

Miscibility, Phase Separation, and Volumetric Properties in Solutions of Poly(dimethylsiloxane) in Supercritical Carbon Dioxide

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ABSTRACT: Miscibility conditions and volumetric properties of solutions of poly(dimethylsiloxane) in supercritical carbon dioxide have been determined as a function of polymer molecular weight, polymer concentration, temperature, and pressure. Measurements have been conducted in a variable volume view cell equipped with an LVDT sensor to identify the position of a movable piston and thus the internal volume of the cell and consequently the density of the solution at a given pressure and temperature. The demixing data (in the form of P-T curves for a given concentration, or as P-x diagrams at a given T) and the density isotherms are presented for solutions of two polymer samples with different molecular weights ($M_w = 38,600$; $M_w/M_n = 2.84$ and $M_w = 94,300$; $M_w/M_n = 3.01$) at several concentrations in the range from 0.05 to 10 mass % over a temperature range from 302–425 K. Solution densities corresponding to the demixing points also have been identified. Representation of the demixing densities on the density isotherms, i.e., pressure-density plots is a new methodology that gives a direct assessment of the volumetric expansion the solution must undergo before phase separation. The temperature–composition diagrams generated at selected pressures show that the poly(dimethylsiloxane) + CO₂ solutions display both lower critical solution and upper critical solution type behavior. The lower critical solution temperature moves to lower temperatures and the upper critical solution temperature moves to higher temperatures with decreasing pressure and they eventually merge together at lower pressures forming an hourglass-shaped region of immiscibility. This behavior is linked to the solvent quality of supercritical carbon dioxide that changes with pressure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1397–1403, 2000

Key words: miscibility; phase separation; poly(dimethylsiloxane); supercritical fluids; carbon dioxide

INTRODUCTION

Because of their tunable properties, supercritical fluids are very useful as solvents and reaction media for polymer synthesis, modifications, and processing.¹ Among some specific examples are:

controlling the solubility to have specific molecular weight and molecular weight distributions during polymerization; controlling the swelling of polymers to regulate impregnation; controlling solubility to have selective extractions or separations; and controlling viscosity to adjust rheological properties of polymer melts or solutions in processing.²

Poly(dimethylsiloxane) (PDMS) is the most important polyorganosiloxane, being the basis of

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most technical silicone oils, greases, and silicone-based rubbers. It has a low glass transition temperature ($T_g \approx -123^\circ\text{C}$) and is a liquid at room temperature.³ It is also known for its high solubility in supercritical carbon dioxide at high pressures.^{2,4-14} For example, at 52°C and 18 MPa, solubility of PDMS in carbon dioxide is about 1 g per liter.⁵ The solubility of carbon dioxide in PDMS melts is also high, reaching 40% by mass level at 26 MPa at 50°C .⁶ The high degree of miscibility of PDMS in carbon dioxide has been of interest for mobility control of carbon dioxide flood in oil recovery,⁵ in fractionation of PDMS,^{7,8,13} and purification of liquid crystalline siloxane oligomers with carbon dioxide.⁹ More recent studies are exploring the reduction of viscosity of PDMS upon addition of supercritical carbon dioxide.^{6,10,11} Additional articles have appeared on the swelling of crosslinked PDMS in supercritical carbon dioxide¹² and adsorption of PDMS from its solutions in carbon dioxide.^{13,14}

Because of the high solubility of PDMS in carbon dioxide, it forms a model system on which more complete data sets on phase boundaries, viscosity, and volumetric properties that cover a wide range of concentrations, pressure, temperature, and molecular weights are highly desirable. In an earlier study,³ we presented data on the phase boundaries for 5% solutions of PDMS of different molecular weights ($M_w = 38,900$; 93,700; 273,500; 396,200), as well as viscosity and density for selected solutions.

