VOLUMETRIC AND VISCOMETRIC STUDIES OF PARACETAMOL IN AQUEOUS SOLUTION OF ALCOHOLS AT DIFFERENT TEMPERATURES

by

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A thesis submitted in partial fulfillment of the requirements for the degree of
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Declaration

This is to certify that the thesis work entitled **“Volumetric and Viscometric Studies of Paracetamol in Aqueous Solution of Alcohols at Different Temperatures”** has been carried out by Shishir Kumar Dey 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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ABSTRACT

Paracetamol in presence of Water, 80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol and 20% Water + 80% n-Butanol were studied through the measurement of viscosity and density at different temperatures (298.15K to 323.15K) with an interval of 5K. The results were discussed on the basis of structure making and breaking mechanism of paracetamol in aqueous and aqueous alcohols solution under experimental conditions. The apparent molar volumes increase with the rise of concentration of paracetamol for all the studied systems indicating the structure making interaction for all the studied systems. The limiting apparent molar volume (φ_v^0) or partial molar volume at infinite dilution of paracetamol are positive and increase when paracetamol content in the solvents increase.

The positive values of transfer apparent molar volume $(\Delta\varphi_v)_{tra}$ suggest the structure making ability through hydrophilic-hydrophilic interactions between polar groups of paracetamol and polar groups of alcohols-water. The values of limiting apparent molar volume expansibilities (E_φ^0) are positive and the values of $(\delta E_\varphi^0/\delta T)_p$ are small which suggest the structure making property in these systems.

Viscosities increase with increasing of paracetamol concentration. The B-coefficients for paracetamol in the studied systems are positive and thus suggest the presence of solute-solvent interactions or structure making properties. The values of D-coefficient are mainly negative showing weak solute-solute interactions.

The changes of free energies ($\Delta G^{\#}$) are increased with the increase of concentration of paracetamol and the values are positive for all the studied systems. It is also seen that the changes of free energies ($\Delta G^{\#}$) of paracetamol in aqueous solutions of n-Propanol and n-Butanol increase very slowly with increasing solute concentration and decrease with increasing temperature. The values of enthalpy of activation ($\Delta H^{\neq}$) indicate the interaction presence in solute-solvent through H-bonding. The entropy ($\Delta S^{\neq}$) values are positive for all the systems and decrease with increase of paracetamol concentration.

The positive values of change of chemical potential ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) for all studied show greater contribution per mole of solute to free energy of activation for viscous flow of the solution and are good agreement with the values of B-coefficient showing structure making properties between solute and solvent.

Contents

LIST OF TABLES

Table No **Description**

LIST OF FIGURES

Nomenclature

¨$_v$	The apparent molar volume
°	Density
°$_1$	Density of solvent
°$_2$	Density of solute
°$_{mix}$	Density of the mixture
V_2	Partial molar volume
¦	Viscosity
c	Molarity
M_1	Molecular mass of solvent in gram
M_2	Molecular mass of solute in gram
V_o	Molar volume of solvent
V_m	Molar volume of solution
a$H^\#$	Enthalpy
a$G^\#$	Free energy
a$S^\#$	Entropy
v_1	Volume of solvent in mL.
v_0	Volume of bottle.
w_e	Weight of empty density bottle
w_0	Weight of density bottle with solvent
w	Weight of density bottle with solution
h	Plank’s constant
N	Avogadro’s number
R	Universal gas constant
PA	Paracetamol

CHAPTER I

Introduction

1.1 General

Physico-chemical behavior and intermolecular interaction provide useful information in pharmaceutical and industrial chemistry. The drug-solvent molecular interaction and their temperature dependence play an important role in the understanding of drug action. The development of solution chemistry is still far from being adequate to account for the properties of solution in terms of the properties of the constituent molecules. It is clear that if the solute and the solvent are interacting, as indeed they do, then the chemistry of the solute in a solvent must be different and the presence of a solvent can modify the properties of a solute. Interactions of drugs with their surrounding environment play an important role in their characteristic properties (1-2).

1.2 Properties of solute in solvent

In chemistry, a solution is a homogeneous mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent. The solution more or less takes on the characteristics of the solvent including its phase and the solvent is commonly the major fraction of the mixture. The concentration of a solute in a solution is a measure of how much of that solute is dissolved in the solvent, with regard to how much solvent is present.

The physicochemical properties involving solute–solvent interactions in mixed solvents have increased over the past decade in view of their greater complexity in comparison with pure solvents (3–5). This puzzling behavior results from the combined effects of preferential solvation of the solute by one of the components in the mixture (6, 7) and of solvent–solvent interactions (8). Preferential salvation occurs when the polar solute has in its microenvironment more of one solvent than the other, in comparison with the bulk composition. The understanding of these phenomena may help in the elucidation of kinetic, spectroscopic and thermodynamic events that occur in solution.

Theoretically, solute-solvent interactions that mean the properties of solutions can be calculated from the properties of the individual components. But, the liquid state creates inherent difficulties and the properties of solution cannot understand properly. The theoretical treatments, therefore, have to assume some model (e.g., lattice model, cell model etc.) for the structure of the components and their solution. Alternatively, it is considered convenient and useful to determine experimentally the values of certain macroscopic properties of solutions for proper understanding of the structure of the solution. Some of the usually experimentally determined macroscopic properties are: density, viscosity, thermodynamic properties, surface tension, etc., which are readily measurable. Investigations, comprising experimental determination of various thermodynamic properties, viscosity etc. on solutions, assume significant importance since it is possible to draw conclusions regarding characteristic molecular interactions between constituent molecules of the components from purely thermodynamic reasoning.

The macroscopic behaviors of any system have to be interdependent, since these essentially originate from the most probable distribution of energy between the constituent molecules comprising the system. Therefore, there has been interest for seeking interrelations between the macroscopic properties of any system. It should be possible to express the value of any macroscopic property in terms of the known values of the other. Since viscosity coefficient is a macroscopic property under non equilibrium condition, there has been a considerable effort for establishing its relationship with thermodynamic properties of a system.

Physical properties like density, viscosity, surface tension, conductivity, dielectric constant, refractive index, group frequency shifts in I.R. spectra etc. provide an indication about the molecular structure as well as the molecular interactions that occur when solute and solvent are mixed together. The density and viscosity are two fundamental physico-chemical properties of which are easy, simple, inexpensive and precise tools, by which one can get the valuable information about the molecular interactions in solid and liquid mixture correlated with equilibrium and transport properties. The thermodynamic data are used subsequently by a variety of physical scientists including chemical kineticists and spectroscopists involved in reaction occurring in solution and by chemical engineers engaged in the operation and design of chemical reactor, distillation columns or other type of separation devices. Solution theory is still far from adequate to account for solution behavior in terms of the properties of the constituent molecules. From the above mentioned properties, quantitative conclusion can be drawn about the molecular interactions even in simple liquids or their mixtures. Our present investigation is based on the methods of physico-chemical analysis, which is a useful tool in getting sound information about the structure of some aqueous alcohols with paracetamol in studying the solute-solvent and solvent-solvent interactions in ternary systems.

1.3 Properties of Paracetamol

Paracetamol also known as acetaminophen or N-acetyl-pamino or N-(4-hydroxyphenyl) phenol is a mild analgesic, antipyretic agent and also a non-steroidal anti-inflammatory drug. Chemically, it consists of a benzene ring core, substituted by one hydroxyl group and the nitrogen atom of an amide group in the para (1,4) pattern. The amide group is acetamide (ethanamide). It is an extensively conjugated system, as the lone pair on the hydroxyl oxygen, the benzene pi cloud, the nitrogen lone pair, the p- orbital on the carbonyl carbon, and the lone pair on the carbonyl oxygen is all conjugated. The presences of two activating groups also make the benzene ring highly reactive toward electrophilic aromatic substitution. As the substituents are ortho, para-directing and para with respect to each other, all positions on the ring are more or less equally activated. The conjugation also greatly reduces the basicity of the oxygens and the nitrogen, while making the hydroxyl acidic through delocalization of charge developed on the phenoxide anion (Fig: 1.2).

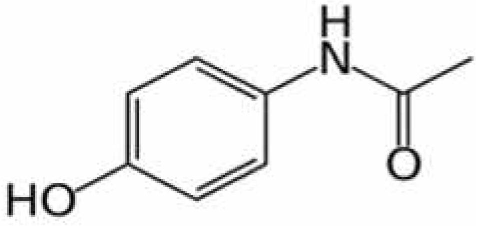

Fig: 1.2 Structure of Paracetamol

Paracetamol is part of the class of drugs known as "aniline analgesics"; it is the only such drug still in use today. Paracetamol is also used for reducing fever in people of all ages. The World Health Organization (WHO) recommends that paracetamol be used to treat fever in children only if their temperature is greater than 38.5 °C (101.3 °F). The efficacy of paracetamol by itself in children with fevers has been questioned and a meta-analysis showed that it is less effective than ibuprofen. Paracetamol is used for the relief of mild to moderate pain. The American College of Rheumatology recommends paracetamol as one of several treatment options for people with arthritis pain of the hip, hand, or knee that does not improve with exercise and weight loss. Paracetamol has relatively little anti-inflammatory activity and has similar effects in the treatment of headache. Paracetamol can relieve pain in mild arthritis, but has no effect on the underlying inflammation, redness, and swelling of the joint. It has analgesic properties comparable to those of aspirin, while its anti-inflammatory effects are weaker. It is better tolerated than aspirin due to concerns with bleeding with aspirin (9-11).

The mode of interactions of aqueous solution of alcohols and paracetamol is of vital importance in the field of solution chemistry and drug industry as it can provide with important information regarding hydrophilic and hydrophobic interactions.

1.4 Properties of alcohols

Most of the common alcohols are colorless liquid at room temperature. Methanol, Ethanol and n-Propanol are free-flowing liquid with fruity odors. The higher alcohols such as 4 to 10 carbon containing atoms are somewhat viscous or oily, and they have fruity odors. Some of the highly branched alcohols and many alcohols containing more than 12 carbon atoms are solids at room temperature.

The boiling point of an alcohol is always much higher than that of the alkane with the same number of carbon atoms. The boiling point of the alcohols increases as the number of carbon atoms increase. For example Ethanol with a MW of 46 has a bp of 78 ^{0}C whereas Propane (MW 44) has boiling point of -42 ^{0}C. Such a large difference in boiling points indicates that molecules of Ethanol are attached to another Ethanol molecule much more strongly than Propane molecules. Most of this difference results from the ability of Ethanol and other alcohols to form intermolecular hydrogen bonds.

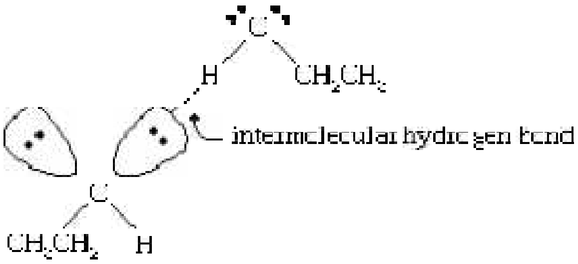

Fig. 1.2

The oxygen atom of the strongly polarized O-H bond of an alcohol pulls electron density away from the hydrogen atom. This polarized hydrogen, which bears a partial positive charge, can form a hydrogen bond with a pair of nonbonding electrons on another oxygen atom (Fig. 1.2).

Alcohols are strongly polar, so they are better solvents than alkanes for ionic and polar compounds. In general, the hydroxyl group makes the alcohol molecule polar. Those groups can form hydrogen bonds to one another and to other compounds (except in certain large molecules where the hydroxyl is protected by steric hindrance of adjacent groups). This hydrogen bonding means that alcohols can be used as protic solvents. Two opposing solubility trends in alcohols are: the tendency of the polar -OH to promote solubility in water, and the tendency of the carbon chain to resist it. Thus, Methanol, Ethanol, and n-Propanol are miscible in water because the hydroxyl group wins out over the short carbon chain. Butanol, with a four-carbon chain, is moderately soluble because of a balance between the two trends. Alcohols of five or more carbons (Pentanol and higher) are effectively insoluble in water because of the hydrocarbon chain's dominance. All simple alcohols are miscible in organic solvents.

Alcohols, like water, can show either acidic or basic properties at the O-H group. With a pK_a of around 16-19, they are, in general, slightly weaker acids than water, but they are still able to react with strong bases such as sodium hydride or reactive metals such as sodium.

1.5 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.

1.6 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 (12). The deviations from regularity indicate some kind of association of water molecules. The notable unique physical properties exhibited by liquid water are (13) : i) negative volume of melting ii) density maximum in normal liquid range (at $4\,^{0}$C) iii) isothermal compressibility minimum in the normal liquid range at ($46\,^{0}$C) iv) numerous crystalline polymorphs v) high dielectric constant vi) abnormally high melting, boiling and critical temperatures for such a low molecular weight substance that is neither ionic nor metallic vii) increasing liquid fluidity with increasing pressure and viii) 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^{0}. For a very long time the physical 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 (14, 15) 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 (16-18) 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 (19), latter developed by Nemethy and scherage (14), 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 (20).

$$(H_2O)_b \rightleftarrows (H_2O)_d$$

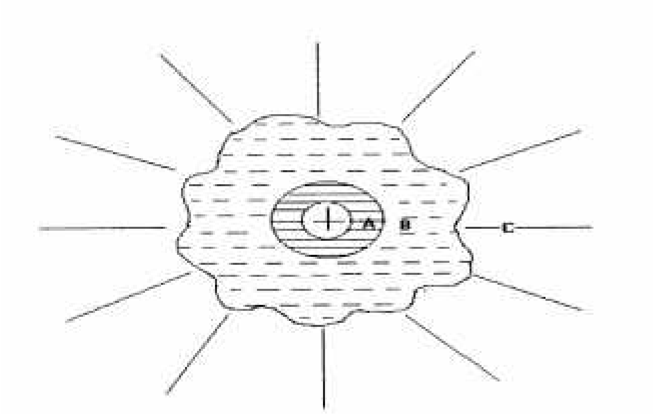

Fig 1.1: Frank and Wen model for the structure modification produce by an ion

The hydrogen bonding in the clusters is postulated (20) to be cooperative phenomenon. So that when one bond forms several others also come into existence. 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.

1.7 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 (21).

1.8 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 (22). 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 a much stronger attractive interaction energy between the nonpolar solutes merged in water than their vander waals interaction in free space (23). The tendency of relativity nonpolar molecules to “stick together” in aqueous solution is denoted as the hydrophobic interaction (24). 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.

1.9 Paracetamol-Solvent systems

The experimental data on macroscopic properties provide valuable information for proper understanding the nature of interaction between the components of the solution. The thermodynamic properties of solution containing paracetamol and alcohols are of interest. The correlation between solute-solvent interactions is complex. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure. The environment of the solute affects the thermodynamic properties; it is of interesting to study the effect of the media changing from water-alcohols with paracetamol on the thermodynamic properties.

Solubility of paracetamol in pure solvents has been measured previously (25). Density and viscosity studies of paracetamol in ethanol +water system have been reported at 301.5K (26). Effect of paracetamol in aqueous sodium malonate solutions with reference to volumetric and viscometric measurements have also been measured (27). Evaluation of free volume, relaxation time of aqueous solution of paracetamol by ultrasonic studies has been presented (28). Ultrasonic investigation of molecular interaction in paracetamol solution at different concentrations has been measured (29). A Study of acoustical behavior of paracetamol in 70% methanol at various temperatures was also measured (30). Density, viscosity, partial molar volume, excess molar volume, and excess viscosity of paracetamol in methanol + water system at 309.15 K was reported (31). Study of physic-chemical properties of paracetamol & aspirin in water - ethanol system were also measured (32).

1.10 The object of the present work

The developments in solution theory are still far from being adequate to account for the properties of the constituent molecules. Accordingly, it is the experimental data on various macroscopic properties (thermodynamic properties, viscosities, surface tension etc), which provide useful information for proper understanding of specific interaction between the components and structure of the solution. The experimental approach of measurements of various macroscopic properties is also useful in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based. Thermodynamic studies on ternary solutions have attracted a great deal of attention and experimental data on a good number of systems are available in a number of review articles (33-35). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, of particular interest has been the determination of densities and viscosities of mixtures (36-38).

Since there has to be the same origin, namely, the characteristic intermolecular interactions, it is natural to seek functional relationships among the volumetric properties, viscometric properties and thermodynamic properties. However, such attempts have not met with much success.

Besides the theoretical importance, the knowledge of physicochemical properties of multicomponent mixtures is indispensable for many chemical process industries. For instance, in petroleum, petrochemical and related industries the above mentioned processes are commonly used to handle the mixture of hydrocarbons, alcohols, aldehydes, ketones etc., which exhibit ideal to non-ideal behavior. For accurate design of equipment required for these processes, it is necessary to have information regarding the interactions between the components. Similarly, knowledge of the viscosity of liquids/mixtures is indispensable, since nearly all engineering calculations involve flow of fluids. Viscosity and density data yield a lot of information on the nature of intermolecular interaction and mass transport.

The experimental data on macroscopic properties such as apparent molar volumes, partial molar volumes, surface tension, and refractive index often provide valuable information for the understanding of the nature of homo and hetero-molecular interactions. The knowledge of the main factors involved in the solute-solvent and solvent-solvent interactions of liquid mixtures is fundamental for a better understanding of apparent molar volumes and thermodynamic properties.

The thermo-physical properties of liquid systems like density and viscosity are strictly related to the molecular interactions taking place in the system (39). These interactions decides the drug actions i.e. drug reaching to the blood stream its extent of distribution, its binding to receptors and producing physiological actions (40). The interactions are of different types such as ionic or covalent, charge transfer, hydrogen bonding, ion-dipole and hydrophobic interactions. There are various papers appeared recently which use viscometric method to access thermodynamic parameters of biological molecule and interpreteted the solute-solvent interactions (41-43). Therefore we decided to study the density and viscometric properties of paracetamol in mixed solvent system.

In the present investigations, (i) densities, apparent molar volumes, partial molar volumes etc. (ii) viscosities and coefficient of B & D and iii) thermodynamic parameters of *n*-Propanol, *n*-Butanol with paracetamol at six different temperatures (298.15-323.15K) have been determined. So far we know, there are no complete data of density, viscosity and molar properties of paracetamol in aqueous solution of *n*-Propanol, *n*-Butanol, at extended temperatures. With these points of view, we have undertaken this research and the measurement of density and viscosity are thought to be powerful tools to investigate the intermolecular interactions of this commonly used medicine paracetamol with alcohols + water which are focused in this study. In order to understand the issue of solute-solvent interactions in aqueous solution of alcohol-paracetamol systems a theoretical and experimental aspect of interactions in terms of apparent molar volume, viscosity coefficient, and thermodynamic properties analysis is necessary.

The specific aims of this study are-

i) to study the density, viscosity and thermodynamic properties of paracetamol in aqueous solution of alcohols through the measurement at different temperatures

ii) to predict about the structure making and breaking mechanism of paracetamol in aqueous alcohols under experimental conditions

iii) to enrich the available data on physico-chemical properties and thermodynamic function of the system.

