Phase Behavior and Density of Polysulfone in Binary Fluid Mixtures of Tetrahydrofuran and Carbon Dioxide under High Pressure: Miscibility Windows

Wei Zhang, Erdogan Kiran

Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

ABSTRACT: Mixtures of tetrahydrofuran (THF) and carbon dioxide (CO_2) were identified as new solvent systems for polysulfone. The miscibility and density of polysulfone in binary fluid mixtures of THF and CO_2 were investigated from 300 to 425 K at pressures up to 70 MPa. The influence of the CO_2 and polysulfone concentrations was studied, with the concentrations of the other two components kept constant. At a 4.5 wt % polymer concentration, the demixing pressures in a 10 wt % CO_2 and 90 wt % THF mixture increased with temperature (310–425 K) from 15 to 40 MPa. With increasing CO_2 concentration (from ca. 10 to 14 wt %), a significant increase (from 15 to 70 MPa at 310 K) was observed in the demixing pressures. Furthermore, with an increasing amount of CO_2, the nature of the phase boundary shifted from lower critical solution temperature behavior to upper critical solution temperature behavior. The influence of the polymer concentration was studied in the 0–5 wt % range at two CO_2 levels, with solvent compositions of 10 wt % CO_2 and 90 wt % THF and 13 wt % CO_2 and 87 wt % THF.

The system with a higher level of CO_2 (13 wt %) showed highly unusual phase behavior: on pressure–composition and temperature–composition diagrams, the system displayed two distinct regions of miscibility. In the system with 10 wt % CO_2, the distinct regions of miscibility that were observed in the system with 13 wt % CO_2 partially overlapped and led to a W-shape phase boundary. The densities of the polymer solutions were measured from the one-phase region through the demixing point into the two-phase region at a constant temperature. No significant change in density was found around the phase boundary; this indicated that the coexisting phases had similar densities, as is often the case with liquid–liquid phase separation in polymer solutions under high pressure. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2357–2362, 2002

Key words: miscibility; polysulfone; supercritical fluids; high pressure

INTRODUCTION

Miscibility windows and islands are relatively new phase behaviors that have been receiving more attention in recent years.[1–7] These phenomena are usually explained by cosolvency effects; that is, a mixture of components B and C has better solubility in A than B or C alone. Most earlier studies have been concerned with fluid mixtures and not systems containing polymers. Schneider and coworkers[1–4] conducted several systematic studies and reported on the cosolvency effects and miscibility windows and islands of ternary systems with carbon dioxide (CO_2), 1-alkanol, and alkane. Wolf and coworkers[5–7] studied the cosolvency of one polymer (e.g., polystyrene) in two solvents (e.g., acetone and diethyl ether), finding that a mixture of two nonsolvents could make a good solvent for a polymer. This appears to be the only publication in the literature that reports on miscibility windows under high pressure for polymer–solvent systems. In the investigations by Wolf and coworkers, the miscibility windows of the ternary polymer systems were identified as a function of the concentration of the solvent mixture, with the polymer concentration kept constant. The study reported in this article was carried out to investigate the phase behavior of polysulfone in mixtures of a good solvent, tetrahydrofuran (THF), and a nonsolvent, CO_2, in the supercritical region and to evaluate these fluid mixtures containing CO_2 as new solvent systems for polysulfones. The results show unique phase behavior with multiple miscibility regions. This system differs from earlier studies in that the miscibility windows are observed in a fluid mixture in which one of the solvent components is already a good solvent for the polymer. Therefore, the observed phenomenon is different from traditional cosolvency effects.