In the present study, we have expanded this database to cover a wider concentration range to permit generation of more complete pressure-composition (P-x) and temperature-composition (T-x) diagrams for two different molecular weight PDMS samples in carbon dioxide. The T-x diagrams that are generated at different pressures provide a clear picture of the changes in the phase behavior of this system. The phase behavior changes from one displaying an hourglass-shaped region of immiscibility at low pressures, to one that displays both upper critical and lower critical solution temperatures (UCST and LCST) with increasing region of miscibility at higher pressures. These reflect clearly the changes in the solvent quality of carbon dioxide with pressure. The present study also provides pressure-density isotherms for these solutions both in the one-phase and two-phase regions of the mixtures. On these isotherms, the density corresponding to demixing conditions are identified as a new and

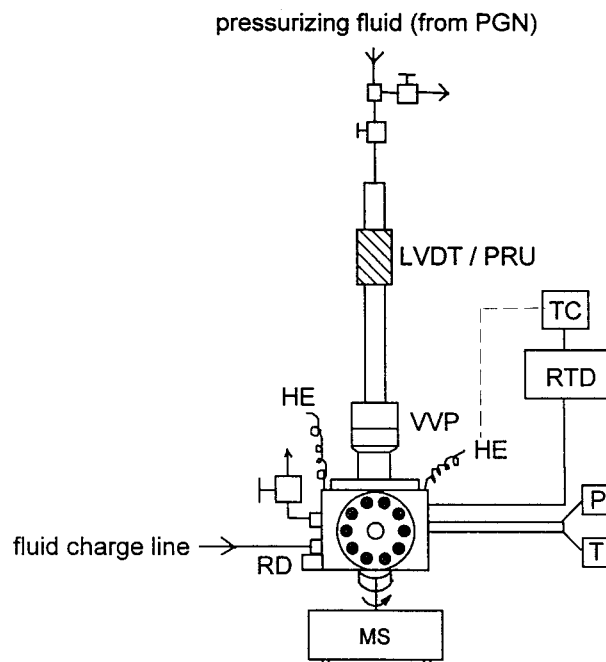


Figure 1 Schematic diagram of the variable-volume view-cell for determination of the demixing pressures and densities. PGN, pressure generator; LVDT/PRU, piston position readout unit; TC, temperature controller; HE, cartridge heating elements; VVP, variable volume part housing the piston; RD, rupture disc; MS, magnetic stirrer.

direct method of assessing the degree of volume expansion needed to bring about phase separation.

EXPERIMENTAL

PDMS samples with molecular weights of $M_w = 94,300$ ($M_w/M_n = 3.01$) and $M_w = 38,600$ ($M_w/M_n = 2.84$) were obtained from Scientific Polymer Products. The miscibility and demixing pressures, as well as densities were determined using the variable-volume view-cell setup shown in Figure 1. The details of the cell and loading procedures are given in our earlier publications.^{4,15} After loading the polymer and carbon dioxide, the system was heated up to ≈ 423 K and pressurized to ≈ 60 MPa. Then, by decreasing the pressure, the conditions where the phase separation takes place were determined by direct observations through the sapphire windows.

For density measurements, the LVDT coil monitors the position of the piston and gives in-

formation on the internal volume at the prevailing temperature and pressure. From the known total mass initially loaded to the cell and the volume, the density is calculated. Densities of the solutions were determined at different pressures covering both the homogeneous one-phase and the heterogeneous two-phase regions, as well as the exact condition of phase separation. The densities that are reported in two-phase regions are the overall densities of the system.

In this system, the densities are determined with an accuracy of $\pm 1\%$.^{15,16} The uncertainty in demixing pressures for the present polymer system was approximately ± 1.5 MPa. For solutions of high concentrations, the cloud point is observed as sharp darkening in the solution, whereas at low concentrations, the solutions become turbid at the incipient phase separation conditions.

