Study of the Effects of Acetonitrile on the Alcohol Solutions by Volumetric and Viscometric Measurements

By

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Declaration

This is to certify that the thesis work entitled "Study of the Effects of Acetonitrile on the Alcohol Solutions by Volumetric and Viscometric Measurements" has been carried out by Monoranjan Mondal 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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Approval

This is to certify that the thesis work submitted by Monoranjan Mondal entitled " Study of the Effects of Acetonitrile on the Alcohol Solutions by Volumetric and Viscometric Measurements " has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of M. Phil. in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh in February, 2013.

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ABSTRACT

Densities and viscosities of binary mixtures of *n*-Propanol + Acetonitrile, *iso*-Propanol + Acetonitrile, *n*-Butanol + Acetonitrile, *iso*-Butanol + Acetonitrile n-Pentanol + Acetonitrile, *iso*-Pentanol + Acetonitrile and Propylene glycol + Acetonitrile have been studied over the entire range of composition $(0 < x_2 < 1)$ at 298.15- 323.15K with an interval of 5K. The studied alcohols or glycols are found to be dissolved completely in acetonitrile solutions at any composition. The density of alcohols or glycols in equi molefraction of acetonitrile solution was found to be order of Propylene glycols> iso-Pentanol> n-Pentanol > *n*-Butanol > iso-Butanol > *n*-Propanol > iso-Propanol. The value of density of alcohols in acetonitrile increases with the increasing of composition of the alcohols. The increase of density with composition of alcohols can be attributed to solute-solvent interaction. The densities of all alcohols increase with the increase of carbon number which may be depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. The density of Propylene glycol is higher than the studied alcohols owing to the higher degree of –OH and increasing unsaturation. The densities decrease regularly with the increasing of temperature. This is due to the thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding are occurred.

The excess molar volumes, V^E were calculated from the densities of the mixtures at different temperatures. The values of V^E for all the systems are positive over the entire range of composition, showing maxima ~ 0.1-0.2 mole fraction of *n*-Propanol and ~ 0.4 mole fraction of *iso*-Propanol, ~ 0.4 mole fraction of *n*-Butanol, ~0.4 mole fraction of *iso*-Butanol, ~ 0.3-0.4 mole fraction of n-Pentanol, ~0.5 mole fraction of iso-Pentanol and ~0.5 mole fraction of Propylene glycol . The excess molar volume, V^E of alcohols in acetonitrile solutions was found to be order of

Propylene glycol >*n*-Pentanol >*n*-Butanol >*n*-Propanol

and

iso-Pentanol > *n*-Pentanol

and

iso-Butanol > *n*-Butanol

and

iso-Propanol > *n*-Propanol.

The increasing of V^E with carbon chain length of alcohol may be related to increase of the size of alcohols. The values of V^E for the studied alcohols increase with the increase of temperature. The observed values of V^E for the mixtures have been explained in terms of physical, chemical and geometrical contributions.

The viscosity coefficients, η of all the above mixtures at all the six different temperatures have also been determined. The viscosities increase initially slowly up to ~0.6 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol, *iso*-Pentanol and Propylene glycol and later on, the viscosity increases sharply until the pure alcohol is reached specially at lower temperature. In pure state the viscosity of alcohols has been found to be in the order of,

propylene glycol > iso-Pentanol ~ *n*-Pentanol > *iso*-Butanol > *n*-Butanol > *iso*-Propanol > *n*-Propanol

There is a marked decrease in the viscosity with increase of temperature for all the studied alcohols. This ascribed that the alcohol solutions are less stable at higher temperature. The increasing of viscosity with carbon number of alcohols ascribed that the solution resistance increases with the increase of carbon chain length. The linear dependence of $\ln\eta$ against 1/T shows for the all studied alcohols. The branched chain isomers are less stable than linear chain isomer at higher temperature.

