Retention of Polyvinylpyrrolidone Swelling Agent in the Poly(ether p-phenylenesulfone) Ultrafiltration Membrane

TADAAKI MIYANO, TAKESHI MATSUURA, and D. J. CARLSSON,
Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6 and S. SOURIRAJAN, *Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Canada K1N 6N5*

Synopsis

The detection and quantification of polyvinylpyrrolidone (PVP) polymer in the top skin layer of the poly(ether p-phenylenesulfone) (PES, Victrex) ultrafiltration membrane was attempted by applying the technique of internal reflection Fourier transform infrared spectroscopy (FTIR-IRS). The effects of the PVP concentration in the casting solution and that of the PVP molecular weight on the residual quantity of PVP were investigated in detail. The PVP content in the membrane was further correlated to the ultrafiltration performance data of PES membranes.

INTRODUCTION

Ultrafiltration is one of the membrane separation processes by which solutes of high molecular weights (> several thousand daltons) are separated from solvents. Polysulfone (PS) has been one of the most popular membrane material for ultrafiltration because of its heat and chemical resistance. Since the early stage of polysulfone membrane development, polyvinylpyrrolidone (PVP) has been used as an additive to the casting solution in order to adjust the casting solution viscosity and the pore size of the membrane.

The role of polyvinylpyrrolidone (PVP) nonsolvent additive in the formation of polysulfone (PS) ultrafiltration membranes is of great interest since PVP polymer is miscible both in PS polymer and water which is used as gelation media in the phase-inversion technique of ultrafiltration membrane preparation. Several reports are documented on the above subject[1-5] but the true role of PVP is not known. Although we have suggested PVP polymer is leached out of the membrane to the gelation bath almost completely since PVP is water miscible,[4] the possibility of PVP being retained in PS membranes has been suggested.[6] Similarly, polyethylene glycol added to the casting solution to prepare polysulfone ultrafiltration membranes may possibly be retained in the polysulfone film during and after the gelation process.[7]

The retention of PVP in PS film is of importance from several view points. If PVP truly remains in the film, the PS membrane has to be regarded as a polymer blend of hydrophobic PS material and hydrophilic PVP material. The hydrophilic nature of the blended polymeric membrane material is, therefore, more intense than that of PS polymer alone. Furthermore, the distribution of

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PVP polymer in PS polymer may have a strong influence on the performance of the ultrafiltration membrane. For example, microdomains of hydrophilic PVP may be formed in the continuous polymer matrix of hydrophobic PS. If so, solvent water can be expected to flow through the PVP phase preferentially. There is also the possibility of a nonuniform distribution of PVP polymer in the through direction, that is from the active surface to the underlying porous support layer of the membrane. This distribution of PVP polymer may give rise to an asymmetric structure in the membrane in terms of hydrophilicity (or −phobicity).

The objective of this work is to confirm the presence of PVP polymer in PS membranes prepared by a gelation procedure and its presence after the subsequent UF operation of the membrane. Poly(ether p-phenylenesulfone) (PES) polymer was chosen instead of PS polymer for membrane material, since PES polymer shows a higher heat resistance than PS polymer and is more adequate for UF membrane.[8] The detection and quantification of PVP polymer in the top skin layer of the UF membrane was a particular objective and the technique of internal reflection Fourier transform infrared spectroscopy (FTIR-IRS) was applied for this purpose. In addition, the effects of the PVP concentration in the casting solution and that of the PVP molecular weight on the residual quantity of PVP were investigated in detail.

EXPERIMENTAL

Materials. Poly(ether p-phenylenesulfone) (PES Victrex 200P) supplied by Imperial Chemical Industries PLC as pellets was dried at 150°C for 4 h before use. A nonwoven fabric (polyethylene, Tyvek 1079D, supplied by DuPont de Nemours & Co.), was used as a backing material on which polymer films were cast. Reagent grade dimethylsulfoxide (DMSO) supplied by J. T. Baker Chemical Co., was used as a solvent. Polyvinylpyrrolidone (PVP) of molecular weight 10,000 and 40,000, supplied by Sigma Chemical Co., and 24,000 and 360,000, supplied by Fluka A.G., were dried at 60°C before use as nonsolvent additive. Polyethylene glycol (PEG) of molecular weight 6000 was supplied by Fluka A.G.

