CHAPTER II
EXPERIMENTAL SECTION

II.1 INTRODUCTION

This chapter covers a discussion on the experimental techniques used to measure the density, speed of sound, viscosity and refractive index of the liquids and liquid mixtures. Density has been measured by using double arm pycnometer, viscosity by Cannon-Fenske viscometer (size 75 & 100), refractive index by the Abbe’s refractometer and speed of sound by the interferometer. Details about the solvents and their uses in addition to the preparation of liquid mixtures are given. Brief information about the numerical analysis and treatment of the data as well as some necessary details about the computer algorithms are presented.

II.2 SOLVENTS USED

The solvents used in this thesis comprise of different classes i.e., alkanes, dipolar aprotics, aromatics, alcohols and esters. These were chosen based on different chemical groups so as to study their varying interactions, with one of the common liquids that have some industrial importance. While handling these liquids, extreme care was taken regarding their toxicity and other properties [1]. The solvents used were of either analytical reagent grade or in some cases, spectroscopic/HPLC grade. Almost all the solvents were used directly because the manufacturers claimed their high purities. The GLC analyses were performed using a flame ionization detector (HP Series 6890, series, with fused silica columns) having a sensitivity better than 10 g of fatty acid/mL of the solvent. The GLC purity analyses for each liquid is given in the corresponding chapters. Information on solvents and their sources are given in Table II.1.
TABLE II.1

Solvents Used and their Sources

<table>
<thead>
<tr>
<th>Solvent (grade)</th>
<th>Formula</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>CH$_3$CN</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>CH$_2$=CHCN</td>
<td>Fluka</td>
</tr>
<tr>
<td>Benzene, HPLC &amp; Spectro.</td>
<td>C$_6$H$_6$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Butan-1-ol, HPLC</td>
<td>HO CH$_2$ CH$_2$ CH$_2$CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>CH$_3$CH$_2$CH$_2$CH$_2$OOCCH$_3$</td>
<td>E.Merck, Darmstadt</td>
</tr>
<tr>
<td>2-Chloroethanol</td>
<td>HO CH$_2$ CH$_2$Cl</td>
<td>E. Merck, Germany</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>CH$_2$(Cl$_2$)$_4$CO</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>n-Decane</td>
<td>CH$_3$(CH$_2$)$_6$CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>1,4-Dimethylbenzene</td>
<td>H$_3$C (C$_6$H$_4$)CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>(CH$_3$)$_2$SO</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>HCON(CH$_3$)$_2$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>N,N-Dimethylacetamide</td>
<td>CH$_3$CON(CH$_3$)$_2$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Dioxane</td>
<td>O</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>CH$_3$(CH$<em>2$)$</em>{10}$CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH$_3$CH$_2$OH</td>
<td>E.Merck, Germany</td>
</tr>
<tr>
<td>2-Ethoxyethanol</td>
<td>C$_2$H$_5$OCH$_2$CH$_2$OH</td>
<td>B.D.H., London</td>
</tr>
<tr>
<td>Ethyl acetate, AR</td>
<td>CH$_3$CH$_2$OOC CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>n-Heptane, HPLC &amp; Spec.</td>
<td>CH$_3$(CH$_2$)$_5$CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>n-Hexane, HPLC &amp; Spec.</td>
<td>CH$_3$(CH$_2$)$_4$CH$_3$</td>
<td>s.d.fine-Chem. Pvt. Ltd., Mumbai</td>
</tr>
<tr>
<td>Hexan-1-ol</td>
<td>HO CH$_2$ (CH$_2$)$_4$CH$_3$</td>
<td>Fluka (Germany)</td>
</tr>
</tbody>
</table>
The physical properties like density, $\rho$ and refractive index, $n_D$ of the liquids are compared at 298.15 K with the literature values in the respective chapters of the thesis.

