CHAPTER- 3
THEORETICAL ASPECTS

3.1 Introduction

Liquid viscosity, density and ultrasonic velocity findings help in understanding ion solvent interaction studies in the recent years [124, 6, 278, 274, 195, and 76]. Ultrasonic waves are very effectively for determination of ion and solvent interaction in liquid solutions containing alkanols (alcohols) [87]. The science of dissemination of ultrasonic wave in various liquids now very well understands using analysis of variety of acoustical and thermal characteristics of the liquids. The data obtain from ultrasonic propagation parameters in liquid mixtures such as ultrasonic velocity and and its variation by changing composition of one of the constituents, Which gives insight into nature of molecular interactions in the provided chemical compositions, also more importantly the theories are also verified related to the structure of different liquid. The ultrasonic propagation parameter gives significant analysis and insight of behavior of variety of liquids. This is due to factors such as association in intra-molecular and intermolecular, dipole interactions, formation of complex as well as changes in association in structures; strongly changes compressibility of the given system alters the given changes of ultrasonic velocity.

The acoustic and thermodynamic variables from ultrasonic investigation suggest the ion salvation can be accompanied with the annihilation or sometimes enhancement in the given solvent structure. Ultrasonic, thermodynamic and physical characteristics of liquid systems are of great importance for obtaining clear cut understanding of intra-molecular and intermolecular interactions, structural and physicochemical variations and also for confirming the different liquid state theories that attempts in founding properties of variety of liquids and liquid mixtures. In the biology, strongness as well as characteristic of intermolecular interactions is under the influence of drug molecule activity and activation energy due to metabolic changes. In the study of departure of some real liquid mixtures from its ideality, thermodynamic as well as transport properties of liquid mixtures are utilized effectively [232].

A different research group carefully analyses the acoustical properties of solution involving alkanols [144, 67]. In solution of ion solute the attraction of the solute and
solvent is dominantly of ion and dipole type. The ion-dipole interactions depend mostly on parameters like size of ion and type of polarity of the given solvent. The strength of attraction between dipole-ion is found to depend upon the magnitude of dipole moment, charge and ion size, and that is reciprocal to the distance between the ion and the dipolar molecule [35, 20]. The dissolution of alcohols in a solvent has effect of a volume contraction because of the interaction of ions and solute molecules and this may have direct impact on other acoustical properties in solution [259, 219, 218, and 139]. This chapter gives theoretical aspects of the present research work.

3.2 Alkanols

Alkanols are also known as alcohols. In alkanol a hydrogen atom of an aliphatic carbon can be replaced by a group of hydroxyl, hence they are called organic compounds. Therefore, alkanol molecules have major two parts; out of which one one is alkyl group and remaining is a group of hydroxyl. Alkanols have odor sweet. Also alkanol show a very unique set of chemical as well as physical characteristics. This unique physical as well as chemical characteristic of alcohols is mainly due to presence of the hydroxyl group. Alkanols or alcohols are compounds, which consist of one or some time more than one groups of hydroxyl. In alkanols, alkyl groups are connected to –OH type group of alkanol [159].

Classification of Alkanols

Classification of alkanols is mainly due to the number of –OH groups which are involved in their molecules. According to above classification, they are mono-, di- and trihydric alcohols. Some examples of mono-, di- and trihydric alcohols are as follows:

\[
\begin{align*}
\text{Ethanol} & \quad \text{Ethane-1,2-diol} & \quad \text{Propane-1,2,3-triol} \\
\text{(Ethyl Alcohol)} & \quad \text{(Ethylene Glycol)} & \quad \text{(Glycerol)} \\
\text{(Monohydric)} & \quad \text{(Dihydrate)} & \quad \text{(Trihydrate)} \\
\end{align*}
\]

Monohydric alkanols are divided into three group namely primary, secondary and tertiary alkanols. This separation is depending upon, whether a hydrogen group is
attached to a primary, secondary or tertiary carbon atom. These are shown as primary (1<sup>0</sup>), secondary (2<sup>0</sup>) and tertiary (3<sup>0</sup>)

\[
\begin{align*}
&\text{H} \quad \text{CH}_3 \quad \text{CH}_3 \\
&\text{CH}_3 - \text{C} - \text{OH} \quad \text{CH}_3 - \text{C} - \text{OH} \quad \text{CH}_3 - \text{C} - \text{OH} \\
&\text{Ethanol} \quad \text{Propan-2-ol} \quad \text{2-methylpropan-2-ol} \\
&\text{Primary} \quad \text{(Secondary)} \quad \text{(Tertiary)} \\
&\text{or} \quad \text{or} \quad \text{or} \\
&\text{1<sup>0</sup> Alcohol} \quad \text{(2<sup>0</sup> Alcohol)} \quad \text{(3<sup>0</sup> Alcohol)}
\end{align*}
\]

a) Physical Characteristics or properties of alcohols

- **Boiling point of alcohol**
  
  As compared to other hydrocarbons of same masses at molecular level, alcohols mostly possesses higher boiling point. This happens due to the presence of intermolecular hydrogen bonding between hydroxyl groups of alcohol molecules. In most of cases, when number of carbon atoms in aliphatic chain of carbon rises there is rise in boiling point of alcohol. Therefore it is observed that, boiling point is inversely proportional to increase in branching in aliphatic carbon chains. Boiling point is higher for alkanols which contain less carbon atoms.

- **Alcohol solubility**
  
  Alcohol solubility with water is mainly due to presence of hydroxyl groups. In liquids, formation of intermolecular hydrogen bonding is only due to hydroxyl group. This causes hydrogen bonds to form in between water and alcohol molecule which easily decides solubility of alcohol in the water. However, hydrophobic nature of alkanolis due to attachment of the alkyl group to the hydroxyl group. Hence, rise in size of alkyl group decreases the solubility of alcohol.

- **Acidic property of alcohol**
  
  When metals like potassium or sodium react with alcohols, they form relevant alkoxide. Above alcohol reactions suggest acidic nature of alcohols and it is mainly because of –OH bonds polarity. If electron donating group is present to hydroxyl group, then there is continuous reduction in acidity, as it enhances the electron density of oxygen atom. Hence, as compared to tertiary and secondary alcohols, primary alcohols
are mostly acidic. Alcohols behave as Bronsted base, because there is reminiscence of unshared electrons in liquids on the oxygen atom.

- **Chemical properties of alkanols**
  
  Very prominent chemicals properties of alkanols are listed below which have direct effect on their physical and chemical properties.

  i. Alkanols undergo full combustion in presence of oxygen producing carbon dioxide with water. Energy is created in the process of the combustion of alkanols, causes alkanols handy utilized as fuels.

  ii. Alkanols easily reacting with active metals to forming a salt and hydrogen gas.

  iii. Alkanols combine to alkanoic acids to give esters.

  iv. Along with strong acid such as sulfuric acid, alkanols can go under elimination reactions and produce alkenes.

  v. Mostly primary and secondary alkanols undergoes oxidation whereas tertiary alkanols never oxidized.