EXPERIMENTAL

Materials

Polysulfone polymers were obtained from Scientific Polymer Products (Ontario, NY). The molecular weights
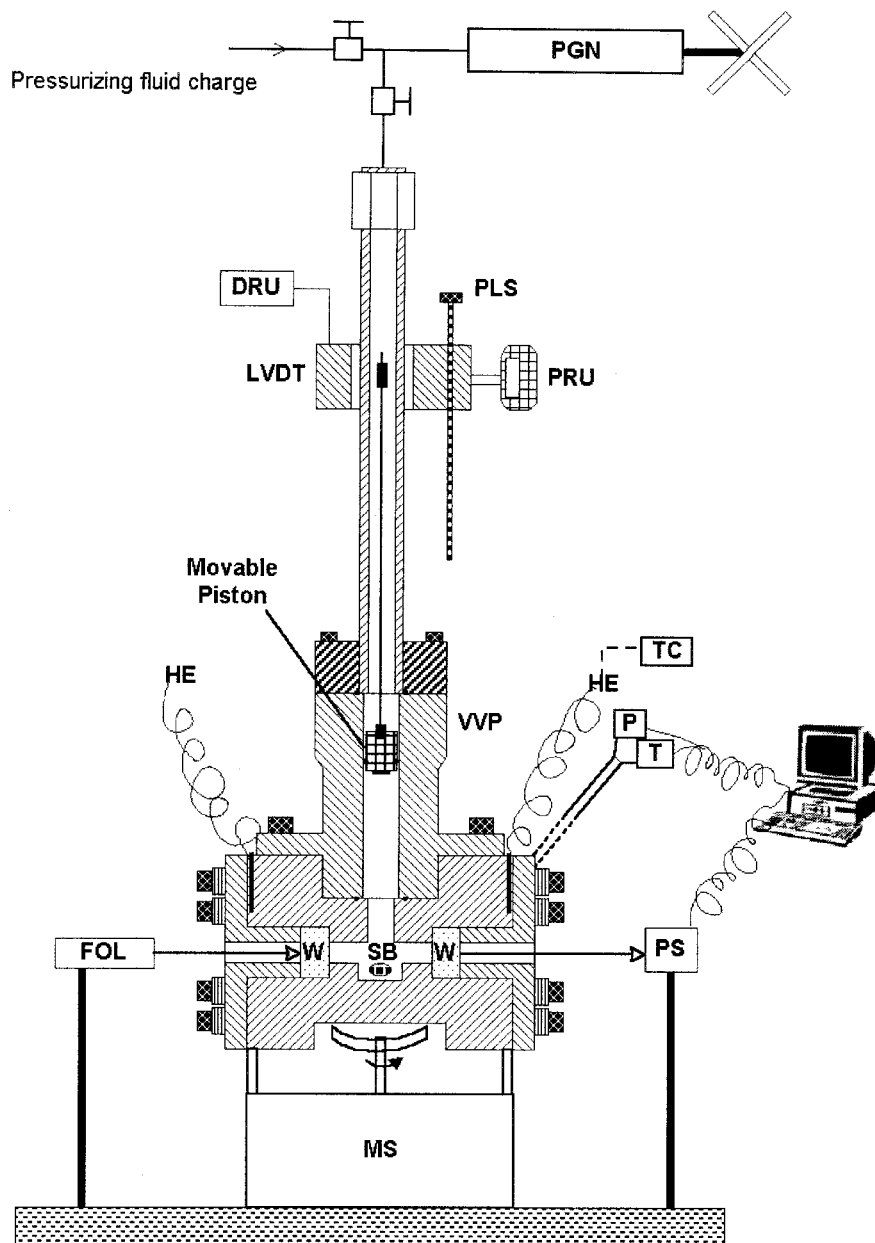
Figure 1 Schematic diagram of the view cell for the determination of the miscibility conditions and densities. PGN = pressure generator; DRU = digital voltage readout unit; PRU = position readout unit; PLS = position locator screw; LVDT = linear variable differential transformer; TC = temperature controller; HE = cartridge heating elements; VVP = variable volume part housing the movable piston; P = pressure; T = temperature; FOL = fiber optical illuminator; W = sapphire window; SB = stirring bar; PS = photodiode sensor; MS = magnetic stirrer.

were (1) M_w = 68,621 and M_n = 37,978 and (2) M_w = 60,206 and M_n = 32,683. THF (purity > 99.5 %) was obtained from Burdick & Jackson (Muskegon, MI). CO_2 was obtained from Air Products and Chemicals (Allentown, PA) with a purity greater than 99.99%. The polymers and solvents were used without further purification.