The excess viscosity, η^E values are found to be negative, indicating that the acetonitrile solutions of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.6-0.9 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-Pentanol and Propylene glycol. The negative excess viscosity, η^E of acetonitrile + all the studied alcohols indicate that the dissociation of components through dispersive forces or steric hindrance. The position of minima virtually does not change remarkably with the variation of temperature. The values of the minima are in the order:

Propylene glycol ~ iso-Pentanol > n-Pentanol> iso-Butanol>n-Butanol
> iso-Propanol> n-Propanol

The hydrophobic effect increases with the increasing of carbon chain length of alcohols. This indicates that the η^E decreases with the decrease of carbon number. The positive V^E, negative η^E, and negative ε for the acetonitrile + studied alcohols systems indicate that dispersion force is dominant. Some disruptive force causing volume expansion may be present and it is more than compensated by volume contraction through the segmental inclusion of acetonitrile.

The thermodynamic parameters such as free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) change of activation for the viscous flow for these systems were examined for the entire range of composition. The free energy (ΔG^*) were found to be positive in magnitude indicating that the kinetic species involved in forming cavities or holes in the liquid medium is given by the work required in forming the hole against surface tension of the solution. The negative excess free energy, ΔG^{*E} indicate that the strong dispersion force in alcohols-acetonitrile solution is dominant. The excess properties (V^E, η^E, ΔG^{*E}) data have been fitted by the least square method to the four parameter Redlich-Kister equation and the values of the parameter a_i and standard deviation have been reported. The volumetric properties are fully consistent with viscometric and thermodynamic properties.

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Nomenclature

ρ	Density
ρ_1	Density of solvent
ρ_2	Density of solute
ρ_{mix}	Density of the mixture
V^E	Excess molar volume
φ_v	The apparent molar volume
φ_v^0	The limiting apparent molar volume
$\bar{V}_2$	Partial molar volume
η	Viscosity
η^E	Excess viscosity
η_{expt}	Experimental viscosity
η_{id}	Ideal viscosity
σ	Standard deviation
ε	Interaction parameter
c	Molarity
X_1	Mole fraction of solvent
X_2	Mole fraction of solute
M_1	Molecular mass of solvent
M_2	Molecular mass of solute
V_o	Molar volume of solvent
V_m	Molar volume of solution
a_i	Fitting coefficient
ΔH^*	Change of Activation Enthalpy
ΔG^*	Change of Activation Free energy
ΔG^{*E}	Excess activation free energy
ΔS^*	Change of Activation Entropy
v_1	Volume of solvent

Nomenclature

V_o	Volume of empty 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

CHAPTER I

Introduction

1.1 Properties of solutions

The liquid state, is an intermediate state between solid and gaseous states, retains some properties of both the gaseous and solid states. Therefore, the liquid state can not be adequately defined as the gaseous and the solid states. The molecular and macroscopic property of liquids varies from liquid to liquid due to characteristic intermolecular interactions. The properties of multi-component mixtures, on account of molecular interactions between dissimilar molecules, become still more difficult to explain. Considering these facts there are serious difficulties in formulation of any general theory of solution (1-3).

It should, in principle, be possible to calculate theoretically, the properties of solution from the properties of individual components. But there are inherent difficulties created by liquid state that is not properly understood. 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 (1-5).

The theoretical treatments need to assume some model for carrying out statistical-mechanical calculations of these properties. The observed discrepancies between theoretically calculated and experimentally determined values are naturally on account of the inadequacies in the theoretical models. Such a comparison often suggests appropriate refinements of the assumed model.

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 (6-8).

The study of physico-chemical properties of binary and ternary mixture has drawn early attention from two main points of view. Firstly, it provides the way for accumulating knowledge about the type of interaction or the type of forces acting during the mixing of two different types of species. Secondly it may show the appearance of a new phenomenon which is absent in the pure liquid.

As for example due to the mixing of liquids their may be either positive or negative deviation of volume and thus different from additivity rule. The negative volume may be caused by the so-called 'compound formation' through association or decrease in the intermolecular distance between the interacting molecules. The positive volume has been explained by the break down of association of the species formed either by chemical forces such as H-bonding or by physical forces such as dipole-dipole and dipole-induced dipole interaction.

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 liquids 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 liquids and liquid mixture correlated with equilibrium and transport properties. The thermodynamic and excess 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. Liquid mixtures frequently appear in chemical research. Most of the mixtures are nonideal and show peculiar behavior. The interpretation of nonideality is a fascinating area and a large number of contributions were made over the last decade. Solution theory is still far from adequate to account for solution nonidealities 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 alcohol with acetonitrile in studying the liquid-liquid interaction in binary systems.