- **Chemical Reactions of Alkanols**
  
  The major functional group in alkanols is –OH. Hence, the chemical properties of alkanols contain the reactions involving –OH group. Alkanols also react to both as nucleophiles as well as electrophiles. The bond between oxygen and hydrogen brake when they react as nucleophiles. The bond between carbon and oxygen is brake when they react as electrophiles. Protonated alcohols can react as following manner of given reaction.

  $\text{RCH}_2\text{-OH} + \text{H} \rightarrow \text{RCH}_2\text{-OH}_2$

  $\text{Br} + \text{H}_2\text{C}\text{-OH}_2 \rightarrow \text{RCH}_2\text{-Br} + \text{H}_2\text{O}$

  (In above reaction protonated alcohols behaves as electrophiles)

A) **Acidic Character**
Alcohols are very weak acids ($Ka = 10^{-16} - 10^{-18}$), ever feeble than water ($Ka = 10^{-14}$). When they treated with active metals like sodium, potassium and aluminum liberate hydrogen along with formation of alkoxides.

$$2 \text{R} - \overset{\ominus}{\text{O}} - \overset{\ominus}{\text{H}} + 2\text{Na} \rightarrow 2\text{R} - \overset{\ominus}{\text{ONa}} + \text{H}_2$$

Sodium Alkoxide

$$2 \text{C}_2\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2 \text{C}_2\text{H}_5 - \overset{\ominus}{\text{ONa}} + \text{H}_2$$

Sodium Ethoxide

Due to the presence of polar O-H group alcohols behave as acid. The order of acidic strength among various types of alkanols is primary > secondary > tertiary. The above order can also be explained in terms of electron releasing inductive effect of alkyl groups. Greater is the number of alkyl groups along with carbon containing -OH group then lowest will be the polarity of OH group and giving lowest acidic properties. In tertiary alcohols, the carbon atom carrying –OH is attached to three alkyl groups, due to which electron density on oxygen is maximum and hence the loss of H+ is most difficult. Alkanols are weaker acid than water depicted in reaction scheme of H$_2$O with alkoxide.

$$\text{R} - \overset{\ominus}{\text{O}} - \overset{\ominus}{\text{H}} \rightarrow 2\text{R} - \overset{\ominus}{\text{O}} - \overset{\ominus}{\text{H}} + \overset{\ominus}{\text{OH}_2}$$

Conjugate Acid

This reaction predicts water is good proton donor and hence mightiest acid than alkanols.

**B) Oxidation**

Alcohols undergo oxidation with oxidizing agent such as chromic anhydride or chromium oxide (CrO$_3$, K$_2$Cr$_2$O$_7$, and KMnO$_4$).

a. A primary alkanols on oxidation with acidified K$_2$Cr$_2$O$_7$ first gives an aldehydes which on further oxidation gives an acid with the equal carbon atom number as the fundamental alcohol.
b. On oxidation secondary alkanols first gives a ketone whose number of carbon atoms is same as original alcohol.

\[
\text{R} - \text{C} - \text{OH} + \text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{O} \xrightarrow{^\oplus} \text{R} - \text{C} - \text{O} + \text{H}_2\text{O}
\]

Secondary alcohol

Ketone

Ethanol

Ethanal

Ethanoic Acid

\[
\text{CH}_3 - \text{C} - \text{OH} + \text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{O} \xrightarrow{^\oplus} \text{CH}_3 - \text{C} - \text{O} + \text{H}_2\text{O}
\]

Propane-2-ol

Propanone

c. Tertiary alkanols are not oxidized with mild oxidizing agent in aqueous, alkaline or under neutral conditions. However, when oxidation is carried out under acidic conditions, tertiary alkanols undergo dehydration to form alkenes [289].

C) Esterification

Alkanols react with mono-carboxylic acid along with tetraoxosulphate acid gives esters. Such reaction is known as Esterification.
The above chemical process is can reverse in direction and the equilibrium can be shifted to the right with removing water at the very moment it is formed. In the reaction with Esterification water molecules are formed with combination carboxylic acid and H form alkanols molecule.

**a) Importance of Alkanols**

Both methanol and ethanol are very precious alkanols. Out of which methanol is mostly synthesized out of petroleum feed stock, on the other hand ethanol synthesized from ethane or some times with process such as fermentation of sugar with starch. Methanol and ethanol is very useful ingredient for industry applications. Some uses are, methanol can be helpful as a solvent and in the formation of ethanoic acid. Second important use ethan-1,2-diol is helpful for the synthesizing polymer. Also propane-1,2,3-triol is helpful in cosmetic products.

Ethanol is a one of the building block of alcoholic beverages out of which some are beer, winery, brandy and other liquor products. A combination ethanol along with water possesses much less freezing point compared to freezing point of water, and hence forth it has application as antifreeze. It is helpful as solvent with resins, fats, oils, fatty acids and hydrocarbons. It can be even used as petrol substitute. Ethanol in mixture with petrol with 25% and found helpful as fuel for internal combustion engines. Ethanol can be used for synthesis of variety of organic compounds viz. chloroform, iodoform, and ethanoic acid [191].

**3.3 The forces between Molecules**
It is well established that all the matter bind together with variety of forces. The force which exists among atoms in a molecule is of intermolecular or chemical force type. Now we are focusing on intermolecular forces.

### 3.3.1 The nature of intermolecular forces

The intramolecular forces which arise because of chemical bonds present inside of fundamental molecule are stronger than intermolecular forces which are forces in between different molecules. This difference is due to the reason that, the molecule in the first place. Fascinating characteristics of matter is a by product property of each molecule which is result of chemical bond and how the large number of identical molecules behaves collectively this is result of intermolecular force [52, 125].

![Fig. 3.1: Strong Covalent bond and weak intermolecular forces](image)

#### 3.3.2 Charge-Charge Forces

The Intermolecular forces mostly long range forces which means they act strongly over large distance when nature of those forces is electrostatic. Interaction of charge monopoles are may be long range electrostatic force. Coulombs law gives force between two charges and it is given as,

\[
F_{\text{charge-charge}} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2}
\]

3.1

For charges of equal sign (+, +) or (-,-), the force is repulsive. And for opposite charges (+,-), the forces are attractive one.

#### 3.3.3 Dipole-Dipole forces

The forces between electric dipole present only for polar molecules those are neutral. Dipole means two equal and opposite charges separated by some distance. Force between these two charges is called dipole force. Thus force between two dipoles
called dipole-dipole forces is the vector sum of force of individual dipole. Electrostatics is unable to clarify the full picture. Electrostatic force does not exist between the round shape molecules having no charge. Hence, question arise that how such round molecules gives liquids or solids.

