CHAPTER 6

VISCOSITY AND DENSITY OF PMMA IN ACETONE + CARBON DIOXIDE MIXTURES

Utilization of high-pressure fluids as process or processing fluids in polymer synthesis and modifications is an area of active research. For practical implementations, there is a continuing need for basic data such as the volumetric properties like density and the transport properties such as viscosity of polymer solutions at high pressures (Kiran, 1994; Brunner, 2004).

Viscosity is a particularly important parameter which influences the mass and heat transfer characteristics of these solutions, and also influences the kinetics of phase separation processes (Dindar and Kiran, 2002). In addition to its practical value for processing and process design, viscosity data on polymer solutions are used to gain fundamental insights on polymer-solvent interactions and whether or not the solvent is a “poor”, or a “good’ solvent. The viscosity data is used to assess the polymer chain dimensions and polymer molecular weights. Indeed, the intrinsic viscosity is related to root-mean square end-to-end distance $<R^2>^{1/2}$, or the hydrodynamic volume, according to the Fox-Flory relationship $[\eta] \sim <R^2>^{3/2}$, and to molecular weight M according to the Mark-Houwink-Sakurada type relations $[\eta] = KM^a$ where K and a are system specific parameters (Kiran and Sen, 1993; Teraoka, 2002; Strobl, 1997; McKee et. al., 2005). The intrinsic viscosity is also related to the critical polymer concentration for chain entanglement and overlap c* according to [η]c* ~1.0. (Teraoka, 2002; Strobl, 1997; McKee et. al., 2005). The knowledge on critical overlap concentration is especially important in fiber spinning from polymer solutions, which has gained a renewed interest recently because of growing activity in electrospinning processes (Shenoy *et. al.*,2005; Levit and Tepper, 2004; Theron et. al., 2004; Pankaj, 2004). The concentration dependence of viscosity is indeed used to differentiate the extent of entanglements. Significantly different exponents are displayed with onset of entanglements, the concentration dependence becoming higher, with typical values in the range 4 to 4.5 in the entangled versus 1.1 to 1.4 in unentangled semidilute solutions in good solvents. In a recent study on PMMA solutions in DMF, intrinsic viscosity values and critical overlap concentrations have been reported at 25 °C and ambient pressures for samples with different molecular weights. For a sample with M_w = 126 K, and M_w/M_n = 1.26, intrinsic viscosity is reported as 37.8 cm3/g and c* = 0.026 g/cm3 (corresponding to 2.7 wt % PMMA on mass basis) (Pankaj, 2004). For semi dilute solutions of PMMA in DMF, the exponent of the concentration dependence of viscosity were observed to change from 0.65 to 5.3 in going from the unentangled to the entangled regime However, there is no information at present if solutions at high pressures display similar exponents and follow similar scaling laws.

The data base for viscosity of polymer solutions at high pressures is not extensive even for common systems such as PMMA + acetone. This is in part due to limitations of available high pressure viscometers that are suitable for such measurements (Sen and Kiran, 1990; Mattischek and Sobczak, 1994). Even though there is extensive data on high- pressure densities for various liquid solvents (Pöhler and Kiran, 1997a; Azevedo et. al., 2004), we were surprised to find out that high-pressure viscosity data were lacking even for acetone. Very limited information on the temperature dependence at ambient pressures up to about 50 ^{o}C is available in the literature (Topallar and Bayrak, 1998). No high pressure viscosity data is available in the open literature for acetone, and acetone + CO_2 mixtures. We were rather surprised with this finding in that acetone is an important solvent used in the polymer industry for production of films, fibers and coatings where viscosity plays a very important role. Acetone is a common solvent in the textile industry for degreasing of wool and degumming of silk. Acetone based solvents are also being explored in high pressure extraction of plant seed oils where viscosity information on the solvent, and the solvent + extracted material becomes important for access and removal of components from the plant matrix (Topallar and Bayrak, 1998). Acetone + CO_2 fluid mixtures have been used in swelling and impregnation studies, with some unique application such as the production of eye protection lenses via supercritical fluid infusion of silver nanoparticles from these mixtures into polymeric lens surfaces (Nakanishi et. al., 2005). A related application is textile dying where the solubility of the dye and its penetration into the textile fibers are adjusted using acetone + CO_2 solvents (Muthukusan et. al., 1999).

Acetone + CO_2 mixtures as tunable solvents for poly (methyl methacrylate) are important in fractionation of PMMA (Coen et. al., 2003) by, for example, the gas anti-solvent method. Acetone + CO_2 fluid mixtures are also being used in biomedical applications such as forming polymeric microspheres of PMMA and poly caprolactone along with specific active components such as cholesterol and albumin (Domingo et. al., 2003), or forming microspheres of other biodegradable polymers such as poly (lactic acid) (Tom and Debenedetti, 1991).

In all these applications, viscosity plays a significant role and there is a need for an expanded data base for viscosity at high pressures. Various techniques can be, and have been used to measure the viscosity of fluids at high pressures. Among these are the (a) the vibrating quartz-crystal viscometers (Vieira dos Santos and Nieto de Castro, 1997), (b) the oscillating-disk viscometers (Yokoyama and Takahashi, 1997), (c) the vibrating-wire viscometer (Padua et. al., 1996), (d) the high-pressure capillary viscometer (Yener et. al., 1998), and (e) the magnetoviscometer (9). However, the most widely used viscometers are based on the principle of a falling (or rolling) body, which are based on measurement of the fall time of a sinker in the fluid under pressure. The falling-body-type viscometers have been used to measure the high-pressure viscosity of dilute polymer solutions in good solvents (Cook et. al., 1992), various hydrocarbon solvents and their mixtures (Et-Tahir, et. al., 1995; Kiran and Sen, 1992), and polymer solutions in supercritical fluids (Dindar and Kiran, 2003; Kiran and Sen, 1993; Mertsch and Wolf, 1994). In these systems, the viscosity is determined at a constant temperature and pressure by measuring the fall time of the sinker (which is converted to terminal velocity V_t), the density difference between the sinker (ρ_s) and the solution (ρ_f), that is (ρ_s-ρ_f), and a calibration constant for the instrument (K) according to:

$$\eta = \frac{1}{V_t}(\rho_s - \rho_f)K \qquad \text{(Eq.6.1)}$$

Depending on the density of sinker used, the measured viscosity range can be varied from that of gaseous fluids to that of polymer solutions at relatively high concentrations. In our laboratory, a home-made falling-cylinder-type viscometer has been used since 1990, and the viscosity data of n-alkanes (Kiran and Sen, 1992), polystyrene solutions in n-butane (Kiran and Sen, 1993), polyethylene in n-pentane (Kiran and Gokmenoglu, 1995), poly (diemethl siloxane) in supercritical CO_2 (Xiong and Kiran, 1995), and polystyrene in n-hexane (Xiong and Kiran, 1997) and in methylcyclohexane (Yeo and Kiran, 1999) have already been generated.

In this paper, we now report on the viscosity and density of solutions of poly (methyl methacrylate) (PMMA) in acetone and in acetone plus CO_2 mixtures which have been determined in the temperature range from 50 to 125 °C in steps of 25 °C over the pressure range from 7 MPa to 35 MPa in steps of 7 MPa.

6.1 Experimental

6.1.1 Materials

Poly (methyl methacrylate)s were obtained from Scientific Polymer Products. Two samples with molecular weights M_w = 15,000 (Mw/Mn = 1.8) and Mw = 540,000 (M_w/M_n = 2.8) were used. Acetone (Burdick & Jackson) with purity of 99.99% and CO_2 (Air Product) with a minimum purity of 99.99% were used without further purification.

6.1.2 Viscometer and operational procedure

The viscometer used has been described in Chapter 4 and shown in Figure 4.6. It is designed to measure the viscosity and also provide information on the phase state and the density of the solutions. This is achieved by combing a view cell with a fall tube and a variable-volume attachment. During operation, the main cell is first loaded with the polymer. Then, solvent is charged to achieve a target concentration. With the aid of the electromagnetic stirrer and the circulation pump, homogeneity is achieved and verified by observations through the sapphire windows. The pressure is adjusted at any loading and temperature, by changing the position of the movable piston.

The fall time of the sinker is monitored by a series of three LVDTs. The signal from each LVDT (as voltage reading) is recorded for the full length of the fall tube as a function of time. The data is then processed to generate distance versus. fall-time plots for the sinker from which the terminal velocity is determined. This determination is usually done using the signal output from he last two LVDT coils. The terminal velocity along with density is then used to determine viscosity using the following equation

$$\eta = \frac{1}{V_t}(\rho_s - \rho_f)K$$

where K is a calibration constant. K is determined by measuring the terminal velocity and density for systems of known viscosity. For the present system K = 0.0199.

Figures 6.1a and 6.1b show the actual LVDT outputs and the velocity of the sinker in pure acetone, at 100 ºC and 34 MPa. Fall time is around 60 seconds. For polymer solutions, the viscosities are higher. This is reflected by the longer fall times as illustrated in Figures 6.2 and 6.3 for a 10 wt % solution of the 15K and 540K molecular weight PMMA samples.

It is important to note that these viscosity measurements with the present system are low-shear measurements. The terminal velocities for the sinker are low, with values such as 0.152

and 0.062 cm/s for the polymer solutions as shown in Figures 6.1 through 6.3. The gap between the skinner and the fall tube is about 0.018 cm, and with these terminal velocities for the sinker, the shear rates experienced by the polymer solutions are around 8.5 to 3.5 s^{-1}. The near zero-shear viscosity data generated with this system is of additional significance because such data are critical for comparisons and modeling.

The system temperature and pressure is controlled with an accuracy of ± 0.1 K and ± 0.06 MPa, respectively. The accuracy of the system is ± 1 % for the density and ± 3 % for the viscosity (Kiran and Gokmenoglu, 1995; Xiong and Kiran, 1995; 1997).

6.2 Results and discussion

Measurements were conducted at concentrations of 2, 5, 10 and 20 wt % with M_w=540,000 and at 10 and 20 wt % with M_w = 15,000 PMMA sample. The viscosity and density data are presented. The effect of temperature, pressure, polymer concentration, and polymer molecular weight on viscosity and density are studied and the activation volume and activation energy are reported. A Doolittle equation is employed to correlate viscosity with density and the closed-packed volume is reported. The effect of adding CO_2 on viscosity is investigated for the 5 wt % solutions with the high-molecular weight (M_w = 540 K) polymer sample.

6.2.1 Acetone

For acetone, the densities and viscosities were determined at 50, 75, 100, and 125 ºC in the pressure range of 7- 35 MPa. The results are shown in Table 6.1, Figures 6.4 and 6.5.

In Figure 6.4, the density data are compared with measurements that were reported in a previous study in our laboratory over a wider pressure range (Pohler and Kiran, 1997), as well as with data from a recent independent publication (Azevedo et. al., 2004). The present results are in good agreement. As expected, densities increase with pressure and decrease with temperature. The pressure sensitivity of density is not high and does not vary much with temperature, which is a consequence of the incompressibility of liquids. Figure 6.5 shows the variation of acetone viscosity with pressure and temperature. Even though the viscosities are lowered with increasing temperature, the pressure sensitivity of viscosity for this solvent is observed to be very low. This is somewhat unexpected compared to the behavior of other solvents where viscosities would typically show an increase with pressure.

6.2.2 Polymer solutions

A. PMMA (15 K) + acetone Densities and viscosities were determined for polymer solutions at 10 and 20 wt % in acetone at 323, 348, 373, and 398 K in the pressure range of 7- 35 MPa. These data are shown in Table 6.2. Figures 6.6 and 6.7 show the variation of densities and viscosities for the 10 wt % solutions at each temperature. The trends are as expected with the viscosity increasing with pressure and decreasing with temperature. Comparison with Figure 6.4 and 6.5 for acetone shows that the viscosity and the density values are higher for the solutions. Figures 6.8 and 6.9 show the variation of density and viscosity with pressure at 373 K, but for different concentrations. The figures illustrate also the values for pure solvent. A 20 wt % solution of this polymer has a density greater about 14 % compared to pure acetone.

The density of PMMA is around 1.2 g/cm^3, and solution densities are not too far from a linear combination.

B. PMMA (540 K) + acetone Table 6.3 shows the data for these solutions. Figures 6.10 and 6.11 are the density and viscosity variations with pressure for the 10 wt % solutions at 50, 75, 100, and 125 ºC. Figures 6.12 and 6.13 compare the density and viscosity data for different concentrations at 373 K. Density data are similar to the data for the lower molecular weight polymer solution (see Figure 6.6). Viscosities are however much higher as would be expected for higher molecular weight polymers. This is demonstrated in Figure 6.14 for 20 wt % solutions at 100 °C for the solutions of PMMA with different molecular weights.

