Isothermal Phase Diagrams and Phase-Inversion Behavior of Poly(vinylidene fluoride)/Solvents/Additives/Water Systems

M. L. Yeow, Y. T. Liu, K. Li

Department of Chemical Engineering, University of Bath, Claverton Down Bath, BA2 7AY, United Kingdom

ABSTRACT: Isothermal ternary phase diagrams of poly(vinylidene fluoride) (PVDF)/solvents/nonsolvent systems were produced using four different solvents, *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and triethyl phosphate (TEP), and using water as a nonsolvent. The effects of the additives polyvinylpyrrolidone (PVP, M_w = 10,000), ethanol, and lithium perchlorate (LiClO$_4$) on the phase-inversion behavior of PVDF/DMAc/water ternary system were investigated, with additive concentrations of 2 and 6 wt %, at temperatures of 25 and 70°C, respectively. Ethanol, glycerol, and water were used to study the cloud points of 10, 15, and 20 wt % PVDF/DMAc concentrations, at solution temperatures ranging from 30 to 70°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2150–2155, 2003

Key words: poly(vinylidene fluoride) (PVDF); phase behavior; phase diagrams; additives; solvents/nonsolvents

INTRODUCTION

Poly(vinylidene fluoride) (PVDF), after being commercially introduced in the 1960s, has been widely regarded as a unique polymer material with great potential for its excellent chemical and thermal resistance.[1] In brief, its high carbon-fluorine dissociation energy gives rise to its outstanding thermal stability and chemical resistance.[2] Unlike other conventional membrane materials, such as polysulfone (PS), polyethersulfone (PESf), and polyacrylonitrile (PAN), PVDF—with its exceptional chemical resistance—remains inert to many corrosive materials such as halogens, oxidants, and inorganic acids (apart from fuming sulfuric acid), as well as aliphatic, aromatic, and chlorinated solvents.[1] This makes it an outstanding membrane material, especially in waste-treatment applications, which often involve harsh chemicals.[3–10] Another main advantage PVDF has to offer as a membrane material is its ease of dissolution in common organic solvents, such as dimethylacetamide (DMAc), dimethylformamide (DMF), and *N*-methyl-pyrrolidinone (NMP). Hence, PVDF membranes can be fabricated by conventional phase-inversion processes.

Research and development of PVDF membranes have been actively pursued by a number of investigators, who have primarily focused on fundamental membrane morphological studies by phase-inversion processes.[11–19] In their publications, a great deal of attention was devoted to studying the effects of various preparation parameters. However, to date the mechanism of PVDF membrane formation has rarely been discussed in the literature. Recently, a few articles dedicated to understanding the phase-separation mechanism of PVDF/DMF systems have been published.[20–24]

As noted by Klein and Smith,[25] one of the persistent difficulties that limit the successful casting of asymmetric membranes is the lack of a predictable and systematic method in solvent selection. Using the Hansen solubility parameter, Bottino et al.[14] identified eight organic solvents out of 46 that were screened to be good solvents for PVDF. Of these solvents, DMAc, DMF, NMP, and DMSO have been widely used as the high boiling point strong solvent, accompanied by either acetone or tetrahydrofuran (THF) as the low boiling point weak solvent.[5–7,11–15]

Precipitation curves, of PVDF polymer using a DMF solvent system, have been reported.[20–24] In the study of phase behavior of the PVDF/DMF/1-octanol system, both liquid–liquid phase separation and crystallization boundaries were computed over a wide temperature range (300–460 K) based on Flory–Huggins theory.[20] Another research group studied the precipitation of crystalline PVDF from PVDF/DMF systems using 1-octanol and water as the nonsolvent at 25°C.[21–23] In their study, the normally inaccessible amorphous phase boundary for PVDF was calculated based on Flory–Huggins interaction parameters and was found to match the experimentally obtained crys-

tallization data.[21–23] This knowledge was then extended to study the PVDF formation mechanism, and for the optimization of membrane structure for microfiltration applications, using both equilibrium thermodynamic and diffusion kinetic theory.[21] The relationship between phase-separation behavior and gelation kinetics for PVDF/tetra(ethylene glycol) dimethyl ether (PVDF/TG) solutions was studied by Hong and Chou[24] using time-resolved light scattering and gelation kinetic analysis. Matsuyama et al.[26,27] investigated the phase separation of a PVDF/DMF system induced by penetration of nonsolvent from the vapor phase.

