

CHAPTER 4

EXPERIMENTAL METHODOLOGY

In this chapter we describe the experimental systems used to determine the phase boundaries, densities and viscosities of fluid mixtures, polymer solutions, and polymerization systems.

Densities and phase boundaries were determined using primarily a view cell system.

Viscosities were determined using a special falling body type viscometer. The viscometer is also used to determine densities. Polymerizations were carried out in either the view cell or the viscometer. All the relevant figures are compiled at the end of the chapter.

4.1 View-cell system

View-cell system is one of the primary apparatus in the present study. The main function of the system is to explore high-pressure phase behavior and determine high-pressure pVT data for fluids, fluid mixtures, and polymer solutions. Additionally, the view cell can also be used as a high-pressure reactor for polymerizations.

The schematic diagram of the view-cell system is shown in Figure 4.1. The system consists of three main sections: a solvent delivery system, a high-pressure variable-volume view-cell, and data acquisition units.

4.1.1 Solvent delivery system

The solvent delivery system has two main subsystems: pressure line (PL) system and solvent line (SL) system, as shown in Figure 4.1. The function of the pressure line is to pressurize the view cell while the solvent line is to deliver solvent into the view cell. Two pump heads (RPH, LPH) of a two-head high-pressure pump (Milton Roy, mini-pump) are employed to deliver CO₂ or solvent into system in the solvent line and the pressure line, respectively. For the delivery of CO₂, a coolant pump (CP) (Little giant pump company) is used to cool the high-pressure pump head to assure liquid state of CO₂ in the pump. Line accessories such as line filters (LF), rupture disks (RD), check valves (CV), and valves are set in the solvent line and pressure line. A manual pressure generator (PGN) (High Pressure Equipment Company) is applied to manipulate the pressure inside the view cell with assistance from the pressure line subsystem.

4.1.2 High-pressure variable volume view-cell

The schematic diagram for the view-cell is shown in Figure 4.2. Two sapphire windows (SW) are set in the opposite direction of the view cell, which permits visual observation or optical measurements (transmitted light intensity measurement) through the view cell. A piston (PI) is positioned in the variable volume part (VVP), whose position is determined by a piston position sensing linear variable differential transformer (PPS LVDT) through detecting the position of a ferromagnetic slug (FS) that is connected to the piston. With the position of the piston known, the inner volume of the view-cell can be calculated. With assistance from the pressure generator (PGN), the piston position can be manipulated to achieve the pressure desired for the view-cell. A high-temperature-high-pressure combined sensor for temperature

and pressure (Dynisco) mounted directly on the view cell helps determine the temperature and pressure inside the view-cell. Four inserted-in cartridge heaters are used to heat the system to the desired temperature. For the transmitted light intensity measurement, a fiber optical illuminator (FOL), and photo sensor (PS/ I_r) are utilized that are set in the proper light path. A magnetic stirrer is used for mixing. During a given experimental operation, pressure and temperature in the view cell, and transmitted light intensity are sent to a control computer and are monitored as a function of time.

4.1.3 Data acquisition units

Temperature, pressure, transmitted light intensity measured in the view cell was acquired and saved on a control computer by a LabView coded data acquisition program via an A/D conversion board (Boss Company).

4.1.4 Operational procedures

A. Polymer loading and solvent charge. The variable volume part (VVP) of the view-cell can be opened for loading polymers (solid or liquid). With assistance of the high-pressure pump head in the solvent line, liquid solvents are charged. However, for gaseous solvent such as CO₂, another coolant pump is needed to cool the head of the high-pressure pump to assure the liquid state of CO₂ in the pump head for efficient charging.

B. Mixing. After the polymers and solvents with known amounts are charged into the view cell, the magnetic stirring is turned on to start mixing.

C. Temperature control. The cartridge heaters are then inserted into the view cell body and the target temperature value is set on the temperature indication and control instrument for temperature control. The control loop that consists of a temperature sensor, temperature indicator and control units and the heaters is used to adjust the temperature to the desired value. It should be pointed that a temperature quench can be imposed whenever desired by changing temperature settings on the temperature controller.

D. Pressure control. Pressure control is achieved with the aid of a pressure generator (PGN) that moves the piston in the variable volume part (VVP) of the cell. Pressure quench can be achieved by the motion of the piston that is manipulated by the pressure generator.

D. Generation of pVT data. The position of the piston is determined by a piston position sensing linear variable differential transformer (PPS LVDT). After knowing the position of the piston, using the inner cross-section area of the variable volume part (1.95 cm^2) and the maximum internal volume (23.46 cm^3), the inner volume of the view cell thus the cell content density is calculated according to the equation below,

$$D = L/(23.46 - 1.95B) \quad (\text{Eq.4.1})$$

where D is the density, g/cm^3 , L is the total loading in gram, and B is the piston position in cm. To measure the B value, the piston position at the top of the variable volume part, which corresponds to the maximum inner volume, is reached and set as “zero” position on the position readout unit (PRU).

E. Determination of demixing conditions. After the polymer and solvent mixtures are loaded, the system is brought to one-phase conditions by adjusting the pressure and/or the temperature. The magnetic stirrer facilitates the dissolution process. Once complete miscibility is achieved, starting from the one-phase region, different paths may be followed (depending on the nature of the experiment) to determine the phase boundaries. Figure 4.3 shows the schematic representation of the different paths that the paths can be used to follow in determining the phase boundaries. These include a constant temperature path (path A), a constant pressure path (path B) and a variable pressure and temperature path (path C).

When temperature is maintained constant, the pressure is reduced with aid of a pressure generator until phase separation takes place. When pressure is maintained constant, the temperature is reduced until the phase separation takes place by turning off the heaters. It is worth noting that the pressure will decrease during the cooling down process if there is no pressure compensation. However, in order to keep the same pressure, compensation for pressure can be provided by moving the piston with manipulation of the pressure generator. 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 the onset of phase separation. During measurements, the temperature, pressure and transmitted light intensity are recorded on the control computer. Based on these data, plots of temperature, pressure, and transmitted light intensity versus time, transmitted light intensity versus temperature or pressure are generated as shown in Figure 4.3. In this figure, for the path A (pressure quench at constant temperature) or C, there

are two characteristic pressures corresponding to beginning and end for the change of transmitted light intensity during phase separation, which are denoted as P_i and P_f , respectively. For the path B (temperature quench at constant pressure) or C, there are two characteristic temperatures corresponding to beginning and end for the change of transmitted light intensity, which are denoted as T_i and T_f , respectively. In the present study, P_i and T_i are taken as demixing pressure and temperature. The path A (constant temperature) is applied to determine the liquid-liquid (LL) phase boundary while the path B (constant pressure) is employed to determine the solid-fluid (SF) phase boundary. Figure 4.4 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.

4.1.5 Accuracy and precision of the measurements

The measurement precision for temperature, pressure, and transmitted light intensity are ± 0.5 K, ± 0.03 MPa, and ± 0.01 AU, respectively. The precision for volume is ± 0.0025 cm³ and for piston position B is ± 0.013 mm, thus for density is ± 1.2 % (Pöhler and Kiran, 1997a).

4.2 Viscometer system

4.2.1 Measurement principle and apparatus

The high pressure high temperature viscometer system and its structure are shown in Figure 4.5 and 4.6. The system was earlier improved (Dindar, 2001; Dindar and Kiran, 2002a, b).

The system consists of four main sections: solvent delivery system, high-pressure viscometer with variable volume cell attachment, control and data acquisition units, and data processing software package.

