

CHAPTER 7

VISCOSITY AND DENSITY OF POLY (ϵ -CAPROLACTONE) IN ACETONE + CARBON DIOXIDE MIXTURES

For processing of polymer solutions at high pressure in dense or supercritical fluids there is a continuing need for basic data on the thermodynamics like phase boundaries, volumetric properties like density, and the transport properties such as viscosity and diffusivity (Kiran, 1994; Brunner, 2004). Viscosity is an especially important parameter, which influences not only the rheological and flow or mixing behavior, but also the mass and heat transfer characteristics of these solutions. Viscosity is an important factor in polymerizations that influences chain termination reactions and thus reaction kinetics (Buback et. al., 2002a; b). Perhaps a lesser-recognized additional factor is the influence of viscosity on the physical rate processes such as phase separation processes in polymer solutions (Dindar and Kiran, 2002a; b). Reducing the viscosity of polymer melts with addition of supercritical fluids like carbon dioxide, or increasing the viscosity of dense fluids with polymeric additives in deep well injections fluids for tertiary oil recovery are among other important application areas where viscosity plays a key role. In addition to its value in such practical applications, viscosity data on polymer solutions are used to gain fundamental insights on polymer-solvent interactions and the goodness of a given solvent and also on crossover concentrations (Teraoka, 2002).

The present study is focused on dissolution and processing of a biodegradable polymer in a new solvent mixture for these polymers. The processing or modification of biodegradable polymers with carbon dioxide or carbon dioxide containing fluid mixtures is of growing interest (Quirk et. al., 2004; Harris et. al., 1998; Shieh and Yang, 2005; Xu et. al., 2004; 2005; Meziani et. al., 2006; Cotugno et. al., 2005) for the well known reasons of (1) the tunability of the properties of supercritical carbon dioxide, (2) the possibility of replacing or significantly reducing the use of toxic organic solvents, and (3) for the possibilities of easier processing and separation. Particle formation and encapsulation of biodegradable polymers with drugs are of much interest in development of controlled-release drugs (Yeo and Kiran, 2005; Vemaverapu et. al., 2005). Foaming and scaffolding of biodegradable polymers are of interest in tissue engineering and organ replacement studies (Quirk et. al., 2004).

Polycaprolactone, $-\text{[(CH}_2\text{)}_5\text{-COO]}_n-$, is a synthetic biodegradable polyester which has been widely used in controlled-release drug formulations (Iojoiu et. al., 2004; Perez et. al., 2000; Rai et. al., 2005). It has the advantage of leading to neutral degradation products which is in contrast to the acidic degradation products of other commonly used biodegradable polymers such as poly (lactide-co-glycolyde) (PLGA) and polylactic acid (PLA). Another feature of PCL is its slower degradation rate that may be advantageous in applications that require prolonged release times (Simha et. al., 2004). There is now a growing interest in processing of PCL in high-pressure fluids especially in carbon dioxide (Shieh and Yang, 2005; Meziani et. al., 2006; Cotugno et. al., 2005). However, the low solubility of PCL in high-pressure CO_2 has been a limitation in some applications, which can be alleviated by adding one or more co-solvents into the PCL + CO_2 mixtures (Byun et. al., 2006). Therefore, most of the

procedures developed to process PCL in high-pressure fluids employed the PCL + CO₂ + co-solvent systems. For example a recent publication has reported on the miscibility of PCL in carbon dioxide + dichloromethane or chloroform. (Kalogiannis and Panayiotou, 2006).

In the present study we have explored the miscibility and viscosity of PCL in acetone + carbon dioxide mixtures. Acetone is an FDA approved GMP (good-manufacture practice) solvent. However, studies on polymer solutions in acetone + carbon dioxide mixtures are not extensive. We have recently reported on the viscosity and density of poly (methyl methacrylate) in such mixtures (Liu et. al., 2006). To our knowledge, no high-pressure viscosity data is available in the open literature for PCL + acetone, and PCL + acetone + CO₂ mixtures.

7.1 Experimental

7.1.1 Materials

Polycaprolactone (PCL) was obtained from Scientific Polymer Products with molecular weights $M_w = 14,300$ and $M_n = 6,100$. The polymer had a melting temperature of 339 K as determined by differential scanning calorimetry at 10 K/min heating rate. Acetone (Burdick & Jackson) with purity of 99.5 % and CO₂ (Air Product) with a minimum purity of 99.99 % were used without further purification.

7.1.2 Apparatus and operational procedure

Measurements have been conducted using a variable-volume view cell and a falling cylinder type viscometer. The details and operational procedures of these systems have been described in previous chapter (See Chapter 4, Sections 4.1 and 4.2).

A. View-Cell. In determination of the phase conditions, once complete miscibility is achieved in the view cell, starting from the one-phase region, the pressure is reduced with aid of a pressure generator until phase separation takes place. Phase separation is noted either by visual observation or by the change in the transmitted light intensity I_{tr} . During these determinations the change in temperature, pressure, and I_{tr} are simultaneously monitored and recorded by the computer. Transmitted light intensity I_{tr} undergoes a rapid decrease with onset of the phase separation. The pressure corresponding to the departure from the baseline transmitted light intensity for the homogeneous solution is noted as the demixing pressure at a given temperature. Figure 7.1 is a representative output from the computer obtained during a pressure reduction experiment from 31 to 20 MPa while holding temperature constant at 354.7 K in a 5 wt % PCL solution containing 40 wt % CO₂. The incipient demixing pressure is identified as 22.3 MPa.

B. Viscometer. The viscometer and its operational procedure were shown in Figure 4.6 and described in Chapter 4. Viscosities are determined by determining the terminal velocity of a cylindrical sinker. The viscosity is given by

$$\eta = \frac{1}{V_t}(\rho_s - \rho_f)K \quad (\text{Eq.7.1})$$

where K is a calibration constant. The viscosity measurements with the present system are low-shear measurements with shear rates about 5 s^{-1} .

7.2 Results and Discussion

Density and viscosity of 5 wt % PCL solution in acetone or in mixtures of acetone + CO_2 (1, 2, 4, 40 wt %) are measured in the temperature range from 323 – 398 K and at pressures up to 35 MPa.

7.2.1 PCL + Acetone

Studies were conducted with 5 wt % solutions at 323, 348, 373 and 398 K in the pressure range from 7 - 35 MPa. The polymer was completely soluble in acetone at these conditions. The results of the density and viscosity determinations based on experiments conducted in the viscometer systems are shown in Table 7.1. The densities determined in the viscometer and the view cell were similar, the difference being less than 1 %. Densities were in the range from 0.7868 to 0.8901 gcm^{-3} . Figure 7.2 shows the increase in density with pressure at each temperature. Viscosities were in the range from 0.283 - 0.595 $\text{mPa}\cdot\text{s}$. Figure 7.3 shows that the variation of solution viscosity with pressure is linear.

7.2.2 PCL + Acetone + CO_2

Densities and viscosities were determined for 5 wt % PCL solutions in acetone plus 1, 2, 4, and 40 wt % CO_2 at 323, 348, 373, and 398 K in the pressure range from 7 - 35 MPa. The density values given in Table 7.2 are once again those determined in the viscometer system.

Figures 7.4 and 7.5 show the variation of density and viscosity of the solution containing 1 wt % CO₂ with pressure. Comparisons with Figures 7.2 and 7.3 show that viscosity values are slightly lowered while the densities are increased upon addition of carbon dioxide to the polymer solution in acetone. Figure 7.6 and 7.7 compare the variation of density and viscosity with pressure at 348 K, but for different CO₂ concentrations in the solutions. The increase in density with carbon dioxide becomes more pronounced at 4 wt % and extremely large at 40 wt %. At 40 wt % addition level, densities are not only significantly higher but also show much higher sensitivity to a change in pressure. The viscosity reductions also become very high at 40 wt % CO₂ additions. However, the pressure sensitivity of viscosity is not much altered as shown in Figure 7.6. While at CO₂ addition levels up to 4 wt % viscosity reductions are small, with 40 wt % addition, nearly 50 % reduction in viscosity is observed.

7.2.3 Miscibility and the effect of phase separation

Phase behavior of all mixtures were also studied in our view-cell system that is dedicated for density and phase boundary measurements with optical techniques. All the solutions except the 5 wt % PCL solution in acetone plus 40 wt % CO₂ were completely miscible at all conditions investigated. In the system containing 40 wt % CO₂, the mixture displayed a liquid-liquid phase separation with the demixing pressures shown in Figure 7.8. Miscible and two-phase regions are indicated in the figure.

For this mixture, densities and viscosities were determined at temperature of 373, 363, 348, 333, and 323 K in the pressure range from 7 - 35 MPa, which are listed in Table 7.2.