1.2 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 °C whereas Propane (MW 44) has boiling point of -42 °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.

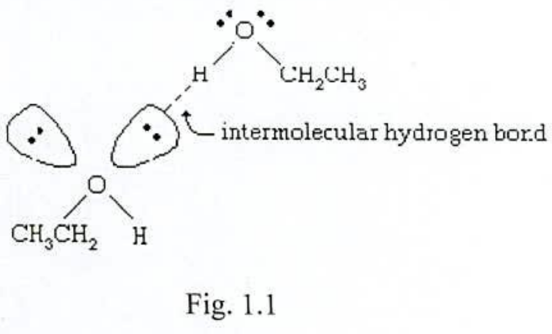

Fig. 1.1

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. 1.1).

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 (9).

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.

1.3 Properties of Acetonitrile

Acetonitrile is the chemical compound with the formula, CH_3CN. This colourless liquid is the simplest organic nitrile. It is produced mainly as a byproduct of acrylonitrile manufacture. It is used as a polar aprotic solvent in organic synthesis and in the purification of butadiene. It is widely used as an electrochemical solvent. In the laboratory, it is used as a medium-polarity solvent that is miscible with water and has a convenient liquid range. With a dipole moment of 3.92D, acetonitrile dissolves a wide range of ionic and nonpolar compounds (e.g. Wohl-Ziegler reaction) and is useful as a mobile phase in HPLC and LCMS (10).

It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. For similar reasons it is a popular solvent in cyclic voltammetry. Its low viscosity and low chemical reactivity make it a popular choice for liquid chromatography. Acetonitrile plays a significant role as the dominant solvent used in the manufacture of DNA oligonucleotides from monomers. Industrially, it is used as a solvent for the manufacture of pharmaceuticals and photographic film (10).

Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole-dipole forces predominate. It is an archetype solvent with simple molecular structure and high solvation power for many solutes (11-12). Consequently, the association or dissociation of solute in acetonitrile has attracted considerable interest. Acetonitrile, a relatively inert and inexpensive solvent, with a high density and low viscosity is also an important solvent with liquid-liquid extraction potential capabilities. It has important technological applications, namely, in battery industry and plating techniques (13).

The mode of interactions of alcohols and acetonitrile is of vital importance in the field of solution chemistry as it can provide with important information regarding hydrophilic and hydrophobic interactions. Binary mixtures of acetonitrile and alkanols are widely used as solvents in chemistry and modern chemical technology. Acetonitrile and alkanol mixtures are also used as very powerful cosolvents of polymers (14). Acetonitriles and alchohols are versatile solvents used in the separation of saturated and unsaturated hydrocarbons, in pharmaceutical synthesis, and serve as solvents for many polymers.

1.4 Acetonitrile-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 acetonitiriles and alcohols are of interest.

The correlation between solute -solvent interaction is complex. Thermodynamic properties of the solution have been reported (15). Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure (16-20). Because the environment of the solute affects the thermodynamic properties, it is of interesting to study the effect of the media changing from water to acetonitrile solvent on the thermodynamic properties of the alcohol.

Acetonitrile, alkanols, and their binary mixtures are used as solvents in chemistry and modern chemical technology (21). Acetonitrile and alkanol mixtures are also used as very powerful cosolvents of polymers (22). Molar excess volumes (23-29) and molar excess enthalpies (30,31) for 1-alkanol + acetonitrile systems have been measured previously. Excess molar functions for butanenitrile + ethanol, 1-butanol, 1-propanol, 2-propanol, 1-hexanol, and 1-octanol systems have been reported for 298.15 K(32-34).The experimental data of the excess molar volumes of 1-alkanol + nitrile mixtures (1-octanol, 1 nonanol, 1-decanol, or 1-undecanol + propanenitrile and 1-undecanol + butanenitrile) at 298.15 K and atmospheric pressure have also been measured (35). Dielectric constants, viscosities, and densities for methanol mixtures have been presented at 298.15 K(36). Density and viscosity of butanenitrile + butanole isomers have been measured (37). Excess Gibbs free energies, excess enthalpies, and volumes were also measured for butanenitrile + 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol (38,39). Excess functions for binary mixtures of butanenitrile + methanol, 1-pentanol, 1-heptanol, 1-nonanol, or 1-decanol have been measured at 298.15 K (40). Excess molar enthalpies and excess molar volumes of alkanol + nitrile compounds were also measured (41).