4.2.2 Solvent delivery system

The solvent delivery system (including solvent delivery line and the pressurization line) is used to load and pressurize the viscometer. A high-pressure liquid pump (Milton Roy), equipped with a cooling jacket, is used in both solvent and pressure lines to deliver the fluid samples and pressurizing fluid. A pressure generator (High Pressure Equipment Company) is connected to the pressure line for pressure manipulation and control by regulating the piston position in the variable volume part of the view cell. A check valve is placed in each line to prevent fluids from back flowing.

4.2.3 Viscometer

The viscometer consists of a view cell, an attachment with movable piston and a fall tube. The view cell equipped with two high-pressure sapphire windows has two sample ports, front load port (FLP) and top load port (TLP), which are used to charge fluids and solids, respectively. A magnetic stirring bar in the mixing cavity is applied to mix the contents in the view cell with help from electromagnetic coils around the cell. The attachment with movable piston equipped with a piston position sensor linear variable differential transformer (PPSLVDT) is used to determine inner volume of the view cell. The fall tube is made of nonferromagnetic 316 stainless steel. The sinker, 0.7781 cm in diameter and 2.094 cm in length (with 4.0 g/cm³ density), is made from an aluminum core and ferromagnetic 416 stainless steel shell and thus magnetically permeable. The leading end of the sink is

hemispherical. The ratio of sink-to-tube radii is 0.9799, which is greater than 0.93 needed to insure concentric fall and error-free fall time measurements. An electromagnetic pull-up magnet is applied to load sinker to the top of the fall tube for each run of viscosity measurement. Three-coil sinker position sensor linear variable differential transformer (sinker position sensor LVDT) is used to generate the voltage-fall time relations for the sinker during its falling process.

4.2.4 Control and data acquisition units

The viscometer is housed in an oven whose temperature is controlled with a PID controller (Omega). The controller is connected to 120 W heaters (Omega) that are attached to the ends of the oven in a way to achieve a uniform temperature distribution. A fan and a circulation pipe are employed to provide good air circulation inside the oven, especially along the height of the fall tube. The viscometer temperature is measured with an accuracy of ± 1.5 K using a J-type thermocouple with resolution of 0.1 K. The temperature is measured at two locations: one being in the view cell of the viscometer (J-type thermocouple) and the other is in the middle of the oven (RTD probe). Both readings agree assuring the uniformity of temperature. The viscometer pressure is measured with an accuracy of ± 0.06 MPa using a flush mount transducer (Dynisco) that is attached to the view cell. The reading is obtained with a digital displayer (Newport) with a resolution of 0.007 MPa.

4.2.5 Data processing software package

The first request is to generate an accurate relation of distance versus fall time. This ever included being carried out manually by relating the position and time for as many points as

possible. This tedious and time-consuming procedure has now been replaced by a software developed in the course of the present research. The new software package is designed to find relations between distance and fall time of the sink by combining voltage-fall time and calibration voltage-distance relations. The process is discussed in detail in Section of 4.2.6 G. The package is developed in Microsoft FORTRAN PowerStation 4.0 language.

4.2.6 Operational procedures

A. Charging solvents. Fluids (nonvolatile organic, volatile organic, and compressed gases) can be charged into the viscometer by properly setting of valves on the solvent line. For this case, V1, V2, and V3 will be open, as shown in Figure 4.5. To measure the amount of fluids charged into the system, a transfer vessel and a balance (Mettler PM6100, accuracy of ± 0.01 g) are used. During the charging process, the exit valves, E 1, E 2, and E 3 are open and closed in turn in order to charge the solvent line.

B. Loading polymers. Liquid polymers are loaded using a syringe through the front loading port (FLP). The weight of polymer charged into the system is determined by the mass difference for the syringe before and after drawing liquid polymer. The loading of solid polymers is done through the top loading port (TLP) by removing the fall tube attachments during the loading process. When working with polymer solutions (mixture), the polymer (solute) is loaded first, and then the solvent is charged.

C. Pressurization. Once the viscometer is charged with the desired amount of polymer and solvent, or pure solvent, the pressurizing fluid (in the present study we access acetone) is

pumped through the pressure line into the pressure generator and to the piston assembly, which holds the backside of the piston. The exit valves (E 4 and E 5) are kept open until some fluid is observed to come out while filling the system to achieve an air-free line. The desired pressure level in the view cell is achieved by the piston movement, which is controlled and manipulated by the pressure generator.

D. Temperature control. The temperature of the view cell is increased or decreased by adjusting the temperature of the circulation air inside the oven that houses the view cell. The heating is carried out slowly to prevent any undesirable temperature gradients across the cell body.

E. Mixing. The electromagnetic stirrer and the circulation pump are used to obtain homogeneity and mixing of the viscometer contents during heating up and at the equilibrium. Electromagnetic stirrer and circulation pump are kept on all the time except at the time of the fall time measurement. By observing the cell through sapphire windows the homogeneity of the solution can be verified.

F. Data acquisition. Once thermal and mechanical equilibrium in the system is achieved, the data collection starts. First, the sinker is pulled up to the top of the fall tube and held there by a magnetized pull-up magnet, which is moved up by a motor. The demagnetization of the magnet makes the sinker fall down in the tube with the effect of gravitational force. At the same time, the data acquisition program starts to record the voltage output from the LVDT coils and fall time. Whenever measurements above are taken, the temperature, pressure, and

piston position are recorded. When examining very high viscosities the fall height can be reduced by loading sinker at the middle height in order to limit the time of one measurement and thus reduce also the effect of the fluctuations of temperature and pressure. The readings from the piston position sensor LVDT and the known total mass of sample loaded are used to calculate the system density in the view cell. This density information and the terminal velocity data of the sinker, which can be drawn from the voltage output of the viscosity LVDT coils and fall time relations stored as computer files in the data acquisition computer, are used to calculate the viscosity of the solutions. The data processing procedure to find out terminal velocity from the computer file of voltage output of the viscosity LVDT coils and fall time relations will be discussed in detail in section of 4.2.6 G.

Several consecutive measurements (normally four) are made at each pressure and temperature level. Between each run sufficient time, typically a period of 30 min is allowed to achieve stability in the system and to prevent the pull-up magnet from overheating system which may affect the temperature of the sample in the viscometer.

G. Data Processing. Figure 4.7 shows a typical voltage output from the three viscosities LVDT coils during fall of the sinker, which was created from the related measurements for viscosity detection for acetone. At first the voltage output is at the zero-baseline. As the sinker falls and enters the first coil, the voltage increases to a positive peak, then passes through a zero point (base-line), which is followed by a negative peak and then passes another zero-base line before entering the second coil. Similar outputs are observed for the second and the third coil.

The data processing software package are shown in Figure 4.8. This package includes 3 programs: “standard”, “zerofinder”, and “dtfinder” program. The raw calibration voltage-distance data from instrument measurement are normalized by using the program of “standard” to generate the normalized calibration voltage-distance data. This normalization process involves three steps. (1) divide all the data into 6 sections according to the 6 peak areas; (2) find maximum for each peaks; (3) normalize all the data by being divided by the 6 corresponding maximum for the 6 peak areas, respectively. The raw and normalized calibration data are shown in Figure 4.9. The same normalization procedure is then conducted to convert the raw experimental voltage-time data from the actual system measurement (for a fluid or polymer solution) to normalized experimental voltage-time data by using program of “zerofinder” and “standard”. The “zerofinder” program is used to provide information about how to divide all the data into 6 sections. Finally, the “dtfinder” program is run to combine the two normalized data to find the distance-time relationships, as shown in Figure 4.10. From the distance-time relationship, the terminal velocity can be deduced.