II.2.1 Alkanes

Alkanes are used in a number of hydrocarbon processing industries. However, their importance in industry depends upon the number of carbon atoms in the $n$-alkane chain. The $n$-alkanes containing carbon atoms $C_8$ to $C_{12}$ are used in the manufacture of surfactants and single cell proteins. Alkanes with $C_{10}$ to $C_{17}$ are used as plasticizers, while $C_{20}$ and the higher
alkanes find applications as additives for lubricating oils. Continued fall in the demand for residual fuels, the rise in the prices of petroleum crudes and eventual shift to fuels derived from oil shale and liquefaction of coal, all contribute to the increasing importance of alkanes. In the present thesis, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, 2,2,4-TMP and cyclohexanone are used.

II.2.2 Monocyclic Aromatics

A number of substituted monocyclic aromatics have been employed. These include benzene, methylbenzene, 1,4-dimethylbenzene, 1,3,5-trimethylbenzene and methoxybenzene. A study of interaction of various substituted monocyclic aromatics with other liquids would have immense engineering applications such as those in separation processes, distillation, etc. Among the aromatic hydrocabons, the parent benzene is nonpolar. Benzene and its homologues are extracted from petroleum products or acetylene. The physical properties of benzene have been well documented in the literature [2,3]. It is used widely in motor fuel due to its high antiknock values. Benzene is also an important raw material in the petrochemical industries. Commercially, it is used as a starting material to synthesize styrene, a useful monomer to produce polystyrene. Recently, benzene is suspected as carcinogenic thereby restricting its wide usage. The vapour threshold limit value (TLV) of benzene is 10 ppm for approximately 8 hours of exposure.

Methylbenzene is a useful raw material in the production of benzene. It is also used as a raw material in the preparation of diisocynates. When strongly nitrated, it forms trinitromethylbenzene (TNT), a powerful explosive. Physical properties of methylbenzene have been well documented in the literature [2,3]. Dimethylbenzenes are important components of gasolene which are used in motor fuels and as solvents in
paints and coatings industries. Methoxybenzene is a colourless liquid and is soluble in alcohols and ether. Methoxybenzene is mainly obtained from sodium phenolate. It finds use in the perfume industry as a solvent. It is also used as a vermicide and as an intermediate. 1,3,5-Trimethylbenzene is a highly symmetrical molecule whose trade name is Ethanox 330. It is used as a noncolouring stabilizer (antioxidant) for plastics, adhesives, rubber and waxes. Just like benzene, 1,3,5-trimethylbenzene has a zero dipole moment.

11.2.3 Alkanols

Alkanols are classified as protic dipolar liquids having intermolecularly hydrogen-bonded structures giving three dimensional networks. They show regularly changing liquid state properties with increasing aliphatic chain length. In view of the importance of higher aliphatic alkanols in industrial applications, an effort was made to study their binary mixtures. Among the alkanols selected in this study are methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol and butan-2-ol. Of these, propan-1-ol is used in the preparation of propionic acid and in making toilet lotions. Other alkanols find extensive use in a number of areas of engineering and pharmaceutical industries.

11.2.4 Esters

Esters are an industrially important class of liquids which are prepared by the esterification method. Methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate are the representative examples of aliphatic esters used in this study. Of these, methyl acetate is mainly used as a solvent for nitrocellulose and acetyl cellulose, along with paints, varnishes and lacquers. Ethyl acetate, a highly polar and somewhat less
toxic liquid, is used in the production of a number of commercial polymers and acrylic esters. Esters are used in flavouring, perfumery and artificial essences. Ethyl acetate is highly flammable and a possible explosion hazard. n-Butyl acetate is used as a solvent and also as a plasticizer in polymer industries.

11.2.5 Other Liquids

Among other liquids, 2-chloroethanol, which has the characteristics of both alcohol and chlorinated hydrocarbon, is soluble in water in all proportions and dissolves in many class of compounds from inorganic salts to cellulose esters. The chief value of 2-chloroethanol is as a source material for many industrially important organic products like ethylene glycol, ethylene oxide and their derivatives. Vapours of 2-chloroethanol possess highly toxic properties due probably to its hydrolysis in the tissue to form hydrochloric acid and therefore, it should be handled only under extreme precautions for the protection against skin and breathing.

