

UNIVERSITY OF CALGARY

Detection of Phase Transitions with Acoustic Resonance

by

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## **Abstract**

In this work, the acoustic resonance (AR) method is used to detect liquid-vapor and liquid-solid phase transitions from reservoir fluids. A thermodynamic model is developed to predict the sonic speed and acoustic theory is used to predict the resonance frequency based on the predicted sonic speed. The predicted trend in the resonance frequency is used to screen the AR measurements for resonance frequencies that correctly identify phase transitions.

Although experiment and theory did not match well, the screening procedure correctly identified liquid-vapor phase transitions in all cases. However, a significant number of false transitions were also identified. The results for liquid-solid phase transitions were less conclusive. Recommendations for the improvement of the AR system are made.

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**To the memory of my parents**

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## Nomenclature

|           |                                                               |
|-----------|---------------------------------------------------------------|
| $a$       | Element of Jacobian matrix                                    |
| $a(T_c)$  | Parameter in equation of state                                |
| $a(T)$    | Parameter in equation of state                                |
| $A$       | Parameter in equation of state or Jacobian matrix             |
| $b$       | Parameter in equation of state                                |
| $B$       | Parameter in equation of state                                |
| $c$       | Sonic speed                                                   |
| $C_p$     | Isobaric heat capacity                                        |
| $C_v$     | Isochoric heat capacity                                       |
| $C_1$     | Constant of ideal gas heat capacity                           |
| $C_2$     | Constant of ideal gas heat capacity                           |
| $C_3$     | Constant of ideal gas heat capacity                           |
| $C_4$     | Constant of ideal gas heat capacity                           |
| $C_5$     | Constant of ideal gas heat capacity                           |
| $E$       | Dimensionless function in multiphase flash calculation        |
| $f$       | Fugacity, frequency, or function in Twu correlations          |
| $F$       | Dimensionless function in ideal gas heat capacity correlation |
| $\hat{f}$ | Reference fugacity                                            |
| $g$       | Dimensionless function in multiphase flash calculation        |
| $h$       | Dimensionless function in multiphase flash calculation        |
| $j$       | Integer                                                       |
| $K$       | Equilibrium ratio                                             |
| $K_w$     | Watson characterization factor                                |
| $l$       | Length                                                        |
| $m$       | Dimensionless function in equation of state                   |
| $M$       | Molecular weight                                              |

|             |                                                                           |
|-------------|---------------------------------------------------------------------------|
| $M_n^+$     | Molecular weight of plus fraction                                         |
| $n$         | Integer in resonance mode, or first single carbon number of plus fraction |
| $N$         | Last single carbon number of plus fraction                                |
| $N_c$       | Number of components                                                      |
| $N_p$       | Number of phases                                                          |
| $N_{pc}$    | Number of pseudocomponents                                                |
| $p$         | Probability density function                                              |
| $P$         | Pressure, or cumulative density function                                  |
| $Q$         | Object function in multiphase flash calculation                           |
| $r$         | Radius                                                                    |
| $R$         | Universal gas constant                                                    |
| $S$         | Parameter in fugacity calculation                                         |
| $SG$        | Specific gravity                                                          |
| $SG_n^+$    | Specific gravity of plus fraction                                         |
| $\Delta SG$ | Function in Twu correlations                                              |
| $t$         | Constant of volume translation                                            |
| $T$         | Temperature                                                               |
| $v$         | Molar volume                                                              |
| $V$         | Volume                                                                    |
| $x$         | Phase composition                                                         |
| $\hat{x}$   | Reference phase composition                                               |
| $y$         | Dimensionless function in gamma distribution                              |
| $z$         | Composition                                                               |
| $z_n^+$     | Mole fraction of plus fraction                                            |
| $Z$         | Compressibility factor                                                    |
| $z_{RA}$    | Rackett compressibility factor                                            |

### **Greek Symbols**

|          |                                                                                |
|----------|--------------------------------------------------------------------------------|
| $\alpha$ | Parameter in gamma distribution, or dimensionless function in Twu correlations |
|----------|--------------------------------------------------------------------------------|

|               |                                                         |
|---------------|---------------------------------------------------------|
| $\alpha_1$    | Dimensionless function in equation of state             |
| $\alpha_{nm}$ | Solution of Bessel function for cylindrical resonator   |
| $\alpha_p$    | Thermal expansivity                                     |
| $\beta$       | Phase amount or parameter in gamma distribution         |
| $\gamma$      | Heat capacity ratio                                     |
| $\delta$      | Binary interaction coefficient                          |
| $\eta$        | Parameter in gamma distribution                         |
| $\theta$      | Function in Kesler-Lee correlations                     |
| $\Theta$      | Dimensionless function in multiphase flash calculation  |
| $\kappa$      | Compressibility                                         |
| $\kappa_T$    | Isothermal compressibility                              |
| $\kappa_S$    | Adiabatic compressibility                               |
| $\lambda$     | Acceleration factor                                     |
| $\rho$        | Density                                                 |
| $\phi$        | Fugacity coefficient                                    |
| $\chi$        | Volume fraction                                         |
| $\psi$        | Function in Twu correlations                            |
| $\omega$      | Acentric factor                                         |
| $\varphi$     | Adjustable parameter for binary interaction coefficient |

### **Subscripts**

|     |                       |
|-----|-----------------------|
| avg | Average               |
| b   | Boiling               |
| c   | Critical or component |
| i   | Component index       |
| I   | Pseudocomponent index |
| j   | Phase index           |
| L   | Liquid                |

|          |                                  |
|----------|----------------------------------|
| <b>M</b> | <b>Molecular weight</b>          |
| <b>p</b> | <b>Phase or isobaric</b>         |
| <b>P</b> | <b>Pressure</b>                  |
| <b>r</b> | <b>Reduced</b>                   |
| <b>S</b> | <b>Adiabatic or Solid</b>        |
| <b>T</b> | <b>Isothermal or temperature</b> |
| <b>v</b> | <b>Isochoric</b>                 |
| <b>V</b> | <b>Volume</b>                    |

### **Superscripts**

|          |                        |
|----------|------------------------|
| <b>0</b> | <b>Ideal gas state</b> |
| <b>k</b> | <b>Iteration index</b> |
| <b>s</b> | <b>Saturation</b>      |

## **CHAPTER ONE: INTRODUCTION**

Phase transitions are an important phenomenon in every stage of oil production. The knowledge of phase transition conditions is necessary for designing optimal operating conditions and for achieving optimal economics. People have long been seeking a versatile technique for detecting phase transitions in a wide range of temperature and pressure conditions. Acoustic resonance is a promising technique and will be tested for its capability in detecting phase transitions.

### **1.1 Phase Transitions in Oil Production**

#### **1.1.1 Vapor-Liquid Transition**

The theory and practice of vapor-liquid phase transition has been well established and documented (Rowlinson et al., 1982; Walas, 1985; McCain, 1990; Smith, et al., 1996; Prausnitz et al., 1999). The process of a vapor-liquid transition can be easily demonstrated with a retrograde gas reservoir which is initially in a single-phase (gas) state (Craft et al., 1991). The reservoir fluid remains single-phase gas during the production until the pressure reaches the dew point. Below this pressure, a liquid drops out of the reservoir fluid which experiences a vapor-liquid transition. This process of condensation continues until the liquid volume reaches its maximum. Further reduction of the pressure will cause the revaporization of the condensed liquid which undergoes a liquid-vapor transition. For an (undersaturated) black oil reservoir, the reservoir fluid is initially in a single-phase (liquid) state. A second phase (gas) will evolve as the pressure drops below the bubble point.

The occurrence of a vapor-liquid transition can have an adverse effect on oil (gas) production. In a retrograde gas reservoir, most of the condensed liquid is trapped in the pore spaces of the rock and is immobile. Hence, it will be left in the reservoir at abandonment, meaning the loss of a valuable resource. In a black oil reservoir, the formation of a second phase (gas) will lead to low recovery, so a pressure maintenance technique is needed to improve the recovery (Craft et al., 1991; Dake, 1994).

### **1.1.2 Liquid-Solid Transition**

Apart from the vapor-liquid transition discussed in Section 1.1.1, liquid-solid phase transitions may also occur during oil production. The liquid-solid transitions of interest in this work involve the precipitation of asphaltene and/or wax from reservoir fluids. Due to their importance and complexity, asphaltene and wax precipitation has been the topic of much research in recent years (Bunger, et al., 1981; Speight, 1991; Yen et al., 1994; Becker, 1997)

Given a crude oil which is initially in the single-phase (liquid) state, as the reservoir pressure declines below the onset of asphaltene precipitation, the reservoir fluid will undergo a liquid-solid transition, resulting in the formation of a solid (asphaltene) phase (Leontaritis, et al., 1994; Leontaritis, 1996). When the pressure is depleted below the bubble point, a vapor phase will appear; hence, three phases (vapor-liquid-solid) coexist in the reservoir.

The problems with asphaltene precipitation have been reported from many areas of the world (Haskett et al., 1965; Lichaa, 1977; Tuttle, 1983; Leontaritis et al., 1988; Mansoori, et al., 1988). In the reservoir, asphaltene precipitation can block pore throats and cause a reduction in permeability. In the wellbore and surface facilities, asphaltene precipitation can reduce the flow and interfere with their proper operations. The Prinos field of the North Aegean Sea (Leontaritis et al., 1988) provides an example of the severe problems caused by asphaltene precipitation. Some wells, with an initial production rate of 3000 barrels per day, ceased flowing only after a few days of production. Due to the presence of sour gas, the cost of workovers could be so high (over a quarter million dollars each) that production from this reservoir appeared to be uneconomic.

Mechanical and chemical techniques have been used to combat asphaltene problems. Mechanical removal was very effective in the Prinos project (Leontaritis et al., 1988). Most oil producers use xylene washes for the removal of asphaltene deposits from wells, transfer lines, and storage facilities (Becker, 1997). These remedial procedures require considerable investment in time, solvent, and lost production.

It is obviously preferable to take preventative measures than to have remedial operations. People have started to test asphaltene inhibitors (de Boer et al., 1995; Jamaluddin et al., 1996) which can be injected into the reservoir to avoid or delay asphaltene precipitation. Thermodynamic modeling is also a useful tool for predicting asphaltene problems. Numerous models have been proposed in the literature (Hirschberg et al., 1984; Won, 1986, 1989; Leontaritis et al., 1987; Park et al., 1988; Nghiem et al., 1993, 1996; Pedersen, 1994). The predictive capabilities of these models are limited partly due to the various assumptions involved in their formulation and partly due to the lack of high quality experimental data necessary to test and tune them.

An ideal way to attack the problems of solids precipitation is to experimentally determine the conditions (e.g., pressure, temperature, and composition) of solids precipitation of an oil and then avoid these conditions during production. The different techniques used for detecting phase transitions will be presented in the next section.

## **1.2 Experimental Techniques for Detection of Phase Transitions**

### **1.2.1 Visual Method**

The visual method is an efficient technique for the detection of bubble point and dew point. The experimental procedures are as follows:

- (1) A certain amount of single-phase reservoir fluid is charged to a windowed PVT cell.
- (2) The PVT cell is heated to the specified temperature.
- (3) The pressure is monitored to ensure the fluid remains in single phase.
- (4) The system is stabilized to reach thermal equilibrium.
- (5) The pressure is slowly decreased and the cell is visually monitored for the appearance of the first bubble (for bubble point) or cloud (dew point).
- (6) The pressure is further reduced into the two-phase region.

During the measurement, the system is equilibrated at each pressure setpoint and the pressure and volume readings are taken.

However, the visual method is sometimes time-consuming and the exact bubble or dew point can be difficult to detect. The bubble point of an oil can also be determined from the measured pressure-volume (PV) relation. The pressure and volume data (in both single and two phases) are plotted on a Cartesian ordinate and the bubble point can be identified from the slope change of the curve.

For a retrograde gas, visual observation is probably the only direct way to detect its dew point. The dew point can also be inferred from the pressure and liquid volume fraction data where available. The pressure and liquid volume data are plotted on a Cartesian ordinate. The curve is then extrapolated to zero liquid volume and the corresponding pressure is identified as the dew point.

### **1.2.2 Light Transmittance**

This technique has been used by many researchers to measure the onset of solids (wax and asphaltene) precipitation (Reichert et al., 1986; Thomas et al., 1992; Kruka et al., 1995; Takhar et al., 1995; Hammami et al., 1995; 1999a; 1999b). It is based on the measurement of changes in transmitted light intensity as a function of precipitant concentration in the oil mixture. The light transmittance of a crude increases when it is diluted with a precipitant and a drastic drop in the signal is observed when the onset of precipitation is reached.

This technique works well for light oils but is not suitable for heavy, dark oils. These dark oils absorb a significant portion of the incident light so that the light signal cannot penetrate the sample.

### **1.2.3 Electrical Conductivity**

This technique is based on the measurement of electrical conductivity of the crude oil and was used by Fotland et al. (1993) to determine the onset and the amount of asphaltene precipitation. The work of Fotland et al. indicated an increase in the electrical conductivity during the titration of pentane followed by a sharp decrease at the onset of asphaltene precipitation. Fotland (1996) extended this technique to high pressure (70

MPa) and temperature (120°C) conditions. However, the measurement conducted by MacMillian et al. (1995) with the same technique did not show this abrupt change in electrical conductivity with asphaltene precipitation. Therefore, more work is needed to verify this technique.

#### **1.2.4 Refractive Index (RI)**

Buckley et al. (1996) used refractive index (RI) measurement to detect the onset of asphaltene precipitation from crude oils. They demonstrated that the RI of non-precipitants-crude oil-solvent mixtures changes linearly with the volume fraction of crude oil in the mixture. A departure from the linear relationship indicates the onset of precipitation.

Based on experimental evidence and assuming that London dispersion forces dominate asphaltene precipitation, Buckley et al. (1998) proposed a theory to account for the precipitation of asphaltenes from precipitants-crude oil-solvent mixtures. With this theory, the experimental RI results at ambient conditions could be extended to reservoir conditions. However, recent work indicates that the linear relationship observed by Buckley et al. does not hold for all systems (Taylor, 2000).

#### **1.2.5 Viscometry**

Escobedo et al. (1995) reported the determination of the asphaltene onset condition by measuring the bulk oil viscosity in a capillary viscometer. The viscosity of a crude decreases smoothly with the addition of a precipitant and the onset of asphaltene precipitation can be identified when a significant shift from the trend is observed.

This technique works for both light and heavy crude oils. Its limitation includes the large number of individual samples required for the measurement and the possibility of capillary plugging by precipitated asphaltenes.

### **1.2.6 Cross Polar Microscopy (CPM)**

The use of this technique to detect the onset of wax precipitation (cloud point) has been reported by Ronningsen et al. (1991), Erickson et al. (1993), and Brown et al. (1994). This technique utilizes the fact that all crystalline materials with noncubic geometry are optically anisotropic. This means that the crystals rotate the plane of polarization of transmitted light. Therefore, if two prisms are crossed on opposite sides of the oil sample, the incident light will be initially blocked and the entire field of view will appear black. During the cooling of the oil, the crystallizing material (wax) appears as bright spots against this black background and hence is visible.

Erickson et al. (1993) indicated that the cloud point measured with CMP is much more accurate than that obtained with viscometry and differential scanning calorimetry. Furthermore, it can be used for both clear and dark oils.

### **1.2.7 Flow Loop Test**

de Boer et al. (1995) reported the use of a flow loop apparatus to detect the onset of asphaltene precipitation from crude oils under dynamic flow conditions. This technique is based on the measurement of the differential pressure (DP) across a section of coiled tubing (1 mm internal diameter) as a function of precipitant concentration in the mixture. The DP decreases when an oil sample is diluted by a precipitant and a sudden increase in the signal indicates the onset of asphaltene precipitation.

The techniques discussed above are difficult to implement for the determination of asphaltene onset from a bitumen sample due to its opacity and high viscosity. To overcome this difficulty, Peramanu et al. (1999) designed a flow loop apparatus to detect the onset of asphaltene precipitation from bitumen. The same principle was followed in the apparatus of Peramanu et al. (1999) and of de Boer et al. (1995), but they have different setup. In the apparatus of Peramanu et al., the bitumen was pumped through an in-line filter. With the gradual injection of precipitant into the stream, asphaltene precipitation can be detected by measuring the differential pressure across the in-line filter.

The apparatus of Peramanu et al. can be operated at high temperatures (160°C) and medium pressures (4.9 MPa). The system pressure is not controlled during the measurement as long as it is above the vapor pressure of the precipitant at a given temperature. One disadvantage of this technique is that the onset condition cannot be determined with great precision due to scatter in the measured pressure drops.

### **1.2.8 Ultrasonic Technique**

This technique was first used by Meray et al. (1993) to study the effect of light ends on the wax crystallization temperature of waxy crudes. In this technique, an ultrasonic signal of a single frequency is transmitted through the fluid and the phase transition can be detected by measuring the velocity and attenuation of the transmitted signal. The velocity of an ultrasonic wave traveling through a medium depends on the density and the elasticity of the medium and a noticeable change in the ultrasonic velocity will occur at the onset of solids precipitation.

In their study of inhibitor selection, de Boer et al. (1995) used this technique to determine the onset of asphaltene precipitation from crude oils. Due to the limited information on this technique, little is known regarding its capability and limitations.

### **1.2.9 Acoustic Resonance (AR) Method**

The AR method has been used by Colgate et al. (1990a, 1990b, 1991a, 1991b, 1992a, 1992b, 1992c) to determine the phase transitions and thermophysical properties of pure components and reservoir fluids. A spherical resonator was used in all their measurements. This technique is based on the relationship of the sonic speed in a fluid to its physical properties. When an acoustic signal is applied to a fluid confined in a resonator cavity, resonances will be set up at certain applied frequencies. The resonance frequency in a spherical resonator is proportional to the sonic speed in the fluid which undergoes a distinct change during a phase transition. Therefore, the phase transition in the fluid can be detected by measuring the change in resonance frequency. With this technique, Colgate et al. reported the measurements of the critical point of CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and a retrograde gas (1991a, 1992a, 1992c), the dew point of a natural gas mixture and a

retrograde gas (1991b), and the onset of wax precipitation in a reservoir fluid (1992b). The sonic speed was also back calculated from the resonance frequency data and reported for some of the measurements.

The advantages of using a spherical resonator have been well documented. One of these advantages is the ease of locating different resonance modes (Moldover et al., 1979; Mehl et al., 1981, 1982). However, the AR method has its limitations. It has mainly been used for gas mixtures at low pressure. Since the spherical resonator has a fixed volume, the change of volume (and hence pressure) cannot be easily implemented in the AR measurements.

### **1.3 The Objective of This Work**

Each of the techniques discussed in Section 1.2 has its own utility and limitations. So far, there has been no versatile technique which is capable of detecting both the vapor-liquid and liquid-solid transitions in any oil over a wide range of temperature and pressure conditions. To overcome the difficulties that exist in various techniques, the AR method has been implemented on an apparatus developed at Hycal Energy Research Laboratories Ltd. A cylindrical resonator rather than a spherical one is used in the new AR setup. The cylindrical geometry permits the use of a piston within the resonator to implement a change in volume (and hence in pressure). The system is designed to work at various temperature and pressure conditions. Although the same acoustic principle is followed in both the cylindrical and spherical resonators, different resonances will be generated due to the difference in their geometry and setup.

Sivaraman et al. (1997a, 1997b, 1998, 1999a, 1999b) have reported the application of the apparatus in detecting phase transitions in reservoir fluids. Although phase transitions have been identified with the apparatus, an experienced operator has always identified the resonance modes by inspection. Discrepancies and uncertainties have been experienced during the interpretation of the AR measurements. The objectives of this work are to develop a systematic approach to interpret the AR measurements and to evaluate the capability of the AR apparatus in detecting phase transitions.

## **1.4 Thesis Structure**

A thermodynamic model for sonic speed calculation is presented in Chapter 2. The relationship between the resonance frequency and the sonic speed is discussed. A multiphase flash algorithm is described to calculate the properties of each phase at equilibrium. The procedures for calculating the sonic speed are presented. The heavy fractions of the reservoir fluid are characterized by a molar distribution function and their physical properties are calculated from suitable correlations. The Peng-Robinson equation of state and its application in the sonic speed calculation are discussed as well as the volume transition technique.

The experimental method is presented in Chapter 3. The setup of the AR apparatus and the experimental procedures are described. AR measurements are conducted to detect the vapor-liquid and liquid-solid phase transitions in seven fluid mixtures.

The data of AR measurements are analyzed and interpreted in Chapter 4. The time domain data collected with the AR measurements are processed into frequency domain data with Fast Fourier Transform (FFT). The characteristics of the AR output signal are discussed. The peaks on the frequency spectrum are tracked and screened for potential resonance modes. Sonic speeds calculated from the Peng-Robinson equation of state are used to predict the resonance frequencies. The expected trend in the resonance modes is established based on the acoustic theory and experimental evidence. The resonance modes that best match theory are selected from the potential resonance modes and then the phase transitions are identified.

Chapter 5 gives a summary of the AR method. Its capability and limitations are discussed and evaluated.

In Chapter 6, conclusions are drawn based on the findings of this work. Recommendations are made to improve the AR method.

## CHAPTER TWO: MODEL DEVELOPMENT

The sonic speed is required for the resonance frequency calculation. However, the sonic speed calculation is not available in commercial phase behavior packages due to its infrequent use in the oil industry. In this chapter, a thermodynamic model is developed to calculate the sonic speed in reservoir fluids. An equation of state (EOS) based multiphase flash algorithm is used to calculate the properties of each phase at equilibrium and the sonic speed is then calculated from thermodynamic relations. The heavy fractions in the reservoir fluids are characterized with a molar distribution function and their properties are calculated from correlations.

### 2.1 Resonance Frequency

Figure 2.1 is the schematic of a cylindrical resonator with a radius of  $r$  and length of  $l$ . The signal emitter and receiver are installed at the top and bottom end of the resonator, respectively.

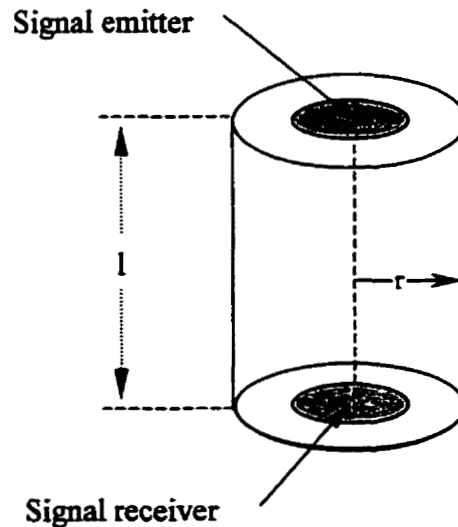


Figure 2.1 Schematic of a cylindrical resonator

Morse (1948) demonstrated that the resonance frequency in a cylindrical space is given by

$$f = \frac{c}{2} \sqrt{\left(\frac{n}{l}\right)^2 + \left(\frac{\alpha_{mn}}{r}\right)^2} \quad (2.1)$$

where  $f$  is resonance frequency;  $c$  is sonic speed;  $l$  and  $r$  are length and radius, respectively;  $n$  is an integer.  $\alpha_{mn}$  is a solution of the equation  $[dJ_m(\pi\alpha)/d\alpha] = 0$  and is tabulated for different values of  $m$  and  $n$  (Morse, 1948).  $J_m$  is the Bessel function of order  $m$ .

The cylindrical resonator used in this work has a radius of 0.3264 cm and a length of 6 cm (variable). A simple calculation shows that, for the resonator used in this work, the second term under the square root in Equation 2.1 can be dropped. For a typical sonic speed of 1000 m/s and the minimum non-zero  $\alpha_{mn}$  of 0.5861, a frequency of 89782 Hz is obtained excluding the first term. This frequency is well above the frequencies used in the AR measurements (0-50000). Therefore, Equation 2.1 is reduced to

$$f = \frac{c}{2} \frac{n}{l} \quad (2.2)$$

Equation 2.2 indicates that the resonance frequency depends on the geometry (length) of the resonator and the property (sonic speed) of the media. Equation 2.2 also contains an integer ( $n$ ) which identifies different resonance modes. The first and second resonance modes are obtained when  $n$  equals 1 and 2, respectively. Only these two modes are meaningful in this work, since the frequencies of the other modes are beyond the range of frequencies used in the AR measurements.

One part of this work is to predict the resonance frequencies using Equation 2.2 and then compare the predicted results with the measured data. Two parameters, the length of the resonator and the sonic speed in the media, are needed for the calculation. The length can be back-calculated from the volume measurement and the radius of the resonator. A thermodynamic model is developed to calculate the sonic speed in the test fluid.

## 2.2 Thermodynamic Relations

Given a mixture that has  $N_c$  components each at an overall composition (mole fraction) of  $z_i$ , it is assumed that the mixture is capable of splitting into  $N_p$  phases at a given temperature and pressure. The following conditions must be satisfied at equilibrium

a. Material balances:

$$\sum_{j=1}^{N_p} \beta_j x_{ij} = z_i \quad (i=1, 2, \dots, N_c) \quad (2.3)$$

where  $\beta_j$  is the molar amount of phase  $j$  and must be nonnegative;  $x_{ij}$  is the mole fraction of component  $i$  in phase  $j$ .

b. Equilibrium relations:

$$f_{i1} = f_{i2} = \dots = f_{iN_p} \quad (i=1, 2, \dots, N_c) \quad (2.4)$$

where  $f_{ij}$  is the fugacity of component  $i$  in phase  $j$ .

c. Summation of mole fractions:

$$\sum_{i=1}^{N_c} x_{ij} = 1 \quad (j=1, 2, \dots, N_p) \quad (2.5)$$

## 2.3 Peng-Robinson Equation of State (PR EOS)

The fugacity (or fugacity coefficient) needs to be calculated in order to solve the set of equations (2.3-2.5). An EOS is used to relate the fugacity to pressure, volume, temperature, and the properties of the mixture (e.g. composition, component properties).

The Peng-Robinson EOS (PR EOS) (Peng et al., 1976) and the Soave-Redlich-Kwong EOS (SRK EOS) (Soave, 1972) are the two most widely used EOS' in the oil industry. Their performance is similar in vapor pressure and equilibrium ratio predictions but the PR EOS gives more accurate liquid density predictions. Therefore, the PR EOS will be used throughout this work. It has the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \quad (2.6)$$

where  $P$ ,  $v$ , and  $T$  are pressure, molar volume and temperature, respectively;  $R$  is the universal gas constant;  $a(T)$  is the attraction parameter and is a function of temperature;  $b$  is the repulsion parameter.  $a(T)$  and  $b$  are calculated with the following equations:

$$a(T) = a(T_c)\alpha_1(T_r, \omega) \quad (2.7)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (2.8)$$

$$\alpha_1 = \sqrt{1 + m(1 - T_r^{0.5})} \quad (2.9)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (2.10)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2.11)$$

where  $P_c$ ,  $T_c$ , and  $\omega$  are critical pressure, critical temperature and acentric factor of a pure component respectively.  $T_r$  is the reduced temperature and is defined as  $T/T_c$ .

The above equations (2.7-2.11) are used for the calculation of pure component parameters. When the PR EOS (Equation 2.6) is used for multicomponent mixtures, mixing rules are necessary to express the parameters of the mixture in terms of the composition and the parameters of the pure components. The following mixing rules are used as recommended by Peng et al. (1976):

$$a = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j (1 - \delta_{ij}) \sqrt{a_{ii} a_{jj}} \quad (2.12)$$

$$b = \sum_{i=1}^{N_c} x_i b_i \quad (2.13)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture.  $\delta_{ij}$  is the binary interaction coefficient and is a measure of the interactions between unlike molecules. During the phase behavior calculation,  $\delta_{ij}$  is usually adjusted to match experimental data. The  $\delta_{ij}$  values between hydrocarbon pairs are calculated with the following equation (Mehra, 1981):

$$\delta_{ij} = 1 - \left[ \frac{2\sqrt{v_{ci}^{1/3} v_{cj}^{1/3}}}{v_{ci}^{1/3} + v_{cj}^{1/3}} \right]^{\varphi} \quad (2.14)$$

where  $v_c$  is the critical volume of a pure component and  $\phi$  is an adjustable parameter.

The PR EOS can also be expressed in polynomial form in terms of the compressibility factor as follows

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2.15)$$

where  $Z$  is the compressibility factor and  $A$  and  $B$  are defined as

$$A = \frac{aP}{R^2T^2} \quad (2.16)$$

$$B = \frac{bP}{RT} \quad (2.17)$$

The fugacity coefficient can be calculated with the following equation

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) + \frac{A}{2.828B} \left( \frac{b_i}{b} - \frac{2S_i}{a} \right) \ln \left( \frac{Z + 2.414B}{Z - 0.414B} \right) \quad (2.18)$$

where  $\phi$  is the fugacity coefficient and  $S_i$  is defined as

$$S_i = \sqrt{a_i} \sum_{j=1}^{N_c} x_j (1 - \delta_{ij}) \sqrt{a_j} \quad (2.19)$$

## 2.4 Volume Translation

One limitation of the PR EOS and the SRK EOS is their inaccuracy in liquid density predictions. Different methods have been proposed to improve the density predictions from EOS (Peneloux et al., 1982; Chien et al., 1986; Mathias et al., 1989; Kokal et al., 1990; Sheng et al., 1990; de Sant' Ana et al., 1999). All these methods are based on the idea of volume translation proposed by Peneloux et al. (1982).

The principle of volume translation is to modify the volume predictions from an EOS with a constant for each component, so that

$$v = v_{eos} - \sum_{i=1}^{N_c} t_i x_i \quad (2.20)$$

where  $v$  is the corrected volume,  $v_{eos}$  is the (uncorrected) volume prediction from an EOS, and  $t_i$  is the constant of volume correction for component  $i$ .

The various methods of volume translation presented in the literature differ from each other in the way that the constants of volume correction are evaluated. According to Peneloux et al. (1982), the best correlating parameter for the pure component volume correction is the Rackett compressibility factor ( $z_{RA}$ ). In the work of Jhaveri et al. (1988), the volume correction was correlated with molecular weight. Mathias et al. (1989) and Shen et al. (1990) proposed that the volume correction should change with temperature. However, the method proposed by Kokal et al. (1990) can greatly improve the volume prediction from an EOS and is easy to implement. Hence, it will be used in this work. The principle of this method is to choose  $t_i$  such that the calculated liquid density from an EOS matches that obtained from the modified Rackett equation which is known to give highly accurate (saturated) liquid densities.

For subcritical components, the procedures for calculating  $t_i$  are:

- (a) Obtain  $z_{RA}$  from the literature (Hankinson et al., 1979). For a pseudocomponent,  $z_{RA}$  can be back-calculated from the following equation (Spencer, et al., 1978) based on its molecular weight and density.

$$v^s = \left[ \frac{RT_c}{P_c} \right] z_{RA}^{[1+(1-T_r)^{2.7}]} \quad (2.21)$$

where  $v^s$  is the saturated liquid volume,  $z_{RA}$  is the Rackett compressibility factor.

- (b) Calculate the saturation pressure of each component at the system temperature from the following equation (Lee et al., 1975).

$$\ln P_r^s = 5.92714 - 6.09648 / T_r - 1.28862 \ln T_r + 0.169347 T_r^6 + \omega(15.2518 - 15.6875 / T_r - 13.4721 \ln T_r + 0.43577 T_r^6) \quad (2.22)$$

where  $P_r^s = P^s / P_c$  and  $P^s$  is the saturation pressure.

- (c) Calculate the saturated liquid molar volume ( $v^s$ ) of each component at the saturation pressure (from Step b) and the system temperature from an EOS.
- (d) Calculate the volume correction  $t$  from

$$t = v^s - \left[ \frac{RT_c}{P_c} \right] z_{RA}^{[1+(1-T_r)^{2.7}]} \quad (2.23)$$

The accurate calculation of the saturated liquid density is guaranteed through the above volume translation. The density prediction can also be improved at other pressures and (subcritical) temperatures if the EOS can give an accurate prediction in the isothermal compressibility  $-\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T$ . The same procedures will be followed for the supercritical components. The only difference is that the constant of volume correction is calculated at the critical temperature of each component.

## 2.5 Multiphase Flash Calculation

For a multicomponent mixture at a specified temperature and pressure, the flash calculation is performed to determine the number of phases present at equilibrium and the composition of each phase. This is achieved by solving the set of equations (2.3-2.5). The algorithm proposed by Heidemann et al. (1997) and by Michelsen (1994) is used in this work. Figure 2.2 shows the flowchart of the program. It can be divided into 4 sections: input, initiation of phases and  $K$ -values, phase distribution calculation, and update  $K$  values.

### 2.5.1 Input

This section reads the parameters required for the EOS calculation. The input data includes overall feed composition, flash temperature and pressure, the properties of each component (critical pressure, critical temperature, acentric factor, critical volume, molecular weight), and binary interaction coefficients. The temperature-independent and composition-independent EOS constants are calculated in this section.

### 2.5.2 Initiation of Phases and $K$ -values

The flash calculation is initiated with the maximum number of phases according to Gibbs' phase rule. Therefore, it starts with  $N_c + 1$  phases if there are  $N_c$  components in the

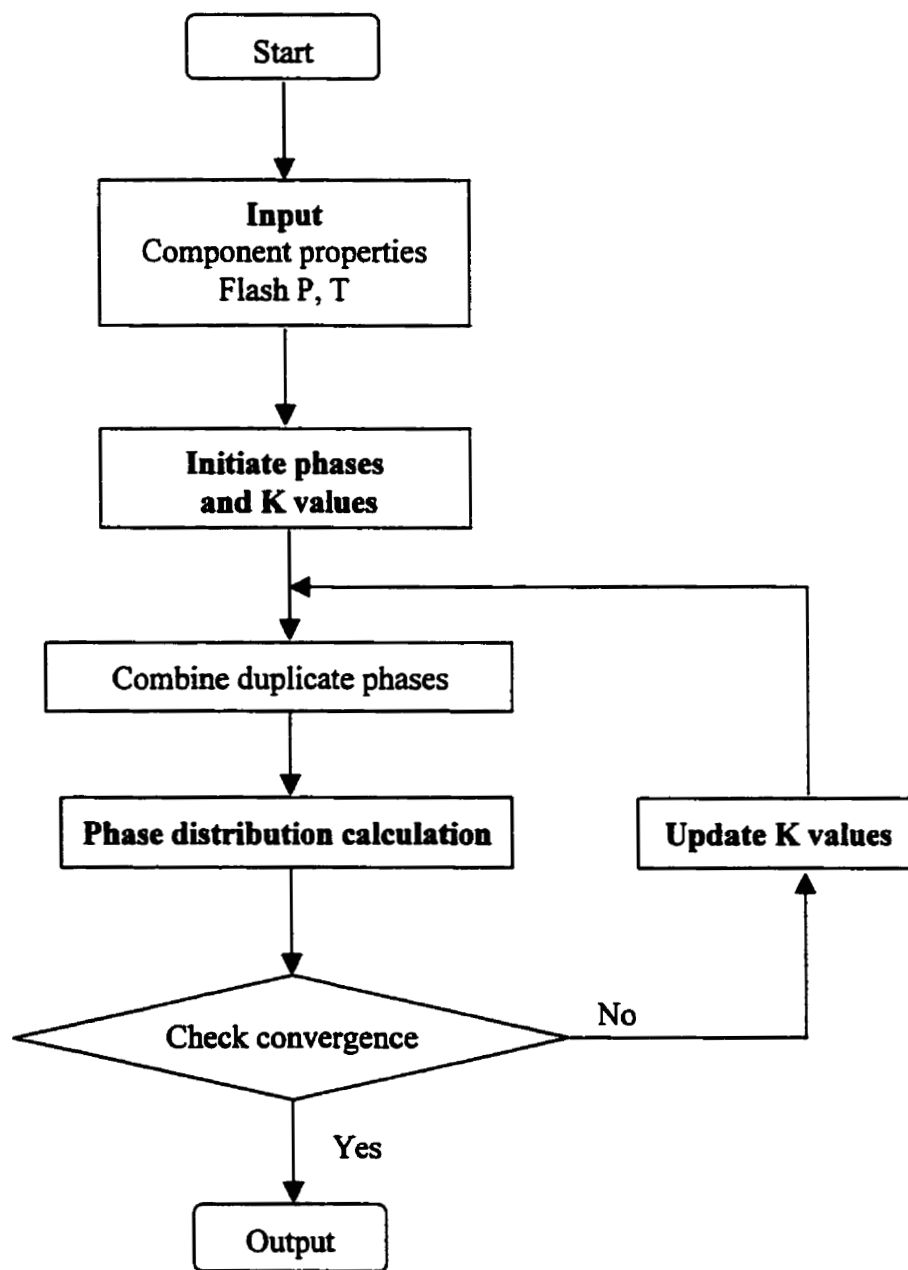


Figure 2.2: Flowchart for multiphase flash calculation

(non-reacting) system. Each of the first  $N_c$  phases is initiated to consist solely of one of the  $N_c$  pure components and the last phase is set to the feed composition.

Given temperature, pressure, and composition, the cubic equation of compressibility factor (Equation 2.15) can be solved. Above the critical temperature, the equation has one root; below the critical temperature, it has one or three roots depending on the pressure. In the case of multiple roots, the intermediate one is of no physical meaning and is discarded. Then the smallest and the largest are compared with  $b$  parameter in the EOS and only those roots greater than  $b$  are kept. Care should be taken to select the correct root for each phase. In a vapor-liquid two-phase equilibrium, the largest is that of the vapor and the smallest that of the liquid. In multiple phase calculation, the identity of each phase with respect to vapor or liquid is not known until the completion of the calculation, so the root corresponding to the lower Gibbs energy will be selected.

Based on temperature, pressure, composition and the  $Z$  factor, the fugacity and fugacity coefficient can be calculated and the calculation is carried out for each component  $i$  in each phase  $j$ . The equilibrium ratios ( $K$  values) are initiated in the following way

$$K_{ij} = \frac{1}{\phi_{ij}} \quad (i=1, \dots, N_c; j=1, \dots, N_p) \quad (2.24)$$

The equilibrium ratio is the mole fraction of component  $i$  in phase  $j$  over the mole fraction of the same component in a reference phase.

### 2.5.3 Phase Distribution Calculation

This section is the most important and most difficult part in the multiphase flash calculation. The purpose of phase distribution calculation is to determine the amount and the composition of each phase at the given temperature and pressure conditions. The algorithm used is a successive substitution procedure which, assuming composition independent fugacity coefficient (or  $K$  values), alternates between calculation of fugacity coefficient and reevaluation of phase amount and composition.

Since the program is initiated with the maximum number of phases, which, in most cases, is much more than the actual number of phases present, a subroutine is called to check if any of the phases is a duplicate of another. Two phases will be combined if their  $K$  values are within 0.5% of each other; however, phases with different  $K$  values will be carried through the calculations even if their amount is zero.

The phase distribution calculation can be formulated as a minimization problem and the objective function is defined as (Michelsen, 1994)

$$Q(\beta) = \sum_{j=1}^{N_p} \beta_j - \sum_{i=1}^{N_c} z_i \ln E_i \quad (2.25)$$

with

$$E_i = \sum_{j=1}^{N_p} K_{ij} \beta_j \quad (2.26)$$

where  $Q$  is the objective function and  $\beta_j$  is the amount (mole fraction) of phase  $j$ . It has been demonstrated (Michelsen, 1994) that the objective function  $Q$  is a strictly convex function defined on the convex set  $\beta$  as long as the number of phases is no more than the number of components, furthermore, a strictly convex function has a unique minimum (Fletcher, 1981).

At the solution, the phase amounts are given by the vector  $\beta$  which minimizes  $Q$  with the condition of  $\beta_j \geq 0$  and the mole fractions are given by,

$$x_{ij} = K_{ij} z_i / E_i \quad (2.27)$$

The problem can be reduced to the solution of the following equations (Heidemann et al., 1997)

$$\partial Q / \partial \beta_j = h_j = 1 - \sum_{i=1}^{N_c} x_{ij} \quad \begin{cases} = 0, \beta_j > 0 \\ > 0, \beta_j = 0 \end{cases} \quad (2.28)$$

or

$$h_j = 1 - \sum_{i=1}^{N_c} \frac{K_{ij} z_i}{E_i} \quad \begin{cases} = 0, \beta_j > 0 \\ > 0, \beta_j = 0 \end{cases} \quad (2.29)$$

The Newton-Raphson method is used to solve the equations with the following iteration procedure

$$\beta^{(k+1)} = \beta^{(k)} - \lambda A^{-1} h^{(k)} \quad (2.30)$$

where superscript  $k$  is the iteration index.  $A$  is the Jacobian matrix and its elements are given by

$$a_{ij} = \partial h_i / \partial \beta_j = \sum_{k=1}^{N_c} x_{ki} x_{kj} / z_k \quad (2.31)$$

Where  $\lambda$  is the acceleration factor used to adjust the change in  $\beta$  between Newton-Raphson iterations.

One feature of this program is the selection of a reference phase. A reference phase is often needed in  $K$  value based phase equilibrium calculations and a liquid phase is often chosen as the reference phase. If the designated reference phase disappears, the calculation cannot continue because  $K$  values approach infinity. In this program, the  $K$  values are defined as

$$K_{ij} = \frac{x_{ij}}{\hat{x}_i} \quad (2.32)$$

where  $\hat{x}_i$  is the composition of an arbitrary reference phase (e.g., the overall composition). Due to cancellation, the reference phase does not appear in the equations used for the final phase distribution calculation. The reference phase is an intermediate used for convenience. Since it will always exist in the calculation scheme, a zero divisor is avoided in Equation 2.32. Hence, any of the phases can vanish without disrupting the calculation.

#### 2.5.4 Update K Values

The phase distribution calculation is the solution of material balance equations at fixed  $K$  values. In order to achieve equilibrium (equality of fugacity),  $K$  values are updated until a convergence criterion is met. The following successive substitution procedure is used for updating  $K$  values,

$$\ln K_{ij}^{(k+1)} = \ln K_{ij}^{(k)} - g_{ij}^{(k)} \quad (2.33)$$

with

$$g_{ij}^{(k)} = \ln f_{ij}^{(k)} - \ln \hat{f}_i^{(k)} - \Theta_j^{(k)} \quad (2.34)$$

where  $\Theta_j = -\ln \sum_i x_{ij}$  and  $\hat{f}_i$  is the reference fugacity defined as

$$\ln \hat{f}_i = \frac{\sum_{j=1}^{N_p} \beta_j \ln f_{ij}}{\sum_{j=1}^{N_p} \beta_j} \quad (2.35)$$

The reference fugacity is a weighted average of the fugacity of each phase. One reason for defining such a reference fugacity for updating  $K$  values is that at equilibrium, a component has the same fugacity in all phases and this fugacity is equal to the average. The calculation is terminated when the following convergence criterion is satisfied

$$\sum_{j=1}^{N_p} \sum_{i=1}^{N_c} \frac{g_{ij}^2}{N_p N_c} < 10^{-11} \quad (2.36)$$

## 2.6 Sonic Speed Calculation

Once the number of phases and the composition of each phase are determined from the multiphase flash calculation, the sonic speed of each phase can be readily calculated. There exists a simple thermodynamic relationship between sonic speed and other properties

$$c = \sqrt{\frac{1}{\rho \kappa_s}} \quad (2.37)$$

where  $c$  is sonic speed,  $\rho$  is density,  $\kappa_s$  is adiabatic compressibility. Theoretically, Equation 2.37 applies to solids, liquids and gases as well as their mixtures (McWilliam, et al., 1969; Douglas et al., 1995). However, only the sonic speed in a single phase fluid (liquid or gas) will be calculated in this work since the parameters involved in the sonic speed calculation are not clearly defined for multiphase mixtures.

