Cosolvency Effect of SF$_6$ on the Solubility of Poly(tetrafluoroethylene-*co*-19 mol % hexafluoropropylene) in Supercritical CO$_2$ and CHF$_3$

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ABSTRACT: Cloud-point data to 280°C and 2800 bar are reported for a binary mixture of poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP$_{19}$) in fluoroform (CHF$_3$) and for ternary mixtures of FEP$_{19}$–CHF$_3$–sulfur hexafluoride (SF$_6$) and FEP$_{19}$–CO$_2$–SF$_6$. FEP$_{19}$ does not dissolve in CHF$_3$ at a temperatures less than 235°C due to strong dipolar CHF$_3$–CHF$_3$ interactions relative to FEP$_{19}$–CHF$_3$ cross interactions. However, FEP$_{19}$ dissolves in CO$_2$ if the temperature is greater than $\approx$185°C and the pressure is in excess of 1000 bar. When SF$_6$ is added to either FEP$_{19}$–CO$_2$ or FEP$_{19}$–CHF$_3$ mixtures, the cloud-point curve is shifted to lower pressures and temperatures due to the increase in favorable dispersion interactions with nonpolar FEP$_{19}$. The magnitude of the shift in cloud-point pressure per amount of SF$_6$ added to solution decreases in a nonlinear manner with increasing amounts of SF$_6$. The Sanchez-Lacombe equation of state can model the binary FEP$_{19}$-SCF data if the FEP$_{19}$–CO$_2$ and FEP$_{19}$–CHF$_3$ binary interaction parameters are allowed to vary with temperature. However, a poor representation is obtained for the ternary phase behavior. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2039–2045, 1999

Key words: supercritical fluids; fluorocopolymer; phase behavior; modeling

INTRODUCTION

Many studies have reported that a polar cosolvent can shift a polymer-supercritical fluid (SCF) solvent cloud-point curve to much lower temperatures and pressures.[1–8] The work presented herein demonstrates the impact of a nonpolar cosolvent, sulfur hexafluoride (SF$_6$), on the phase behavior of a nonpolar fluorocopolymer, poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP$_{19}$), in two SCF solvents, CO$_2$ and

fluoroform (CHF$_3$). A cosolvent can enhance copolymer solubility if it possesses physical properties that increase favorable energetic interactions with the copolymer of interest. Dispersion-type forces are expected to be the dominant attractive forces between segments of FEP$_{19}$ given that tetrafluoroethylene and hexafluoropropylene repeat units exhibit characteristics of nonpolar fluorinated alkanes. The FEP$_{19}$ used in this study has a weight-average molecular weight of $\approx$210,000[9] and is end-capped with carboxylic acid groups that amount to approximately 1000 mass-ppm groups, which should have only a modest effect on the phase behavior of this copolymer.[10] Mertdogan et al.[11] have also shown that CO$_2$ is a rather weak solvent for FEP$_{19}$ due to the CO$_2$ quadrupolar self-interactions that are much

Table I   Physical Properties of the Solvents Used in this Study[23,28,29]

Solvent	Critical Temperature (°C)	Critical Pressure (bar)	Critical Density (g/cm^3)	Polarizability (Å^3)	Dipole Moment (Debye)
CO_2	31.0	73.8	0.469	27.1	0.0
CHF_3	26.2	48.6	0.528	26.5	1.6
SF_6	45.5	37.6	0.735	54.6	0.0

The polarizabilities of CHF_3 and SF_6 were calculated using the method of Miller and Savchik.[30] CO_2 has a quadrupole moment of -4.3 erg$^{1/2} \cdot$ cm$^{5/2} \cdot 10^{-26}$.

greater than FEP_{19}–CO_2 or FEP_{19}–FEP_{19} interactions at temperatures below 185°C. The experimental study described herein is similar in principle to data reported by Kiran and coworkers for polyethylene-alkane-CO_2 mixtures.[12–15] Kiran uses CO_2 as an antisolvent because it adds polar interactions to the solvent mixture, which decreases the SCF alkane solvent quality for nonpolar polyethylene. In addition, CO_2 dilates the alkane solvent, which lowers the solvent mixture density and further reduces solvent quality.

