

Experimental Methods

In any experimental work on the thermodynamic properties, the purity of chemicals employed is of extreme importance. Impurities such as water which is absorbed by the chemicals, dissociation of chemicals on standing or exposure, association etc. all gives rise to errors in experimental measurements. Thus, apart from initial purification, a continuous check of the purity of substances and purification is important in any experiment on thermodynamics.

Excess volume

Excess volumes of the binary liquid mixtures can be determined in two ways:

- i. directly by observing the change in volume upon mixing the components in a dilatometer
- ii. indirectly by measuring densities of pure liquids and liquid mixtures

The different methods for the determination of excess volumes have been critically reviewed by Battino [1], Marsh [2], and Handa and Benson [3].

2.1 Measurement of Density: Review and Measurement

A number of methods can be employed to measure the density of a liquid. Conventionally specific gravity bottle is used to determine the density of liquids. Different methods for measurement of density of liquids are reviewed briefly here.

2.1.1 Balancing Column Method

It is based on the principle that the hydrostatic pressure of a given weight of liquid is proportional to its density. This method is quite useful when small quantities of liquid are available. It is capable of offering an accuracy of 2 in 10^4 parts.

2.1.2 Buoyancy Method

It is based on Archimedes' principle. This method [4,5] is rapid and useful for temperature variation studies. However, it is less widely used due to the difficulty of maintenance of temperature and due to surface tension effects. Under optimum conditions the method is capable of yielding an accuracy of 2 in 10^6 parts.

2.1.3 Magnetic Float Method

This is another form of buoyancy method. It is used for very accurate measurements of densities and density changes. It makes use of submerged float containing an iron core, the buoyancy of which is delicately counter balanced by the pull of a current carrying solenoid. The method is particularly suitable for determination of excess volumes of mixtures. Benjamin [6] designed a magnetic float method, with an accuracy of $\pm 0.001\%$ in density measurements. Franks and Smith [7] described a magnetic float technique with a sensitivity of $\pm 0.0001\%$ for a cell with 600 cm^3 capacity. Millero [8] surveyed the earlier literature on magnetic float densitometers and described a highly versatile new apparatus with a precision of $\pm 0.0002\%$, a capacity of about 32 c.m^3 and a useful temperature range greater than from 293.15 to 325.15 K. Drost-Hensen et al.[9] gave details on magnetic float densimeter and Masterton and Seiler [10] fully described their apparatus which had a reproducibility of 3 ppm. Further developments are proposed by Kupke and Beams [11], Keramati and Wolgemuth [12], Kupke and Crouch [13] and Haynes and co-workers [14-16].

2.1.4 Dilatometer Method

The density (ρ) of the mixtures is also evaluated using the molar volumes V_1 and V_2 ; molecular weights M_1 and M_2 of the component liquids and the excess molar volume V^E of the mixture using the relation.

$$\rho = \frac{M_1 X_1 + M_2 X_2}{(V_1 X_1 + V_2 X_2) + V^E} \quad (2.1)$$

where ' X_1 ' and ' X_2 ' are mole fractions. The measurement of V^E thus enables one to determine the density of the mixture. Neubeck [17] described a basic weight dilatometer wherein a mixture or a pure liquid was maintained by mercury. Volume changes which occur on change of temperature are determined by the weight of mercury expelled or added to the dilatometer. Improved versions in this method are reported by Burlew [18], Wood and Brusie [19] and Wirth and Losourdo [20]. Washington and Battino [21] described a dilatometer convenient to use in the temperature range 263.15 – 353.15 K and utilized for density measurements accurate to $\pm 0.003 \text{ cm}^3 \cdot \text{mol}^{-1}$ in V^E . Continuous dilatometers which are capable of measuring

the excess volumes with an accuracy of $\pm 0.0005 \text{ cm}^3 \cdot \text{mol}^{-1}$ are developed [22, 23] and reported in recent times.

2.1.5 Pycnometers Method

In this method the mass of a known volume of the liquid is weighed. Many types of Pycnometers are described by Bauer and Lewis [24]. Pycnometers are employed to determine the densities of the mixtures and the excess volumes are derived from these densities provided the compositions of the mixtures are known. Battino [25] used an improved version of the single arm pycnometer described by Wood and Brusie [19] which can be used to determine the density accurate to fifth decimal place. Parker and Parker [26], Kohler and Rott [27] and Ruiter [28] reported other good designs of mixing bottles for the measurement of densities.

2.1.6 Digital Densimeter

Kratky and co-workers [29-31] designed a digital densimeter in which the density of a fluid is determined by measuring the resonant frequency of a mechanical oscillator in a 'U' shaped glass tube, filled with the fluid. The method assumes a linear relationship.

$$\rho = AT_2 + B \quad (2.1.2)$$

Between density ' ρ ' of the fluid and the square of the time period 'T' of the oscillator, 'A' and 'B' are constants of the instrument and their values are determined by calibration with two fluids of known densities. Water and air are generally used for this purpose, Anton Parr K.G. manufactured a digital densimeter (Model DMA 020) based on this principle.

Kiyohara and Benson [32] employed this densimeter and found its usefulness for determination of densities accurately. Under favourable circumstances density can be determined, within $\pm 1.5 \times 10^{-6} \text{ g cm}^{-3}$. However, this accuracy is limited to differences which are less than about 0.05 g cm^{-3} . It is especially useful for the study of dilute aqueous solutions and to the determination of partial molar volumes. Recently, it has been used to determine densities of mixtures of organic liquids. Other models are also used by Letcher [33] (Model PAAR DMA 601 which gives an accuracy of $\pm 0.007 \text{ cm}^3 \text{ mol}^{-1}$), Picker [34] and Roux et al [35].

2.1.7 Anton Paar Model

The density of the sample was measured with an Anton Paar model DMA 5000 oscillating U-tube densimeter, provided with automatic viscosity correction, two integrated pt 100 platinum thermometers (DKD traceable), and a stated accuracy of $5 \times 10^{-6} \text{ g cm}^{-3}$. The temperature in the cell was regulated to $\pm 0.001 \text{ K}$ with a solid state thermo stat. The apparatus was calibrated once a day with dry air and bi-distilled freshly degassed water.

All liquids were boiled or heated to remove dissolved air. Solutions of different composition were prepared by mass in a 10 cm^3 rubber-stoppered vial to prevent evaporation using a Mettler A G 204 balance accurate to $\pm 10^{-4} \text{ g}$. To minimize the errors in composition, the heavier component was changed first and the sample kept in the water. Total uncertainty (ISO 9001) in the mole fraction is 9.86×10^{-5} , precision of the density (duplicate) measurement. $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$, and of the temperature $\pm 0.002 \text{ K}$. Total uncertainty in the density measurement as reported by the equipment manufacture, was $5 \times 10^{-6} \text{ g .cm}^{-3}$. Proper safety measures were taken when handling all the materials.