World demand for acrylonitrile has been increasing every year by at least 10% for the last three decades. It is mainly used for acrylic fibres which contain at least 85% of acrylonitrile and are known as “madacrylics”. Because of their wool-like aesthetics, acrylic fibres have their main outlets in knit-wear, carpets and upholstery. Acrylonitrile-butadiene copolymers (perbunan-GR-N) have good resistance to oils, solvents and has superior abrasion resistance property.

Cyclohexanone is used chiefly as a chemical intermediate in nylon manufacture and solvent for synthetic resins and polymers, thinner for lacquers specially those containing nitrocellulose and vinylchlorides polymers and co-polymers, dyes and insecticides. It is also use as a building block in the synthesis of many organic compounds like pharmaceuticals, and
2-ethoxy ethanol is a versatile organic liquid used in chemical industries as a solvent for lacquers, oils, and resins and as an antifreeze for explosives. 2-Ethoxyethanol is employed as a solubilizing agent and as a solvent in several plastic industries and those which manufacture enamels and lacquers. It is soluble in water in all proportions. Being an ether-alcohol, it is readily miscible with many classes of organic solvents.

Several polar liquids such as 1,4-dioxane, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF) have been used. 1,4-Dioxane finds a wide number of applications. It is an useful ingredient in paint, varnish and lacquer remover and is almost a common component of cleaning materials like dry cleaning spotting fluids. It is employed in certain pharmaceutical processes for solvent extraction. Dioxane is also a suggested solvent in cryoscopic determination of molecular weight of solutes.

Dimethyl sulfoxide is a highly hygroscopic liquid miscible with water in all proportions. It is a versatile organic liquid having a special solvent power to promote a chemical reaction when used as a reaction medium. It also exerts a solvent effect sufficient to accelerate a reaction brought about by another reagent. As such, it is used as a reaction medium in the syntheses of a variety of organic compounds. It is also used as a solvent for polymerization reactions displacement reactions because of its high dielectric constant value (i.e., \( \varepsilon = 46.45 \)). A majority of organic fungicides, insecticides and herbicides are soluble in dimethyl sulfoxide. DMSO is used as a solvent for the crystallization of vitamins, hormones and sulphonamides. It is most effective in influencing the structure and molecular dynamics of water. Even at very low temperatures, dimethyl sulfoxide is able to prevent water crystal formation and to protect living cells from freezing damage.
N,N-Dimethyl formamide is a useful solvent in industrial processes especially for polar polymers having strong intermolecular forces such as in poly(vinyl chloride) and poly(acrylonitrile). Dimethylformamide solutions of high molecular weight polymers are processed to make fibres, thin films and reverse osmosis polymer membranes. In pharmaceutical industries, it is used as a solvent for crystallization of vitamins, hormones and sulphonamides. Dimethylformamide is used as a solvent to dissolve polymers for membrane casting with the technique of phase inversion wherein, a polymer film solution spread on a flat surface is immersed in a large bath of a poor solvent that induces membrane precipitation [12,13].

DMAc is a good solvent for a wide range of organic and inorganic compounds synthetic/natural resins and copolymers of acrylonitrile and vinyl formate. The polar nature of DMAc enables it to act as a solvent as well as a reaction catalyst, often producing higher yields and pure products in a shorter time. DMAc is capable of converting many organic and inorganic molecules into reactive forms by solvation.

THF is a cyclic ether which is produced mainly from furfural. Due to its proton accepting capability, THF is regarded an extensively used solvent for reactions involving organo-lithium compounds and Grignard reagent and as a solvent in synthetic research [14-16]. Moreover, it has been used as a very useful solvent for the production of vinyl polymers.

Acetonitrile is the starting material for a number of industrially important products such as acetophenone and vitamin B<sub>1</sub> (thiamine). It is a good solvent for organic compounds and is used in the extraction of rough fractions of fatty acids. Aqueous mixtures of acetonitrile serve to be good reaction media in electrochemical research [17].
II.3 BINARY MIXTURES

Binary mixtures were prepared by mass in specially designed ground glass stoppered bottles. Totally, a set of nine compositions were made with an increment of 0.1 mole fraction for each mixture. The possible error in mole fraction is estimated to be ± 0.0001. Mixture compositions are expressed as mole fractions, $x_i$ and also, as volume fractions, $\phi_i$ defined respectively, as:

$$x_i = \frac{g_i}{\sum g_i/M_i} \quad (II.1)$$

$$\phi_i = \frac{x_i V_i}{\sum x_i V_i} \quad (II.2)$$

Here, $g_i$, $M_i$ and $V_i$ refer to mass, molecular weight and molar volume of the $i$-th component of the mixture.