Figures 7.9 and 7.10 show the variation of density and viscosity with pressure for the 5 wt % PCL solution in acetone plus 40 wt % CO₂ at 373, 363, 348, 333, and 323 K. The demixing pressure at these temperatures as determined from Figure 7.8 (26.9, 24.2, and 20.2 MPa, respectively) are also included in the figure. In these figures, the data points that lie to the left of the demixing points correspond to liquid-liquid demixed system, while the points to the right correspond to one-phase homogeneous conditions. As shown by these figures, the liquid-liquid phase separation does not lead to a sharp change in either the density or the viscosity, possibly because the properties of the two liquid-liquid phases do not differ significantly, which would not be the case if there was a liquid-vapor type phase separation taking place. Because of the physical geometry of the attachment of the viscometer tube, when system is phase separated, the fluid mixture in the fall tube is expected to be more representative of the polymer-lean phase. That the viscosity did not show a sharp change suggests that the composition of the polymer-lean phase that forms upon phase separation is not significantly different from the concentration of the initial solution; or that the concentration of the polymer-lean and polymer-rich-phase are close to each other, which would, for example, be the case near the critical polymer concentration.

7.2.4 Correlation of viscosity with pressure, temperature and density

The pressure (P) dependence of viscosity at a given temperature (T) was correlated in terms of a flow activation volume (V^\ddagger) using Eq 2 (Xiong and Kiran, 1995; Yeo and Kiran, 1999),

$$\eta = A \exp(V^\ddagger P / RT) \quad (\text{Eq.7.2})$$

Only the homogeneous one-phase data were used for the 40 wt % CO₂ containing solutions. The activation volume ranged from 12 - 29 cm³ mol⁻¹. As shown in Table 7.3, they were observed to increase with temperature at all concentrations, which would suggest that at higher temperatures the viscosity of these solutions may become more sensitive to pressure. The actual data show only a modest sensitivity to pressure at these temperatures. There appears to be a large increase in activation volume for the 40 wt % CO₂ addition.

The temperature dependency of the viscosity at a given pressure was correlated in terms of activation energy (E^\ddagger) according to Eq 3 (Xiong and Kiran, 1995; Yeo and Kiran, 1999),

$$\eta = B \exp(E^\ddagger / RT) \quad (\text{Eq.7.3})$$

The activation energies as shown in Table 7.3, ranged from 7 - 9 kJ mol⁻¹. Generally, the activation energies were observed to decrease with pressure at all concentrations, suggesting that at a higher pressure, the viscosity becomes less temperature dependent.

Figure 7.11 shows the variation of viscosity as a function of density for these solutions.

These data correspond to a temperature range of 323 – 398 K and a pressure range of 7 - 35 MPa that are illustrated in Table 7.1 and 7.2. The density (ρ) dependent variation of viscosity was correlated in terms of a characteristic close-packed volume (V_0) according to the well-known Doolittle equation as expressed in Eq 4 (Xiong and Kiran, 1995; Yeo and Kiran, 1999).

$$\eta = A \cdot \exp\left(\frac{B}{1 - V_0 \cdot \rho}\right) \quad (\text{Eq.7.4})$$

The solid curves in Figure 7.11 correspond to these correlations. The optimal values of V_0 that were determined by fitting the three parameters in Eq 4 by the Hooke-Jeeves and quasi-Newton method (with $A = 0.000625$ mPa•s, $B = 3.19$ and a convergence criterion of 0.0001) are included in Table 7.3. The close-packed volumes in this system ranged from 0.5 to 0.6, with the close-packed volumes becoming smaller as CO_2 content in the system is increased.

7.2.5 Comparison of PCL + Acetone + CO_2 system with PMMA + Acetone + CO_2 system

In a recent study (Liu et. al., 2006), we determined the high-pressure density and viscosity of poly (methyl methacrylate) solutions in acetone + CO_2 binary fluid mixtures. Determinations were carried out with two PMMA samples with different molecular weights ($M_w = 14$ K, $M_w/M_n = 1.8$; and $M_w = 540$ K, $M_w/M_n = 2.8$) at a 5 wt % PMMA concentration in the presence of 1, 2 and 4 wt % CO_2 at temperature and pressure conditions employed in the present study.

Figures 7.12 and 7.13 provide a comparison of the density and viscosity of these systems at 373 K at 2 and 4 % carbon dioxide levels. Figure 7.12 shows that increasing the CO_2 amount in the mixture leads to higher densities for all polymer systems. For PMMA solutions, the higher molecular weight polymer system shows lower densities. At a given CO_2 addition level, the PCL solutions show densities that are in between the densities of the solutions of the low and high molecular weight PMMA samples. The change in density in going from 2 to 4 wt % carbon dioxide in the mixture is smaller in the PCL solution than the change that takes place in PMMA solutions. Figure 7.13 shows that in all polymer systems, increasing the CO_2 content in the solution reduces the viscosity. The viscosity reductions for all the

solutions are close. Figure 7.12 and 7.13 demonstrate that when the solutions of PCL and PMMA with similar molecular weight (i.e., 15 K) are compared, the PCL solutions show a lower density but higher viscosity. Lower density would also suggest larger molar volume for the PCL solutions. As discussed in the previous section, the close-packed volumes in PCL solutions were in the range of 0.5 - 0.6 cm³/g, while for the PMMA solutions, the close-packed volumes were found to be in the range of 0.7 – 0.9 cm³/g. A larger molar volume and a smaller close-packed volume would indicate a higher free volume and correspondingly lower viscosities. This is in contrast with the higher viscosities of the PCL solutions that are observed, which however can be reconciled if polymer chain expansion for PCL in the solvent were to be greater. Although the free volume in the PCL solutions is larger than that of low molecular weight PMMA solutions, the larger chain expansion of PCL in the acetone + CO₂ solvent and potential entanglements of the chain can offset the effect of free volume and result in the higher viscosities. This would suggest that acetone - CO₂ mixtures, in the temperature and pressure ranges studied, must be a “better” solvent for PCL than PMMA.

7.3 Summary and conclusions

In this chapter, we have reported on the high-pressure viscosity and density of poly (ϵ -caprolactone) solutions in acetone and in acetone plus CO₂ mixtures over a temperature range from 323 to 398 K over a pressure range from 7 MPa to 35 MPa. The effect of adding CO₂ on viscosity was investigated for the 5 wt % solutions at CO₂ concentrations of 1, 2, 4, and 40 wt %. The effect of phase separation on viscosity was studied for the 5 wt % polymer solution in the binary fluid mixture with high (40 wt %) carbon dioxide content. The solution

viscosities ranged from 0.2 to 0.6 mPa·s with flow activation energies in the range 7 - 9 kJ/mol and flow activation volumes in the range from 12 - 29 cm³/mol. Close-packed volumes estimated from correlation of the data to Doolittle equation were in the range 0.5 - 0.6 cm³/g. In ternary solutions containing carbon dioxide, solution densities were higher, reflecting the higher density of compressed CO₂ compared to that of acetone, but viscosities were lowered. A viscosity reduction of about 50 % was observed with 40 wt % CO₂ addition. The density and viscosity data for the PCL solutions have been compared with data for solutions of poly (methyl methacrylate) (PMMA) with similar molecular weight ($M_w = 14$ K and 15 K) in acetone + CO₂. The results show that the acetone + CO₂ binary mixtures are “better” solvents for PCL than PMMA.

Acknowledgements: This chapter is in part based on the publication “*Liu, K., and Kiran, E. (2006). Miscibility, viscosity and density of poly (ϵ -caprolactone) in acetone + carbon dioxide binary fluid mixtures, Journal of Supercritical Fluids, 39, 192-200.*”. The Journal of Supercritical Fluids is a publication of Elsevier, and the reproduction here is with the publisher’s permission.