Despite the extensive use of PVDF/DMAc/water systems in the fabrication of asymmetric PVDF membranes,[3,4,8–10,16–19] no information on the phase separation behavior of PVDF polymer has been reported. Indeed, information of such a nature is extremely useful in providing important thermodynamic and kinetic information on the membrane-making process.[28] Because of its crystallinity, phase-inversion behavior of PVDF polymer is more complicated than that of amorphous polymers such as polysulfone (PSf) and polyethersulfone (PESf).[29] It is therefore very important to study and understand its phase-inversion behavior, to use such information in a membrane-making process. Here, we study the precipitation curves of PVDF Kynar® K-760 polymer, from four different solvent systems (i.e., DMAc, DMF, NMP, and TEP), using water as the nonsolvent. Also included in this report is the effect of three additives, ethanol, lithium perchlorate (LiClO$_4$), and polyvinylpyrrolidone (PVP, M_w = 10,000), on the phase-inversion behavior of a PVDF/DMAc system, again using water as the nonsolvent. Finally, the cloud points of 10, 15, and 20 wt % PVDF/DMAc systems were investigated using ethanol, glycerol, and water as the nonsolvent.

EXPERIMENTAL

Materials

Kynar K760 poly(vinylidene fluoride) (PVDF) polymer pellets used were purchased from Elf Autochem (City, State), and were predried at 50°C before use. *N,N*-Dimethylacetamide (DMAc) [99.9+%, HPLC grade] and 1-methyl-2-pyrrolidone (NMP) [99+%, spectrophotometric grade], *N,N*-dimethylformamide (DMF) [99.8%, ACS reagent grade], and triethyl phosphate [99%, GC grade] were used as solvents. Ethanol [reagent grade], lithium perchlorate (LiClO$_4$) [99+%, ACS reagent grade], and polyvinylpyrrolidone (PVP) [99.9+%, M_w = 10,000] were used as additives. Ultrapure water, ethanol [reagent grade] and glycerol [F_w = 92.09, 99%] were used as nonsolvents. All chemicals were purchased from Sigma Aldrich (St. Louis, MO) and used as received.

Measurement of cloud points

Cloud point data were measured by means of a titration method. The solution to be titrated was poured into a sealed Quickfit round flask and kept at controlled temperature. Nonsolvent was slowly added into the polymer, with a magnetic stirrer constantly agitating the solution. In cases where localized precipitation occurred, especially at higher polymer concentration, further addition of nonsolvent was performed only after the solution became homogeneous again. This was carried out until the titration end point was reached (i.e., the solution became permanently turbid or showed signs of gelation).

Measurement of solution viscosity

Viscosities of 15 wt % PVDF polymer solutions in four different solvents (i.e., DMAc, DMF, NMP, and TEP) were measured using a Bohlin Rheometer Measuring System 4/40, at 30-s delay time and 30°C operating temperature. This equipment uses the ramp stress test method, whereby a gradually increasing ramped stress (0.07892–6.662 Pa) was applied onto the sample solution, and the induced shear rate was continuously monitored. The viscosity of the sample solution was calculated, based on the ratio of the two parameters (i.e., shear stress versus shear rate). Viscosity measurements were also made on 10, 15, and 20 wt % PVDF/DMAc solutions, as well as on 15 wt % PVDF/DMAc solutions with 2 and 6 wt % of additives (ethanol, LiClO$_4$, and PVP).

RESULTS AND DISCUSSION

Isothermal ternary phase diagram of PVDF/solvent/water systems

Solvent plays a very important role in determining the final outcome of membrane structure and performance.[15,25] A good solvent is essential in formulating a uniform polymer solution, and in obtaining membranes with narrow pore size distribution, or even good mechanical strength. Out of the eight good solvents for PVDF polymers identified by Bottino et al.,[13] four were tested in fundamental PVDF phase-inversion studies, including DMAc, DMF, NMP, and TEP. It was found that PVDF polymer dissolved fairly easily in DMAc, DMF, and NMP; however, it did not easily dissolve in TEP.

