

# Preparation, Structure, and Transport Properties of Ultrafiltration Membranes of Poly(vinyl chloride) and Poly(vinyl pyrrolidone) Blends

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**ABSTRACT:** Ultrafiltration (UF) membranes based on poly(vinyl chloride) and poly(vinyl pyrrolidone) blends were prepared by the phase inversion method, and the factors governing membrane properties were investigated. The membranes were characterized by scanning electron microscopy and atomic force microscopy. The fouling characteristics of the membranes were determined by UF of aqueous solutions of bovine serum albumin (BSA) over a pH range of 2–9 and varying salt concentrations. The maximum adsorption of the protein on the membrane surface occurred near the isoelectric point (pI 4.8) of BSA, and the presence of the salts increased the fouling of the membrane. The results can be explained in terms of the nature of the membrane polymer and the effect of different ionic environments on the permeability of the deposited protein layer. The net charge on the BSA molecules appears to be a dominant factor in determining the flux of water through the blend membranes. The UF flux is correlated by a model based on the membrane resistance, adsorbed protein resistance, and time dependent resistance of the concentration polarization layer near the membrane surface. The  $\zeta$  potentials of the membranes were also determined before and after UF to characterize the surface potential of the membrane. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2606–2620, 2000

**Key words:** ultrafiltration; membranes; poly(vinyl chloride) and poly(vinyl pyrrolidone) blend; scanning electron microscopy analysis; atomic force microscopy analysis; bovine serum albumin; fouling studies; concentration polarization;  $\zeta$  potential

## INTRODUCTION

Despite the technological relevance of ultrafiltration (UF) in a wide range of applications, its main limitation is flux decline due to fouling.<sup>1,2</sup> Fouling is an irreversible process caused by solute adsorption and pore blocking, which can be minimized by using more hydrophilic membranes. Many of the thermostable and chemical resistant poly-

mers used for UF membranes, such as polysulfone (PS), polyether imide, poly(vinylidene fluoride), and cellulose triacetate, are quite hydrophobic and it is not always possible to prepare a new polymer with requisite properties for a specific application. The performance of the polymeric membranes can be improved by blending the original polymer with other polymers having more suitable properties.<sup>3</sup> Blending of polymers is a very interesting way of producing materials with improved bulk properties. However, the main problem in blending is that most polymer pairs are rather immiscible.<sup>4,5</sup> The miscibility of polymers occurs in three situations: polymers of low molecular weights that no longer have negligible

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entropy of mixing; polymers that are chemically very similar and have a very small unfavorable heat of mixing; and polymers that show specific interactions between the molecules, resulting in a favorable heat of mixing.

However, it is not easy to predict the miscibility of polymers. Immiscible blends are known for their poor mechanical properties that are due to bad adhesion between their polymer domains. The early work of Cabasso<sup>6</sup> on blend membranes is by far the most informative. Using PS and poly(vinyl pyrrolidone) (PVP) blends in the casting solution of dimethyl acetamide (DMA) or dimethyl formamide (DMF), it was shown that the blend membranes show better performance than membranes prepared from polysulfone alone. Sourirajan and Matsuura<sup>7</sup> similarly studied the spinning of a solution of poly(ether sulfone) (PES) and PVP in DMA with water as an external coagulant for preparation of hollow fiber membranes.

Apart from the coagulant solvent, which is water in most cases, several additives can affect properties of the membrane when present in the casting solution or coagulant bath. Liu et al.<sup>8</sup> investigated the effect of several additives such as *n*-propionic acid, *n*-butyric acid, sulfuric acid, and formamide in the coagulant bath for blend membranes. Their results showed that the pure water permeation rate and pore size vary depending upon the composition of the coagulant bath. Asymmetric hollow fibers with a skin layer on the outside of the fiber were made by Espenan et al.<sup>9</sup> from a solution of PS in DMF in the presence of a nonionic surfactant (Triton X-100) as an additive (pore-forming agent). The membrane permeability could be increased by decreasing the polymer concentration and/or by adding additives to the solution.<sup>10</sup>

Myong et al.<sup>11</sup> demonstrated that a coating of PVP on a hydrophobic membrane surface decreases the rate of fouling, because PVP forms hydrophilic spikes on the membrane surface. However, PVP has an amphiphilic character, which contains highly hydrophilic amide groups, and a loose random coil conformation in solution. During the UF process the hydrophilic matrix on the membrane surface acts as a water reservoir and reduces fouling.<sup>11</sup>

Recently, we investigated blends of poly(vinyl chloride) (PVC) with carboxylated PVC (CPVC) for preparation of UF membranes.<sup>12</sup> The blends show better performance because of the hydrophilic CPVC present in the blend membrane. In comparison with CPVC, PVP is more hydrophilic. PVP contains highly hydrophilic amide groups

regularly arranged in every segment throughout the polymer matrix whereas in CPVC the carboxylic content is small (2 g/kg of polymer), which is randomly placed in the polymer matrix. Hence, we expected that the membranes obtained with a PVC/PVP blend may show still better performance than the PVC/CPVC blend membranes. It was expected that the presence of PVP would make the blend membrane more hydrophilic and less susceptible to fouling by adsorption of proteins. The preparation, structure, and transport properties of UF membranes made of PVC/PVP blends are discussed in the following report.

## EXPERIMENTAL

The PVC resin was obtained from Reliance Industries Ltd. (India) with a *K* value of 57.01; PVP (MW 36,000) and bovine serum albumin (BSA, MW 68,000, V fraction >97% pure) were obtained from Loba Chemie (Mumbai). Sodium dodecyl sulfate (SDS) and Triton X-100 (TX-100) were obtained from S. D. Fine Chemicals (Mumbai), and cetyl pyridinium bromide (CPB) was obtained from Aldrich Chemicals.

The thermal behavior of the polymer blends was determined using a differential scanning calorimeter (Perkin–Elmer, DSC 7) to verify the miscibility of the polymers. The sample (~5 mg) encapsulated in a platinum pan was heated from 20 to 350°C at a rate of 10°C/min under a nitrogen atmosphere to measure the glass-transition temperature ( $T_g$ ).

The membranes were prepared by the phase inversion method as described earlier.<sup>12</sup> The casting solution was prepared at 60–65°C for dissolution of the polymers in DMF with the concentration of the polymer at 10–12% (w/v). A film was cast on a glass plate and, after a predetermined evaporation time ranging from 5 to 240 s, the film was immersed in a coagulation bath maintained at 10–15°C. The membranes were removed from the glass plate and leached overnight in running water to remove any traces of the solvent.

By changing the concentration of the polymer in the casting solution, membranes with various properties and structures were obtained. The blend membranes were cast from 11% PVC + 0.5% PVP, 11% PVC + 1.0% PVP, 11% PVC + 2% PVP, 10% PVC + 1.0% PVP, and 9% PVC + 2% PVP (w/v) in DMF solutions.