Table 7.1 Density and viscosity data for 5 wt % PCL solution in acetone

	Pressure (MPa)	Density (g/cm ³)	Viscosity (mPa·s)
T = 398 K	7.91	0.7868	0.283
	14.70	0.8000	0.300
	21.61	0.8132	0.319
	28.55	0.8231	0.334
	34.97	0.8331	0.346
T = 373 K	7.63	0.8185	0.346
	14.86	0.8300	0.363
	21.16	0.8392	0.377
	28.13	0.8489	0.392
	35.31	0.8581	0.406
T = 348 K	7.71	0.8490	0.418
	14.39	0.8596	0.446
	21.26	0.8678	0.469
	28.31	0.8754	0.486
	33.99	0.8802	0.493
T = 323 K	7.74	0.8607	0.529
	14.39	0.8681	0.547
	21.52	0.8764	0.560
	28.07	0.8826	0.580
	35.24	0.8901	0.595

Table 7.2 Density and viscosity data for 5 wt % PCL (14 K) solutions in acetone + CO₂ at different CO₂ concentrations (C)

	Pressure (MPa)	Density (g/cm ³)	Viscosity (mPa·s)
<u>C = 1 wt %</u>			
T = 398 K	7.71	0.7888	0.277
	14.50	0.8027	0.295
	21.55	0.8153	0.314
	28.20	0.8259	0.327
	35.07	0.8359	0.344
T = 373 K	7.25	0.8188	0.333
	14.82	0.8304	0.360
	21.19	0.8400	0.377
	27.84	0.8491	0.392
	35.54	0.8589	0.403
T = 348 K	7.63	0.8503	0.404
	14.96	0.8603	0.422
	21.45	0.8690	0.445
	28.37	0.8770	0.457
	35.30	0.8832	0.463
T = 323 K	8.10	0.8638	0.516
	15.02	0.8723	0.532
	21.74	0.8799	0.554
	28.51	0.8850	0.585
	35.16	0.8918	0.595
<u>C = 2 wt %</u>			
T = 398 K	6.91	0.7889	0.271
	14.07	0.8040	0.289
	21.25	0.8172	0.310
	27.96	0.8299	0.322
	35.24	0.8404	0.336
T = 373 K	7.28	0.8210	0.331
	14.59	0.8331	0.348
	21.39	0.8431	0.370
	28.73	0.8530	0.382
	35.11	0.8616	0.395

T = 348 K	7.14	0.8510	
	14.39	0.8608	0.410
	21.56	0.8703	0.434
	28.14	0.8776	0.448
	35.01	0.8860	0.457
T = 323 K	7.76	0.8769	0.509
	14.19	0.8839	0.526
	21.30	0.8871	0.563
	28.36	0.8884	0.568
	35.19	0.8921	0.589
<u>C = 4 wt %</u>			
T = 398 K	6.98	0.7908	0.261
	14.28	0.8076	0.281
	21.21	0.8200	0.301
	28.18	0.8326	0.315
	35.08	0.8432	0.334
T = 373 K	7.18	0.8235	0.323
	14.38	0.8361	0.340
	21.65	0.8474	0.358
	28.27	0.8569	0.370
	35.10	0.8661	0.383
T = 348 K	7.03	0.8550	0.386
	13.87	0.8648	0.397
	21.46	0.8755	0.409
	28.15	0.8833	0.428
	34.88	0.8906	0.445
T = 323 K	7.64	0.8638	0.500
	14.41	0.8723	0.520
	20.94	0.8799	0.536
	28.07	0.8850	0.549
	34.88	0.8918	0.574
<u>C = 40 wt %</u>			
T = 373 K	25.09	0.8773	0.204
	28.26	0.8872	0.211
	34.99	0.9075	0.225
T = 363 K	19.10	0.8867	0.219
	21.41	0.8942	0.221
	27.91	0.9175	0.238
	35.04	0.9384	0.254

T = 348 K	9.56	0.8617	0.205
	15.06	0.8825	0.215
	20.99	0.9020	0.235
	28.04	0.9223	0.248
	34.61	0.9394	0.265
T = 333 K	7.42	0.8943	0.222
	14.55	0.9174	0.234
	21.13	0.9354	0.247
	27.78	0.9531	0.264
	35.14	0.9697	0.279
T = 323 K	7.42	0.8943	0.222
	14.55	0.9174	0.234
	21.13	0.9354	0.247
	27.78	0.9531	0.264
	35.14	0.9697	0.279

Table 7.3 Activation volume, activation energy and close-packed volume for 5 wt % PCL solutions in acetone and acetone + CO₂ mixtures

System	Activation energy, E^\ddagger (kJ/mol)					Activation volume, V^\ddagger (cm ³ /mol)				Close-packed volume, V_0 (cm ³ /g)
	Pressure (MPa)					Temperature (K)				
	7	14	21	28	35	398	373	348	323	
PCL (5 wt %, 14 K) + acetone	9	9	8	8	8	25	18	18	12	0.60
PCL (5 wt %, 14 K) + acetone + CO ₂ (1 wt %)	9	9	8	8	8	26	21	15	15	0.60
PCL (5 wt %, 14 K) + acetone + CO ₂ (2 wt %)	9	8	8	8	8	25	20	15	14	0.59
PCL (5 wt %, 14 K) + acetone + CO ₂ (4 wt %)	9	9	8	8	8	29	19	15	13	0.58
PCL (5 wt %, 14 K) + acetone + CO ₂ (40 wt %)	-	-	-	7	7	-	-	25	24	0.50

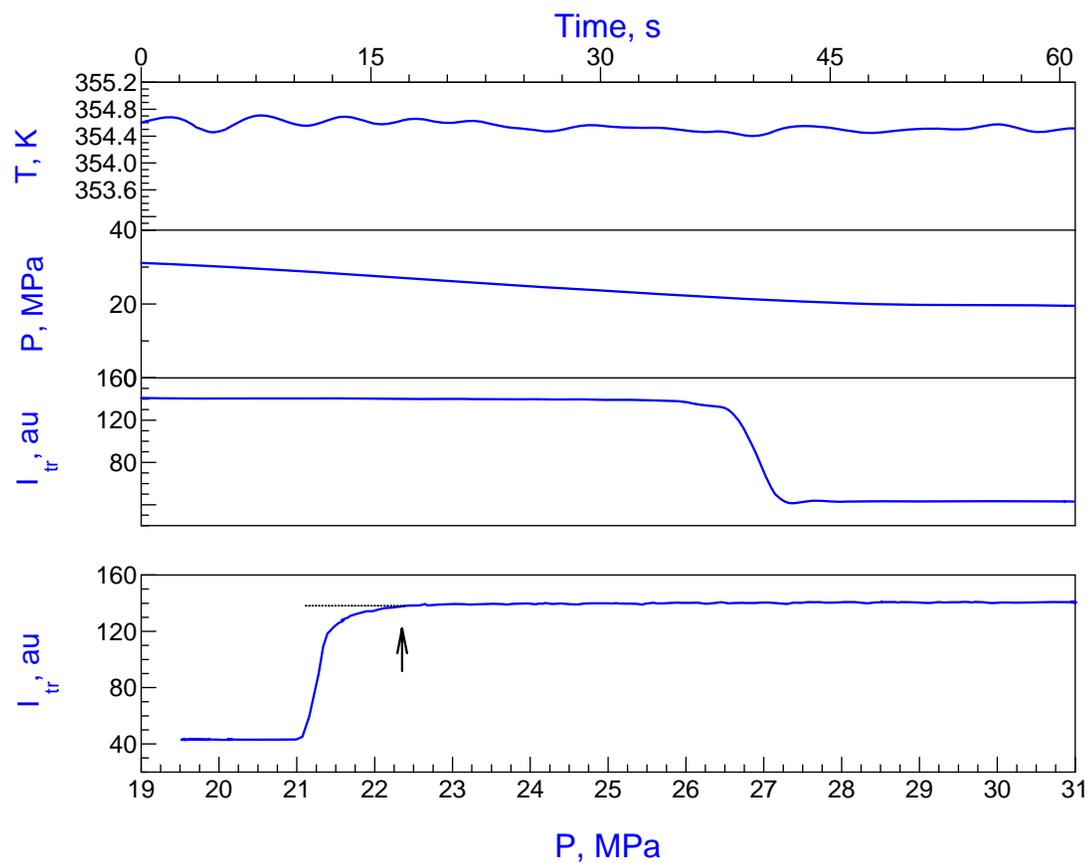


Figure 7.1. Variation of temperature, pressure, and transmitted light intensity with time (top three figures), and the determination of the phase separation (demixing) pressure from variation of I_{tr} with pressure (lower figure) during depressurization at constant temperature of 354.7 K in the view cell for 5 wt % PCL solution in acetone.