2.1.8 Measurement of density in the present investigation (Rudolph Research Analytical digital densimeter)

In the present investigation all the binary liquid mixtures were prepared by weighing an appropriate amount of pure liquids using an electronic balance (Afoset, ER -120A, India) with a precision of $\pm 0.1 \text{ mg}$ by syringing each component into airtight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogenous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDM-2911 Model) equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of $303.15 \text{ K} \pm 0.03 \text{ K}$. The uncertainty in density measurement liquid mixtures was $\pm 2 \times 10^{-5} \text{ gm.cm}^{-3}$. Proper calibrations at each temperature were achieved with doubly distilled, de-ionised water and with air as standards.

Specifications of the Rudolph Research Analytical digital densimeter**(DDM-2911 Model)**

Measurement of Density	:	0 to 3 g/cm ³
Temperature range	:	0 °C to 90 °C(Controlled via Peltier)
Pressure	:	0 to 10 bars
Modes	:	Continuous, Single, Multiple
Technique	:	Mechanical Oscillator Method
Accuracy	:	Density 0.00005 g/cm ³ Temperature 0.03 °C
Repeatability	:	Density 0.00001 g/cm ³ Temperature 0.01 °C
Resolution	:	Density 0.00001 g/cm ³ Temperature 0.01 °C
Minimum Sample Volume	:	Less than 1ml
Materials	:	Borosilicate glass, Teflon
Display	:	10.4 inch diagonal, 800-600 pixels, colour, Flat Panel Monitor with Resistant Touch Screen Interface, 200 nits' brightness, gasketed for spill Protection
Communication Interface	:	Touch Screen User Interface 3 – USB Ports, 2 – RS232 Ports, Ethernet Port for Network Connection, Keyboard Mouse, Network Capabilities
Video	:	Video assisted view of cell,
Magnification	:	Capable approximately 10X magnification
Internal Memory	:	8 GB Non-removable Compact Flash Shipping
Dimensions	:	36 in. (L) x 19 in. (W) x 18 in. (H) 91.44 cm (L) x 48.26 cm (W) x 45.72 cm (H)
Shipping Weight	:	70 lbs. (31.75 kg)
Power Supply	:	85 to 260 VAC 1; 48 to 62 Hz
Power Consumption	:	150 – 200 Watts



Figure 2.1: Rudolph Research Analytical Digital Densimeter (DDM-2911 Model)

Review of experimental techniques, Measurement of speed of sound

2.2 Measurement of Sound: review and method adopted

Techniques used for the measurement of speed of sound are, in general, classified into two categories [36-38]. They are 1) continuous wave methods and 2) pulse techniques.

2.2.1 Continuous wave methods

Some of the important continuous wave methods namely, Striation method, Optical diffraction method, Interferometer method and Brillouin scattering involve the measurement of frequency and wavelength of sound wave in a given medium. The velocity of ultrasound is the product of frequency and wavelength of the wave. The basic fact involved in Optical methods [39-44] is that when a sound beam passes through a medium it alters the local density and hence the refractive index of the medium. Striation or Schlieren method is developed by Toepler [45] for measuring wavelength of sound waves. In this method, sharp image of a vertical slit is focused on a vertical wire through a cell containing the liquid. Stationary sound waves are setup in the cell by a crystal and plane parallel reflector arrangement. A series of alternate bright and dark fringes can be seen by focusing a telescope on the wire. The distance of separation between these fringes is proportional to the wavelength of sound. The acoustic wave remains virtually stationary because of slowness of speed of sound compared with speed of light.

The optical diffraction method is invented almost simultaneously by Debye–Sears [46] and Lucas – Biquard [47, 48]. In this method a parallel beam of ultrasonic waves in a transparent medium acts as a diffraction grating for light which moves with the speed of sound. It is virtually stationary because velocity of sound is very much less compared to that of light. Since the order of diffraction and wavelength of light are known, wavelength of sound can be determined by measuring the angle of diffraction. The velocity of sound can be computed by multiplying wavelength of sound with its frequency. The outstanding advantage of optical methods is that they do not require any precision mechanical system and use small quantities of test liquids. One

disadvantage with this method is that normal acoustic beam is not a plane wave, and several distortions appear in the resultant light image. The accuracy in velocity measurements with this technique is $\pm 0.1\%$.

The interferometer method is the most widely used technique for the measuring of sound speed with high accuracy. It is easy to maintain the temperature steady for the sample. Subba Rao and Ramchandra Rao [49] developed a simple and accurate interferometer method by modifying the fixed path type to determine the temperature coefficient of sound speed. Kor and Tripathi [50] followed the method devised by Fox. Stationary waves are produced in this method and the effect of varying path length is investigated. A reversible crystal transducer is used in a variable path interferometer to both generate and detect the sound waves. The frequency of vibration of transducer crystal is adjusted such a way that the crystal vibrates at its natural frequency. As the crystal attains resonance it vibrates with maximum amplitude. The sound waves generated by the crystal travel through the liquid medium to a plane reflector which is maintained accurately parallel to crystal surface. When the distance between transducer and reflector is an integral multiple of half wavelength of sound, standing waves are set up between reflector and the crystal. The reflected sound waves are arriving back to crystal surface after being reflected by reflector which is 180° out of phase with the motion of the crystal. This results in the drop of current through the crystal due to decrease of amplitude of vibration.

Accuracy up to few parts per million in velocity measurements is attained due to recent advances in this technique. The NRL [51] measurements are accurate to $\pm 0.0013\%$. The interferometer method is a versatile technique. Wavelength of sound can be easily measured by varying the acoustic path length. The frequency of crystal oscillation is easy to determine when compared to tedious measurement of transition time in pulse technique. The temperature of the cell can be maintained steadily with ease. Frequency stability of oscillator is high due to high Q-factor of quartz crystal. Several workers have found interferometer technique more suitable for the determination of temperature coefficient of sound velocity. The superiority of this technique is well documented by Del Grasso [52].

Leonard and Suguin [53] designed an acoustic interferometer for simultaneous velocity and attenuation measurements in liquids over a wide range of frequencies and a temperature range from room temperature to cryogenic temperatures. A modified method was mentioned by Raghupathi Rao and Krishna Rao [54]. Leha et al [55] developed an interferometer for measuring ultrasonic velocities in electrolytes.