The slope of the distance-time plot is the terminal velocity of the sinker. Thus, along with the density data determined before, the viscosity η of the polymer solution can be found by using the equation below

$$\eta = (K/V_t)(\rho_s - \rho_f) \quad (\text{Eq.4.2})$$

where V_t is the terminal velocity of the sinker, ρ_s is the density of the sinker, ρ_f is the density of the solution, K is a instrument constant, which is determined as 0.0199 in previous study (Dindar, 2001).

In Figure 4.10, only the second and the third coil data (without the last to points) were utilized to get the terminal velocity. The first coil is neglected in order to ensure that the sinker has reached its terminal velocity. The last two points of the third coil are neglected to avoid the deviations that set in (end effect of the fall tube) as the sinker approaching the bottom of the fall tube. Figures 4.7 and 4.10 showed the actual LVDT outputs and the velocity of the sinker in pure acetone, at 100 °C and 35 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 4.11 and 6.12 for 10 wt % solutions of the 15K and 540K molecular weight PMMA samples.

4.2.7 Accuracy and precision of measurement

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 (Dindar and Kiran, 2002a;b).

4.3 Other characterizations

A. Gel permeations chromatography (GPC) tests. The GPC tests for all the polymers formed are conducted in chemistry department to find out polymer molecular weight and

polydispersity index. Typically, the THF is used as solvent and narrow-PDI polystyrene is used as standard.

B. Nuclear magnetic resonance (NMR) test. The ^1H and ^{13}C NMR tests for all the copolymers formed are conducted in chemistry department to gain information of comonomer sequence and comonomer composition in the copolymer chain. Generally, the THF is used as solvent.

C. Fourier transform infrared spectroscopy (FTIR) tests. FTIR tests are conducted to determine the polymer molecular structure by identifying the atomic groups through their characteristic absorption bands. These tests are conducted in our lab using the FTS 3100 from DIGILAB. The KBr disks containing polymer samples are made for tests and a pure KBr is used for background test.

D. Differential scanning calorimetry (DSC) tests. DSC tests are conducted to characterize the thermal properties of the polymers by determining the glass transition temperature and melting temperature. These tests are also conducted in our lab using a Perkin-Elmer DSC unit with Pyris control program. Typically, the heating/cooling rate is 10 K/min.

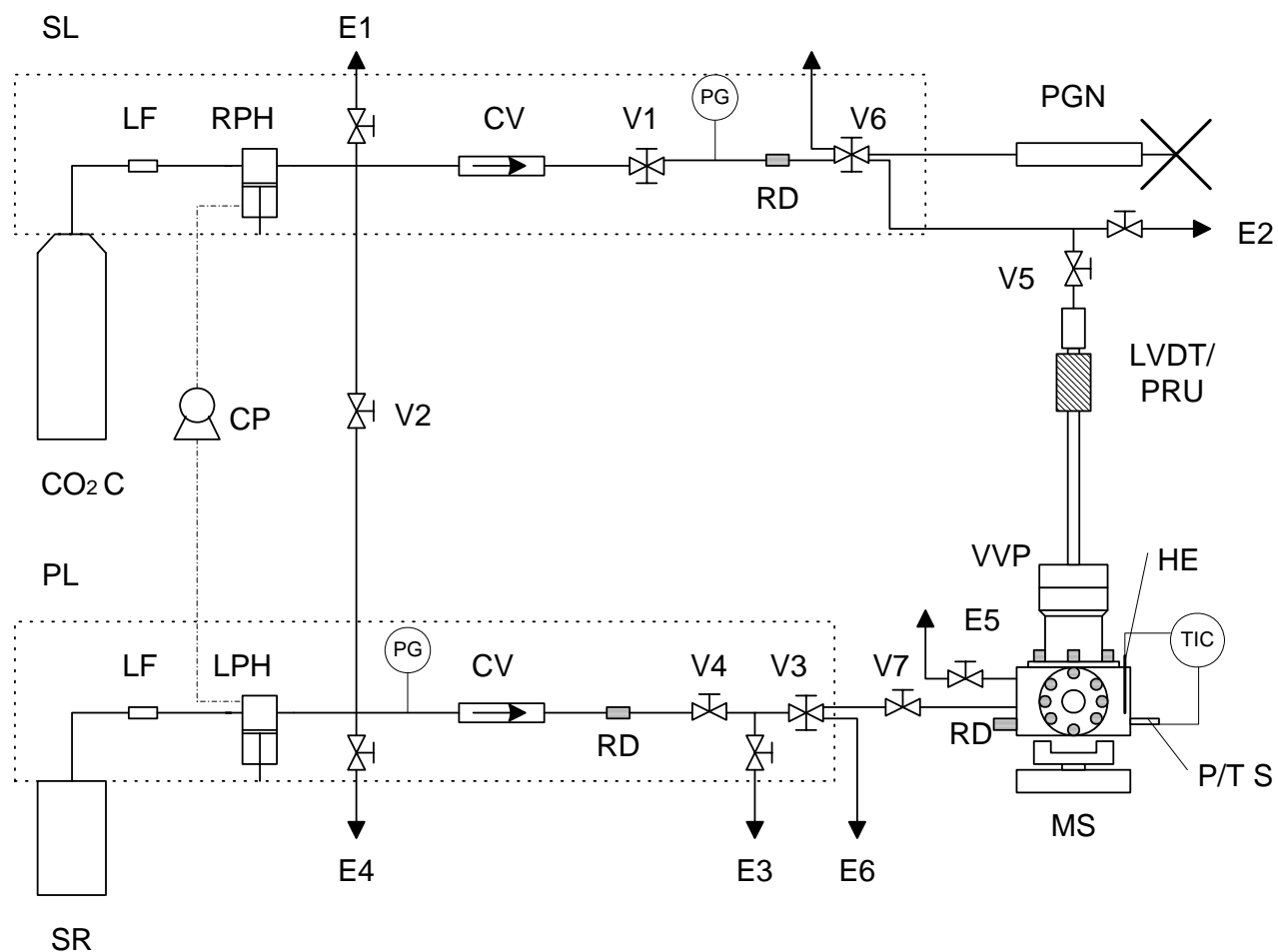


Figure 4.1 Schematic diagram of the view cell system. SL: solvent line, PL: pressure line, CO₂ C: CO₂ cylinder, SR: solvent reservoir, RPH: right pump head, LPH: left pump head, PG: pressure gauge, CV: check valve, RD: rapture disk, PGN: pressure generator, LVDT/PRU: linear variable differential transformer / position readout unit, VVP: variable volume part, HE: cartridge heater, MS: magnetic stirring, P/T S: pressure/temperature sensor, V1-V7: valves, E1-E6: exits.

