

Preparation of Polysulphone Ultrafiltration Membranes for Milk Concentration: Effect of Additives on Morphology and Performance

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ABSTRACT

In this study, polysulphone membranes were prepared from quaternary systems containing *N,N*-dimethylacetamide as solvent, polyvinylpyrrolidone as constant additive and acetic acid, acetone and formamide as variable additives. Phase inversion via immersion precipitation was employed for manufacturing of membranes. The prepared films were immersed in the mixture of pure water and 2-propanol (30/70 v%) as non-solvent. The morphology and performance of the prepared membranes were investigated by scanning electron microscopy and separation experiments using milk as the feed. The porosity of the prepared membrane was slightly increased with addition of acetic acid due to faster exchange rate between the solvent and non-solvent, and therefore it has resulted in a minor increase in flux. The presence of acetone and formamide in the casting solution declined the flux due to formation of membranes with denser skin layers. Evaporation and delay demixing are responsible for tighter membrane structures in the case of addition of acetone and formamide, respectively.

Key Words:

membrane;
ultrafiltration;
polysulphone;
phase inversion;
milk.

INTRODUCTION

A common technique for the preparation of polymeric membranes with the asymmetric structure is the phase inversion where a thin layer of the polymer dissolved in an appropriate solvent is cast on a suitable support and phase separation is introduced by

a non-solvent [1,2]. In order to obtain membranes with special properties additional additives can be dissolved in the casting solution.

In the formation process, two types of phase inversion can be distinguished. In dry phase inversion,

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the phase separation is introduced by evaporation of volatile solvent and/ or by absorption of water as non-solvent from the air moisture. The wet phase inversion is carried out by immersing the polymer solution film into a coagulation bath of a non-solvent where an exchange of solvent and non-solvent takes place. A combination of both processes may also be considered.

The membrane formation mechanisms of polysulphone (PS)/*N,N'*-dimethylacetamide (DMAc)/water and PS/*N*-methyl-2-pyrrolidone (NMP)/water ternary systems were studied by Wijmans et al [3]. Similar studies for PS/*N,N'*-dimethylformamide (DMF)/water have been carried out by Brons et al. [4]. These studies indicated that PS membranes are consolidated by nucleation and growth of the polymer lean phase. Some precipitation paths of the PS/DMAc/ propanol ternary system were proposed by Radovanovic et al. [5] using mass transfer model for early stages of phase inversion. The liquid-liquid phase separation in the ternary system of a polymer in the mixture of solvent and non-solvent was studied by Altena et al. [6].

The macrovoids have a great influence on the performance of membranes. Several studies were carried out to understand the phenomena of macrovoid formation [7-12]. The effect of thermodynamic conditions on performance of asymmetric formed polysulphone and polyethersulphone membranes was studied by Barth et al. [13]. They showed that the presence of 3 wt% acetone in 16 wt% polymer solution has no obvious effect on the cross-section structure of the membrane. A comparison between morphology and separation properties of PS and PES membranes indicates that more finger-like pores exist for PES membranes.

The structure and water flux of membrane formation by ternary system of PS/DMAc/water was studied by Kaiser et al. [14]. Ping et al [15] studied the mechanism of addition of organic additives in the polysulphone membrane casting solution. Yamasaki et al. [16] employed phase inversion process for preparation of polysulphone membrane with 2-propanol and water. They obtained lower flux and higher retention after storing the membrane forming film in 2-propanol for prolonged times.

In this study, the effects of acetic acid, acetone and formamide as additive in quaternary casting solution systems (PS/PVP/DMAc/additive) on morphology and performance of polysulphone membranes have been studied.

EXPERIMENTAL

Materials

Polysulphone (Udel-P1700) was provided by Amoco. The molecular weight of PS was 45000 g/mol ($\bar{M}_w = 45000$). Polyvinylpyrrolidone (PVP), acetic acid, acetone, formamide and *N,N'*-dimethylacetamide (DMAc) were obtained from Merck. The molecular weight of PVP was 25000 g/mol ($\bar{M}_w = 25000$). Distilled water was used for all experiments.