McCartney and Drouin [56] configured an acoustic interferometer capable of measuring ultrasonic velocity with an accuracy of 0.03%. Theory and performance of differential optical interferometer for measuring velocities of both surface acoustic waves and bulk waves are described by Palmer et al [57] Wright and Campbell [58] developed an ultrasonic interferometer for a range of frequencies 0.1 to 1.5 GHz.

These continuous wave methods are not adequate for measuring sound velocities in the GHz frequency range. Scattering technique developed by Brillouin [59] is useful in the frequency range of 1 to 10 GHz.

The random thermal motion of the molecules in a liquid can be considered as a result of a large number of longitudinal waves. It is very difficult to generate hypersonic waves of fixed frequency and amplitude. As such it is quite convenient to study the sound waves naturally present in the liquid at hypersonic frequencies. Brillouin predicted that scattering of light beam may occur when a monochromatic light beam is passed through a medium in which a sound wave is propagating. This Brillouin scattering is equivalent to a Bragg reflection from the acoustic diffraction grating. Light scattered by an acoustic grating suffers a Doppler shift as the acoustic grating is moving with the velocity of sound. Thus the scattered light consists of a doublet split symmetrically about the incident frequency. The frequency difference between scattered and incident light equals the frequency of the sound wave responsible for scattering. The wavelength (λ) of sound wave is given by the Bragg's relation

$$n\lambda = 2d \sin\theta \quad (2.2)$$

where λ is the wavelength of light and θ is the angle of scattering between the incident beam and plane of grating. Piercy and Hanes [60] proposed a simple model for

scattering process which yields the same results. This method is useful at hypersonic frequencies. Different methods for determination of hypersonic velocities are reviewed by Sette [61].

2.2.2 Pulse techniques

Ultrasonic velocity is determined by electronically measuring the time required for an ultrasonic pulse to traverse a given acoustic path length in pulse techniques. Pulse methods include the pulse echo method, pulse echo overlap method, pulse superposition method, pulse comparison method and ring around method. Some of the inherent disadvantages of continuous wave methods such as streaming and sample heating are virtually eliminated in pulse methods. A distinct advantage of pulse method is that velocity and absorption can be measured simultaneously.

In the single transducer pulse technique [62], a piezo-electric crystal transducer generates a short train of periodically repeated sound pulses. These pulses are propagated through the liquid medium to a plane reflector. The reflector is maintained accurately flat and parallel to the transducer's face. The reflector can be moved normal to the transducer to and fro. The reflected pulses are received by the transducer, which then serves as the receiver. Each time a pulse returns to the transducer, a part of energy is converted to an electrical signal and the rest energy being reflected. Repetition of this process leads to a series of detected echoes, each of which has made one more round trip through the sample than its predecessor. The attenuation and sound velocity are determined from the echo amplitudes and transit times. The transit time of a given pulse is electronically measured and sound velocity in the medium is directly evaluated.

Two transducer pulse technique is generally used when 1) the medium is highly attenuating which requires short acoustic path lengths and 2) keeping echoes separated from applied signal is difficult. The first transducer converts radio-frequency electrical pulses into ultrasonic pulses. The second transducer receives these pulses and reconverts them into electrical signals. The two transducers must possess exactly the same natural frequency. In case of single transducer pulse

technique electronic circuit is complicated because it is essential to block receiver input during the time interval of transmitted signal. But the size of measuring cell is generally small in single transducer pulse technique. The received pulse is amplified and displayed on a cathode ray oscilloscope. The time base of CRO is synchronized to pulse repetition frequency. A change in acoustic path length causes a change in transit time. This time delay is used for determination of speed of sound. Short wavelengths and high absorption coefficients make it difficult to extend the range of frequency beyond 300 MHz below 5 MHz this technique is not reliable due to diffraction problems. The accuracy in velocity measurement by this technique is $\pm 0.2\%$. Parthasarathy and Pancholy [63-65] used pulse technique to determine velocity of liquids at 21 MHz in the temperature range 10°C to 50°C .

Fairley and Mc Clements [66] described an ultrasonic pulse-echo reflectometer useful for measurement of ultrasonic velocity, attenuation and characteristic impedance of liquid samples. The device may be used for determining density, particle size and concentration of dispersed phases.

Pulse superposition method [67, 68] is a variant of pulse technique. A single transducer is generally used in this method. The pulse generated by the transducer traverses the medium and gets reflected by a plane parallel reflector. Each time a reflected pulse returns to the transducer, a part of energy is converted to electrical energy and the rest being reflected. Repetition of this process leads to a series of detected echoes each of which has made a round trip. A radio frequency oscillator excites the transducer. The frequency of radio frequency oscillator is adjusted until its period is equal to the round trip transit time of ultrasonic pulse in the specimen. Thus, radio frequency pulse generator triggers the transducer once per round trip of ultrasonic pulse. In this method the reflected echo is superposed by the triggering pulse. It is essential to trigger the transducer from a definite phase point of the signal. This method is accurate, but not as versatile as pulse echo overlap method as buffer rods cannot be employed. In pulse methods, generally, a pulse of sinusoidal radio frequency voltage is applied to the transducer. Typically, the voltage amplitude is

between a few volts to a few hundred volts. The pulse width varies between 1-10 μ s and pulse repetition frequency between 100 to 1000 pulses per second.

In the pulse echo overlap method [69-72] there is no superposition of elastic waves themselves but rather of the received echo signals when they reach the oscilloscope. Only one signal pulse is present in the sample at a time. The oscilloscope sweep is triggered by Continuous Wave Audio Oscillator (CWAO). CWAO frequency is adjusted such that time between sweeps is an integral multiple of the round trip transit time of acoustic pulse in the sample. The repetition rate of the applied signal is controlled by the same oscillator following a frequency division by 1000. The repetition rate is sufficiently low such that each pulse is dissipated in the sample before the next pulse is generated. Overlap of any two successive echoes is achieved by adjusting the CWAO frequency such that it is equal to round trip transit time. The reciprocal of CWAO frequency gives the transit time. Absolute accuracy arises in this method from the fact that this method is capable of measuring accurately from any cycle of one echo to the corresponding cycle of next echo. This method is highly accurate method yielding an accuracy of few parts per million in the velocity measurements.

In the phase adjustment method, the frequency of a gated pulse is varied such that the second pulse and reflected echo of the pulse through the medium reach the receiving transducer with a phase difference that is an integral multiple of $2\pi q_E$. This is achieved by varying the frequency until the superposed signal (on CRO screen) reaches a null. This is repeated for several nulls and single pass travel time can be computed.

Phase comparison technique [73-77] is used in the frequency range 10-200 MHz. In this method a fused quartz spacer of known thickness separates two delay lines precisely fixed distance apart. A pulse of sound waves from the transducer is reflected at both the liquid interfaces. Comparison of phase of the reflected echoes at the transducer is used to compute the transit time.