RESULTS AND DISCUSSION

Demixing Pressures

Figures 2 and 3 show the demixing pressures for two PDMS samples in carbon dioxide at different concentrations. The region above each curve is the one-phase homogeneous region for these solutions. As seen from Figures 2 and 3, at temperatures above 320 K, the solutions show typical LCST behavior and demixing pressures increase as temperature increases. However, at tempera-

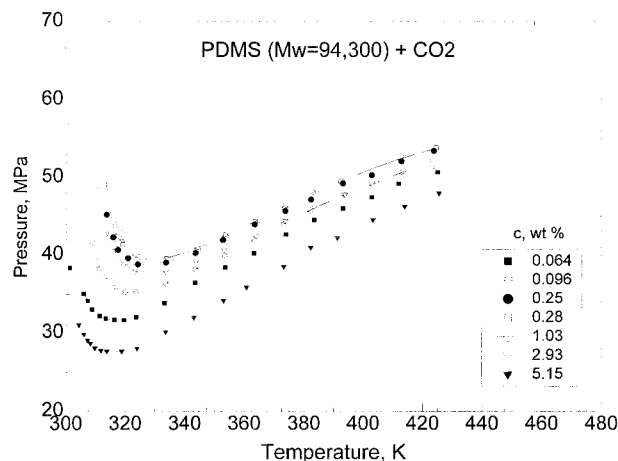


Figure 2 Demixing pressures of poly(dimethyl siloxane) ($M_w = 94,300$; $M_w/M_n = 3.01$) in carbon dioxide. Polymer concentrations given in the inset are in mass %. The region above each curve is the one-phase region corresponding to that concentration.

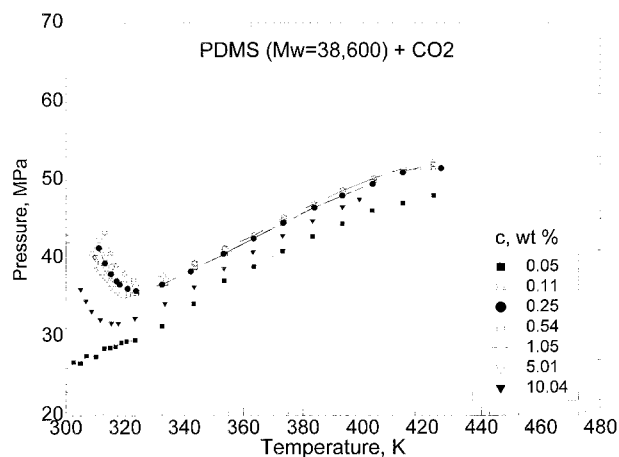


Figure 3 Demixing pressures of poly(dimethyl siloxane) ($M_w = 38,600$; $M_w/M_n = 2.84$) in carbon dioxide. Polymer concentrations given in the inset are in mass %. The region above each curve is the one-phase region corresponding to that concentration.

tures below 320 K, the character of the system shifts to that of a system showing UCST where the one-phase regions are entered upon increasing the temperature. It is noted that dP/dT along the UCST branch is high and the demixing pressures increase sharply upon a decrease in temperature. These solutions thus display both UCST and LCST.

The LCST and UCST character of these solutions has been reported previously for these molecular weight samples based on data at 5 mass % concentration,⁴ and for a wider range of molecular weights based on data at 1 mass % concentration in another study.¹⁴ The present demixing pressures for 1% solution for $M_w = 38,600$ compare well with the literature data for 1% solution for a sample with $M_w = 39,000$.¹⁴ The data, despite some differences, are also in basic agreement with the data that were reported previously for 5% solutions.⁴ In the earlier work,⁴ we demonstrated that the PDMS-carbon dioxide system can be described using the Sanchez-Lacombe model provided that a temperature-dependent interaction parameter (that may need to be further adjusted for a given molecular weight and concentration) is used. Modeling, however, is not the focus of the present study.

Figure 4 shows the demixing pressures as a function of polymer concentration ($M_w = 94,300$) that are generated by taking constant temperature cuts from Figure 2 at 323, 353, 373, 393, 413, and 424 K. In this temperature range, the demix-