The thesis presents the density, apparent molar volumes, partial molar volumes, viscosity, and coefficient of B & D, thermodynamic parameters data of paracetamol in aqueous solution of alcohols (n-Propanol and n-Butanol) over the concentration range from 0.02M to 0.10M at six temperatures from 298.15 K to 323.15 K.

CHAPTER II

Theoretical Background

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 interatomic 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 weight 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 (44).

(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 parachor, molar refraction, molecular viscosity etc. are the other example 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.

2.2 Density

The density of a liquid may be defined as the mass per unit volume of the liquid unit of volume being the cubic centimeter (cm^3) or milliliter (mL). Since the milliliter is defined to be the volume occupied by one gram of water at temperature of maximum density (i.e, at 4^0C), the density of water at this temperature in gmL^{-1} is unity and the density of water at any other temperature is expressed relative to that of water at 4^0C and expressed by (d^{10}_4).

The relative density of a substance is the ratio of the weight of a given volume of the substance to the weight of an equal volume of water at the same temperature (d^{10}_4). The absolute density of a certain substance temperature t^0C is equal to the relative density multiplied by the density of water at the temperature. The density of a liquid may be determined either by weighing a known volume of the liquid in a density bottle or picnometer or by buoyancy method based on “Archimedes principle”.

In our present investigation, the densities of the pure components and the mixture were determined by weighing a definite volume of the respective liquid in a density bottle.

2.3 Density and temperature

An increase in temperature of a liquid slightly increases the volume of the liquid, thus decreasing its density to some extent. The temperature increase brings about an increase in molecular velocity. These energetic molecules then fly apart causing more holes in the bulk of the liquid. This causes the expansion of the liquid, thereby decreasing the number of molecules per unit volume and hence the density.

2.4 Molarity

Molarity (C) is defined as the number of moles of solute per litre of solution. If n_2 is number of moles of solute and V liters is the volume of the solution then,

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

$$\text{Or, } C = \frac{n_2}{V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

For one mole of solute dissolved in one liter of solution, C=l i.e. molarity is one. Such a solution is called 1 molar. A solution containing two moles of solute in one liter is 2 molar and so on. As evident from expression (2.1), unit of molarity is $molL^{-1}$ (45).

2.5 Molar volume of Mixtures

The volume in mL occupied by one gram of any substance is called its specific volume and the volume occupied by 1 mole is called the molar volume of the substance. Therefore, if ρ is the density and M be the molar mass, we have the molality (m) of a solution is defined as the number of moles of the solute per 1000 g of solvent (45). Mathematically,

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

$$\text{or, } \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M}_2} \times 1000}{\text{Volume of solvent in mL} \times \text{Density of solvent in g cm}^{-3}}$$

$$\text{or, } \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M}_2} \times 1000}{\mathrm{V}_1 \times \rho_0}$$

$$\text{or, } \mathrm{m} = \frac{\mathrm{a}}{\mathrm{M}_2} \times \frac{1000}{\mathrm{V}_1 \times \rho_0} \qquad \ldots\ldots\ldots\ldots(2.2)$$

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}

$$\text{Specific volume, (V)} = \frac{1}{\rho} mLg^{-1} \qquad \ldots\ldots\ldots\ldots(2.3)$$

$$\text{and Molar volume, } (V_m) = \frac{M}{\rho} mLmol^{-1} \ldots\ldots\ldots\ldots(2.4)$$

when two components are mixed together, there may be either a positive or a negative deviation in volume. The positive deviation in volume i.e. volume expansion has been explained by the break down of the mode of association through H-bonding of the associated 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.

2.6 Apparent/ partial molar volume

The apparent molar volume of a solute in solution, generally denoted by is defined by φ_v the relation (44)

$$\varphi_v = \frac{V - n\overline{V}_1^{\,0}}{n_2} \qquad \text{……………………………………………….(2.5)}$$

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 molal 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 (45),

$$\varphi_v = \frac{1}{n_2}\left[\frac{n_1M_1 + n_2M_2}{\rho} - n_1\overline{V}_1^{\,0}\right] \qquad \text{……………………………………….. (2.6)}$$

where, V=$\frac{n_1M_1 + n_2M_2}{\rho}$ 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 molal concentration, n_2 = m, the molality and n_1 = 55.51, the number of moles of solvent in 1000g of solvent (water), the equation for apparent molal volume takes the form (37, 38),

$$\varphi_v = \frac{1}{m}\left[\frac{1000 + mM_2}{\rho} - \frac{1000}{\rho_0}\right]$$

$$\text{or, } \varphi_v = \left[\frac{M_2}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho\rho_0}\right] \qquad \text{…………………………….(2.7)}$$

$$\text{or, } \varphi_v = \frac{1}{\rho}\left[M_2 - \frac{1000}{m}\left(\frac{W - W_0}{W_0 - W_e}\right)\right] \qquad \text{…………………………….(2.8)}$$

where, ρ_o and ρ are the densities of the solvent and solution and W_e, W_0 and W are the weight of empty bottle, weight of bottle with solvent and weight of bottle with solution respectively.

If the concentration is expressed in molarity (C), the equation 2.8 takes the form (47):

$$\phi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0}\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.9)$$

where,the relation, $C = \dfrac{m.\phi_v.1000}{1000 + \phi_v.m.\rho_0}$ ……………………………………(2.10)

is used for inter conversion of the concentration in the two scales (47).

The partial molal 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 molal 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:

$$\overline{Y_1} = \left(\frac{\partial Y}{\partial n_1}\right)_{n_2,P,T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (2.11)$$

Similarly for component 2,

$$\overline{Y_2} = \left(\frac{\partial Y}{\partial n_2}\right)_{n_{12},P,T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2.12)$$

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,

$$Y_{(n_1,n_2)} = n_1\overline{Y_1} + n_2\overline{Y_2}\,, \qquad \text{at constant T and P} \qquad \text{……………………..(2.13)}$$

In respect of the volume of solution, equation 2.5 gives directly

$$V = n_1\overline{V_1} + n_2\overline{V_2}\,, \qquad \text{at constant T and P} \qquad \text{……………………..(2.14)}$$

The partial molar volumes of solute and solvent can be derived using the equation 2.5 as follows (46):

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{P,T,n_1} = \varphi_v + n_2\left(\frac{\partial \varphi_v}{\partial n_2}\right)_{P,T,n_1} = \varphi_v + m\left(\frac{\partial \varphi_v}{\partial m}\right)_{P,T,n_1} \qquad \text{…………………….(2.15)}$$

and,

$$\overline{V_1} = \frac{\left(V - n_2\overline{V_2}\right)}{n_1} = \frac{1}{n_1}\left[n_1\overline{V_1^0} - n_2^2\left(\frac{\partial \varphi_v}{\partial n_2}\right)\right]_{P,T,n_1} = \overline{V_1^0} - \frac{m^2}{55.51}\left(\frac{\partial \varphi_v}{\partial m}\right)_{P,T,n_1} \qquad \text{…………..(2.16)}$$

For solutions of simple electrolytes, the apparent molar volume (φ_v) vary linearly with √m, even up to moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (46):

$$\frac{\partial \varphi_v}{\partial m} = \frac{\partial \varphi_v}{\partial \sqrt{m}}.\frac{\partial \sqrt{m}}{\partial m} = \frac{1}{2\sqrt{m}}.\frac{\partial \varphi_v}{\partial \sqrt{m}} \qquad \text{……………………….……………(2.17)}$$

If φ_v is available as a function of molal concentration, the partial molar volumes of solute and solvent can be obtained from equation 2.15 and 2.16 as (47):

$$\overline{V_2} = \varphi_v + \frac{\sqrt{m}}{2}\left(\frac{\partial \varphi_v}{\partial \sqrt{m}}\right) = \varphi^0_v + \frac{3\sqrt{m}}{2}\left(\frac{\partial \varphi_v}{\partial \sqrt{m}}\right) \qquad \text{……………………………(2.18)}$$

and

$$\overline{V_1} = \overline{V_1^0} - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2}.\frac{\partial \varphi_v}{\partial \sqrt{m}}\right) = V_1^0 - \frac{M_1 m^{3/2}}{2000}\left(\frac{\partial \varphi_v}{\partial \sqrt{m}}\right) \text{…………………………..…(2.19)}$$

Where, φ^0_v is the apparent molal volumes at zero concentration.

When molar concentration scale is used to express φ_v as a function of concentration, then

$$\overline{V_2} = \varphi_v + \left[\frac{1000 - C\varphi_v}{2000 + C^{3/2}\left(\frac{\partial\varphi_v}{\partial\sqrt{C}}\right)}\right]\sqrt{C} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.20)$$

and

$$\overline{V_1} = \frac{2000\overline{V}_1^{0}(18.016/\rho_0)}{2000 + C^{3/2}\left(\frac{\partial\varphi_v}{\partial\sqrt{C}}\right)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.21)$$

From equation 2.18 and 2.20, it follows that at infinite dilution, (m or c → 0), the partial molar volume and the apparent molar volume are identical (48). 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 (49).

The concentration dependence of the apparent molar volume of electrolytes has been described by the Masson equation (50), the Redlich-Mayer equation (52) and Owen-Brinkley equation (51). Masson (50) found that the apparent molar volume of the non-electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v C \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.22)$$

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

Redlich and Rosenfeld (52) predicated that a constant limiting 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,

$$S_v = KW^{3/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.23)$$

where, the terms K and W are given by

$$K = N^2 e^3 \left(\frac{8\text{®}}{100 D^3 RT} \right)^{1/2} \left\{ \left(\frac{\text{¢} \ln D}{\text{¢°}} \right) - \left(\frac{}{3} \right) \right\} \quad \text{……………………………..…..(2.24)}$$

and $W = 0.5 \sum \text{¥}_i Z_i^2$ ……………………………………….(2.25)

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 (52). For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of non-electrolytes is given by the equation,

$$\ddot{}_v = \ddot{}_v^{\,0} + KW^{3/2} C \quad \text{………………………………………..(2.26)}$$

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

$$\ddot{}_v = \ddot{}_v^{\,0} + S_v C + b_v C \quad \text{……………………………………...(2.27)}$$

where, S_v, is the theoretical limiting law slope and b_v an empirical constant for 1:1 electrolyte, the limiting law slope at 298.15K is 1.868 $\text{cm}^3\text{mol}^{-3/2}.\text{L}^{1/2}$.

2.7 Viscosity

Viscosity means viscous ability. It's more generalized definition is "the internal friction which 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 centre of the tube, the layer in the centre of the tube having the maximum velocity. There thus exists a velocity gradient.

In case of liquid, 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, 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 $\frac{dv}{dx}$

Thus, $f \infty \; A \; \frac{dv}{dx}$

or $$f = \eta \; A \; \frac{dv}{dx} \qquad \text{……………………………………………(2.28)}$$

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.

$$\phi = \frac{1}{\eta} \qquad \text{……………………………………………………………..(2.29)}$$

It is measure of the case with which a liquid can flow.

The C.G.S 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. Since viscosity of liquid is usually very small, it is usually expressed in millpoise (mP) or centipoise (cP) or mPa.S.
When a liquid flows through a narrow tube it is probable that the thin layer of liquid in contact with the wall is stationary; as a result of viscosity, therefore, the next layer will be slowed down to some extent, and this effect will continue up to the centre of the tube where the flow rate is maximum.

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation (53). 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 (53):

$$\eta = \frac{\pi P r^4 t}{8lV} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2.30)$$

This equation known as Poiseuille's equation holds accurately for stream-line flow but not for the turbulent flow which sets as higher velocities. A small error arises in practice, because the liquid emerging from a capillary tube possesses appreciable kinetic energy and since this is not accounted for in Poiseuille’s equation, a correction term is introduced. After correction for kinetic energy, the equation becomes,

$$\eta = \frac{\pi P r^4 t}{8lv} - \frac{\rho V}{8\pi lt} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2.31)$$

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

The driving pressure P = hρg, 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 (2.35) becomes,

$$\eta = \frac{\pi h \rho g r^4 t}{8vl} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2.32)$$

For a particular viscometer h, l, r and V are fixed, so the equation (2.37) becomes,

$$\eta = A \rho t \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.38)$$

where $A = \frac{\pi h g r^4}{8vl}$, called the calibration constant of the viscometer used. For flow of water, therefore,

$$\eta_{H_2O} = A \rho_{H_2O} t_{H_2O} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2.33)$$

$$\text{or, } A = \frac{\eta_{H_2O}}{\rho_{H_2O} t_{H_2O}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.34)$$

knowing the value of $¦_{H_2O}$ and $°_{H_2O}$ at the experimental temperature and measuring the time of flow for water, the calibration constant A for a particular viscometer can be determined. Putting the value of and of the experimental liquid/solution and the value of viscometer constant A in equation (2.33), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

2.8 Viscosity and temperature

The viscosity of a liquid is generally decrease with the increase of temperature, i.e., a liquid becomes more free moving at higer temperatures. This in sharp contrast with the gas behavior, viscosity of gases increases with the increase of temperature. Numerous equations, connecting viscosity and temperature, have been proposed, but those of the exponential type, first derived independently by S. Arrhenius (1912) and J. De Guzmann(1913), are preferred due to their theoretical practical importance.

$$¦ = Ae^{E/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.35)$$

Where ‘A’ and ‘E’ are constants for the given liquid. It follows from equation (2.41) that the plot of log η versus 1/T will be a straight line. By analogy with the Arrhenius theory of reaction rates, ‘E’ has the dimension of work and can be regarded as the activation energy of viscous flow. It is probably related to the work needed to form ‘holes’ in the liquid, into which molecules can move, thus permitting relative motion to take place.

It has been suggested that before a molecule can take part in liquid flow, it must acquire sufficient energy ‘B’ to push aside the molecules which surround it. As the temperature increases, the number of such molecules increases in proportion to the Boltzmann factor $e^{-E/RT}$ as in equation 2.41.

At low temperature the viscosity of a liquid is usually greater because the intermolecular attractive forces simply dominate the disruptive kinetic forces. At elevated temperatures the kinetic energy of the molecules increases at the expense of intermolecular forces which diminish progressively. Therefore, the molecules of a liquid at high temperature offer less resistance to the flow and hence less viscosity.

Viscosity also depends on pressure, molecular weight or mass of the molecule, molecular size and particularly chain length, the magnitude of intermolecular forces, such as association in pure liquids. Non polar liquids e.g., benzene, toluene etc. have low viscosities, whereas liquids in which direct bonding can occur between the molecules, e.g., glycerin, water etc. have high viscosities where H-bonding occurs extensively.

2.9 Viscosity of liquid mixtures

To represent the Viscosity of liquid mixtures, many equations have been proposed, without, an adequate theoretical basis it was not possible to assign to those corresponding to ideal behavior. Support at one time was obtained for the equation of E. C. Bingham (1906)

$$\varphi = X_1 \varphi_1 + X_2 \varphi_2$$

where φ is the fluidity of the mixture, φ_1 and φ_2 are the corresponding values for the pure components 1 and 2, whose mole fraction are $X_1$and X_2 respectively.

In liquid mixtures, there may be either a positive or a negative deviation in viscosity. The positive deviation from ideal behavior, i.e. higher viscosities than the calculated values indicate that constituents of mixtures from complexes in the liquid state or, association between components may increase for the associated liquids. Water and alcohol mixture exhibit this type of behavior probably as a result of H-bonding formation between water and alcohol molecules. The negative deviation of viscosities i.e., lower viscosities than the ideal values indicate the decrease in association of associated liquids (H-bonded) or increase in the internuclear distance between them. Again, this type of behavior may also arise due to the trapping of smaller molecules into the matrices of larger species.

2.10 Viscosity as a rate process

Liquids in a tube are considered as combination of concentric layers and it flows as a rate processes.

To treat the viscosity of a liquid as a rate process it is assumed that

i) The motion of one layer with respect to another is assumed to involve the passes of a molecule from one equilibrium position to another is the same layer.

ii) In order to move a molecule from one equilibrium position to another, a suitable ‘hole’ or site should be available.

iii) The production of a site requires the expenditure of energy because work must be done in pushing back the molecules.

iv) The jump of the moving molecules from one equilibrium position to the next may thus be regarded as equivalent to the passage of the system over a plot of energy barrier.

Eyring and his co-workers (55) using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, η as follows:

$$\eta = \frac{hN}{V_m} e^{\Delta G^{\#}/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.36)}$$

Where, $\Delta G^{\#\ \text{is}}$ the free energy of activation per mole for viscous flow, V_m is the molar volume for pure liquids or solutions and h, N, R and T have their meanings. The values of change of free energy of activation ($\Delta G^{\#}$) can be calculated by using the Nightingle and Benck equation (48):

$$\Delta G^{\#} = RT \ln \left(\frac{\eta V_m}{Nh} \right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.37)}$$

The experimental term in equation 2.48 depends on the temperature and is typical for the processes which require activation energy. The activation process to which $\Delta G^{\#}$ refers can not be precisely described but in general terms, it corresponds to the passes of the system into some relatively favorable configuration, from which it can then easily go to the final state of the molecular process. For example, in normal liquids the activation step may be the creation in the body of the liquid of a vacancy or holes into which an adjacent molecule can move. For associated liquids, it might be the breaking of enough intermolecular bonds to permit a molecule to move into available vacancy.

Enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation for viscous flow:

Enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution can be obtained with the help of Eyring equation (55):

$$\eta = \left(\frac{hN}{V_m}\right) e^{\Delta G/RT}$$

$$\text{or } \ln\eta + \ln\frac{hN}{V_m} + \frac{\Delta G^{\#}}{RT}$$

$$\text{or,}\ln\frac{\eta V_m}{Nh} = \frac{\Delta G^{\#}}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.38)$$

Since,

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.39)$$

The Eyring equation takes the form,

$$\ln\frac{\eta V_m}{Nh} = \frac{\Delta H^{\#}}{RT} - \frac{\Delta S^{\#}}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.40)$$

Assuming $\Delta H^{\#}$ and $\Delta S^{\#}$ to be almost independent in the temperature range studied, a plot of $\ln \eta V_m / Nh$ against $1/T$, will give a straight line with slope $= \frac{\Delta H^{\#}}{R}$ and intercept $\frac{\Delta S^{\#}}{R}$

From the slope of this straight line, $\Delta H^{\#}$ can be calculated as,

$$\Delta H^{\#} = \text{slope} \times R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.41)$$

and from of the intercept of this straight line, $\Delta S^{\#}$ can be calculated as

$$\Delta S^{\#} = -\text{ intercept} \times R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.42)$$

$\Delta H^{\#}$ and $\Delta S^{\#}$ respectively the enthalpy of activation per mole for viscous flow and $\Delta S^{\#}$ is the entropy of activation. Since $\Delta S^{\#}$ does not change much within a range of temperature, so when in $\ln\eta V_m$ / hN is plotted against 1/T, will be found. From the slope and intercept, $\Delta H^{\#}$ and $\Delta S^{\#}$ respectively can be calculated.

