Chapter 3

3.1 Materials:

In the present work, the liquid substances such as benzyl alcohol, phenol, substituted phenols, viz: p-nitrophenol, p-chlorophenol, m-chlorophenol, p-cresol and the solvents like diethylether, acetone, n-hexane, DMSO, used were of analytical grade (s.d.fine chemicals, India). The solids employed in this study including sodium chloride, potassium dichromate, succinic acid, p-hydroxy benzoic acid and micellisable surfactants like sodium laurylsulphate, cetyltrimethylammonium bromide and tetraheptylammonium bromide were also analytical grade (s.d.fine chemicals, India) with 99.9% purity. The pesticides such as lindane, methylparathion and chloropyrifos which have been used in the degradation studies were of commercial grade from Bayer India Ltd, Mumbai, India.

3.2 Methods

3.2.1 Purification

The chemicals were purified by standard procedure reported in the literature [68]. The purity of the liquid samples was checked by their boiling points and their refractive indices. In the case of solids, they were recrystallised with appropriate solvents, followed by comparison of melting point with literature values.
Table 3.1 Comparison between experimental values and literature values of solid samples:

<table>
<thead>
<tr>
<th>Name</th>
<th>Melting point (°C)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Literature [69]</td>
<td></td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>795</td>
<td>801</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>184</td>
<td>184</td>
<td></td>
</tr>
<tr>
<td>Sodium lauryl sulphate</td>
<td>205</td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>Cetyl trimethyl ammoniumbromide</td>
<td>239</td>
<td>241</td>
<td></td>
</tr>
<tr>
<td>p-Hydroxy Benzoic acid</td>
<td>215</td>
<td>214.5</td>
<td></td>
</tr>
<tr>
<td>p-Cresol</td>
<td>35</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>p-Methoxy Benzyl alcohol</td>
<td>23</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>p-Nitro Benzyl alcohol</td>
<td>93</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>p-Hydroxy Benzy alcohol</td>
<td>115</td>
<td>114-122</td>
<td></td>
</tr>
<tr>
<td>p-Amino Benzyl alcohol</td>
<td>62</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2 Preparation of binary liquid mixture

The binary liquid mixtures have been prepared by mixing appropriate volumes of the chosen pair of liquids so that maximum ranges of mole fractions are covered. However, in ternary systems involving a solid; first a known amount of the solid component is dissolved in one of the liquid components and appropriate volume of this solution is mixed with the required volume of the second liquid component.

3.2.3 Preparation of pesticide sample:

The commercially available samples of pesticides have been extracted with ether as follows. A definite amount of pesticide sample has been mixed with required amount of ether; the mixture is then shaken very well for a while to get homogeneous phase. It is then transfer to a china dish. The mixture is allowed to left-over for a while to facilitate the evaporation of ether. Then the ether extract of lindane have been dissolved in hexane, where as methyl parathion and chloropyrifos have been dissolved in acetone to get homogenous solution.

3.2.4 Preparation of tetra heptyl ammonium dichromate (THADC):

The THADC was prepared by adopting a simple ion exchange process. K$_2$Cr$_2$O$_7$ (1.47g, 0.1M) in 50 mL of water slowly to an aqueous solution of tetra heptyl ammonium bromide (THAB, 2.47g, 0.1M) with continuous stirring in a 250 mL beaker kept on a magnetic stirrer at room temperature. A yellow color compound appeared immediately. Stirring was continued for some time after the completion of K$_2$Cr$_2$O$_7$ solution. The resulting yellow precipitate is filtered off and
washed with water several times, vacuum dried and kept in a desiccators in an air-tight container covered with silver-foil.

3.2.5. Preparation of stock solution for kinetic experiment:

(a) Benzyl alcohol: Stock solution of benzyl alcohol (BA, 0.01M) was prepared by weighing 1.0818 g of BA (M.wt = 108.18) in a 100 mL standard flask using DMF as the solvent.

(b) Potassium dichromate: A stock of solution of 0.01M of K₂Cr₂O₇ was prepared by weighing accurately 2.9418 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made upto the mark.

(c) THDAC: A stock of solution of 0.01M of THDAC was prepared by weighing accurately 4.906 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made up to the mark.

