Studies on syntheses and permeabilities of special polymer membranes.
27. Concentration of poly(styrene sulphonic acid) in various aqueous solutions using poly(vinylidene fluoride) membranes

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The permeation characteristics of poly(vinylidene fluoride) membranes in the separation and concentration of poly(styrene sulphonic acid), from various aqueous solutions were investigated under various conditions. The rejection of the polymer from its aqueous solution was high, because electrostatic repulsions between the charges along polymer chains cause chain extension. When a salt, such as sodium chloride, and sulphuric acid were added to the aqueous solution and the pH was changed, the configuration of the poly(styrene sulphonic acid) molecules changed significantly with the added amounts of salt. The permeation characteristics were influenced markedly by the conformational changes of polymer molecules and the viscosities of permeating liquids. The rejections were dependent on the conformational changes: the permeation rates were mainly governed by the viscosities. Poly(vinylidene fluoride) membranes had much superior resistance to acid, i.e. even when immersed in concentrated sulphuric acid for 7 days, the permeation characteristics did not change at all. The membranes were also effective for the concentration of poly(styrene sulphonic acid) and the removal of sulphuric acid from aqueous mixtures since the concentration of these solutes were optimum.

INTRODUCTION

The permeation characteristics of poly(vinylidene fluoride) membranes and their dependence on preparation and the permeation conditions have been reported in an earlier paper[1]. The relationships of formation process of microporous poly(vinylidene fluoride) membranes, the structures of the resulting membranes and the permeation characteristics of these membranes with changes in mixed casting solvent and time allowed for evaporation have also been discussed[2].

Here, we discuss the permeation characteristics of poly(vinylidene fluoride) membranes which have high resistance towards acid, and the effects of conformational changes of poly(styrene sulphonic acid) molecules in aqueous solutions, aqueous solutions containing various salts, and in aqueous solutions of different pH; the effects of permeated solution viscosity are also examined. The ability to concentrate poly(styrene sulphonic acid) and remove sulphuric acid from mixed aqueous solutions are investigated from the viewpoint of their feed concentrations.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVF_2), whose average degree of polymerization was 1000 (produced by Kureha Chemical Co. Ltd), was used as the membrane substrate. Pure commercial dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF) were used as solvents for the casting solutions. Poly(vinyl alochols) (supplied by Kurary Co. Ltd) used as solutes for the feed solutions were PVA 205 and PVA 217, whose average degrees of polymerization were 550 ± 50 and 1725 ± 25, respectively. Sodium chloride (NaCl), sodium hydroxide (NaOH), concentrated sulphuric acid (conc. H_2SO_4), and silver sulphate were pure commercial reagents. Polystyrene, whose number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) were 75 800 and 205 000 respectively ($\bar{M}_w/\bar{M}_n = 2.70$), was used for the synthesis of poly(styrene sulphonic acid).

Poly(styrene sulphonic acid) was synthesized by stirring the mixture of polystyrene (50 g and silver sulphate (0.5 g) dissolved in 97% concentrated sulphuric acid (470 g) at 100–110°C for 6 h. The mixture was then dissolved in pure water (1 l), insoluble material was removed by filtration, and the excess unreacted sulphuric acid was removed by dialysis with cellophane tube membrane (produced by Union Carbide Co.) for 5 days, until the sulphate ions in the product solution could not be detected with an aqueous solution of barium chloride. The solution in the cellophane tube was concentrated by distillation under reduced pressure, poured into concentrated hydrochloric acid, and the solid product was obtained. This product was dissolved in a small amount of pure water and reprecipitated with concentrated hydrochloric acid. After repeating this reprecipitation process, hydrochloric acid in the aqueous solution of poly(styrene sulphonic acid) was removed by repeating the distillation under reduced pressure with the addition of pure water. The ion exchange capacity of the

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poly(styrene sulphonic acid) obtained was 3.58 meq g^{-1}.

Preparation of membranes

The casting solution was prepared from the ratio poly(vinylidene fluoride):tetrahydrofuran:dimethyl sulphoxide 7:48:45 (wt %). The membranes were made by pouring the casting solution onto a rimmed glass plate, exposing for 2 h at 25°C and 50–60% humidity, and immersing the glass plate together with the membrane, which was removed from the glass plate and treated with hot water at 40°C for 20 min.