The physical structure of the membranes was determined by analyzing the photographs made by

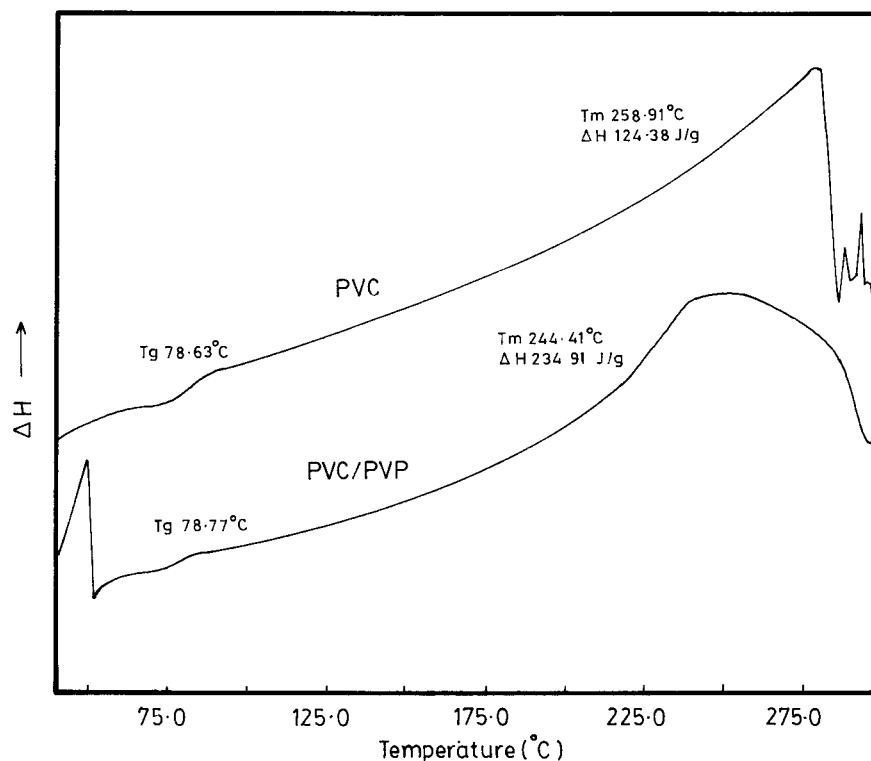


Figure 1 DSC analysis of PVC and PVC/PVP blend membranes.

means of a JSM-35 scanning electron microscope (Jeol, Japan) and an atomic force microscope (Digital Inc.) at Tata Institute for Fundamental Research (TIFR, Mumbai). For the scanning electron microscopy (SEM) the membranes were carefully dehydrated by inserting them successively in a water-ethanol mixture, pure ethanol, an ethanol-hexane mixture, and then in pure hexane. After careful dehydration of the membranes, they were fractured in liquid nitrogen and then covered with metallic gold to obtain an adequate contrast of the membrane fracture. For the atomic-force microscopy (AFM) analysis the membranes were cast on a nonwoven polyester fabric and subsequently coagu-

lated. From this membrane a small section ( $1 \times 1 \text{ cm}^2$ ) was cut from the center of the membrane sheet for the analysis. This small section was placed in pure ethanol for 10 s and then exposed to air for 10 min to allow the excess ethanol on its surface to evaporate. The membrane was placed in ethanol before examination because this approach improved the resolution of the AFM image.<sup>13</sup>

The performance of the membranes was tested by UF experiments in a flat sheet module with an effective membrane area of  $112 \text{ cm}^2$  and a 0.4-cm channel height. The transport properties of the membrane with reference to water and the BSA solution ( $0.75 \text{ g/dm}^3$ ) were tested at a constant

Table I Effect of PVC Concentration on Membrane Characteristics

PVC/PVP Content (%)	Flux with Water ( $\text{dm}^3/\text{m}^2/\text{h}$ )	Flux with BSA ( $\text{dm}^3/\text{m}^2/\text{h}$ )	Rejection (%)
11 + 0	174.1	56.2	96.5
11 + 0.5	211.4	58.3	96.7
11 + 1.0	592.4	76.5	96.6
11 + 2.0	645.5	78.9	95.9
10 + 1.0	2336.6	116.5	81.0
9 + 2	2996.5	108.9	80.3

**Table II Effect of Various Additives on Performance of 11% PVC + 1% PVP Membrane**

Additive	Flux with Water (dm <sup>3</sup> /m <sup>2</sup> /h)	Flux with BSA (dm <sup>3</sup> /m <sup>2</sup> /h)	Rejection (%)
0.5% TX-100	832.5	119.6	89.4
1.0% TX-100	1022.5	108.9	83.0
2.0% TX-100	2303.6	112.6	80.3
0.5% SDS	404.6	67.8	94.8
1.0% SDS	512.5	86.5	97.8
2.0% SDS	717.5	74.3	98.2
0.5% CPB	598.3	95.7	90.5
1.0% CPB	910.7	93.7	94.1
2.0% CPB	1928.5	78.6	95.5

temperature (303 K), pressure (98 kPa), and flow rate ( $14 \frac{\text{dm}^3}{\text{h}}$ ) unless otherwise stated. All the membranes were pressurized at 48 kPa for 30 min prior to the UF experiment. The water flux was obtained using distilled water.

The  $\zeta$  potential of the membrane was measured by the Dip cell method.<sup>14</sup> The membrane was placed in a cell dipped in an electrolyte medium with the active layer facing the bottom platinum electrode. The medium was 0.01 mol/dm<sup>3</sup> KCl with a conductivity of  $1.71 \times 10^{-3}$  S/cm. The

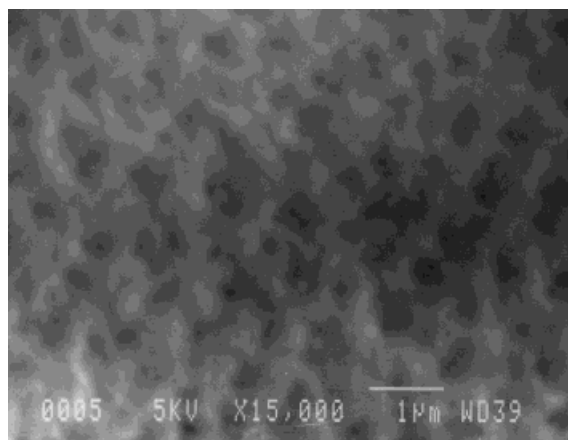
electroosmotic flux was measured by the weight gain on an electronic balance. Measurements were made over only the initial 10 min to avoid heating the solution. A fresh solution was used for each measurement. All measurements were carried out in duplicate and averaged.

## RESULTS AND DISCUSSION

The  $T_g$  characterizes the segmental motion of the polymers. For an immiscible multiphase system,

**Table III Effect of Gelating Media on Membrane Performance**

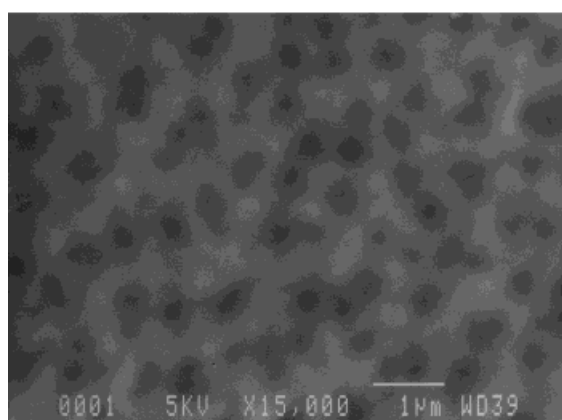
Membrane	Gelating Medium	Flux with BSA (dm <sup>3</sup> /m <sup>2</sup> /h)	Rejection (%)
11% PVC + 1% PVP	Water	66.2	96.0
	10% Acetic acid	75.0	95.0
	10% NaOH	83.6	94.2
	10% Methanol	71.4	95.0
	10% NaCl	70.0	93.1
	10% DMF	96.4	93.2
11% PVC + 1% PVP with 1% SDS	Water	68.1	94.8
	10% Acetic acid	82.8	93.3
	10% NaOH	76.8	91.0
	10% Methanol	89.3	96.6
	10% NaCl	78.2	94.4
	10% DMF	90.3	94.6
11% PVC + 1% PVP with 1% CPB	Water	95.7	93.5
	10% Acetic acid	92.4	94.1
	10% NaOH	90.2	96.5
	10% Methanol	101.5	93.1
	10% NaCl	84.1	92.2
	10% DMF	106.5	94.0



