3.1 VARIOUS EXPERIMENTAL TECHNIQUES

The different methods for measurement of ultrasonic velocity are

1) Optical Diffraction Method,
2) Pulse Echo Technique,
3) Interferometer method.

A brief description of various techniques is given below while an interferometer method which is used in the present work has been described in details.

3.1.1 Optical Diffraction Method

The optical method of measuring sound absorption and dispersion in liquids is based on the fact that successive compressions and rarefactions of sound wave alter the refractive index of the medium and a pulse grating is formed [154,155]. If a beam of monochromatic light and ultrasonic wave are allowed to propagate at right angles to each other through a liquid, then a light wave gets diffracted by the sinusoidal grating formed due to acoustic wave. The pattern of this diffraction can be used to determine ultrasonic velocity.

If \( \lambda \) and \( \lambda \) denote the wavelengths of light and sound respectively, then the deflection of the mth order spectrum is given by

\[
\sin \alpha = \frac{m \lambda}{\lambda}
\]  \( \ldots \ldots \ 3.1 \)
OPTICAL SYSTEM FOR OBSERVATION OF DIFFRACTION BY ULTRASONIC WAVES.

**fig. 3.1 (a)**

PULSE REFLECTION SYSTEM

**fig 3.1 (b)**
If a photograph of diffraction pattern is taken on the plate at a distance sufficiently large compared to the distance $i$ between the consecutive fringes, then ultrasonic velocity $u$ is obtained as

$$u = \sqrt{fd/i} \quad \ldots \ldots \quad 3.2$$

where $f$ is the frequency of ultrasonic waves. Bachem et al. [156] evolved a better technique to measure acoustic velocities in liquids by directly photographing the compressional wave set up by ultrasonic beam.

3.1.2 Pulse Echo Technique

Pulse echo technique devised by Pinkerton[157], Pellam et al [158] and Carstensen [159] have been found to be of immense use in studying ultrasonic velocity in liquids as well as in solids. A square wave pulse of about 25 µsec. pulse width is used to modulate RF signal which drives a suitable transducer. When the crystal vibrates, it emits waves of frequency which is about five times larger than that of RF signal. This acoustic pulse is received either by a second transducer or is first reflected and then arrives back at the emitting transducer where it is amplified and presented on the screen of C.R.O.

There are two main advantages of the pulse technique over the continuous wave methods, for the measurement of velocity and absorption. One is, formation of the standing waves is eliminated. And the other is, it minimizes the local heating
effects because even with the high peak powers, the average heating effect of the R.F. pulse is small.

An extremely high precision pulse method known as the differential phase comparison technique has been devised by Badar [160] for the measurement of very small changes in ultrasonic velocities in liquids. In this technique, an ultrasonic wave takes two separate paths, one in the liquid under study and second in a reference liquid, used as a delay line. Velocity dispersion measurements in the frequency range 3.3 MHz to 7.2 MHz give an accuracy of 0.1%.

But there are certain drawbacks in pulse technique. It requires a large quantity of liquid under study and also requires a sophisticated electronic circuitry for recording pulse reflecting rates.

3.1.3 Interferometer Method

An interferometer method introduced by Pierce [161] and improved by Hubbard and Loomis [162] is based on the formation of standing waves between an ultrasonic transducer and a plane parallel reflector. The distance of reflector from the transducer is altered and for different positions of reflector, where it is an integral multiple of half wavelength, can be used to determine ultrasonic velocity in liquids. This method gives better accuracy in low attenuating liquids than highly attenuating liquids. But the
method is not very well suited for highly viscous liquids. Recently, Rao[163] recommended zirconate titinate(PZT) crystal to take an advantage of its special piezoelectric properties, such as large frequency band width, low impedance and high electroacoustical conversion efficiency. Rao and Rao [164] developed a modified ultrasonic interferometer for liquids, giving accuracy of 1 in 1000. Vander borgh et al [165] suggested a new cell for ultrasonic absorption measurement. Raghupati Rao [166] employed a double crystal interferometer technique for determining temperature coefficients of ultrasonic velocities in liquids. Resonance conditions are reached in a double crystal interferometer either by changing frequency ($\Delta f$) or by changing temperature ($\Delta T$).

3.1.4 Other Techniques

The techniques of Gorden and Cohen[167] and of Montrose and Pritsch [168] are of special significance for Brillouin scattering in electrolytic solutions. Cedrone and Curren [169], Garnsey et al [170] and D'Arrigo et al[171] obtained better accuracy by using the sing around technique. Coherent detection technique for variable path lengths in fluid has been used by Williamson and Eden [172]. Burrundukov and Lobernov[173] made noteworthy contributions in the development of ultra high precision techniques for velocity, dispersion and absorption measurements in liquids.

The advantages of interferometer method than the other
methods are (i) its simplicity & (ii) it requires about 10-12 ml of the liquid. The heating effect of an ultrasonic wave can be removed by suitable external temperature control. The effect of the reflection of waves from the walls of the cell can be minimised by corrugating the inner surface. With these improvements, accuracy of better than 0.001% comparable with the accuracies claimed by the pulse methods can be obtained by this technique.

Due to the above merits, it was thought worthwhile to prepare a set up of an interferometer for measuring ultrasonic velocities in the present study.

3.2 Interferometer Method

3.2.1 Principle

This method is based upon the formation of standing waves in liquid, between the transducer and a flat receiver. By measuring wavelength of these waves, according to a formula

\[ u = f \cdot \lambda \]  

\[ \ldots \ldots \quad 3.3 \]

and by knowing frequency \( f \), the velocity \( u \) can be determined.

Ultrasonic waves of known frequency are produced by an X-cut quartz crystal which is fitted at the bottom of the cell. These waves travel through the liquid and get reflected from a movable flat metallic plate, kept parallel to the crystal surface. When distance between the transducer and the reflector, is an integral multiple of half wavelength, stationary waves are formed, in the
The reflected waves received back at the crystal are out of phase. The resulting decrease in the amplitude of crystal oscillations is accompanied by an alternating current through the crystal. The driving oscillator is loosely coupled with the LC circuit having quartz crystal in parallel with the condenser. Both LC circuit and an oscillator are tuned to the resonating frequency of the crystal and the crystal current is measured. When the position of the reflector is changed, there is variation in crystal current (Fig 3.2). The distance between the successive maxima or minima is half of the wavelength in the medium, which can be measured with the help of screw movement on the scale along with the reflector and by knowing \( \lambda \) and frequency \( f \), velocity of waves can be calculated.