Membrane Preparation and Ultrafiltration Experiment. The casting solutions of compositions specified in Table I were cast at 245 μm thickness on a backing cloth in the ambient atmosphere (20 to 23°C, $<$ 60 RH %). The cast film on the backing cloth was immersed in water (5 ± 0.5°C) after 20 s of solvent evaporation in the ambient atmosphere. The film was then allowed to gel in water for more than 20 min and kept in fresh water thereafter.

Ultrafiltration experiments were carried out using a conventional continuous flow cell.[9] The operating pressure and the feed flow rate were kept at 345 kPag (50 psig) and 2.76 L/min, respectively. There are two types of ultrafiltration experiments involved in this study. In one type pure water permeation alone was carried out to prepare membrane samples for the spectroscopic study. The pure water permeation experiment was continued for a specified period, after which the membrane was removed from the UF cell and rinsed with pure water. In the second type of UF experiments the membranes were characterized by the separation of PEG-6000 solute. The pure water permeation rate (PWP)

TABLE I
Compositions of Membrane and Film Casting Solutions[a]

Solution no.	PES content, wt %	PVP content, wt %	M.W. of PVP	C_s[b] wt %
Asymmetric UF membranes				
1	20	2.6	10,000	11.5
2	20	5.7	10,000	22.3
3	20	8.1	10,000	28.8
4	20	10.6	10,000	34.6
5	21	2.7	10,000	11.4
6	21	6.0	10,000	22.2
7	21	8.0	10,000	27.6
8	23	0	10,000	0.0
9	23	0.3	10,000	1.3
10	23	0.8	10,000	3.4
11	23	1.8	10,000	7.3
12	23	2.3	10,000	9.1
13	23	3.0	10,000	11.5
14	23	4.6	10,000	16.7
15	23	6.5	10,000	22.0
16	23	9.8	10,000	29.9
17	23	10.5	10,000	31.3
18	26	3.7	10,000	12.5
19	26	6.0	10,000	18.8
20	26	9.0	10,000	25.7
21	23	3.0	24,000	11.5
22	23	6.5	24,000	22.0
23	23	9.6	24,000	29.4
24	23	3.1	40,000	11.9
25	23	6.5	40,000	22.0
26	23	9.4	40,000	29.0
27	23	3.0	360,000	11.5
28	23	6.5	360,000	22.0
Calibration films				
29	11.5	0.15	10,000	1.3
30	11.5	0.40	10,000	3.4
31	11.5	1.15	10,000	9.1
32	11.5	3.25	10,000	22.0

[a] Solvent, dimethylsufoxide.

[b] C_s = PVP weight in the casting solution × 100/(total polymer weight (PVP + PES) in the casting solution).

was measured after 4.5 h of continuous pure water operation. Then, the feed solution containing 200 ppm of PEG-6000 solute was supplied to the UF cell and, after 30 min of feed circulation, the permeate sample was collected. The feed and permeate samples were then subjected to an analysis by a Beckman Total Carbon Analyzer Model 915B for the determination of the PEG concentration. All the ultrafiltration experiments were performed at room temperature (23 to 25°C), and the solute separation, f, is defined as

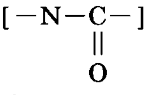
$$f = \frac{\text{feed PEG ppm} - \text{product PEG ppm}}{\text{feed PEG ppm}} \times 100\% \qquad (1)$$

In addition the pure water permeation rate (PWP) and product rate (PR) were estimated. PWP and PR are defined as the permeation rate per effective membrane area in the absence and in the presence of the solute in the feed, respectively, and both have the dimension of g/h. All PWP and PR data are those corrected to 25°C using relative density and viscosity data of water. The effective membrane area was 14.5 cm^2.