Preparation of Membranes

Homogeneous solutions of the polymer dissolved in DMAC were prepared using various additives by stirring for 4 h at room temperature. The stirring was carried out at low speed (50 rpm). The solution was cast on a smooth glass plate by film applicator at room temperature. The membrane thickness was maintained at 100 μm . The film was immediately immersed in the coagulation bath containing a mixture of distilled water and 2-propanol (30/70 v %) at room temperature. In order to guarantee complete phase separation, the membrane was stored in the coagulation bath for 24 h. This allows the water soluble components in the membrane to be leached out. As the final stage, membrane was dried by placing between two sheets of filter paper for 24 h at room temperature. The different compositions of casting solutions are listed in Table 1. It is worth to notify that for 6 wt % of formamide, preparation of a homogeneous polymer solution was not accessible in the experimental conditions.

Scanning Electron Microscopy (SEM)

The cross-sections of the prepared membrane were inspected with a scanning electron microscope (SEM, Philips). The samples of the membranes were frozen in liquid nitrogen and fractured. After sputtering with gold, they were viewed with the microscope at 25 kV.

Flux and Retention

The performances of the prepared membranes were characterized using cross-flow system. All filtration experiments were carried out in a cross flow cell. The retentate was circulated by a centrifugal pump. The detailed of the experimental set up is shown in Figure 1. Milk was used as the feed for all trials. The retention of protein was investigated for prepared membranes by

Table 1. Composition of casting solutions.

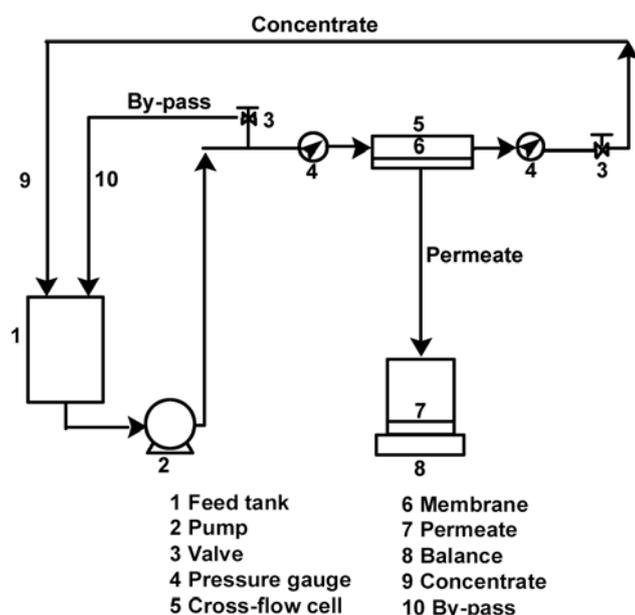
PS (wt%)	Solvent (DMAC) (wt%)	Acetic acid (wt%)	Acetone (wt%)	Formamide (wt%)	PVP (wt%)
16	82	-	-	-	2
16	80	2	-	-	2
16	78	4	-	-	2
16	76	6	-	-	2
16	80	-	2	-	2
16	78	-	4	-	2
16	76	-	6	-	2
16	80	-	-	2	2
16	78	-	-	4	2

measuring the amount of protein in the permeate using the standard Brathford method [17]. The fluxes of each membrane were determined at 15 min with a trans-membrane pressure of 2, 4 and 6 bars. The experiments were carried out at 20°C.

RESULTS AND DISCUSSIONS

Membrane Morphology

The phase inversion process is determined by interac-

**Figure 1.** The cross flow system for milk concentration.

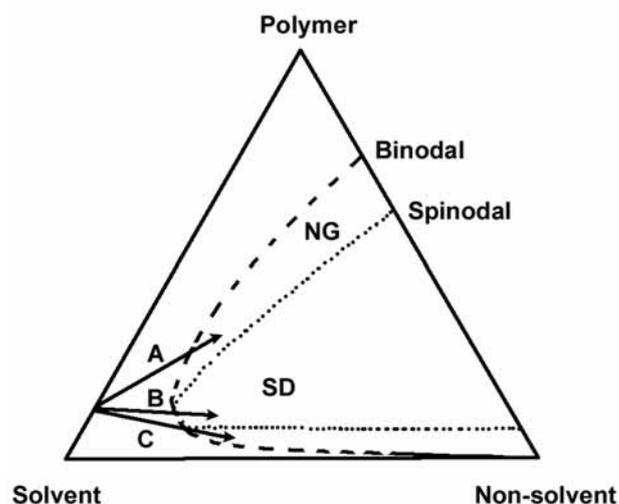
tion between the components and kinetic factors. Figure 2 shows the possible pathways of membrane forming film during the phase inversion in a schematic Gibbs triangle. Pore formation is determined by the movement of mixture into the miscibility gap and within it [13]. The mechanism follows path A or C is called nucleation and growth (NG) and the other following path B is called spinodal decomposition (SD).