### 3.2.2. Interferometer Assembly

An interferometer used in the present study was supplied by Messrs Mittal Enterprises, New Delhi. The line diagram and the photograph are shown in the Fig 3.3 and 3.4. It consists of:

(i) Quartz crystal  
(ii) R.F. Oscillator  
(iii) The cell and the measuring assembly  
(iv) Thermostat.

### 3.2.2a Quartz Crystal

Crystalline form of Silicon dioxide (SiO₂) is called as
Quartz Crystal. It is a crystal of the trigonal class possessing three polar axes at 60° to each other. These are the X-axes of the crystal and all are equivalent. Y-axes lie in the same plane but are perpendicular to this plane. In the case of quartz, the piezoelectric modulus tensor has five components, only two of which are independent. A widely used transducer is the X-cut crystal whose flat faces are perpendicular to the X-axes. For such a cut, the application of stresses in X direction produces a polarization component in the same direction. Similarly, an application of electric field in the X direction gives rise to the strain in the X direction. Thus, such a cut of crystal is of use in producing and detecting compressional waves in the X direction.

A transducer for producing ultrasonic waves is a circular plate of diameter 1 cm, cut from X-cut crystal. This plate is coated with gold from both sides to act as electrodes. When a P.D. V is applied between them, the thickness changes by

$$u' = d \cdot V$$ .................................. 3.4

where \( d = 2\mu /V \). On the other hand, if the plate is compressed by a force \( F \), the electrodes acquire electric charge

$$q = d \cdot F$$ .................................. 3.5

where \( d \) is precisely the same value as before, or expressed in a slightly different though equivalent way, is approximately \( 2\mu \text{coul}/\text{N} \). If the voltage is reversed, the strain changes sign.
i.e. changes from extension to contraction or vice-versa. So when alternating voltage is applied across such transducer, it vibrates and when the natural frequency of vibration of the crystal is equal to the frequency of applied voltage, resonance takes place and amplitude of vibration is increased 100 fold, being limited only by damping. If the amplitude of oscillation becomes very large, great strains are produced which may crack the quartz plate. Hence a.c. voltage applied across the crystal is kept low.

3.2.2b R.F. Oscillator

This is a fixed frequency oscillator, the frequency of which is controlled by quartz crystal in the power amplifier of the circuit (fig. 3.5). When R.F. power is drawn, the microammeter shows constant current, due to D.C. voltage applied across it. An oscillator provides the voltage of about 400 volts across the crystal. R.F. generator is used to excite the X-cut quartz crystal, fitted at the bottom of the measuring cell.

3.2.2c Cell and The Measuring Assembly.

Different parts of an interferometer can be described as follows. These parts can be separated from each other.

1) The Base

It is a rectangular metallic heavy base having a space at the centre equal to the outer diameter of the cell, so that it can
VARIATION OF CRYSTAL CURRENT WITH REFLECTOR POSITION IN AN INTERFEROMETER

fig. 3.2
be placed in the base. At its centre, there is an electrode isolated from the base and pointed upwards to make an electrical contact with the crystal at the bottom of the cell. Electrical contact of crystal is made with an oscillator from the side of the base by a shielded cable. Cell can be tightly fitted into the base by a side screw present in the base.

ii) The Cell

It is a specially designed double walled cylindrical vessel made of stainless steel having outer diameter 3.96 cm, inner diameter 0.87 cm and height 9.25 cm. It has a capacity of 12 ml of liquid. For maintaining temperature of the liquid constant, water can be circulated through the annular space between the walls. It has an X-cut quartz crystal of diameter 10 mm fixed at its bottom exactly at its center. Upper surface of the crystal plate is covered with a diaphragm to prevent the liquid from coming in direct contact with the crystal surface. The inner wall of the cell is corrugated to prevent the wall reflections. The Cell has got a small hole in its bottom from lower side upto the crystal so as to fit it in the base and to have contact of an electrode with the crystal.

iii) Measuring Assembly

The reflector is connected with the plunger(E) which slides through a tightly fitting cylindrical bore(F), ensuring a self
SECTION DIAGRAM OF CELL

fig. 3-3
parallel displacement of the reflector. Upper end of the plunger is connected to the lower end of the screw by means of a locking ring. The screw forms the part of the screwguage which has a least count of 0.0001 cm. Hence the position of the reflector can be accurately measured upto the fourth place of decimal. The distance of 2.5 cm is available for the movement of the micrometer screw. The whole assembly can be screwed on the top of the cell as a cap.

3.2.2d Thermostat Assembly

Velocity of ultrasonic waves in liquid is extremely sensitive to changes in temperature. Hence it becomes necessary to obtain a good stability of temperature. Thermostat U-10 of temperature stability 0.02°C with a double action pump was used for this purpose. The temperature can be controlled to an accuracy of 0.1°C in the temperature range -60°C to +300°C.

The ultra thermostat U-10 incorporates the following main units. The thermostat bath, thermostat relay, the contact thermometer, the control thermometer, thermostat pump, cooling receiver and valve relay.

3.2.2d(1) Thermostat Bath

The thermostat bath comprises a rectangular reservoir with a bath capacity of approximately 12 litres. The cover plate is provided with a bath opening and the filling aperture. Beneath both
the opening, there is an adjustable lifting platform able to take an insert pot, the useful capacity of pot being 5 litres. The filling aperture is closed by the lid. Covering the bath opening is possible optionally with the insert lid or water bath rings. The coverplate is provided with sockets for accommodating the contact thermometer (0°C to 100°C) as well as protecting the tube and a rotary magnet for the contact thermometer.

3.2.2d(ii) **Thermostat Relay**

The thermostat relay is fixed on the coverplate of the thermostat bath. The seven contact switch serves for switching on the instrument and adjusting the required degree of heating power from 270 watt to 1200 watts in four stages. The signal lamp indicates the connection state of contact thermometer. The signal socket serves as pump drive connection. The left socket is paralleled with the heating element. This is connected with the thermostat when the cooling accessories are used. The connecting cable provides the connection between the thermostat relay and the contact thermometer. The mains cable connects the thermostat to mains supply through a safety socket.

