Volumetric and Viscometric Study of Dimedone in Ethanol-Water Mixtures

by

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Dedicated

To

My Beloved Parents

Declaration

This is to certify that the thesis work entitled **"Volumetric and Viscometric Study of Dimedone in Ethanol-Water Mixtures**" has been carried out by **Md. Jahangir Hossain** in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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Acknowledgement

Abstract

Density and viscosity of binary (Dimedone-Ethanol) and ternary (Dimedone-Ethanol – Water) mixtures of Dimedone, Water and Ethanol were determined at various temperatures (298.15 to 318.15 K at 5 K intervals) in between a concentration range of 0.05 to 0.25 mol L^{-1} of Dimedone with a view to determining the molecular interactions among Dimedone, Water and Ethanol. Dimedone is an organic substance which has the applications in colorimetry, crystallography, luminescence and spectrophotometric analysis. And it can also be used for chemistry involving organic compounds of low electrical resistance. Ethanol is a colourless organic polar solvent has led to its large-scale production in recent years with negligible toxicity. Ethanol is completely miscible with universal solvent water. So Ethanol– Water mixture can be a vital binary solution in investigating Dimedone that was taken as topic of research in this study. The apparent molar volumes, (φ_v) were obtained from the experimental density data. In the Dimedone–Ethanol and Dimedone–Water–Ethanol system, the apparent molar volume of Dimedone increases. In addition, apparent molar volume at infinite dilution (φ_v^u), apparent molar Expansivity and S_v (values of experimental slopes) were also calculated according to the experimental density data. The apparent molar volume at infinite dilution gives an idea about the presence of solute–solvent interactions whereas S_v is the experimental slopes which give an idea about the prevailing solute–solute interactions in the mixtures. The calculated data indicate that there may be solute-solute and solute-solvent interactions present in the binary and ternary solutions. It is seen that Dimedone has good structure making property in ternary solutions than the binary systems. Both binary and ternary systems shows rapid increase of viscosity values with the increased Dimedone concentration but the values of viscosity decreased with the increase of temperature. The viscosity data were employed to determine the viscosity coefficients (A&B), change of free energy, ΔG^*, change of enthalpy, ΔH^* as well as change of entropy, ΔS^*. From these thermodynamic parameters state of the spontaneity of the investigated systems were known. Moreover, positive A co-efficients and negative B co-efficients suggesting that strong solute-solute but weak solute-solvent interaction present in the binary and ternary solution. On the basis of this data, the predominant molecular interactions occurring between Dimedone-Ethanol and Dimedone–Water–Ethanol were found to be solute-solute interaction. The results suggest that there is a significant effect of Dimedone on Water and Ethanol.

Contents

List of the symbols and abbreviations

Symbols/ Abbreviations		Explanation
K_d	:	Dissociation Constant
$\}_i$	:	Ionic conductance
y	:	Viscosity
$\}_1^0$	:	Limiting Ionic conductance
A	:	Area of contact between the two layers
f	:	Tangential force
w	:	Fluidity
l	:	Length
Pa.s	:	Pascal-Second
cP	:	centipoise
mPa.s	:	Milli-Pascal-second
v	:	Velocity
r	:	Radius
P	:	Pressure
t	:	Flow time
ρ	:	Density of the liquid/solution
φ_v	:	Apparent molar volume
φ_E^0	:	Apparent molar expansivity at infinite dilution
ΔG^*	:	Free energy
ΔH^*	:	Change of Enthalpy and
ΔS^*	:	Entropy
h	:	Difference in height of the surface of the two reservoirs
g	:	Acceleration due to gravity
IUPAC	:	The International Union of Pure and Applied Chemistry

Introduction

1.1.1   General

Dimedone is a cyclic diketone used in organic chemistry to determine whether a compound contains an aldehyde group. Cyclohexanediones in general can be used as catalysts in the formation of transition-metal complexes. Other uses include applications in colorimetry, crystallography, luminescence and spectrophotometric analysis. It can also be used for chemistry involving organic compounds of low electrical resistance. Dimedone usually comes in the form of white crystals. It is stable under ambient conditions and soluble in water, as well as ethanol and methanol. It has a melting point range of 147–150 °C (420–423 K). Dimedone is prepared from mesityl oxide and diethyl malonate [1]. Dimedone is in equilibrium with its tautomer in solution in a 2:1 keto to enol ratio in chloroform [2].

Crystalline dimedone contains chains of molecules, in the enol form, linked by hydrogen bonds [3].

1.1.2   The phenomena of solute-solvent interaction

Explanation of the nature of ion-solvent interaction [4–5] and interpretation of the thermodynamic and transport processes in terms of such parameters as effective size of the solvated ions in solutions have been two of the most difficult problems in the understanding of electrolytic solutions. This is because there is not satisfactory model to represent the various phenomena that occur in solution and the incompleteness in the understanding of the structure of the liquids in general. There are a number of evidences

of solvation of ions [4–5] or solute molecules a number of studies have discussed the effect of solvation on the equilibrium properties of liquids.

The process of solvation and the process of dissolution are known to be close related. When ionic crystal is added to a solvent, the electrostatic force of attraction between the oppositely charged ions in the crystal have to be overcome by interposing solvent layers around each of the ions. The ability of a solvent to dissolve a crystal is reflected by the following properties, its dielectric properties, polarity, degree of self-association and its ability to solvate. Studies on the phenomena of solvation have led to the conclusions that:

(i)   The ionic compounds are moderately soluble in dipolar aprotic solvents of relatively high dielectric constant but are much more soluble in water and other hydroxylic solvents like methanol. A number of inorganic salts are dissociated in acetonitrile, which is otherwise known to solvate cations and anions rather poorly [6].

(ii)   The dielectric constant alone is not an adequate measure of solvating ability and may even play a major role in determining the solvation of ionic species. Cations should be better solvated in solvents having atoms with an unshared electron pair like nitrogen and oxygen. The cations have been found to be strongly solvated in highly polar solvents with the negative charge localized on an oxygen atom, e.g. in sulphur dioxide, dimethyl sulfoxide, phosphorus oxide, dimethyl formamide [7]. Potassium iodide is less soluble than sodium iodide in methanol or water [8], but in dimethyl sulfoxide or dimethyl formamide the reverse is true, which could be due to differences of cation solvation.

The anions have been found to be solvated in two ways:

(i)   Small ions are mostly solvated by hydrogen bonding which is superimposed upon solvation by ion-dipole interactions, and

(ii)   Large ions are solvated by interaction due to mutual polarizability of the anions and the solvent superimposed upon solvation by dipole interactions. Thus while the anions are more strongly solvated in hydrogen bonding solvents than in dipolar aprotic solvents, the cations are better solvated in the latter type of solvents.

The solubility of halides in various solvents generally follows the order:

Iodides > bromides > chlorides > fluorides.

The alkaline halides are more soluble in hydroxylic solvents than in the dipolar aprotic solvents like acetonitrile and acetone. These are found to be more soluble in acetonitrile than in acetone [9]. Electrolytes may be divided into two categories: ionophores and ionogens. While the former are ionic in character in the crystalline state as well as in the fused state and in highly dilute solutions, the latter have molecular crystal lattice and ionize in solution only if suitable interaction occurs with the solvent molecules.

The ionophores may exist in solution as an equilibrium mixture containing ion-pairs and free ions [10].

$$M^+X^- \rightleftharpoons M^+ + X^-$$
$$\text{solvated} \qquad \text{solvated} \quad \text{solvated}$$
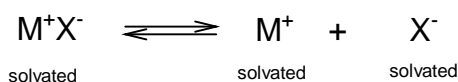
The ion-pairs are of oppositely charged ions having life terms sufficiently long to be recognized as kinetic entities in solution and in which only electrostatic forces are assumed [1]. Fuoss *et al*. [11] have studied intensely the dependence of the dissociation constant, K_d, on the dielectric constant, the temperature and the nature of the salt. It was found to be large for solvents having high dielectric constant. It has also been found to be dependent on the distance of closest approach of the ions in the ion pairs. For hydroxylic solvents, large ions have larger K_d values and lower conductance values than smaller ions, which doesn't hold for other solvents.

Interaction of the ions with the solvent molecules causes low conductance. Na^+ ion behaves as a large ion as the K_d of iodides of Bu_4N^+ and Na^+ are found to be of the same order. Small ions like Li^+, F^- have low conductance in acetone [9] but have low K_d values which have been attributed to the loss of the solvent molecules from the ion-pairs [12]. Solute-solvent interactions have been studied in details by various methods; some important ones may be listed as follows:

    (i)   Study of the solute-solvent interactions through transference experiments.

    (ii)   The effect of solvation on the ionic conductance.

(iii)   The experiments applying stake's law and their relevance to the nature of solvation.

(iv)   Polaro graphic measurements of solutions.

(v)   The spectral results due to the presence of the ions in solutions.

A relationship between the values of the limiting equivalent ionic conductance, λ_i and the viscosity, η value was advocated and utilized by Walden and others to study the solute-solvent interactions [13]. In one approach which assumes the constancy of the product $\lambda_i \eta$ the effects of variation of temperature, viscosity and variation of the solvent were studied. For large organic ions , the temperature co-efficient was found to be nearly constant in water as well as other non-aqueous solvents, while for the other ions it showed variations. For changing solvents, the product was found to vary widely in the case of inorganic ions which have been interpreted to be due to differences in solvation numbers of the ion in the various solvents. In another approach to this study Pure and Sherrington [14] used the relation between viscosity η_t, and limiting ionic conductance λ_i^0, to measure the radii of interaction of solvent and solute, called Stoke's law radii, r. They compared the crystallographic radii of some cations and anions with Stoke's law radii in the case of dimethyl amide and dimethyl sulphoxide solvents. They found the degree of solvation to decrease from lithium to cesium and to be less for silver and ammonium ions which have nearly comparable crystallographic radii. They postulated the anions to be unsolvated in dipolar aprotic solvents as the radii obtained are of the same order as that of the crystallographic radii, and that the negative end of the dipole in the solvent molecule is unshielded while the positive end is protected by two methyl groups, so that the cations, but not the anions are solvated by these solvents. Volumetric and viscometric measurement provides valuable tool for the determination of interaction among solutes and solvents.

1.1.3   Viscosity

Viscosity means viscous ability. Simply, viscosity of a material is resistance to flow. The internal friction which opposes the relative motion of the adjacent layers of a fluid causes for the resistance to flow. When a fluid is flowing through a cylindrical tube, this internal

friction arises because of intermolecular friction. Molecules are a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa.

Viscosity is really a frictional effect experienced by one layer of a liquid in moving past another in much the same way as an object experiences frictional resistance when dragged on a surface. The friction force, f, resisting the flow of one layer of fluid past the adjacent layer is proportional to the area, A, of the interface between the layers and to $\frac{d}{d}$, the velocity gradient. This is Newton's law and is given by

$$f = \eta A \frac{du}{dr}$$

Where, η (eta, a Greek letter), the constant of proportionality, is called the co-efficient of viscosity. When the velocity gradient is unity and the area is 1 sq-cm, η is equal to the force; or the co-efficient of viscosity, η may be defined as the force per 1 sq-cm required to maintain a difference of velocity of 1 cm per second between two parallel layers 1 cm apart. The reciprocal of the co-efficient of viscosity is known as the fluidity, $\varnothing$, or

$$\varnothing = \frac{1}{\eta}$$

Fluidity is a measure of the ease with which a liquid can flow. The connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation [15]. If a liquid with a coefficient of viscosity (y) flows with a uniform velocity, at a rate of v cm^3 in t seconds through a narrow tube of radius r cm, and length 1 cm under a driving pressure of P dynes cm^{-2} then [15]:

$$\eta = \frac{\pi\ r^4 t}{8l_1} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.1.1)$$

This equation known as Poiseuille's equation holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities.

Where, y is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. The CGS unit of viscosity i.e., dynes sec cm^{-2} = g cm^{-1}sec^{-1} is

called poise, in honor of J.L.M. Poiseuille who is the pioneer in the study of viscosity. The SI unit of viscosity is the Pascal-second (Pa.S). Since viscosity of liquid is usually very small, it is usually expressed in millipoise (mP) or centipoise (cP) or mPa.s.

1.1.4   Factors affecting viscosity

Viscosity is the first and foremost function of material. Most ordinary liquids have viscosities on the order of 1 to 1000 mPa·s, while gases have viscosities on the order of 1 to 10µPa·s. Pastes, gels, emulsions, and other complex liquids are harder to summarize. Some fats like butter or margarine are so viscous that they seem more like soft solids than like flowing liquids.

Temperature: The viscosity of a simple liquid decreases with increasing temperature (and vice versa). As temperature increases, the average speed of the molecules in a liquid increases and the amount of time they spend "in contact" with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces decrease. The exact manner in which the two quantities vary is nonlinear and changes abruptly when the liquid changes phase.

Pressure: Viscosity is normally independent of pressure, but liquids under extreme pressure often experience an increase in viscosity. Since liquids are normally incompressible, an increase in pressure doesn't really bring the molecules significantly closer together. Simple models of molecular interactions won't work to explain this behavior and to my knowledge, there is no generally accepted more complex model that exists. The liquid phase is probably the least well understood of all the phases of matter.

While liquids get runnier as they get hotter, gases get thicker. The viscosity of gases increases as temperature increases and is approximately proportional to the square root of temperature. This is due to the increase in the frequency of intermolecular collisions at higher temperatures. Since most of the time the molecules in a gas are flying freely through the void, anything that increases the number of times one molecule is in contact with another will decrease the ability of the molecules as a whole to engage in the coordinated movement. The more these molecules collide with one another, the more disorganized their motion becomes.

Cohesive forces: Cohesive forces are the intermolecular forces (such as those from hydrogen bonding and Van der Waals forces) which cause a tendency in liquids to resist separation. These attractive forces exist between molecules of the same substance. For instance, rain falls in droplets, rather than a fine mist, because water has strong cohesion which pulls its molecules tightly together, forming droplets. This force tends to unite molecules of a liquid, gathering them into relatively large clusters due to the molecules' dislike for its surrounding. The materials having stronger cohesive forces normally exhibit lower viscosities and vice-versa.

Adhesive force: Adhesive forces are the attractive forces between unlike molecules. They are caused by forces acting between two substances, such as mechanical forces (sticking together) and electrostatic forces (attraction due to opposing charges). In the case of a liquid wetting agent, adhesion causes the liquid to cling to the surface on which it rests. When water is poured on clean glass, it tends to spread, forming a thin, uniform film over the glasses surface. This is because the adhesive forces between water and glass are strong enough to pull the water molecules out of their spherical formation and hold them against the surface of the glass, thus avoiding the repulsion between like molecules. The materials having stronger adhesive forces normally reveal higher viscosities and vice-versa.

1.1.5 Properties of alcohol

In chemistry, an alcohol is any organic compound in which a hydroxyl group (–OH) is bound to a carbon atom of an alkyl or substituted alkyl group. It is composed of carbon, oxygen, and hydrogen and the general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$ where n=1, 2, 3, etc. The saturated carbon chain is often designated by the symbol R, so that ROH can represent any alcohol in the homologous series. The –OH group bonded to sp³ hybridized carbon as shown above. It can therefore be regarded as a derivative of water, with an alkyl group replacing one of the hydrogen. The oxygen in an alcohol has a bond angle of around 109 ° (c.f. 104.5 ° in water) and two non-bonded electron pairs.

The properties of any given aliphatic alcohol depend on the nature of the alkyl group in the molecule and on the properties of the hydroxyl group. Generally, alcohols are clear, volatile and burn (oxidize) easily. Alcohols react with organic acids to form Esters. The reaction proceeds slowly but the rate of esterification is increased by the presence of hydrogen ions, which act as a catalyst in the reaction. Alcohols are very weak acids,

intermediate in strength between acetylene and water. They undergo substitution with strongly electropositive metals such as sodium. Alcohols react with phosphorus penta chloride when the hydroxyl group is replaced by a chlorine atom.

No gaseous alcohols are known at standard laboratory temperature. The lower members of the homologous series of aliphatic alcohols (containing C_1 to C_{10}) are clear colorless liquids at room temperature. They have varying solubility in water, the higher alcohols being less soluble. The alcohols higher than C_{12} are solids and are insoluble in water. Methanol, ethanol and propanol are miscible with water. The alcohols are miscible in all proportions with most organic liquids. The boiling points of the straight chain alcohols increase as the number of carbon atoms in the molecule increase. For a given molecular mass, there is a decrease in the boiling point when branching of carbon atoms occurs. Thus, the primary alcohols boil at a higher temperature than the secondary alcohols of the same molecular mass and similarly secondary alcohols have higher boiling points than the tertiary alcohols. The boiling points are much higher than is to be expected from their molecular masses. Hydrogen bonds alcohols associate neighboring molecules causes the boiling points high. These intermolecular bonds are considered to be intermediate in strength between weak Van der Waals forces and the strong forces between ions. The extra energy required to break the hydrogen bonds leads to an increase in boiling point.

The hydroxyl group is referred to as a hydrophilic group as it forms hydrogen bonds with water and enhances the solubility of alcohol in water. Methanol, ethanol, propanol, etc. are all miscible with water. Alcohols with higher molecular masses tend to be less water-soluble as the hydrocarbon part of the molecule which is hydrophobic ("water-hating") in nature. In this thesis, Ethanol was used as solvent to find out the interaction of Dimedone from the point of view of biological interests. Some of ethanol properties are listed in Table1.1.

Table 1.1: Some properties of Ethanol

Property	Data
Chemical Name	Ethanol
Chemical formula	C_2H_5OH
Appearance	Colourless liquid
Molecular mass	46.07 g mol^{-1}
Melting point	- 114 °C
Boiling point	78.37 °C
Density	0.789 g cm^{-3}
Viscosity	1.2 mPa.s (at 20 °C)
Vapor pressure	5.95 kPa (at 20 °C)
Solubility	Soluble in water

Ethanol shows the normal reactions of a primary alcohol. Thus it can be converted to alkyl halides; for example red phosphorus and iodine produce ethyl iodide while PCl_3 with catalytic $ZnCl_2$ gives ethyl chloride. Reaction with acetic acid in the presence of an H_2SO_4 catalyst under Fischer esterification conditions gives ethyl acetate while refluxing ethanol overnight with formic acid alone can produce ethyl formate. Oxidation of ethanol with $Na_2Cr_2O_7$ and H_2SO_4 gives only a yield of Ethanaldehyde and therefore for this type of reaction higher yielding methods using PCC or the Swern oxidation are recommended. Oxidation with chromic acid yields Ethanoic acid. Ethanol is not only the oldest synthetic organic chemical used by man but it is also one of the most important solvent. In industry ethanol is widely used as a solvent and a medium for chemical reactions. In addition, it is an important raw material for synthesis.

Some common reaction schemes of ethanol have given below:
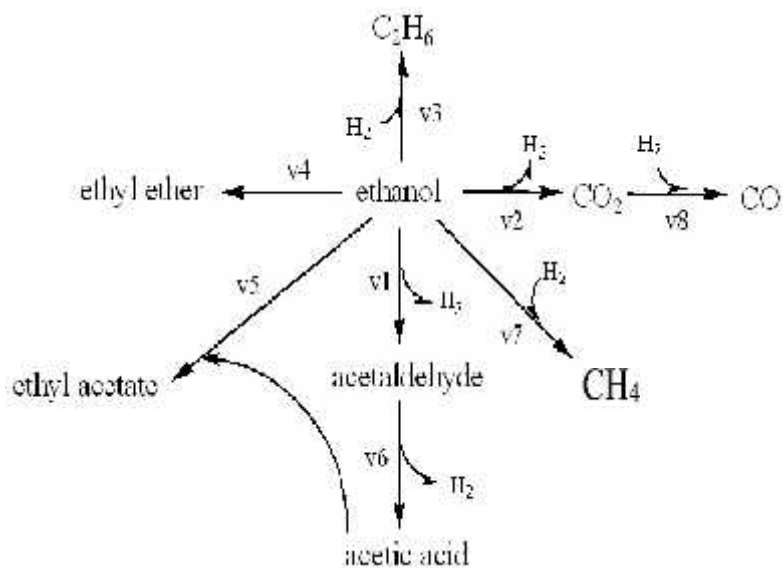
Fig: Common reaction scheme of ethanol

1.1.6 Properties of Water

Water has a very simple atomic structure. The nature of the atomic structure of water causes its molecules to have unique electrochemical properties. The hydrogen side of the water molecule has a slight positive charge. On the other side of the molecule a negative charge exists. This molecular polarity causes water to be a powerful solvent and is responsible for its strong surface tension.

When the water molecule makes a physical phase change its molecules arrange themselves in distinctly different patterns. The molecular arrangement taken by ice (the solid form of the water molecule) leads to an increase in volume and a decrease in density. Expansion of the water molecule at freezing allows ice to float on top of liquid water.