Zegers and Somsen (42) reported the volumetric properties of DMF + alcohol mixtures. In order to give a better description of the solvation of DMF by water and by alcohol molecules in the ternary mixture DMF + alcohol + water (43-44) published of papers on the excess molar volumes of the ternary mixtures at 313.15 K. Several empirical expressions are used to correlate the ternary excess molar volumes from experimental results on the constituent binaries. Density and viscosity studies of acetonitrile with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl propan-1-ol and 2-methyl propan-2-ol at (298.15 -313.15) have been reported (45).

1.5 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 binary 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 (46-50). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, (51-55) of particular interest has been the determination of densities and viscosities of mixtures.

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 excess molar volumes, excess viscosities, 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 nonideality of liquid mixtures is fundamental for a better understanding of excess molar volumes and excess viscosities. Alcohol-nitrile solutions are of practical importance. Acetonitrile to some extent is associated by means of dipole–dipole interactions. Significant structural effects are absent due to the lack of hydrogen bonds. Therefore it acts as an aprotic solvent of high dielectric constant (ϵ=36.71) of molecules with a large dipolemoment (μ=3.8 D) at 298.15 K (10). Because of its miscibility with almost all common solvents (10) it is classified as so-called super solvent. A acetonitile molecule can interact with an alkanol molecule by virtue of dipole -dipole interaction, resulting in structural and packing effects.

In the present investigations, (i) densities and excess molar volumes, (ii) viscosities and excess viscosities and iii) thermodynamic parameters of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol with Acetonitrile at five different temperatures (298.15-323.15K) have been determined. Although in this study out of seven binary systems, three systems (n-Propanol, iso-Propanol, n-Butanol) of them are similar with the Nikam et al reported system (45), but most of the studied conditions and parameters i.e. mole fraction, temperature, excess viscosity, interaction parameters, thermodynamic parameters etc) are different. At this point our studied systems and parameters are different from the reported system (45). Considering these, we have chosen these systems for the study. In order to understand the issue of solute-solvent interactions in alcohol-acetonitrile systems a theoretical and experimental aspect of interactions in terms of excess molar volume, excess viscosity, and excess thermodynamic properties analysis is necessary.

The specific aims of this study are-

(i) to examine the volumetric, viscometric and thermodynamic properties of the mixture of acetonitriles and alcohols in different compositions and different temperatures.

(ii) to understand the effect of acetonitriles on alcohol solutions to generalize the type of interactions among them.

(iii) to enrich the available data on Physico-chemical properties and thermodynamic function of the systems .

The thesis presents the density, excess molar volumes, viscosity, excess viscosities, thermodynamic parameters data of acetonitriles + some alcohols or glycols over the whole range of compositions 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 (56).

(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 liter of solution. If n_2 is number of moles of solute and V liters is the volume of the solution then,

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

$$\text{or } C = \frac{n_2}{V} \qquad \text{...(2.1)}$$

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 $molL^{-1}$ (57).

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 (57). Mathematically,

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

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

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

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

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}

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

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

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 φ_v the relation (58)

$$\varphi_v = \frac{V - n\overline{V}_1^{0}}{n_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.5)$$

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 (58),

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

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 (59, 60),

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

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

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

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 (61):

$$\varphi_v = \left[\frac{M_2}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0}\right] \quad \text{...(2.9)}$$

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

is used for inter conversion of the concentration in the two scales (61).

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:

$$\overline{Y_1} = \left(\frac{\delta Y}{\delta n_1}\right)_{n_2,P,T} \quad \text{.......... (2.11)}$$

Similarly for component 2,

$$\overline{Y_2} = \left(\frac{\delta Y}{\delta n_2}\right)_{n_{12},P,T} \quad \text{..........(2.12)}$$

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,

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

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

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

The partial molar volumes of solute and solvent can be derived using the equation 2.5 as follows (34):

