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Comparison of the Solubility of PVF and PVDF in Supercritical CH$_2$F$_2$ and CO$_2$ and in CO$_2$ with Acetone, Dimethyl Ether, and Ethanol

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Cloud-point data are reported at temperatures to 245 °C and pressures to 2700 bar for poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF) in CO$_2$, CH$_2$F$_2$, dimethyl ether (DME), acetone, and ethanol and in mixtures of CO$_2$ with acetone, DME, and ethanol. PVF does not dissolve in CO$_2$ even at 245 °C and 2700 bar, but, PVF does dissolve in CH$_2$F$_2$ at 180 °C and pressures in excess of 1500 bar. To dissolve PVF in DME, pressures in excess of 550 bar and temperatures in excess of 130 °C are needed although it only takes ∼100 bar to maintain a single phase to temperatures of ∼220 °C with ethanol and acetone. Compared to the conditions needed to dissolve PVF, it takes hundreds of bar less pressure to dissolve PVDF in CO$_2$, CH$_2$F$_2$, and DME and ∼60 bar less pressure to dissolve it in acetone, but it does take ∼60 bar more pressure to dissolve it in ethanol. With CO$_2$, ethanol is a better cosolvent than acetone for both fluoropolymers at high temperatures and at low ethanol concentrations. However, when the temperature is decreased or the ethanol concentration is increased, it acts as an antisolvent probably due to ethanol self-association. Compared to ethanol and acetone, DME is not as good a cosolvent more than likely as a result of its lower density and smaller dipole moment. For all three cosolvents, their impact on the reduction of the cloud-point pressure diminishes with increasing cosolvent concentration. It is also evident that CO$_2$ is an effective antisolvent since small amounts of it added to the polymer−cosolvent mixtures greatly increase the pressures needed to obtain a single phase.

Introduction

Carbon dioxide has been touted as the supercritical fluid (SCF) solvent of choice for many industrial applications because it is nonhazardous and inexpensive. A large body of work has been generated demonstrating that CO$_2$ dissolves hydrocarbon−fluorocarbon polymers containing fluorinated octyl acrylate groups[1−10] and hydrocarbon−fluorocarbon block and graft copolymers.[1,11−13] Fluorocopolymer solubility depends on the number of fluorinated side groups and on the molecular weight of the side groups relative to the molecular weight of the hydrocarbon main chain. It has also been suggested that CO$_2$ either forms a weak complex or preferentially clusters near the fluorine of the C−F bonds that are more polar than C−H bonds.[14−16] These studies establish that fluorinating a polymer enhances its solubility severalfold in CO$_2$ but that fluorination alone does not ensure that the polymer will remain soluble in CO$_2$ at temperatures below 100 °C.[17] However, to predict quantitatively the solubility of a polymer in an SCF solvent still remains a challenge due to the difficulty in accounting for the intra- and intersegmental interactions of the many segments of the polymer relative to the small number of segments in a solvent molecule. It is also difficult to model the density dependence of the intermolecular potential functions since polymer−SCF solutions are highly compressible. In the work presented here, cloud-point data are obtained for poly(vinyl

TABLE 1: Properties of the Poly(vinyl fluoride) (PVF) and Poly(vinylidene fluoride) Used in This Study[a]

polymer	M_w	M_n	T_m (°C)
PVF	125 000	40 100	187
PVDF	200 000	unknown	168

[a] M_w is the weight average molecular weight, M_n is the number average molecular weight, and T_m is the melting temperature.

fluoride) (PVF) in CH$_2$F$_2$ and for poly(vinylidene fluoride) (PVDF) in CO$_2$ with three different cosolvents since these two fluoropolymers represent one end of the backbone composition spectrum for many of the fluorocopolymers studied with SCF solvents (see Table 1). Cloud-point data reported in the literature for PVDF in CH$_2$F$_2$ and CO$_2$[18] are compared to PVF cloud-point data for these two SCF solvents to ascertain the impact of solvent−polymer polar interactions on the pressures needed to obtain a single phase.