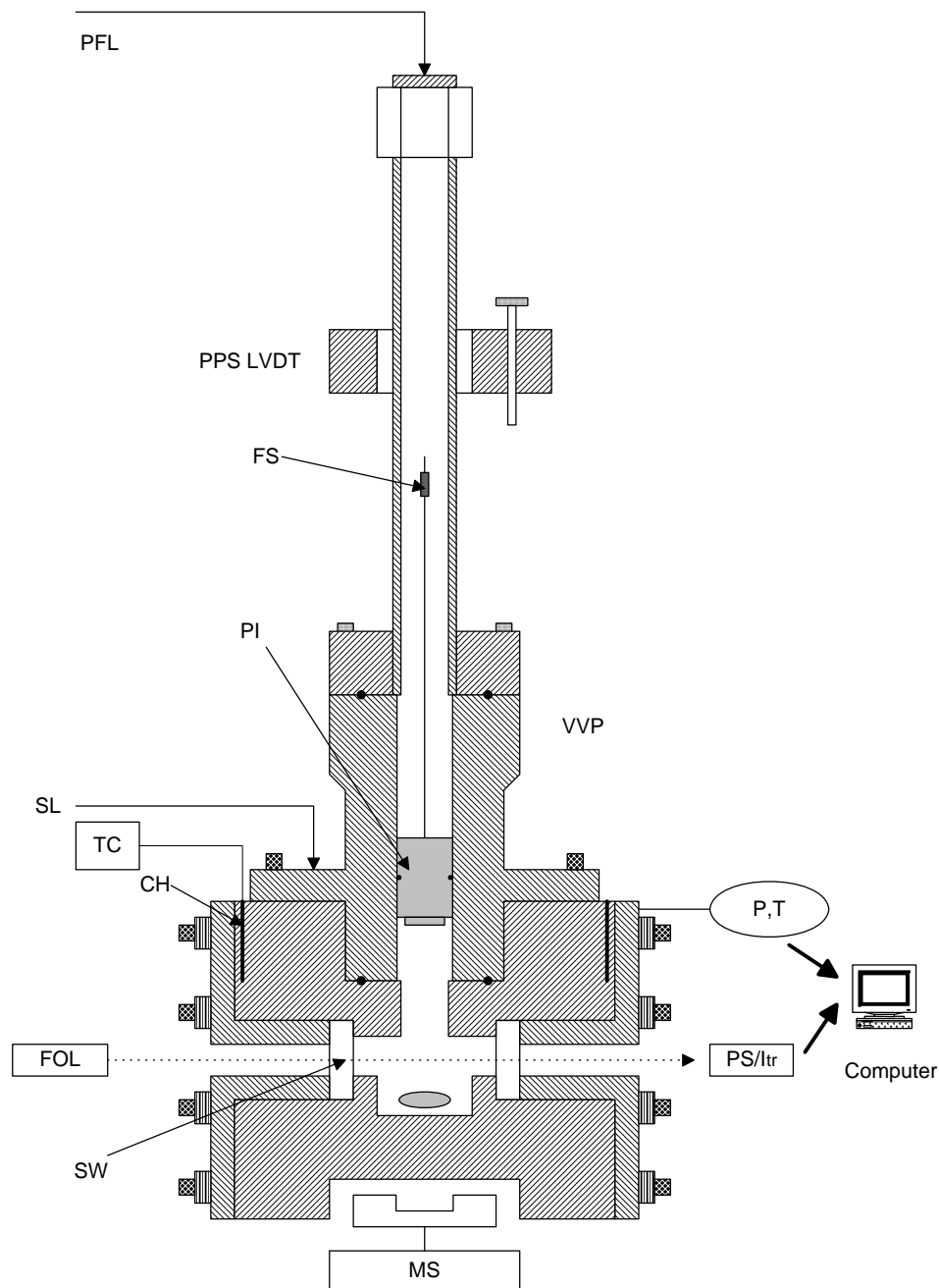


Figure 4.2 Schematic diagram of the view-cell for density and phase behavior determinations. PFL: pressurized fluid line, PPS LVDT: piston position sensor linear variable differential transformer, FS: ferromagnetic slug, PI: piston, SL: solvent line, TC: temperature controller, CH: cartridge heater, VVP: variable volume part housing the piston, P = pressure; T = temperature, FOL: fiber optical illuminator, SW: sapphire window, PS/ I_{tr} : photo sensor/ transmitted light intensity, MS: magnetic stirrer.

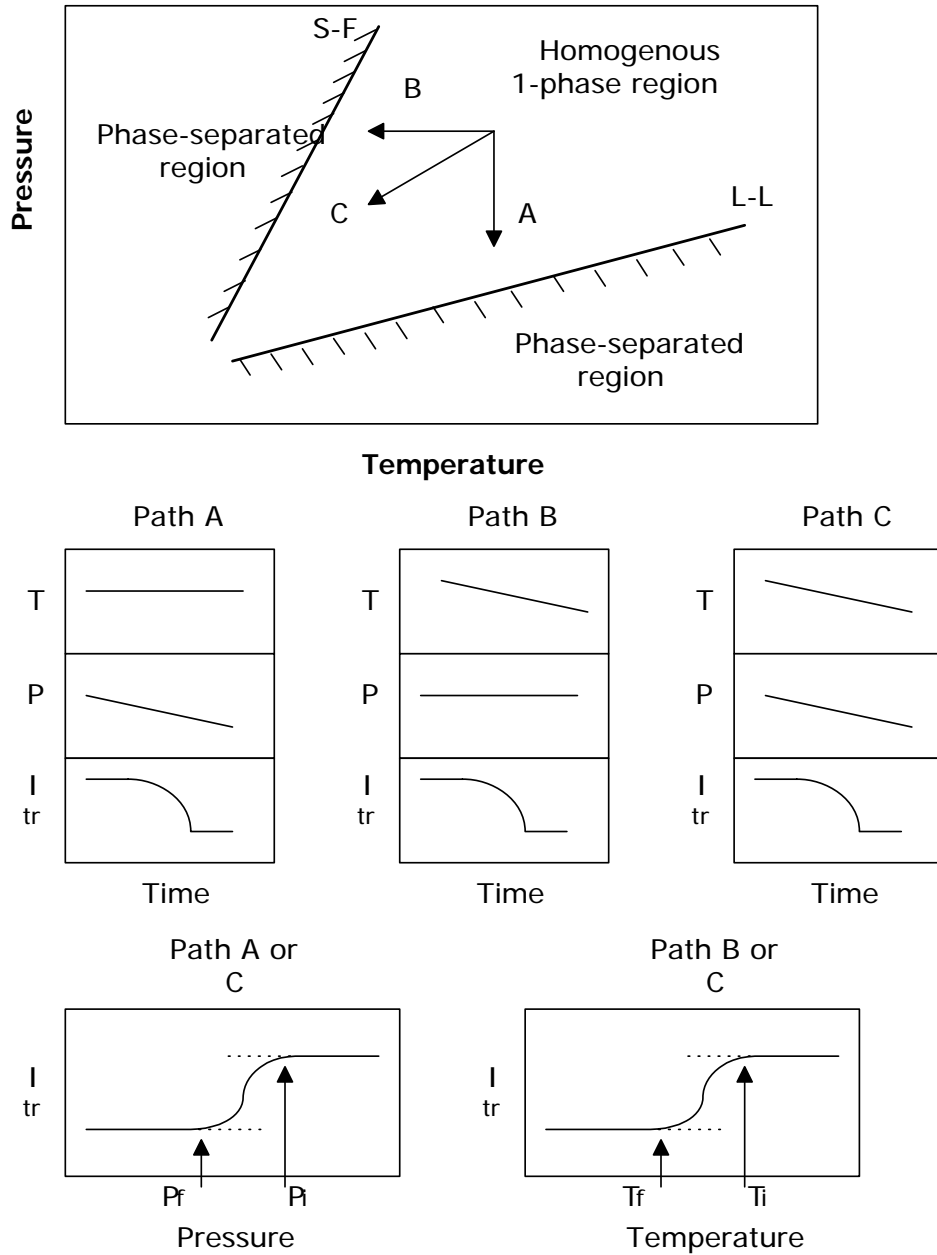


Figure 4.3 Illustration of the different paths followed to determine phase boundaries (liquid-liquid (L-L) and solid-fluid (S-F)) and the corresponding changes in temperature (T), pressure (P) and transmitted light intensity (I_{tr}) with time. The lower part of this figure demonstrates the incipient demixing pressure (P_i) and temperature (T_i) and the condition corresponding to transmitted light intensity going to minimum (P_f and T_f). Path A: constant temperature, Path B: constant pressure, Path C: variable pressure and temperature.