C. PMMA (540 K) in acetone + CO_2 We have investigated the change in the density and viscosity of the high molecular weight PMMA solutions in acetone upon addition of 1, 2, and 4 wt % CO_2. The results are given as Table 6.4. Figures 6.15 and 6.16 are comparative plots showing the change in density and viscosity for these solutions at 373 K. Upon addition of CO_2, as shown in Figure 6.15, densities are increased. This is expected because of the higher density for CO_2 compared to acetone at those temperatures and pressures (Pohler and Kiran, 1997). Viscosities - on the other hand were lowered when CO_2 is present. The viscosity reduction in this system is nearly 30 % for the 4 wt % CO_2 addition.

6.2.3. Effect of pressure on viscosity

The pressure dependence of viscosity at a constant temperature can be described in terms of flow activation volume through the following equation (Yeo and Kiran, 1999):

$$\eta = A\exp(V^{\neq}P/R) \quad \text{(Eq.6.2)}$$

where η is viscosity, A is constant, $V^{\neq}$ is the flow activation volume, P is the pressure, R is the gas constant and T is the temperature. According to Eq.6.2, the activation volumes of acetone, PMMA + acetone binary solutions and PMMA + acetone + CO_2 ternary solutions were calculated from the slopes of $\ln\eta$ versus P plots at each temperature and concentration. The results are listed in Table 6.5. The values of activation volume ranged from 5-37 cm^3 mol^{-1}. The activation volumes were observed to increase with temperature at all concentrations and molecular weights, showing that, at a higher temperature, the viscosity becomes more pressure dependent for these solutions. A larger activation volume was obtained for the higher molecular weight sample. There appears to be a reduction in activation volume for higher CO_2 additions.

6.2.4 Effect of temperature on viscosity

The temperature dependency of viscosity for polymer solutions can be determined by an Arrhenius type equation (Billmeyer, 1984):

$$\eta = B\exp\left(E^{\neq}/RT\right) \quad \text{(Eq.6.3)}$$

The activation energies for all the systems were evaluated from the slope of $\ln\eta$ versus 1/T plots at each pressure and concentration. The results are summarized also in Table 6.5. The calculated activation energies ranged from 5-10 kJ mol^{-1}. Generally, the activation energies were observed to decrease with pressure at all concentrations and molecular weights, showing that at a higher pressure, the viscosity becomes less temperature dependent. The activation energy was found to be essentially not affected by concentration and molecular weight in the range investigated in the present study, which is consistent with the results of previous study (Yeo and Kiran, 1999).

6.2.5. Correlation of viscosity with density

Figures 6.17 - 6.19 show 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 8- 35 MPa. Figures 6.18 and 6.19 include both also 3D representations of the data.

In these figures, viscosity at different pressures and temperatures essentially tend to collapse to a single curve, even though some temperature dependence can be still differentiated. Density is indeed a well - known scaling factor for the viscosity (Kiran and Sen, 1992; Kiran and Gokmenoglu, 1995; Xiong and Kiran, 1995, 1997). A Doolittle-type equation (Dindar and Kiran, 2002) with three parameters has been used to correlate the experimental data, i.e.:

$$\eta = A \cdot \exp\left(\frac{B}{1 - V_0 \cdot \rho}\right) \qquad \text{(Eq.6.4)}$$

where A and B are constants, ρ is the density of the solutions and V_0 is the closed-packed volume for the solutions. All the experimental data were used to calculate the optimal values for the three parameters in Eq.6.4 by the Hooke-Jeeves and quasi-Newton method with convergence criterion of 0.0001. The parameters are summarized in Table 6.6. The equations with these values of parameters are represented by the solid curves in Figures 6.17 – 6.19. These equations correlate the data well except for the 20 wt % solution for the 540 K polymer. These correlations suggest a closed - packed volume of about 0.9 cm^3g^{-1} for all the systems investigated. Figure 6.19 shows the results for the systems containing CO_2. The significance of this figure is two-fold. One is that, it visually demonstrates that to achieve a given viscosity, the solutions containing CO_2 must be compressed to higher densities. If the density is sustained at a given value, then it demonstrates that viscosity is lowered with increasing CO_2 content. The dotted cross – lines that are superimposed in this figures should facilitate this visualization of change in viscosity at constant density, or change in density at constant viscosity.

6.2.6 Effect of concentration on viscosity

Figure 6.20 shows the variation of viscosity with polymer concentration in solution of PMMA with M_w = 540 K in acetone at two different temperatures (323 and 398 K) holding pressure constant (at 35 MPa) and two different pressures (7 and 35 MPa) holding temperature constant (at 398 K). The concentrations have been expressed here in units of g/cm^3 at each T and P. (The data points correspond to the 2, 5, 10 and 20 wt % solutions). Expressing the concentrations in g/cm^3 units, which are the traditional units commonly used for polymer solutions, is simple with this viscometer system since the densities of the solutions are directly measured at any T/P condition. This figure demonstrates a significant change in viscosity in the concentration range from 0.045 - 0.075 g /cm^3. The concentration exponents outside this range are similar. The figure suggests that the overlap concentration for these solutions is likely to be around 0.045 g/cm^3. At ambient pressure for PMMA solutions in DMF, the overlap concentrations have been reported to be 0.06 for a polymer with M_w = 34,000 and PDI = 1.6; and 0.013 for a sample with M_w =366,000 and PDI = 1.8. (These concentrations were reported to correspond to 6.2 and 1.3 wt %, respectively).

6.3 Summary and conclusion

In this chapter, we have reported on the high-pressure viscosity and density of solutions of poly (methyl methacrylate) (PMMA) in acetone and in acetone plus CO_2 mixtures in the temperature range from 50 to 125 °C in steps of 25 °C over the pressure range from 7 MPa to 35 MPa. Measurements were conducted with PMMA samples of two different molecular weights (M_w = 15,000, M_w/M_n = 1.8 and M_w = 540,000, M_w/M_n = 2.8) at concentrations of 2, 5, 10 and 20 wt % with M_w=540,000 and at 10 and 20 wt % with M_w = 15,000 sample. The effect of adding CO_2 on viscosity was investigated for the 5 wt % solutions with the high molecular weight polymer sample. The viscosities were observed to be relatively low, with values in the range from 0.2 to 1.6 mPa·s for these solutions. The flow activation energies were around 5 - 10 kJ/mol. Flow activation volumes were in the range from 5 - 40 cm^3/mol. Closed packed volumes correlated from density correlation were around 0.9 cm^3/g. The overlap concentrations were estimated to be around c* = 0.045 g/cm^3. In the presence of CO_2, densities of the solution show an increase, reflecting the higher density of compressed CO_2 compared to that of acetone, but viscosity were significantly lowered, with a reduction of about 30 % at 4 wt % CO_2 addition. The density dependence of viscosity is used to visually illustrate the need for higher pressures in the presence of CO_2 to sustain same viscosity level.

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Table 6.1 Density and viscosity data for acetone

	Pressure (MPa)	**Density** (g/cm^3)	**Viscosity** (mPa·s)
T = 125 °C	8.20	0.6919	0.169
	13.49	0.7058	0.162
	20.48	0.7174	0.182
	27.90	0.7282	0.184
	33.71	0.7374	0.205
T = 100 °C	8.27	0.7177	0.200
	14.66	0.7285	0.203
	21.31	0.7384	0.215
	28.55	0.7474	0.214
	35.26	0.7555	0.232
T = 75 °C	8.14	0.7370	0.244
	14.42	0.7462	0.253
	21.40	0.7546	0.255
	28.25	0.7623	0.262
	35.13	0.7697	0.264
T = 50 °C	7.53	0.7584	0.290
	14.30	0.7631	0.367
	21.40	0.7704	0.362
	27.80	0.7773	0.377
	34.95	0.7838	0.383

Table 6.2 Density and viscosity data for PMMA (15 K) solutions in acetone at different concentrations (c)

	Pressure (MPa)	**Density** (g/cm^3)	**Viscosity** (mPa·s)
C = 10 wt %			
T = 125 °C	7.64	0.7575	0.308
	14.57	0.7671	0.315
	22.28	0.7805	0.332
	28.25	0.7911	0.343
	33.95	0.8015	0.355
T = 100 °C	7.18	0.7806	0.344
	15.01	0.7918	0.369
	22.21	0.8025	0.390
	28.64	0.8126	0.407
	35.97	0.8212	0.423
T = 75 °C	8.08	0.8098	0.426
	14.41	0.8196	0.447
	21.55	0.8295	0.469
	28.94	0.8373	0.491
	35.58	0.8449	0.508
T = 50 °C	7.67	0.8343	0.519
	14.38	0.8428	0.542
	21.32	0.8498	0.566
	28.88	0.8566	0.588
	35.26	0.8600	0.615
C = 20 wt %			
T = 125 °C	10.33	0.7777	0.512
	13.43	0.7842	0.518
	21.56	0.7951	0.552
	28.38	0.8041	0.587
	35.48	0.8129	0.612
T = 100 °C	7.78	0.8002	0.600
	14.45	0.8085	0.631
	21.40	0.8172	0.661
	28.37	0.8254	0.708
	35.12	0.8327	0.726
T = 75 °C	7.33	0.8245	0.745

	15.14	0.8325	0.786
	21.93	0.8397	0.813
	28.28	0.8461	0.858
	35.63	0.8534	0.880
T = 50 °C	9.05	0.8504	0.950
	14.63	0.8546	1.011
	21.23	0.8605	0.973
	28.80	0.8675	1.032
	35.15	0.8722	1.058

Table 6.3 Density and viscosity data for PMMA (540 K) solutions in acetone at different concentrations (c)

	Pressure (MPa)	**Density** (g/cm^3)	**Viscosity** (mPa·s)
c = 2 wt %			
T = 125 °C	7.95	0.7598	0.184
	14.33	0.7760	0.196
	21.53	0.7900	0.211
	28.35	0.8027	0.224
	34.66	0.8139	0.232
T = 100 °C	7.72	0.8011	0.227
	14.75	0.8133	0.244
	21.58	0.8250	0.257
	28.18	0.8357	0.265
	35.99	0.8460	0.279
T = 75 °C	7.91	0.8383	0.275
	14.55	0.8485	0.288
	21.54	0.8578	0.302
	28.41	0.8693	0.318
	35.58	0.8762	0.332
T = 50 °C	8.24	0.8713	0.335
	14.51	0.8805	0.349
	20.92	0.8892	0.371
	28.48	0.8968	0.379
	34.72	0.9029	0.398
c = 5 wt %			
T = 125 °C	7.21	0.7279	0.193
	14.64	0.7437	0.218
	20.35	0.7545	0.230
	26.67	0.7663	0.240
	33.95	0.7770	0.258
T = 100 °C	7.92	0.7583	0.249
	14.56	0.7692	0.265
	21.63	0.7802	0.280
	27.63	0.7903	0.290
	35.36	0.7991	0.306
T = 75 °C	8.34	0.7871	0.304

	14.80	0.7976	0.319
	21.37	0.8065	0.335
	28.36	0.8146	0.350
	35.38	0.8222	0.362
T = 50 °C	7.94	0.8145	0.369
	14.43	0.8221	0.384
	21.25	0.8306	0.399
	28.49	0.8372	0.418
	35.31	0.8444	0.433

c = 10 wt %

T = 125 °C	11.09	0.7566	0.717
	13.36	0.7673	0.744
	21.40	0.7800	0.824
	28.32	0.7920	0.872
	34.85	0.8021	0.926
T = 100 °C	7.88	0.7836	0.821
	14.64	0.7950	0.880
	20.87	0.8056	0.963
	28.40	0.8167	0.994
	35.11	0.8266	1.048
T = 75 °C	7.79	0.8157	1.014
	14.22	0.8248	1.049
	21.33	0.8333	1.101
	28.12	0.8415	1.132
	35.13	0.8495	1.260
T = 50 °C	7.43	0.8411	1.251
	14.30	0.8498	1.140
	21.33	0.8575	1.226
	27.98	0.8656	1.309
	34.72	0.8726	1.368

c = 20 wt %

T = 125 °C	7.13	0.7577	0.776
	14.34	0.7714	0.840
	21.03	0.7822	0.909
	27.81	0.7921	0.979
	35.22	0.8014	1.070
T = 100 °C	7.9	0.7881	0.847
	13.83	0.7968	0.938
	21.53	0.8072	0.978
	28.06	0.8146	1.118
	35.65	0.8219	1.162

T = 75 °C	7.35	0.8098	1.034
	14.27	0.8180	1.095
	21.07	0.8240	1.290
	28.17	0.8268	1.274
	34.94	0.8275	1.318
T = 50 °C	8.22	0.8171	1.157
	14.1	0.8219	1.336
	21.13	0.8229	1.456
	27.41	0.8236	1.506
	34.38	0.8238	1.507