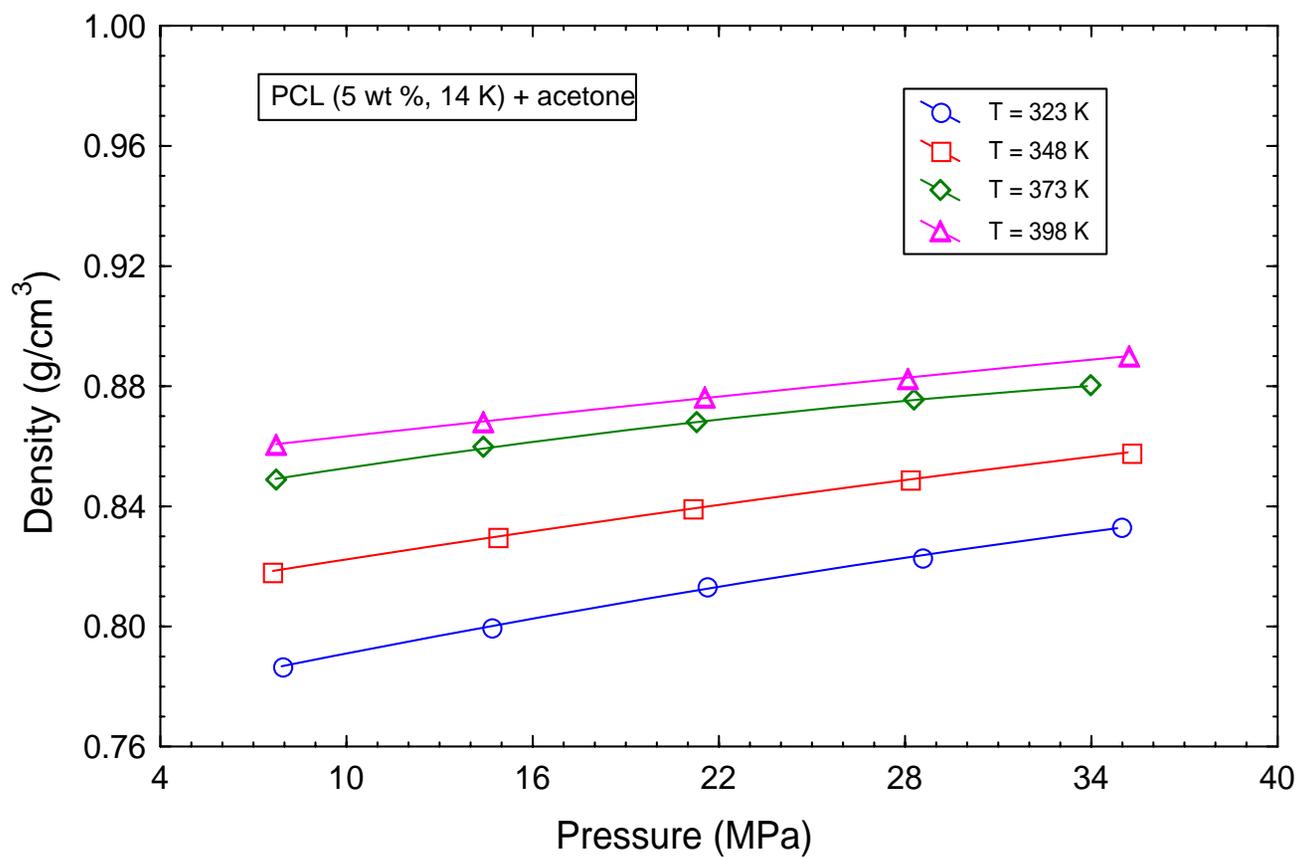


Figure 7.2 Variation of density with pressure at 323, 348, 373, and 398 K for 5 wt % solution of PCL in acetone.

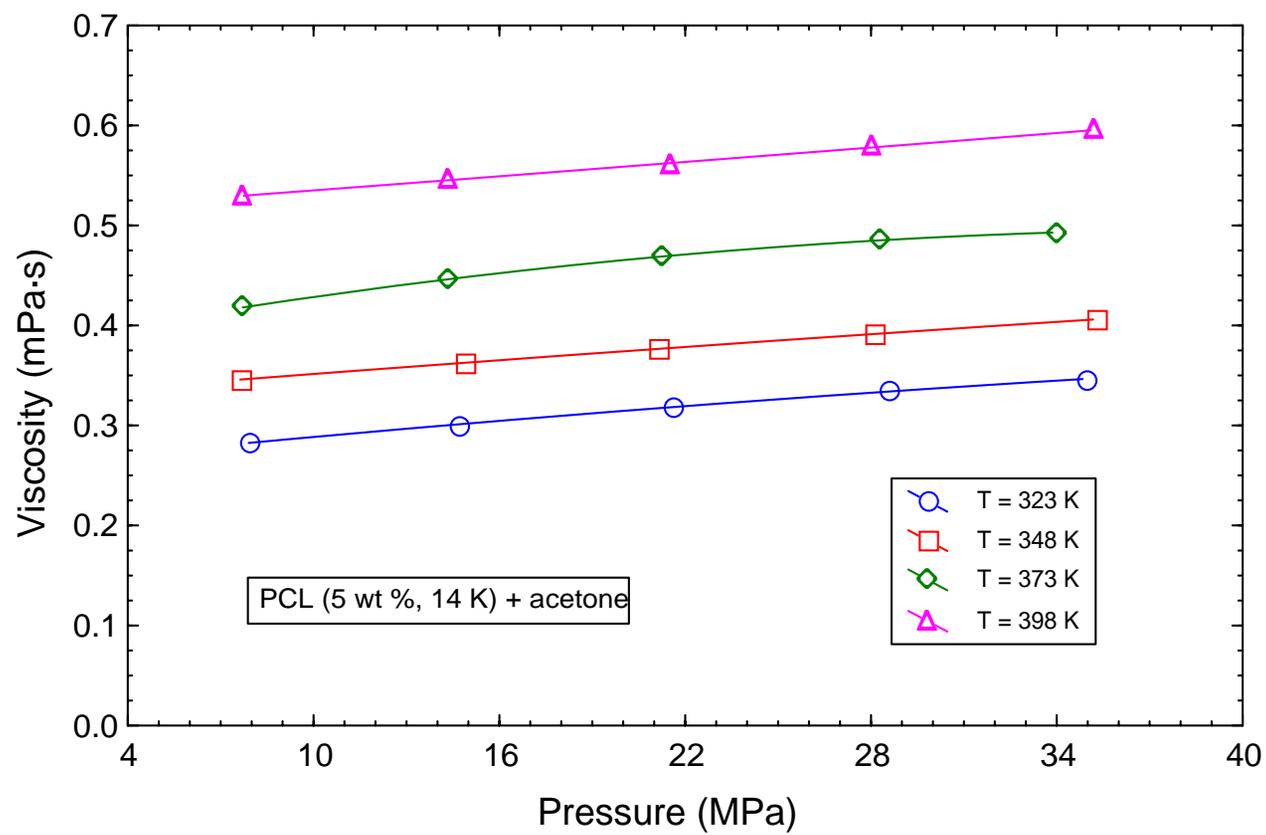


Figure 7.3 Variation of viscosity with pressure at 323, 348, 373, and 398 K for 5 wt % solution of PCL in acetone.