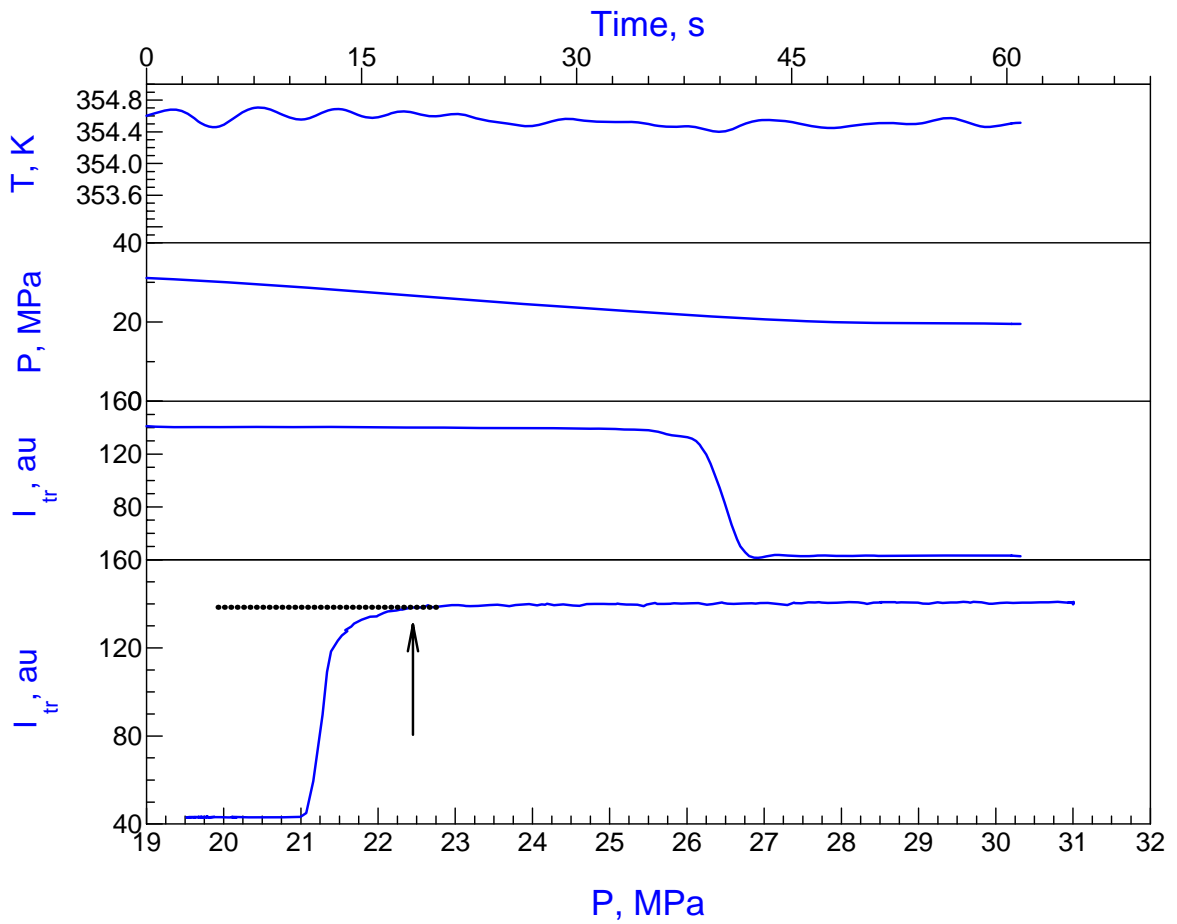


Figure 4.4 Variation of temperature, pressure, and transmit light intensity with time during depressurization at constant temperature of 354.7 K in the view cell for the solution of 5 wt % PCL in acetone containing 40 wt % CO₂.

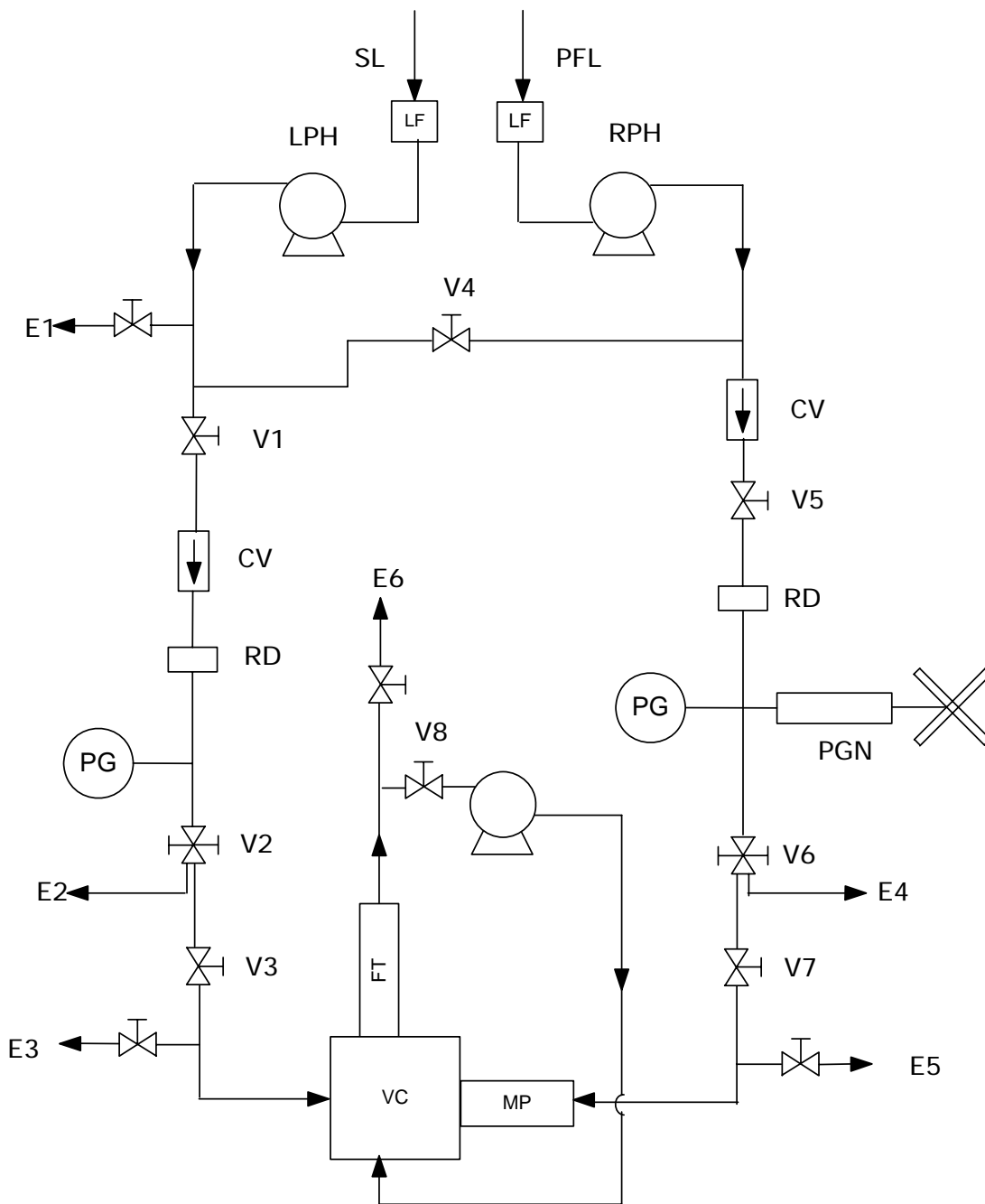


Figure 4.5 Flow sheet of the viscometer system. VC: view cell, FT: falling tube, MP: movable piston, V's: valves, E's: exit valves, CV: check valve, RD: rupture disk, PG: pressure gauge, SL: solvent line, PL: pressurized line, LPH: left pump head, RPH: right pump head, PGN: pressure generator, CP: circulation pump.