Two equivalent forms of Equation 2.37 are (Ye et al., 1992a)

$$c = \sqrt{\frac{\gamma}{\rho \kappa_T}} \quad (2.38)$$

and

$$c = \sqrt{\frac{1}{\rho(\kappa_T - \alpha_p^2 v T / C_p)}} \quad (2.39)$$

where  $\gamma (= C_p/C_v)$  is the ratio of isobaric heat capacity ( $C_p$ ) to isochoric heat capacity ( $C_v$ ).  $\kappa_T$  and  $\alpha_p$  are isothermal compressibility and thermal expansivity respectively.  $\kappa_T$  and  $\alpha_p$  are defined as

$$\kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = -\frac{1}{v(\partial P / \partial v)_T} \quad (2.40)$$

$$\alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P = -\frac{1}{v} \frac{(\partial P / \partial T)_v}{(\partial P / \partial v)_T} \quad (2.41)$$

Sonic speed can be calculated in two different ways: from the PR EOS or from measured PV data. The former is discussed in this section and the later will be discussed in Chapter 4 along with the experimental data. The sonic speed calculation from the PR EOS is based on Equation 2.39. To ensure the consistency of the calculation, all the parameters in Equation 2.39 will be obtained from the PR EOS. The procedures are as follows:

- (1) Run the flash calculation at a given temperature ( $T$ ) and pressure ( $P$ ).
- (2) Calculate density ( $\rho$ ) and molar volume ( $v$ ) from the flash calculation.
- (3) Calculate  $\kappa_T$  and  $\alpha_p$  from their definitions (Equations 2.40 and 2.41).

First obtain the partial derivatives from the PR EOS, then calculate  $\kappa_T$  and  $\alpha_p$  from the results of the flash calculation.

- (4)  $C_p$  can be calculated from the following relation:

$$C_p - C_p^\circ = T \int_{\infty}^v \left( \frac{\partial^2 P}{\partial T^2} \right)_v dv - T \frac{(\partial P / \partial T)_v^2}{(\partial P / \partial v)_T} - R \quad (2.42)$$

where  $C_p^\circ$  is the ideal gas heat capacity which can be calculated from the following correlation (Aly et al., 1981):

$$C_p^\circ = C_1 + C_2 \left[ \frac{C_3 / T}{\sinh(C_3 / T)} \right]^2 + C_4 \left[ \frac{C_5 / T}{\cosh(C_5 / T)} \right]^2 \quad (2.43)$$

where  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ , and  $C_5$  are constants known for each pure component. A different correlation (Kesler et al., 1976) is used for pseudocomponents:

$$C_p^0 = -0.32646 + 0.02678K_w - (1.3892 - 1.2122K_w + 0.03803K_w^2) \times 10^{-4}T - 1.5393 \times 10^{-7}T^2 - F[0.084773 - 0.080809SG - (2.1773 - 2.0826SG) \times 10^{-4}T + (0.78649 - 0.70423SG) \times 10^{-7}T^2] \quad (2.44)$$

with

$$F = [(12.8 / K_w - 1)(10 / K_w - 1)100]^2 \quad (2.45)$$

where  $K_w$  is the Watson characterization factor and  $SG$  is specific gravity.  $C_p^0$  is in Btu/lb.°F and  $T$  is in °R.  $K_w$  is defined as

$$K_w = T_b^{1/3} / SG \quad (2.46)$$

where  $T_b$  is true boiling point.

The  $C_p^0$  calculated from Equations 2.43 and 2.44 is the property of a pure component. For a mixture, it is given by

$$C_p^0 = \sum_{i=1}^{N_c} x_i C_{pi}^0 \quad (2.47)$$

In summary, the calculation of  $C_p$  can be performed by: (a) obtaining the partial derivatives and the integral from the PR EOS; (b) calculating  $C_p^0$  from the correlations (Equations 2.43-2.44); and (c) calculating  $C_p$  from the results of flash calculations and Equation 2.42.

(5) Calculate the sonic speed from Equation 2.39.

## 2.7 Characterization of Hydrocarbon Heavy Fractions

The EOS method described in Sections 2.2-2.6 can be applied to any system for which the composition and component properties are known. However, reservoir fluids consist of a limited number of pure well defined components (e.g. CO<sub>2</sub> and CH<sub>4</sub>) and numerous heavy fractions which are not clearly defined. These heavy fractions have a significant effect on phase behavior predictions. Unfortunately, they are often reported as a single plus fraction with very limited information (such as mole fraction, molecular weight and

specific gravity) which is not adequate for EOS based phase behavior calculations. A technique based on gamma distribution is described to properly characterize the heavy fractions.

For convenience, the plus fraction is given a symbol of  $C_n^+$ , which contains all the fractions with a carbon number equal to or great than  $n$ . The characterization of  $C_n^+$  involves three parts: (1) split  $C_n^+$  into single carbon number (SCN) groups with mole fractions, molecular weights, and specific gravities which match measured  $C_n^+$  properties, (2) calculate the properties of the SCN groups, and (3) regroup the SCN groups into a reasonable number of pseudocomponents.

### 2.7.1 Molar Distribution Model

Whitson (1983) indicated that the continuous molar distribution of the  $C_n^+$  fraction (usually  $C_7^+$ ) can be represented by the three-parameter gamma function

$$p(M) = \frac{(M - \eta)^{\alpha-1} \exp[-(M - \eta) / \beta]}{\beta^\alpha \Gamma(\alpha)} \quad (2.48)$$

where  $p(M)$  is the probability density function,  $M$  is the molecular weight used as the independent variable, and  $\alpha$ ,  $\beta$ , and  $\eta$  are distribution parameters.

The above distribution will be completely set once the three parameters are determined.  $\alpha$  defines the shape of the distribution. It can be estimated from a full or partial compositional analysis or from an empirical relation and is usually in the range of 0.5-3.0.  $\eta$  is the minimum molecular weight to be included in the  $C_n^+$  fraction and can be calculated from

$$\eta = 14n - 6 \quad (2.49)$$

where  $n$  is the minimum carbon number expected to occur in the  $C_n^+$  fraction. After  $\alpha$  and  $\eta$  are determined,  $\beta$  is calculated from the following equation

$$\beta = (M_n^+ - \eta) / \alpha \quad (2.50)$$

where  $M_n^+$  is the molecular weight of the  $C_n^+$  fraction and is measured directly.

The cumulative density function,  $P(M \leq M_0)$ , is the integral of  $p(x)$  from  $\eta$  to  $M_0$ ,

$$P(M \leq M_0) = \int_{\eta}^{M_0} p(M) dM \quad (2.51)$$

This integral represents the frequency of occurrence (normalized mole fraction) in the interval of  $\eta$  to  $M_0$  and can be expressed analytically as

$$P(M \leq M_0) = \frac{e^{-y} y^{\alpha}}{\Gamma(\alpha)} \sum_{j=0}^{\infty} \frac{y^j}{(\alpha + j)!} \quad (2.52)$$

with  $y = (M_0 - \eta)/\beta$ .

For the components having molecular weight between  $M_{i-1}$  and  $M_i$ , the cumulative frequency of occurrence,  $f_i$ , is calculated from

$$f_i = \int_{M_{i-1}}^{M_i} p(M) dM = P(M \leq M_i) - P(M \leq M_{i-1}) \quad (2.53)$$

The mole fraction is given by

$$z_i = f_i z_n^+ \quad (2.54)$$

where  $z_i$  is the mole fraction of the components having molecular weight between  $M_{i-1}$  and  $M_i$ , and  $z_n^+$  is the mole fraction of the  $C_n^+$  fraction. The average molecular weight in the same interval is given by

$$M_{avg} = \eta + \alpha\beta \frac{P(M \leq M_i, \alpha + 1) - P(M \leq M_{i-1}, \alpha + 1)}{P(M \leq M_i, \alpha) - P(M \leq M_{i-1}, \alpha)} \quad (2.55)$$

where  $M_{avg}$  is the average molecular weight for the components in the range of  $M_{i-1}$  and  $M_i$ .

The mole fraction and the molecular weight of each SCN group can be calculated from the molar distribution model. The input data includes  $\alpha$ ,  $\beta$ ,  $\eta$ , which have been discussed above, and  $z_n^+$  and  $M_n^+$  which come from the compositional measurement. The lower bound of the molecular weight distribution and the magnitude of the increment in SCN groups are required. The upper bound of the molecular weight distribution then depends on the number of the increments. For example, starting from  $C_7$  and using 50 SCN groups and a constant molecular weight interval of 14, an upper bound of 792 in the molecular weight distribution is determined.

## 2.7.2 Physical Property Calculation

The physical properties of each component are required in phase behavior calculations and the minimum requirement for each component includes its critical pressure, critical temperature, and acentric factor. The properties of pure components are given in handbooks (Reid et al., 1987) and those of heavy fractions can be calculated from the many correlations available in the literature. Most of the correlations use specific gravity ( $SG$ ) and true boiling point ( $T_b$ ) as input parameters. Therefore, these two properties need to be calculated first and the other properties are then computed from the correlations.

### 2.7.2.1 Calculation of $SG$ and $T_b$

The  $SG$  of each SCN group is calculated from the following relation (Riazi et al., 1980)

$$K_w = 4.5579 M^{0.15178} SG^{-0.84573} \quad (2.56)$$

In Equation 2.56,  $M$  is obtained from the molar distribution.  $K_w$  is assumed constant for all SCN groups and can be estimated from Equation 2.56 where  $M$  and  $SG$  are replaced by the measured molecular weight and specific gravity of the  $C_n^+$  fraction,  $M_n^+$  and  $(SG)_n^+$ , respectively. The average  $SG$  for all SCN groups is calculated by

$$(SG)_{avg} = \frac{\sum_{i=n}^N x_i M_i}{\sum_{i=n}^N x_i M_i / SG_i} \quad (2.57)$$

where  $n$  and  $N$  are the first and the last SCN in the  $C_n^+$  fraction, respectively. The calculated  $(SG)_{avg}$  is compared with the measured  $(SG)_n^+$ . If they do not match,  $K_w$  should be adjusted until a match is obtained.

Given the  $K_w$  and  $SG$  of each SCN group, the  $T_b$  is calculated from

$$T_b = (SG \times K_w)^3 \quad (2.58)$$

### 2.7.2.2 Property Correlations

Numerous correlations are available for estimating the physical properties of petroleum fractions, such as those proposed by Kesler et al. (1976), Riazi et al. (1980,1987), Lin et

al. (1984), Twu (1984), and Watansiri et al. (1985). Voulgaris et al. (1991) compared the performance of over 25 different methods in calculating critical temperature, critical pressure and acentric factor for non-polar compounds, petroleum and coal liquid fractions. They concluded that for petroleum fractions, Twu, Riazi-Daubert and Kesler-Lee correlations gave the most accurate predictions. The use of Kesler-Lee and Twu correlations has also been recommended by Whitson (1983) and James (1987). Therefore, Kesler-Lee and Twu correlations are used in this work to calculate the physical properties of the  $C_n^+$  fraction. These properties include critical pressure ( $P_c$ ), critical temperature ( $T_c$ ), critical volume ( $V_c$ ), acentric factor ( $\omega$ ), and molecular weight ( $M$ ).

#### (1) Kesler-Lee Correlations

In their attempt to improve the accuracy of enthalpy predictions, Kesler and Lee (1976) proposed a set of correlations to calculate  $P_c$ ,  $T_c$ ,  $\omega$  and  $M$  of petroleum fractions. The equations are as follows:

Critical pressure:

$$\begin{aligned} \ln(P_c) = & 8.3634 - 0.0566 / SG \\ & - (0.24244 + 2.2898 / SG + 0.11857 / SG^2) 10^{-3} T_b \\ & + (1.4685 + 3.648 / SG + 0.47227 / SG^2) 10^{-7} T_b^2 \\ & - (0.42019 + 1.6977 / SG^2) 10^{-10} T_b^3 \end{aligned} \quad (2.59)$$

Critical temperature:

$$\begin{aligned} T_c = & 341.7 + 81.1SG + (0.4244 + 0.1174SG)T_b \\ & + (0.4669 - 3.2623SG) 10^5 / T_b \end{aligned} \quad (2.60)$$

Molecular weight:

$$\begin{aligned} M = & -12272.6 + 9486.4SG + (4.6523 - 3.3287SG)T_b \\ & + (1 - 0.77084SG - 0.02058SG^2)(1.3437 - 720.79 / T_b) 10^7 / T_b \\ & + (1 - 0.80882SG + 0.02226SG^2)(1.8828 - 181.98 / T_b) 10^{12} / T_b^3 \end{aligned} \quad (2.61)$$

Acentric factor:

For  $\theta = T_b / T_c > 0.8$ ,

$$\omega = -7.904 + 0.1352K_w - 0.007465K_w^2 + 8.359\theta + (1.408 - 0.01063K_w) / \theta \quad (2.62)$$

For  $\theta < 0.8$ ,

$$\omega = \frac{-\ln(P_c / 14.696) - 5.92714 + 6.09648 / \theta + 1.28862 \ln(\theta) - 0.169347\theta^6}{15.2518 - 15.6875 / \theta - 13.4721 \ln(\theta) + 0.43577\theta^6} \quad (2.63)$$

Where  $T_c$  and  $T_b$  are in °R and  $P_c$  is in psia.  $K_w$  is the Watson factor as defined in Equation 2.46.

## (2) Twu Correlations

In the work of Twu (1984), the properties of the reference system (n-alkanes) were first correlated with the normal boiling point ( $T_b$ ). The properties of a real system were then obtained from those of the reference system through the perturbation expansion.

The correlations for the reference system are:

Critical pressure:

$$P_c^0 = (3.83354 + 1.19629\alpha^{1/2} + 34.8888\alpha + 36.1952\alpha^2 + 104.193\alpha^4)^2 \quad (2.64)$$

Critical temperature:

$$T_c^0 = T_b (0.533272 + 0.191017 \times 10^{-3} T_b + 0.779681 \times 10^{-7} T_b^2 - 0.284376 \times 10^{-10} T_b^3 + 0.959468 \times 10^{28} / T_b^{13})^{-1} \quad (2.65)$$

Critical volume:

$$V_c^0 = [1 - (0.419869 - 0.505839\alpha - 1.56436\alpha^3 - 9481.70\alpha^{14})]^{-8} \quad (2.66)$$

Specific gravity:

$$SG^0 = 0.843593 - 0.128624\alpha - 3.36159\alpha^3 - 13749.5\alpha^{12} \quad (2.67)$$

Molecular weight is solved from:

$$T_b = \exp(5.71419 + 2.71579\psi - 0.286590\psi^2 - 39.8544 / \psi - 0.122488 / \psi^2) - 24.7522\psi + 35.3155\psi^2 \quad (2.68)$$

where

$$\alpha = 1 - T_b / T_c^0 \quad (2.69)$$

$$\psi = \ln M^0 \quad (2.70)$$

The correlations for a real system are:

Critical temperature:

$$T_c = T_c^0 [(1 + 2f_T) / (1 - 2f_T)]^2 \quad (2.71)$$

$$f_T = \Delta SG_T [-0.362456 / T_b^{1/2} + (0.0398285 - 0.948125 / T_b^{1/2}) \Delta SG_T] \quad (2.72)$$

$$\Delta SG_T = \exp[5(SG^0 - SG)] - 1 \quad (2.73)$$

Critical volume:

$$V_c = V_c^0 [(1 + 2f_V) / (1 - 2f_V)]^2 \quad (2.74)$$

$$f_V = \Delta SG_V [0.466590 / T_b^{1/2} + (-0.182421 + 3.01721 / T_b^{1/2}) \Delta SG_V] \quad (2.75)$$

$$\Delta SG_V = \exp\{4[(SG^0)^2 - SG^2]\} - 1 \quad (2.76)$$

Critical pressure:

$$P_c = P_c^0 (T_c / T_c^0) (V_c^0 / V_c) [(1 + 2f_P) / (1 - 2f_P)]^2 \quad (2.77)$$

$$f_P = \Delta SG_P [(2.53262 - 46.1955 / T_b^{1/2} - 0.00127885 T_b) \\ + (-11.4277 + 252.140 / T_b^{1/2} + 0.00230535 T_b) \Delta SG_P] \quad (2.78)$$

$$\Delta SG_P = \exp[0.5(SG^0 - SG)] - 1 \quad (2.79)$$

Molecular weight:

$$\ln M = \ln M^0 [(1 + 2f_M) / (1 - 2f_M)]^2 \quad (2.80)$$

$$f_M = \Delta SG_M [|x| + (-0.0175691 + 0.193168 / T_b^{1/2}) \Delta SG_M] \quad (2.81)$$

$$|x| = |0.0123420 - 0.328086 / T_b^{1/2}| \quad (2.82)$$

$$\Delta SG_M = \exp[5(SG^0 - SG)] - 1 \quad (2.83)$$

In Equations 2.64-2.83,  $T_c$  and  $T_b$  are in °R,  $P_c$  is in psia, and  $V_c$  is in ft<sup>3</sup>lb<sup>-1</sup>mol<sup>-1</sup>.

## 2.7.3 Regrouping

### 2.7.3.1 Number of Pseudocomponents

The plus fraction was split into about 50 SCN groups with the molar distribution model. This, together with the components lighter than  $C_n^+$ , amounts to about 60 components in the mixture. Due to computational limitations, the total number of components used in EOS based phase behavior calculations seldom exceeds 10-15 (Young, 1987), where only a few of these components represent the  $C_n^+$  fraction. Therefore, an algorithm is necessary to lump these components into fewer groups.

Pedersen et al. (1983) proposed grouping individual fractions together so that each pseudocomponent had an equal weight fraction of the fluid. In the work of Lee et al. (1981), the available properties of each fraction were first plotted as a function of the boiling point. Then the fractions with similar slopes were grouped together. Lee's method is not practical since the boiling point data is usually unavailable. Li et al. (1984) proposed a lumping scheme in which the fractions whose K values fell within a certain range were grouped together. The lumping scheme proposed by Whitson (1983) is used in this work since, compared with other methods, it is easy to implement and has great flexibility.

According to Whitson (1983), the number of pseudocomponents in the  $C_n^+$  fraction is estimated by

$$N_{pc} = \text{Int}[1 + 3.3 \log(N - n)] \quad (2.84)$$

where  $N_{pc}$  is the number of pseudocomponents;  $n$  and  $N$  are the first and the last SCN in the  $C_n^+$  fraction, respectively. For example, assigning  $n$  and  $N$  a value of 7 and 50 respectively gives  $N_{pc}$  a value of 6. The molecular weight boundaries for each pseudocomponent are given by

$$M_i = M_n \left\{ \exp \left[ (i / N_{pc}) \times \ln(M_N / M_n) \right] \right\}^i \quad (2.85)$$

where  $M_n$  and  $M_N$  are the molecular weight of the first and the last SCN group in the  $C_n^+$  fraction respectively. The SCN groups whose molecular weights fall within two neighboring  $M_i$ 's are lumped into the same pseudocomponent.

### 2.7.3.2 Mixing Rules

Mixing rules are necessary to express the parameters of a pseudocomponent in terms of the parameters of its components. The mixing rules recommended by Lee et al. (1975) are used in this work:

$$\omega = \sum_i x_i \omega_i \quad (2.86)$$

$$V_c = \frac{1}{8} \sum_i \sum_j x_i x_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (2.87)$$

$$T_c = \frac{1}{8V_c} \sum_i \sum_j x_i x_j (V_{ci}^{1/3} + V_{cj}^{1/3})^3 (T_{ci} T_{cj})^{1/2} \quad (2.88)$$

$$Z_c = 0.2905 - 0.085\omega \quad (2.89)$$

$$P_c = Z_c R T_c / V_c \quad (2.90)$$

where  $Z_c$  is the critical compressibility factor.

The flash calculation program developed in this work has been tested using standard mixtures. The results of this program agree well with those obtained from WinProp of CMG. The results of sonic speed calculations will be discussed in Chapter 4. The source code for all programs is given in the attached diskette.

### **CHAPTER THREE: EXPERIMENTAL METHOD**

The acoustic resonance apparatus is owned and operated by Hycal Energy Research Laboratories Ltd. on a commercial basis. Therefore, some details of the apparatus such as the acoustic source and signal processing techniques are confidential and are not reported here. Furthermore, the oils available for testing were largely limited to samples submitted by Hycal clients. While these samples were known to exhibit liquid-vapor and liquid-solid phase transitions, it was not possible to verify the liquid-solid transition with other techniques.

The AR technology is based on the detection of resonance frequencies as an acoustic signal is transmitted through the fluid confined in a cylindrical resonator. The resonance frequency changes with the physical properties of the fluid and a distinct change in resonance frequency is expected during a phase transition.

#### **3.1 Experimental Setup**

Figure 3.1 is a schematic illustration of the AR system. The AR apparatus is essentially a modified PVT cell. It consists of a cylindrical resonator, an air bath, pressure, volume and temperature multimeters, an acoustic control system, and a PVT control system.

##### **3.1.1 Acoustic Resonator**

The key component of the system is a cylindrical resonator of 0.65 cm in diameter (Figure 3.2). The resonator is made of Hastelloy material to resist corrosion from reservoir fluids. The resonator assembly is housed in a well insulated air bath. Two pistons with hollow center are installed in the resonator: one at the top and the other at the bottom. The bottom piston is stationary and the movement of the top piston changes the volume and pressure of the cavity. Each piston is provided with a piezoelectric transducer at one end and a diaphragm at the other end. The top transducer vibrates in response to an applied voltage and this vibration is transmitted to the top diaphragm through a vibration pin located at the center of the top piston. The acoustic stimulation is

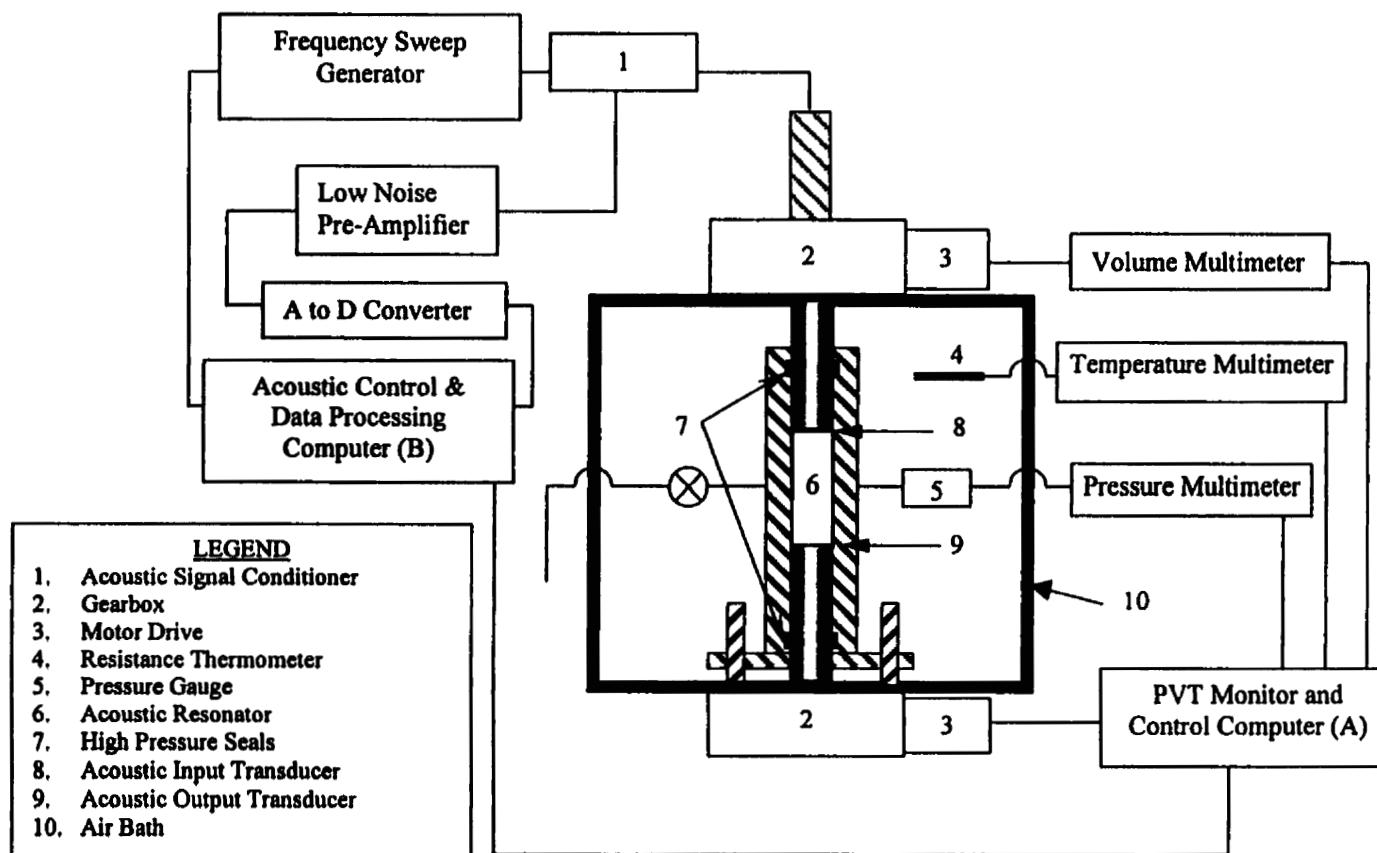


Figure 3.1: High pressure cylindrical acoustic resonator system

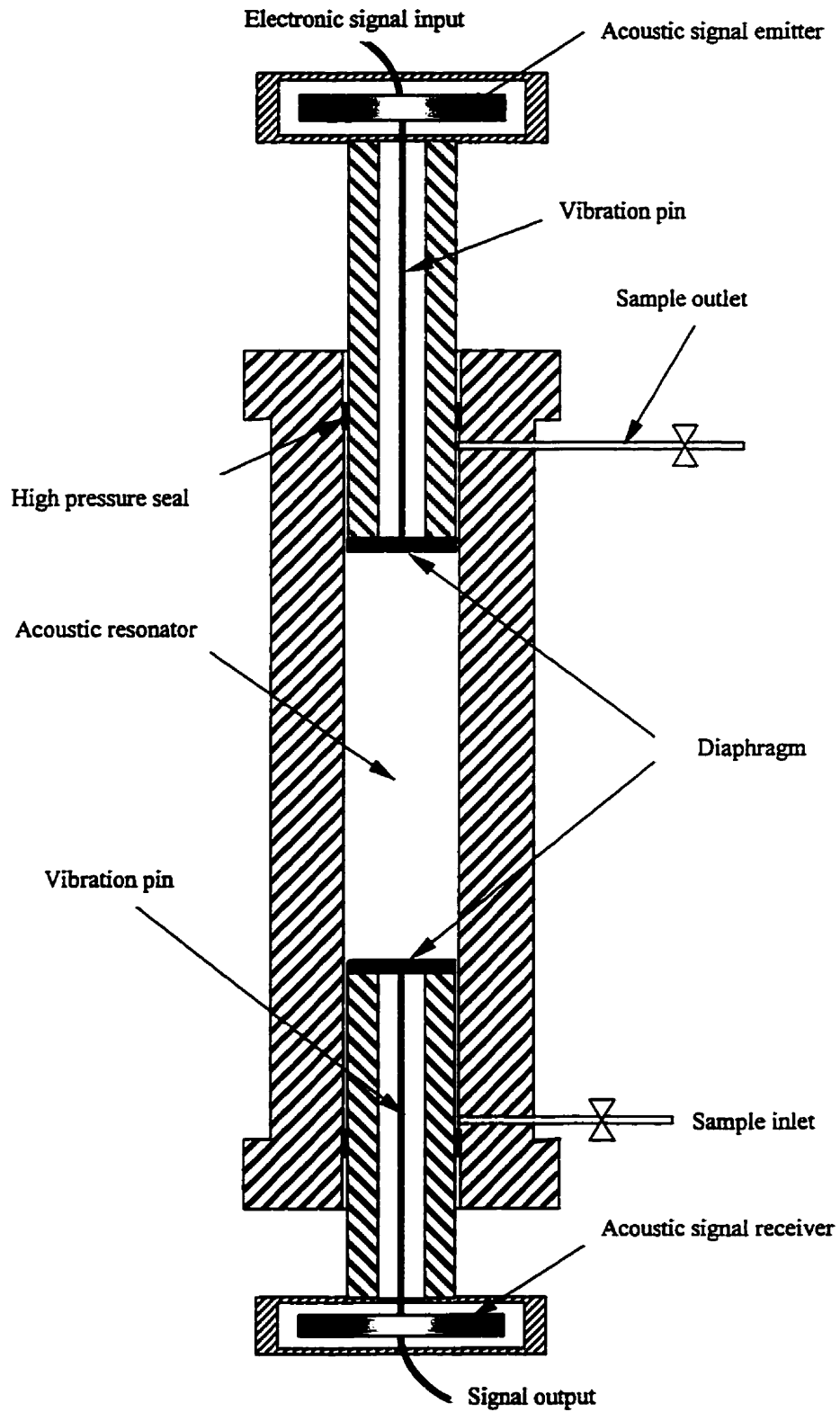


Figure 3.2: Structure of the acoustic resonator

subsequently applied to the test fluid. The bottom diaphragm receives the response from the stimulated oscillations in the fluid and in turn, these vibrations are transmitted to the bottom transducer through a vibration pin located at the center of the bottom piston. At certain applied stimulation frequencies, resonances will be established in the fluid. The patterns of these resonances depend on the geometry of the cavity and the properties of the fluid. Since the resonator is vertically oriented, the resonance patterns depend on the distribution of any multiple phases present. Therefore, the phase transition can be inferred by measuring the change of resonance frequencies as a function of pressure or temperature conditions.

### **3.1.2 System Control**

Two computers are used in the system. Computer A (control computer) is a PVT monitor which controls all the system functions except acoustic control and data acquisition. Computer B (acquisition computer) is used for the acoustic control and data acquisition.

The piston movement in the resonator is controlled by a worm gear assembly and a Stepper motor. The volume is measured by a Linear Velocity Displacement Transducer (LVDT) and the pressure measured by a high precision strain gauge transducer. The temperature is measured by a calibrated platinum resistance thermometer and controlled by a well insulated air bath. Liquid nitrogen is available for cryogenic measurements. The values of pressure, volume and temperature are read by precision Keithley multimeters interfaced to the control computer. The control program uses a Proportional Integral Differential (PID) type algorithm. The custom software allows the operator to see immediately the results of any tuning change for each control variable (pressure, volume and temperature) in real time through a graphical interface. Therefore, one can control the setup and operation of pressure, volume and temperature very precisely through the control computer.

Computer B controls the acoustic excitation of the resonator and acquires acoustic response data. The signal necessary to excite the transmitter is supplied by an interfaced function generator. The acoustic signal is processed through a low noise pre-amplifier

and then through a fast high precision analog to digital converter (ADC). A low pass filter and a high pass filter are used to screen out the frequencies below 10,000 Hz and above 35,000 Hz respectively. The sampling rate used in the measurement is 100,000 Hz. The acoustic data acquired by ADC is synchronized by a trigger signal generated by the function generator. This computer is interfaced to the control computer in a network configuration and it displays pressure, volume, temperature, and the acoustic spectrum (frequency domain) in real time through a graphic interface. The raw time domain data is stored along with pressure, volume and temperature data gathered during acoustic data acquisition.

### 3.1.3 Working Conditions

The AR system can be operated in a wide range of conditions which are summarized in Table 3.1.

Table 3.1 Working conditions for the AR system

| Working Conditions                  | Range                                     |
|-------------------------------------|-------------------------------------------|
| Pressure, MPa                       | 0.1~69                                    |
| Temperature, °C                     | -40~150                                   |
| Sample volume, cm <sup>3</sup>      | 0~5                                       |
| Acoustic signal (Frequency), Hz     | 0~50,000                                  |
| Sampling rate (Acoustic signal), Hz | 100,000                                   |
| Frequency resolution, Hz            | 1.5 Hz at 50,000 Hz full scale excitation |
| Amplitude resolution, Bit           | 16                                        |
| Pressure transducer accuracy        | ±0.05% full scale                         |
| Volume measurement accuracy         | ±0.01% total volume                       |
| Temperature accuracy                | ±0.01°C                                   |

### 3.1.4 Operating Modes

The system can be operated in the following three different modes:

**(1) Isothermal mode**

Maintain a constant temperature and vary the volume and record the acoustic spectrum with varying pressures and volumes. This mode is often used for the detection of bubble point, dew point, and the onset of asphaltene precipitation.

**(2) Isobaric mode**

Maintain a constant pressure and vary the temperature and record the acoustic spectrum with varying temperatures and volumes. This mode is often used for the detection of the onset of wax precipitation.

**(3) Isochoric mode**

Maintain a constant volume and vary the temperature and record the acoustic spectrum with varying temperatures and pressures. This mode is used for isochore measurements.

All the experiments reported in this thesis were performed in isothermal or isobaric mode.

### **3.2 Experimental Procedure**

- a. The system is assembled as required.
- b. The resonator and all the lines are cleaned with toluene.
- c. The system is pressure tested.

The pressure test is conducted at a pressure higher than the expected operating pressure and there should be no leak before going to the next step.

- d. The system is initiated.

The volume of the resonator cavity is set to the required value and this is achieved by moving the piston upward or downward.

- e. The system is evacuated with a vacuum pump.

- f. The temperature of the oven is set and raised to the required value and is stabilized for 2 hours.
- g. Sample (test fluid) is transferred to the system from a sample-containing cylinder.
- h. The resonator is isolated by closing the valves at its top and bottom end.
- i. The system is stabilized for 4 hours.
- j. Typically, the initial pressure is well above bubble point and the sample is a single phase liquid. If any small amount of gas is undissolved, it is purged from the top of the apparatus.
- k. Set up the control parameters (pressure, volume, temperature, sampling rate) and then start the measurement. The system will stop itself when the preset end conditions are satisfied.

The operation of the AR system is highly automated and can be finished in a single step (k). The steps from a-j are preparations for the measurement. Proper step sizes in pressure, volume and temperature should be used in the measurement to secure the smoothness of the data and the thermodynamic equilibrium of the process. For an isothermal depressurization process, the initial rate of pressure reduction of 40 psi/min is found to be appropriate. The rate of depressurization decreases with time and reaches about 5 psi/min towards the end of the experiment. For an isobaric cooling process, a cooling rate of 0.1°C/min is often used.

### **3.3 Data Acquisition**

The data collected from the AR measurements include pressure, volume, temperature, and time domain acoustic data. The time domain data are processed with fast Fourier transforms to obtain frequency domain data (frequency spectrum). The frequency domain data is then tracked with the pressure or temperature and phase transitions are detected from the results of the analysis. The interpretation of the AR measurements will be discussed in details in Chapter 4.

### 3.4 Materials

Eight fluid mixtures are considered in this work and their properties are listed in Tables 3.2 and 3.3. Mixture A is a binary mixture and the remainder are live oils. The known information for each mixture (except E) includes the composition and the saturation pressure (bubble point pressure). The saturation pressure was found by Hycal with a visual technique in a conventional PVT cell. Mixture E was obtained by mixing 60% (by volume) of mixture D and 40% of toluene. Mixture B is taken from Ye et al. (1991) and is only used for sonic speed comparison. Asphaltene precipitation has been experienced in the reservoirs where Mixtures C and D were taken. No solids precipitation has been reported for other mixtures. AR measurements were conducted for all of these mixtures except Mixture B. These mixtures were tested for liquid-vapor and/or liquid-solid transitions.

Table 3.2: Properties of test mixtures

| Component                      | Composition                 |             |              |                               |
|--------------------------------|-----------------------------|-------------|--------------|-------------------------------|
|                                | A                           | B           | C            | D                             |
| N <sub>2</sub>                 | 0.679                       | 0.00225     | 0.00117      | 0.00480                       |
| CO <sub>2</sub>                |                             | 0.00777     | 0.00675      | 0.00920                       |
| H <sub>2</sub> S               |                             | 0.00000     | 0.01728      | 0.00000                       |
| C1                             |                             | 0.42524     | 0.33705      | 0.43390                       |
| C2                             |                             | 0.08238     | 0.06652      | 0.11010                       |
| C3                             |                             | 0.06062     | 0.08503      | 0.06540                       |
| i-C4                           |                             | 0.01431     | 0.02157      | 0.00790                       |
| n-C4                           |                             | 0.03284     | 0.06344      | 0.03700                       |
| i-C5                           |                             | 0.01306     | 0.01181      | 0.01280                       |
| n-C5                           |                             | 0.01593     | 0.01668      | 0.02250                       |
| n-C16                          | 0.321                       |             |              |                               |
| C6+ Mol. weight, g/mol         |                             |             | 211.02       | 214.74                        |
| C6+ Mole fraction              |                             | 0.3456      | 0.3727       | 0.2964                        |
| C6+ Density, g/cm <sup>3</sup> |                             |             | 0.8521       | 0.8570                        |
| Reservoir temp., °C            |                             | 139         |              | 116                           |
| Reservoir pressure, MPa        |                             | 26.0        |              | 58.61                         |
| Saturation pressure, MPa       | 33.3 (67°C)<br>33.0 (100°C) | 25.5(139°C) | 13.13 (70°C) | 22.48 (99°C)<br>23.17 (110°C) |

Table 3.3: Properties of test mixtures

| Component                      | Composition    |                |                |
|--------------------------------|----------------|----------------|----------------|
|                                | F              | G              | H              |
| N <sub>2</sub>                 | 0.00170        | 0.00700        | 0.00530        |
| CO <sub>2</sub>                | 0.00520        | 0.00510        | 0.00400        |
| H <sub>2</sub> S               | 0.00000        | 0.00000        | 0.00000        |
| C1                             | 0.38950        | 0.36810        | 0.38220        |
| C2                             | 0.02410        | 0.02360        | 0.02430        |
| C3                             | 0.00310        | 0.00390        | 0.00430        |
| i-C4                           | 0.00150        | 0.00130        | 0.00240        |
| n-C4                           | 0.00140        | 0.00080        | 0.00210        |
| i-C5                           | 0.00150        | 0.00150        | 0.00220        |
| n-C5                           | 0.00090        | 0.00060        | 0.00100        |
| n-C16                          |                |                |                |
| C6+ Mol. weight, g/mol         | 300.26         | 299.76         | 296.36         |
| C6+ Mole fraction              | 0.5711         | 0.5881         | 0.5722         |
| C6+ Density, g/cm <sup>3</sup> | 0.8906         | 0.8907         | 0.8895         |
| Reservoir temperature, °C      | 62.5           | 62.8           | 60.3           |
| Reservoir pressure, MPa        | 19.12          | 19.18          | 18.66          |
| Saturation pressure, MPa       | 17.51 (62.5°C) | 17.82 (62.8°C) | 17.51 (60.3°C) |

## CHAPTER FOUR: AR MEASUREMENTS

The interpretation of AR measurements is discussed in this chapter. First, the nature of the AR signal is discussed. Second, an attempt is made to identify the correct resonance peak from the AR frequency spectrum, which consists of multiple peaks. The expected trend for the resonance peak is established from acoustic theory and experimental observations. Finally, measured peaks are compared with the expected trend and potential resonance peaks are identified for seven fluid mixtures. Note that all figures for Chapter 4 are provided at the end of the chapter.

Mixture A will be used to demonstrate the procedures used in the interpretation of AR measurements and then the same procedures will be followed for other mixtures.

### 4.1 Source of AR Signal

The frequency spectra for Mixture A at 48.95 and 33.38 MPa (67°C) are shown in Figures 4.1 and 4.2, respectively. Each frequency spectrum shows the change of amplitude with frequency at specified temperature and pressure conditions. There are 9 to 10 peaks in each spectrum and their frequencies are in the range from 12500 to 37500 Hz. These frequencies correspond to the energetic region of the acoustic source signal (Figure 4.3) as will be discussed in more detail in Chapter 5.

A number of different factors can contribute to the output signal in AR measurements: ambient noise, vibration from the chamber, and response from the fluid, etc. The response from the test fluid is what is of interest in this work; however, the contributions from other sources cannot all be ignored due to their omnipresence and magnitude. Comparing the spectra at different conditions (Figures 4.1, 4.2), the output signals are found to be quite stable in terms of the number, amplitude and location of the peaks on each spectrum. This is an indication of the non-randomness of the signal. The ambient noise level was determined by measuring the output signal with no input applied. It was found to be several orders of magnitude lower than the typical AR output. Hence, the

ambient noise does not appear to affect the AR measurement. The vibration of the chamber itself is expected to occur only at frequencies below the range of interest. In addition, the echo and reflection of the signal within the chamber can also have a share in the output. As will be discussed in Chapter 5, the output signal from AR measurements appears to be a combination of signals from these different sources. The fact that it is very difficult to quantify the contribution from each source makes the interpretation of AR measurements a real challenge.

## **4.2 Interpretation of AR Measurements**

### **4.2.1 Frequency Spectrum of AR Measurements**

Our purpose is to detect phase transitions by investigating the changes in resonance frequency as a function of pressure. There are nine distinguishable peaks in Figure 4.1 which are numbered from 1 to 9 with ascending frequencies. Since we do not know which peak(s) is the resonance modes, they are tracked one by one. The frequency of each peak is expressed as a function of pressure as shown in Figures 4.4-4.12. Slope changes are obvious in these plots and the pressures at which slope changes occur are indicated by arrows on the plots and are summarized in Table 4.1. There is one slope change in Peaks 1, 2, 5, 6, 7, and 9, two slope changes in Peaks 3 and 8, and three slope changes in Peak 4. These slope changes occur at very different pressures which are between 24 and 43 MPa.

The bubble point pressure of this mixture at 67°C is 33.3 MPa which is the pressure where liquid-vapor phase transition occurs. Therefore, a slope change in frequency is expected to appear at around this pressure. Among the 9 peaks tracked, there are 6 peaks (Peaks 1, 2, 3, 4, 7 and 8) which have a slope change close to this pressure. However, it is still not clear which peak(s) is the correct one. It may be possible to identify the correct peak if the resonance frequency can be predicted and then compared with the measured data.

Table 4.1: Change of slope in frequency for Mixture A

| Peak No. | Change of slope at pressure (MPa) |                 |                 |                 |                 |                 |
|----------|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|          | 67°C                              |                 |                 | 100°C           |                 |                 |
|          | 1 <sup>st</sup>                   | 2 <sup>nd</sup> | 3 <sup>rd</sup> | 1 <sup>st</sup> | 2 <sup>nd</sup> | 3 <sup>rd</sup> |
| 1        |                                   | 30±2            |                 | 25              | 36±1            |                 |
| 2        |                                   | 32±2            |                 |                 |                 | 43              |
| 3        | 25±1                              | 33±2            |                 |                 |                 | 39±1            |
| 4        | 27                                | 29±1            | 43              | 25              |                 |                 |
| 5        | 27                                |                 |                 |                 | 30±1            |                 |
| 6        |                                   |                 | 40±1            |                 | 34±1            |                 |
| 7        |                                   | 36±1            |                 |                 |                 |                 |
| 8        | 28                                | 29±1            |                 | 30±2            | 38              | 41              |
| 9        | 28                                |                 |                 |                 | 36              | 40              |
| 10       | -                                 | -               | -               | 28              | 35±1            | 41              |

#### 4.2.2 Prediction of Sonic Speed

Based on Equation 2.2, the resonance frequency can be calculated from the sonic speed and the length of the resonator. The length of the resonator can be easily obtained from the volume measurement and the known chamber diameter. The sonic speed can be calculated from an EOS as discussed in Chapter 2 or from PV data. We will demonstrate that the sonic speed predicted from EOS is fairly accurate and will be used to predict resonance frequencies.

Sonic speed data for pure hydrocarbons have been reported in the literature (Boelhouwer, 1967; Niepmann, 1984; Muringer, et al., 1985), however, sonic speed data in multicomponent reservoir fluids at elevated temperature and pressure conditions are scarce. Wang et al. (1988) reported the sonic speed measurement in 8 dead oils and 1 live oil and the sonic speed was correlated with temperature, pressure and oil properties (e.g. molecular weight and API gravity). They did not report the composition of their oils, so comparison with their data is not possible. Ye et al. (1991, 1992a, 1992b) reported the sonic speed data in 3 binary mixtures and 3 live oils and the detailed composition and the saturation pressure of these mixtures are also available.

For the purpose of comparison, AR measurements were conducted for Mixture A which is the same as one of Ye's binary mixtures (Ye et al., 1992b). The sonic speed of Mixture

A is calculated from both EOS and PV data and compared with the literature data. Mixture B is a live oil taken from Ye et al. (1991) and the sonic speed calculated from EOS is compared with the literature data.