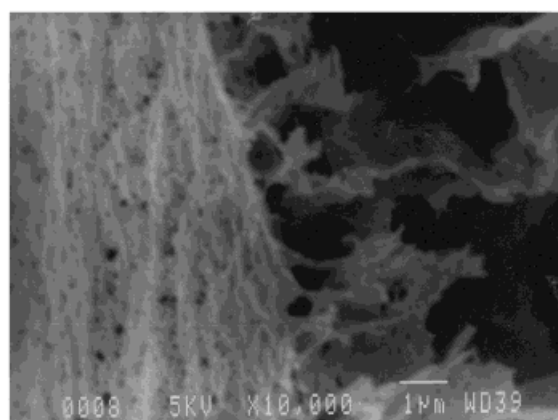
(a) PVC/PVP



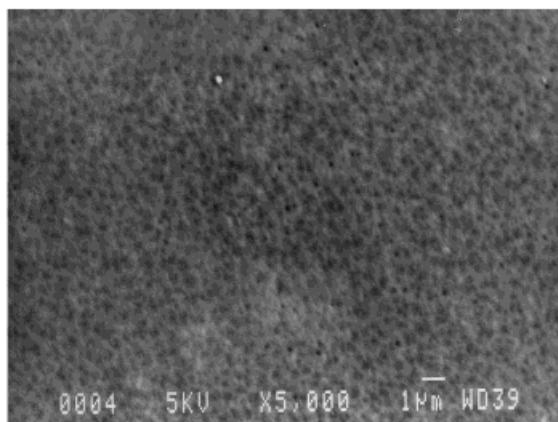
(b) PVC/PVP CROSS SECTION



(c) PVC/PVP WITH SDS



(d) PVC/PVP WITH SDS CROSS SECTION

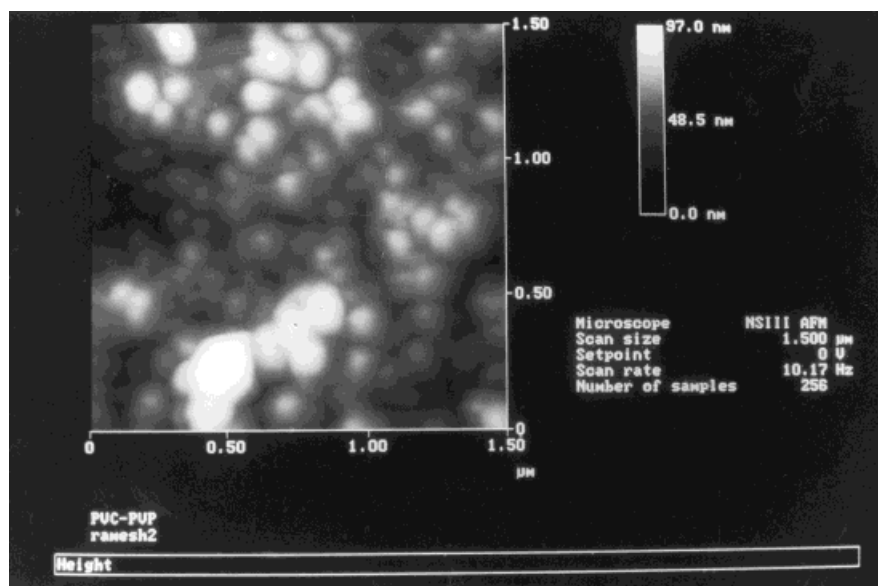


(e) PVC/PVP USED

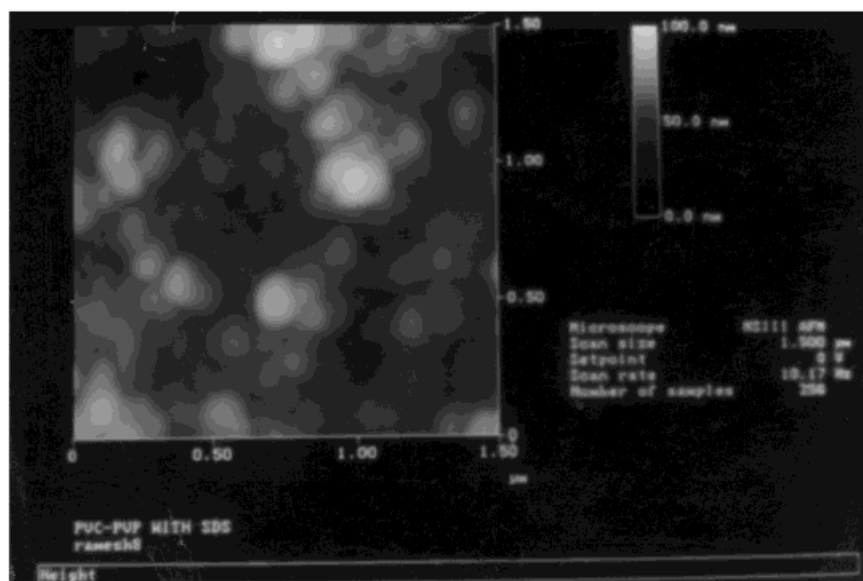
**Figure 2** The surface characteristics of PVC/PVP blend UF membranes obtained by SEM before and after UF experiments.

every phase should possess its own  $T_g$ . The observation of a single  $T_g$  in blend polymers is usually taken as proof for of the miscibility of the

polymer mixtures.<sup>15</sup> From the heat-flow versus temperature plots (Fig. 1) we found that PVC and a PVC/PVP blend show single  $T_g$  values. Both of



(a) PVC/PVP



(b) PVC/PVP WITH SDS

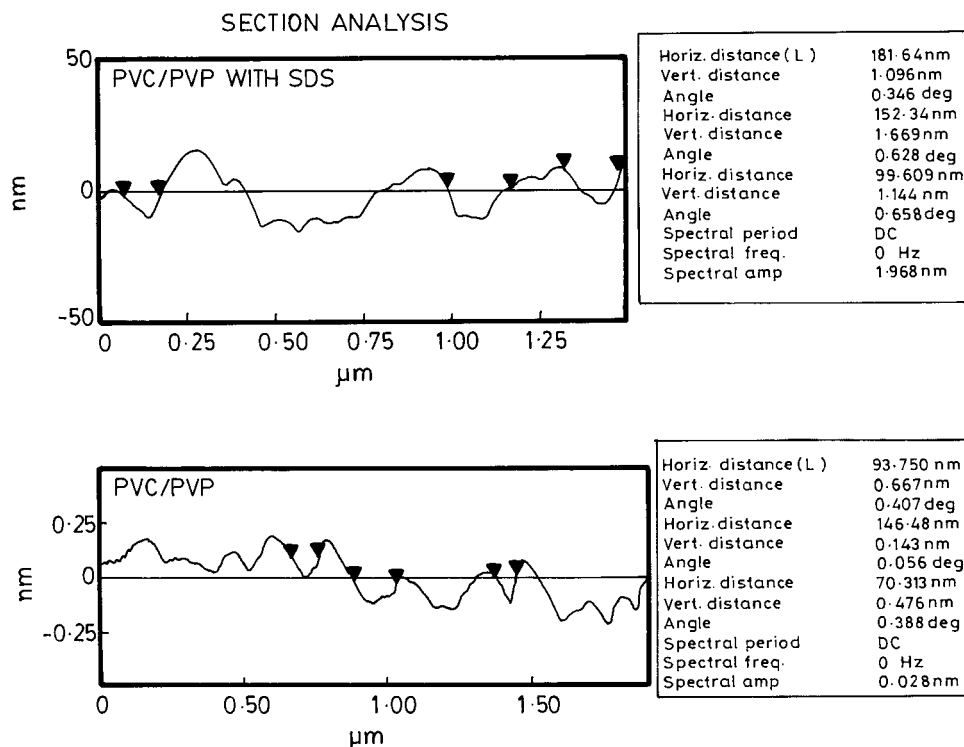
**Figure 3** A top view image of PVC/PVP blend and PVC/PVP with SDS additive UF membrane surfaces taken with AFM. The bar at the right side of the image denotes the vertical deviation in the samples, the white regions indicate the highest points, and the dark regions indicate the depressions.

the polymers show almost similar  $T_g$  values. However, there is a considerable difference in their melting temperatures and heats of fusion ( $\Delta H$ ). The PVC/PVP blend showed a higher  $\Delta H$  value (234.91 J/g) as compared to PVC ( $\Delta H = 124.4$  J/g), suggesting that the addition of PVP

to PVC increases the crystallinity in the polymer blend.