Polymer−solvent interactions must be greater than $^1/_2$ the sum of polymer−polymer and solvent−solvent interactions for a polymer to dissolve in a given solvent.[19] Interaction energy is intimately linked to the physical properties of the solvents and cosolvents listed in Table 2 for CO$_2$, CH$_2$F$_2$, acetone, dimethyl ether (DME), and ethanol. Consider first the two SCF solvents, CO$_2$ and CH$_2$F$_2$. Neither CO$_2$ nor CH$_2$F$_2$ is expected to be a particularly good solvent for PVF or PVDF at high temperatures where dispersion interactions should dominate since the polarizabilities of these solvents are only ∼60−70% of that of ethane. However, both CO$_2$ and CH$_2$F$_2$ have significant polar moments that are enhanced at elevated pressures as both SCF solvents are easy to densify. Hence, the quality of these two SCF solvents

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Comparison of the Solubility of PVF and PVDF

J. Phys. Chem. B, Vol. 103, No. 14, 1999 **2819**

TABLE 2: Properties of the Solvents and Cosolvents Used in This Study[a]

solvent	critical temperature (°C)	critical pressure (bar)	polarizability ($cm^3 \times 10^{25}$)	dipole moment (D)	quadrupole moment (($erg^{1/2}cm^{5/2}$) $\times 10^{26}$)
CO_2	31.0	73.8	29.1	0.0	−4.3
CH_2F_2	78.3	58.2	32.4	1.96	
acetone	234.9	47.0	63.7	2.86	
dimethyl ether	126.8	53.0	52.2	1.30	
ethanol	240.8	63.0	51.1	1.73	

[a] References 19, 25, 33, and 34.

for polar PVF and polar PVDF should improve as the temperature is lowered since polar interactions scale inversely with temperature.

Each of the three cosolvents considered in this study, acetone, DME, and ethanol, has a significant dipole moment although ethanol is the only one of these cosolvents that can self-associate and cross-associate by hydrogen bonding. The addition of these cosolvents to CO_2 is expected to enhance polymer−solvent interactions that will favor the dissolution of polar PVF and PVDF. Solvent density increases as each of these cosolvents is added to the solution, which has the effect of decreasing the free volume difference between the solvent and the polymer and, thus, makes it easier to dissolve the polymer. To correctly interpret the effect of a cosolvent, it is important to know the phase behavior of the solvent−cosolvent mixture. Each binary mixture of CO_2 with acetone, DME, and ethanol has a continuous critical-mixture curve that exhibits a maximum pressure at approximately 40 mol % of the heavy component at temperatures between the critical points of CO_2 and of the other component. The pressure maximum is approximately 120 bar for the CO_2−acetone system,[20] 80 bar for the CO_2−DME system,[21] and is expected to be less than 160 bar for the CO_2−ethanol system.[22−24] These pressure maximums are much lower than the pressures investigated in this study, which means that phase separation does not occur due to the separation of the mixed solvent.

Table 1 lists the properties of PVF and PVDF. Both polymers are polar since the dipole moment is 1.37 D for vinylidene fluoride monomer and 1.43 D for vinyl fluoride monomer.[25] The larger dipole moment of vinyl fluoride is probably due to the more significant structural asymmetry of vinyl fluoride relative to that of vinylidene fluoride. PVF also has a higher melting temperature (187 °C) than PVDF (168 °C). Spectroscopy data suggest that a very weak electrostatic attraction exists between the carbon atom of CO_2 and the fluorine in PVF,[14] which should help promote the dissolution of this polymer into CO_2. The magnitude of this electrostatic attraction is similar to that of dispersion and polar interactions; therefore, it is not expected to have a dominating effect on the phase behavior.

