

Thermodynamic Phase Behavior of Fluoropolymer Mixtures with Supercritical Fluid Solvents

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Abstract—Cloud-point experimental data were presented at temperatures up to 260 °C and pressures up to 2,500 bar for poly(vinylidene fluoride) (PVDF) [M_w =180,000 and 275,000] in CO₂, CHF₃, CHClF₂, and dimethyl ether (DME). Also, phase behavior curves were shown for the PVDF [M_w =180,000] in CO₂ with 1-propanol and 1-pentanol. Poly(vinyl fluoride) does not dissolve in CO₂ even at 215 °C and 2,500 bar, while poly(vinylidene fluoride) does dissolve in CO₂ at 220 °C and pressures of 1,700 bar. To dissolve poly(vinylidene fluoride) in dimethyl ether, pressures in excess of 200 bar and temperatures in excess of 165 °C are needed. The cloud-point behavior between the ternary PVDF [M_w =180,000]-CO₂-DME mixture shows a temperature range of 100-195 °C and pressure range of 350-1,360 bar by adding the 11, 29, and 60 wt% DME in cosolvent. The phase behavior for PVDF [M_w =180,000]-CHF₃-9, 19, and 40 wt% CHClF₂ system shows a temperature at below 200 °C and pressure up to 1,700 bar. The effect of CHClF₂ as a cosolvent for PVDF [M_w =275,000] in CO₂ decreased with the pressure increasing 10, 26, 40 and 61 wt% of cosolvent (CHClF₂) contents. Also, the effect of 15 and 40 wt% DME for the PVDF [M_w =275,000]-CHF₃ mixture shows temperature ranges of 120-206 °C and pressures up to 1,570 bar.

Key words: Phase Behavior, Poly(vinylidene fluoride), Supercritical Fluid Solvents, 1-Alcohol, Fluoropolymer

INTRODUCTION

Supercritical fluid solvents have been used in polymer processes such as monomer polymerization [DeSimone et al., 1992], fractionation [Mertdogan et al., 1997], extraction [Chang et al., 2000], swelling [Chun and Kim, 2002] and sustainable industries [Sarbu et al., 2000; Perrut, 2000]. Also, supercritical fluid solvents have been an attractive alternative to incompressible organic liquid solvents, since they can have liquid-like dissolving power while exhibiting transport properties of a gas. Particularly, supercritical carbon dioxide has been touted as the solvent of choice for many industrial applications because it is nonhazardous, inexpensive, nonflammable, nontoxic, and readily available.

Fluoropolymers are useful for a wide range of applications since they possess a unique combination of chemical, mechanical, and electrical properties. The solubility fluoropolymers depend on the number of fluorinated side groups and on the molecular weight of the hydrocarbon main chain. Especially, poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF) are important polymers due to chemical resistance, hard (good) mechanical properties and unique electrical properties [Newman et al., 1979; Hsu and Geil, 1984]. In the reported related research in this work, Lora et al. [1999] recently reported on the solubility of poly(vinyl fluoride) and poly(vinylidene fluoride) in supercritical CH₂F₂ and CO₂ and in CO₂ with acetone, dimethyl ether, and ethanol. The experimental data of reported cloud-point are presented at temperature to 245 °C and pressure to 2,700 bar for the binary and ternary systems. Also, Mertdogan et al. [1996, 1999] reported on the solubility of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in supercritical CO₂ and halogenated

supercritical solvents, and cosolvency effect of SF₆ on the solubility of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) in supercritical CO₂ and CHF₃.

In this work, the high pressure phase behavior of fluoropolymers (PVDF: M_w =180,000 and 275,000) in compressed liquid and supercritical CO₂, CHF₃, dimethyl ether and CHClF₂, with CO₂ in 1-propanol and 1-pentanol was measured at temperatures up to 260 °C and pressures as high as 2,500 bar.

