CHAPTER - II

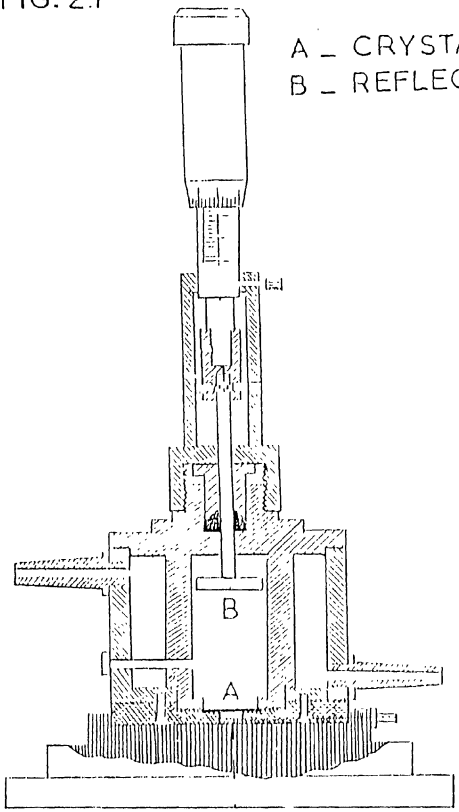
EXPERIMENTAL PROCEDURE

The experimental techniques employed in the present study to determine the ultrasonic velocity, ultrasonic attenuation and density were described in this chapter. All the chemicals used in this present research work are of AR/BDH quality. Measurement of ultrasonic velocity is generally made either by continuous wave method or pulse methods. Continuous waves are used in optical diffraction, reverberation and interferometry methods. In pulse echo or pulse superposition methods RF pulses of short duration are used.

2.1 CONTINUOUS WAVE METHOD:

In the fixed frequency variable path ultrasonic interferometer, The acoustic wave length is measured which in turn is used to compute the ultrasonic velocity. The ultrasonic cell is a double walled brass cell with chromium plated surfaces. The capacity of the cell is 10 ml. The schematic diagram is shown in figure 2.1. In the figure 2.1, A is the crystal holder from which the leads are taken out. B is the metallic reflector attached to the shaft C which moves up or down by the action of a spring and a micrometer screw. The micrometer screw has a least count of 0.001 cm and the length of the pitch scale is 25 mm. The cell has an