1.1.6.1 Structure of water

It has been recognized that water is an 'anomalous' liquid many of its properties is differ essentially from normal liquids of simple structures [16]. The deviations from regularity indicate some kind of association of water molecules. The notable unique physical properties exhibited by liquid water are [17]

- negative volume of melting

- density maximum in normal liquid range (at 4 °C)

- isothermal compressibility minimum in the normal liquid range at (46 °C)

- numerous crystalline polymorphs

- high dielectric constant

- abnormally high melting, boiling and critical temperatures for such a low molecular weight substance that is neither ionic nor metallic

- increasing liquid fluidity with increasing pressure and

- high mobility transport for H^+ and OH^- ions pure water has a unique molecular structure.

The O-H bond length is 0.096 nm and the H-O-H angle 104.5 °. For a very long time the physicist and the chemist have pondered over the possible structural arrangements that may be responsible for imparting very unusual properties to water. To understand the solute water interaction the most fundamental problem in solution chemistry the knowledge of water structure is a prerequisite. The physico-chemical properties of aqueous solution in most of the cares are interpreted in terms of the structural change produced by solute molecules. It is recognized that an understating of the structural changes in the solvent may be crucial to study of the role of water in biological systems. Various structural models that have been developed to describe the properties of water may generally be grouped into two categories, namely the continumm model and the mixture models. The continumm models [18, 19] treat liquid water as a uniform dielectric medium, and when averaged over a large number of molecules the environment about a particular molecules is considered to be the same as about any other molecules that is the behavior of all the molecules is equivalent. The mixture model theories [20-22] depict the water as being a mixture of short lived liquid clusters of varying extents consisting of highly hydrogen bonded molecules which are mixed with and which alternates role with non-bonded monomers . Among the mixture models, the flickering cluster of Frank and Wen [23] later developed by Nemethy and scherage [15] is commonly adopted in solution chemistry. Properties of dilute aqueous solutions in terms of structural changes brought about by the solutes can be explained more satisfactorily using this model than any other model. According to this model the

tetrahedraly hydrogen bonded clusters referred to as bulky water $(H_2O)_b$ are in dynamic equilibrium with the monomers referred to as dense water $(H_2O)_d$ as represented by [19].

$$(H_2O)_b \; \rightleftharpoons \; (H_2O)_d$$
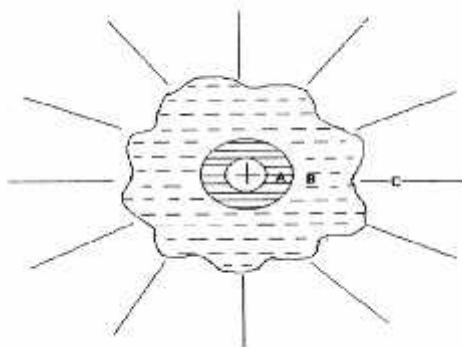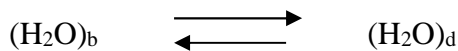
Fig 1.1: Frank and Wen model for the structure modification produce by an ion

The hydrogen bonding in the clusters is postulated [24] to be cooperative phenomenon. So when one bond forms several other also come into existence will be dissolved. The properties of solution can be accounted for in terms of solvent-solvent, solvent-solute and solute-solute interaction. In terms of thermodynamics, the concentration dependence of a given property extrapolated to the limit of infinite dilution provides a measure of solute-solvent interactions. Solute-water interaction or hydration phenomenon can be conveniently classified into three basic types:

i.   Hydrophilic Hydration

ii.   Ionic hydration

iii.   Hydrophobic hydration

The introduction of a solute into liquid water produces changes in the properties of the solvent which are analogous to these brought about by temperature or pressure. The solute that shifts the equilibrium to the left and increase the average half-life of the clusters is termed as structure maker whereas that which has an effect in the opposite direction is called 'Structure breaker. The experimental result on various macroscopic properties provides useful information for proper understanding of specific interactions between the components and the structure of the solution. The thermodynamic and

transport properties are sensitive to the solute-solvent, solute-solute and solvent-solvent interaction. In solution systems these three types of interaction are possible but solute-solute interaction are negligible at dilute solutions. The concentration dependencies of the thermodynamic properties are a measure of solute-solute interaction and in the limit of infinite dilutions these parameters serve as a measure of solute-solvent interactions. The solute induced changes in water structure also result in a change in solution viscosity.

1.1.6.2 Hydrophilic hydration

Solvation occurs as the consequences of solute-solvent interactions different from those between solvent molecules themselves. The solubilization of a solute molecule in water is characterized by changes in the water structure that depend on the nature of the solute. Dissolution of any solute will disrupt the arrangement of water molecules in the liquid state and create a hydration shell around the solute molecule. If the solute is an ionic species, then this hydration shell is characterized to extend from an inner layer where water molecules near the charge species are strongly polarized and oriented by the electrostatic field through an intermediate region where water molecules are significantly polarized but not strongly oriented to an outer solvent region of bulk water where the water molecules are only slightly polarized by the electric field of the ion [25].
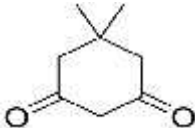
1.1.6.3 Hydrophobic hydration and hydrophobic interaction

The hydrophobic effect refers to the combined phenomena of low solubility and the entropy dominated character of the solvation energy of non-polar substances in aqueous media [26]. It is also reflected by anomalous behavior in other thermodynamic properties such as the partial molar enthalpies, heat capacities and volumes of the nonpolar solutes in water. This effect originated from as much stronger attractive interaction energy between the nonpolar solutes merged in water than their van der waals interaction in free space [27]. The tendency of relativity nonpolar molecules to "stick together" in aqueous solution is denoted as the hydrophobic interaction [28]. It results from hydrophobic hydration of a nonpolar molecule. Because hydrophobic hydration plays an important role in facilitating amphiphiles to aggregates in the aqueous bulk phase and to absorb excessively at the aqueous solution/air interface. It has been an ongoing objective of chemists working in these areas to seek a clearer understanding of the molecular nature behind the subtle hydration phenomenon occurring between nonpolar solutes and water.

A brief but detailed account of the general aspects of hydrophobic hydration which is essential to the rationalization of the results obtained in this work is given at this point.

1.1.7 Dimedone

Table: 1.2 Properties of Dimedone

Property	Data
Chemical formula	$C_8H_{12}O_2$
Chemical Structure	
Molar mass	140.17968
Appearance	Yellow crystals
Melting point	147 to 150 °C (297 to 302 °F; 420 to 423 K) (decomposes)

Dimedone is an alicyclic compound having 1,3-dicarbonyl groups flanked by a Methylene group and exists in a tautomeric trans-enolized form where intramolecular hydrogen bonding is not possible [29]. The inherent structural features in 1 have created various reactive centers: C-1, C-2, and to a less extent C-6 in addition to C-3 in or 3-O. Such phenomenon attracted much attention for using it as a synthetic reagent for the characterizations of aldehydes, since its discovery by the formation of readily crystalizable derivatives; determination of formaldehyde in textiles has been done by a colorimetric method [30]. Moreover, Dimedone is an excellent precursor for partially hydrogenated fused heterocycles [31] where two of the carbon-atoms of Dimedone are part of the backbone of the formed heterocycles. Its structural features and its reactivity to form more functionalized derivatives have led to the construction of a wide range of fused or spiral bi-heterocycles. This chapter will emphasize the role of 1 in the synthesis

off used heterocycles, classified according to the size of the ring and the number of hetero atoms in the heterocycle fused to the cyclohxane ring and subdivided according to the hetero atoms and their arrangement in the ring. The titles are given as annulated heterocycles to 1 which are mostly saturated or partially saturated heterocycles. However, for the simplicity the subtitle is given between two brackets as benzo heterocycles.

Condensation of dimedone with 1, 1, 2-tribenzoylethylene provided pentaketone where the position of the keto-enol equilibrium in the dibenzoyl methane fragment depended on external factors. In reactions with N-nucleophiles the pentaketone behaves as 1,4-diketone, affording with ammonium acetate, methylamine and hydroxylamine hydrochloride functional derivatives of 4,5,6,7-tetrahydroindole and with hydrazine hydrate, a pyridazine derivative. 5-Phenyl-4-ethoxycarbonyl-1H pyrrole-2,3-diones react with acetonitriles and dimedone to form ethyl 2-amino-7,7-dimethyl-2',5-dioxo-5'-phenyl-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-pyrrole]-4'-carboxylates.The crystal and molecular structure of ethyl2-amino-1'-benzyl-7,7-dimethyl-2',5-dioxo-5'-phenyl-3-cyano-1',2',5,6,7,8-hexahydro Spiro[chromene-4,3'-pyrrole]-4'-carboxylate was proved by XRD analysis.

The reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with dialdehydes resulting from periodate oxidation of the 3 '-hydroxyl terminus of RNA has been studied as a terminal-labeling technique in polynucleotide sequence analysis, One molar equivalent of dimedone-2- 4C is incorporated per free 3' terminus of oxidized AMP, tRNA, rRNA, or bacteriophage f2 RNA. Little or no dimedone is associated with unoxidized RNA. The labeling process does not result in appreciable nonspecific incorporation or detectable polynucleotide degradation. The terminal label is sufficiently stable at neutral pH, except in the presence of amines, to permit identification of only predicted terminally labeled oligonucleotide fragments from RNA upon nuclease digestion followed by DEAE-cellulose chromatography.

A simple, two-step synthesis of 9-phenylxanthene-1,8-dione from dimedone and benzaldehyde was developed for second-semester undergraduate organic chemistry. Both reactions afford crystalline solids in excellent yield by simply precipitating the product from solution. Reaction times are very short, and no specialized equipment, reagents, or purification techniques are needed. Multiple spectroscopic methods (IR and ^{1}H, ^{13}C, and DEPT NMR) are employed to solve the structures of the intermediate and final product,

which are unknown to students. The products are not ones students would initially predict, but rather are derived from careful analysis of the spectroscopic data in conjunction with logical mechanistic steps. 1H NMR peaks are well resolved, even at low field. Students have responded favorably over the five years this experiment has been used as a culminating experience in organic chemistry lab.

All of the organic materials and reagents used in this experiment pose the standard safety risks: flammability and irritation of the skin and respiratory tract. Piperidine causes burns to the skin and smells unpleasant. Gloves and chemical splash goggles must be worn for this experiment. The experiment should be conducted in a fume hood. The filtrate from the first reaction should be placed in a standard organic waste bottle. The filtrate from the second reaction can be disposed of down the drain after neutralization.

The reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) with dialdehydes resulting from periodate oxidation of the 3 '-hydroxyl terminus of RNA has been studied as a terminal-labelling technique in polynucleotide sequence analysis. Terminal-labelling techniques have played an important role in the development of protein chemistry. Cyclohexanediones can be applicable for the industry of Transition-metal complex catalyst chemistry, Luminescence chemistry and spectrophotometric analysis, Organic synthesis, Crystallography and Crystal Chemistry, Organic low electrical resistance Chemistry, Colorimetry dimedone is a versatile precursor for annulated heterocycles.

The properties of the substance in liquid mixtures basically depend on its local structure, expressed in terms of packing density, free volume or radial distribution function [32] [33]. However, this local structure depends on forces between molecules and their forms and volume of molecules. It changes with compositions. This change in composition changes thermodynamic properties of mixtures. The investigations regarding the molecular association in organic or aqueous or organic-aqueous mixed solvents are of particular interest, to understand the chemical behavior between polar and non-polar moieties. Water is universal protic solvent, highly associated and is used in daily life. Ethanol is aprotic but strongly associated due to polar -OH group, is the molecule having large dipole moment. So investigation of interaction between dimedone and water, dimedone and ethanol or dimedone and ethanol-water mixture could be quite interesting and applicable as well that has not been investigated earlier so far. Recently volumetric and viscometric study of N-acetylcysteine in ethanol and ethanol-water systems [71] and

Dimethylsulfoxide (DMSO) and DMSO-H_2O [72] were performed. From the results it was seen that NAC showed more interaction in ethanol-water and DMSO-H_2O mixture than those for individual solvents. To the best of our knowledge, still there is no explicit data of viscometric and volumetric properties of dimedone in ethanol and aqueous system are available. The purpose of this study is to evaluate the miscibility of dimedone in water, ethanol and aqueous-ethanol mixed solution systems with a view to determining the molecular interaction among them.

1.2.1 Physical Properties and chemical constitutions

In interpreting the composition, the structure of molecules and the molecular interaction in the binary and ternary systems, it is inevitable to find out the size and the shape of the molecules and the geometry of the arrangement of their constituent atoms. For this Purpose the important parameters are bond lengths or inter atomic distance and bond angles. The type of atomic and other motions as well as the distribution of electrons around the nuclei must also be ascertained; even for a diatomic molecule a theoretical approach for such information would be complicated. However, the chemical analysis and molecular mass determination would reveal the composition of the molecules, and the study of its chemical properties would unable one to ascertain the group or sequence of atoms in a molecule. But this cannot help us to find out the structures of molecules, as bond length, bond angles, internal atomic and molecular motions, polarity etc. cannot be ascertained precisely.

For such information it is indispensable to study the typical physical properties, such as absorption or emission of radiations, refractivity, light scattering, electrical polarization, magnetic susceptibility, optical rotations etc. The measurement of bulk properties like, density, surface tension, viscosity etc. are also have gained increased importance during the recent years, because not only of their great usefulness in elucidating the composition and structure of molecules, but also the molecular interaction in binary and ternary systems.

The various physical properties based upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc., have been found to fall into the following four categories [34].

(i) **Purely additive properties:** An additive property is one, which for a given system, is the sum of the corresponding properties of the constituents. The only strictly additive property is mass, for the mass of a molecule is exactly equal to the sum of the masses of its constituent atoms, and similarly the mass of a mixture is the sum of the separate masses of the constituent parts. There are

other molecular properties like molar volume, radioactivity etc. are large additive in nature.

(ii) **Purely constitutive properties:** The property, which depends entirely upon the arrangement of the atoms in the molecule and not on their number is said to be a purely constitutive property. For example, the optical activity is the property of the asymmetry of the molecule and occurs in all compounds having an overall asymmetry.

(iii) **Constitutive and additive properties:** These are additive properties, but the additive character is modified by the way in which the atom or constituent parts of a system are linked together. Thus, atomic volume of oxygen in hydroxyl group (−OH) is 7.8 while in ketonic group (=CO) it is 12.2. The molar refraction, molecular viscosity etc. are the other examples of this type.

(iv) **Colligative properties:** A colligative property is one which depends primarily on the number of molecules concerned and not on their nature and magnitude. These properties are chiefly encountered in the study of dilute solutions. Lowering of vapor pressure, elevation of boiling point, depression of freezing point and osmotic pressure of dilute solutions on the addition of non-volatile solute molecules are such properties.

1.2.2 Molarity

Molarity (C), is defined as the number of moles of solute per liter of solution. If n is number of moles of solute and V liters is the volume of the solution then,

$$Molarity\ (C) = \frac{Number\ of\ moles\ of\ solute}{Volume\ of\ solution}$$

$$or\ \ = \frac{n}{V} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.1)$$

The unit of molarity is mol L^{-1}.

1.2.3 Molar volume of Mixtures

The volume in mL occupied by 1 mole of any substance is called the molar volume. On the other hand, if ρ is the density and M be the molar mass, molality (m) of a solution is defined as the number of moles of the solute per 1000 g of solvent. Mathematically,

$$Molality\ (m) = \frac{Number\ of\ moles\ of\ solute}{Weight\ of\ solvent\ in\ gram} \times 1000$$

$$or,\ m = \frac{\frac{a}{M_2} \times 1000}{Volume\ of\ solvent\ in\ mL. \times density\ of\ solvent\ in\ g\ cm^{-3}}$$

$$or,\ m = \frac{a}{M_2} \times \frac{1000}{V_1 \times \rho_0} \qquad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.2)$$

Where, a   = weight of solute in gram.

          M_2 = molecular weight of solute in gram.

          V_1 = volume of solvent in mL

          ρ_0 = density of solvent in g cm^{-3}.

Specific volume, $(V) = \frac{1}{\rho} mL\,g^{-1}$ $\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ (1.2.3)

Molar volume, $(V_m) = \frac{M}{\rho} m\ L\,mol^{-1}$ $\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$ (1.2.4)

When two components are mixed together, there may be either a positive or a negative deviation in volume. One of cause of positive deviation in volume i.e. volume expansion has been explained by the disruption of the mode of association through H–bonding of liquids. The negative deviation in molar volume i.e. volume contraction has been thought of by many observers, as arising from the

    I.   compound formation through association

    II.   decrease in the intermolecular distance between the interacting molecules

    III.   interstitial accommodation of smaller species in the structural network of the larger species and

    IV.   change in the bulk structure of either of the substance forming the mixture.

1.2.4 Apparent molar volume

The apparent molar volume of a solute in solution, generally denoted by is defined by φ_v the relation [27]

$$\phi_v = \frac{V - n_1 \overline{V}_1^{\,0}}{n_2} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.5)$$

Where, V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute and $\overline{V}_1^{\,0}$ is the molar volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molar volume (ϕ_v) of an electrolyte in an aqueous solution is given by [35],

$$\phi_v = \frac{1}{n_2}\left[\frac{n_1 M_1 + n_2 M_2}{\dots} - n_1 \overline{V}_1^{\,0}\right]\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.6)$$

Where, $V = \dfrac{n_1 M_1 + n_2 M_2}{\dots}$ and

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molar concentration, $n_2 = m$, the molality and n_1, the number of moles of solvent in 1000g of solvent, the equation for apparent molar volume takes the form [36,37]

$$\phi_v = \frac{1}{m}\left[\frac{1000 + mM_2}{\dots} - \frac{1000}{\dots_0}\right]$$

$$\text{or,}\ \phi_v = \left[\frac{M_2}{\dots} - \frac{1000(\dots - \dots_0)}{m\dots\dots_0}\right]\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.7)$$

$$\text{or,}\ \phi_v = \frac{1}{\dots}\left[M_2 - \frac{1000}{m}\left(\frac{W - W_0}{W_0 - W_e}\right)\right]\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.8)$$

where, ρ_o and ρ are the densities of the solvent and solution .

If the concentration is expressed in molarity (C), the equation (1.2.7) takes the form [30]:

$$\{_v = \left[\frac{M_2}{\cdots_0} - \frac{1000(\cdots - \cdots_0)}{C\cdots_0} \right] \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.9)$$

Where, the relation,

$C = \dfrac{m\{_v 1000}{1000 + \{_v m\cdots_0}$ is used for inter conversion of the concentration in the two scales

[38].The partial molar property of a solute is defined as the change in property when one mole of the solute is added to an infinite amount of solvent, at constant temperature and pressure, so that the concentration of the solution remains virtually unaltered. If 'Y' represents partial molar property of a binary solution at constant temperature and pressure, Y will then be a function of two independent variables n_1 and n_2 which represent the number of moles of the two components present. The partial molar property of component one is then defined by the relation:

$$\overline{Y_1} = \left(\frac{\delta}{\delta n_1} \right)_{n_2, P, T} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.10)$$

Similarly for component 2,

$$\overline{Y_2} = \left(\frac{\delta}{\delta n_2} \right)_{n_1, P, T} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.11)$$

The partial molar property is designated by a bar above the letter representing the property and by a subscript, which indicates the components to which the value refers. The usefulness of the concept of partial molar property lies in the fact that it may be shown mathematically as,

$$Y_{(n_1, n_2)} = n_1 \overline{Y_1} + n_2 \overline{Y_2} \text{ at constant T and P} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.12)$$

In respect of the volume of solution, equation 1.2.4 gives directly

$$V = n_1 \overline{V_1} + n_2 \overline{V_2} \text{ at constant T and P} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.13)$$

At infinite dilution, (m or c →0), the partial molar volume and the apparent molar volume are identical. To obtain reliable φ_v values, it is necessary to measure the density ρ, with great precision because errors in ρ contribute, considerably to the uncertainties in φ_v.

The concentration dependence of the apparent molar volume of electrolytes have been described by the Masson equation [39], the Redlich-Mayer equation [33] and Owen-Brinkley equation [40]. Masson [41] found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

$$\{_v = \{_v^0 + S_v \sqrt{c} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.14)$$

Where, S_v is the experimental slope depending on the nature of the electrolyte.

Redlich and Rosenfeld [42] predicated that a constant limiting law slope S_v, should be obtained for a given electrolyte charge type if the Debye-Huckel limiting law is obeyed. By differentiating the Debye-Huckel limiting law for activity coefficients with respect to pressure, the theoretical limiting law slope S_v, could be calculated using the equation,

$$S_v = KW^{3/2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.15)$$

Where, the terms K and W are given by

$$K = N^2 e^3 \left(\frac{8f}{100D^3 RT}\right)^{1/2} \left\{\left(\frac{u \ln D}{u_{...}}\right) - \left(\frac{s}{3}\right)\right\} \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.16)$$

And, $\quad W = 0.5 \sum x_i Z_i^2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.17)$

where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valency Z_i formed by one molecule of the electrolyte and the other symbols have their usual significance [43]. For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

$$\{_v = \{_v^0 + KW^{3/2} \sqrt{C} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.18)$$

and for not too low concentrations, the concentration dependence can be represented as,

$$\{_v = \{_v^0 + S_v \sqrt{C} + b_v C \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1.2.19)$$

Where, S_v is the theoretical limiting law slope and b_v an empirical constant.

