface because the rejection is 100%.

Effect of membrane thickness

The relationship between the membrane thickness and the permeation characteristics is shown in *Figure* 2 where the casting solution composition is the proportion of poly(vinylidene fluoride):tetrahydrofuran:dimethyl sulphoxide being 7:53:40 (wt%), and the exposure period is kept constant at 2 h. Both the rate of pure water permeability, and the permeation rate for aqueous solution of PVA 205, decrease with an increase in membrane thickness, whilst the rejection for PVA 205 increases. The permeation characteristics for pure water and an aqueous solution of PVA 205 are a function of thickness of the resuting membranes (i.e. the amount of casting solution poured on the glass plate). Since the conditions of membrane preparation other than the amount of casting solution are kept constant, these permeation characteristics are influenced by pore sizes and porosities in the resulting membranes, and differences of the membrane compaction under pressure based on the pore size and porosity. In an aqueous solution of PVA 210, the permeation rate and the rejection increase up to 150 μm of membrane thickness. Over 150 μm both are constant. Such a special behaviour for the permeation characteristics of aqueous solutions of PVA 210 may be dependent on the interactions between the PVA 210 molecules and the pore sizes or pore wall. That is, it is presumed that the permeation rate and the rejection for the membranes below 150 μm are smaller, because the pore sizes do not block the PVA 210 molecules (being approximately equal to the molecular sizes of PVA 210) and consequently, the permeation resistance of polymer solute through the membrane becomes larger. The fact that the permeation rate and the rejection are not changed over 150 μm, is attributed to the compaction of membrane and the concentration polarization of PVA 210 molecules onto the membrane surface. Also, the permeation rates for aqueous solution of PVA 217 which are constant regardless of the membrane thickness, are due to the sinificant concentration polarization of PVA 217 molecules.

EFFECT OF POLYMER CONCENTRATION

The effect of poly(vinylidene fluoride) concentration on the permeation characteristics is shown in *Figure* 3 where

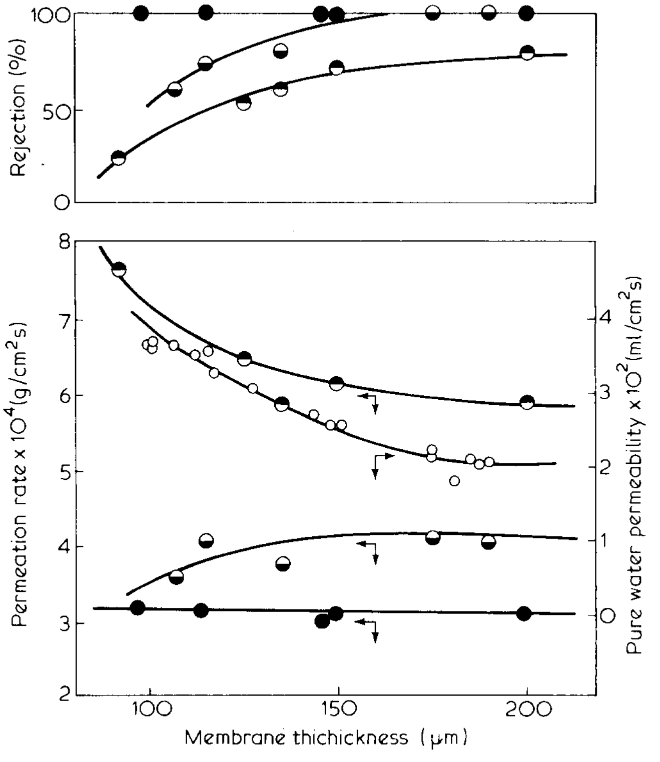

Figure 2 Effect of membrane thickness on permeation characteristics at 2 h in exposure period. Casting solution composition, PVF$_2$/THF/DMSO = 7/53/40 (wt %); heat treatment, 40°C, 20 min; feed, (○) pure water, (◓) 1% PVA 205, (◒) 1% PVA 210, (●) 1% PVA 217 aqueous solutions; operating conditions, 40°C, 2 kg cm^{-2}