FIG. 2.1



ULTRASONIC
INTERFEROMETER CELL

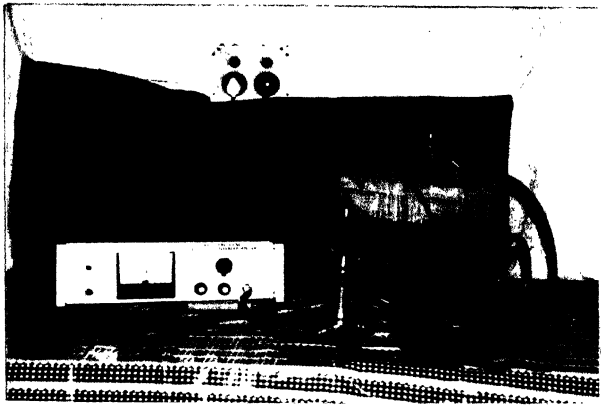


FIG. 2.2 : EXPERIMENTAL SETUP FOR VELOCITY MEASUREMENT

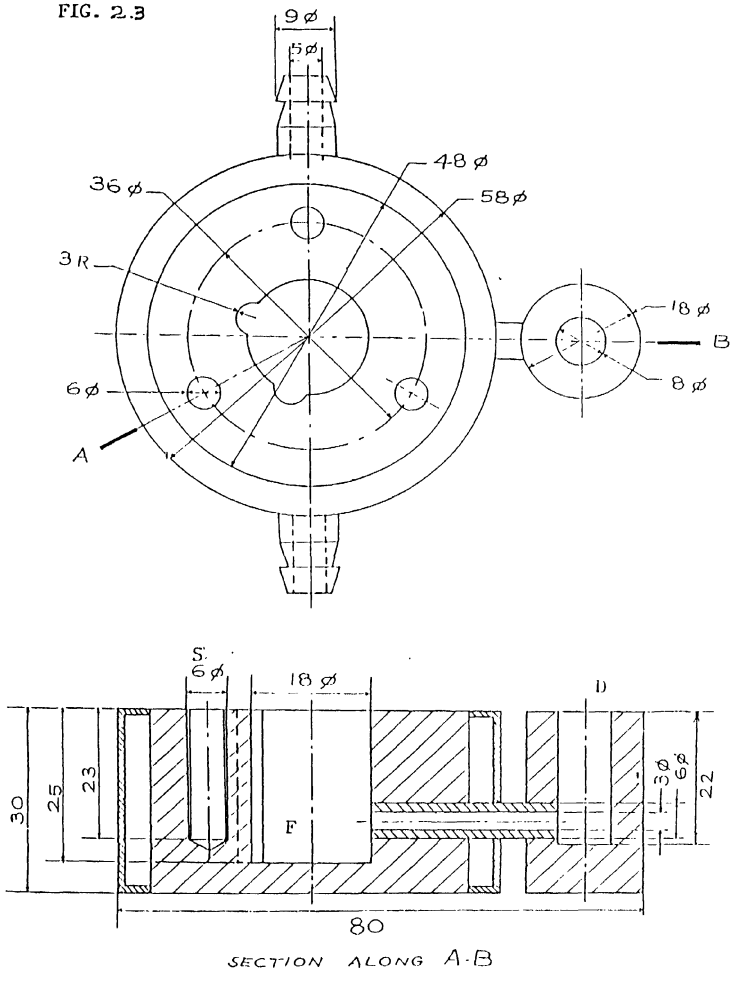
outer shell through which water is circulated. The temperature of the circulating water is maintained at a fixed temperature by a thermostatically controlled water bath. The temperature is maintained constant within ±0.1K.

At the bottom of the cell an X-cut quartz crystal of resonant frequency 2 MHz is fixed. The crystal is excited at 2 MHz by an RF oscillator. With liquid sample in the cell, the standing waves are formed between the reflector and the crystal. This alters the anode current and the changes in the anode current is measured in a differential amplifier configuration using a micro ammeter. The complete experimental set up is shown in figure 2.2.

The principle used in the measurement of velocity (C) is based on the accurate determination of the wavelength (λ) in the medium. If the separation between the quartz plate and reflector is exactly a whole multiple of the sound wavelength (λ), standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelength ($\lambda/2$) or multiple of it, anode current again becomes maximum. From the knowledge of wavelength (λ) the velocity (C) can be obtained from the relation $C = \lambda F$, where F is the frequency of the ultrasonic waves.

When the solutions attain the required temperature, the micrometer is operated and the distance d (mm) is measured and $d = n\lambda/2$. Therefore by knowing (λ) from above, C the ultrasonic velocity can be calculated. In practice, d