Stewart and Stewart [78] used normal incidence reflection technique at high frequencies up to 10 GHz. In this technique change in amplitude on reflection of sound wave incident normally at the delay line gives the longitudinal impedance. Longitudinal impedance data can be used to evaluate sound velocity, if the density of liquid is known precisely.

In the sing around technique [79, 80], a pulse of sound waves from a transducer passes through the liquid to a second transducer. Here acoustic pulse is converted to an electrical signal. This signal is amplified, reshaped and fed back to the transmitting crystal transducer. The repetition frequency of the complete cycle is determined to facilitate evaluation of sound velocity. This technique gives accuracy better than 1 in 10^4 parts. Sing around technique developed by Garnesey et al [81] is capable of determining difference between velocities in dilute aqueous solutions with an accuracy of $\pm 0.003\%$. Brammer [82] improved the technique and obtained an accuracy of 0.000001% in solids. Satyabala et al [83] developed sing around technique in which velocity measurement was performed with an accuracy of ± 0.5 m/s. Sanjeeva Chadda [84] developed singlaround technique with capability of digitally displaying sound velocity with an accuracy of $\pm 0.3\%$.

Some of the techniques for measurement of sound velocity are described in detail in Handbook der Physik [85].

2.2.3 Measurement of speed of sound in the present investigation (Interferometer Technique)

In the present investigation a variable path ultrasonic interferometer (Mittal enterprises, New Delhi Model M-82) was used to measure the speed of sound of pure liquids and liquid mixtures. The working frequency of variable path ultrasonic interferometer was 2 MHz.

2.2.3.1 Principle

Ultrasonic interferometer employs an x-cut quartz crystal as transducer. The opposite faces of the crystal are gold plated and connected to an oscillator. The oscillator

excites the X-cut quartz crystal at its natural frequency. Due to resonance, crystal vibrates with maximum amplitude. The vibrating face of the crystal generates an ultrasonic wave that passes through the liquid medium. The wave gets reflected by a reflector, which is held accurately parallel to crystal surface and can be moved at right angles to crystal surface in the direction of wave propagation. Stationary waves are formed in the liquid medium, when the distance between crystal and reflector is an integral multiple of the half wave length of the sound wave. The motional impedance of quartz crystal increases due to rigorous vibration of liquid medium. The wave reflected back to crystal arrives at 180° out of phase with the motion of the crystal. This results in appreciable decrease in the amplitude of crystal vibration. This is accompanied by the decrease in current through the crystal.

The current measured through the crystal/ voltage measured across the crystal, as a function of distance between crystal and reflector, exhibits series of minima separated by a distance equal to half the wavelength of sound wave in the liquid. If the frequency of crystal oscillation is f , then sound velocity u in the liquid medium is given by the formula

$$u = f\lambda \quad (2.2.1)$$

where λ = wavelength of sound wave.

Generally, a trite crystal controlled oscillator is used to excite the x-cut quartz transducer. The variation of voltage across the crystal is observed using a FET Voltmeter. Water from a constant temperature water bath is circulated through the double walls of the interferometer cell to maintain the temperature of the liquid sample in the cell. The constant temperature water bath (thermostat) can maintain the temperature of water at any desired temperature within $\pm 0.01^\circ\text{C}$.



Figure 2.2: Ultrasonic interferometer (Model M-82)

The major sources of error in the interferometer technique are

- i. Diffraction and wave guide effects
- ii. Irregularities in the vibrations of the transducer
- iii. Lack of parallelism between transducer and reflector

Errors due to diffraction are generally minimized by confining the velocity measurements to Fresnel zone.

2.2.3.2 Description of the equipment

The interferometer assembly consists of the following major parts

- i. High frequency oscillator (generator) assembly
- ii. Liquid cell
- iii. Reflector assembly with vernier micrometer
- iv. Base to hold the cell and a shielded co-axial cable

2.2.3.3 High frequency oscillator assembly

High frequency oscillator/generator is used to excite the transducer at the required frequency (2 MHz) in the present study. The oscillator assembly is provided with a micro-ammeter (0-50 μ A) to observe the changes in current.

2.2.3.4 The Measuring Cell

This is a specially designed double walled cell for maintaining the constant temperature of the liquid during the experiment. A fine micrometer screw has been provided at the top, which can lower or raise the reflector plate in the cell through a known distance. It has quartz plate fixed at its bottom.

A sketch of the interferometer cell is shown in Fig. 2.2.1. The interferometer cell is made of stainless steel, which is in the form of tube of inner diameter 1.6 cm with capacity 12 cm³. A gold plated quartz plate of diameter 0.9 cm is cemented at the bottom of the interferometer cell. The ultrasonic waves start from the quartz plate and they are reflected back from the movable reflector. The reflector used in this

interferometer is a fused quartz rod with a reflecting surface of 1.4 cm in diameter. This is coupled to a micrometer screw assembly reading up to 0.01 cm using a Teflon coupler via the steel rod. The micrometer screw activates the steel rod, which is spring loaded to take care of any backlash. The micrometer assembly along with the reflector is fixed to the liquid cell with the help of a threaded cup and Teflon ring. The required stability for measuring the cell is given by heavy pedestal; provision is made for circulating water at any desired temperature from a thermostatically controlled bath into a jacket around the measuring space to maintain the experimental liquid at a constant temperature during the experiment. A crystal controlled r.f. Oscillator Fig. 2.2.2 is used to excite the transducer at a fixed frequency of 2 MHz. The HT current to the output tube is fed through a bridge network including a micrometer in such a way that the changes in the plate current can be easily observed on the microammeter. Two controls are provided for the purpose of sensitivity regulation and initial current adjustment of the meter. The interferometer consists of an electrically dried quartz plate coupled to the liquid column.

The length of the liquid column can be varied by moving the quartz reflector, keeping its plane parallel to the quartz plate.