(d) p-Methoxy Benzyl alcohol (p-OMeBA): A stock of solution of 0.01M of THDAC was prepared by weighing accurately 1.3816 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made up to the mark

(e) p-Nitro Benzyl alcohol (p-NO₂BA): A stock of solution of 0.01M of THDAC was prepared by weighing accurately 1.5314 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made up to the mark

(f) p-Hydroxy Benzyl alcohol (p-OHBA): A stock of solution of 0.01M of THDAC was prepared by weighing accurately 1.2414 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made up to the mark

(g) p-Amino Benzyl alcohol (p-NH₂BA): A stock of solution of 0.01M of THDAC was prepared by weighing accurately 1.2315 g and transferring in to a 100 mL standard flask, dissolved in distilled water and made up to the mark
3.2.6 Density measurement:

The density ($\rho$) of the pure liquid and liquid mixtures has been determined by relative measurement method. Specific gravity bottle has been used for this purpose. Throughout the experiment, the temperature is maintained constant. Using the following relation, the densities of liquid mixtures were determined.

$$\rho = (W/W_w) \times \rho_w$$

where $\rho_w$ is the density of water, $W$ and $W_w$ are the weight of mixture and water respectively.

3.2.7 Viscosity measurement:

An Ostwald’s viscometer (10 mL capacity) was used for the viscosity measurement of pure liquids and liquid mixtures by the relative method. The viscometer is first filled with double distilled water and then immersed in the electrically controlled water bath, maintained at the experimental temperature. The time of flow of water ($t_2$) and that of solution ($t_1$) were measured with digital stop clock having accuracy of 0.01s (Model CASIO HS – 10W). Knowing the flow time of reference liquid (double distilled water) and the liquid mixture, the viscosity of the mixture can be determined using the following relation,

$$\frac{\eta_1}{\eta_2} = \frac{t_1d_1}{t_2d_2}$$

where $\eta_1$ and $\eta_2$ are viscosities of the liquid and water respectively; $d_1$ and $d_2$ are the densities of liquid and water respectively. The measured viscosity values were accurate to $\pm 0.001$ Nsm$^{-2}$.

3.2.8 Ultrasonic Velocity Measurement:

Measurements of ultrasonic velocities are made in liquids in order to get an idea of their physical functions. A large number of such measurements have been made and reported in the literature [70-77]. Three techniques namely echo-pulse, optical diffraction and interferometric technique are generally employed for the
measurement of ultrasonic velocity in liquids. In the present work, the ultrasonic velocity measurements were made by interferometric method.

3.2.9 Principle of Interferrometric technique:

The interferometer is an instrument for exact measurement of wavelength of any wave motion. One of the most accurate ways of measuring ultrasonic constants in fluids is, to set up stationary wave resonances. This is usually done in a column at one end of which the source is located and at the other end of which is placed a reflector. The working of such a device can be illustrated with the help of a schematic diagram (fig 3.1) where T represents an X-cut quartz crystal transducer which is silvered or gold polished to provide metallic contacts to an oscillator O. When the frequency of driving oscillator O coincides with the natural frequency of piezoelectric transducer T, it vibrates with appreciable amplitude. The moving surface of the crystal generates a plane sound wave which travels through the medium towards a plane reflecting plate R, maintained parallel to the crystal surface. A crystal source transmits ultrasonic wave into the medium; they impinge upon a parallel reflector and are reflected back to the source. The parallel reflector is ordinarily mounted on a very fine screw, which can move the reflector in small fractions of a centimeter at a time. Standing waves are setup in the medium, when the distance between the reflector and the crystal is an integral number of half wavelengths. The reflected wave arriving back at the crystal is then 180° out of phase with the vibration of the crystal. As the reflector is moved through a given distance, the plate current of the oscillator that provides the driving force for the sending crystal is observed and points during which the current is a minimum are noted. The distance between two successive minima (or maxima) is \( \lambda/2 \), where \( \lambda \) is the wavelength of the sound wave in the medium between crystal and reflector.

Once the wavelength is known, the ultrasonic velocity (u) in the liquid can be obtained using the following relation:
\[ u = \text{frequency (f)} \times \text{wavelength (\lambda)} \quad (3.3) \]

The interferometer consists of two important components.