Table I lists the properties of the three SCF solvents chosen for the study. Because nonpolar SF_6 has been shown to be an excellent SCF solvent for FEP_{19},[11] varying amounts of SF_6 are added to a solution of FEP_{19} in CO_2 to determine the concentration of SF_6 that is needed to diminish the impact of quadrupolar CO_2–CO_2 interactions on the phase behavior. The cloud-point curve of the FEP_{19}–CHF_3 system is also measured so that the impact of dipolar solvent-solvent interactions can be compared with quadrupolar CO_2–CO_2 interactions. Likewise, SF_6 cosolvent data are determined for the FEP_{19}–CHF_3 system to ascertain the magnitude of the shift of the cloud-point curve with cosolvent concentration.

EXPERIMENTAL

Experimental cloud-point data are obtained using equipment and techniques described in detail elsewhere.[11,16] Polymer solubilities are reported as cloud points obtained at a fixed polymer composition of ≈5 wt %, the expected maximum in the P-x isotherms.[11,17–19] 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 the point at which there is a 90% drop in transmitted light through the solution. Each cloud point is mea-

sured to within ±3 bar and ±0.4°C and are reproduced two or three times to within ±5.0 bar and ±0.4°C.

Materials

The FEP_{19} was kindly donated by The DuPont Company. More detailed information on the characteristics of FEP_{19} are given by Tuminello,[9] where FEP_{19} is designated LMFEP-2 and by Mertdogan et al.[10] The hexafluoropropylene content (19.3 mol %) was determined spectroscopically and the weight-average molecular weight (210,000) was calculated from low strain rate melt viscosity. CO_2 (Bone Dry grade, 99.8% minimum purity) was obtained from Airgas Inc. (Baltimore, MD) CHF_3 (98% minimum purity) was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). SF_6 (CP grade, 99.0% minimum purity) was obtained from MG Industries (Allentown, PA). All of the solvents were used as received.

RESULTS AND DISCUSSION

Figure 1 shows the cloud-point behavior of the FEP_{19}–CHF_3, –CO_2, and –SF_6 systems as an initial reference for binary FEP_{19}-SCF solvent phase behavior. CO_2 is a poor quality solvent for FEP_{19} because pressures in the range of 1000 bar are needed to obtain a single phase, as shown in Figure 1. The sharp rise in the cloud-point pressure near 185°C is attributed to the increase of enhanced CO_2–CO_2 quadrupolar interactions relative to FEP_{19}–CO_2 cross interactions with decreasing temperature. At temperatures below 185°C, increased pressure does not help dissolve nonpolar FEP_{19} in quadrupolar CO_2.

The cloud-point pressures of the FEP_{19}–CHF_3 system in Figure 1 range from ≈1500 bar at

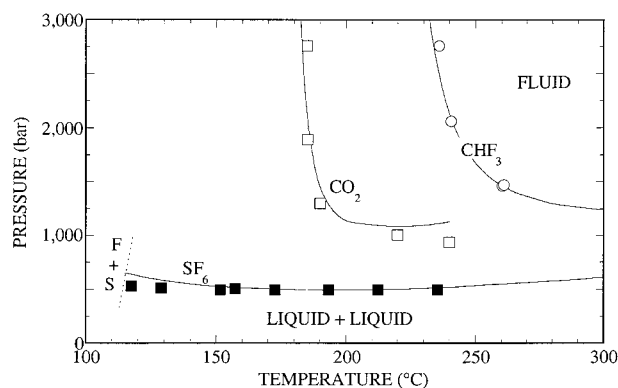**Figure 1** Experimental cloud-point data for mixtures of ≈5 wt % poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP$_{19}$) in SF$_6$, CO$_2$,[11] and CHF$_3$ where the symbols represent experimental data and the solid lines represent the cloud-point curve calculated using the Sanchez-Lacombe equation of state. The dashed line represents a crystallization boundary below which FEP$_{19}$ falls out of solution as a solid.

260°C to pressures in excess of 2000 bar as the temperature is lowered to 230°C. Compared with CO$_2$, CHF$_3$ is an even weaker solvent for FEP$_{19}$ due most likely to strong CHF$_3$–CHF$_3$ interactions that result from the large dipole moment, 1.6 Debye, of CHF$_3$. The characteristic shape of the FEP$_{19}$–CHF$_3$ cloud-point curve resembles that of the FEP$_{19}$–CO$_2$ system, which is the signature behavior of a binary mixture with a nonpolar and a polar component.[11,20,21]

Mertdogan and coworkers[11] have shown that nonpolar SF$_6$ is an excellent solvent for FEP$_{19}$. However, Figure 2 reveals that 5 wt % (2 mol %) SF$_6$ is not enough to prevent CO$_2$–CO$_2$ quadrupolar interactions from dominating favorable FEP$_{19}$–SF$_6$ interactions at temperatures below 170°C where the cloud-point curve rises rapidly in pressure. With 26 wt % (10 mol %) SF$_6$, the cloud-point curve does not exhibit a sharp rise in pressure but it does intersect an FEP$_{19}$ crystallization boundary at ≈150°C. With 47 wt % (23 mol %) SF$_6$, cloud-point pressures are reduced to ≈800 bar and the crystallization boundary is also lowered to ≈120°C, which is close to that observed for the FEP$_{19}$–SF$_6$ system.