1.2.5 Determination of Apparent Molar Expansivities

From the apparent molar volumes determined at different temperatures, it is possible to derive the apparent molar expansivities through the thermodynamic relation given by equation 1.2.20.

$$\varphi_E = \left(\frac{\delta\varphi_v}{\delta}\right)_P \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1.2.20)$$

Where, φ_E is the apparent molar expansivity, t is the temperature, and P is the pressure. The slope of φ_v versus t plot gave φ_E. The linearity of the φ_v versus t plot over a certain temperature range indicates that φ_E is constant over that range and given by the slope of the line. The apparent molar expansivity at infinite dilution, φ_E^0, can be obtained if φ_v^0 values are used for φ_v in this treatment.

1.2.6 Viscosity

Viscosity means viscous ability. The internal friction opposes the relative motion of adjacent layers of a fluid. When a fluid is flowing through a cylindrical tube, layers just touching the sides of the tubes are stationary and velocities of the adjacent layers increases towards the center of the tube, the layer in the center of the tube having the maximum velocity. There thus exists a velocity gradient. Molecules are a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa, with a result that some tangential force is required to maintain uniform flow. This tangential force will depend upon two factors,

(i) Area of contact 'A' between the two layers and

(ii) Velocity gradient $\dfrac{dv}{dx}$

Thus, $f \infty \ A \ \dfrac{dv}{dx}$

Or $\quad f \ = \ y \ A \ \dfrac{dv}{dx} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1.2.21)$

Where, η is a proportionality constant, known as the coefficient of viscosity or simply viscosity of the liquid. Thus, the coefficient of viscosity may be defined as the force per unit area required to maintain unit difference in velocity between two parallel layers of liquid unit distance apart.

The reciprocal of viscosity called the fluidity (φ) is given by the relation.

$$\varphi = \frac{1}{\eta} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1.2.22)$$

If a liquid with a coefficient of viscosity (η) flows with a uniform velocity, at a rate of V cm^3 in t seconds through a narrow tube of radius r cm, and length 1 cm under a driving pressure of p dynes cm^{-2} then according to J.L.M. Poiseuille [44],

$$\eta = \frac{f\, Pr^4 t}{8lv} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1.2.23)$$

This equation known as Poiseuille's holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities. After correction for kinetic energy, the equation becomes,

$$\eta = \frac{f\, Pr^4 t}{8lv} - \frac{...V}{8flt} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1.2.24)$$

Where ρ represents the density of the liquid/solution. However, in practical purposes, the correction factor is generally ignored.

The driving pressure P=h...g, where h is the difference in height of the surface of the two reservoirs, since the external pressure is the same at the surface of both reservoirs, g = acceleration due to gravity and ρ= the density of liquid. Thus the equation (1.2.23) becomes,

$$\eta = \frac{fh...gr^4 t}{8vl} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1.2.25)$$

For a particular viscometer h, l, r and v are fixed, so the equation (1.2.25) becomes,

$$\eta = A...t \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1.2.26)$$

Where $A = \dfrac{f h g r^4}{8vl}$, called the calibration constant of the viscometer used.

Putting the values of $A,...$and to f the investigated liquid in equation (1.2.26), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

The CGS Unit of viscosity is poise, in honor of J.L.M. Poiseuille. The SI unit of viscosity is the pascal-second (Pa·s). Since viscosity of liquid is usually very small, it is usually expressed in centipoise (cP) or mPa.s.

1.2.7 Viscosity and temperature

The viscosity of a liquid generally decreases with the increase of temperature. Evaluation of energy of activation for viscous flow can be stated by the Arrhenius equation as follows:

$$\eta = Ae^{-\epsilon_a / R} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.27)$$

Where, A is Arrhenius constant and ε is energy of activation for viscous flow. The linear form of the equation 1.2.27 is as follows:

$$\ln\eta = \ln A - \frac{\epsilon_a}{RT} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.28)$$

$\ln\eta$ vs $\frac{1}{T}$ offer straight line. From the slope and intercept the energy of activation and Arrhenius constant can be determined.

1.2.8 Different thermodynamic parameters

Eyring and co-workers [45] are using absolute reaction rate theory and partition functions corrected viscosity, η as follows:

$$\eta = \frac{hN}{V} . e^{\frac{\Delta G^*}{R}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.30)$$

Where, ΔG^* is the change of free energy of activation per mole for viscous flow, V_m is the molar volume for liquids or solutions and h, N, R and T have usual meaning. The values of change of free energy of activation (ΔG^*) can be calculated by using the Nightingle and Benck equation [46],

$$\Delta G^* = RT\ln\left(\frac{\eta}{hN}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.31)$$

And values for the corresponding thermodynamic parameters, enthalpy of activation, ΔH^* and entropy of activation ΔS^* for per mole for viscous flow of the liquids or solutions have been calculated from the relationship (1.2.30) [47]

$$\ln\frac{\eta V}{hN} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.32)$$

Assuming ΔH^* and ΔS^* to be almost independent in the temperature range studied, a plot of $\ln\frac{\eta V_m}{N}$ against $\frac{1}{T}$, will give a straight line. From the slope and intercept ΔH^* and ΔS^* can be determined respectively.

1.15 Viscosity Coefficients A and B Measurement

The Jones-Dole coefficient A, reflects the effect of solute-solute interaction and B is a measure of structural modifications induced by the solute-solvent interaction. The coefficients A and B for the electrolyte solutions can be measured by using the empirical equations of Jones-Dole [108]

$$\eta_r = 1 + A\sqrt{C} + B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.31)$$

Where, η_r is the relative viscosity.

Relative viscosity, $\eta_r = \dfrac{V \quad o\ s \quad , \ \eta}{V \quad o\ s \quad , \ \eta_c}$

The values of the coefficients *A* and *B* were obtained from the intercept and slope of the plot $\frac{y_r - 1}{\sqrt{C}}$ against $\sqrt{C}$ respectively.

<center>**CHAPTER II**</center>

<center>**Literature Review**</center>

2.1   Literature Review

Dimedone (5,5-dimethylcyclohexane-1,3-dione) belongs to the cyclic 1,3-diketones, a very important class of organic compounds. A wide range of practical dimedone applications include its use as a versatile precursor for synthesis of numerous hetero and spirocyclic compounds [48], xanthene derivatives with their industrial [49] and synthetic [50] applications, and as a reagent for various analytical determinations [51]. The reaction of Dimedone with aliphatic and aromatic aldehydes gives the well-known acyclic Vorlander adducts [52].

Like all 1,3-diketones, dimedone can exist as an equilibrium mixture of the diketo and enol tautomers. However, as distinct from acyclic 1,3-diketones, the enol form of dimedone cannot be stabilized by the intramolecular hydrogen bond. In the solid state, dimedone exists as the enol tautomer stabilized by intermolecular hydrogen bonds network [53].

Diketone is a molecule which contains two ketone carbonyl groups. Diacetyl ($CH_3COCOCH_3$), 2,3 butadione is the simplest aliphatic diketone. It is an alpha-diketone which has two ketone groups side by-side. Usually, alpha-diketone imparts a carmel like or buttery flavor. Diketone compounds take a role in creating various fragrances. Bezil ($C_6H_5COCOC_6H_5$) is an aromatic diketone, the fundamental structure of photo sensitive molecule which is broken down into free radicals upon exposure to ultraviolet radiation. Acetoacetone is a beta-diketone which two ketones are separated only by one carbon. The beta-ketone is stable as a conjugated enol rather than a diketone due to the delocalization which makes the counter ion more stable and less likely to regain the proton. Ascorbic acid is an example of enol compound. Enol compounds form complexes with many transition metal ions. These compounds are readily soluble in organic solvents. They are widely used as chelating agents, ligands, and catalyst precursors. Acetoacetic acid and its esters contain active methylene groups which have relatively acidic alpha-protons due to H atom adjacent to two carbonyl groups. The

reactivity of its methylene group provide the sequence of reactions of alkylation, hydrolysis of the esters and decarboxylation resulting in substituted ketones. Acetoacetic acid derivatives are important aliphatic parts adjoining azo dyes and pigments. Aacetoacetate is one of ketone bodies which are the end-products of rapid or excessive fatty acid breakdown in the human body. Para-benzoquinone and its derivatives belong to 1,4-diketone family. Benzoquinone is used as an oxidizing agent in organic chemistry and is a common constituent of biologically molecules like Vitamin K1. Quinone serves as electron acceptors in electron transport chains such as in photosynthesis and aerobic respiration. Diketene derivatives find versatile applications in making biomolecules, agrochemicals, dyes, pigments, pharmaceuticals including vitamins and stabilizers for PVC and polyester. They are used as components for fragrances and as solvents. Diketones undergo the reversible and irreversible addition reactions include; Aldol Reactions, Alkylation of Enolate Anions, Clemmensen Reduction, Cyanohydrin Formation, Enamine Formation, Hemiacetal and Acetal Formation, Hydration Formation, Imine Formation and Wolff-Kishner Reduction.

2.2   Aim of the Research

Dimedone is a cyclic diketone used in organic chemistry to determine whether a compound contains an aldehyde group. Cyclohexanediones in general can be used as catalysts in the formation of transition-metal complexes. It can also be used for chemistry involving organic compounds of low electrical resistance.

The specific aims of this study are:

i)   to be aware of the probable interaction between Water−Ethanol solution, Dimedone−Ethanol solution, Dimedone−Water−Ethanol ternary solution

ii)   to explore the data on physico-chemical properties of the systems mentioned above

iii)   to explore the role of Ethanol in physico-chemical interactions of all the systems

iv)   to understand the change in thermodynamic properties of Ethanol in Water, Dimedone and Dimedone−Water mixture.

CHAPTER III

Experimental

3.1 General

During the course of the present work a number of techniques were involved which were in general standard ones. Constant efforts for attaining the ideal conditions for the experiments were always attempted.

The thoroughly cleaned glass pieces were dried in electric oven. The smaller pieces of apparatus were dried in electric oven and stored in desiccators, while larger pieces of apparatus were used directly from the oven.

Cannon-Fenske Opaque Viscometers viscometers were used for measurement of viscosity. The inside wall of the viscometer was cleaned thoroughly with warm chromic acid so that there was no obstruction in the capillary and the liquid could run clearly without leaving any drop behind. It was then rinsed thoroughly with distilled water followed by rectified spirit and finally with acetone and dried.

3.2 Apparatus

Viscosities of various liquids were measured using Cannon-Fenske Opaque Viscometer. And the densities were measured by Density and Sound Velocity Meter (DSA 5000M) Anton Paar, Austria. Electronic balance (HR 200, made in Japan) with an accuracy of ±0.0001g was used for weighing. The flow time of liquids were recorded by a stop-watch capable to read up to 0.01 sec. The temperature was controlled by water thermostat (Fisher Scientific ET-150, HAKKE, Germany) with an accuracy of $\pm$ 0.05 °C. The experimental temperatures were 298.15 to 323.15 K at 5 K intervals. Both the density bottle and viscometer were calibrated with doubled-distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

3.3   Preparation and Purification of Reagents

High quality analytical grade reagents were used in all the experiments, where necessary further purifications were done.

3.4   Distillation of water

First time water was distilled by water distillation apparatus. First time distilled water was further purified by a quick-fit glass made distillation apparatus. About 1.5 L water was taken in a round bottom reservoir of which the capacity was 2.0 L. Then it was distilled in presence of $KMnO_4$. Distilled water was collected at only 100 °C. Other liquids of which the temperatures were below and above the mentioned boiling point were discarded. In all the experiments double distilled water was used.

3.5   Chemicals

Dimedone (Reagent for aldehydes) was collected from Loba Chemie Pvt. Ltd. Mumbai, India. High performance liquid chromatography (HPLC) grade. Ethanol was collected from E-Merk, Germany, and was 99.99% pure. All chemicals and reagents were of analytical grade and were used without further purification.

3.6   Preparation of solution

Solutions were prepared by mixing appropriate volumes of components. The volume taken by using burettes and pipettes were correct up to 0.1 cm^3. The volume of each component used as taken converted into mole fraction, special precaution was taken to prevent evaporation and introduction of moisture into the experimental samples.

3.7   Density measurement

The densities were measured by Density and Sound Velocity Meter (DSA 5000M) Anton Paar, Austria. The densities of solvents and solutions were measured separately. For this solvent and solutions were poured into the Density and Sound Velocity Meter through injection by syringe. The investigated temperatures were selected manually and the experimental data of density values were recorded automatically in the machine. Then the results were collected from the data memory. Precautions were taken in every injection and after each ejection machine was cleaned properly by ethanol, water on the basis of inorganic and organic solvents. The density measurement was performed for

each of the solutions at the temperature of 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K respectively.

3.8 Viscosity measurements

Viscosity of water, ethanol and several solutions were measured by using the Cannon-Fenske Opaque Viscometer. The interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind. It was then rinsed with acetone and dried in and oven at about 85 °C. The viscometer was then clamped vertically in the thermostatic water bath such that the upper mark of the top bulb was well below the water level. 10.0 mL of doubled-distilled water was poured into the viscometer by a pipette.

Then it was allowed to keep in the thermostatic bath for about 30 minutes to attain the bath temperature. With the help of pipette filler attached to the narrower limb of the viscometer, the water was sucked up above the upper mark of the bulb. The water of bulb was then allowed to fall into the capillary and the time of fall between the two marks was noted with the help of stop-watch capable of reading up to 0.01 second. The reading at each temperature was repeated three or four times, in order to check the reproducibility of the flow time, the temperature being maintained at the same value. Since the accurate viscosity and density of water at different temperatures are known (from literature) calibration constant A of the viscometer for different temperature were obtained by using equation,

$$\eta = A \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1.2.26)$$

Where, $A = \dfrac{\eta_{H_2O}}{\rho_{H_2O} \cdot t_{H_2O}}$

Like water the flow time of different solutions were determined. Then putting the values of the calibration constant, density and time of flow of the experimental solutions, the viscosities of the solutions were determined by using the equation 1.2.26.

3.9 Apparent molar volumes measurement:

Apparent molar volumes were determined from measured densities of solvent and solution by using the following equation 1.2.8.

$$\varphi_V = \left[\frac{1000(\rho_0 - \rho)}{C\rho_0}\right] + \frac{M_2}{\rho_0} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.8)$$

Where φ_V is the apparent molar volume, C is the molarity, M_2 is the molecular mass of the solute (Dimedone) and ρ_0 and ρ are the densities of the solvent and the solution respectively. In general, φ_V was found to vary linearly with concentration for the systems studied. Thus, φ_V data were fitted into equation 1.2.14 and 1.2.19.

$$\{_v = \{_v^0 + S_v \sqrt{c} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.14)$$

$$\{_v = \{_v^0 + S_v \sqrt{C} + b_v C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.19)$$

Where φ_V is the apparent molar volume at infinite dilution and b_v is an experimentally determined parameter.

3.10 Determination of apparent molar expansivities

From the apparent molar volumes determined at different temperatures, it is possible to derive the apparent molar expansivities through the thermodynamic relation given by equation 1.2.20.

$$\varphi_E = \left(\frac{\delta\varphi_V}{\delta t}\right)_P \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.20)$$

Where, φ_E the apparent molar expansivity, t is is the temperature, and P is the pressure. The slope of φ_V versus t plot gave φ_E. The linearity of the φ_V versus t plot over a certain temperature range indicates that φ_E is constant over that range and given by the slope of the line. The apparent molar expansivity at infinite dilution, φ_E^0 can be obtained if φ_V^0 values are used for φ_V in this treatment.

3.11 Determination of thermodynamic parameters

The activation energy for viscous flow is determined from logarithmic form of Eyring equation as:

$$\ln\eta = \ln A - \frac{\epsilon_a}{RT} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1.2.28)$$

The slope and intercept of the straight line of plot of $\ln\eta$ vs $\frac{1}{T}$ presented the values of activation energy for viscous flow and Arrhenius constant respectively.

Values of enthalpy of activation, ΔH^* and entropy of activation, ΔS^* for per mole for viscous flow of solutions have been calculated from the relationship (1.2.30)

$$\ln \frac{\eta V}{hN} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2.30)$$

Assuming ΔH^* and ΔS^* to be almost independent in the temperature range studied, a plot of $\ln \frac{\eta V_m}{N}$ against $\frac{1}{T}$, will give a straight line. From the slope and intercept ΔH^* and ΔS^* can be determined respectively.

CHAPTER-IV

Results and Discussion

4.1 Investigated Systems

The whole research work has been designed within seven investigated systems to identify the change of interaction in various concentrations of Dimedone in different binary and ternary solution of ethanol and water, which will provide the change of information in volumetric, viscometric and thermodynamic properties of solutions to determine the molecular interactions among Dimedone, Ethanol and Water. The investigated systems are:

i)   Dimedone in Ethanol

ii)   Dimedone in [1:4] [Water–Ethanol]

iii)   Dimedone in [2:3] [Water–Ethanol]

iv)   Dimedone in [3:2] [Water–Ethanol]

v)   Dimedone in [4:1] [Water–Ethanol]

vi)   Dimedone in [1:1] [Water–Ethanol]

vii)   Dimedone in [1:3] [Water–Ethanol]

4.2 Volumetric Properties

4.2.1 Density of Pure Solvent

The density at different temperatures of the pure solvents; ethanol and water have been tabulated in Table 4.1 with the literature values [37, 96] for possible comparison. The larger density values of ethanol indicate that ethanol is denser than water at all investigated temperatures. From the table it is also seen that densities of the solvents decreased with the increasing temperature as expected and provide almost same results

as mentioned in the cited literatures. It indicates that the solvents being used in the experiments were pure and analytical grade as declared by suppliers.

Table 4.1: Density, values of Ethanol and Water at 298.15 to 318.15 K at 5 K interval

Temp. (K)	Density (g cm^{-3}) of Ethanol		Density (g cm^{-3}) of Water	
	Literature Value	Experimental Value	Literature Value	Experimental Value
298.15	0.7858[55]	0.7976	0.9971[56]	0.9971
303.15	0.7813[55]	0.7932	0.9957[56]	0.9957
308.15	0.7761[55]	0.7887	0.9940[56]	0.9940
313.15	0.7718[55]	0.7842	0.9922[56]	0.9922
318.15	0.7651[55]	0.7796	0.9902[56]	0.9902

4.2.2 Density of Dimedone>Ethanol system

The density values, of different concentration of Dimedone (0.05, 0.10, 0.15, 0.20 and 0.25) M in water solutions have been investigated at 298.15, 303.15, 308.15, 313.15 and 318.15 K temperatures. The density values are shown in Table 4.2. The density values of (Dimedone−Water) systems at 5 investigated temperatures are higher than those of ethanol even the values increased with increasing the amount of Dimedone in Ethanol. It is seen from the result that densities of ethanolic Dimedone solution increased with increasing concentration within the investigated composition of Dimedone in Ethanol. Comparing the results in Table 4.1 with the density values of Ethanol, it can be stated that density values of solution of Dimedone in Ethanol are higher than those of pure ethanol. Density values of the Dimedone−Ethanol in Table 4.2 have fitted in Figure 4.1. From the Figure 4.1 it is seen that density values of Dimedone in Ethanol increased linearly with the concentration of the Dimedone within the temperature range of 298.15 K to 318.15 K at 5 K interval. This increase of density in Dimedone−Ethanol binary system may be due to solute-solute, solute-solvent interaction through strong hydrogen bond, dipole-dipole as well as acid-base interaction between Dimedone and Water. Detail mechanism of dissolution of Dimedone in Ethanol is still unknown. It is also seen that density values of the investigated binary systems decreased with increasing

temperature at a specific concentration. With increasing temperature internal energy of the molecules present in the systems increases. As we know from the first law of thermodynamics, if energy of a system is increased then work is done on the system and changed it mode of dimension blindly, e.g., increase in volume, plus some heat is absorbed. In other words, heat and work are equivalent ways of changing a system's internal energy [57]. So with increasing temperature as well as the internal energy solute−solvent interaction may be weaken and the volume is increased; the resultant is the lessen of densities.