### 3.3.4 Hydrogen bonding

Water molecule is a polar molecule. Formation of water is due to hydrogen bonding, in which unique type of intermolecular force present. In water, two hydrogen atoms are attached to every oxygen atom to form hydrogen bonds. Every water molecule is bonded to adjacent water molecules through hydrogen bonding. This intermolecular hydrogen bonding is responsible for the relatively high boiling point of water. Hydrogen atom contain single electron called valence electron. Due to this hydrogen is novel amongst the elements. In polar covalent bonding, this single is hogged by another atom. Due to this, hydrogen nucleus in very significant fraction turns out to be uncovered and the bare nucleus desperate for covering of electrons from the other atom.

Nature hydrogen bond is attractive, because attractive interaction present between the two closed shell species. This interaction arises in form of C-H-D; in this, elements C and D are highly electronegative. In most of the cases, hydrogen bond present only for atoms like nitrogen, oxygen, and fluorine etc. Hydrogen bonding is having significance role in the function of proteins. Because, these attractive interactions decide the way by which protein fold, also this depicts how their interactions within cell take place. Bonding between fluorine and hydrogen atoms are hard to recognize in biochemistry, but can be significant in some synthetic material characteristics.

### 3.3.5 Charge-dipole forces

Electric dipole moment is also present in neutral molecules. Dipole moment arises due to separation of opposite and equal charges by some distance which is shown in Fig. 3.2. Polar molecules have permanent electric dipole moment. Water is having permanent dipole moment and referred as polar molecule and has a dipole moment of magnitude approximately 1.9 Debye (1 Debye = 3.336 x 10^{-30} Coulomb-meter). If salt is dissolved in water, it forms homogeneous solution, in which Na^+ ions and
Cl ions dissociate from each other. After that they combine with dipole of the water molecules. It should be kept in mind that, dependens of forces between charge-dipole is on relative orientation of molecules.

![Fig. 3.2: Charge-Dipole forces](image)

### 3.3.6 Instantaneous Dipole–Induced Dipole Forces

These interactions are present in non-polar molecules. Cl₂, I₂, O₂, N₂ and monoatomic molecules like He, Ne, Ar, etc. are the examples of non-polar molecules which have no dipole moments. Fritz London [162] has explained the origin of van der Waal’s forces. These forces are present between the non-polar molecules in the liquid and solid state. Their characteristics are understands with the help of quantum physics.

The electrons surrounding the nucleus in the atom of every non-polar molecule are symmetrical, distributed around the nucleus. According to London [162], these electrons are in continuous and rapid motion with respect to the nucleus and hence it is possible that at any moment, the electron density around the nucleus may be concentrated in the other region of the same molecule [255].
This results in unsymmetrical distribution of the electron density around the nucleus and hence the non-polar molecule possesses temporary dipole. When this temporary dipole becomes closer to another non-polar molecule, the other non-polar develops an induced dipole in it. These two dipoles are then attracted towards each other by electrostatic forces which are called London forces. These forces are also called dispersive or dispersion forces.

The magnitude of van der Waal's forces is directly proportional to the number of electrons present in the given molecule. Boiling point of molecules increases due to the van-der-Waal’s forces. If larger is the molecular size or larger the molar mass, the stronger is the van-der-Waal’s force and hence boiling point also increases. Magnitude of dispersive force depends upon volume, shape, and surface area of molecules. Dispersion force is greater for bigger size molecules, as shown in Fig. 3.3.
Factors influencing the strength of the molecular interactions

It is well established that five types of molecular interactions are present between the molecules of respective solute and solvent. The strength five interactions with decreasing strength are like following order [119].

1. ion-ion
2. ion-dipole
3. dipole-dipole
4. dipole-induced dipole
5. induced dipole-induced dipole

### 3.4.1 Ion-Ion Interactions

The strength of ionic attraction depends on the charge and inter-ionic distance. This is obtained by Born - Lande equation

\[
E = \frac{Z^+ Z^- \epsilon^2}{4\pi\epsilon_0 r}
\]
Sizes and charge number determine the ion-ion interaction energy.

### 3.4.2 Ion-Dipole interactions

Ion-Dipole forces may be thought as directional so they result in preferred orientations of molecules. The potential energy of an ion-dipole interaction is given by

\[ E = \frac{z^\pm \mu_r}{4\pi\varepsilon_0 r^2} \]  \hspace{1cm} \text{(3.3)}

Where, \( z^\pm \) is the charge on the ion and \( r \) is the distance between ion and molecule and \( \mu_r \) is the molecular dipole? Ion-dipole interactions are same to ion-ion interaction except that they are more sensitive to distance \([(1/r^2) \text{ instead of } (1/r)] \) and seem to be somewhat weaker as shown in (Fig. 3.6).

![Fig. 3.6: Ion-Dipole Interactions](image)

Belonging to non-polar and polar molecules as constituents, two types of major interactions are present in liquid mixtures. Dipole-induced dipole and dipole-dipole interactions are the two interactions.

### 3.4.3 Dipole-induced dipole interactions

Dipolar molecule disturbs cloud of electrons in the non-polar molecules and this type of polarization of neutral species will depend upon the inherent polarizability of systems and on the polarizing field offered by the dipole. The interaction energy is much weaker than the energy of dipole-dipole interaction. The energy of interaction is given by

\[ E = -\frac{\mu^2 \alpha}{r^6} \]  \hspace{1cm} \text{(3.4)}

Where ‘\( \mu \)’ is the dipole moment of inducing dipole. Since the energy varies inversely with higher power of ‘\( r \)’, so they are effective at very short distances.
3.4.4 Induced Dipole-Induced Dipole interactions

The molecules those have no permanent dipole moment, instantaneous dipoles will arises as a result of momentary imbalances in electron distribution. These dipoles are capable of inducing dipoles in adjacent molecules. Induced dipole-induced dipole attractions are very short ranged and very weak. The interaction energy may be expressed as

$$E = \frac{2\mu \alpha}{r^6}$$  \hspace{1cm} (3.5)

Where ‘\(\mu\)’ is the mean instantaneous dipole and ‘\(\alpha\)’ is the polarizability. London forces are external short range in action and weakest of all attractive forces of interest of chemists and physicists. At very short distances, the electronic clouds of the interacting molecules begin to overlap and Pauli repulsion becomes extremely large. The repulsive energy is expressed as

$$E = +\frac{k}{r^n}$$  \hspace{1cm} (3.6)

Where, ‘\(k\)’ is constant and ‘\(n\)’ may have various values (5 to 10). Repulsive energies come in to play only at extremely short distances.