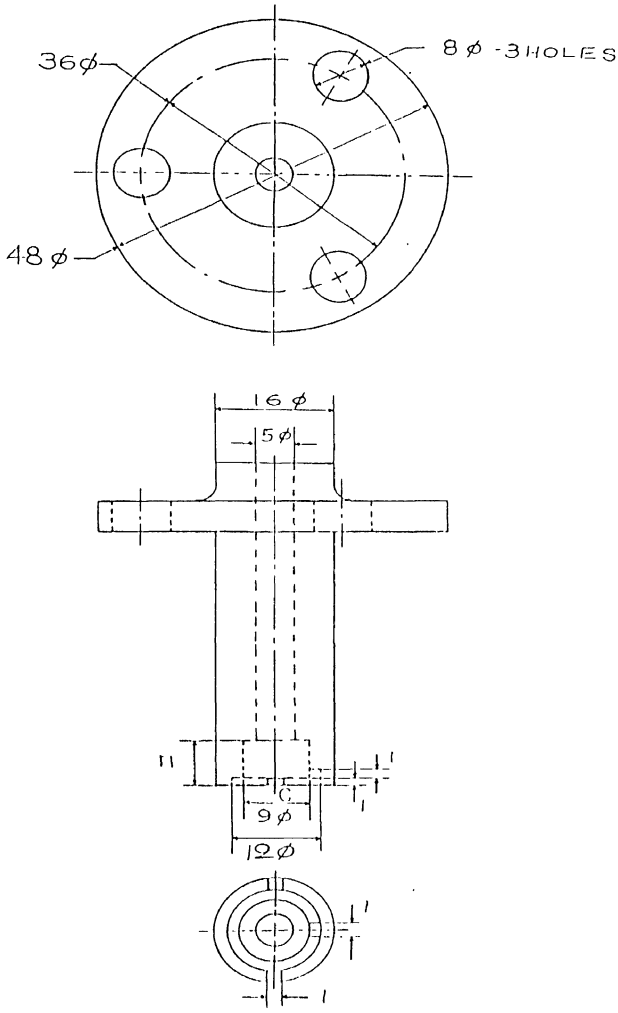
FIG. 2.3



SECTION ALONG A-B

FIG. 2.4

CRYSTAL HOLDER



for 20 maxima is measured so that F = 2MHz and n=20, C = 200 d m/sec. Thus C in meters/second can be readily obtained by multiplying the measured values of d for 20 maxima by 200. The velocity is measured to an accuracy of ±0.001%.

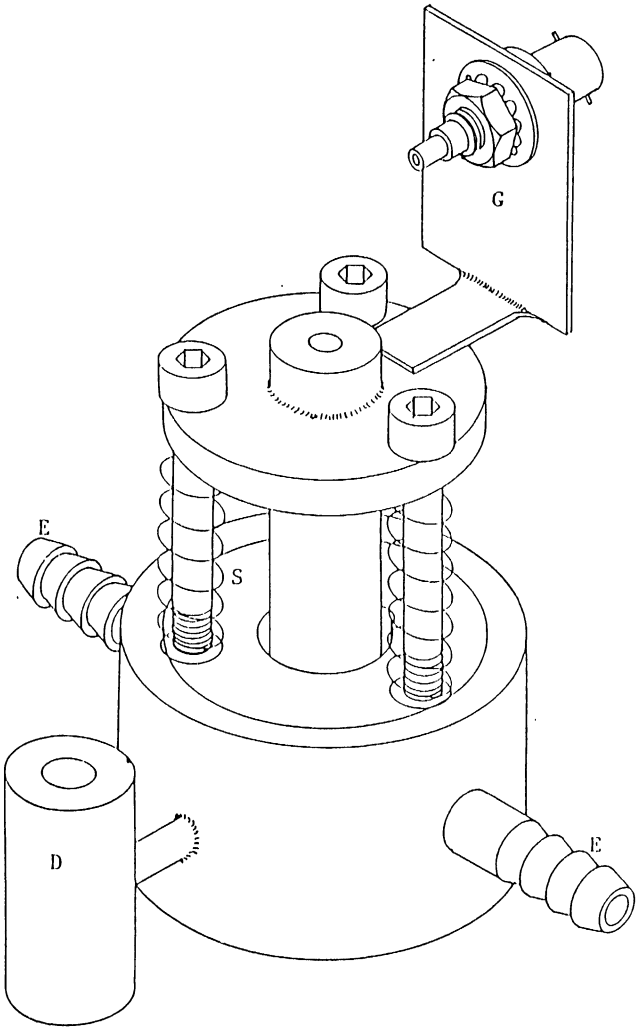
2.2 PULSE ECHO TECHNIQUE:

The ultrasonic velocity and absorption can be determined with the pulse echo technique. A cell is designed and fabricated in this laboratory for the measurement of absorption.

The cell fabricated in this laboratory is a double walled stainless steel cell with a central uniform bore of 18 mm diameter and a depth of 25 mm with a perfectly plane, highly polished bottom surface F (floor). The section along A-B with details of measurement are shown in the figure 2.3. A stainless steel shaft of 16 mm diameter and 40 mm length with a circular head on one side and a provision to mount the quartz crystal on the other side C (fig. 2.4) moves up and down in the bore of the cell by the action of three adjustable 8 mm Allen bolts and springs. A bore of 5mm diameter at the centre of the shaft helps in taking the leads from the quartz crystal to pulsed RF of pulse echo interferometer. The length of the liquid cell can be suitably altered by the movement of the shaft inside the bore. Through the fine adjustment of the Allen bolts with a key, parallelism can be achieved between the floor of the cell `F' which acts as a reflector and the quartz crystal `C'. Through a side provision `D' liquid under investigation can be poured in or out to the cell without