Table 4.2: Density values, of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone–Ethanol	0.05	0.7993	0.7949	0.7904	0.7859	0.7813
	0.10	0.8010	0.7966	0.7921	0.7876	0.7830
	0.15	0.8026	0.7982	0.7937	0.7892	0.7846
	0.20	0.8043	0.7998	0.7954	0.7908	0.7862
	0.25	0.8059	0.8015	0.7970	0.7924	0.7878
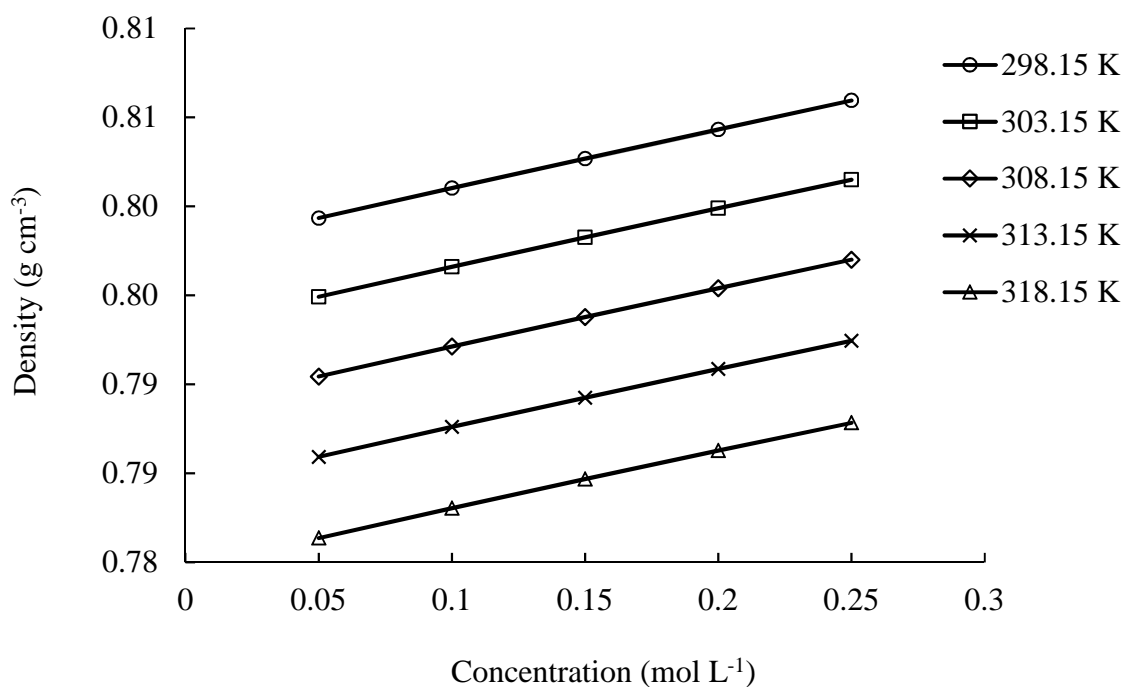
Figure 4.1: Density values vs concentration of Dimedone in Ethanol system at 298.15 to 318.15K at 5 K interval

4.2.3 Density of Dimedone−Water−Ethanol System

The densities, of the five specific concentration of Dimedone in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water−Ethanol] systems at 298.15K to 318.15 K at 5K interval has been investigated. The density values have shown in Table 4.3-4.8. The density values of Dimedone in [1:4] [Water−Ethanol] ternary systems are the highest than all other ternary and also than those of Dimedone−Ethanol binary systems. The density values increased with increasing concentration of Dimedone in [Water−Ethanol] at the entire investigated composition range, (0.05 to 0.25) M Dimedone in mixed solvents. The values of the Table 4.3-4.8 are fitted in Figure 4.2-4.7. From the figures it is seen that the densities of Dimedone in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water−Ethanol] systems increased linearly with the concentration of the Dimedone within the temperature range of 298.15 K to 318.15 K at 5 K interval. It is seen that with increasing amount of Ethanol in Dimedone−Water−Ethanol systems density values increased. Ethanol is a polar aprotic

solvent (having−OH group) along with water a polar inorganic solvent whose polarity and dipole moment is 1 and 1.84 D [58] respectively. At the same time Dimedone is also a polar organic solute. So with increasing the ratio of ethanol in Ethanol−Water systems amount of solvation with strong interaction took place between Dimedone and increased amount of ethanol as a result densities increased. It is also seen that density values of the investigated ternary systems decreased with increasing temperature at a specific concentration as shown in Table 4.6 and Figure 4.6, 4.8, 4.10 & 4.12. It is already mentioned that with increasing temperature internal energy increased which affect or increase the vibrational, rotational and translational state of the system. As a result volume of the system increased and density values decreased.

In case of ternary systems, the highest densities observed for Dimedone in [1:4] [Water −Ethanol] system, probably highest dipole-dipole interactions in addition to other forces. On the other hand Dimedone in [4:1] [Water−Ethanol] system showed lowest interaction might be due to minimum dipole-dipole forces, comparison to other ternary systems. In ternary systems the interaction increased with the increase of the ratio of ethanol and the order is:

Dimedone in [1:4] [Water−Ethanol]>Dimedone in [2:3] [Water−Ethanol]>Dimedone in [1:1] [Water−Ethanol]>Dimedone in [3:2] [Water−Ethanol]>Dimedone in [1:3] [Water−Ethanol]>Dimedone in [4:1] [Water−Ethanol]

Detail mechanism of dissolution or solvation of Dimedone in [Water−Ethanol] system is still unknown.

Table 4.3: Density values, of Dimedone in [1:4] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:4] [Water–Ethanol]	0.05	0.8642	0.8599	0.8555	0.8511	0.8466
	0.10	0.8652	0.8608	0.8565	0.8521	0.8475
	0.15	0.8661	0.8618	0.8574	0.8531	0.8485
	0.20	0.8671	0.8627	0.8583	0.8539	0.8494
	0.25	0.8679	0.8636	0.8592	0.8548	0.8502

Figure 4.2: Densities vs concentration of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.4: Density values,   of Dimedone in [2:3] [Water–Ethanol] systems at 298.15 to
318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [2:3] [Water–Ethanol]	0.05	0.9099	0.9058	0.9017	0.8975	0.8933
	0.10	0.9103	0.9063	0.9022	0.8981	0.8937
	0.15	0.9108	0.9067	0.9026	0.8984	0.8941
	0.20	0.9112	0.9071	0.9030	0.8988	0.8945
	0.25	0.9116	0.9075	0.9034	0.8991	0.8948

Figure 4.3: Densities vs concentration of Dimedone in [2:3] [Water–Ethanol] system at
298.15 to 318.15 K at 5 K interval

Table 4.5: Density values, of Dimedone in [3:2] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [3:2] [Water–Ethanol]	0.05	0.9475	0.9441	0.9406	0.9369	0.9332
	0.10	0.9482	0.9448	0.9413	0.9377	0.9340
	0.15	0.9489	0.9455	0.9420	0.9384	0.9347
	0.20	0.9496	0.9462	0.9427	0.9390	0.9353
	0.25	0.9503	0.9469	0.9433	0.9397	0.9359

Figure 4.4: Densities vs concentration of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.6: Density values,   of Dimedone in [4:1] [Water–Ethanol] systems at 298.15 to
318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [4:1] [Water–Ethanol]	0.05	0.9734	0.9713	0.9690	0.9665	0.9638
	0.10	0.9743	0.9722	0.9699	0.9674	0.9647
	0.15	0.9752	0.9731	0.9707	0.9682	0.9655
	0.20	0.9761	0.9739	0.9716	0.9690	0.9662
	0.25	0.9770	0.9748	0.9724	0.9698	0.9669

Figure 4.5: Densities vs concentration of Dimedone in [4:1] [Water–Ethanol] system at
298.15 to 318.15 K at 5 K interval

Table 4.7: Density values,   of Dimedone in [1:1] [Water–Ethanol] systems at 298.15 to
318.15 K at 5 K interval

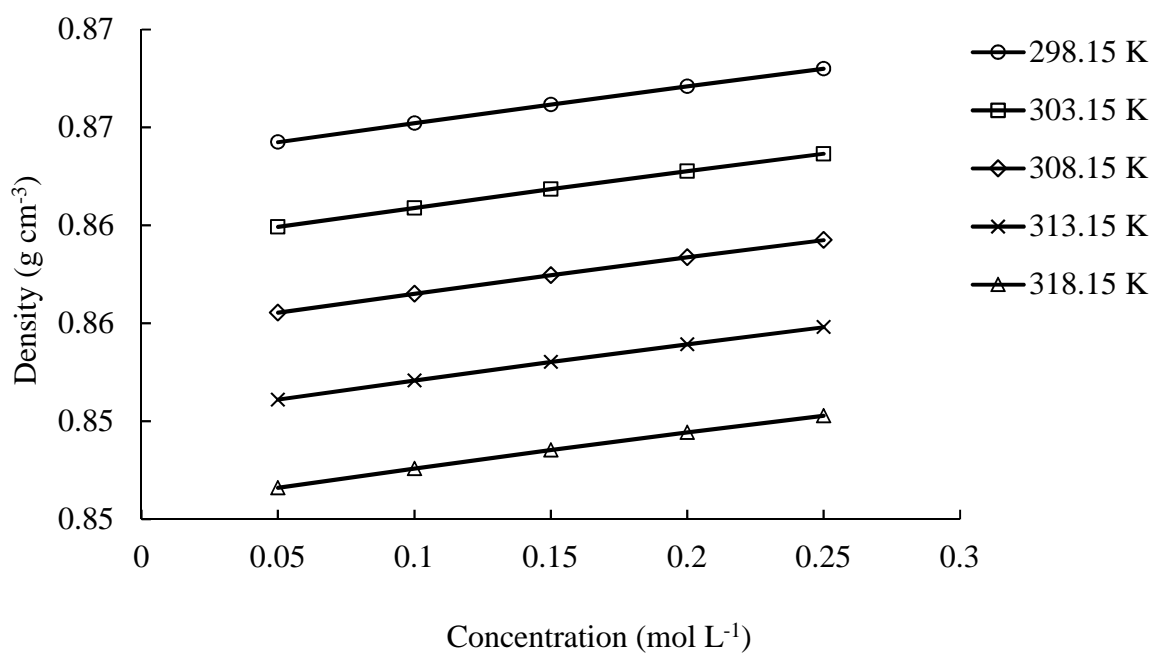| Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:1] [Water–Ethanol]	0.05	0.9293	0.9257	0.9219	0.9181	0.9142
	0.10	0.9303	0.9267	0.9229	0.9191	0.9152
	0.15	0.9313	0.9276	0.9239	0.9200	0.9160
	0.20	0.9322	0.9285	0.9248	0.9209	0.9169
	0.25	0.9331	0.9294	0.9256	0.9216	0.9176
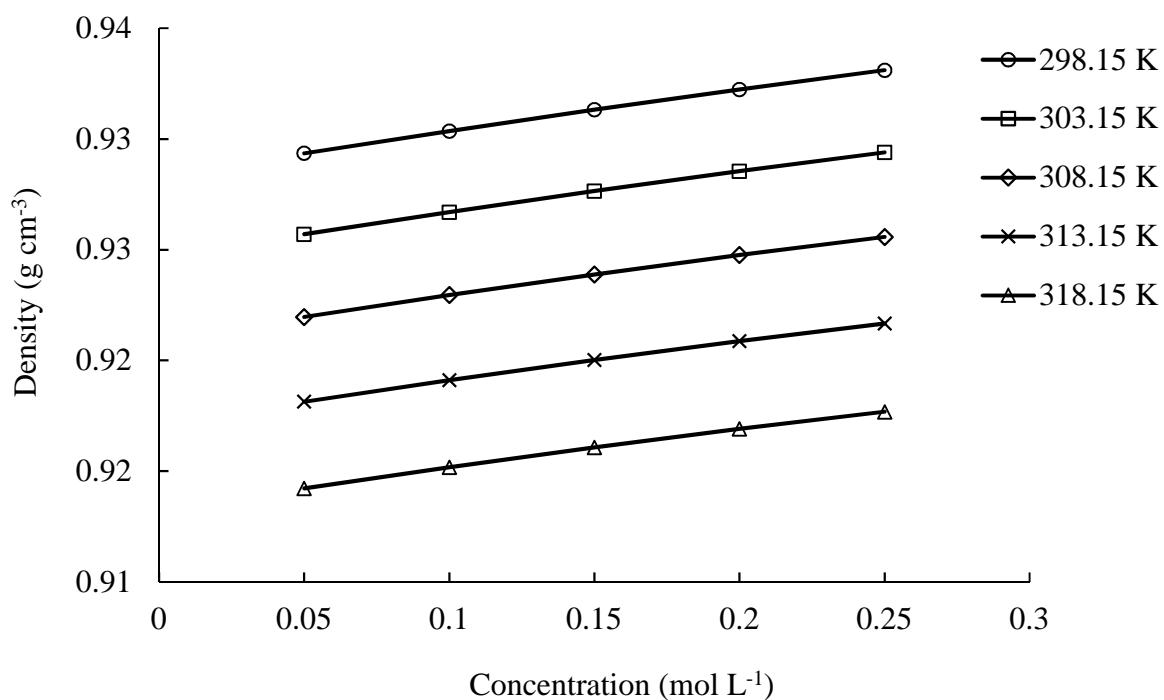
Figure 4.6: Densities vs concentration of Dimedone in [1:1] [Water–Ethanol] system at
298.15 to 318.15 K at 5 K interval

Table 4.8: Density values, of Dimedone in [1:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

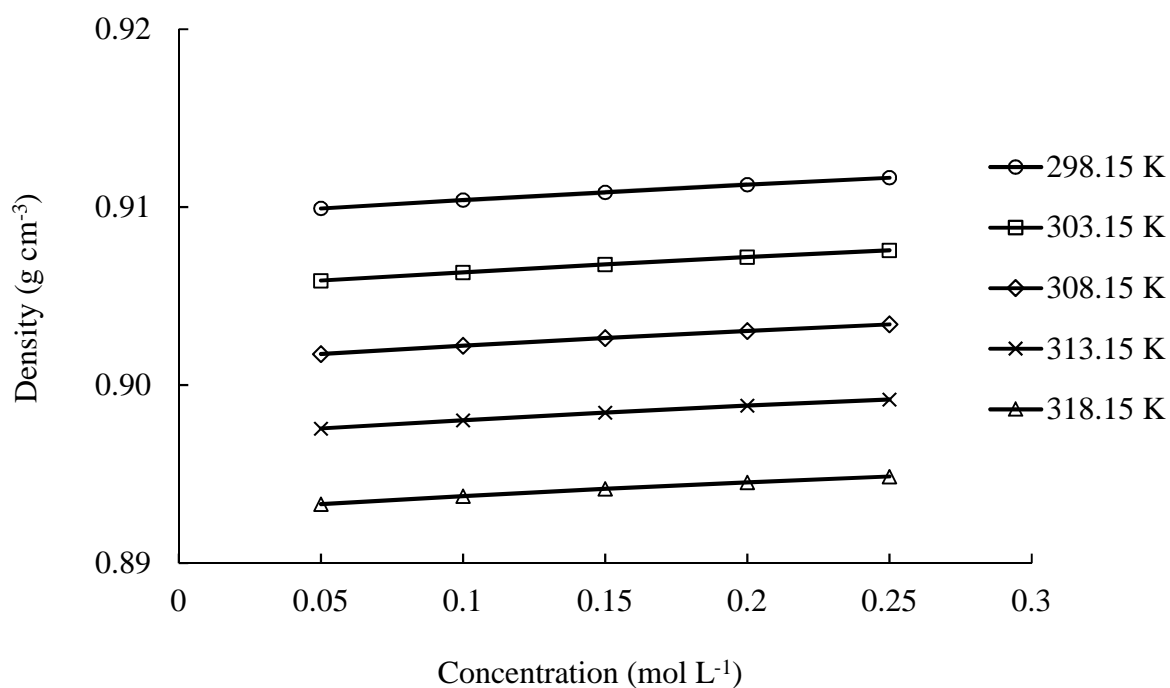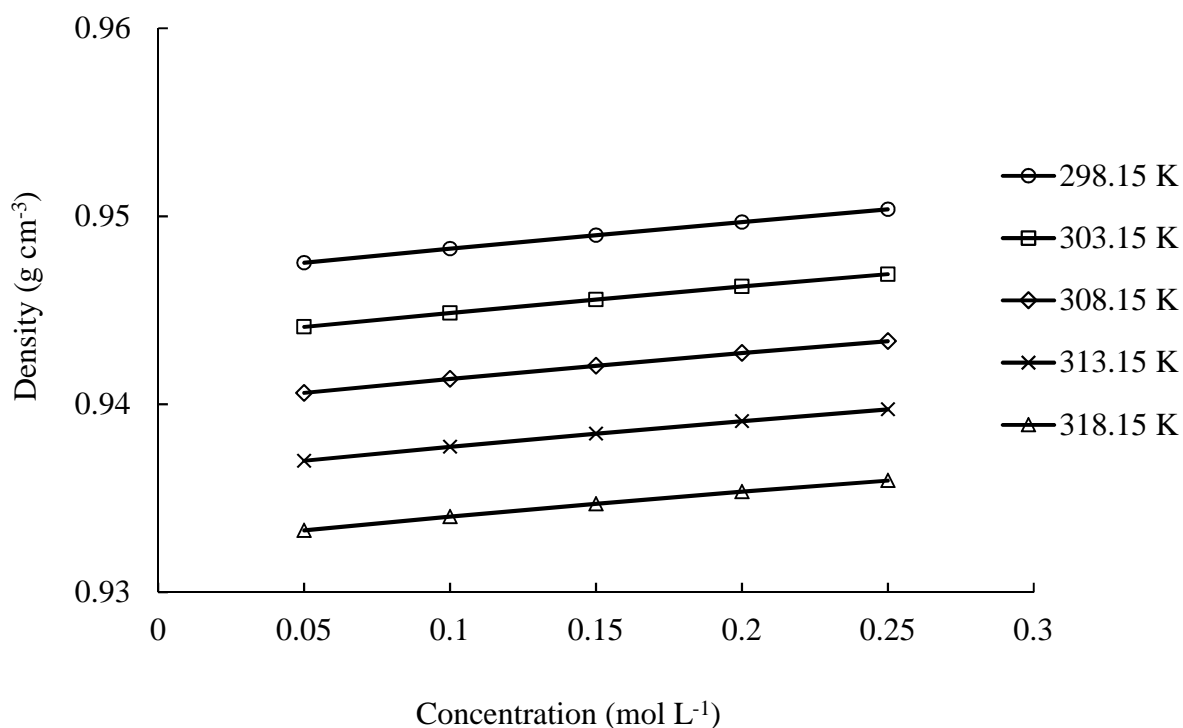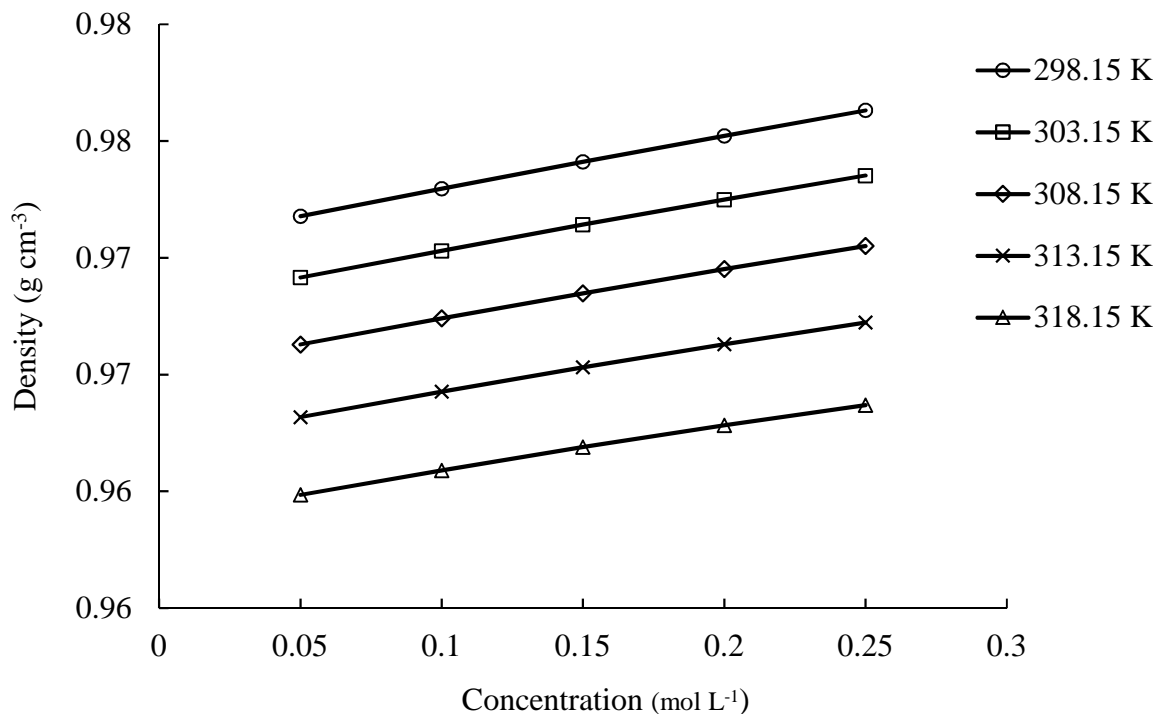| Name of the system	Conc. (mol L^{-1})	Density, (g cm^{-3})				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:3] [Water–Ethanol]	0.05	0.8753	0.8711	0.8668	0.8623	0.8579
	0.10	0.8771	0.8729	0.8685	0.8641	0.8597
	0.15	0.8789	0.8746	0.8703	0.8658	0.8614
	0.20	0.8807	0.8763	0.8719	0.8675	0.8630
	0.25	0.8824	0.8780	0.8736	0.8691	0.8646

Figure 4.7: Densities vs concentration of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

4.3 Apparent molar volume

The volumetric properties of Dimedone in solution can provide useful information in elucidating the interactions which occur in water, ethanol as well as ethanol–H_2O mixed solutions. Dimedone possessing both polar and non-polar groups have potential effects on the structure or molar volume of water, ethanol as well as ethanol–H_2O mixed solutions exhibit interactions of particular important applications. Hydrophobic interactions between the organic parts of Dimedone and ethanol may play an important role in the stability in the mixture even when water is added to it. From a theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume since these values depend only on the intrinsic size of the ion and on ion-solvent interaction. Moreover, the interactions of solutes with water may influence their accession to, and binding with, receptor sites, thus influencing their perception properties. In order to investigate the nature of the solute-solute and solute–solvent interactions of Dimedone in aqueous ethanol solution, the apparent molar volume and apparent molar volume at infinite dilution were determined.