Table 6.4 Density and viscosity data for 5 wt % solutions of PMMA (540 K) in acetone + CO_2 mixtures

	Pressure (MPa)	**Density** (g/cm^3)	**Viscosity** (mPa·s)
Acetone/PMMA/CO_2: 94:5:1			
T = 125 °C	8.06	0.7666	0.193
	14.26	0.7828	0.221
	21.31	0.7975	0.218
	28.48	0.8103	0.231
	34.36	0.8221	0.240
T = 100 °C	7.17	0.8016	0.229
	14.30	0.8130	0.242
	21.65	0.8256	0.253
	28.22	0.8368	0.266
	35.28	0.8536	0.276
T = 75 °C	7.11	0.8350	0.268
	14.80	0.8435	0.283
	21.30	0.8541	0.293
	28.19	0.8640	0.303
	35.03	0.8726	0.313
T = 50 °C	7.33	0.8742	0.312
	13.55	0.8723	0.324
	21.60	0.8808	0.336
	28.20	0.8893	0.346
	35.34	0.8960	0.355
Acetone/PMMA/CO_2: 93:5:2			
T = 100 °C	15.39	0.8196	0.204
	21.41	0.8315	0.209
	27.76	0.8426	0.217
	34.93	0.8521	0.225
T = 75 °C	8.94	0.8433	0.231
	14.25	0.8508	0.236
	21.01	0.8601	0.251
	28.06	0.8692	0.257
	35.1	0.8779	0.266
T = 50 °C	7.53	0.8724	0.273
	14.69	0.8809	0.278

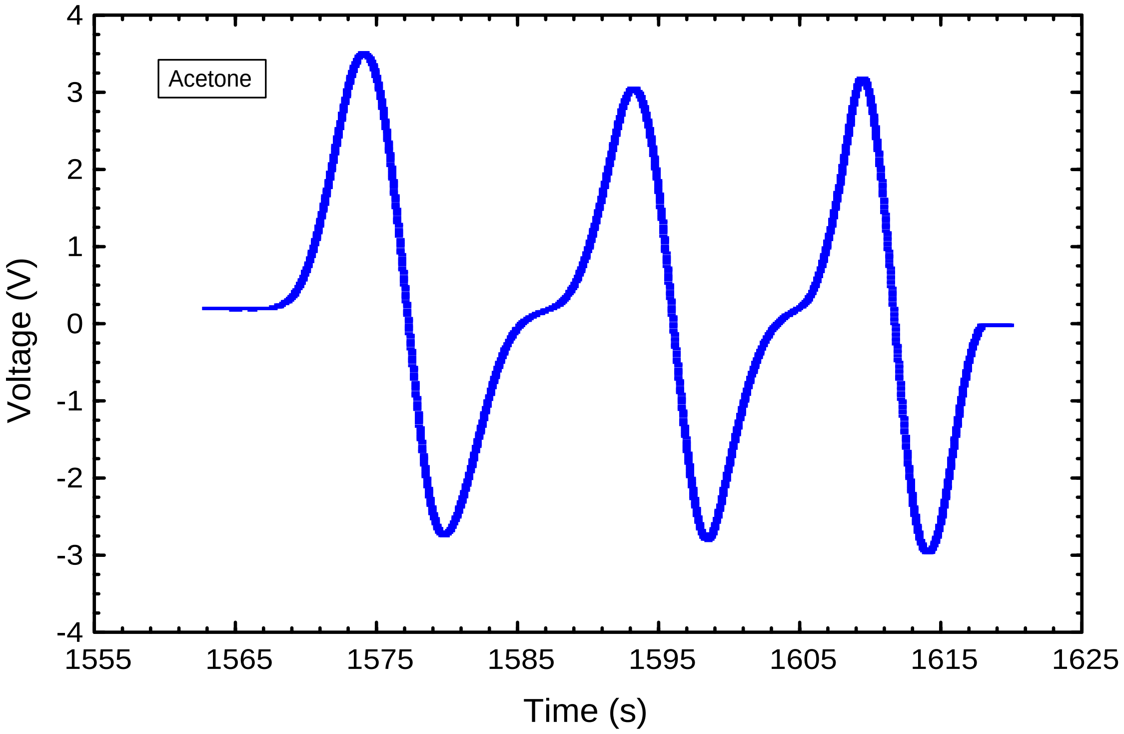
	22.22	0.8894	0.283
	27.76	0.8966	0.297
	34.95	0.9005	0.307
Acetone/PMMA/CO_2: 92:5:4			
T = 100 °C	7.31	0.8337	0.188
	14.33	0.8433	0.192
	21.16	0.8555	0.196
	27.95	0.8662	0.201
	34.87	0.8763	0.206
T = 75 °C	7.31	0.863	0.219
	13.94	0.8732	0.225
	21.14	0.8835	0.231
	28.03	0.8927	0.238
	34.9	0.9011	0.245
T = 50 °C	7.36	0.896	0.264
	14.17	0.9017	0.273
	21.05	0.9095	0.281
	28.08	0.9161	0.288

Table 6.5 Activation volumes and activation energies for PMMA solutions in acetone and acetone + CO_2.

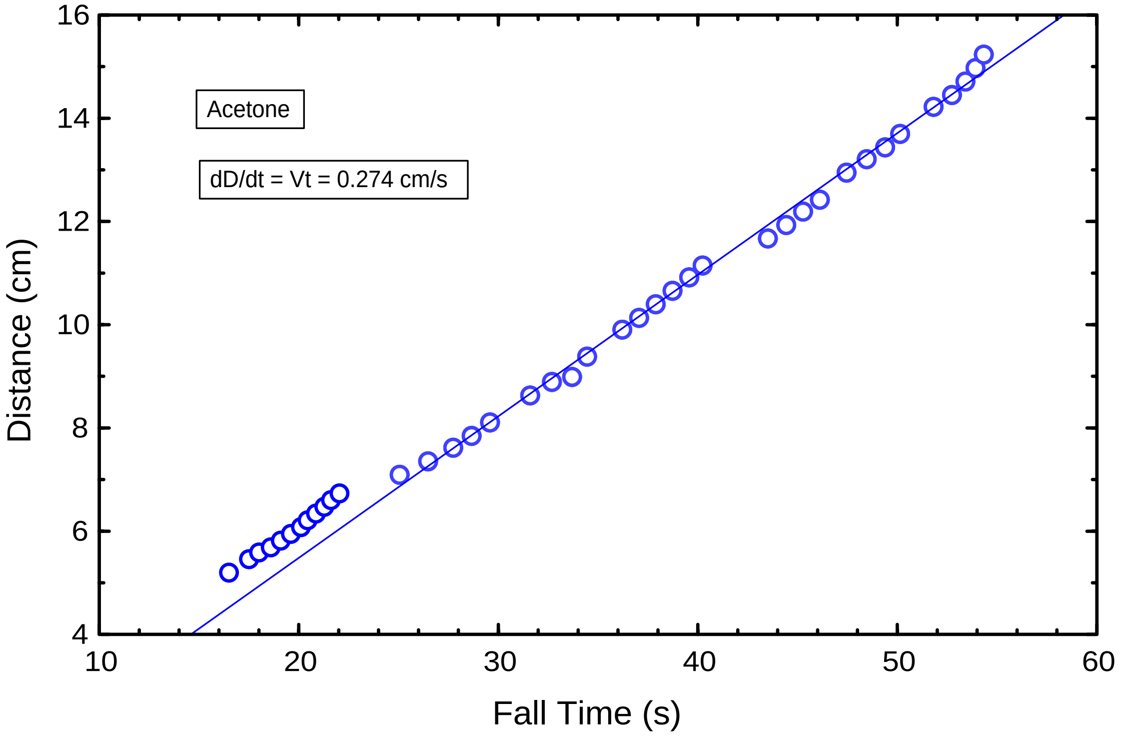
System	**Activation Energy** (kJ/mol)					**Activation Volume** (cm^3/mol)			
	Pressure (MPa)					Temperature (°C)			
	7	14	21	28	35	125	100	75	50
Acetone	8	10	8	8	6	26	16	9	5
Acetone + PMMA (2wt%, 540K)	9	8	8	8	8	30	22	20	16
Acetone + PMMA (5wt%, 540K)	9	8	8	8	7	33	22	20	16
Acetone + PMMA (5wt%, 540K) + CO_2 (1wt%)	7	6	6	6	6	23	22	14	13
Acetone + PMMA (5wt%, 540K) + CO_2 (2wt%)	7	7	7	7	7		16	14	11
Acetone + PMMA (5wt%, 540K) + CO_2 (4wt%)	7	7	7	7	8		9	12	11
Acetone + PMMA (10wt%, 15K)	8	8	8	8	8	20	22	17	16
Acetone + PMMA (20wt%, 15K)	9	10	8	8	8	23	22	17	11
Acetone + PMMA (10wt%, 540K)	8	6	6	6	6	36	28	20	13
Acetone + PMMA (20wt%, 540K)	6	7	7	6	5	36	37	26	16

Table 6.6 Density correlation parameters for viscosity using Doolittle equation.

Molecular Weight	Concentrations		Doolittle equation Parameters			Correlation Coefficient
(g/mol)	PMMA (wt %)	CO_2 (wt %)	A (mPa•s)	B (-)	V_0 (cm^3/g)	R
-	0	0	1.2E-02	0.80	0.98	0.91
15,000	10	0	3.1E-02	0.80	0.85	0.99
	20	0	4.6E-02	0.80	0.86	0.98
540,000	2	0	2.6E-02	0.80	0.78	0.99
	5	0	2.4E-02	0.80	0.86	0.99
	5	1	2.9E-02	0.80	0.76	0.99
	5	2	2.4E-02	0.80	0.76	0.98
	5	4	2.0E-02	0.80	0.77	0.95
	10	0	9.9E-02	0.80	0.80	0.98
	20	0	7.0E-02	0.80	0.88	0.89

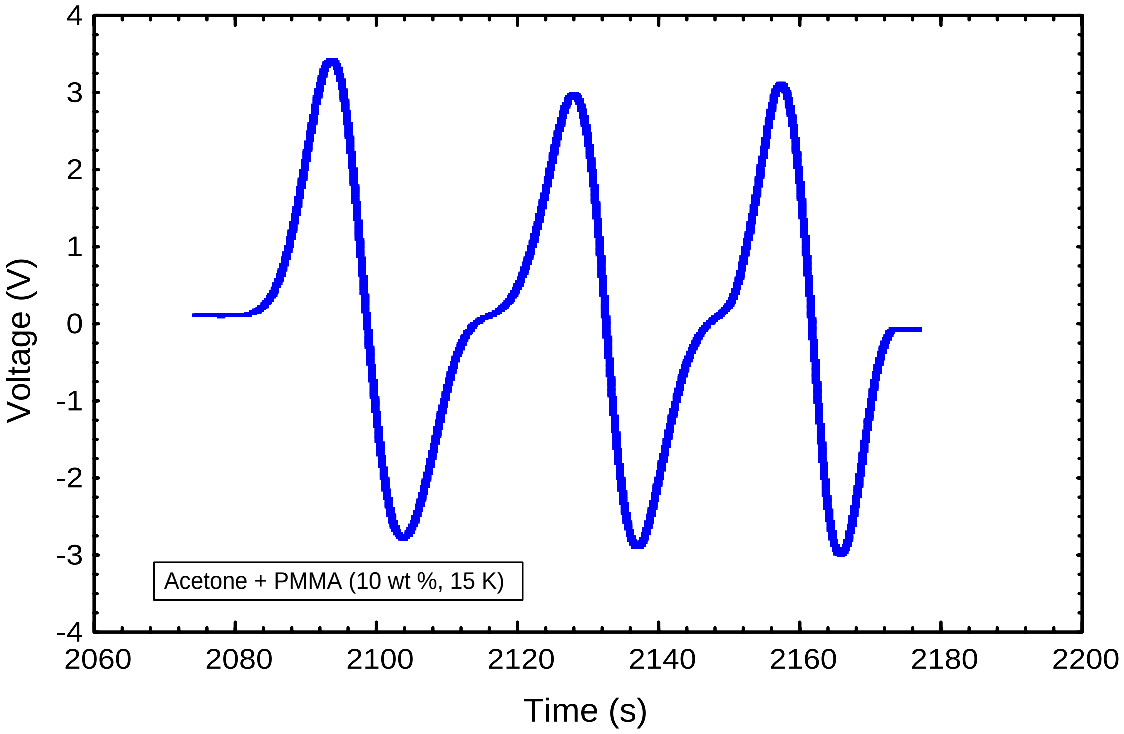


(a)