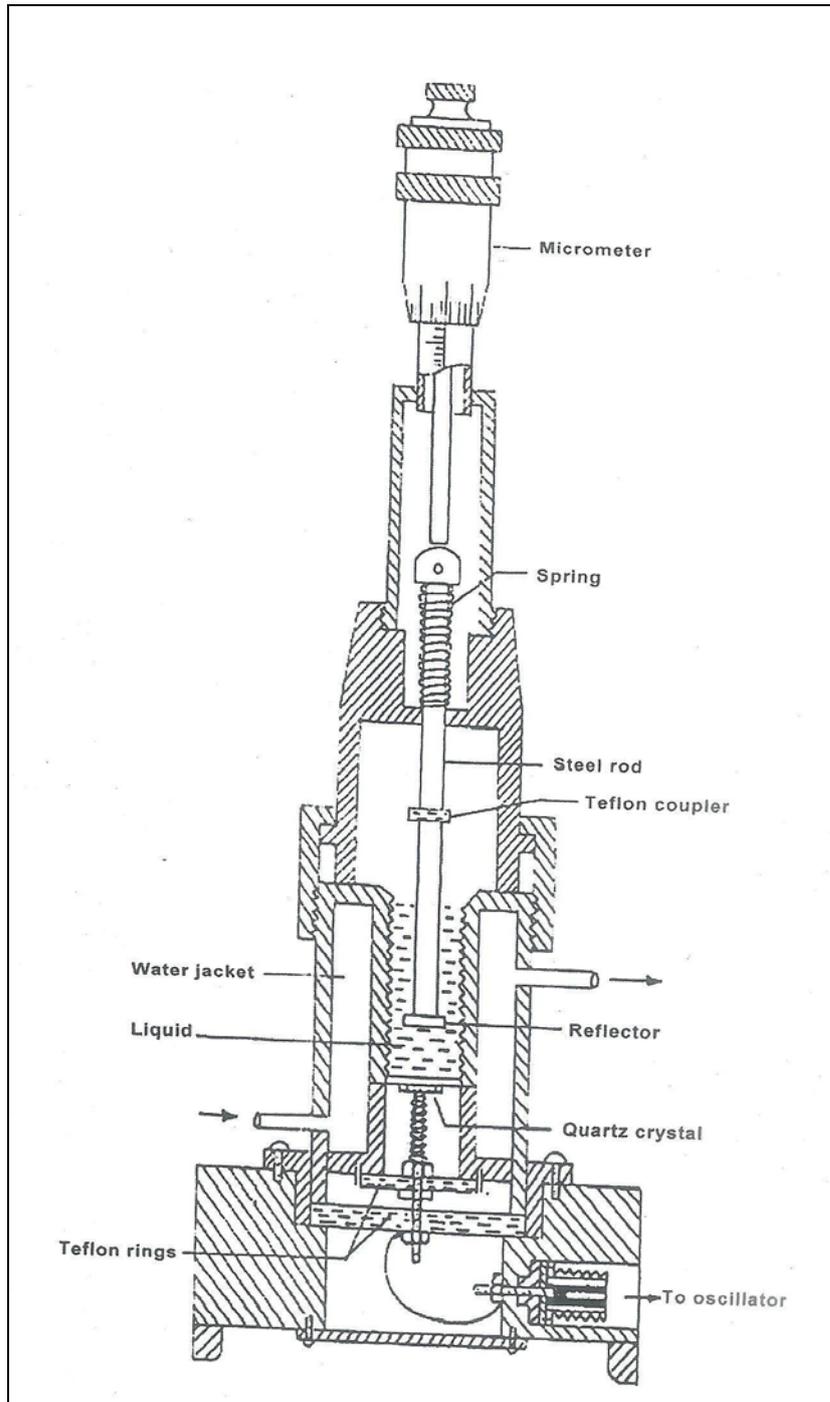


Figure 2.2.1: Interferometer cell

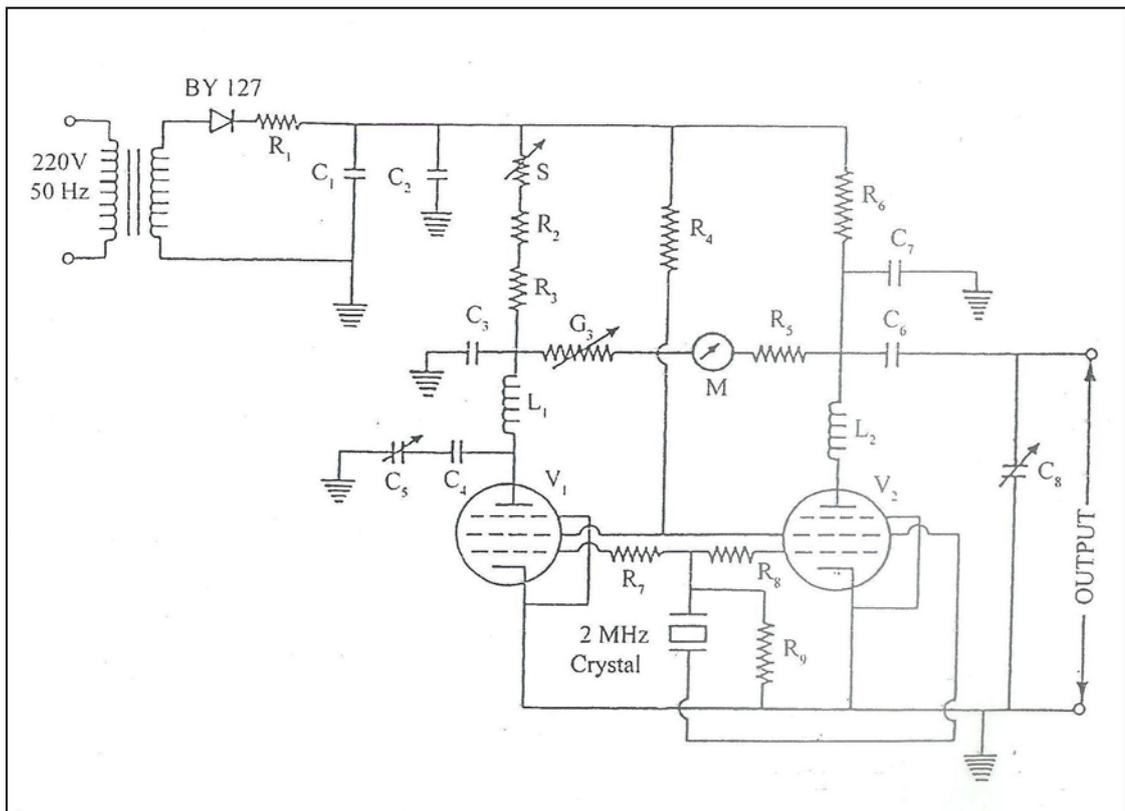


Figure 2.2.2: Oscillator Circuit

Whenever the distance between the transducer and the reflector corresponds to an integral number of half-wavelengths, the liquid column vibrates in resonance resulting in an increase of the motional impedance of the transducer. This leads to a sharp dip in the r.f. Voltage across the transducer. The current vibrations are noted in the micro-ammeter. The distance covered by the reflector between any two consecutive dips corresponds to one-half wavelength, $\lambda/2$.

