CHAPTER - III

EXPERIMENTAL TECHNIQUES
3.0 Experimental techniques:

The experimental techniques employed in the present study to determine the ultrasonic velocity, ultrasonic absorption and density are described in this chapter. All the chemicals used in this present research work are of AR quality.

3.1 Ultrasonic techniques:

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. In the present study continuous wave (low amplitude) variable path interferometer is used.

In fixed frequency variable path 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 18 ml. The schematic diagram is shown in figure 1. In the figure 1, A is the crystal holder from which the leads are taken out. B is a metallic reflector attached to a shaft C which moves up or down by the action of a spring and a micrometer screw. The micrometer screw has a least count 0.001 cm and the length of the pitch
FIG. 1

A - CRYSTAL
B - REFLECTOR

ULTRASONIC INTERFEROMETER CELL
The cell has an outer shell through which the 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 ± 0.1°C.

At the bottom of the cell an X-cut quartz crystal of resonant frequency 2 MHz is fixed. This 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 microammeter. The complete experimental set up is shown in figure 2.

The principle used in the measurement of velocity (C) is based on the accurate determination of the wave length (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 (λ)/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
FIG. 2 EXPERIMENTAL SET UP FOR ULTRASONIC VELOCITY MEASUREMENTS.
\[ C = (\lambda) X F, \text{ where } F = \text{frequency of ultrasonic wave when the solution attains the required temperature, the micrometer is operated and the distance } d \text{ (mm) is measured and } d = n X (\lambda)/2. \] Therefore by knowing (\lambda) from above, C, the ultrasonic velocity can be calculated. In practice d for 20 maxima is measured so that F = 2 MHz 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 ±0.5 m/sec.

3.2 Measurement of density:

To measure the density of solution (\( \rho \) kg m\(^{-3} \)) at different temperatures (303K, 313K and 323K), a dilatometer was used. The dilatometer made in the Institute Workshop 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 dilatometer and hence the mass of the solution was found using a single pan electronic balance (Sartorius) with an accuracy of ±0.001 gm. The dilatometer was kept in a constant temperature water bath. The volume expansions were measured using a traveling microscope which was previously calibrated to measure the volumes to an accuracy of 0.001 c.c. From the measurements of volumes at different
FIG. 4

CRYSTAL HOLDER

36 φ

48 φ

8 φ 3 HOLES

16 φ

5 φ

11

9 φ

12 φ

1
FIG. 5
ULTRASONIC CELL FOR LIQUID MIXTURES
temperatures (303K, 313K, and 323K) the density of the solution at these temperatures were determined.

3.3 Co-efficient of volume expansion (\(\alpha\)):

The co-efficient of volume expansion (\(\alpha\)) 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 calculated using the formula,

\[
\alpha = \frac{1}{V_T} \left( \frac{dV}{dT} \right)
\]

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

3.4 Shear Viscosity measurement:

The shear viscosities of the solutions are determined using ostwalds viscometer kept in a constant temperature bath at 30 ± 0.1°C, using the value of viscosity of water at 30 ± 0.1°C from literature.

3.5 Pulse echo technique for absorption:

Ultrasonic absorption may be determined with the pulse echo technique. A cell is designed and fabricated by the author in this laboratory for the measurement of absorption.

3.5.1 Description of the cell:

The cell is a double walled stainless steel cell with a central uniform bore of 18 mm diameter and a depth of
FIG. 6 EXPERIMENTAL SET UP FOR ULTRASONIC ABSORPTION MEASUREMENTS
25 mm with a perfectly plane, highly polished bottom su-
tface F(floor). The section along A-B with details of mea-
urement are shown in the figure 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.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 5 mm 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 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 provi-
sion '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 circu-
lating water is maintained at a fixed temperature by a
thermostatically controlled water bath. The temperature is
maintained constant within ± 0.1°C. An X-cut quartz
FIG. 7 OSCILLOSCOPE TRACE OF PULSE ECHO PATTERN
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 5.

A sharp R.F. electrical pulse with variable pulse duration from 2 us to 20 us is applied to the crystal with a suitable repetition frequency. The reflected wave returns to the transducer and part of its energy is converted into electrical signal. The signal is amplified and displayed on the oscilloscope. The trace on 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 set up is shown in figure 6 and the oscilloscope trace is shown in the figure 7.

The schematic block diagram of the pulse interferometer is shown in the figure 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 rate 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.
FIG. 8. ULTRASONIC PULSE ECHO INTERFEROMETER
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 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 \( A e^{-ax} \) and the value of \( a \) is evaluated and expressed in nepers. The distance between crystal and reflector is measured and the absorption per unit length is calculated and expressed as nepers/cm. It is assumed that the reflector in the interferometer reflects all the sound energy incident upon it. The acoustic impedances 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

\[
R = \left[ \frac{\sigma_1 - \sigma_2}{\sigma_1 + \sigma_2} \right]^2
\]

where \( \sigma \) 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 meas-

63
ured absorption was also made using carbon tetrachloride as a standard liquid. The measured absorption \((\alpha/f^2)\) for carbon tetrachloride at a frequency of 10 MHz is \(0.560 \times 10^{-14}\) NP/cm which compares well with the earlier reported value of \(0.540 \times 10^{-14}\) NP/cm (Vigaroux, 1952).