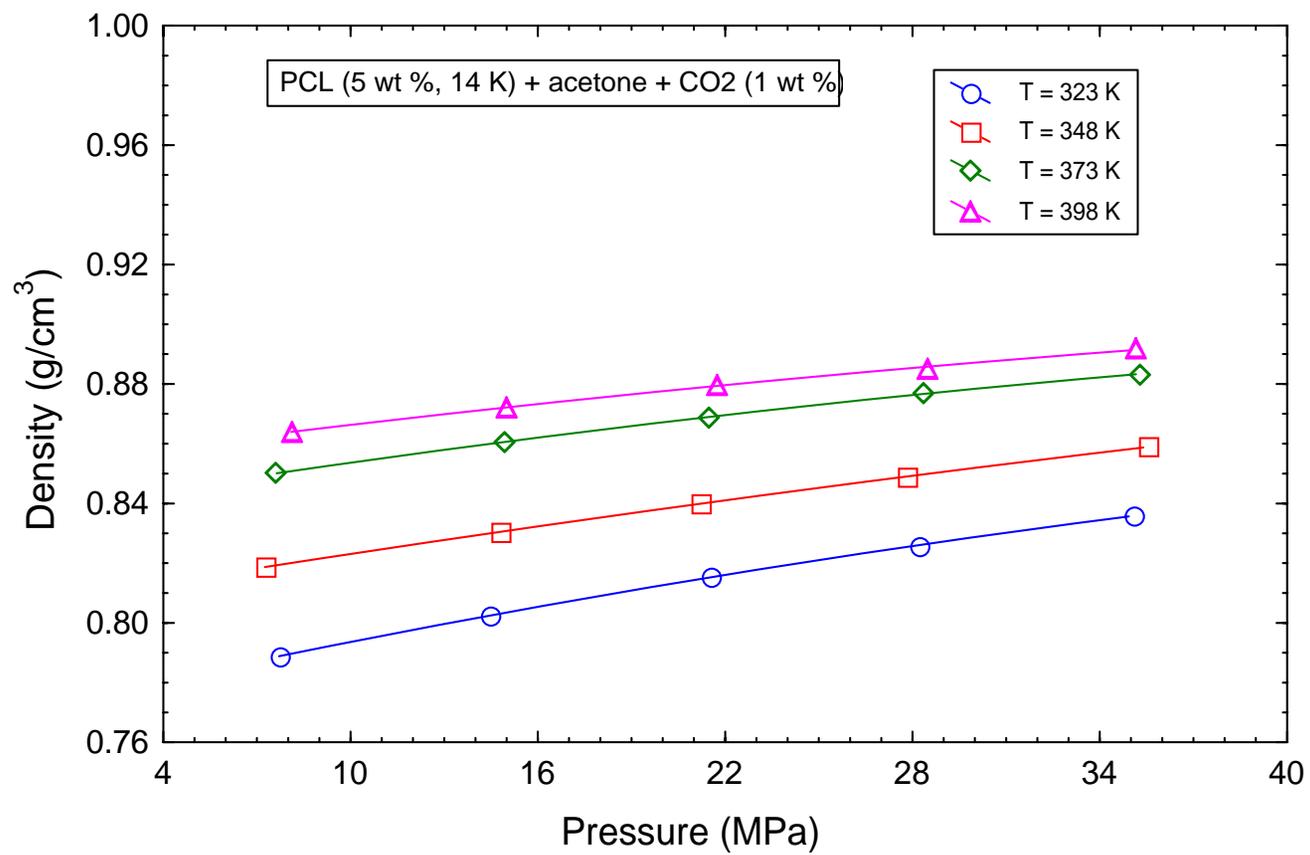


Figure 7.4 Variation of density with pressure at 323, 348, 373, and 398 K for mixtures of PCL (5 wt%) + acetone + CO₂ (1 wt %).

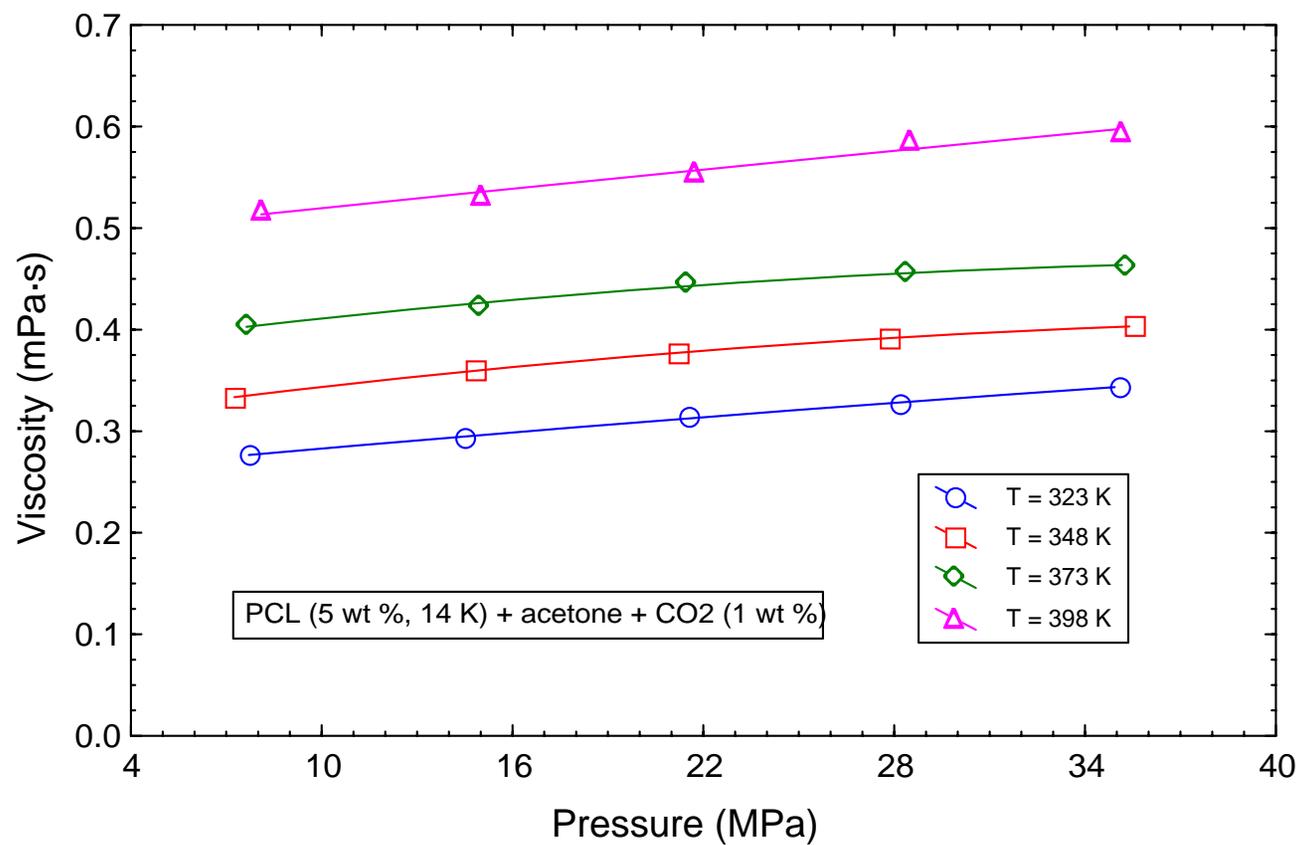


Figure 7.5 Variation of viscosity with pressure at 323, 348, 373, and 398 K for mixtures of PCL (5 wt%) + acetone + CO₂ (1 wt %).

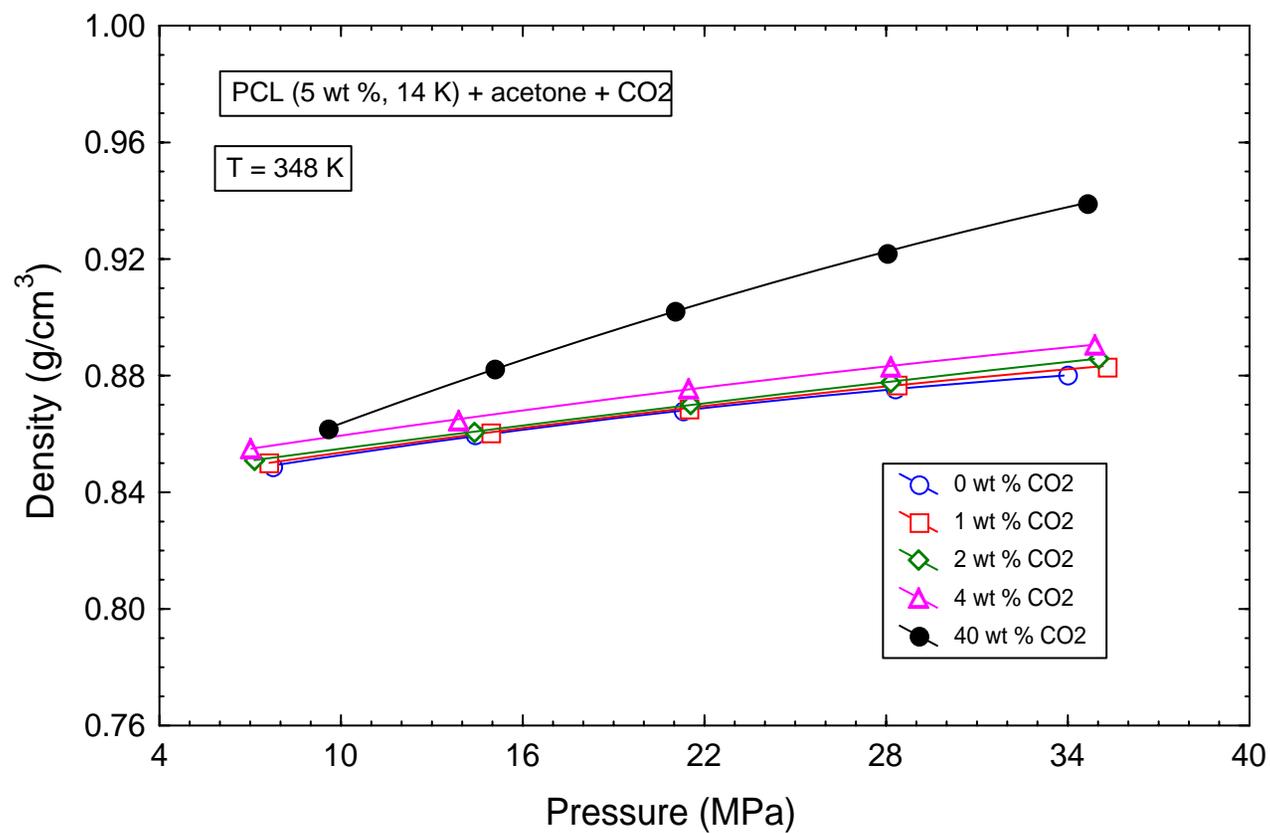


Figure 7.6 Variation of density with pressure at 323, 348, 373, and 398 K MPa for mixtures of PCL (5 wt%) + acetone + CO₂ containing 0, 1, 2, 4, 40 wt % CO₂.