Apparatus and measurements

The ultrafiltration cell has been described in earlier papers[3,4]. The suction filtration apparatus consisted of a membrane filter as shown in *Figure 1*. The operating conditions for the suction filtration were 25°C and 30 mmHg. The experimental procedure and analysis of feed and membrane-permeated liquid have already been reported[3].

RESULTS AND DISCUSSION

Ultrafiltration and suction filtration

The permeation characteristics in ultrafiltration and suction filtration, using aqueous solutions of poly(vinyl alcohols) as feed solutions are summarized in *Table 1*. The permeation rate for pure water in suction filtration is constant regardless of the filtration period, but the permeation rates for aqueous solutions of poly(vinyl alcohols) in suction filtration decrease with the permeation period. The former phenomenon is due to the fact that the compaction of the membrane under suction pressure is small. The latter is attributed mainly to an increase in feed concentration with the concentration of poly(vinyl alcohol) molecules. As can be seen from *Table 1*, in spite of the fact that the rate of pure water permeability in the suction filtration is about half that of the ultrafiltration, the permeation characteristics for aqueous solutions of poly(vinyl alcohols) are approximately equal. The results indicate that the concentration polarization of poly(vinyl alcohol) molecules onto the membrane surface in the suction filtration is smaller than that in ultrafiltration. Consequently, it was found that in the separation and concentration of polymers from their aqueous solutions the suction filtration is relatively useful, and was used for this study.

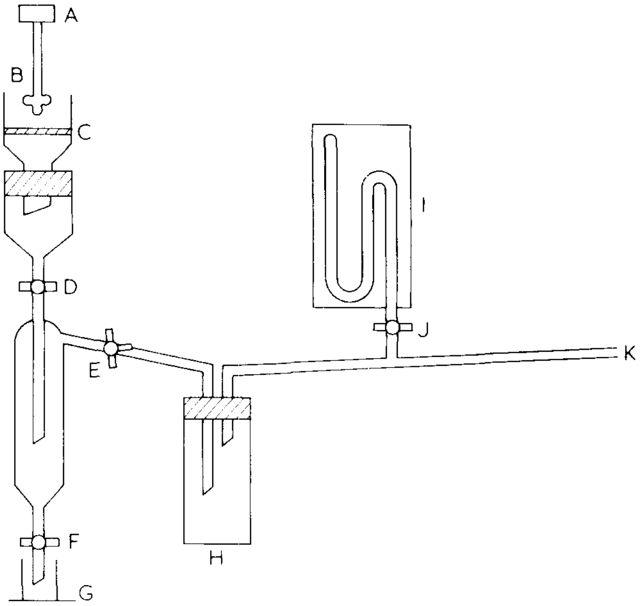

Figure 1 Schematic diagram of suction filtration. A, mini motor; B, stirrer; C, membrane; D, F, J, two-way stopcocks; E, three-way stopcock; G, vessel of permeated liquid; H, trap; I, manometer; K, reduced pressure

Separation in aqueous solution of poly(styrene sulphonic acid)

The relationship between the permeation characteristics and the permeation period is shown in *Figure 2*, where an aqueous solution of poly(styrene sulphonic acid) is used as the feed. In spite of the fact that when the poly(styrene sulphonic acid) molecules dissolve in pure water, the viscosity is high and the polymer chains are extended by electrostatic repulsions of the charges along the polymer chains. However, the poly(styrene sulphonic acid) molecules are not rejected completely. This result is attributed to the fact that the lower molecular weight poly(styrene sulphonic acid) cannot be rejected. The permeation rates decrease with increasing permeation period and concentration of poly(styrene sulphonic acid) in the feed. These phenomena are caused mainly by the increase in viscosity at the feed solution side and the decrease in effective pressure. If concentration polarization of poly(styrene sulphonic acid) molecules onto the membrane surface occurs, the rejection should increase with increasing permeation period. However, the rejections are constant. This may indicate that the concentration polarization of poly(styrene sulphonic acid) molecules onto the membrane surface is small, and this is supported by the fact that the permeation rate at 90 min, when the feed of 0.5 wt % is concentrated to about 1 wt %, approximately equals the permeation rate of the earlier permeation period for a starting feed concentration of 1.0 wt %.