The explanation for the cosolvency effect of SF$_6$ is twofold. First, SF$_6$ decreases the free volume of the solvent, or equivalently, increases the solvent density because SF$_6$ is more than twice as dense as CO$_2$. Second, SF$_6$ decreases the polarity of the mixed solvent because it is nonpolar. Note that the addition of SF$_6$ to the FEP$_{19}$–CO$_2$ mixture
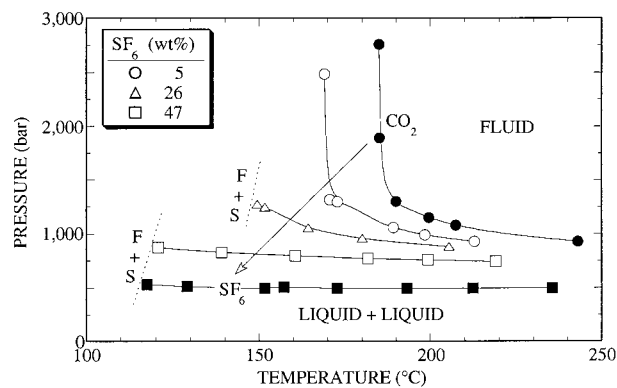

Figure 2 Effect of SF$_6$ as a cosolvent for 5 wt % poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) in CO$_2$ with the crystallization boundary denoted by the dashed lines.

causes a nonlinear decrease in cloud-point conditions. The cloud-point curve with 47 wt % SF$_6$ is much closer to the binary FEP$_{19}$–SF$_6$ curve than to the FEP$_{19}$–CO$_2$ curve even though on a molar basis the mixed solvent is predominantly CO$_2$.

In this study SF$_6$ is also used as a cosolvent to reduce the impact of dipolar CHF$_3$–CHF$_3$ interactions on the FEP$_{19}$–CHF$_3$ phase behavior. Figure 3 shows that SF$_6$ has a dramatic impact on the location of the cloud-point curve. Cloud-point pressures drop from 1500 bar to 1150 bar at 260°C with the addition of 9 wt % (5 mol %) SF$_6$. The addition of 51 wt % (35 mol %) SF$_6$ further lowers the cloud-point pressures to ≈800 bar. Once again the cloud-point conditions of the FEP$_{19}$-CHF$_3$-SF$_6$ system decrease in a nonlinear manner with SF$_6$ content. The curve with 51 wt %
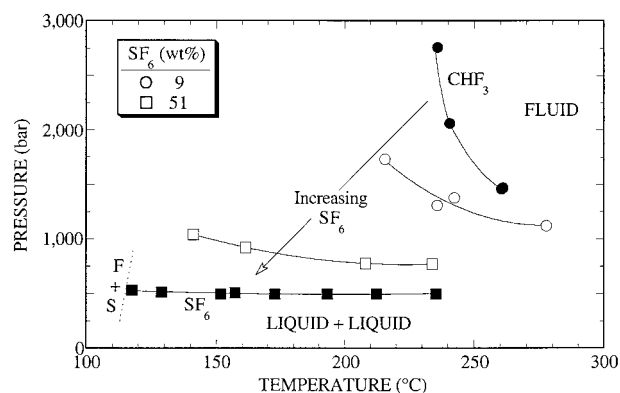

Figure 3 Effect of SF$_6$ as a cosolvent for 5 wt % poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) in CHF$_3$ with the crystallization boundary denoted by the dashed line.

SF_6 is much closer to the binary FEP_{19}–SF_6 curve than to the FEP_{19}–CHF_3 curve even though the solvent is predominantly CHF_3, on a molar basis. These cosolvent phase behavior studies suggest that it may be possible to process nonpolar fluorocopolymers in polar solvents, such as CO_2, if an appropriate cosolvent is used. The large decrease in cloud-point pressures with the addition of a small amount of cosolvent provides another advantage for using cosolvents as a processing aid.