II.4 EXPERIMENTAL TECHNIQUES

In this section, details of the experimental techniques such as pycnometer, viscometer, refractometer and ultrasonic interferometer are given.

II.4.1 Density Measurements

Density is one of the most fundamental properties of a liquid from which many thermodynamic parameters like thermal expansivity, molar volume, partial molar volume, excess molar volume, etc., can be calculated. Therefore, it is essential to have accurate values of density of
liquids and liquid mixtures in order to investigate the detailed molecular interactions in liquid mixtures.

In the present thesis, densities of liquids and of binary mixtures were measured using a capillary pycnometer (Lurex, NJ, USA) having a volume capacity of 10 cm$^3$ with a diameter of 1 mm. Pycnometer was calibrated with double distilled water at the desired experimental temperatures. After routine cleaning and calibrations, the pycnometer was weighed empty by supporting it with a plastic stand of known weight kept on the pan. It was then filled with the double distilled water and suspended in a constant temperature bath for at least 10-15 minutes so as to ensure attainment of the thermal equilibrium. Before taking final weight of the pycnometer with water, its outer surface was dried thoroughly using filter paper wraps. The same procedure was followed for other liquids. Density of the liquid was then calculated from a knowledge of the density and weight of water at that temperature. The measured density values of liquids were reproducible within $\pm 0.0002$ g.cm$^{-3}$.

Standard deviations in the calculation of densities of liquids and their mixtures were generally within $\pm 0.01\%$. For each measurement, sufficient time was given to attain thermal equilibrium in the constant temperature water bath,

the temperature of which was monitored to $\pm 0.01K$ on a digital display which was also checked by using a $1/10$th degree calibrated thermometer (made in England). Fluctuations in the bath temperature did not exceed $\pm 0.01K$ and evaporation losses in mixtures was almost insignificant during the entire time of actual measurements. The measured densities were considered significant to four figures. An average of triplicate measurements was taken into account and these were reproducible within $\pm 0.05\%$. 
II.4.2 Viscosity Measurements

All liquids possess resistance to flow and this property is called viscosity [4]. It is represented by the symbol, $\eta$, and is expressed in dyne-seconds per cm or Poise, or mPa.s. with the dimensions of $M^1 L^{-1} T^{-1}$. If the tangential force per unit area exerted by a layer of liquid upon one adjacent layer is one dyne for a space rate of variation of tangential velocity of unity, then viscosity is one Poise. On the other hand, the kinematic viscosity is the ratio of viscosity to density. The cgs unit of kinematic viscosity is Stoke. The flow of liquids through a tube of length, $L$ and radius, $r$ having a pressure difference of $\Delta P$ at the ends, the coefficient of viscosity, $\eta$ i.e., liquid volume, $V$ escaping per second is given by the well-known Poiseuille's relation:

$$V = \frac{\pi \cdot \Delta P r^4}{8L \cdot \eta}$$  \hspace{1cm} (II.3)

where the liquid flow volume is given in cm$^3$. sec$^{-1}$; if $L$ and $r$ are given in the units of cm and $P$ in dynes.cm$^{-2}$, then $\eta$ would be in the units of Poise or dyne-sec. cm$^2$. In SI units, one centiPoise is mPa.s. In the present thesis, we have used mPa.s as the unit of viscosity.

Viscosities of pure liquids and binary mixtures were measured in the temperature range of 298.15 to 308.15 K using Cannon-Fenske viscometer (ASTM D 445, supplied by the Industrial Research Glassware Ltd., NJ, USA). Three different sizes 75, 100 and 150 were used depending on the flow times of the liquids and liquid mixtures.