3.4.5 Dipole-Dipole Interactions

The energy of the interaction of the dipoles is given by equation

$$E = \frac{-2\mu_1 \mu_2}{4\pi \varepsilon_0 r^3}$$  \hspace{1cm} (3.7)

This energy corresponds to head to tail arrangement as shown in figure 3.7. An alternative arrangement is anti-parallel (Fig. 3.7) which will be more stable if the molecules are not too fat. At moderate temperature and in gas phase, there will be a tendency for internal motion to randomize the orientation of dipoles and the energy of interaction will be reduced. However, in liquid mixtures at room temperature, the dipole-dipole interaction energy is greater than that in gas phase containing the same molecular components.

Dipole-dipole interactions tend to be weaker than ion-dipole interaction and fall more rapidly with distance \((\frac{1}{r^6})\) and they are decreasing in character.
3.5 Jacobson Free Length Theory

Jacobson [119, 117] has been coined the concept of intermolecular free length credited to Eyring et al. [89]. This free length theory is used for evaluation of speed of sound in liquid mixture solutions as well as in pure liquid. Propagation of a sound wave in liquid is in accordance with Eyring theory [89]. Sound wave propagates with large velocity within molecules equal to kinetic velocity in gas. Space between molecules is known as available volume. Distance between the surfaces of two molecules is referred as intermolecular free length denoted by $L_f$. This distance is covered by ultrasonic wave shown by the following formula.

$$L_f = \frac{2V_a}{Y} \quad \text{(3.8)}$$

Where $V_a$ is available volume per mole and $Y$ is surface area per mole. $V_a$ as well as $Y$ also given by formula as,

$$V_a = V - V_0 \quad \text{(3.9)}$$

And

$$Y = (36\pi N_A V_0^2)^{1/3} \quad \text{(3.10)}$$

Where $V$ is molar volume at temperature $T$

$V_0$ is molar volume at absolute zero temperature

$N_A = 60.23 \times 10^{23}$ mole$^{-1}$ Avogadro’s number constant.

By considering shape of the molecules to be spherical, molar volume of liquid at absolute zero temperature is calculated using equation.

$$V_0 = V \left[1 - \frac{T}{T_c}\right]^{0.3} \quad \text{(3.11)}$$
In above equation $T_c$ means critical temperature. In case of pure liquid, $L_f$ is obtained using Jacobson’s relation \[121\]

$$L_f = K\beta^{1/2}$$  \hspace{1cm} 3.12

In above equation, $K$ is Jacobson’s constant (varies with temperature), the $\beta$ is called as adiabatic compressibility. The dependence of $K$ with temperature is given by following equation,

$$K = (93.875 + 0.375T) \times 10^{-8}$$  \hspace{1cm} 3.13

In above equation, $T$ is absolute temperature of liquid measured accurately. It is well established that both relations given by equations 3.9 and 3.13 are used effectively for determination of free length between molecules [117]. In present work, $L_f$ for solute-solvent mixture for different concentrations and temperatures is evaluated using Jacobson’s relation given by equation 3.13.

3.6 Solvent Used in the Present Study

3.6.1 Dimethylsulphoxide

Dimethyl sulphoxide is shortly known as DMSO. It is a chemical having molecular formula $(\text{CH}_3)_2\text{SO}$. In the year 1866, Russian scientist Alexander Saytzeff was first prepared Dimethyl sulphoxide and they published findings in a German chemistry journal in the year of 1867. DMSO is a polar solvent in which polar and non-polar compound dissolves. DMSO is soluble in water as well as in organic solvents. DMSO is easily penetrated into skin, so that, when DMSO comes in to contact with skin one can taste it easily. DMSO has taste like oyster or garlic [192]. When DMSO comes in contact with human body, it causes harmful effects on human body. These effects are headache, sensitivity to light, stomach upset, visual disturbance and so on. When DMSO is applied on skin, irritation of skin takes place.

**Table 3.1: Dimethylsulphoxide (DMSO) Structure & Properties**

![Dimethylsulphoxide (DMSO) Structure & Properties](image)
1) DMSO as a Solvent

Because of low boiling point, distillation of dimethyl sulfoxide takes place under vacuum. As compared to solvents like dimethyl formamide, dimethyl acetamide, N-methyl-2-pyrrolidone, dimethyl sulphoxide is less toxic. Dimethyl sulphoxide has good solvating power, therefore as a solvent it can be used regularly for chemical reactions with salts. Reactions like nucleophilic substitution reactions as well as Finkelstein reactions dimethyl sulfoxide is continuously used. Dimethyl sulfoxide shows weak acidic nature. Due to weak acidic nature, it can tolerate comparatively strong bases and hence it is helpful for studying carbanion. A significant set of some non-aqueous pKa values such as carbon-hydrogen, oxygen-hydrogen, sulphur-hydrogen, nitrogen-hydrogen and acidity value for many organic compound have been reported in dimethyl sulfoxide solution [155].

DMSO posses's high boiling point. Which implies that, rate of evaporation of dimethyl sulfoxide at normal temperature and atmospheric pressure is slow. For phase separate product reaction of DMSO is always diluted with water. As compared to nitromethane and di-chloromethane, dimethyl sulfoxide is safer and beneficial paint

<table>
<thead>
<tr>
<th>Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CHEMICAL FORMULA</td>
<td>C₂H₆OS</td>
</tr>
<tr>
<td>MOLAR MASS</td>
<td>0.07813 Kg/mole</td>
</tr>
<tr>
<td>Appearance</td>
<td>Liquid has no colour</td>
</tr>
<tr>
<td>Density</td>
<td>1100.4 Kg/m³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>292 kelvin</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>462 kelvin</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Water Soluble</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.479</td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.996×10⁻² poise</td>
</tr>
</tbody>
</table>

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stripper. Dimethyl sulfoxide has solid phase due to its comparatively large freezing point. This large freezing point put some limitation on its applications in chemical processes like crystallization on cooling. Dimethyl sulfoxide is helpful in production microelectronic devices [88]. DMSO is largely helpful in order to strip photo resist in TFT-liquid crystal display. It is also used in modern packaging applications like wafer level packaging and solders bump patterning etc.

b) Reactions

In dimethyl sulfoxide, center of sulfur is nucleophilic and directed toward flexible electrophiles. While, oxygen is nucleophilic towards electrophiles which are rigid. In dimethyl sulfoxide, methyl group is little acidic in nature having pKa value 35. This pKa is due to the stabilization of final carbanion of S-(O)-R groups. Therefore they are deprotonated with strong bases such as sodium hydride and lithium diisopropylamide. For deprotonation of ketones, sodium salt of dimethyl sulfoxide produced by above method is used as base to synthesize phosphonium salts and sodium enolates. It is also used to produce witting reagents and salts of formamidinium.