Table 1 Permeation characteristics of ultrafiltration and suction filtration

Ultrafiltration (2 kg cm^{-2} s^{-1}, 40°C)					Suction filtration (30 mmHg, 25°C				
	PVA205 1 wt % (aq. soln)		PVA217 1 wt % (aq. soln)			PVA205 1 wt % (aq. soln)		PVA217 1 wt % (aq. soln)	
PWP ml cm^{-2} s^{-1}	*PR* g cm^{-2} s^{-1}	*R* %	*PR* g cm^{-2} s^{-1}	*R* %	*PWP* ml cm^{-2} s^{-1}	*PR* g cm^{-2} s^{-1}	*R* %	*PR* g cm^{-2} s^{-1}	*R* %
2.02 x 10^{-2}	5.85 x 10^{-4}	59	2.55 x 10^{-4}	100	1.06 x 10^{-2}	5.00 x 10^{-4}	64	2.35 x 10^{-4}	100

PWP is rate of pure water permeability, *PR* is permeation rate for aqueous solution of poly(vinyl alcohol), *R* is rejection

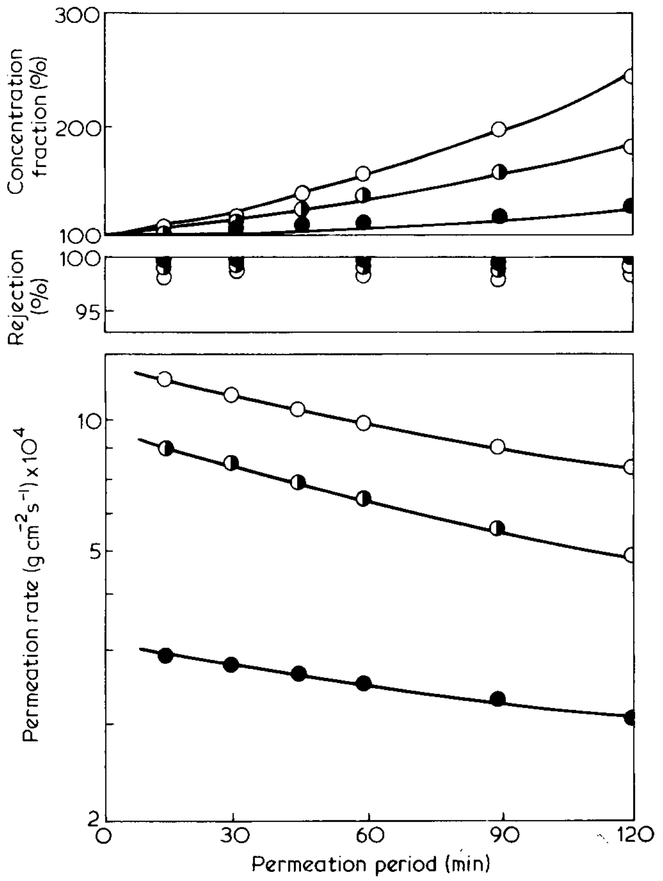

Figure 2 Effect of permeation period on permeation characteristics. Feed: ○, 0.5 wt % PSA; ◑, 1.0 wt % PSA; ●, 2.0 wt % PSA aqueous solutions; operating conditions, 25°C, 30 mmHg

Separation of aqueous solutions poly(styrene sulphonic acid)/sodium chloride

The effect of addition of sodium chloride into aqueous solutions on the permeation characteristics of poly(styrene sulphonic acid) is shown in *Figure 3*, where the concentration of poly(styrene sulphonic acid) is kept constant at 1.0 wt %. Poly(styrene sulphonic acid) molecules dissociate completely in aqueous solution, but the pH of its solution is far higher than the value expected from complete dissociation, since the activity coefficient of the proton is small. Accordingly, with the ion exchange between the protons and the sodium ions, the protons occur in a free state and the activity coefficient increases, and consequently the pH of solution lowers. The ion exchange capacity of poly(styrene sulphonic acid) used in this work is 3.58 meq g^{-1}. The theoretical amount of sodium ion exchanged by the poly(styrene sulphonic acid) molecules is 0.082 g per gramme of poly(styrene sulphonic acid), which corresponds to 0.207 g of sodium chloride, in close agreement with the pH curve in *Figure 3*. The permeation rate and the rejection change significantly in the lower concentration region of sodium chloride. These results depend on the significant variation of configuration of the poly(styrene sulphonic acid) molecules. The decrease in rejection is due to the decrease of apparent molecular size based on the shrinkage of poly(styrene sulphonic acid) chains. The decrease in permeation rate is dependent on an increase in viscosity of the permeated liquid and on an osmotic back pressure caused by the fact that the poly(styrene sulphonic acid) molecules permeate through the membrane.