(i) **High Frequency Generator:**

This is a high frequency crystal controlled oscillator based on modified Pierre circuit operating in the megahertz region. It is used to excite the piezoelectric transducer which is a quartz crystal fixed at the bottom of the measuring cell to produce ultrasonic waves at its resonant frequency in the experimental liquid filling the cell. To observe the changes in current, the oscillator is provided with a micro-ampermeter and two trimmer condensers marked A and B on the back side of the generator assembly. These are used to adjust or tune the instrument so that sufficient deflection in anode current can be observed. Two controls are provided for the adjustment of micro-ampere meter and controlling gain respectively (in fig. 3.1).

(ii) **Measuring Cell**

The coupling of the generator to the crystal is such that it prevents high-voltage breakdown and also provide a maximum transfer of power. A cylindrical metal container placed vertically and stably on a heavy metal base which also works as the coupler between piezoelectric crystal and the high frequency generator. Cylindrical container is a double walled jacket. Outer wall has provision for circulation of water or any other liquid for maintaining the temperature of the experimental liquid which is filled in this cell (fig.3.2). A quartz crystal is fixed at the bottom of the cell. A movable metallic reflector plate graduated from outside by micrometer screw arrangement and kept parallel to the crystal is housed inside cell. A digital screen is also attached with cell to give direct micrometer reading. The measuring cell can be easily dismantled into three pieces viz. metal base, container, and reflector such that the experimental liquid can be easily poured into
the cell. The transducer is coupled to the high frequency oscillator by a coaxial cable.

The detailed technical specifications about measuring cell are as under:
(a) Maximum displacement of the reflector- 25 mm
(b) Capacity of liquid cell- 12ml
(c) Least count of micrometer- 0.001 mm.

The calibration of ultrasonic interferometer was done by measuring the velocity in AR grade benzene ($C_6H_6$) and carbon tetra chloride ($CCl_4$). Experimental values of $u$ in $C_6H_6$ at 293, 298, 303 and 313 K were found to be 1316, 1294, 1273, and 1223 ms$^{-1}$ and in $CCl_4$ the corresponding values of $u$ were found to be 932, 927, 919, and 904 ms$^{-1}$ respectively. These values of $u$ agree closely with the corresponding standard values. Standard values of $u$ for $C_6H_6$ and $CCl_4$ at aforementioned temperatures were calculated using the value of $u$ at 298K and the rate of change of velocity with temperature ($-du/dt$). The maximum estimated error has been found to be $+0.08 \%$. The temperature was maintained by circulating water around the liquid cell from thermostatically controlled adequately stirred water bath and covering the measuring cell along with its base with a specially made insulated jacket with a window for noting down micrometer readings.
Fig 3.1 Utrasonic interferometer
Fig.3.2 Cross section of the liquid cell
3.3 Principle of UV-Visible spectra:

This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since transition among electronic energy levels of the molecule leads to the absorption of ultraviolet or visible radiation it is also often called electronic spectroscopy. The information provided by this spectroscopy when combined with those provided by NMR and IR spectral data leads to valuable structural proposals.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also the function of length of the path of radiation through the sample, and is given as

\[ A = \log \frac{I_0}{I} = \varepsilon c l \]  

(3.4)

where, \( A \) = absorbance;
\( I_0 \) = Intensity of the incident light (or the light intensity passing through a reference cell)
\( I \) = Intensity of light transmitted through the sample solution
\( c \) = concentration of the solution in mol. l\(^{-1}\)
\( l \) = path length of the sample in cm
\( \varepsilon \) = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation.
3.4 Measurement of $\lambda_{\text{max}}$ using UV-Visible spectrophotometer

Most of the modern UV-spectrophotometer (fig. 3.3) consists of following important components,