#### 4.2.2.1 Sonic Speed Prediction from PV Relation

Ideally, the sonic speed can be calculated directly from the PV data using Equation 2.38. Three parameters are required for the calculation: density ( $\rho$ ), heat capacity ratio ( $\gamma$ ), and isothermal compressibility ( $\kappa_T$ ). One density measurement, conducted at the initial pressure of the experiment, is adequate since the densities for other pressures can be calculated from this point and the PV data using a material balance. The density can be calculated from an EOS if experimental data is not available. The  $\gamma$  values are usually not known. Wang et al. (1988) indicated that for light oils,  $\gamma$  can take values from 1.2 to 1.3 and can be assumed to be independent of temperature and pressure. The  $\gamma$  term can also be computed from an EOS, but from our experience, it is usually underestimated by EOS (for example,  $\gamma$  calculated from an EOS is always below 1.2 for the oils in this work).

The isothermal compressibility can be calculated from Equation 2.40 in which the slope of the PV relation is required. The PV relation is available from the AR measurement and Figure 4.13 shows the measured PV relation for Mixture A at 100°C. There are 3 steps in the compressibility calculation: (1) the volume is regressed against pressure and expressed as a polynomial function of pressure; (2) the derivative of the volume is calculated with respect to pressure; and (3) the isothermal compressibility is calculated from Equation 2.40. Once density, heat capacity ratio and compressibility are available, the sonic speed can be calculated from Equation 2.38.

Figure 4.14 shows the sonic speed calculated from the AR measured PV data at 100°C (assuming  $\gamma=1$ ) together with the literature data. The literature sonic speed decreases with pressure and there is an approximately linear relation between sonic speed and pressure. The sonic speeds from the PV data are obtained by assuming  $\gamma=1$  and should be corrected to the correct  $\gamma$  before they are compared with the literature data. The predicted

sonic speed does not follow the correct trend at pressures between 45 and 47 MPa and deviates, in both magnitude and slope, significantly from the literature data even after correcting  $\gamma$  to values as high as 1.3.

Table 4.2 shows the deviations of the calculated sonic speed (at three  $\gamma$  values) with respect to the literature data reported by Ye et al. (1992b). The absolute average deviation (AAD) is calculated with

$$AAD\% = \frac{100}{n} \sum_{i=1}^n \left| \frac{c_{lit} - c_{cal}}{c_{lit}} \right| \quad (4.1)$$

where  $n$  is the number of data points,  $c_{lit}$  and  $c_{cal}$  are the literature and calculated sonic speed, respectively. The sonic speeds calculated from the PV relation of the AR measurements at 100°C have large AAD with the smallest error at  $\gamma=1.3$  still 29.9%.

Table 4.2: Summary of sonic speed calculation for Mixture A

|        | $\gamma$ | AAD%  |       |
|--------|----------|-------|-------|
|        |          | 100°C | 67°C  |
| EOS    |          | 1.51  | 1.38  |
| EOS-PV | 1.0      | 16.79 | 15.54 |
|        | 1.2      | 8.84  | 7.48  |
|        | 1.3      | 5.12  | 3.70  |
| AR-PV  | 1.0      | 38.48 | 43.86 |
|        | 1.2      | 32.61 | 38.51 |
|        | 1.3      | 29.85 | 36.00 |

The discrepancy between the calculated sonic speed from the PV relation and the literature data can be explained by analyzing the parameters involved in the calculation: heat capacity ratio ( $\gamma$ ), density ( $\rho$ ), and isothermal compressibility ( $\kappa_T$ ). We know the range of  $\gamma$  and the related error is less than 5%. The density affects the sonic speed result and 10% error in density leads to about 5% error in sonic speed. If density measurement is not available, which is the case for Mixture A, it can be calculated from the volume translated PR EOS with an error less than 1%. Therefore, the error in the sonic speed calculation due to density is negligible. The remaining factor is the isothermal

compressibility whose accuracy depends on the accuracy of pressure and volume measurement.

In order to evaluate the accuracy of the PV measurement, a PV relation is predicted from the PR VT (volume translated PR EOS). This is achieved by calculating from the PR VT the molar volume (or density) for each pressure point used in the AR measurement. The absolute volume can also be obtained if the amount of sample used in the measurement is known. Figure 4.15 compares the measured PV and the PR VT prediction and Figure 4.16 shows the isothermal compressibility calculated with these PV relations. The measured PV differs from the PR VT prediction and the deviation increases with decreasing pressure. The compressibility calculated from the measured PV is unreasonably large at low pressures: it is 2.7 times as large as that predicted from the PR VT at 34.53 MPa. It is clear that the overestimation of the compressibility from the AR measured PV results in the underestimation of the sonic speed. The sonic speed calculated from the PR VT predicted PV ( $\gamma=1$ ) is also shown in Figure 4.14 and Table 4.2 and it has an AAD of 5.12% ( $\gamma=1.3$ ).

The above calculation is for Mixture A at 100°C and the same calculation is repeated for Mixture A at 67°C. Figure 4.17 shows the predicted sonic speed as well as the literature data and the AAD is given in Table 4.2. The sonic speed calculated from the AR PV has an incorrect trend at the high pressure end (45-49.3 MPa) and has a deviation of 36% ( $\gamma=1.3$ ). It is clear that the sonic speed calculated from the AR PV data is not accurate enough to be used for the resonance frequency prediction. The source of this error is discussed in Section 5.3.

#### 4.2.2.2 Sonic Speed Prediction from EOS

Sonic speed calculation with the PR EOS involves 3 steps: (a) match the bubble point by adjusting the binary interaction coefficients; (b) run a flash calculation to generate the composition of each phase at equilibrium; (c) calculate sonic speed from the equations presented in Chapter 2.

### (1) Mixture A

The results of sonic speed prediction from the PR EOS are shown in Figure 4.14 (100°C), Figure 4.17 (67°C), and Table 4.2. The predicted sonic speed matches the trend of the literature data in the whole pressure range of interest. It has an AAD of 1.51% and 1.38% at 100°C and 67°C, respectively. This is in contrast with the large AAD in the sonic speed calculated from the PV data.

Density is an important parameter in the sonic speed calculation. Compared with the PR EOS, the volume translated PR EOS (PR-VT) can give very accurate density prediction. Therefore, the sonic speed is also calculated with the PR VT. Unfortunately, the sonic speed predictions from the PR VT are unreasonably higher than the measured data. For example, the PR EOS predicts a sonic speed of 1050 m/s for Mixture A at 47.07 MPa and 100°C, while the PR VT gives an prediction of 2594 m/s at the same condition; that is, 1.48 times larger than the measured value (1045 m/s). One explanation is that the volume translation changes the values of the partial differentials among those thermodynamic equations (Equations 2.39-2.42) involved in the sonic speed calculation.

### (2) Mixture B

Mixture B is a live oil from Ye et al. (1991). The sonic speed at different temperatures has been reported and this provided an opportunity to test the model in this work.

The same procedure as in Mixture A is followed to do the calculation. The properties of each component used in the calculation are shown in Table 4.3 and the sonic speed results from the PR EOS are given in Table 4.4 and Figure 4.18. The sonic speed predictions follow the trend of the literature data and they have an AAD of 3.86% and 3.53% at 100.1°C and 60.2°C, respectively. This shows that the PR EOS can give quite accurate predictions of sonic speed in live oils.

Table 4.3: Properties of Mixture B used in sonic speed calculation  
(Pc, critical pressure; Tc, critical temperature;  $\omega$ , acentric factor; M, molecular weight)

| Component       | Mole Fraction | Pc, (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|-----------------|---------------|-----------|-----------|----------|-----------|
| N <sub>2</sub>  | 0.0022500     | 33.50000  | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub> | 0.0077700     | 72.80000  | 304.20000 | 0.22500  | 44.01000  |
| C1              | 0.4252400     | 45.40000  | 190.60000 | 0.00800  | 16.04300  |
| C2              | 0.0823800     | 48.20000  | 305.40000 | 0.09800  | 30.07000  |
| C3              | 0.0606200     | 41.90000  | 369.80000 | 0.15200  | 44.09700  |
| iC4             | 0.0143100     | 36.00000  | 408.10000 | 0.17600  | 58.12400  |
| nC4             | 0.0328400     | 37.50000  | 425.20000 | 0.19300  | 58.12400  |
| iC5             | 0.0130700     | 33.40000  | 460.40000 | 0.22700  | 72.15100  |
| nC5             | 0.0159300     | 33.30000  | 469.60000 | 0.25100  | 72.15100  |
| C6              | 0.0388000     | 32.37303  | 507.86260 | 0.27128  | 84.00000  |
| C7              | 0.0225800     | 31.01017  | 542.90570 | 0.31094  | 96.00000  |
| C8              | 0.0346300     | 29.08266  | 570.68600 | 0.34931  | 107.00000 |
| C9              | 0.0315700     | 26.97314  | 598.28240 | 0.39295  | 121.00000 |
| C10             | 0.0215400     | 24.92712  | 622.62780 | 0.43782  | 134.00000 |
| C11             | 0.0201800     | 23.20247  | 643.38150 | 0.47993  | 147.00000 |
| C12             | 0.0160800     | 21.64369  | 663.81240 | 0.52327  | 161.00000 |
| C13             | 0.0160800     | 20.45472  | 682.21480 | 0.56180  | 175.00000 |
| C14             | 0.0129000     | 19.30980  | 700.87890 | 0.60243  | 190.00000 |
| C15             | 0.0129000     | 18.19352  | 719.05520 | 0.64481  | 206.00000 |
| C16             | 0.0107000     | 17.16445  | 734.40100 | 0.68514  | 222.00000 |
| C17             | 0.0107000     | 16.31046  | 749.54180 | 0.72327  | 237.00000 |
| C18             | 0.0085000     | 15.62885  | 760.68940 | 0.75432  | 251.00000 |
| C19             | 0.0085000     | 15.02167  | 771.36900 | 0.78406  | 263.00000 |
| C22             | 0.0299200     | 13.26394  | 804.29330 | 0.88023  | 300.00000 |
| C27             | 0.0192200     | 11.11691  | 849.84950 | 1.01565  | 360.00000 |
| C35             | 0.0191700     | 8.90231   | 906.04990 | 1.17752  | 445.00000 |
| C45             | 0.0116200     | 7.13012   | 957.99790 | 1.32850  | 539.00000 |

Table 4.4: Summary of sonic speed results for Mixture B\*

|        | $\gamma$ | AAD%    |        |
|--------|----------|---------|--------|
|        |          | 100.1°C | 60.2°C |
| EOS    |          | 3.86    | 3.53   |
| EOS-PV | 1.0      | 16.78   | 15.83  |
|        | 1.2      | 8.83    | 7.80   |
|        | 1.3      | 5.11    | 4.23   |

\*The literature data for Mixture B is read from the plot in Ye et al. (1991) and small errors are expected.

The capability of the PR EOS and the PR VT in predicting density and sonic speed is compared where experimental data is available (Table 4.5). Compared with the PR EOS, the PR VT can give highly accurate density prediction (with error less than 1%), but the predicted sonic speed is much higher than the measured data. Based on the above findings, the sonic speed calculated from the PR EOS will be used to predict resonance frequencies.

It should be mentioned that the sonic speed calculation discussed above is only valid for single phase fluids (liquid or vapor). No attempt has been made to predict the sonic speed in two or three phase mixtures since the parameters involved in the sonic speed calculation (density, heat capacity ratio, compressibility, etc) are not clearly defined in multiphase mixtures. Because the sonic speed calculation is only valid for single phase fluids, the resonance frequency calculation will only be made for single phase fluids.

Table 4.5: Comparison of the PR EOS and the PR VT in predicting density and sonic speed for Mixture B

| Temp.<br>(°C) | Pres.<br>(MPa) | Density (g/cm <sup>3</sup> ) |          |          | Sonic speed (m/s) |          |          |
|---------------|----------------|------------------------------|----------|----------|-------------------|----------|----------|
|               |                | PR<br>EOS                    | PR<br>VT | Measured | PR<br>EOS         | PR<br>VT | Measured |
| 139           | 26             | 0.567                        | 0.615    | 0.621    | 701               | 1004     |          |
| 15.56*        | 0.1            | 0.712                        | 0.829    | 0.833    | 1402              | 1291     |          |
| 60.2          | 65             | 0.658                        | 0.727    |          | 1331              | 4690     | 1275     |
| 100.1         | 65             | 0.641                        | 0.703    |          | 1191              | 2714     | 1170     |

(\* This row is the properties of stock tank oil for Mixture B)

#### 4.2.3 Identification of the Resonance Modes

We have so far obtained the two parameters needed for the resonance frequency calculation: sonic speed from the PR EOS, the length of the resonator from the volume measurement. Then the resonance frequency can be calculated from Equation 2.2.

The frequencies of the first and second resonance mode are calculated for Mixture A (67°C) and are shown in Figures 4.19 and 4.20, respectively, along with the 9 peaks tracked before. The pressures involved in the calculation are between 34.63 and 49.38

MPa which are above the bubble point (33.3 MPa), therefore, the mixture is a single phase liquid. A few observations can be made from these plots:

- (1) The calculated resonance frequency decreases significantly and approximately linearly with decreasing pressure and has a change of 18.9% in the pressure range between 34.63 and 49.38 MPa.
- (2) The measured frequency changes only slightly with pressure. For example, for the two peaks which intersect the first resonance mode, Peaks 1 and 2, each has a change of only 0.3% in the pressure range of 34.63–49.38 MPa. Peak 8, which intersects the second resonance mode, has a change of 0.6% in the same pressure range.
- (3) Not all the peaks follow the predicted trend of the resonance modes. The trend of the peaks can be identified more easily from Figures 4.4–4.12 since they are presented on an expanded scale. Among the 9 peaks, 5 peaks (Peaks 1, 2, 6, 7 and 8) follow the same trend as the resonance mode; Peak 4 follows the trend only partly (in the pressure range of 43–49.38 MPa); Peak 3 has a reverse trend; Peak 5 is invariant; and Peak 9 does not have a clear trend.

The above comparisons clearly indicate that we still have difficulties in identifying the resonance modes. Ideally, if there are peaks which follow the path of the predicted resonance modes, they can be identified as resonance modes. Unfortunately, this is not the case in this work. A temporary solution to this problem is to take those peaks which follow the same trend as the predicted resonance modes to be the potential resonance modes. The frequencies of Peaks 1, 2, 8, and 9 are close to those of the resonance modes and Peaks 1, 2, and 8 follow the same trend as the resonance modes. Can we declare Peaks 1, 2, and 8 as the resonance modes?

The answer to this question is no. We have only predicted the trend of the resonance modes in the high pressure end (single phase liquid region) and the trend will be different at lower pressures where phase transition occurs. What is the trend of the resonance

modes along the path of the depressurization, especially during phase transitions? This issue will be addressed in the next section.

#### **4.2.4 Expected Trend of the Resonance Modes**

Based on acoustic theory, the resonance frequency is related to sonic speed through Equation 2.2. Although the resonance frequency is not strictly proportional to the sonic speed due to the presence of a non-constant term (length of the chamber), it can be shown that the resonance frequency follows the same trend as that of the sonic speed. In the following, the phase transition will be explained in terms of changes in sonic speed.

##### **4.2.4.1 Single Phase Liquid**

It has been demonstrated that the sonic speed for a single phase liquid can be calculated from an EOS. Both the literature data (Ye et al., 1991, 1992a, 1992b; Wang et al., 1988) and the calculation results (as shown in Section 4.2.2) indicate that the sonic speed in a liquid decreases with decreasing pressure at fixed temperature and increases with decreasing temperature at fixed pressure.

##### **4.2.4.2 Liquid-Solid Phase Transition**

Liquid and solid phases coexist during a liquid-solid phase transition and the corresponding sonic speed behavior can be qualitatively analyzed using Equation 2.37. For convenience, it is duplicated here

$$c = \sqrt{\frac{1}{\rho \kappa}} \quad (4.2)$$

For simplicity, the subscript *s* is dropped from the adiabatic compressibility. Theoretically, Equation 4.2 holds for liquid-solid mixtures. However, sonic speed in such a mixture cannot be readily calculated since  $\rho$  and  $\kappa$  are not clearly defined in the mixture.

The liquid-solid phase transition of interest in this work involves the precipitation of asphaltene and/or wax from reservoir fluids. If  $\chi$  is the volume fraction of the solid phase, the density and compressibility of the mixture can be expressed as (Meray et al., 1993)

$$\rho = \chi\rho_S + (1 - \chi)\rho_L \quad (4.3)$$

$$\kappa = \chi\kappa_S + (1 - \chi)\kappa_L \quad (4.4)$$

where the subscripts  $S$  and  $L$  refer to the solid and liquid phase respectively.

During the liquid-solid phase transition, the change in density when passing from the liquid to the solid state is insignificant, while the variation in compressibility is quite high, so that the bulk properties can be estimated with (Meray et al., 1993)

$$\rho = \rho_L \quad (4.5)$$

$$\kappa = (1 - \chi)\kappa_L \quad (4.6)$$

$$c = c_L / \sqrt{1 - \chi} \quad (4.7)$$

where  $c_L$  is the sonic speed in a single phase liquid. It can be inferred that the sonic speed increases during liquid-solid phase transition and this will cause a slope change in sonic speed. The experimental results of Meray et al. (1993) confirmed the increase of ultrasonic velocity during the cooling of a waxy oil which was an indication of wax precipitation. The reverse of this observation is that the dissolution of solids in the liquid-solid mixture will cause a decrease in the sonic speed. Wang et al. (1988) indicated that the melting of solid materials (asphaltene, wax, etc.) in heavy oils due to heating resulted in a substantial decrease in sonic speed and this is in agreement with the above analysis.

#### 4.2.4.3 Liquid-Vapor Phase Transition

The liquid-vapor phase transition, however, behaves differently from the liquid-solid transition. Theoretically, the presence of gas bubbles in a liquid dramatically reduces the sonic speed in the liquid (McWilliam et al., 1969; Kieffer, 1977). In particular, the sonic speed should be much lower in a vapor-liquid mixture than in either the vapor or the liquid phases because the mixture actually assumes the density of a liquid but the compressibility of a vapor. However, a different picture regarding the sonic speed change

was presented by Wang et al. (1988). Experimental results of Wang et al. showed that when the bubble point pressure of a live oil was reached, there was a small slope change in sonic speed. Further reduction of the pressure around the bubble point caused the sonic speed to increase slightly. Reducing the pressure still further caused the sonic speed to drop sharply and the sonic signal to disappear from the monitor screen. These results reflect the complexity of the acoustic behavior during a phase transition.

To summarize the discussion about the changes in sonic speed during phase transitions, Figure 4.21 shows the sonic speed behavior along the path of pressure reduction. Three sections, with different sonic speed behavior, are shown in the figure: single phase liquid (A-B), liquid-solid mixture (B-D), and vapor-liquid-solid mixture (D-E).

#### Section A-B:

The mixture is in single phase liquid when pressure is dropped from A to B and the sonic speed decreases with decreasing pressure.

#### Section B-D:

The solid phase starts to form when pressure reaches the onset pressure ( $P_s$ ) of solids precipitation and the sonic speed reverses its trend and increases with decreasing pressure. During the early stage of the liquid-solid transition, the effect of solids precipitation dominates the sonic speed behavior and the role of solids in enhancing the sonic speed has been discussed in Section 4.2.4.2. Experimental results of Ferworn (1995) showed that once the solids (asphaltene) start to form, they grow very quickly and precipitate out of solution instantaneously. With the formation of a solid phase as the pressure drops, the effect of pressure begins to dominate and the liquid phase behaves more or less like the original single phase liquid. This, together with the increased damping of the sonic signal caused by the solid phase, gives rise to a slope reversal in sonic speed which drops again with decreasing pressure. Therefore, a local maximum in sonic speed (point C) is expected during liquid-solid transition. However, the decrease of sonic speed during liquid-solid phase transition has not been experimentally verified.

#### Section D-E:

The sonic speed behavior of the mixture is further complicated with the formation of a third phase (vapor) when the pressure reaches the bubble point ( $P_b$ ). It is expected that the vapor-liquid transition, compared with the liquid-solid transition, has a larger effect on sonic speed behavior due to the high compressibility of the vapor. The effects of liquid-solid and vapor-liquid transitions have been discussed in Sections 4.2.4.2 and 4.2.4.3 respectively.

It should be mentioned that for a mixture that can only undergo a vapor-liquid transition under the experimental conditions of interest, the section from B to D in Figure 4.21 will not appear. The case of more than one liquid phase has been neglected in the discussion. Ye et al. (1992b) reported uncommon behavior in sonic speed in binary mixtures with high CO<sub>2</sub> content which was found to be caused by the formation of a second liquid phase.

#### 4.2.5 Procedure for Identifying Resonance Modes

The theoretical behavior of the sonic speed has been elaborated and the resonance frequency is expected to follow the same trend. Thus, two guidelines, the predicted resonance frequency and the expected trend in resonance modes, are formulated to help identify the resonance modes and detect phase transitions from AR measurements. The procedures used for screening the resonance modes are as follows:

- (1) Discard the peaks which do not have a clear trend.
- (2) Discard the peaks which do not follow the expected trend in the single phase liquid region.
- (3) Discard the peaks which do not exhibit an increase in frequency upon a phase transition.

Note that in many cases, the expected downward trend in frequency in the liquid-vapor region did not appear. The reason for this is not clear. The peaks that pass the screening procedure are potential resonance modes. Any peaks which appear to respond at the actual phase transitions, but do not fulfill the selection criteria will also be noted.

Two terms, false positives and false negatives, will be used in the analysis of AR measurements. False positives represent the peaks which pass the screening procedure but do not give the correct phase transitions, while false negatives stand for the peaks which fail to pass the screening procedure but give the correct phase transitions. A peak is said to have the correct response if it gives a liquid-vapor phase transition within  $\pm 4$  MPa of the measured bubble point from the visual method.

### **4.3 Analysis of AR Measurements for Seven Fluids**

#### **4.3.1 Mixture A**

##### **(1) Measurement at 67°C**

The data of Mixture A at 67°C has been discussed in Section 4.2. Among the 9 peaks tracked (Figures 4.4–4.12), Peaks 1, 2, 7 and 8 are found to pass the screening procedure. All four peaks indicate a phase transition between 28 and 34 MPa. It is possible that all four peaks are some form of resonance modes.

##### **(2) Measurement at 100°C**

Figure 4.22 shows the frequency spectrum at 47.08 MPa. A total of 10 peaks are tracked with pressure and the results are shown in Figures 4.23–4.32. The slope changes in these peaks are summarized in Table 4.1. Figures 4.33 and 4.34 show the predicted resonance modes.

Among the 10 peaks tracked, Peaks 2, 6, and 9 passed the screening. Peaks 2 and 9 are false positives since they do not give the correct phase transition (33.0 MPa). However, it was observed that Peak 2 split into two peaks at about 30 MPa. This split is believed to be caused by the formation of the second phase (vapor) as will be discussed in Chapter 5. Figure 4.24 shows both the new peak and the original one. The frequency of the original peak continues to decrease with pressure but the new peak represents a slope change. Peak 5 is a false negative since it failed to pass the screening procedure but has a slope change close to the measured bubble point.

### 4.3.2 Mixture C

Note that for Mixture C and all the other mixtures, only the peaks that pass the screening procedure will be shown. Figure 4.35 shows the PV relation for Mixture C at 70°C and two slope changes are observed at about 16.2 and 13.2 MPa respectively. This is uncommon since there exists usually only one slope change in PV relation which is the bubble point. The bubble point of this oil measured by visual method is 13.13 MPa (70°C) which indicates that the slope change at 13.2 MPa is the result of a liquid-vapor transition. Then what is the slope change at 16.2 MPa? Intuitively, it might be said to come from a liquid-solid transition as will be discussed later. Another possibility is that an error was made in the sample preparation and the bubble point for the experiment is really 16.2 MPa.

Figure 4.36 shows the frequency spectrum at 24.11 MPa. The predicted resonance modes are shown in Figures 4.37-4.38 along with the tracked peaks. Peaks 1-8 are not shown since they are far below the predicted resonance modes. The characterization of Mixture C used in the prediction is shown in Table 4.6.

A surprising slope change in the predicted resonance frequency at 16.2 MPa is noticed in Figures 4.37-4.38 and this change may be speculated to be the result of a liquid-solid transition. As has been mentioned in Section 4.2.2, the predicted sonic speed and resonance frequency are only valid for a single phase liquid, i.e., for pressures above both the onset of solids precipitation and the bubble point. Therefore, no distinct slope change is expected to occur in the predicted sonic speed and resonance modes. The predicted sonic speed for Mixture C is shown in Figure 4.39 which is indeed close to a straight line. Rechecking the equation (Equation 2.2) used in the resonance frequency calculation, it is found that the length of the resonator causes the slope change in the predicted resonance modes. Since the length of the resonator is calculated from the volume measurement, the slope change in the predicted resonance modes is actually caused by the slope change in the measured PV relation (Figure 4.35). This can be easily verified since these two slope changes occur at exactly the same pressure (16.2 MPa). It should also be kept in mind

that if a liquid-solid transition really occurs at 16.2 MPa, the predicted sonic speed and resonance modes below 16.2 MPa will be no longer valid and should be ignored.

The nature of the slope change at 16.2 MPa in the measured PV relation (Figure 4.35) is still not clear. Usually only a liquid-vapor transition can cause this kind of PV behavior due to the high compressibility of the vapor phase. One speculation is that the slope change is caused by a liquid-solid transition, or by the formation of a second liquid phase. However, none of these can be easily verified.

Table 4.6: Characterization of Mixture C used in sonic speed prediction

| Component        | Mole fraction | Pc (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|------------------|---------------|----------|-----------|----------|-----------|
| N <sub>2</sub>   | 0.00117       | 33.50000 | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub>  | 0.00675       | 72.80000 | 304.20000 | 0.22500  | 44.01000  |
| H <sub>2</sub> S | 0.01728       | 88.20000 | 373.20000 | 0.10000  | 34.08000  |
| C1               | 0.33705       | 45.40000 | 190.60000 | 0.00800  | 16.04300  |
| C2               | 0.06652       | 48.20000 | 305.40000 | 0.09800  | 30.07000  |
| C3               | 0.08503       | 41.90000 | 369.80000 | 0.15200  | 44.09700  |
| IC4              | 0.02157       | 36.00000 | 408.10000 | 0.17600  | 58.12400  |
| NC4              | 0.06344       | 37.50000 | 425.20000 | 0.19300  | 58.12400  |
| IC5              | 0.01181       | 33.40000 | 460.40000 | 0.22700  | 72.15100  |
| NC5              | 0.01668       | 33.30000 | 469.60000 | 0.25100  | 72.15100  |
| C6-C16           | 0.2565897     | 23.68455 | 651.32068 | 0.49777  | 154.74848 |
| C17+             | 0.1161103     | 12.16348 | 861.07733 | 0.99157  | 323.30665 |

Among the 14 peaks tracked, Peaks 2 and 9 (Figures 4.40–4.41) passed the screening. Peak 2 gives an apparent solids onset of 22.5 MPa and a bubble point of 13.7–16.0 MPa. Peak 9 gives an apparent solids onset of 19.2 MPa and a bubble point of 13.5–14.5 MPa. Two possibilities need to be considered for this measurement: bubble point at 13.2 MPa or at 16.2 MPa.

#### (1) Bubble point at 13.2 MPa

There are 5 false negatives with respect to the liquid-vapor transition. (These five peaks have a slope change at about 13.2 MPa).

(2) Bubble point at 16.2 MPa

There are 2 false negatives if the bubble point is at 16.2 MPa.

### 4.3.3 Mixture D

(1) Measurement at 99°C

Figure 4.42 shows the frequency spectrum at 64.47 MPa. One difficulty in this case is that the data of the AR measurement is only available in the pressure range of 32.52-64.47 MPa which is well above the measured bubble point (22.48 MPa). This means the lack of a reference point (bubble point) in the interpretation.

The predicted resonance modes are shown in Figure 4.43-4.44 and are found to intersect all the peaks except Peak 4. The characterization of this oil used in the prediction is shown in Table 4.7. Peaks 1, 2, and 3 (Figures 4.45-4.47) passed the screening and give an apparent solids onset of 52, 60, and 57.5 MPa, respectively.

Table 4.7: Characterization of Mixture D used in sonic speed prediction

| Component       | Mole fraction | Pc (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|-----------------|---------------|----------|-----------|----------|-----------|
| N <sub>2</sub>  | 0.0048000     | 33.50000 | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub> | 0.0092000     | 72.80000 | 304.20000 | 0.22500  | 44.01000  |
| C1              | 0.4339000     | 45.40000 | 190.60000 | 0.00800  | 16.04300  |
| C2              | 0.1101000     | 48.20000 | 305.40000 | 0.09800  | 30.07000  |
| C3              | 0.0654000     | 41.90000 | 369.80000 | 0.15200  | 44.09700  |
| IC4             | 0.0079000     | 36.00000 | 408.10000 | 0.17600  | 58.12400  |
| NC4             | 0.0370000     | 37.50000 | 425.20000 | 0.19300  | 58.12400  |
| IC5             | 0.0128000     | 33.40000 | 460.40000 | 0.22700  | 72.15100  |
| NC5             | 0.0225000     | 33.30000 | 469.60000 | 0.25100  | 72.15100  |
| C6-C16          | 0.1999557     | 23.68862 | 653.61268 | 0.49970  | 155.48931 |
| C17+            | 0.0964443     | 12.14283 | 864.92680 | 0.99610  | 325.74704 |

(2) Measurement at 110°C

Figure 4.48 shows the frequency spectrum at 64.01 MPa and Figures 4.49-4.50 show the predicted resonance modes along with the tracked peaks. All 6 peaks intersect the predicted resonance modes. Peaks 1 and 2 (Figures 4.51-4.52) passed the screening. Peak

1 gives a bubble point of 23 MPa and an apparent solids onset of 51 MPa. Peak 2 gives a bubble point of 38 MPa and an apparent solids onset of 51 MPa. Peak 2 is a false positive since it gives a bubble point inconsistent with the measured value (23.17 MPa) from the visual method.

#### **4.3.4 Mixture E**

This mixture is obtained by mixing 60% (by volume) of Mixture D and 40% of toluene. Bubble point and/or onset of solids precipitation are not available from other sources. However, the onset of solid precipitation for this mixture, if any, is not expected to be higher than that of Mixture D at the same temperature (99°C), since toluene is known as an inhibitor for asphaltene precipitation.

The frequency spectrum at 64.1 MPa is shown in Figure 4.53. No prediction for the resonance modes is made for this mixture due to the lack of data necessary to tune the model. Among the 8 peaks tracked, Peaks 5, 6, and 8 (Peaks 4.54–4.56) passed the screening. Peaks 5 and 8 give an apparent solids onset of 56 and 58 MPa, respectively. Due to its high content of toluene, this mixture is not expected to undergo a liquid-solid transition at such high pressures. Hence, Peaks 5 and 8 are probably false positives. Peak 6 has a slope change at 23.5 MPa which can be interpreted as a bubble point.

#### **4.3.5 Mixture F (isothermal)**

This oil is tested for asphaltene and/or wax precipitation, if any. Based on the different mechanism of asphaltene and wax precipitation, the former is expected to dominate during an isothermal depressurization measurement, while the latter dominates during an isobaric cooling measurement. Both the depressurization measurement and the cooling measurement were conducted for this mixture. The cooling measurement will be discussed separately in Section 4.3.8.

The frequency spectrum at 38.53 MPa is shown in Figure 4.57. The predicted resonance modes are shown in Figures 4.58–4.59 together with the tracked peaks. Peaks 1–3 are not

shown since they are far below the predictions. The characterization of the mixture is given in Table 4.8.

Among the 11 peaks tracked, Peaks 4 and 11 (Figures 4.60-4.61) passed the screening. Peak 4 gives an apparent solids onset of 33.5 MPa and a bubble point of 18 MPa. Peak 11 also gives a bubble point of 18 MPa. This bubble point can be verified by the visually measured bubble point (17.51 MPa). Peaks 1, 2, 6, and 10 have a slope change at about 17 MPa and are false negatives. Peak 11 has another slope change at 27 MPa which does not match the expected trend for a liquid-solid transition. It may be caused by the spurious signals or interpreted as an apparent solids onset.

Table 4.8: Characterization of Mixture F used in sonic speed prediction

| Component       | Mole fraction | Pc (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|-----------------|---------------|----------|-----------|----------|-----------|
| N <sub>2</sub>  | 0.0017000     | 33.50000 | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub> | 0.0052000     | 72.80000 | 304.20000 | 0.22500  | 44.01000  |
| C1              | 0.3895000     | 45.40000 | 190.60000 | 0.00800  | 16.04300  |
| C2              | 0.0241000     | 48.20000 | 305.40000 | 0.09800  | 30.07000  |
| C3              | 0.0031000     | 41.90000 | 369.80000 | 0.15200  | 44.09700  |
| IC4             | 0.0015000     | 36.00000 | 408.10000 | 0.17600  | 58.12400  |
| NC4             | 0.0014000     | 37.50000 | 425.20000 | 0.19300  | 58.12400  |
| IC5             | 0.0015000     | 33.40000 | 460.40000 | 0.22700  | 72.15100  |
| NC5             | 0.0009000     | 33.30000 | 469.60000 | 0.25100  | 72.15100  |
| C6-C16          | 0.2529013     | 21.11291 | 669.43233 | 0.55462  | 171.13824 |
| C17+            | 0.3181987     | 9.66141  | 911.90306 | 1.16006  | 392.16028 |

#### 4.3.6 Mixture G

Figure 4.62 shows the frequency spectrum at 38.52 MPa. The predicted resonance modes are shown in Figure 4.63 and the characterization of this oil is given in Table 4.9.

Peaks 3 and 8 (Figures 4.64-4.65) passed the screening. Both peaks have a slope change at about 18 MPa consistent with the measured bubble point from the visual method (17.82 MPa). Peaks 5 and 7 have a slope change at about 17 MPa and are false negatives. Peak 8 gives an apparent liquid-solid transition at 34 MPa. Peak 3 has a slope change at

27 MPa which does not match the expected trend for a liquid-solid transition. It may be caused by the spurious signals or interpreted as an apparent solids onset.

Table 4.9: Characterization of Mixture G used in sonic speed prediction

| Component       | Mole fraction | Pc (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|-----------------|---------------|----------|-----------|----------|-----------|
| N <sub>2</sub>  | 0.0070000     | 33.50000 | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub> | 0.0051000     | 72.80000 | 304.20000 | 0.22500  | 44.01000  |
| C1              | 0.3681000     | 45.40000 | 190.60000 | 0.00800  | 16.04300  |
| C2              | 0.0236000     | 48.20000 | 305.40000 | 0.09800  | 30.07000  |
| C3              | 0.0039000     | 41.90000 | 369.80000 | 0.15200  | 44.09700  |
| IC4             | 0.0013000     | 36.00000 | 408.10000 | 0.17600  | 58.12400  |
| NC4             | 0.0008000     | 37.50000 | 425.20000 | 0.19300  | 58.12400  |
| IC5             | 0.0015000     | 33.40000 | 460.40000 | 0.22700  | 72.15100  |
| NC5             | 0.0006000     | 33.30000 | 469.60000 | 0.25100  | 72.15100  |
| C6-C16          | 0.2609556     | 21.13944 | 669.43010 | 0.55417  | 171.02308 |
| C17+            | 0.3271444     | 9.68184  | 911.77839 | 1.15886  | 391.72395 |

#### 4.3.7 Mixture H

Figure 4.66 shows the frequency spectrum at 36.93 MPa. The predicted resonance modes as well as the tracked peaks are shown in Figure 4.67. The characterization of this mixture is given in Table 4.10.

Table 4.10: Characterization of Mixture H used in sonic speed prediction

| Component       | Mole fraction | Pc (atm) | Tc (K)    | $\omega$ | M (g/mol) |
|-----------------|---------------|----------|-----------|----------|-----------|
| N <sub>2</sub>  | 0.0053000     | 33.50000 | 126.20000 | 0.04000  | 28.01300  |
| CO <sub>2</sub> | 0.0040000     | 72.80000 | 304.20000 | 0.22500  | 44.01000  |
| C1              | 0.3822000     | 45.40000 | 190.60000 | 0.00800  | 16.04300  |
| C2              | 0.0243000     | 48.20000 | 305.40000 | 0.09800  | 30.07000  |
| C3              | 0.0043000     | 41.90000 | 369.80000 | 0.15200  | 44.09700  |
| IC4             | 0.0024000     | 36.00000 | 408.10000 | 0.17600  | 58.12400  |
| NC4             | 0.0021000     | 37.50000 | 425.20000 | 0.19300  | 58.12400  |
| IC5             | 0.0022000     | 33.40000 | 460.40000 | 0.22700  | 72.15100  |
| NC5             | 0.0010000     | 33.30000 | 469.60000 | 0.25100  | 72.15100  |
| C6-C16          | 0.2574474     | 21.24643 | 668.54521 | 0.55153  | 170.25263 |
| C17+            | 0.3147526     | 9.77664  | 909.64244 | 1.15195  | 388.76776 |

Among the 8 peaks tracked, Peaks 5, 7 and 8 (Figures 4.68–4.70) passed the screening. All the 3 peaks have a slope change at 18 MPa consistent with the measured bubble point from the visual method (17.51 MPa). Peak 1 has a slope change at 17 MPa and is a false negative. Peak 5 gives an apparent solids onset of 29.5 MPa. Peak 8 has a slope change at 26.5 MPa but its trend is not clear. It may be caused by the spurious signals or interpreted as an apparent solids onset.

#### **4.3.8 Mixture F (isobaric)**

An AR measurement was conducted on Mixture F to identify the onset of wax precipitation, if any. This measurement is different than the previous ones in that it is an isobaric cooling process rather than an isothermal depressurization process.

The expected trend of sonic speed shown in Figure 4.21 is only valid for an isothermal depressurization process and different behavior is expected for isobaric cooling measurement. The sonic speed of a single phase liquid increases with decreasing temperature at fixed pressure and increases further during liquid-solid phase transition (as discussed in Section 4.2.4). Therefore, a slope change in sonic speed is expected during a liquid-solid transition. The measurement was conducted at 19.03 MPa which is above the bubble point in the entire temperature range (25–65°C). Therefore, only liquid-solid transition is possible during the measurement.

The frequency spectrum at 65°C is shown in Figure 4.71. Twelve peaks are tracked with temperature. The predicted resonance modes as well as the track results are shown in Figure 4.72. Peaks 1 and 6 are not shown due to their unclear trend. Although the prediction has been made in the whole temperature range (25–65°C), it is only valid above the (unknown) wax onset. The characterization of this mixture is shown in Table 4.8.

Among the 12 peaks tracked, only Peak 9 (Figure 4.73) passed the screening. It has a slope change at 43°C which is the possible wax onset. Peaks 4, 5, 7, and 8 have a slope change at about 43°C and are probably false negatives.

#### 4.4 Summary of AR Data Interpretation

Table 4.11 is a summary of the AR data interpretation for liquid-vapor transitions. Multiple resonance modes have been detected for all the seven mixtures. For Mixtures A (67°C), C, F (isothermal measurement), G, and H, all the peaks that passed the screening give correct L-V transitions. For Mixtures A (100°C) and D (110°C), there is at least one false positive among the identified resonance modes. For all the AR measurements except Mixture A (67°C) and Mixture D (110°C), false negatives are also observed.

Table 4.11: Summary of AR data interpretation for L-V transitions

| Mixture         | No. of peaks * | No. of peaks ** | Correct responses | False positives | False negatives |
|-----------------|----------------|-----------------|-------------------|-----------------|-----------------|
| A (67°C)        | 9              | 4               | 4                 | 0               | 0               |
| A (100°C)       | 10             | 3               | 1                 | 2               | 1               |
| C (Pb=13.2 MPa) | 14             | 2               | 2                 | 0               | 5               |
| C (Pb=16.2 MPa) | 14             | 2               | 2                 | 0               | 2               |
| D (110°C)       | 6              | 2               | 1                 | 1               | 0               |
| E               | 8              | 3               | Unknown           | Unknown         | Unknown         |
| F (isothermal)  | 11             | 2               | 2                 | 0               | 4               |
| G               | 8              | 2               | 2                 | 0               | 2               |
| H               | 8              | 3               | 3                 | 0               | 1               |

\*Number of peaks tracked.

\*\*Number of peaks that passed the screening.

Table 4.12 is a summary of the liquid-vapor transitions identified from the AR measurements. The pressures for the liquid-vapor transitions are read from the peaks which give correct responses. The numbers with plus-minus sign represent the errors in the pressure readings. The errors (percent) given in Table 4.12 represent the relative deviations of the liquid-vapor transitions (pressure) identified from AR measurements with respect to the correct transitions obtained from the visual method. Except from the large deviations for Mixture A (67°C), the liquid-vapor transitions detected from the AR measurements are within 5% of the visually observed bubble point. For Mixture C, the pressure of 13.13 MPa is more likely to be the correct bubble point (compared with 16.2

MPa) since both of the resonance modes identified for this mixture respond favorably to this pressure.

Table 4.12: Summary of L-V transitions

| Mixture    | Correct L-V transition (MPa)* | Peak No.** | AR L-V transition (MPa) | Error %*** |
|------------|-------------------------------|------------|-------------------------|------------|
| A (67°C)   | 33.3                          | 1          | 30±2                    | 9.91       |
|            |                               | 2          | 32±2                    | 3.90       |
|            |                               | 7          | 36±1                    | 8.11       |
|            |                               | 8          | 29±1                    | 12.91      |
| A (100°C)  | 33.0                          | 6          | 34±1                    | 3.03       |
| C (70°C)   | 13.13                         | 2          | 13.3                    | 1.29       |
|            |                               | 9          | 13.5±0.5                | 2.82       |
| C (70°C)   | 16.2                          | 2          | 13.3                    | 17.90      |
|            |                               | 9          | 13.5±0.5                | 16.67      |
| D (110°C)  | 23.17                         | 1          | 23±2                    | 0.73       |
| F (62.5°C) | 17.51                         | 4          | 18                      | 2.80       |
|            |                               | 11         | 19±1                    | 8.51       |
| G (62.8°C) | 17.82                         | 3          | 17.5                    | 1.80       |
|            |                               | 8          | 18±1                    | 1.01       |
| H (60.3°C) | 17.51                         | 5          | 17±1                    | 2.91       |
|            |                               | 7          | 18±1                    | 2.80       |
|            |                               | 8          | 17±1                    | 2.91       |

\*Obtained from the visual method.

\*\*For peaks that have correct responses.

\*\*\*Relative deviation with respect to the correct L-V transition.

Table 4.13 is a summary of the AR data interpretation for the possible liquid-solid transitions. Apparent liquid-solid transitions have been detected for Mixtures C, D, F, G, and H. Multiple resonance modes are detected for all the mixtures except Mixture F (isobaric). For Mixtures C, D, F, and G, all the peaks that passed the screening give possibly correct L-S transitions. For Mixtures E and H, there are possible false positives among the identified resonance modes. For all the measurements except Mixtures D (99°C) and E, possible false negatives are also observed.

Table 4.14 is a summary of the possible liquid-solid transitions identified from the AR measurements. Although these results are not confirmed with other techniques, they are

self-consistent since the liquid-solid transitions detected from different peaks for the same mixture are close to each other. Mixtures F, G, and H are from the same reservoir and have similar properties. The liquid-solid transitions detected for these three mixtures are also very close. For these three mixtures, the liquid-solid transitions are more likely to occur at 27 MPa than 34 MPa since the latter is much higher than the current reservoir pressure.

Table 4.13: Summary of AR data interpretation for L-S transitions

| Mixture        | No. of peaks * | No. of peaks ** | Possible correct responses | Possible false positives | Possible false negatives |
|----------------|----------------|-----------------|----------------------------|--------------------------|--------------------------|
| C (70°)        | 14             | 2               | 2                          | 0                        | 5                        |
| D (99°C)       | 6              | 3               | 3                          | 0                        | 0                        |
| D (110°C)      | 6              | 2               | 2                          | 0                        | 3                        |
| E              | 8              | 3               | N/A                        | 2                        | N/A                      |
| F (isothermal) | 11             | 2               | 2                          | 0                        | 5                        |
| G              | 8              | 2               | 2                          | 0                        | 3                        |
| H              | 8              | 3               | 2                          | 1                        | 2                        |
| F (isobaric)   | 12             | 1               | 1                          | 0                        | 4                        |

\*Number of peaks tracked.