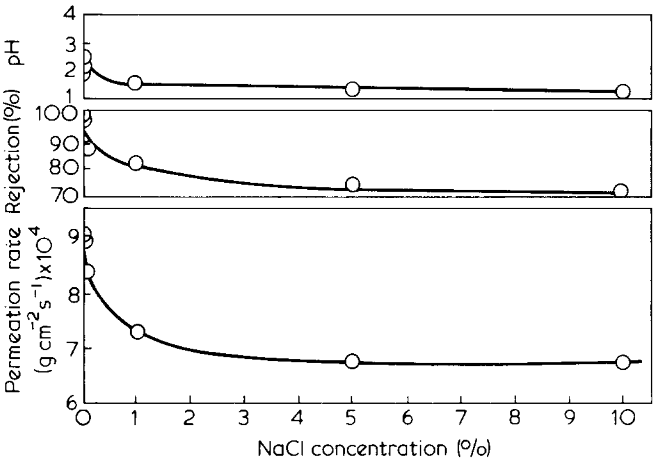

Figure 3 Effect of NaCl concentration on permeation characteristics. Feed: 1.0 wt % aqueous solution of PSA: operating conditions, 25°C, 30 mmHg

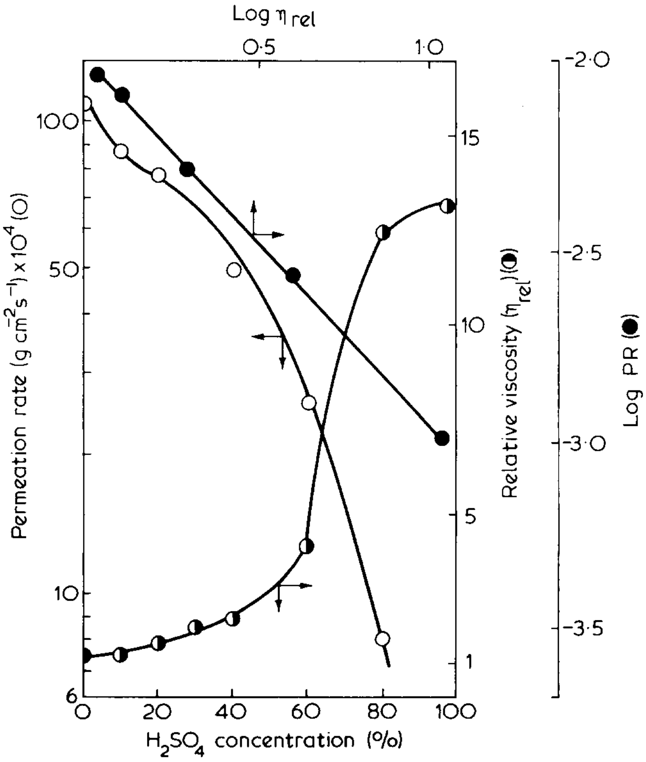

Figure 4 Effect of H_2SO_4 concentration on permeation rate of H_2SO_4 aqueous solution. *PR* is permeation rate (g cm^{-2} s). η_{rel} is relative viscosity of H_2SO_4 aqueous solution for viscosity of water. Feed is H_2SO_4 aqueous solution. Operating conditions are 25°C, 30 mmHg

Separation of poly(styrene sulphonic acid) in aqueous solution of sulphuric acid

Poly(vinylidene fluoride) has high resistance to acid, and hence we investigated the effects of concentrated sulphuric acid on the permeation characteristics, by immersing in concentrated sulphuric acid for 7 days. The permeation rate for pure water and the rejection for aqueous solutions of poly(vinyl alcohol) do not change at all. From these results, it is found that the poly(vinylidene fluoride) membranes are highly stable in acidic solution.