For determining $\lambda_{\text{max}}$, the solution under investigation is placed in the sample cell and pure solvent is placed in the reference cell; then it is scanned over appropriate wavelength span. The output is presented as an absorbance-wavelength profile. The wavelength corresponding to the maximum absorbance is the $\lambda_{\text{max}}$ of the solution.
Fig 3.3 UV-Visible spectrophotometer
3.5 Kinetic measurements:
All kinetic measurements were made spectrometrically using Elico 210 model UV-Visible double beam spectrophotometer at a wave length of 480 nm. The reaction mixture was homogeneous throughout the course of the experiments. Several trial experiments were run to arrive at the standard conditions. All experiments were carried out under pseudo-first order conditions by keeping large excess of substrate over oxidant. The reactions were conducted at room temperature in 10% DMF-90%water binary solvent medium. The progress of the reaction was observed as the function of decrease in absorbance of the dichromate ion with respect to time. Reduction of Cr(vi) was confirmed by the color change of the reaction mixture from yellow to pale green. The first order rate constant was evaluated from the conventional log(a-x) versus time plots. In a typical experiment, the volume corresponding to the requisite concentration of BA and dichromate stock solution were taken in a reaction vessel were maintained by appropriately adjusting their volumes. The reaction mixture was shaken thoroughly and absorbance was measured at 480 nm at regular intervals of time. A gradual decrease in absorbance was observed throughout the period of time followed. The reaction was monitored at least for one half life period. This procedure, with appropriate modification has been followed for the oxidation of the substituted benzyl alcohols by dichromate as well as THDAC.
3.6 Theoretical Ultrasonic velocity:

Comparison of theoretical values of ultrasonic velocities with those obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of interaction between component molecules in the mixture. Such theoretical study is useful in finding the comprehensive suitable theoretical model for the liquid mixtures.

Many theoretical models have been proposed to accommodate the experimentally observed ultrasonic velocities of binary liquid mixtures with varying compositions. Some of them briefly mentioned below.

3.6.1 Nomoto's Relation (U_{NR})

Nomoto established the following relation for the ultrasonic velocity of binary liquid mixtures:

\[ R = \frac{M}{\rho U^{1/3}} \]  

(3.5)

where \( U \) and \( \rho \) are determined experimentally, and \( M \) is the mean molecular weight in a binary liquid mixture:

\[ M = (X_1M_1 + X_2M_2) \]  

(3.6)

where, \( M_1 \) and \( M_2 \) are molecular weights of constituent components.

Simple manipulation yields the following relation:

\[ U_{NR} = \frac{(X_1R_1 + X_2R_2)^3}{(X_1V_1 + X_2V_2)} \]  

(3.7)
3.6.2 The Impedance Relation (UR)

Impedance is the product of ultrasonic velocity $U$ and the density $\rho$ of a liquid mixture. Hence the impedance relation predicts the ultrasonic velocity of the given mixture by simply using the values of impedance and the density values.

Impedance relation is given as

$$U_{IR} = \frac{\sum X_i Z_i}{\sum X_i \rho_i} \quad (3.8)$$

where $X_i$ mole fraction, $\rho_i$ is the density of the mixture and $Z_i$ is the acoustic impedance.

3.6.3 The Jungie Equation (UJ)

The Jungie equation is given as

$$U_j = \left[\frac{1}{(x_1 M_1 + x_2 M_2)}\right]^{1/2} \times \left[\frac{x_1}{M_1 U_1^2} + \frac{x_2}{M_2 U_2^2}\right]^{1/2} \quad (3.9)$$

where, $M_1$ and $M_2$ are molecular weights of constituent components, $U_1$ and $U_2$ are the velocities of constituent components, $x_1$ and $x_2$ are the mole fraction of components 1 and 2 respectively.

3.6.4 Ideal Mixing Relation (Uimx)

Van Deal and Vangeel suggested the following relation for the velocity of sound:

$$U_{imx} = \left[(\frac{x_1}{M_1 U_1^2} + \frac{x_2}{M_2 U_2^2})(x_1 M_1 + x_2 M_2)\right]^{1/2} \quad (3.10)$$

Where, $U_{imx}$ is the ideal mixing ultrasonic velocity in liquid mixture, $U_1$ and $U_2$ are the velocities of the individual components.
The degree of molecular association called as interaction parameter ($\chi$) given by Gruenberg and Nissan equation

$$\chi = \left( \frac{U_{\exp}}{U_{\text{mix}}} \right)^{-1} \quad (3.11)$$

3.7 Calculation of acoustic parameters:

The acoustic parameters are so significant that they can throw light on the nature of intermolecular interactions and hence help us to understand the nature of network in the liquid structure. Such parameters are discussed below.