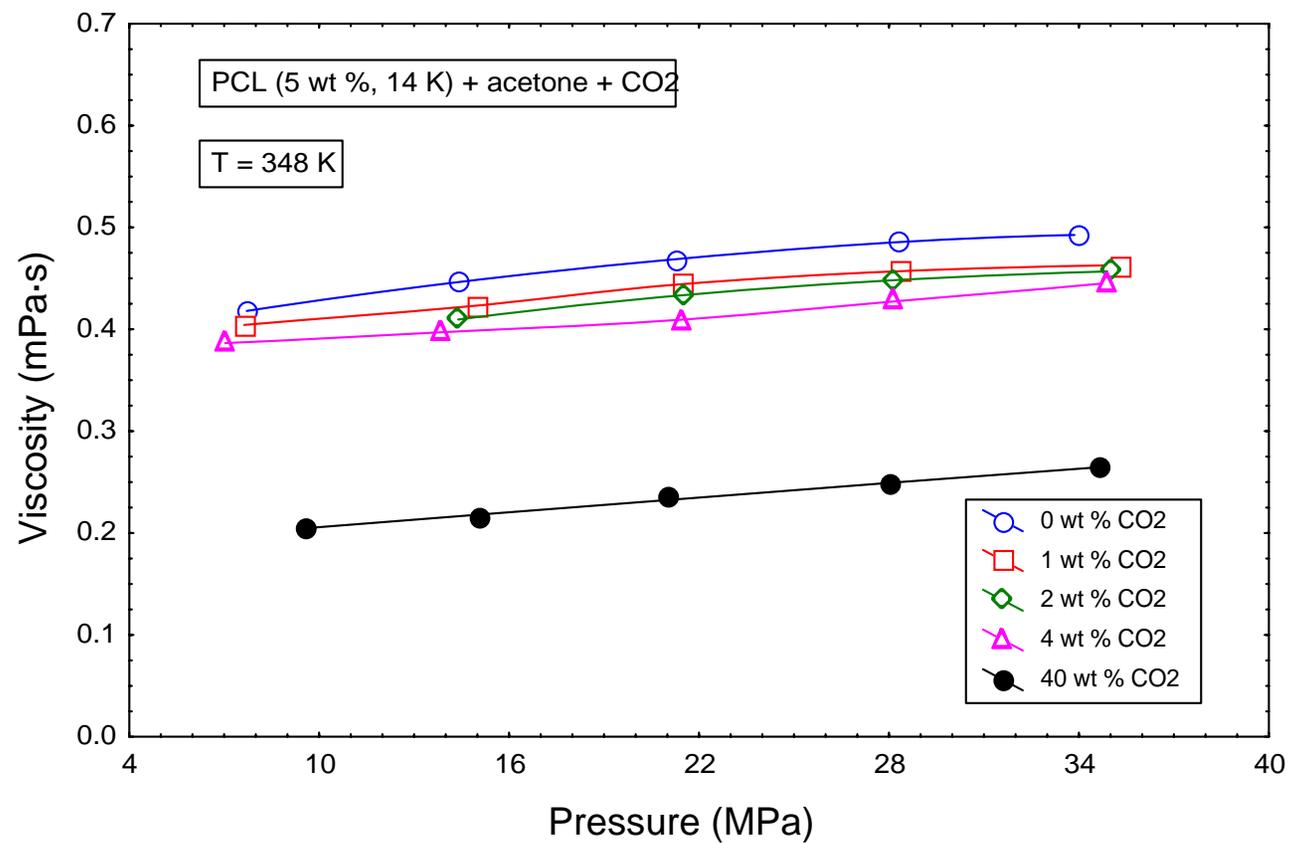


Figure 7.7 Variation of viscosity with pressure at 323, 348, 373, and 398 K MPa for mixtures of PCL (5 wt%) + acetone + CO₂ containing 0, 1, 2, 4, 40 wt % CO₂.

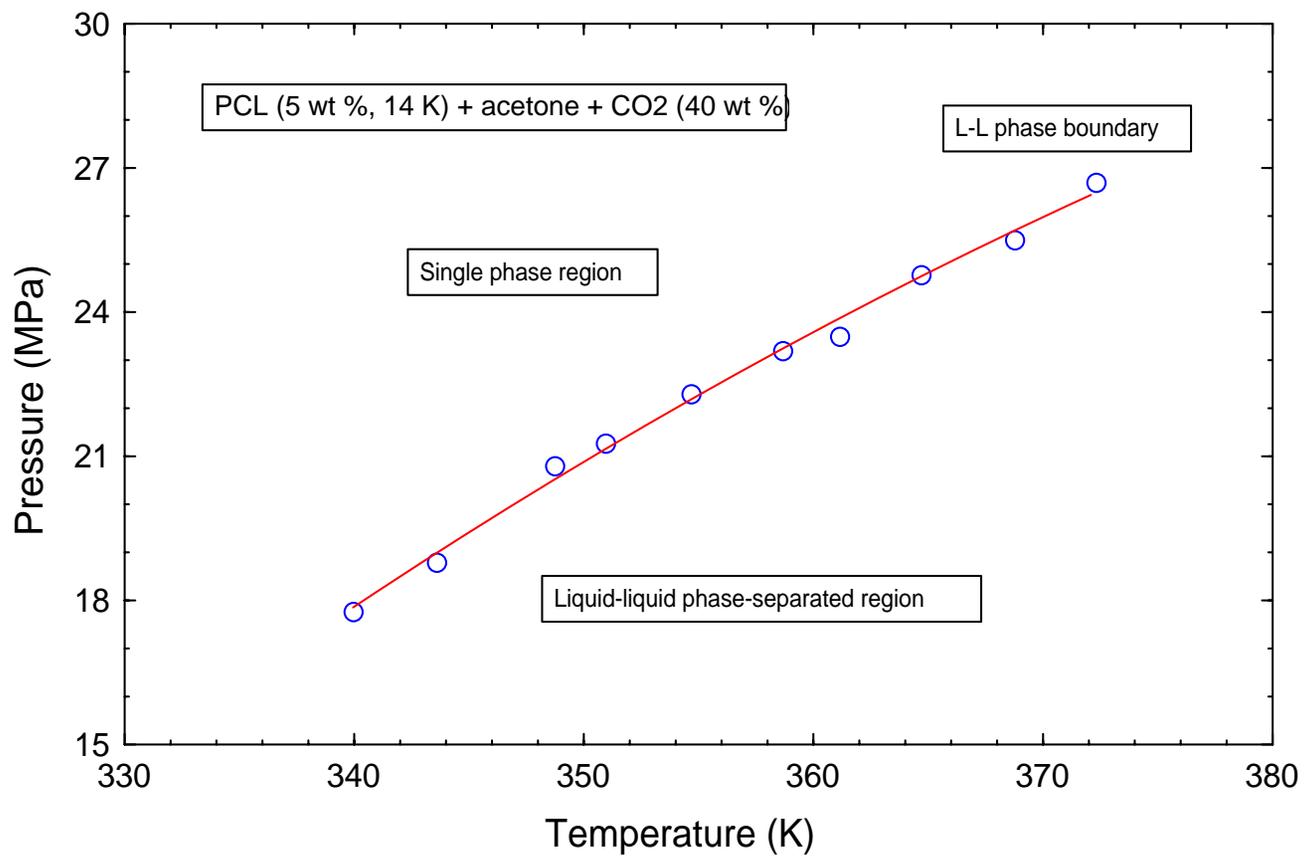


Figure 7.8 Liquid-liquid phase boundary for mixture of PCL (5 wt %, 14 K) + acetone + CO₂ (40 wt %) as determined in the view cell.