Viscosities were calculated from the flow times. In the actual measurement, a thoroughly cleaned viscometer was used. The liquid under
examination was introduced through one of the arms of the viscometer by means of a pipette. The viscometer was then kept in the thermostat for 10-15 minutes for attainment of thermal equilibrium. The liquid was then sucked from the capillary side of viscometer and allowed to flow under gravity. The time required to cover definite positions marked on one limb of the viscometer was noted by means of a stop watch with a precision of 0.01 sec. This process was repeated several times and the mean time, $t_1$ was taken into account for the calculations. The same procedure was repeated for water. Thus knowing the density, $\rho_1$ and of water, $\rho_2$ and the viscosity of water, $\eta_2$, the viscosity of the liquid, $\eta_1$, was then calculated as:

$$\eta_1 = \eta_2 \left( \frac{\rho_1 t_1}{\rho_2 t_2} \right) \quad \text{(II.4)}$$

In the actual determinations, the flow times of pure liquids or mixtures have been compared with that of double distilled water. Similarly, flow times for benzene, carbon tetrachloride and cyclohexane were measured. Using the flow times, viscosities and densities of these liquids, the viscometer constants, $A$ and $B$ were determined by using the relation:

$$\frac{\eta}{\rho} = At - B/t \quad \text{(II.5)}$$

The viscosities of the above mentioned liquids were then calculated with these constants and are found to be in good agreement with the literature data.

**II.4.3 Refractive Index Measurements**

Refractive index, $n_0$, for the sodium-D line was measured using a thermostated Abbe refractometer (Bellingham and Stanley Ltd., England or Atago 3T, Made in Japan). The precision of the instrument is ± 0.0001.
The refractometer is fitted with hollow prism casings through which water is circulated. The temperature of the prism casings is observed with a digital display (±0.1K). The instrument is provided with two prisms placed one above the other in front of the telescope. Upon inserting a few drops of the liquid using a hypodermic syringe, the incident ray forms the line of demarcation between the light and the dark portions of the field, when viewed with a telescope which smoothly moves with the scale. From the scale of the instrument, values of $n_D$ are obtained.

The refractive index measurements were carried out at 298.15, 303.15 and 308.15 K by circulating water from a thermostat using a 1/40 HP water pump. In order to obtain the precise data, refractometer was calibrated frequently using a glass piece of known refractive index supplied with the instrument. It was also double checked by measuring the refractive index of pure water. A built-in sodium-D lamp was used as a light source and an average of triplicate measurements was considered in all the calculations. In earlier measurements, Abbe refractometer (Bellingham and Stanley Ltd., London) with a separate sodium-D lamp was used. The $n_D$ values of the liquids studied are compared well with the literature as given in tables of the subsequent chapters of the thesis and these agreed reasonably well.

### 11.4.4 Speed of Sound Measurements

Speed of sound measurements are useful in understanding the intermolecular interactions in liquid mixtures. Theoretically, ultrasonics is a rapidly developing branch of modern physics. Ultrasonic methods have been used in several scientific disciplines in order to tackle numerous theoretical and practical problems. Considerable literature exists on the speed of sound measurements of liquids and liquid mixtures. The multifrequency ultrasonic interferometer, model M-84, supplied by Mittal
Enterprises, New Delhi is used in this research. The instrument measures speed of sound in liquids and their mixtures within the precision of $+2 \text{ m.s}^{-1}$. A schematic diagram of the instrument is shown in Figure II.1.

In the ultrasonic interferometer, ultrasonic waves of known frequency, $v$ generated by a quartz crystal are reflected by a movable metallic plate kept parallel to it. Increase or decrease in the distance between two plates produces the acoustic resonance, giving rise to an electrical signal on a generator driving the quartz crystal with the anode current reaching maximum, when the separation between two plates is exactly one half the wave length, $\lambda$, or its multiple. From a knowledge of $\lambda$, the speed of sound, $u$ in liquids can be calculated as:

$$u = v\lambda$$  \hspace{1cm} (II.6)

The ultrasonic interferometer consists of a measuring cell and a high frequency generator. The measuring cell is a specially designed double-walled metallic cell with two chutes in it for water circulation in order to maintain a constant temperature of the liquid filled in the central portion of the cell. A fine micrometer screw reading up to $\pm 0.001 \text{ mm}$ is provided at the top which raises or lowers the reflector plates in the liquid within the cell through a known distance. A quartz crystal is fixed at the bottom of the cell.