Sample Preparation for Infrared Spectroscopy. Membranes, both with and without being subjected to the UF experiment, were partially air-dried before complete drying under vacuum at 40°C. These dry membranes were examined directly by infrared spectroscopy and they are of asymmetric structure. Film samples for IR calibration, called calibration films hereafter, were prepared in the following way. The casting solution of compositions specified in Table I was cast to the thickness of 49 μm on a smooth glass plate. The cast film was kept in an oven at 75°C overnight to evaporate the solvent. Then, the film was removed from the glass plate and kept under vacuum at 80°C for 2 days to complete the solvent removal. The thin film so obtained was transparent and is considered to be of symmetric structure.

Determination of the PVP Content. The determination of PVP content in the surface layers of each asymmetric UF membrane was made by Fourier Transform-Internal Reflection-Spectroscopy (FTIR-IRS). The IRS spectra were recorded on a Nicolet 7199 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. Surface spectra were recorded by squeezing the selected membrane surface against both sides of a germanium, parallelogram, IRS element (45° facets, 50 × 20 × 2 mm) mounted on a 2-mirror optical stage (Buck Scientific, Model 59), with a 45° facet at the focal point of the spectrometer, as described previously.[10] These conditions yield spectra in the ~ 1600 cm^{-1} region corresponding to a surface layer of about 0.5 μm in thickness for the surface in contact with the Ge reflection element. Normally 200 IR scans were averaged to give a high signal-to-noise ratio. The transmission spectra of the calibration films were measured on this spectrometer and on a Perkin Elmer 1500 (DTGS detector); both spectrometers gave virtually identical ratios of PVP to PES absorptions. PVP to PES concentration ratios were established from the 1680 cm^{-1} to 1580 cm^{-1} absorption ratios, after correcting for a small PES absorption at 1680 cm^{-1}.

RESULTS AND DISCUSSION

For the analysis of the Infrared spectroscopy data, the absorption peaks at 1680 cm^{-1} and 1580 cm^{-1}, each corresponding to the amide carbonyl  $[-N-\underset{\underset{O}{\|}}{C}-]$ and the $-C{=}C-$ stretching vibrations of the para substituted ring, respectively, were considered to represent the concentrations of PVP and PES in the membrane sample. Thus, the absorption ratio of both peaks was correlated to the weight ratio of PVP to PES of the calibration membrane as illustrated in Figure 1. The PVP content in the surface layer of the asymmetric UF membrane, designated as C_m,

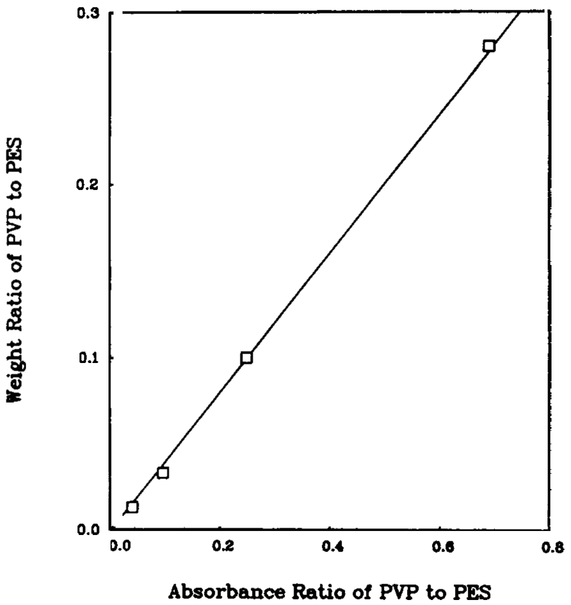


Fig. 1. Calibration curve for the determination of PVP content. Determined by transmission IR on thin, cast films of PVP and PES.

$$\left[C_m = \frac{\text{PVP weight in membrane surface} \times 100}{(\text{total weight of polymer in the surface})}\right] \qquad (2)$$

was then determined by using the calibration curve prepared above after making the correction for the wavelength dependence of intensities in the IRS data. This correction is small (1.06) for the two close bands in the PVP/PES spectra.