The contact thermometer lies in the grid circuit of an electronic valve. Interpolated into the anode circuit of this valve is the coil of a mercury relay, controlling the heating power of the thermostat.
3.2.2d(iii) **Thermostat Pump**

The double acting pump is fitted into an appropriate hole on the coverplate of the thermostat bath and fixed by means of quick acting fastening devices. The pump keeps the temperature regulating liquid in a constant flow and feed it, in case of necessity, to an external user. The pressure pump pushes the temperature regulating liquid from the bath to the external consumer whereas the suction pump gets it from the external consumer back into the bath.

3.2.2d(iv) **Cooling Receiver**

The cooling receiver has a capacity of approximately 4 kg of ice. In its porcelain vessel, there is a cooling coil made of copper and wound in the shape of a basket. Its ends are connected to hoses. Further the cooling receiver has an outlet cock and it is closed by a cover made of P.V.C. board, which is fastened suitably on the top of the porcelain vessel.

3.2.2d(v) **Valve Relay**

It is housed in a plastic casting. The connection to the thermostat relay is carried out with a cable attached to the valve relay. For connecting the hoses (for return pipe and cooling receiver), the valve relay is fitted with four olives.
The electrically controlled valves of the valve relay function such that when the temperature is below the setting, the whole liquid stream coming from the consumer flows back direct to the thermostat whereas when it is above the setting, the liquid is led through the cooling receiver.

The valve relay controls the temperature of the thermostat bath and thus the consumer by supplying cooled liquid intermittently. In this case a good stability of temperature is achieved.

3.3 Density measurement

While applying different theories to mixtures of liquids, it is observed that volume factor is the most important one in case of mixture. Hence stress was given to measure densities of different liquid solutions very accurately.

Densities of the experimental liquids were measured by the hydrostatic plunger method. A cell was designed and fabricated specially for this purpose. It consists of a double walled, cylindrical glass vessel, of length 12 cm, inner diameter 1.7 cm, and an outer diameter 3 cm with inlet and outlet. A small glass tube of length 3.2 cm and diameter 0.7 cm sealed with a glass hook at the upper end and filled with mercury was used as plunger. The above dimensions of plunger and mercury in it were used so as to dis-
place large volume of an experimental liquid in order to obtain higher accuracy in density measurement. And the dimensions of the cell are taken as stated above so as to consume as less liquid as possible but as compared to plunger length, liquid height is sufficient in the cell. A monopan digital balance was used having least count as 0.0001 gm. so that it could record changes in weight of plunger dipped in solutions correct to fourth place of decimal. A special nylon thread was tied to the plunger not to have a chemical reaction with the strong organic liquids used in the present study.

Plunger was suspended from the balance passing through the hole of the table and dipping the plunger fully in liquid in the cell. Having so small the dimensions of the cell, care was always taken not to touch the plunger to the walls of the cell and it should suspend freely dipping completely upto the hook of the plunger in the liquid.

3.4. The Experimental Set Up

Filling the thermostat bath upto 3/4th of its volume with distilled water, a desired temperature was adjusted at the Jumbo contact thermometer by means of the rotary magnet. Thermostat was connected to the interferometer so as to have an exact temperature of the liquid equal to the temperature of the bath for measurement of velocity. The outlet of interferometer was connected to the
density cell. It then went to the relay, through relay to cooling vessel and back to the thermostat bath. The density measurement cell was fixed vertical to the stand. It was covered by woolen material thick string from outside so as to prevent heat radiations from outside. This is needed specially when low temperature readings are taken. Ultrasonic cell was also covered from outside by thick black cloth. The cooling vessel was filled by ice-pieces.

3.5. Systems Investigated

Ultrasonic velocities and densities of the following mixtures and of the pure components were measured.

1. Benzene - Furan
2. Acetone - Furan
3. Benzene - Tetrahydrofuran
4. Acetone - Tetrahydrofuran
5. Benzene - Pyridine
6. Acetone - Pyridine
7. Benzene - Piperidine
8. Acetone - Piperidine

3.6. Sample Preparation

The liquids used were of B.D.H. Analar grade and were thrice redistilled before use. The samples of different concentrations were prepared by mixing the components in volume proportions of liquids. Everytime, fresh sample was prepared just before the
starting of the experiment. Total sample prepared was 50 ml, 10 ml was used for ultrasonic study, 10 ml for density measurement and the rest was used for rinsing the two cells. Density cell was covered by a round cork type disc having hole at the center, for thread to pass over the plunger without touching and to prevent direct contact with the solution inside the cell. The experimental readings were taken within 5 hours of duration after preparation of the sample.

3.7. Experiment

Interferometer cell, its parts and density cell were cleaned repeatedly with acetone. It was dried completely with the help of dryer and the same was rinsed with sample solution twice. Taking 10ml of solution in ultrasonic cell and 10ml in density cell, thermostat was switched on, activating the seven contact switch. Adopting heating power of thermostat to the desired working conditions is a requisit for a high regulating accuracy. The most favourable conditions in the regulating circuit exist when the switching time i.e. on and off interval indicated by the neon signal lamp of the thermostat relay are as short as possible and are in the ratio 1:1. The condition was achieved by keeping the cooling receiver at 4°C below the contact thermometer value. When a reading at temperature above the room temperature was required, cold water at room temp. was circulated through the coil dipping in thermostat bath to take out the excess heat and stability
Experimental Set-up. fig 3.4
condition of temperature was ensured in this way.

When steady temperature was achieved, the reflector of the interferometer and plunger dipped in density cell was moved up and down many times, by micrometer screw and lever of monopan balance respectively. This was done in order to remove thermal gradient, if any inside the two cells. Reading was then noted for the first maxima. Then the readings for successive fourth maxima were obtained. All the readings were taken by moving the screw only in one direction to avoid backlash error if any. In this way the readings were obtained at temperatures from 10°C to 40°C at the interval of 5°C for all the systems except Benzene-Furan and Acetone-Furan. For Furan containing systems, readings were taken from 5°C to 25°C at the interval of 5°C. The constancy of oscillator frequency was checked using a digital frequency counter FC734(ecil) was found to be \( \pm 4 \) in \( 10^4 \). The micrometer screw (least count \( 5 \times 10^{-4} \text{cm} \)) driving the reflector across 20 maxima permitted an overall accuracy of better than 1 in \( 10^3 \) in velocity measurement.