\*\*Number of peaks that passed the screening.

Table 4.14: Summary of L-S transitions

| Mixture                  | Reservoir Pressure (MPa) | Peak No. | Possible AR L-S transition (MPa) |
|--------------------------|--------------------------|----------|----------------------------------|
| C (70°C)                 |                          | 2        | 22.5                             |
|                          |                          | 9        | 19.2                             |
| D (99°C)                 | 58.61 (116°C)            | 1        | 52                               |
|                          |                          | 2        | 60                               |
|                          |                          | 3        | 57.5                             |
| D (110°C)                | 58.61 (116°C)            | 1        | 51                               |
|                          |                          | 2        | 51                               |
| F (62.5°C) (isothermal)  | 19.12                    | 4        | 33.5                             |
|                          |                          | 11       | 27                               |
| G (62.8°C)               | 19.18                    | 3        | 27                               |
|                          |                          | 8        | 34                               |
| H (60.3°C)               | 18.66                    | 5        | 29.5                             |
|                          |                          | 8        | 26.5                             |
| F (19.03 MPa) (isobaric) | 19.12 (62.5°C)           | 9        | 43 (°C)                          |

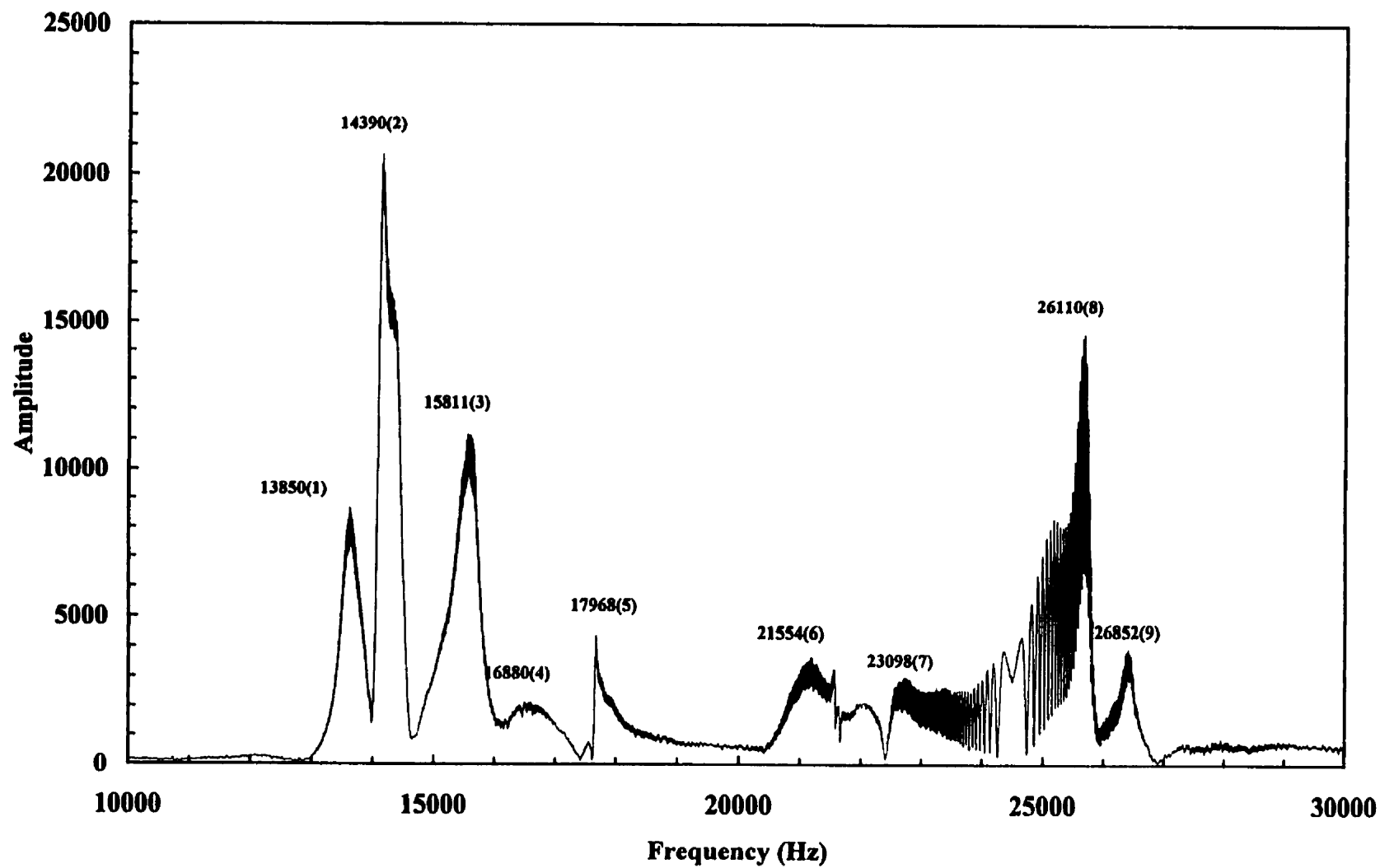
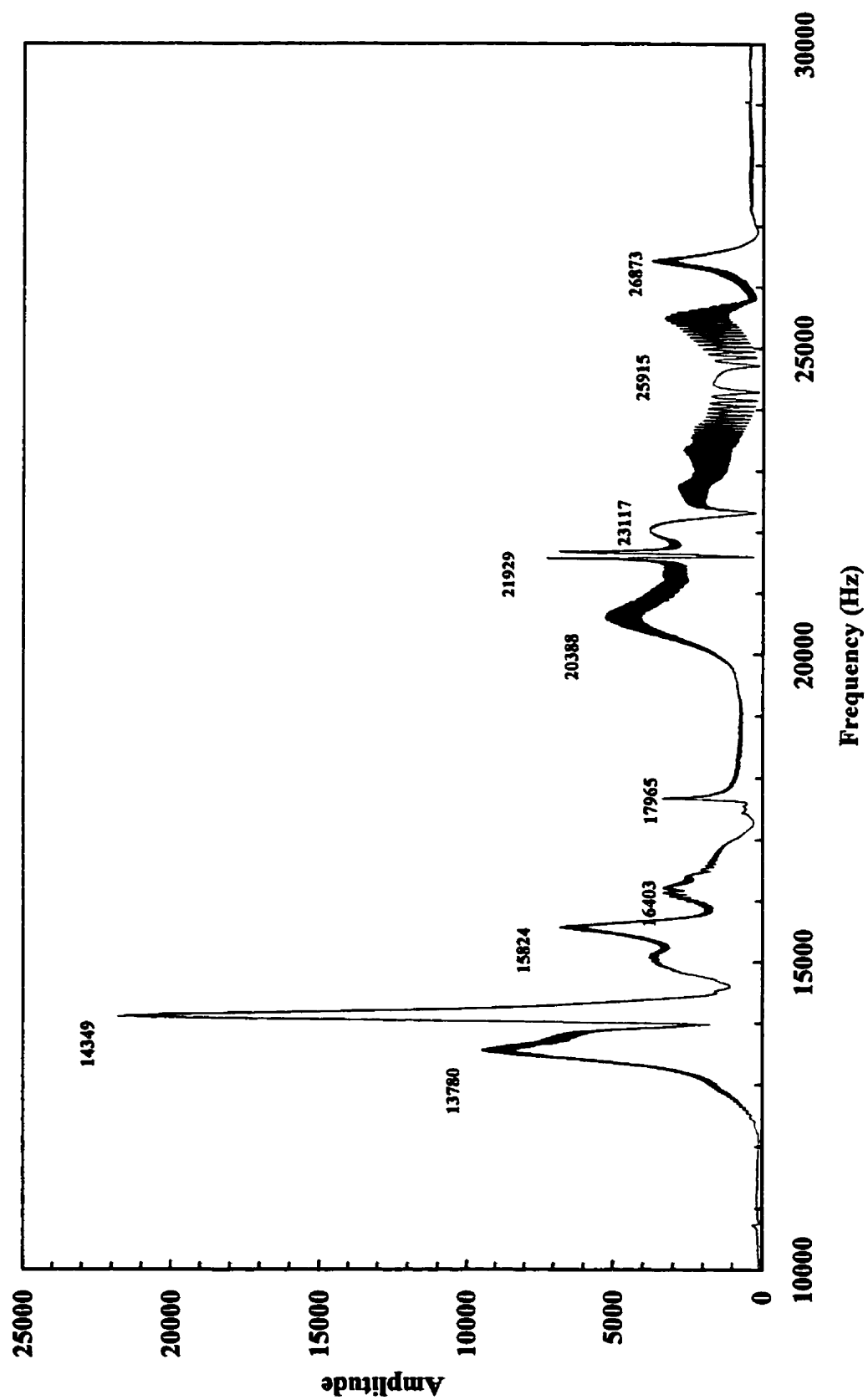


Figure 4.1: Frequency spectrum for Mixture A (67°C, 48.95MPa)



**Figure 4.2: Frequency spectrum for Mixture A (67°C, 33.38MPa)**

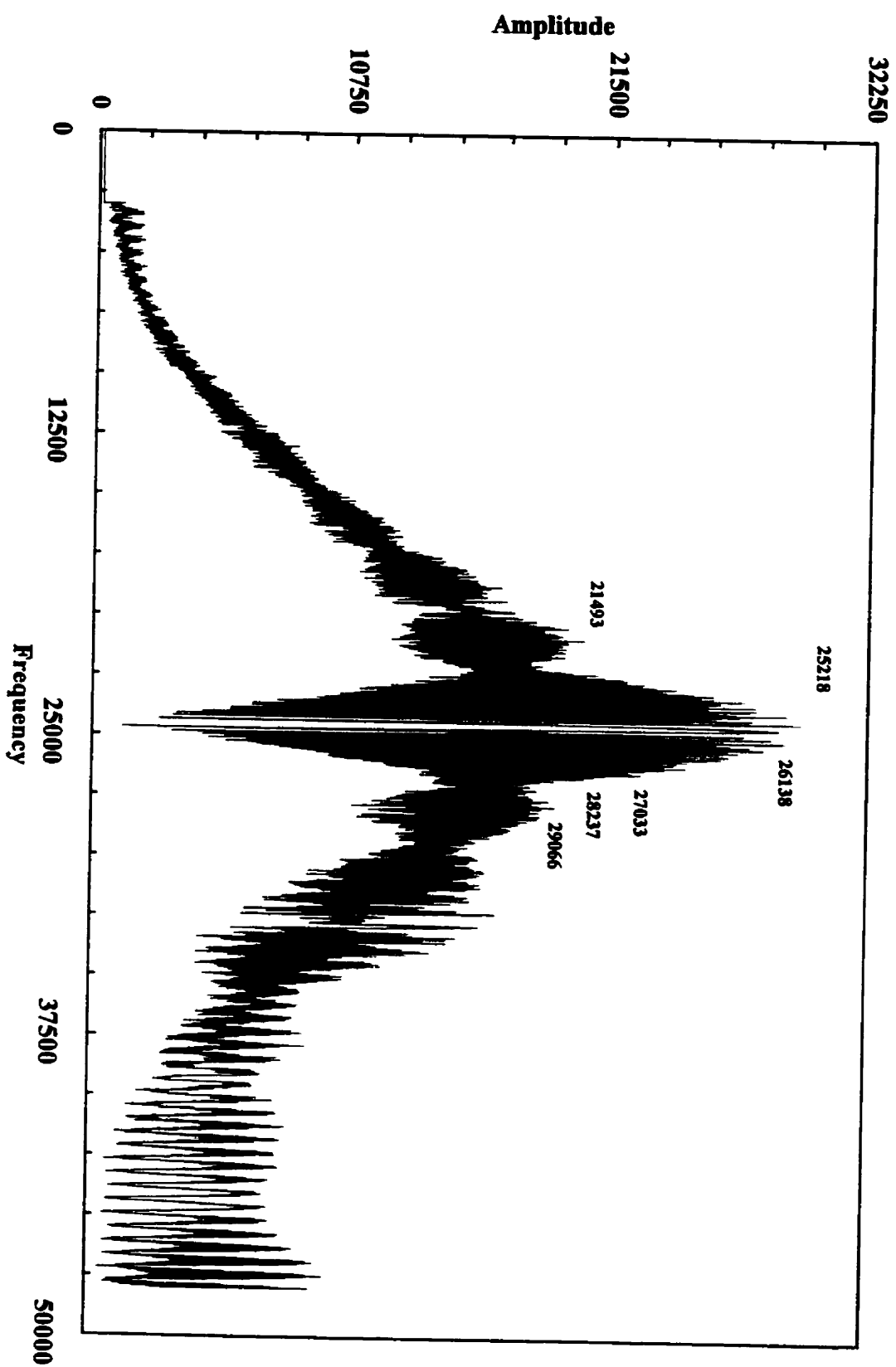
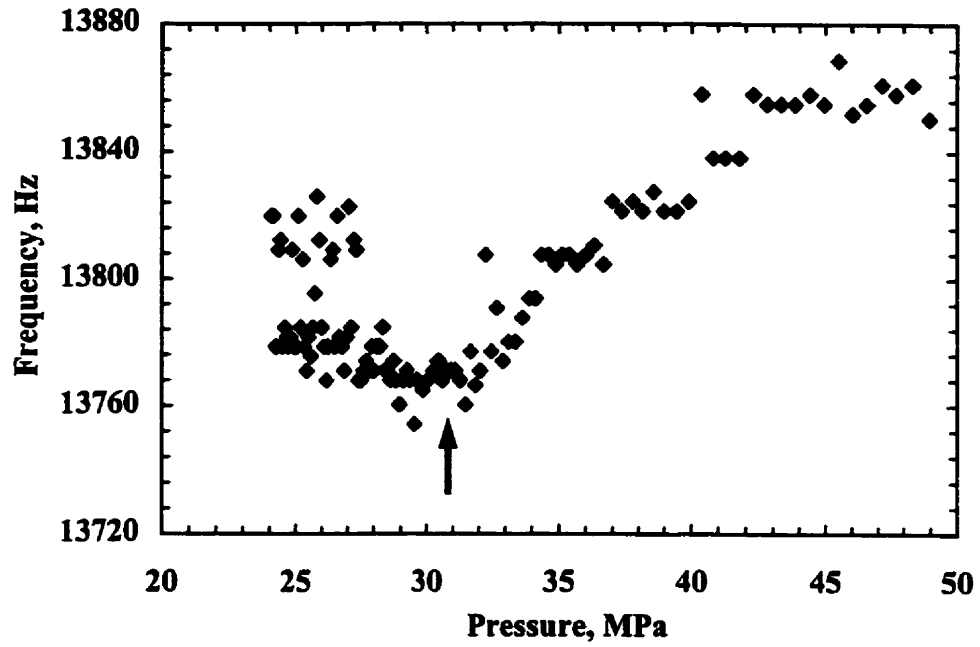
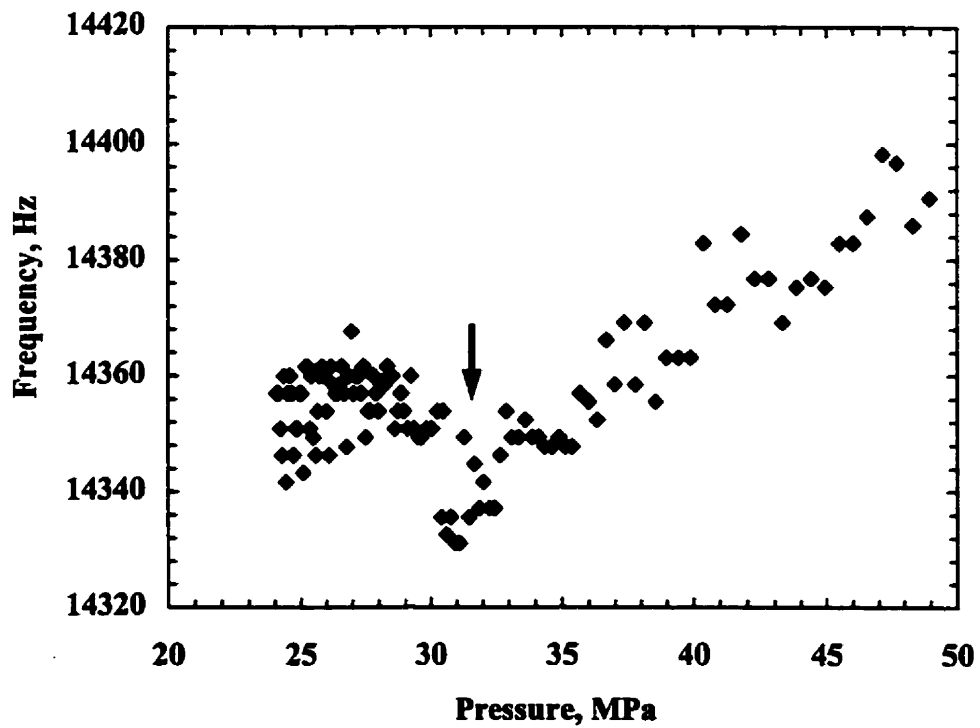


Figure 4.3: Frequency spectrum of the acoustic source signal



**Figure 4.4: Frequency versus pressure  
for Mixture A (67°C) (Peak 1)**



**Figure 4.5: Frequency versus pressure  
for Mixture A (67°C) (Peak 2)**

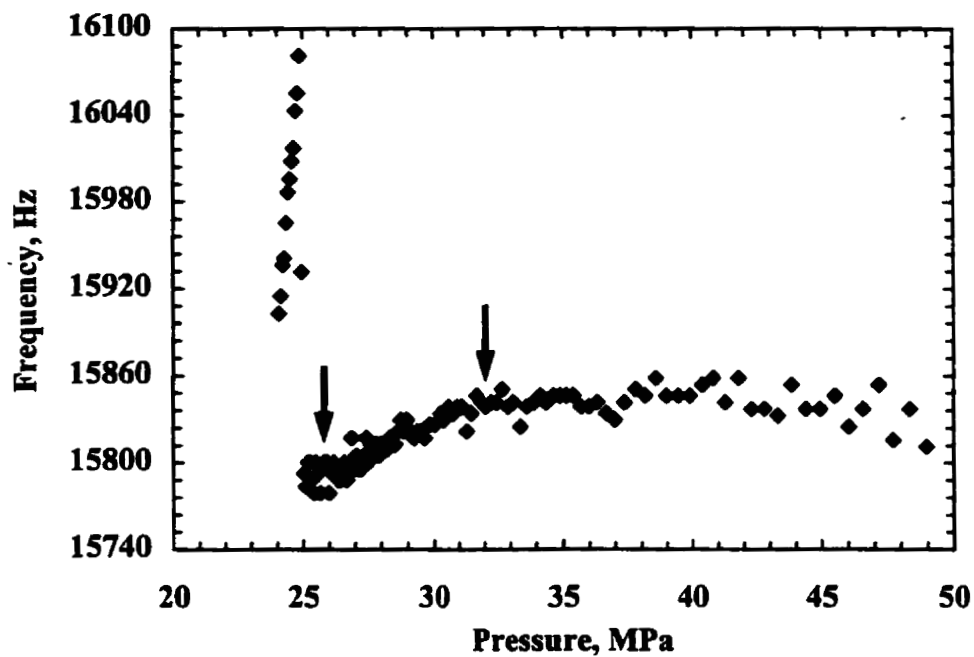


Figure 4.6: Frequency versus pressure  
for Mixture A (67°C) (Peak 3)

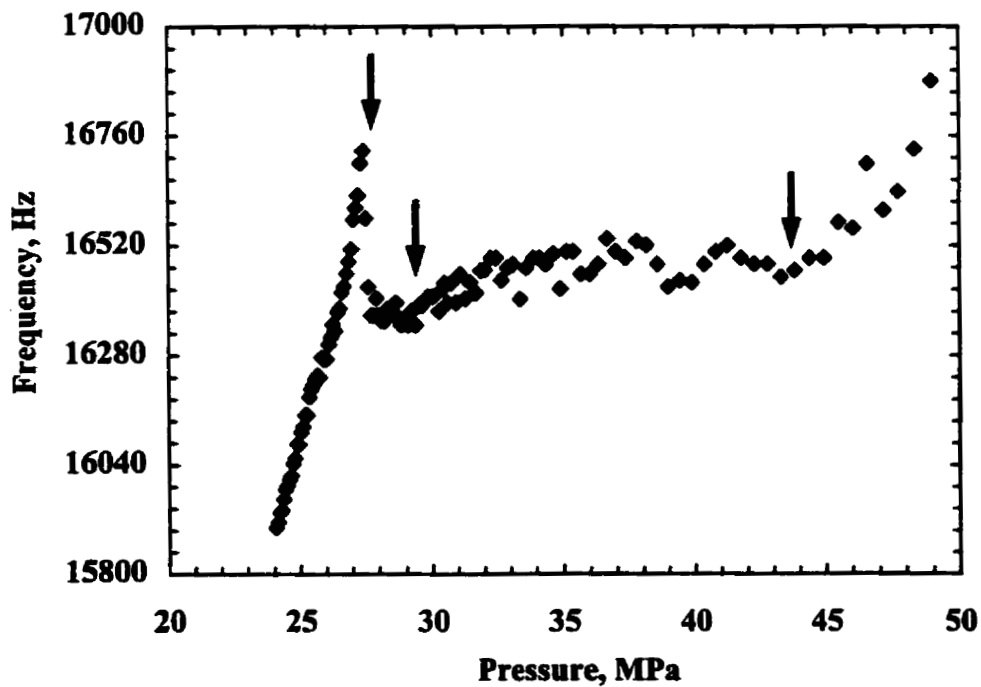


Figure 4.7: Frequency versus pressure  
for Mixture A (67°C) (Peak 4)

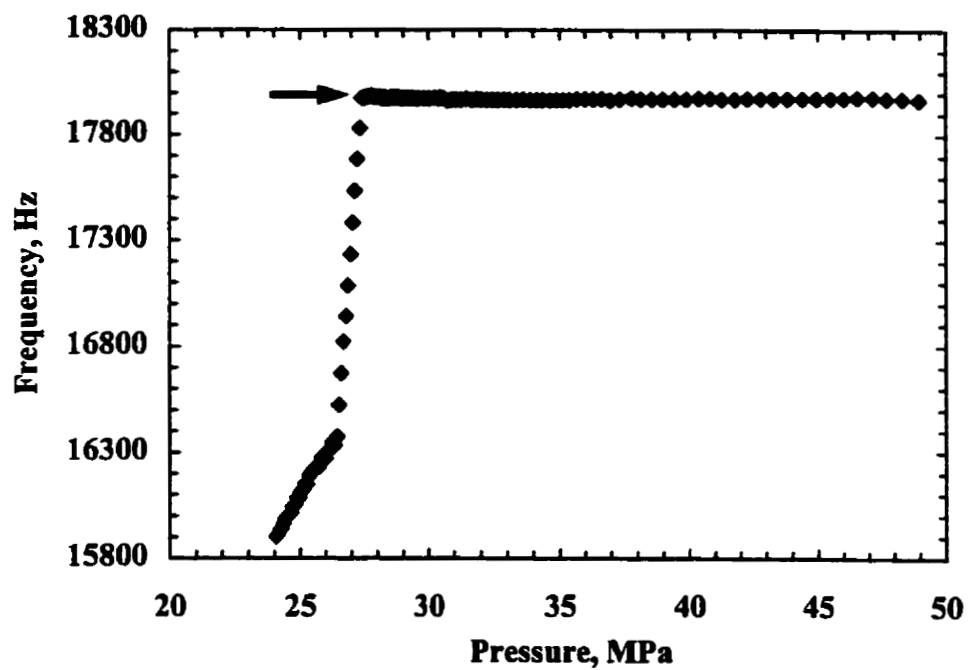


Figure 4.8: Frequency versus pressure  
for Mixture A (67°C) (Peak 5)

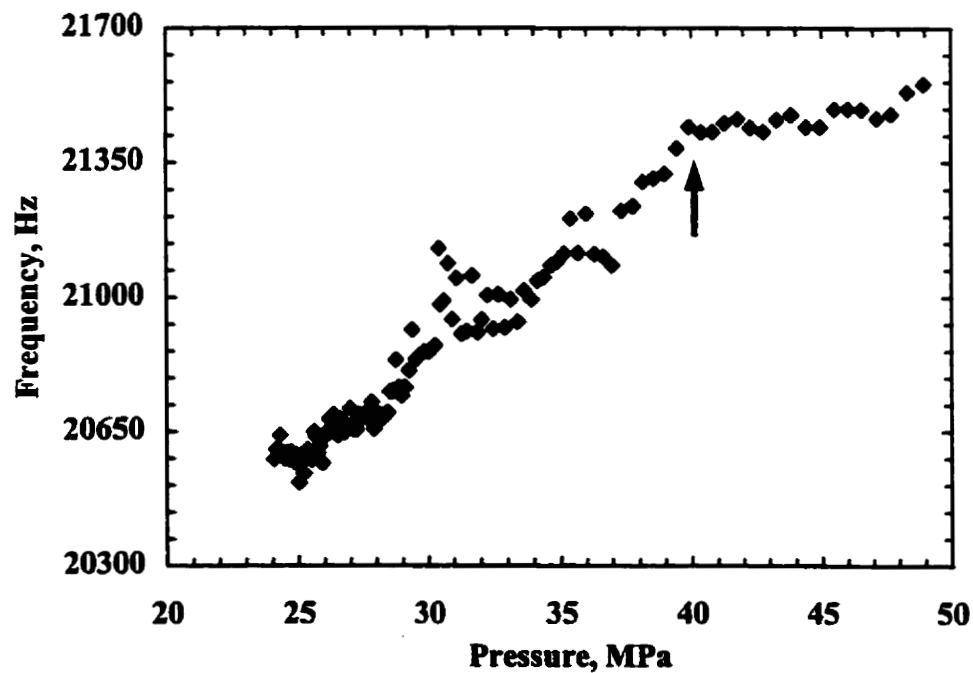
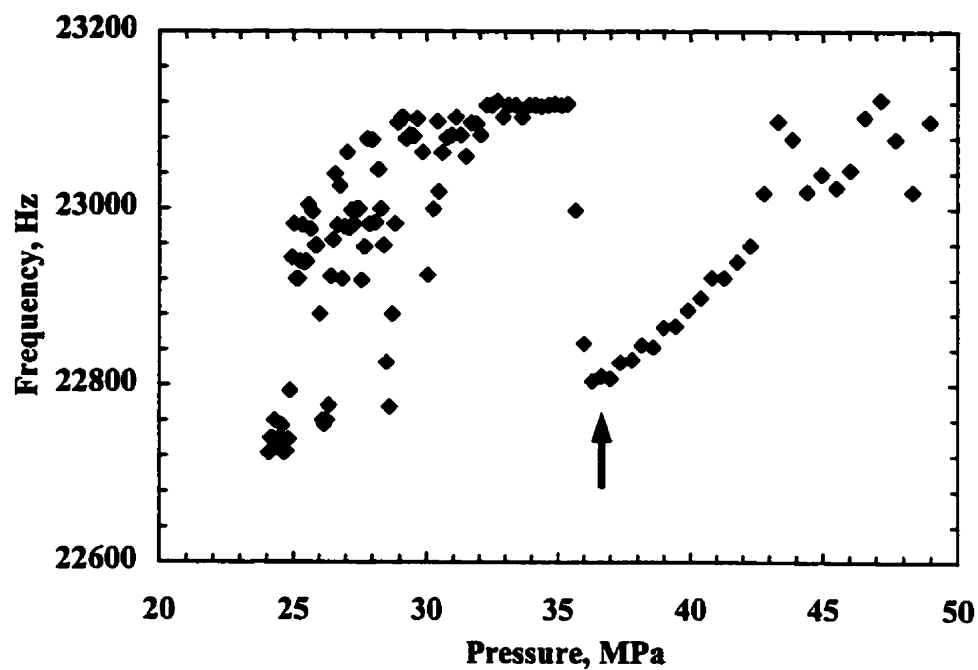
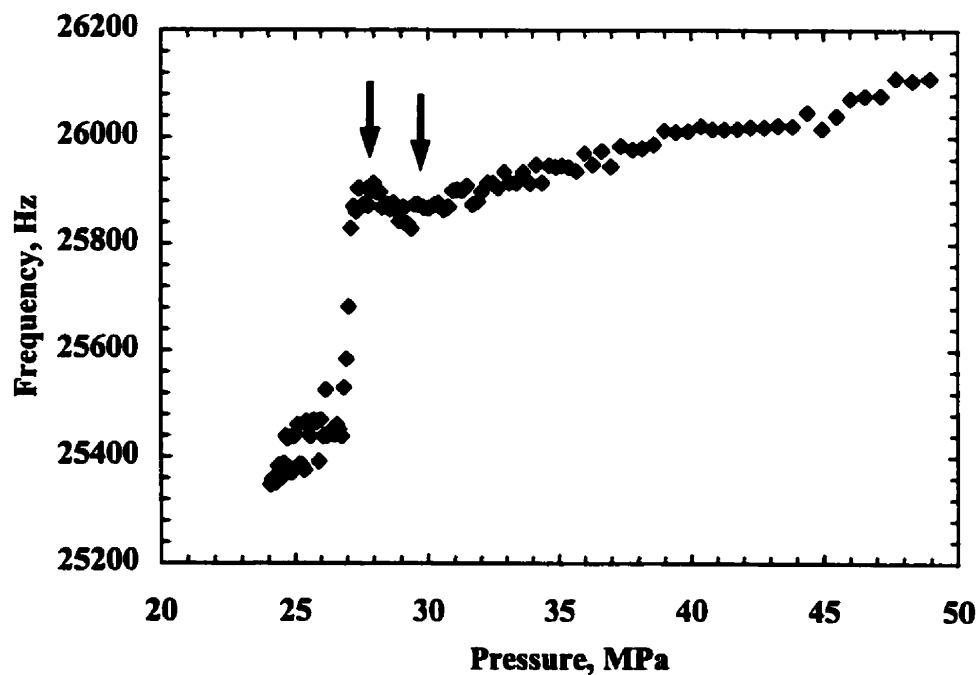


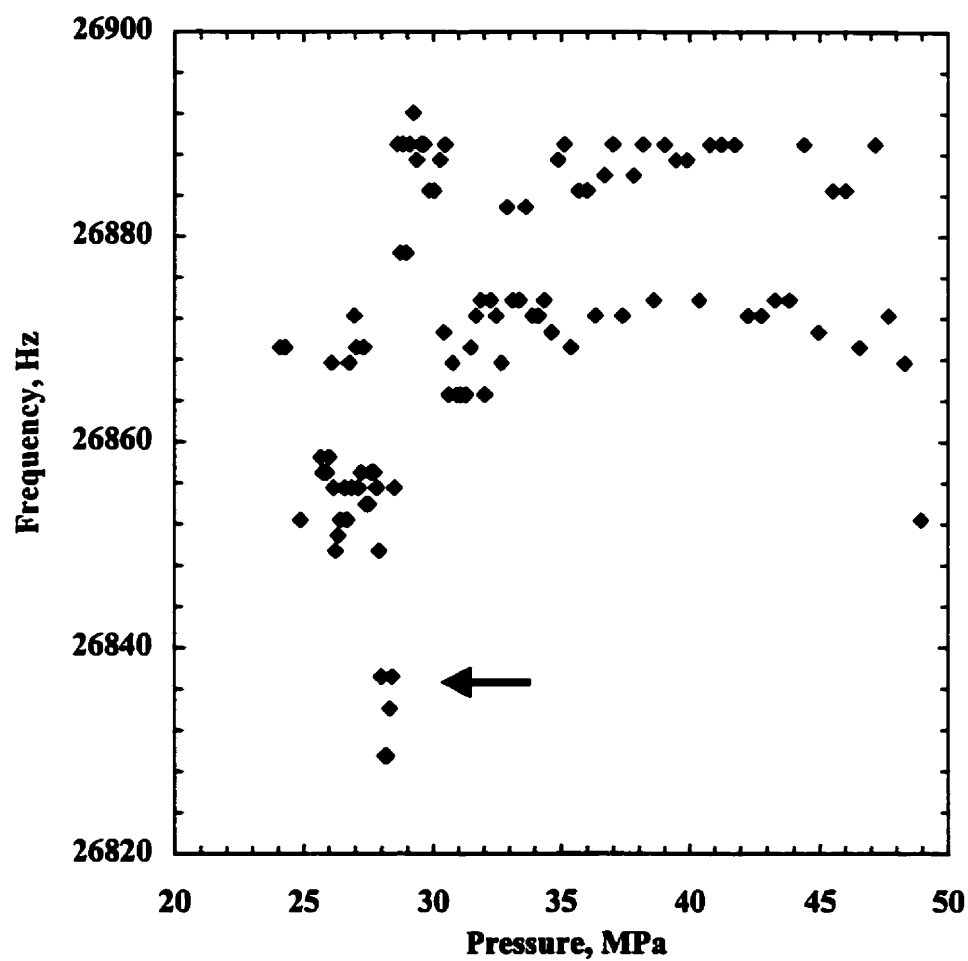
Figure 4.9: Frequency versus pressure  
for Mixture A (67°C) (Peak 6)



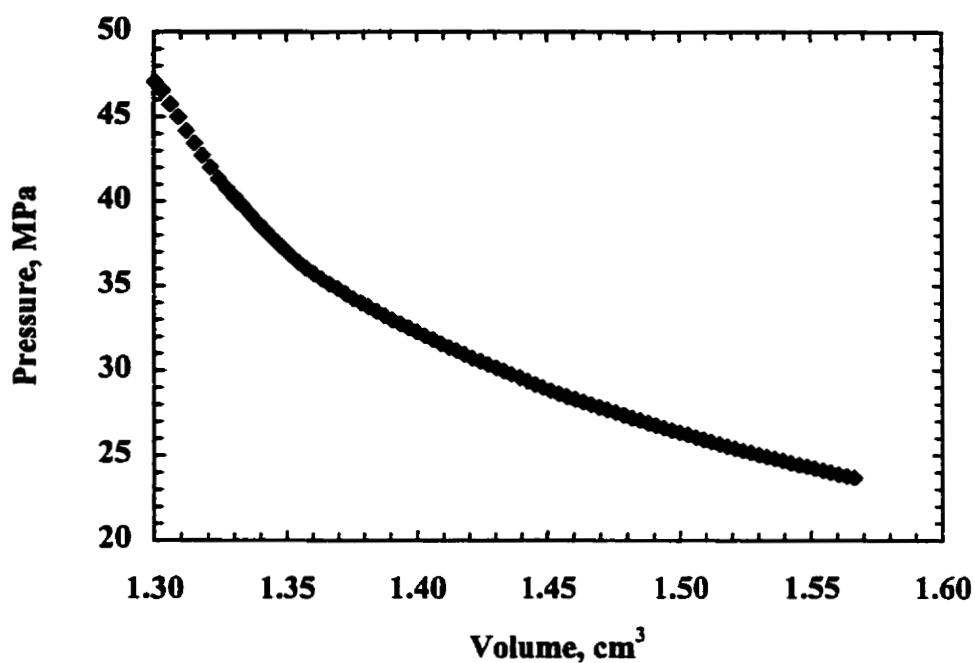
**Figure 4.10: Frequency versus pressure  
for Mixture A (67°C) (Peak 7)**



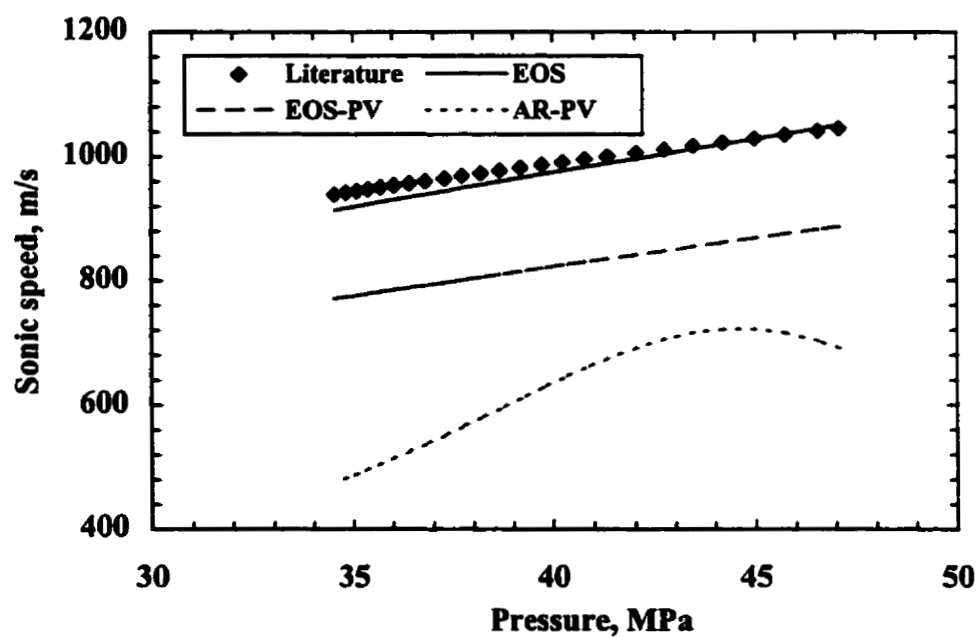
**Figure 4.11: Frequency versus pressure  
for Mixture A (67°C) (Peak 8)**



**Figure 4.12: Frequency versus pressure  
for Mixture A (67°C) (Peak 9)**



**Figure 4.13: Pressure-volume relation  
for Mixture A (100°C)**



**Figure 4.14: Sonic speed versus pressure for Mixture A  
(100°C) (Literature, Ye et al. (1992); EOS, predicted  
from EOS; EOS-PV, calculated from EOS predicted  
PV; AR-PV, calculated from AR measured PV)**

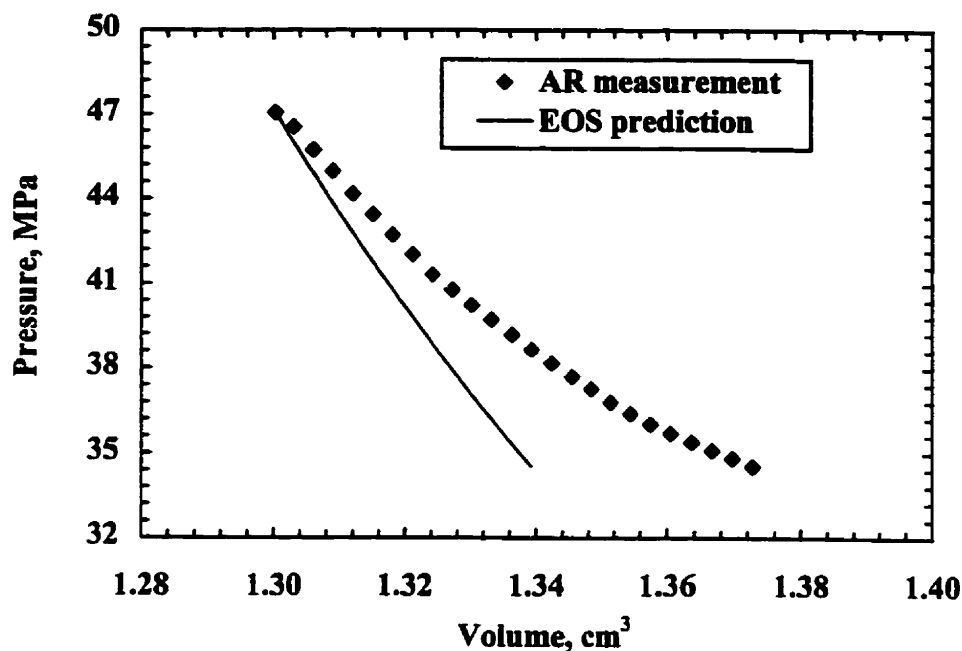


Figure 4.15: Pressure-volume relation for Mixture A (100°C)

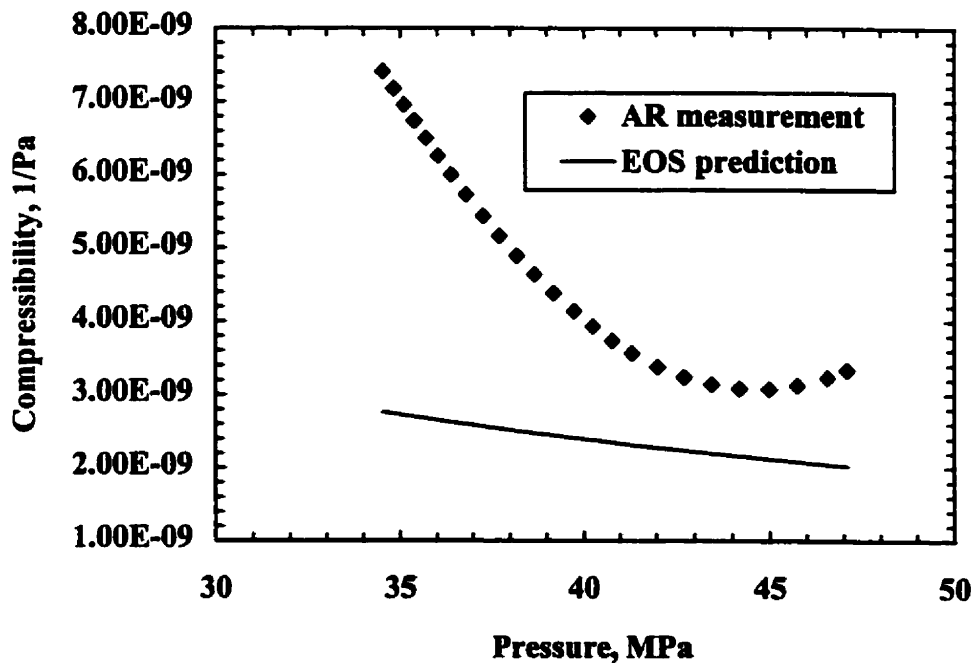
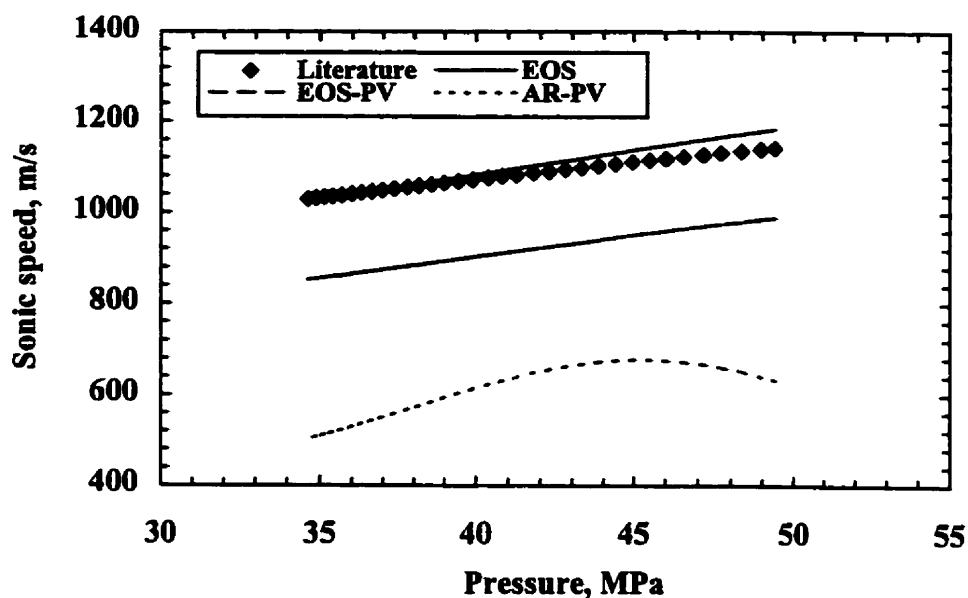
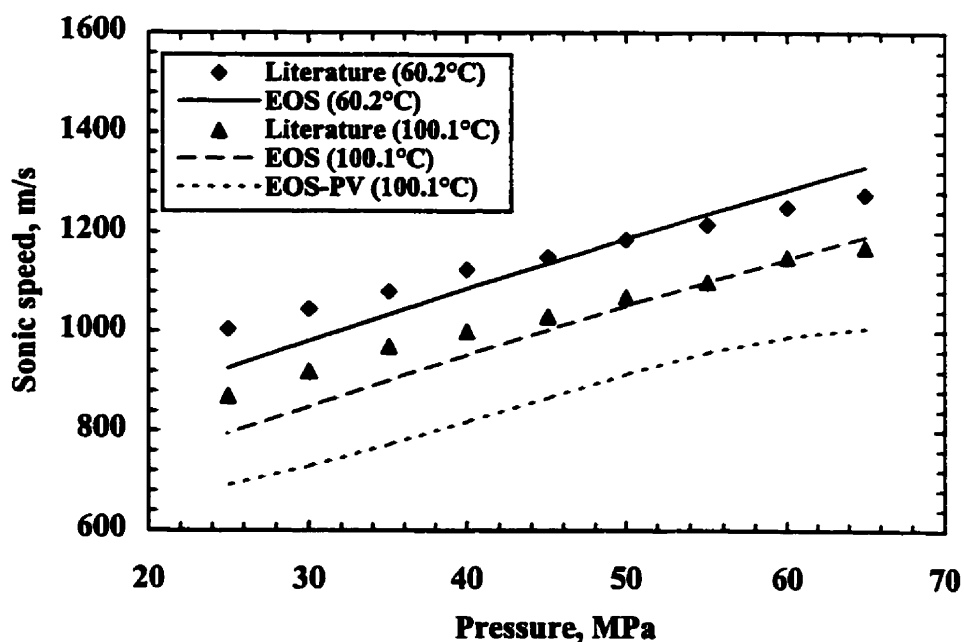