2.11 Different thermodynamic parameters

2.11.1 Free energy ($\Delta G^{\#}$) for viscous flow

In any liquid, for a molecule to take part in flow, a hole must be available. This hole is not necessarily the full size of a molecule but the additional volume required by the activated state as compared with the initial state. The energy required to make a hole of a molecular size is equal to the energy of activation E_{vap} and so the free energy of activation may be expected to be some fraction of the energy of vaporization.

2.11.2 Enthalpy ($\Delta H^{\#}$) for viscous flow

A plot of $\ln\eta V_m$/hN VS 1/T [according to Eyring equation] will give a straight line of slope $\Delta H^{\#}/R$ and intercept $-\Delta S^{\#}/R$. Assuming that $\Delta H^{\#}$ and $\Delta S^{\#}$ to be almost independent of temperature. The value of $\Delta H^{\#}$ as found by this procedure are almost constant, for normal liquids over a range of temperature under ordinary condition.

2.11.3 Entropy ($\Delta S^{\#}$) for viscous flow

In view of high activation energy for the flow of associated liquids, it is a striking fact that the free energy of activation shows no such abnormality. The explanation is that, $\Delta G^{\#}$ is equivalent to ($\Delta H^{\#} - T\Delta S^{\#}$) and that the high value of the enthalpy of activation $\Delta H^{\#}$ is compensated by the large positive value of $\Delta S^{\#}$, so that $\Delta G^{\#}$ remains normal. If as suggested above the unit of even in associated liquids is a single molecule and the formation of the activated state involves of a number of hydrogen–bonds, it is evident that the entropy of the activated state will be appreciably greater than that of the initial state. In other words, the entropy of activation $\Delta S^{\#}$ for flow should be relatively large positive, in agreement with the experimental fact that $\Delta G^{\#}$ is normal in spite of the volume of the $\Delta H^{\#}$ for associated liquids.

CHAPTER III

Experimental

3.1 General Techniques

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 a desiccator, while larger pieces of apparatus were used directly from the oven.

Ostwald viscometer of British standard institution form was 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 Materials

The chemicals used for study were - Paracetamol, *n*-Propanol, *n*-Butanol. All chemicals were of analytical reagent (A.R) grade. Specifications and structural formula for all of them are given below:

Chemicals	**Molecular formula**	**Molar mass**	**Reported purity**	**Producer**
Paracetamol	$C_8H_9NO_2$	151.163	97.80%	Ganosasto Pharmaceutical bd. Ltd.
n-Propanol	C_3H_8O	60.10	98.90%	E. MERCK Germany
n-Butanol	$C_4H_{10}O$	74.12	99.98%	E. MERCK Germany

3.3 Preparation and Purification of Solvent

Ordinary distilled water was purified by a quick-fit glass made distillation apparatus. About 1.5L water was taken in a round bottom flux of which the capacity was 2L. 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 and deionized water was used. Conductivity of this redistilled water was found to be less than 1×10^{-6} $S.cm^{-1}$. This redistilled water was used for the preparation of sample solutions for volumetric and viscometric studies.

3.4 Apparatus

The glass-ware used for the measurement for density of solvents and solutions were of the density bottle (25ml). Viscosities of various liquids were measured using the calibrated ostwald type viscometer. A & D company, (Model; HR 200, Made in Japan) electronic balance with an accuracy of ± 0.0001g was used for weighting. The flow time of liquids were recorded by a stop-watch capable to read up to 0.01 seconds. The temperature was controlled by water thermostat (Model: Huber, Made in Germany) with an accuracy of $\pm 0.01^0$C. The experimental temperatures were 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K respectively. Both the density bottle and viscometer were calibrated with doubly distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

3.5 Conductance measurements

Conductance of water was measured by using a digital conductivity meter (EXTECH INATRUMENTS Model no. 407303). Rinsed the cell with one or more portions of sample and adjust sample temperature about 25^0. Immerse cell in sample: sample level above vent holes then read and noted conductivity of sample.

3.6 Density measurements

The densities of the solutions were determined by weighing a definite volume of the solution in a density bottle at specified temperature. The volumes were obtained by measuring the weight of water at that temperature and using the density of water from literature. The density of solution was determined from the relation.

$$\circ = \frac{w - w_e}{v_0} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3.1)$$

where, ρ = density of the solution, w = weight of bottle with solution, w_e = weight of empty bottle, v_0 = volume of bottle.

The density bottle was first thoroughly cleaned with warm chromic acid and then with enough distilled water. Then it was rinsed with acetone and finally dried at 85^0C for more than two hours. The weight of the dried empty density bottle was noted after proper cooling. The density bottle was calibrated at experimental temperature with doubly distilled water.

The solution under investigation was taken in a density bottle up to the mark. The density bottle was clamped carefully with stand in the thermostatic water bath maintained at the desired temperature. As the solution started to gain the temperature of the bath excess liquid overflowed through the capillary. Then it was allowed to keep in the bath for about 30 minutes to attain the thermal equilibrium. When no overflowed observed through the capillary the density bottle was taken out from the thermostatic water bath, wiped with tissue-paper, dried and weighed in the analytical balance. The difference between the two weights (weight with solution and without solution) gave the weight of the solution in the density bottle. The density measurement was performed for each of the solutions at the temperature 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K respectively in this way using equation 3.1.

3.7 Apparent/ Partial molar volume measurements

The apparent molar volumes of the solution for binary and ternary systems were determined from density measurement using the following equation (46, 47):

$$\phi_v = \frac{1}{\rho}\left\{M_2 - \frac{1000}{m}\left(\frac{\rho - \rho_0}{\rho_0}\right)\right\}$$

$$\text{or, } \phi_v = \frac{1000}{m\rho\rho_0}\left(\rho_0 - \rho\right) + \frac{M_2}{\rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.2)$$

where, ρ is the density of the experimental solution, M_2 and m are the molar mass and molality of the electrolyte respectively and ρ_0 is the density of the solvent. The molality 'm' of a solution was calculated from mole fraction of solute and solvent

$$m = \frac{X_2 \times 1000}{X_1 M_1}$$

Where, M_1 and M_2 = the molecular weight of solvent and solute

And also from molarity C,

$$m = \frac{1}{\left(\frac{\rho}{C} - \left(\frac{M_2}{1000}\right)\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3.3)$$

Where, C is the molarity, M_2 is the solute molecular weight and ρ is the density of the solution respectively.

The molarity 'C' of a solution was calculated from the following equation:

$$C = \frac{1}{M_2} \times \frac{a}{\text{vol. of solution in liter}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.4)$$

Where, a = weight of the solute (electrolyte) in gm, M_2 = solute molecular weight.

Molar volume of solvent (pure water) at experimental temperature was calculated using the following equation (46).

$$\overline{V_1}^0 = \frac{\text{Molecular masses of solvent}}{\text{Density of solvent (at expt. temp.)}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.5)$$

The partial molar volumes of the solute and solvent can be obtained from density measurement using the following equation.

$$\overline{V_2} = \phi_v + \frac{\sqrt{m}}{2}\left(\frac{\partial \phi_v}{\partial \sqrt{m}}\right) = \phi_v^0 + \frac{3\sqrt{m}}{2}\left(\frac{\partial \phi_v}{\partial \sqrt{m}}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.6)$$

Where, ϕ_v^0 = apparent molar volumes at zero concentration.

and $$\overline{V_1} = V_1^0 - \frac{M_1 m^{3/2}}{2000}\left(\frac{\partial \phi_v}{\partial \sqrt{m}}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.7)$$

The values of $\frac{\partial \phi_v}{\partial \sqrt{m}}$ were obtained from the slope of the plot of φ_v against $\sqrt{C}$ by the use of Masson (50) equation and the apparent molar volume of solutes at infinite dilution ($\varphi_v^0 \approx \overline{V_2}^0$) were determined from the intercept of the plot, at C equal to zero.

3.8 Transfer apparent molar volume of measurements

Limiting apparent molar volume of transfer can be obtained from using the following equation

$(\Delta\varphi_v)_{tra} = \varphi_v$ (in aq.solution) - φ_v (in water) ……………………………….(3.8)

where, φ_v is limiting apparent molar volume.

3.9 Temperature dependent limiting apparent molar volume measurements

At infinite dilution, the variation of limiting apparent molar volumes i.e. (Φ_v^0) with the temperature can be expressed by the general polynomial equation as follows:

$\varphi_v^0 = A + B\,(T - T_m) + C\,(T - T_m)^2$ ……………………………………………..(3.9)

where T is the temperature in Kelvin, T_m is the average temperature, A, B, and C are the empirical constants.

The limiting apparent molar expansibilities are calculated as follows:

$E_{\varphi}^{0} = B + 2C\,(T-T_m)$ ……………………………………………………(3.10)

Hepler developed the general thermo-dynamic expression to determine the capacity of solute as a structure maker or structure breaker in mixed solvent system using general thermodynamic expression (56):

$(\delta E_{\varphi}^{0}/\delta T)_p = 2C$ ……………………………………………………..(3.11)

3.10 Viscosity measurements

Viscosity of water, the binary solution of Paracetamol-water, n-Propanol-Water, n-Butanol-Water, Paracetamol-n-Propanol, Paracetamol-n-Butanol and ternary solution of Paracetamol -Water- n-Propanol, Paracetamol -Water- n-Butanol were measured by using the British standard Ostwald U-type 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 75^0C. 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 mL of doubly distilled water was poured into the viscometer. 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,

$¦ = A°t$ ……………………………………………………...(3.12)

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

Putting the values of the calibration constant, density and time of flow of the experimental solution, the viscosity of that solution was determined by using the equation 3.40.

3.11 Coefficient B and D determinations

The coefficients A and B for the electrolyte solutions were calculated using the empirical equations of Jones-Dole:

$$\eta_r = 1 + A\sqrt{C} + BC$$

$$\text{or, } \frac{\eta_r - 1}{\sqrt{C}} = A + B\sqrt{C}$$

where, η_r is the relative viscosity = $\dfrac{\text{Viscosity of solution}}{\text{Viscosity of solvent}}$

and C is the molar concentration.

For non-electrolyte solute, the modified Jones-Dole equation was used for calculating coefficients B and D (57):

$$\frac{\eta_r - 1}{C} = B + CD \text{ ....(3.13)}$$

The values of the coefficients B and D were obtained from the intercept and slope of the plot $\dfrac{\eta_r - 1}{C}$ against C respectively.

3.12 Thermodynamic parameters

The change of free energy of activation ($\Delta G^{\#}$) was calculated by the help of Nightingle and Benck equation (58):

$$\Delta G^{\#} = RT \ln (\eta V_m / Nh) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.14)}$$

Where η = Viscosity of the liquid in SI unit ($Kg\ m_1^{-1}S^{-1}$)

V_m = Average molar volume of solution (m_1^3)

N= Avogadro's constant = 6.023×10^{23} mol^{-1}

h = Plank's constant = 6.626×10^{-34}Js

T = Absolute temperature (K)

R = Universal gas constant = 8.314 JK^{-1} mol^{-1}

Energy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution were determined y using the Eyring equation:

$$\eta = \left(\frac{Nh}{V_m}\right) e^{\frac{\Delta G^{\#}}{RT}}$$

$$\text{or,} \quad \text{In}\ \frac{\eta V_m}{Nh} = \frac{\Delta G^{\neq}}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.15)}$$

Since, $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$

$$\therefore \ln\left(\frac{\eta V_m}{Nh}\right) = \frac{\Delta H^{\#}}{RT} - \frac{\Delta S^{\#}}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.16)}$$

Assuming $\Delta H^{\#}$ and $\Delta S^{\#}$ are almost independent of temperature in this range, a plot of ln $\frac{\eta V_m}{Nh}$ against $\frac{1}{T}$ will give a straight line with slope = $\frac{\Delta H^{\#}}{R}$ and intercept = - $\frac{\Delta S^{\#}}{R}$ from which,

$$\Delta H^{\#} = \text{slope} \times R \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.17)}$$

and $$\Delta S^{\#} = \text{-intercept} \times R \qquad \text{……………………………………………..(3.18)}$$

3.13 Change of chemical potential (($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$)) for viscous flow

Although a complete theory of B coefficient is not known, even then it has been used for a long time by workers to interpret the interaction between the ions and solvent molecules. The study of B –coefficient is very important for qualitative determination of the effects of ions on the structure of solvents. According to Feakins, Freemantle and Lawrence coefficient B is related to the difference in chemical potential for the flow of one mole of solution having concentration C and that of solvent by the relation (59),

$$X_2\left(\Delta\mu_1^{*} - \Delta\mu_0^{*}\right) = RT \ln \frac{(1 + BC)V_m}{V_0} \qquad \text{…………………… (3.22)}$$

CHAPTERE IV

Results and Discussion

The experimental results and the properties derived from experimental data are presented in this chapter. The results have been discussed in the light of recent developments of the subject. The studied systems are:

- **a) Paracetamol + Water**
- **b) Paracetamol + 80% Water + 20% n-Propanol**
- **c) Paracetamol + 20% Water + 80% n-Propanol**
- **d) Paracetamol + 80% Water + 20% n-Butanol**
- **e) Paracetamol + 20% Water + 80% n-Butanol**

The above-mentioned systems were studied precisely at six equidistant temperatures ranging from 298.15K to 323.15K at interval of 5K by volumetric and viscometric methods. The volumetric properties such as, apparent molar volume (φ_v), transfer apparent molar volume $(\Delta\varphi_v)_{tra}$, partial molar volume (V_2), limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume expansibilities (E_φ^0), limiting apparent molar volume transfer $(\Delta\varphi_v^0)_{tra}$ and $(\delta E^0\varphi/\delta T)_p$ are determined from density data and viscometric properties like coefficient of B and D and thermodynamic properties like viscous free energy ($\Delta G^\#$), enthalpy ($\Delta H^\#$), entropy ($\Delta S^\#$) and change of chemical potential ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) are determined from viscosity data. The obtained information of these systems are presented in various sections and discussed in the light of theories mentioned in the earlier chapter.

4.1 Volumetric Properties

The densities, ρ of paracetamol in water-alcohols systems were determined at temperatures ranging from (298.15K, 303.15K, 308.15K, 313.15k, 318.15K and 323.15K) with the interval of 5K over the concentration ranging from 0.02M to 0.10M. The densities of the solvents have been shown in table 4.1. The densities of these systems have been shown in tables 4.2-4.6 at different temperatures. Figures 4.1-4.5 show the plots of densities as a function of concentration of paracetamol in aqueous solution of n-Propanol and n-Butanol. It shows that densities increase with the increase of concentration of paracetamol and decrease with temperature. The experimental densities of paracetamol (PA) have been found to be in the order of:

PA + Water > PA + 80% Water + 20% n-Propanol
and
PA + Water > PA + 80% Water + 20% n-Butanol
and
PA + Water > PA + 20% Water + 80% n-Propanol
and
PA + Water > PA + 20% Water + 80% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 20% Water + 80% n-Propanol
and
PA + 80% Water + 20% n-Butanol > PA + 20% Water + 80% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 80% Water + 20% n-Butanol
and
PA + 20% Water + 80% n-Propanol > PA + 20% Water + 80% n-Butanol

The densities of paracetamol in Water have been found higher than all the studies systems (80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol, 20% Water + 80% n-Butanol) and it is also observed that the densities are changed significantly during the altering of solvent. The densities of paracetamol are more in high percentage of water containing systems than in low percentage of water containing systems. This is due to the notable unique properties exhibited by liquid water that has high density. Here, the density of paracetamol in 20% Water + 80% n-Propanol is higher than paracetamol in 20% Water + 80% n-Butanol. This is due to the small size of n-

Propanol than n-Butanol; which causes higher interstitial accommodation. The densities decrease linearly with temperature for all the systems. This is due to the increase of thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding is occurred (60).

The apparent molar volumes (φ_v) of these systems are calculated from density data using the equation (2.9). The value of apparent molar volume of paracetamol at different temperatures (298.15, 303.15, 308.15, 313.15, 318.15, 323.15) K are given in tables 4.7-4.11 and figures 4.6-4.10 show the plots of apparent molar volume as a function of concentration of paracetamol at different temperatures.

Examinations of the figures 4.6-4.10 reveal that:

a) The apparent molar volumes increase with the rise of concentration of paracetamol and also with rise of temperatures.
b) Such trends indicate the interactions between solute-solvent as well as solvent-solvent change with temperatures and solvent compositions (61).
c) The values of apparent molar volume for all systems are positive.
d) The positive apparent molar volumes have been found to be in the order of:

PA + 80% Water + 20% n-Propanol > PA + Water
and
PA + 80% Water + 20% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + Water
and
PA + Water > PA + 20% Water + 80% n-Butanol
and
PA + 20% Water + 80% n-Propanol > PA + 80% Water + 20% n-Propanol
and
PA + 80% Water + 20% n-Butanol > PA + 20% Water + 80% n-Butanol
and
PA + 80% Water + 20% n-Butanol > PA + 80% Water + 20% n-Propanol

and

PA + 20% Water + 80% n-Propanol > PA + 20% Water + 80% n-Butanol

The values of transfer apparent molar volume $(\Delta\varphi_v)_{tra}$ have been reported in tables 4.16-4.20 and the values of $\Delta\varphi_v$ are positive for all the studied systems except Paracetamol + 20% Water + 80% n-Butanol system. The observed positive values of $\Delta\varphi_v$ suggest strong solute-solvent interactions of paracetamol with aqueous alcohols solution through H-bonding.

The limiting apparent molar volume (φ_v^0) which is also called the standard partial molar volume of paracetamol in aqueous alcohols solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K are reported in tables 4.16-4.20. The limiting apparent molar volumes (φ_v^0) of paracetamol reflect the true volume of the solute. However, limiting apparent molar volumes at infinite dilution (φ_v^0) of the solute can provide further information regarding (solute + solvent) or (solute + solvent) interactions (62). The apparent molar volumes (φ_v) were observed to correlate linearly with solution concentration (C) at all experimental temperatures, hence standard partial molar volumes (φ_v^0) were obtained from Masson equation (50).The intercept (φ_v^0), i.e., the standard partial molar volume provides a measure of solute-solvent interactions and the slope S_V provides information regarding solvent-solvent interactions (63). The tables 4.16-4.20 show that (φ_v^0) values are positive and increase when both the experimental temperature and paracetamol content in the solvents increase. This trend in limiting apparent molar volume (φ_v^0) indicate the presence of strong (solute + solvent) interactions and such interactions further strengthen at elevated temperatures and such a trend in (φ_v^0) values is at par the trends in (φ_v) values for the studied solutions. The values of experimental slope (S_V) for paracetamol in different aqueous alcohols solutions at the experimental temperatures are reported in tables 4.16-4.20. The tables show that the experimental slopes (S_V) are positive for all the studied systems indicating the structure forming properties of paracetamol in water-alcohols solvents.

The increase of φ_v^0 with temperature may be due to the result of the following effects (64):

a) At higher temperature the thermal energy of the water molecules is increased, causing fast movement of the bulk electrostricted water molecules from the interaction region of -OH and -NH groups, resulting in a positive volume change.
b) An increase in temperature decreases the solute-solute interaction, giving rise to a small negative volume change.
c) A decrease in paracetamol-water interactions causes a positive volume change.
d) The water-water interactions decrease with increasing temperature, giving rise to a small negative change in volume.