Chemical reaction of dimethyl sulfoxide with methyl iodide gives salts of sulfoxonium. Further it can be deprotonated with sodium hydride producing sulfurylide. The reaction scheme is as shown in following chemical equation.

\[
(CH_3)_2SO + CH_3I \rightarrow [(CH_3)_3SO]I
\]

3.14

\[
[(CH_3)_3SO]I + NaH \rightarrow (CH_3)_2CH_2SO + NaI + H_2
\]

3.15

For organic production, DMSO is helpful and works as mild oxidant [289], which is reported by Swernas well as Pfitzner-Moffatt oxidation [55]. In co-ordination chemistry dimethyl sulfoxide is a basic legend. If dimethyl sulfoxide is combined to Ru with oxygen and sulfur, it gives complex dichlorotetrakis (dimethylsulphoxide) ruthenium (II), and RuCl₂ (dimethyl sulfoxide).

c) Medicine

In cryobiology, dimethyl sulphoxide is helpful for cryoprotectant. In cryoprotectant vitrification compound, it is still an essential element, which is used for preserving different organs, tissues, as well as cells. In absence of DMSO, more than 80% frozen cells become useless and inactive. In freezing and long time storage of hematopoietic
stem cell, embryonic stem cell dimethyl sulfoxide play significant role. For low temperature preservation of heteroploid cell lines a mixture of 10% DMSO with 90% EMEM is used. This mixture is composition of 70% EMEM + 30% fetal bovine serum and antibiotic. In autologous bone marrow transplant, dimethyl sulphoxide can be infused together with patient’s own hematopoietic stem cell. Implementation of dimethyl sulphoxide in medicine was started around year nineteen sixty three. Especially, team of Oregon Medical School University invented that; dimethyl sulphoxide goes through skin as well as other membrane of cell without causing hazards to them. Dimethyl sulphoxide is helpful in carrying other mixtures in to biological system.

Today, area of medicine effectively uses dimethyl sulphoxide as analgesic vehicle for topical application in pharmaceutical industries, as anti-oxidant and anti-inflammatory [25]. Dimethyl sulphoxide enhances rate of absorption of some compounds in organic tissues containing the skin. Hence it is helpful for delivery of drugs in the system. Many times dimethyl sulphoxide is combined with antifungal medications for driving them, when penetrated into skin, finger nails as well as toe.

Large number of organic substance such as polymers, peptides, carbohydrates and many inorganic salts can be dissolve by dimethyl sulphoxide. Commonly observed loading level is about 50 to 60 percent of weight, but for typical solvents it is 10 to 20 percent of weight. Due to above reason, dimethyl sulphoxide is used in management of samples and screening mechanisms for design and delivery of drug [270]. In veterinary medicine, dimethyl sulphoxide is frequently used as liniment for horses, together with other ingredient or alone. When dimethyl sulphoxide present with other medicine, it acts as solvents and carries other constituents across the skin. For animals like horses, single or with other medicine, dimethyl sulphoxide is used intravenously. For cerebral edema of horses or treatment of enhanced intracranial pressure, single dimethyl sulphoxide is used [233].

d) Safety

Choice of glove is very crucial while handling DMSO. For safety reasons always thick rubber gloves are recommended. The very popular gloves are nitrile gloves, mostly used in chemistry research laboratories, nitrile gloves dissolve fully with exposure to DMSO. Due to which, dimethyl sulphoxide can go through the skin.
Dimethyl sulphoxide rapidly absorbs substances which are soluble in it. For example, mixture of dimethyl sulphoxide and sodium cyanide gives poisons cyanide. Dimethyl sulphoxide possesses less toxicity [128]. Dimethyl sulphoxide will start an explosive chemical reaction when comes in contact with acid.

### 3.6.2. 1- Hexanol

Hexane 1-ol is an organic alcohol containing a 6 carbon atom chain and a have chemical formula \( \text{CH}_3(\text{CH}_2)_5\text{OH} \). Hexanol is a colorless liquid and partially dissolve in water, but insoluble in diethyl ether and ethanol at normal temperature and pressure. Hexanol possess 2 extra straight chain isomers of hexan-1, hexan-2 and hexan-3, both vary with the position of the hydroxyl group. Large number of isomeric alcohols posses' chemical formula as \( \text{C}_6\text{H}_{13}\text{OH} \). Hexanol is synthesized on large scale for industrial applications with the oligomerization of ethylene with the help of triethyl aluminum followed by producing oxidation of the alkyl aluminum. This is shown in following chemical reaction.

\[
\begin{align*}
\text{Al (C}_2\text{H}_5)\text{Al} & + 6\text{C}_2\text{H}_4 & \rightarrow & \text{Al (C}_6\text{H}_{13})\text{Al} \\
\text{Al (C}_6\text{H}_{13})\text{Al} & + 1\frac{1}{2} \text{O}_2 & + 3\text{H}_2\text{O} & \rightarrow & 3\text{HOC}_6\text{H}_{13} + \text{Al (OH)}_3
\end{align*}
\]

**Uses:**

1. Hexanol commonly used as part of the head incense applicable in fragrance base and refined essential oil such as geraniol oil.
2. A trace of hexanol is helpful in violet, sweet scented osmanthus, magnolia, ylang type flavor to change or to enhance the tender environment, and also for edible coconut formula, barriers and different categories of fruit flavor.
3. Hexanol is also solvent and analytical reagent, particularly in medicinal industry for conservative and sleeping tablets.
4. Hexanol is used for chromatography reagent and organic synthesis of large number of chemical compounds.
5. Hexanol is used in gas chromatography studies.
6. Hexanol also studied as a perturbing agent on octomyosin resulting to change the function of octomyosin motor using intermediate predefined structural perturbation.
Table 3.2: 1- Hexanol Structure & Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C₆H₁₄O</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>0.1029 Kg/mole</td>
</tr>
<tr>
<td>Appearance</td>
<td>Liquid has no colour</td>
</tr>
<tr>
<td>Density</td>
<td>820 Kg/m³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>228 kelvin</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>430 kelvin</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>5.9 gm/lit at 20 °C</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.479</td>
</tr>
<tr>
<td>Viscosity</td>
<td>4.590×10⁻² poise</td>
</tr>
</tbody>
</table>

3.6.3 1- Heptanol (heptan-1-ol):

Heptan-1 is long chain alkanes having chemical formula H₃C (H₂C)₅ CH₃ or sometimes C₇H₁₆. While used as a test fuel ingredient in anti knock study engines, a one hundred percent heptane fuel is the zero point of the octane rating scale. Octane number co-pares to the anti knock properties of a comparison compound of heptane and iso-octane this is represented as the percentage of iso-octane in heptane and is remarked on pumps for gasoline i.e. petrol used world wide.