3.7.1 Adiabatic compressibility

The structural changes of molecules in the mixture take place due to the existence of electrostatic field between the interacting molecules. Thus, the structural arrangement of molecules results in the effect of adiabatic compressibility.

Adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It can be found by the following Newton-Laplace equation as follows.

$$\beta = \frac{1}{\rho U^2} \quad (3.12)$$

3.7.2 Intermolecular free length:

The free length ($L_f$) is the distance between the surfaces of the neighboring molecules given by the equation

$$L_f = K_T \beta^{1/2} \quad (3.13)$$

where $K_T$ is the temperature dependent constant.

The free length can be written using the available volume ($V_a$) and the surface area per molecule $Y$ as

$$L_f = 2V_a / Y \quad (3.14)$$
Here, the surface area per molecule, in the case of spherical molecule is given as

\[ Y = (36\pi N V_o^2)^{1/3} \]  \hspace{1cm} (3.15)

and for non-spherical molecule

\[ Y = (36\pi N V_o^2)^{1/3} f \]  \hspace{1cm} (3.16)

where \( V_o \) is the molecular volume at absolute zero temperature, \( N \) is the Avogadro number and \( f \) is the form factor, which is the ratio between the surface of the molecule and the imagined spherical surface which encloses the same volume as the volume of the molecule. For spherical molecule \( f=1 \).

### 3.7.3 Free Volume \( (V_f) \):

Free volume in terms of ultrasonic velocity \( (U) \) and viscosity \( (\eta) \) of the liquid can be defined as

\[ V_f = M_{\text{eff}} U / K \eta \]  \hspace{1cm} (3.17)

where \( K \) is the temperature dependent constant which is equals to \( 4.28 \times 10^9 \) for all liquids and \( M_{\text{eff}} \) is effective molecular weight \( (M_{\text{eff}} = \sum m_i X_i \) in which \( m_i \) and \( X_i \) are the molecular weight and the mole fraction of the individual constituents).

### 3.7.4 Internal Pressure \( (\pi_i) \):

It is the cohesive force, which is resultant force of attraction and force of repulsion between molecules present in the liquid system. It may be regarded as a measure of the pressure in the interior of the liquid. The attractive forces mainly comprise hydrogen bonding, dipole-dipole interactions. Repulsive forces, acting over a very small intermolecular distances, play a minor role in the cohesion.

\[ (\pi_i) = b RT [K \eta / U]^{1/2} \left[ \rho^{2/3} / M_{\text{eff}}^{7/6} \right] \text{atm} \]  \hspace{1cm} (3.18)

where \( b \) stands for cubic packing factor which is assumed to be 2 for liquids including solutions.
K is the temperature dependent constant $4.28 \times 10^9$.
R is gas constant.
T is absolute temperature and $M_{\text{eff}}$ is the effective molecular weight of the liquid mixtures.

3.7.5 Acoustic Impedance ($Z$)
It is the velocity of light in the liquid medium given by
$$Z = U \rho$$
(3.19)
where $U$ and $\rho$ are velocity and density of the liquid respectively.

3.7.6 Relaxation Time ($\tau$)
Relaxation time describes the rate at which molecules return to their original positions after being displaced by force. It is estimated from the following relation
$$\tau = 4/3 \eta \beta$$
(3.20)
knowing the viscosity($\eta$) and compressibility($\beta$) of the liquid $\tau$ can be calculated.

3.7.7 Absorption coefficient ($\alpha/f^2$):
It reflects the quantity of sound absorption by the medium in which it penetrates and it depends on the external condition like temperature, pressure and frequency of sound.
$$\alpha/f^2 = 8 \Pi^2 \eta/[3 U^3 \rho]$$
(3.22)
where $\eta$ is the viscosity of liquid, $\rho$ and $U$ are the density and velocity of the liquid.

3.7.8 Molecular interaction parameter ($\chi_u$):
It can be calculated by using the following relation,
$$(\chi_u) = [U^2_{\text{exp}}/U^2_{\text{ideal}} -1]$$
(3.23)
where $U_{\text{exp}}$ and $U_{\text{ideal}}$ are the experimental and ideal ultrasonic velocity of mixture of component in the solution under study.
The sign of molecular interaction parameter predicts the strength of interaction between the molecules in the solution. If $\chi_u$ are negative, then interaction will be stronger between the molecules and the interaction will be weak are repulsive if the $\chi_u$ is positive.