The permeation rate for aqueous sulphuric acid solution depends significantly on viscosity as shown in *Figure 4*. Since the membrane is rough and porous,

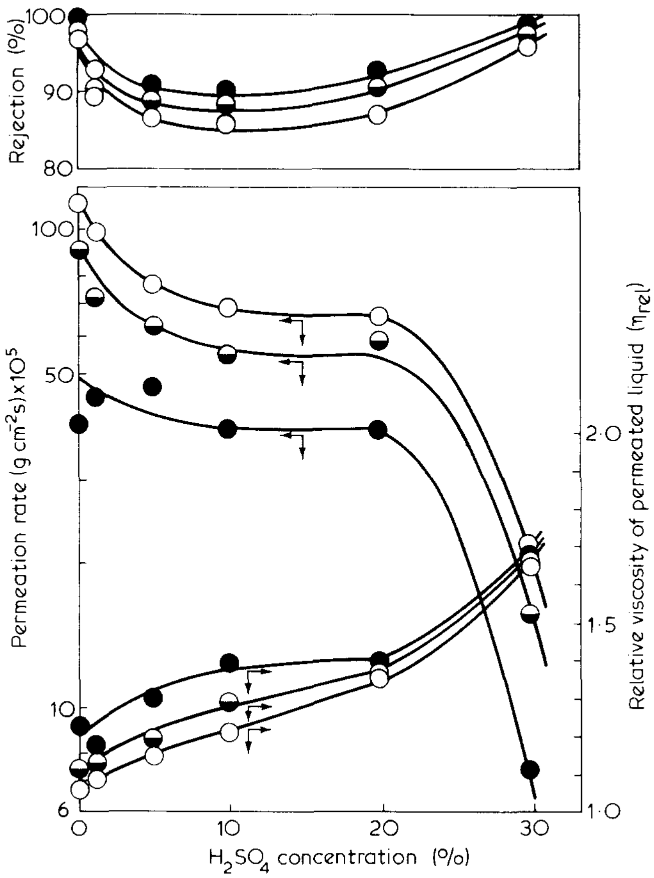

Figure 5 Effect of H_2SO_4 concentration in PSA aqueous solution on permeation characteristics. Feed: ○, 0.5 wt % PSA; ◒, 1.0 wt % PSA; ●, 2.0 wt % PSA in H_2SO_4 aqueous solutions; operating conditions, 25°C, 30 mmHg

sulphuric acid molecules are not completely rejected. A plot of log *PR* (logarithm of permeation rate) vs. log η_{rel} (logarithm of relative viscosity in dilute aqueous sulphuric acid) gives a straight line with slope −1.0. This relation may thus be represented by the following equation:

$$PR = 1/\eta_{rel}$$

It can be seen that permeations through PVF_2 membranes swollen with water, at various concentrations of aqueous sulphuric acid solution obey viscous flow, and consequently the permeation rates are governed by the viscosities of the permeating liquids. In other words, the interactions between the permeating species and the membranes are small.

Figure 5 shows the effect of concentration of sulphuric acid on the permeation characteristics for the system poly(styrene sulphonic acid)–aqueous sulphuric acid solution. The change in viscosity with increasing sulphuric acid concentration in aqueous solution is shown in *Figure 6*, where there is a marked decrease in viscosity as a result of the significant conformational change of poly(styrene sulphonic acid) molecules up to 5% sulphuric acid concentration, but is small over 5%. The permeation rates in *Figure 5* do not correspond to the feed viscosities with such conformational changes in poly(styrene sulphonic acid) molecules. *Figure 5* also includes the viscosities of permeating liquids, which increase as the concentration of sulphuric acid in the feed increases. The increases in these viscosities are caused mainly by the viscosities of aqueous sulphuric acid solutions. The permeation rates correspond to the viscosities of permeating solutions. Alternatively, the rejection for poly(styrene sulphonic acid) molecules decreases up to 10% sulphuric acid concentration, but increases over 10%. The former phenomenon may be attributed to a decrease in apparent molecular size based on a decrease in terminal distance of poly(styrene sulphonic acid) molecules rather than the 10% sulphuric acid concentration, and consequently an increase in permeation resistance. The large decrease in permeation rate over 20% is related to this permeation resistance.

