Phase Separation Phenomena of Polysulfone/Solvent/Organic Nonsolvent and Polyethersulfone/Solvent/Organic Nonsolvent Systems

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SYNOPSIS

The precipitation values (PVs) of several organic nonsolvents in polysulfone (PSf)/solvent and polyethersulfone (PESf)/solvent systems were measured in temperatures ranging from 10 to 80°C by the direct titration method and compared with those of water in the same systems. The solvents used were N-methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAC); the organic nonsolvents employed were methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, ethylene glycol, and diethylene glycol as well as acetic acid and propionic acid. The compositions of nonsolvent, polymer, and solvent at the precipitation points for different polymer concentrations up to 10 wt % were also determined at 30°C with respect to both the polymers and six nonsolvents presented. These results were used to obtain the polymer precipitation curves in the polymer–solvent–nonsolvent triangular phase diagrams and to determine the theta composition of solvent–nonsolvent for a polymer. The results show that the precipitation value of nonsolvent in polymer/solvent systems depends on both the nature of polymer, solvent, and nonsolvent used and the temperature. The effect of temperature on the precipitation value was observed to be dramatically different for different polymer/solvent/nonsolvent systems. These results were explained on the basis of polar and nonpolar interactions of the polymer, solvent, and nonsolvent system. The results indicate that the precipitation values of the type presented in this paper not only give a relative measure of the nonsolvent tolerance of the polymer/solvent system involved and the strength of solvent and nonsolvent for the polymer, but also determine the relative location of the polymer precipitation curve in the triangular phase diagram. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Most commercial organic polymer membranes currently used in reverse osmosis, ultrafiltration, microfiltration, gas separation, and pervaporation are asymmetric membranes prepared by the so-called phase-inversion process developed by Loeb and Sourirajan.[1] In this process, a solution consisting of a polymer and a suitable solvent or a solvent–additive mixture is immersed into a nonsolvent to bring about phase separation, which forms the membrane. To make good membranes suitable for a desired application, membrane researchers and manufacturers have to identify parameters that govern the phase inversion and the resulting membrane morphology and performance. The phase-separation behavior of a polymer solution with a nonsolvent plays an important role in the selection of a membrane solution composition and a coagulant as well as the indication of the subsequent formation of membranes. It can provide useful thermodynamic and kinetic information on membrane-making processes.

Nonsolvents used in phase-inversion processes may be categorized as either strong nonsolvents or weak nonsolvents. For polysulfone (PSf) and polyethersulfone (PESf), water is usually treated as a strong nonsolvent, whereas the organic solvents that cannot dissolve the polymer are classified as weak

nonsolvents, i.e., organic nonsolvents. Many researchers have reported phase-separation phenomena of water as nonsolvent in the PSf/solvent and PESf/solvent systems.[2-6] The polymer precipitation curves in the triangular phase diagram of polymer/solvent/water systems have been obtained by a simple titration method. Recent studies show that addition of organic nonsolvents in polymer film casting solutions can greatly improve the performance and structure of the asymmetric membranes, especially for gas-separation applications.[7-10] Substantially defect-free skin asymmetric membranes for gas separation have been prepared by using C_1 — C_3 alcohols as coagulants.[11-14] It is evident that the introduction of these organic nonsolvents plays an important role in the development of practical membranes. In view of its practical significance, this study focuses attention on phase separation of several organic nonsolvents in PSf/solvent and PESf/solvent systems at different temperatures.

The polymer precipitation curve in the triangular phase diagram has been often used to study phase separation of polymer, solvent, and nonsolvent systems. It requires extensive experimental measurements to obtain the polymer precipitation curves of polymer/solvent systems for various nonsolvents at different temperatures; on the other hand, identification of the polymer precipitation point in a concentrated or viscous polymer solution is difficult. Therefore, to obtain information easily on the phase separation of polymer solutions with different nonsolvents at different temperatures, the concept of the precipitation value (PV) has been introduced in this paper. The PV is defined as the grams of nonsolvent required to cause visual turbidity in a solution containing 100 g solvent and 2 g polymer. Based on the PV, phase-separation phenomena of PSf/N-methylpyrrolidone (NMP), PSf/dimethylacetamide (DMAC), PESf/NMP, and PESf/DMAC systems with different organic nonsolvents at different temperatures were investigated. The relationship between the PV and the polymer precipitation curve in the triangular phase diagram was also examined.