EXPERIMENTAL SECTION

The cloud-point curves for the fluoropolymer-supercritical low molecular weight hydrocarbon mixtures were determined at pressures up to 3,000 bar and temperatures to 250 °C. Fig. 1 shows the schematic diagram of the experimental apparatus used for the fluo-

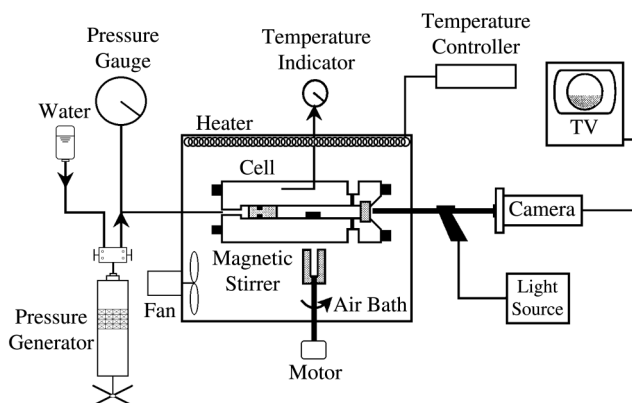


Fig. 1. Schematic diagram of the high-pressure experimental apparatus used in this study.

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ropolymer-SCF solvent phase behavior studies [Byun, 2002; Byun and Choi, 2002].

Experimental cloud-point data were obtained by using a high-pressure, variable-volume view cell. The variable-volume cell used to obtain the cloud-point curves was a static-type with a 1.59 cm I.D., an O.D. of 7.0 cm, and a working volume of $\sim 28 \text{ cm}^3$. A 1.9 cm thick sapphire window was fitted in the front part of the cell to allow observation of the phases. Typically $0.500 \pm 0.002 \text{ g}$ of fluoropolymer was loaded into the cell which was subsequently purged at room temperature with the solvent of interest at 3 to 6 bar to remove any entrapped air and organic solvents. Generally, 7.0 to $10.0 \pm 0.020 \text{ g}$ of solvent were transferred into the cell gravimetrically by using a high-pressure bomb. For the fluoropolymer-solvent-monomer systems, the liquid monomer was transferred into the cell to within $\pm 0.002 \text{ g}$ by using a syringe. The fluoropolymer mixture was compressed to the desired operating pressure by moving a piston located within the cell. The piston was moved by using water pressurized by a high-pressure generator (HIP Inc., model 37-5.75-60). The pressure of the mixture was measured with a Heise gauge (Dresser Ind., model CM-108952, 0 to 3,450 bar, accurate to within ± 3.5 bar). The temperature of the cell was measured with a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Yokogawa, model 7563, accuracy to within $\pm 0.005\%$). The system temperature was typically maintained to within $\pm 0.2^\circ\text{C}$ below 200°C , and $\pm 0.4^\circ\text{C}$ above 200°C . The mixture inside the cell could be viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model F100-038-000-50) placed against the outside of the sapphire window. A fiber optic cable connected to a high density illuminator (Dolan-Jenner Industries, Inc., model 180) and to the borescope was used to transmit light into the cell. The solution in the cell was well mixed by using a magnetic stir bar activated by an external magnet beneath the cell.

At a fixed temperature, the solution in the cell was compressed to a single phase. The solution was maintained in the one-phase region at the desired operating temperature for at least 30–40 min so that the cell could reach thermal equilibrium. The pressure was then slowly decreased until the solution reached cloud-point. The cloud-point pressure is defined as the point at which the mixture becomes so opaque that it is no longer possible to see the stir bar in the solution. The cell was again pressurized to a single phase, at least 150 bar above the cloud-point pressure, and maintained for at least 10 minutes. Cloud point measurements were repeated at least twice at each temperature, and were typically reproducible to within ± 3.0 bar at the highest temperatures. In the P-T region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within ± 5.0 bar. Typi-

cally, the lowest temperature of the cloud-point curves presented in this work represents either the highest pressure of the experimental apparatus or the location of the crystallization boundary of the fluoropolymer.