The FTIR-IRS spectra clearly show that PVP remains in the UF membrane after the gelation step even though PVP polymer is water soluble. Figure 2 shows the FTIR-IRS spectra for membranes prepared from casting solutions without (a) and with (b) PVP additive. The absorption peak at 1680 cm^{-1} which is characteristic of the amide carbonyl stretching vibration appears only in the spectrum of the membrane prepared from a casting solution with PVP additive.

The PVP content in the surface layer, designated above as C_m, was measured after specified periods of pure water permeation and the results are reported in Table II. During the pure water permeation experiment the pure water permeation rate (PWP) decreased significantly, probably due to the contamination on the membrane surface or restructuring of the skin. Although a close examination of the membrane revealed coloring of the membrane surface, no new absorption peaks in the IR spectrum were detected.

In Table II the PVP concentration in each casting solution, C_s, is defined as

$$C_s = \frac{(\text{PVP weight in the casting solution}) \times 100}{(\text{total polymer weight (PVP + PES) in the casting solution})} \qquad (3)$$

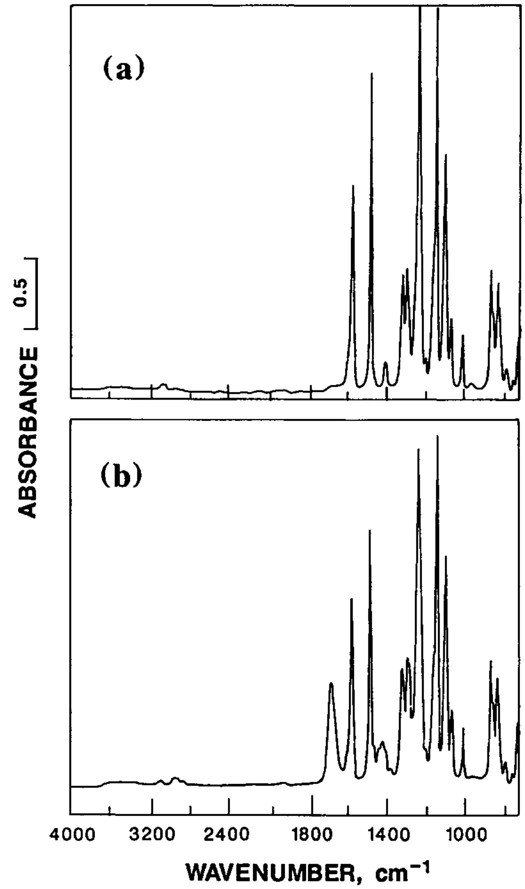


Fig. 2. FTIR-IRS spectra of the active layer of PES membranes (a) prepared from a PVP-free casting solution and (b) prepared from the casting solution containing PVP polymer, composition corresponding to No. 15 in Table I.

Therefore, if there is no escape of PVP during the gelation and subsequent ultrafiltration steps, C_m should be equal to C_s. Looking at the data of zero hour pure water permeation, C_m is 10 to 11% when C_s is 11%, while C_m is ca 17% when C_s is 22%. The above results do not depend on the molecular weight (M_w) in the 10,000 to 360,000 range. Thus, we are able to conclude that the loss of PVP during the gelation step depends only on C_s and when C_s is low the loss is insignificant. C_m is almost unchanged during the following 73 h of pure water permeation experiment when either the molecular weight is high or C_s is low. However, when neither is the case (film No. 15) C_m drops from 17 to 13% during the first 2 h and remains at almost the same level during the rest of the pure water permeation experiment.