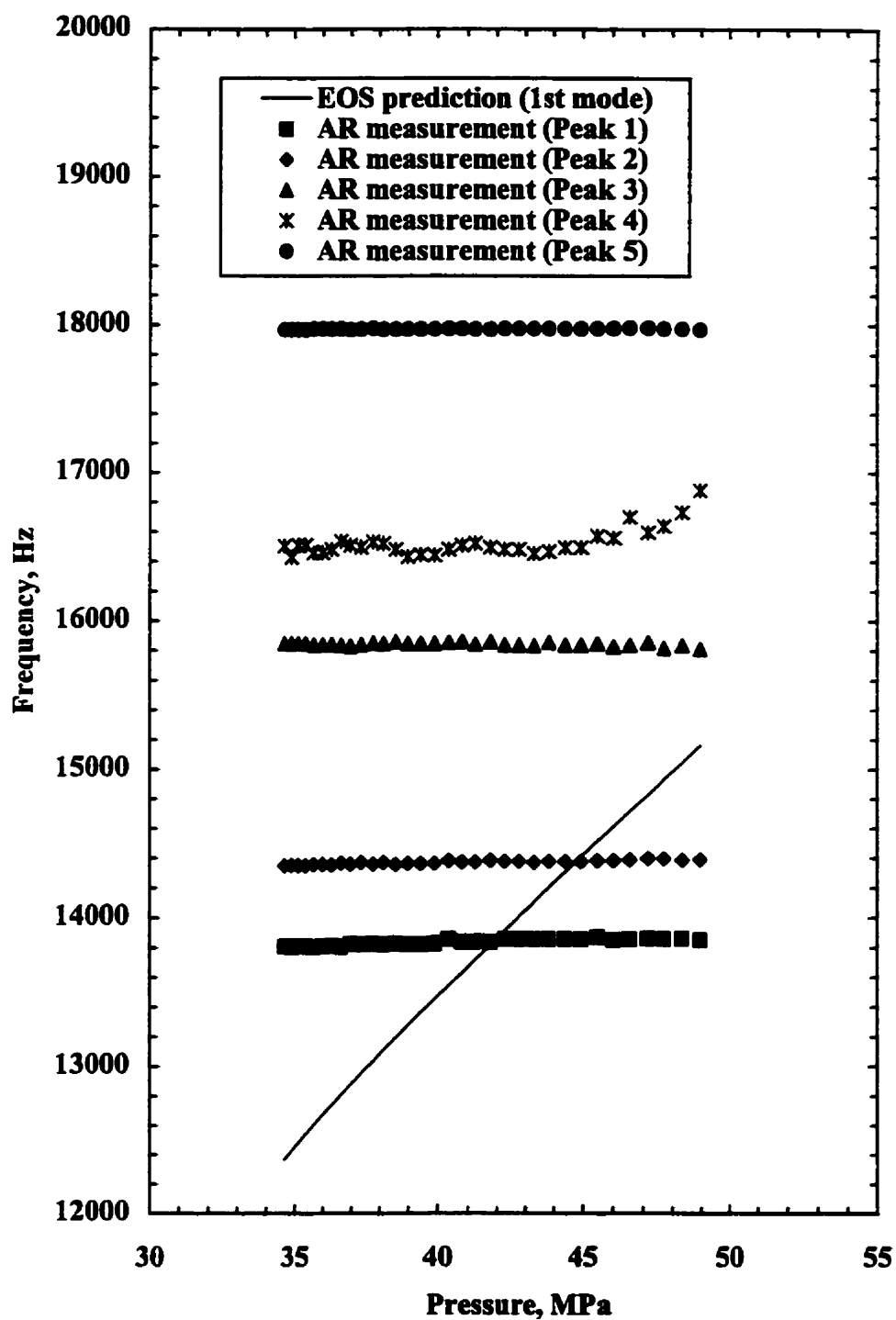
Figure 4.16: Isothermal compressibility versus pressure for Mixture A (100°C)



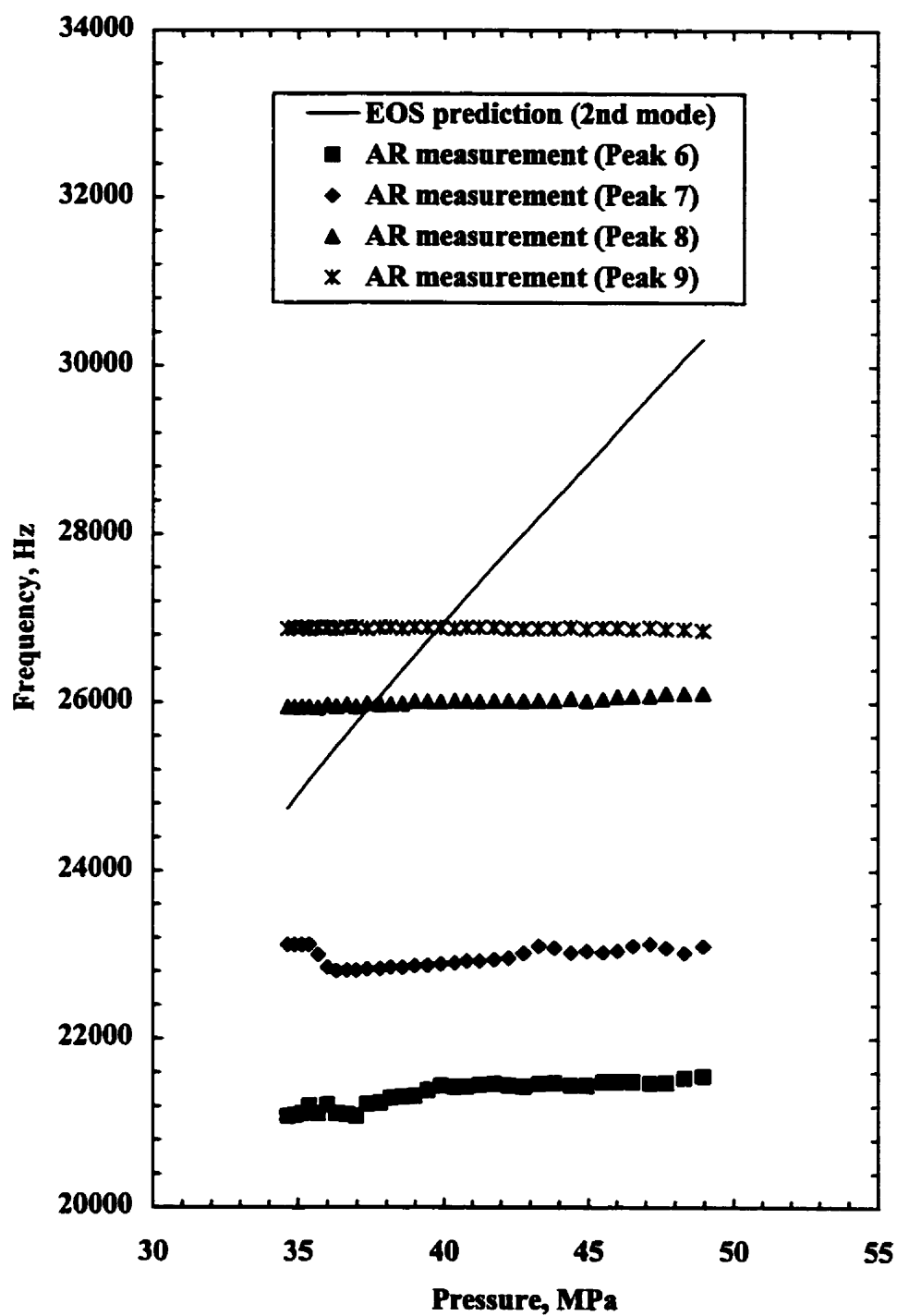
**Figure 4.17: Sonic speed versus pressure for Mixture A (67°C) (Literature, Ye et al. (1992); EOS, predicted from EOS; EOS-PV, calculated from EOS predicted PV; AR-PV, calculated from AR measured PV)**



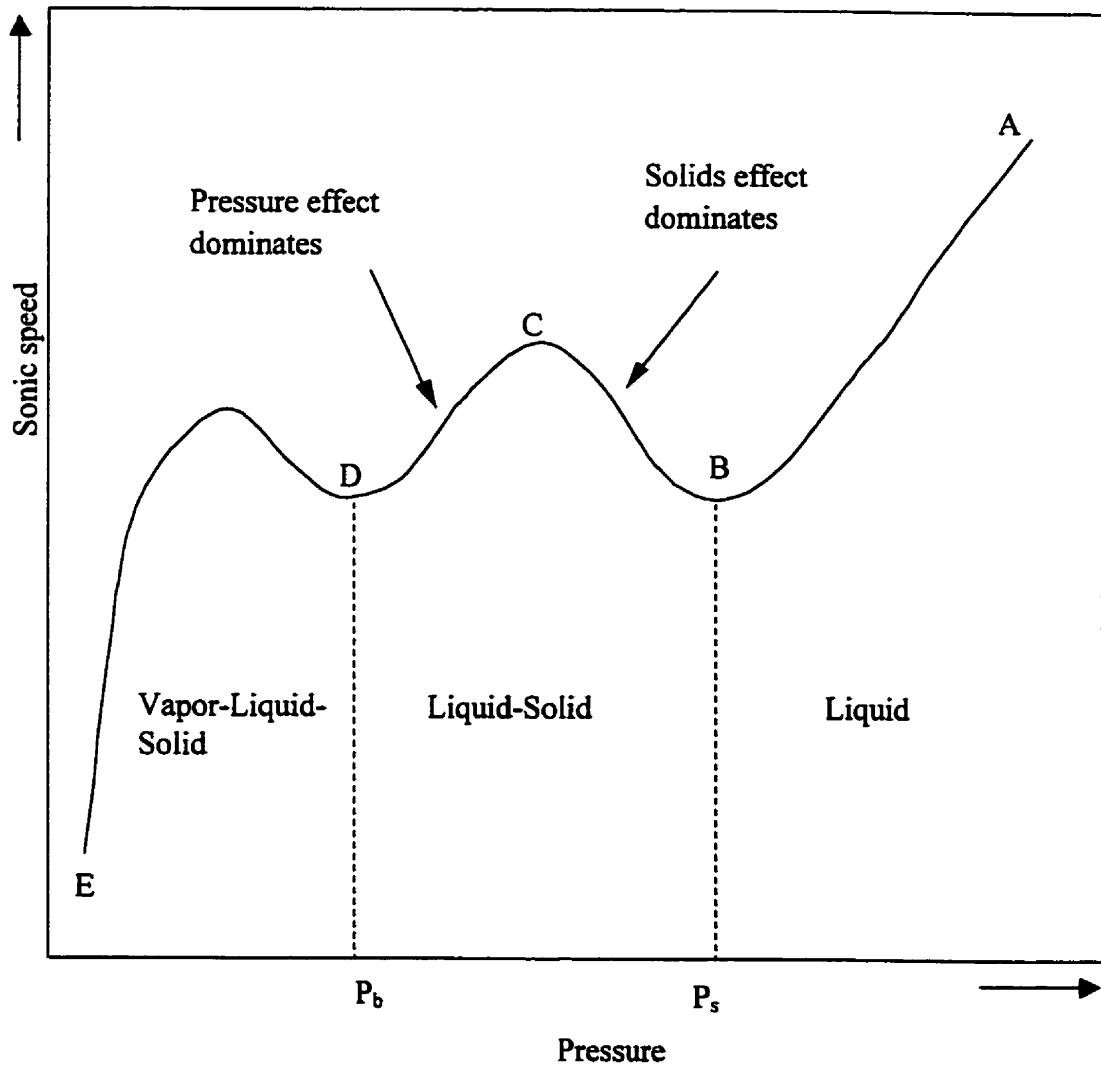
**Figure 4.18: Sonic speed versus pressure for Mixture B (Literature, Ye et al. (1991); EOS, predicted from EOS; EOS-PV, calculated from EOS predicted PV)**



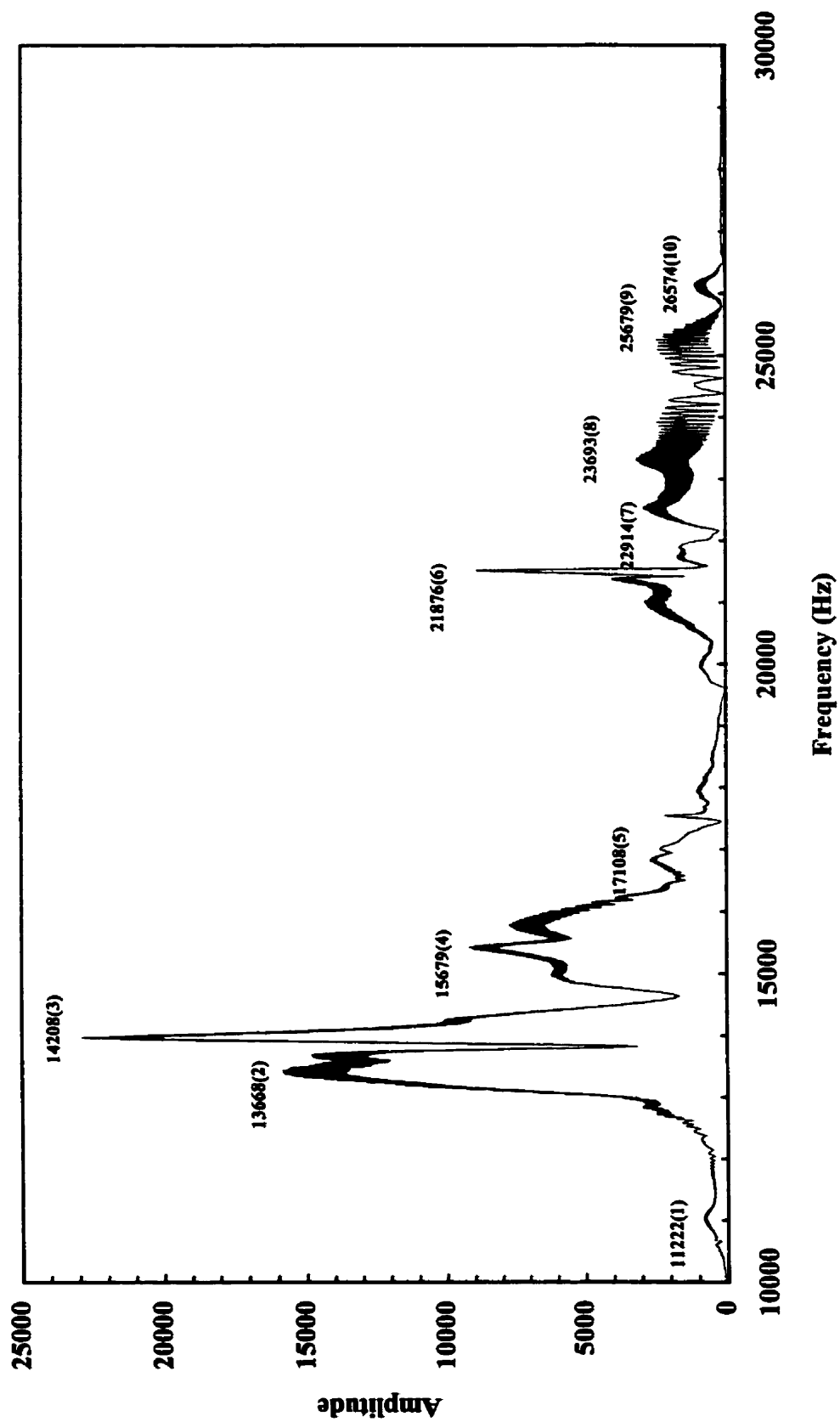
**Figure 4.19: Frequency versus pressure  
for Mixture A (67°C)**



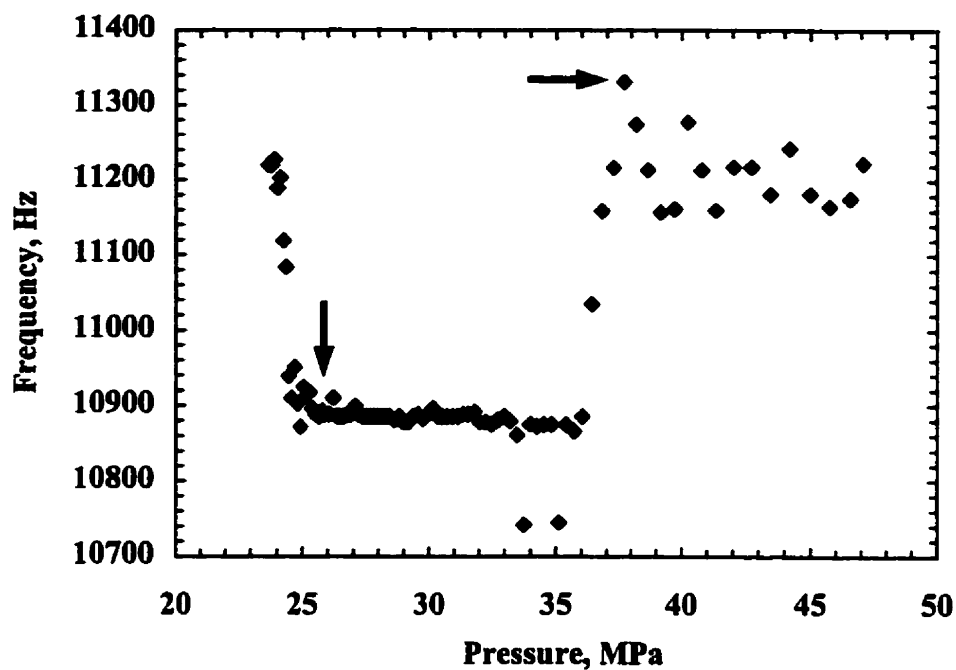
**Figure 4.20: Frequency versus pressure  
for Mixture A (67°C)**



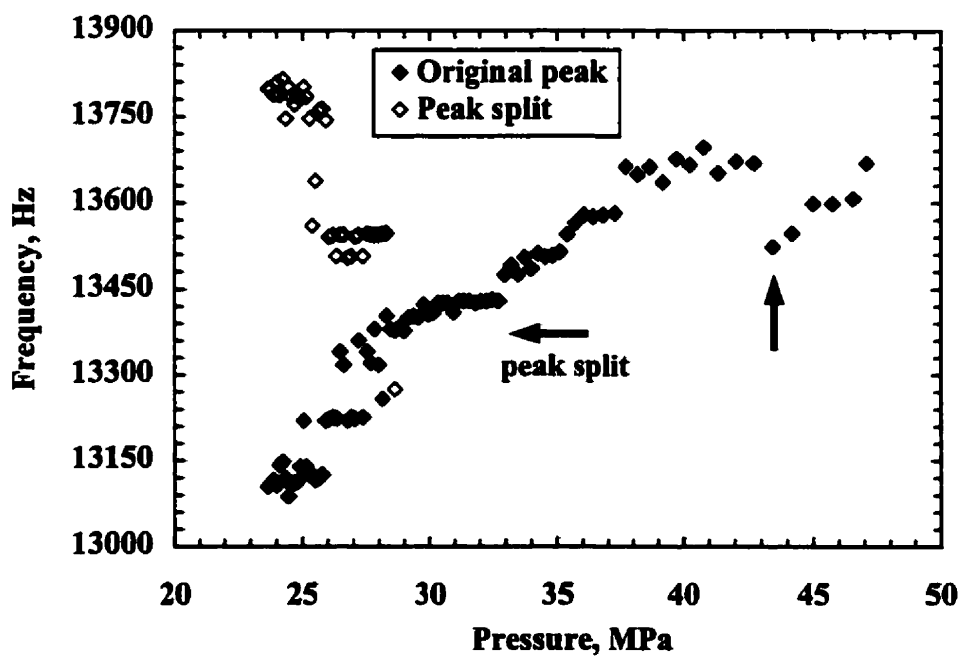
**Figure 4.21: Change of sonic speed with pressure**



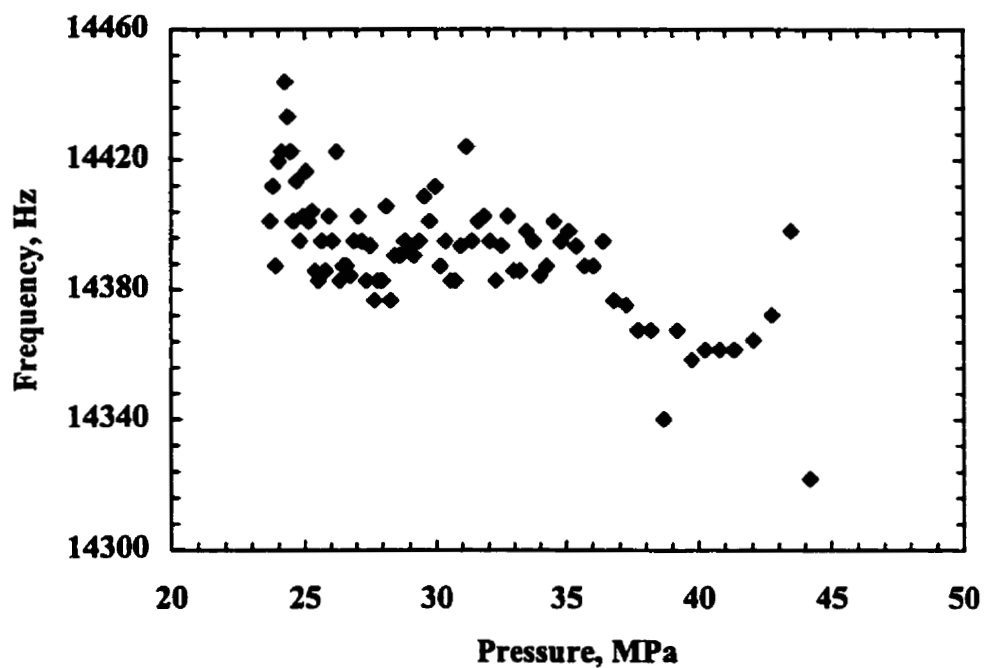
**Figure 4.22: Frequency spectrum for Mixture A (100°C, 47.08MPa)**



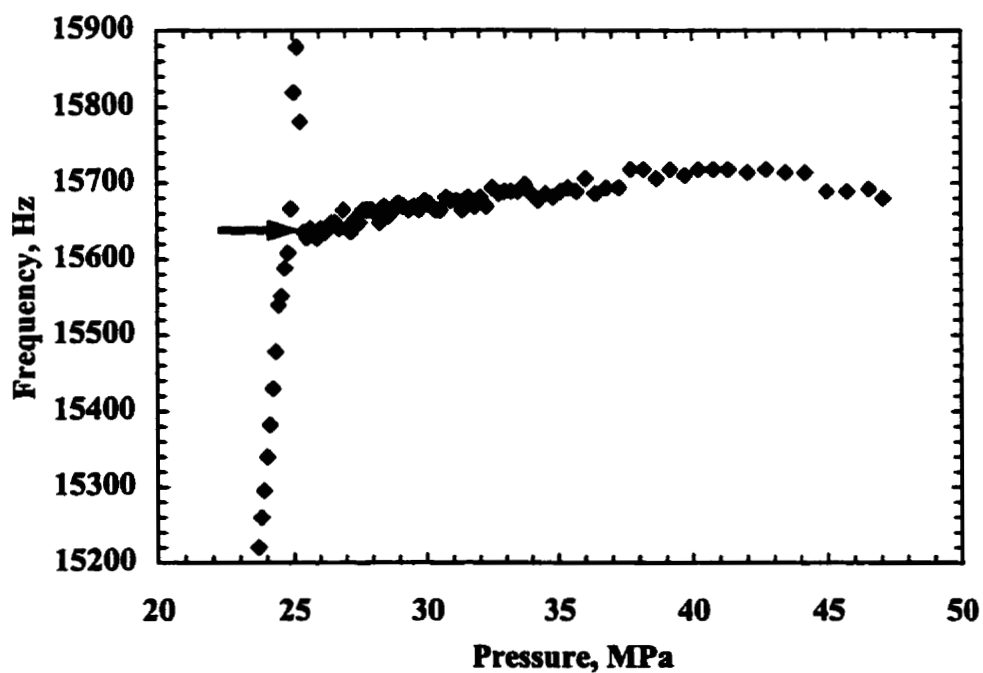
**Figure 4.23: Frequency versus pressure  
for Mixture A (100°C) (Peak 1)**



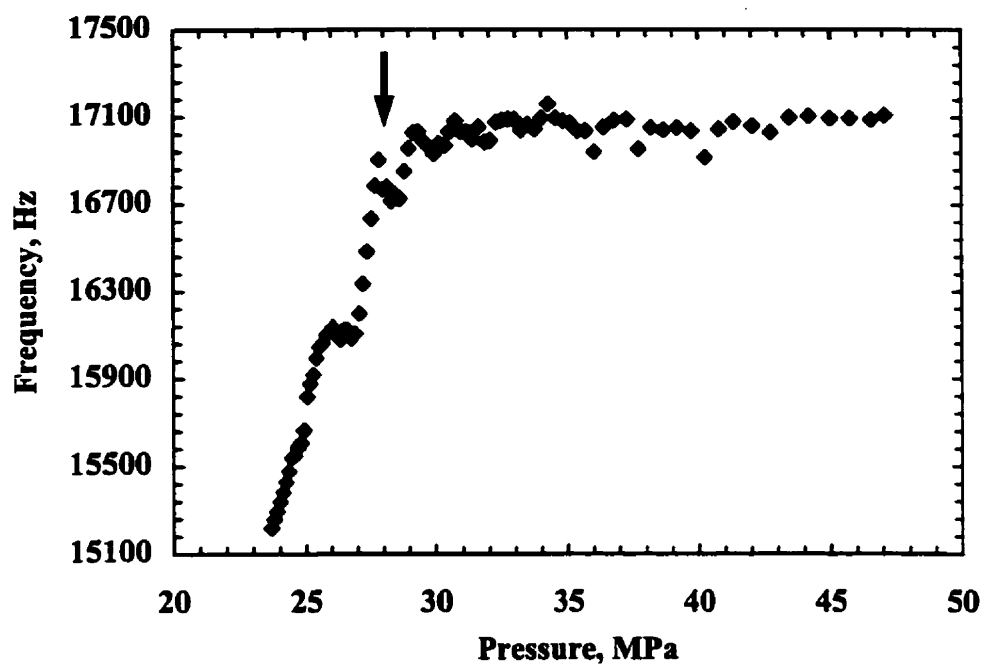
**Figure 4.24: Frequency versus pressure  
for Mixture A (100°C) (Peak 2)**



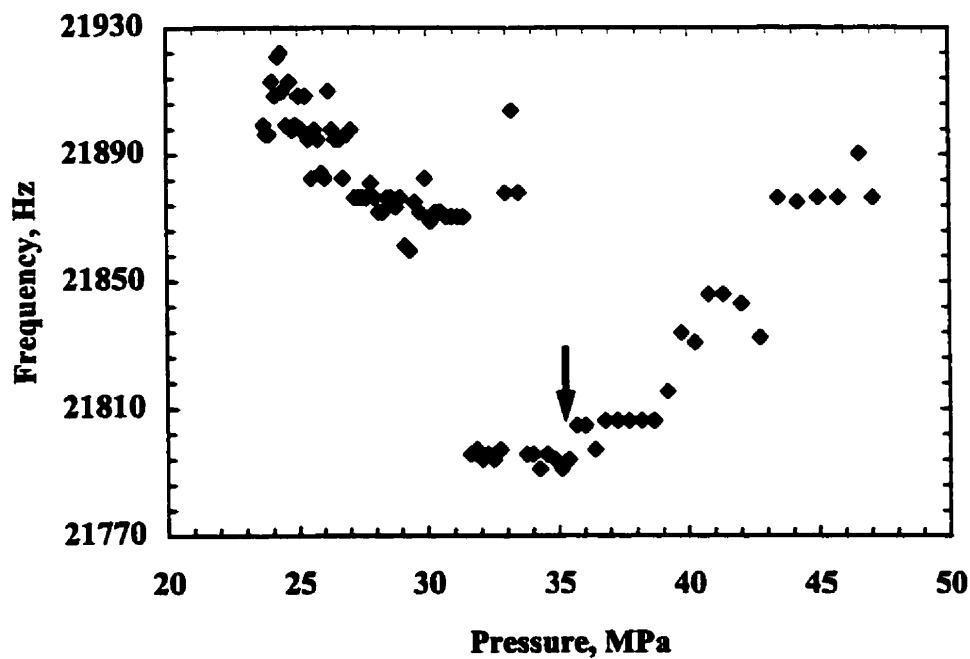
**Figure 4.25: Frequency versus pressure  
for Mixture A (100°C) (Peak 3)**



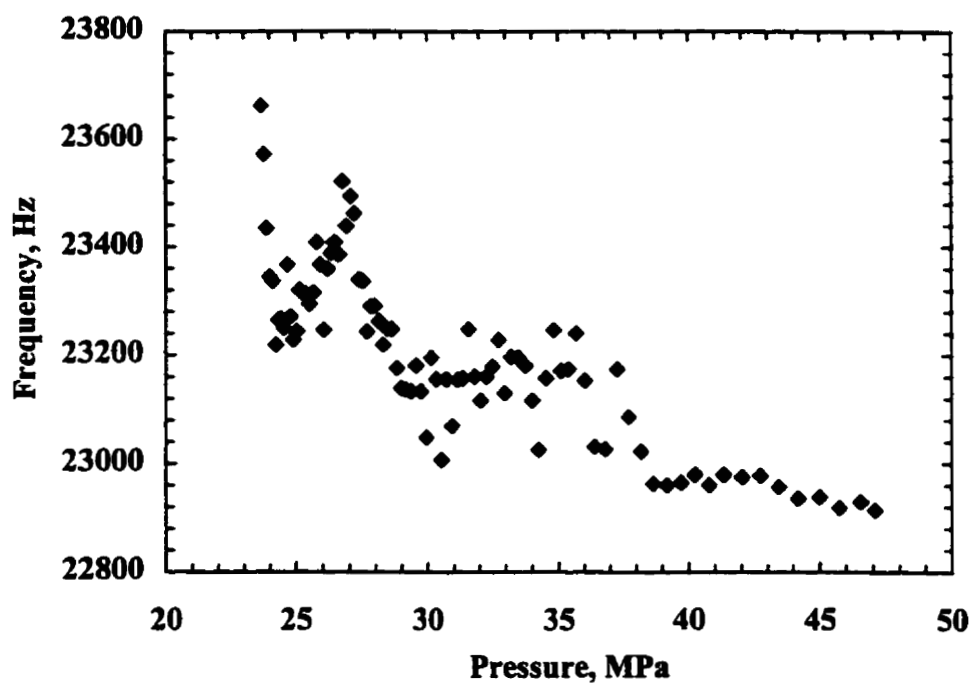
**Figure 4.26: Frequency versus pressure  
for Mixture A (100°C) (Peak 4)**



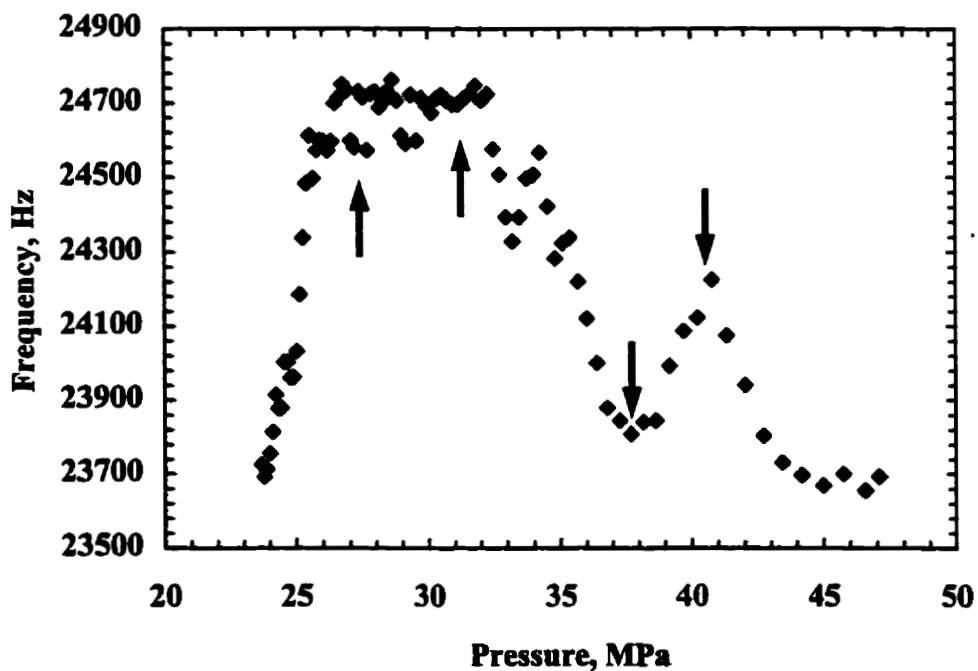
**Figure 4.27: Frequency versus pressure  
for Mixture A (100°C) (Peak 5)**



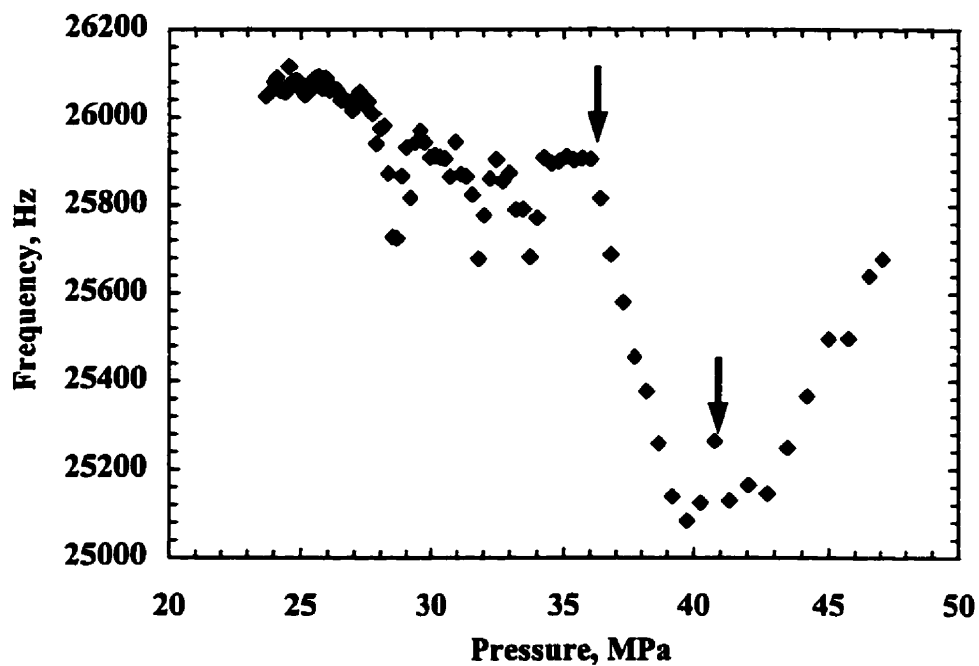
**Figure 4.28: Frequency versus pressure  
for Mixture A (100°C) (Peak 6)**



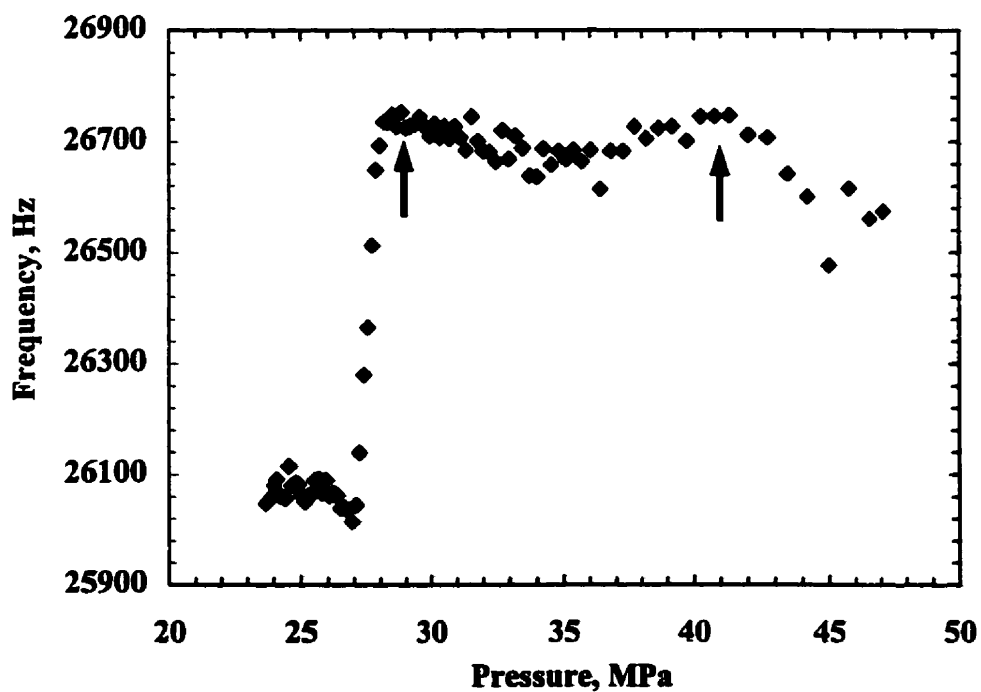
**Figure 4.29: Frequency versus pressure  
for Mixture A (100°C) (Peak 7)**



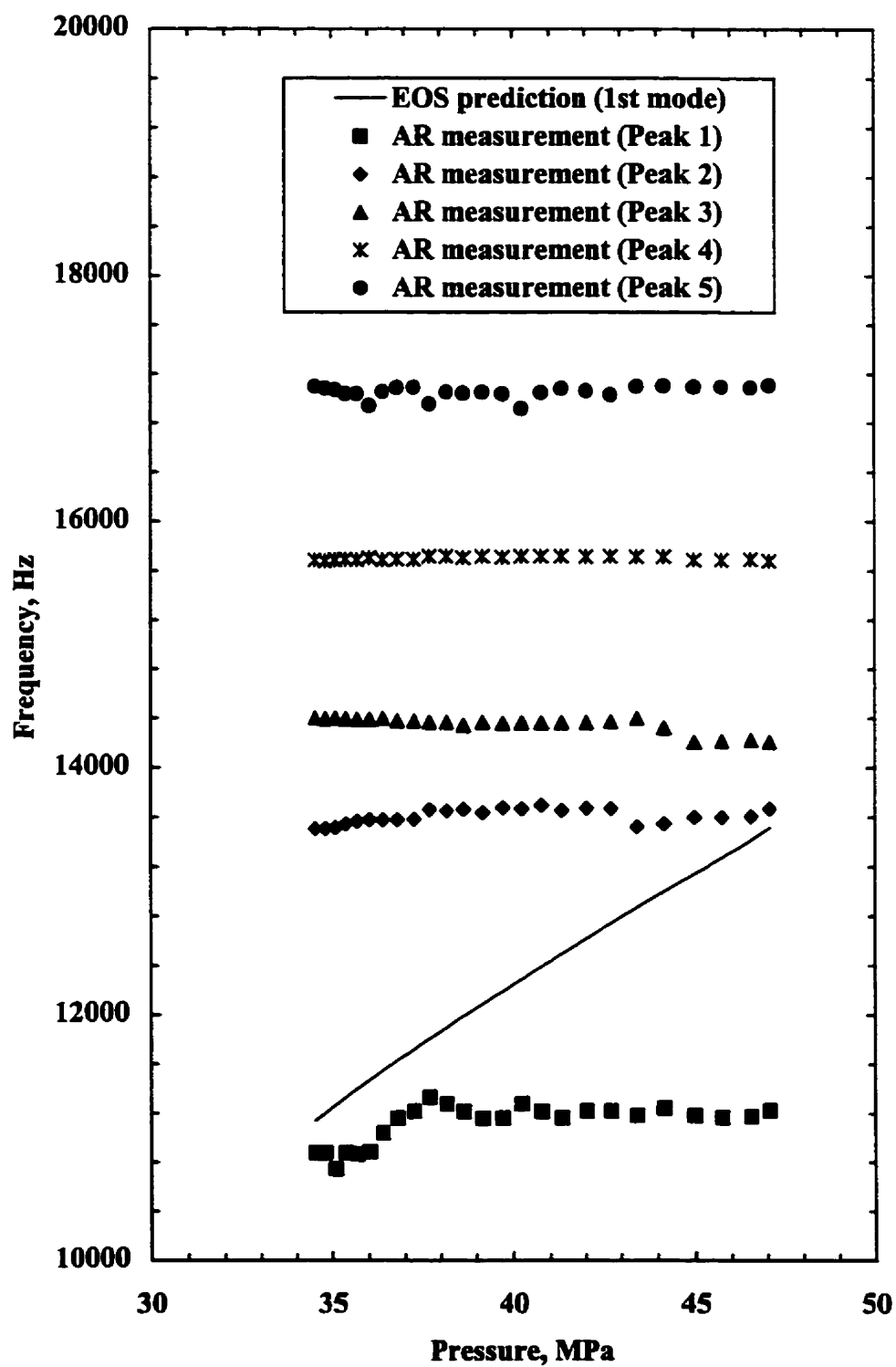
**Figure 4.30: Frequency versus pressure  
for Mixture A (100°C) (Peak 8)**