The effect of the PVC/PVP ratio on the membrane performance is shown in Table I. We observed that as the PVP content increased, the flux through the membrane increased but the rejec-





**Figure 4** A vertical displacement profile of PVC/PVP blend and PVC/PVP with SDS additive membrane surfaces from the diagonal line across the insert image by AFM with cursor pairs more readily identified.

tion of the protein decreased. It was also observed that as the PVC/PVP content varied, the rejection efficiency varied between 80 and 97% for the BSA solution. With 1 and 2% PVP content (with 11% PVC) the flux and rejection were maximum for BSA (with 1% PVP the flux =  $76.5 \text{ dm}^3/\text{m}^2/\text{h}$  and rejection = 96.6%; with 2% PVP the flux =  $79.0 \text{ dm}^3/\text{m}^2/\text{h}$  and rejection = 95.8%). The decrease in the PVC content of the blend increases the flux but decreases the rejection efficiency of the membrane. To obtain a compromise between the rejection and flux for the protein (BSA), the PVP content in the casting solution was selected at 1% for all further studies.

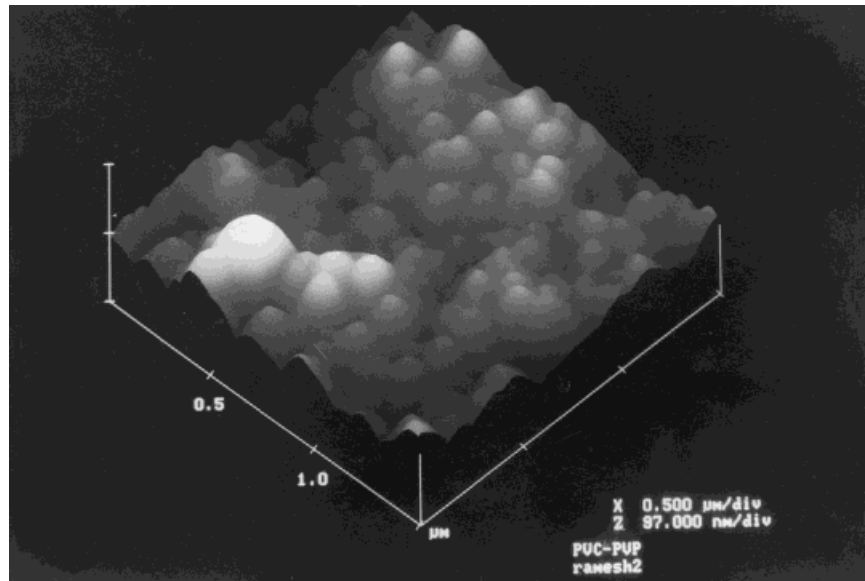
The additives in the casting solution were different types of surfactants that are hydrophilic in nature. The amount of the surfactant was varied from 0.5 to 2.0% (w/v). They migrate to the surface of the polymer and provide a charged layer on the membrane surface. This layer is more effective if the surfactant is ionic in nature.<sup>15</sup> These additives also reduce the solvency of the solvents and give membranes with different pore structures.<sup>16</sup> The effect of the type and amount of the additive is thus an important factor in preparing

the membranes. The membrane performance with different additives is given in Table II.

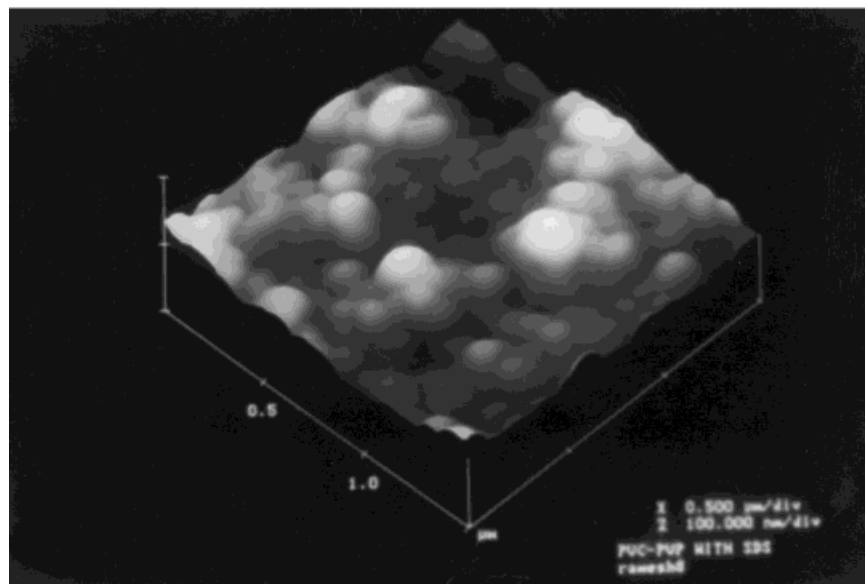
The best compromise between the flux and rejection was when 1% (w/v) SDS and 1% (w/v) CPB were used as additives. On the other hand, membranes obtained with TX-100 as the additive had higher flux but a poorer rejection efficiency. Hence, the membranes prepared with TX-100 were not considered for further studies.

The membranes were prepared at different evaporation times with the optimum polymer compositions and additives. The membranes obtained with shorter evaporation times exhibit a more asymmetric structure<sup>17</sup> whereas the structure of membranes with longer evaporation times is compact and homogeneous. This leads to a compromise situation between the active layer thickness and the width of the pore, which controls the permeability and rejection efficiency. Evaporation time was optimized at 15–30 s for all the membranes.

Gelating conditions are also important for UF characteristics of the membrane. The relationship between membrane morphology and kinetic effects suggests that mass transfer of the gelation



**(a) PVC/PVP**



**(b) PVC/PVP WITH SDS**

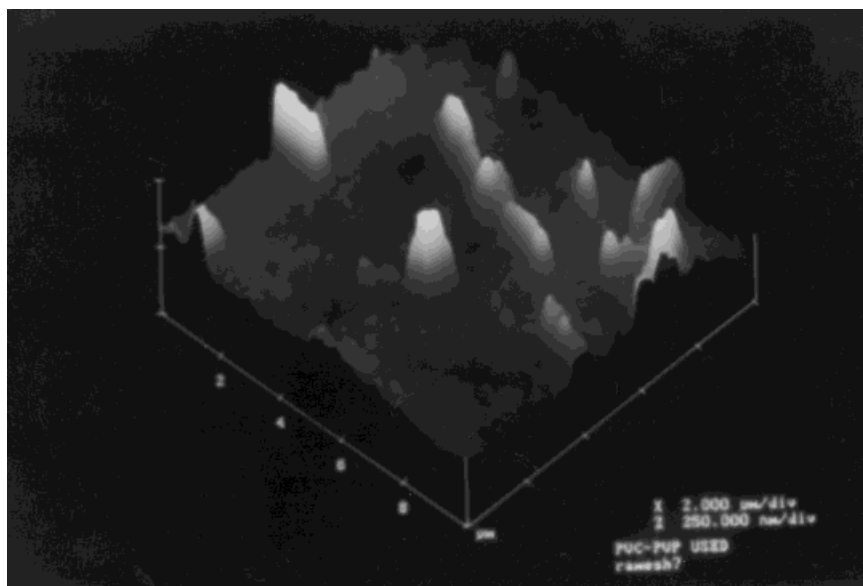
**Figure 5** A 3-dimensional surface image of a PVC/PVP blend, PVC/PVP with SDS additive, and used PVC/PVP UF membranes at  $1.5 \times 1.5 \mu\text{m}^2$ .

medium plays an important role in determining the structure of the membrane. Mass transfer mainly occurs at the interface between the polymer solution and the gelation medium by diffusion processes. Exchange of the solvent and non-solvent across the interface introduces a phase separation, leading to various asymmetric structures.<sup>18</sup> Table III shows the effect of the gelating medium on the membrane performance; 10% DMF in water seems to give comparatively better flux and rejection.