If phase separation follows the mechanism of nucleation and growth, discrete polymer-lean nuclei would involve in the bulk polymer rich phase [8]. The polymer-lean nuclei formed in this region are commonly referred to as closed-cell pores. Spinodal decomposition occurs when large temperature gradients induce phase separation [8]. This process is commonly called thermally-induced phase separation.

Effect of Acetic Acid

Figure 3 shows micrographs of cross sections of membranes cast from 16 wt% PS, 2 wt% PVP (Figure 3a) and 2, 4 and 6 wt% acetic acid added (Figures 3b-3d). DMAC was used as solvent and mixture of water and 2-propanol (30/70 vol%) was employed as non-solvent.

The flat membranes obtained from 16 wt% PS exhibit highly heterogeneous structure owing to the presence of large voids and cavities of different sizes and shapes beneath the upper layer. The porosity of the membranes increases with addition of acetic acid in the casting solution. Addition of acetic acid in the casting solution causes a fast exchange rate between solvent

**Figure 2.** Different pathways of a binary casting solution into the miscibility gap of ternary membrane forming system.

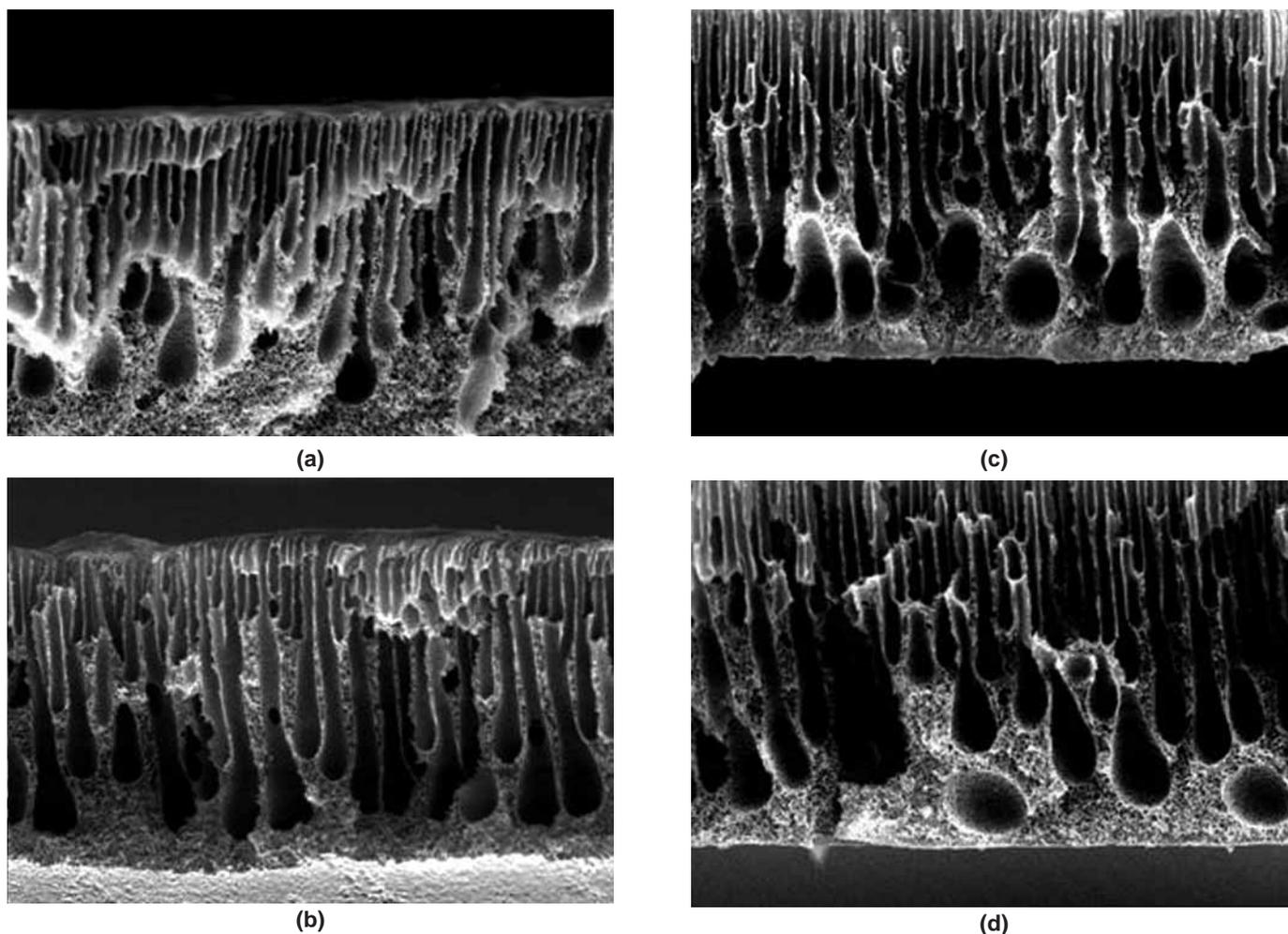