3.8. **Excess molar volumes calculation:**

On mixing two liquids namely $L_1$ and $L_2$, it may lead to any one or more of the following processes:

1. Breaking down the intermolecular forces in $L_1$-$L_1$ or $L_2$-$L_2$ and reorganizing the liquid structure.
2. Formation of intermolecular forces between unlike molecules of $L_1$ and $L_2$.
3. Close or loose packing of liquid molecules, thus modifying the intrinsic viscosity of the binary liquid system.

These processes would result in an increase or decrease of the net volume of the binary liquid mixture on mixing a given quantity of each.

The thermodynamic conditions for an ideal liquid mixture is given as $\Delta V = 0$ and $\Delta H = 0$; hence, ideally there would be no change in volume of the mixture compared to the sum of the volume of the individual components added. In short, the volumes are additive in ideal mixtures. Similarly, the ideal mixture formation is neither exothermic nor endothermic ($\Delta H = 0$). Thus for an ideal binary liquid mixture the excess molar volume $V^E$ is zero. Whereas for a real binary liquid mixture $V^E$ may be negative or positive value depending upon the molecular nature of the two liquids and whether they attract or repel each other. Consequently, by determining excess molar volume it will be possible to predict the molecular interaction pattern.
For example, the excess molar volume for both the binary mixtures of acetonitrile-nitrobenzene and benzonitrile-nitrobenzene are negative, suggesting that attractive forces operative between the molecules in both the systems; however, the $V^E$ is more negative for the former than the later indicating greater attractive forces in acetonitrile-nitrobenzene system than that in the other. On the other hand, positive value of $V^E$ for the styrene-octane mixture pointing to a loose structure in the binary system.

3.8.1. Determination of excess molar volume:

Excess molar volume can be determined directly or indirectly by measuring volume change. In the direct determination a batch dilatometer or a continuous dilatometer is used to determine the excess molar volume. The principle involved in the batch dilatometer method is the determination of mercury level in a calibrated capillary tube which separates two liquids. The change in height of the mercury is proportional to the volume change and hence excess molar volume can be calculated. In the continuous dilatometer method, liquid 1 is taken in a reservoir and the second liquid is successively added in aliquots; the change in mercury level is determined. The change in height of the mercury is proportional to the volume change and hence excess molar volume can be calculated. In the indirect method the density of the liquid is measured using a pycnometer. The density data are used to determine the excess molar volume.

Using the following equation excess molar volume of a liquid binary mixture has been calculated from its density data,

$$V^E = x_i m_i / \rho_i - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2$$  \hspace{1cm} 3.24
where \( x_1 \) and \( x_2 \) are mole fractions, \( M_1 \) and \( M_2 \) are the molar masses and \( \rho_1 \) and \( \rho_2 \) are the densities of component 1 and 2 respectively; quantities with subscripts ‘i’ refer to the mixtures.

### 3.8.2 Redlich-Kister polynomial equation:

The excess acoustic values viz: \( V^E \), \( \beta^E \), \( \pi^E \) and \( L_i^E \) for each of the mixtures were fitted to the Redlich-Kister polynomial equation given as

\[
Y^E = X_1 X_2 \sum A_i (2X_1-1)^i
\]

where \( A_i \) and \( x_1 \) are adjustable parameters and mole fraction of component 1.

In each case the optimum number of coefficients \( A_i \) was determined from an examination of the variation of the standard deviation given by

\[
\sigma (Y^E) = \left[ \sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E) / (n - m) \right]^{1/2}
\]

where \( n \) is the total number of experimental values and \( m \) is the number of parameters.

### 3.8.3 Calculation of Partial molar volume at infinite dilution:

The partial molar volume for a binary liquid mixture (\( V_{1\infty} \) and \( V_{2\infty} \)) could be calculated from the Redlich-Kister polynomial equation coefficients \( A_i \) using the following relationship

\[
Y_{1\infty} = \sum A_i \quad \text{and} \quad Y_{2\infty} = (-1)^i \sum A_i
\]