### Physical Structure of Membranes

The surface of the membranes obtained from PVC/PVP, PVC/PVP with SDS as the additive, and PVC/PVP after UF was characterized by SEM. Figure 2(a–d) compares the membranes obtained from PVC/PVP and PVC/PVP with 1% (w/v) SDS as the additive. The morphology of membranes made in the presence of additives is somewhat different than those prepared in the absence of the additive. Membranes prepared





(c) PVC/PVP USED

Figure 5 (Continued from the previous page)

without additives have a fingerlike pore structure whereas membranes obtained with the SDS additive show more open and porous structures in the support. The surface structure of the membrane after UF [Fig. 2(e)] looks more grainy in the scanning electron micrograph but not significantly different from the fresh membrane. The effect of fouling on the membrane surface is more closely examined by AFM.

The structures of the surface of PVC/PVP and PVC/PVP with SDS as revealed by AFM are shown in Figure 3(a,b). These are the top view images of the surface of the membranes, showing an area of  $1.5 \times 1.5 \mu\text{m}^2$ . The surface seems to be a smooth globular structure with depressions indicating possible pores available for the solvent flow during UF.

Table IV  $\zeta$  Potentials of Membranes before and after UF

Membrane	$\zeta$ Potential (mV)	
	Before UF	After UF
PVC/PVP	-34.1	-8.5
PVC/PVP with 1% SDS	-33.1	-10.5
PVC/PVP with 1% CPB	-15.3	-7.1

The AFM permits the measurement of the distance variations in the sample's surfaces, as seen in Figure 4(a,b). These lines yield profiles of surface structures and are shown in the upper portion of each figure. Distance variations along these profiles are determined by the measurement of the horizontal and the vertical distances between the pair of cursors that are also shown in Figure 4(a,b). The cursors can be pointed to locate the valleys in the surface at the horizontal line, most of them indicating the pores in the surface. The distance between the cursor positions can therefore be used as an indication of the pore size.

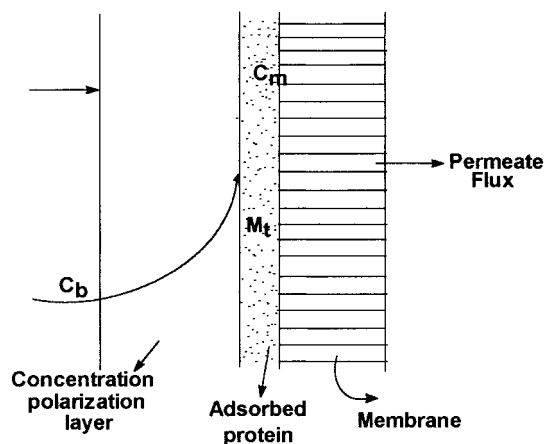


Figure 6 A schematic diagram of the UF process.

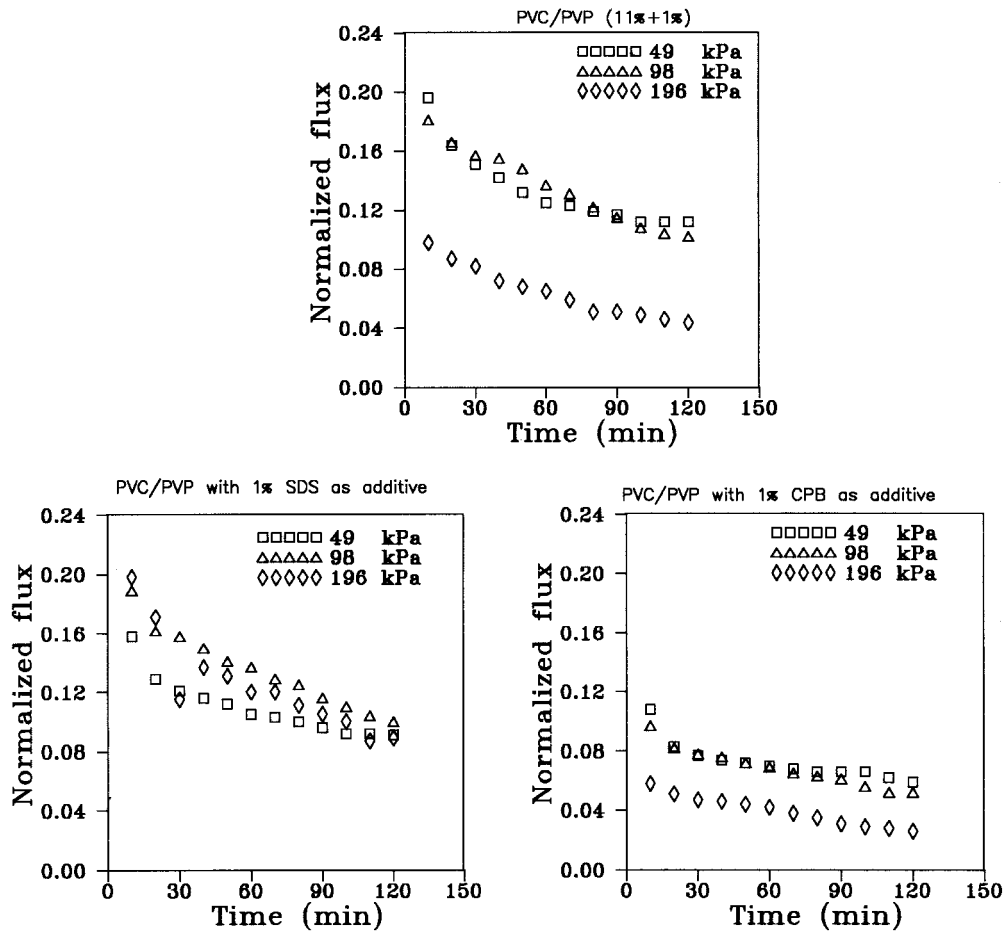
**Table V Membrane Resistance and Fouled Protein Layer Resistance for PVC/PVP Blend Membranes with BSA Solution**

Membrane	Pressure (kPa)	$R_m \times 10^{-15}$ (1/m)	$R_a \times 10^{-15}$ (1/m)
PVC	49	1.08	0.21
	98	1.12	1.23
	196	1.09	2.26
PVC/PVP	49	0.67	0.21
	98	0.69	0.56
	196	0.67	0.69
PVC/PVP with SDS	49	0.79	0.21
	98	0.78	0.50
	196	0.81	0.91
PVC/PVP with CPB	49	0.42	0.18
	98	0.44	0.39
	196	0.42	1.09