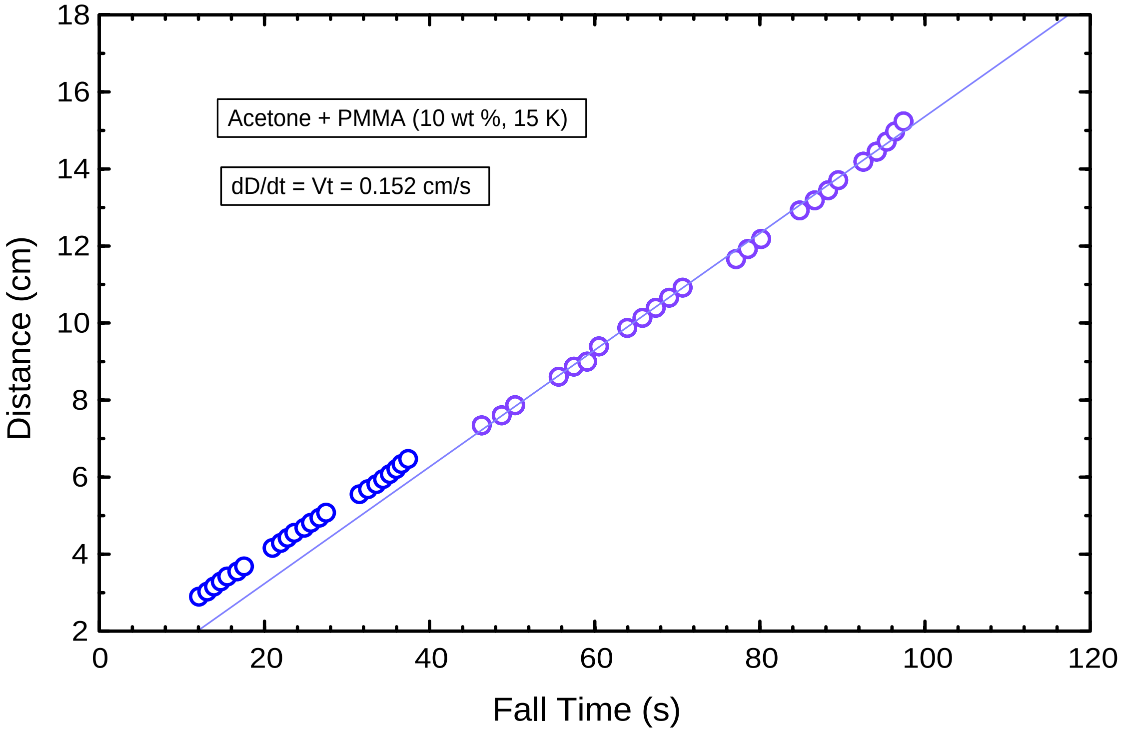


(b)

Figure 6.1 (a). Sinker LVDT signal (V) versus time, and (b) Sinker travel distance (D) versus time during viscosity determination for acetone at 35 MPa and 100 °C. The sinker terminal velocity determined from the response of the 2nd and 3rd LVDT coils (the slope of the fitted line) is 0.274 cm/s.

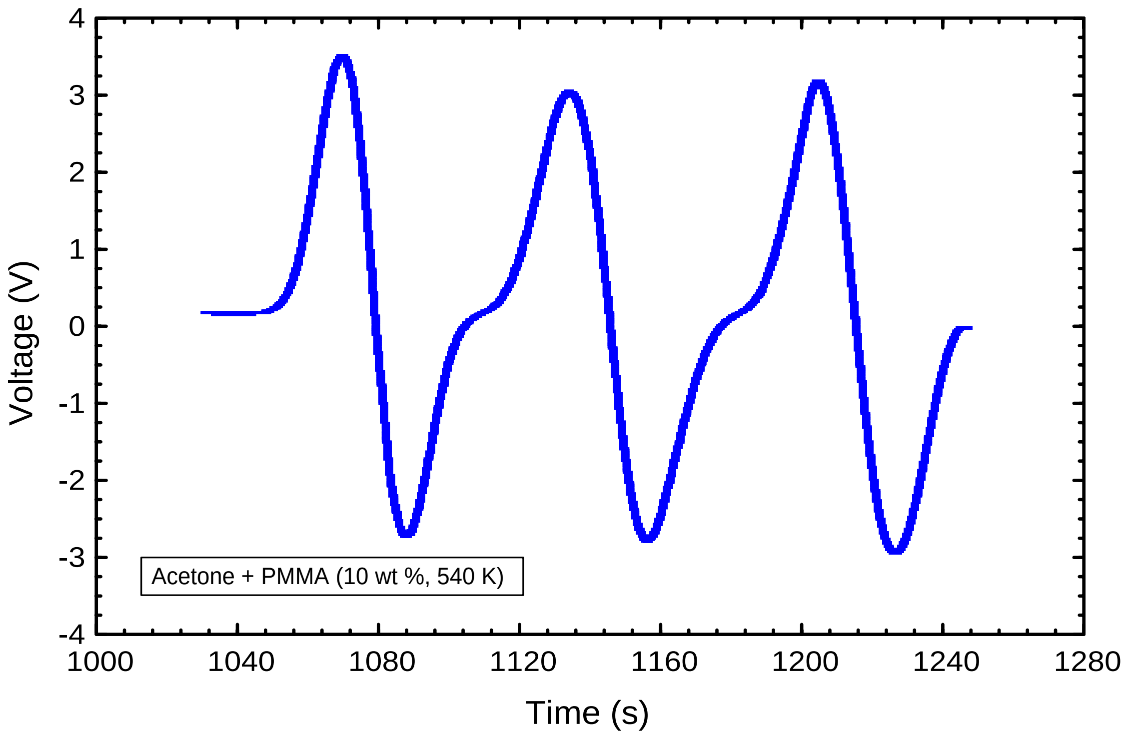


(a)

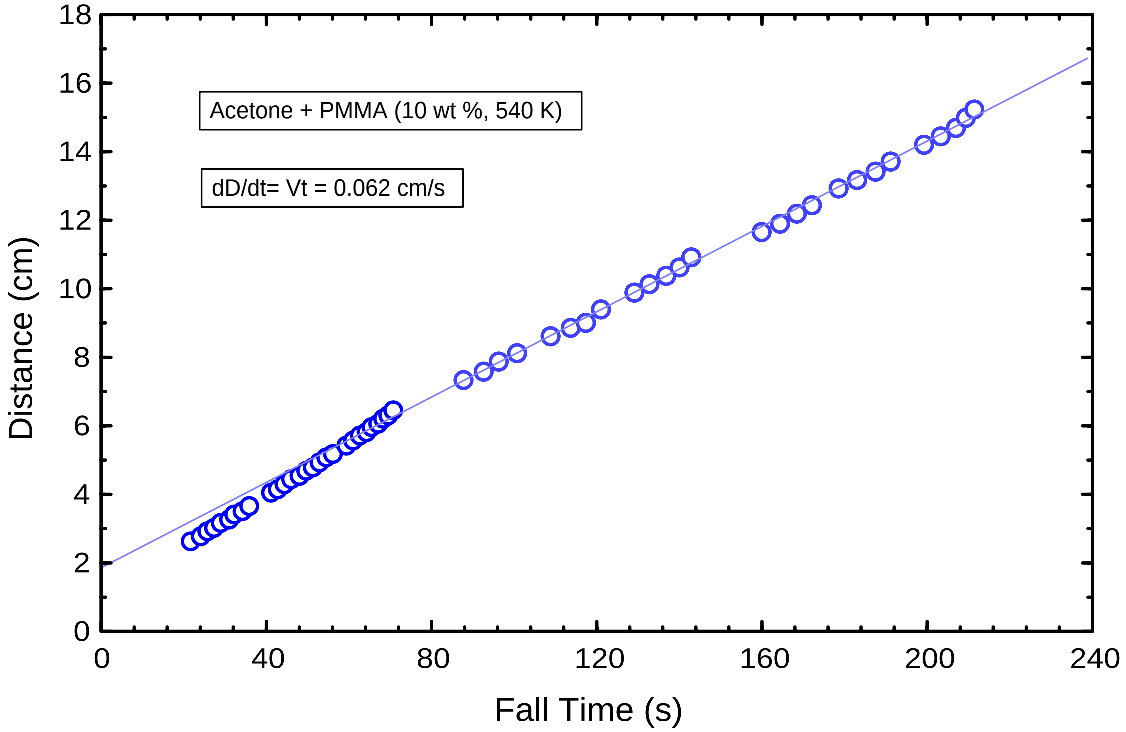


(b)

Figure 6.2 (a). Sinker LVDT signal (V) versus time, and (b) Sinker travel distance (D) versus time during viscosity determination for system of acetone + PMMA (10 wt%, 15 K) at 35 MPa and 100 °C. The sinker terminal velocity is 0.152 cm/s.



(a)



(b)

Figure 6.3 (a). Sinker LVDT signal (V) and (b). Sinker travel distance (D) versus time during viscosity determination for system of acetone + PMMA (10 wt%, 540 K) at 35 MPa and 100 °C. The sinker terminal velocity is 0.062 cm/s.

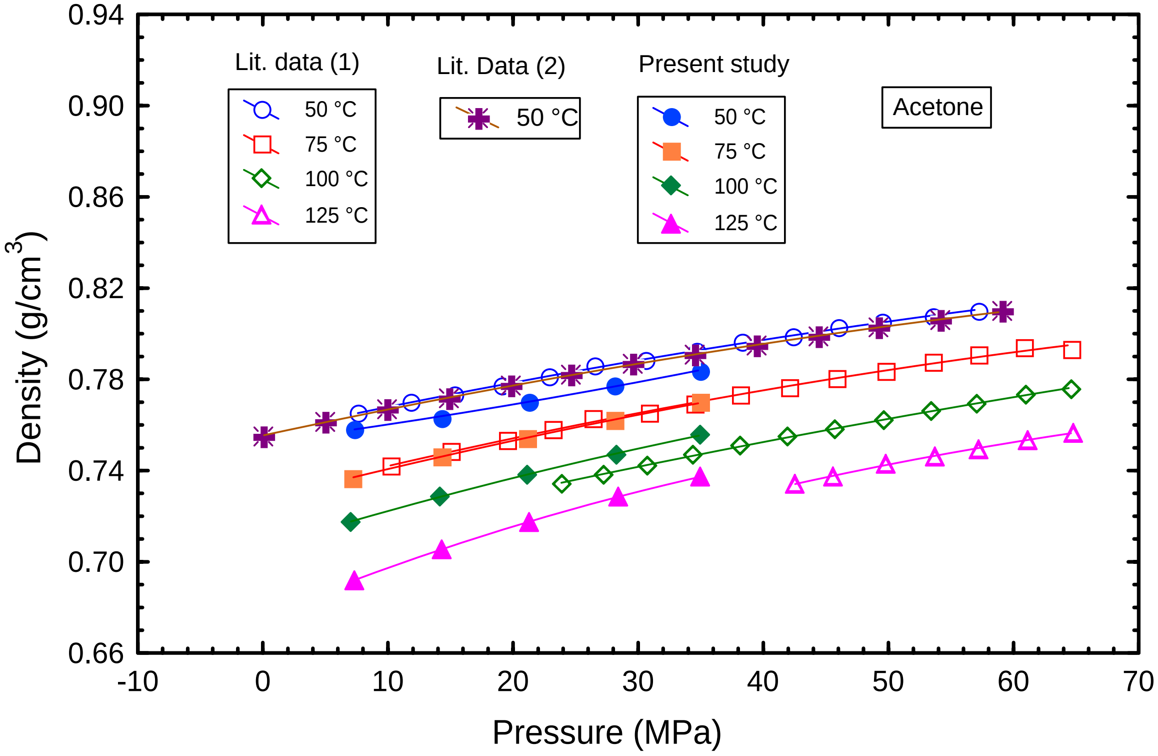


Figure 6.4 Variation of density with pressure at 50, 75, 100, and 125 °C for acetone. Literature data are from references (Lit. data (1): Pohler and Kiran, 1997a; Lit. data (2): Azevedo et. al., 2004).