Precipitation point curves of PVDF in these four solvent systems, using water as the nonsolvent, are presented in Figure 1. The solvent power could be ranked in the order of DMAc > NMP > DMF > TEP, as suggested by the width of the one-phase homogeneous gap in the ternary phase diagram. The stronger the solvent power, the greater the amount of nonsolvent (in this case water) that is required to disturb the
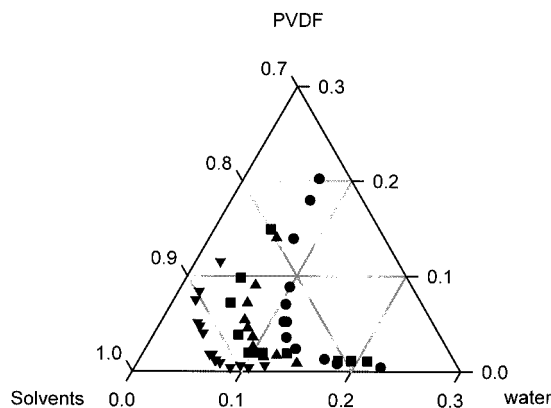
Figure 1 Isothermal phase diagram for PVDF K-760/water/solvents ternary system at 25°C.

system equilibrium and induce the polymer precipitation. As noted by Lau et al.,[26] this miscibility region can also be considered as a measure of the system's resistance or tolerance to polymer precipitation by the nonsolvent (in this case water). Because DMAc is the strongest solvent of PVDF, it was subsequently used for investigating the effect of additives on the phase-inversion behavior of PVDF polymer solutions.

It is also worth mentioning here that the end points of the titration differ remarkably between low-concentration and high-concentration polymer solutions. When the polymer concentration is low, the solvent–solute effect dominates the solution behavior, with negligible macromolecule–macromolecule interaction, and the titration end points, marked by the presence of persistence solution turbidity that could be detected visually. At high polymer concentration, the interaction between macromolecules starts to interfere: the polymer solution shows signs of crystallization and becomes gel-like. Indeed, we cannot conclude that these points, obtained at high polymer concentration, are the so-called binodal point attributed to the occurrence of gelation. However, they mark the point after which the solution became thermodynamically unstable and not suitable to be used as a polymer dope. In short, the establishment of these isothermal ternary phase diagrams is especially useful in identifying the region(s) where the high-concentration polymer solution remains indefinitely stable thermodynamically. This information is crucial in the preparation of a stable casting or dope solution for membrane fabrication.

Effect of additives on the PVDF/DMAc/water isothermal ternary phase diagram

The effects of three additives, PVP (M_w = 10,000), ethanol, and LiClO$_4$, on the phase-inversion behavior of PVDF/DMAc system were studied at both 25 and 70°C.

In general, the addition of additive was found to reduce the system's degree of tolerance for water. At 25°C, the impact of the 6 wt % additive used in reducing the envelope of the one-phase homogeneous region follows the trend of LiClO$_4$ > PVP (10K) > ethanol, as shown in Figure 2(a). The impact differences between these additives were found to be less apparent at the high temperature of 70°C, as shown in Figure 2(b).