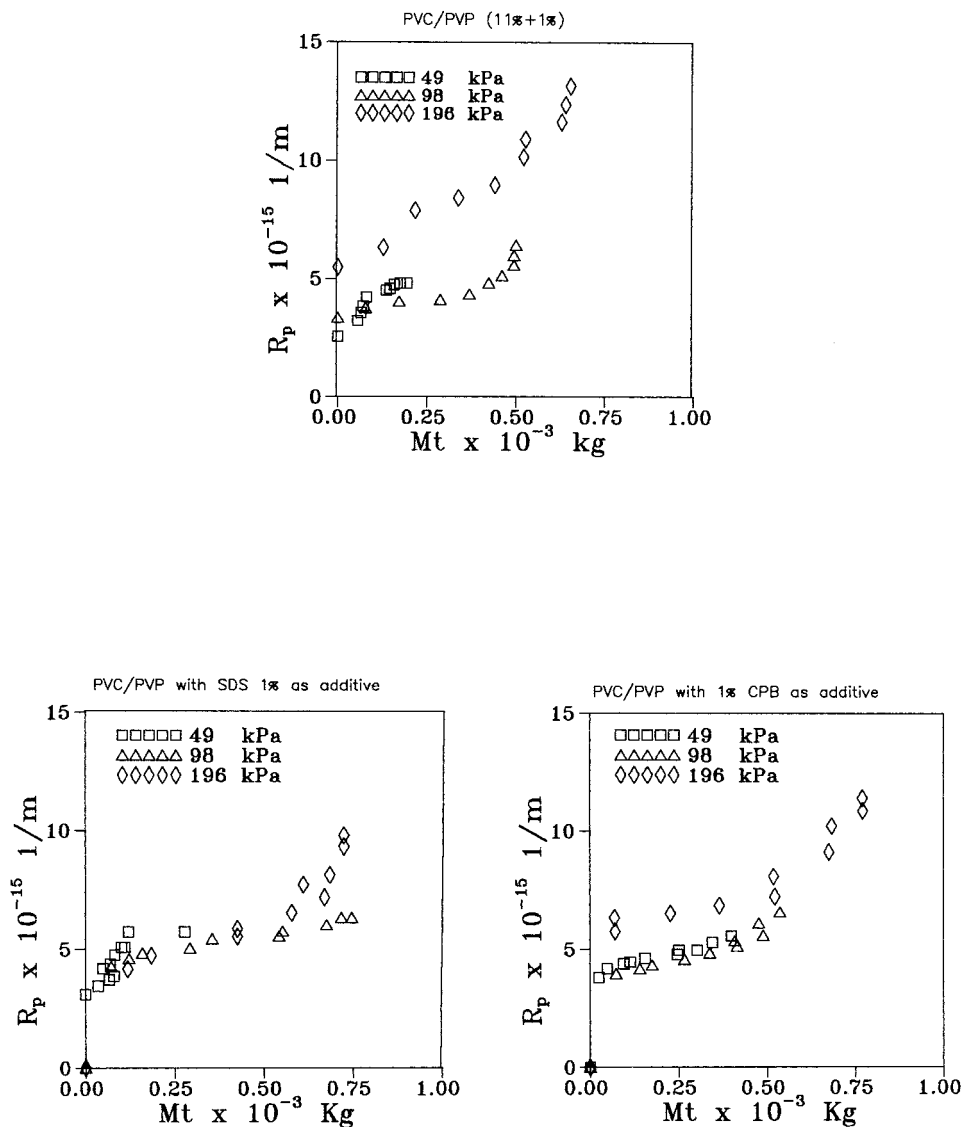
$C_b = 0.75 \text{ g/dm}^3$ , flow rate =  $14 \text{ dm}^3/\text{h}$ , pH 6.5.

These measurements indicate that the pore diameters are in the range of 7–14 Å for PVC/PVP and somewhat wider at 9.9–18.1 Å for PVC/PVP with SDS membranes.

The samples can also be viewed at a plane perpendicular to the horizontal as shown in Figure 5(a–c). These structures result from portions of impinging assemblies of nodule aggregates that constitute the surface of UF membranes. The membranes obtained with surfactants as additives are more uniform with a porous structure with a smoother surface. However, the used membranes show remarkably different surface characteristics. The AFM shows complete loss of the smooth structure of the virgin membrane after UF because of fouling. The surface is characterized by sharp spikes all over the surface, some of them projecting into the solution. These spikes introduce irregular structures on the membrane



**Figure 7** The normalized permeate fluxes at different pressures with PVC/PVP and PVC/PVP with SDS and CPB additives membranes at a flow rate of  $14 \text{ dm}^3/\text{m}^2/\text{h}$  and a pH of 6.5.



**Figure 8** The variation of  $R_p$  and  $M_t$  with pressure for PVC/PVP and PVC/PVP with SDS and CPB additives membranes.

surface. The fouling layer of the adsorbed protein contributes to this apparently rough surface. This feature is not clear in the SEM and could be distinguished only with AFM.

#### Electrostatic Characteristics of Membranes

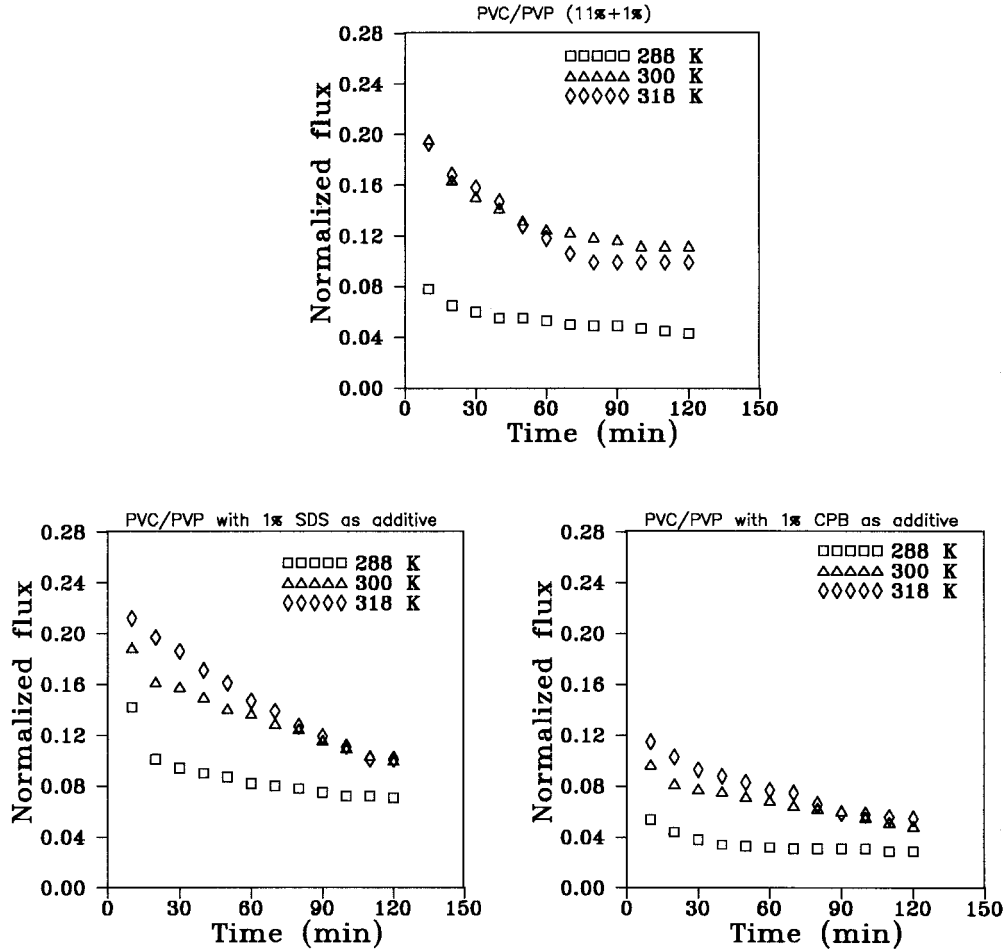
The  $\zeta$  potentials of each membrane were determined before and after UF using the Smoluchowski equation<sup>14</sup> (Table IV). The fouled membranes show reduced negative  $\zeta$  potentials compared to fresh membranes. Because the fouling layer of protein decides the  $\zeta$  potential of the fouled surface, the measured value essentially indicates the  $\zeta$  potential of the fouling layer.