Modeling

The Sanchez-Lacombe (SL) equation of state is used to model the FEP_{19}–SCF solvent–cosolvent phase behavior presented in this study. Previous results have shown that it is possible to model the phase behavior of a nonpolar fluorocopolymer in nonpolar or slightly polar solvents with the SL equation of state if one of the two semiempirical mixture parameters is allowed to vary with temperature.[11]

The SL equation of state is:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \quad (1)$$

where $\tilde{T}, \tilde{P}, \tilde{V},$ and $\tilde{\rho}$ are the reduced temperature, pressure, volume and density, respectively, that are defined as

$$\tilde{T} = T/T^* \quad T^* = \varepsilon^*/R \quad (2)$$

$$\tilde{P} = P/P^* \quad P^* = \varepsilon^*/v^* \quad (3)$$

$$\tilde{\rho} = 1/\tilde{v} = V^*/V \quad V^* = N(rv^*) \quad (4)$$

$$\rho^* = M/(rv^*) \quad (5)$$

where ε^* is the mer–mer interaction energy, v^* is the close-packed molar volume of a mer, M is the molecular weight, N is the number of molecules, r is the number of sites (mers) a molecule occupies in the lattice, and R is the universal gas constant. The equation for the chemical potential is given elsewhere.[16]

Table II lists the three characteristic, pure component parameters, $T^*, P^*,$ and ρ^*, obtained from a fit of the SL equation to the vapor pressure curves and saturated liquid densities of CO_2, CHF_3, and SF_6. The parameters are fit to a minimum of five vapor pressure and liquid density

Table II   Characteristic Pure-Component Parameters for the Solvents and Polymer of Interest for Use with the Sanchez-Lacombe Equation of State

Component	T^* (K)	P^* (bar)	ρ^* (g/cm^3)
CO_2	305.0	5745	1.510
CHF_3	287.2	4805	1.783
SF_6	336.4	2497	2.290
FEP_{19}	641.0	2771	2.134

The parameters for FEP_{19} are those reported for teflon.[25]

data points[22–24] to within 50°C of the critical temperature for each solvent. The calculated critical temperatures for these solvents are $\approx$4% too high; the calculated critical pressures are $\approx$13% too high for CHF_3 and $\approx$22% too high for CO_2 and SF_6; the calculated liquid densities are typically 20% too low for all of these solvents. An improved fit of the liquid densities could be obtained but it results in a worse fit of the critical temperature and pressure. Because experimental pure component data are not available for FEP_{19}, the characteristic parameters for PTFE are used for the calculations presented here.[25]

Mixing rules are needed to calculate the close-packed molar volume, v^*_{mix}, and the characteristic interaction energy, ϵ^*_{mix}, of the mixture. The mixing rule for v^*_{mix} is

$$v^*_{\text{mix}} = \sum_{i=1}\sum_{j=1} \varphi_i\varphi_j v^*_{ij} \quad (6)$$

where φ_i and φ_j are volume fractions and the subscripts i and j represent the two pure components. The cross term, v^*_{ij} is the arithmetic mean of the two pure-component characteristic volumes,

$$v^*_{ij} = \frac{1}{2}(v^*_{ii} + v^*_{jj})(1 - \eta_{ij}) \quad (7)$$

where η_{ij} is a fitted mixture parameter that adjusts the close-packed volume of polymer-solvent pair. The mixing rule for ϵ^*_{mix} is

$$\varepsilon^*_{\text{mix}} = \frac{1}{v^*_{\text{mix}}}\sum\sum \varphi_i\varphi_j\varepsilon^*_{ij}v^*_{ij} \quad (8)$$

where

$$\varepsilon_{ij}^* = (\varepsilon_{ii}^* \varepsilon_{jj}^*)^{0.5}(1 - k_{ij}) \qquad (9)$$

in which k_{ij} is a mixture parameter that corrects the energy of the mixture by accounting for specific binary interactions between components i and j not accounted for by the simple geometric-mean average.