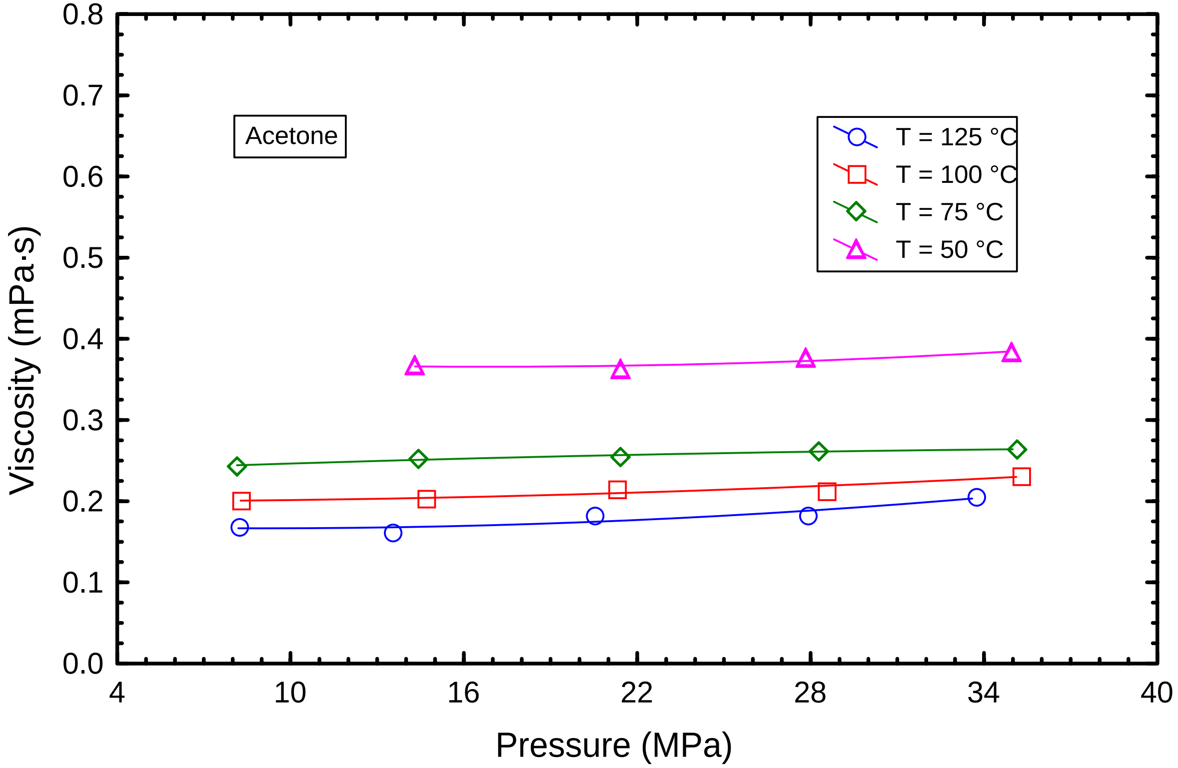


Figure 6.5 Variation of viscosity with pressure at 50, 75, 100, and 125 °C for acetone.

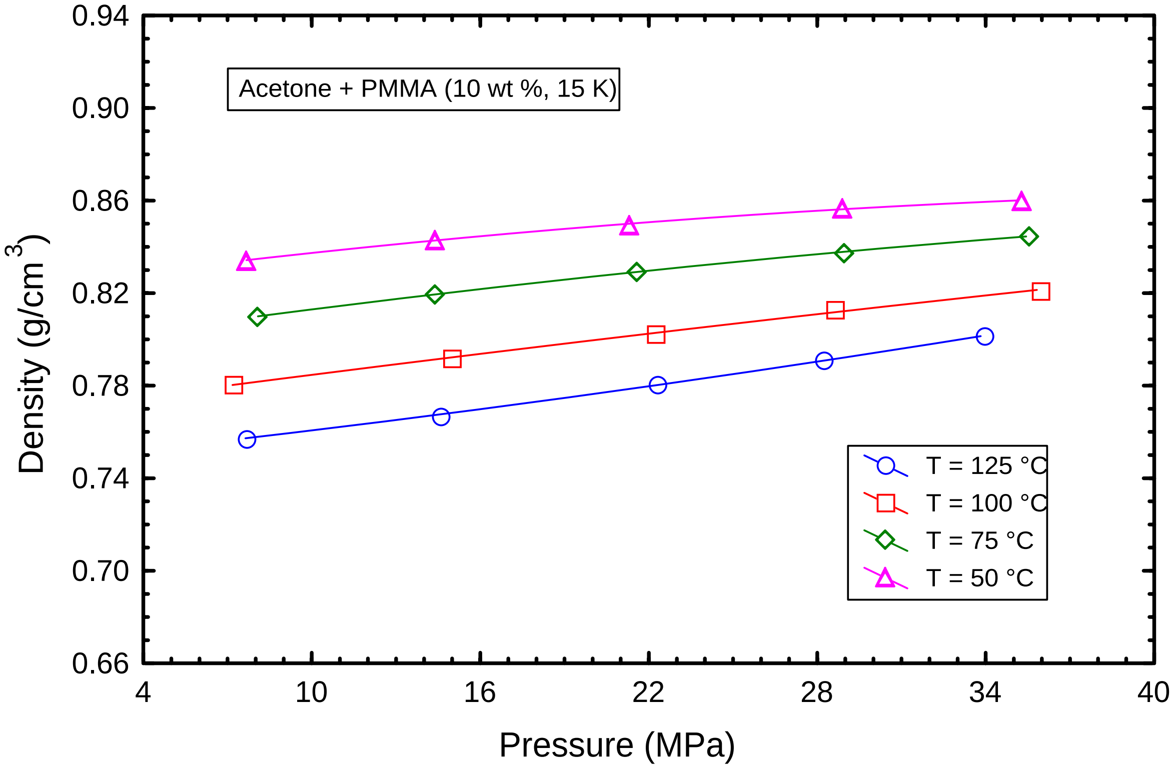


Figure 6.6 Variation of density with pressure for PMMA (10 wt %, M_w = 15 K) in acetone at 50, 75, 100, and 125 °C.

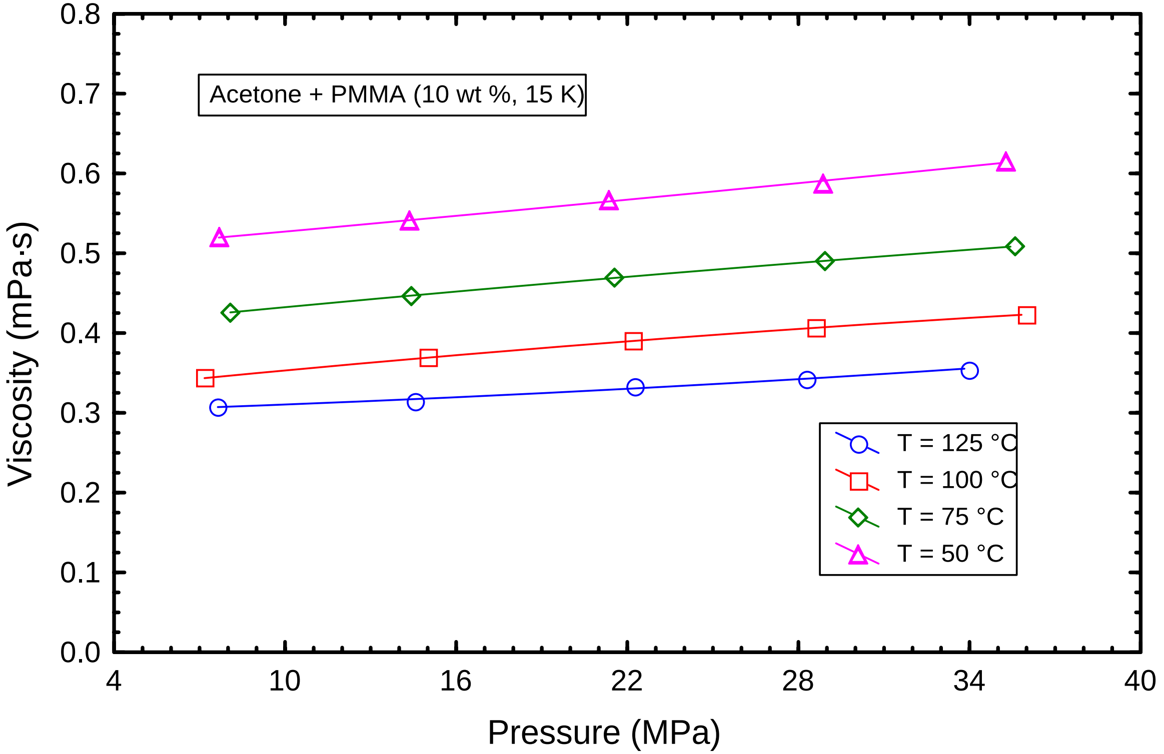


Figure 6.7 Variation of viscosity with pressure for PMMA (10 wt %, M_w = 15 K) in acetone at 50, 75, 100, and 125 °C.

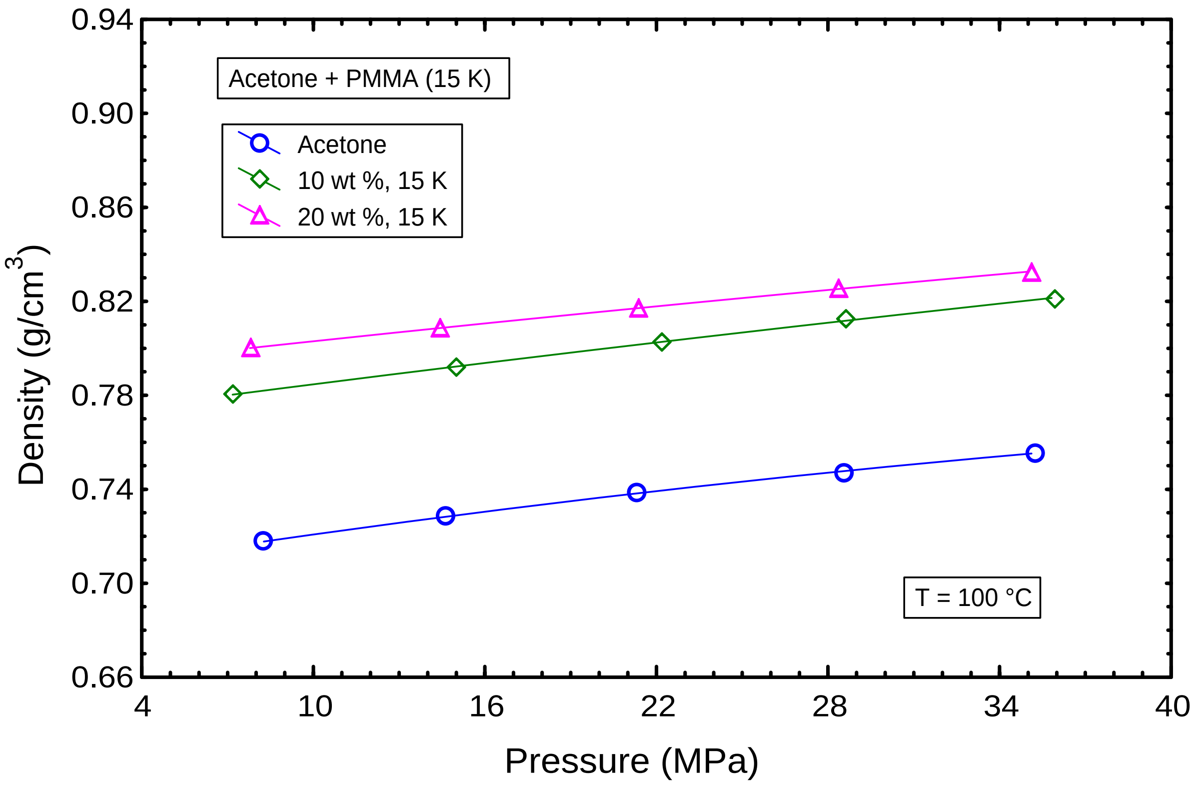


Figure 6.8 Comparison of the variation of density with pressure for PMMA (M_w = 15 K) solutions (0, 10, 20 wt %) in acetone at 100 °C.