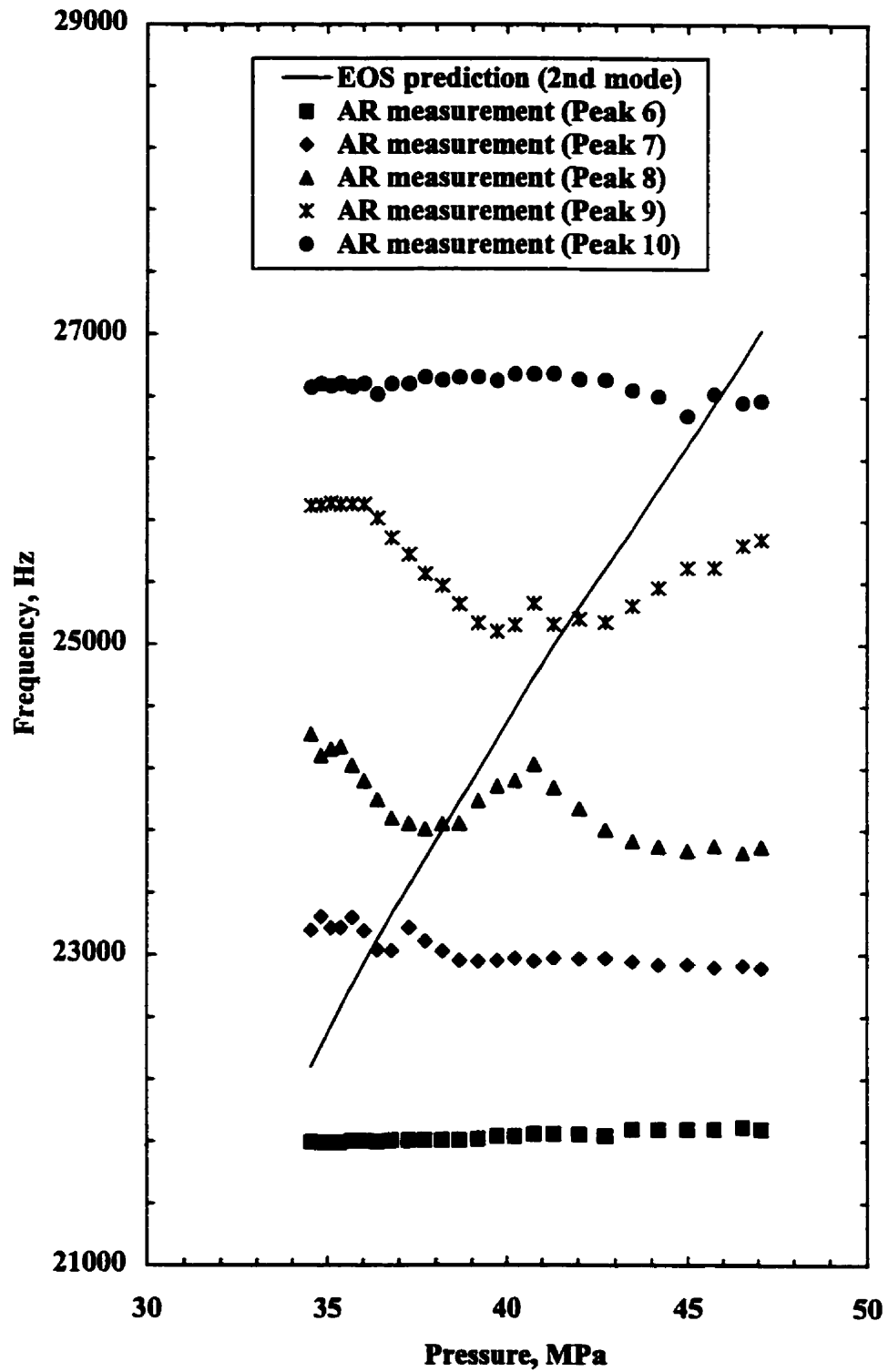
**Figure 4.31: Frequency versus pressure  
for Mixture A (100°C) (Peak 9)**



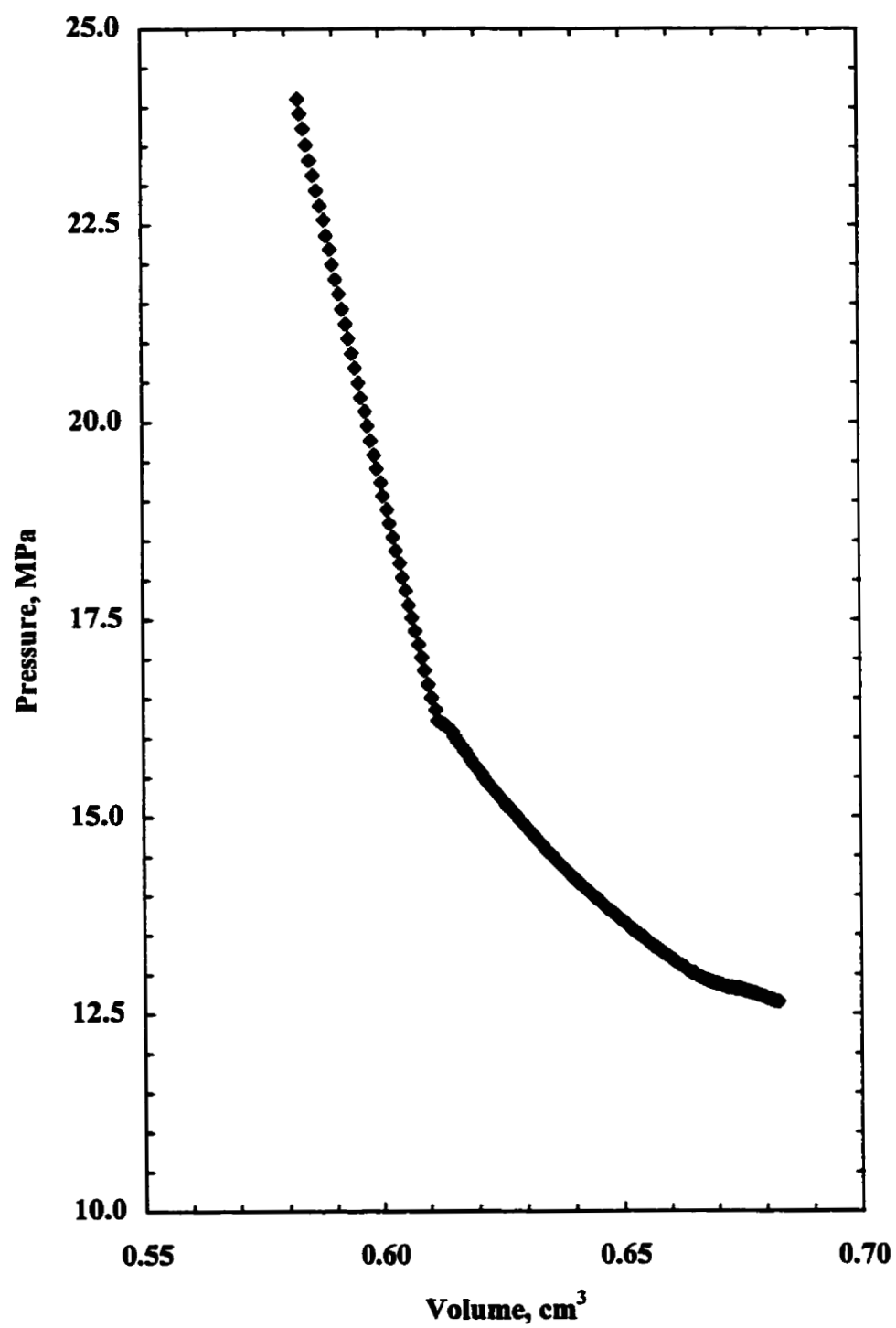
**Figure 4.32: Frequency versus pressure  
for Mixture A (100°C) (Peak 10)**



**Figure 4.33: Frequency versus pressure  
for Mixture A (100°C)**



**Figure 4.34: Frequency versus pressure  
for Mixture A (100°C)**



**Figure 4.35: Pressure-volume relation  
for Mixture C (70°C)**

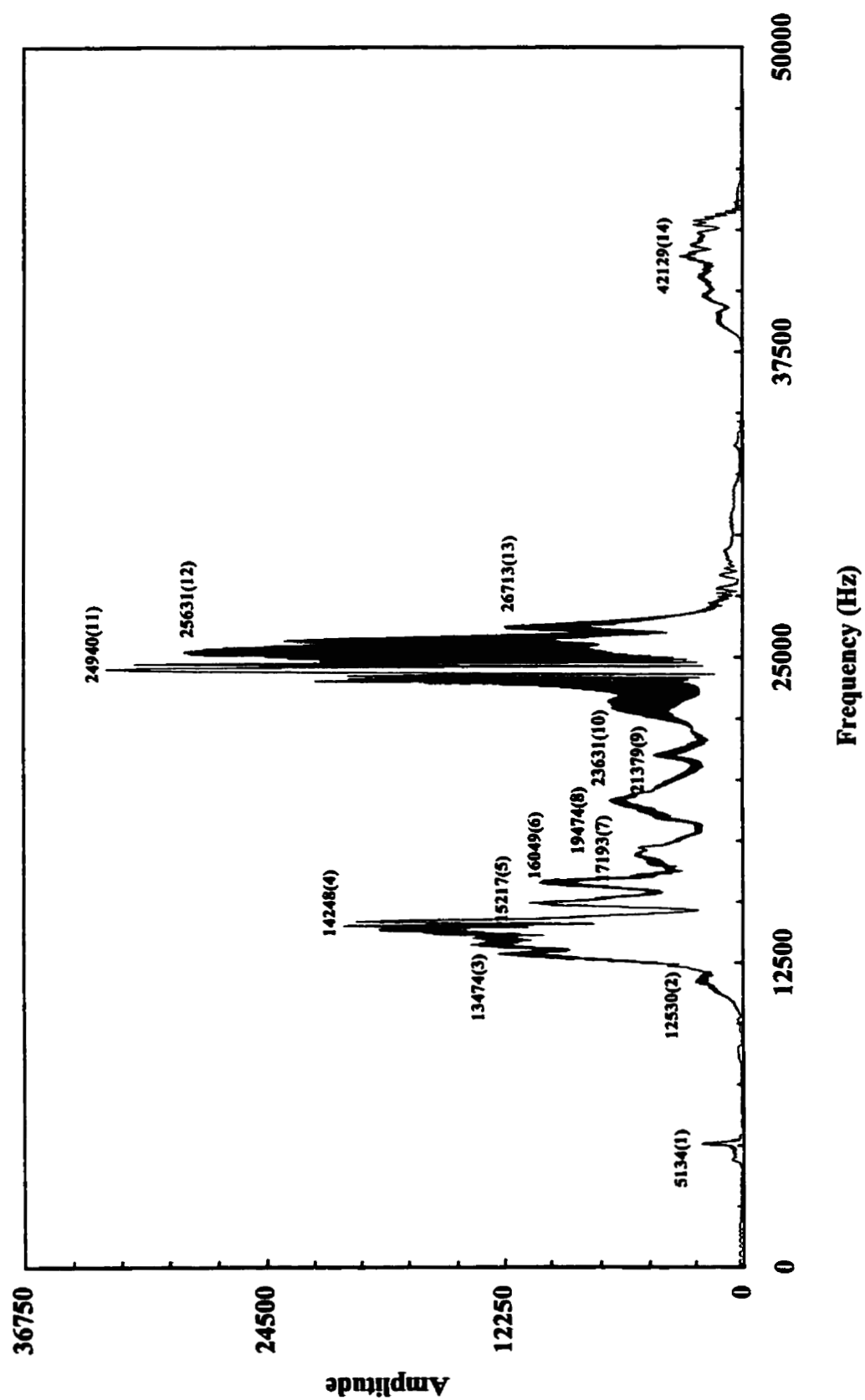
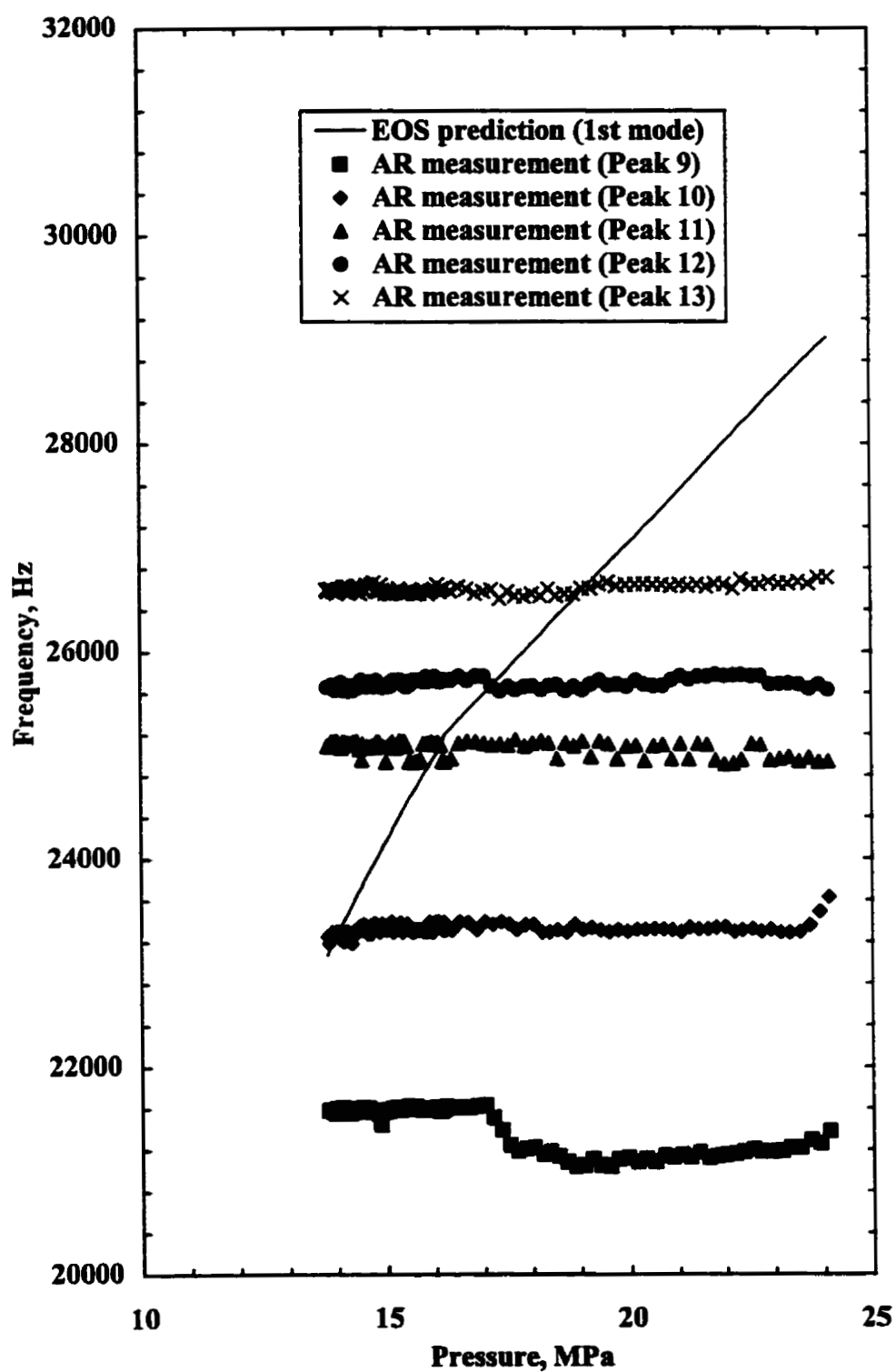
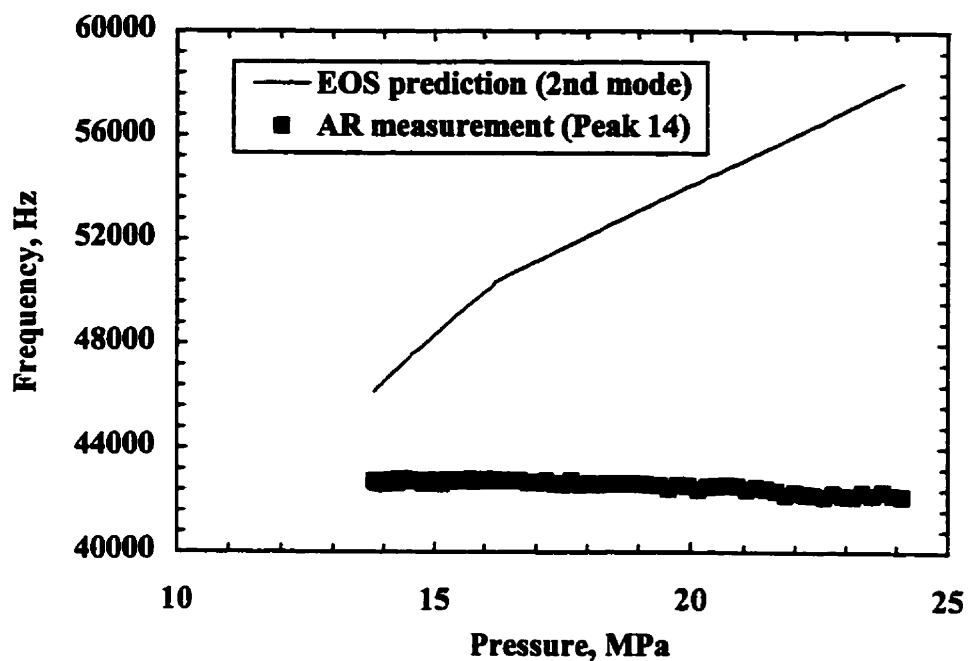


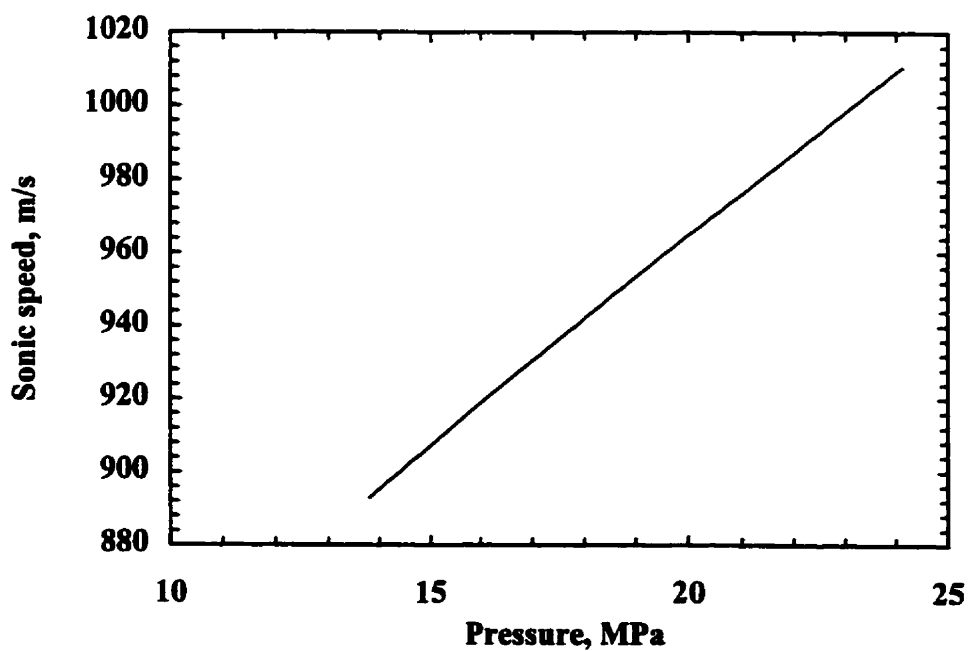
Figure 4.36: Frequency spectrum for Mixture C (70°C, 24.11MPa)



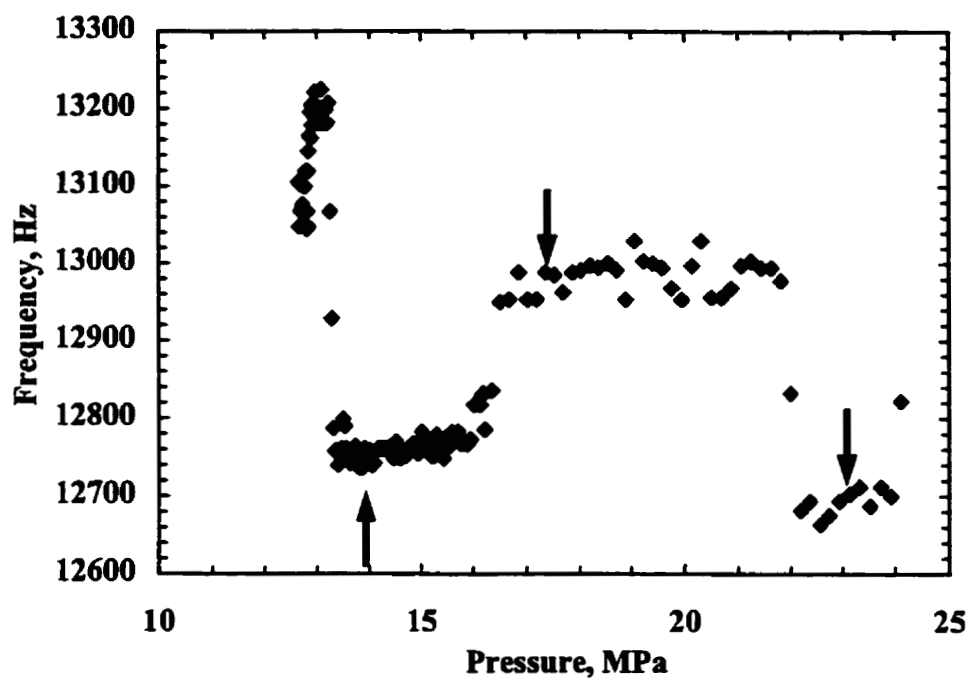
**Figure 4.37: Frequency versus pressure for Mixture C (70°C)**



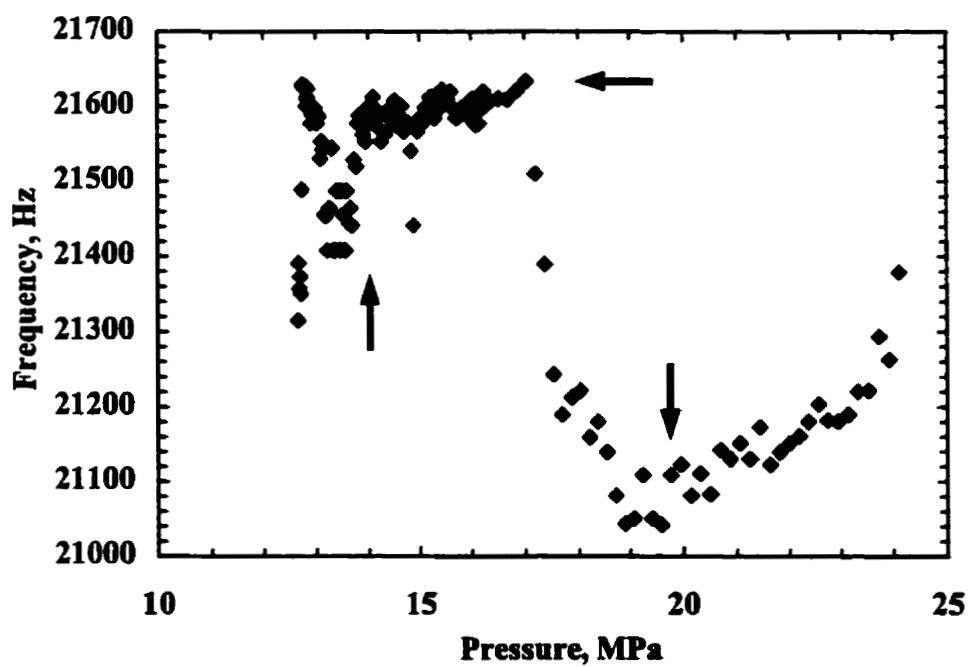
**Figure 4.38: Frequency versus pressure  
for Mixture C (70°C)**



**Figure 4.39: Sonic speed versus pressure  
for Mixture C (70°C) (EOS prediction)**



**Figure 4.40: Frequency versus pressure  
for Mixture C (70°C) (Peak 2)**



**Figure 4.41: Frequency versus pressure  
for Mixture C (70°C) (Peak 9)**

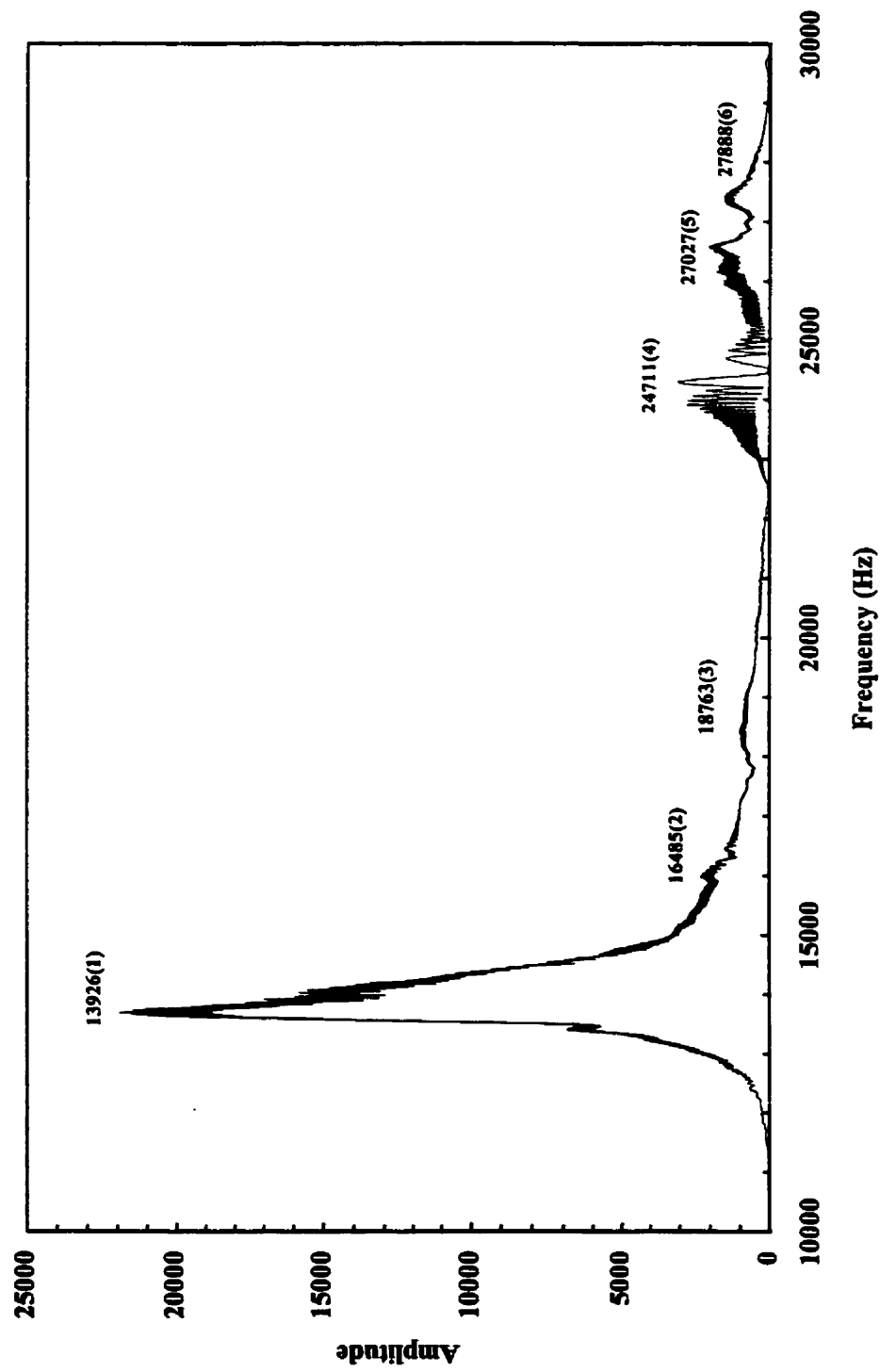


Figure 4.42: Frequency spectrum for Mixture D (99°C, 64.47MPa)

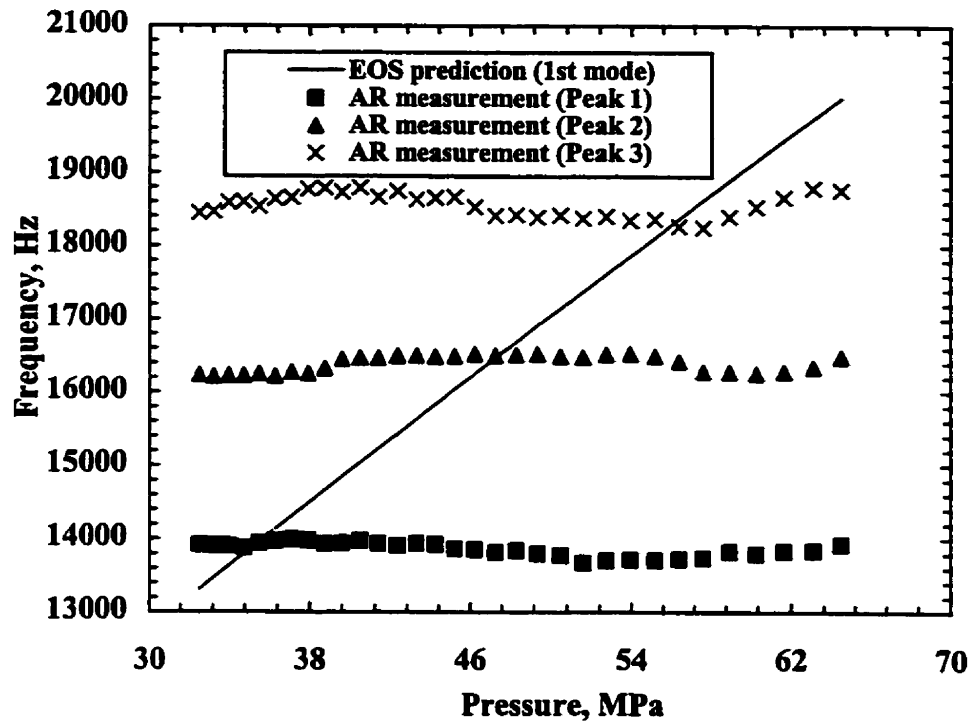


Figure 4.43: Frequency versus pressure  
for Mixture D (99°C)

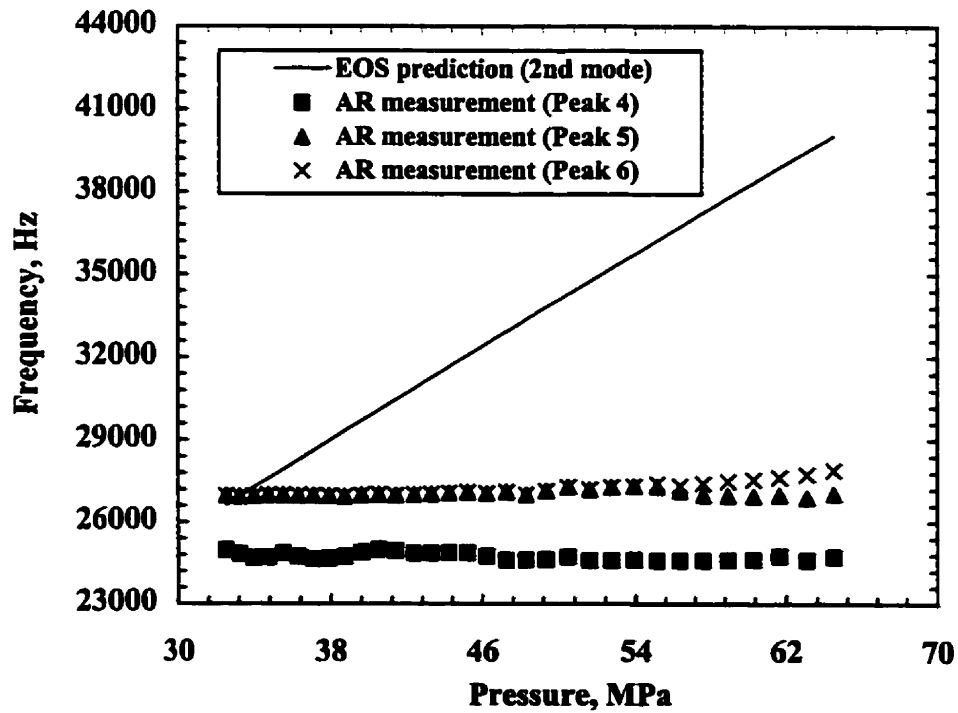
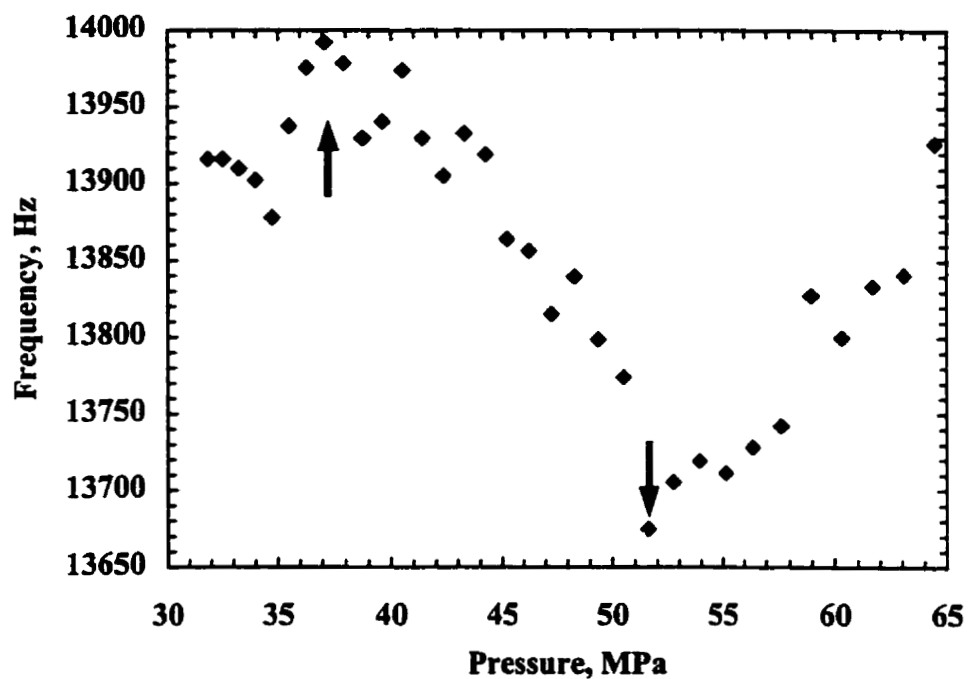
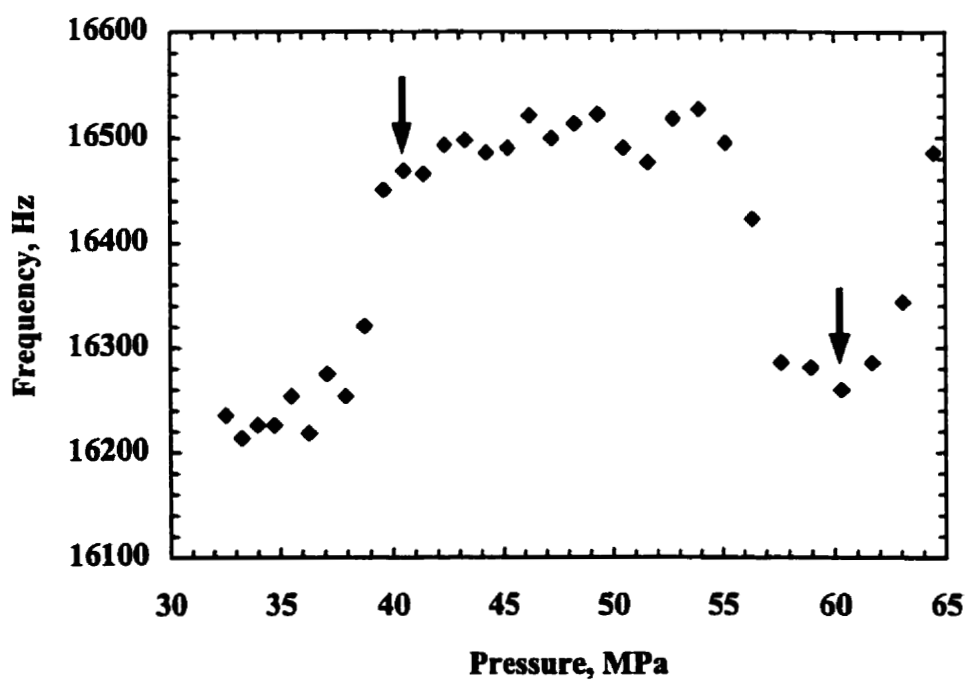


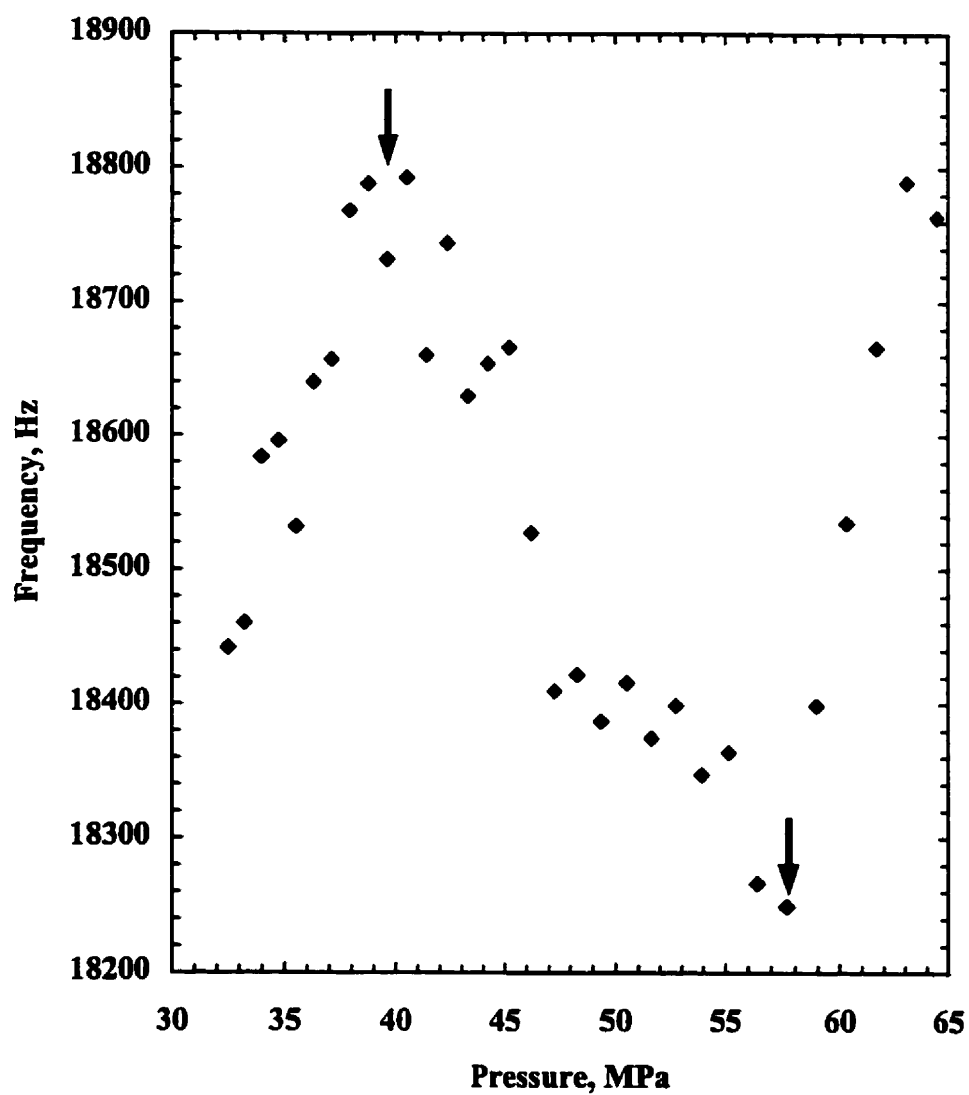
Figure 4.44: Frequency versus pressure  
for Mixture D (99°C)



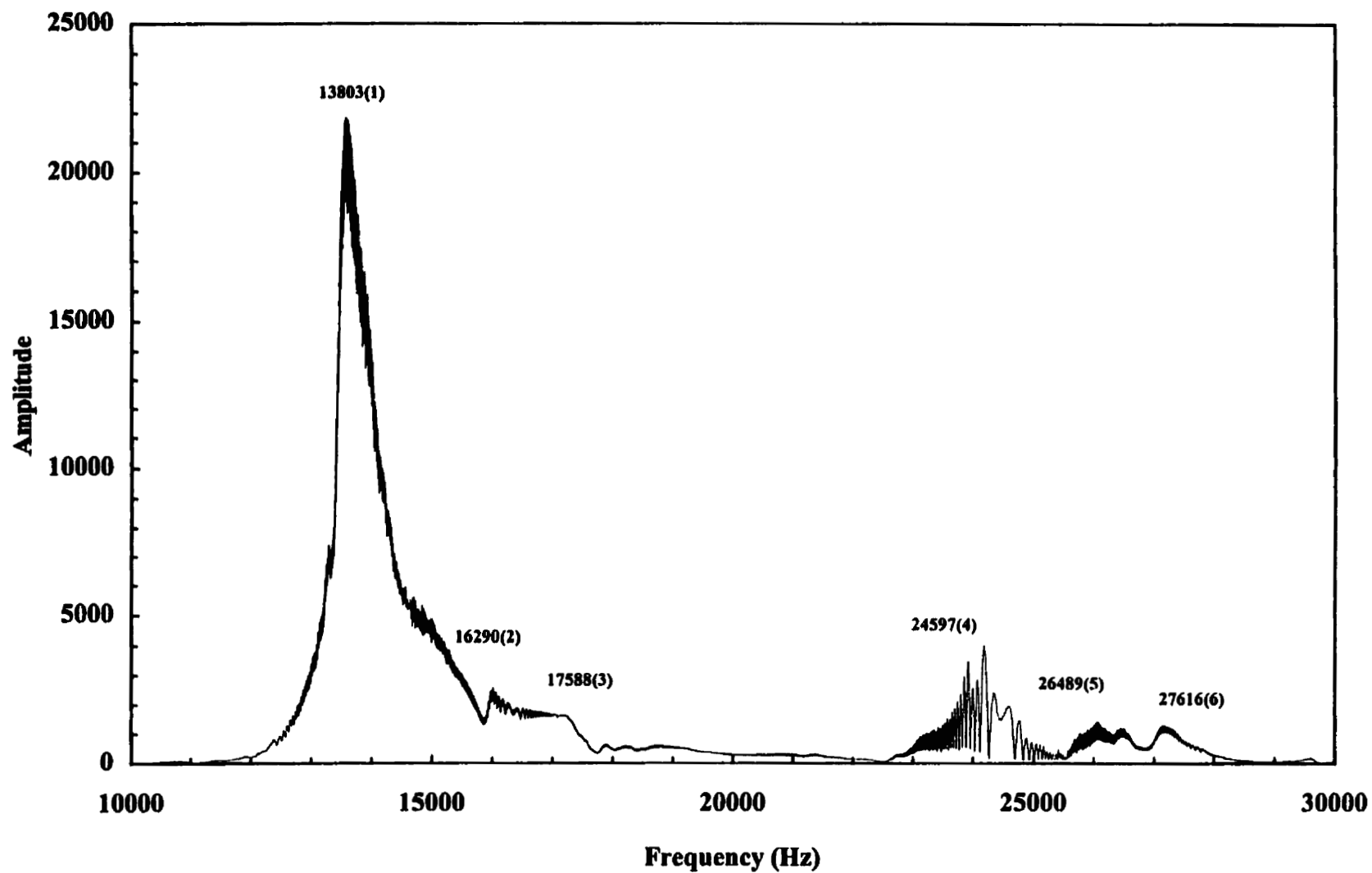
**Figure 4.45: Frequency versus pressure  
for Mixture D (99°C) (Peak 1)**