FIG. 2.5

ULTRASONIC CELL FOR LIQUID MIXTURES



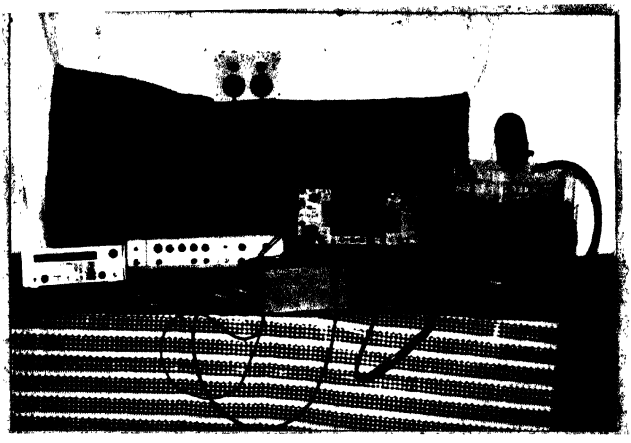


FIG. 2.6 : EXPERIMENTAL SETUP FOR VELOCITY AND ABSORPTION MEASUREMENTS.

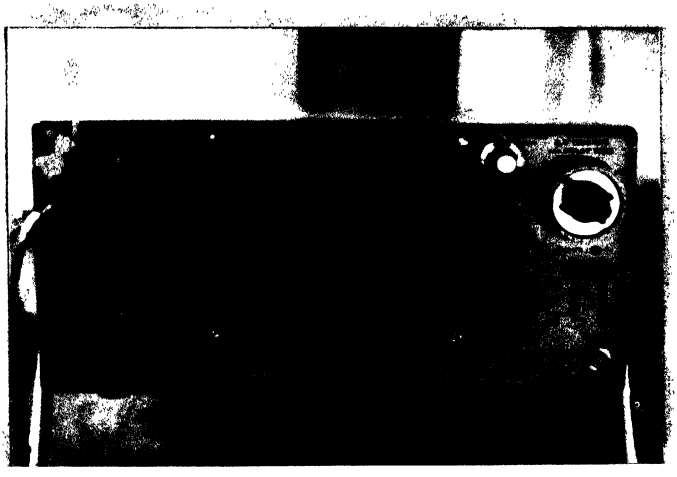


FIG. 2.7 : OSCILLOSCOPE TRACE OF PULSE ECHO PATTERN.