3.6 Computation of parameters:

The adiabatic compressibility \(\beta_s\), Rao's number \(R\), intermolecular freeness \(L_f\), internal pressure \(\Psi P_1\), classical absorption \(\alpha/f^2\)_c, volume viscosity \(\eta_v\), relaxation time \(T\) are computed using the relations 1.3, 1.4, 1.9, 1.12, 1.14, 1.17, and 1.21 respectively.

3.7 Ultrasonic velocity and absorption measurements in solids:

The velocity and absorption measurements in solids were done using VT 1005E (HITACHI) ultrasonic instrument. Again velocity was checked using ultrasonic wall thickness / velocity meter (CALIPER CL204).

3.7.1 Velocity measurements:

The UT 1500E ultrasonic instrument is broadly divided into four major components (i) power supply unit (ii) ultrasonic pulsar / receiver (CRT) unit (iii) data processor and display (iv) auto-alarm unit. The measurements were carried out at frequency of 2 MHz. The crystal used is X-cut longitudinal wave crystal. The time base knob of the instrument is set at the desired thickness range of the sample.
First, the measurements were done in the standard samples such as iron, steel, brass etc. The velocity measurements were done as explained below; First, for the known standard samples, the instrument has been calibrated. The crystal, which is connected to a pulsar/receiver unit, was placed over the sample. Silicon grease was used as bonding material between crystal and the sample. The transmitting wave and the corresponding echoes were be displayed on the screen of the cathode ray oscilloscope. Then the following adjustments were done.

(a) By adjusting velocity and pulse position-knob unit the transmission wave (T) was set to point 0 and the maximum echo, the first echo \((h_1)\) near 25th division on the time base (fig.9).

(b) Next the second echo \((h_2)\) was located at 50th division without moving the probe.

(c) Then first echo \((h_1)\) and second echo \((h_2)\) were shifted to 25th and 50th division respectively by adjusting the knobs.

Then velocity and pulse position were locked. By using the known velocity samples (iron, stainless steel) the instrument was standardised. After standardisation, the sample of unknown velocity can be read directly from the display, after bonding the sample with crystal. The thickness of the sample measured using Vernier caliper was given
to the data processing unit, using the data/function keys present in the front panel control. The microcomputer attached to the calculation unit automatically calculate the velocity from the given value of thickness and from the measured time taken by the ultrasonic wave to pass through the thickness of the sample. The computed value was displayed in the display unit.

The block diagram of the instrument caliper CL 204 is shown in fig.16. It contains simply 3 toggle switches for power, thickness and velocity. There is one micrometer knob for adjusting the thickness numerical read-out value, which display on the display screen. For the velocity measurement, the probe was coupled to the test specimen, the wall thickness numerical readout was adjusted to the known thickness value at the measuring point. Then, sound velocity was read off from the display by operating the toggle switch. There are two probes available for two different range of thickness. The probe CLF4 was used for measuring in the range 0.250–9.999 mm and probe CLF5 is used in the range 1.50–99.99 mm.

3.7.2 Absorption coefficient measurements in solids:

By using UT1005E ultrasonic instrument, the amplitude of the echoes were noted. From the measured values of echo amplitudes and thickness, the absorption coefficient was calculated using the relation
FIG. 9 ULTRASONIC INSTRUMENT UT-1005E AND PULSE POSITION ADJUSTMENTS
FIG. 10 ULTRASONIC WALL THICKNESS/VELOCITY METER
(CALIPER CL-204)
\[ A = A_0 e^{-\alpha x} \]

where \( A_0 \) and \( A \) are amplitudes of initial and next echoes, \( x \) is the distance traveled by the wave and \( \alpha \) is the absorption coefficient.

3.8 Nuclear Magnetic Relaxation time measurements:

The relaxation times \( T_1 \) and \( T_2 \) are determined by using commercially available Bruker PC 120 NMR process analyser. The major components of the instrument are magnet module, control module and the printer and a keyboard.

**Magnet module:**

The magnet module houses the magnet unit, the radiofrequency preamplifier, and the probe head. The latter includes the transmitter/receiver coil and associated tuning circuitry. The magnet unit consists of a paramagnet and a magnet temperature control unit. The magnet has tested field strength of 4.7 Kilo gauss. The temperature control unit employs multiple temperature sensors and dual heater/fan units to thermostat the magnet.

**Control Module:**

The control module contains three main sections, the power supply, the radiofrequency circuitry, 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 digital converter.

**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, parameter values used in the analysis, sample identification and date.

**Key board:**

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

**Measurement of \( T_1 \) and \( T_2 \):**

The experiment definition module (EDM) 510-A was used to measure \( T_1 \). This measurement was by 'inversion Recovery' method, employing the 180°-( \( T \))-90° pulse sequence. \( T_2 \) was measured using the EDM-610-A, with the CPMG pulse sequence. The measurements were carried out at 40°C.