A high frequency generator is designed to excite the quartz crystal at its resonance frequency in order to generate an ultrasonic wave in the test liquid taken in the measuring cell. The measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. A microammeter is used to observe the changes in the current. Two controls are provided on the panel of the high frequency generator for sensitivity regulation and initial adjustment of the microammeter. Microammeter is used to observe the maximum of each of the deflections.
Fig. II.1: Schematic Diagram of Interferometer Cell
In actual measurements, the measuring cell with a quartz crystal of desired frequency (1 to 4 MHz depending upon the nature of the liquid) was fixed. Water was circulated from a thermostat so as to maintain a constant temperature of the test liquid. A high frequency generator at the known value was switched on after the liquid in the measuring cell attained thermal equilibrium. The micrometer was then turned to obtain maximum or minimum of the anode current as indicated by deflections on the microammeter. The successive maximum deflections, n, moved on the microammeter scale, which indicates the successive maxima in the anode current were counted. The total distance, d covered by the micrometer for n = 10 was read to give the wave length as: \( \lambda = \frac{2d}{n} \). Values of d were measured five or six times and these were reproducible within ± 0.002 mm. The mean of these readings was considered for the calculations. The speed of sound in the liquid within the precision of ± 2 m.s\(^{-1}\) was then calculated using Eq.(I1.6).

Precautions like maintenance of accurate temperature, low liquid evaporation losses, constant voltage input, etc., were taken while making the measurements. Care was taken to avoid any possible damage of the quartz crystal while cleaning operations and filling cell with the liquids. From the results of \( u \), the isentropic compressibility, \( k_s \) was calculated by using the relation:

\[
k_s = \frac{1}{(u^2 \rho)} \quad (I1.7)
\]

where \( \rho \) is density of the liquid. The average uncertainty in \( k_s \) is generally around ± 0.01%. In all the cases, triplicate measurements were taken at each temperature and for each composition of the mixture. Average values of \( u \) were used in all the calculations.
II.4.5 Constant Temperature Water Bath, Balance and Immersion Cooler

In order to obtain precise experimental values of liquids and liquid mixtures, a good temperature control is necessary. In this research, with a digital display of the bath, a temperature precision up to ± 0.01K was used. Temperature was also checked using a calibrated certified thermometer. A single pan Mettler balance (model AT 20, Switzerland) with an accuracy of ± 2µg was used for mass measurements.

The Julabo immersion cooler (FT 200), Julabo Labortechnik GmbH, Germany was employed to cool the water bath. This unit was installed at the intake of a heating circulator to draw the heat away from the circulating bath liquid. The immersion probe was connected to the instrument with a flexible and insulated tube. To prevent the immersion probe from icing, it was completely immersed into the bath liquid.

II.5 COMPUTATION OF MIXING FUNCTIONS

One of the goals of the present thesis is to calculate the excess functions of mixtures. Such excess functions represent the properties of mixtures which are in excess of those of an ideal mixture under the same conditions of temperature, pressure and composition. Thus, several excess quantities have been calculated from the measured physical properties of the mixtures. All these excess quantities have been fitted to Redlich and Kister equation [6] to estimate the needed parameters by the method of least squares using Marquardt algorithm [7]. The standard deviations, σ between the computed and the experimental values have also been calculated for different binary mixtures and these data will be presented in different chapters of the thesis.
II.6 REGRESSION ANALYSIS

Depending upon the nature of the experimental data, various regression equations have been adopted in the literature for the statistical analysis of the experimental data. The regression model consists of an equation or a set of equations that allows the calculation of a dependent variable, \( Y \) from the values of an independent variable, \( x \) and a set of \( k+1 \) parameters \([B(i)]\). A general mathematical form of such a model for \( j = 0 \) to \( k \) data points is:

\[
Y_j \text{(calc)} = F\{x_j, B(0), B(1),..., B(k)}\quad (II.8)
\]

While several independent variables can be used, we limit ourselves to one independent variable.