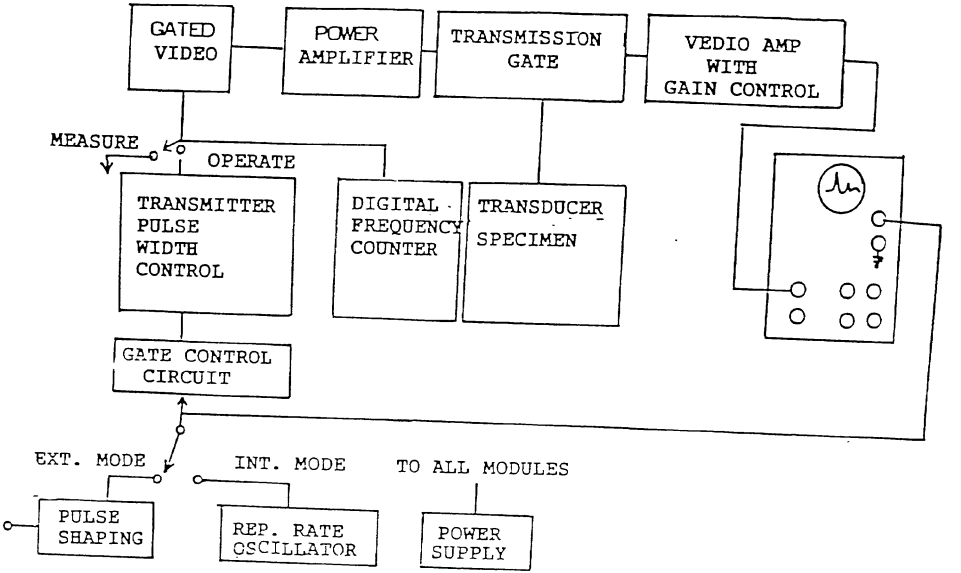


FIG.2.8.ULTRASONIC PULSE ECHO INTERFEROMETER

disturbing the parallelism between the crystal and the floor of the cell. Temperature of the sample can also be recorded by inserting a thermometer in this side provision `D'. The cell has an outer shell through which water can be circulated. EE represents the inlet and outlet of the water circulating jacket. The temperature of the circulating water is maintained at a fixed temperature by a thermostatically controlled water bath. The temperature is maintained constant within ±0.1K. An X-cut quartz crystal of 10 MHz fundamental frequency (supplied by Bharat Electronics Limited, Bangalore) is rigidly fixed by suitable adhesive in the crystal mounting space `C' of the shaft. An overall view of the cell is shown in figure 2.5.

A sharp RF electrical pulse with variable pulse duration from 2 μs to 20 μs is applied to the crystal with a suitable repetition frequency. The reflected wave returns to the transducer and a part of its energy is converted into electrical signal. This signal is amplified and displayed on the oscilloscope. The trace of the oscilloscope is a series of echoes with decreasing amplitude. The decrease in the amplitude is a measure of absorption. The photograph of the experimental setup is shown in figure 2.6 and the oscilloscope trace is shown in figure 2.7.

The schematic block diagram of the pulse echo interferometer is shown in the figure 2.8. The transmitter signal starts from a gated video oscillator connected in Weins bridge configuration. It generates RF pulses centered around 10 MHz. The repetition frequency of the RF generator is variable from 40 kHz to 400 kHz. The pulsed RF signal is

amplified by means of an RF power amplifier and then fed to the quartz transducer through the transmission gate. The transmission gate is used to isolate the input of the receiver amplifier circuit from the high voltage transmitter signal. The typical RF signal is 20 V peak to peak across the transducer through 50 ohm coaxial cable.

The receiver amplifier has four stages and the overall voltage gain is more than 60 db. The output of the amplifier is fed to the triggered oscilloscope (Phillips, dual beam oscilloscope PM 3226). All the power supplies of the system are electronically regulated.

The echo heights are fitted to an exponentially decaying wave of the form $Ae^{-\alpha x}$ and the value of α is evaluated and expressed in nepers. The distance between crystal and reflector is measured and the absorption per unit length is calculated and expressed in Nepers/cm. It is assumed that the reflector reflects all the sound energy incident upon it. The acoustic impedences of the solution and the reflector, are approximately 1,42,500 gm $cm^{-2}s^{-2}$ and 41,92,400 gm $cm^{-2}s^{-2}$. Hence the reflection coefficient estimated using the relation

$$R = \left[\frac{\sigma_1 - \sigma_2}{\sigma_1 + \sigma_2}\right]^2 \qquad (2.1)$$

where σ represents the impedance and the suffixes 1,2 represent the medium and the reflector. The calculated value is 0.87 which shows that only a negligible fraction is transmitted. A further check on the accuracy of the measured absorption was also made using carbon tetrachloride