Figure 3. SEM Micrographs (magnification 500) of cross-sections of membranes prepared from PS/PVP/DMAc/acetic acid/water+2-propanol (30/70 v %). The composition of casting solution: (a)16 wt% PS, 2 wt% PVP; (b)16 wt% PS, 2 wt% PVP and 2 wt% acetic acid; (c)16 wt% PS, 2 wt% PVP and 4 wt% acetic acid; (d)16 wt% PS, 2 wt% PVP and 6 wt% acetic acid.

and non-solvent in the coagulation bath. This leads to an increment in the number and size of the cavities in the sub layer.

Effect of Acetone

Figures 4a-4c demonstrates SEM images of cross-sections of membranes cast from 16 wt% PS, 2 wt% PVP and 2, 4 and 6 wt% acetone. DMAc was used as solvent and mixture of water and 2-propanol (30/70 vol%) was employed as non-solvent. These Figures compared to Figure 3a, show that the addition of acetone in the casting solution decreases the size and the number of finger-like pores in the sub layer.

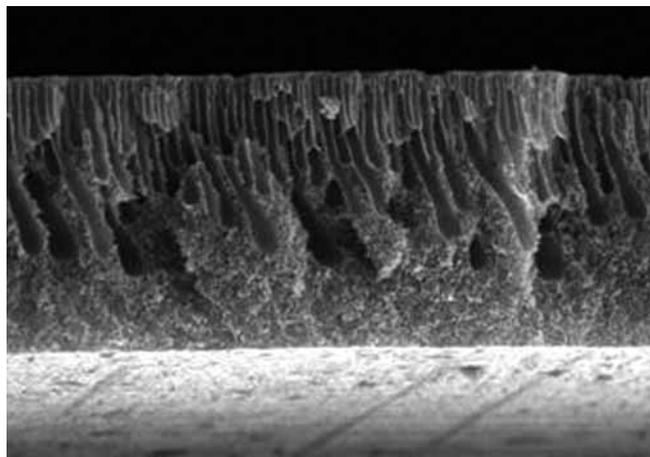
Acetone is lost by evaporation from the film surface before the wet phase separation. This results in higher polymer concentration in the upper layer with

smaller pores in the final membrane [13].

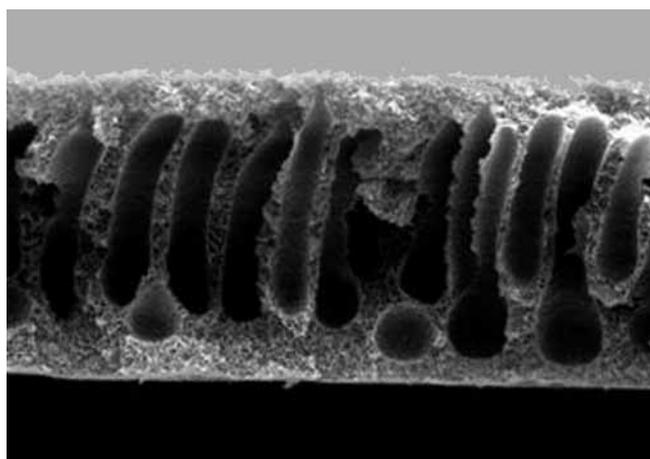
Effect of Formamide

The SEM micrographs of membranes prepared by addition of 2 and 4 wt% formamide in the casting solution (16 wt% PS and 2 wt% PVP as shown in Figure 3a) are represented in Figures 5a and 5b. The solvent used was DMAc and the non-solvent was a mixture of water and 2-propanol (30/70 v%).