For density measurement, reading of the monopan balance with its vernier scale was taken and the same was repeated for different temperatures. A separate set of mass of water displaced for the same temperatures was taken for distilled water. The density measurement had an accuracy of 1 in \( 10^4 \).
3.8 COMPUTATIONAL ASPECTS

3.8.1 Ultrasonic Parameters

As the distance between two successive maxima is $\lambda/2$, mean is calculated from the readings of micrometer of interferometer and by using the relation,

$$u = f \cdot \lambda$$  \hspace{1cm} (3.6)

$f$ being the frequency equal to 2 MHz., $u$ was calculated for different compositions at different temperatures. In all the cases it was found that the ultrasonic velocity was linear with the temperature. Hence a method of least squares was applied and then values of $u$ for different temperatures were calculated from the equation,

$$u = u(o) + (du/dT)T$$  \hspace{1cm} (3.7)

Similarly densities were also found linear with the temperatures hence densities were computed from the equation

$$\rho = \rho(o) + (d\rho/dT)T$$  \hspace{1cm} (3.8)

Adiabatic compressibility was calculated from

$$\beta_a = (u^2\rho)^{-1}$$  \hspace{1cm} (3.9)

Vander Wall's parameter $b$ was calculated from
For comparing different systems, a following formula for a function (say Y) is used

\[ \frac{Y_{\text{expt}} - Y_{\text{ideal}}}{Y_{\text{ideal}}} \times 100 \]

\[ \Delta Y = \frac{Y_{\text{expt}} - Y_{\text{ideal}}}{Y_{\text{ideal}}} \times 100 \]

where \( Y_{\text{ideal}} \) is obtained using volume additive rule in all cases given by

\[ Y_{\text{ideal}} = (1 - x)Y_1 + xY_2 \]

where \( x \) is the mole/volume fraction of second component.

using eqn 3.11, excess parameters as adiabatic compressibility \( b_a^E \), molar volume \( V^E \), and VDW parameter \( b^E \) were calculated. The error for each of the excess parameters was estimated and the deviations from the additive law were found to be outside the limit of error (3%). A least square fit is obtained in case of \( V^E \) with mole fraction and for \( b_a^E \) with volume fraction giving a second degree polynomial equation of a curve where the variation is symmetrical. The values of coefficients are listed in the table B.

3.8.2 Scaled Particle Theory

In each mixture which is experimented, molecules of two
species are assigned one of the following shapes:

a) Spherical,

b) Cubical,

or
c) Tetrahedral.

If R, S, V denote the Radius, Surface area and Volume of a molecule respectively, then shape factor denoted by Z(3) is given by

\[ Z(3) = \frac{RS}{V} = X \]

As obtained earlier for pure liquids,

\[ \frac{\mu^2}{\gamma RT} = \frac{[1+(X-1)\eta]^2}{[1-\eta]^4} \] \[ 3.12 \]

where \( \eta = \frac{V_N^P}{\rho N} \); \( \rho \) being the number density, \( \gamma \) = hard core volume and other quantities have their usual meaning.

A solution of above equation is obtained as,

\[ \eta = A = B - J(B^2 + C - 1) \] \[ 3.13 \]

where

\[ B = 1 + CY/2 \] \[ 3.14 \]

\[ C = J(G/M)/\gamma \] \[ 3.15 \]

\[ G = \gamma RT \] \[ 3.16 \]

and

\[ Y = Z(3) - 1 \] \[ 3.17 \]

using experimental ultrasonic velocity \( \mu \), molecular weight \( M \) and \( \gamma \), calculated in Flory's calculations, \( \eta \) is calculated for pure liquids.
Now \( N = v \cdot \rho_N \)

\[
\begin{align*}
N &= \frac{\rho_N}{H/V} = \frac{\rho}{H/P/M} \\
&= \frac{\rho}{H/P'/M} 
\end{align*}
\]

by knowing \( N \), molecular weight \( M \), molecular density, and Avogadro's number \( \text{H} \), \( \nu \) can be calculated.

For a spherical molecule, volume \( \nu = \frac{4\pi A^3}{3} \), hence \( A = \left(\frac{3\nu}{4\pi}\right)^{1/3} \)

or

\[
A = Z(5)\nu^{1/3} \tag{3.20}
\]

area of a molecule \( B = 4\pi A^2 \)

\[
B = Z(7)A^2
\]

\[
C = A^2
\]

and volume \( \nu \)

\[
\nu \equiv \frac{4\pi}{3}A^3 \tag{3.21}
\]

For pure liquids, these \( A, B, C \) and \( \nu \) are denoted by

\[
A_1 = l(1), B_1 = K(1), C_1 = N(1), \nu_1 = P(1) \text{ and } A_2 = l(2), B_2 = K(2), C_2 = N(2), \nu_2 = P(2)
\]

respectively.

Now, molecular weight of the mixture is given as

\[
M = R(1) + x[R(2) - R(1)] \tag{3.22}
\]

where \( x \) is the volume fraction.

\( R(1) \) and \( R(2) \) are molecular weights of two components. Let \( T(1) \) and \( T(2) \) be the densities of pure liquids. Then from 3.19

\[
\frac{\nu_1}{\nu} = \frac{N_1}{HT(1)/R(1)} \text{ and } \frac{\nu_2}{\nu} = \frac{N_2}{HT(2)/R(2)} \tag{3.23}
\]
Volume of mixture is given by, 
\[
V_0 = \frac{R(1)}{T(1)} + \frac{R(2)}{T(2)} + \frac{R(1)}{T(1)} \cdot x
\]

i.e.
\[
V_0 = V_1 + \left[ (V_2 - V_1) \cdot x \right]
\]

For a binary mixture, different molecular dimensions are
\[
\begin{align*}
I(3) &= I(1) + x[I(2) - I(1)] = A \quad \ldots \ldots \quad 3.24 \\
K(3) &= K(1) + x[K(2) - K(1)] = B \quad \ldots \ldots \quad 3.25 \\
N(3) &= N(1) + x[N(2) - N(1)] = C \quad \ldots \ldots \quad 3.26 \\
P(3) &= P(1) + x[P(2) - P(1)] = \nu \quad \ldots \ldots \quad 3.27
\end{align*}
\]

By substituting these values in an eqn.
\[
\frac{\mu u^2}{\rho R T} = \frac{1 + 2AB(\rho_0^3/(1 - \rho_0 \nu)) + B^2C(\rho_0^3/(1 - \rho_0 \nu))^2}{(1 - \rho_0 \nu)^2}
\]

\[
\text{where } \rho_0 = \frac{H}{V_0}
\]

ultrasonic velocity "u" for a mixture is calculated. This gives the velocity of a mixture at temperature T from the parameters of pure liquids assuming no interaction in the mixture.