4.3.1 Apparent molar volume of Dimedone–Ethanol Binary System

The apparent molar volume of different concentration (0.05 to 0.25) M of Dimedone in water solution has been determined at 298.15 to 318.15 K temperature at 5 K interval by using equation 1.2.8. The values of apparent molar volume of Dimedone–Water binary system has been shown in the Table 4.7. The graphical representation of the φ_v values of Dimedone–Water binary system has been shown in Figure 4.13. The apparent molar volume values vary linearly with square root of concentration of Dimedone solution.

It is seen that apparent molar volume is dependent upon the concentration of Dimedone as well as on temperature. The values have been found to be positive throughout the whole concentration range for Dimedone in Ethanol medium. The apparent molar volumes of Dimedone in Ethanol were found to be increased with the increasing concentration at all temperatures. Moreover the increase in magnitude of φ_v values with an increase in molarities of Dimedone suggest that the presence of ion-ion interactions [59].

The increase of apparent molar volume values of Dimedone with concentrations may be attributed to the increase in solvent-solvent, solute-solvent and the solute-solute interactions.

However the φ_v values of Dimedone in Ethanol also increase with a rise in temperature in the system which suggests that at higher temperature significant solute-solvent interactions present in the mixtures.

Table 4.9: Apparent molar volume, φ_v of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone–Ethanol	0.05	133.09	133.69	134.34	135.07	135.76
	0.10	133.34	134.00	134.70	135.49	136.27
	0.15	133.61	134.31	135.05	135.91	136.76
	0.20	133.86	134.63	135.41	136.32	137.27
	0.25	134.11	134.93	135.77	136.74	137.77
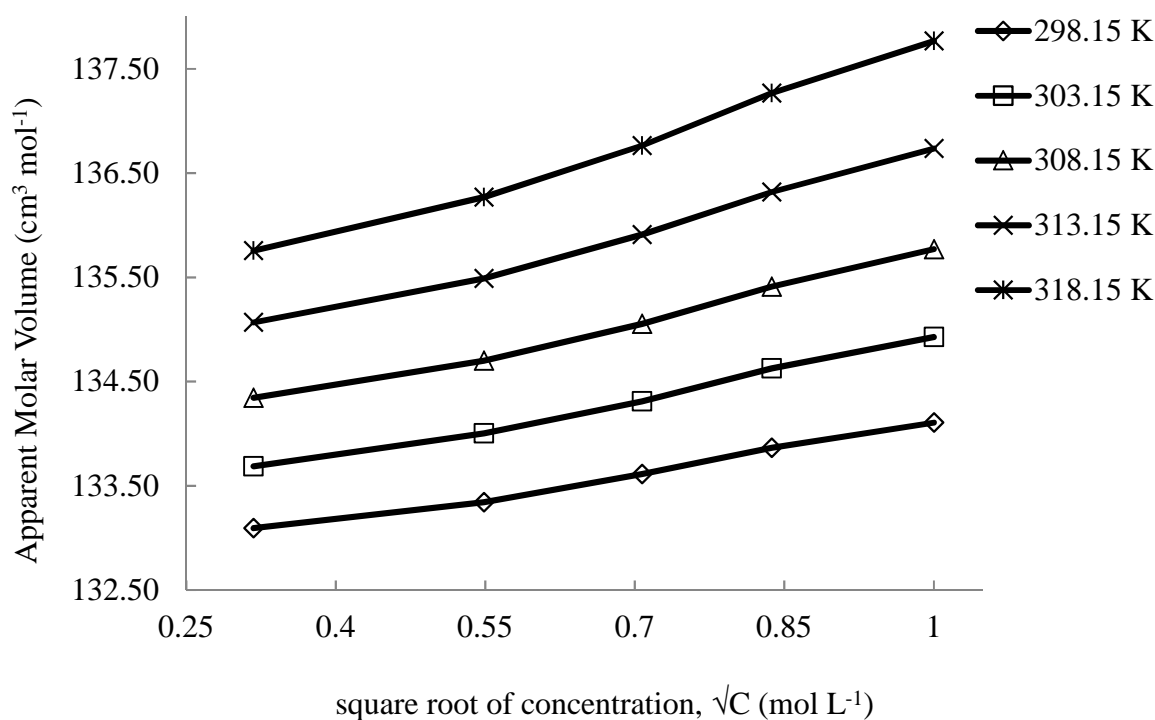
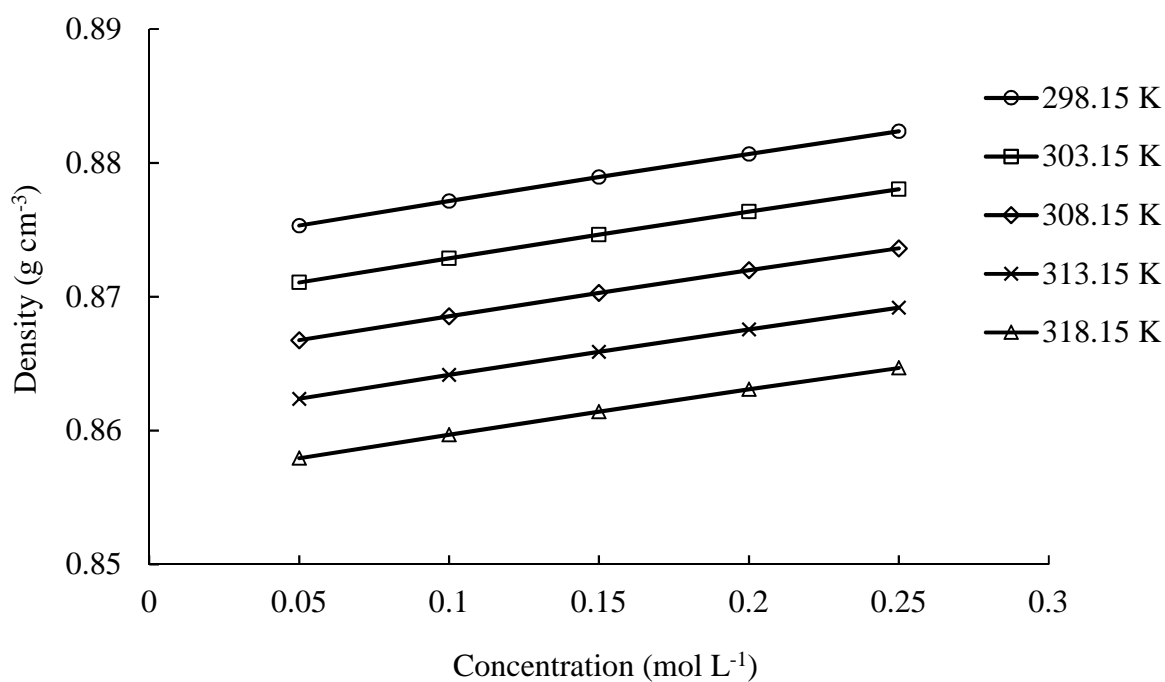Figure 4.8: Apparent molar volume vs square root of concentration of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

4.3.3 Apparent molar volume of Dimedone>Water>Ethanol Ternary System

The apparent molar volume of Dimedone in Water−Ethanol mixture systems have been determined at various concentration (0.05 to 0.25) M of Dimedone from 298.15 to 318.15 K temperature at 5 K interval by using equation 1.2.8. The values of apparent molar volume of the ternary systems have been shown in the Table 4.9. It is seen that like binary systems, apparent molar volume is also dependent upon the concentration of Dimedone as well as on temperature. The values have been found to be positive throughout the whole concentration range for Dimedone in all ternary solution. The apparent molar volume of Dimedone−Water−Ethanol system has found to be increased with increasing the concentration of Dimedone which suggested that in addition to ion-dipole interaction, ion-ion interaction might be supplemented there but solute-solute interaction became predominant in the ternary Dimedone−Water−Ethanol systems [59]. Moreover, apparent molar volumes were found to be increased with increasing

temperature at any concentration of the solution and the reason has been discussed earlier for the binary systems in section 4.3.1 and 4.3.2.

The graphical representation of the φ_V values of ternary systems has been shown in Figure 4.15-4.20. It is seen from the Figure 4.15-4.20 the stacked line of apparent molar volumes, φ_V versus concentration of Dimedone in Water−Ethanol solutions; represent the trend of the contribution of each apparent molar volume over concentration. From the Figure 4.15, 4.16, 4.17, 4.18, 4.19 and 4.20 it is seen that φ_v values increase against concentration of Dimedone in all cases of Dimedone−Water−Ethanol ternary solutions. From the above discussion about apparent molar volume reveals the following characteristics:

- ➢ Solute−solvent interaction in the Dimedone−Ethanol systems happened significantly
- ➢ Solute-solute interaction predominant in Dimedone−Ethanol system at higher concentration of Dimedone
- ➢ Significant presence of solute−solute, solute−solvent interaction in the ternary systems
- ➢ The apparent molar volume, φ_V are positive and large in magnitude
- ➢ φ_v increases with increasing temperature i.e., temperature effect on φ_v is quite significant
- ➢ With increasing concentration of Dimedone, φ_V is increased i.e., concentration effect is also significant.

Table 4.10: Apparent molar volume, φ_v of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

| Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [1:4] [Water–Ethanol]	0.05	139.43	140.11	140.66	141.14	141.61
	0.10	139.65	140.33	141.01	141.53	142.06
	0.15	139.89	140.57	141.33	141.92	142.51
	0.20	140.15	140.88	141.71	142.37	143.02
	0.25	140.41	141.21	142.04	142.76	143.53
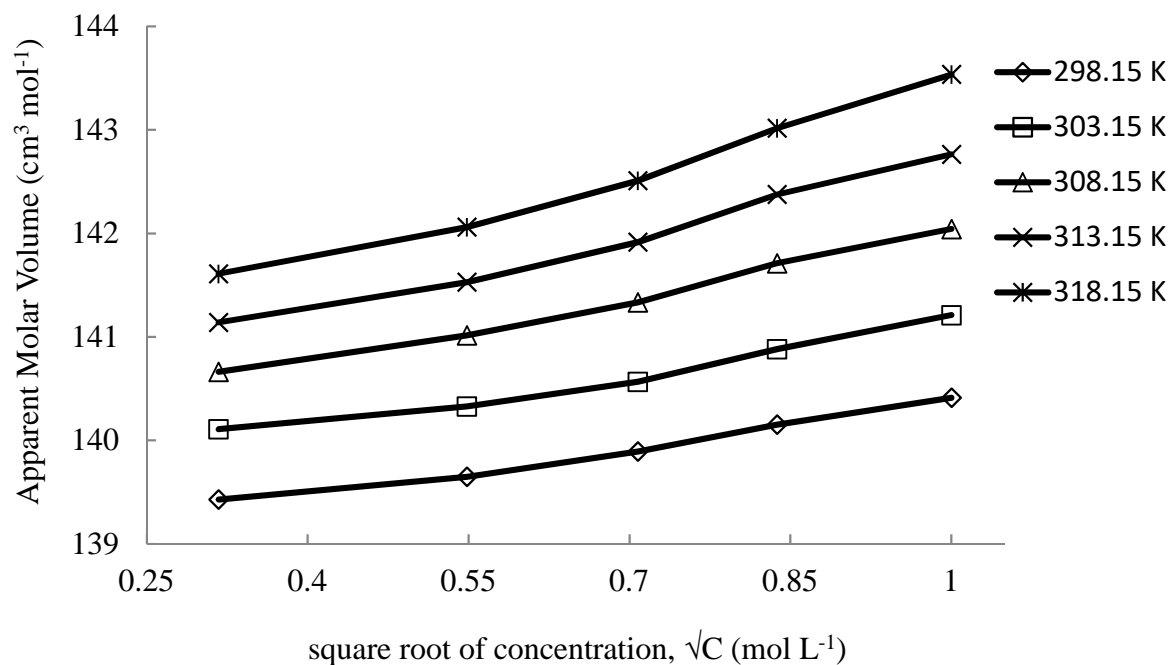
Figure 4.9: Apparent molar volume vs square root of concentration of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.11: Apparent molar volume of Dimedone in [2:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [2:3] [Water–Ethanol]	0.05	143.3873	143.6292	143.8931	144.1405	144.3989
	0.10	143.8752	144.1955	144.5084	144.8195	145.1166
	0.15	144.5335	144.9219	145.2510	145.6098	145.9538
	0.20	145.1414	145.5561	145.9514	146.3565	146.7734
	0.25	145.7662	146.2815	146.7892	147.3063	147.8092
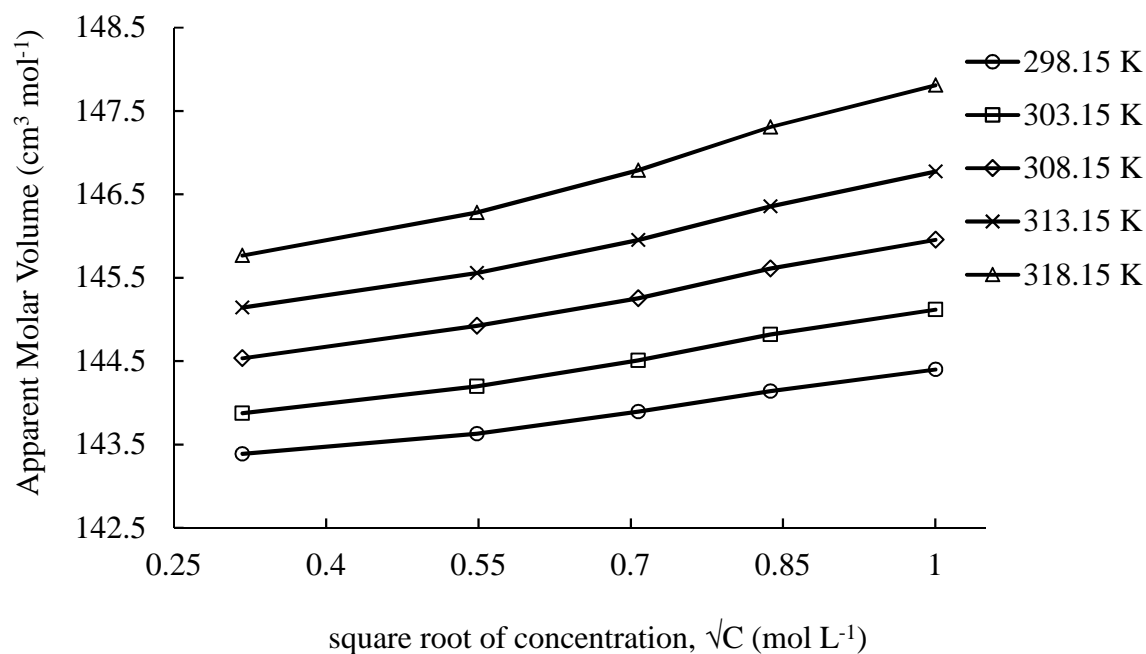
Figure 4.10: Apparent molar volume vs square root of concentration of Dimedone in [2:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.12: Apparent molar volume, φ_v of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [3:2] [Water–Ethanol]	0.05	131.80	132.21	132.71	133.13	133.60
	0.10	132.05	132.51	133.07	133.54	134.11
	0.15	132.31	132.82	133.43	133.94	134.61
	0.20	132.56	133.12	133.78	134.34	135.11
	0.25	132.80	133.43	134.14	134.74	135.62
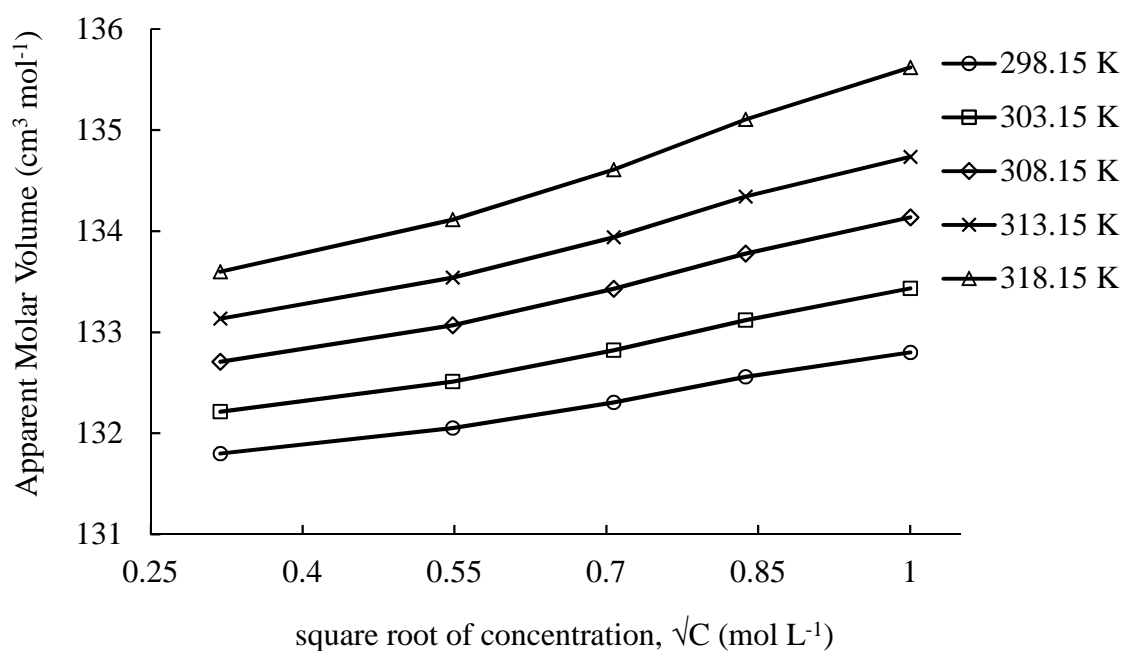
Figure 4.11: Apparent molar volume vs square root of concentration of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.13: Apparent molar volume, φ_v of Dimedone in [4:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [4:1] [Water–Ethanol]	0.05	124.24	124.90	125.61	126.36	127.06
	0.10	124.51	125.22	125.96	126.76	127.56
	0.15	124.74	125.51	126.32	127.15	128.07
	0.20	125.01	125.84	126.67	127.57	128.58
	0.25	125.26	126.15	127.03	127.98	129.10
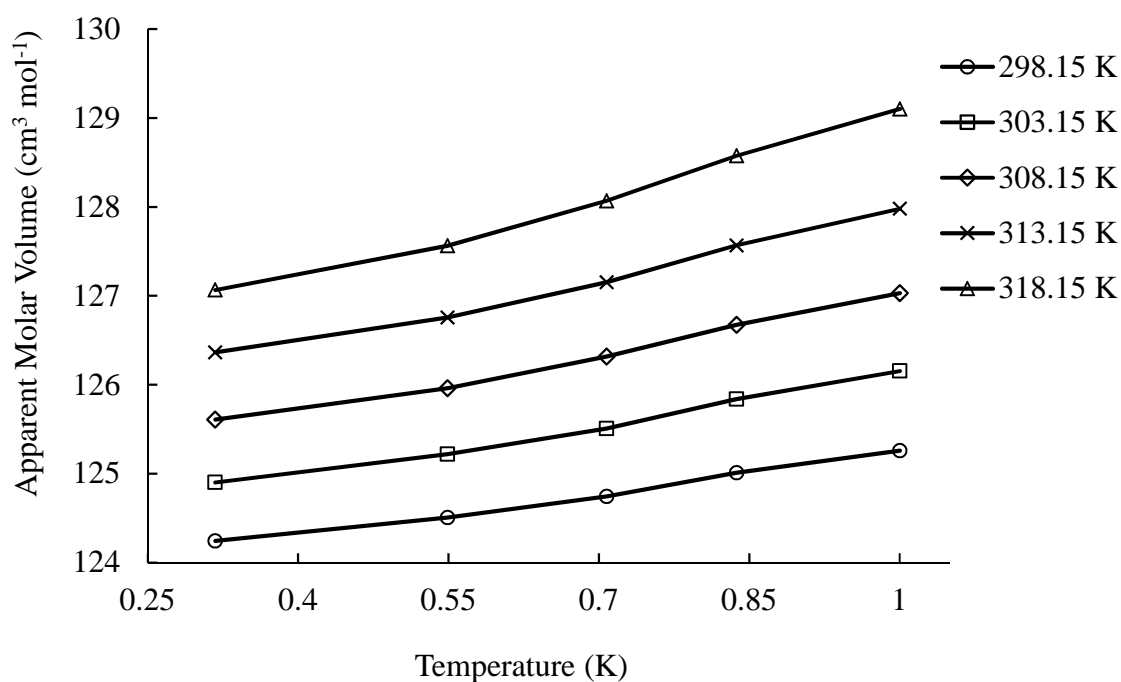
Figure 4.12: Apparent molar volume vs square root of concentration of Dimedone in [4:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.14: Apparent molar volume, φ_v of Dimedone in [1:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

| Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [1:1] [Water–Ethanol]	0.05	128.26	128.92	129.59	130.35	131.17
	0.10	128.78	129.45	130.19	131.01	131.83
	0.15	129.29	130.01	130.78	131.64	132.51
	0.20	129.80	130.55	131.39	132.30	133.19
	0.25	130.29	131.09	131.98	132.95	133.87
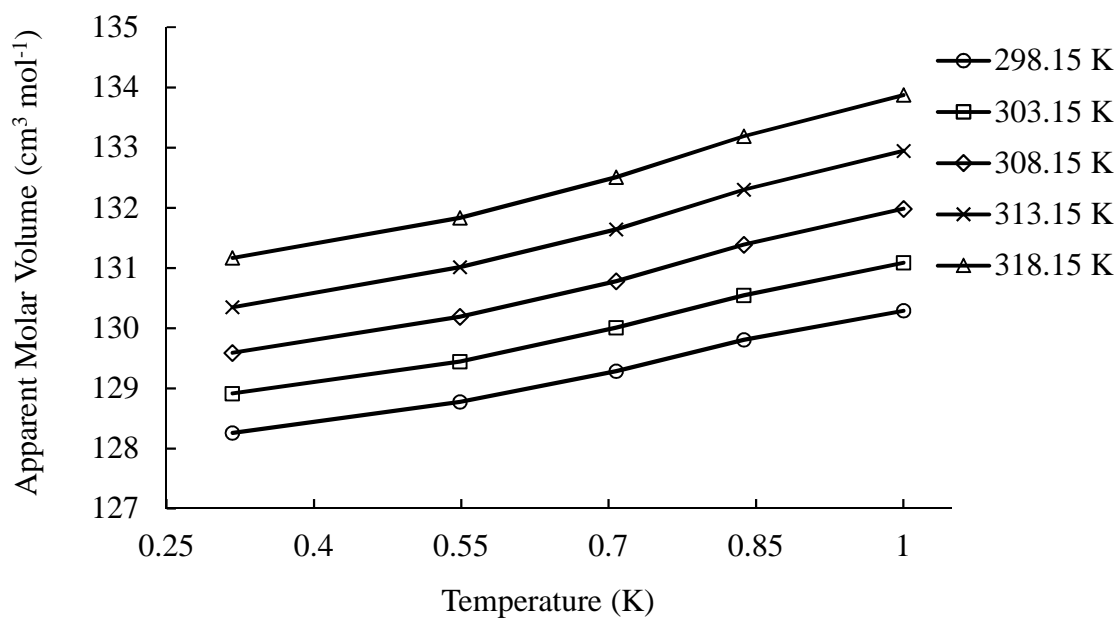
Figure 4.13: Apparent molar volume vs square root of concentration of Dimedone in [1:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.15: Apparent molar volume, φ_v of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

| Name of the system	Conc. (mol L^{-1})	Apparent molar volume, φ_v (cm^3 mol^{-1})				
		298.15K	303.15 K	308.15 K	313.1 K	318.15 K
Dimedone in [1:3] [Water–Ethanol]	0.05	117.45	118.58	119.64	120.67	121.71
	0.10	118.00	119.06	120.12	121.17	122.22
	0.15	118.55	119.60	120.67	121.72	122.72
	0.20	119.10	120.14	121.24	122.24	123.23
	0.25	119.62	120.70	121.84	122.83	123.84
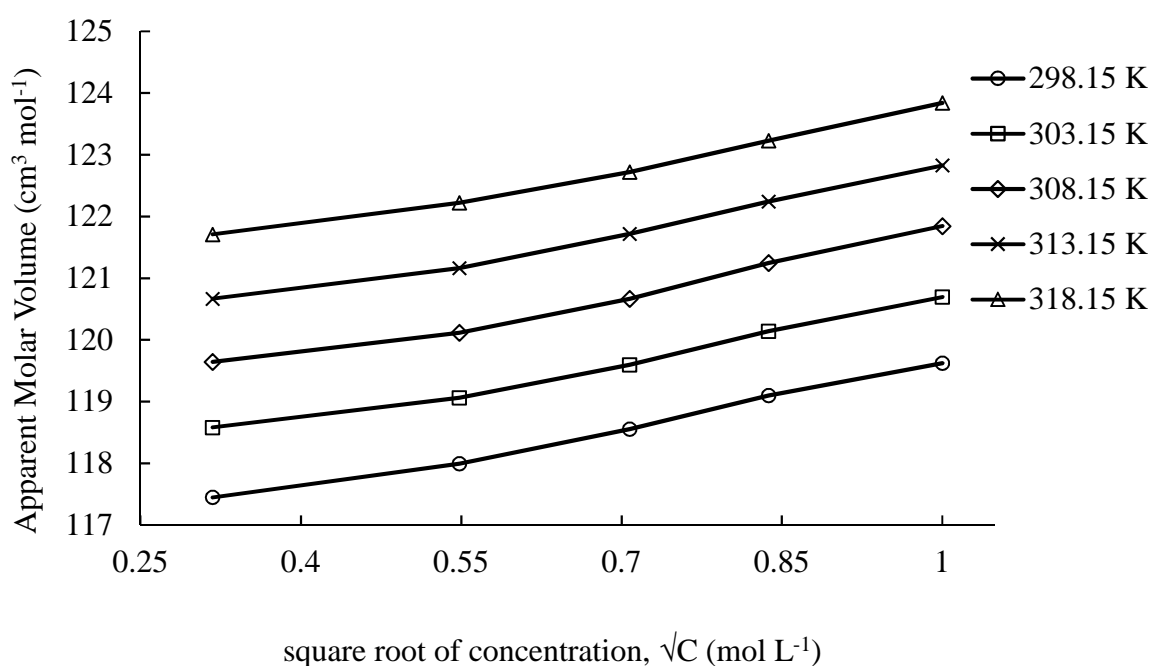
Figure 4.14: Apparent molar volume vs square root of concentration of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

4.4 Apparent molar volume at infinite dilution

Apparent molar volume at infinite dilution, φ_v^0 varies with the molarity of Dimedone as represented by the following equation. The apparent molar volume at infinite dilution gives an idea about the presence of solute−solvent interactions. The S_v is the experimental slopes which give an idea about the prevailing solute−solute interactions in the mixtures. The apparent molar volumes at infinite dilution, φ_v^0 values of Dimedone in Ethanol and Water−Ethanol mixtures have been tabulated in Table 4.16. The results can be revealed as a function of both temperature and the structure of Dimedone. The φ_v^0 values of Dimedone reflect the true value of Dimedone at the specified temperatures. Apparent molar volumes at infinite dilution were computed from intercept of the plot between φ_v and $C^{1/2}$ as per following Masson equation 1.2.13.

$$\varphi_v = \varphi_v^0 + S_v \sqrt{c}$$

The apparent molar volumes, φ_v and square root of concentration, $C^{1/2}$ have been computed formerly to evaluate the value of apparent molar volume at infinite dilution which is the experimental intercept of graph between φ_v and $C^{1/2}$ and is a function of ion−solvent interactions. In case of Dimedone−Ethanol solution the increase in φ_v^0 values with an increase in Dimedone molarity represents the volume expansion [59] due to less hydrophobic interactions. In the remaining ternary systems the same effect has been found. However the φ_v^0 values increase with a rise in temperature in all systems due to weaken all sorts of interactions at higher temperature present in the mixtures.

Table 4.16: Apparent molar volume, φ_v^0 at infinite dilution of Dimedone (DMD) in Ethanol and in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Temp. (K)	Apparent molar volume at infinite dilution, φ_v^0 (cm³ mol⁻¹)						
	DMD in Ethanol	DMD in [1:4] [Water– Ethanol]	DMD in [2:3] [Water– Ethanol]	DMD in [3:2] [Water– Ethanol]	DMD in [4:1] [Water– Ethanol]	DMD in [1:1] [Water– Ethanol]	DMD in [1:3] [Water– Ethanol]
298.15	132.2248	138.5757	142.5192	130.9447	123.717	126.5265	115.5886
303.15	132.6290	139.1399	142.8192	131.1691	124.249	127.0538	116.7534
308.15	133.1291	139.4819	143.3409	131.4926	124.8655	127.5464	117.7257
313.15	133.6486	139.7332	143.7566	131.7692	125.5157	128.1387	118.8108
318.15	134.0453	139.9533	144.0239	131.8847	125.9989	128.8549	119.9048

4.5 S_v parameter

The S_v parameter is the resultant of experimental slope of graph between φ_v and $C^{1/2}$ and is a function of ion–ion interactions. Sign of S_v gives information about the structural influence of solute on solvent system that is, whether solute acts as a structure promoting or structure breaker [60] of solvent or solvent mixture. The values of experimental slopes (S_v) have been represented in Table 4.17.

The positive values of S_v in Dimedone–Ethanol and Dimedone–Water–Ethanol solution predicts there is a strong solute-solute interaction present here [61].
It is found that values of S_v are positive for all binary and ternary solutions. It is seen from the table that Dimedone in [1:3] [Water–Ethanol] system having more solute–solute interactions in comparison to all other systems.

Table 4.17: S_v parameter of Dimedone (DMD) in Ethanol and in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Temp. (K)	DMD in Ethanol	DMD in [1:4] [Water–Ethanol]	DMD in [2:3] [Water–Ethanol]	DMD in [3:2] [Water–Ethanol]	DMD in [4:1] [Water–Ethanol]	DMD in [1:1] [Water–Ethanol]	DMD in [1:3] [Water–Ethanol]
298.15	3.6792	3.5500	3.6561	3.6260	3.6608	7.3520	7.8835
303.15	4.4848	3.9446	4.4917	4.4025	4.5060	7.8628	7.6357
308.15	5.1382	4.9890	5.1033	5.1532	5.1312	8.6396	7.9435
313.15	6.0148	5.8982	5.8664	5.7848	5.8220	9.3645	7.7727
318.15	7.2543	6.9153	7.3800	7.2659	7.3310	9.7626	7.5769

4.6 Apparent molar expansivity

The parameter that measures the variation of volume with temperature is the apparent molar expansivity, φ_E which was defined by the equation 1.2.19. These values of apparent molar expansivities at infinite dilution φ_E^0 are shown in Table 4.18. The expansivity values are positive at all the investigated temperatures. Positive values indicate that, on heating some Dimedone molecules may be released from the solvation layer of ion. It may also be conferred that the positive φ_E^0 values may be originated from the hydrophobic character and steric effect of the Dimedone. As a whole there is a hydrophilic/hydrophobic balance among the solute and solvent molecules.

The φ_E^0 values are found to be positive at all temperatures and concentrations of Dimedone. It is observed that the values of φ_E^0 for all ternary solutions of Dimedone decrease with increase in temperature. The positive values of φ_E^0 as reported in Table 4.18 suggests the presence of solute-solvent interactions in these systems, as already indicated by apparent molar volume data [62].

Table 4.18: Apparent molar expansivity at infinite dilution φ_E^0 values of Dimedone (DMD) in ethanol and in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water–Ethanol] mixtures at 298.15 to 318.15 K at 5 K interval

Temp. (K)	Apparent molar expansivity at infinite dilution, φ_E^0 (cm³ mol⁻¹ K⁻¹)						
	DMD in Ethanol	DMD in [1:4] [Water–Ethanol]	DMD in [2:3] [Water–Ethanol]	DMD in [3:2] [Water–Ethanol]	DMD in [4:1] [Water–Ethanol]	DMD in [1:1] [Water–Ethanol]	DMD in [1:3] [Water–Ethanol]
298.15	0.1341	0.1078	0.1204	0.0903	0.1420	0.1449	0.2122
303.15	0.1467	0.1203	0.1333	0.1030	0.1530	0.1537	0.2111
308.15	0.1581	0.1316	0.1447	0.1143	0.1658	0.1615	0.2092
313.15	0.1699	0.1444	0.1573	0.1262	0.1771	0.1703	0.2071
318.15	0.1825	0.1559	0.1695	0.1387	0.1901	0.1806	0.2113

4.7 Viscometric Properties

Having enormous medicinal and biological applications of Dimedone in human body, its viscometric investigation in versatile solvent water and in common organic solvent Ethanol as well as in Water–Ethanol mixed solvents might be interesting. Water–Ethanol mixtures are very important systems exhibiting properties that are of great interest in physics, chemistry and biology. Due to this reason viscometric behavior of Dimedone in Ethanol and Water–Ethanol mixture system is also fascinating and has been discussed.

4.7.1 Viscosity of pure solvent

The viscosity at different temperatures of the pure solvents; ethanol and water have been tabulated in Table 4.19 with the literature values [38-40 and 56] for possible comparison. The larger viscosity values of ethanol indicate that ethanol is more viscous than water at all investigated temperatures. From viscosity values of ethanol and water it is seen that viscosities of ethanol are higher at all temperatures than those of water which correlate the density results of the solvents in Table 4.1. From the table it is also seen that viscosities of the solvents decreased with the increasing temperature as expected and provide almost similar results as mentioned in the cited literatures. It indicates that the solvents being used in the experiments were pure and analytical grade as declared by suppliers.

Table 4.19: Viscosity, values of Ethanol and Water at 298.15 to 318.15 K at 5 K interval

Temp. (K)	Viscosity (mPa.s) of Ethanol		Viscosity (mPa.s) of Water	
	Literature Value	Experimental Value	Literature Value	Experimental Value
298.15	1.0820[63]	1.0843	0.8926 [56]	0.8927
303.15	0.9870[63]	0.9972	0.8007 [56]	0.8011
308.15	0.9015[64]	0.9113	0.7234 [56]	0.7235
313.15	0.8284[65]	0.8029	0.6579 [56]	0.6578
318.15	0.7642[64]	0.7037	0.6017 [56]	0.6007

Table 4.20: Experimental viscosity values, η of [4:1], [3:2], [2:3] [1:4], [1:1] and [1:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Experimental Value, η (mPa.s)				
	298.15K	303.15K	308.15K	313.15K	318.15K
[1:4] [Water–Ethanol]	1.6653	1.4049	1.2640	1.0697	0.9249
[2:3] [Water–Ethanol]	2.1518	1.7755	1.5845	1.3507	1.1728
[3:2] [Water–Ethanol]	1.9944	1.7039	1.4192	1.2289	1.0406
[4:1] [Water–Ethanol]	1.3218	1.1418	0.9726	0.8239	0.7532
[1:1] [Water–Ethanol]	1.9805	1.7350	1.4850	1.2918	1.1172
[1:3] [Water–Ethanol]	1.7451	1.5569	1.3545	1.1825	1.0718

4.7.2 Viscosity of Dimedone-Ethanol Binary Solvent

The viscosities, η of binary system Dimedone-Ethanol have been studied at 298.15, 303.15, 308.15, 313.15, and 318.15 K temperature over a concentration range of (0.05 to 0.25) M of Dimedone. The experimented results are tabulated in Table 4.21. The viscosity values in Dimedone-Ethanol systems increased with the increase of concentration as expected and the graphical presentation has been shown here in Figure 4.15. The values of the binary systems are also greater than the values of the pure solvents which have been shown in Table 4.19. The increase of η values of Dimedone with concentration can be attributed to the increase in solute–solvent, solvent–solvent and solute–solute interactions in solution. The wide range of dissolution of Dimedone in Ethanol might have intriguing aspects which may be the consequence of the great ability of ethanol to make dipole-dipole, ion-dipole and hydrogen bonds with Dimedone. At the same time it is seen that the viscosity values decrease considerably with the rise in temperature at a constant molarity. In both cases with the increase of temperature in binary systems the internal energy of the system increased and as because of this the solute-solute or solute-solvent interaction may be depleted.

Table 4.21: Viscosities, η of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

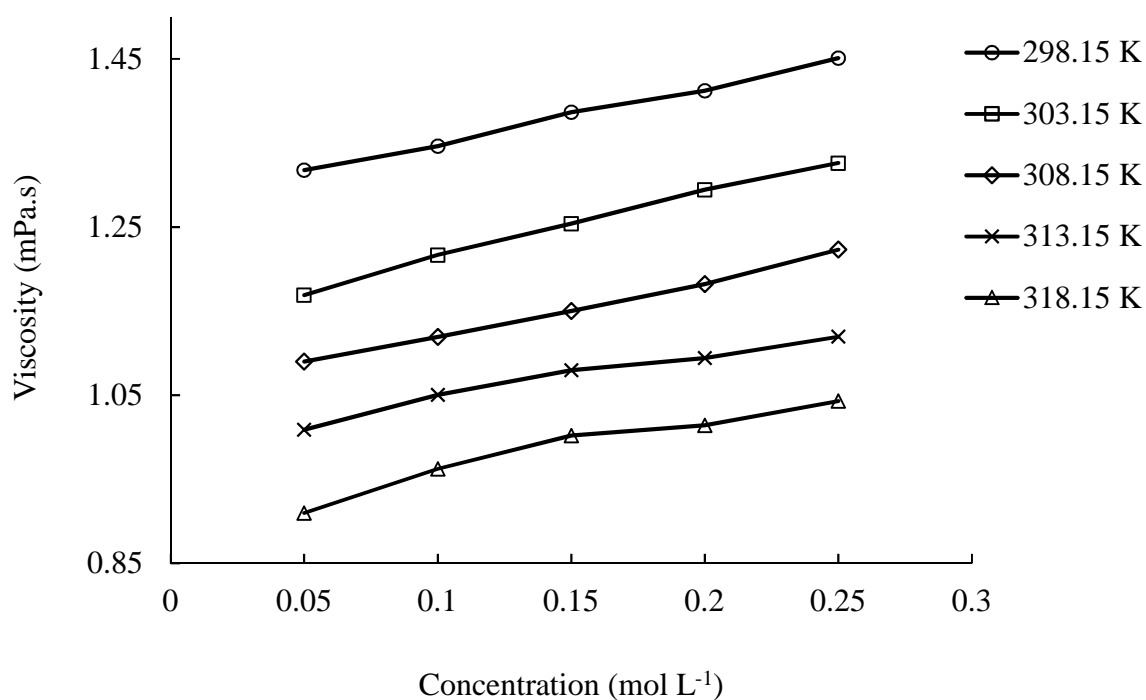| Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone-Ethanol	0.05	1.3178	1.1691	1.0900	1.0090	0.9100
	0.10	1.3464	1.2167	1.1195	1.0506	0.9625
	0.15	1.3865	1.2542	1.1504	1.0796	1.0023
	0.20	1.4123	1.2945	1.1822	1.0941	1.0145
	0.25	1.4510	1.3262	1.2232	1.1196	1.0432

Figure 4.15: Viscosities vs concentration of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