EXPERIMENTAL

Materials

The polymers, polysulfone (PSf, P3500) and polyethersulfone (PESf, VIC-TREX) were purchased from Union Carbide and ICI, respectively. N-Methylpyrrolidone (NMP) and dimethylacetamide (DMAC), the most important solvents for PSf and PESf membrane preparation, were supplied by Merck. The organic nonsolvents studied are methanol (MeOH), ethanol (EtOH), propanol (PrOH), butanol (BuOH), pentanol (PeOH), ethylene glycol (EgOH), diethylene glycol (DegOH), acetic acid (AA), and propionic acid (PA) purchased also from Merck. All liquid solvents were reagent grade and used without further purification. PSf and PESf were dried for at least 5 h at 100°C before being used in the experiments.

Measurement of Precipitation Values (PVs)

The polymer solution with the ratio of 2 g PSf or PESf and 100 g NMP or DMAC was placed in a glass-jacketed bottle that can be easily used at different temperatures. The temperature was controlled in a range of 10–80°C by a water thermostat. Pure nonsolvent (alcohols, acids, or water) was slowly added through a burette into the polymer solution under agitation until the initially clear solution became cloudy visually. By adjusting the temperature of the cloudy solution, the formed precipitate redissolved and then this solution became clear again. This process could be repeated. Addition of the nonsolvent into this solution was continued until the solution became turbid again. The quantity in mass or volume of the nonsolvent required to make the polymer solution turbid was obtained by the change in weight or volume of the nonsolvent in the burette. Based on the definition mentioned above, the precipitation value can, therefore, be easily calculated from the grams of nonsolvent and the polymer solution in the bottle.

Measurement of the Precipitation Point Composition

The solution containing the polymer and the solvent with different concentrations up to 10 wt % was placed in the glass-jacketed bottle accordingly. The polymer solution was titrated with several alcohols and distilled water at 30°C, respectively. The volume of nonsolvent at the precipitation point were measured by a decrease in level of the burette. The volume fractions of the polymer and the solvent in the bottle at the precipitation point can, therefore, be obtained with the use of the densities of the polymer and the solvent. These values were used to obtain the relationship between the concentration of nonsolvent and that of the polymer.

RESULTS AND DISCUSSION

Precipitation Values (PVs) of Alcohols and Water in PSf/Solvent Systems

The PVs of MeOH, EtOH, PrOH, BuOH, PeOH, EgOH, DegOH, and H_2O in PSf/NMP and PSf/DMAC systems were first measured in the temperature range from 10 to 80°C. The results are shown in Figures 1 and 2, respectively. In both systems, the PVs for water are far lower than those of alcohols, indicating the low nonsolvent tolerance of the PSf–solvent solution for water. Water is a stronger nonsolvent compared to the alcohols. With NMP as the solvent (Fig. 1), the PVs of alcohols are 4–10 times higher than those of water and they are in the order DegOH > BuOH > PeOH > EtOH > PrOH > MeOH > EgOH at temperatures of less than 60°C. Further, the PVs of MeOH, EtOH, and DegOH decrease; those of H_2O, PrOH, BuOH, and PeOH increase; and those of EgOH remain practically unchanged with increase in temperature. With DMAC solvent (Fig. 2), the PVs were about one-half of those obtained with NMP solvent; in other respects, the trends in PVs are essentially similar to those obtained with the NMP solvent.