In a mixture, the deviation in the value of a thermodynamic property from that of ideal mixture is indicative of an interaction between the molecules of the two species i.e. an AB interaction. The AB interaction may cause the formation of new molecules if the interaction is strong enough. But in the case of weak AB interaction, it may cause a distortion in molecules. The distortion can be either in the shape of a molecule or a change in
the volume (size) of both the molecules or both types of distortions may occur. Considering only the changes in shape without the changes in size, the mixture can be considered as an assembly of non-interacting distorted molecules.

(1) Assuming AB interaction taking place in a mixture, volume of the mixture is modified as

\[ V_0 = V_1 + (V_2 - V_1)x + (x - x^2)(\alpha + \beta x) \]  

where \( \alpha \) and \( \beta \) are taken as adjustable parameters. If densities, taking volume additive, do not differ from experimental values, then the mixture is supposed to have no interaction but as density values are different, eqn 3.29 is used. \( \alpha \) and \( \beta \) values are adjusted to get experimental values of densities for a given set of different compositions of two liquids. In the present work, calculations are done with the help of computer giving values to \( \alpha \) and \( \beta \) from -5 to +5 at a difference of 0.0001, trying all possible combinations of numbers to get the minimum deviation from experimental values of densities.

E.g. taking the case of Benzene + Tetrahydrofuran system, for \( \alpha = \beta = 0 \), sum deviation = ADEV = 1.112E-2 and for \( \alpha = 0.37, \beta = 0.504 \), the minimum sum deviation is found to be equal to 1.5137E-3. These values of \( \alpha \) and \( \beta \) are kept constant for a given system for different compositions which indicate the measure of interaction.

Let the basic parameters used to modify the equation of
bulk volume be 'a' and 'b'. By the use of 'a' and 'b', they give the
corrected volumes of individual liquids in mixture as

\[ V'_1 = V_1[1 + a(x-x^2)] \]
\[ V'_2 = V_2[1 + b(x-x^2)] \]

Volume of the mixture \( V = (1-x)V'_1 + xV'_2 \)

\[ V = (1-x)V_1[1 + a(x-x^2)] + xV_2[1 + b(x-x^2)] \]

hence,

\[ V = (x-x^2)[V_1a + x(V_2b-V_1a)] \]

\[ = (x-x^2)[\alpha + x.\beta] \]

i.e. \( V_1a = \alpha \), \( (V_2b-V_1a) = \beta \)

\( \alpha \) and \( \beta \) give non-ideal contribution to bulk volume of the mixture.

\( a \) and \( b \) parameters when compared to each other can suggest which
liquid is contributing to the change in volume after mixing.

Therefore bulk volume of the mixture is considered as

\[ V = V_1(1-x) + V_2.x + (x-x^2)[\alpha + \beta.x] \]

where \( V_1 = M_1/\rho_1 \), \( V_2 = M_2/\rho_2 \) for two constituent liquids. Hence \( \alpha \) and \( \beta \)
parameters can be called as transfer parameters which ultimately
are indicative of the dominance of either first or second liquid
which give non-ideal part in the volume equation.

(2) Assuming distortion of molecules in case of weak inter­
actions, correction is applied to hard core volumes as,
FLOWCHART SHOWING THE PROGRAM EXECUTION OF SCALED PARTICLE THEORY

- Densities of pure liquids and mixtures
- Shape parameters for different combinations & A1 and A2 from
- Experimental us velocities of pure liquids
- Us velocities of mixtures (A)

Molar Volume

Pure liquids & mixtures (R)

Ideal mixing molar volume
\( \alpha = \beta = 0(T) \)

Use of different values of \( \alpha \) & \( \beta \) by computer iter.

Calculation of molar volumes (Q)

Through computer program Ghosh1 to Ghosh8

Velocities of mixtures with adjustment parameters \( Y=Z=0 \), according to SPT (B)

Use of different \( Y \) & \( Z \) (comp. iter.)

Us velocities of mixtures (B)

Is \( A=B \) ?

Print \( Y, Z, \chi^2 \) (min. SDEVW)

Is \( R=Q \) ?

ADEV?

Is \( R=T \) ?

Yes

Yes

No

No
\[ v^C_1 = v_1[1+Y(x-x^2)] \]

and

\[ v^C_2 = v_2[1+Z(x-x^2)] \]

Taking these values of \( v^C_1 \) and \( v^C_2 \), corrected volume of the mixture is obtained as

\[ v = v^C_1 + (v^C_2 - v^C_1)x \]

and proceeded in the same manner for calculation of ultrasonic velocity. By keeping \( a, b \) constant as adjusted earlier and by varying the values of \( Y \) and \( Z \) between -5 to +5 at the interval of 0.0001, all combinations are tried to get the minimum deviation from the experimental velocities. e.g. in the system, Benzene + Tetrahydrofuran, for \( Y = Z = 0 \), sum deviation \( SDEVW = 92.556 \text{ m/s} \) and for \( Y = 0.0282, Z = 0.014 \), min \( SDEVW = 4.1282 \text{ m/s} \) for sph + sph combination.

The same is repeated by considering different shapes of component molecules in a mixture such as,

1. spherical + spherical
2. spherical + cubical
3. spherical + tetrahedral
4. cubical + spherical
5. cubical + cubical
6. cubical + tetrahedral
7. tetrahedral + spherical
8. tetrahedral + cubical
9. tetrahedral + tetrahedral.