**Figure 4.46: Frequency versus pressure  
for Mixture D (99°C) (Peak 2)**



**Figure 4.47: Frequency versus pressure  
for Mixture D (99°C) (Peak 3)**



**Figure 4.48** Frequency spectrum for Mixture D (110°C, 64.01MPa)

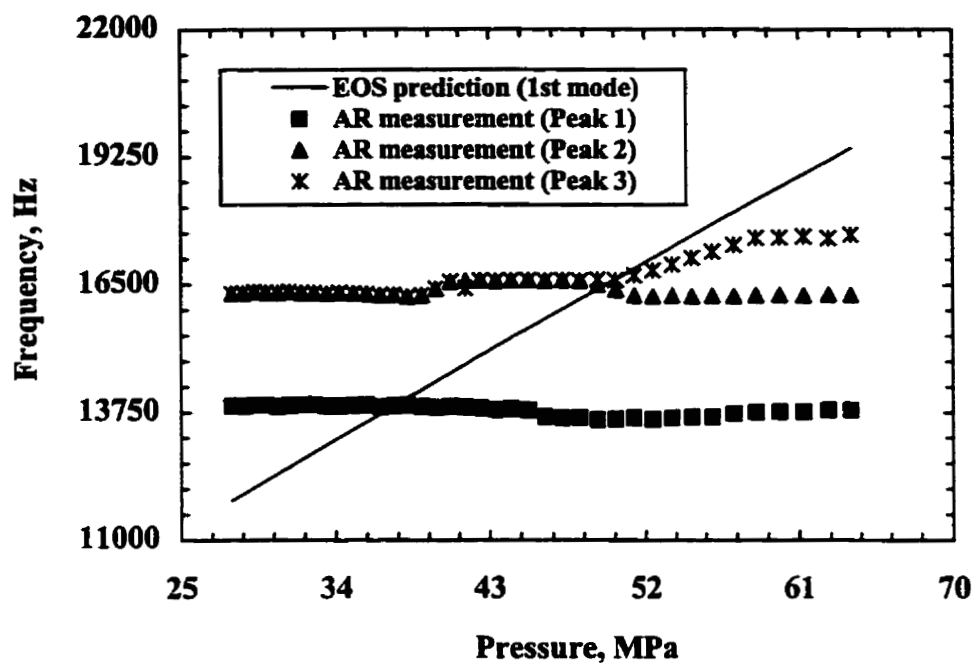


Figure 4.49: Frequency versus pressure  
for Mixture D (110°C)

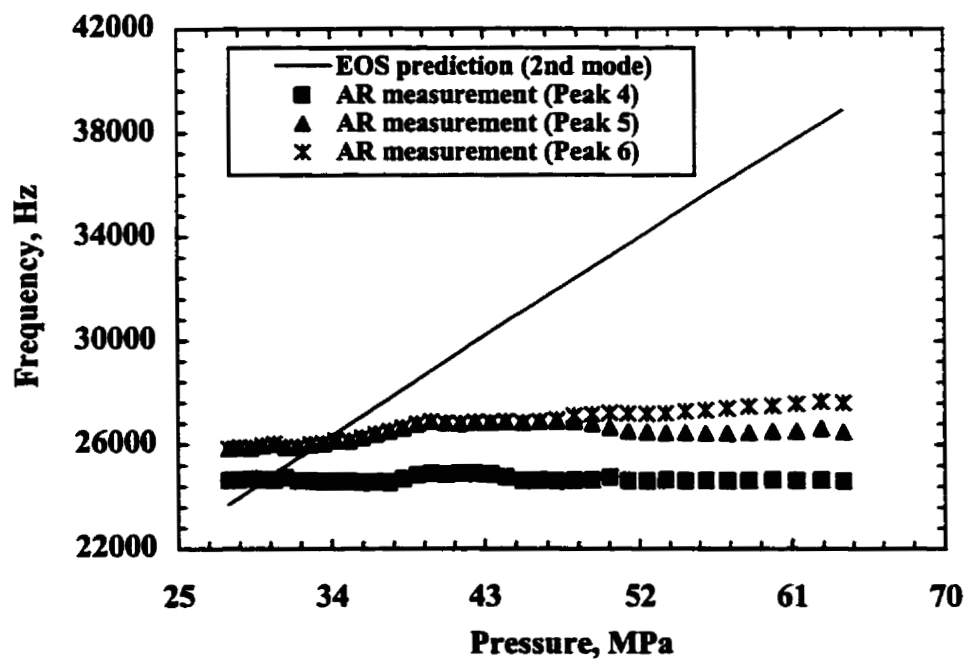
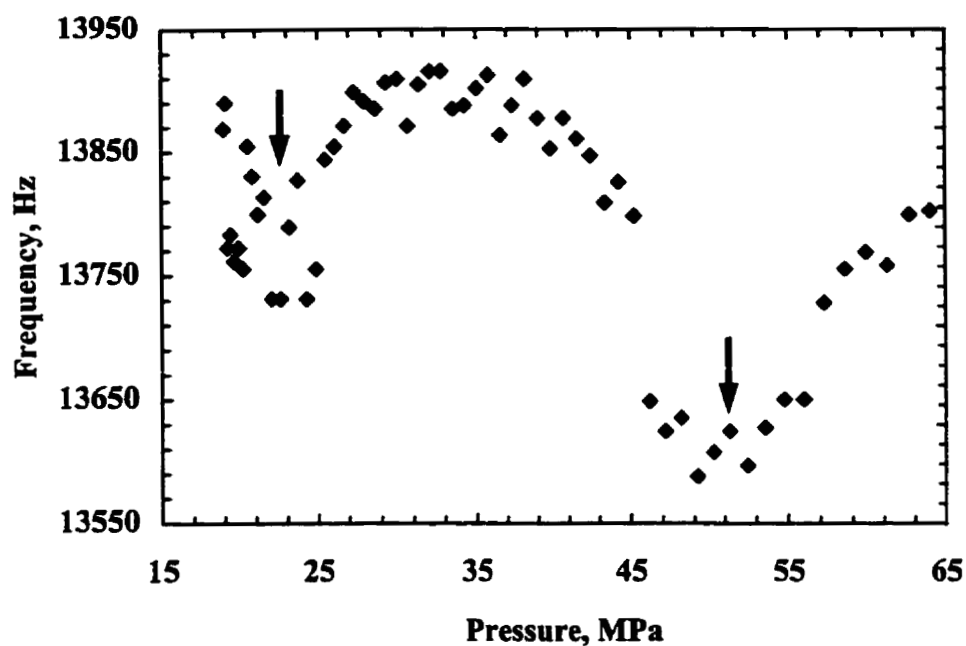
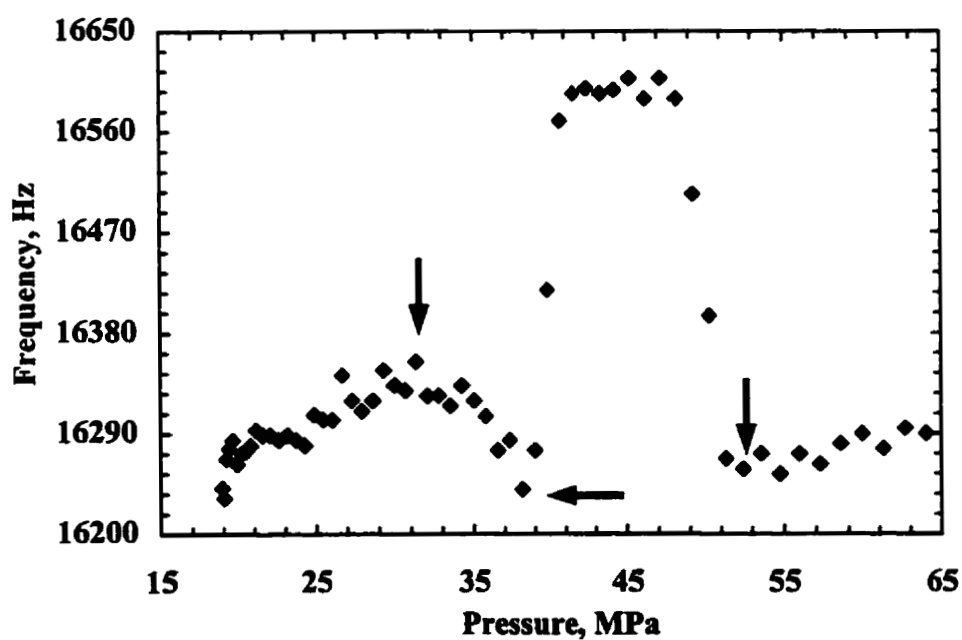


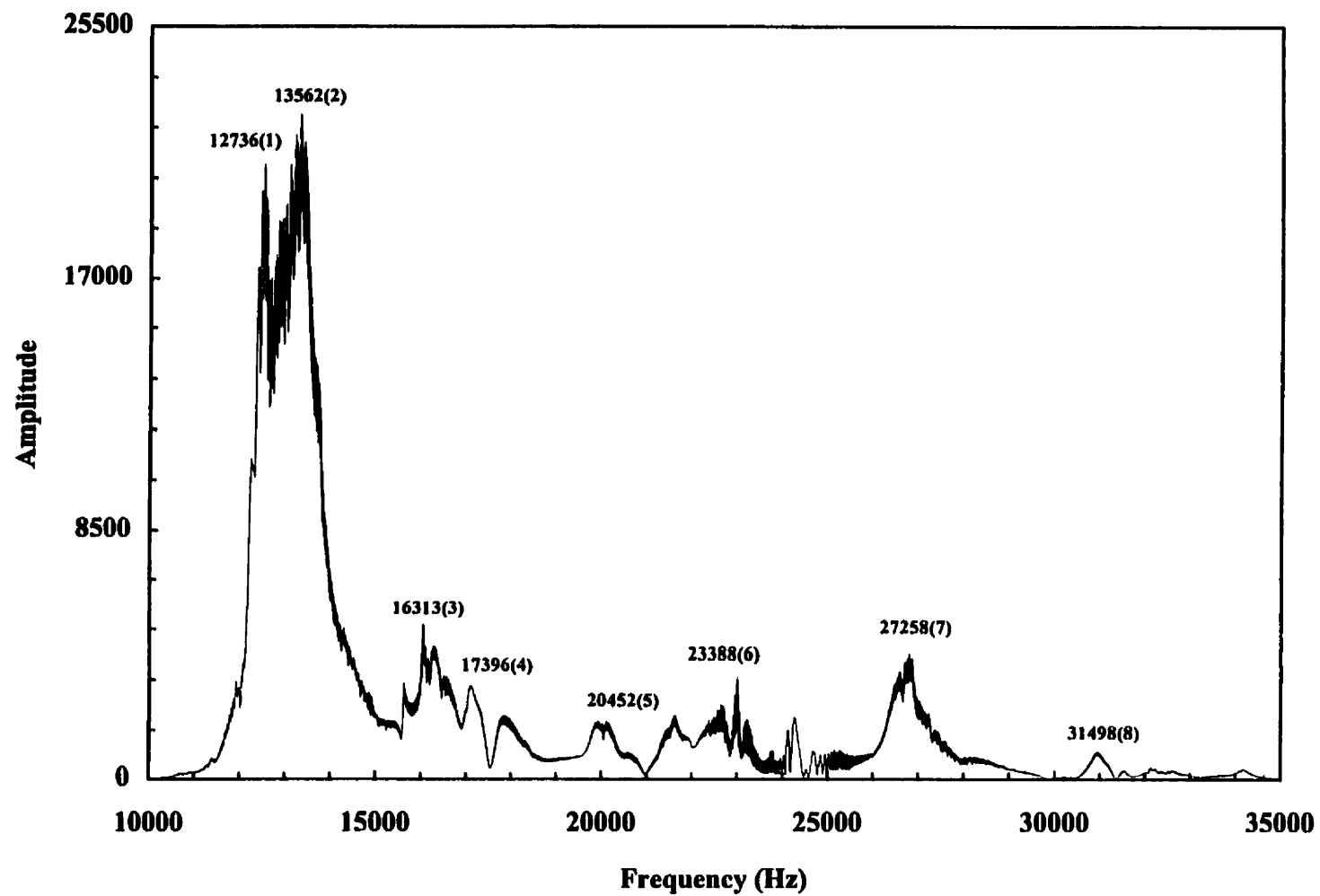
Figure 4.50: Frequency versus pressure  
for Mixture D (110°C)



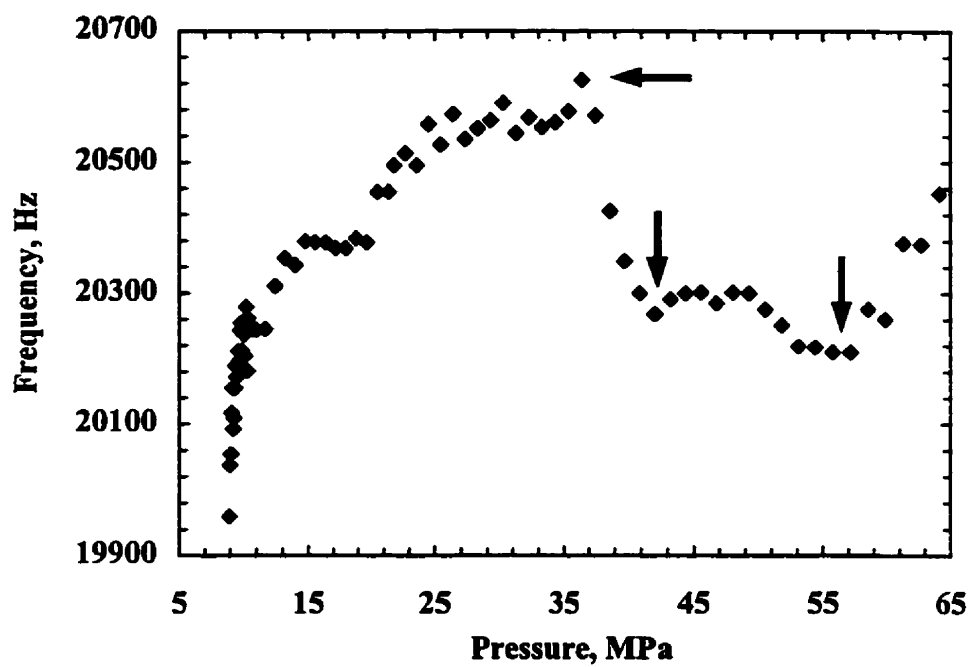
**Figure 4.51: Frequency versus pressure  
for Mixture D (110°C) (Peak 1)**



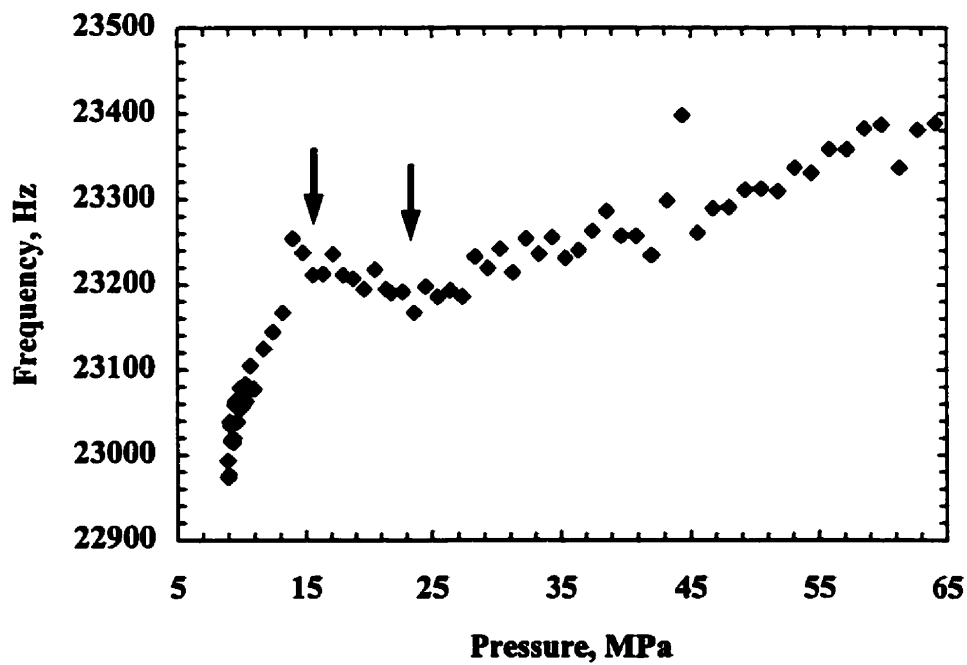
**Figure 4.52: Frequency versus pressure  
for Mixture D (110°C) (Peak 2)**



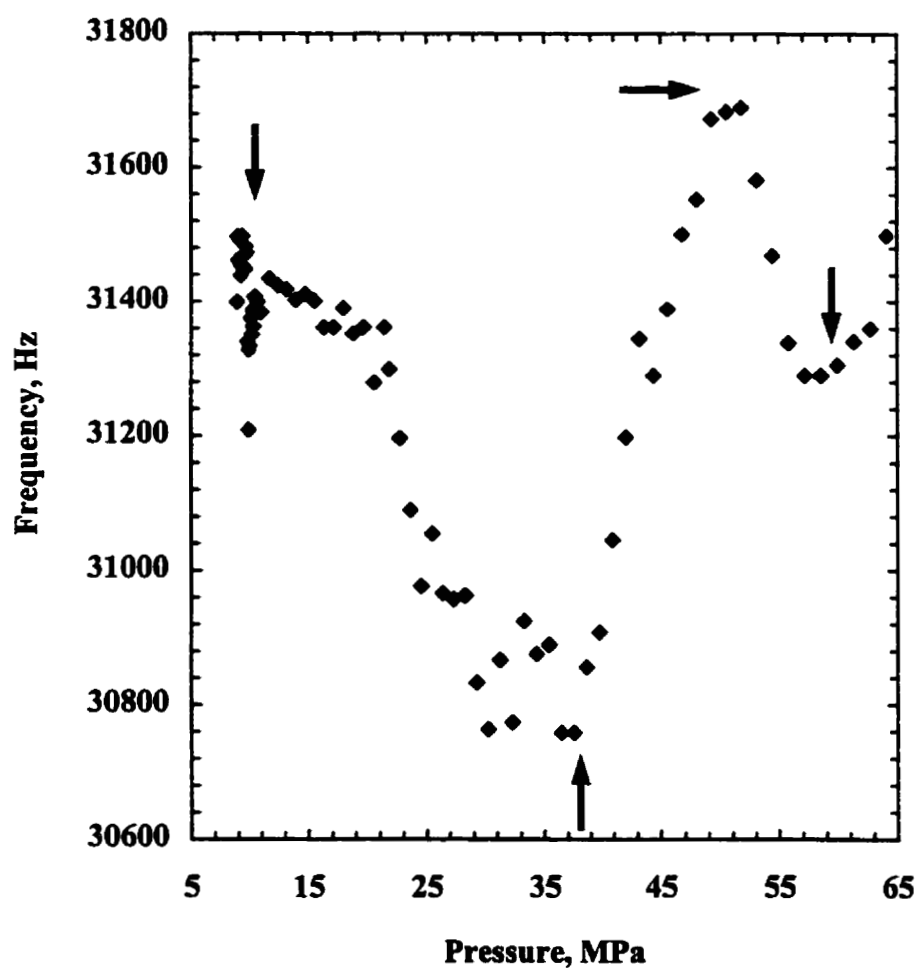
**Figure 4.53: Frequency spectrum for Mixture E (99°C, 64.1MPa)**



**Figure 4.54: Frequency versus pressure  
for Mixture E (99°C) (Peak 5)**



**Figure 4.55: Frequency versus pressure  
for mixture E (99°C) (Peak 6)**



**Figure 4.56: Frequency versus pressure  
for Mixture E (99°C) (Peak 8)**

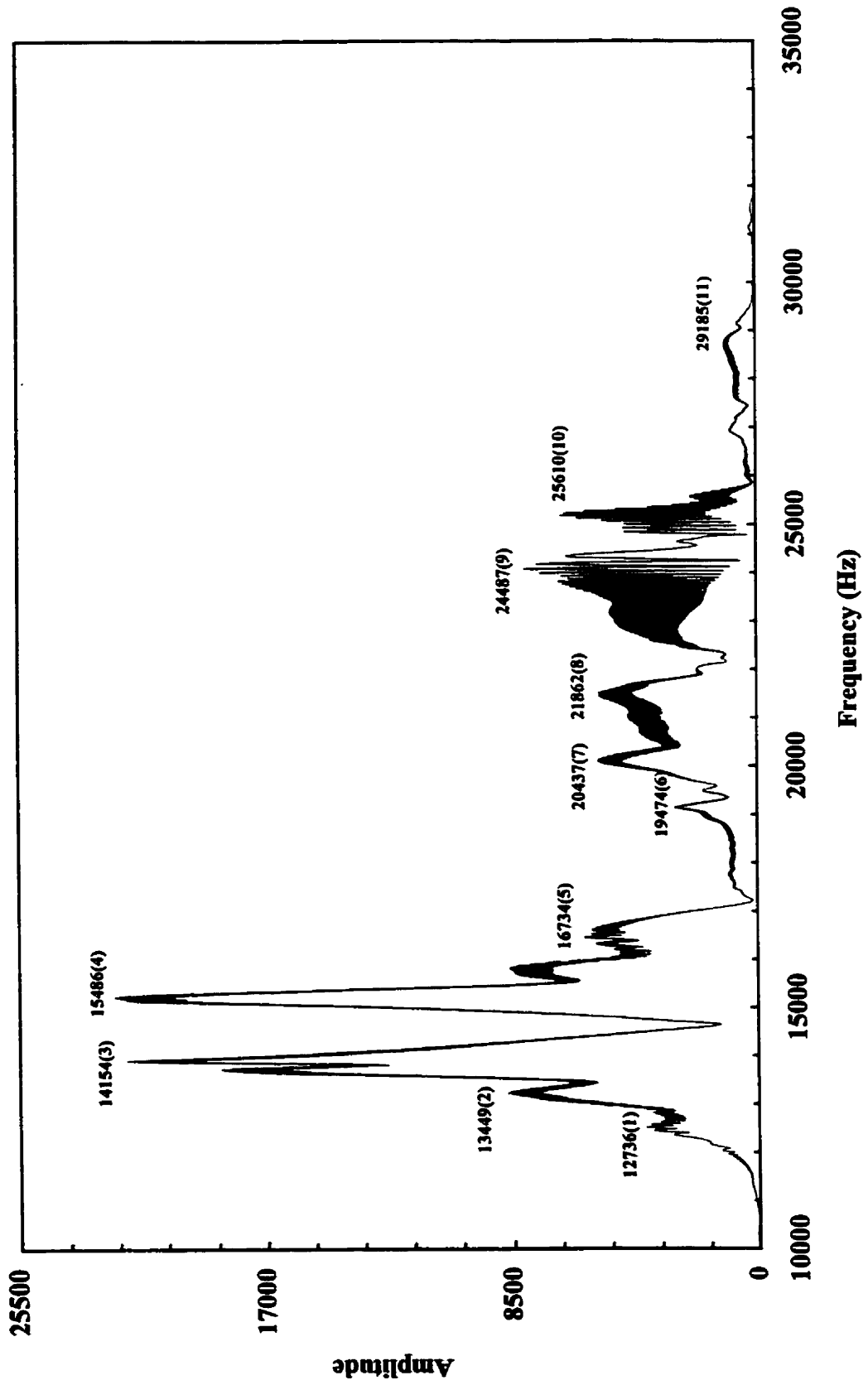
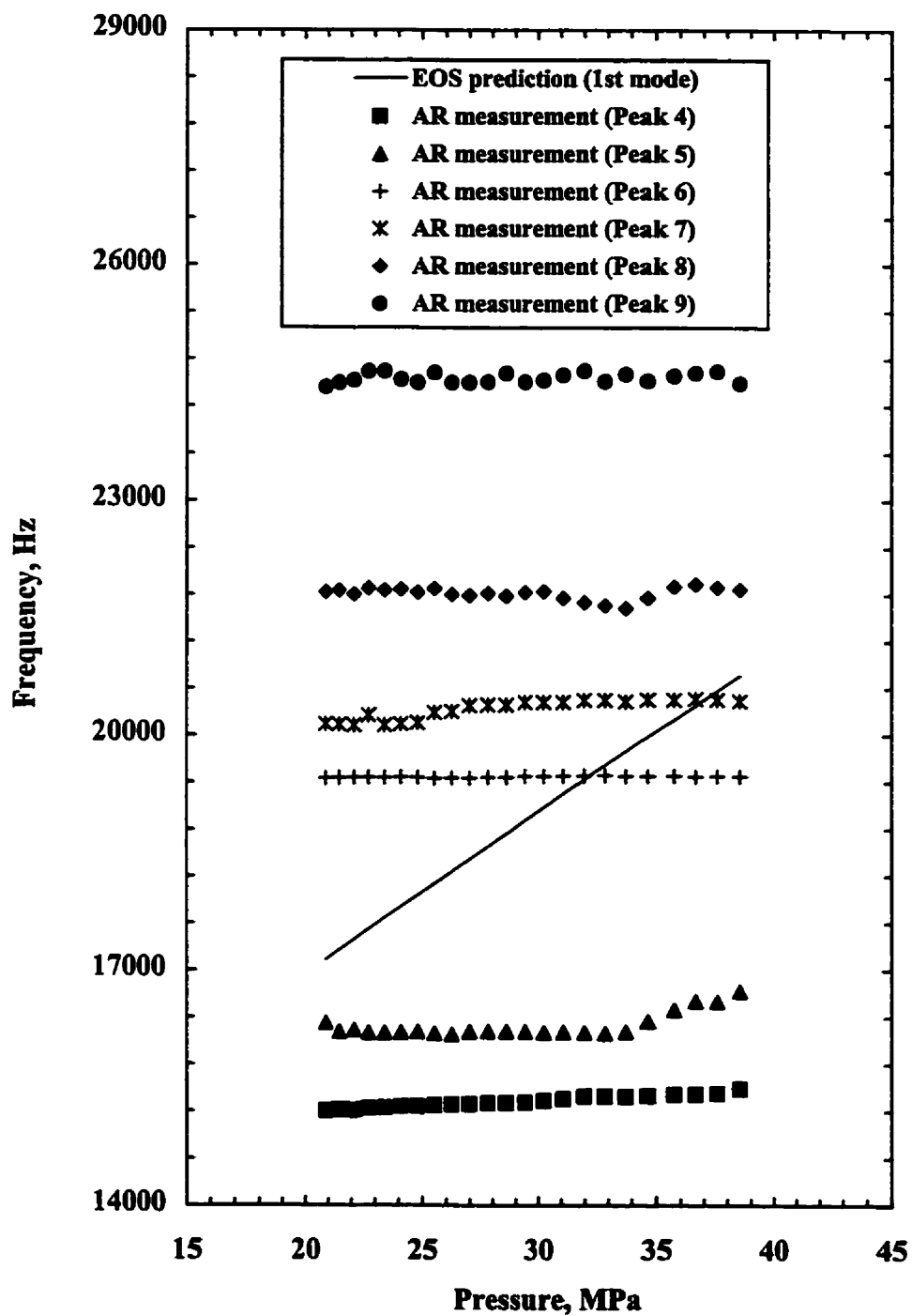
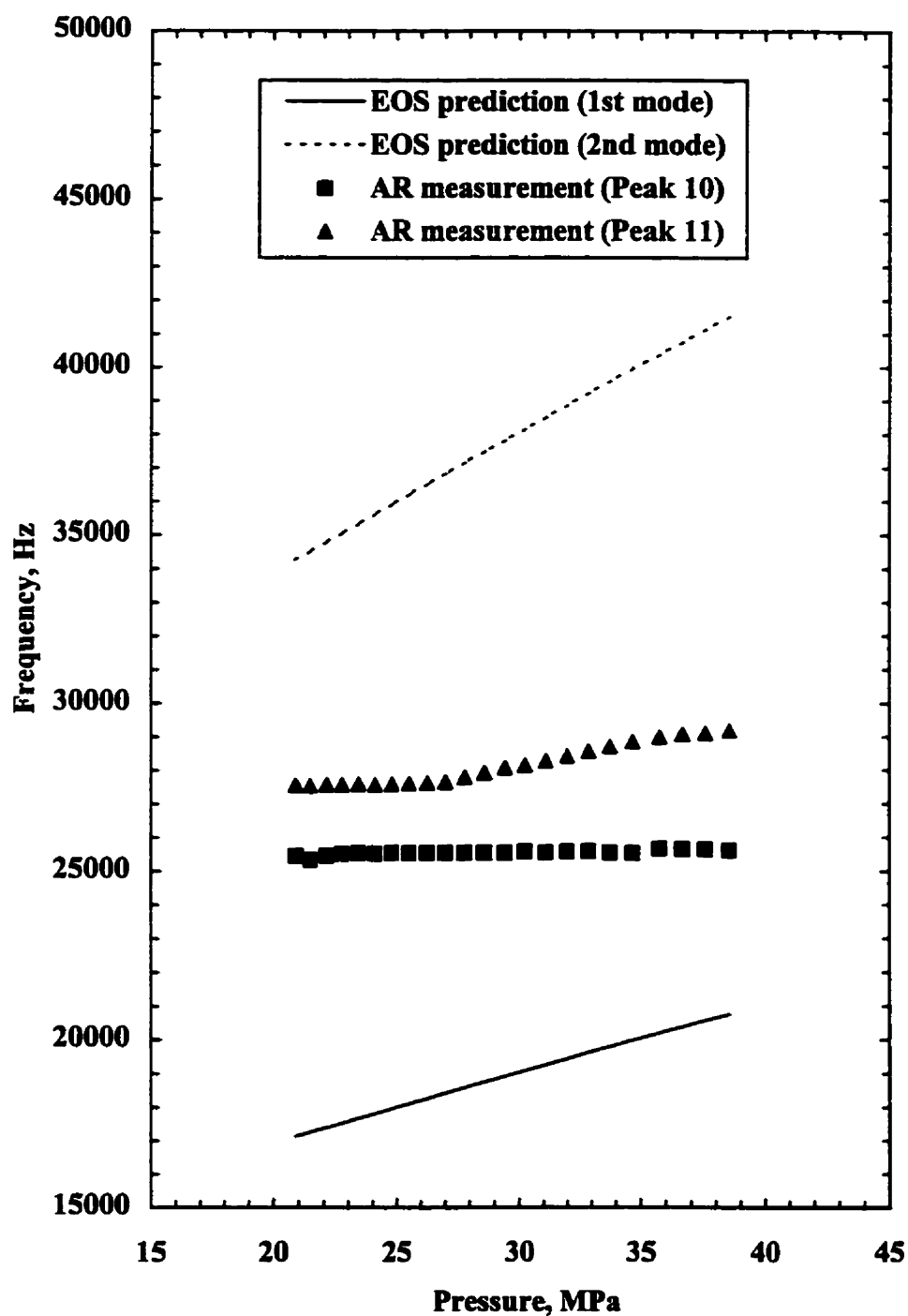


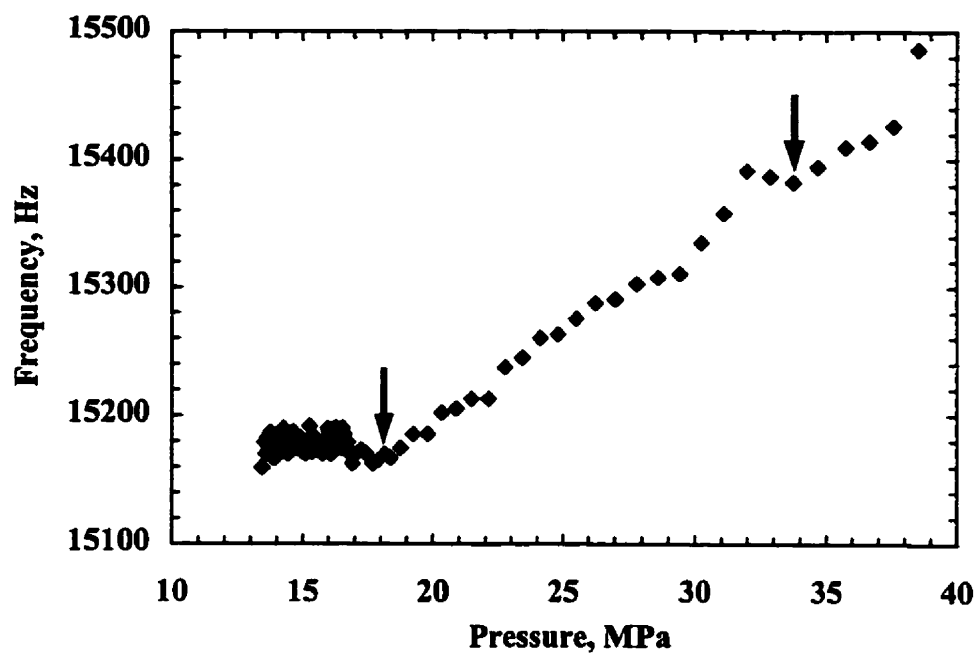
Figure 4.57: Frequency spectrum for Mixture F (62.5°C, 38.53MPa)



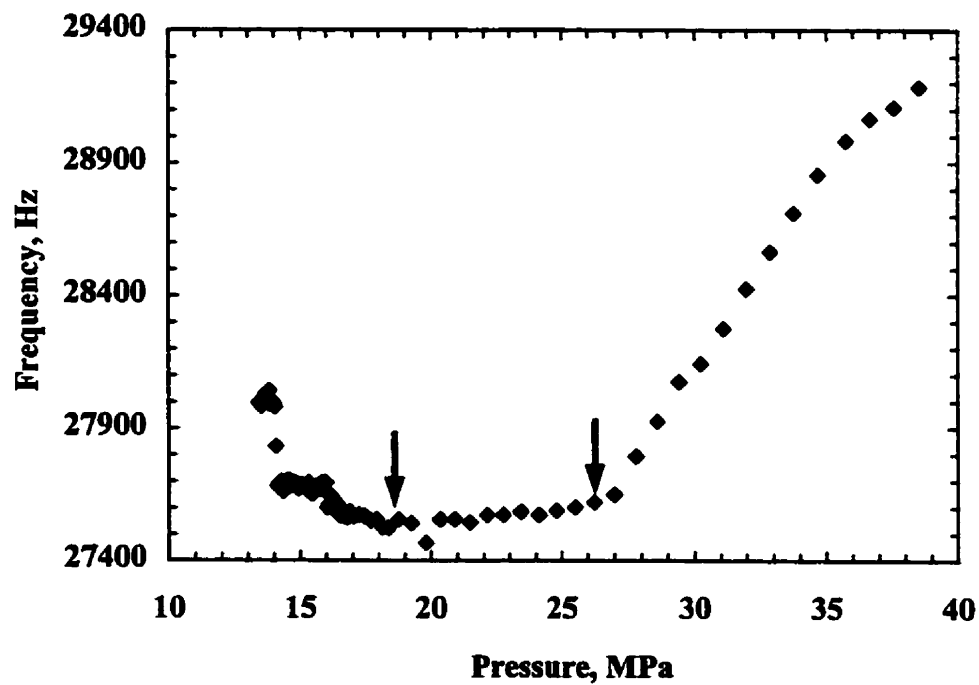
**Figure 4.58: Frequency versus pressure  
for Mixture F (62.5°C)**



**Figure 4.59: Frequency versus pressure  
for Mixture F (62.5°C)**



**Figure 4.60: Frequency versus pressure  
for Mixture F (62.5°C) (Peak 4)**



**Figure 4.61: Frequency versus pressure  
for Mixture F (62.5°C) (Peak 11)**

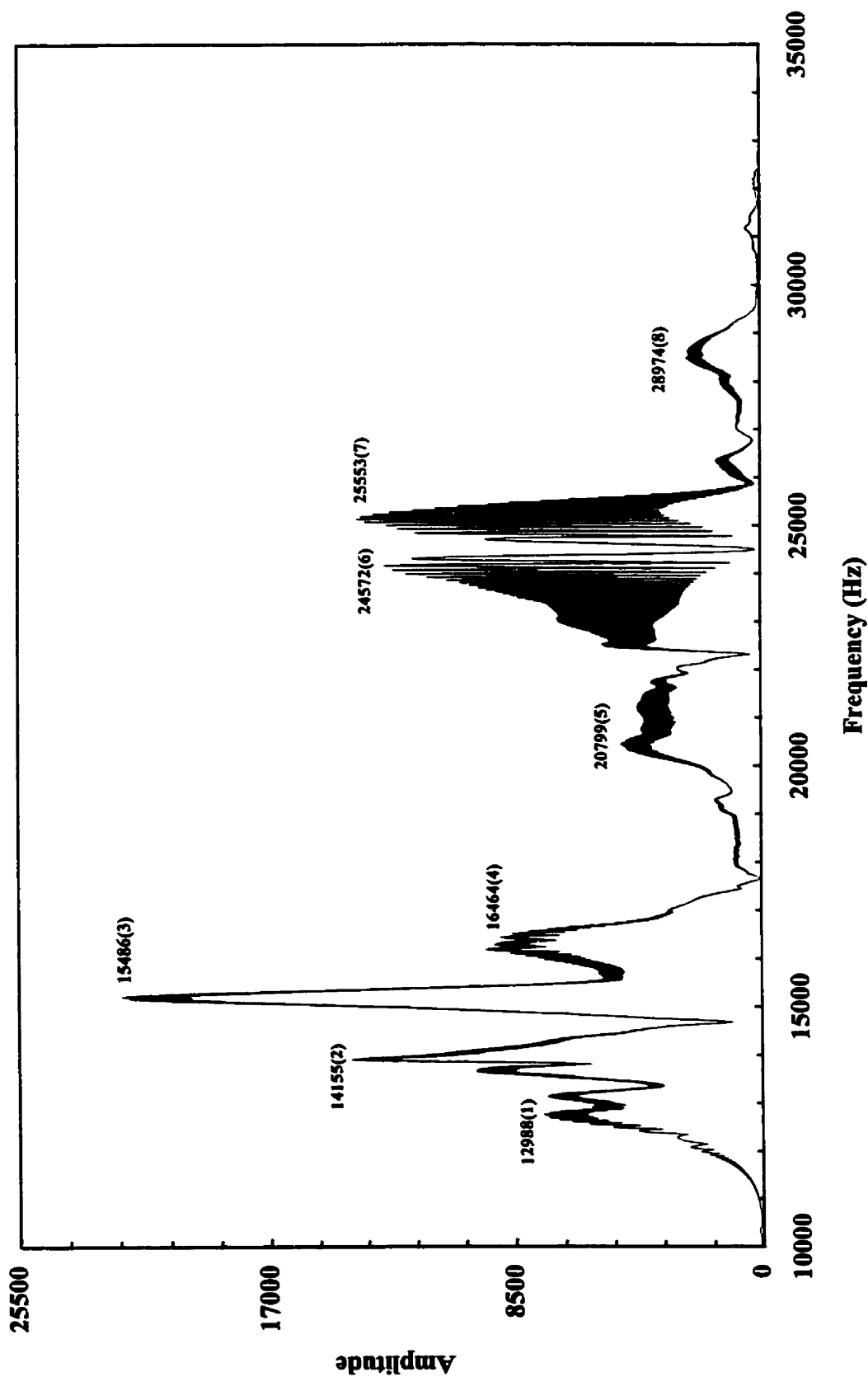
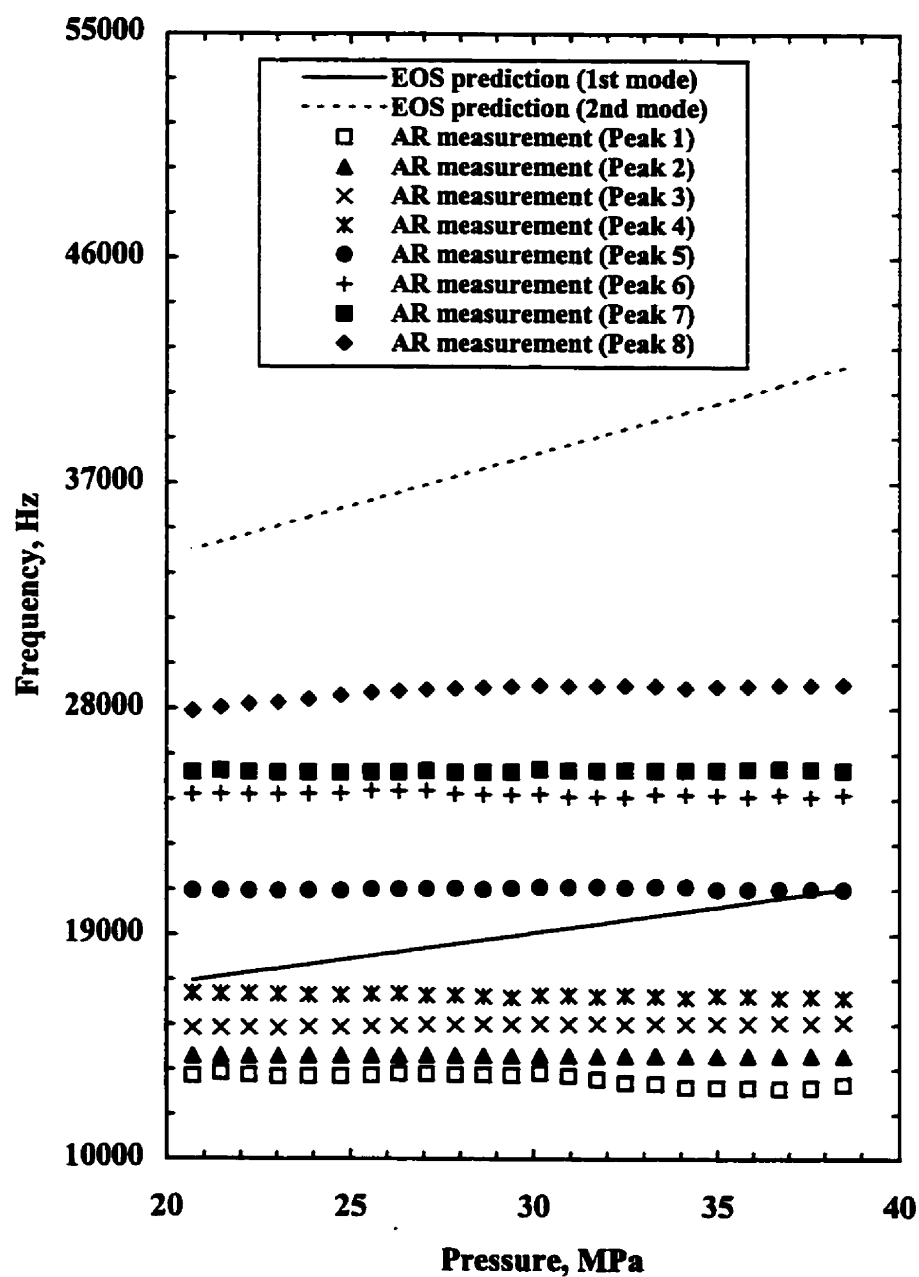
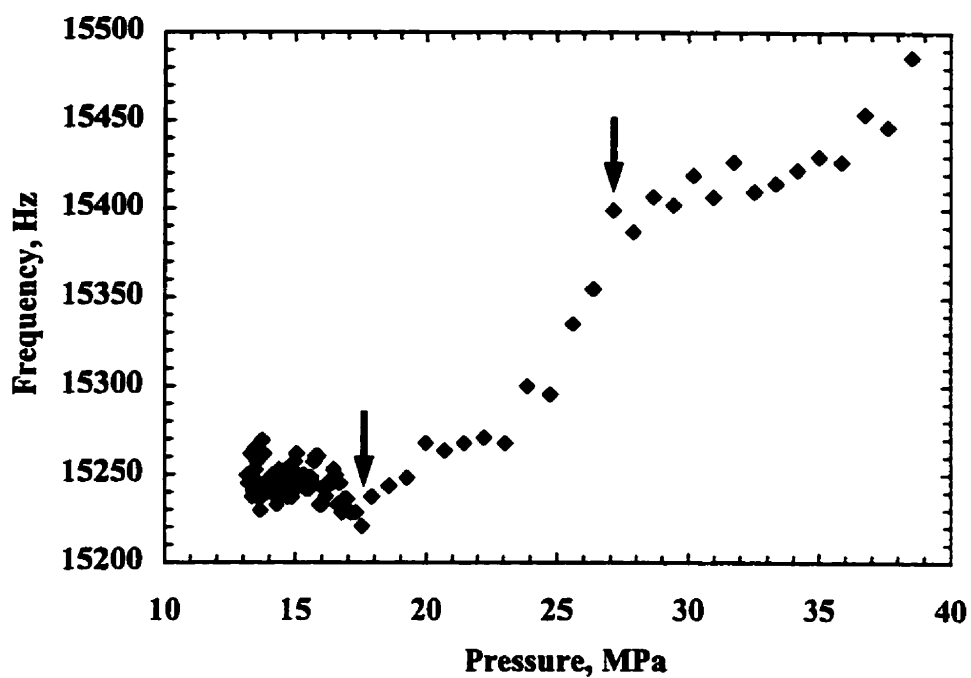