The regression analysis consists of simultaneous variation of the parameters in the model with respect to a set of experimental data \([Y_j \text{ expt}), x_j]\) until the \( Y_j \text{(calc)} \) computed from Eq. (II.8) are as close as possible to the experimental values i.e., \( Y_j \text{(expt)} \). This is called "fitting" the model to the experimental data. It is usually done by using the principles of least squares, which holds that the "best" values of the parameters as found when the error sum \( S \),

\[
S = \sum_{j=1}^{n} w_j \left[ Y_j \text{(expt)} - Y_j \text{(calc)} \right]^2 \quad (II.9)
\]

has its minimum value with respect to the parameters. The \( Y_j \text{ (expt)} \) in Eq.(II.9) are the experimental data and the \( Y_j \text{(calc)} \) are computed from Eq.(II.8). The \( w_j \) in Eq.(II.9) are the weighting factors.
Computer programmes for the nonlinear regression analysis are commercially available. General programmes have a "model subroutine" into which the user writes programme code for the desired regression model. With \( w_j = 1 \), \( S \) in Eq.(11.9) is called an unweighted error sum. The approach to minimum \( S \) starting from a set of arbitrary initial "best guesses" for \( k \) parameters is viewed as the journey of a point toward the minimum of an error surface in a \( k+1 \) dimensional orthogonal coordinate system. One axis of the coordinate system corresponds to \( S \) and the others correspond to the parameters.

The error surface has three dimensions. The \( Z \) axis is associated with the error sum \( S \), while the \( X \) and \( Y \) axes are identified with the parameters \( A \) and \( k \), respectively. From the initial guesses of \( A_i \) and \( k_i \), an initial point, \( p_i [A_i, k_i, S_i] \) is located on the error surface. By a systematic variation of the parameters, the algorithm employed by the programme to minimize \( S \) causes this point to travel toward the point, \( P_o[A_o, k_o, S_o] \). This is the point of convergence where \( S_o \) is at the absolute minimum on the error surface. The quantities \( A_o \) and \( k_o \) are the best values of the parameters, optimized with respect to the experimental data.

General programmes for the nonlinear regression differ mainly in the algorithm used to minimize \( S \). One of the most commonly used algorithms is that of the steepest descent method, in which the search for the minimum \( S \) travels on the gradient of the error surface. The progress of travel is monitored at each iteration or cycle and adjusted when necessary. The steepest descent provides a fast convergence in the initial stages of the computation, but slows down considerably near the convergence point. Such programmes written with conservative tolerances for the convergence are extremely reliable.

The Gauss-Newton, another frequently used algorithm, approximates nonlinear models for \( Y_j(\text{calc}) \) by linear Taylor's series expansions [7,8].
After initial guesses, new values of the parameters at each cycle are found by methods similar to the linear least squares, using expressions involving the first derivatives of S with respect to each parameter. Ideally, each iterative cycle gives successively better estimates for the parameters until an absolute minimum in S is reached. Unlike the steepest descent method, convergence is often fast in the vicinity of the minimum.

The Marquardt or Levenberg-Marquardt algorithm [7,9] contains elements of both steepest descent and Gauss-Newton methods, but converges more rapidly than either of these. The Marquardt algorithm behaves like a steepest descent method under conditions for which the latter is efficient, i.e., far from the minimum S. However, close to the minimum, it behaves like the Gauss-Newton method, again under conditions where the latter is efficient.

The nonlinear regression programmes should include criteria to automatically test for convergence and terminate the programme when preset conditions for the convergence are reached. Reliable tests for the convergence are based on the rate of change of S or on the rate of change of the parameters. For example, one programme commonly terminates when the rate of change of S over ten cycles is < 0.02%. Another converges normally when the change in all the parameters in a given cycle is smaller than 0.005%. In an algorithm as fast as the Levenberg-Marquardt [9], testing over a series of cycles is self defeating in terms of the computational time and is usually unnecessary.

In this thesis, all the numerical calculations were done by using a pentium personal computer (AST, USA and Vintron, India) with programmes written in GW/TURBO BASIC languages. These results will be discussed in subsequent chapters of the thesis.
II.7 LITERATURE CITED