All the above shapes of molecules are tried using equivalent radius, corresponding area and volume [174] (Tab G) of molecules and that shape has been fixed which gives ultrasonic velocity values in close agreement to the experimental values (for which the total sum of deviations is minimum).
3.8.3 **Flory's Theory**

Flory et al. [151] calculated theoretically for various mixtures, the excess quantities such as excess enthalpy, $H^E$, excess molar volume $V^E$ and the excess molar entropy $S^E$ and compared them with the experimental values. Dividing these systems into four different groups, they are discussed separately in which one group consists of molecules approximately spherical. Second consists of molecules differing in size considerably. Flory's theory is applied to mixtures having homopolar species, small & non-polar components [175], or mixtures consisting of component liquids having approximately spherical shape [139], or molecules of two species differing in size and shape [176] etc., means all types of mixtures are considered [177].

J.D. Pandey [178] has calculated excess thermodynamic functions for piperidine-tetrahydropyran, piperidine-cyclohexane and tetrahydropyran-cyclohexane. He had also evaluated Van der Waal's constant, internal pressure and sound velocity in binary liquid mixtures from Flory's theory [179].

D. Patterson and A.K. Rastogi [180] plotted two distinct empirical curves of reduced surface tension, against reduced temperature, one containing data for simple liquids and the other data for polymers and polyatomic liquids. Using several methods of the liquid state, Flory theory gave them best results.
Using Patterson and Rastogi's formula for surface tension as

\[ \sigma^* = k^{1/3} (p^*)^{2/3} (T^*)^{1/3} \]  \quad \ldots \quad 3.31

J.D. Pandey [181] used the equation of reduced surface tension as

\[ \bar{\sigma}(\bar{V}) = M \bar{V}^{5/3} - \frac{\bar{V}^{1/3} - 1}{\bar{V}^2} \log \frac{\bar{V}^{1/3} - 0.5}{\bar{V}^{1/3} - 1} \]  \quad \ldots \quad 3.32

where surface tension of liquid in Flory's theory is expressed as

\[ \sigma = \sigma^* \cdot \bar{\sigma}(\bar{V}) \]  \quad \ldots \quad 3.33

and according to Auerback relation, the velocity of sound has been calculated by

\[ u = \left[ \frac{\sigma}{6.3 \times 10^{-4} \rho} \right]^{2/3} \]  \quad \ldots \quad 3.34

Using this method, he calculated sound velocities at different temperatures and elevated pressures (whereas Flory has stated that all attempts to apply the theory at elevated pressures failed) and he found good agreement between calculated and observed velocities of Ar, Kr and Xe whereas liquid nitrogen showed a deviation of not more than 9%.

Flory's theory was applied by Subhash Sharma et al [182] to solutions of PTMO in Benzene. Calculating the parameter \( \chi_{12} \) from excess enthalpy data, they calculated excess volume, reduced
residual potentials, partial molar residual entropy which are
given by

\[ V^* = \left[ \frac{x_1 M_1 + x_2 M_2}{\rho} \right] - \left[ \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] \]

chemical potential

\[ \mu = \ln a_1 - \ln \phi_1 - \left( 1 - \frac{V^*_1}{V^*_2} \right) \frac{\phi_1}{\phi_2} \]

reduced residual chemical potential

\[ \bar{\mu} = \left( \frac{\rho^*_1 V^*_1}{RT \phi^*_1} \right) \left[ 3 \ln \frac{V^*_1}{T^*_1} + \left( \frac{V^*_1}{V} - \frac{V^*_1}{T^*_1} \right) + V^*_1 \left( \frac{\chi_{12}}{V} - T Q_{12} \right) \frac{\theta^*_2}{RT \phi^*_2} \right] \]

partial molar volume enthalpy

\[ \chi_v = \left( \frac{\rho^*_1 V^*_1}{RT \phi^*_1} \right) \left[ \left( \frac{V^*_1}{V} - \frac{V^*_1}{T^*_1} \right) + \left( \frac{V^*_1}{V} \right) \left( \frac{\rho^*_1}{\rho^*_2} \right) \right] \]

where \[ \alpha T = 3 \left( \frac{V^*_1}{V} - 1 \right) / \left[ 1 - 3 \left( \frac{V^*_1}{V} - 1 \right) \right] \]

Discrepancies are found between theory and experimental values and
are more in case of PTMO 650 solutions. According to them, as the
systems involve complex molecular interactions, better agreement
is not expected.

K.S. Reddy et al [152] calculated excess isothermal
compressibility and excess thermal pressure coefficient \( \beta_T^E, \gamma_T^E \)
and found that the theory successfully predicts the sign of \( \gamma_T^E \) in
case of mixtures of CCl\(_4\) with toluene, o-xylene and m-xylene where
as the theory fails to predict even the sign in the system CCl\textsubscript{4} with p-xylene. Recently K. Purnachandra Rao et al [183] discussed the excess isothermal compressibilities calculated by Flory's theory in terms of difference in molecular size and shape of components and specific interactions between unlike molecules.

M. Rafiqul Islam [184] calculated the excess molar volume and sound velocity by

\[ V_{\text{calcd}} = (x_1V_1^* + x_2V_2^*)(\bar{V}_0)^{7/3} \left[ \frac{4}{3} - \frac{1}{3}(\bar{V}_0)^{1/3}(\bar{T} - T_0) \right]^{-1} \]

\[ u = \left[ \frac{\sigma}{6.3E-4\rho} \right]^{2/3} \quad \text{where} \quad \sigma = \sigma^* \cdot \bar{\sigma} \]

Percentage deviation of calculated sound velocity is given using Flory's theory. The deviation is thought due to size effects of components and their moments or approximation in formulation of interaction parameter \( \chi_{12} \).

An attempt here has been made to calculate \( \varphi_1 \varphi_2 \chi_{12} \) and then \( \rho^* \) from observed excess volume.

Also another way has been tried to get \( \chi_{12} \) and \( \vartheta_2 \) from molecular dimensions assuming different shapes of component molecules.
3.8.3a Characteristic and Reduced Thermodynamic Parameters for Pure Liquids

Starting with the reduced equation of state,

\[
\frac{\bar{p} \bar{v}}{\bar{T}} = \frac{\bar{v}^{1/3}}{\bar{T} - 1} \left( \bar{v} \bar{T} \right)
\]

where \( \bar{p}, \bar{v}, \bar{T} \) are reduced parameters given by \( \bar{p} = p/p^*, \bar{v} = v/v^*, \bar{T} = T/T^* \) \( p^*, v^*, T^* \) being characteristic parameters.