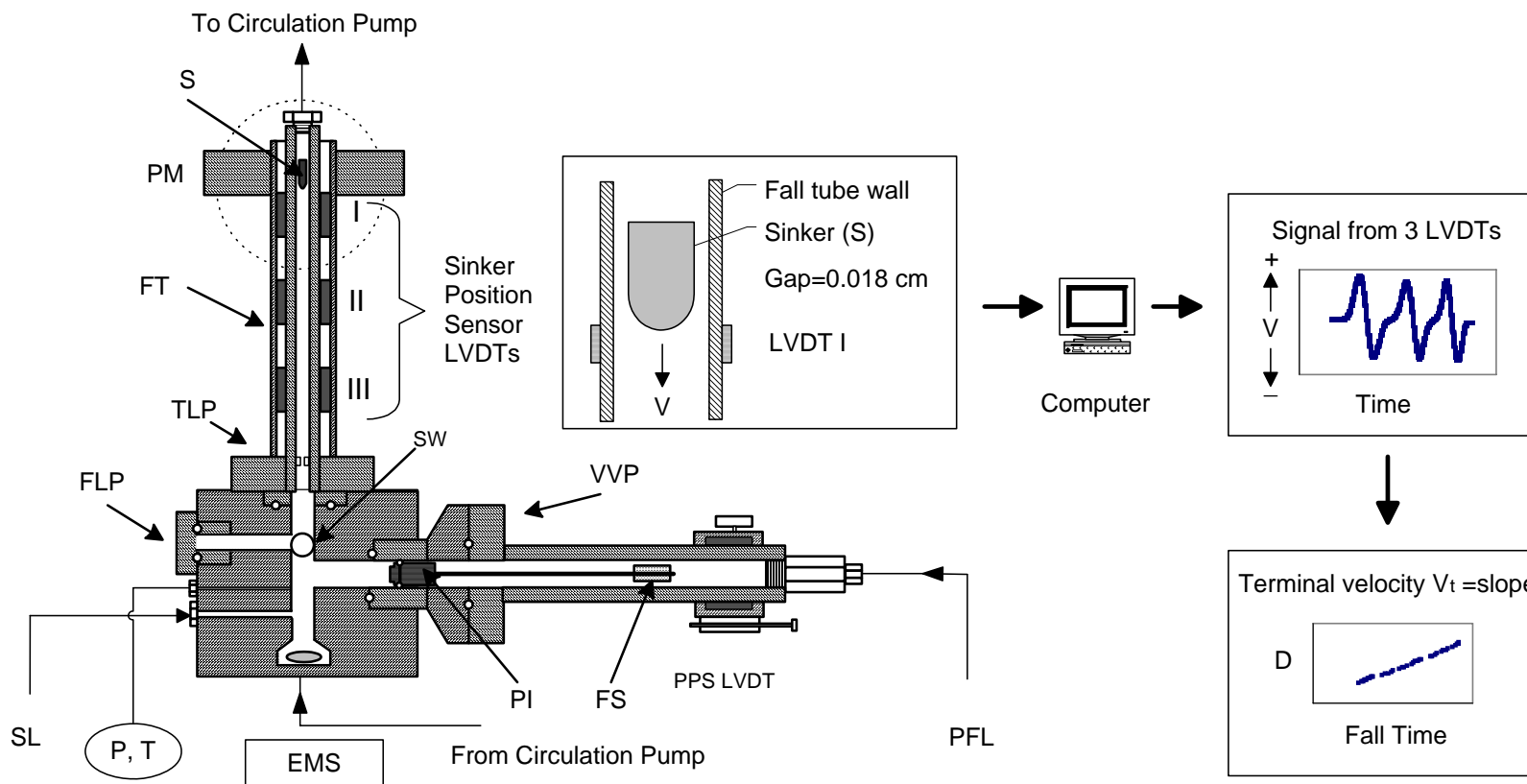


Figure 4.6 Schematic diagram of the viscometer and the data processing procedure. SL: solvent line, PFL: pressurizing fluid line, PM: pull-up magnet, TLP: top loading port, FLP: front loading port, SW: sapphire window, EMS: electromagnetic stirrer, PI: movable piston, FS: ferromagnetic slug, PPS LVDT: piston position sensor linear variable differential transformer, S: sinker, V: LVDT signal; D: sinker fall distance.

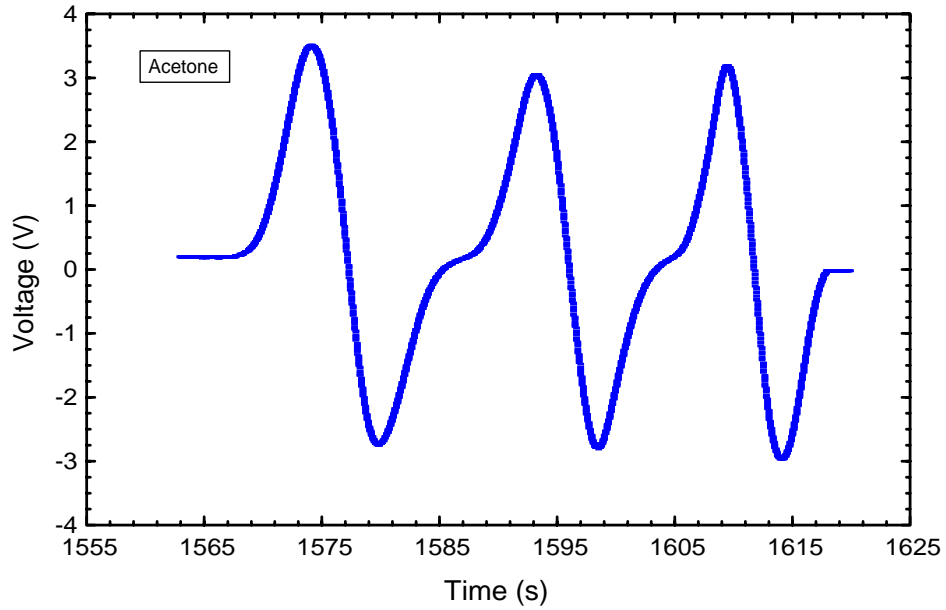


Figure 4.7 Sinker LVDT signal (V) versus time during viscosity determination for acetone at 35 MPa and 100 °C.