When a nonsolvent is added to a polymer–solvent solution, it reduced the dissolving power of the solvent used for polymer and changes the solution structure, i.e., the thermodynamic state of the so-
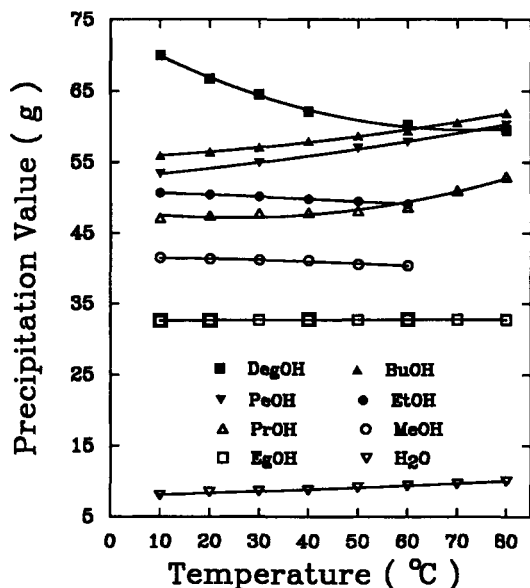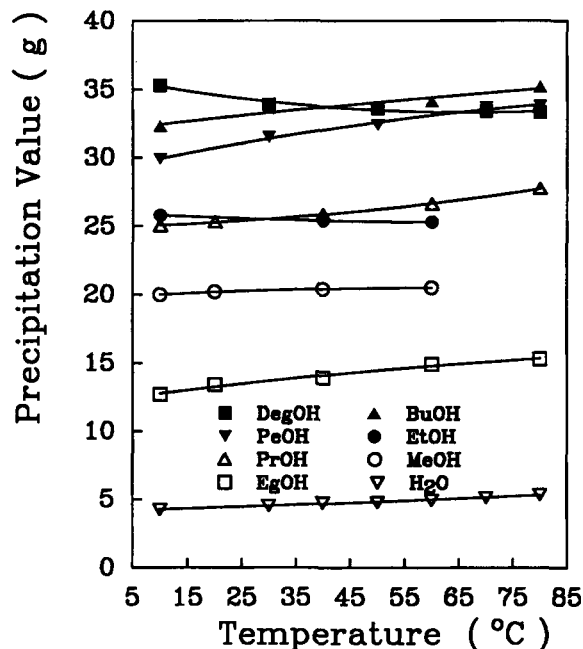

Figure 2 The precipitation values of alcohols and water in the PSf/DMAC system as a function of temperature.

lution. When the addition of nonsolvent in polymer solution is continued sufficiently, phase separation eventually takes place and the polymer solution becomes thermodynamically unstable. The PVs of nonsolvent in a polymer/solvent system give a quantitative measure of the nonsolvent tolerance of the polymer solution. They can be understood in terms of the polar and nonpolar interactions governing the solution structure of the polymer–solvent–nonsolvent system involved. Greater interaction of the nonsolvent and solvent decreases the dissolving power of the solvent for the polymer; on the other hand, greater interaction of the nonsolvent and polymer promotes greater polymer aggregation. Both these effects tend to decrease the PVs.

For a given polymer/solvent system, the polar interaction of the nonsolvent depends on its hydrogen-bonding ability represented by the δ_h component of its solubility parameter, given in Table I. A lower value for δ_h signifies lower hydrogen-bonding ability, hence, lower nonsolvent–solvent interaction and, consequently, an increase in the PV. The nonpolar interaction depends on the hydrophobic nature of the nonsolvent. As increase in the carbon number of the alcohol increases its hydrophobicity and its tendency to promote polymer aggregation, resulting in a decrease in the PV. In the case of C_1—C_5 monohydric alcohols, both these effects are notice-

Figure 1 The precipitation values of alcohols and water in the PSf/NMP system as a function of temperature.

Table I Hansen Solubility Parameters for the Solvents and Nonsolvents Used in This Study[15]

Compounds	δ_h	δ_d	δ_p
N-Methyl-2-pyrolidone (NMP)	3.5	8.8	6.0
N,N-Dimethyl acetamide (DMAC)	5.0	8.2	5.6
Water	20.7	7.6	7.8
Methanol (MeOH)	10.9	7.4	6.0
Ethanol (EtOH)	9.5	7.7	4.3
1-Propanol (PrOH)	8.5	7.8	3.3
1-Butanol (BuOH)	7.7	7.8	2.8
1-Pentanol (PeOH)	6.8	7.8	2.2
Ethylene glycol (EgOH)	12.7	8.3	5.4
Diethylene glycol (DegOH)	10.0	7.9	7.2
Acetic acid (AA)	6.6	7.1	3.9
Propionic acid (PA)	5.9	7.2	3.0