Determination of the demixing pressures and densities

Figure 1 shows a schematic diagram of the variable-volume view cell used in this study to determine the

phase boundaries and densities at pressures up to 70 MPa and at temperatures up to 200°C. The design details and the operation procedure were described in previous publications.[8–10] Briefly, it consists of (1) a view cell equipped with two sapphire windows for visual observation or optical determination of the demixing conditions, (2) a movable piston attachment with position sensing and a readout unit to determine the internal volume of the cell at any temperature and pressure, and (3) a computerized data acquisition system that records the temperature, pressure, and trans-
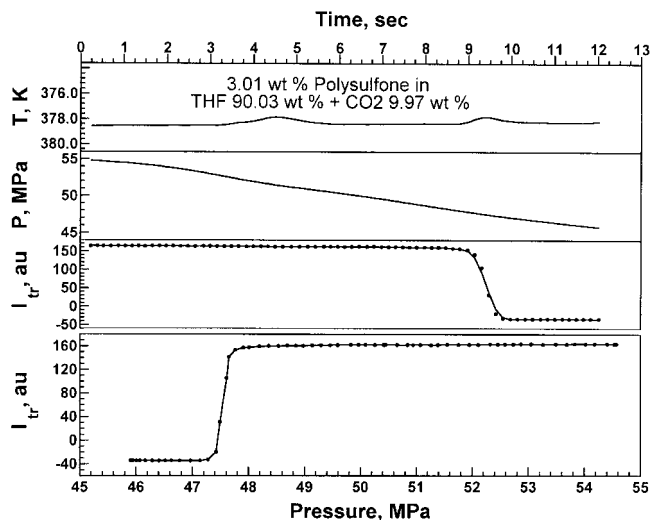
Figure 2 Variation of the temperature (T), pressure (P), and transmitted light intensity (I_{tr}) with time during a pressure reduction in a 3.01 wt % solution of polysulfone in a solvent mixture of 90.03 wt % THF and 9.97 wt % CO_2. The demixing pressure was determined from the variation of I_{tr} with time or pressure (the lower curve).

mitted light intensity (I_{tr}) and permits the determination of the demixing conditions.

After the polymer and solvent mixtures are loaded, the system is brought to the region of complete miscibility by the adjustment of the temperature and pressure. Pressure adjustments at a given temperature are achieved by the movement of the piston in the variable-volume part of the cell. The magnetic stirrer facilitates the dissolution process. Once complete miscibility is achieved, initially starting from the one-phase region, the pressure is reduced with the aid of a pressure generator until phase separation takes place. Phase separation is noted either by visual observation or by the change in I_{tr}. The pressure, temperature, and I_{tr} are simultaneously monitored and recorded by the computer. I_{tr} undergoes a rapid decrease with the onset of phase separation. In this work, we refer to the pressure corresponding to the departure from the baseline of I_{tr} as the demixing pressure at a given temperature. Figure 2 presents the typical output from the computer for the determination of the phase-separation conditions in a solution containing 3.01 wt % polysulfone and a 90.03 wt % THF and 9.97 wt % CO_2 mixture, in which the demixing pressure at 378.4 K has been identified as 47.8 MPa. A linear variable differential transformer coil is used to monitor the position of the movable piston to determine the internal volume in the view cell at any given temperature and pressure, from which the density of the polymer solutions can be calculated with the initial mass loading.