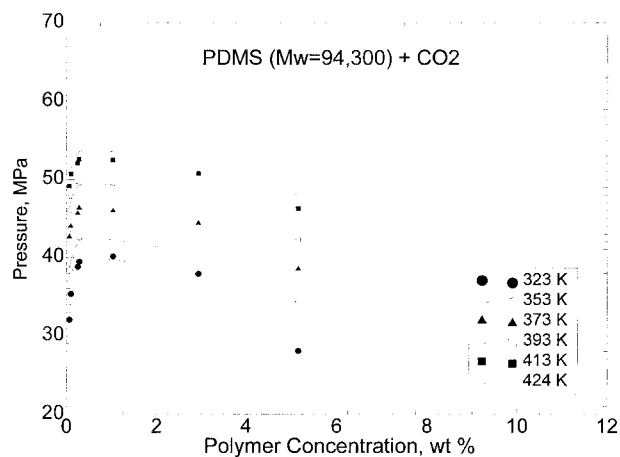


Figure 4 Variation of the demixing pressures with concentration at selected temperatures >320 K for solutions of PDMS ($M_w = 94,300$) in carbon dioxide. The region above each curve is the one-phase homogeneous region. Demixing pressures increase with increasing temperature in this temperature range.

ing pressures increase with increasing temperature. Figure 5 shows the demixing pressures for the same solution as a function of polymer concentration at 313 and 319 K, which are below the temperature at which the system behavior shifts from LCST to UCST. In contrast with Figure 4, in this temperature range, the demixing pressures decrease with increasing temperature.

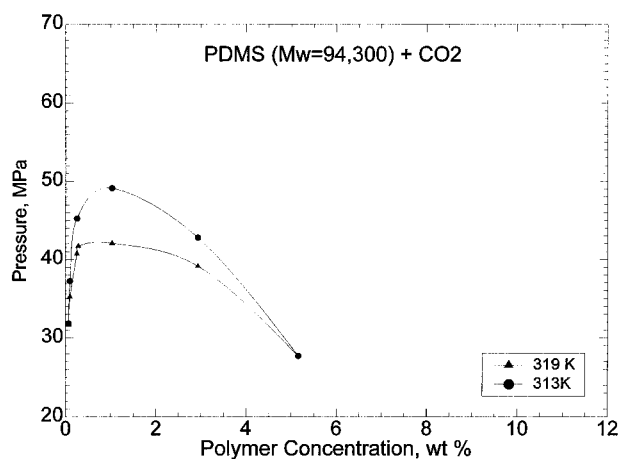


Figure 5 Variation of the demixing pressures with concentration at selected temperatures <320 K for solutions of PDMS ($M_w = 94,300$) in carbon dioxide. The region above each curve is the one-phase homogeneous region. Demixing pressures decrease with increasing temperature in this temperature range.

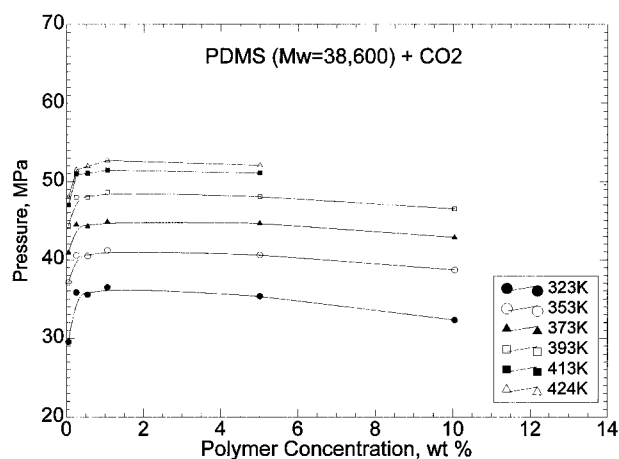


Figure 6 Variation of the demixing pressures with concentration at selected temperatures >320 K for solutions of PDMS ($M_w = 38,600$) in carbon dioxide. The region above each curve is the one-phase homogeneous region. Demixing pressures increase with increasing temperature in this temperature range.

Figure 6 shows the P-x diagram for the polymer solution with the lower molecular weight ($M_w = 38,600$) at temperatures >320 K. In this range, the demixing pressures increase with temperature. Even though not shown, P-x diagrams at temperatures <320 K will show the opposite behavior as shown in Figure 5 for the higher molecular weight polymer sample.