The retention of all or most of the PVP from the casting solution for low C_s values or high C_s with high molecular weight, yet less of PVP when high C_s levels are used with low molecular weight polymer implies a complex interplay of association and entanglement effects. The plateau level of C_m ($\simeq$ 12% PVP) for the low molecular weight polymer after exhaustive water permeation implies

TABLE II
Change in PVP Content During Pure Water Permeation Experiment[a]

Pure water permeation time, h	Surface PVP concentration (C_m) wt %[b]
Film No. 13, M_w = 10,000, C_s = 11.5 wt-%	
0	11.3
2	10.8
4.5	10.2
25	10.1
Film No. 15, M_w = 10,000, C_s = 22.0 wt-%	
0	16.5
2	12.8
4.5	13.6
7.5	12.4
20	11.0
73	12.4
Film No. 27, M_w = 360,000, C_s = 11.0 wt-%	
0	10.1
2	10.6
4.5	10.1
20	10.8
73	10.5
Film No. 28, M_w = 360,000, C_s = 22.0 wt-%	
0	17.1
2	17.6
4.5	17.0
25	17.1
73	17.6

[a] Film No. is the same as the number of the casting solution in Table I from which the film was prepared.

[b] The error limit is ±0.5%.

some specific PVP-PES interaction at a ratio of pyrrolidone to ether sulfone repeats of ~ 1 : 3.5. It is interesting to note that this value agrees with the level at which a deviation from linearity of the intrinsic viscosity of PVP-PES solutions was observed.[4]

The higher levels of PVP (> 11%) present in the as-cast membranes prepared from low molecular weight PVP (for example, Film 15; Table II) are probably an artifact of the gelation processes. That is the level of PVP is controlled by solvent evaporation, the gelation speed, and the postgelation immersion time. For the high molecular weight PVP (360,000), entanglement effects may begin to control the extraction-resistant PVP levels.

Effect of the Composition of the Membrane Casting Solution. Figure 3 shows the correlation between C_m and C_s for different PES concentrations in the casting solution. The PVP molecular weight was fixed at 10,000 in these experiments. Furthermore, the PVP content in each membrane, C_m, is the maximum after gelation. C_m was determined with membrane samples which had not been subjected to the pure water permeation experiment.

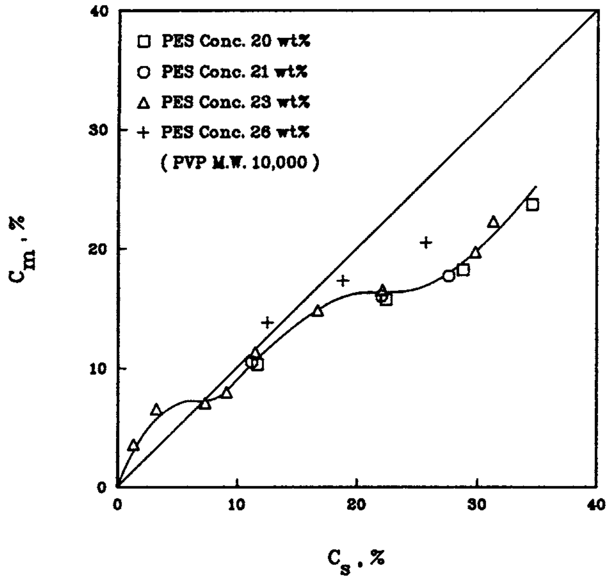


Fig. 3. Effect of PES concentration on the retention of PVP polymer (C_s measured immediately after gelation, before water permeation).

The correlation lines, which could be generated by connecting the data points corresponding to PES concentrations of 20 to 23 wt-%, can be split into 4 regions (Fig. 3). When $0 \leqq C_s < 8\%$, $C_m > C_s$, i.e., PVP is preferentially concentrated in the active surface layer. When $8 \leqq C_s < 15\%$, $C_m \simeq C_s$. When $15 \leqq C_s < 27\%$, C_m is lower than C_s and has a plateau at $C_m > 17\%$. When $C_s \geqq 27\%$, C_m starts to increase once again with an increase in C_s but is still clearly below C_s. The data for the PES concentration of 26 wt-% in the casting solution are consistently higher than the correlation line. The data for $C_s < 8\%$ suggests the presence of a nonuniform PVP distribution in the membrane cross-section. However, the difference between C_s and C_m is close to the experimental error in C_m when C_s is $\leq 8\%$. Therefore, an attempt was made to confirm the aforementioned PVP distribution at low PVP levels by measuring PVP contents both on the top and on the bottom sides of membrane No. 12 after removing the backing cloth from the PES membrane. From FTIR-IRS, the PVP content at the bottom was in fact 30% lower than that of the active surface.