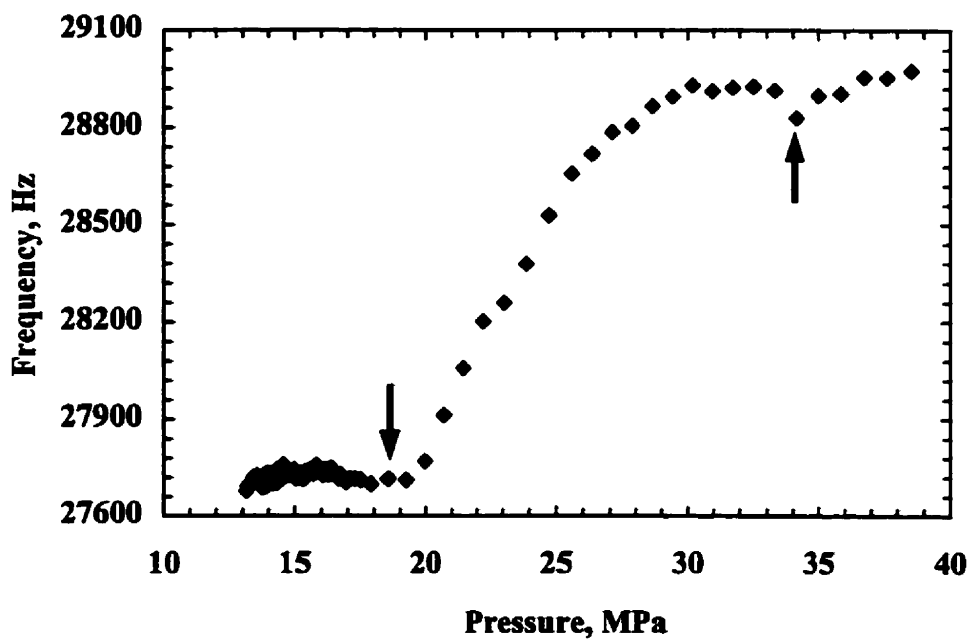
Figure 4.62: Frequency spectrum for Mixture G (62.8°C, 38.52MPa)



**Figure 4.63: Frequency versus pressure  
for Mixture G (62.8°C)**



**Figure 4.64: Frequency versus pressure  
for Mixture G (62.8°C) (Peak 3)**



**Figure 4.65: Frequency versus pressure  
for Mixture G (62.8°C) (Peak 8)**

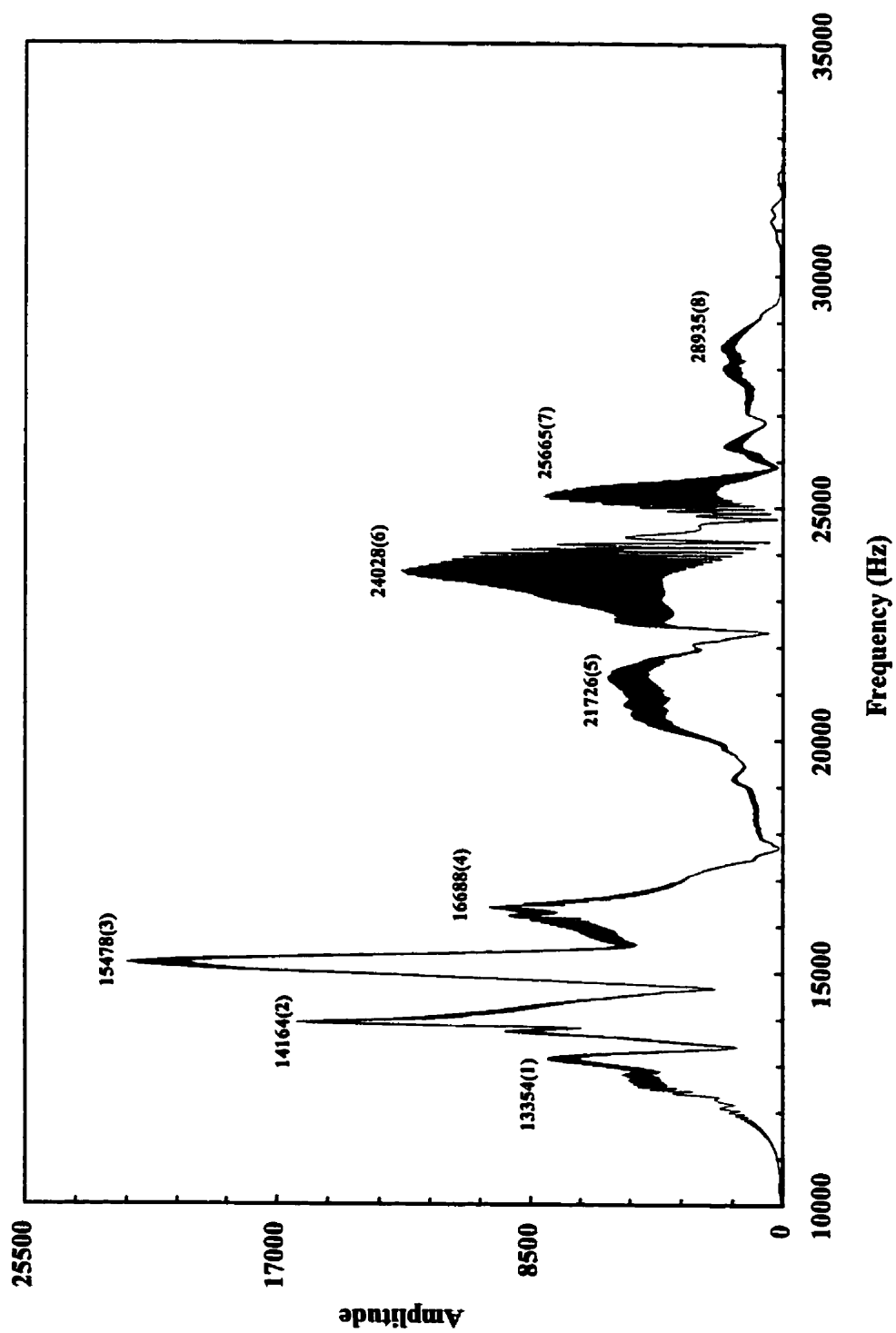
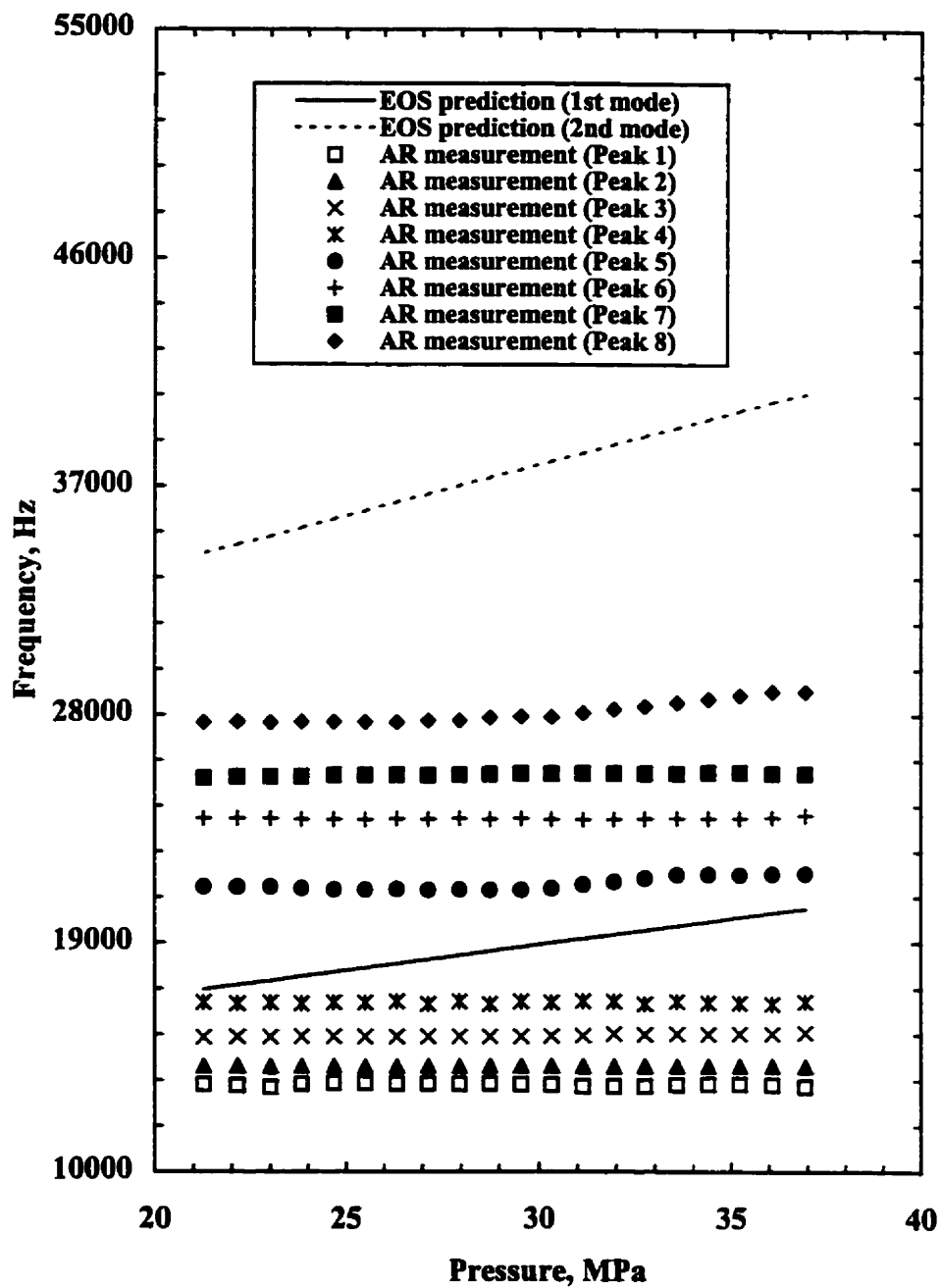
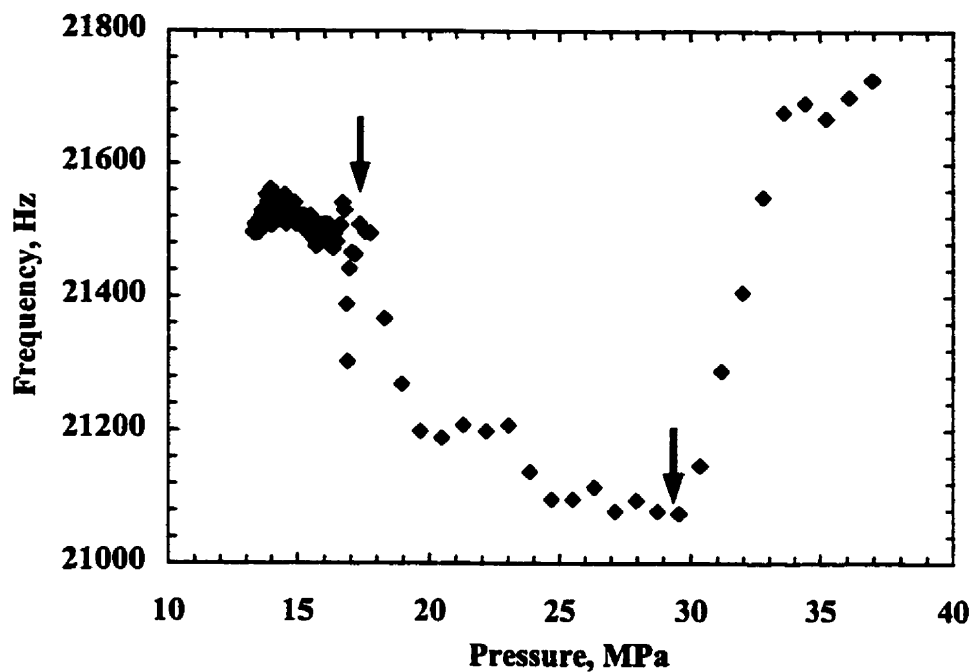


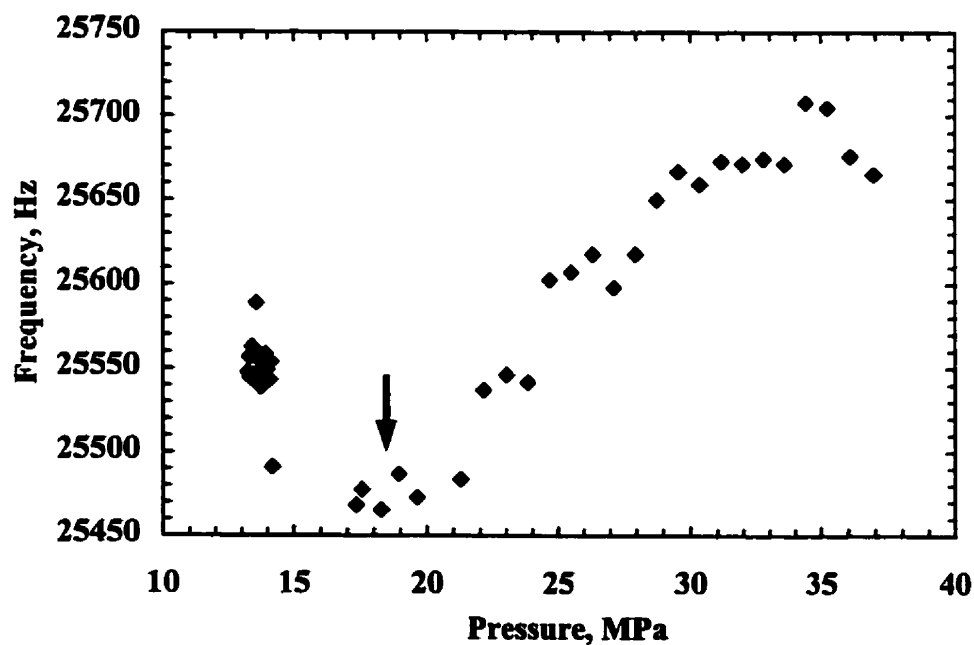
Figure 4.66: Frequency spectrum for Mixture H (60.3°C, 36.93MPa)



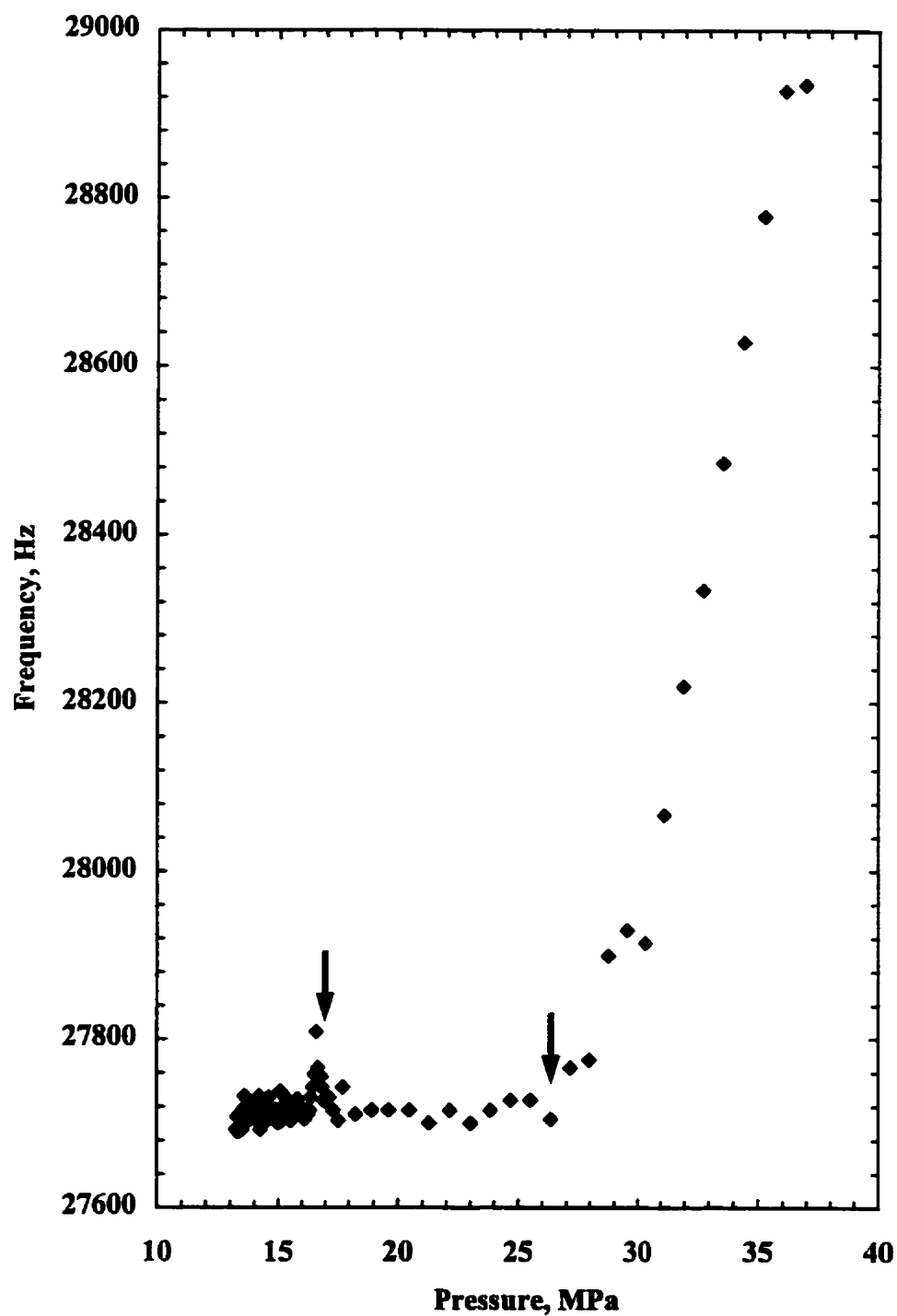
**Figure 4.67: Frequency versus pressure  
for mixture H (60.3°C)**



**Figure 4.68: Frequency versus pressure  
for Mixture H (60.3°C) (Peak 5)**



**Figure 4.69: Frequency versus pressure  
for Mixture H (60.3°C) (Peak 7)**



**Figure 4.70: Frequency versus pressure  
for Mixture H (60.3°C) (Peak 8)**

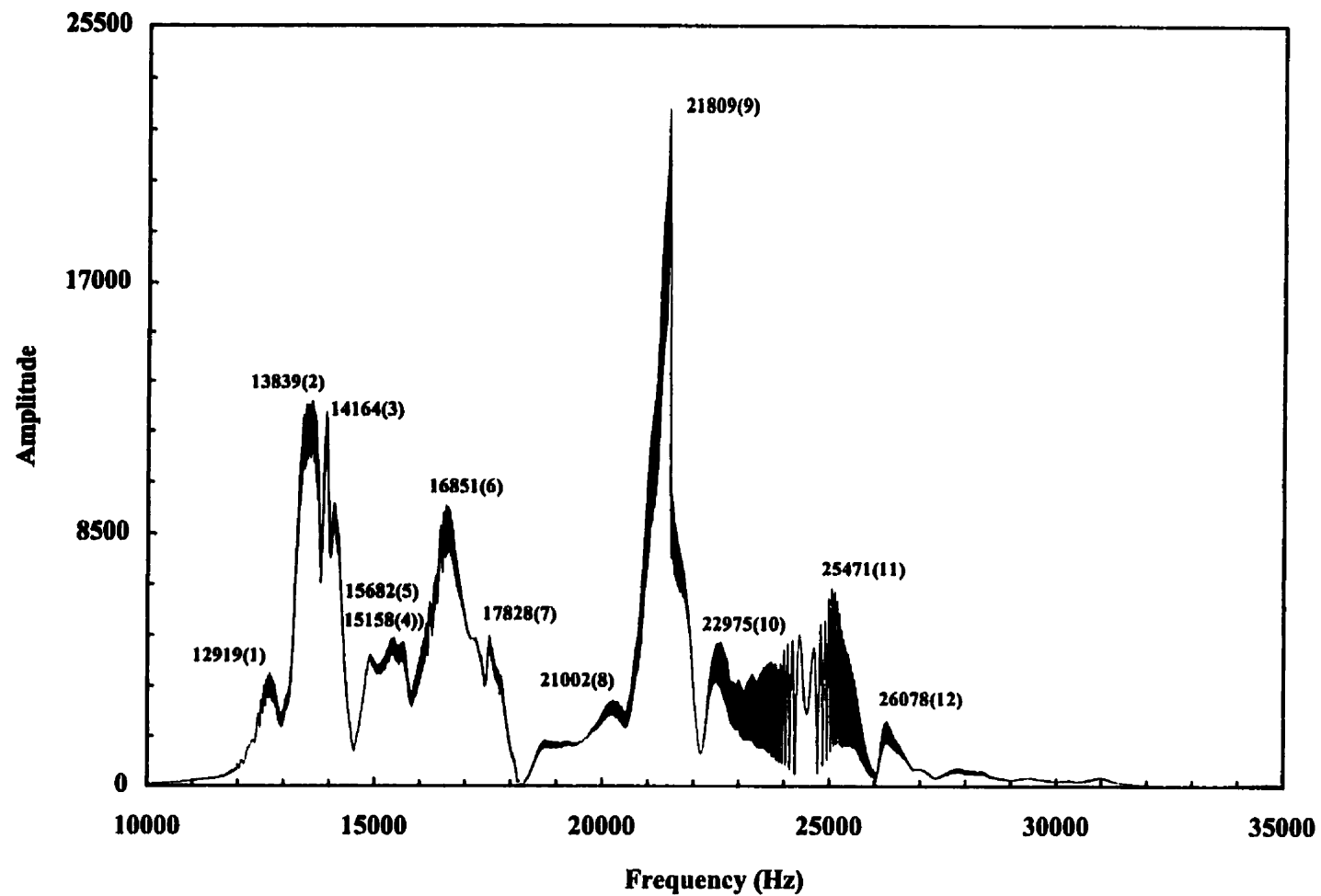
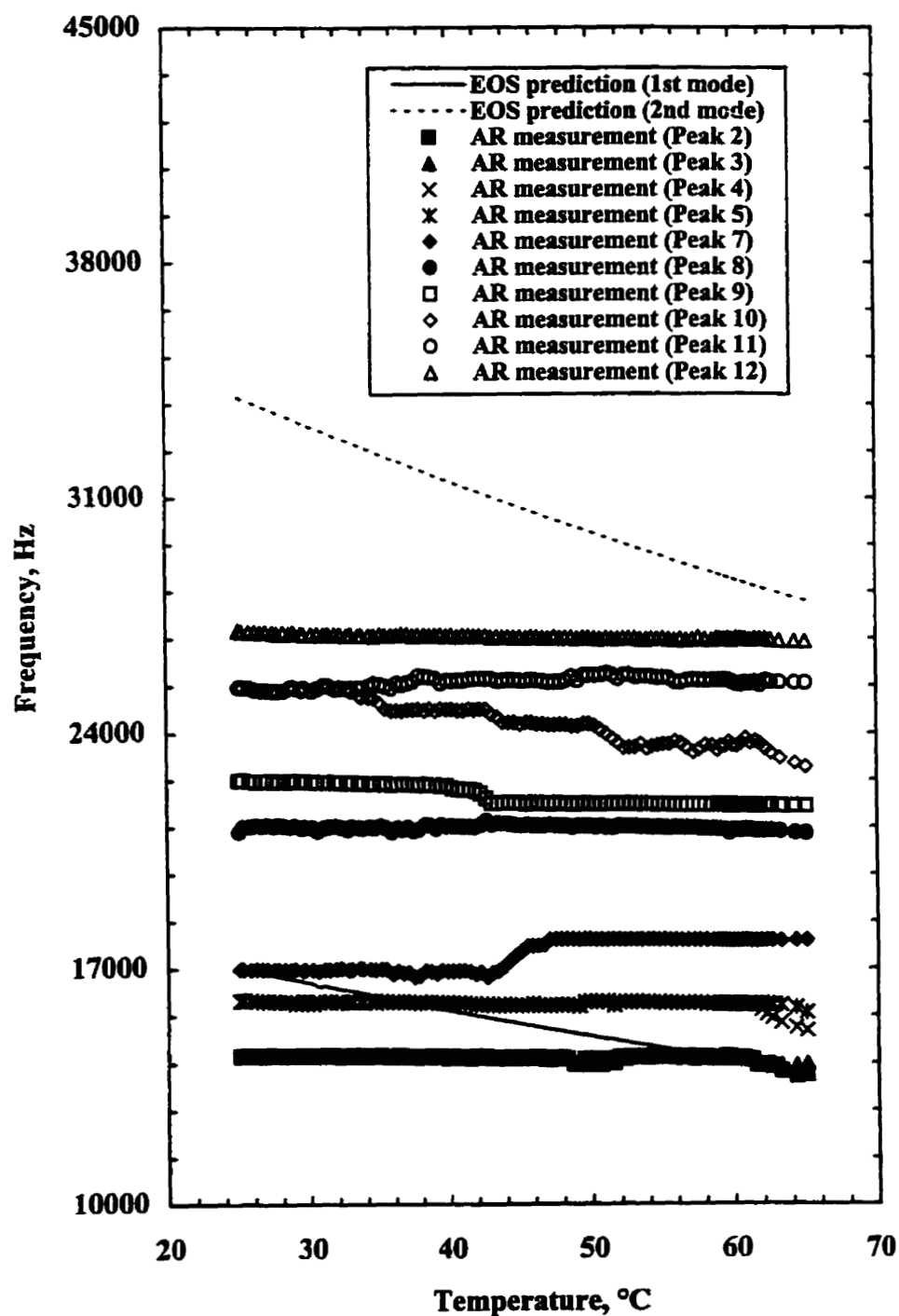
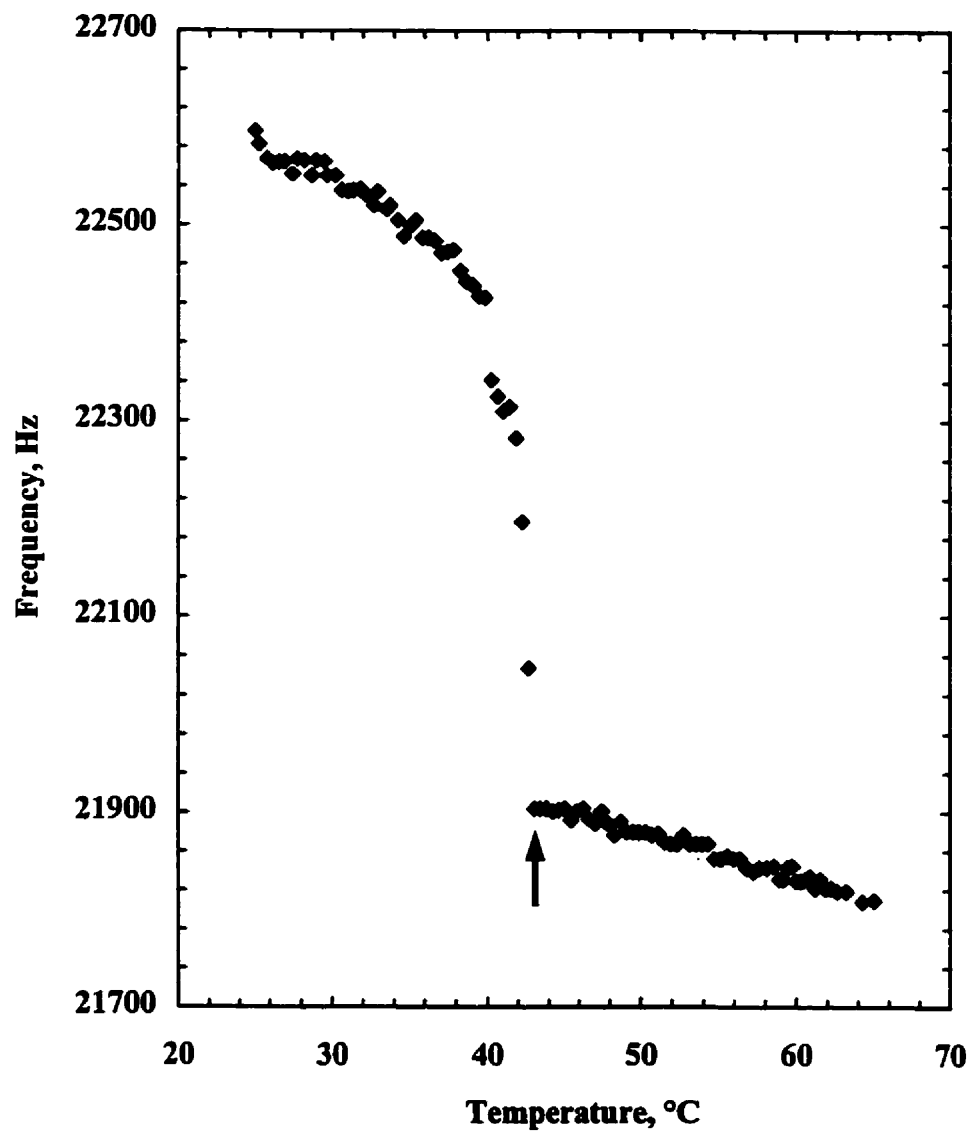


Figure 4.71: Frequency spectrum for Mixture F (65°C, 19.03MPa)



**Figure 4.72: Frequency versus temperature  
for Mixture F (19.03 MPa)**



**Figure 4.73: Frequency versus temperature  
for Mixture F (19.03 MPa) (Peak 9)**

## **CHAPTER FIVE: UNRESOLVED ISSUES IN THE AR METHOD**

The scope of this thesis was to apply thermodynamic and acoustic theory to aid in the interpretation of the results obtained from the existing AR apparatus. Clearly, theory and experiment do not agree. There is reason to believe that the discrepancy is caused by the design of the AR system. Therefore, the capability and limitations of the AR method are briefly discussed.

### **5.1 The Acoustic Source Signal**

The source signal used in the AR method is a chirp signal whose frequency increases from 0 to 50,000 Hz in 0.6 second. The real source signal used in the AR measurements is not available. Figure 4.3 is believed to be an approximation of the source signal. This signal was obtained by placing the two transducers (emitter and receiver) in contact at ambient conditions. The relationship between amplitude and frequency as shown in Figure 4.3 is close to a normal distribution with a peak frequency of about 25,000 Hz. While it is not clear how close this signal is to the real signal, the observed output falls within the same frequency range.

In the AR apparatus, both of the transducers are not in direct contact with the test fluid. The vibrations of the top transducer are transmitted first to a diaphragm through a vibration pin and then to the test fluid. This setup can cause a portion of the source signal generated by the top transducer to be lost before it reaches the test fluid. It is unknown how effectively the vibration pin can transmit the signal between the transducer and the diaphragm. Since the diaphragm is subjected to elevated temperature and pressure conditions during the AR measurement, the change of temperature or pressure can affect the vibrations of the diaphragm and hence the source signal. The echo and reflection of the signal within the resonator can also interfere with the source signal.

## 5.2 AR Output Signal

The nature of the AR output signal has been discussed in Section 4.1. The output signal is a combination of the responses from several sources: the response from the test fluid, the vibration of the chamber, the echo of the signal, etc. The setup of the receiver end of the resonator is similar to that of the emitter end. The bottom transducer (receiver) is not in contact with the test fluid. The vibrations in the fluid are first applied to a diaphragm and then transmitted to the transducer through a vibration pin. The vibrations of the diaphragm are affected by the temperature and pressure conditions. It is not clear how much of the signal is lost when transmitted from the diaphragm to the transducer.

There are about ten peaks in each frequency spectrum. These peaks can be divided into two groups based on their location and energy (amplitude). The first group is centered at about 15,000 Hz and the second group at 25,000 Hz. The resonance frequencies of the seven mixtures presented in Chapter 4 are in the range of 10,000-35,000 Hz which fall within the energetic region of the acoustic source signal.

The consistency of the AR output seems to confirm that some resonances are created. However, it is not clear if the resonances result from the fluid, the chamber or the apparatus. The results in Chapter 4 indicate that liquid-vapor transitions can be detected from these peaks for all the experiments. However, the observed trends do not match theoretical predictions for resonances in the fluid. One possible explanation is that the fluid and apparatus are coupled and more complex resonances are formed.

## 5.3 Quality of PVT Data

The AR apparatus is a well-controlled system. The accuracy of the pressure, volume, and temperature measurement is 0.1 psi, 0.001 cm<sup>3</sup>, and 0.01°C, respectively. The results of the sonic speed calculation presented in Section 4.2.2.1 indicate that large errors exist in the sonic speed calculated from the AR PV data. These errors are probably caused by an error in the measured compressibility. The compressibility is sensitive to very small errors in the volume measurement. While the volume measurement itself is accurate to

0.001 cm<sup>3</sup>, the size of the chamber can change with pressure. In particular, the diaphragms at each end of the chamber (Figure 3.2) are less rigid than the walls of the chamber and may shrink and expand with a change in pressure.

No information is available regarding the volume calibration. To ensure the accuracy of the volume measurement, the volume should be calibrated using standard substances with known compressibility.

#### **5.4 Data Processing**

In this work, the time domain data collected with the AR measurements were processed into frequency domain data with Fast Fourier Transform (FFT). The chirp signal used in the AR measurements is a non-stationary signal and FFT is not well suited for processing such a signal. Therefore, many characteristics of the signal may have been lost after the processing. The wavelets and short time Fourier transform (STFT) techniques are better suited for this type of analysis and should be tested in future.

#### **5.5 Qualitative Analysis of the AR Data**

Amplitude is a measure of the acoustic energy and the frequency spectrum is an indication of the acoustic energy distribution. During the AR measurements, the physical properties and acoustic properties (e.g. sonic speed) change with temperature and pressure and these changes will cause the redistribution of the acoustic energy. For example, for the AR measurement of Mixture D, the amplitudes of the peaks in the first group at 15,000 Hz (mentioned in Section 5.2) decrease with decreasing pressure, while the peaks in the second group at 25,000 Hz experience an increase in amplitude.

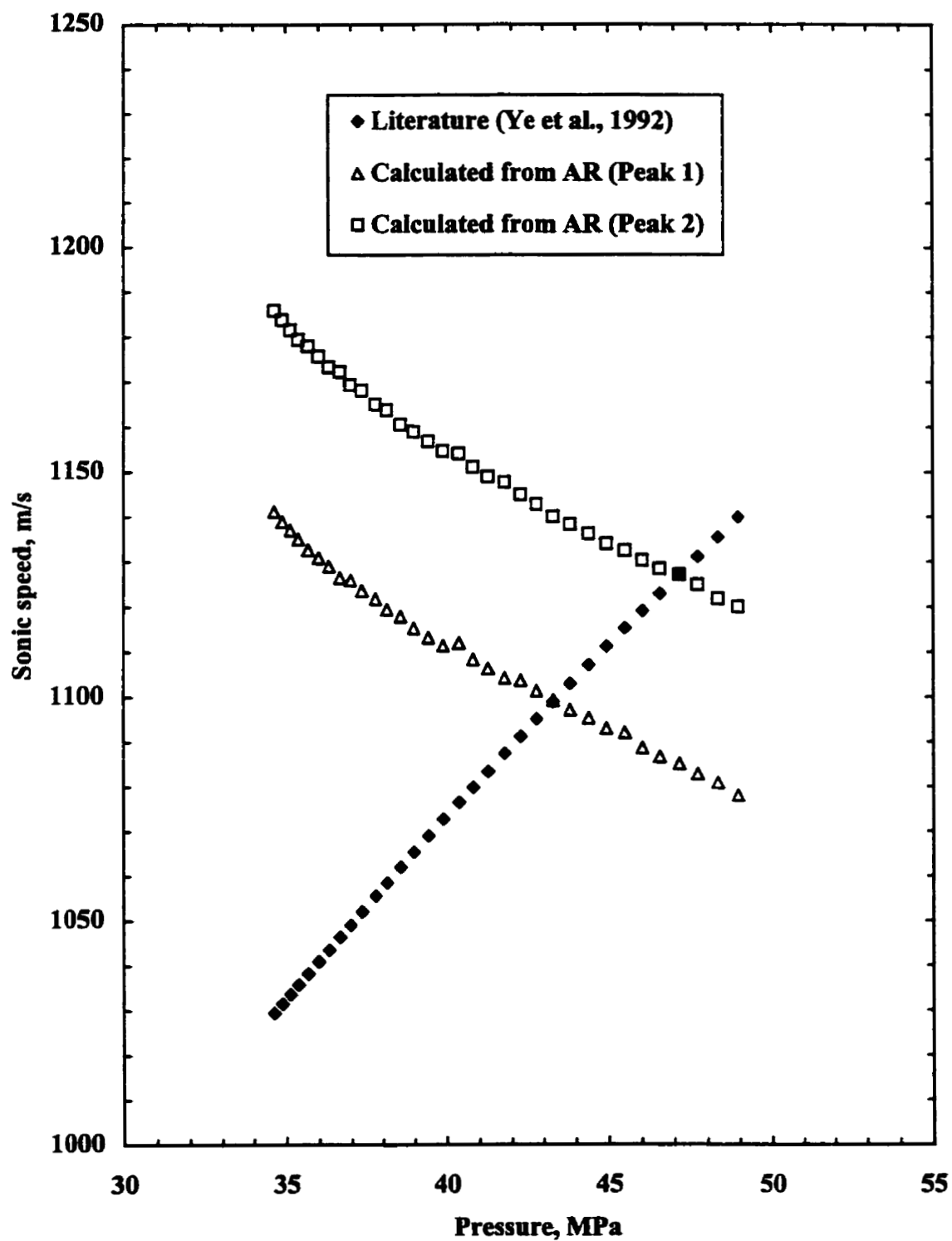
Drastic changes in acoustic properties can occur during phase transitions. For example, the sonic speed goes to zero when a pure component approaches its critical point (Colgate et al., 1991a). The changes in sonic speed and resonance frequency during liquid-solid and liquid-vapor phase transitions have been discussed in Chapter 4. Changes in the acoustic energy distribution are expected during phase transitions. For example, Peak 2 of Mixture A (100°C) undergoes a peak split at about 30 MPa consistent with the liquid-

vapor transition detected by the visual method. This indicates that a phase transition can sometimes be inferred from the changes in acoustic energy distribution. However, due to the overlapping of the peaks in the frequency spectrum, it is difficult to detect phase transitions by mere inspection of the spectra. It is recommended to attempt a more detailed analysis of the energy distribution in the AR spectra.

## 5.6 Sonic Speed from Resonance Frequency

When the trends of the resonance frequencies are considered more carefully, another inconsistency with theory is apparent. Based on Equation 2.2, the sonic speed can be back-calculated from the measured resonance frequency. Figure 5.1 shows the sonic speed calculated from two potential resonance modes (Peaks 1 and 2) of the AR measurement for Mixture A (67°C). The literature data is also shown for comparison. The data in Figure 5.1 is in the single phase (liquid) region. The trend of the calculated sonic speed is in contradiction to the literature data. At first glance, it is surprising that the trend in the calculated sonic speed increases with decreasing pressure since the frequencies of these two peaks have a decreasing trend with decreasing pressure. Consider the equation used for the sonic speed calculation,  $c=2fl$  (for  $n=1$ ). The trend of the calculated sonic speed depends on that of the product of frequency ( $f$ ) and length ( $l$ ). Since the frequency has a decreasing trend and the length has an increasing trend with decreasing pressure, the rate of frequency decrease must be larger than the rate of length increase to result in a decreasing trend in sonic speed. Checking the measured data, it is found that, for Peak 2, the frequency decreased by only 0.297% and the volume (and hence the length) increased by 6.2% in the pressure range of 34.63–48.95 MPa and this caused the increasing trend in the calculated sonic speed.

The measured volume consists of the cylindrical cavity and the volume of a short piece of tubing (sample outlet in Figure 3.2). This dead volume is less than 5% of the total volume. When calculating the sonic speed from the measured data, the volume should have been corrected for the dead volume. However, this correction can only shift the calculated sonic speed up or down along the sonic speed axis and cannot reverse its



**Figure 5.1: Sonic speed versus pressure  
for Mixture A (67°C)**

increasing trend with decreasing pressure. This means that the error in the volume measurement alone cannot cause the incorrect trend in the calculated sonic speed.

There is no obvious explanation for the incorrect trend in sonic speed. At face value it casts in doubt the entire validity of the AR measurements and the screening procedure developed in Chapter 4. However, the apparent resonance frequencies do appear to show a slope change at phase transitions. As mentioned previously, it is possible that the fluid and apparatus are somehow coupled and hence the observed responses do not follow theory exactly, or the FFT signal processing may mask or distort the change in resonance frequency. If so, with improvement in design and signal processing, the AR technique may still be used to detect phase transitions.

### **5.7 Redesign of AR Apparatus**

The results in Chapter 4 demonstrate the potential of the AR method for detecting phase transitions. However, the interpretation of the AR measurements has been complicated by the presence of spurious signals. Therefore, modifications of the apparatus are desired to make it an independent and reliable tool.

The main problems with the AR apparatus are related to the nature of the input and output signal. The transducers (emitter and receiver) are not in direct contact with the test fluid. Since the vibrations to and from the transducers are transmitted through a vibration pin, part of the input signal and output signal may have been lost or changed. Since the diaphragms used as the relay for the signal transmission are under elevated temperature and pressure conditions, the change of temperature or pressure can affect the vibration of the diaphragms and hence the signal.

If the acoustic response can be confined to the fluid, it is likely that clear unambiguous resonance signals can be obtained. With some equipment modifications and a variety of signal processing techniques, the AR method has the potential to be a useful tool for detecting phase transitions particularly for opaque fluids.

## **CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS**

### **6.1 Conclusions**

- (1) The AR method has been used to detect the vapor-liquid and liquid-solid phase transitions from reservoir fluids. The AR system can be operated in a wide range of temperature and pressure conditions. Preliminary results have verified its potential in detecting phase transitions.
- (2) The output signal of AR measurements contains responses from different sources: the test fluid, the vibration of the chamber, and the echo of the signal. It is difficult to quantify the contribution from each source. The interpretation of the AR measurements is sometimes complicated by the presence of spurious signals.
- (3) A thermodynamic model is developed to predict the sonic speed in reservoir fluids and acoustic theory is used to predict the resonance frequency based on the predicted sonic speed. The expected trend in the resonance frequency is established from acoustic theory and experimental observations. The screening procedure greatly assisted in the interpretation of the AR measurements. A better understanding of the acoustic behavior of the AR system has been achieved with the help of these predictions. The screening criteria need to be refined when more experimental data is available.
- (4) Liquid-vapor phase transitions have been detected for all the seven mixtures (a total of eight experiments) tested in this work. Among the seven experiments with known liquid-vapor transitions, correct phase transitions are detected from all the identified resonance peaks for five experiments. False positives exist for two experiments. False negatives are observed for five experiments.
- (5) Apparent liquid-solid phase transitions have been detected for five mixtures. The results appear to be self-consistent. However, these liquid-solid transitions are not verified with other techniques.

- (6) While liquid-vapor and liquid-solid transitions are detected from the AR system, the AR response did not match theory. There are two possible explanations for the discrepancy between measurement and theory. One possible explanation is that the FFT signal processing used to obtain the frequency domain data loses critical information since it employs time-averaging. Another possible explanation is that the fluid and AR apparatus form a coupled system with complex resonances.
- (7) The data processing technique used in this work may not be the best choice for the AR system. Different techniques can be applied and a best choice can be made from among them.

## **6.2 Recommendations**

- (1) Identify the sources of AR output signal and evaluate the contribution from each source. Put the transducers in contact with the test fluid to decrease the level of the spurious signals. Try different transducers with the AR system.
- (2) Test the AR system against clearly defined mixtures with known phase transitions. Test the system with reservoir fluids exhibiting both vapor-liquid and liquid-solid transitions. The results of AR measurements need to be verified with other techniques.
- (3) Try different signal processing techniques with the AR measurements and identify the best technique. A combination of different techniques may be needed to achieve the best effect.
- (4) Calibrate the volume of the AR system and minimize the dead volume.

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