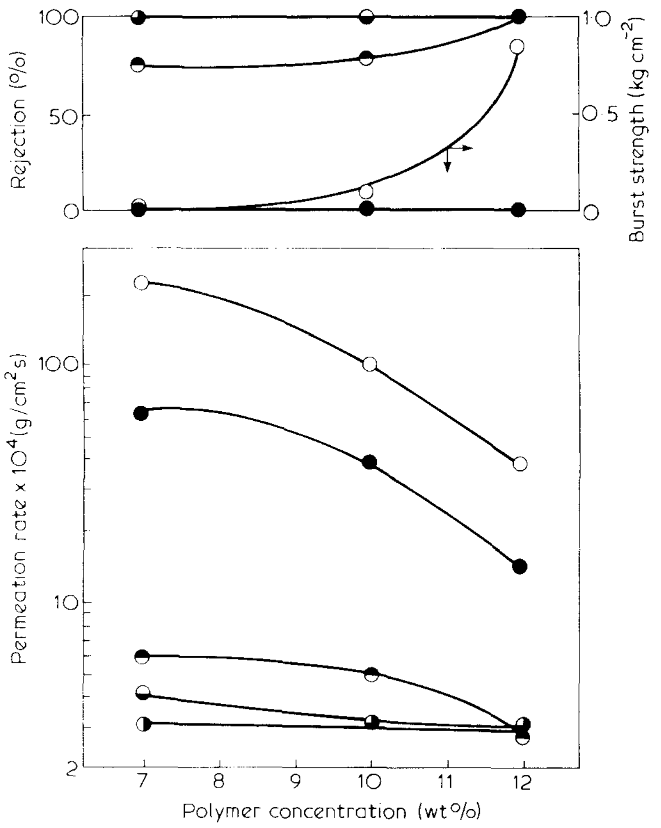

Figure 3 Effect of polymer concentration in casting solution on permeation characteristics at 2 h in exposure period. Casting solvent composition, THF/DMSO = 53/40 (wt %); heat treatment, 40°C, 20 min; feed, (○) pure water, (●) 1% PEG 20000, (◓) 1% PVA 205, (◒) 1% PVA 210, (◑) 1% PVA 217 aqueous solutions; operating conditions, 40°C, 2 kg cm^{-2}

the exposure period and the ratio of tetrahydrofuran/dimethyl sulphoxide are kept constant at 2 h and 53/40 (wt%), respectively, and the polymer content in the casting solution is changed in the range of 7–12 wt%. The permeation rates for pure water and aqueous solutions of PVA 205 and PVA 210 decrease markedly with an increase in polymer concentration. The rejections for PVA 205 and PVA 210 molecules and the burst strength of the membranes increase with it. These phenomena suggest that the membrane of higher polymer concentration is denser than lower ones. Similar results were obtained for cellulose acetate membranes[3]. The permeation rate and the rejection for aqueous solution of PVA 217 are constant, and independent of polymer concentration. Only water molecules are permeated through the membrane from the feed solution because the rejections are 100%. The permeation rates, therefore, should be equal to those of pure water; however, the former rates are smaller than the latter. This implies that the concentration polarisation layer of PVA 217 molecules onto the membrane surface is a rate-determining step in the permeation through the membrane. This is supported by the fact that when the polymer concentration is 12 wt%, the rejections for PVA 205, PVA 210, and PVA 217 are 100% and the permeation rates are approximately equal.

PVA 205 and PEG 20000 have similar *MWD*, (i.e. PVA 205 $\bar{D}\bar{P}=550\pm50$ and PEG 20000 $\bar{D}\bar{P}=350\pm50$) and similar relative viscosities in 1.0% aqueous solutions (i.e. PVA 205 is 1.417 and PEG 20000 is 1.412 at 40°C). However, the results show that there is a great difference between permeation and rejections rates. Even though the *MWDs* of PEG 20000, having the ether bonds in the main chain, and of PVA 205, having hydroxyl groups on the side chain, are approximately equal, the form in these aqueous solutions may differ. It is presumed also that there is a great difference in the interactions between PVA 205 molecules and poly(vinylidene fluoride) membrane, and between PEG 20000 molecules and this membrane. Water molecules, around the ether oxygen atoms in PEG 20000 molecules, are liable to rotate freely. Free rotation of PVA 205 molecules is more difficult than that for PEG molecules. When the polymer solute molecules are permeated through the polymer membrane, the PEG molecule permeates preferentially to the PVA molecule. The permeation and rejection rates, therefore, depend on complex interactions between polymer solute molecules and membrane materials, and on the physical nature of polymer solute molecules in aqueous solution.