The values of limiting apparent molar volume transfer ($\Delta\varphi_v^0$) have been reported in tables 4.17-4.20. The calculated values of $\Delta\varphi_v^0$ as reported in tables 4.17-4.20 are positive for all the studied systems except Paracetamol + 20% Water + 80% n-Butanol system. The observed positive values of $\Delta\varphi_v^0$ suggest strong solute-solvent interactions of paracetamol with aqueous alcohols solution. Since the structural moiety of paracetamol and aqueous alcohols contain polar groups, so interactions between them promote the structure maker ability of solute in the solvent. Hence, the mentioned positive values of transfer volume indicate structure promoter nature of the solute according to co-sphere overlap model (65, 66). Depending upon the co-sphere overlap model regarding the values of $\Delta\varphi_v^0$, there is negligible contribution from solute-solute interactions and hence they provide information regarding solute-solvent interactions. The various interactions that occur between paracetamol and aq. alcohols molecules can be categorized by hydrophilic-hydrophilic interactions between polar groups of paracetamol and polar groups of alcohols and water. According to co-sphere overlap model, hydrophobic- hydrophobic interactions contribute positively to the $\Delta\varphi_v^0$ values. Therefore, in our present study, it is deduced that hydrophilic-hydrophilic interactions are mainly dominating. The negative values of $\Delta\varphi_v^0$ for Paracetamol + 20% Water + 80% n-Butanol show the weak solute-solvent interaction or structure breaking ability in solute in solvent.

The sign of $(\delta E_\varphi^0/\delta T)_p$ determines the tendency of a dissolved solute as a structure maker or structure breaker in a solvent which suggests that positive and small negative $(\delta E^0\varphi/\delta T)_p$ values are observed for solutes having structure making capacity. The values of limiting apparent molar volume expansibilities E_φ^0 and $(\delta E_\varphi^0/\delta T)_p$ are reported in tables 4.12-4.16. The E_φ^0 values are found to be positive at all temperatures and concentrations of paracetamol. The positive values of E_φ^0 as reported in tables 4.16-4.20 suggest the presence of solute-solvent interactions in these systems, as already indicated by apparent molar volume data. The positive values of E_φ^0 may occur due to phenomenon of packing effect or caging which further suggests interaction between paracetamol and aq. alcohols molecules. The E_φ^0 values show an irregular trend with an increase of temperature. The positive and small negative values of $(\delta E_\varphi^0/\delta T)_p$ for studied systems show the structure making ability of paracetamol in all aq. alcohols solutions (67-72).

The value of partial molar volume (V_2) of solute and the value of partial molar volume (V_1) of solvent are shown in tables 4.21-4.30 and figures 4.11-4.20 show the plots of partial molar volume as a function of concentration of paracetamol in aqueous solution of n-Propanol and n-Butanol. The value of partial molar volume (V_2) increases with increasing of concentration of paracetamol and the value of (V_1) slightly decreases for all the systems. This suggests that solute-solvent interactions increase with increasing concentration of paracetamol.

4.2 Viscometric Properties

The viscosities of paracetamol in water-alcohols systems were determined at temperatures ranging from (298.15K-323.15K) with the interval of 5K are shown in tables 4.31-4.35. The variations of viscosities at these temperatures as a function of the concentration of paracetamol are shown in figures 4.21-4.25. The following characteristic features of viscosity are observed:

a) Viscosities increase with increasing of concentration of paracetamol.
b) Viscosity decreases with increasing of temperatures.
c) The viscosities of paracetamol at 298.15K temperature have been found to be in the order of:

PA + 80% Water + 20% n-Propanol > PA + Water

and

PA + 80% Water + 20% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + Water
and
PA + 20% Water + 80% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + 80% Water + 20% n-Propanol
and
PA + 20% Water + 80% n-Butanol > PA + 80% Water + 20% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 80% Water + 20% n-Butanol
and
PA + 20% Water + 80% n-Propanol > PA + 20% Water + 80% n-Butanol

The increase of viscosity (η) with concentration may be interpreted by the fact that paracetamol molecules penetrate in the void spaces of the hydrogen bonded framework of water and alcohols and may have positive interaction with the solvent. The interaction seems to be strong. Thus paracetamol may be considered as water structure maker at the temperature range of 298.15K-323.15K. The structure making concept is reasonable on the grounds that paracetamol may enter into cluster formation in aqueous solutions due to its available hydrogen bonding groups –OH and -NH_2.

- Examinations of the figures 4.21-4.25 reveal that:

a) In the presence of paracetamol in general, the values of viscosity decreases with the increase of percentage of water in mixed solvent. This may be due to the interaction between water and alcohols molecules through H-bonds (73).
b) The value of viscosity increases with the increase of concentration of paracetamol. This indicates that, there is a interaction between the molecules of paracetamol and the solvent (water and alcohols).This may be due to the presence of hydroxyl group in all the three studied molecules (water, alcohols and paracetamol) (74).

The B-coefficients of different solutions containing paracetamol at different temperature are presented in tables 4.31-4.35. The B-coefficient reflects the net structural effects of polar groups and hydrophobic benzene ring and also the effects of solute-solvent interactions on the solution and provides information about the structure making or breaking properties between solute and solvent. Tables 4.16-4.20 show that the B-coefficients for paracetamol in the studied solvent systems are positive and thus suggest the presence of solute-solvent interactions or structure making properties in the all studies solutions.

Tables 4.31-4.35 also reveal that:

a) There is no systematic change of viscosity B-coefficients in Paracetamol + Water binary system; but has positive values showing structure making properties between water and paracetamol.
b) In the cases of Paracetamol + 80% Water + 20% n-Propanol and Paracetamol + 20% Water + 80% n-Butanol systems, the viscosity B-coefficients increase with the rise of temperature suggesting the structure-making tendency is more in the low concentration of paracetamol through H-bonding.
c) Similar tendency is also shown for viscosity B-coefficient of Paracetamol + 20% Water + 80% n-Propanol and Paracetamol + 80% Water + 20% n-Butanol systems except 308.15K temperature.

The values of D-coefficient for paracetamol in water-alcohols mixed solvent were presented in tables 4.31-4.35. The values are mainly negative and also irregular. The D-coefficient value indicates the solute–solute interactions coupled with size and shape effect of the solute and to some extent solute–solvent interactions. Due to lack of adequate theoretical knowledge, its significance is not fully understood (75). The negative D-value obtained in this case may represent that the increase in viscosity with the solute concentration is due to some additional factors other than the solute-solvent interactions (i.e., B-coefficient) which imparts negative contribution to the increase in viscosity (76).

4.3. Thermodynamic properties

The thermodynamic parameters such as free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) for the viscous flow of these systems are calculated by using equations 3.14, 3.17 and 3.18. Free energy ($\Delta G^{\#}$) for the viscous flow of the systems is shown in tables 4.37-4.41. The variation of free energy ($\Delta G^{\#}$) at these temperatures as a function of concentration of paracetamol is shown in figures 4.26-4.30.

The following characteristic features of free energies ($\Delta G^{\#}$) are observed:

a) The free energy ($\Delta G^{\#}$) increase with the increase of concentration of paracetamol.
b) The $\Delta G^{\#}$ value is positive for all the studied systems.
c) The $\Delta G^{\#}$ decrease with the increase of temperature.
d) The $\Delta G^{\#}$ of paracetamol at 298.15K temperature has been found to be in the orders:

PA + 80% Water + 20% n-Propanol > PA + Water
and
PA + 80% Water + 20% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + Water
and
PA + 20% Water + 80% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + 80% Water + 20% n-Propanol
and
PA + 20% Water + 80% n-Butanol > PA + 80% Water + 20% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 80% Water + 20% n-Butanol
and
PA + 20% Water + 80% n-Butanol > PA + 20% Water + 80% n-Propanol

The positive free energy for viscous flow can be interpreted with help of the Furth model (77), which states that the kinetic species involved in forming cavities or holes in the medium is given by the work required in forming the hole against surface tension of these systems. The solute-solvent interaction is also reflected by positive $\Delta G^{\#}$-values. It is seen that the $\Delta G^{\#}$ values of paracetamol in aqueous solutions of n-Propanol and n-Butanol increase very slowly with increasing solute concentration and decrease with increasing temperature (Figs. 4.26-4.30). The slow increase in $\Delta G^{\#}$-values for aqueous paracetamol solutions indicates that the structure-making property is rise with increasing solute concentration.

The enthalpy and entropy of flow process are obtained from the temperature dependence of viscosity which is presented in tables 4.42- 4.46. It shows that the value of enthalpy increases with the increase of concentration of paracetamol and the value of entropy decrease with the increase of concentration of paracetamol for most of the systems. An investigation of the $\Delta H^{\neq}$ values of paracetamol of these systems reveals the following order:

PA + 80% Water + 20% n-Propanol > PA + Water
and
PA + 80% Water + 20% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + Water
and
PA + 20% Water + 80% n-Butanol > PA + Water
and
PA + 20% Water + 80% n-Propanol > PA + 80% Water + 20% n-Propanol
and
PA + 20% Water + 80% n-Butanol > PA + 80% Water + 20% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 80% Water + 20% n-Butanol
and
PA + 20% Water + 80% n-Butanol > PA + 20% Water + 80% n-Propanol

The change of chemical potential ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) of the studied systems is shown in tables 4.47-4.51. According to Freemantle and Lawrence, (59), the viscosity B-coefficient is related to the difference in chemical potential for the flow of 1 mole of solute. The change in chemical potential values ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) indicates the solute-solvent interactions presence in the studied systems. A positive and high value of ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) indicates strong interaction between solute and solvents, whereas a low and negative value of ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) indicates structure disorder (78, 79). An examination of the data indicates that positive values of ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) are obtained for all the systems, corresponding to strong solute-solvent interaction. The positive change of chemical potential ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) of paracetamol is found in the order of:

PA + Water > PA + 80% Water + 20% n-Propanol
and
PA + Water > PA + 80% Water + 20% n-Butanol
and
PA + Water > PA + 20% Water + 80% n-Propanol
and
PA + Water > PA + 20% Water + 80% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 20% Water + 80% n-Propanol
and
PA + 80% Water + 20% n-Butanol > PA + 20% Water + 80% n-Butanol
and
PA + 80% Water + 20% n-Propanol > PA + 80% Water + 20% n-Butanol
and
PA + 20% Water + 80% n-Propanol > PA + 20% Water + 80% n-Butanol

However, for paracetamol in the aqueous solution of alcohols (n-Propanol and n-Butanol) solvent system, the values of ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) decrease with increasing paracetamol concentration for all the studied systems. It is also observed that the values of ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) are greater in Paracetamol + Water, Paracetamol + 80% Water + 20% n-Propanol and Paracetamol + 80% Water + 20% n-Butanol systems than Paracetamol + 20% Water + 80% n-Propanol and Paracetamol + 20% Water + 80% n-Butanol systems. This indicates the greater contribution per mole of solute to free energy of activation for viscous flow of the higher percentage of water containing solutions than lower percentage of water containing solutions and are good agreements with the values of B-coefficient showing structure making properties between solute and solvent.

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Table 4.1: Density (ρ) of solvents (Water, 80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol and 20% Water + 80% n-Butanol) at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Solvent	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Water	0.99709	0.99581	0.99391	0.99231	0.99021	0.98803
80% Water + 20% n-Propanol	0.976202	0.976008	0.975812	0.975572	0.975412	0.975212
20% Water + 80% n-Propanol	0.864384	0.860508	0.857684	0.854188	0.850788	0.846612
80% Water + 20% n-Butanol	0.971092	0.969988	0.969012	0.968036	0.967092	0.966052
20% Water + 80% n-Butanol	0.845286	0.842946	0.859024	0.855871	0.852581	0.848850

Table 4.2: Density (ρ) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	0.998023	0.996934	0.995483	0.994065	0.992165	0.990031
0.0399	0.998191	0.997338	0.9960278	0.994567	0.992178	0.990812
0.0600	0.998223	0.997687	0.996543	0.994661	0.992295	0.990795
0.0800	0.998304	0.998045	0.997054	0.995643	0.992276	0.991023
0.0999	0.998412	0.998226	0.997099	0.996387	0.993078	0.992058

Table 4.3: Density (*ρ)* of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	0.977058	0.976843	0.976629	0.976371	0.976190	0.975971
0.0399	0.977909	0.977675	0.977442	0.977165	0.976963	0.976727
0.0600	0.978757	0.978502	0.978251	0.977955	0.977733	0.977478
0.0800	0.979600	0.979326	0.979056	0.978741	0.978498	0.978225
0.0999	0.980441	0.980147	0.979859	0.979523	0.979260	0.978966

Table 4.4: Density (*ρ*) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	0.865044	0.861168	0.858336	0.854823	0.851418	0.847233
0.0399	0.865696	0.861817	0.858979	0.855447	0.852036	0.847840
0.0600	0.866340	0.862455	0.859614	0.856058	0.852642	0.848431
0.0800	0.866976	0.863082	0.860240	0.856657	0.853237	0.849006
0.0999	0.867604	0.863699	0.860858	0.857245	0.853821	0.849567

Table 4.5: Density (ρ) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	0.971548	0.970425	0.969432	0.968447	0.967495	0.966449
0.0399	0.971986	0.970845	0.969833	0.968839	0.967875	0.966819
0.0600	0.972403	0.971246	0.970217	0.969217	0.968234	0.967163
0.0800	0.972807	0.971628	0.970582	0.969574	0.968570	0.967483
0.0999	0.973187	0.971993	0.970921	0.969913	0.968885	0.967778

Table 4.6: Density (ρ) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\circ}{g.cm^{-3}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	0.859024	0.855871	0.852581	0.848850	0.847057	0.844703
0.0399	0.860842	0.857675	0.854375	0.850631	0.848824	0.846454
0.0600	0.862657	0.859476	0.856166	0.852409	0.850587	0.848203
0.0800	0.864468	0.861275	0.857952	0.854184	0.852347	0.849949
0.0999	0.866275	0.863067	0.859735	0.855954	0.854102	0.851692

Table 4.7: Apparent molar volume (φ_v) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{\psi_V}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	105.10	106.12	107.31	108.20	109.25	110.19
0.0399	105.15	106.16	107.36	108.24	109.29	110.23
0.0600	105.20	106.21	107.40	108.28	109.33	110.33
0.0800	105.30	106.25	107.44	108.44	109.49	110.39
0.0999	105.54	106.43	107.64	108.53	109.75	110.54

Table 4.8: Apparent molar volume (φ_v) of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{\psi_V}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	111.03	112.08	113.04	114.01	115.11	116.07
0.0399	111.02	112.06	113.05	114.02	115.11	116.08
0.0600	111.23	112.29	113.26	114.23	115.32	116.28
0.0800	111.34	112.39	113.35	114.34	115.43	116.39
0.0999	111.38	112.43	113.40	114.41	115.48	116.47

Table 4.9: Apparent molar volume (φ_v) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\psi_V}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	136.70	137.34	138.23	139.78	140.67	141.85
0.0399	136.83	137.55	138.39	140.03	140.91	142.20
0.0600	137.16	137.96	138.74	140.48	141.35	142.75
0.0800	137.40	138.27	138.99	140.83	141.69	143.20
0.0999	137.59	138.54	139.20	141.14	141.99	143.6151

Table 4.10: Apparent molar volume (φ_v) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\psi_V}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	132.18	133.29	134.34	134.93	135.49	135.95
0.0399	132.59	133.70	134.76	135.36	136.01	136.58
0.0600	133.15	134.23	135.28	135.82	136.63	137.31
0.0800	133.58	134.71	135.75	136.29	137.20	137.96
0.0999	134.06	135.15	136.28	136.74	137.75	138.59

Table 4.11: Apparent molar volume (φ_v) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{\psi_V}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	70.07	71.11	72.04	73.06	74.09	75.12
0.0399	69.91	70.95	71.88	72.91	73.94	75.04
0.0600	70.28	71.34	72.25	73.28	74.31	75.39
0.0800	70.39	71.42	72.36	73.39	74.42	75.48
0.0999	70.39	71.44	72.36	73.39	74.43	75.47

Table 4.12: Transfer apparent molar volume $(\Delta\varphi_v)_{tra}$ of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{(\Delta\varphi_v)_{tra}}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	5.93	5.96	5.73	5.81	5.86	5.88
0.0399	5.87	5.90	5.69	5.78	5.82	5.85
0.0600	6.03	6.08	5.86	5.95	5.99	5.95
0.0800	6.04	6.14	5.91	5.90	5.94	6.00
0.0999	5.84	6.00	5.76	5.88	5.73	5.93

Table 4.13: Transfer apparent molar volume $(\Delta\varphi_V)_{tra}$ of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. (*mol.L^{-1}*)	$\frac{(\Delta\varphi_V)_{tra}}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	31.60	31.22	30.93	31.58	31.42	31.66
0.0399	31.68	31.39	31.04	31.80	31.63	31.98
0.0600	31.96	31.75	31.34	32.20	32.02	32.42
0.0800	32.10	32.02	31.55	32.39	32.20	32.81
0.0999	32.05	32.11	31.56	32.61	32.24	33.08

Table 4.14: Transfer apparent molar volume $(\Delta\varphi_V)_{tra}$ of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. (*mol.L^{-1}*)	$\frac{(\Delta\varphi_V)_{tra}}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	27.08	27.17	27.03	26.73	26.24	25.76
0.0399	27.44	27.54	27.40	27.12	26.72	26.35
0.0600	27.96	28.02	27.88	27.54	27.30	26.98
0.0800	28.29	28.46	28.31	27.85	27.71	27.57
0.0999	28.53	28.72	28.64	28.21	28.00	28.05

Table 4.15: Transfer apparent molar volume $(\Delta\varphi_V)_{tra}$ of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{(\Delta\varphi_V)_{tra}}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	-35.03	-35.01	-35.27	-35.14	-35.16	-35.07
0.0399	-35.24	-35.21	-35.48	-35.33	-35.35	-35.19
0.0600	-34.92	-34.87	-35.15	-35.00	-35.02	-34.94
0.0800	-34.91	-34.83	-35.08	-35.05	-35.07	-34.91
0.0999	-35.15	-34.99	-35.28	-35.14	-35.32	-35.07

Table 4.16: Limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume expansibilities (E_φ^0) and $(\delta E_\varphi^0/\delta T)_p$ of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Temp (K)	Conc. (mol.L^{-1})	φ_v^0 (cm^3.mol^{-1})	S_V	E_φ^0 (cm^3.mol^{-1}.K^{-1})	$(\delta E_\varphi^0/\delta T)_p$
298.15K	0.0200	104.95	5.17	0.22	-0.002
	0.0399				
	0.0600				
	0.0800				
	0.0999				
303.15K	0.0200	106.02	3.56	0.22	
	0.0399				
	0.0600				
	0.0800				
	0.0999				
308.15K	0.0200	107.21	3.71	0.23	
	0.0399				
	0.0600				
	0.0800				
	0.0999				
313.15K	0.0200	108.08	4.32	0.20	
	0.0399				
	0.0600				
	0.0800				
	0.0999				
318.15K	0.0200	109.06	6.02	0.19	
	0.0399				
	0.0600				
	0.0800				
	0.0999				
323.15K	0.0200	110.08	4.32	0.18	
	0.0399				
	0.0600				
	0.0800				
	0.0999				