2.2.3.5 Reflector assembly

The pitch of the screw employed to move the reflector is 0.5mm and the head of the screw is divided into 50 equal divisions. The least count of this setup is 0.001 cm. The bottom of the screw is coupled to the reflector rod through a steel ball which eliminates errors arising due to non-axiality between them, besides keeping the reflector free to move axially without rotating along with the screw. To avoid backlash error, the reflector is spring loaded. The reflector can be firmly mounted on the top of the interferometer cell. The reflector is tightly coupled to the interferometer cell with the help of knurled cap.

2.2.3.6 Base to hold the interferometer cell

A heavy cylindrical base is used to hold the cell. The cell is clamped in the socket of the base with the help of a screw provided on the side of the base. In addition to acting as a rigid mount for the interferometer cell, base provides contacts to the upper and lower surfaces of the crystal transducer, so that exciting electrical signal is passed from high frequency oscillator assembly. The base is connected to high frequency oscillator assembly with a high quality co-axial cable provided with suitable sockets.

2.2.3.7 Experimental procedure

Ultrasonic velocities in aqueous/non-aqueous liquid mixtures at different temperatures have been measured in the present investigation at a frequency of 2 MHz. The detailed method of measurement of ultrasonic velocity using ultrasonic interferometer is described below.

The interferometer cell is cleaned with acetone and then dried using an air blower. The cell is filled with experimental liquid. The reflector assembly is coupled to the cell tightly by screwing the knurled cap. The cell is inserted into the base socket and clamped rigidly with the help of side screw provided to the base. The inlet and outlet of the double walled construction are connected to constant temperature water bath by means of transparent plastic tubes. Water is pumped into the double walled cell with the help of an electrical motor provided with the constant temperature water bath. Water of constant temperature is circulated at least for 30 minutes so that the temperature in the cell stabilizes. After the required temperature is attained in the interferometer cell, high frequency oscillator assembly is connected to the base of the cell using shielded co-axial cable. The high frequency oscillator assembly is switched on.

The reflector is gently moved towards the crystal with the help of micrometer screw. Variation of current through the crystal transducer due to the motion of the reflector is observed with the help of micro-ammeter provided with high frequency oscillator assembly.

Readings of positions of micrometer screw corresponding to ten successive maxima (or minima) of current in the micro-ammeter are noted. Then counting maxima (or minima) up to 20, the readings of 21st to 30th consecutive maxima (or minima) are noted. The difference between 1st and 21st, 2nd and 22nd, 3rd and 23rd... are calculated. These differences should be almost equal. Otherwise, another set of fresh readings are to be taken. Since the difference between successive sharp maxima (or minima) corresponds to half wave length of sound wave, the average of the ten differences corresponds to ten wavelengths. From this data, wavelength of ultrasonic wave is determined. The ultrasonic velocity is determined by multiplying the wavelength of ultrasonic wave with the frequency of crystal oscillation (2 MHz in this investigation). The measured ultrasonic velocities have an accuracy of $\pm 0.2\%$.

2.2.3.8 Effect of diffraction on the velocity measurement

Diffraction of ultrasonic beam introduces considerable error in the measurement of ultrasonic velocity and absorption [86]. These errors are predominant near the radiator and decrease for differential distance farther from it. The velocities measured near the source are higher than the plane wave velocities. These errors are systematic in nature and are amenable to theoretical and empirical studies.

Several workers [87-93] made attempts to evaluate diffraction errors. Errors arising due to diffraction are discussed in detail by Kranushkin [94]. The excess velocities (Δv) are given by

$$(\Delta v/v) = \lambda^2/31.5a^2 \quad (2.2.2)$$

where λ is the wavelength and “a” is the radius of the piston source.

The theoretical expression of free field diffraction error due to Bass and Williams as cited by Mc Skimin [95,96] is given by

$$(\Delta v/v) = \lambda^2/2\pi^2az^{1/2} \quad (2.2.3)$$

where λ is the wavelength, “a” is the diameter of the beam and z is the distance of the source from reflector at which measurement is made. Mc Skimin confirmed the above relation by measuring velocities in solids. The diffraction effects in liquids are studied by Ilgunas et al [97]. But they have not correlated their results with theory.

Subramanyam et al [98] found that diffraction errors are 3.2 times the value predicted by Bass and Williams theory.

$$(\Delta v/v) = 3.2(\lambda^2/2\pi^2az^{1/2}) \quad (2.2.4)$$

The above relation was used to evaluate diffraction errors in the present investigation. The experimental velocities were corrected accordingly.

2.3 Viscosity Measurement: Review and Measurement

Viscosity is a measure of resistance of fluids to flow. It is due to friction between adjacent layers of fluid. The property of a liquid by virtue of which it opposes

relative motion between its different layers is known as viscosity [99]. A brief review of some important methods for determining viscosity is prescribed here.

Viscosities of liquid and liquid mixtures can be determined by two methods: (i) absolute method and (ii) relative method. The determination of viscosity by absolute method requires the determination of the constants of the apparatus. Hence, viscosities of liquids and binary solutions were determined by the relative method. In this method, it is easy to measure the viscosity of a liquid by comparison with a reference standard liquid of known viscosity. Different types of viscometers and their modifications and conditions of viscosity measurements are given below.

1. Stokes falling Sphere Viscometer
2. Ostwald's viscometer
3. Ubbelohde suspended level Viscometer

2.3.1 Stokes falling Sphere Viscometer Method

Stokes' method is suitable for highly viscous liquids. When a body falls through a viscous medium, its motion is opposed by frictional force which increases with the velocity of the body. This frictional force increases until it becomes just equal to the motive of driving force. Then the body attains a constant velocity called terminal velocity. The coefficient of viscosity can be determined by measuring the terminal velocity.

Rotational viscometer consists of two coaxial cylinders, with the space between them filled up with a fluid. The inner cylinder is suspended by means of a long thin wire. When the outer cylinder is rotated with a constant velocity about their common axis, a torque is communicated to the inner cylinder through the intervening fluid. This torque tends to rotate the inner cylinder. This motion is opposed by the torque of suspension and the cylinder comes to equilibrium after rotating through an angle θ . The angle is measured by an optical lever arrangement in which a mirror is attached to the suspension.

The viscometer consists of a vertical cylindrical tube filled with the liquid under test and immersed in a thermostat at the desired temperature. A steel ball, of density ‘ ρ ’ and the diameter suitable to give a slow rate of fall, is now dropped through the neck of the tube, and the time of fall between two marks is determined with a stop watch. If the process is repeated with a liquid of known density and viscosity then Eq. 2.3

$$\eta = \frac{2r^2(\rho - \rho_m)g}{9V} \quad (2.3)$$

- r = radius of spherical body
 ρ = density of spherical body
 ρ_m = density of fluid
 g = acceleration due to gravity
 V = volume of the liquid taken in the tube.