Effect of heat treatment

Figure 4 shows the effect of heat treatment time on the permeation characteristics. The permeation rate increases up to 20 min in heat treatment time, and is kept constant over 20 min. The rejection does not change. Poly(vinylidene fluoride) molecules do not lengthen, entanglements between poly(vinylidene fluoride) molecules are very small, and consequently, intramolecular hydrogen bonds are stronger than intermolecular hydrogen bonds. Tetrahydrofuran and dimethyl sulphoxide cannot dissolve poly(vinylidene fluoride) molecules and the burst strength of the resulting membrane is very weak. Therefore, since intramolecular hydrogen bonds occur

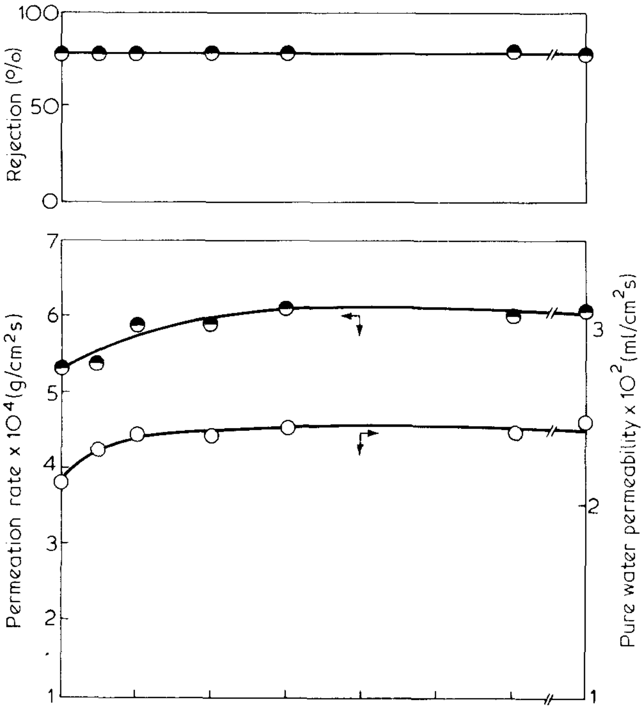

Figure 4 Effect of heat treatment time on permeation characteristics at 2 h in exposure period. Casting solution composition, PVF$_2$/THF/DMSO = 7/53/40 (wt %); heat treatment temperature, 60°C; membrane thickness, 150 μm; feed, (○) pure water, (○) 1% aqueous solution of PVA 205; operating conditions, 40°C, 2 kg cm^{-2}

preferentially after heat treatment, spacings between poly(vinylidene fluoride) molecules are extended and the permeation rate, up to 20 min, is increased. This is in part due to the increase of desolvation of dimethyl sulphoxide molecules that cannot be desolvated into water during gelation process and therefore, remain in the membrane as the heat treatment time increases. Similar results are obtained in acrylonitrile–styrene copolymer membrane[5].