δ: Solubility Parameter, $cal^{0.5}/cm^{1.5}$. The subscripts h, d, and p represent hydrogen bonding, dispersion, and polar.

able. For MeOH and EtOH, the predominant effect is due to the decrease in the δ_h value, whereas for PrOH and BuOH, both the decrease in δ_h value and increase in carbon number affect the PVs. In the case of PeOH, the decreased polar interaction is partially offset by the increased nonpolar interaction. The PVs of the dihydric alcohols are also similarly understandable. The PVs of EgOH are lower than those of EtOH due to the increased δ_h value for EgOH. The PVs of DegOH are higher than those of EgOH due to the lower δ_h value for DegOH.

Both the polar and nonpolar interactions of the nonsolvent–solvent and the nonsolvent–polymer and the dissolution power of solvent for polymer may be expected to increase with increasing temperature. The consequent effect on the PVs depends on the relative magnitudes in the increase in polar and nonpolar interactions relative to the polymer–solvent interaction. With respect to the NMP–solvent system, for MeOH, EtOH, and DegOH, the effect of nonpolar and polar interactions of polymer–nonsolvent and solvent–nonsolvent is relatively greater; in the case of H_2O, PrOH, BuOH, and PeOH, the effect of polymer–solvent interaction is relatively greater; and in the case of EgOH, the effect of polar and nonpolar interactions seem to essentially cancel by the polymer–solvent interaction.

DMAC is relatively more polar than is NMP as indicated by their δ_h values (Table I). Hence, the DMAC dissolution power for PSf is less than that of NMP; on the other hand, the polar interactions of the alcohols and DMAC are relatively more extensive than in the case of PSf/NMP system. This explains the significantly lower PVs obtained for all

the nonsolvents used in the PSf/DMAC system; this also explains the slight increase in PVs obtained for EgOH and the relatively less steep decrease in PVs for DegOH with increase in temperature (Fig. 2).

Precipitation Values (PVs) of Alcohols and Water in PESf/Solvent Systems

Figures 3 and 4 give the PVs of water and those of the alcohols used in the temperature range 10–80°C for PESf/NMP and PESf/DMAC systems, respectively. As in the case of PSf/solvent systems, the PVs for water are far lower than those of the alcohols; the PVs for all the nonsolvents are higher in the NMP solvent than in the DMAC solvent. However, the PVs of all the nonsolvents used, including water, are significantly higher than those obtained for the corresponding PSf/solvent systems. Further, with respect to the PESf/solvent systems, the differences among the PVs obtained for the C_1—C_5 monohydric alcohols are very narrow for both PESf/NMP and PESf/DMAC systems; the PVs of EgOH are higher than those of C_1—C_5 monohydric alcohols. Except in the case of water, the PVs of all the alcohols tend to decrease with increasing temperature, and this tendency is particularly remarkable for the DegOH.

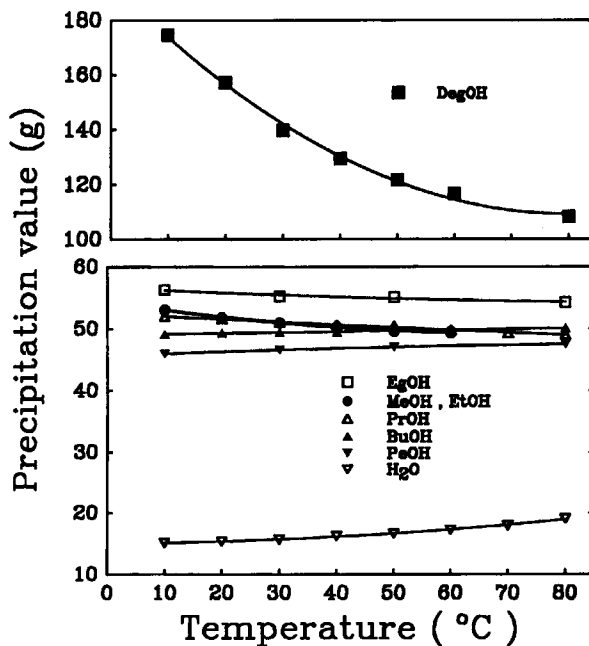All the above observations are again understandable on the basis of changes in polar and nonpolar