Materials: Poly(vinylidene fluoride) [$M_w=180,000$, $M_w/M_n=2.53$ and $M_w=275,000$, $M_w/M_n=2.57$] were obtained from Aldrich Chemical Co., Inc. Also, poly(vinyl fluoride) [fluoride content 41%, $T_g=41^\circ\text{C}$] was obtained from Scientific Polymer Products, Inc. The 1-propanol (99.5% purity) and 1-pentanol (98% purity) were obtained from Aldrich Chemical Co. and Junsei Chemical Co., respectively. Carbon dioxide (99.9% minimum purity) was obtained from Daesung Oxygen Co. (Yeosu, Chonnam). Fluoroform (98+ % minimum purity) was obtained from Aldrich Chemical Co., Inc. CHClF_2 (99.9% minimum purity) was obtained from Dongil Gas Co. Dimethyl ether (99.9% minimum purity) was obtained from Yeosu NCC Company. All of the solvents were used as received.

RESULTS AND DISCUSSION

The properties of the solvents and cosolvents used in this study are shown in Table 1 [Reid et al., 1987; Daubert and Danner, 1989]. For the poly(vinylidene fluoride)-solvents systems, CO_2 , CHF_3 , CHClF_2 and DME were used as solvents. For the poly(vinylidene fluoride)-solvents-cosolvents, 1-propanol and 1-pentanol were used as cosolvents.

CO_2 have the critical pressure, critical temperature, critical density and polarizabilities. However, CO_2 has a quadrupole moment but does not have a dipole moment. CHF_3 has the critical pressure, critical temperature, critical density, dipole moment and polarizabilities. CHClF_2 possesses a dipole moment (1.4 D). DME has both polarizability and dipole moment. The dipole moment increases in the order of $\text{CHF}_3 > \text{CHClF}_2 > \text{DME} > \text{CO}_2$. The polarizability has a CO_2 ($2.71 \times 10^{-25} \text{ cm}^3$), CHF_3 ($2.65 \times 10^{-25} \text{ cm}^3$), CHClF_2 (no literature) and DME ($52.2 \times 10^{-25} \text{ cm}^3$).

The critical temperatures for 1-propanol and 1-pentanol increase as the molecular weight increases, while the critical pressure and critical density for them decrease. The dipole moment has similar 1-propanol and 1-pentanol.

1. Phase Behavior of Binary System

The impact of polymer backbone architecture on fluoropolymer solubility in supercritical fluid solvents is studied by systematically varying the chemical type of the repeat units in the main chain. A variable-volume view cell, capable of operating to high temperatures and high pressures, was designed and implemented to meet these extreme operating conditions.

Fig. 2 shows the comparison between the phase behavior of ~ 5

Table 1. Properties of the solvent and cosolvent used in this study

Solvents	M_w	T_c ($^\circ\text{C}$)	P_c (bar)	ρ_c (g/cm^3)	Polarizability ($\text{cm}^3 \times 10^{-25}$)	Dipole moment (D)	ω
CO_2	44.0	31.0	73.8	0.469	26.5	0.0	0.225
CHF_3	70.	26.2	48.6	0.528	26.5	1.6	0.260
CHClF_2	86.5	96.1	49.7	0.525		1.4	0.221
DME	46.1	126.8	52.4	0.271	52.2	1.3	0.200
1-Propanol	60.1	263.6	51.7	0.274		1.7	0.623
1-Pentanol	88.1	315.0	39.1	0.270		1.7	0.579