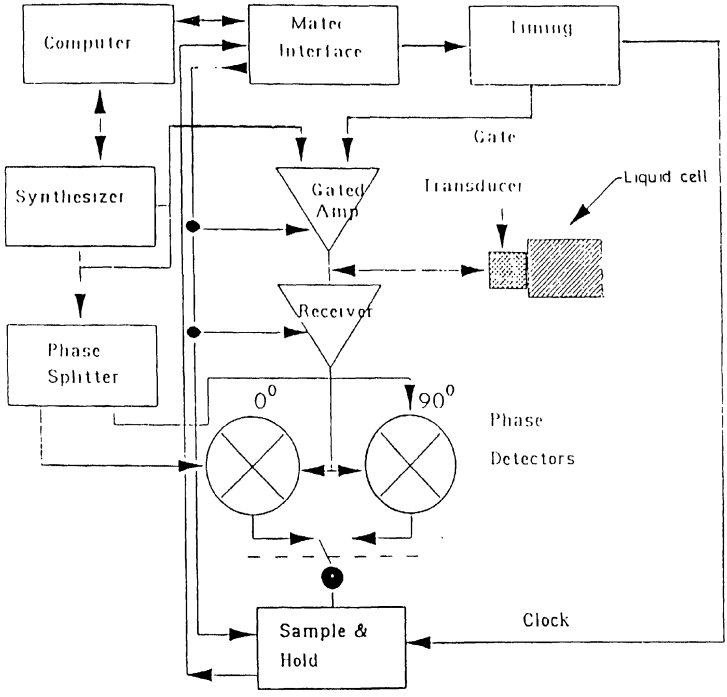


Figure 2.9 Block Diagram of the MBS 8000 Measurement System

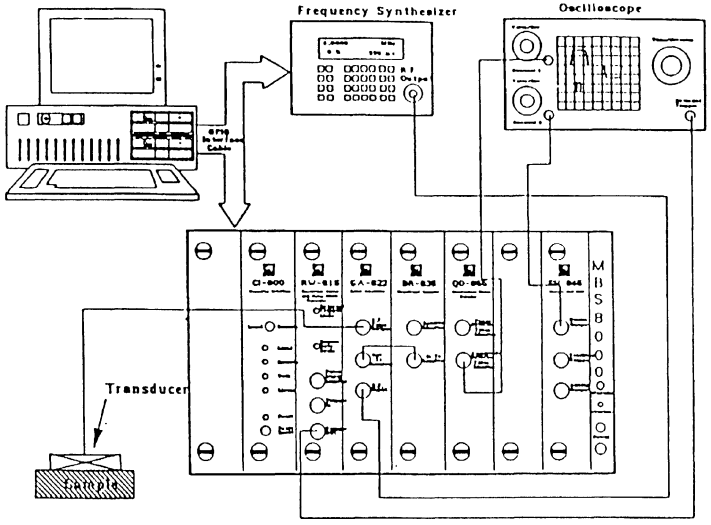


Figure-2.10 MATEC - MBS 8000 Ultrasonic system

as a standard liquid. The measured absorption $(\alpha/f^2)_{obs}$ for carbon tetrachloride at a frequency of 10MHz is 0.560 X 10^{-14} Np/cm which compares well with the earlier reported value of 0.540 X10^{-14} Np/cm. The accuracy in the measurement of velocity and absorption is 0.01% and 5% respectively.

2.3 MATEC MBS-8000 Ultrasonic Interferometer

The MBS-8000 Measurement system uses an innovative approach in determining the attenuation and velocity of sound through materials. A block diagram of the MBS 8000 measurement system is shown in figure 2.9 which shows the interrelationships of the various modules. The whole experimental setup is shown in figure 2.10.

First, the user must determine some operational parameters for the experiment to be performed, such as

1. Correct Frequency of Operation for the transducer chosen
2. Pulse Width and the Repetition Period for the high power R.F. Pulse
3. Receiver gain
4. Strobe Width and Position of the SH-865
5. Video Filtering

After the initial setup conditions have been defined in the software, the computer will address the MBS-8000 and program the modules to the above variables. If the initial conditions are not to the user's liking, the software will allow the re-programming of any or all of the parameter

values. For instance, if the frequency of operation needs to be optimized slightly, or changed completely, the software function key labelled frequency will allow the user to completely re-program this function. Likewise, the other variables in the system can be changed just as easily.

When the system has been optimized to the proper operational settings the MBS-8000 amplifier module (GA-822) will generate an R.F tone burst of upto 2500 Watts into 50 ohms, sending this tone burst to the transducer bonded to the material under study. The acoustic signals (echoes) which propagate through the material are then sent to the receiver (BR-835 or TR-833), to be amplified. The amplified acoustic signals are then sent to a phase sensitive detector module (QD-855 or TR-833). Here, incoming CW is used to generate both 0^{o} and 90^{o} phase reference which, together with the amplified signal echoes, are sent to phase sensitive detector stage. The resulting signals, which are filtered and multiplexed onto a common line, represent the real and imaginary component of the acoustic signal. The signal which results from the 0^{o} phase detector represents $A\sin\phi$, where A is the amplitude and ϕ is the phase angle. Likewise, the signal resulting from the 90^{o} phase detector represent $A\cos\phi$. It can easily be seen that if these two pieces of information are known, the magnitude of the acoustic signal will equal the square root of the sum of the squares, which, in mathematical form is:

$$A = \sqrt{A_1^2 \sin^2 \phi + A_2^2 \cos^2 \phi} \qquad (2.2)$$

Where A is the amplitude of the acoustic signal. A_1 is the coefficient of sine term, while A_2 is the coefficient of the cosine term.