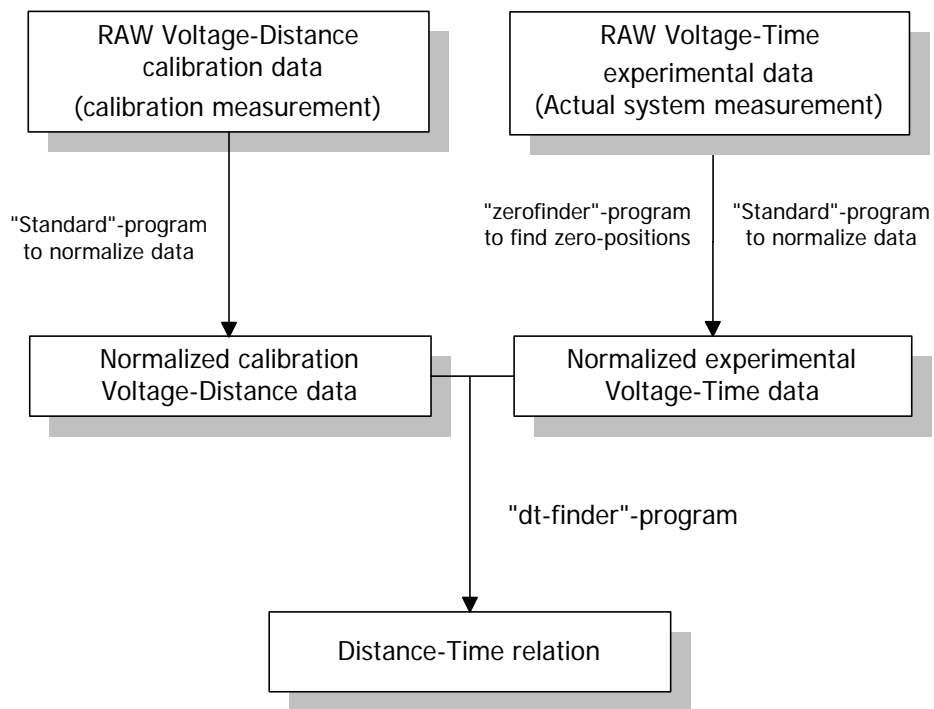
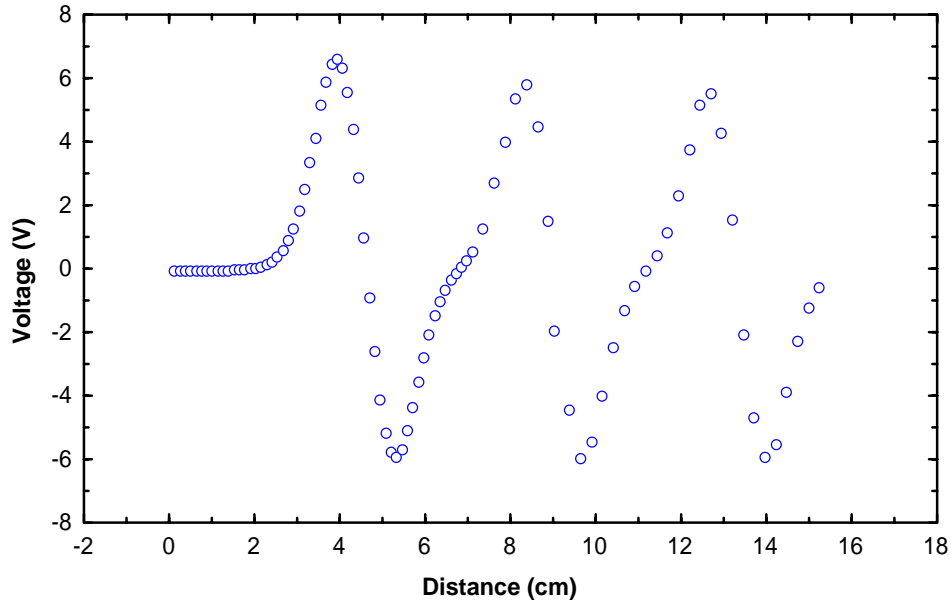
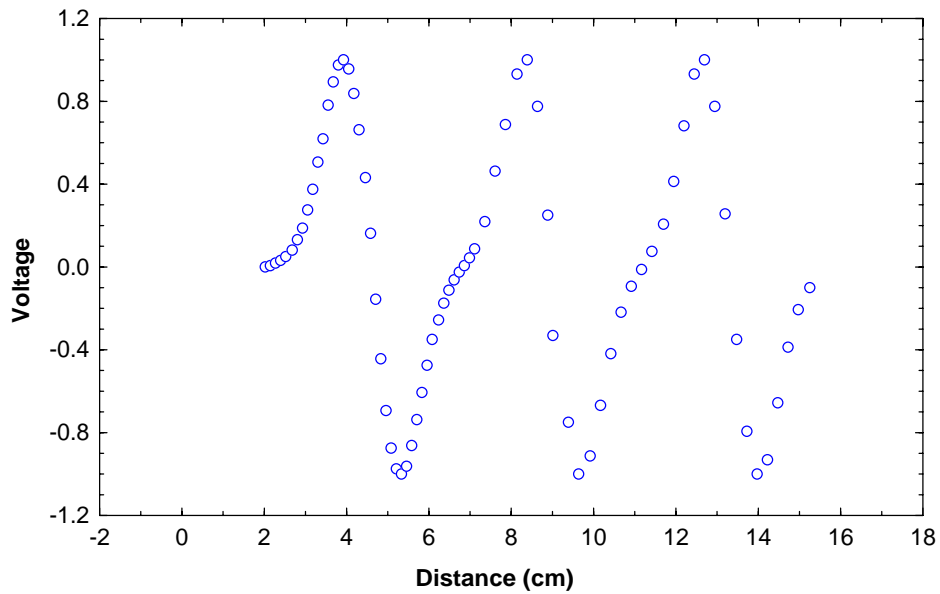


Figure 4.8 Working diagram for data processing software package



(a)



(b)

Figure 4.9 Calibration voltage-distance relations for the sinker position in the falling tube of the instrument. Raw calibration voltage-distance data (a); normalized calibration voltage-distance data (b). The normalized data (b) are derived from the raw data by 1) divide all the data into 6 sections according to the 6 peak areas; 2) find maximum for each peaks; 3) normalize all the data by being divided by the 6 maximum for the 6 peak areas, respectively. Some points that are at the beginning are deleted in the normalized figure (b).