Experimental Section

Described elsewhere are the techniques used to obtain cloud-point curves for polymer−SCF solvent−cosolvent ternary mixtures.[26] Cloud-points are measured for the polymer solutions at a fixed polymer concentration of ~5 wt % which should be close to the maximum in the pressure-composition loop.[27,28] Cloud points are measured and reproduced at least twice to within ±2.8 bar and ±0.4 °C. The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. Cloud points obtained in this manner are identical to those defined as
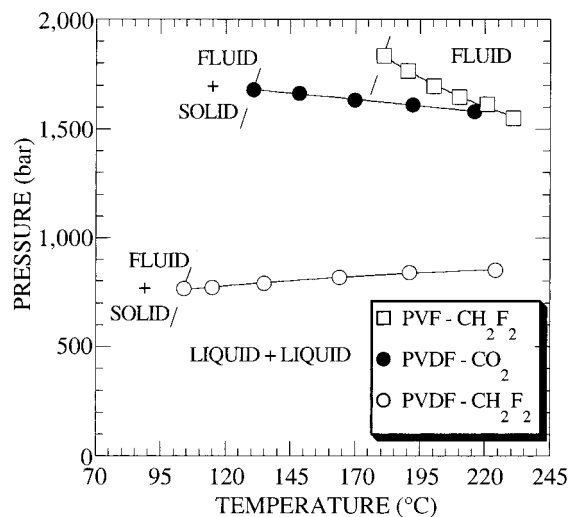

Figure 1. Experimental cloud-point curves for the PVF−CH_2F_2 system obtained in this study compared to the PVDF−CO_2 and PVDF−CH_2F_2 systems reported in the literature.[18] The fluoropolymer concentration is ~5 wt % in each case. A single phase exists at conditions above each of the curves in this figure.

the point at which there is a 90% drop in transmitted light through the solution.

Materials

Table 1 lists the properties of the PVF, obtained from Scientific Polymer Products (Ontario, NY), and the PVDF (Kynar 741), obtained from Elf Atochem (King of Prussia, PA). Acetone (99.9% minimum purity, HPLC grade) and DME (99% minimum purity) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and ethanol (USP grade) was obtained from the Warner Graham Company (Cockeysville, MD). CO_2 (99.8% minimum purity) was obtained from Airgas Inc (Baltimore, MD) and CH_2F_2 was kindly donated by ICI-Klea (Wilmington, DE). All of the polymers and solvents were used as received.

Binary Phase Behavior

Figure 1 shows the phase behavior of the PVDF−CO_2,[18] PVF−CH_2F_2, and PVDF−CH_2F_2[18] systems. PVF is not soluble in CO_2 even to temperatures of 245 °C and pressures of 2700 bar probably as a result of the high dipole moment of PVF that favors PVF−PVF interactions relative to PVF−CO_2 interactions. PVF does dissolve in CH_2F_2 although temperatures in excess of 180 °C and pressures of 1500 bar and higher are needed. A PVF crystallization boundary is observed in CH_2F_2 at 180 °C and ~1900 bar. CH_2F_2 is a better solvent for PVF compared to CO_2 since CH_2F_2 has a large dipole moment in addition to a high density at cloud-point conditions. A dramatic difference is also reported between the phase behavior of PVDF in CO_2 and in CH_2F_2.[18] It is possible to dissolve PVDF in CH_2F_2 at pressures from 750 to 900 bar and temperatures from 100 to 225 °C. However, to dissolve PVDF in CO_2 it takes pressures in excess of 1600 bar at temperatures of 130 to 215 °C although in an earlier study it was reported that PVDF did not dissolve in CO_2 at temperatures as high as 300 °C and pressures to 2750 bar.[29] It is important to note that the PVDF used in an earlier study contained significant amounts of cross-linked gel material resulting from the polymerization process used to synthesize this material. This gel material remains insoluble even in liquid solvents. The PVDF used in the present cosolvent study is synthesized by a different process, which does not result in the formation of cross-linked polymer gel. The less severe condi-
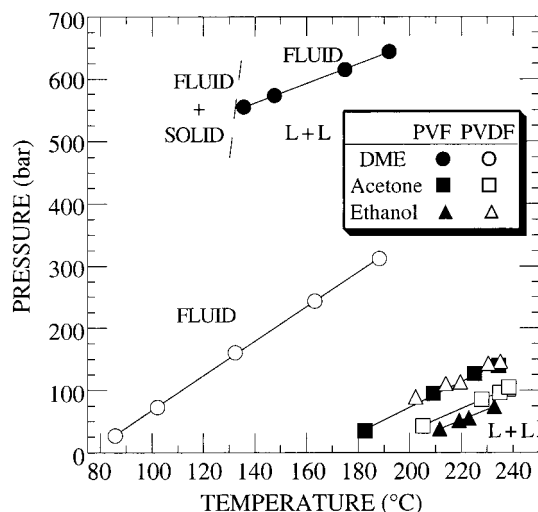
Figure 2. Experimental cloud-point curves for PVDF and PVF in acetone, DME, and ethanol. The fluoropolymer concentration is ~5 wt % in each case.
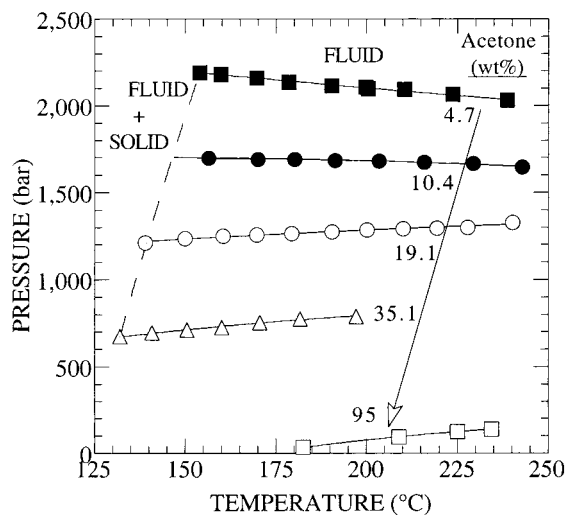