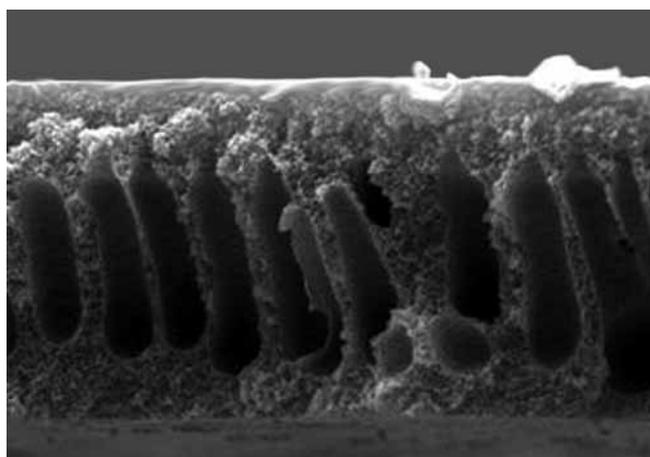
Addition of formamide in a ternary system (PS/PVP/DMAc) causes a delay in demixing for immersed film in the coagulation bath. Two distinct types of membrane preparation processes can be distinguished: instantaneous demixing and delay demixing. Generally instantaneous demixing is accompanied with an asymmetric porous structure and delayed demixing with



(a)

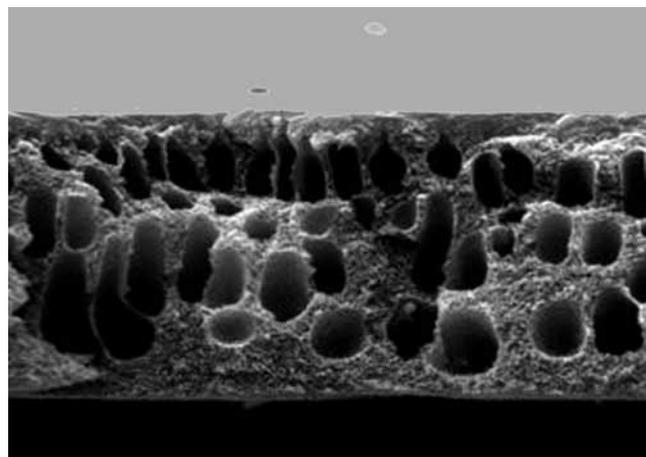


(b)

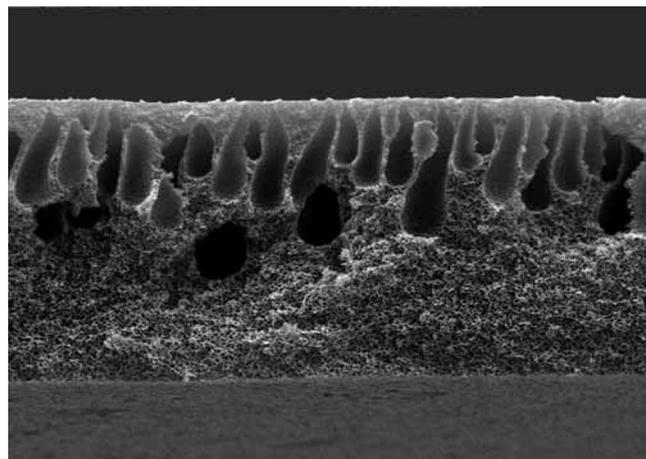


(c)

Figure 4. SEM Micrographs (magnification 500) of cross-sections of membranes prepared from PS/PVP/DMAc/acetone/ water+2-propanol (30/70 vol%). The composition of casting solution: (a) 16 wt% PS, 2 wt% PVP and 2 wt.% acetone; (b) 16 wt% PS, 2 wt% PVP and 4 wt% acetone; (c) 16 wt% PS, 2 wt% PVP and 6 wt% acetone.



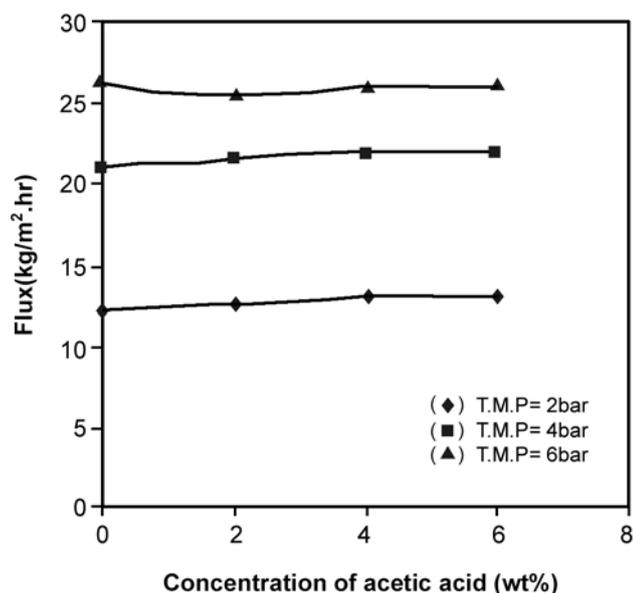
(a)