Figure 3 The precipitation values of alcohols and water in PESf/NMP system as a function of temperature.
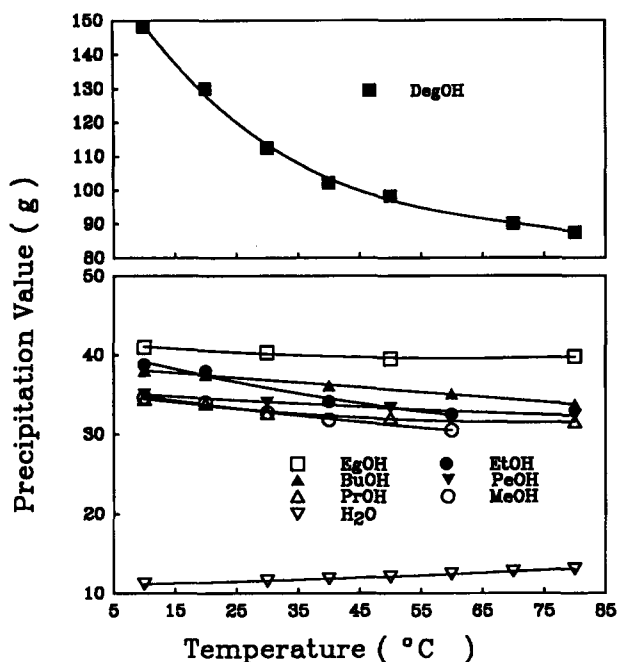
Figure 4 The precipitation values of alcohols and water in PESf/DMAC system as a function of temperature.

interactions in the polymer/solvent/nonsolvent systems. The presence of ether linkage in PESf makes the polymer amenable to more extensive polar interactions. Consequently, in the PESf/solvent/nonsolvent systems under consideration, the nonsolvent–polymer polar interactions particularly reduce both the nonsolvent–solvent polar interactions and also the nonsolvent–polymer nonpolar interactions. Both these effects tend to decrease polymer aggregation (polymer–polymer interaction) and, consequently, increase the PVs of nonsolvents in PESf/solvent systems. This explains the higher PVs obtained for all the nonsolvents tested as reported in Figures 3 and 4. With increasing temperature, the polar and nonpolar interactions of polymer–nonsolvent and nonsolvent–solvent seem to be sufficiently more extensive than that of polymer–solvent. As a result, increase in solution temperature promotes polymer aggregation and reduces the PVs, as shown in Figures 3 and 4.

PVs of Organic Acids in PSf/Solvent and PESf/Solvent Systems

Organic acids capable of forming Lewis acid : base complexes with solvents such as NMP constitute another important class of organic nonsolvents for use in polymer film casting solutions. The success of the Permea (Monsanto) PRISM Alpha gas-sep-

aration membrane is attributed entirely to the possibility of controlling the morphology of the skin layer by including additives such as acetic acid (AA), propionic acid (PA), butyric acid (BA), and isobutyric acid (IBA) in the PSf/NMP solution system.[10] To compare the PVs obtained in such systems with those reported in Figures 1–4, two organic acids, namely, AA and PA were chosen for study in this work. These PVs in PSf/NMP, PSF/DMAC, PESf/NMP, and PESf/DMAC systems were determined as before, and the results obtained are shown in Figures 5 and 6, which indicate that the PVs of PA are higher than those of AA in all the polymer/solvent systems tested. These results are consistent with the membrane performance data presented by Kesting.[10] Further, the PVs of PA and AA are higher for the NMP solvent system than for DMAC solvent system; with respect to each solvent used, the PVs are higher for the PESf polymer than for the PSf polymer. The PVs tend to increase, decrease, or remain essentially unchanged with increase in temperature for different polymer/solvent/nonsolvent systems. These results are similar to those observed and discussed with respect to the alcohols reported in Figures 1–4.