The phase angle ϕ can easily be determined by taking the arc-tangent of the sine divided by the cosine or:

$$\phi = \tan^{-1}\left[\frac{A\sin\phi}{A\cos\phi}\right] \qquad (2.3)$$

Once both the amplitude and the phase angle of the acoustic signal is known, it is a simple matter to determine the attenuation of sound between two different echoes by acquiring additional data from another acoustic signal. This is accomplished by changing the position of the sample and the hold gate; to the next echo or any other echo in the field. Additional information could also be generated by changing the frequency; perhaps to an odd harmonic of the transducer. When amplitude information from two acoustic signals is known, the attenuation can be calculated from:

$$Attenuation = 20 \log\left[\frac{A_2}{A_1}\right] \qquad (2.4)$$

Where A_2 is the magnitude of the amplitude of the echo number two, and A_1 is the magnitude of the amplitude of echo number 1. All of the data which the computer uses in its calculations, is provided by the SH-865 Sample and Hold module which returns the value of the signal which is at the trailing edge of the sample and hold gate. As was mentioned previously, this gate can be changed in both width and position. Each time the computer requests data, the SH-865

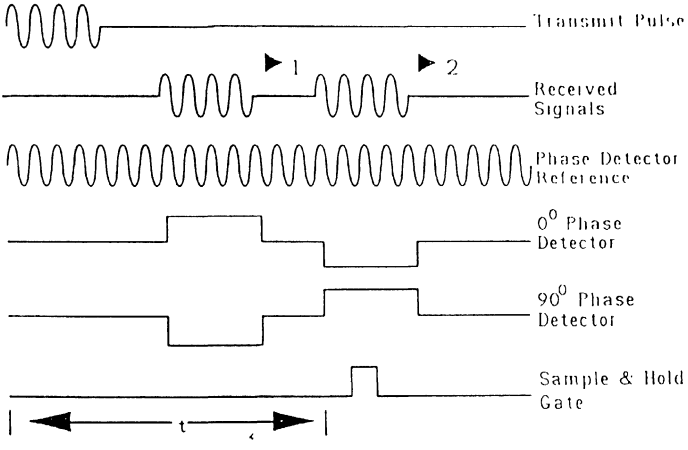


Figure 2.11 Time Relationships of Typical Signals

returns one data point. The accuracy in the measurement of absorption in this method is 3%.

Since the frequency, amplitude, and phase angle are known, information about the acoustic velocity can now be determined.

The use of phase detection has two major advantages. Automated measurements are much easier to achieve than with most other methods, and signals may be recovered from noise using computer averaging techniques. The technique used in the MBS-8000 measurement software involves interactive automatic control of the frequency, and measurement of phase relationships. The relationship between the time separating the initial R.F. tone burst, the received acoustic signals, the frequency and the phase is shown in figure 2.11, and mathematically represented by:

$$t = -\frac{\phi}{2\pi f} \qquad (2.5)$$

Where ϕ is phase angle much greater than 2π and f is the frequency in hertz.

Since it is impossible to directly measure ϕ except as an angle between $-\pi$ and $+\pi$, the above equation may be differentiated and written in terms of small change in frequency, and a measured change in the phase in angle.

$$t = -\frac{\Delta\phi}{2\pi\Delta f} \qquad (2.6)$$

A change in frequency can be controlled by the computer, addressing the frequency synthesizer, and the consequent change in phase angle determined by taking the difference of

two phase angle measurements. The change in frequency must be made in such a way that the change in phase is measurable, but less than π, since the computer cannot distinguish between $+\pi$ and $-\pi$. This is not a problem since the frequency can be changed in increments small enough to prevent a single large change in the phase angle. Therefore, the frequency is changed until the phase angle of each of the echoes is increased approximately by an integer value of π. The phase shifts of all of the echoes need not be equal, just a multiple of π.

When the desired phase shift is approached, the computer will calculate the frequency change required to make the phase angle change $M\pi$, where M is some integer. Several iterations of this procedure may be required to bring the value of the change in phase angle within the desired limits. Error limits of ± 0.02 radians are relatively easy to maintain. The values for $\Delta\phi/2\pi\Delta f$ are then calculated for each echo using the actual phase and frequency shifts for each echo. When this has been accomplished, the transit time is then determined from the slope of the $\Delta\phi/2\pi\Delta f$ versus echo number (N) curve. The slope is determined from a linear least squares fit of the data.