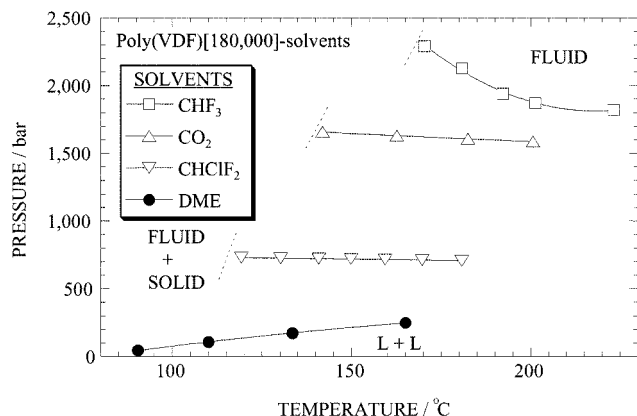


Fig. 2. Comparison of the cloud-point curve of poly(vinylidene fluoride) [$M_w=180,000$] in CO_2 , CHF_3 , CHClF_2 and DME. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

wt% PVDF [$M_w=180,000$] in CO_2 , DME, CHF_3 and CHClF_2 . As shown in Fig. 2, the phase behavior of the ~ 5 wt% PVDF [$M_w=180,000$]- CHF_3 mixture presents a negative slope with dissolution at a temperature of $\sim 225^\circ\text{C}$ and a pressure of $\sim 2,300$ bar. The cloud-point of the ~ 5 wt% PVDF [$M_w=180,000$] in CO_2 shows a plate slope at a temperature range of 140 – 200°C and a pressure of $\sim 1,600$ bar. Also, the solubility of the ~ 5 wt% PVDF [$M_w=180,000$]- CHClF_2 and -DME mixture presents a positive slope in lower pressure at a range of temperature of 90 to 180°C and a range of pressure of 45 to 730 bar. At 170°C , the phase behavior boundary has shifted from $2,100$ bar (CHF_3), $1,600$ bar (CO_2), 700 bar (CHClF_2) to 300 bar (DME).

Fig. 3 shows the phase behavior curve of PVDF [$M_w=275,000$] dissolved in supercritical CO_2 , DME, CHF_3 and CHClF_2 . The cloud-point behavior for PVDF [$M_w=275,000$]- CO_2 , CHF_3 and CHClF_2 system exhibits UCST curves with a negative slope. The phase behavior of PVDF [$M_w=275,000$]-DME mixture exhibits LCST curve

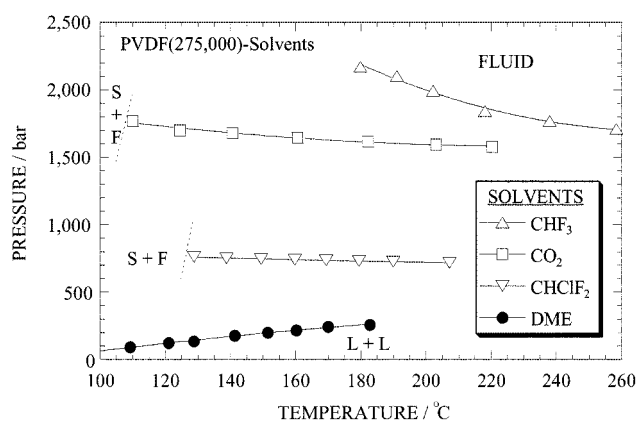


Fig. 3. Comparison of the cloud-point curve of poly(vinylidene fluoride) [$M_w=275,000$] in CO_2 , CHF_3 , CHClF_2 and DME. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

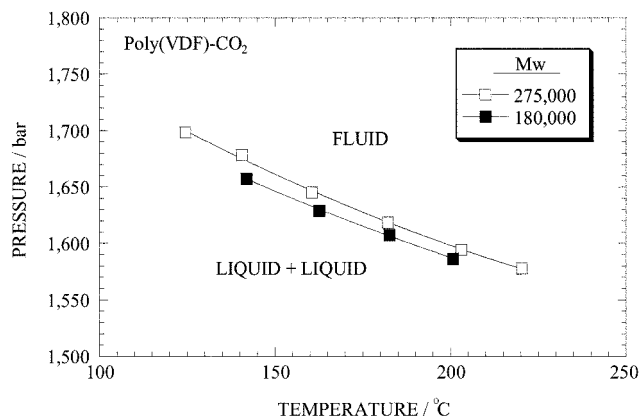


Fig. 4. Comparison the cloud-point curve of poly(vinylidene fluoride) [$M_w=180,000$ and $275,000$] in CO_2 . The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