At zero pressure,

\[
\frac{-1/3}{\bar{v}^{1/3}} = 1 - \frac{1}{\bar{v} \bar{T}}
\]

i.e.

\[
\bar{v}^{1/3} - 1 = \bar{v}^{4/3} \bar{T}
\]

If \( \alpha \) is coefficient of thermal expansion, then

\[
\frac{-1/3}{\bar{v}} - 1 = \frac{\alpha T}{1 + \alpha T}
\]

from 3.37,

\[
\bar{v}^{1/3} - 1 = \frac{T}{\bar{v}^{4/3}}
\]

From experimental values of adiabatic compressibility \( \beta_a \) and specific heat at constant pressure \( C_p \), thermal pressure coefficient is calculated from

\[
\gamma = \frac{\alpha C_p}{\beta_a C_p + \alpha^2 T \bar{v}}
\]
which gives \( p^* = \gamma T \nu^2 \) ........ 3.41

Isothermal compressibility is given by

\[ \beta_T = \alpha / \gamma \]

Adiabatic compressibility is obtained from experimental ultrasonic velocity and density.

Thus the parameters \( \nu, T, \nu^*, T^*, p^*, \gamma, \beta_a, \beta_T \) etc are calculated for pure liquids from above equations and are presented in the form of the table.

3.8.3b Mixture Parameters

The following analysis is confined to binary mixtures, the components being indexed by subscripts 1 and 2.

From ideal molar volume of the mixture \( V_{\text{ideal}} \), reduced volume is given by

\[ \frac{V_{\text{ideal}}}{\nu} = \frac{1}{x_1 \nu_1 + x_2 \nu_2} \] ........ 3.42

Characteristic volume of the mixture is used in the form

\[ [x_1 \nu_1^* + x_2 \nu_2^* + x_1 x_2 (Y + Z x_2)] \]

instead of \( [x_1 \nu_1^* + x_2 \nu_2^*] \) in equation 3.42

where \( Y \) and \( Z \) are adjustment parameters.

Segment fractions \( \phi_1 \) and \( \phi_2 \) are given by
\[ \phi_1 = \frac{x_1v_*^1}{x_1v_*^1 + x_2v_*^2} \quad \text{and} \quad \phi_2 = \frac{x_2v_*^2}{x_1v_*^1 + x_2v_*^2} \quad \ldots \quad 3.43 \]

The molecular element or segment is defined in correspondence for the two species such that \( r_1 \) and \( r_2 \) are taken in the ratio of respective molar core volumes \( v_*^1 \) and \( v_*^2 \) \([150]\).

i.e.

\[ \frac{r_1}{r_2} = \frac{v_*^1}{v_*^2} \]

Number of sites \( r_iS_i \) per molecule are taken proportional to the surface area of a sphere of the same core volume.

Thus,

\[ \frac{r_1}{r_2} \frac{S_1}{S_2} = \left( \frac{v_*^1}{v_*^2} \right)^{2/3} \quad \text{and} \quad \frac{r_1}{r_2} \frac{v_*^1}{v_*^2} = \frac{r_1}{r_2} \frac{v_*^1}{v_*^2} \]

which gives

\[ \frac{S_1}{S_2} = \left( \frac{v_*^2}{v_*^1} \right)^{1/3} \]

Site fraction is given by

\[ \phi_2 = \frac{\phi_2}{(S_1/S_2)\phi_1 + \phi_2} \quad \ldots \quad 3.44 \]

Interaction parameter is given by

\[ X_{12} = p^* \left[ 1 - \left( \frac{S_1}{S_2} \right)^{1/2} \left( \frac{\phi_2}{p_2} \right)^{1/2} \right] \quad \ldots \quad 3.45 \]

And \( p^* \) is calculated from this value of \( X_{12} \) by using an equation,

\[ p^* = \phi_1p_1^* + \phi_2p_2^* - \phi_1\phi_2X_{12} \quad \ldots \quad 3.46 \]

for the mixture.
FLOWCHART SHOWING THE PROGRAM EXECUTION OF FLOYD'S SYSTEM - I

Experimental densities & Ultrasonic velocities of pure liquids (six in all)

Experimental Ultrasonic velocities of mixtures (B) (A)

Through Computer Programmes ESS1 to ESS6 (six in all)

Parameters of pure liquids (volume, adiabatic compress, \( \Gamma \), thermal pressure coeff. \( V, \bar{p}, T, V^*, p^*, T^* \)

Introduction of shape factors (nine shapes)

Through computer programmes Flory1 to Flory6 (8 in all)

Ultrasonic velocities of mixtures with adjustment parameters, (taking \( Y=Z=0 \)) [Ideal mixing]

Use of different values of \( Y \) & \( Z \) using computer iteration

Calculation of Ultrasonic velocities of mixtures (8) (B)

is \((A) = (B)\)?
Use Chi-sq. test

Yes

No

PRINT
Then proceeding in the same manner as explained in chapter two, adiabatic compressibilities and ultrasonic velocities are calculated.

In above considerations, \( \frac{S_1}{S_2} \) is calculated as follows from different shapes.

(\( ^{\text{i}} \) Considering molecules of two species spherical (sph+sph)

\[
\frac{S_1}{S_2} = \left( \frac{\nu_2^*}{\nu_1^*} \right)^{1/3} \quad \ldots \ldots \quad 3.47
\]

(\( ^{\text{ii}} \) Spherical + Cubical

As stated earlier,

\[
\text{Ratio of surface areas of two molecules} = \frac{r_1S_1}{r_2S_2} \]

Therefore, from table G,

\[
\frac{S_1}{S_2} = \frac{4\pi r_1^2}{6} \cdot \frac{r_2}{r_1} \]

but ratio of segments in two molecules, \( \frac{r_1}{r_2} = \frac{\nu_1^*}{\nu_2^*} \)

Hence,

\[
\frac{S_1}{S_2} = \frac{4\pi(3/4\pi)^{2/3}}{6} \cdot \frac{\nu_2^*}{\nu_1^*} \quad \frac{1}{3} \]

\[
= 0.805866 \left( \frac{\nu_2^*}{\nu_1^*} \right)^{1/3} \quad \ldots \ldots \quad 3.48
\]

(\( ^{\text{iii}} \) Cubical + Spherical

\[
\frac{S_1}{S_2} = \frac{6l_1^2}{4\pi R_2^2} \cdot \frac{r_2}{r_1} \]
(iv) Spherical + Tetrahedral

\[
\frac{S_1}{S_2} = \frac{4\pi R_1^2}{\sqrt{3} l_2^2} \cdot \frac{r_2}{r_1}
\]

For sphere, \( v = \frac{4\pi R^3}{3} \) and for tetrahedron, \( v = \frac{\sqrt{2} l^3}{12} \).