Table 4.17: Limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume transfer ($\Delta\varphi_v^0$), limiting apparent molar volume expansibilities (E_φ^0) and $(\delta E_\varphi^0/\delta T)_p$ of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Temp (K)	Conc. (mol.L^{-1})	φ_v^0 (cm^3.mol^{-1})	S_V	$\Delta\varphi_v^0$ (cm^3.mol^{-1})	E_φ^0 (cm^3.mol^{-1}.K^{-1})	$(\delta E_\varphi^0/\delta T)_p$
298.15K	0.0200	110.90	5.07	5.95	0.20	0.0001
	0.0399					
	0.0600					
	0.0800					
	0.0999					
303.15K	0.0200	111.94	5.12	5.92	0.20	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
308.15K	0.0200	112.91	5.11	5.70	0.19	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
313.15K	0.0200	113.87	5.61	5.79	0.20	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
318.15K	0.0200	114.97	5.31	5.91	0.20	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
323.15K	0.0200	115.93	5.56	5.85	0.20	
	0.0399					
	0.0600					
	0.0800					
	0.0999					

Table 4.18: Limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume transfer ($\Delta\varphi_v^0$), limiting apparent molar volume expansibilities (E_φ^0) and $(\delta E_\varphi^0/\delta T)_p$ of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Temp (K)	Conc. (mol.L^{-1})	φ_v^0 (cm^3.mol^{-1})	S_V	$\Delta\varphi_v^0$ (cm^3.mol^{-1})	E_φ^0 (cm^3.mol^{-1}.K^{-1})	$(\delta E_\varphi^0/\delta T)_p$
298.15K	0.0200	136.43	11.74	31.49	0.18	0.002
	0.0399					
	0.0600					
	0.0800					
	0.0999					
303.15K	0.0200	137.00	15.62	30.98	0.19	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
308.15K	0.0200	137.95	12.65	30.75	0.17	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
313.15K	0.0200	139.40	17.61	31.32	0.21	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
318.15K	0.0200	140.30	17.11	31.24	0.22	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
323.15K	0.0200	141.37	22.62	31.29	0.23	
	0.0399					
	0.0600					
	0.0800					
	0.0999					

Table 4.19: Limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume transfer ($\Delta\varphi_v^0$), limiting apparent molar volume expansibilities (E_φ^0) and $(\delta E_\varphi^0/\delta T)_p$ of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Temp (K)	Conc. (mol.L^{-1})	φ_v^0 (cm^3.mol^{-1})	S_V	$\Delta\varphi_v^0$ (cm^3.mol^{-1})	E_φ^0 (cm^3.mol^{-1}.K^{-1})	$(\delta E_\varphi^0/\delta T)_p$
298.15K	0.0200	131.69	23.81	26.74	0.24	-0.008
	0.0399					
	0.0600					
	0.0800					
	0.0999					
303.15K	0.0200	132.80	23.63	26.78	0.20	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
308.15K	0.0200	133.82	24.35	26.61	0.26	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
313.15K	0.0200	134.46	22.78	26.38	0.12	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
318.15K	0.0200	134.90	28.58	25.84	0.08	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
323.15K	0.0200	135.28	33.34	25.20	0.04	
	0.0399					
	0.0600					
	0.0800					
	0.0999					

Table 4.20: Limiting apparent molar volume (φ_v^0), experimental slope (S_V), limiting apparent molar volume transfer ($\Delta\varphi_v^0$), limiting apparent molar volume expansibilities (E_φ^0) and $(\delta E_\varphi^0/\delta T)_p$ of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Temp (K)	Conc. ($mol.L^{-1}$)	φ_v^0 ($cm^3.mol^{-1}$)	S_V	$\Delta\varphi_v^0$ ($cm^3.mol^{-1}$)	E_φ^0 ($cm^3.mol^{-1}.K^{-1}$)	$(\delta E_\varphi^0/\delta T)_p$
298.15K	0.0200	69.87	5.64	-35.08	0.18	0.002
	0.0399					
	0.0600					
	0.0800					
	0.0999					
303.15K	0.0200	70.91	5.68	-35.11	0.19	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
308.15K	0.0200	71.43	5.68	-35.77	0.17	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
313.15K	0.0200	72.86	5.78	-35.22	0.21	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
318.15K	0.0200	73.89	5.78	-35.17	0.22	
	0.0399					
	0.0600					
	0.0800					
	0.0999					
323.15K	0.0200	74.96	5.67	-35.12	0.23	
	0.0399					
	0.0600					
	0.0800					
	0.0999					

Table 4.21: Partial molar volume (V_2) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_2}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	105.11	106.13	107.32	108.21	109.26	110.20
0.0399	105.17	106.18	107.38	108.26	109.31	110.25
0.0600	105.23	106.24	107.43	108.31	109.36	110.36
0.0800	105.34	106.29	107.48	108.48	109.53	110.43
0.0999	105.59	106.48	107.69	108.58	109.80	110.59

Table 4.22: Partial molar volume (V_2) of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_2}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	111.04	112.09	113.05	114.02	115.12	116.08
0.0399	111.04	112.08	113.07	114.04	115.13	116.10
0.0600	111.26	112.32	113.29	114.26	115.35	116.31
0.0800	111.38	112.43	113.39	114.38	115.47	116.43
0.0999	111.43	112.48	113.45	114.46	115.53	116.52

Table 4.23: Partial molar volume (V_2) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_2}{\mathrm{cm^3.mol^{-1}}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	136.71	137.35	138.25	139.79	140.68	141.86
0.0399	136.85	137.57	138.42	140.06	140.94	142.23
0.0600	137.19	137.99	138.77	140.51	141.38	142.78
0.0800	137.44	138.31	139.03	140.87	141.73	143.24
0.0999	137.64	138.59	139.25	141.19	142.04	143.66

Table 4.24: Partial molar volume (V_2) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_2}{\mathrm{cm^3.mol^{-1}}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	132.19	133.30	134.35	134.94	135.50	135.96
0.0399	132.61	133.72	134.78	135.38	136.03	136.60
0.0600	133.19	134.26	135.31	135.85	136.66	137.34
0.0800	133.63	134.75	135.79	136.33	137.24	138.00
0.0999	134.12	135.20	136.33	136.79	137.80	138.64

Table 4.25: Partial molar volume (V_2) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_2}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	70.08	71.12	72.05	73.07	74.10	75.13
0.0399	69.93	70.97	71.90	72.93	73.96	75.06
0.0600	70.31	71.37	72.28	73.31	74.34	75.42
0.0800	70.43	71.46	72.40	73.43	74.46	75.52
0.0999	70.44	71.49	72.41	73.44	74.48	75.52

Table 4.26: Partial molar volume (V_1) of Water in Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_1}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	18.05	18.09	18.11	18.13	18.18	18.21
0.0399	18.05	18.08	18.11	18.14	18.18	18.21
0.0600	18.05	18.08	18.10	18.14	18.17	18.21
0.0800	18.05	18.07	18.10	18.14	18.17	18.21
0.0999	18.05	18.07	18.09	18.13	18.17	18.21

Table 4.27: Partial molar volume (V_1) of Water in Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_1}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	18.43	18.44	18.44	18.45	18.45	18.45
0.0399	18.43	18.44	18.43	18.45	18.45	18.45
0.0600	18.4	18.44	18.43	18.44	18.45	18.45
0.0800	18.43	18.44	18.42	18.44	18.45	18.45
0.0999	18.43	18.44	18.41	18.44	18.45	18.45

Table 4.28: Partial molar volume (V_1) of n-Propanol in Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	$\frac{V_1}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	69.53	69.84	70.07	70.35	70.63	70.99
0.0399	69.53	69.84	70.07	70.35	70.63	70.98
0.0600	69.52	69.83	70.07	70.35	70.63	70.98
0.0800	69.52	69.83	70.06	70.35	70.63	70.98
0.0999	69.52	69.83	70.06	70.35	70.63	70.98

Table 4.29: Partial molar volume (V_1) of Water in Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L^{-1}*)	$\frac{V_1}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	18.53	18.56	18.58	18.59	18.61	18.63
0.0399	18.53	18.56	18.57	18.59	18.61	18.63
0.0600	18.52	18.55	18.57	18.59	18.60	18.62
0.0800	18.52	18.55	18.57	18.58	18.60	18.62
0.0999	18.52	18.54	18.56	18.58	18.60	18.62

Table 4.30: Partial molar volume (V_1) of n-Butanol in Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L^{-1}*)	$\frac{V_1}{cm^3.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	86.47	86.79	87.12	87.50	87.68	87.93
0.0399	86.47	86.78	87.12	87.50	87.69	87.93
0.0600	86.47	86.78	87.13	87.50	87.69	87.93
0.0800	86.47	86.78	87.13	87.50	87.69	87.93
0.0999	86.47	86.78	87.12	87.50	87.68	87.92

Table 4.31: Viscosity (η) of solvents (Water, 80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol, 20% Water + 80% n-Butanol) at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Solvent	$\frac{\eta}{mPa.s}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
Water	0.8890	0.7982	0.7222	0.6531	0.5964	0.5474
80% Water + 20% n-Propanol	1.6676	1.4429	1.2578	1.0994	0.9601	0.8492
20% Water + 80% n-Propanol	2.4473	2.0912	1.8152	1.5784	1.3612	1.1888
80% Water + 20% n-Butanol	1.1767	1.0504	0.9439	0.8410	0.7555	0.6835
20% Water + 80% n-Butanol	2.3277	1.9738	1.6812	1.4375	1.2344	1.0682

Table 4.32: Viscosity (η), Coefficient B and D of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	0.8905	1.42	18.79	0.8150	1.22	-5.29	0.7450	1.65	-9.48
0.0399	0.8921			0.8309			0.7572		
0.0600	0.8937			0.8438			0.7648		
0.0800	0.8962			0.8550			0.7706		
0.0999	0.8998			0.8576			0.7806		

Conc. (*mol.L*$^{-1}$)	313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	0.6730	1.58	-6.24	0.6110	1.11	-5.43	0.5490	1.24	2.57
0.0399	0.6894			0.6193			0.5743		
0.0600	0.6916			0.6211			0.5858		
0.0800	0.7106			0.6417			0.5884		
0.0999	0.7206			0.6468			0.6035		

Table 4.33: Viscosity (*η*), Coefficient B and D of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	1.6972	0.77	3.58	1.4773	1.09	0.32	1.2889	1.13	-0.97
0.0399	1.7256			1.5026			1.3087		
0.0600	1.7632			1.5304			1.3289		
0.0800	1.8076			1.5682			1.3594		
0.0999	1.8603			1.6159			1.4013		
Conc. (*mol.L*$^{-1}$)	313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	1.1351	1.51	-3.83	0.9978	1.87	-6.96	0.8843	1.98	-8.11
0.0399	1.1511			1.0136			0.8990		
0.0600	1.1760			1.0339			0.9145		
0.0800	1.2036			1.0582			0.9370		
0.0999	1.2353			1.0874			0.9633		

Table 4.34: Viscosity (η), Coefficient B and D of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	2.5027	1.12	1.26	2.1591	1.61	-2.65	1.8735	1.54	-2.19
0.0399	2.5660			2.2127			1.9119		
0.0600	2.6202			2.2677			1.9663		
0.0800	2.6864			2.3241			2.0143		
0.0999	2.7542			2.3817			2.0635		
Conc. (*mol.L*$^{-1}$)	313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	1.6316	1.68	-3.63	1.4271	2.42	-10.46	1.2474	2.49	-11.74
0.0399	1.6709			1.4609			1.2765		
0.0600	1.7110			1.4955			1.3063		
0.0800	1.7522			1.5309			1.3317		
0.0999	1.7942			1.5671			1.3627		

Table 4.35: Viscosity (η), Coefficient B and D of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	1.1919	0.65	-1.07	1.0655	0.72	-1.40	0.9575	0.71	-1.31
0.0399	1.2043			1.0775			0.9677		
0.0600	1.2169			1.0894			0.9774		
0.0800	1.2293			1.1012			0.9892		
0.0999	1.2418			1.1133			1.0011		
Conc. ($mol.L^{-1}$)	**313.15K**			**318.15K**			**323.15K**		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	0.8565	0.93	-2.51	0.7705	1.01	-2.76	0.6974	1.02	-3.12
0.0399	0.8674			0.7821			0.7067		
0.0600	0.8782			0.7925			0.7160		
0.0800	0.8895			0.8033			0.7252		
0.0999	0.9002			0.8130			0.7347		

Table 4.36: Viscosity (*η*), Coefficient B and D of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. (*mol.L*$^{-1}$)	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	2.3679	0.76	4.45	2.0138	0.92	4.97	1.7212	1.07	3.43
0.0399	2.4115			2.0636			1.7588		
0.0600	2.4758			2.1163			1.8072		
0.0800	2.5315			2.1802			1.8593		
0.0999	2.6095			2.2552			1.9246		

Conc. (*mol.L*$^{-1}$)	313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D	$\frac{\eta}{mPa.s}$	B	D
0.0200	1.4775	1.29	1.43	1.2744	1.45	-1.71	1.1082	1.79	-3.58
0.0399	1.5112			1.2937			1.1331		
0.0600	1.5517			1.3238			1.1616		
0.0800	1.5962			1.3621			1.1941		
0.0999	1.6510			1.4076			1.2324		

Table 4.37: Free energy ($\Delta G^{\#}$) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta G^{\#}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	9.14	9.15	9.07	8.96	8.85	8.59
0.0399	9.23	9.25	9.17	9.08	8.94	8.69
0.0600	9.32	9.34	9.25	9.14	8.99	8.80
0.0800	9.39	9.43	9.32	9.26	9.15	8.90
0.0999	9.47	9.52	9.40	9.35	9.22	9.11

Table 4.38: Free energy ($\Delta G^{\#}$) of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta G^{\#}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	10.87	10.70	10.53	10.37	10.19	10.03
0.0399	10.96	10.80	10.62	10.46	10.29	10.13
0.0600	11.07	10.89	10.71	10.57	10.40	10.23
0.0800	11.18	11.01	10.82	10.68	10.51	10.35
0.0999	11.30	11.13	10.95	10.80	10.64	10.48

Table 4.39: Free energy ($\Delta G^{\#}$) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta G^{\#}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	15.08	14.97	14.86	14.75	14.64	14.53
0.0399	15.15	15.04	14.92	14.83	14.72	14.60
0.0600	15.21	15.12	15.01	14.90	14.79	14.67
0.0800	15.29	15.19	15.08	14.97	14.87	14.74
0.0999	15.36	15.26	15.15	15.05	14.94	14.81

Table 4.40: Free energy ($\Delta G^{\#}$) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta G^{\#}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	10.00	9.89	9.78	9.66	9.53	9.42
0.0399	10.08	9.98	9.87	9.75	9.63	9.51
0.0600	10.16	10.06	9.95	9.83	9.72	9.61
0.0800	10.24	10.14	10.03	9.92	9.81	9.70
0.0999	10.32	10.22	10.12	10.01	9.90	9.79

Table 4.41: Free energy ($\Delta G^{\#}$) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta G^{\#}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	15.34	15.19	15.05	14.91	14.76	14.63
0.0399	15.39	15.26	15.11	14.97	14.81	14.69
0.0600	15.46	15.33	15.19	15.05	14.87	14.76
0.0800	15.52	15.41	15.27	15.13	14.95	14.84
0.0999	15.60	15.50	15.36	15.22	15.05	14.93

Table 4.42: Enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$
0.0200	15.51	21.09
0.0399	13.88	15.42
0.0600	14.40	16.86
0.0800	15.05	18.71
0.0999	13.34	12.88

Table 4.43: Enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$
0.0200	20.86	33.53
0.0399	20.89	33.29
0.0600	20.94	33.13
0.0800	20.96	32.84
0.0999	21.04	32.69

Table 4.44: Enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$
0.0200	21.61	21.90
0.0399	21.65	21.81
0.0600	21.63	21.51
0.0800	21.78	21.74
0.0999	21.84	21.70

Table 4.45: Enthalpy (*$\Delta H^{\#}$*) and entropy (*$\Delta S^{\#}$*) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$
0.0200	17.06	23.65
0.0399	16.93	22.96
0.0600	16.83	22.34
0.0800	16.72	21.73
0.0999	16.64	21.19

Table 4.46: Enthalpy (*$\Delta H^{\#}$*) and entropy (*$\Delta S^{\#}$*) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$
0.0200	23.82	28.45
0.0399	23.85	28.36
0.0600	23.92	28.35
0.0800	23.81	27.75
0.0999	23.79	27.41

Table 4.47: Change of chemical potential ($\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$) of Paracetamol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	41.03	38.48	45.43	44.30	36.69	40.59
0.0399	40.52	38.04	44.81	43.71	36.30	38.94
0.0600	40.03	37.62	44.20	43.14	35.91	38.35
0.0800	39.55	37.21	43.62	42.59	35.54	37.77
0.0999	39.09	36.81	43.06	42.06	35.17	37.28

Table 4.48: Change of chemical potential ($\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$) of Paracetamol + 80% Water + 20% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	30.36	35.99	36.62	42.65	48.32	50.22
0.0399	30.07	35.60	36.22	42.10	47.59	49.35
0.0600	29.79	35.22	35.83	41.56	46.88	48.56
0.0800	29.51	34.85	35.45	41.04	46.20	47.81
0.0999	29.24	34.49	35.08	40.55	45.56	47.11

Table 4.49: Change of chemical potential ($\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$) of Paracetamol + 20% Water + 80% n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$ $KJ.mol^{-1}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	19.45	26.65	25.67	27.62	37.87	42.38
0.0399	19.27	26.29	25.34	27.23	37.09	39.80
0.0600	19.09	25.94	25.02	26.86	36.36	38.42
0.0800	18.92	25.61	24.71	26.50	35.66	37.40
0.0999	18.76	25.29	24.41	26.15	35.01	36.54

Table 4.50: Change of chemical potential ($\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$) of Paracetamol + 80% Water + 20% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$ $KJ.mol^{-1}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	28.41	30.01	29.85	33.35	34.62	34.78
0.0399	28.15	29.72	29.57	33.02	34.26	34.42
0.0600	27.89	29.44	29.29	32.68	33.91	34.06
0.0800	27.63	29.17	29.02	32.36	33.56	33.71
0.0999	27.39	28.91	28.76	32.05	33.23	33.38

Table 4.51: Change of chemical potential ($\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}$) of Paracetamol + 20% Water + 80% n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively

Conc. ($mol.L^{-1}$)	$\frac{\Delta\mu_1^{\neq} - \Delta\mu_o^{\neq}}{KJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0200	13.46	15.94	18.04	21.11	23.34	30.03
0.0399	13.38	15.81	17.88	20.88	23.05	28.61
0.0600	13.29	15.69	17.72	20.65	22.77	27.86
0.0800	13.21	15.58	17.56	20.44	22.50	27.30
0.0999	13.13	15.46	17.41	20.23	22.24	26.82

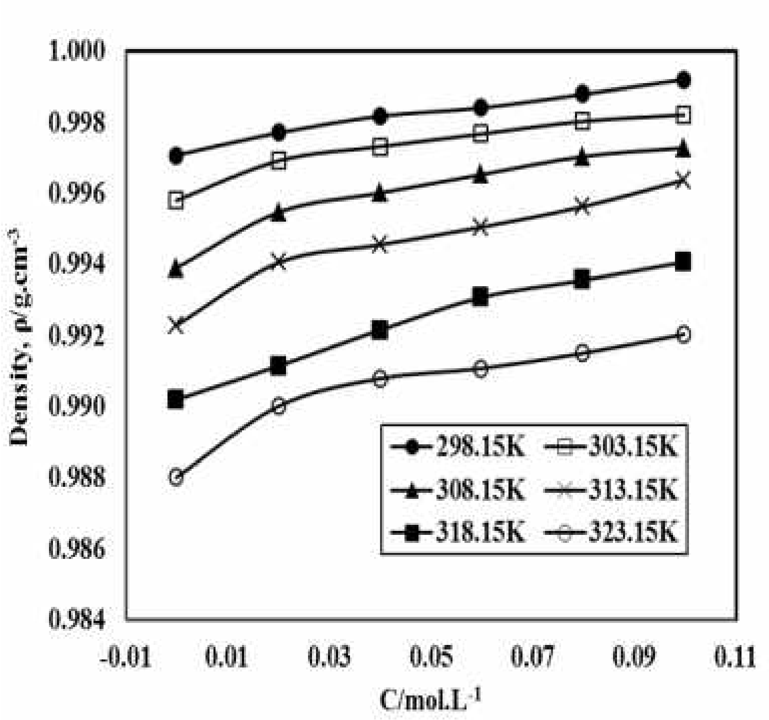

Figure 4.1**:** Plots of Density (ρ) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

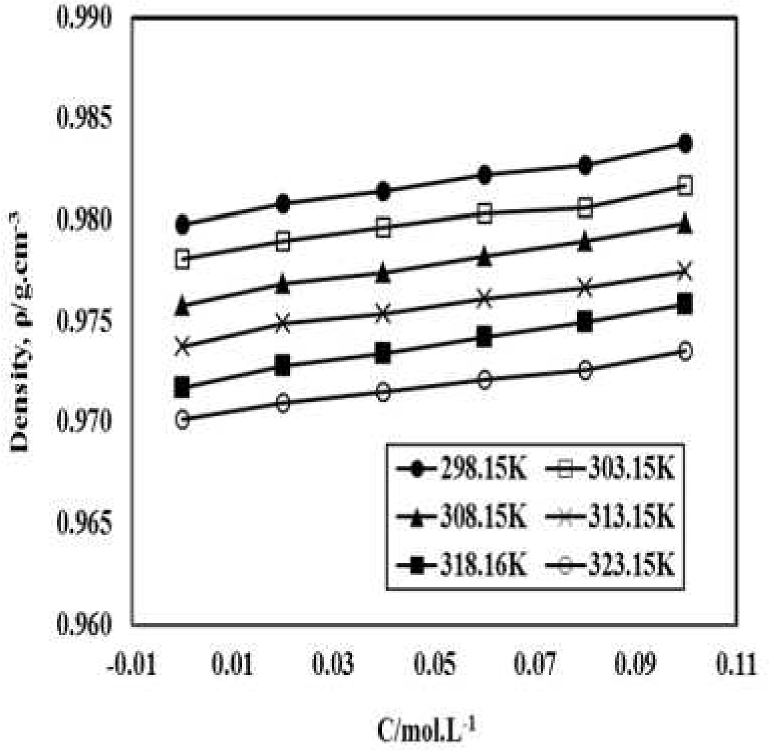

Figure 4.2: Plots of Density (ρ) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

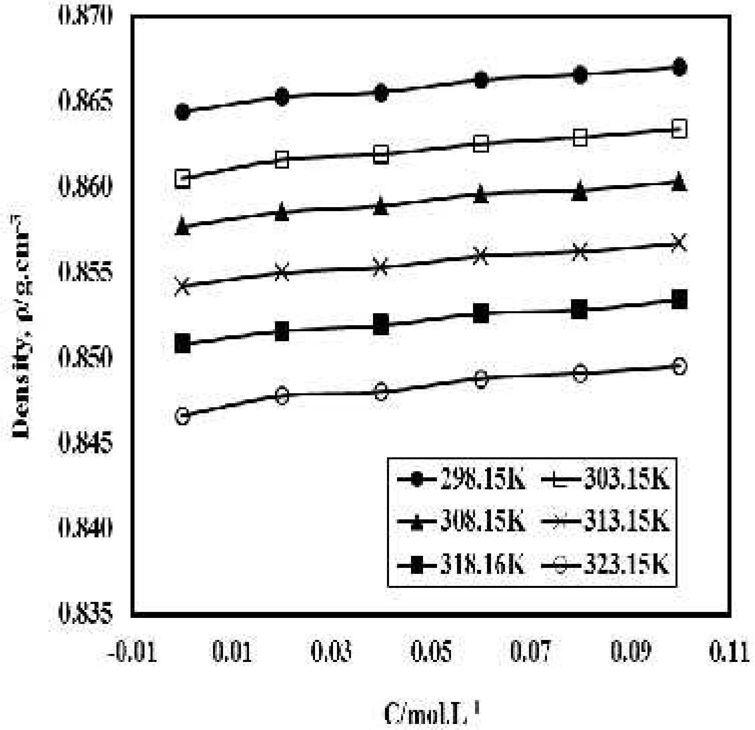

Figure 4.3: Plots of Density (ρ) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) systems at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

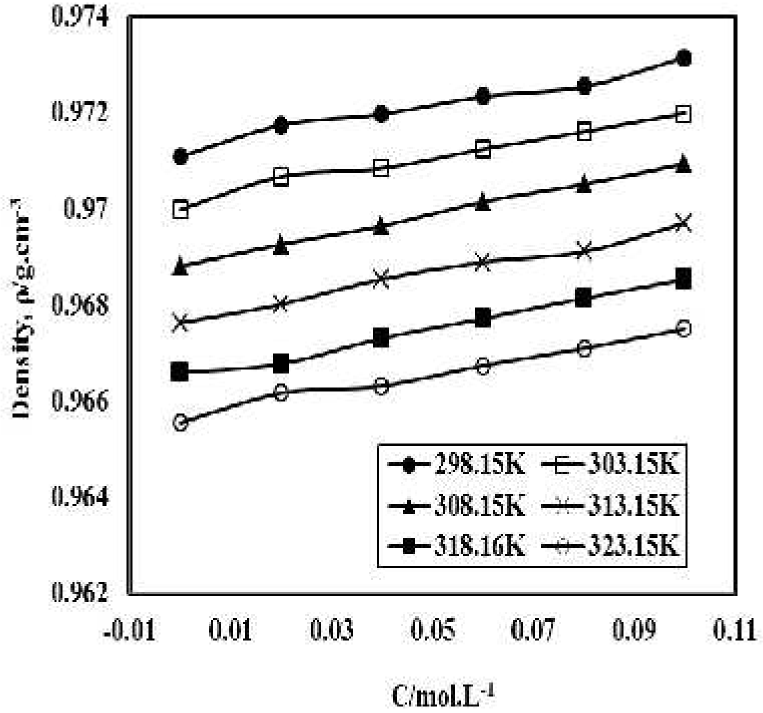

Figure 4.4: Plots of Density (ρ) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

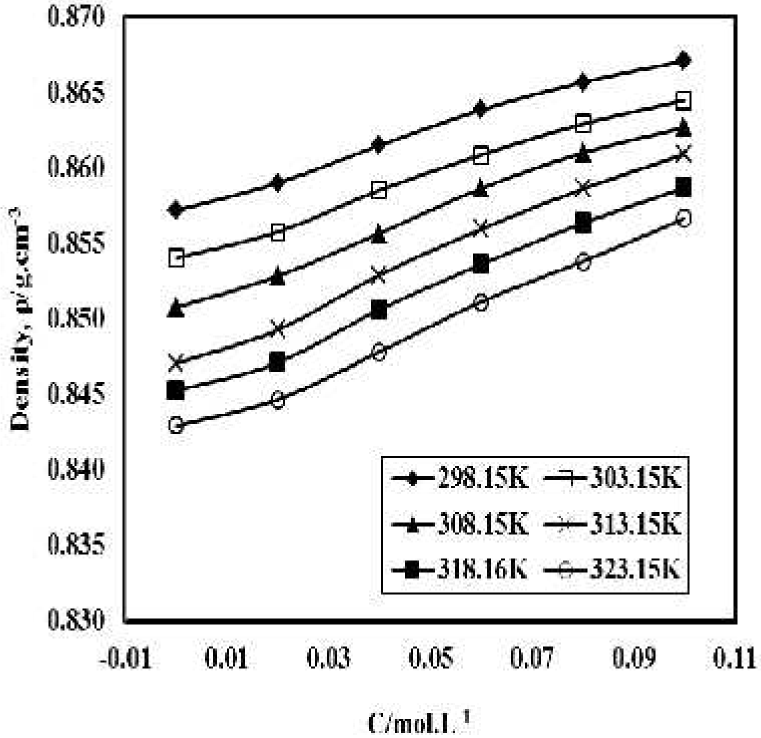

Figure 4.5: Plots of Density (ρ) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

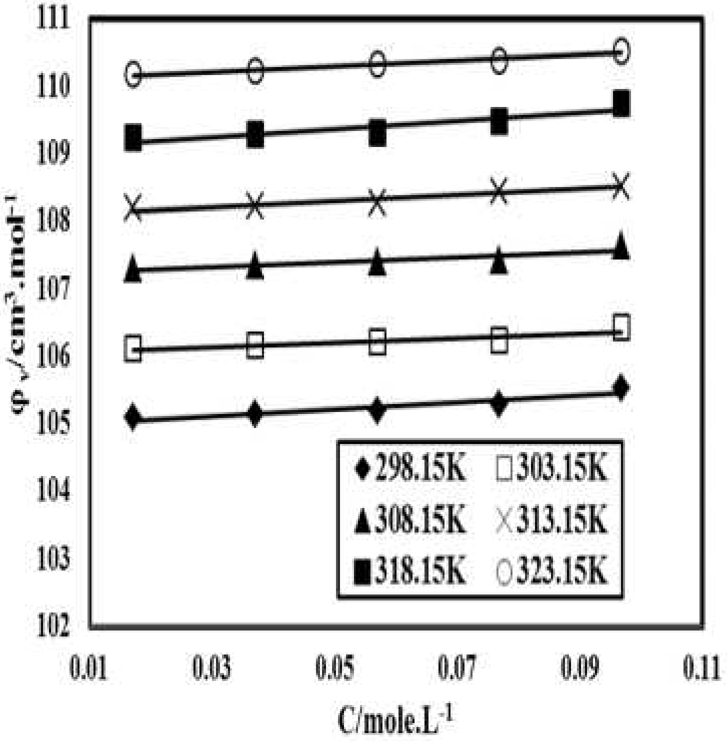

Figure 4.6: Plots of Apparent molar volume (φ_v) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

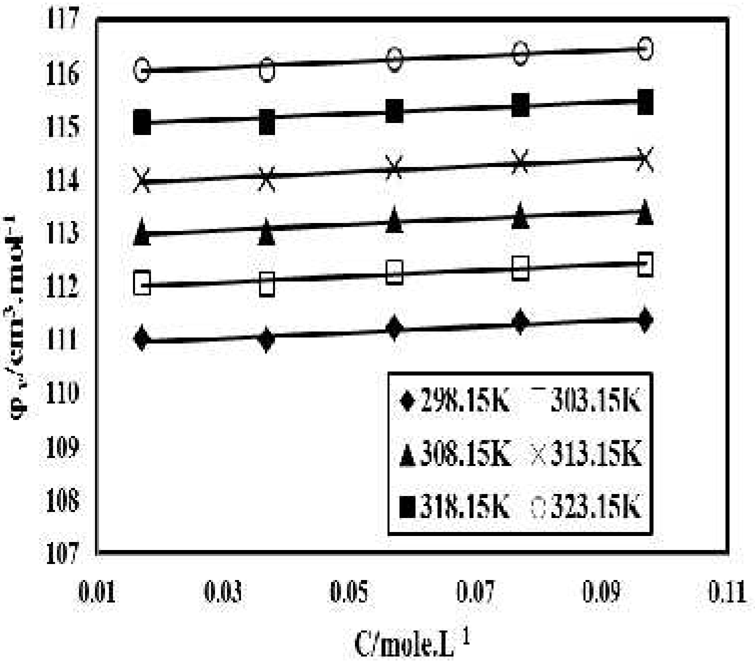

Figure 4.7: Plots of Apparent molar volume (φ_v) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

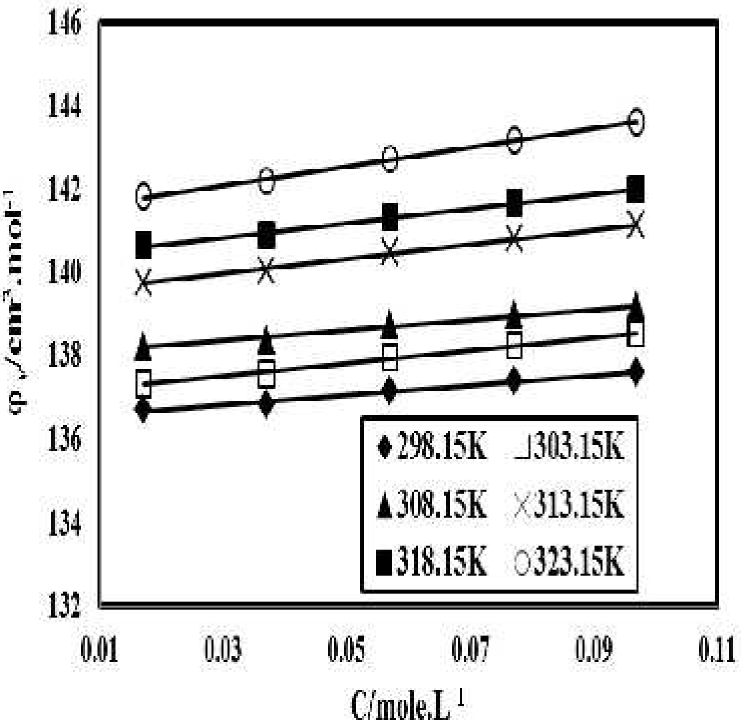

Figure 4.8: Plots of Apparent molar volume (φ_v) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

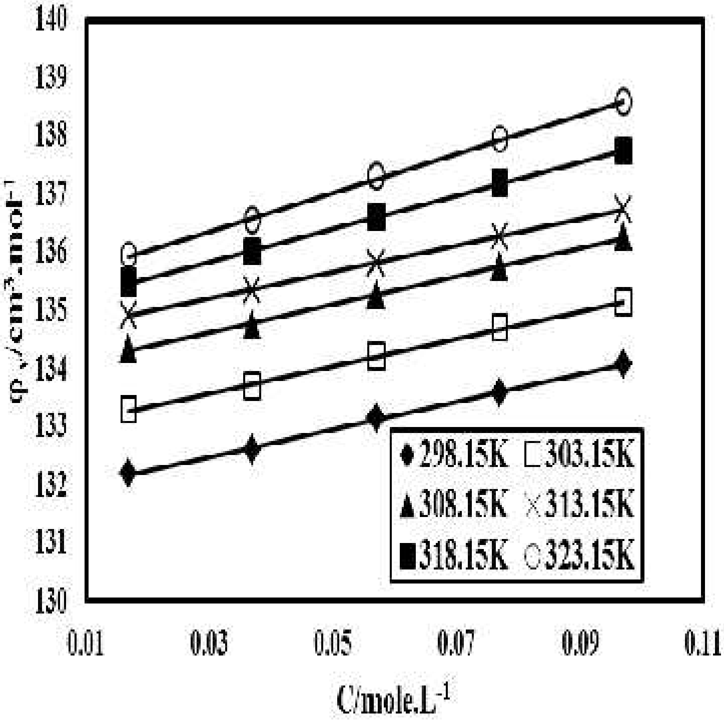

Figure 4.9: Plots of Apparent molar volume (φ_v) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

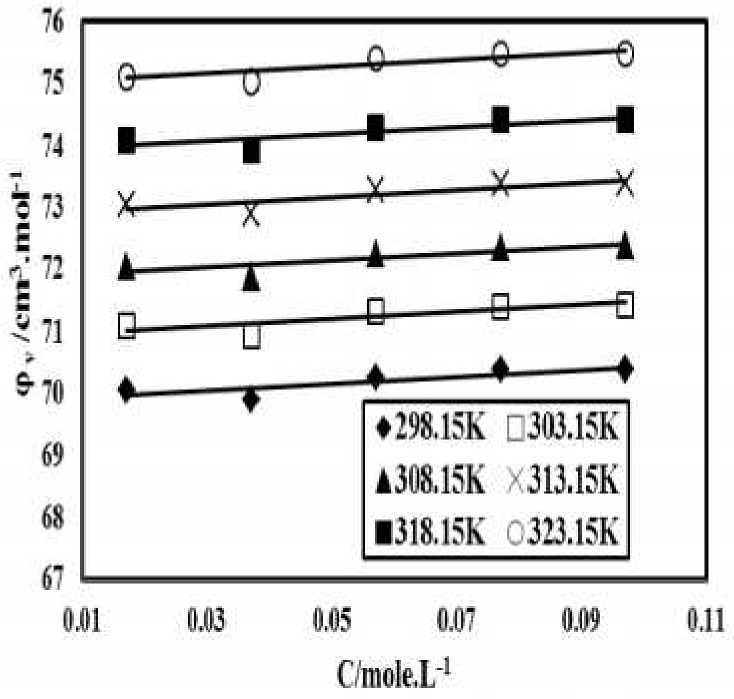

Figure 4.10: Plots of Apparent molar volume (¨$_v$) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