with a positive slope. The PVDF [$M_w=275,000$]- CO_2 , CHF_3 and CHClF_2 system is present at the temperature range of 90 – 260°C and pressure to $2,170$ bar. At 180°C the phase behavior boundary has shifted from $2,200$ bar (CHF_3) to 300 bar (DME) and it is due to the polarizability difference of CHF_3 ($2.65 \times 10^{-25} \text{ cm}^3$) and DME ($52.2 \times 10^{-25} \text{ cm}^3$).

Fig. 4 shows a comparison between the cloud-point of ~ 5 wt% PVDF [$M_w=180,000$]- CO_2 and ~ 5 wt% PVDF [$M_w=275,000$]- CO_2 mixture. At 170°C , the pressure difference of solubility curve for ~ 5 wt% PVDF [$M_w=180,000$]- CO_2 and ~ 5 wt% PVDF [$M_w=275,000$]- CO_2 system has shifted from $1,620$ bar to $1,630$ bar, and this is due to the molecular weight difference.

Fig. 5 shows the comparison between the phase behavior of ~ 5 wt% PVDF [$M_w=180,000$]- CHClF_2 and ~ 5 wt% PVDF [$M_w=275,000$]- CHClF_2 system at a temperature range of 120 – 215°C and a pressure range of 706 – 760 bar. The pressure difference of the solubility curve for two systems has about 25 bar at 170°C .

2. Phase Behavior of Ternary System

Fig. 6 shows the effect of CHClF_2 on the cloud-point curves of the ~ 5 wt% PVDF [$M_w=180,000$]- CHF_3 system obtained in this study. The PVDF [$M_w=180,000$] does dissolve in pure CHF_3 to tem-

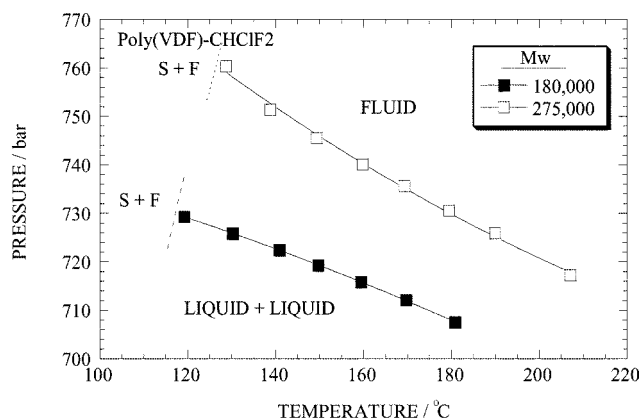


Fig. 5. Comparison the cloud-point curve of poly(vinylidene fluoride) [$M_w=180,000$ and $275,000$] in CHClF_2 . The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

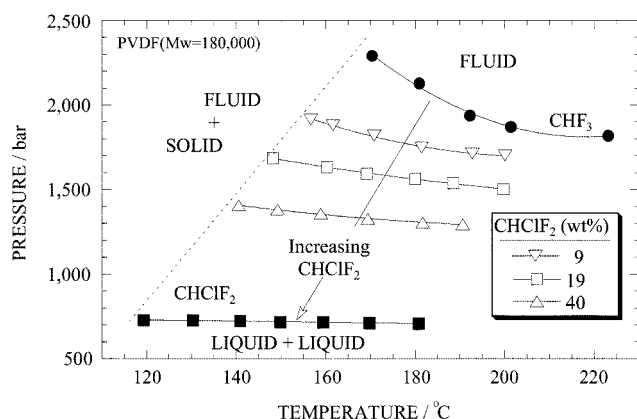


Fig. 6. Effect of CHClF_2 on the phase behavior of the poly(vinylidene fluoride) [$M_w=180,000$] in CHF_3 system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