These  $\zeta$  potential values obtained for the fouled membranes may correspond to the surface potential of the BSA molecule.<sup>19</sup>

#### Transport Properties

Transmembrane pressure plays an important role in UF because it decides the flux. Three different pressures (49, 98, and 196 kPa) were studied with PVC/PVP, PVC/PVP with SDS as the additive, and PVC/PVP with CPB as the additive.

The permeation rate ( $J$ ) in UF is limited by the formation of an adsorbed protein layer, as well as the concentration polarization layer near the



**Figure 9** The effect of temperature on flux decline for PVC/PVP and PVC/PVP with SDS and CPB additives membranes at a pressure of 98 kPa, a flow rate of 14 dm<sup>3</sup>/m<sup>2</sup>/h, and a pH of 6.5.

membrane surface as shown in Figure 6; it can be expressed as follows

$$J(t) = \frac{P - \sigma\Delta\Pi}{\mu(R_m + R_a + R_p)} \quad (1)$$

where  $R_m$  is the membrane resistance,  $R_a$  is the resistance offered by the adsorbed protein layer,  $R_p$  is the resistance of the accumulated protein in the concentration polarization layer, and  $\sigma$  is the rejection coefficient. The adsorbed protein resistance ( $R_a$ ) can be obtained from the water flux through the fouled membrane. The estimated values of  $R_m$  and  $R_a$  are given in Table V. The total amount of protein accumulated near the membrane surface ( $M_t$ ) can be obtained by the mass balance on the feed and retentate streams for the protein.

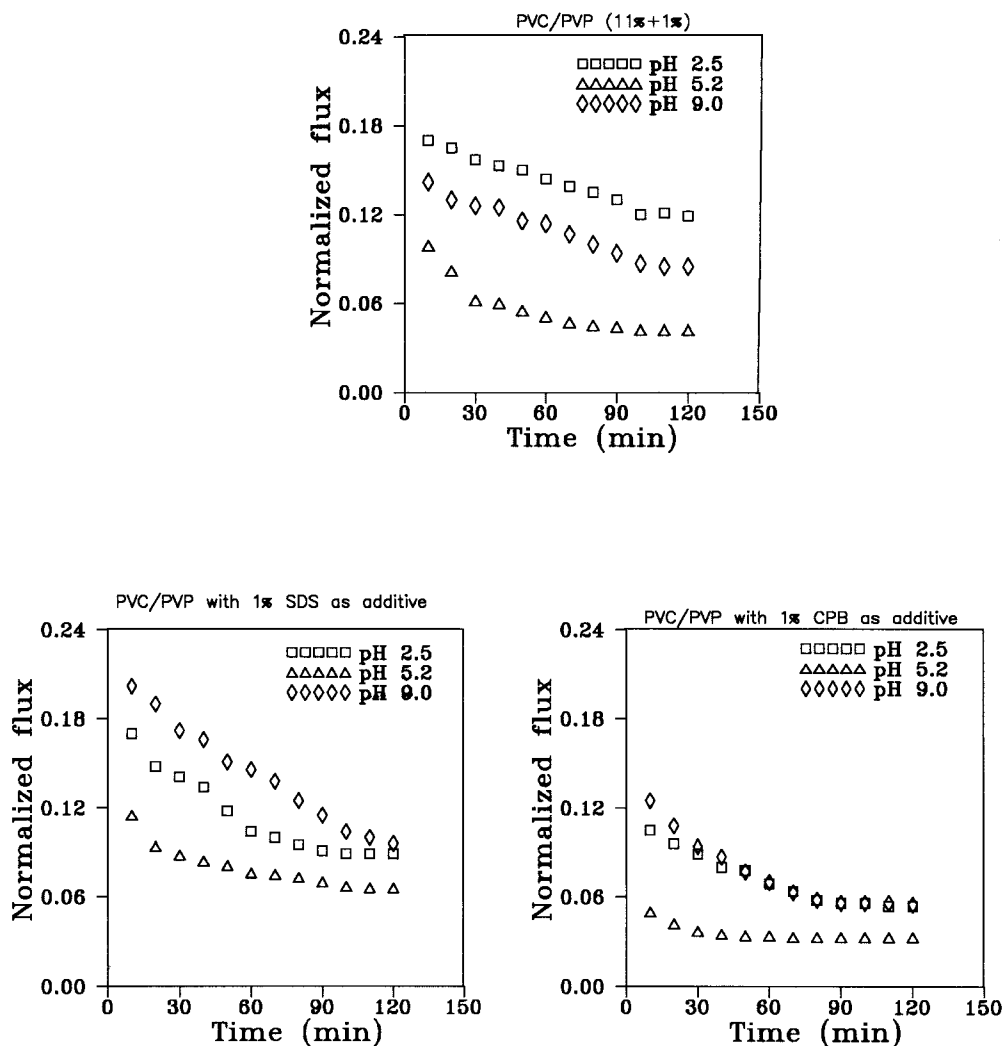
$$M_t = \int_0^t \{(V_0 C_b) - C_r(V_0 - JA_m) - C_p JA_m\} dt \quad (2)$$

where  $C_b$  is the feed concentration,  $C_r$  is the retentate concentration,  $C_p$  is the permeate concentration,  $A_m$  is the active membrane area of the membrane, and  $V_0$  is the volumetric flow rate through the unit. Because the concentration of BSA in the solution is very low, the osmotic pressure difference ( $\Delta\pi$ ) in eq. (1) can be neglected.

The normalized flux is defined as

$$\text{normalized flux} = \frac{\text{flux of solute}}{\text{flux of pure water}} \quad (3)$$

The comparison among different membranes becomes easier on the basis of normalized fluxes.