Figure 3 shows isothermal precipitation curves for all three additives used in relation to their concentrations added (i.e., 2 and 6 wt %) as well as the isothermal condition employed (i.e., 25 and 70°C, respectively). Based on the experiment carried out at 25°C, the following observations were recorded: in the case where ethanol was used as the additive, the titration end point was noted as the solution became visibly turbid and remained in liquid form at isothermal conditions for more than 24 h. In the case of PVP, the low-concentration solution titration end point was also noted as the solution exhibiting visually detectable turbidity, with a very noticeable
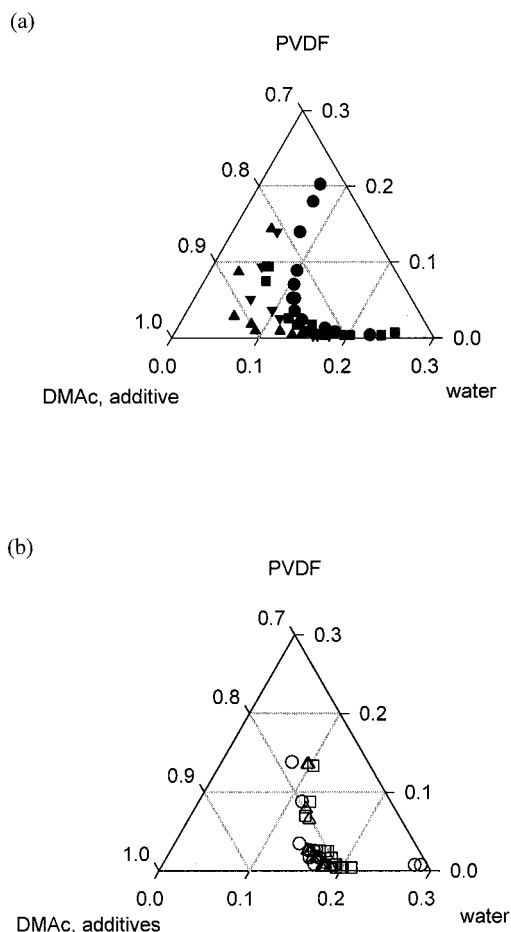
(a)

(b)

Figure 2 Effects of additives on the precipitation curves of PVDF/DMAc/water ternary system at (a) 25°C: ● plain PVDF, ▼ 6% PVP, ▲ 6% LiClO$_4$, ■ 6% ethanol; and (b) 70°C: ○ 6% PVP, △ 6% LiClO$_4$, □ 6% ethanol.
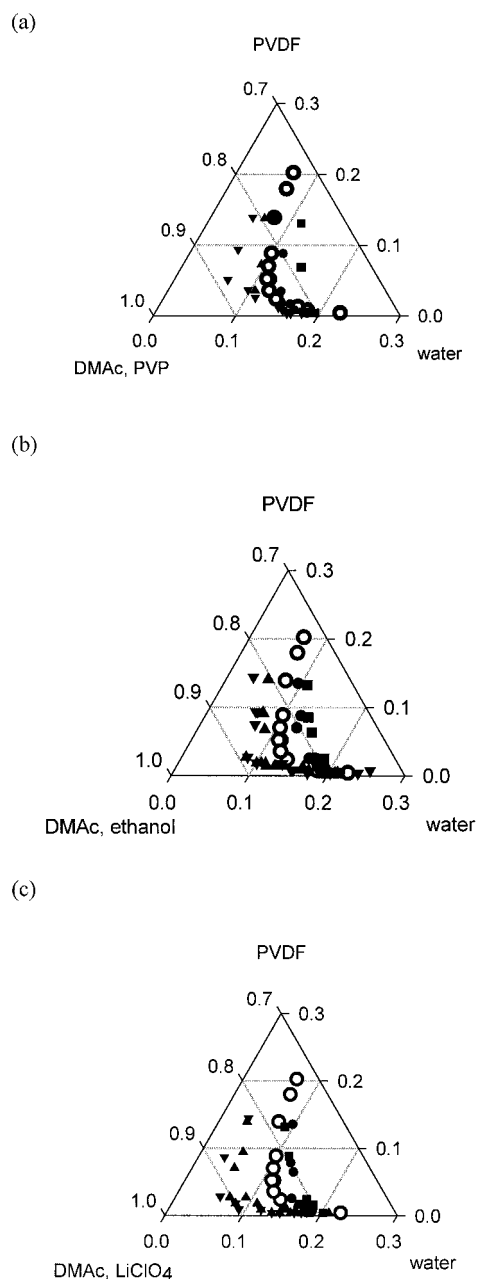
(a)

(b)

(c)

Figure 3 Effects of additives on the precipitation curves of PVDF/DMAc/water ternary system at 25 and 70°C: (a) PVP, (b) ethanol, (c) LiClO₄. ▲ 2% at 25°C, ▼ 6% at 25°C, ● 2% at 70°C, ■ 6% at 70°C.

precipitate when seen under light. At higher solution concentration (>10 wt % PVDF concentration), the turbid solution exhibited gelling behavior after being kept at a constant temperature of 25°C for more than 24 h. When LiClO₄ was used as the additive, the already cloudy solution showed gelling behavior similar to that of PVP at a lower PVDF concentration of 8 wt %, within a shorter period of time. At higher PVDF concentration, the solution was found to be gelled without showing any sign of cloudiness. In short, these results suggest that the

presence of additives facilitates polymer crystallization at a low temperature of 25°C.