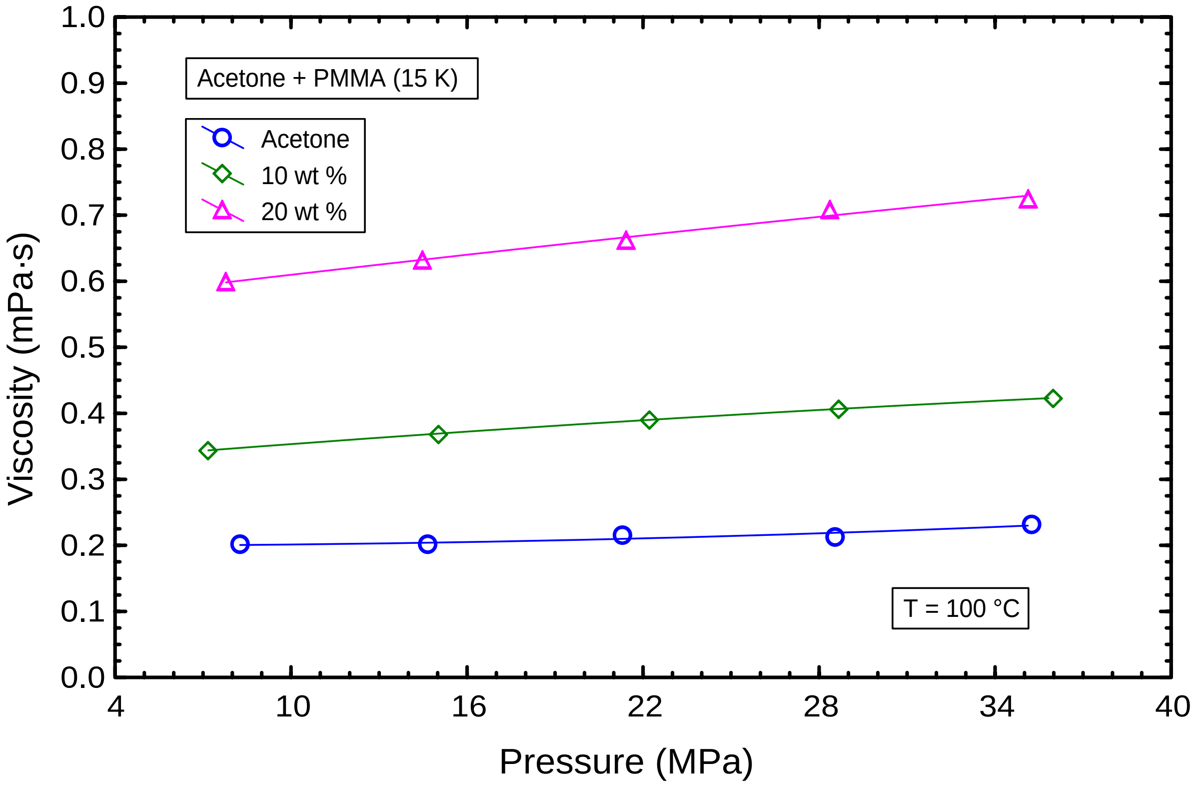


Figure 6.9 Comparison of variation of viscosity with pressure for PMMA (M_w = 15 K) solutions (0, 10, 20 wt %) in acetone at 100 °C.

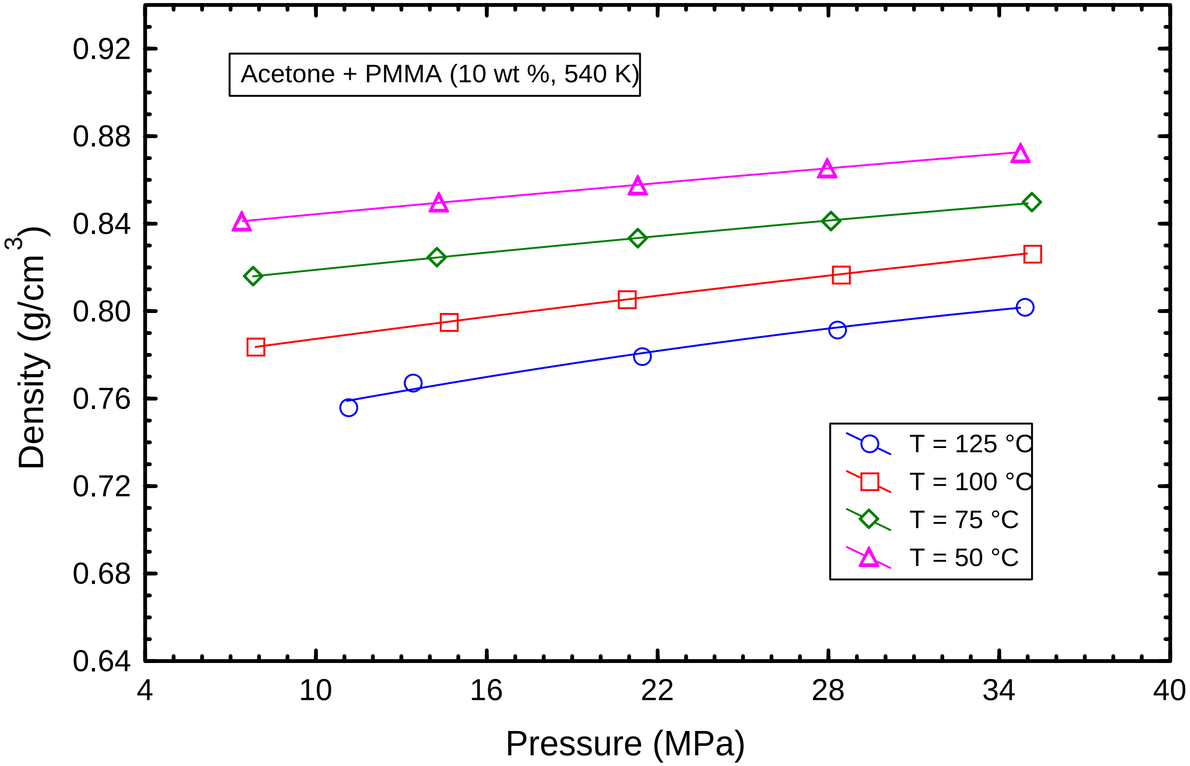


Figure 6.10 Variation of density with pressure for PMMA (10 wt %, M_w = 540 K) in acetone at 50, 75, 100, and 125 °C.

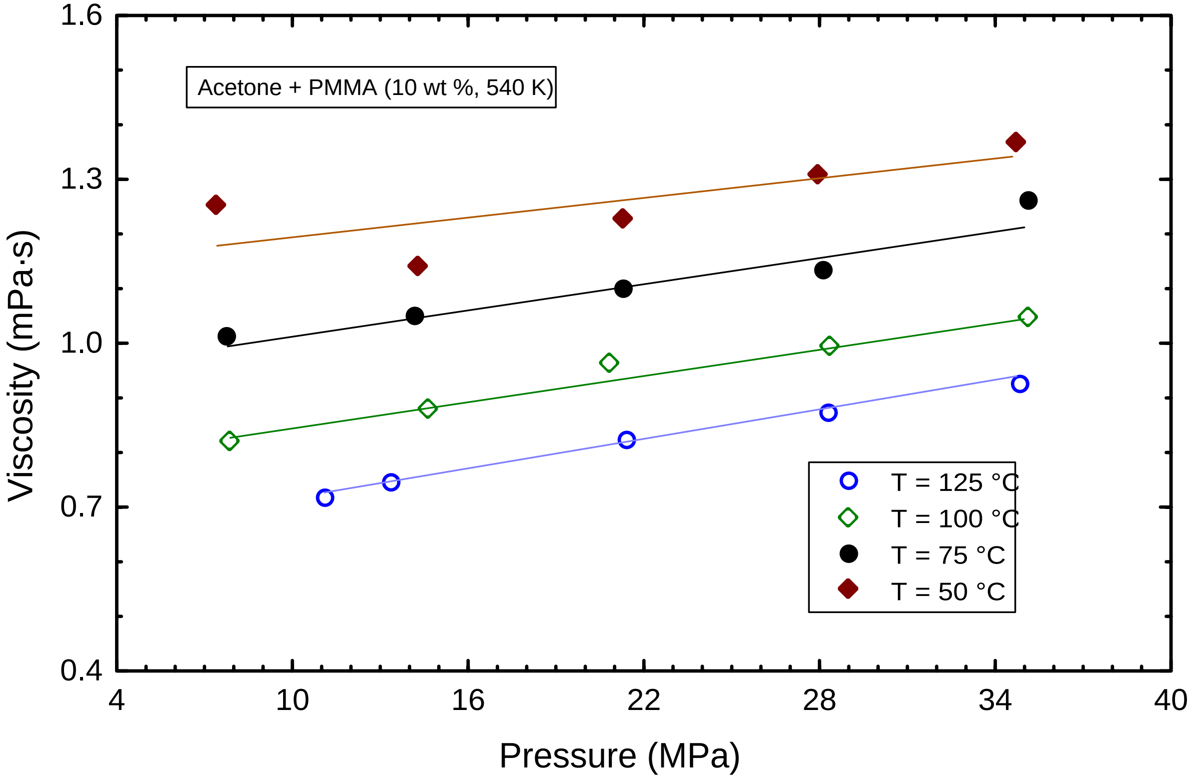


Figure 6.11 Variation of viscosity with pressure for PMMA (10 wt %, M_w = 540 K) in acetone at 50, 75, 100, and 125 °C.

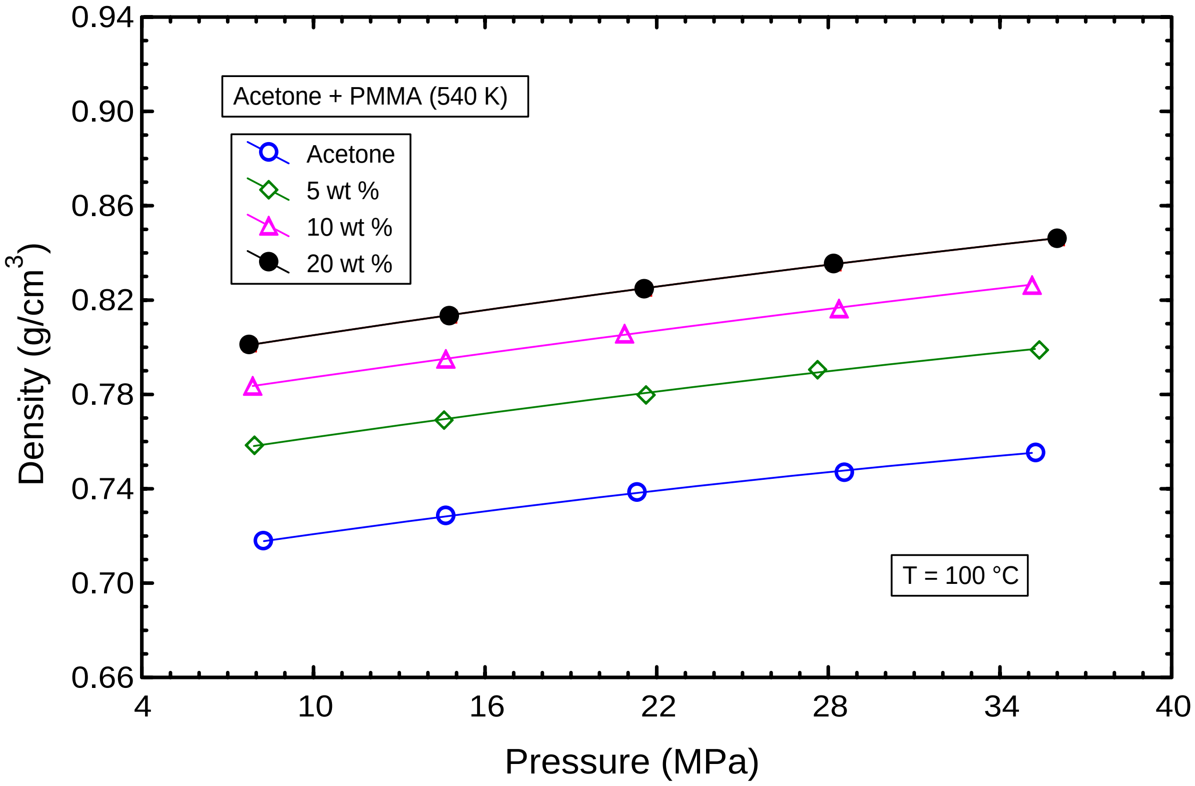


Figure 6.12 Comparison of variation of density with pressure for PMMA (M_w = 540 K) solutions (0, 5, 10, 20 wt %) in acetone at 100 °C.