In general, PES ultrafiltration membranes appeared opaque and uniform when dried. However, there were notable exceptions in the appearance when the C_s value in the casting solution was above 30%. Transparent spots were observed in the continuous opaque phase when these were dried. From FTIR, the PVP contents of both transparent and opaque parts were equal. The above observation suggests a structural change of polymer at $C_s = 30\%$. The same change in the appearance of the dry membrane occurred at $C_s = 26\%$ when the PES concentration in the casting solution was 26 wt %. Referring to Figure 3, the above results mean that the change in the polymer structure occurs when $C_m \geqq 20\%$.

Effect of PVP Molecular Weight. In Figure 4, C_m is plotted versus C_s for different molecular weights of PVP polymer. The PES concentration in the

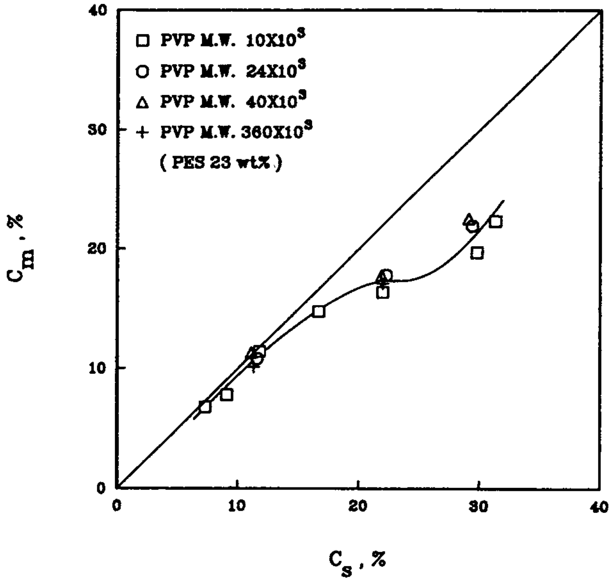


Fig. 4. Effect of PVP molecular weight on the retention of PVP polymer (C_s measured immediately after gelation, before water permeation).

casting solution was fixed at 23 wt % in this experiment while the amount of PVP additive in the casting solution was changed. Like Figure 3, C_m in Figure 4 is the PVP content before the membrane was subjected to pure water permeation experiments. Although a 36-fold increase in the PVP molecular weight was involved in the experiment all the data points fall along a single correlation line. Furthermore, the shape of the latter correlation line is exactly the same as that in Figure 3. The above results confirm the conclusion obtained from Table II, i.e., C_m before pure water permeation experiments depends only on C_s and is independent of PVP molecular weight.

Effect of PVP Additive on the Membrane Performance. The membrane performance is summarized in Figures 5 and 6 as separation data of PEG 6000 solute and as PWP. While PES concentration in the casting solution was fixed at 23 wt %, PVP concentration was changed. PVP molecular weight was also changed. In order to compare these figures with Figure 4, the PVP concentration can be converted to C_s by

$$C_s = \frac{\text{PVP wt \%}}{(\text{PES wt \%} + \text{PVP wt \%})} \times 100 \qquad (4)$$

Figures 5 and 6 show that PWP decreases and the separation increases with an increase of PVP concentration in the casting solution, consistent with the suggestion that the pore size becomes smaller as PVP concentration increases. The solute separation levels off at PVP concentration of about 6%, which corresponds to a C_s value of 20.7%. It is interesting to note that C_m value, the amount of PVP which remains in the membrane, also levels off in Figure 4 at the above C_s value. Therefore, there is some correlation between the amount