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

and,

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

For solutions of simple electrolytes, the apparent molar volumes (φ_v) vary linearly with $\sqrt{m}$, even upto moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (58):

$$\frac{\delta\varphi_v}{\delta m}=\frac{\delta\varphi_v}{\delta\sqrt{m}}\cdot\frac{\delta\sqrt{m}}{\delta m}=\frac{1}{2\sqrt{m}}\cdot\frac{\delta\varphi_v}{\delta\sqrt{m}} \quad \text{..(2.17)}$$

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:

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

and

$$\overline{V_1}=\overline{V_1^0}-\frac{m}{55.51}\left(\frac{\sqrt{m}}{2}\cdot\frac{\delta\varphi_v}{\delta\sqrt{m}}\right)=V_1^0-\frac{M_1m^{3/2}}{2000}\left(\frac{\delta\varphi_v}{\delta\sqrt{m}}\right) \text{..................................(2.19)}$$

Where, $\varphi^0{}_v$ is the apparent molal volumes at zero concentration.

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

$$\overline{V_2}=\varphi_v+\left[\frac{1000-C\varphi_v}{2000+C^{3/2}\left(\frac{\delta\varphi_v}{\delta\sqrt{C}}\right)}\right]\sqrt{C} \quad \text{...(2.20)}$$

and

$$\overline{V}_1 = \frac{2000\overline{V}_1^0(18.016/\rho_0)}{2000 + C^{3/2}\left(\frac{\delta\varphi_v}{\delta\sqrt{C}}\right)} \quad \text{.......(2.21)}$$

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. To obtain reliable φ_v values, it is necessary to measure the density ρ, with great precision because errors in ρ contribute, considerably to the uncertainties in φ_v.

The concentration dependence of the apparent molar volume of electrolytes has been described by the Masson equation (62), the Redlich-Mayer equation (63) and Owen-Brinkley equation (64). Masson (62) found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \quad \text{.......(2.22)}$$

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

Redlich and Rosenfeld (63) 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,

$$S_v = KW^{3/2} \quad \text{.......(2.23)}$$

where, the terms K and W are given by

$$K = N^2e^3\left(\frac{8\pi}{100D^3RT}\right)^{1/2}\left\{\left(\frac{\delta \ln D}{\delta\rho}\right) - \left(\frac{\beta}{3}\right)\right\} \quad \text{.......(2.24)}$$

and $$W = 0.5\sum \gamma_i Z_i^2 \quad \text{.......(2.25)}$$

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

$$\varphi_v = \varphi_v^0 + KW^{3/2}\sqrt{C} \qquad (2.26)$$

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

$$\varphi_v = \varphi_v^0 + S_v\sqrt{C} + b_v C \qquad (2.27)$$

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 $cm^3mol^{-3/2}.L^{1/2}$.

2.7 Excess molar volume

For binary systems the molar volumes of pure components, ρ^0 and of mixtures, ρ_{mix} is given by the relation

$$V^0 = \frac{M}{\rho} \qquad (2.28)$$

The mixture molar volume is,

$$V_{mix} = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} \qquad (2.29)$$

and the ideal molar volume of this system is given by

$$\text{or, } V_{ideal} = \frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2} \qquad (2.30)$$

The excess molar volumes, V^E were calculated using the following equation.

$$V^E = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \qquad (2.31)$$

Where X_1, M_1, and ρ_1 are the mole fraction, molar mass and density of component 1(solvent); X_2, M_2, and ρ_2 are the corresponding values of component 2 (organic solutes); and ρ_{mix} is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich Kister polynomial equation of the form,

$$V^E/\text{cm}^3\text{mol}^{-1} = X_1X_2\sum_{i=0}^{n} a_i(1-2X_1)^i \qquad \text{.....................(2.32)}$$

Where a_i is the ith fitting coefficient. Using n = 3 four a_i coefficient and the standard deviation σ were obtained through the least square method.