It is of particular interest to compare the PVs of CH_3OH with those of CH_3COOH and also those of C_2H_5OH with those of C_2H_5COOH. Except in the
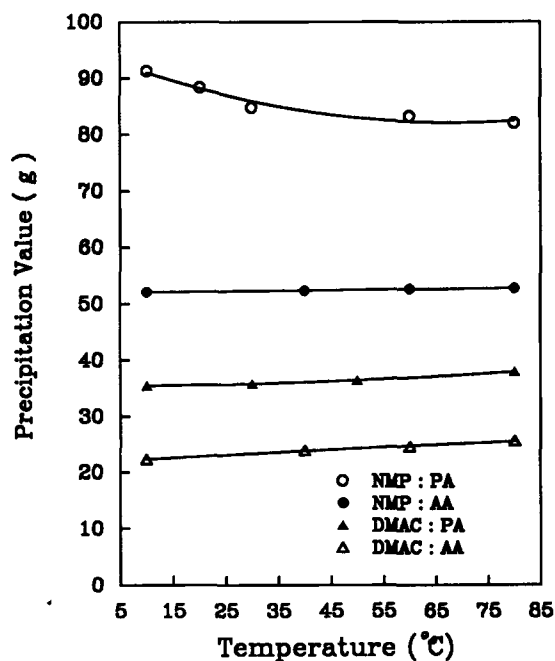

Figure 5 The precipitation values of PA and AA in PSf/NMP and PSf/DMAC systems as a function of temperature.
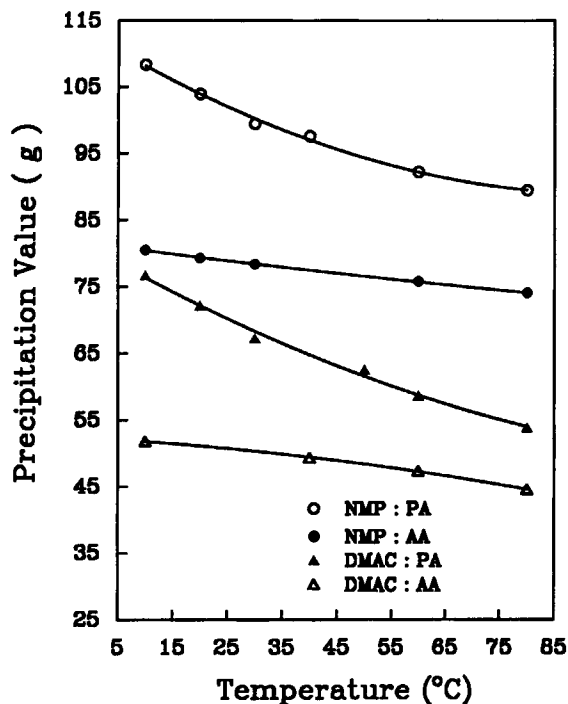
Figure 6 The precipitation values of PA and AA in PESf/NMP and PESf/DMAC systems as a function of temperature.

case of the PSf/DMAC system, for which the PVs of MeOH and AA are almost equal, in all the other cases tested, the PVs of AA and PA are significantly higher than the corresponding values for MeOH and EtOH. These results indicate that the tolerance power of the polymer solution for the functional group —COOH is much higher than that for the functional group —OH associated with a given substituent group in the polar organic nonsolvent.

The nonsolvent tolerance of polymer solution is inversely proportional to the strength of nonsolvent for polymer and directly proportional to the strength of solvent. The PVs may be used to sensitively indicate the strength of solvent and nonsolvent for polymer.

Precipitation Point Compositions of PSf and PESf in NMP and Nonsolvents

Previously, several authors[2-5] made use of the concept of the precipitation curve to explain the phase-separation phenomena in polymer/solvent/nonsolvent systems. These curves were obtained from the measurements of the precipitation point composition of polymer/solvent/nonsolvent at various polymer concentrations. The location of this curve

in the triangular phase diagram is an indication of a system's tolerance for nonsolvent. Because it is very difficult to exactly measure the composition of the precipitation point at higher polymer concentrations, the full precipitation curve could not be determined experimently.