RESULTS AND DISCUSSION

Phase behavior of mixtures of polysulfone, THF, and CO_2

Influence of the CO_2 concentration on miscibility

We determined the miscibility and demixing conditions for 4.5 wt % polysulfone solutions in CO_2/THF mixtures. In these experiments, the polymer concentration was kept constant, and the solvent fluid concentrations were varied, with the CO_2 concentration ranging from 9.9 to 13.9 wt %. Figure 3 shows the demixing conditions as determined from the change in I_{tr} (see Fig. 2). The pressure region above each pressure–temperature curve corresponds to the one-phase homogeneous region, whereas the lower pressure side of each curve is the phase-separated region. The increase in the CO_2 concentration in the solvent fluid mixture causes a remarkable increase in the demixing pressures, which is even greater at lower temperatures. For example, at 308 K, the shift is from about 16 to 67 MPa, but at 368 K, the shift is from about 31 to 65 MPa. For 9.9, 11.4, and 12.9 wt % CO_2, the system shows lower critical solution temperature (LCST) behavior (phase separation occurs with increasing temperature) within the temperature range investigated. However, upper critical solution temperature (UCST) behavior (miscibility rather than phase separation takes place with increasing temperature) is observed with a 13.9 wt % CO_2 solution.

Influence of the polymer concentration on miscibility

Figure 4 shows the demixing curves for the miscibility of polysulfone as a function of the polymer concentration in a solvent mixture in which the weight ratio of the THF and CO_2 is kept constant at 87:13. (The fluid concentration was achieved in each experiment within an error margin of less than 0.03 wt %.) At a 0.28 wt %
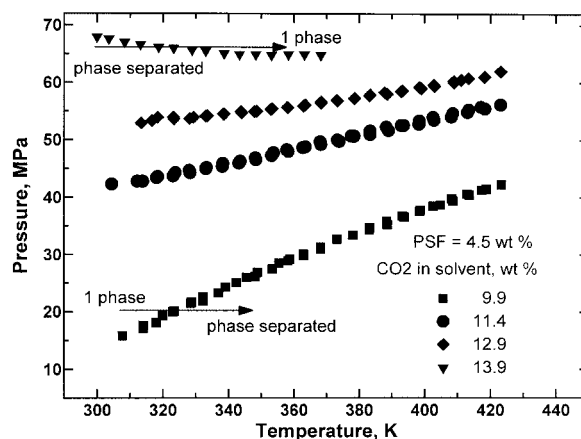
Figure 3 Variation of the demixing pressures for 4.5 wt % polysulfone solutions in THF/CO_2 binary solvents with CO_2 concentrations of 9.9, 11.4, 12.9, and 13.9 wt %.
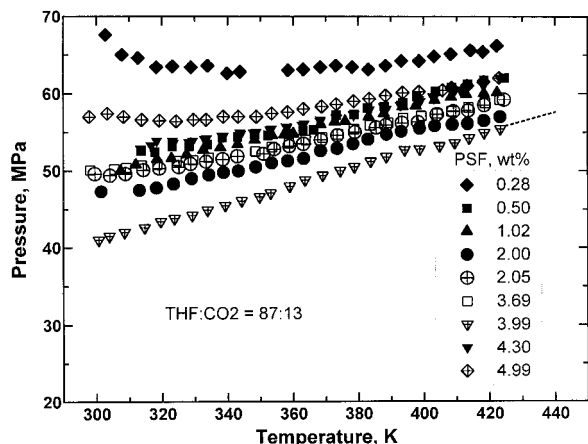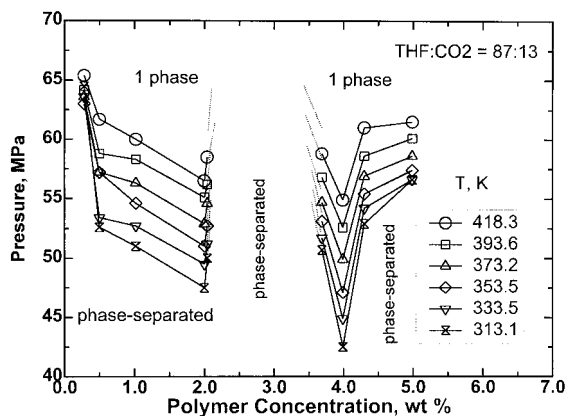
Figure 4 Variation of the demixing pressures for polysulfone solutions in 87:13 THF/CO_2 binary solvents at polymer concentrations of 0.28, 0.50, 1.02, 2.00, 2.05, 3.69, 3.99, 4.30, and 4.99 wt %.
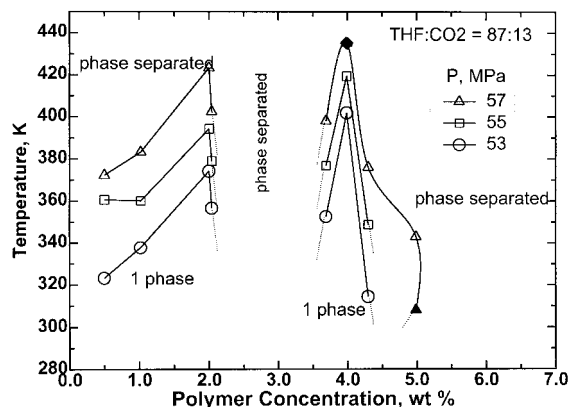