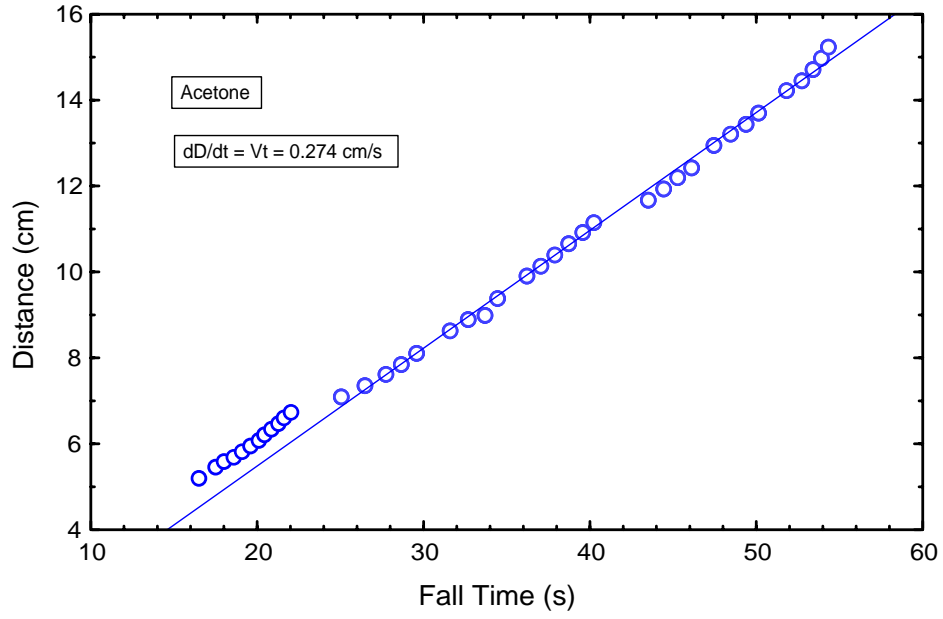
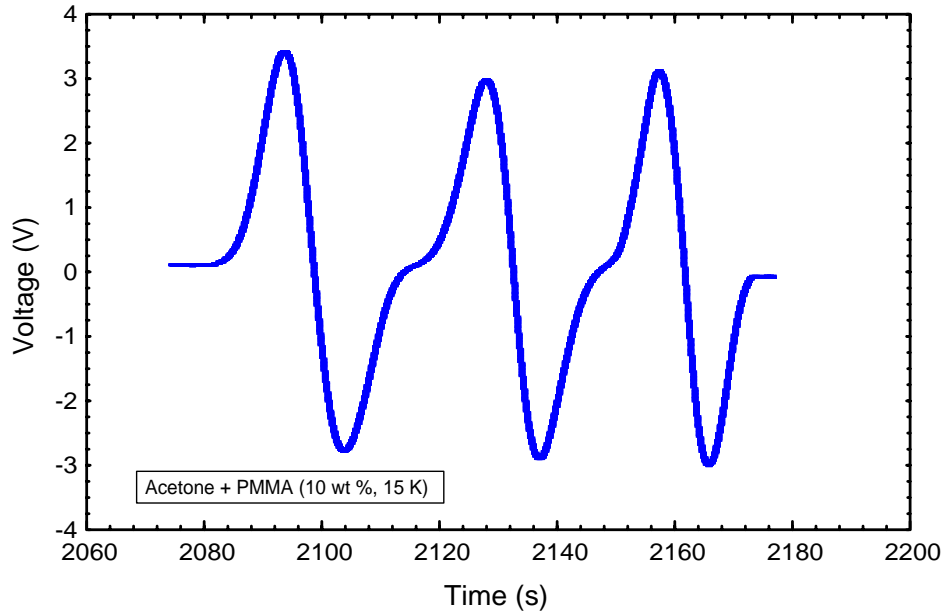
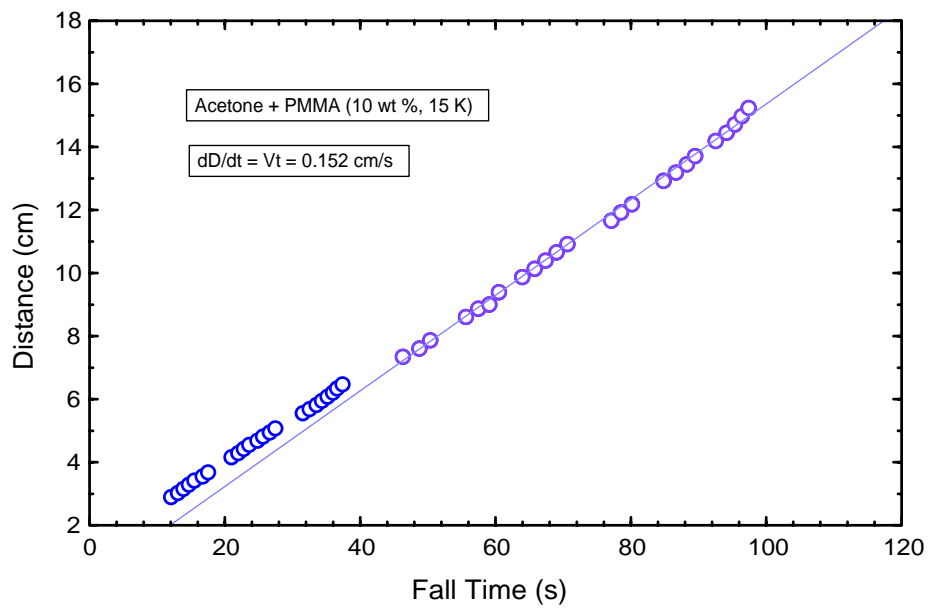


Figure 4.10 Sinkers travel distance (D) versus time during viscosity determination for acetone at 35 MPa and 100 °C. The sinker terminal velocity determined from the response of the 2nd and 3rd LVDT coils (the slope of the fitted line) is 0.274 cm/s.

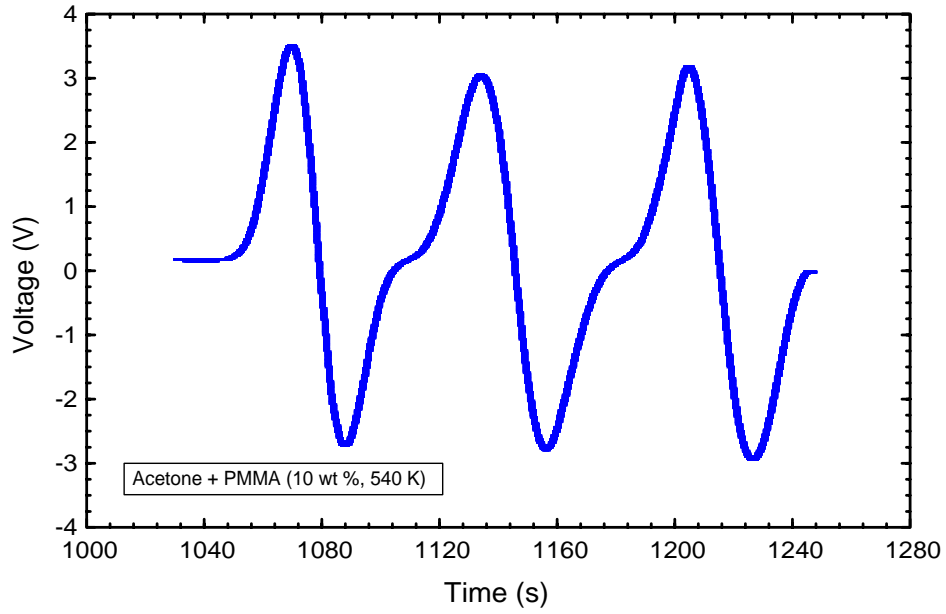


(a)

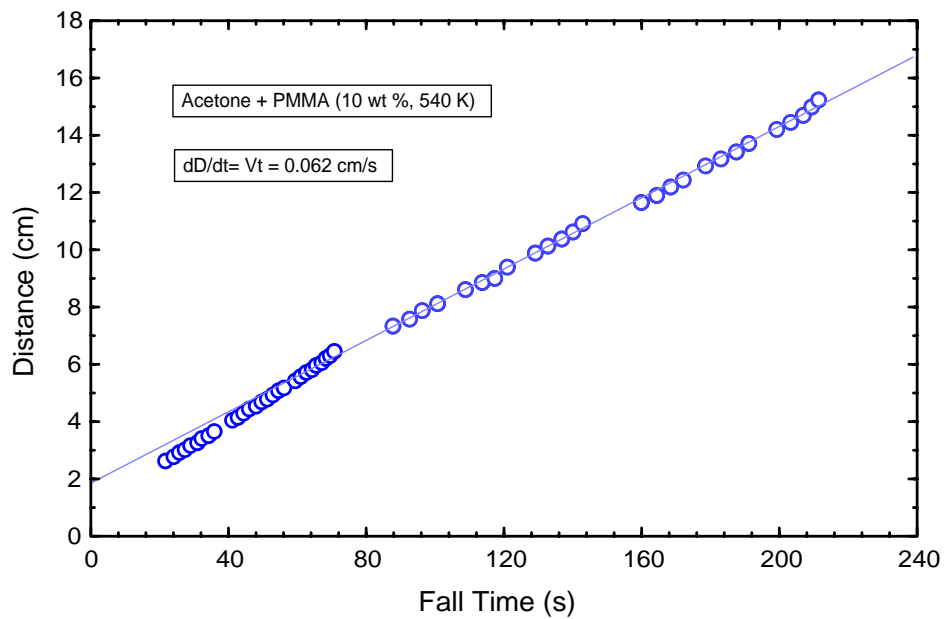


(b)

Figure 4.11 (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 4.12 (a). Sinkers LVDT signal (V) and (b). Sinkers travel distance (D) versus time during viscosity determination for system of acetone + PMMA (10 wt%, 540 K) at 35 MPa and 100 °C. The sinkers terminal velocity is 0.062 cm/s