Figure 3. Effect of acetone on the phase behavior of the PVF−CO_2 system. The PVF concentration is ~5 wt % in each case.

Figure 4. Effect of DME on the phase behavior of the PVF−CO_2 system. The PVF concentration is ~5 wt % in each case.

tions needed to dissolve PVDF in CH_2F_2 likely result from a closer match of the polar character of a PVDF repeat unit with the dipolar character of CH_2F_2 as compared to the quadrupolar character of CO_2 since the polarizabilities of these two SCF solvents are reasonably close. These phase behavior results suggest that a polar cosolvent should have a large impact on the phase behavior of either of these two fluoropolymers in CO_2.

Figure 2 shows the phase behavior of PVDF and PVF in dimethyl ether (DME), acetone, and ethanol, the three cosolvents used in this study. Although DME is polar, it is not as good a solvent for either fluoropolymer as are ethanol and acetone. PVF crystallizes from solution in DME at approximately 130 °C and 550 bar which is ~50 °C lower than that observed from CH_2F_2. It is interesting that ethanol is a better solvent for PVF than for PVDF, whereas just the opposite behavior is observed with acetone. Nevertheless, both ethanol and acetone are excellent solvents for these fluoropolymers since a single-phase region is maintained at pressures as low as ~100 bar to temperatures as high as 220 °C.