To investigate whether the precipitation value can indicate the location of the polymer precipitation curve, we measured the composition of the precipitation point for various polymer concentrations up to 10 wt % in PSf/NMP/nonsolvent and PESf/NMP/nonsolvent systems at 30°C. The resulting volume fraction (C_n) of the nonsolvent was plotted against the volume fraction (C_p) of the polymer in logarithmic form according to the Elias method.[16] The results are shown in Figures 7 and 8 for PSf and PESf, respectively. As shown, the concentration of alcohols varies linearly with the polymer concentration in a semilog plot. This is the same as in the case of water as a nonsolvent. The alcohol with the higher precipitation value has a corresponding higher volume fraction of the nonsolvent. The larger PV, therefore, means that the polymer precipitation curve is closer to the polymer–nonsolvent axis in the triangular phase diagram. As a result, the phase-separation region becomes smaller.

The effect of temperature on the phase-separation region can also be indicated through the precipitation value. If the PV decreases with temperature, the precipitation curve moves away from the non-solvent–polymer axis with increasing temperature
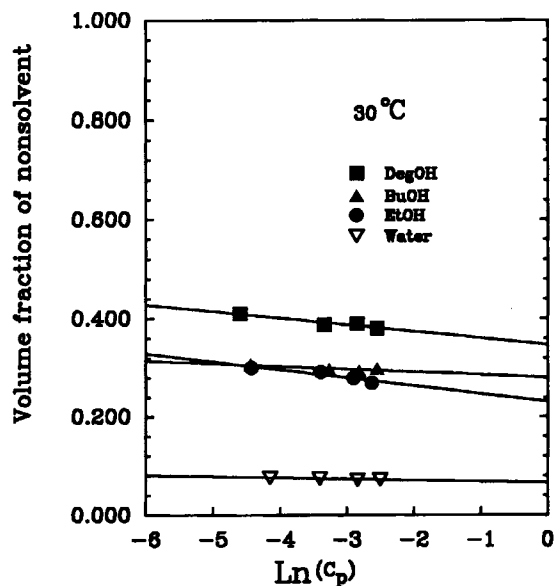

Figure 7 Volume fraction of nonsolvent vs. the volume fraction of PSf at the precipitation point.
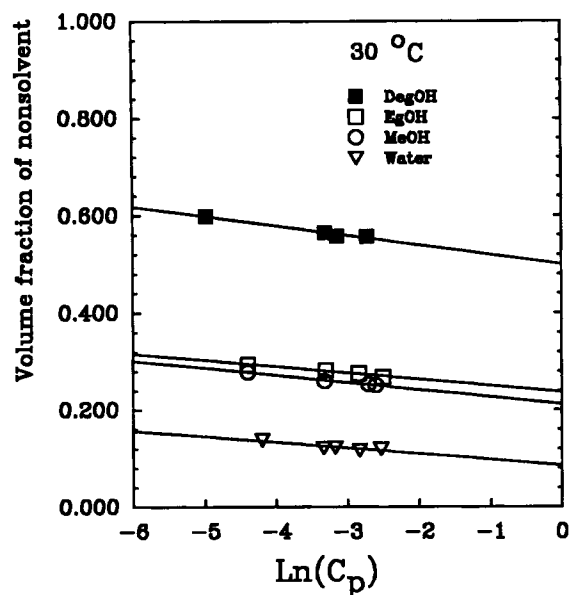
Figure 8 Volume fraction of nonsolvent vs. the volume fraction of PESf at the precipitation point.

and the corresponding phase-separation region becomes larger. The reverse is true if the PV increases with temperature. Among the alcohols and acids studied, DegOH and PA, which have the highest PVs, are predicted to have the smallest phase-separation region in PSf/solvent/nonsolvent and PESf/solvent/nonsolvent triangular phase diagrams. When these nonsolvents are used as the coagulant in the coagulation step, the low precipitation rate will cause delay in phase separation, resulting in the formation of the asymmetric membrane whose skin is rather thick and sublayer macrovoid can be suppressed. On the other hand, if these nonsolvents are used as additives in polymer solution, higher nonsolvent concentration in the polymer solution can be obtained. This accelerates phase separation of the polymer solution with the coagulant. Membranes with uniform pore structure and a thin skin separating layer can then be expected.