Uses:
The uses of heptanol are enlisted here

1. It is largely used in research labs as a non polar solvent.
2. For the grease spot test, heptanol soluble in oil spot to indicating the previous presence of organic compound on a stained paper.
3. Liquid bromine may be classified from aqueous iodine by its appearance after removing into heptane.

4. In water bromine as well as iodine appears brown. While, iodine changes colour to purple when dissolved in heptane, on the other hand the bromine remains brown.

5. In industries, heptane is used in paints and for coating purposes.

**Table 3.3: 1- Heptanol Structure & Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>$C_6H_{16}$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>100.21 gm/mole</td>
</tr>
<tr>
<td>Colour</td>
<td>It has no colour</td>
</tr>
<tr>
<td>Density</td>
<td>679.5 Kg/m$^3$</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>$3 \times 10^{-4}%$ at 20 $^\circ$C</td>
</tr>
<tr>
<td>Odor</td>
<td>Petrolic</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$5.690 \times 10^{-2}$ poise</td>
</tr>
</tbody>
</table>

3.6.4. 1-octanol

Octanol is commonly organic compound having molecular formula $H_3C\,(H_2C)_7\,OH$. Octanol was synthesized by the Oligomerization of ethylene with the help of triethyl aluminum giving oxidation of alkyl aluminum products. Reaction is given as,

$$Al\ (C_2H_5)_3 + 9C_2H_4 \rightarrow Al\ (C_8H_{17})_3$$

$$Al\ (C_8H_{17})_3 + 3O + 3H_2O \rightarrow 3HOC_8H_{17} + Al\ (OH)_3$$

Octanol is insoluble in water. Coefficient of partition of molecule is derived from distribution of compound between Octanol and water. Partitioning between cytosol and lipid membrane of living system is better approximation of partitioning between Octanol and water.

**Uses:**

Some applications of octanol are enlisted below.
a) 1-Octanol is a transparent liquid, possessing little viscous property makes it useful as a deforming or wetting agent applications.
b) 1-octanol used as a solvent for protective layer, waxes and oils, and as a crude material for plasticizers. Octanol found naturally in the form of esters in some daily routine used oils.
c) It is also one of many compounds derived from tobacco and tobacco smoke that increases the permeability of the membranes of human lungs fibroblasts [309].
d) Octanol used as starting material for making of perfumes.
e) Octanol helpful for treatment of essential tremors as well as even some involuntary neurological tremors.
f) Octanol helpful for study the lipophilicity of pharmaceutical industries.

Table 3.4: 1- Octanol Structure & Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nonanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C₈H₁₈O</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>130.23 g/mole</td>
</tr>
<tr>
<td>Appearance</td>
<td>Liquid has no colour</td>
</tr>
<tr>
<td>Density</td>
<td>824 Kg/m³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>257 kelvin</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>468 kelvin</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>0.46 gm/lit</td>
</tr>
<tr>
<td>Viscosity</td>
<td>7.36×10⁻² poise</td>
</tr>
</tbody>
</table>

3.6.5. 1- Nonanol

Nonanol is long chain fatty alcohol having 9 carbon atoms with chemical formula CH₃(CH₂)₈OH. Nonanol is found in citrus and oils of orange, citronella and lemon. It is also found in cheese, prickly pears and bread. In perfume as well as flavor purpose
different derivative of nonanols are used. Nonanol-1 has some harmful chemical properties. When it penetrates through skin, it causes painful irritation to eyes. Vapors of nonanol rupture lungs of human giving pulmonary edema in extreme situations. On consumed with mouth it shows symptoms like consumption of ethanol or poisoning due to ethanol to those of ethanol poisoning, and like ethanol consumption, which may destroy liver of human being.

**Table 3.5: 1- Nonanol Structure & Properties**

<table>
<thead>
<tr>
<th>Uses:</th>
<th>Nonanol has main application in synthesis of artificially produced lemon oil and its product.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Different types of esters of nonanol, like nonyl acetate, useful for perfumery and obtaining pleasant flavors.</td>
</tr>
</tbody>
</table>

**3.6.6 1-Decanol**

It is straight chain fatty alcohols having 10 carbon atoms with chemical formula as C\textsubscript{10}H\textsubscript{21}OH. Decanol is transparent light yellow viscous liquid that immiscible to water possessing aromatic smell. Decanol can be synthesized by the hydrogenation of decanoid acid that present in coconut oil in the amount of about 10 percent and palm kernel oil with the amount of about 4%. Decanol may also synthesized artificially by the Ziegler process which was explained in Octanol preparation topic.
It is used in the formation of chemical plasticizers, lubricants, surfactants and even as a solvent. Decanol is also used as a penetration modifier for transdermal drug delivery due to its capacity to penetrate the skin [160].

### 3.6: 1- Decanol, Structure & Properties

<table>
<thead>
<tr>
<th>Uses:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
</tr>
<tr>
<td>Molar mass</td>
</tr>
<tr>
<td>Nature</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Melting Point</td>
</tr>
<tr>
<td>Boiling Point</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
</tbody>
</table>

1. Decanol is used as chemical intermediate in synthesis of esters and fragrances and as an artificial odor of edible products.
2. Decanol is very helpful for artificial detergents, lube additives, pharmaceutical products, cosmetic products, and even in rubber and textiles industries also.

### 3.7 Mechanism action of alkanols

Synaptosomal membranes of rat brain are used to examine carefully the impact of different alkanol on central nervous system of human being. Fluidity of membranes and activity of Ca²⁺ + Mg²⁺ was studied using alkanol. Enhancement in molar inhibition of ATPase activity and enhancement in the carbon chain length to Octanol-1 are due to alkanols. Biphasic effect on the ATPase activity was created by alkanols such as Octanol and decanol. Stimulation of the ATPase activity was created by dodecanol. Such findings show that, effect of alkanols on ATPase activity depends on binding of alkanols with enzyme molecule, variation in border layer of the membrane as well as surrounding medium [309].
3.8 Water

Water is famous as the universal solvent due to its property that it can completely
dissolve great number of substances. Water is the chemical liquid possessing chemical
formula H\textsubscript{2}O. Water consists of two hydrogen atom and single oxygen atom which are
covalently bonded forming water molecule.

Water is neutral in taste, smell and transparent in less amount but it has its
characteristic very light blue colour. The main cause of state of water as liquid is oxygen
have more electronegative property compared to other elements (excepting fluorine).
Oxygen attracts electrons with greater Coulomb force than hydrogen, resulted in charge
separation. Hydrogen atom acquire net positive charge and oxygen atom acquire net
negative charge. Separation of net charges on each atom gives permanent electric
dipole moment to each water molecule. Due to dipole, Coulomb's force of attraction is
present between water molecules. This dipole force pulls water molecules close
together making it harder. Boiling point of water is higher due to hardness. Therefore,
H\textsubscript{2}O can be considered as a polar solvent which normally separates different
proportionality into the hydronium ion chemical formula as H\textsuperscript{3}O\textsuperscript{+} and an associated
hydroxide ion chemical formula of OH\textsuperscript{-}. This dissociation factor is may be represented
as Kw with a value of 10\textsuperscript{-14} at 25\textdegree\textsuperscript{C} [53, 310].