Ternary Phase Behavior with CO_2

Experimental cloud-point curves are reported in Figure 3 for the PVF−CO_2−acetone system. The strong dipole moment of
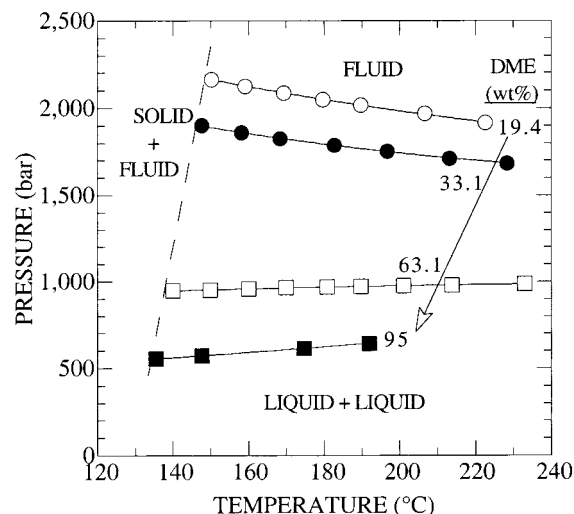
acetone significantly lowers the pressures needed to obtain a single phase. With 4.7 wt % acetone it is now possible to solubilize PVF at pressures of 2200 bar at 200 °C. Note that the effect of acetone diminishes with the increasing amount of acetone added to CO_2. This "diminishing returns" effect with increasing cosolvent concentration is observed with all of the cosolvents, and it has been observed with many other polymer−SCF mixtures.[28] All of the cloud-point curves shown in Figure 3 are virtually flat, and they terminate at a PVF crystallization boundary with the exception of the PVF−acetone curve which intersects the liquid/vapor boundary at a lower critical end point.[27] The crystallization boundary decreases from 187 °C for neat PVF, to 155 °C with 4.7 wt % acetone added to the mixture, and to 130 °C with 35.1 wt % acetone added to the mixture. The location of the crystallization boundary is a compromise between the effect of hydrostatic pressure, which increases the crystallization temperature, and the solubility of the solvent mixture in the polymer-rich phase, which depresses the crystallization temperature. The data in Figure 3 also suggest that CO_2 would make an ideal antisolvent to force the precipitation of PVF from a PVF−acetone mixture based on the location of the pure acetone curve and the 35.1 wt % acetone curve, i.e., a small amount of CO_2 has a large impact on the location of the cloud-point curve.

Experimental cloud-point curves are reported in Figure 4 for the PVF−CO_2−DME system. It is apparent that DME is not as effective a cosolvent as acetone since much higher pressures are needed to obtain a single phase. For example, 19.4 wt % DME is needed to shift the cloud-point curve to ~2100 bar, whereas the same cloud-point pressures are obtained with only 4.7 wt % acetone. Cloud-point pressures with ~63 wt % DME, ~900 bar, are similar to those obtained with ~27 wt % acetone. Acetone is a better cosolvent than DME since acetone has a higher dipole moment and it is denser than DME at the same temperatures and pressures. Once again it is apparent that the reduction in cloud-point pressure decreases with increasing amount of DME added to the solution. Note that the crystallization temperature of PVF changes less with increasing DME concentration than it does with increasing acetone concentration, which also implies that DME is not a particularly strong cosolvent.

The cosolvent effect of ethanol is also less than that of acetone for PVF as indicated by the location of the PVF−CO_2−ethanol cloud-point curves shown in Figure 5. As reported for the other
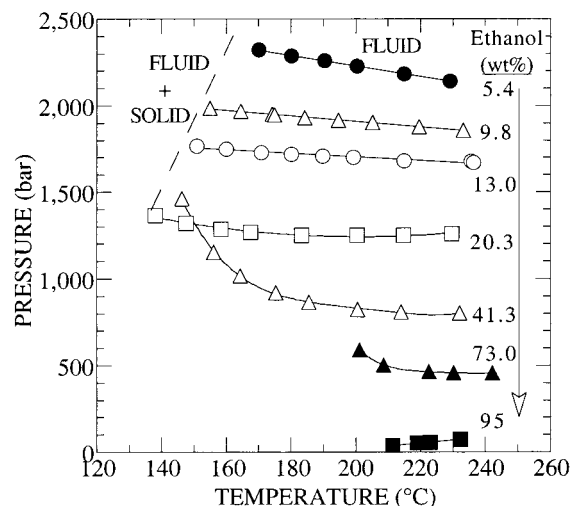
Comparison of the Solubility of PVF and PVDF

J. Phys. Chem. B, Vol. 103, No. 14, 1999 **2821**

Figure 5. Effect of ethanol on the phase behavior of the PVF$-CO_2$ system. The PVF concentration is ∼5 wt % in each case.

Figure 6. Effect of acetone on the phase behavior of the PVDF$-CO_2$ system. The PVDF concentration is ∼5 wt % in each case.