Cloud points are calculated at 5 wt % copolymer in solution, neglecting the molecular weight distribution of the copolymer. Calculations are done first for the FEP$_{19}$–SF$_6$ system with the mixture parameters k_{ij} and η_{ij} set to zero. However, the slope of the calculated cloud-point curve was slightly positive rather than slightly negative as observed experimentally and the calculated cloud-point pressures were as much as 1000 bar too high. For nonpolar copolymer-solvent mixtures, such as FEP$_{19}$–SF$_6$, k_{ij} is not expected to be function of temperature because temperature-independent dispersion forces are the dominant type of interaction in operation. Therefore, in this instance, the mixture parameter, η_{ij} is adjusted to fit the FEP$_{19}$–SF$_6$ data. Figure 1 shows calculated results reported earlier[11] for the FEP$_{19}$–SF$_6$ cloud-point curve with k_{ij} equal to -0.240 and

$$\eta_{ij} = -0.003 \cdot (T(K) - 463) \qquad (10)$$

For the FEP$_{19}$–CO$_2$ and FEP$_{19}$–CHF$_3$ systems, k_{ij} is expected to vary inversely with temperature since quadrupolar and dipolar interactions are inversely proportional to temperature. Figure 1 shows the fit of the FEP$_{19}$–CO$_2$ curve with η_{ij} fixed at zero and

$$k_{ij} = 1954 \cdot [1/T(K)) - (1/463.2)] \qquad (11)$$

and the fit of the FEP$_{19}$–CHF$_3$ system also with η_{ij} fixed at zero and

$$k_{ij} = 966 \cdot [(1/T(K)) - (1/517)] \qquad (12)$$

For ternary phase behavior calculations it is necessary to determine binary mixture parameters for the CO$_2$–SF$_6$ and the CHF$_3$–SF$_6$ systems. Unfortunately, there is only a small amount of binary data for the CO$_2$–SF$_6$ system available in the literature[26,27] and, to the best of our knowledge, there are no data for CHF$_3$–SF$_6$ system available in the literature. Enick and coworkers[27] and Kiran and coworkers[26] present volumetric data for CO$_2$–SF$_6$ mixtures from 21 to 157°C for a variety of concentrations ranging from 0 to 100%
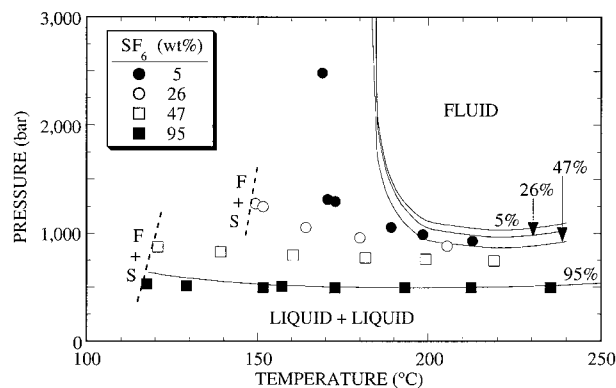

Figure 4 Comparison of the calculated and experimental cloud-point data of ≈5 wt % poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) in CO$_2$ with SF$_6$ as a cosolvent where the symbols represent experimental data, the solid lines represent cloud-point curves calculated using the Sanchez-Lacombe equation of state, and the dashed lines represent experimental crystallization boundaries.

SF$_6$, but the authors do not report the phase boundaries for these mixtures. It is not possible to obtain a quantitative fit of CO$_2$–SF$_6$ liquid densities over the entire concentration and temperature range with single values for the two binary parameters. Values of k_{ij} near -0.050, give a reasonable fit of the densities at low SF$_6$ concentrations whereas larger values of k_{ij} near 0.050 give a better fit of mixture densities at high SF$_6$ concentrations. Likewise, values of η_{ij} greater than zero give a better fit of densities at low SF$_6$ concentrations whereas values less than zero give a better fit of densities at high SF$_6$ concentrations. Therefore, to minimize the number of adjustable parameters, both k_{ij} and η_{ij} for the CO$_2$–SF$_6$ binary pair are set equal to zero because these values provide an adequate fit of the densities at midconcentrations of SF$_6$. There are no CHF$_3$–SF$_6$ data available in the literature, hence both k_{ij} and η_{ij} for this binary pair are set equal to zero.