Comparison of Figure 6 with Figure 4 shows that for the lower molecular weight sample, the P-x diagram is broader. The demixing pressures are higher for the higher molecular weight sample at concentrations less than $\approx 3\%$. At higher concentrations, the data show that the P-x curves cross each other and higher molecular weight samples may require lower pressures for miscibility. This seemingly unexpected behavior may be an outcome of the broad molecular weight distributions of these polymer samples which influence the shape of the P-x diagrams.

Demixing Temperatures

Figures 7 and 8 show the temperature composition diagrams for the two molecular weight samples at three different pressures. These are generated from Figures 2 and 3 by taking constant pressure cuts. The filled circles are the actual data points, and the open circles are extrapolated values. At 50 MPa, both systems clearly display the LCST and UCST, the miscible one-phase re-

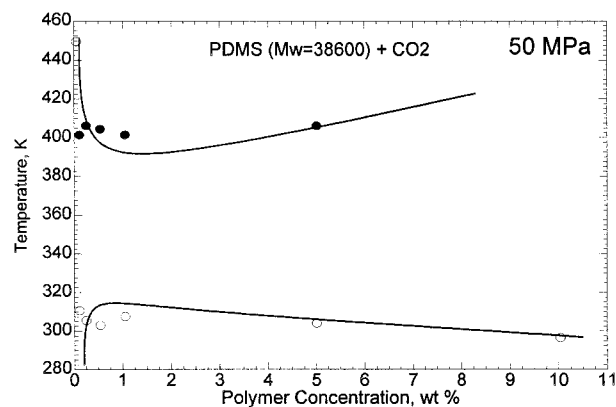
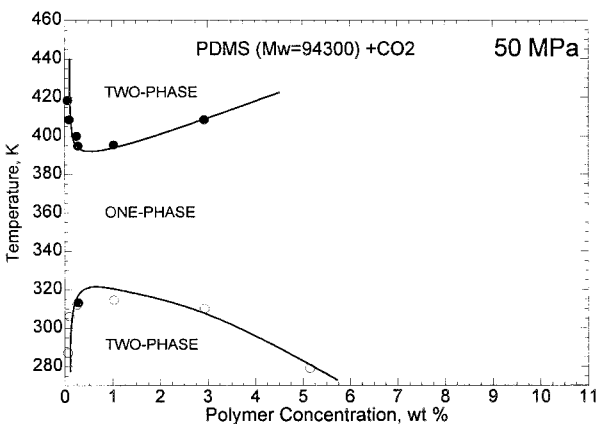
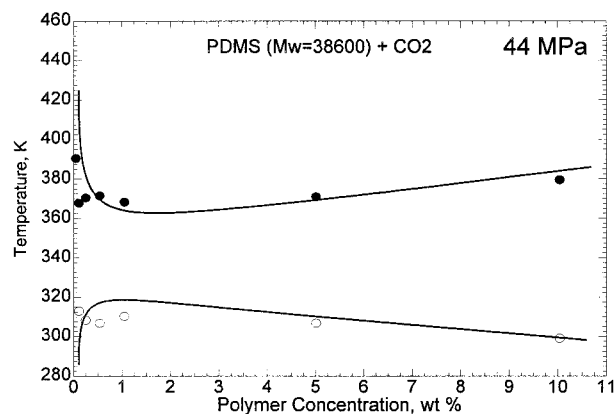
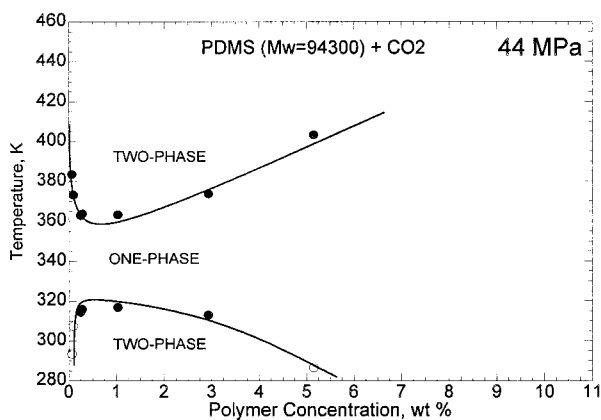
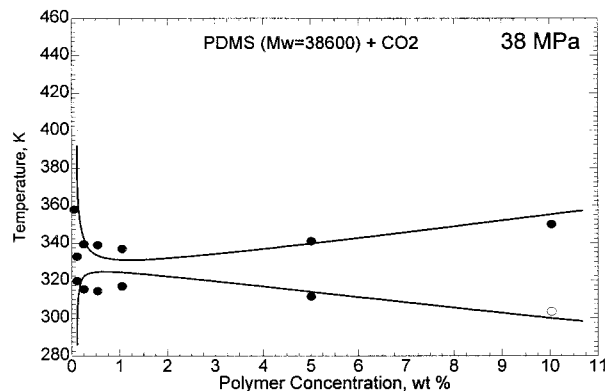
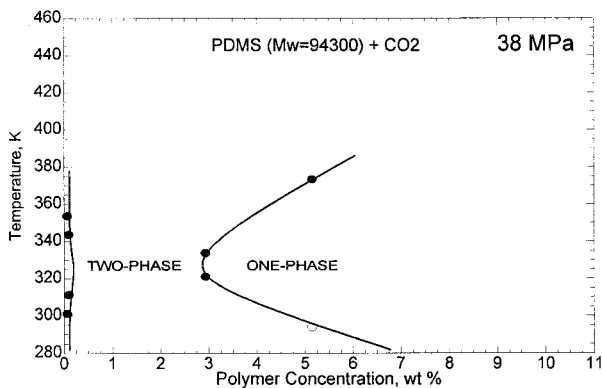