Figure 7. Effect of DME on the phase behavior of the PVDF$-CO_2$ system. The PVDF concentration is ∼5 wt % in each case.

Figure 8. Effect of ethanol on the phase behavior of the PVDF$-CO_2$ system. The PVDF concentration is ∼5 wt % in each case.

cosolvents, the magnitude in the reduction in cloud-point pressure decreases with increasing amounts of ethanol added to the solution. Also note that the 41.4 wt % ethanol cloud-point curve increases in pressure when the temperature is lowered below 170 °C which suggests that the interchange energy favors ethanol−ethanol interactions relative to ethanol−PVF interactions at these lower temperatures. This is not surprising since cross association between ethanol and PVF repeat units is not expected to occur to any great extent although ethanol self-association will occur as the concentration of ethanol in solution increases and as the temperature is lowered. With 73.0 wt % ethanol in solution the cloud-point curve increases in pressure at the higher temperature of ∼190 °C in agreement with the expectation that ethanol−ethanol hydrogen bonding should increase with decreasing temperature. Hence, ethanol is a good cosolvent for polar PVF as long as the concentration is modest or the temperature is high as has also been observed in several other copolymer−SCF−ethanol studies.[30−32] Pure ethanol is an excellent solvent for PVF as shown in Figure 5. Once again it is apparent that CO_2 is an excellent antisolvent for PVF−ethanol mixtures since it only takes small amounts to precipitate PVF from solution. The crystallization temperature of PVF also decreases in a manner similar to that exhibited by acetone except at high ethanol concentrations as just noted. The phase behavior shown in Figures 3, 4, and 5 suggest that to dissolve PVF a polar, non-hydrogen bonding cosolvent is needed with supercritical CO_2 so that extreme pressures are not required.

The phase behavior of the PVDF−CO_2−cosolvent system is expected to exhibit many of the same trends already described for the PVF systems. However, the pressures needed to obtain a single phase should be lower with PVDF compared to PVF since CO_2, by itself, can dissolve PVDF although it does not dissolve PVF. Figure 6 shows the phase behavior for the PVDF−CO_2−acetone system. As expected, the PVDF−CO_2−acetone cloud-point curves are at lower pressures relative to those of PVF−CO_2−acetone system with the same amount of acetone. Moreover, the slopes of the PVDF−CO_2−acetone cloud-point curves are more positive than those of the PVDF−CO_2−acetone system. The same diminishing returns for lowering cloud-point pressures with increasing acetone concentration is observed here with PVDF as with PFV. Likewise, the crystallization of PVDF is also decreased quite significantly with increasing acetone concentration.