At 70°C, however, all titration end points were marked by the solution becoming visibly cloudy, without any sign of gelation. Hence, it is proposed that elevated temperature was in fact suppressing polymer crystallization and enhancing liquid–liquid demixing from the amorphous region. When removed from heat and maintained at 25°C, the already turbid low-concentration solutions were found to regain limited clarity with visible precipitates seen floating in the solution, whereas those of high concentration gelled within a short time span.

Regardless of the temperature, it was found that the region occupied by a one-phase homogeneous solution decreased with the increase of additive concentration used, as shown in Figure 3(a)–(c). Therefore, it can be said that these additives act as antisolvents, reducing the solvent power and system tolerance for water, and thus favoring the phase-inversion process of the polymer solution.

Similar to the observation made by Cheng,[22] the isothermal precipitation curves obtained in this study (Fig. 3) were found to be nearly parallel to each other, with the curve shifting to the left with increasing quantity of additive used, and shifting to the right when the solution temperature was increased.

Cloud points of 10, 15, and 20 wt % PVDF/DMAc system induced with different nonsolvents (i.e., water, ethanol, and glycerol) were investigated over a temperature range of 30 to 70°C. The cloud points obtained consistently followed the trend of water > glycerol > ethanol, demonstrating that water is the strongest nonsolvent, whereas ethanol is the weakest nonsolvent of the three studied, as illustrated in Figure 4.

Effect of solvent, additives, and polymer concentration of solution viscosity

Viscosity is a basic parameter in membrane-formation processes. In the casting of flat-sheet membranes, solution viscosity influences the thickness of the resulting membrane. In the spinning of hollow fibers, solution viscosity is one of the key factors in determining solution spinnability (i.e., in the extrusion of hollow fibers), in addition to such factors as spinneret size and coagulation medium used. Additionally, solution viscosity has a strong influence on the interdiffusion of solvent and nonsolvent during the phase-inversion process, which then controls the kinetic aspect of membrane-formation processes, including both skin formation and substructure morphology. Information on solution viscosity is thus crucial because of its influence on the resulting membrane morphology and performance.
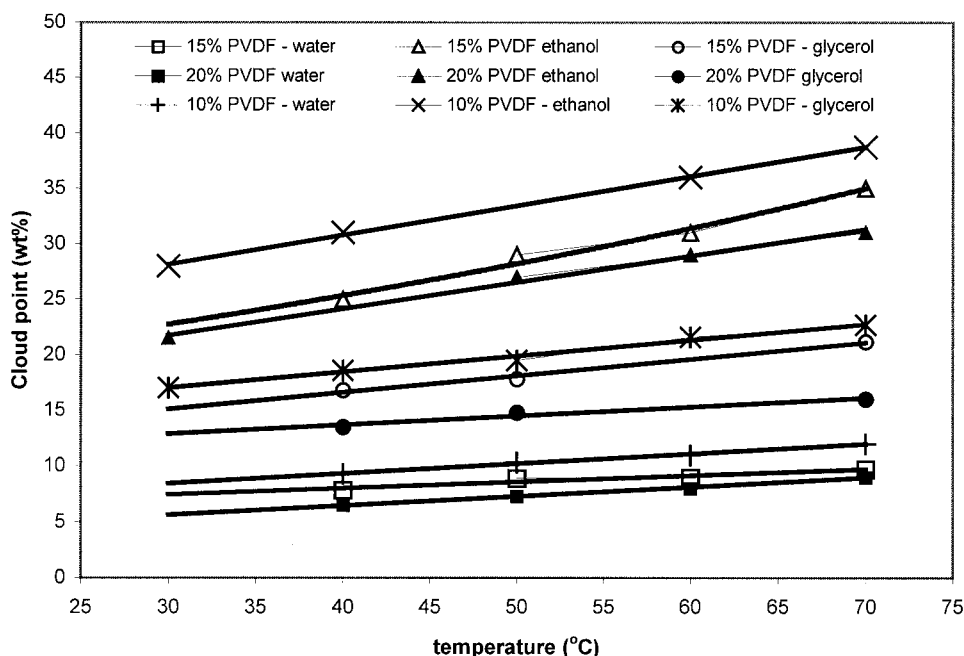
Figure 4 Cloud point of water, ethanol, and glycerol for 10, 15, and 20 wt % PVDF/DMAc system at various temperatures.