Figure 6 Temperature–composition curves for polysulfone solutions in 87:13 THF/CO_2 binary solvents at pressures of 53, 55, and 57 MPa: (▲) a second phase-separation point at 57 MPa at a concentration of 4.99 wt %; (◆) an extrapolated point from the dotted portion of the 3.99 wt % curve in Figure 4.

polysulfone concentration, the system shows UCST-type behavior at low temperatures (<340 K) but shifts to LCST-type behavior as the temperature is increased (>380 K). At 4.99 wt %, the crossover from UCST to LCST is shifted to lower temperatures, to about 325 K. For the other polymer concentrations, only LCST-type phase behavior was observed within the temperature range investigated.

Figure 5 shows the pressure–composition (polymer concentration) curves at six temperatures ranging from 313 to 418 K. These curves were generated from constant-temperature cuts from Figure 4. Figure 6 shows the temperature–composition (polymer concentration) curves at three pressures also generated from Figure 4 from constant-pressure cuts that include most of the concentrations.

The pressure–composition diagrams show two separated miscibility domains at each temperature within this concentration range. For example, at 418.3 K the
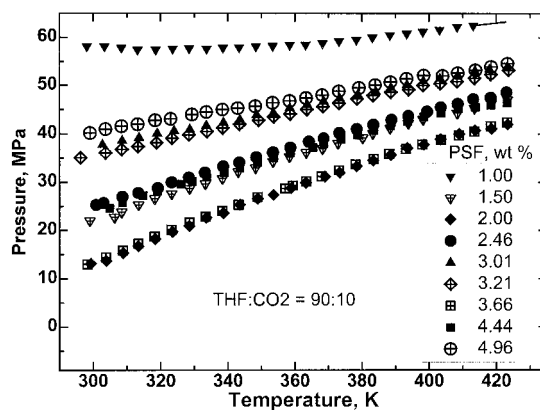
first miscibility domain is at a pressure greater than 57 MPa in the polymer concentration range of 0.3–2.0 wt %. The second domain is observed at concentrations greater than 3.6 wt % and at pressures greater than 55 MPa. Remarkably, this system is not miscible in the polymer concentration range from 2.0 to 3.6 wt %, and the demixing pressures increase extremely rapidly.