Figure 7 shows the cloud-point curves for the PVDF−CO_2−DME system. As with the PVF system, DME is not as effective
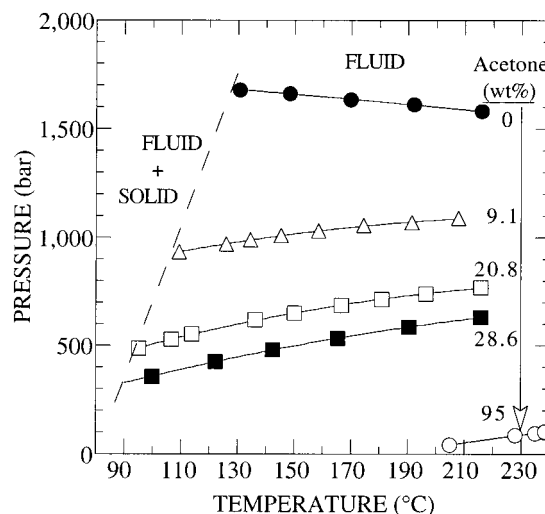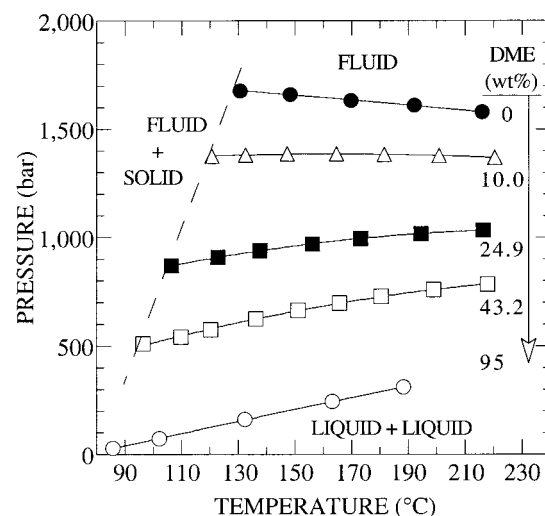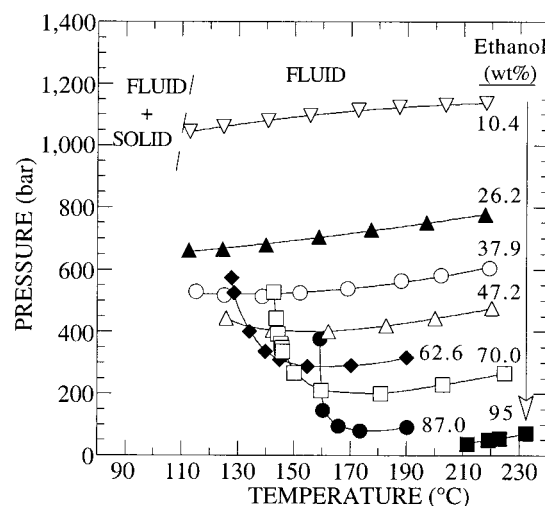
a cosolvent for PVDF as is acetone since DME has a smaller dipole moment and it has a lower density at the same temperatures and pressures. Figure 8 shows that ethanol is a better cosolvent for PVDF than it is for PVF even though Figure

2 showed that ethanol is a slightly better pure solvent for PVF than PVDF. However, it is now very apparent that large amounts of ethanol in solution can cause the cloud-point curve to increase quite rapidly as the temperature is decreased. The cloud-point pressure increases at ~140 °C with 62.6 wt % ethanol in solution, at ~150 °C with 70.0 wt % ethanol, and at ~160 °C with 87.0 wt % ethanol. A single phase is obtained at 210 °C with pure ethanol which is apparently a high enough temperature so that ethanol–ethanol interactions do not dominate the interchange energy and cause the cloud-point curve to increase sharply in pressure. Acetone is the preferred cosolvent for PVDF even though the decrease in pressure with increasing cosolvent concentration is virtually identical to that observed with ethanol since acetone does not self-associate and, hence, behave as an antisolvent.

Conclusions

A polar supercritical fluid solvent is needed to solubilize polar PVF and PVDF. Not surprisingly, the cloud-point pressures of these two polymers are lower in CH_2F_2 than those in CO_2 since CH_2F_2 has a significant dipole moment and it is a very dense solvent. PVF is more difficult to solubilize than PVDF because it is slightly more polar and it has a higher melting temperature which reflects stronger monomer–monomer interactions. To increase the solvent power of CO_2, a polar cosolvent is used. Acetone is a better cosolvent for both PVF and PVDF, compared to DME since acetone is also a better pure component solvent for these two fluoropolymers. Although ethanol is a good cosolvent, it self-associates at high solution concentrations and low temperatures, causing it to act as an antisolvent rather than a cosolvent. It is also interesting to note that small amounts of CO_2 added to the polymer–cosolvent mixtures causes a large increase in the pressures needed to obtain a second phase. At these low concentrations, CO_2 acts as an effective antisolvent.

It remains a challenge to model high-pressure, fluoropolymer–SCF solvent–cosolvent phase behavior. In preliminary modeling studies with the SAFT equation of state it is possible to mimic the phase-behavior trends observed in this study; however, the calculated behavior is only qualitatively correct, and empirical methods are used for calculating pure component fluoropolymer parameters. More work with the SAFT equation of state is in progress.

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