Effects of co-ion and counterion

The effects of co-ion and counterion on the permeation characteristics are summarized in *Table 2*, where the added amounts of sodium chloride and sulphuric acid are

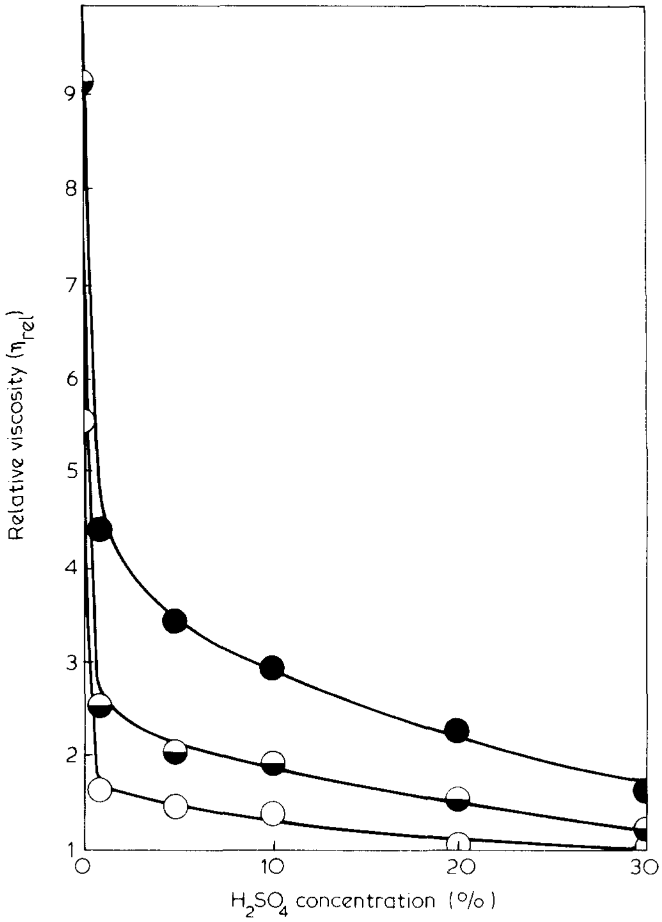

Figure 6 Relations between concentration of PSA and H_2SO_4 and relative viscosity. ○, 0.5 wt % PSA; ◒, 1.0 wt % PSA; ●, 2.0 wt % PSA in H_2SO_4 aqueous solution

Table 2 Effects of co-ion and counterion on permeation characteristics

Additional electrolyte		*PR* (g cm^{-2} s)	*R* (%)	η_{rel}
NaOH(pH = 6.68)	$-SO_3^-Na^+$	7.38×10^{-4}	97	8.25
NaCl	$-SO_3^-Na^+$, H^+, Cl^-	8.15×10^{-4}	88	3.40
H_2SO_4	$-SO_3^-H^+$, H^+, SO_4^{2-}	7.85×10^{-4}	93	3.75

PR is permeation rate, *R* is rejection, and η_{rel} is relative viscosity for viscosity of aqueous salt solution

Table 3 Diameter of hydrated ion

Ion	Diameter (Å)
H^+	9
Na^+	3.5
SO_4^{2-}	4
Cl^-	3
OH^-	3.5

equal to the concentration of sodium hydroxide counterion used to neutralize the poly(styrene sulphonic acid). In neutralization with sodium hydroxide, the sulphonic acid groups in the poly(styrene sulphonic acid) molecules become sodium sulphonate groups and protons react with the hydroxyl ions to form water. That is, there is little change in the amounts of ion in aqueous solution. In the sodium chloride system (which gives rise to the same sodium sulphonate groups) the rejection for poly(styrene sulphonic acid) molecules is lower and the permeation rate is higher than those in the sodium hydroxide system because of the existence of excess counterions and co-ions in aqueous solutions; the electrostatic repulsions between the charges on the poly(styrene sulphonic acid) chains are weakened in this manner, and consequently the molecular size of poly(styrene sulphonic acid) becomes smaller, i.e. the relative viscosity becomes small. In the comparison between the sodium chloride system and the sulphuric acid system in which the excess co-ions and counterions exist, the rejection in the sulphuric acid system is higher and the permeation rate is smaller than for sodium hydroxide. These phenomena depend on the feed viscosity; the polymer chains of sulphonic acid-type are extended more than those of the sodium sulphonate species. It is presumed that this factor is influenced by the difference in the hydrated ion sizes for sodium and protons, or the difference in co-ion such as chloride and sulphate. *Table 3* summarizes the diameter of the hydrated ions calculated by Debye–Hückel theoretical formulation using the activity coefficient of individual ions in aqueous solution. The diameter of hydrated protons and sulphate ions are larger than those of sodium ions and chloride ions. Therefore, poly(styrene sulphonate) ions in the aqueous sulphuric acid solution system are less influenced by an electric field than in the sodium chloride system and consequently the poly(styrene sulphonic acid) chains become extended.