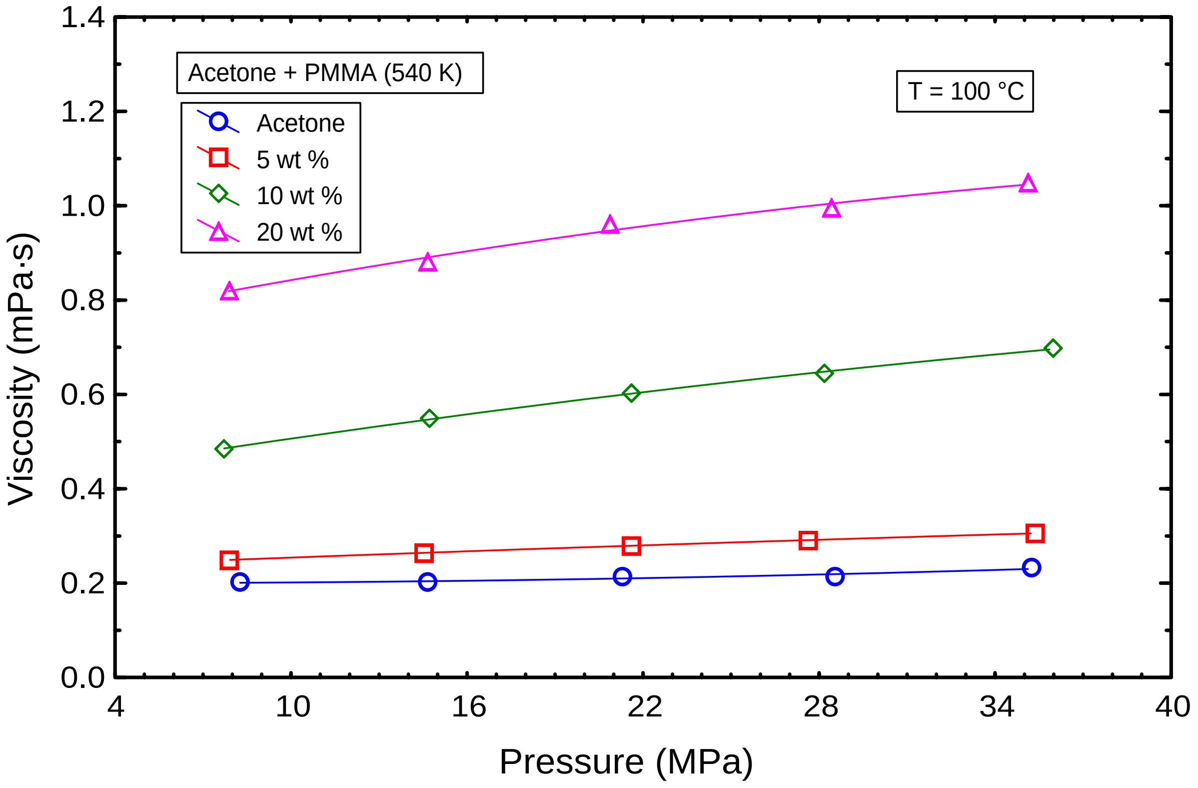


Figure 6.13 Comparison of the variation of viscosity with pressure for PMMA (M_w = 540 K) solutions (0, 5, 10, 20 wt %) in acetone at 100 °C.

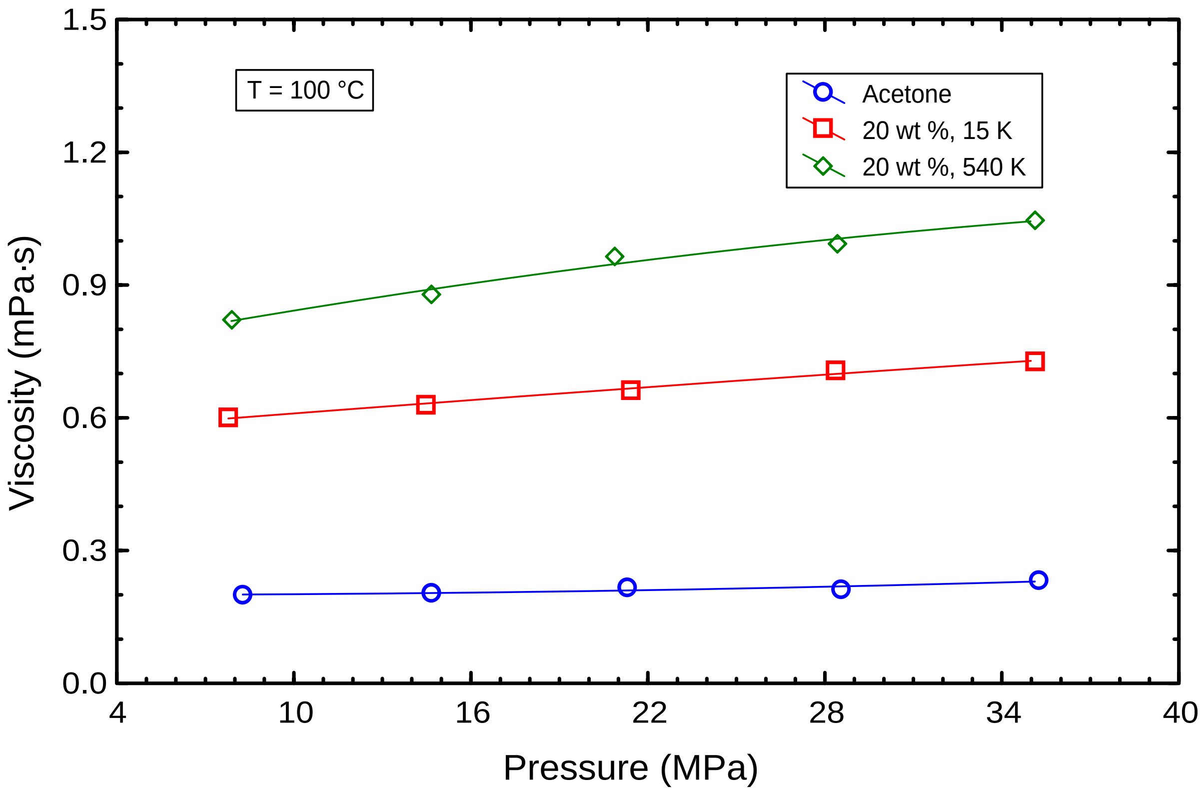


Figure 6.14 Comparison of the variation of viscosity with pressure for solutions of PMMA (20 wt %) in acetone at 100 °C.

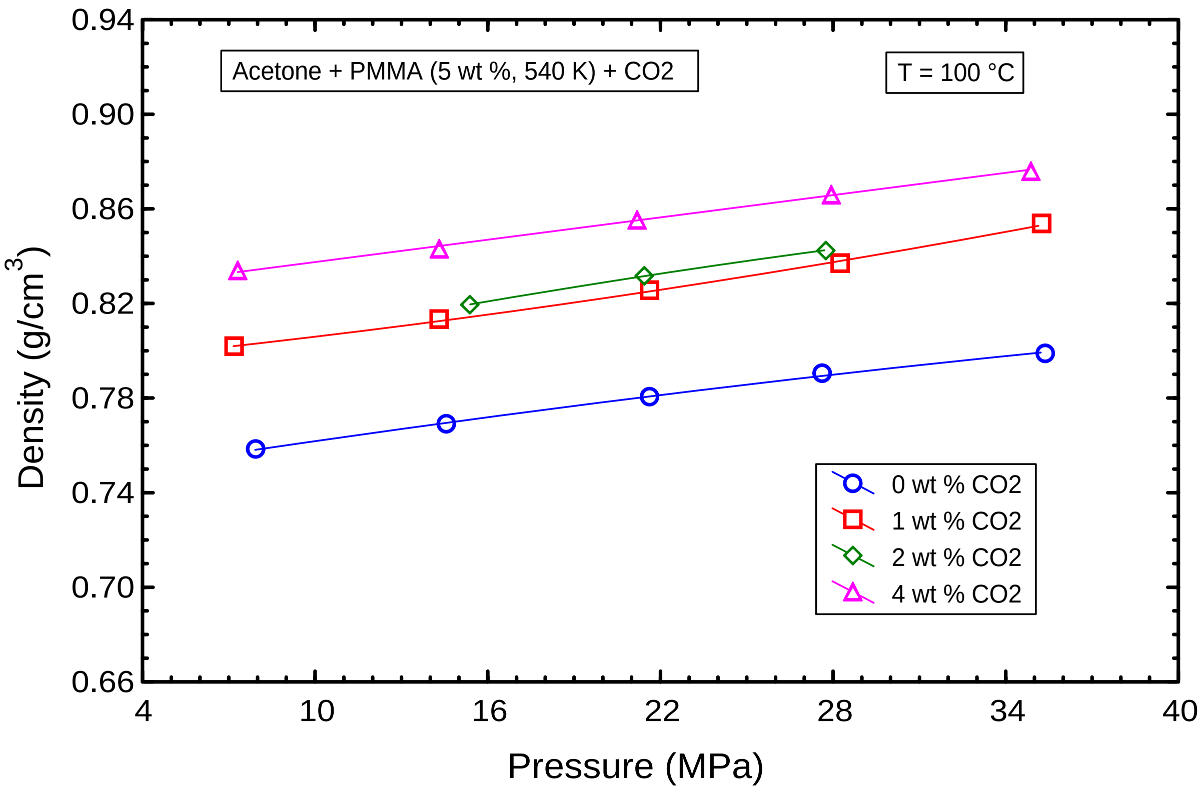


Figure 6.15 Variation of density with pressure for solutions of PMMA (5 wt %, M_w = 540 K) in acetone + CO_2 mixtures at different CO_2 levels at 100 °C.

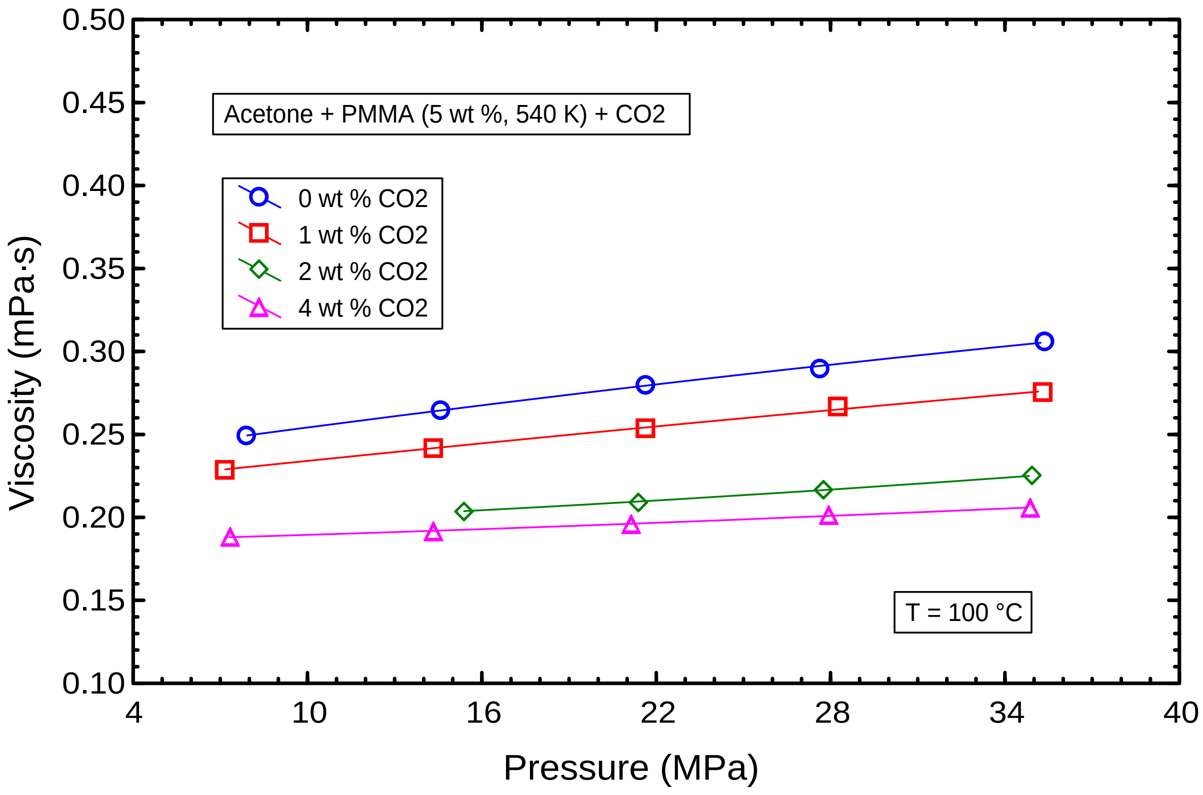


Figure 6.16 Variation of Viscosity with pressure for solutions of PMMA (5 wt %, M_w = 540 K) in acetone + CO_2 mixtures at different CO_2 levels at 100 °C.