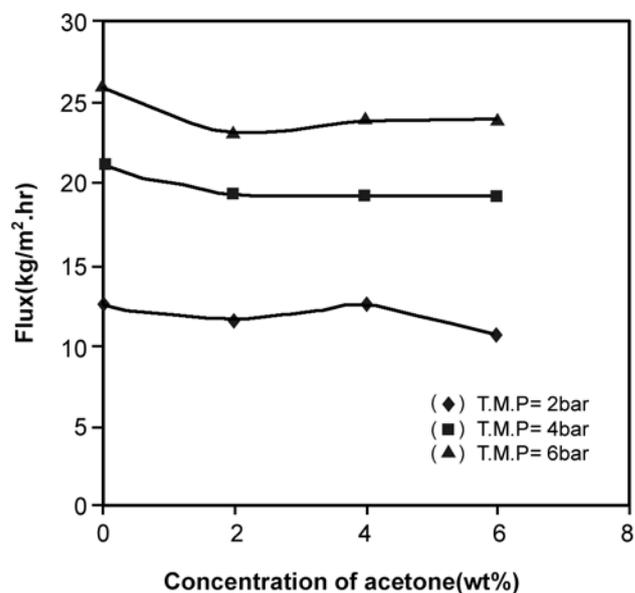
(b)

Figure 5. SEM micrographs (magnification 500) of cross-sections of membranes prepared from PS/ PVP/ DMAc/ formamide/ water+2-propanol (30/70 v %). The composition of casting solution: (a) 16 wt% PS, 2 wt% PVP and 2 wt% formamide; (b) 16 wt% PS, 2 wt% PVP and 4 wt% formamide.

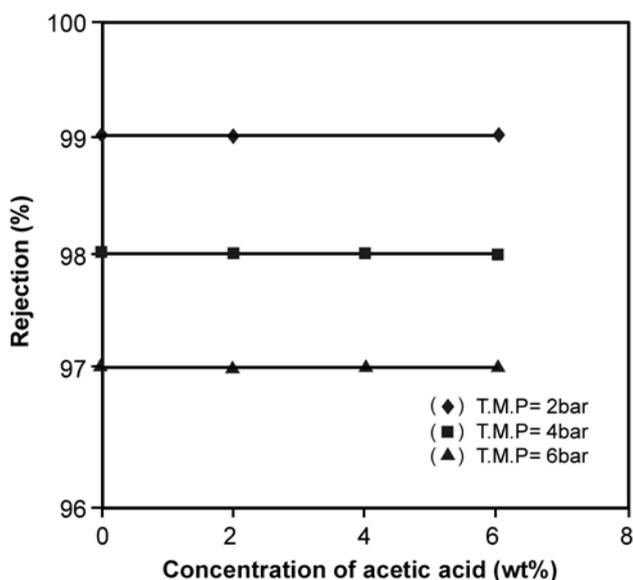
symmetry in the porous part. The type of top layer (porous or dense) and the presence of macrovoids depend on the delay time. Delayed demixing is often associated with the formation of a dense layer. However, delayed demixing structures do not always contain a dense top layer but in all cases an almost symmetric porous structure in the sub layer is generated. Delayed demixing can only be linked to the formation of a dense top layer under certain conditions: the generation of a high polymer concentration at the interface between polymer solution and coagulation bath [18]. An increase in formamide concentration causes formation of a membrane with a dense top layer.