Yields for the ratio of the viscosities of the two liquids

$$\frac{\eta_1}{\eta_2} = \frac{(\rho - \rho_{m1})t_1}{(\rho - \rho_{m2})t_2} \quad (2.3.1)$$

Therefore, knowing the viscosities of one of the liquid, the density of the ball, and the densities of the two liquids, the viscosity of the liquid under study can be calculated by means of eq. (2.3.1) from the observed values of t_1 and t_2 .

2.3.2 Ostwald Viscometer Method

Viscosity measurements can also be made with a modified Ostwald type viscometer with a flow time of 300s for water at 298.15 K. The viscometer contains two bulbs A & B. A definite quantity of liquid is introduced into the bulb (B) of the viscometer and is kept immersed in the thermostat. After equilibration, the liquid is drawn up by suction into the bulb (A) until the liquid level is raised above the mark ‘a’. The liquid is then allowed to drain and the flow time (t_1) taken by the liquid to drain from ‘a’ to ‘b’ is measured with a stop watch which reads 1/10 sec. The viscometer is cleaned, the reference liquid is added and the procedure is repeated to determine the flow time (t_2).

The viscosity of the test liquid can be calculated by using the eq. (2.3.2)

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \quad (2.3.2)$$

where

η_1 = viscosity of the test liquid

ρ_1 = density of the test liquid

t_1 = flow time of the test liquid

η_2 = viscosity of the reference liquid (water)

ρ_2 = density of the reference liquid

t_2 = flow time of the reference liquid

At least eight determinations are required to be made for each liquid and difference of any two readings should not exceed 0.2 sec. The reported viscosity data will be reproducible within ± 0.005 Cp.

2.3.3 Experimental techniques that were employed in the present investigation (Viscosity Measurement: Ubbelohde Viscometer Method)

Viscosity measurements were made with the help of Ubbelohde suspended level viscometer using 10-15 cm³ of solution. The design of this viscometer eliminates pressure corrections and minimizes surface tension effects [100]. Choice of viscometer dimensions are limited by consideration of two factors.

- (i) Volume of solution required: Unlike Kaminsky's work on aqueous systems [101] preparation of purified solvent limits the volume to 10-15 cm³.
- (ii) Capillary dimensions: The capillaries are too narrow which are found to be very sensitive to small quantities of impurities or dust, while broad capillaries require a large kinetic energy correction, together with introducing errors due to heating and drainage effects.

For absolute viscosities the viscometer is calibrated with water at temperature over the range 288.15 - 318.15 K and with 30% aqueous sucrose solution, using an equation of the form

$$\eta = \rho (at - b/t) \quad (2.3.3)$$

Which may be derived for a capillary viscometer [102] and where ‘ η ’ is the dynamic viscosity, ‘ ρ ’ is the density of the liquid, ‘ t ’ is the efflux time and ‘ a ’ and ‘ b ’ are the viscometer constants. Majority of the work is concerned solely with relative viscosities, η/η_0 and it is found sufficiently precise to take

$$\eta_1/\eta_0 = \frac{\rho t}{\rho_0 t_0} \quad (2.3.4)$$

where ‘ η ’, ‘ t ’ and ‘ ρ ’ refer to the solution and ‘ η_0 ’, ‘ t_0 ’ and ‘ ρ_0 ’ to the solvent. ‘ t_0 ’ and ‘ ρ_0 ’ are determined for every batch of solvent used.

The viscometers are to be mounted in a thermostated water bath of 45 dm³ capacity by means of rigid metal clamps which can be individually leveled.

Efflux times are measured with an accuracy of ± 0.001 s by means of photocell/lamp assemblies firmly attached to the viscometers and coupled to an electronic timing and programming system.

Eicher and Zwolonski [103] reported a heating effect due to lamps in a similar detector unit. When times of a continuous series of measurements on water are plotted over a time scale of several hours, no trend is apparent and the efflux times are varied by less than 0.02% from the mean. The first efflux time is generally discarded as subsequent measurements are usually slightly shorter due to an initial wetting effect.

In the present study, viscosities of liquids and liquid mixtures were determined by relative method using Ubbelohde viscometer Fig. 2.3 as this is superior over the Ostwald type of viscometer. In the Ubbelohde viscometer the liquid is allowed to flow only down the walls of the bulb below the capillary, thus forming a suspended level in the form of a hallow hemisphere at the lower end of the capillary to discharge into an

air space. This eliminates the uncertainty regarding the position of the lower liquid level and balance the effect of surface tension at the upper meniscus.

The viscometer was fabricated with a heavy walled glass so that the instrument was resistant to shock. The bulb between etched lines (Ubbelohde) had a capacity about 4 ml and the capillary tube had a length of about 90 mm and 0.5 mm internal diameter. The reservoir of the viscometer was filled with the sample liquid by tilting the viscometer to about 30° from the vertical and its limbs closed with Teflon caps.

The viscometer was kept for about 30 minutes in a thermostat maintained at 308.15 K temperature. This permitted the contents of the viscometer to attain the experimental temperature. Then the Teflon caps were removed and the sample was raised to the middle of the upper most bulbs by applying suction, with the air vent being closed by the finger tip. The efflux time was measured between the marks on either side of the bulb with a stopwatch, which had an accuracy of ± 0.1 sec. The efflux time of each sample was measured at least eight times.

The average efflux time and density at the same temperature were employed in the calculation of viscosity, the viscosities (η) of pure liquids and liquid mixtures were computed from the efflux time and densities using the relation

$$\eta = K_V \rho t \quad (2.3.5)$$

where ' K_V ' is viscometer constant, ' ρ ' and ' t ' are density and efflux time for a given sample respectively. At the experimental temperature (308.15 K) ' K_V ' was evaluated using viscosity and density of pure water from the

$$K_V = \frac{\eta_w}{\rho_w t_w} \quad (2.3.6)$$

The calibration of viscometer was checked by measuring the viscosities of pure liquids like benzene, chlorobenzene and carbon tetrachloride at 298.15 K. The measured values of viscosity were accurate to $\pm 0.1\%$