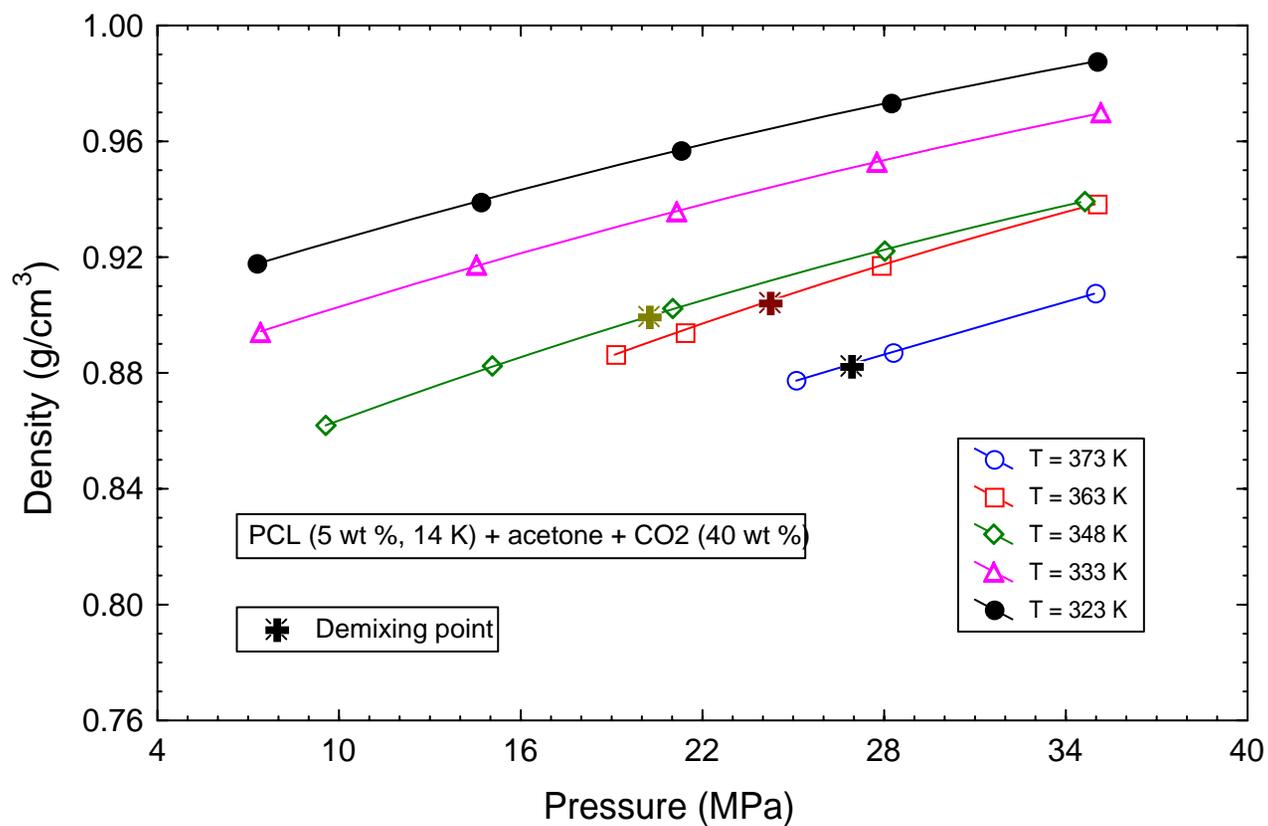


Figure 7.9 Variation of density with pressure at 323, 348, 373, and 398 K MPa for mixtures of PCL (5 wt%) + acetone + CO₂ (40 wt %). (The demixing points are also included (See Figure 7.8)).

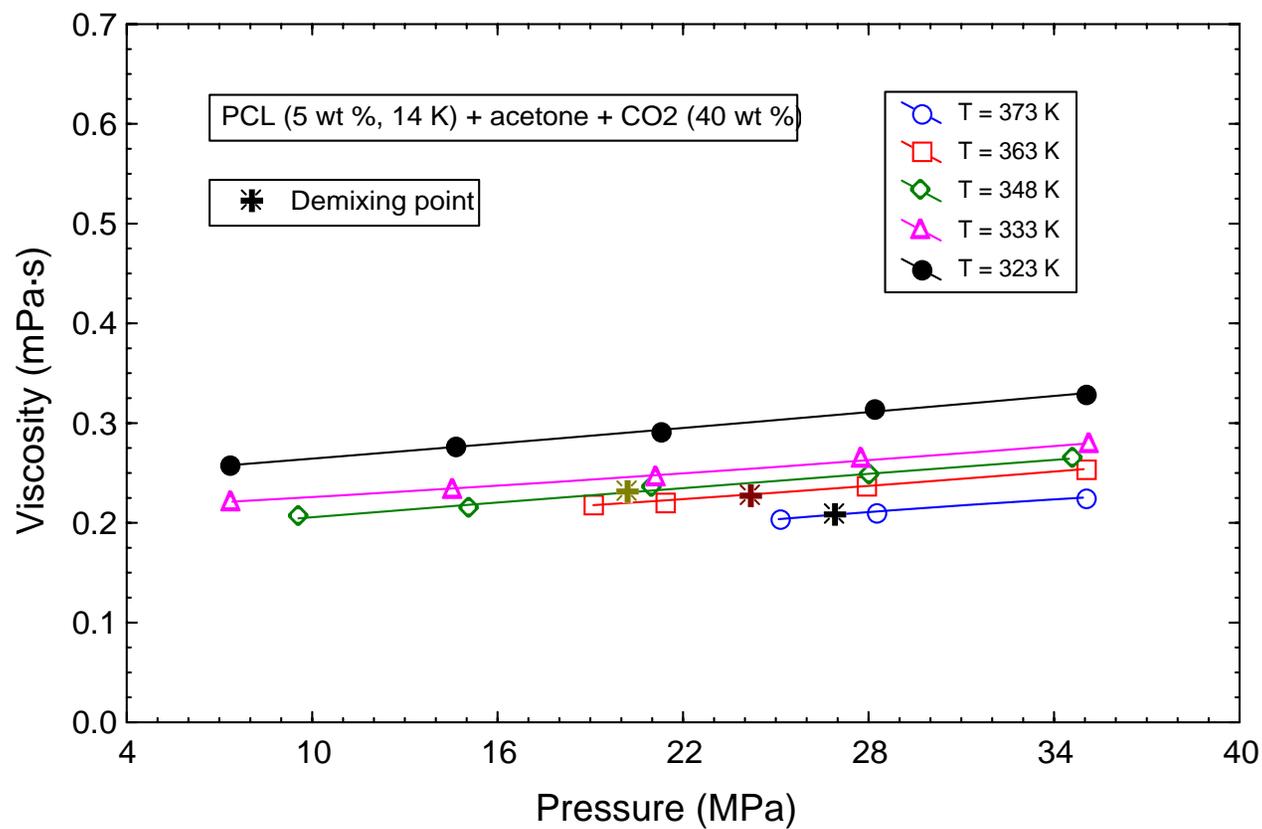


Figure 7.10 Variation of viscosity with pressure at 323, 348, 373, and 398 K MPa for mixtures of PCL (5 wt%, 14 K) + acetone + CO₂ (40 wt %). (The demixing points are also included (See Figure 7.8)).