4.7.3 Viscosity of Dimedone–Water–Ethanol Ternary Systems

The viscosities, η of Dimedone in [4:1], [3:2], [2:3], [1:4], [1:1] and [1:3] [Water–Ethanol] systems have been described at 298.15, 303.15, 308.15, 313.15, and 318.15 K temperature over a concentration range of (0.05 to 0.25) M. The values of the viscosity of ternary systems have been tabulated in Table 4.22-4.27. The results are also presented graphically in Figure 4.16, 4.17, 4.18, 4.19, 4.20 and 4.21. From the table we can see that the viscosity values are positive in all ternary systems and are greater than (Dimedone–Ethanol) binary systems as shown in Table 4.20 and even those of the solvents (Table 4.19). So there may be much more solute-solute or solute-solvent interactions in the ternary systems than the others. Viscosity values increased significantly with the increase in concentration of Dimedone. At the same time it is seen that the viscosity values decreased considerably with temperature at a constant molarity as expected. The reason is been discussed earlier in the section 4.7.2. The reason of more interactions in ternary systems may be due to the fact that Ethanol, Water and Water–Ethanol systems can be stabilized by hydrogen-bonded structure. Also each Dimedone consists of two methyl group which provide hydrophobic interaction with Ethanol. So water is polar it attracts –OH group of ethanol and aliphatic group on the other hand can have the hydrophobic interaction with the non-polar group of Dimedone. Thus the solubility of ternary solution is therefore become facile or make available more of the interactions and offer more organized structures. At the same time the polar groups of Dimedone get easily mixed with the polar solvent Water. Because of the strength of the attraction of the –OH group, ethanol is completely miscible with water [66]. It dissolves in water in any amount. On the other hand Dimedone contains two polar groups; –CO and –OH. Using this, Dimedone make strong interactions in Dimedone–Water–Ethanol ternary systems. In case of ternary, binary and solvent systems the viscosity maxima follow the order:

Dimedone in [4:1] [Ethanol−Water] > Dimedone in [3:2] [Ethanol−Water] > Dimedone in [1:1] [Ethanol−Water] > Dimedone in [2:3] [Ethanol−Water] > Dimedone in [1:3] [Ethanol−Water] > Dimedone in [1:4] [Ethanol−Water]

Table 4.22: Viscosities, η of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:4] [Water–Ethanol]	0.05	1.8617	1.6562	1.4398	1.2748	1.1315
	0.10	2.0003	1.7618	1.5244	1.3476	1.2079
	0.15	2.0648	1.8160	1.5841	1.3815	1.2526
	0.20	2.1015	1.8544	1.6237	1.4304	1.2942
	0.25	2.1512	1.8946	1.6751	1.4724	1.3566

Figure 4.16: Viscosities vs concentration of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.23: Viscosities, η of Dimedone in [2:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [2:3] [Water–Ethanol]	0.05	2.3269	2.0196	1.7043	1.5000	1.30442
	0.10	2.4308	2.1096	1.8030	1.5551	1.3847
	0.15	2.5233	2.1716	1.8509	1.6066	1.4381
	0.20	2.5911	2.2460	1.8972	1.6785	1.4915
	0.25	2.6390	2.3047	1.9588	1.7274	1.5549

Figure 4.17: Viscosities vs concentration of Dimedone in [2:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.24: Viscosities, η of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [3:2] [Water–Ethanol]	0.05	2.1873	1.8649	1.5739	1.3693	1.2051
	0.10	2.2398	1.9726	1.6759	1.4619	1.2729
	0.15	2.2747	2.0306	1.7297	1.5266	1.3278
	0.20	2.3253	2.0805	1.7835	1.5697	1.3627
	0.25	2.3933	2.1346	1.8337	1.6170	1.4117

Figure 4.18: Viscosities vs concentration of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.25: Viscosities, η of Dimedone in [4:1] [Water–Ethanol] system at 298.15 to
318.15 K at 5 K interval

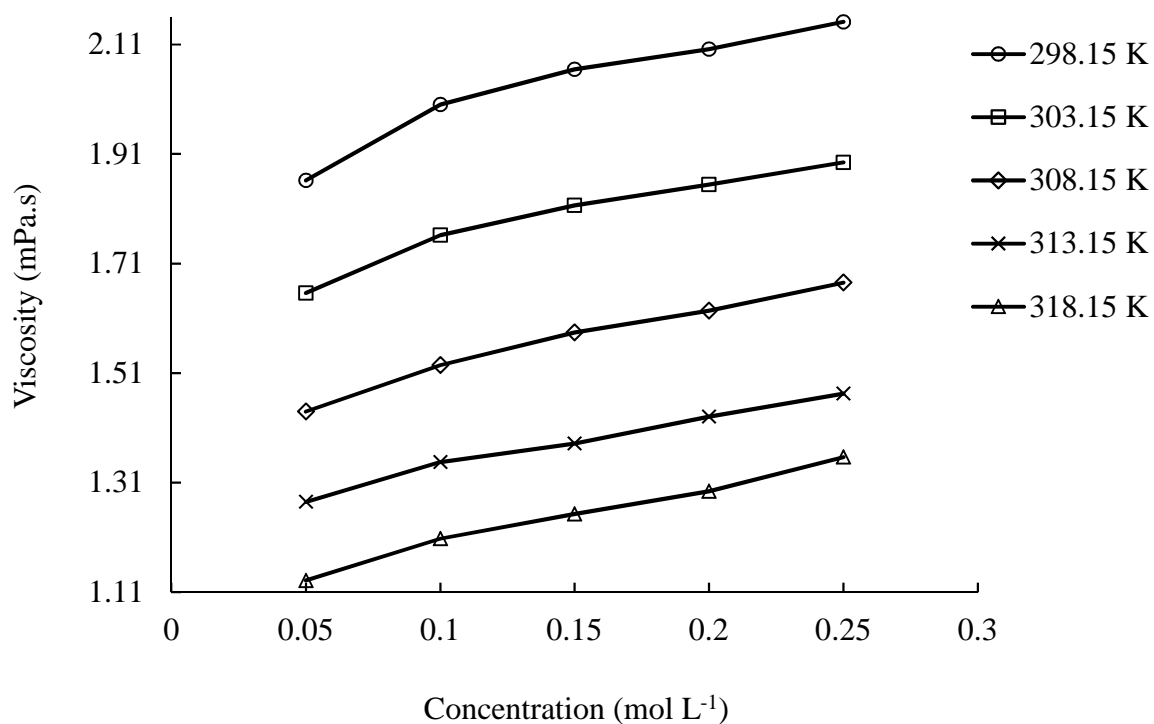| Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [4:1] [Water–Ethanol]	0.05	1.4747	1.2747	1.1083	0.9709	0.8699
	0.10	1.5354	1.3643	1.1955	1.0479	0.9322
	0.15	1.6050	1.4234	1.2514	1.1034	0.9830
	0.20	1.6744	1.4750	1.2964	1.1561	1.0363
	0.25	1.7397	1.5355	1.3594	1.2089	1.0810

Figure 4.19: Viscosities vs concentration of Dimedone in [4:1] [Water–Ethanol] system
at 298.15 to 318.15 K at 5 K interval

Table 4.26: Viscosities, η of Dimedone in [1:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

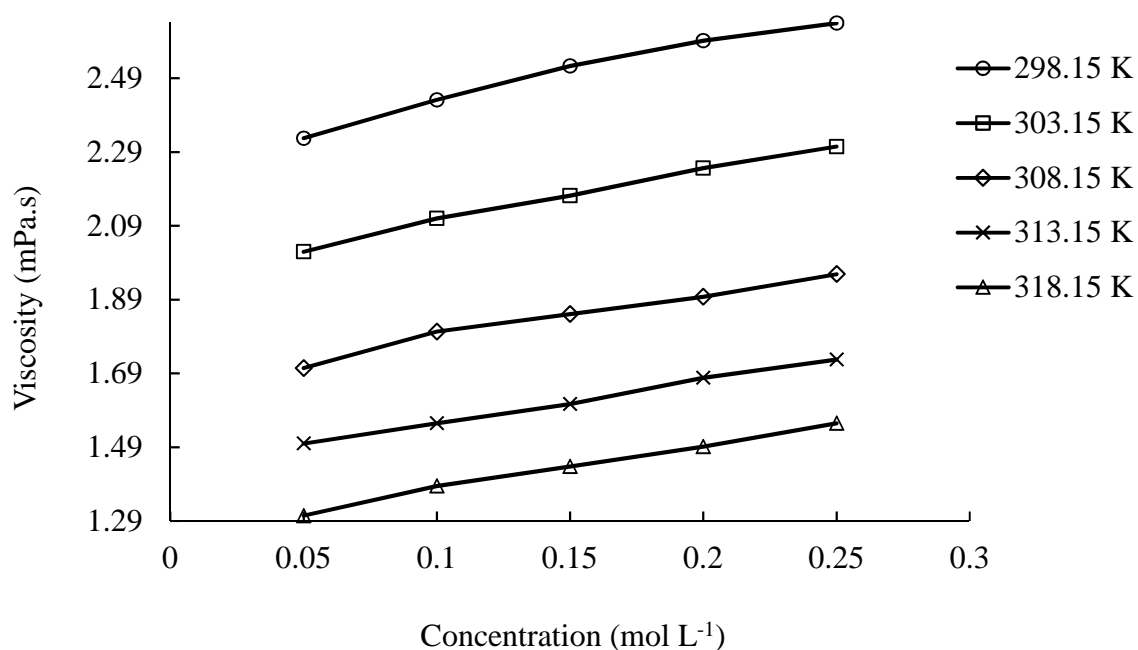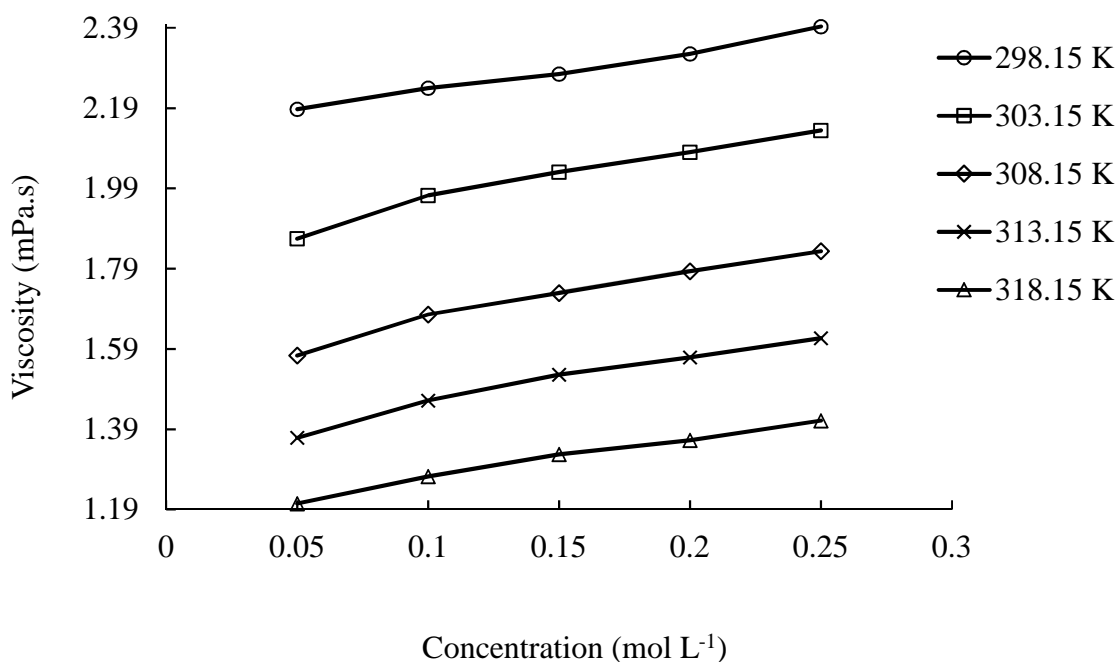| Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:1] [Water–Ethanol]	0.05	2.2862	1.9503	1.6884	1.4492	1.2580
	0.10	2.3454	2.0046	1.7469	1.5087	1.3106
	0.15	2.4050	2.0492	1.8060	1.5628	1.3520
	0.20	2.4794	2.0993	1.8710	1.6158	1.4139
	0.25	2.5404	2.1595	1.9392	1.6610	1.4742

Figure 4.20: Viscosities vs concentration of Dimedone in [1:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Table 4.27: Viscosities, ɤ of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

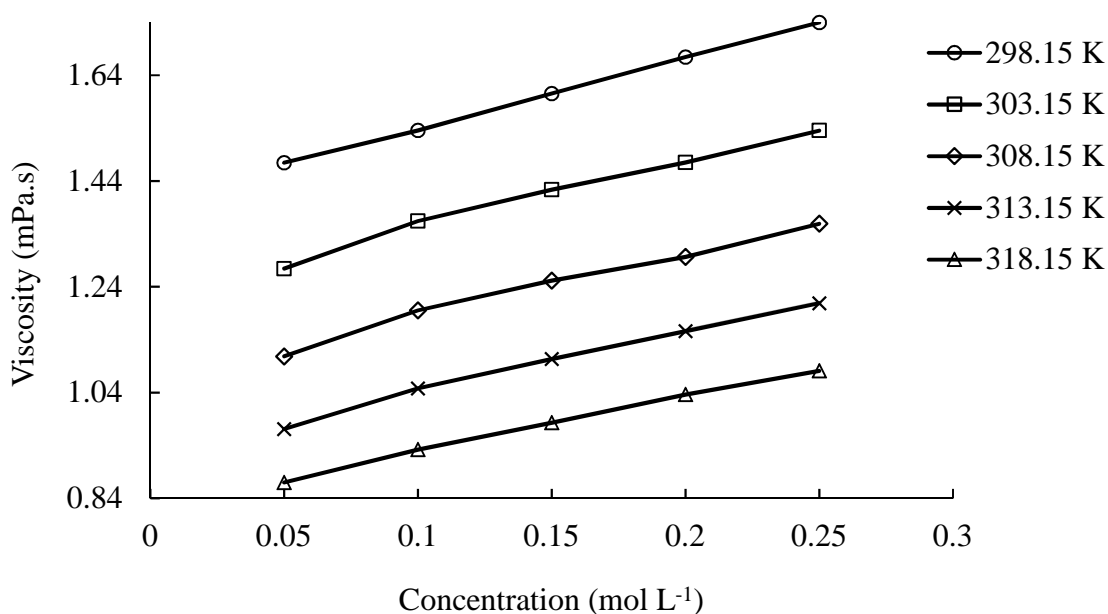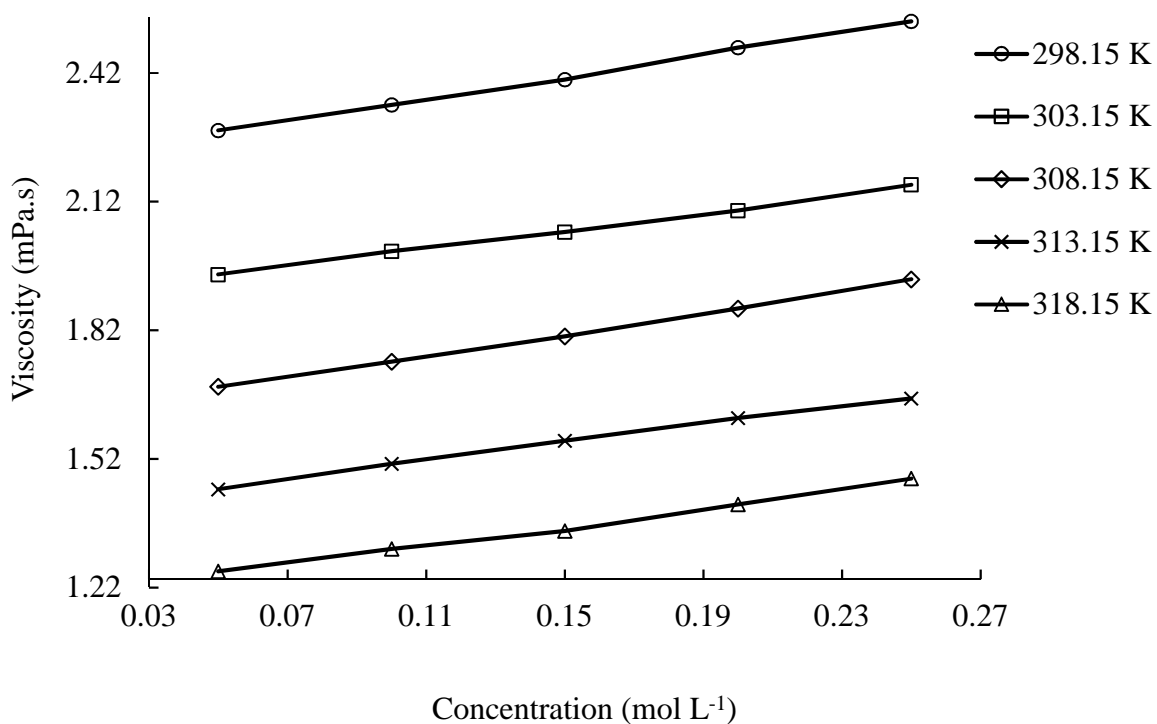| Name of the system	Conc. (mol L^{-1})	Viscosity, η (mPa.s)				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:3] [Water–Ethanol]	0.05	2.0097	1.7952	1.5834	1.3920	1.2244
	0.10	2.1338	1.9105	1.6729	1.4619	1.3011
	0.15	2.2374	1.9878	1.7412	1.5235	1.3841
	0.20	2.3089	2.0579	1.8162	1.5959	1.4447
	0.25	2.3739	2.1169	1.8865	1.6512	1.5152
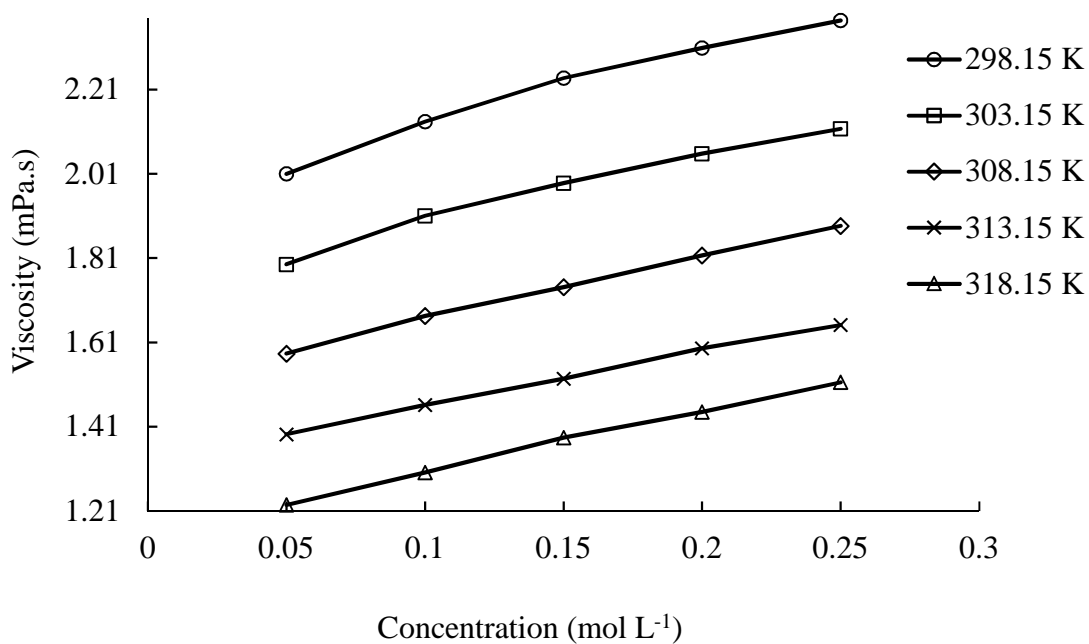
Figure 4.21: Viscosities vs concentration of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

4.7.4 Jones-Dole co-efficient

The Jones-Dole co-efficient, A, reflects the effect of solute-solute interaction and B, is a measure of structural modifications induced by the solute-solvent interaction. The viscosity co-efficient A and B were obtained from the intercept and slope of the plots (η_{rel} -1)/$C^{1/2}$ against $C^{1/2}$. The values of A and B are listed in Table 4.28-4.31 shows that A and B co-efficient has positive and negative values respectively. Positive values of A co-efficient indicate the presence of strong solute-solute interactions and the negative values of B co-efficient point out the existence of weak ion-solvent interaction in the investigated systems at the all specific temperatures [67]. Both values show variation with the increasing temperature.

A and B co-efficient support the behavior of φ_V, S_v and φ_v^0 which all suggest that solute-solute interactions are predominant over solute-solvent interaction in all experimented systems.