2.8 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 $$f = \eta\ A\ \frac{dv}{dx} \qquad \text{.....................(2.33)}$$

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.

$$\phi = \frac{1}{\eta} \qquad \text{.....................(2.34)}$$

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 (65). 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 (65):

$$\eta = \frac{\pi \mathrm{Pr}^4 t}{8lV} \qquad \text{...(2.35)}$$

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,

$$\eta = \frac{\pi \mathrm{Pr}^4 t}{8lv} - \frac{\rho V}{8\pi l t} \qquad \text{...(2.36)}$$

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,

$$\eta = \frac{\pi h\rho g r^4 t}{8vl} \qquad \text{..(2.37)}$$

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

$$\eta = A\rho t \qquad \text{..(2.38)}$$

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

$$\eta_{H_2O} = A\rho_{H_2O}t_{H_2O} \qquad \text{..(2.39)}$$

$$\text{or, } A = \frac{\eta_{H_2O}}{\rho_{H_2O}t_{H_2O}} \qquad \text{..(2.40)}$$

knowing the value of η_{H_2O} and ρ_{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.

2.9 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 higher 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 due to their theoretical practical importance.

$$\eta = Ae^{E/RT} \qquad \text{... ....(2.41)}$$

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.

2.10 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,

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

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 form 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.

2.11 Excess viscosity measurements

The theoretical viscosities, η_{id} of the mixtures are given by using the relation,

$$\ln \eta_{id} = X_1 \ln \eta_1 + X_2 \ln \eta_2$$

$$\text{or } \eta_{id} = \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \quad \text{..........(2.42)}$$

The excess viscosity, η^E of a mixture is given by, subtracting the theoretical (ideal) viscosity from the observed (experimental) value, η_{expt}

$$\eta^E = \eta_{expt.} - \eta_{id} \quad \text{..........(2.43)}$$

The excess viscosities, η^E were fitted to a Redlich–Kister polynomial equation of the form,

$$\eta^E = X_1 X_2 \sum_{i=0}^{n} a_i (1-2X_1)^i \quad \text{..........(2.44)}$$

where a_i is the ith fitting coefficient. Using $n = 3$, four a_i coefficients and the standard deviation σ were obtained through the least squares method.

2.12 Interaction parameter measurements (ε)

Interaction parameter, ε for viscosity for all compositions of the mixtures at different temperatures have been calculated by using Grunberg-Nissan equation (66),

$$\varepsilon = \frac{\ln \eta_{expt} - \ln \eta_{id}}{X_1 X_2} \quad \text{..........(2.45)}$$

Where , ε = Interaction parameter.

$\eta_{expt.}$ = observed viscosity

η_{id} = calculated viscosity

$$=\exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \quad \text{.......................}(2.46)$$

η_1 and η_2 are the viscosities of the pure component 1 and 2 respectively and x_1 and x_2 are the mole fractions respectively.

Interaction parameter, ε has been usually regarded as an approximate measure of the strength of the interactions between components. The negative value of ε indicates there is no specific interaction between the components present in the mixture and the positive value of ε indicates the presence of strong interaction.

2.13 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.

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 such 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 (67) using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, η as follows:

$$\eta = \frac{hN}{V_m} e^{\Delta G^* / RT} \quad \text{.......................}(2.47)$$

Where, ΔG^* is the change of 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 (ΔG^*) can be calculated by using the Nightingle and Benck equation (68):

$$\Delta G^{*} = RT \ln\left(\frac{\eta V_m}{Nh}\right) \qquad \text{....(2.48)}$$

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 ΔG^{*} 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.

2.13.1 Enthalpy (ΔH^{*}) and entropy (ΔS^{*}) of activation for viscous flow:

Change of enthalpy of activation (ΔH^{*}) and change of entropy of activation (ΔS^{*}) for viscous flow for the solution can be obtained with the help of Eyring equation (67):

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

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

$$\text{or, } \ln\frac{\eta V_m}{Nh} = \frac{\Delta G^{*}}{RT} \qquad \text{....(2.49)}$$

Since,

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \qquad \text{....(2.50)}$$

The Eyring equation takes the form,

$$\ln\frac{\eta V_m}{Nh} = \frac{\Delta H^{*}}{RT} - \frac{\Delta S^{*}}{R} \qquad \text{....(2.51)}$$

Assuming ΔH^{*} and ΔS^{*} 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, ΔH^* can be calculated as,

$\Delta H^* = \text{slope} \times R$ ……………………………………………………….(2.52)

and from of the intercept of this straight line, ΔS^* can be calculated as

$\Delta S^* = - \text{intercept} \times R$ ………………………..……………………….(2.53)

ΔH^* and ΔS^* respectively the enthalpy of activation per mole for viscous flow and ΔS^* is the entropy of activation. Since ΔS^* 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, ΔH^* and ΔS^* respectively can be calculated.