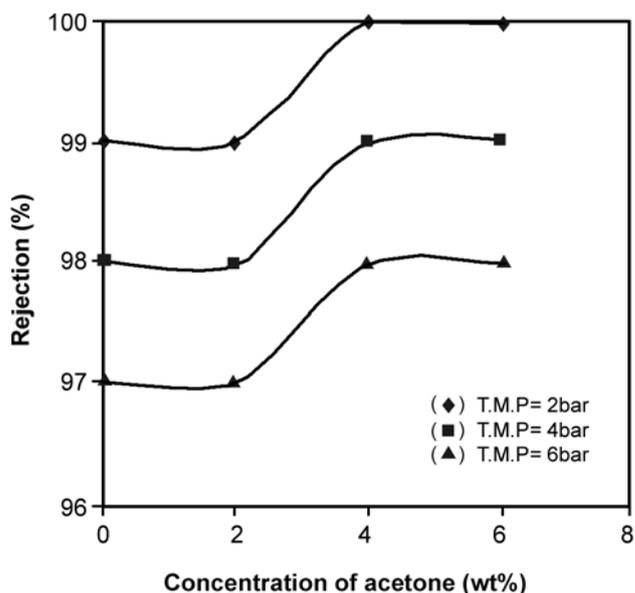
(a)



(a)



(b)



(b)

Figure 6. Effect of acetic acid concentration: (a) on flux and (b) on rejection of protein.

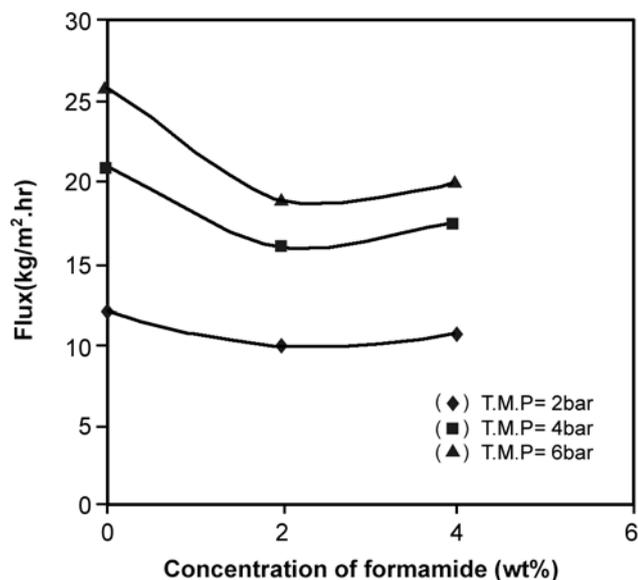
Figure 7. Effect of acetone concentration: (a) on flux and (b) on rejection of protein.

Membrane Performance

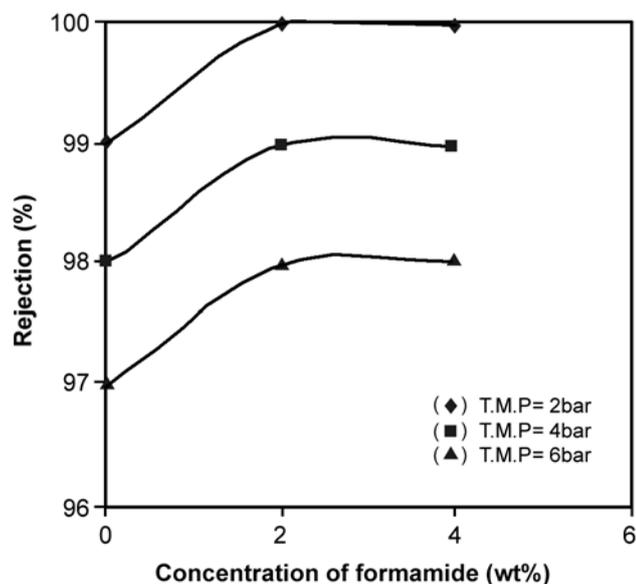
Effect of Acetic Acid

The influences of the presence of acetic acid in the casting solution on flux and retention of prepared membrane at 16 wt% of PS are presented in Figure 6. DMAC was used as solvent and mixture of water and 2-propanol (30/70 v %) was employed as non-solvent.

The data indicate that the addition of acetic acid in the casting solution slightly increases the permeability without any pronounced change in the selectivity of membrane. As investigated in morphology section, the porosity of the PS membranes increases with addition of acetic acid in the casting solution. The membrane performance is a reflection of membrane morphology, i.e. the slight increase in the flux may be attributed to the slight increase in the membrane porosity.



(a)



(b)

Figure 8. Effect of formamide concentration: (a) on flux and (b) on rejection of protein.

Effect of Acetone

Figure 7 demonstrates the influence of addition of acetone in the casting solution at 16, wt% PS. DMAc was used as solvent and mixture of water and 2-propanol (30/70 v %) was employed as non-solvent. The presence of acetone in the casting solution causes a decline in flux of prepared membranes and an improvement in the retention of membranes. Addition of acetone in the casting solution results in higher polymer concentration

in the upper layer of the membrane forming films and a denser layer with smaller pores in the final membranes. This is due to low exchange rate between solvent and non-solvent in the coagulation bath [13].