Figure 7 Variation of the demixing temperatures with composition at different pressures for PDMS ($M_w = 94,300$) solutions in carbon dioxide. Top: hourglass-shaped region of immiscibility at 38 MPa; middle: distinct LCST and UCST branches with a region of miscibility in between at 44 MPa; bottom: increased region of miscibility with LCST moving to much higher temperatures and UCST moving to lower temperatures at 50 MPa.

Figure 8 Variation of the demixing temperatures with composition at different pressures for PDMS ($M_w = 38,600$) solutions in carbon dioxide. Top: distinct LCST and UCST branches with a very narrow region of miscibility in between at 38 MPa; middle: distinct LCST and UCST branches with a greater region of miscibility in between at 44 MPa; bottom: increased region of miscibility with LCST moving to higher temperatures and UCST moving to lower temperatures at 50 MPa.

gion being in between. At lower pressures, i.e., 44 MPa, the LCST moves to lower temperatures and UCST moves to higher temperatures. The one-phase miscible region is decreased. At an even lower pressure of 38 MPa, the LCST and UCST boundaries overlap for the higher molecular weight polymer case, leading to an hourglass-shaped immiscibility region. Comparison of Figures 7 and 8 show that at the same pressures, the region of miscibility is greater for the lower molecular weight polymer sample. At 38 MPa, the distinct LCST and UCST are still observable, even though the region of miscibility is greatly reduced for the lower molecular weight sample. Again, examination of Figures 2 and 3 would show that if T-x diagrams were generated at very high pressures, only the UCST branch may be observed, the LCST having been shifted to experimentally inaccessible temperatures.