Dipolar Properties

Water molecule is polar in nature, in which center of gravity if positive and center
of gravity of negative charge is separated with finite distance. In polar structure of water
molecule, hydrogen atom is at the tips and oxygen atom is at the vertex making some
angle. Oxygen atom is present at the vertex, because it has higher electro-negativity
due to higher molecular weight compared to hydrogen molecule. The side of the
molecule with the oxygen atom has a small negative charge. An equal and opposite
charges separated by distance is called electric dipole. This variation in charge makes
water molecules to be attracted to each other and also attract other polar molecules.
This attraction result in formation of hydrogen bond, which is unique characteristic of
H\textsubscript{2}O. When electrically charged object is placed in the vicinity of a small falling stream of
water, makes the stream to be directed towards the charged object. From this one can
understood dipolar nature of water molecule.
Water as a Solvent

Due to its polarity, water is a good solvent. The materials which can completely miscible in water are called as hydrophilic sometimes water-loving materials. On the other hand, hydrophobic material is one which is immiscible in water such as fats or oils. When water is added in substance of polar molecules, substance is surrounded by water molecules. Single molecule of substance is surrounded by many water molecules due to comparatively less size of water molecules. At this time, positive ends of dipole of the substance are attracted toward negative dipole ends of water. This process is reversed for positive end of dipole [43].

Hydrogen Bonding

A water molecule can form as many as 4 hydrogen bonds due to it can accept 2 and loose 2 hydrogen atoms.

![Fig. 3.8: Water molecules showing hydrogen bonding](image)

3.9 Formulae used for the calculations

The brief description of the different formulae employed for the calculations of different thermodynamic as well as acoustical variables in the present study are as follows

1. Ultrasonic Velocity (U)

Different formulations have been published in the research papers for calculation of ultrasonic velocity [279]. The ultrasonic velocity calculated by ultrasonic interferometer technique is more accurate and reliable. In ultrasonic interferometer, wavelength (λ) of the ultrasonic wave in variety of liquids and liquid mixtures are calculated. The following equation is used for calculation of ultrasonic velocity.
In above equation, \( f \) is number of waves per unit time of ultrasonic wave generated in this case by crystal. In the present work, a constant frequency 2MHz interferometer was employed and hence the value of ‘\( f \)’ is \( 2 \times 10^6 \) Hz.

\[
U = f \lambda = 2 \times 10^6 \times 2d = 4d \times 10^6 \text{ cm/sec}
\]

\[
= 4d \times 10^6 \times 10^{-2} \text{ m/sec} = 4d \times 10^4 \text{ m/sec}
\]

2. **Density (\( \rho \))**

Liquid densities are essential in large engineering applications like process formulation, simulations and liquid metering studies. Very large number of precise correlations is available for saturated liquid density calculations of pure liquids.

Liquid density is determined from equation of state of the liquid. In most of the cases the accuracy of liquid density determination with equation of state is not to the point. Flory has given an equation for calculating excess volume by with the help of density values. Flory also developed theoretical model to find of density of the liquid mixtures. This theoretical model is useful in calculation of precise compressible density below critical point of given liquid mixture.

Aalto and Keshkinen developed a modified model by removing drawbacks of Hankinson and Thomson model as using saturated liquid density. Nasrifar has proposed compressed liquid density model that is also based on Hankinson and Thomson model using saturated liquid density. Correlation of liquid density of mixture of poly glycols was proposed by Francesconi and Ottani. The precision of many models is the major concern for liquid mixtures, because of difficulty in using the mixing rules. The density of a liquid can be given as ratio of mass to volume. Universal symbol of density is \( \rho \) pronounces as rho which is Greek alphabet. The equation is given below

\[
\text{Density (\( \rho \))} = \frac{\text{Mass of solution (M)}}{\text{Volume of the solution (V)}}
\]

3. **Viscosity (\( \eta \))**

Viscosity is a fundamental transport property of material. Viscosity is useful in petroleum engineering and other chemical industries. Viscosity is useful in transportation of fluid, transfer of heat into mechanical work and agitation mixing. As compared to pure liquids, calculation of viscosity of liquid mixture is harder. In large
number of industrial, chemical techniques or research works it is essential to obtain
practical information of viscosity.
Viscosity is indicating factor of the resistance of a fluid which is being under force and
tension with shear stress and/or extensional stress. In daily terminology, viscosity
referred as thickness. Hence water known to be thin having less viscosity value, on the
other hand honey called thick because of its greater viscosity.

\[ \eta_s = \frac{\rho_s \cdot t_s}{\rho_w \cdot t_w} \eta_w \]

Where, \( \eta_s \) = viscosity of solution
\( \rho_s \) = density of solution in gm/cm\(^3\)
\( \rho_w \) = density of water
\( t_s \) = mean time flow for solution in sec.
\( t_w \) = mean time flow for water
\( \eta_w \) = viscosity of water

4. Adiabatic Compressibility (\( \beta \))

Adiabatic compressibility defined to be association or dissociation or repulsion
exists between molecules. The adiabatic compressibility is defined as very small
decrease in volume per unit rise in pressure, with the condition that there is exchange of
heat in or out from liquid. Singh and Kalsh [262] reported that the adiabatic
compressibility must be constant with respect to temperature and pressure of weekly
associated molecules and changes with time in case of other molecules. The phase of
solvent molecules is also studies by adiabatic compressibility factor. For calculation of
adiabatic compressibility following equation is employed [36].

\[ \beta = \frac{1}{\rho U^2} \text{Kg}^{-1} \text{ms}^2 \]

5. Intermolecular Free Length (\( L_f \))

It is defined as distance travelled by wave at the time of propagation between
surfaces of adjacent atoms. Strength of attraction among molecules in the solution is
indicated by free length. Strengthening and weakling of attraction between molecules
depends upon change in length. It is known that, speed of sound is directly proportional
to concentrations and inversely proportional to free length. The intermolecular free length obtained by reported formula given of Jacobson [117, 89, and 121].

\[ L_f = \frac{K}{\sqrt{\rho U^2}} = K\sqrt{\beta} \text{ m} \quad 3.24 \]

In above equation, K is called as Jacobson's constant. K changes with change in temperature.