Table 4.28: Jones-Dole co-efficient for Dimedone in Ethanol and in [1:4] [Water–Ethanol] system

Temp (K)	Dimedone-Ethanol		Dimedone in [1:4] [Water–Ethanol]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	0.7705	-0.4805	0.4222	-0.1258
303.15	0.6026	-0.2982	0.6489	-0.3147
308.15	0.6865	-0.3898	0.4782	-0.1625
313.15	0.9447	-0.5973	0.6789	-0.3299
318.15	1.0758	-0.6373	0.7788	-0.3483

Table 4.29: Jones-Dole co-efficient for Dimedone in [2:3] and [3:2] [Water–Ethanol] system

Temp (K)	Dimedone in [2:3] [Water–Ethanol]		Dimedone in [3:2] [Water–Ethanol]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	0.2639	-0.0330	0.3271	-0.1496
303.15	0.4695	-0.1880	0.3199	-0.0668
308.15	0.2467	-0.0101	0.3671	-0.0749
313.15	0.3502	-0.0851	0.3791	-0.0593
318.15	0.3579	-0.0399	0.5388	-0.1979

Table 4.30: Jones-Dole co-efficient for Dimedone in [4:1] and [1:1] [Water–Ethanol] system

Temp (K)	Dimedone in [4:1] [Water–Ethanol]		Dimedone in [1:1] [Water–Ethanol]	
	A co-efficient	B co-efficient	A co-efficient	B co-efficient
298.15	0.3556	-0.0532	0.5345	-0.2824
303.15	0.3729	-0.0301	0.4265	-0.2073
308.15	0.4554	-0.0644	0.4517	-0.1711
313.15	0.5861	-0.1303	0.4037	-0.1309
318.15	0.4899	-0.0622	0.4003	-0.1040

Table 4.31: Jones-Dole co-efficient for Dimedone in [1:3] [Water–Ethanol] system

Temp (K)	Dimedone in [1:3] [Water–Ethanol]	
	A co-efficient	B co-efficient
298.15	0.5144	-0.1593
303.15	0.5231	-0.1712
308.15	0.5641	-0.1925
313.15	0.5904	-0.2174
318.15	0.4392	-0.0339

From the above discussion following possible interaction mechanism may be proposed:

Dimedone and water may be interacted through hydrogen bond as follows:

Two types structures i) Case formation and ii) Linear structure may be attained.

i) Case formation mechanism
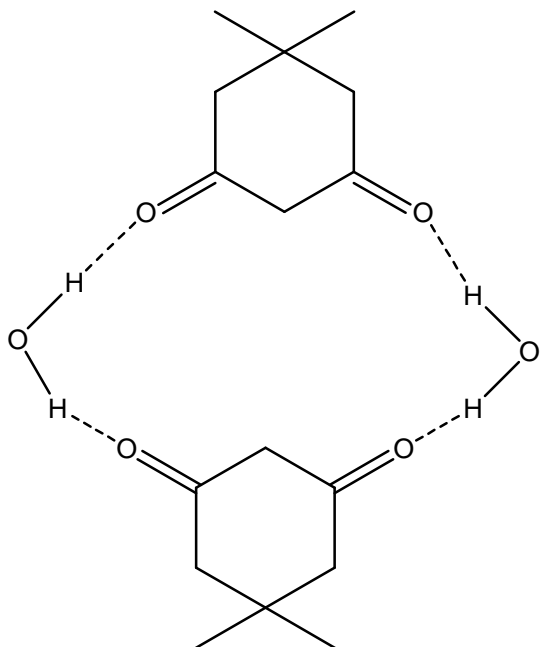
ii) Linear structure formation
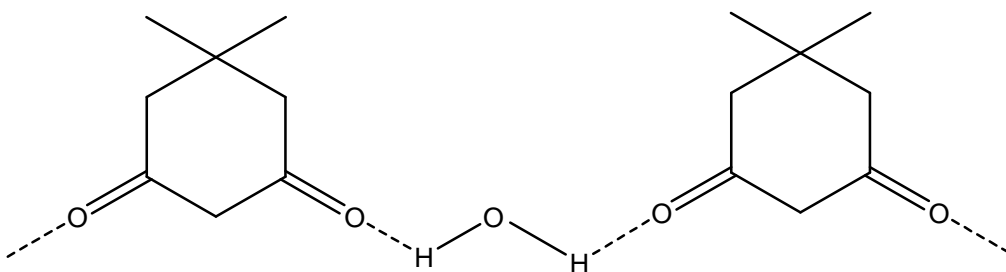
In Water-ethanol solvent system interaction mechanism can be explained by the following H- bonded:
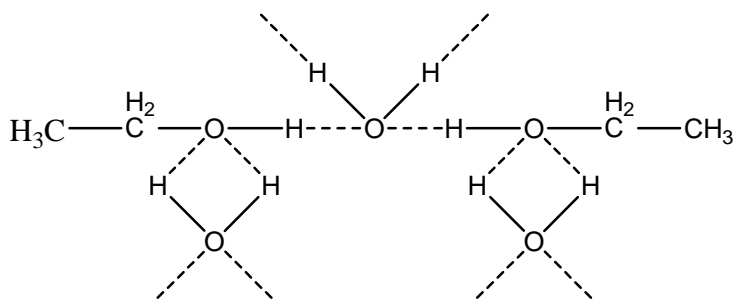
Dimedone in ethanol may form hemiacetal according to following reaction mechanism. The mechanistic steps are:

i) Protonation of the carbonyl
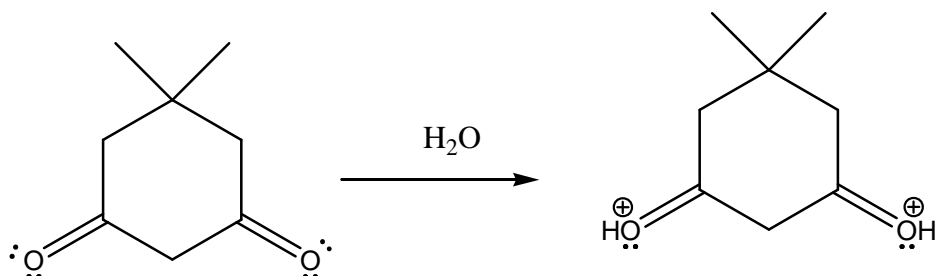
ii) Nucleophilic attack by the alcohol
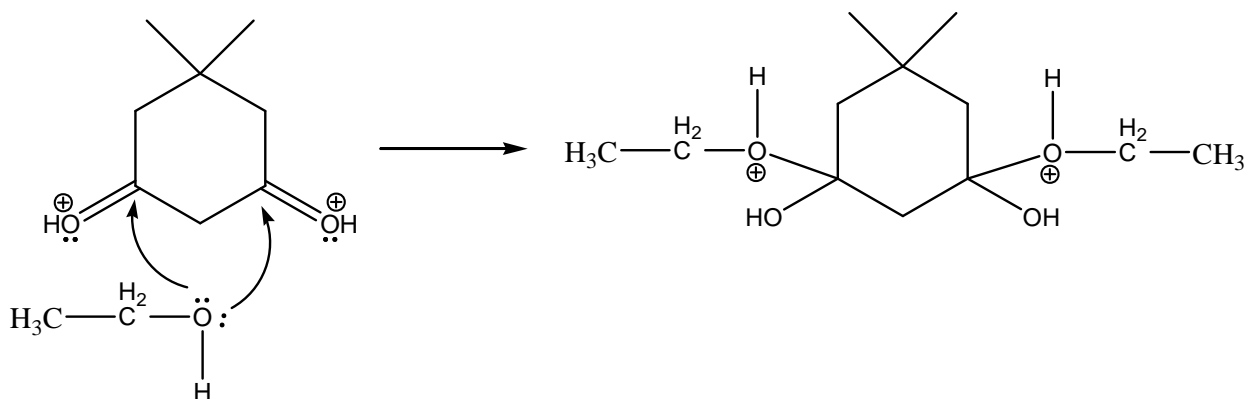
iii) Deprotonation to form hemiacetal

Hemiacetal
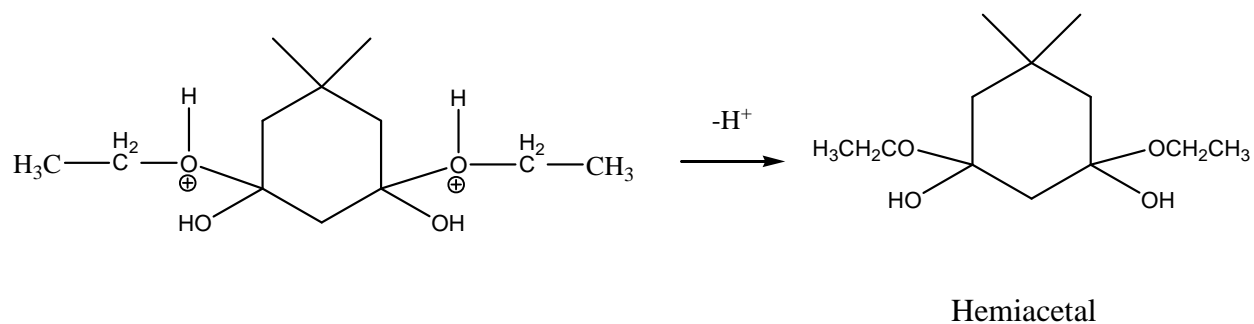
4.8 Thermodynamics Properties

The change in viscosity of Dimedone in different solvents can make a significant contribution to thermodynamic properties of the solution, such as enthalpy, entropy, and other properties in solution. So in this section different thermodynamic parameters such as, change of free energy, ΔG^*, change of enthalpy, ΔH^*, change of entropy, ΔS^* for viscous flow for Dimedone in different solvent systems have been discussed.

Thermodynamic properties, change of free energy, ΔG^*, change of enthalpy, ΔH^*, change of entropy, ΔS^* for viscous flow have been calculated from viscometric data via Eyring equation. Gibbs free energy is a thermodynamic function and the energy of the system which is ready to work. The Gibbs free energy is used when considering processes that occur under constant pressure and temperature conditions. For a process that occurs at constant temperature and pressure, spontaneity can be determined using the change in Gibbs free energy, which is given by the sign, ΔG; depends on the changes in enthalpy (ΔH) and entropy (ΔS), as well as on the absolute temperature (T).

In cases where ΔG [68] is:

- Negative, the process is spontaneous and may proceed in the forward direction as written.
- Positive, the process is non-spontaneous as written, but it may be proceed spontaneously in the reverse direction.
- Zero, the process is at equilibrium, with no net change taking place over time.

The ΔG^*, values are positive for all the studied systems Dimedone−ethanol and Dimedone−Water−Ethanol indicate that studied systems are non-spontaneous for the flow process as shown in Table 4.32 to 4.38 and it is spontaneous in the reverse direction. The positive free energy change, ΔG^* for viscous flow may be interpreted by Furth model [69] which states that kinetic species involved in forming holes in the investigated solution systems may be stated by the work is required in forming the holes against surface tension of the solution. Positive ΔG^* values also explain the interstitial incorporation, solute−solvent interaction that render the binary and ternary systems are more structured.

Enthalpy is the thermodynamic quantity equivalent to the total heat content of a system. It is defined as the sum of internal energy of a system and the product of the pressure and volume of the system or pressure-volume work. Internal energy is the sum of translational energy, rotational energy, vibrational energy and the kinetic energy of a matter. The change in enthalpy is the sum of the change in the internal energy and the work done. Entropy is a measure of disorder or randomness of a system. In other words, it's a measurement of the degree of randomness of energy in a system. An ordered system has low entropy. A disordered system has high entropy.

The set of rules can be used to determine four distinct cases by examining the signs of the ΔS and ΔH [68].

- When $\Delta S > 0$ and $\Delta H < 0$, the process is always spontaneous as written.
- When $\Delta S < 0$ and $\Delta H > 0$, the process is never spontaneous but the reverse process is always spontaneous.
- When $\Delta S > 0$ and $\Delta H > 0$, the process will be spontaneous at high temperatures and non-spontaneous at low temperatures.
- When $\Delta S < 0$ and $\Delta H < 0$, the process will be spontaneous at low temperatures and non-spontaneous at high temperatures.
- For the latter two cases, the temperature at which the spontaneity changes will be determined by the relative magnitudes of ΔS and ΔH.

The change enthalpy, ΔH^* values are positive for all the studied system as shown in Table 4.39-4.45.The positive ΔH values indicate that work has to be done for all the investigated systems. That is, the viscous flow is not thermodynamically favored for the systems studied. The change of entropy, ΔS^* of the investigated systems are shown in same Table 4.39-4.45. The ΔS^* values are negative for all the systems studied except Dimedone–Ethanol system. This means that except Dimedone–Ethanol system other binary and ternary systems are regular than those of the pure one. Here one point may be remarked that as $\Delta S < 0$ and $\Delta H > 0$, so the processes (except Dimedone–Ethanol systems) are never spontaneous but the reverse process is always spontaneous. In case of my studied temperatures these systems were found to be non-spontaneous.

Table 4.32: Free energy, ΔG* of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone-Ethanol	0.05	15774.57	15751.47	15846.30	15917.28	15913.74
	0.10	15827.83	15852.05	15914.60	16022.43	16062.08
	0.15	15900.62	15928.46	15984.33	16093.45	16169.21
	0.20	15946.27	16008.22	16054.25	16128.19	16201.22
	0.25	16013.21	16069.24	16141.57	16188.07	16274.94

Table 4.33: Free energy, ΔG*of Dimedone in [1:4] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:4] [Water–Ethanol]	0.05	16435.10	16428.68	16353.90	16316.11	16275.14
	0.10	16613.09	16584.33	16500.19	16460.57	16448.15
	0.15	16691.73	16660.77	16598.58	16525.26	16544.18
	0.20	16735.45	16713.53	16661.96	16615.84	16630.68
	0.25	16793.36	16767.49	16741.79	16691.25	16755.07

Table 4.34: Free energy, ΔG*of Dimedone in [2:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [2:3] [Water–Ethanol]	0.05	16858.79	16795.85	16649.63	16599.51	16507.66
	0.10	16967.06	16905.74	16793.96	16693.44	16665.63
	0.15	17059.66	16978.67	16861.05	16778.28	16765.64
	0.20	17125.37	17063.63	16924.33	16892.20	16862.07
	0.25	17170.84	17128.61	17006.26	16966.92	16972.29

Table 4.35: Free energy, ΔG*of Dimedone in [3:2] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [3:2] [Water–Ethanol]	0.05	16605.78	16491.49	16338.44	16250.59	16182.99
	0.10	16664.51	16632.90	16499.28	16421.26	16327.81
	0.15	16702.86	16706.01	16580.24	16534.08	16438.85
	0.20	16757.46	16767.12	16658.68	16606.50	16508.09
	0.25	16828.84	16831.86	16729.76	16683.90	16601.66

Table 4.36: Free energy, ΔG*of Dimedone in [4:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [4:1] [Water–Ethanol]	0.05	15562.16	15460.36	15363.86	15275.35	15236.03
	0.10	15662.18	15632.38	15558.02	15474.07	15418.90
	0.15	15772.07	15739.42	15675.03	15608.24	15559.30
	0.20	15876.97	15829.05	15765.51	15729.71	15698.95
	0.25	15971.86	15930.41	15887.08	15846.04	15810.51

Table 4.37: Free energy, ΔG*of Dimedone in [1:1] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:1] [Water–Ethanol]	0.05	16648.99	16533.11	16442.38	16318.06	16211.60
	0.10	16712.31	16602.26	16529.65	16422.81	16319.92
	0.15	16774.52	16657.80	16614.82	16514.52	16402.21
	0.20	16850.12	16718.59	16705.39	16601.35	16520.62
	0.25	16910.32	16789.83	16797.11	16673.13	16631.11

Table 4.38: Free energy, ΔG^* of Dimedone in [1:3] [Water–Ethanol] system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Free energy, ΔG^* J mol^{-1}				
		298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Dimedone in [1:3] [Water–Ethanol]	0.05	16329.51	16324.19	16277.82	16213.22	16139.92
	0.10	16477.94	16481.13	16418.79	16340.82	16300.69
	0.15	16595.47	16581.05	16521.23	16448.31	16464.39
	0.20	16673.52	16668.48	16629.25	16569.05	16577.72
	0.25	16742.33	16739.72	16726.64	16657.85	16703.66

It is evident from Table 4.39-4.45 in all cases of Dimedone–Ethanol and Dimedone−Water–Ethanol system, positive value of G increases with the increase in solute concentration and the rise of temperature. This behavior of G [70] suggests that the work is required for viscous flow. Lower values of G at higher temperatures may be due to weaken solute–solvent and solvent–solvent interactions for greater thermal agitation. The positive value of H increases with the increase of solute composition. This indicates that to overcome the energy barrier, some positive work has to be done. Thus the viscous flow is not favoured for all the Dimedone molecules in solution systems. This might be due to the fact that the ground state of the binary and ternary systems is more organized than the transition states.

For Dimedone−Ethanol system S > 0 and H > 0, the process is never spontaneous, but the reverse process is always spontaneous. In fact, change of enthalpy, ΔH^* and change of entropy, ΔS^* are derived from viscosity and molar volume as secondary derived data. It can also be here mentioned that the instrumental limitations during the experiments especially during determination of flow of time by Cannon-Fenske Opaque Viscometers may hamper of the data of investigated system in both binary and ternary system. So

some irregularities as well as some ambiguity may be present in change enthalpy, ΔH^* and change entropy, ΔS^* values.

Table 4.39: Change of Enthalpy, ΔH^* and Entropy, ΔS^* of Dimedone in Ethanol system at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H*	Change of Entropy, S*
Dimedone-Ethanol	0.05	13107.50	8.87
	0.10	12014.26	12.73
	0.15	11718.02	13.95
	0.20	12195.74	12.56
	0.25	12186.03	12.82

Table 4.40: Change of Enthalpy, ΔH^* and Entropy, ΔS^* of Dimedone in [1:4] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [1:4] [Water–Ethanol]	0.05	19020.44	-8.63
	0.10	19331.93	-9.12
	0.15	19274.99	-8.67
	0.20	18580.14	-6.19
	0.25	17721.88	-3.16

Table 4.41: Change of Enthalpy, ΔH* and Entropy, ΔS* of Dimedone in [2:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [2:3] [Water–Ethanol]	0.05	22227.80	-17.99
	0.10	21843.98	-16.35
	0.15	21781.44	-15.88
	0.20	21309.11	-14.07
	0.25	20527.58	-11.29

Table 4.42: Change of Enthalpy, ΔH* and Entropy, ΔS* of Dimedone in [3:2] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [3:2] [Water–Ethanol]	0.05	23101.18	-21.83
	0.10	21949.52	-17.65
	0.15	20882.37	-13.92
	0.20	20690.83	-13.08
	0.25	20424.03	-11.97

Table 4.43: Change of Enthalpy, ΔH* and Entropy, ΔS* of Dimedone in [4:1] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [4:1] [Water–Ethanol]	0.05	20565.94	-16.83
	0.10	19510.95	-12.86
	0.15	19094.51	-11.11
	0.20	18598.84	-9.15
	0.25	18400.85	-8.15

Table 4.44: Change of Enthalpy, ΔH* and Entropy, ΔS* of Dimedone in [1:1] [H_2O–ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [1:1] [Water–Ethanol]	0.05	23144.57	-21.79
	0.10	22456.17	-19.27
	0.15	22055.75	-17.73
	0.20	21465.98	-15.53
	0.25	20926.43	-13.52

Table 4.45: Change of Enthalpy, ΔH* and Entropy, ΔS* of Dimedone in [1:3] [Water–Ethanol] systems at 298.15 to 318.15 K at 5 K interval

Name of the system	Conc. (mol L^{-1})	Change of Enthalpy, H* J K^{-1}mol^{-1}	Change of Entropy, S* J K^{-1}mol^{-1}
Dimedone in [1:3] [Water–Ethanol]	0.05	19246.55	-9.70
	0.10	19432.24	-9.83
	0.15	18964.56	-7.93
	0.20	18417.77	-5.82
	0.25	17702.78	-3.21

Conclusion

Volumetric, viscometric and thermodynamic properties of Dimedone were studied in Ethanol, Water and also in Ethanol−Water. Dimedone was found to be readily dissolved in Ethanol, Water and Ethanol−Water over a concentration range of 0.05-0.25 M. Some interesting solution properties of these Dimedone in different systems were observed as follows:

(i) Volumetric, viscometric and thermodynamic properties are dependent upon Dimedone concentration as well as on the temperature.

(ii) The order of density of Dimedone in [4:1] [Ethanol−Water] > Dimedone in [3:2] [Ethanol−Water] > Dimedone in [1:1] [Ethanol−Water] > Dimedone in [2:3] [Ethanol−Water] > Dimedone in [1:3] [Ethanol−Water] > Dimedone in [1:4] [Ethanol−Water]

(iii) The apparent molar volume, $_V$ values increased at all concentrations and temperatures.

(iv) The apparent molar volumes at infinite dilution φ_V^0 values of Dimedone in Water, Ethanol, Ethanol−Water mixtures are positive and provide worthy understanding between solute–solvent interaction.

(v) Positive S_v values for Dimedone in all solution predict that solute-solute interactions are predominant as compared to solute-solvent interactions

(vi) The viscosity values, η increased with concentration but decreased with temperature for all systems.

(vii) The change of free energy, ΔG^* values for viscous flow are found to be positive for all the studied systems indicate that work has to be done to overcome the energy barrier for the flow process.

(viii) The positive H values indicate that the viscous flow is not thermodynamically favored for the systems studied.

(ix) The ΔS^* values are negative for all the systems studied except Dimedone–Ethanol system means that the system of its other binary and ternary systems are regular that those of the pure one.

(x) In all the cases A co-efficients are positive whereas those of B co-efficients are negative, suggesting strong solute-solute but weak solute-solvent interaction present in the binary and ternary solution.

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