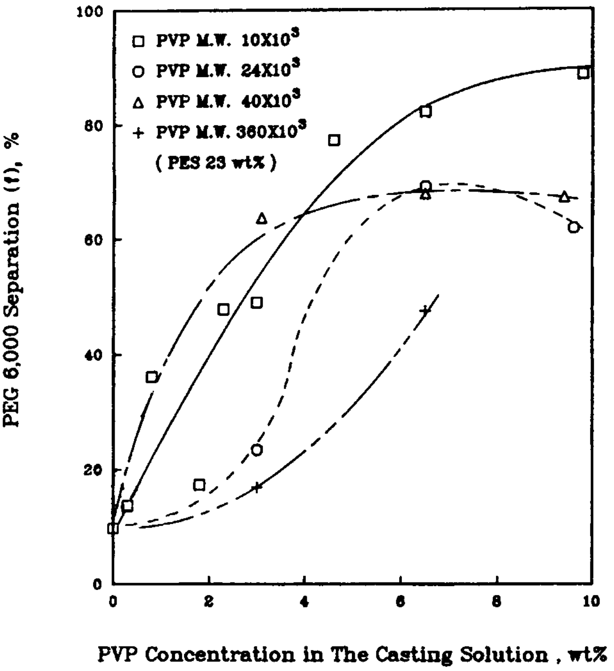


Fig. 5. PEG 6000 separation versus PVP concentration in the casting solution (ultrafiltration experiment, at 50 psig and room temperature with 200 ppm PEG 6000 solution).

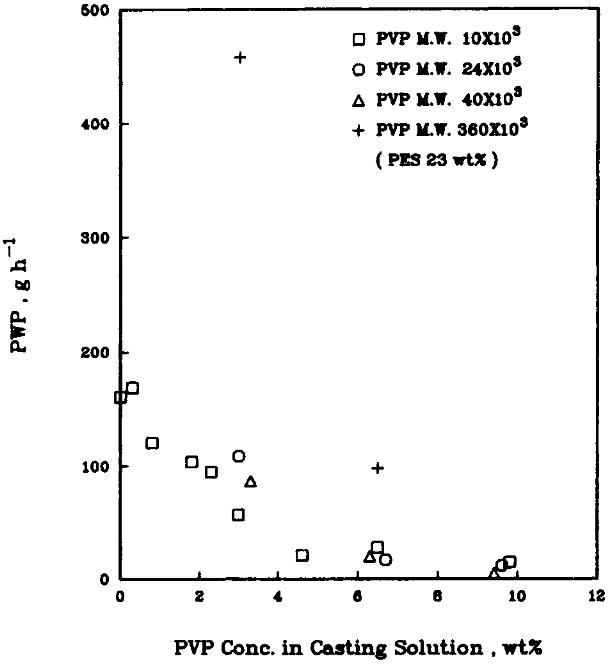


Fig. 6. Pure water permeation rate (PWP) versus PVP concentration in the casting solution (ultrafiltration experiment, at 50 psig and room temperature).

of PVP retained in the PES membrane and its performance. In Figure 4, however, C_m values start to increase when C_s is above 27%. However, Table II indicates that C_m is further lowered during ultrafiltration operations, when the molecular weight is sufficiently small (data for film No. 15). Therefore, the gain in C_m at $C_s > 27\%$ may be only a temporary one and the excessive PVP will be washed away leaving only PVP polymer strongly interacted with PES polymer.

The data for the PVP molecular weight of 360,000, which are quite abnormal on Figures 5 and 6 as compared with other PVP molecular weights, are probably the reflection of the strong interaction force between PVP polymer and PES polymer for such a high molecular weight. Figures 5 and 6 indicate also that the best PEG solute separation is obtained with the lowest molecular weight PVP while the best permeation rate is obtained with the highest molecular weight PVP.

CONCLUSION

The FTIR-IRS method has revealed that PVP added to the casting solution of PES ultrafiltration membranes is still retained in the membrane, even after 73 h of ultrafiltration operation. The amount of PVP retained in PES membranes is a complicated function of the PES concentration in the casting solution, PVP wt-% in the total amount of polymer present in the casting solution, and the molecular weight of PVP. The experimental observations also suggest the nonuniform distribution of PVP polymer in the membrane cross-section. Some relationships were also found between the PVP content in the membrane after gelation and the ultrafiltration performance of the membrane.

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