After the transit time information is known, this information can be used to determine the velocity of the sound through the material if the exact dimensions of the sample piece are known.

2.4 COMPUTATION OF PARAMETERS

The adiabatic compressibility (β_s), hydration number, intermolecular free length (L_f), internal pressure ($_{\nu}P_i$), classical absorption $(\alpha/f^2)_{cl}$, volume viscosity (η_v), relaxation time (τ) and relaxation frequency (f_r) are computed using the the relations 1.3, 1.4, 1.9, 1.12, 1.15, 1.18, 1.21 and 1.22 respectively.

2.5 MEASUREMENT OF DENSITY

To measure the density of the solution at different temperatures (303K, 313K and 323K), a dilatometer used. The dilatometer consists of a long graduated tube. The capacity of the bulb is 3 ml. The dilatometer was filled with the solution upto a fixed marking at the temperature 303K. The mass of the solution was found using a single pan electronic balance (Sartorius, Germany) with an accuracy of ±0.001 gm. The dilatometer was kept in a constant temperature bath. The volume expansions were measured using a travelling microscope which was previously calibrated to measure the volumes to an accuracy of 0.001%. From the measurement of volumes at different temperatures namely 303K, 313K and 323K, the density of the solution at these temperatures were determined. The buoyancy correction has been applied in determining the density of the solutions.

2.5.1 Co-efficient of volume expansion (α_v)

The co-efficient of volume expansion (α_v) of the given solution was measured using the same dilatometer. The volumes of the solution at different temperatures were

measured and a graph was plotted between volume and temperature. The coefficient of volume expansion was then calculated using the formula,

$$\alpha_v = -\frac{1}{V_T}\left[-\frac{dV}{dT}\right] \qquad (2.7)$$

where (dV/dT) is the slope of the straight line at the volume V_T.

2.6 Shear viscosity measurement

The shear viscosities of the solutions are determined using an Ostwald's viscometer kept in a constant temperature bath, using the value of viscosities of water at 303K, 313K and 323K from literature using the formula

$$\eta_s = \frac{\rho_1 t_1}{\rho_o t_o} \times \eta_o \qquad (2.7)$$

where ρ_1, ρ_o are the densities of the solution and water, t_1, t_o are the corresponding flow times and η_o is the shear viscosity of water at the measuring temperature.

2.7 Nuclear Magnetic Relaxation time measurements

The relaxation times T_1 and T_2 are determined by using commercially available Brucker PC 120 NMR process analyser. The major components of the instrument are magnet module, control module and printer and the key board.

2.7.1 Magnet module:

The magnet module houses the magnet unit, the radio frequency preamplifier, and the probe head. The later

includes the transmitter/receiver coil and associated tuning circuitary. The magnet unit consists of a permanent magnet and a magnet temperature control unit. The magnet has tested field strength of 4.7 Kilogauss. The temperature control unit employes multiple temperature sensors and dual heater/fan units to thermostat the magnet.

2.7.2 Control module:

The control module contains three main sections, the power supply, the radiofrequency circuitary and the microprocessor unit. The microprocessor unit is the brain of the minispec monitoring and controlling the operation of the instrument. It is the most complex portion of the minispec and consists of four major sub-assemblies. 1. The central processing unit, 2. The interface control, 3. The programmable pulse sequence generator, 4. The analog to digital converter.

2.7.3 Thermal printer:

The thermal printer consists of the print mechanism and interfacing electronics. It uses a 5 by 7 dot matrix and prints 15 characters per line. The printer provides a record of results, parameters values used in the aralysis of samples.

2.7.4 Key board:

This is used to change the various parameters of the pulse sequences, mode of detection of the signal (diode or phase sensitive detection) gain of the amplifier etc.

2.7.5 Measurement of T_1 and T_2:

The experiment definition module (EDM) 510A was used to measure T_1. This measurement was done using `Inversion Recovery' method, employing the $180^{\circ} - \tau - 90^{\circ}$ pulse sequence. T_2 was measured using the EDM 610A, with the CPMG pulse sequence. The measurements were carried out at 303± 0.1K.