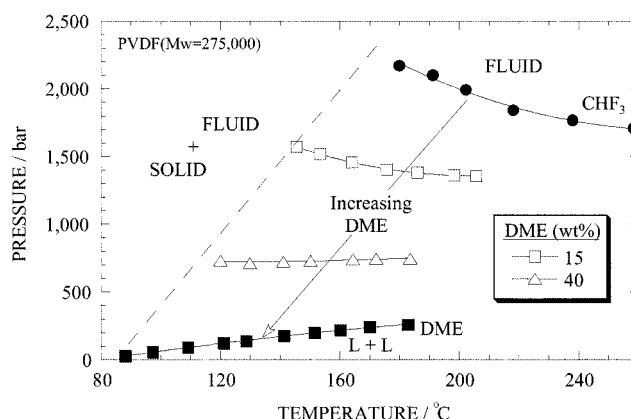


Fig. 8. Effect of DME on the phase behavior of the poly(vinylidene fluoride) [$M_w=275,000$] in CHF_3 system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

perature of 225 °C and pressure of 2,300 bar. When 9 wt% CHClF_2 is added to the PVDF [$M_w=180,000$]- CHF_3 solution, the cloud-point curve exhibits UCST-type phase behavior of the negative slope at temperature range from 157 to 200 °C. With 19 wt% CHClF_2 added to the solution, the cloud-point curve exhibits UCST-type phase behavior of a negative slope. The cloud-point curve shows a slight slope at 1,500–1,680 bar and at a temperature range of 148 to 200 °C. Also at 170 °C, the cloud-point pressure of the PVDF [$M_w=180,000$]- CHF_3 - CHClF_2 system decreases by ~ 200 bar with the first 9 wt% CHClF_2 addition to the solution, and it decreases by another ~ 400 bar with the addition of 18 wt% CHClF_2 . The phase behavior curve with 40 wt% CHClF_2 has a slightly negative slope at a temperature range from 140 to 190 °C and pressure to 1,400 bar.

Fig. 7 presents the cloud-point experimental behavior of the PVDF [$M_w=180,000$]- CO_2 -x wt% DME system data obtained in this study. The PVDF [$M_w=180,000$] does dissolve in pure CO_2 to a temperature of 200 °C and pressure of 1,658 bar. When 11 wt% DME is added to the PVDF [$M_w=180,000$]- CO_2 solution, the phase behavior exhibits UCST-type phase behavior of the slightly negative slope

at temperature range from 130 to 195 °C. Also with 29 wt% DME added to the solution, the cloud-point curve exhibits LCST-type phase behavior of the positive slope. At 160 °C, the cloud-point pressure of the PVDF [$M_w=180,000$]- CO_2 -DME system decreases by ~ 450 bar with the first 11 wt% DME addition to the solution, and it decreases by another ~ 350 bar with the addition of 31 wt%. When 60 wt% DME is added to the solution, the phase behavior curve exhibits LCST-type cloud-point behavior with a positive slope. The phase behavior curve with 60 wt% DME shows at a temperature range of 100 to 190 °C and a pressure range from 350 to 540 bar.

Fig. 8 shows the impact of the phase behavior of PVDF [$M_w=275,000$]- CHF_3 -x wt% DME mixture obtained in this work. With 15 wt% DME added to the solution, the cloud-point curve exhibits UCST type phase behavior with a negative slope. With 40 wt% DME in solution the cloud-point pressure remains virtually flat at 700 bar over a temperature range of 120 to 185 °C. As shown in Fig. 8, the PVDF [$M_w=275,000$]- CHF_3 -15 and 40 wt% DME system has lower cloud-point pressure as the DME increases.