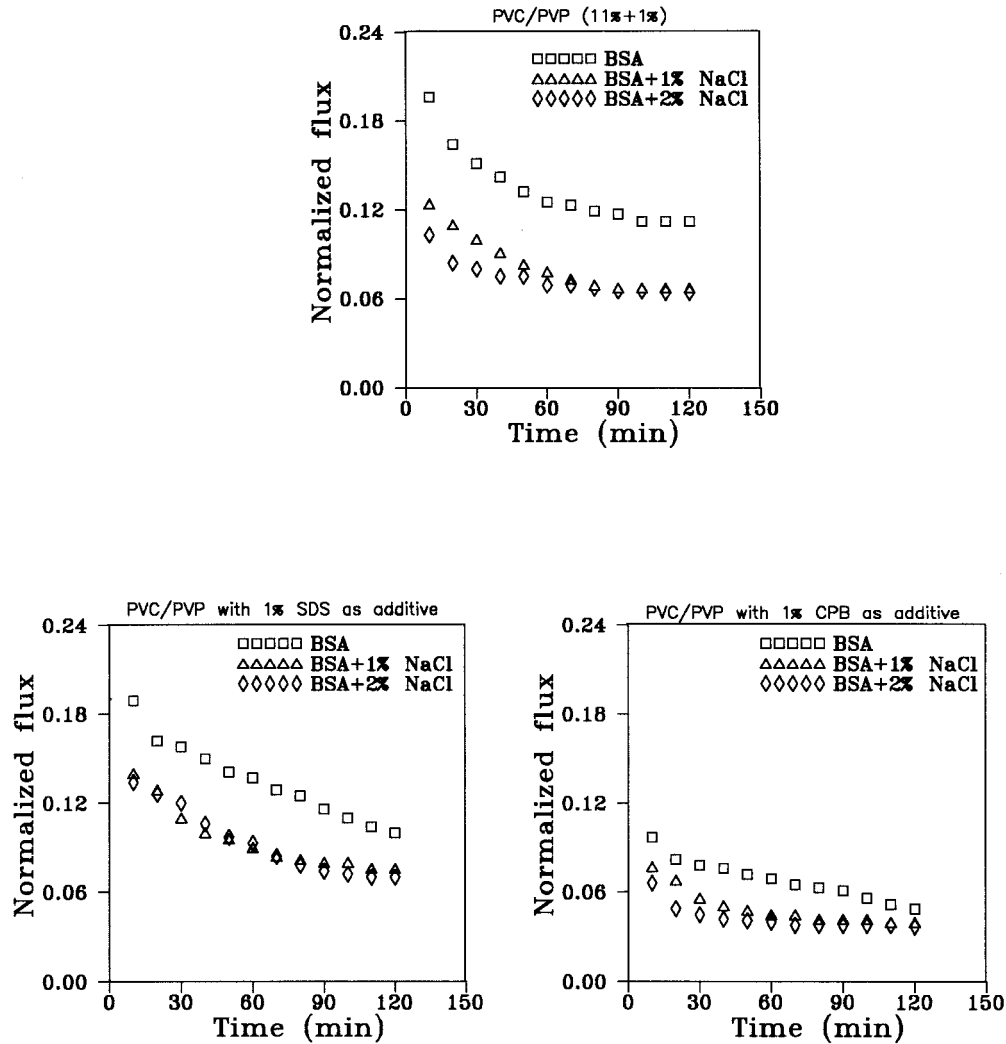


**Figure 10** The effect of pH on flux decline for PVC/PVP and PVC/PVP with SDS and CPB additives membranes at a pressure of 98 kPa and a flow rate of  $14 \text{ dm}^3/\text{m}^2/\text{h}$ .

Figure 7 shows the normalized flux at different pressures on the three membranes. The normalized flux at a constant pressure reduces to as low as 8–10% of the initial value. The fouling resistance ( $R_a$ ), which characterizes the resistance offered by the adsorbed protein layer, increases with the increase in the operating pressure. The pressure probably has a compacting effect on the adsorbed protein layer as shown by the higher values of  $R_a$  at higher pressure (Table V). The PVC/PVP membranes prepared with surfactants as additives show less of a fouling tendency than PVC/PVP alone at lower pressure. At higher pressures membranes prepared with surfactants as additives show more of a fouling tendency than the PVC/PVP membrane. Figure 8 shows the effect of pressure on the adsorbed protein layer

resistance ( $R_p$ ), which increases with the accumulated protein layer ( $M_t$ ) and reaches a constant value after some time. If the concentration polarization layer were to remain unchanged with time, one would expect a linear relation between these two quantities. But the highly nonlinear variation that is also dependent on the operating pressure indicates probable changes in the polarization layer with time.

Figure 9 shows the effect of temperature on UF performance of PVC/PVP, PVC/PVP with SDS as the additive, and PVC/PVP with CPB as the additive membranes. The viscosity of the BSA solution decreases from 0.041 P at 288 K to 0.0065 P at 318 K. The dispersion of protein molecules from the polarization layer on the membrane surface is assisted by this decrease in viscosity at higher tem-



**Figure 11** The effect of salt concentration on flux decline for PVC/PVP and PVC/PVP with SDS and CPB additives membranes at a pressure of 98 kPa, a flow rate of 14 dm<sup>3</sup>/m<sup>2</sup>/h, and a pH of 6.5).

peratures. With the increase in the temperature the normalized flux increases and the fouling resistance decreases for all three membranes. At a lower temperature (288 K) the membranes prepared with PVC/PVP with SDS additive and PVC/PVP with CPB additive show less fouling resistance than the PVC/PVP membrane. The  $R_a$  values for PVC/PVP, PVC/PVP with SDS additive and PVC/PVP with CPB additive are  $0.71 \times 10^{15}$ ,  $0.62 \times 10^{15}$ , and  $0.52 \times 10^{15}$  1/m, respectively. However, the membranes obtained from PVC/PVP with SDS additive show marginally higher fouling resistance than the PVC/PVP membrane with CPB additive. The same trend was observed at a higher temperature (318 K).

Figure 10 shows the flux at different pH values in the absence of an electrolyte. It was observed

that at pH 2.5 and 9.0, membranes show higher permeation flux. At these pH values away from the isoelectric point of the protein (pI 4.8) the BSA molecules acquire significant net charge and thus enlarge because of electrostatic repulsion. These effects would yield a more permeable deposited layer, resulting in a higher permeation flux of water through the UF membranes.

The effect of ionic strength was studied with all three membranes at 98 kPa. Electrolytes are expected to have a buffering effect on the structure of the proteins. A higher concentration of the salt can either lead to the formation of a compact structure of the protein molecules in the adsorbed layer or enhance the hydrophobic interactions among the protein molecules. Sodium chloride (NaCl) was used



as a representative electrolyte and the salt concentration was kept as 1 and 2% (w/v). Figure 11 shows the effect of the NaCl addition to the BSA solution on the UF characteristics of all three membranes. The normalized fluxes further decrease on the addition of the salt. The fouling resistance ( $R_f$ ) increases with an increase in the salt concentration and is minimum with PVC/PVP with CPB membrane. With an increase in the salt concentration (from 1 to 2%), there is not much of an increase in the fouling resistance with all three membranes. However, PVC/PVP and PVC/PVP with SDS membranes show fouling resistances that are more than twice that of the PVC/PVP with CPB membrane. The  $R_f$  values are  $0.99 \times 10^{15}$ ,  $0.96 \times 10^{15}$ , and  $0.49 \times 10^{15}$  1/m for PVC/PVP, PVC/PVP with SDS, and PVC/PVP with CPB, respectively, in the presence of 2% NaCl under identical conditions. The increase in the ionic strength leads to more counterion binding on the protein molecule, which may enhance the hydrophobic interactions between the protein molecules. This leads to the formation of compact layering on the membrane surface and thereby a decrease in the flux through the membrane.

As compared to PVC/PVP with SDS additive membranes, PVC/PVP with CPB additive membranes show less of a fouling tendency at all UF parameters. However, the normalized fluxes are less with PVC/PVP with CPB membranes. The membranes obtained with PVC/PVP with CPB additive are probably more porous because of the bulky head group of CPB.

## CONCLUSIONS

The membrane performances using PVC/PVP blends as a membrane material for UF membranes were verified under various conditions. The concentration of PVC in the casting solution was optimized at 11% while the PVP content was optimized at 1%. The addition of 1% SDS and CPB to the casting solution gives membranes with better performance. The evaporation time was optimized at 15–30 s for all three membranes. The PVC/PVP with CPB additive membrane gave higher fluxes ( $84\text{--}106 \text{ dm}^3/\text{m}^2/\text{h}$ ) and comparable rejection efficiency (97%) as compared to the other two membranes. The pore sizes of the membranes in the range of 7–18 Å were found to be suitable for UF.

The fouling resistance increases with an increase in the pressure and decreases with an increase in the temperature and is also decided by the pH of the

solution. The pH influences the interaction between the membrane and BSA. The UF flux is at a minimum at pH 5.2, which is close to the isoelectric point of BSA. The variation in flux can be explained on the basis of conformational changes of the BSA molecules at different pH conditions, the nature of the membrane material, and the hydrophobic and electrostatic interactions among BSA molecules and between the membrane and BSA.

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