Effect of Formamide

Figure 8 illustrates the influence of addition of 2 and 4 wt% formamide in the casting solution at 16 wt% PS concentration. DMAc was used as solvent and mixture of water and 2-propanol (30/70 v %) was employed as non-solvent. The data indicate that the addition of formamide causes flux decline and retention improvement. The presence of formamide as an additive in the casting solution results in formation of membranes with lower porosity in the sub layer and small pores in the skin layer. This leads to lower flux and higher retention.

CONCLUSION

Addition of additives such as acetic acid, acetone and formamide in the casting solution exhibits a great influence on membrane structure and performance. Addition of acetic acid increases the porosity and results in higher flux. Addition of acetone and formamide in the casting solution results in the formation of a dense upper coating and a decline in the size and number of finger-like pores on the sub layer. This provides lower flux and higher retention of protein.

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REFERENCES

1. Kesting R.E., *Synthetic Polymeric Membranes*, McGraw-Hill, New York (1971).
2. Koros W.J., Pinnau I., Membrane formation for gas separation processes, in: D.R Paul, Y. Yampolskii (Eds.), *Polymeric Gas Separation Membranes*, CRC, Boca Raton, FL, 209-271 (1994).
3. Wijmanes J.G., Baaij J.P.B., Smolders C.A., The mecha-

- nism of formation of microporous or skinned membrane produced by immersion precipitation, *J. Member. Sci.*, **14**, 263-274 (1983).
4. Brons L., Altena F.W., Smolders C.A., Asymmetric membrane structure as a result of phase separation phenomena, *Desalination*, **32**, 33-45 (1980).
 5. Radovanovic P., Thiel S.W., Hwang S.T., Formation of asymmetric PS membranes by immersion precipitation. Part I. Modelling mass transport during gelation, *J. Member. Sci.*, **65**, 213-229 (1992).
 6. Altena F.W., Smolders C.A., Calculation of liquid-liquid phase separation in a ternary system of polymer in a mixture of a solvent and non-solvent, *Macromolecules*, **15**, 1491-1497 (1982).
 7. Strathmann H., Kock K., Aimar P., The formation mechanism of asymmetric membranes, *Desalination*, **16**, 179-203 (1975).
 8. Mckelvey S.A., Koros W.J., Phase separation, vitrification and the manifestation of macrovoids in polymeric asymmetric membranes, *J. Member. Sci.*, **112**, 29-39 (1996).
 9. Smolders C.A., Reuvers A.J., Boom R.M., Wienk I.M., Microstructure in phase inversion membranes. Part I. Formation of macrovoids, *J. Member. Sci.*, **73**, 259-275 (1992).
 10. Matz R., The structure of cellulose acetate membranes. The development of porous structure in anisotropic membranes, *Desalination*, **10**, 1-15 (1972).
 11. Termonia Y., Fundamental of polymer coagulation, *J. Polym. Sci. Polym. Phys. Ed.*, **33**, 279-288 (1995).
 12. Frommer M.A., Messalem R.M., Mechanism of membrane formation. VI. Convective flows and large void formation during membrane precipitation, *Ing. Eng. Chem. Prod. Res. Develop.*, **12**, 328-333 (1973).
 13. Barth C., Goncalves M.C., Pires A.T.N., Roeder J., Wolf B.A., Asymmetric PS and PES membranes: Effect of thermodynamic conditions during formation on their performance, *J. Memb. Sci.*, **169**, 287-299 (2000).
 14. Kaiser R., Stropnik C., Membranes formation PS/DMAc/water systems; structure and water flux, *Acta Chim. Slov.*, **47**, 205-213, (2000).
 15. Ping H.T., Hua D.S., Ying Z.L., The study of mechanism of organic additives action in the PS membranes casting solution, *Desalination*, **83**, 343-360 (1991).
 16. Yamasaki A., Tyagi R.K., Fouda A.E., Matsuura T., Jonason K., Effect of gelation conditions on gas separation performance for asymmetric PS membranes, *J. Memb. Sci.*, **123**, 89-94 (1997).
 17. Bradford M.M., A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, *Anal. Biochem.*, **72**, 248-254 (1976).
 18. Van den Boomgaard A., Membrane formation by phase inversion in multi-component polymer systems, PhD Thesis, University of Twente, The Netherlands, Ch. 5 (1998).