In Figure 6, these miscibility domains are demonstrated for constant-pressure cuts. Once again, the system is not miscible in the concentration range from 2 to 3.6 wt %. At 57 MPa, for a 4.99 wt % solution, phase separation is encountered at two temperatures (filled and open triangles), which must be on the miscibility loop defining this region. A more complete picture of a miscibility loop with closure on the lower part of the loop can perhaps be observed, but would require generation of more data at lower temperatures, going to subambient conditions.
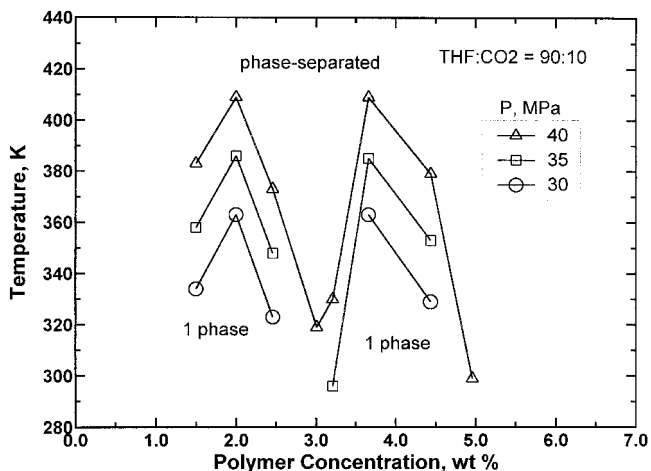

Figure 5 Variation of the demixing pressures with polymer compositions for polysulfone solutions in 87:13 THF/CO_2 binary solvents at temperatures of 313.1, 333.5, 353.5 373.2, 393.6, and 418.3 K.

Figure 7 Variation of the demixing pressures for polysulfone solutions in 90:10 THF/CO_2 binary solvents at polymer concentrations of 1.00, 1.50, 2.00, 2.46, 3.01, 3.21, 3.66, 4.44, and 4.96 wt %.
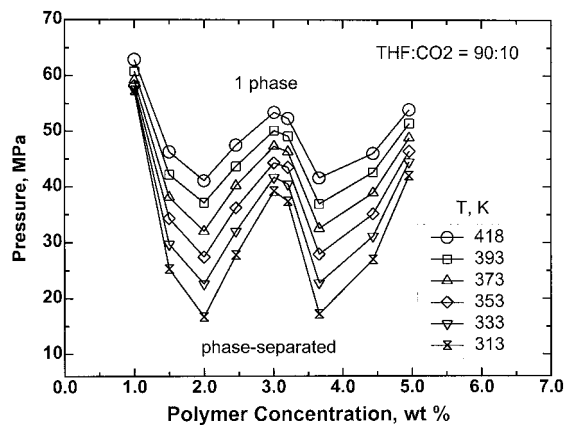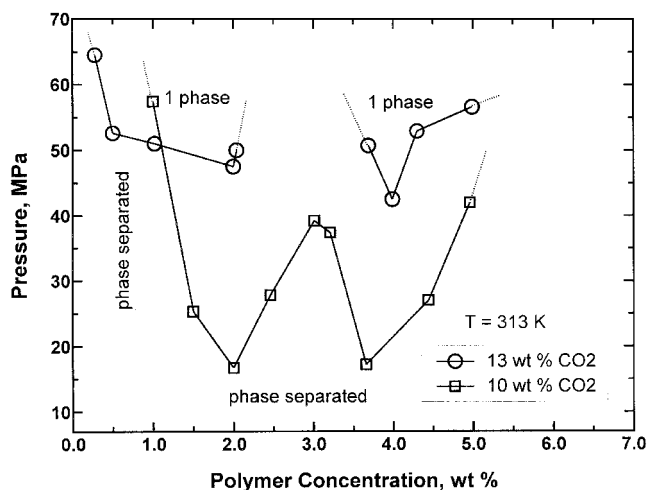
Figure 8 Variation of the demixing pressures with polymer compositions for polysulfone solutions in 90:10 THF/CO$_2$ binary solvents at temperatures of 313, 333, 353 373, 393, and 418 K.

Figure 7 shows the pressure–temperature diagram of this ternary system in a solvent mixture with a lower CO$_2$ level (10 wt % instead of 13 wt %) for polymer concentrations of 1.0–5.0 wt %. Figures 8 and 9 show pressure–composition and temperature–composition diagrams generated from Figure 7. The general features are similar to those observed in the 87:13 mixture.