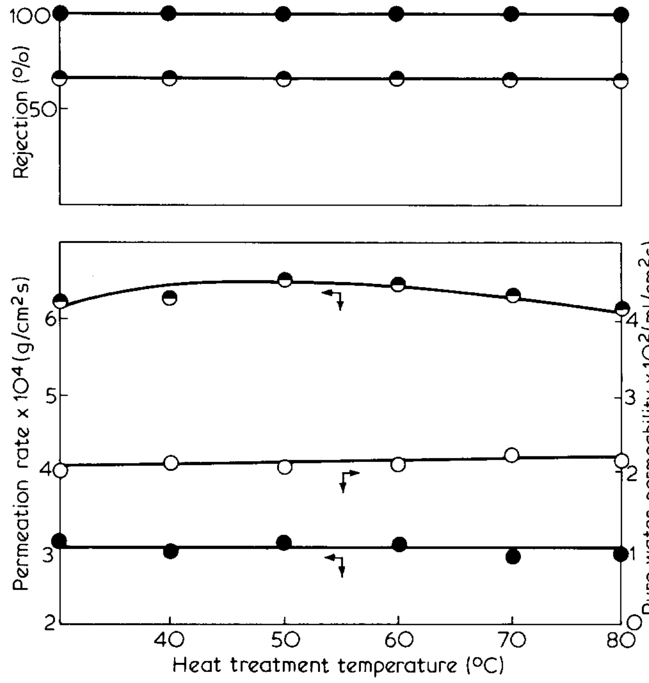

Figure 5 Effect of heat treatment temperature on permeation characteristics at 2 h in exposure period. Casting solution composition, PVF_2/THF/DMSO = 7/53/40 (wt %); heat treatment time, 20 min; membrane thickness, 150 μm; feed, (○) pure water, (○) 1% PVA 205, (●) 1% PVA 217 aqueous solutions; operating conditions, 40° C, 2 kg cm^{-2}

The effect of heat treatment temperature on the permeation characteristics is shown in *Figure* 5, where the heat treatment time is 20 min. When cellulose acetate[3], cellulose nitrate[6], and nylon 12 membranes[4] are treated with heat, the ability of separation becomes higher and the permeation rate lowers — depending on the structural change of membranes. Strathman[7] has found by X-ray diffraction that when the membranes were treated with higher temperature, the crystallinity of membranes increased. The permeation characteristics of poly(vinylidene fluoride) membrane are not changed with heat treatment temperature (*Figure* 5). In this range of heat treatment temperature, poly(vinylidene fluoride) molecules are stable. Therefore the structural change of poly(vinylidene fluoride) membrane does not occur.

Effect of operating temperature

The effect of operating temperature on the permeation characteristics is summarized in *Table* 1. When the operating temperature is raised, the viscosity of feed decreases, because of increasing molecular movement of solvent and solute in the feed, and the permeation rate increases. However, the probabilities of PVA 205 molecules entering the pores that PVA 205 molecules can permeate become high and the permeation of PVA 205 molecules through the membrane is promoted with an increase in operating temperature while the rejection for PVA 205 decreases. As the operating temperature is increased, the molecular movement of PVA 217 should also be activated. However, the rejection for PVA 217 remains unchanged. This phenomenon is due to the fact that the molecular size of PVA 217 is larger than the pore

Table 1 Effects of operating temperature and feed concentration on permeation characteristics for various solutions

Feed solution		Operating temperature 30° C	40° C	50° C	60° C	70° C
Pure water	η	0.802	0.653	0.550	0.470	0.406
	PWP	1.62 x 10^2	1.82 x 10^2	1.95 x 10^2	2.36 x 10^2	2.71 x 10^2
PEG 20 000 1% aq. soln.	η_{rel}	1.435	1.412	1.356	1.330	1.283
	PR	6.72 x 10^3	8.48 x 10^3	1.03 x 10^2	1.21 x 10^2	1.34 x 10^2
	R	0	0	0	0	0
PVA 205 0.5% aq. soln.	η_{rel}	1.195	1.179	1.161	1.153	1.134
	PR	7.61 x 10^4	8.95 x 10^4	1.01 x 10^3	1.22 x 10^3	1.31 x 10^3
	R	72	65	58	48	35
PVA 205 1% aq. soln.	η_{rel}	1.469	1.417	1.383	1.354	1.324
	PR	4.60 x 10^4	5.17 x 10^4	7.05 x 10^4	9.35 x 10^4	9.99 x 10^4
	R	75	68	58	48	38
PVA 205 2% aq. soln.	η_{rel}	2.077	1.952	1.845	1.821	1.731
	PR	2.53 x 10^4	3.50 x 10^4	3.53 x 10^4	4.74 x 10^4	6.22 x 10^4
	R	78	74	60	50	42
PVA 217 0.5% aq. soln.	η_{rel}	1.393	1.370	1.356	1.323	1.278
	PR	3.39 x 10^4	4.09 x 10^4	4.51 x 10^4	5.57 x 10^4	5.70 x 10^4
	R	100	100	100	100	100
PVA 217 1% aq. soln.	η_{rel}	2.148	2.061	1.874	1.796	1.738
	PR	2.50 x 10^4	2.90 x 10^4	3.25 x 10^4	3.55 x 10^4	3.99 x 10^4
	R	100	100	100	100	100
PVA 217 2% aq. soln.	η_{rel}	4.180	3.844	3.550	3.360	3.064
	PR	1.15 x 10^4	1.30 x 10^4	1.45 x 10^4	1.70 x 10^4	2.17 x 10^4
	R					