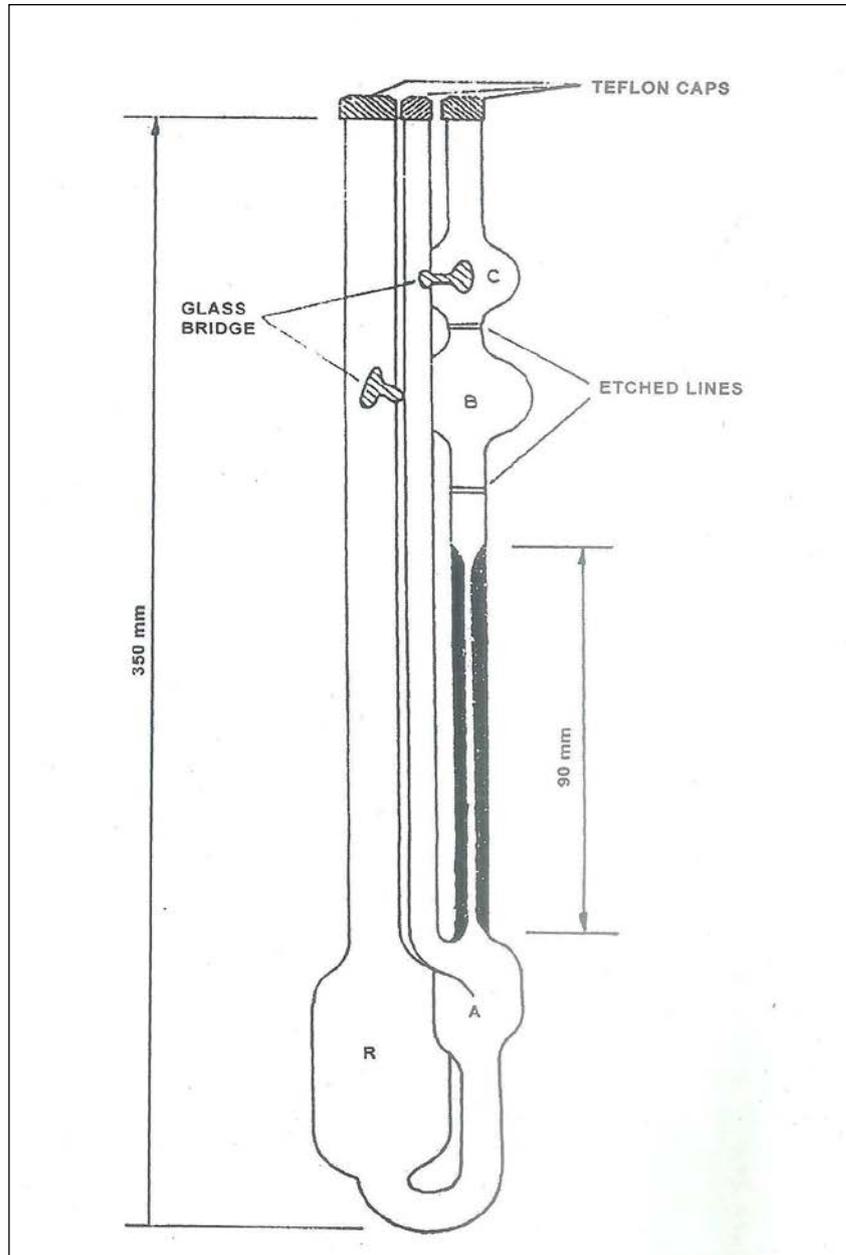


Fig. 2.3: Ubbelohde Viscometer

2.4 Source of Materials :

Material	Supplier	Purity of mass fraction (%)
3-chloroaniline	Merck	99.5
1,2-dichlorobenzene	Merck	99.5
1,3-dichlorobenzene	Merck	99.5
1,2,4-trichlorobenzene	Merck	99.6
o-chlorotoluene	Merck	99.5
m-chlorotoluene	Merck	99.0
p-chlorotoluene	Merck	99.0
2-phenylethanol	Merck	99.0
2-chloroethanol	Merck	99.5
2-aminoethanol	Merck	99.0
Bromobenzene	Merck	99.5
Chlorobenzene	Merck	99.0
Nitrobenzene	Merck	99.7

Purification Methods

2.4.1 Purification of chemicals

The following chemicals are used in the present work.

01. 3-Chloroaniline
02. 1,2-Dichlorobenzene
03. 1,3-Dichlorobenzene
04. 1,2,4-Trichlorobenzene
05. o-Chlorotoluene
06. m-Chlorotoluene
07. p-Chlorotoluene
08. 2-aminoethanol
09. 2-chloroethanol
10. 2-phenylethanol
11. Chlorobenzene
12. Bromobenzene
13. Nitrobenzene

In the present investigation all chemicals supplied by S.D. Fine chemicals and Merck Ltd, which were purified by standard procedures [104,105] like distillation, fractional distillation under reduced pressure and middle fractions were collected. Before use, the chemicals were stored over 0.4 nm molecular sieves approximately for 72 h to remove water content and degassed. The measured density and speed of sound of the pure components were compared with literature [105-119] values at 303.15 K and these were in good agreement with literature values and were given in Table 2.4.2.

Table: 2.4.2: Literature [105-119] values and these were in good agreement with literature values at 303.15 K

Pure components	Density $\rho / \text{g}\cdot\text{cm}^{-3}$		speed of sound $u / \text{m}\cdot\text{s}^{-1}$		Viscosity $\eta / \text{m Pa}\cdot\text{s}$	
	Experimental	Literature	Experimental	Literature	Experimental	Literature
3-chloroaniline	1.20532	1.20530 [106]	1517.5	1517.0[106]	4.2554	4.2560[107]
o-chlorotoluene	1.07285	1.07283[108]	1285.0	1284.0[109]	0.886	0.884[109]
m-chlorotoluene	1.06283	1.06281[108]	1281.1	1280.0[109]	0.743	0.746[108]
p-chlorotoluene	1.05953	1.05951[108]	1273.0	1271.0[109]	0.782	0.782[108]
2-aminoethanol	1.00872	1.00874[110]	1703.1	1703.1[111]	14.424	14.423[112]
2-chloroethanol	1.19212	1.19210[113]	1342.8	1343.6[114]	2.578	2.580[113]
2-phenylethanol	1.01234	1.01238[115]	1508.4	1510.5[115]	9.045	-
chlorobenzene	1.09554	1.09553[116]	1248.2	1249.0[116]	0.712	0.7105[118]
bromobenzene	1.48152	1.48150[105]	1136.0	1138.0[116]	0.982	0.985[119]
nitrobenzene	1.19345	1.19347[117]	1438.0	1437.0[116]	1.627	1.628[119]
1,2-dichlorobenzene	1.29474	1.29472[109]	1263.0	1265.0[109]	1.234	1.2350[109]
1,3-dichlorobenzene	1.27777	1.27779[109]	1235.0	1238.0[109]	0.945	0.9460[109]
1,2,4-trichlorobenzene	1.44242	1.44243[109]	1255.0	1256.0[109]	1.762	1.7600[109]

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