However, as shown in Figure 8, the two miscibility regions now partially merge, forming one region of miscibility with a local maximum in pressure below which the two-phase region could still be entered in the concentration range from about 2.0 to 3.6 wt %. This W-shape phase boundary evolves from the double U-shape phase boundary as the CO$_2$ level in the solvent mixture is reduced. In the temperature–composition diagrams, the phase boundary at 40 MPa gives an M-shape phase diagram indicating that two


Figure 9 Temperature–composition curves for polysulfone solutions in 90:10 THF/CO$_2$ binary solvents at pressures of 30, 35, and 40 MPa.

Figure 10 Comparison of the demixing pressures as a function of the polymer composition at 313 K for polysulfone/ THF/CO$_2$ systems with 10 and 13 wt % CO$_2$ in the solvent mixtures.

homogeneous regions merge somewhere around a 3.0 wt % polysulfone concentration. However, at other pressures, the constant-pressure cuts from the pressure–temperature diagram can only give two portions of curves; this means that either the potential merge temperature of the two separated one-phase regions is beyond the temperature range of measurement in this study or that they still remain separated at this CO$_2$ level.

Figures 10 and 11 offer a clearer comparison of these data and the merging of the miscibility regions with the CO$_2$ level. These show pressure–composition phase diagrams at 313 and 418 K. The transition from the W-shape phase boundary to the double U-shape boundary with increasing CO$_2$, which leads to two
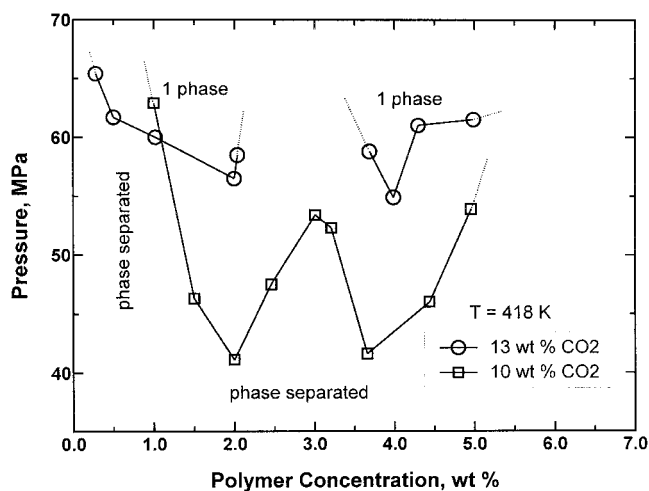

Figure 11 Comparison of the demixing pressures as a function of the polymer composition at 418 K for polysulfone/ THF/CO$_2$ systems with 10 and 13 wt % CO$_2$ in the solvent mixtures.

identifiable miscibility regions in the fluid mixture, is clearly observed.