Concentration of poly(styrene sulphonic acid) and removal of sulphuric acid

We have examined the effects of concentration of poly(styrene sulphonic acid) and aqueous sulphuric acid on the permeation characteristics of poly(vinylidene fluoride). The results obtained are shown in *Figure 7*. When the concentrations of poly(styrene sulphonic acid) and sulphuric acid are 2 and 30 wt %, respectively, the rejection for poly(styrene sulphonic acid) is greater, but the residual fraction of sulphuric acid in the feed side is 80% and the concentration fraction of poly(styrene sulphonic acid) is no more than 120% after 7 h. In the system with 0.34 wt % poly(styrene sulphonic acid) and 5 wt % sulphuric acid, the concentration fraction is twice that of the starting feed concentratiohn, and the residual fraction of sulphuric acid is 40%. In the aqueous 0.68 wt % poly(styrene sulphonic acid) solution and 10% sulphuric acid feed solution, the permeation rate is relatively large, the concentration fraction is 4.5 times greater, and the residual fraction is 20%. This system is effective for the concentration of poly(styrene sulphonic acid) and the removal of sulphuric acid from their aqueous solutions. The results suggest that the feed concentration is an important factor.

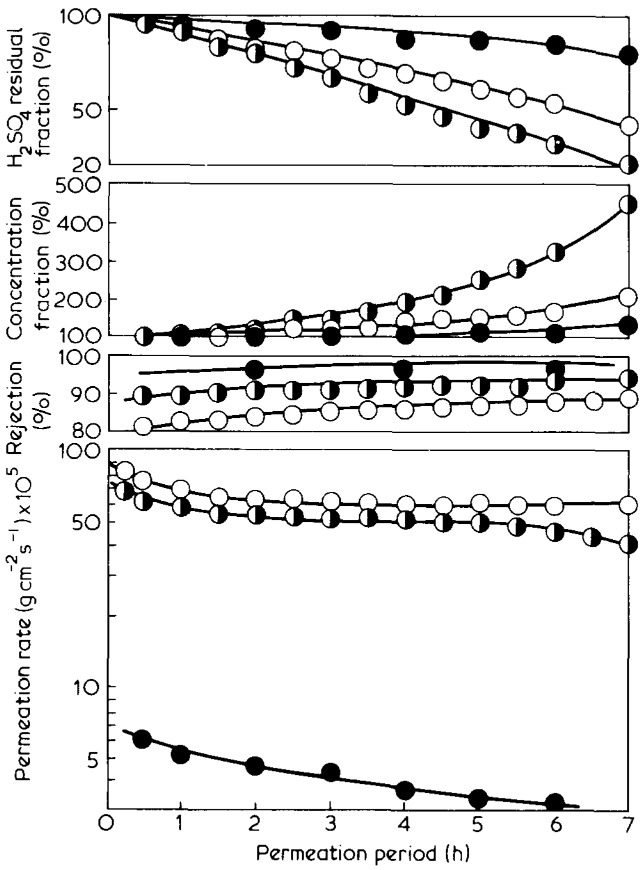

Figure 7 Effect of permeation period on permeation characteristics in various concentrations of PSA and H_2SO_4 in feed solution. Feed: ●, 2.0 wt % PSA and 30 % H_2SO_4; ◑, 0.68 wt % PSA and 10 % H_2SO_4; ○, 0.34 wt % PSA and 5 % H_2SO_4, aqueous solution. Operating conditions, 25°C, 30 mmHg

The effectiveness of the poly(vinylidene fluoride) membranes for the concentration of poly(styrene sulphonic acid) and the removal of sulphuric acid is indicated by the fact that the time for these processes is not only shorter than the dialysis using the cellophane tube membranes, but they can also simultaneously concentrate the poly(styrene sulphonic acid) molecules and remove low molecular weight compounds of poly(styrene sulphonic acid). It may be expected that the circulation-type rather than the batch-type examined in this work and the combination of the membrane technique and the ion exchange resin technique are more effective.

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