Fig. 9 shows the effect of CHClF_2 on the phase behavior of the

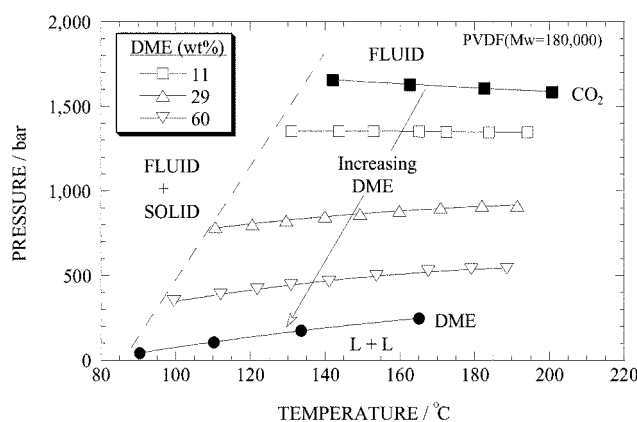


Fig. 7. Effect of DME on the phase behavior of the poly(vinylidene fluoride) [$M_w=180,000$] in CO_2 system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

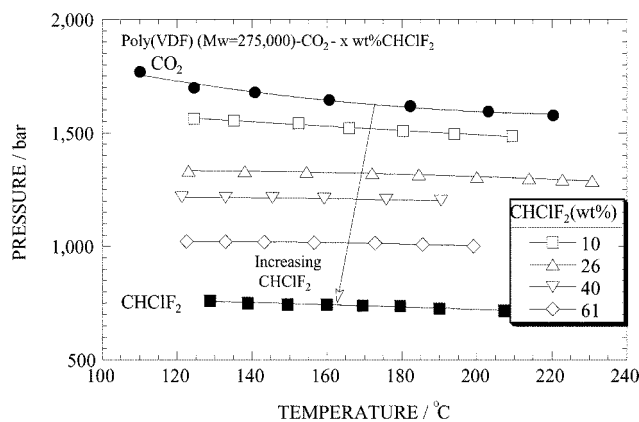


Fig. 9. Effect of CHClF_2 on the phase behavior of the poly(vinylidene fluoride) [$M_w=275,000$] in CO_2 system. The crystallization boundary is denoted by the dashed line. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

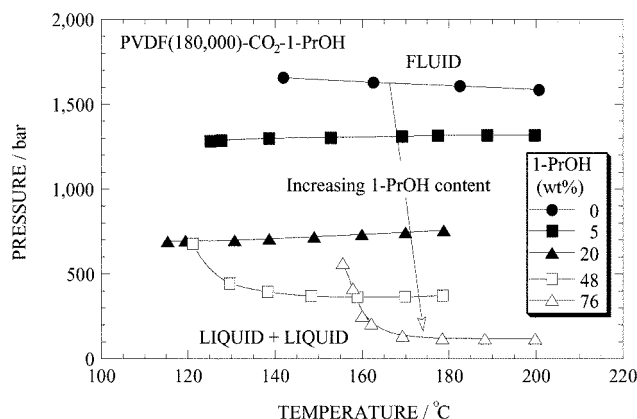


Fig. 10. Effect of 1-propanol on the phase behavior of the poly(vinylidene fluoride) [$M_w=180,000$] in CO_2 system. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

PVDF [$M_w=275,000$]- CO_2 mixture. The PVDF [$M_w=275,000$]- CO_2 -10, 26, 40, and 61 wt% CHClF_2 system presents a virtually flat pressure of 1,500 bar, 1,300 bar, 1,200 bar and 1,000 bar at constant temperature of 170 °C, respectively.