6. Acoustic Impedance (Z)

Sound propagates from material medium by variation in pressure of sound. In solid, atoms or molecules are elastically bound to each other and acts like a spring. Variation in excess pressure is responsible for motion of wave through solid. In another way, there are some analogies between acoustics and electricity, one of them is direct impedance analogy. Acoustic pressure \( P_a \) is the analogue of voltage, acoustic velocity \( U \) is the analogue of current and specific acoustic impedance \( Z \) is the analogue of resistance. Specific acoustic impedance (Z) is defined by Ohms analogue [239].

\[ Z = \frac{P_a}{U} \]

Beyer and Letcher [36] considered the case of plane harmonic wave and obtained equation for \( Z \) as

\[ Z = \rho \ U \quad 3.25 \]

7. Free Volume (\( V_f \))

It is very important factor for understanding of changes in different chemical and physical of liquid used in my work. Free volume and properties related to it has considerable effect on structure of molecules and shows fascinating characteristics of interaction among molecules in the two or more liquid mixtures. Such interaction among dissimilar and similar molecules is affected due to structural alignment together with size and shape of molecules in liquid. Liquid is considered as, it formed due to molecules. In liquid, individual molecule is moving randomly in given volume \( V_f \) with average potential because of environment and other molecules. One way of saying this, as we know that, molecules in liquid are not closely packed but have some space between them. Hence among molecules there exist free space for random motion and this volume and this \( V_f \) referred as free volume.
In free volume molecules are in random motion like gas molecules as reported by Eyring and Kincaid and they obey perfect gas equation. The relation among free volume, sound speed, and viscosity [244] is depicted by following relation,

\[ V_f = \left( \frac{M_{\text{eff}}U}{K\eta} \right)^{1/2} \]  

Equation 3.26

In above equation, \( M_{\text{eff}} \) is effective molecular weight. K is constant which remains constant with temperature having value \( K = 4.28 \times 10^9 \) for almost all liquids.

8. Available Volume (Va)

Available volume defined to be deciding factor of together holding power of molecules and closeness among molecules of liquid mixtures. The available volume obtained using following equation [102],

\[ V_a = \left[ 1 - \frac{U}{U_\infty} \right] \text{m}^3 \text{mol}^{-1} \]  

Equation 3.27

Where, \( U_\infty \) is the Schaalff's limiting value taken as 1.6 km/s for almost all liquids.

9. Relaxation time (\( \tau \))

Relaxation phenomenon in liquids can be attributed to certain reactions between molecules. If there is no sound wave, the molecules maintain an equilibrium whose level depends on pressure and temperature. When the sound waves are passed through a liquid, the pressure and temperature will fluctuate periodically, so the equilibrium level is displaced periodically. The longitudinal motion of the acoustic wave is sometimes turned into rotational and vibrational motions of the liquid molecules. This is because of the collisions of molecules and requires a certain characteristic relaxation time. When the angular frequency of the sound wave multiplied by the relaxation time is unity, and then there is increase in the attenuation and dispersion in the velocity of ultrasonic wave. These interactions are called relaxations, which satisfy certain thermodynamic principle and the measured results can be related with the molecular properties of liquids.

The relaxation process in liquids accounts for the attenuation of sound and heat conduction process. Thermal relaxation occurs in the liquid due to the molecules structural re-alignment. Structurally relaxing liquids form a bridge between gas like behavior of liquids and the solid like behavior of glasses. Several relaxation processes take place within a liquid. In case if time scale of relaxation process is rapid or slow as compared to the time interval for which the stress is applied. The time scale of the
process is similar to the time interval or stress considerations. In relaxation process excitation energy of molecules is transformed into translational energy. Time required in the transformation of energy is called relaxation time. Relaxation time changes with impurities present in the solution and variation of temperature. Relaxation time of relaxation process is responsible for dispersion in speed of ultrasonic wave. It is obtained by reported equation such as [231].

$$\tau = \frac{4}{3} \beta \eta$$

The fraction ‘\(X\)’ of a relaxation process that has been completed up to time ‘\(t\)’ can be described by relation,

$$X = 1 - e^{-t/\tau}$$

Where, \(\tau\) is called the relaxation time. When \(t = \tau\), \(X = 0.63\), then the value of relaxation time is 63% of the relaxation to perform and is an important parameter to specify the time scale of a relaxation process. Relaxation process in liquid has large range of time spectrum in between \(10^{-13}\) second for atomic vibration to \(10^{6}\) second for the viscous flow of grain boundaries. For a particular process, the relaxation time is changes with temperature and reciprocal to temperature have slow variation because it appears in exponential form.

10. Internal pressure (\(\pi\))

In the field of research related to thermodynamic properties of liquid mixture, it is essential to measure internal pressure. This internal pressure can be considered as one form of cohesive force, that is vector sum of repulsive and attraction forces which exists among molecules. Cohesive force among molecules produces pressure inside liquid of the order of \(10^{4}\) atm. Hence internal pressure describes the idea of liquid solubility. Interactions between solvent and dissolved solute are a result of hydrogen bonding, charge transfer and van-der-Waal’s interaction which are described earlier. In van-der-Waal’s equation of state the term \(a/V^2\) is measure of attractive force between molecules known to be internal pressure.

Internal pressure changes because of variety of interactions taking place between solvent-solute, solute-solute as well as solvent-solvent interactions. Internal pressure is given by following reported formula [244],
\[ \pi_i = bRT \left[ \frac{Kn}{U} \right]^{1/2} \left[ \frac{\rho^{2/3}}{M^{1/6}} \right] \]  

3.29

In above equation, \( K \) is a constant of liquid. \( T \) known as absolute temperature in Kelvin, \( \eta \) known as viscosity of liquid, \( U \) being sound speed; \( \rho \) is density of liquid under study.

11. Coefficient of absorption (\( \alpha/f^2 \))

Coefficient of absorption is sometime referred as coefficient of attenuation. It is important fundamental characteristic of medium which changes with temperature, pressure and frequency. Absorption coefficient calculated from following equation,

\[ \frac{\alpha}{f^2} = \frac{8\eta \pi^2}{3\rho U^3} \]  

3.30

12. Rao’s constant (\( R \))

It is also known as molar sound velocity and it is an additive property. For organic or inorganic liquid, it remains constant with temperature and pressure. Value of \( R \), is evaluated from following reported equation [83],

\[ R = \left[ \frac{M_{mol}}{\rho} \right] U^{1/3} \]  

3.31

13. Gibb’s free energy (\( \Delta G \))

For given transition, relaxation time is related to the activation free energy. Change in relaxation time with respect to temperature is given by Eyring salt process theoretical model. The Gibb’s free energy is given by equation [145].

\[ \Delta G = -kT \log \left[ \frac{h}{m} \right] \]  

3.32

14. Enthalpy (\( H \))

Enthalpy has been evaluated using formula,

\[ H = \pi_i \times V_m \]  

3.33

15. Excess Parameters (\( A^E \))

In this work, excess parameter is obtained using following equation

\[ A^E = A_{exp} - A_{id} \]  

3.34