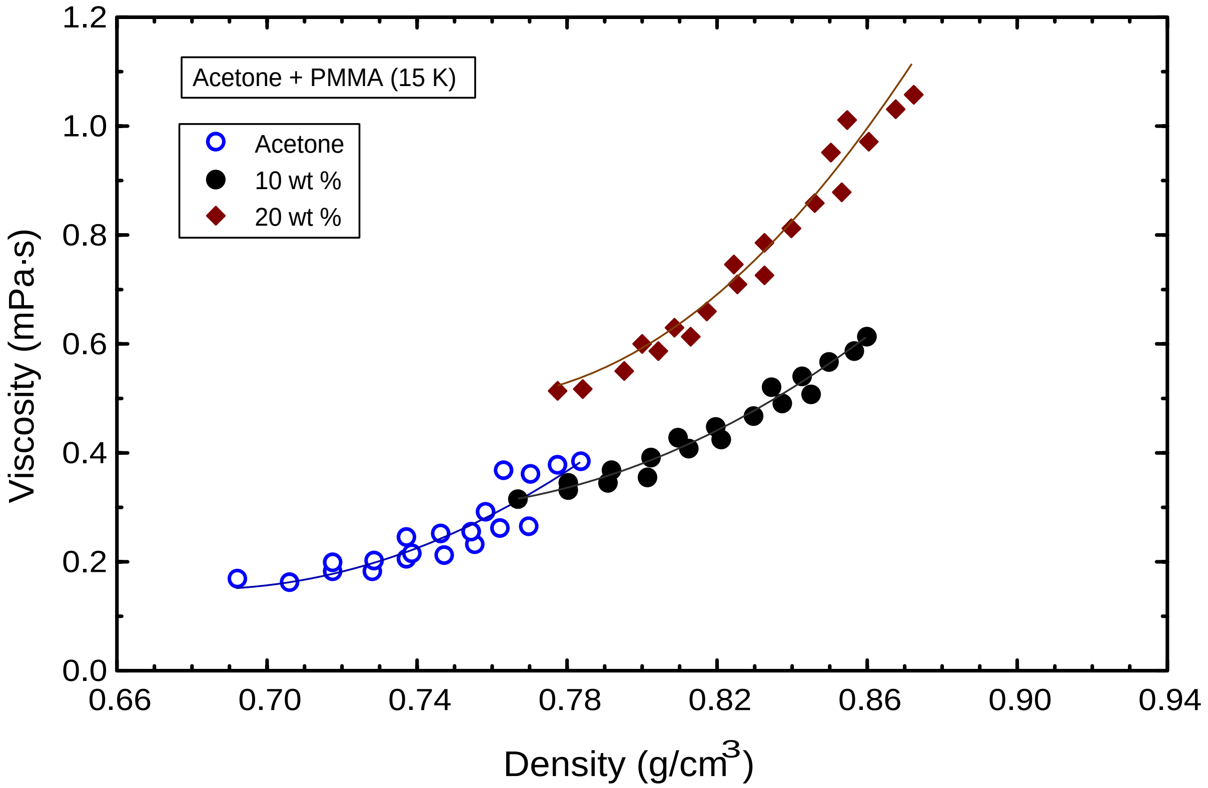
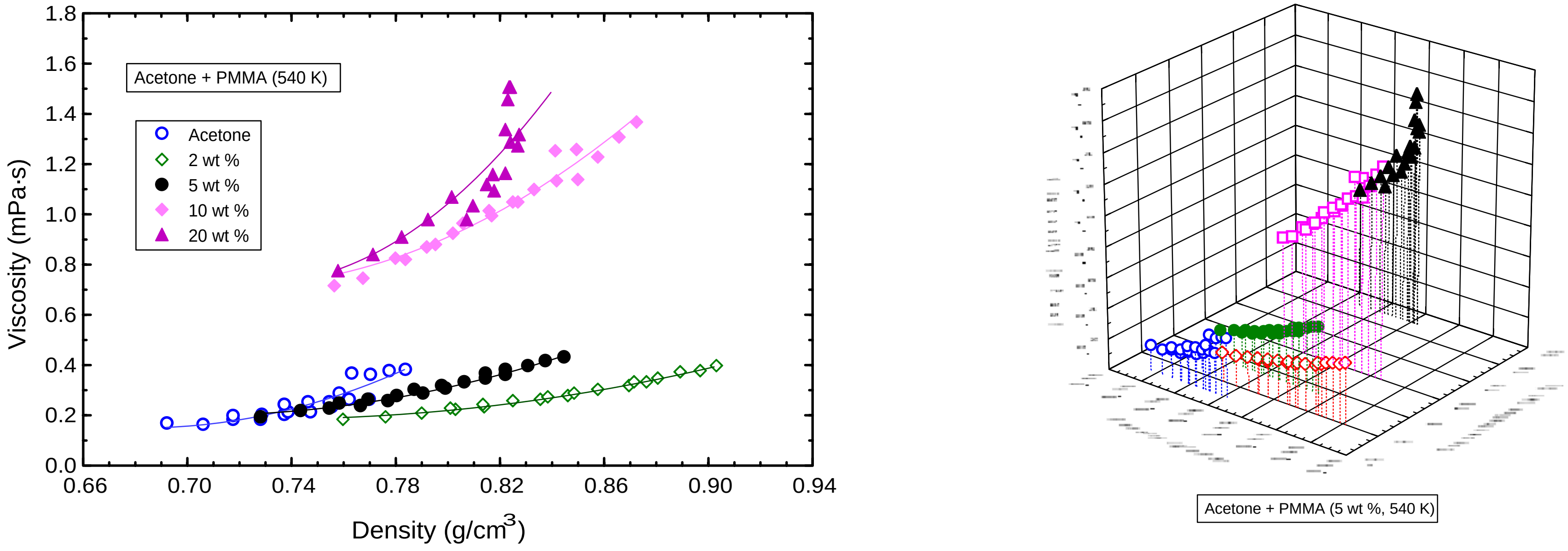


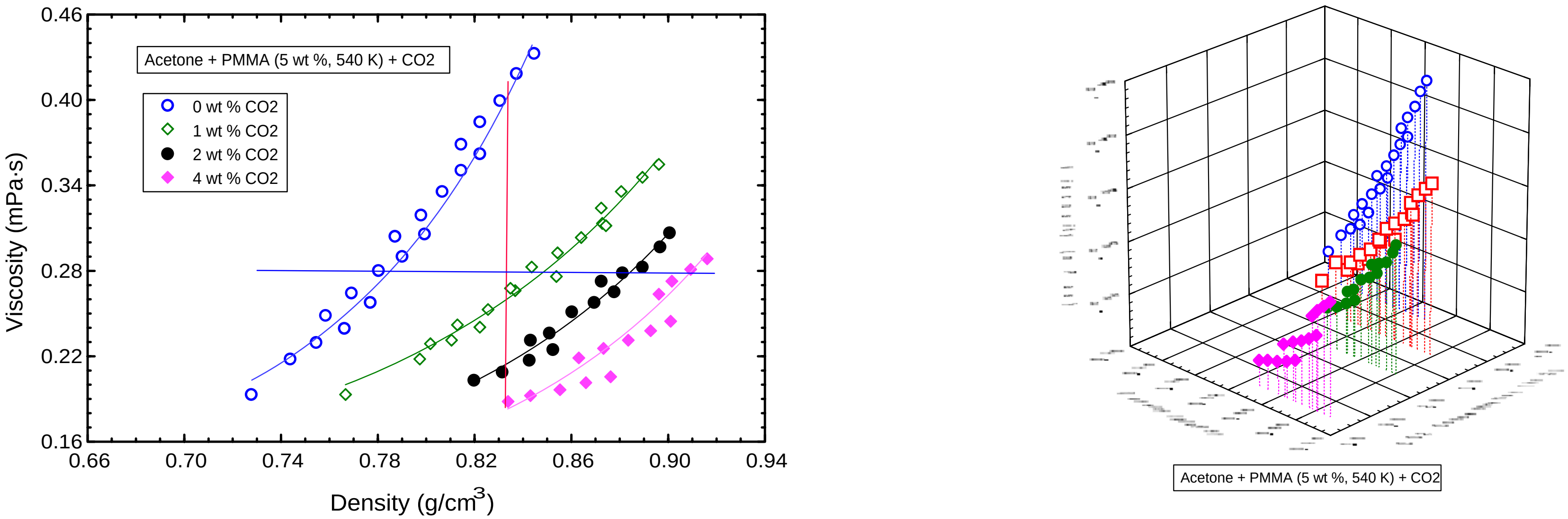
Figure 6.17 Variation of viscosity with density for PMMA (M_w = 15 K) solutions (0, 10, 20 wt %) in acetone.



(a)

(b)

Figure 6.18 Variation of viscosity with density and concentration for PMMA (M_w = 540 K) solutions (0, 2, 5, 10, 20 wt %) in acetone. (a). Viscosity versus density; (b) 3-D representation.



(a)

(b)

Figure 6.19 Variation of viscosity with density and composition for PMMA (5 wt %, M_w = 540 K) solutions in acetone + CO_2 mixtures at CO_2 addition levels of 0, 1, 2, 4 wt %. (a). Viscosity versus density; (b) 3-D representation.

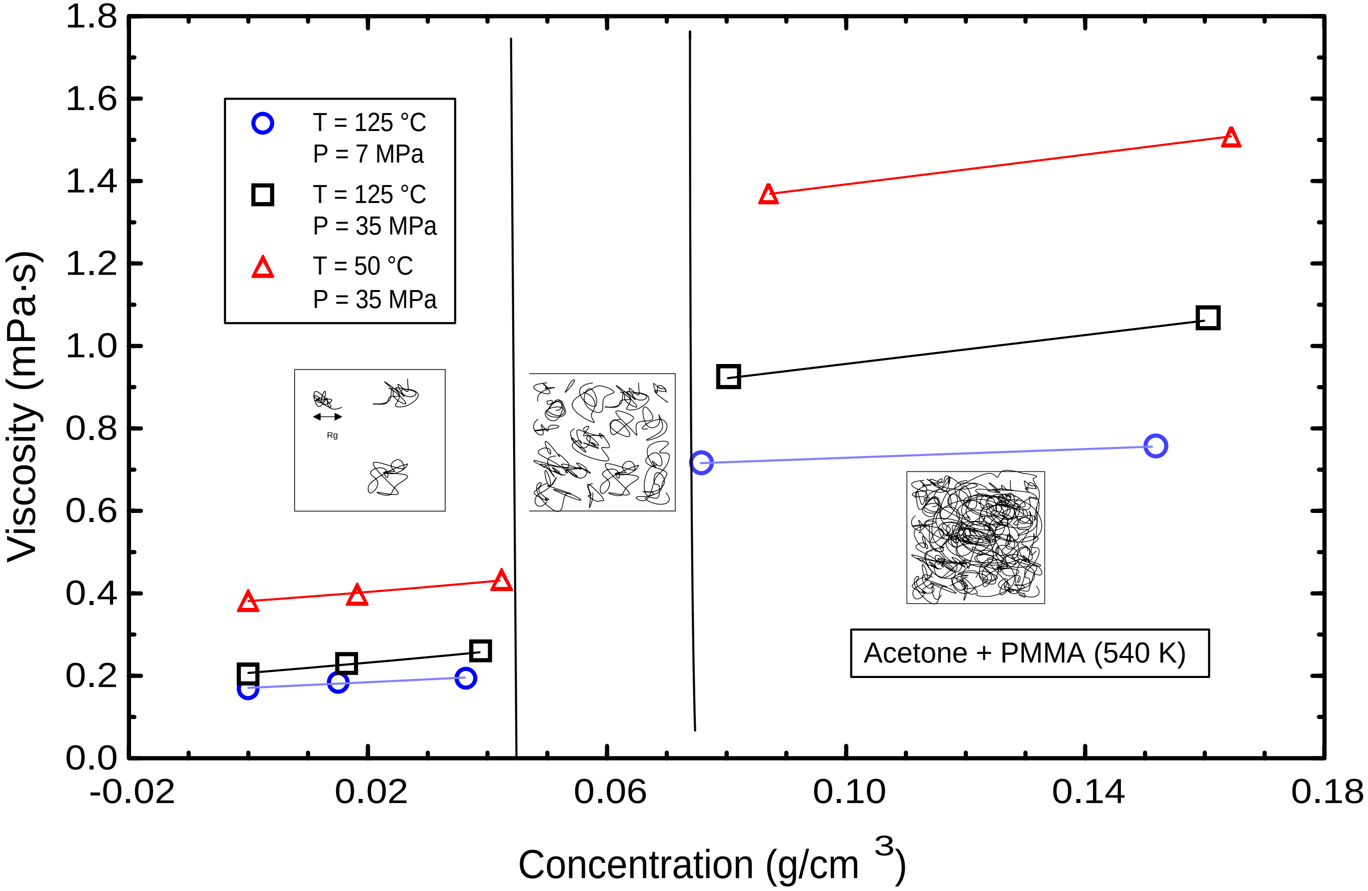


Figure 6.20 Variation of the viscosity with concentration for PMMA (540 K) solutions in acetone. The pressure/temperature conditions are as indicated in the figure inset. A significant jump in viscosity takes place in the concentration range between 0.4 to 0.8 g/cm^3 which is interpreted to be related to the onset of entanglements.