Wijmans et al.[5] measured the precipitation curves for PSf in DMAC/water, DMAC/EtOH, CHCl$_3$/MeOH, CHCl$_3$/EtOH, and CHCl$_3$/PrOH mixtures and found that the precipitation curves shifted close to the polymer–nonsolvent axis in the sequence of water, EtOH, and PrOH. This sequence is consistent with the precipitation values in our experiments. Thus, it is shown that the precipitation values can be used to determine the relative location of the polymer precipitation curves.

Nonsolvent/Solvent Theta-composition

The preparation of membrane casting or spinning dopes depends on polymer solubility in the solvent or the mixture of solvent and additive as well as on the critical miscibility composition at a given temperature. In the limit of infinite polymer chain length, the solvent/nonsolvent mixture becomes a theta-solvent for the polymer. This theta-composition can be determined by the method developed by Elias[16] based on precipitation data. In this method, the concentration of nonsolvent is plotted against the corresponding polymer concentration in a semi-logarithmic form at the precipitation point. The theta-composition of the nonsolvent was obtained by extrapolating the plot to 100% polymer. From Figures 7 and 8, theta-compositions in volume fraction of alcohols and water over NMP for PSf and PESf were obtained and are summarized in Table II. As can be seen, the larger the PV, the larger is the ratio of the nonsolvent to solvent at the theta-condition.

CONCLUSIONS

The precipitation values (PVs) of several alcohols and acids in PSf/NMP, PSf/DMAC, PESf/NMP, and PESf/DMAC systems at various temperatures have been measured and compared with the corresponding values of water in the same systems. The

Table II Volume Fraction of Nonsolvent/Solvent Mixtures at the Theta-condition for PSf and PESf

Nonsolvents	DegOH	EgOH	MeOH	EtOH	BuOH	H$_2$O
$\dfrac{\text{Nonsolvent}}{\text{NMP}}$ in PSf	$\dfrac{.35}{.65}$	—	—	$\dfrac{.238}{.762}$	$\dfrac{.28}{.72}$	$\dfrac{.065}{.935}$
$\dfrac{\text{Nonsolvent}}{\text{NMP}}$ in PESf	$\dfrac{.52}{.48}$	$\dfrac{.239}{.761}$	$\dfrac{.215}{.785}$	—	—	$\dfrac{.09}{.91}$

PVs of organic nonsolvent such as methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, ethylene glycol, and diethylene glycol as well as AA and PA in the polymer/solvent systems studied are significantly higher than those of water in the same polymer/solvent systems. Among the alcohols and acids examined, diethylene glycol and PA were found to have the highest precipitation values, which generally decrease with increasing temperature. The effect of temperature on the phase-separation region of the polymer, solvent, and nonsolvent system is dramatically different for different systems, as indicated by the relationship between the precipitation value and temperature. With increasing temperature, the phase-separation region of some systems is increased, while others decreased. For PSf/solvent systems, the solubility of polymer/solvent system with the nonsolvents examined increases with increasing temperature for most of the nonsolvents used with exception of methanol, ethanol, and diethylene glycol. However, for the PESf/solvent systems, the reversed trend was observed for almost all the nonsolvents studied.

The results are understandable on the basis of polar and nonpolar interactions governing the structure of polymer solution. The results show that the precipitation value can be used as a measure of the nonsolvent tolerance of polymer solution for nonsolvent and the strength of solvent and nonsolvent for polymer. It can also be used for determining the relative locations of the polymer precipitation curve in the polymer–solvent–nonsolvent triangular phase diagram. Consequently, the precipitation value of the type presented in this paper may offer a rational physicochemical basis for the choice of polymer film casting composition and the coagulant composition as well as film-casting conditions for making polymeric membranes.

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