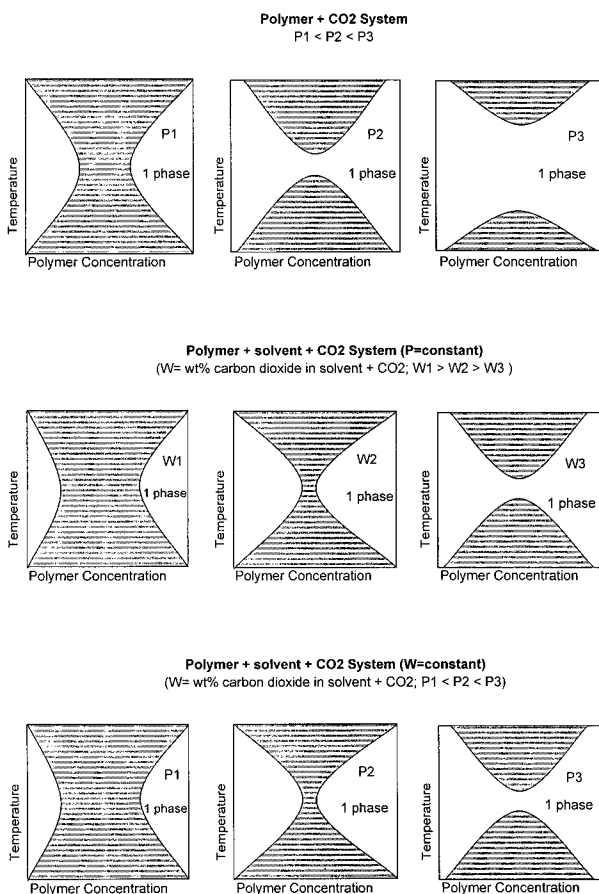


Figure 9 Schematic representation of the changes in the phase behavior of the polymer solvent systems with pressure or the solvent composition that alter the quality of the solvent. See the text for explanations.

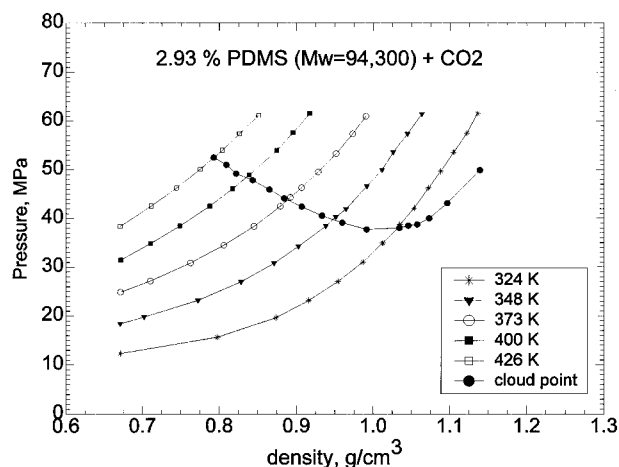


Figure 10 Pressure-density isotherms and the demixing pressures (densities) for 2.93% PDMS ($M_w = 94,300$) in carbon dioxide. Along each isotherm, the density domain below the cloud point density corresponds to the two-phase region.

Similar shifts with pressure in the T-x phase diagrams have been reported earlier in “polystyrene + *n*-butane” binary and “polyethylene + *n*-pentane + carbon dioxide” ternary systems.^{1,17} At a fixed pressure, the phase behavior in polymer + solvent + carbon dioxide systems can be moved from one showing an hourglass-shaped immiscibility region, to a system showing both LCST and UCST by decreasing the carbon dioxide content in the solvent mixture. If the solvent/carbon dioxide ratio is held constant, then the same shifts are observed with increasing pressure.

The behavior that is observed for PDMS + CO₂, and more generally in polymer + solvent + carbon dioxide systems, can be described with the schematic representation shown in Figure 9. The common denominator is the fact that these trends in each case follow the trends in the quality of the solvent system. Increasing the system pressure for a given solvent, or improving the nature of the solvent at a given pressure give similar results.

Volumetric Properties and Demixing Density

The densities for some of the solutions were determined at selected temperatures by changing the pressure in known increments.

Figure 10 shows the variation of the overall density of the mixture with pressure for 3% solution for $M_w = 94,300$ PDMS at selected tempera-

tures in the range 324–426 K. In Figure 10, we have included the densities corresponding to the cloud point line which indicates the demixing densities identified by the demixing pressures of the system at a given temperature. It is important to note that the demixing densities do not remain constant at different temperatures, and they show an increase with decreasing temperature.

Along each isotherm, the pressure-density domain that is below the line corresponding to the cloud point densities represents the two-phase regions, whereas the region above the line represents the one-phase regions. The inclusion of phase information on pressure-density isotherms in terms of demixing densities is a relatively new method of presentation¹⁸ that permits easy identification of the volume expansion needed to cause phase separation at a given temperature. Data of this nature has been previously shown for solutions of cellulosic polymers in binary fluid mixtures of carbon dioxide.¹⁸

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