2.14 Different thermodynamic parameters

2.14.1 Change of free energy of activation (ΔG^*) 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.

2.14.2 Change of enthalpy of activation (ΔH^*) 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 ΔH^* and ΔS^* to be almost independent of temperature. The value of ΔH^* as found by this procedure are almost constant, for normal liquids over a range of temperature under ordinary condition.

2.14.3 Change of entropy of activation (ΔS^*) 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, ΔG^* is equivalent to (ΔH^* - $T\Delta S^*$) and that the high value of the enthalpy of activation ΔH^* is compensated by the large positive value of ΔS^*, so that ΔG^* 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 ΔS^* for flow should be relatively large positive, in agreement with the experimental fact that ΔG^* is normal in spite of the volume of the ΔH^* for associated liquids.

2.15 Redlich-Kister equation

The experimentally obtained values of excess properties, i.e. excess molar volume (V^E), excess viscosities (η^E) and excess free energy of activation (ΔG^{*E}), excess enthalpy of activation (ΔH^{*E}), excess entropy of activation (ΔS^{*E}) for viscous flow of all compositions for a system were fitted by the least square method of the four coefficient Redlich-Kister equation :

$$\mathrm{PROP}^E = X_1(1-X_1)\sum_{i=0}^{3} a_i(2X_1-1)^i \quad \ldots\ldots(2.54)$$

Where PROP^E represents any excess property (excess molar volume or excess viscosity etc.) for a binary liquid mixture composition and X_1 is the corresponding mole fraction of component one. a_i ($i = 0,1,2,3$) is the coefficient of the Redlich-Kister equation. A computer programme was developed in BASIC language to fit the excess property values and the corresponding mole fractions which computes four coefficients of Redlich-Kister equation along with the calculated excess property values.

The standard deviation of all excess properties of each system was calculated by using the following equation:

$$\mathrm{SD} = \left[\frac{\Sigma(PROP^E_{\exp} - PROP^E_{calcd})^2}{n-p-2}\right]^{1/2} \quad \ldots\ldots(2.55)$$

Where, $\mathrm{PROP}^E_{\exp}$ = experimental excess property, i.e. excess molar volume or excess viscosity etc.

$PROP^{E}_{calcd}$ = calculated excess property,

n = total number of compositions for each system,

p = number of coefficient of the Redlich-Kister equation,

and SD = standard deviation.

All the calculated excess properties, their corresponding polynomial coefficients and the standard deviation values have been presented in the tables. In the figures solid lines have been drawn by using the calculated excess property values with the aid of a computer program; whereas, the symbols represent the corresponding experimental excess property values.

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 (British standard) 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 n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol, iso-Pentanole, Propylene glycol and Acetonitrile. 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**
Ethanol	C_2H_5OH	46.07	99%	MERCK Germany
n-Propanol	$CH_3CH_2CH_2OH$	60.10	99%	E. MERCK India
iso-Propanol	$(CH_3)_2CHOH$	60.10	99%	MERCK Germany
n-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	99.5%	Scharlau Chemie U.S.A.
iso-Butanol	$(CH_3)_2CHCH_2OH$	74.12	99.%	E. MERCK India
n-Pentanol	$C_5H_{11}OH$	88.15	99 %	BDH, England
iso-Pentanol	$C_5H_{11}OH$	88.15	99 %	LOBA Chemical, India
Propylene glycol	C_3H_8O $(CH_2OHCH_2CH_2OH)$	76.10	99 %	MERCK Germany
Acetonitrile	CH_3CN	41.05	99.8%	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 calibaration of viscometer and density bottle.

3.4 Apparatus

The glass-ware used for the measurement for density of solvents and solutions were of the density bottle. Viscosities of various liquids were measured using the calibrated ostwald type viscometer. A & D company, HR 200 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 with an accuracy of $\pm 0.05^0$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 Methods (preparation of solution)

The binary solution of alcohol-acetonitrile in the whole range of composition ($X_2 = 0 - 1$) were prepared by mixing appropriate volumes of components. The volume taken by using burettes and pipettes were correct upto 0.1 cm^3. The volume of each component used as taken converted into mole fraction, special precaution was taken to prevent evaporation and introduction of moisture into the experimental samples.