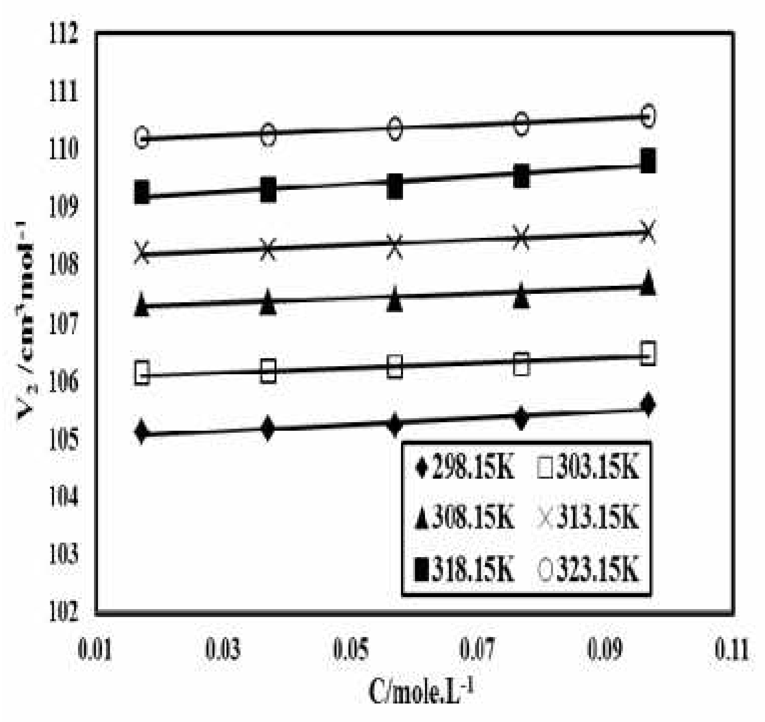

Figure 4.11: Plots of Partial molar volume (V_2) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

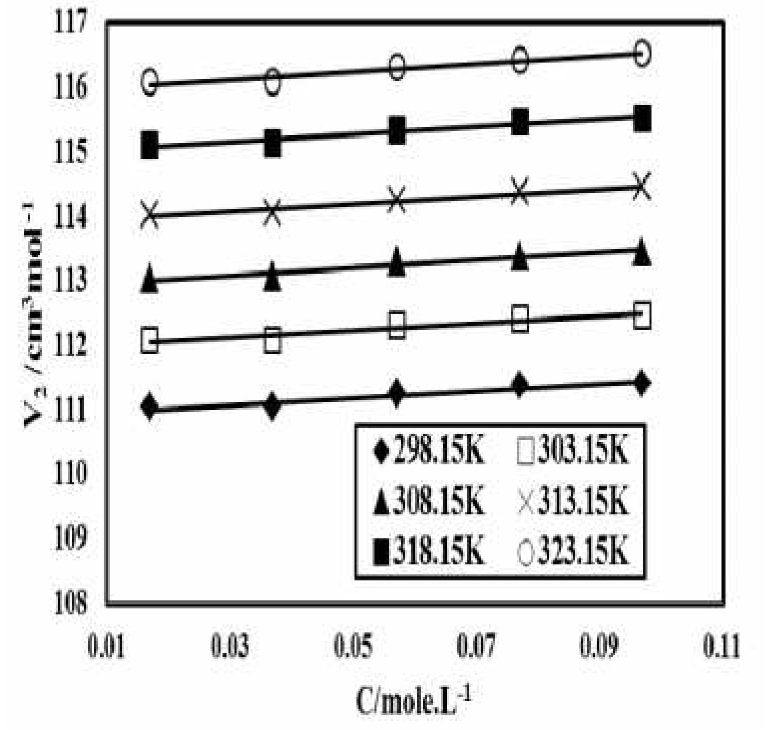

Figure 4.12: Plots of Partial molar volume (V_2) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

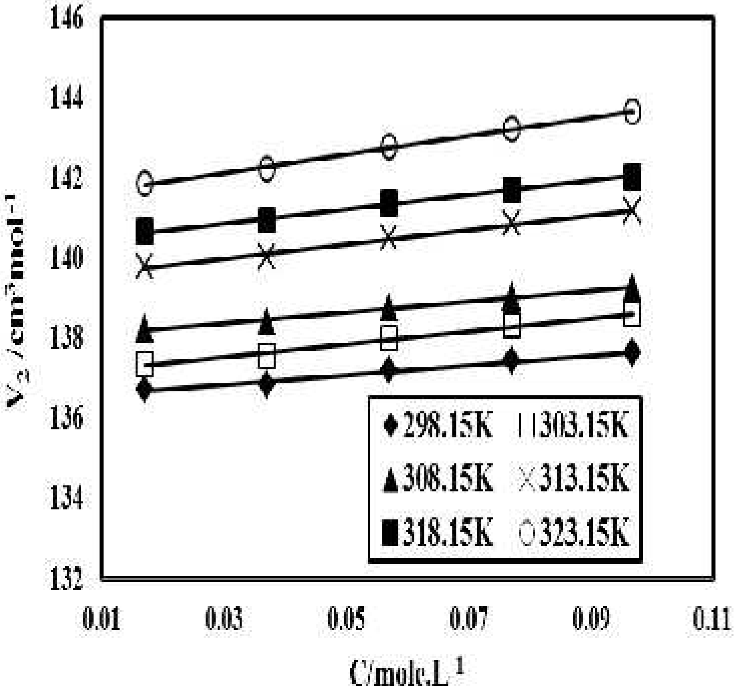

Figure4.13: Plots of Partial molar volume (V_2) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) systems at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323K respectively.

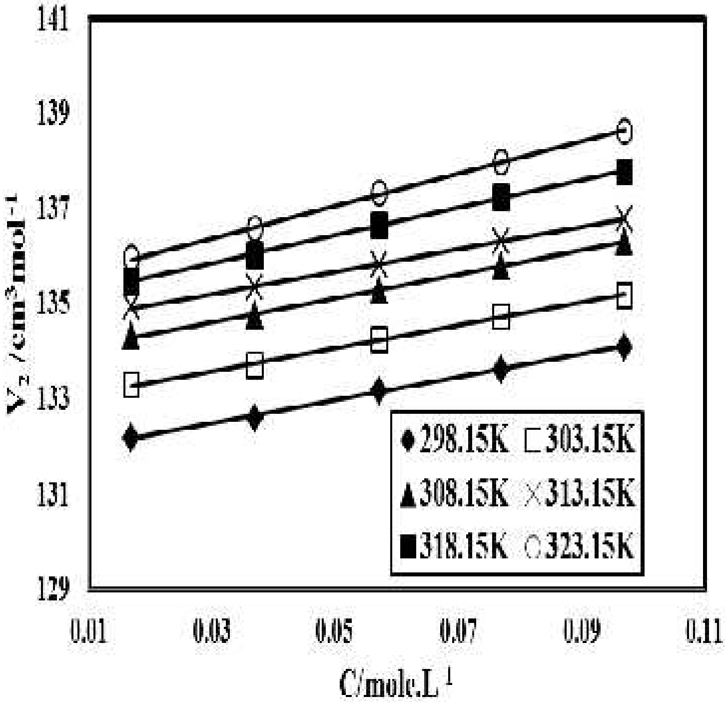

Figure 4.14: Plots of Partial molar volume (V_2) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

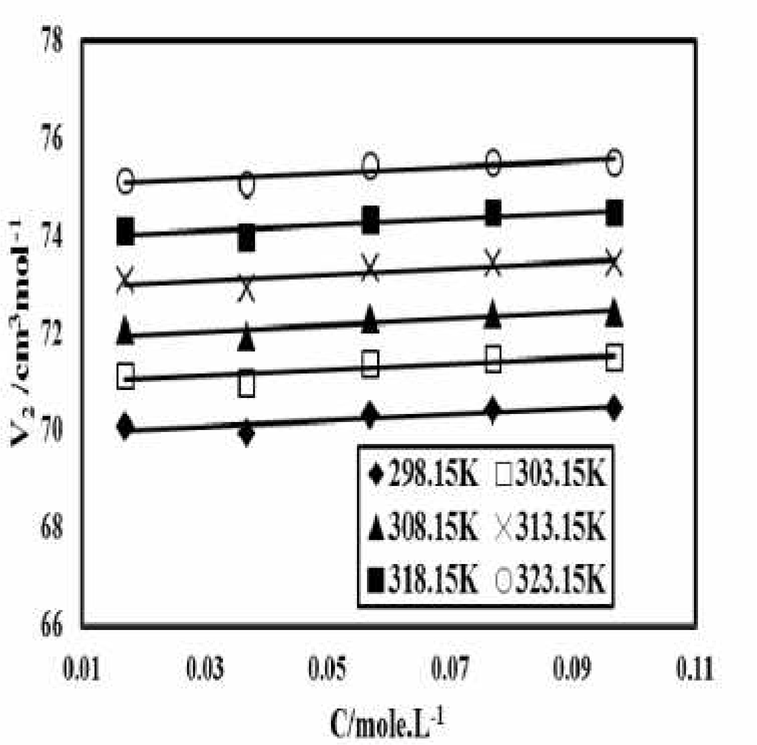

Figure 4.15: Plots of Partial molar volume (V_2) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

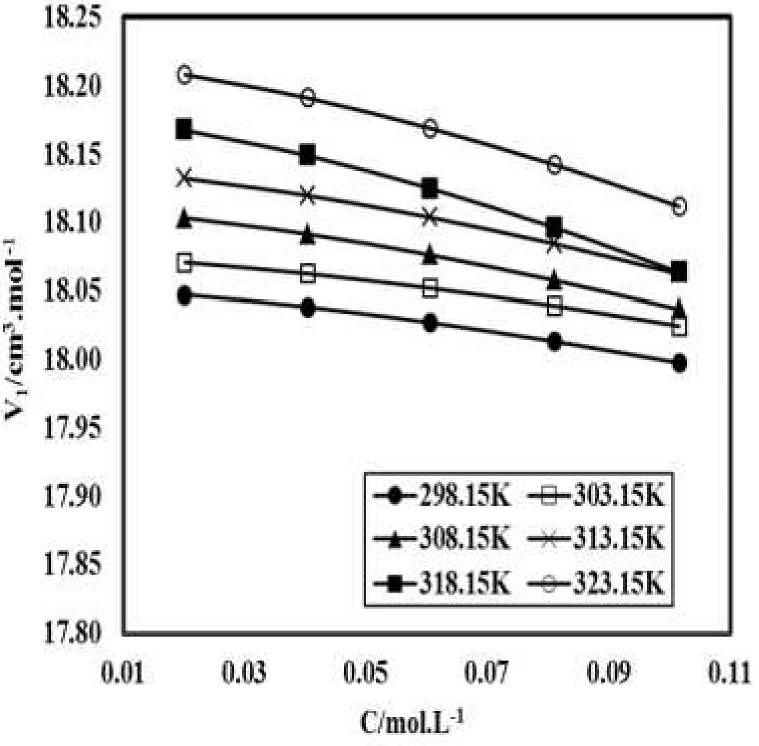

Figure 4.16: Plots of Partial molar volume (V_1) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

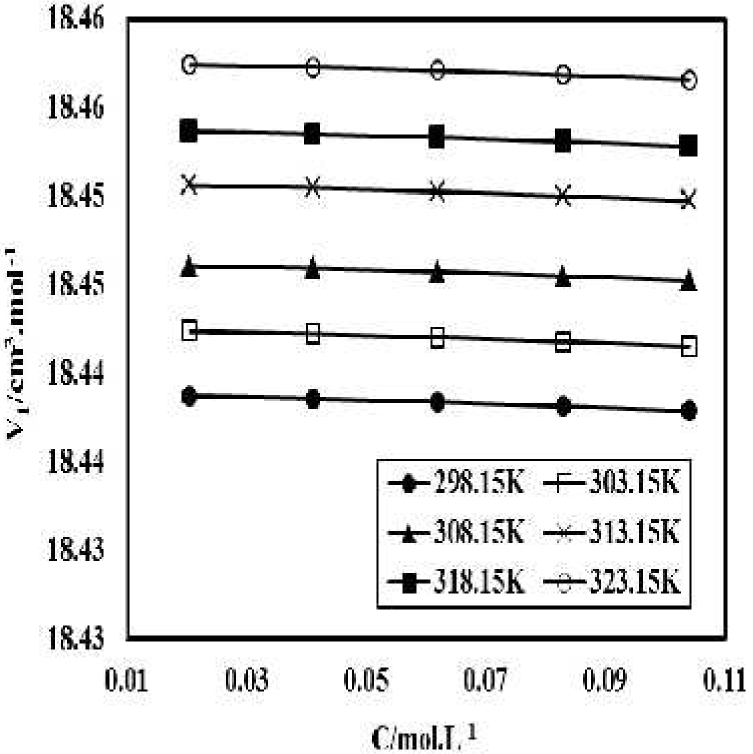

Figure 4.17: Plots of Partial molar volume (V_1) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

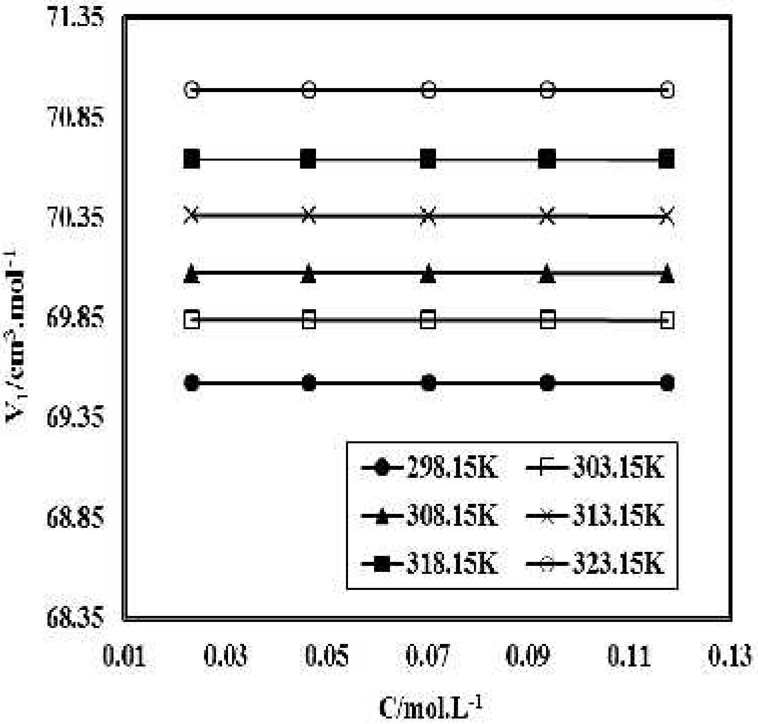

Figure 4.18: Plots of Partial molar volume (V_1) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

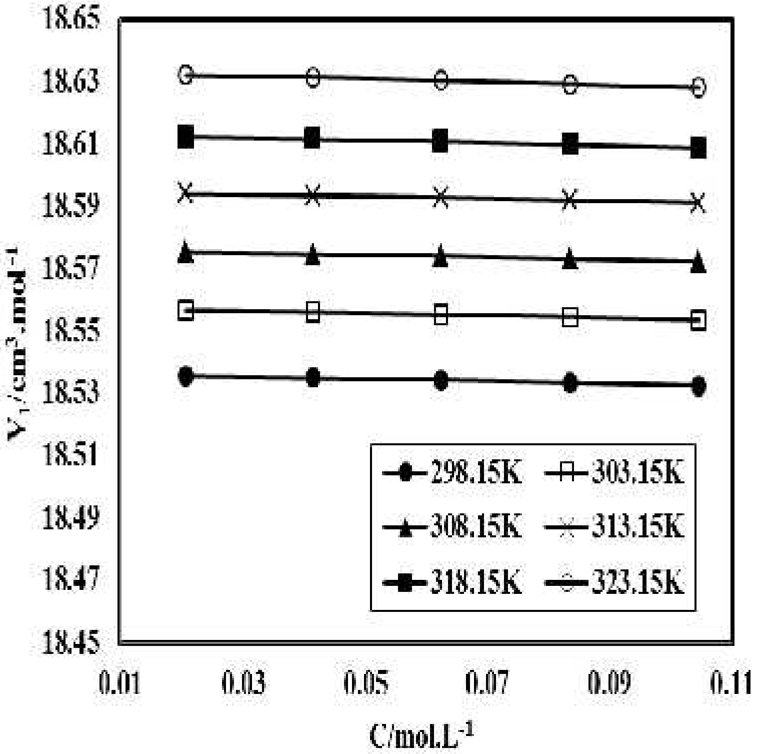

Figure 4.19: Plots of Partial molar volume (V_1) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

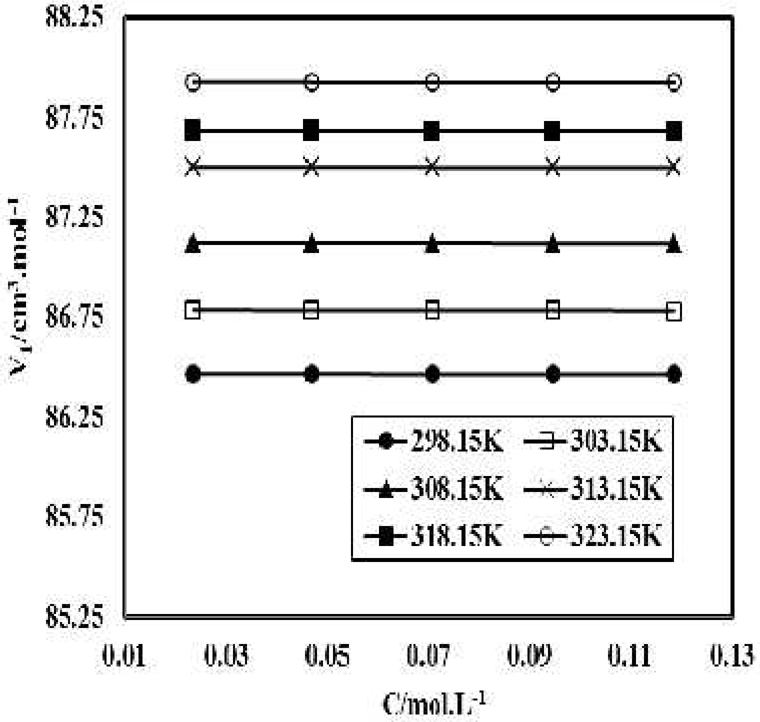

Figure 4.20: Plots of Partial molar volume (V_1) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

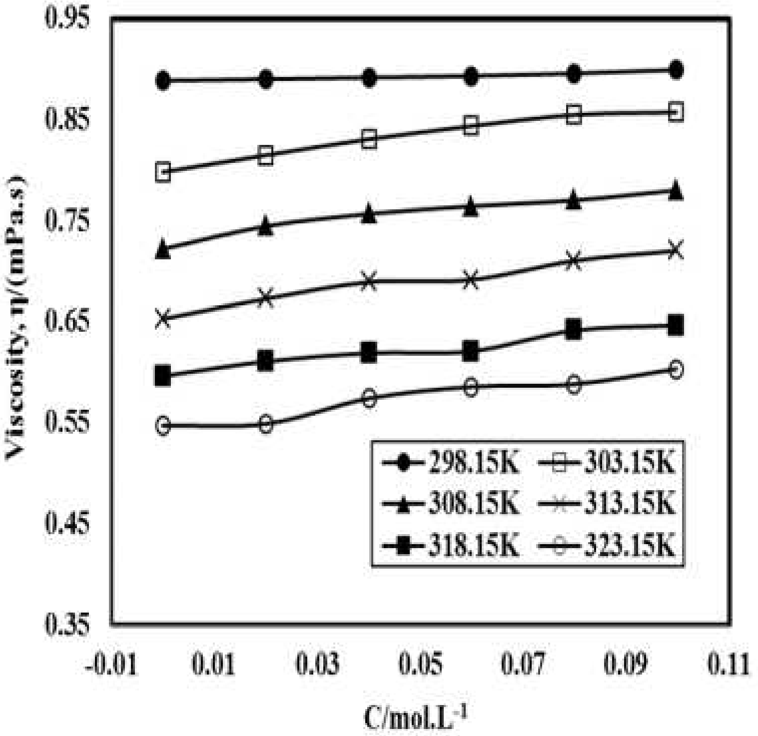

Figure 4.21: Plots of Viscosity (η) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