The viscosities of 15 wt % PVDF polymer solutions prepared using different solvents, DMAc, DMF, NMP, and TEP, were found to follow the order of TEP (1211 cP) > NMP (1167 cP) > DMAc (619.5 cP) > DMF (488 cP), in accordance with their respective formula weights [i.e., TEP (M_w = 182.16), NMP (M_w = 99.13), DMAc (M_w = 87.12), and DMF (M_w = 73.10), as summarized in Table I]. Generally, viscosity is inversely proportional to the solvent strength in dissolving the polymer. It is clearly not the case here: according to our cloud point experiment the solvent strength was in the order of DMAc > NMP > DMF > TEP. This is attributed to the complicated solute–solvent interaction in the presence of macromolecules. Detailed verification in this aspect is beyond the scope of the present study.

Using DMAc as solvent, viscosities of 10, 15, and 20 wt % PVDF/DMAc polymer solutions were measured, as listed in Table II. As expected, solution viscosity increases with increased polymer concentration: 112.3, 619.5, and 2137.5 cP for 10, 15, and 20 wt % PVDF/DMAc polymer solution, respectively. Measurements were also made to investigate the effect of

additives on 15 wt % PVDF/DMAc solution viscosity, as summarized in Table II. The addition of both PVP (M_w = 10,000) and LiClO$_4$ increases the solution viscosity, with a greater viscosity increase noted in the case of LiClO$_4$. Increase in viscosity was found to be correlated to the amount of additive added. On the contrary, the addition of 2 wt % ethanol had little or no impact on the solution viscosity; however, a slight decrease in solution viscosity was detected with the addition of 6 wt % ethanol (i.e., 584.3 cP), compared to 613.6 cP for the plain 15 wt % PVDF/DMAc polymer solution.

CONCLUSIONS

Polymer precipitation curves for poly(vinylidene fluoride) (PVDF) were generated for four different or-

TABLE I
Viscosity of 15 wt % PVDF Polymer Solution with Different Solvents

Solvent	Viscosity (cP)
TEP	1211
NMP	1167
DMF	619.5
DMAc	488.0

TABLE II
Viscosity of PVDF/DMAc Polymer Solution

PVDF polymer concentration (wt %)	Additive	Viscosity (cP)
10	Nil	112.3
15	Nil	619.5
20	Nil	2137.5
	2 wt % ethanol	613.1
	6 wt % ethanol	584.3
15	2 wt % PVP (M_w = 10,000)	654.2
	6 wt % PVP (M_w = 10,000)	863.3
	2 wt % LiClO$_4$	694.1
	6 wt % LiClO$_4$	1309.0

ganic solvents, DMAc, DMF, NMP, and TEP, using water as a nonsolvent. Experimental results show solvent strengths to be in the order of DMAc > NMP > DMF > TEP. Using DMAc as solvent, the presence of additives [i.e., ethanol, LiClO$_4$, and PVP (M_w = 10,000)] decreased the width of the one-phase homogeneous region on PVDF/DMAc/water ternary phase diagram following the trend of LiClO$_4$ > PVP > ethanol at both 25 and 70°C. The effect of additive concentrations was found to be less significant at the higher temperature of 70°C. Elevated temperature was found to suppress crystallization and favor liquid–liquid demixing; thus it is expected to result in a more porous membrane structure. Cloud point data for 15 wt % PVDF/DMAc system obtained using water, glycerol, and ethanol as nonsolvent aimed at investigating the tolerance of the PVDF/DMAc system before gelation. Water was found to be the strongest nonsolvent, whereas ethanol was the weakest.

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