Figure 4 shows a comparison of the calculated and experimental cloud-point data for mixtures of ≈5 wt % FEP$_{19}$ in CO$_2$ with SF$_6$ as a cosolvent. Calculations are performed allowing k_{ij} for the FEP$_{19}$–CO$_2$ binary pair to vary for temperatures between 240 and 185°C, but then remain fixed at the value at 185°C, 0.048, for calculations at lower temperatures. A very poor prediction of the FEP$_{19}$-CO$_2$-SF$_6$ phase behavior is obtained because the calculated cloud-point curves rise sharply with decreasing temperature for all combinations of cosolvent concentrations examined.
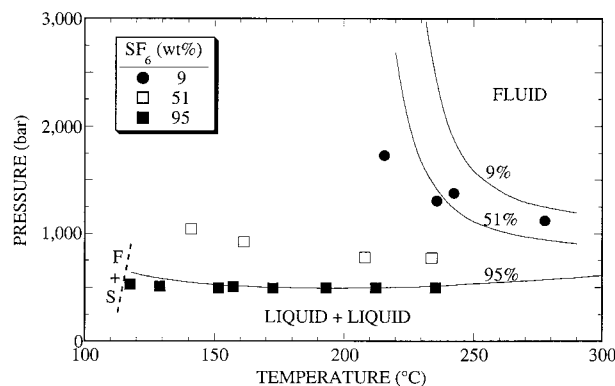
Figure 5 Comparison of the calculated and experimental cloud-point data of ≈5 wt % poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) in CHF_3 with SF_6 as a cosolvent where the symbols represent the experimental data, the solid line represents cloud-point curves calculated using the Sanchez-Lacombe equation of state, and the dashed line represents an experimental crystallization boundary.

The fit of the ternary data is not improved with nonzero k_{ij} values for the CO_2–SF_6 binary pair. Neither is the fit of the calculated curves improved if k_{ij} for the FEP_{19}–CO_2 binary pair is determined by extrapolating eq. (11) to temperatures below 185°C. Apparently, the k_{ij} parameter of the FEP_{19}–CO_2 binary pair dominates the phase behavior calculations even at high temperatures. The results from these calculations suggest that it is not feasible to extrapolate k_{ij} for the FEP_{19}–CO_2 binary pair to temperatures lower than those used to determine k_{ij}.

Figure 5 shows a very poor fit of experimental cloud-point data for mixtures of ≈5 wt % FEP_{19} in CHF_3 with SF_6 as a cosolvent. Calculations are performed allowing k_{ij} for the FEP_{19}–CHF_3 binary pair to vary for temperatures between 280 and 240°C, but then fixing the value determined at 240°C, 0.014, for calculations at lower temperatures. Once again, the fit of the data below 240°C is not improved if k_{ij} is allowed to vary according to equation 12 or if nonzero values of k_{ij} are used for the FEP_{19}–CHF_3 binary pair.

CONCLUSIONS

CO_2 is a feeble solvent for FEP_{19} because pressures in the range of 1000 bar are needed to obtain a single phase at temperatures above 185°C. Below 185°C, the cloud-point pressures rise sharply with decreasing temperature, which

is attributed to the increase in the strength of CO_2–CO_2 interactions relative to FEP_{19}–CO_2 interactions. The phase behavior of FEP_{19} in dipolar CHF_3 shows similar trends as those observed with CO_2. Pressures in excess of 1500 bar and temperatures greater than 230°C are needed to dissolve FEP_{19}. It is well known that the strength of polar interactions decreases with increasing temperature. Hence, because both CO_2 and CHF_3 have similar polarizability values, the strength of quadrupolar CO_2–CO_2 interactions must be less than that of dipolar CHF_3–CHF_3 interactions because FEP_{19} dissolves in CO_2 at lower temperatures compared with CHF_3. Lower pressures are needed to dissolve FEP_{19} in CO_2 compared with CHF_3 because CO_2 is the denser solvent at similar temperatures and pressures.

If nonpolar SF_6 is added as a cosolvent to FEP_{19}–CO_2 or FEP_{19}–CHF_3 mixtures, lower cloud-point pressures are observed and the cloud-point curve extends to lower temperatures. Interestingly, the impact of SF_6 for lowering cloud-point pressures and temperatures is highly nonlinear with respect to its molar amount in solution. These results suggest that it is feasible to use a small amount of a cosolvent to substantially improve the solvent quality of a supercritical fluid solvent for a polymer, consistent with the use of a cosolvent for nonpolymeric solutes.

Although the SL equation of state can capture the characteristics of the binary cloud-point behavior observed in this study if an empirical, temperature-dependent k_{ij} is used for the polar solvent-nonpolar polymer pair, it is not possible to predict the phase behavior for ternary mixtures. An alternative equation of state should be investigated for predicting the phase behavior of fluoropolymer-solvent solutions that contain a polar component.

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