3. Phase Behavior of PVDF-Supercritical Solvents-1-Alkanol System

Fig. 10 shows the effect of 1-propanol on the cloud-point of the PVDF [$M_w=180,000$]- CO_2 system obtained in this work. The PVDF [$M_w=180,000$]- CO_2 -5 wt% 1-propanol mixture shows a virtually flat curve at a temperature range of 125–200 °C and pressure up to $\sim 1,300$ bar. When 20 wt% 1-propanol is added to the solution, the phase behavior exhibits LCST region cloud-point behavior with slightly positive slope. With 48 wt% 1-propanol in solution, the cloud-point curve is presented as almost virtually flat at a temperature range from 130 °C to 180 °C, and the phase behavior pressure increases rapidly at below 130 °C which suggests that the interchange energy favors 1-propanol 1-propanol interactions relative to 1-propanol PVDF interactions at these lower temperatures. If 76 wt% 1-propanol is added to the solution, the cloud point curve increases in pressure at the higher temperature of 165 °C in agreement with the expectation that 1-propanol 1-propanol hydrogen bonding should

increase with decreasing temperature.

Fig. 11 shows the impact of 1-pentanol on the phase behavior of the PVDF [$M_w=180,000$]- CO_2 -x wt% 1-pentanol system obtained in this work. With 5 and 16.7 wt% 1-pentanol in solution, the phase behavior shows virtually flat at a temperature range from 120 °C to 195 °C and pressure to $\sim 1,400$ bar and ~ 950 bar, respectively. The PVDF [$M_w=180,000$]- CO_2 -35, 53 and 77 wt% 1-pentanol mixtures shows the phase behavior curves of slowly increase at below 140 °C (35 wt%), 160 °C (53 wt%) and 180 °C (77 wt%).

CONCLUSION

A supercritical fluid solvent was used to solubilize polar PVDF. The cloud point pressures of these two poly(vinylidene fluoride) [$M_w=180,000$, $M_w/M_n=2.53$ and $M_w=275,000$, $M_w/M_n=2.57$] are lower in DME than those in CO_2 since DME is a very dense solvent and has a significant dipole moment.

The phase behavior for the systems supercritical CO_2 , CHF_3 , CHClF_2 and DME in PVDF is measured in changes of the pressure-temperature slope, and with cosolvent concentrations. The PVDF- CO_2 -DME (11, 29 and 60 wt%) and CHClF_2 (10, 26, 40 and 61 wt%) solution shows the appearance of a typical LCST and UCST region. The DME (15 and 40 wt%) and CHClF_2 (9, 19 and 40 wt%) for the PVDF- CHF_3 mixture shows a typical UCST region.

The solubility curve up to ~ 200 °C and 1,320 bar for PVDF ($M_w=180,000$)- CO_2 -1-propanol system shows the change of pressure-temperature and with 1-propanol concentration of 0, 5, 20, 48 and 76 wt%. The high pressure phase behavior for PVDF ($M_w=180,000$)- CO_2 -0, 5, 17, 35, 53 and 77 wt% 1-pentanol system shows the change of pressure-temperature curve from LCST region to U-LCST region as the 1-pentanol concentration increases.

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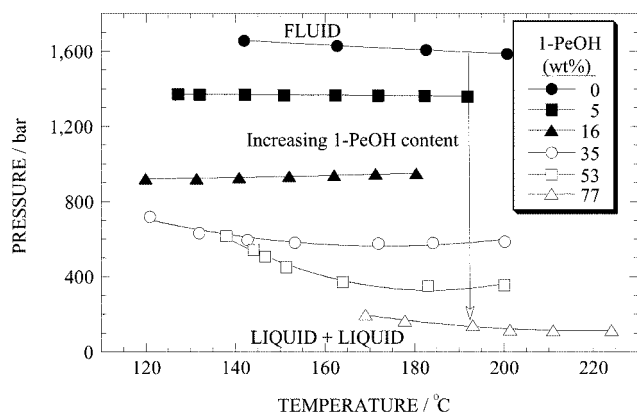


Fig. 11. Effect of 1-pentanol on the phase behavior of the poly(vinylidene fluoride) [$M_w=180,000$] in CO_2 system. The poly(vinylidene fluoride) concentration is ~ 5 wt% in each case.

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