η is viscosity of pure water (cp), η_{rel} is relative viscosity for pure water, *PWP* is pure water permeability (ml/cm^2. s), *PR* is permeation rate (g/cm^2, s), *R* is rejection (%)

Table 2 Activation energies for permeation and viscous flow

	Permeant	E_p (kcal mol^{-1})	E_η (kcal mol^{-1})	E'_η (kcal mol^{-1})	E_p/E'_η*
	Pure water	3.14	3.35	3.35	0.94
PEG 20 000	1.0% aq. soln.	4.01	4.12	4.12	0.97
PVA 217	0.5% aq. soln.	3.33	3.96	3.35	0.99
PVA 217	1.0% aq. soln.	3.39	4.65	3.35	1.01
PVA 217	2.0% aq. soln.	3.51	5.18	3.35	1.05

*$PR \propto \eta^{-E_p/E'_\eta}$

size. The fluity of liquid, φ, in the viscous flow theory is given by:

$$\varphi \propto 1/\eta \qquad (1)$$

where η is the viscosity of liquid. When the activation energy for the viscous flow of liquid, E_η, is considered, equation (1) is rewritten:

$$\varphi \propto e^{-E_\eta/RT} \qquad (2)$$

From equations (1) and (2)

$$\eta = 1/\varphi \propto e^{E_\eta/RT} = Ae^{E_\eta/RT} \qquad (3)$$

where A is constant.

The permeation rate, PR, is represented as[8]:

$$PR = P_0 e^{-E_p/RT} \qquad (4)$$

where E_p is the overall activation energy for the permeation of liquid; P_0 is defined:

$$P_0 = S_0 D_0 \qquad (5)$$

where S_0 is the solubility coefficient of the permeating molecule into the membrane and D_0 is the diffusive coefficient of the permeating species through the membrane.

Table 2 summarizes activation energies determined from Arrhenius plots using the above equations. Since the value of E_η is based on the capillary model, the interaction between liquid and capillary wall is not considered. The value of E_p involves the activation energies for the physical and chemical interactions between permeating molecules and membrane, for the molecular sieve on the membrane surface or in the membrane, for permeation through the concentration polarization layer, and for viscosity of permeating liquid. In *Table* 2, E_p is the overall activation energy for the permeation, E_η is the activation energy for the viscous flow of feed, and E'_η is the activation energy for the viscous flow of liquid which permeates across the membrane. The rejections for PEG 20 000 and PVA 217 are 0 and 100%, respectively. Therefore, in PEG 20 000 the activation energy for the viscous flow of feed, and in PVA 217 that of pure water, are adopted.

Equation (6) is obtained from equations (3) and (4):

$$PR \propto \eta^{-E_p/E'_\eta} \qquad (6)$$

The values of E_p/E'_η for all permeants in *Table* 2 approximately equal unity. Therefore, equation (6) is represented by:

$$PR \propto 1/\eta \qquad (7)$$

It is found that the permeation through poly(vinylidene fluoride) membrane in this work is due to the viscous flow. Yasuda[9] and Paul[10] reported that the permeation through very swollen membrane was not diffusive flow but was due to viscous flow. The results in this work are the same as theirs. The error in activation energy obtained from Arrhenius plots is ~0.05 kcal mol^{-1}. However, the values of E_p are smaller over the measurement error than the values of E_η. It is presumed that the hydrogen bonds in a water cluster are severed partly because of the polarity of fluoride group in poly(vinylidene fluoride) molecules. The viscosity of liquid in the membrane is lower than the actual viscosity, and consequently the permeating molecules are liable to permeate the membrane. The activation energy for aqueous solutions of PVA 217 is larger than that for pure water. These activation energies also increase with an increase in feed concentration. These results are attributed to the concentration polarization of PVA 217 molecules onto the membrane surface, and suggest that the thickness of the concentration polarization layer increases as the concentration of PVA 217 in the feed increases. This discussion is supported by the fact that the permeation rate decreases with an increase in feed concentration.

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