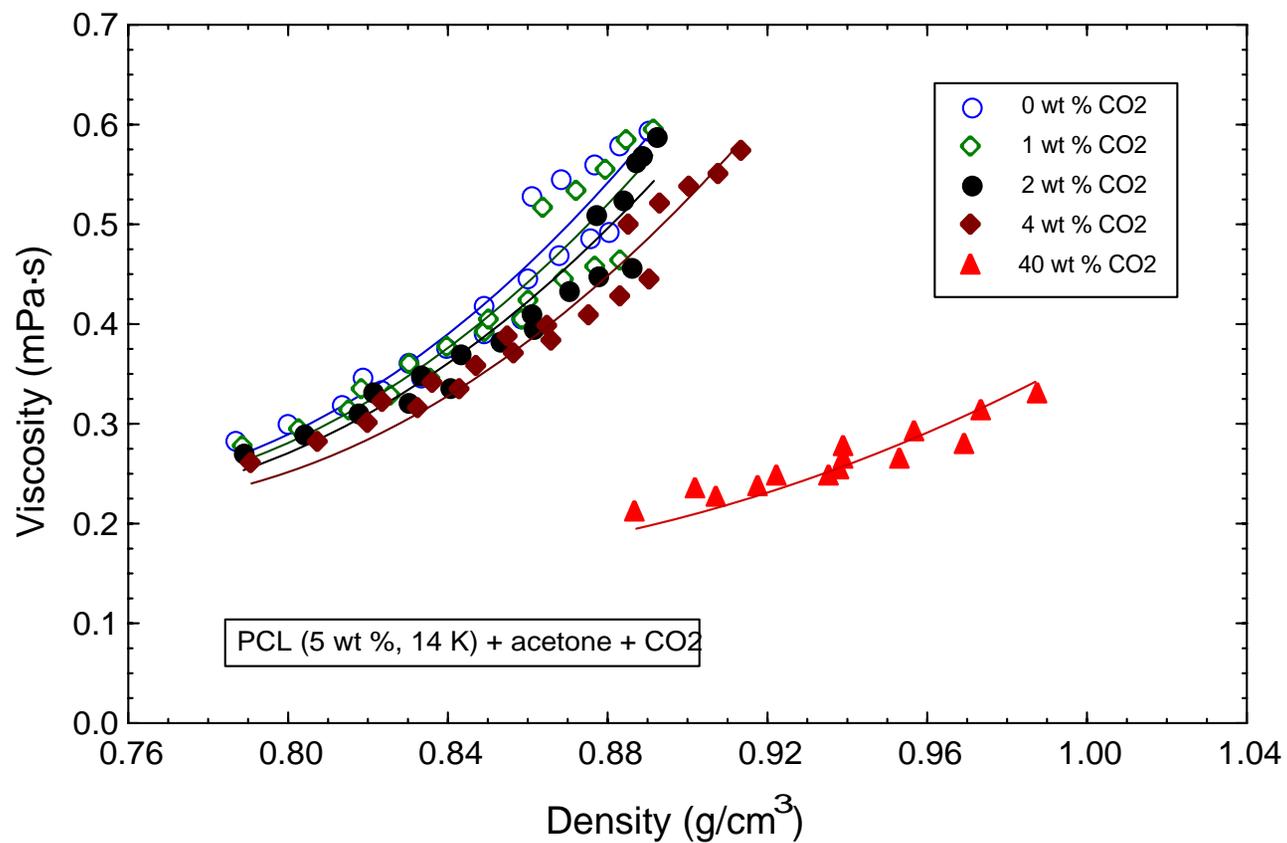


Figure 7.11 Variation of viscosity with density for mixtures of PCL (5 wt %, 14 K) + acetone + CO₂ (0, 1, 2, 4, 40 wt %). The solid curves are correlations based on Doolittle equation.

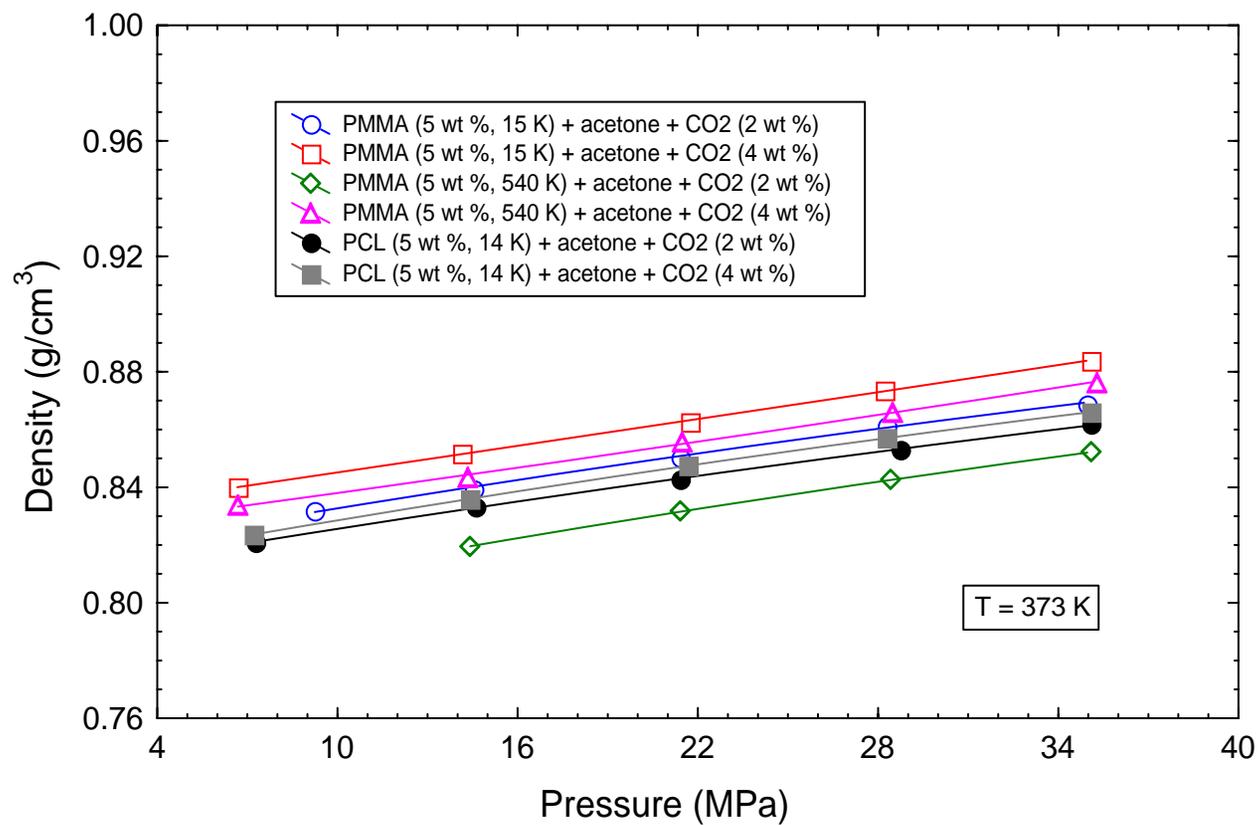


Figure 7.12 Comparison of the variation of density with pressure at $T = 373\text{ K}$ for the mixtures of PMMA (15 K) + acetone + CO_2 , PMMA (540 K) + acetone + CO_2 , and PCL (15K) + acetone + CO_2 .

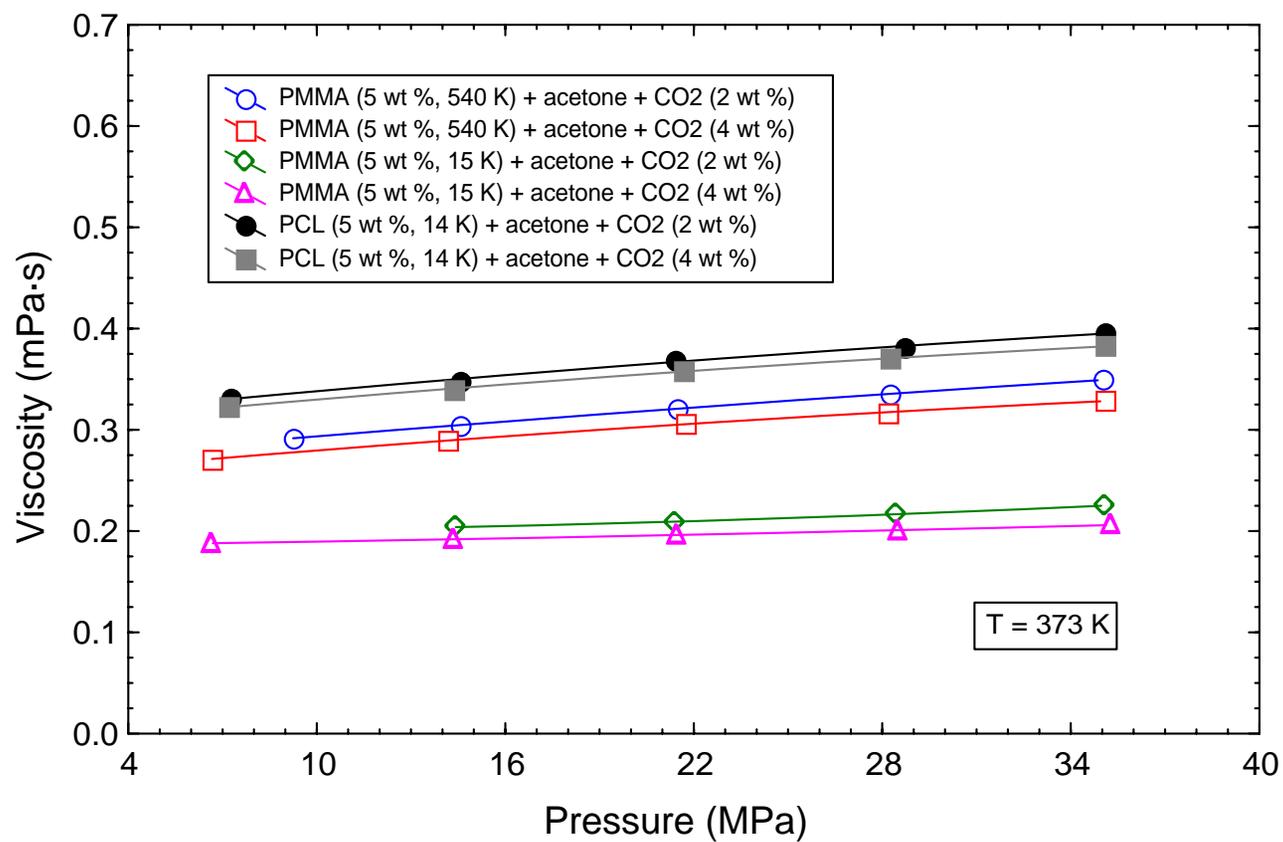


Figure 7.13 Comparison of the variation of viscosity with pressure at $T = 373\text{ K}$ for the mixtures of PMMA (15 K) + acetone + CO_2 , PMMA (540 K) + acetone + CO_2 , and PCL (15K) + acetone + CO_2 .