Hence,

\[
\frac{S_1}{S_2} = \left(\frac{\pi}{2}\right)^{1/3} \frac{1}{\sqrt{3}} \left(\frac{v_2^{1/3}}{v_1^{1/3}}\right)
\]

\[= 0.671026 \left(\frac{v_2^{1/3}}{v_1^{1/3}}\right) \quad \ldots \ldots \quad 3.50\]

In a similar manner, for,

(v) Tetrahedral + Spherical

\[
\frac{S_1}{S_2} = \frac{\sqrt{3} l_2^2}{4\pi R_2^2} \cdot \frac{r_2}{r_1}
\]

\[= \sqrt{3} \frac{2}{\pi} \left(\frac{v_2^{1/3}}{v_1^{1/3}}\right) \]

\[= 1.49025 \left(\frac{v_2^{1/3}}{v_1^{1/3}}\right) \quad \ldots \ldots \quad 3.51\]

(vi) Cubical + Tetrahedral

\[
\frac{S_1}{S_2} = \frac{6 l_2^2}{\sqrt{3} l_2^2} \cdot \frac{r_2}{r_1}
\]
\[
\frac{S_1}{S_2} = 1.20093 \left( \frac{\frac{v_2}{v_1}}{\frac{v_2^*}{v_1^*}} \right) \quad \text{......... 3.53}
\]

(vii) Tetrahedral + Cubical

For molecules of same shapes, i.e. cubical-cubical or tetrahedral-tetrahedral, \( S_1/S_2 \) is same as obtained for spherical-spherical. Calculations are done with these different values of \( S_1/S_2 \) denoted by "C" to obtain ultrasonic velocities and an attempt has been made to predict the shape of the molecule in a given mixture.

3.8.3c Velocity calculation from Excess Volume

In Flory's calculations, \( \rho^* \) (the parameter denoting the characteristic pressure of the mixture) is not taken as additive but \( \theta_2 x_2 \) is introduced in the eqn of \( \rho^* \). Here, excess volume is found out from the experimental densities and the same is used to find out \( \theta_2 x_2 \). Following procedure of calculations is adopted. Excess Reduced Volume is obtained as \([177]\]

\[
\bar{v}^E = \frac{v^E}{x_1 v_1^* + x_2 v_2^*} \quad \text{......... 3.54}
\]

Ideal reduced volume \( \bar{v}^o \) is given by

\[
\bar{v}^o = \phi_1 \bar{v}_1 + \phi_2 \bar{v}_2 \quad \text{......... 3.55}
\]
\( T^0 \) is calculated from
\[
\frac{V^{01/3} - 1}{V^{04/3}} \quad \ldots \ldots \quad (3.56)
\]

\( T_1 \) and \( T_2 \) for pure components are calculated in the same way from eqn 3.56 by taking reduced volumes \( \bar{V}_1 \) and \( \bar{V}_2 \) for them respectively instead of \( V^0 \).

The reduced excess volume is also given approximately by [151]
\[
\bar{V}^E = (T - T^0) \left( \frac{\bar{V}}{\bar{V}} \right) \\
\text{i.e.} \quad \bar{V}^E = (V^0)^{7/3} \left( \frac{4/3 - (V^0)^{1/3}}{(V^0)^{1/3}} \right)^{-1} (T - T^0) \quad \ldots \ldots \quad (3.57)
\]
from which \( \bar{T} \) is evaluated.

And from
\[
\bar{T} = (\phi_1 \bar{T}_1 + \phi_2 \bar{T}_2) \left( \phi_1 \bar{P}_1 + \phi_2 \bar{P}_2 - \phi_1 \phi_2 X_{12} \right)^{-1} \quad \ldots \ldots \quad (3.58)
\]
\( (\phi_1 \phi_2 X_{12}) \) is calculated for the given mixture.

By substituting this in an eqn,
\[
\bar{p}^* = \phi_1 \bar{p}_1 + \phi_2 \bar{p}_2 - \phi_1 \phi_2 X_{12} \quad \ldots \ldots \quad (3.59)
\]
\( \bar{p}^* \) for the mixture is obtained. And proceeding in the same manner, using thermodynamic parameters of pure components (evaluated from experimental readings), as \( \beta_T, \beta_B, \bar{P}_1, \bar{P}_2, \bar{V}_1, \bar{V}_2 \) etc, ultrasonic velocities of the mixture are calculated.

The tables D-1 to D-8 give the ideal velocities calculated from excess volume data by applying Flory's theory. The
FLOWCHART SHOWING THE PROGRAM EXECUTION OF FLORY'S SYSTEM-2

Experimental densities & Ultrasonic velocities of Pure liquids (6 in all)

Experimental Ultrasonic velocities of mixtures (A)

Through Computer program SSS1 to SSS6 (six in all)

Parameters of pure liquids (volume, adiabatic, isothermal compressibilities, \( \Gamma \), thermal pressure coefficient, \( \bar{V} \), \( \bar{p} \), \( \bar{T} \), \( \bar{v} \), \( \bar{p} \), \( \bar{T} \))

Excess Volumes

Through computer programmes Flory9 to Flory16 ((8 in all))

Calculation of Ultrasonic velocities of mixtures (8)

Ultrasonic velocities of mixtures for \( x=0.1 \) to \( x=0.9 \) (B)

\% Dev

is conforming with theory? chi-square test

Print \% dev, chi-sq
The percentage deviation of calculated velocities is also found out. The graphs are plotted to compare these velocities of systems of different compositions \([x = 0.1, 0.2, \ldots, 0.9]\) with experimental values at temperature 293 K.