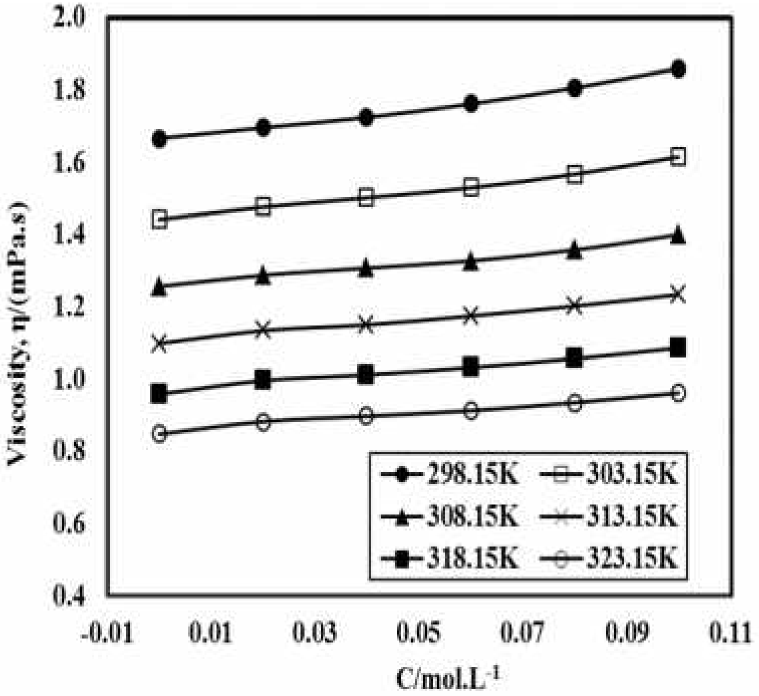

Figure 4.22: Plots of Viscosity (η) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

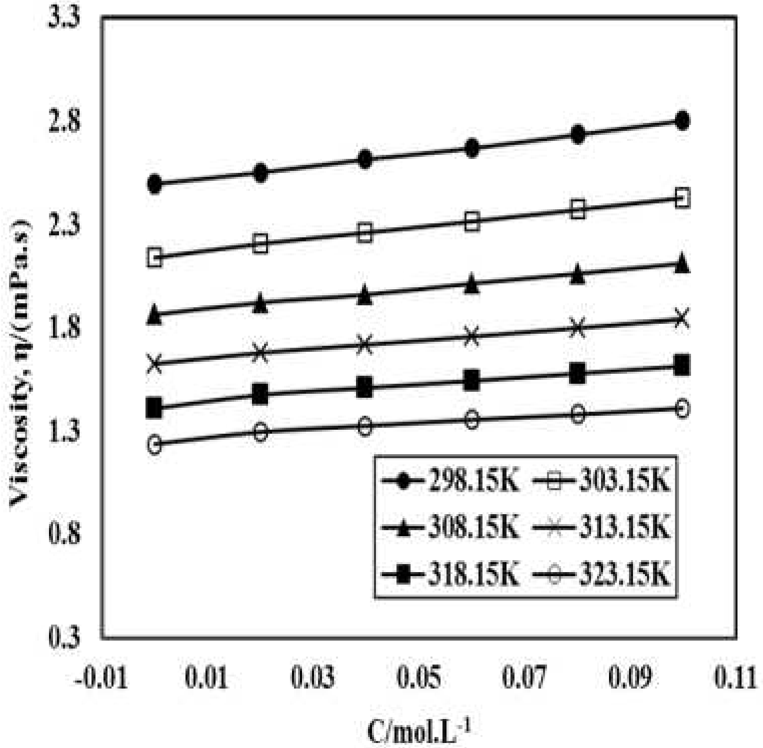

Figure 4.23: Plots of Viscosity (*η*) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

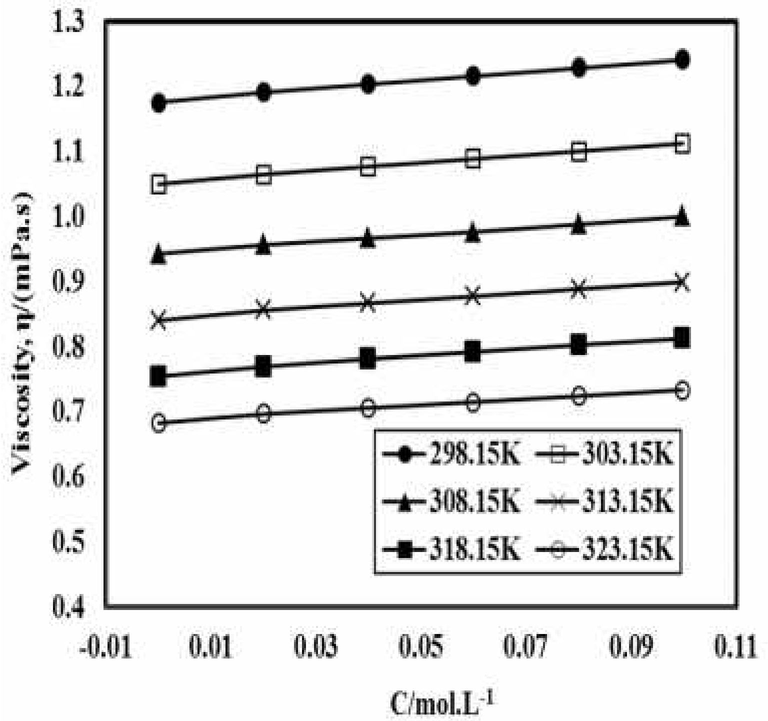

Figure 4.24: Plots of Viscosity (*η*) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

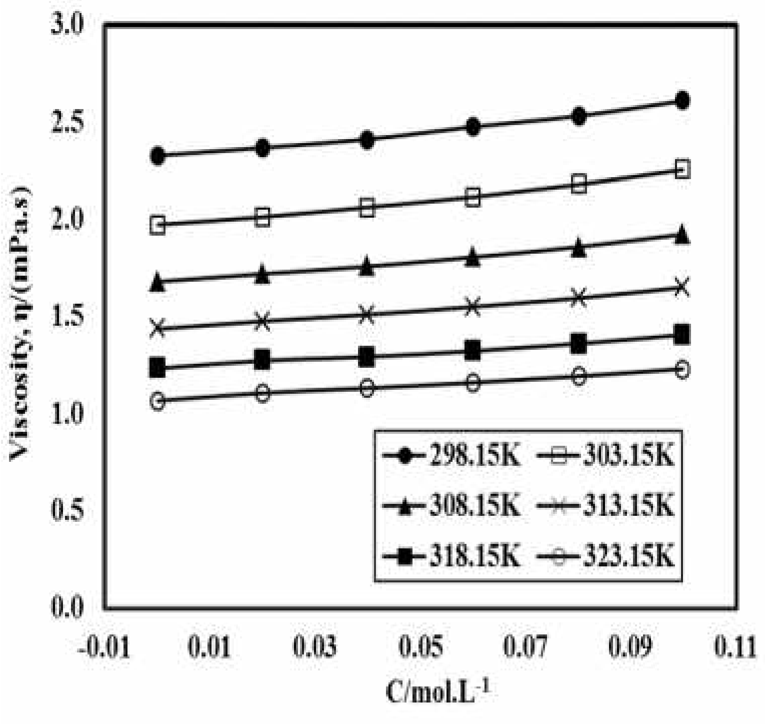

Figure 4.25: Plots of Viscosity (η) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

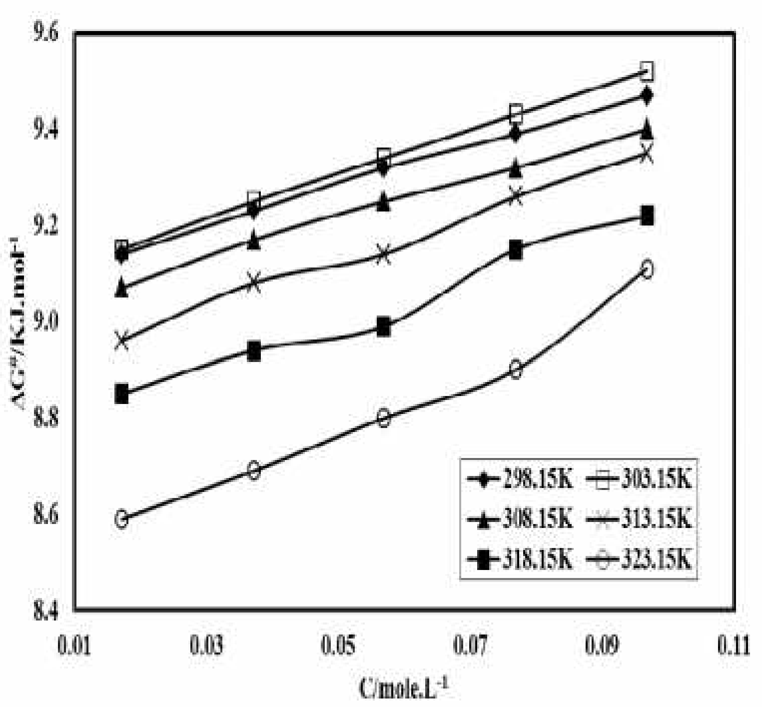

Figure 4.26: Plots of free energy ($\Delta G^{\#}$) vs. Conc. of Paracetamol in Water at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

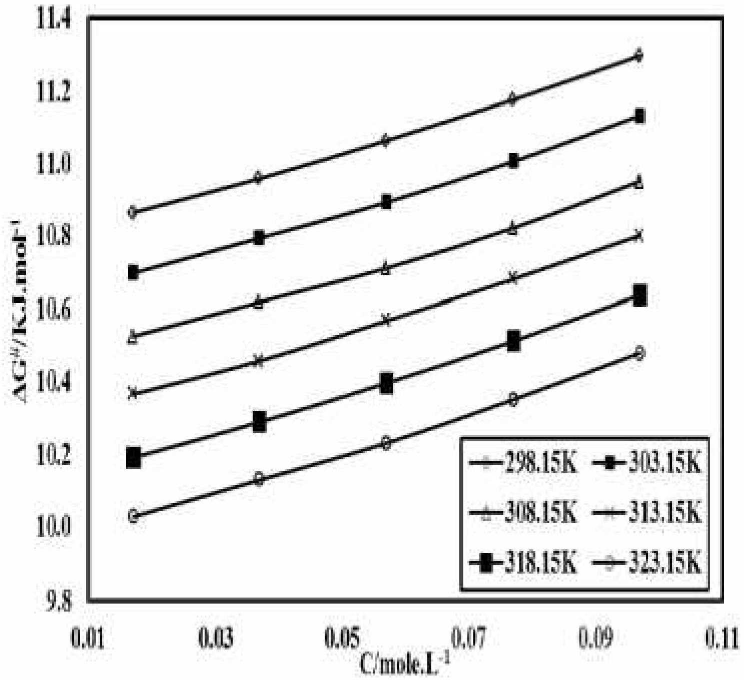

Figure 4.27: Plots of free energy (*ΔG*$^{\#}$) vs. Conc. of Paracetamol in (80% Water + 20% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

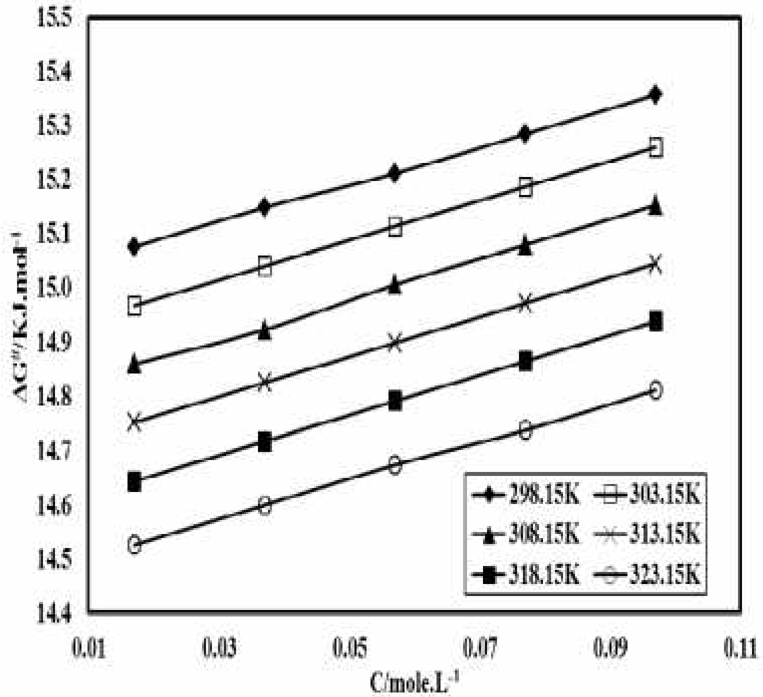

Figure 4.28: Plots of free energy (*ΔG*$^{\#}$) vs. Conc. of Paracetamol in (20% Water + 80% n-Propanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

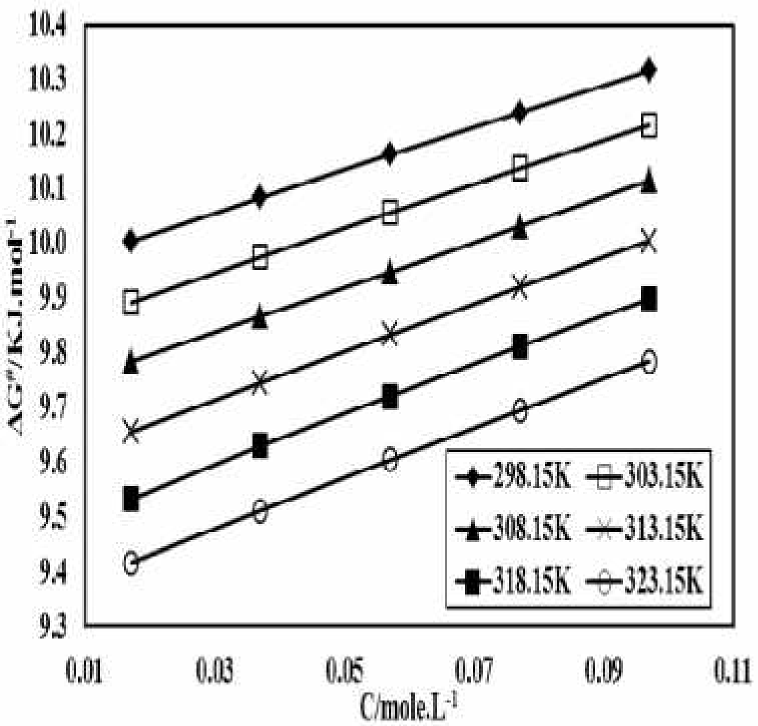

Figure 4.29: Plots of free energy (*ΔG*#) vs. Conc. of Paracetamol in (80% Water + 20% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

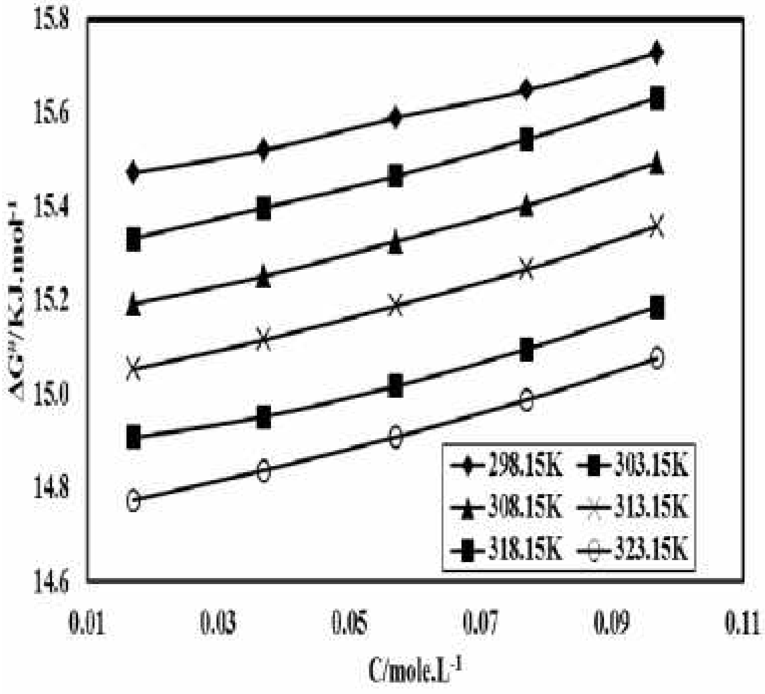

Figure 4.30: Plots of free energy (*ΔG*#) vs. Conc. of Paracetamol in (20% Water + 80% n-Butanol) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

CHAPTER V

Conclusions

The densities of Paracetamol in Water, 80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol and 20% Water + 80% n-Butanol are measured and the densities increase with increasing of concentration of Paracetamol and decreases with increasing of temperature.

The apparent molar volumes (φ_v) of Paracetamol are determined from density data and the values of φ_v are found to be positive and increased with the increase of concentration of Paracetamol.

The values of transfer apparent molar volume $(\Delta\varphi_v)_{tra}$ are obtained from apparent molar volume data and the values are found to be positive for these systems except Paracetamol + 20% Water + 80% n-Butanol system. The values of limiting apparent molar volume expansibilities (E_φ^0) are positive and the values of $(\delta E_\varphi^0/\delta T)_p$ are very small.

The viscosities of Paracetamol in Water, 80% Water + 20% n-Propanol, 20% Water + 80% n-Propanol, 80% Water + 20% n-Butanol and 20% Water + 80% n-Butanol are found to increase with increasing of paracetamol concentration. The B-coefficients for Paracetamol in the studied systems are positive and the values of D-coefficient are mainly negative.

The free energy ($\Delta G^{\#}$) is found to be positive in magnitude for all these systems indicating that the kinetic species involved in forming cavities or hole in liquid is given by the work required in forming the hole against surface tension of the solution.

The values of change of chemical potential ($\Delta\mu_1^{\neq}$ - $\Delta\mu_o^{\neq}$) are positive for all studied systems showing greater contribution per mole of solute to free energy of activation for viscous flow of the solution.

So, the above experimental results show the structure making properties of Paracetamol in water and aqueous alcohols solution.

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