Density

The density data were taken along the pressure reduction path, first at a high pressure in the one-phase region and then with the pressure reduced in approximately 3.45-MPa increments until the two-phase region was entered. The temperature was kept constant and controlled with an accuracy of 0.4°C during these measurements. For measurements close to the demixing pressure, pressure intervals were adjusted so that the density data right at the demixing point could be determined. Figures 12 and 13 show the density as a function of pressure at several selected temperatures for the ternary system containing 2 wt % polymer in solvent mixtures containing 13 wt % CO_2 and 87 wt % THF and 10 wt % CO_2 and 90 wt % THF, respectively. The density data for this solution and other concentrations will be published separately.[11] The filled symbols represent the demixing pressures at each temperature. This type of information is useful in that the data show how much the volume will need to be expanded at a given temperature to induce phase separation. The density increases almost linearly as the pressure increases without any significant observable change around the phase-separation point. This
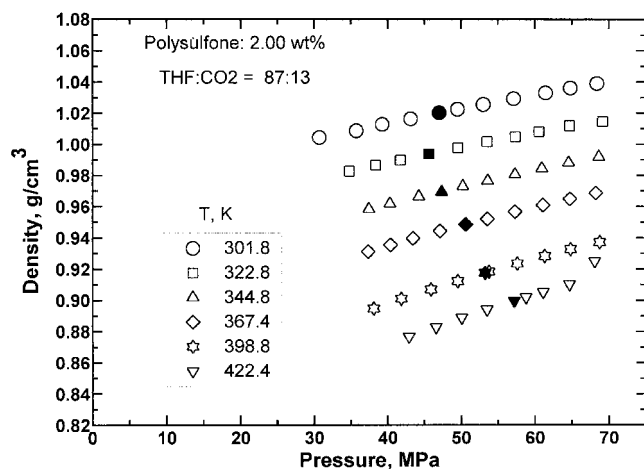
Figure 12 Pressure dependence of the density for a 2.00 wt % polysulfone solution in an 87:13 THF/CO_2 solvent mixture at 301.8, 322.8, 344.8, 367.4, 398.8, and 422.4 K. Filled data points are the densities at the phase-separation points.
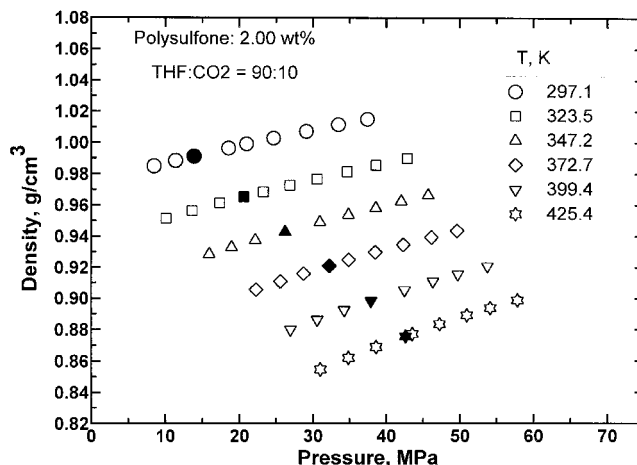
Figure 13 Pressure dependence of the density for a 2.00 wt % polysulfone solution in a 90:10 THF/CO_2 solvent mixture at 297.1, 323.5, 347.2, 372.7, 399.4, and 425.4 K. Filled data points are the densities at the phase-separation points.

suggests that the coexisting phases must have similar densities, which is often the case for liquid–liquid phase separation in polymer solutions under high pressure.

CONCLUSIONS

A new solvent system for polysulfone has been identified and a new type of phase behavior has been observed in a ternary polysulfone/THF/CO_2 system. This system shows double miscibility regions that tend to merge when the CO_2 level in the solvent mixture is reduced.

References

1. Gauter, K.; Peters, C. J.; Scheidgen, A. L.; Schneider, G. M. Fluid Phase Equilib 2000, 171, 127.
2. Pöhler, H.; Schneider, G. M. Fluid Phase Equilib 1995, 110, 151.
3. Scheidgen, A. L.; Schneider, G. M. J Chem Thermodyn 2000, 32, 1183.
4. Schneider, G. M.; Scheidgen, A. L.; Klante, D. Ind Eng Chem Res 2000, 39, 4476.
5. Wolf, B. A.; Blaum, G. Makromol Chem 1976, 177, 1073.
6. Wolf, B. A.; Molinari, R. J. Makromol Chem 1973, 173, 241.
7. Blaum, G.; Wolf, B. A. Macromolecules 1976, 9, 579.
8. Kiran, E.; Liu, K. Korean J Chem Eng 2002, 19, 153.
9. Bayraktar, Z.; Kiran, E. J Appl Polym Sci 2000, 75, 1397.
10. Kiran, E.; Pöhler, H.; Xiong, Y. J Chem Eng Data 1996, 41, 158.
11. Zhang, W.; Kiran, E. J Chem Thermodyn, to appear.