3.6 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 ($g.cm^{-3}$) of solution was determined from the relation.

$$\rho = \frac{w - w_e}{v_0} \qquad \text{..(3.1)}$$

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 Excess molar volume measurements

The excess molar volumes, V^E (cm^3 mol^{-1}) were calculated using the following equation.

$$V^E = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \dots\dots (3.8)$$

Where X_1, M_1 and ρ_1 are the mole fraction, molar mass and density of component 1(solvent);

X_2, M_2 and ρ_2 are the corresponding values of component 2(organic solutes); and ρ_{mix} is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich-Kister polynomial equation of the form,

$$V^E = X_1X_2 \sum_{i=0}^{n} a_i(1-2X_1)^i \dots\dots (3.9)$$

Where a_i is the ith fitting coefficient. Using $n = 3$ four a_i coefficient and the standard deviation σ were obtained through the least square method.

3.8 Viscosity measurements

Viscosity (mPa.S) of water, acetonitrile, alcohols and their mixtures 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^{0}C. The viscometer was then clamped vertically in the thermostatic water bath such that the upper mark of the top bulb was well below the water level. 10 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,

$$\eta = A\rho t \quad \ldots\ldots\ldots\ldots\ldots\ldots(3.10)$$

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.

3.9 Excess viscosity measurements

The excess viscosities, η^E (mPa.S) were calculated using the following equation:

$$\eta^E = \eta_{\text{expt.}} - \eta_{id} \ldots\ldots\ldots\ldots\ldots\ldots(3.11)$$

where, η_{expt} is the observed viscosity. The ideal viscosity of mixture, η_{id} may be represented as:

$$\ln \eta_{id} = X_1 \ln \eta_1 + X_2 \ln \eta_2 \ldots\ldots\ldots\ldots\ldots\ldots(3.12)$$

The excess viscosities, η^E were fitted to a Redlich–Kister polynomial equation of the form,

$$\eta^E = X_1 X_2 \sum_{i=0}^{n} \mathrm{a_i}(1\text{-}2X_1)^{\mathrm{i}} \ldots\ldots\ldots\ldots\ldots\ldots(3.13)$$

where a_i is the ith fitting coefficient. Using $n = 3$, four $\mathrm{a_i}$ coefficients and the standard deviation σ were obtained through the least squares method.

3.10 Interaction parameter measurements

Interaction parameter, ε for viscosity for all compositions of the mixtures at different temperatures have been calculated by using Grunberg-Nissan equation (66),

$$\varepsilon = \frac{\ln \eta_{\mathrm{expt}} - \ln \eta_{id}}{X_1 X_2} \qquad \text{...(3.14)}$$

Where , ε = Interaction parameter.

$\eta_{\mathrm{expt.}}$ = observed viscosity

η_{id} = calculated viscosity

$= \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2)$

η_1 and η_2 are the viscosities of the pure component 1 and 2 respectively and x_1 and x_2 are the mole fractions respectively.

Interaction parameter, ε has been usually regarded as an approximate measure of the strength of the interactions between components. The negative value of ε indicates there is no specific interaction between the components present in the mixture and the positive value of ε indicates the presence of strong interaction.

3.11 Thermodynamic parametes

The change of free energy of activation (ΔG^*/ kJ mol^{-1}) was calculated by the help of Nightingle and Benck (68) equation:

$$\Delta G^* = RT \ln \left(\frac{\eta V_m}{Nh} \right) \text{ .... (3.15)}$$

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}

Enthalpy of activation (ΔH^* /kJ mol^{-1}) and entropy of activation (ΔS^* /J mol^{-1}) for viscous flow for the solution was determined y using the Eyring equation (67):

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

$$\text{or,} \quad \text{In } \frac{\eta V_m}{Nh} = \frac{\Delta G^*}{RT} \quad \ldots\ldots(3.16)$$

Since, $\Delta G^* = \Delta H^* - T\Delta S^*$

$$\therefore \ln\left(\frac{\eta V_m}{Nh}\right) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \quad \ldots\ldots(3.17)$$

Assuming ΔH^* and ΔS^* 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,

$$\Delta H^* = \text{slope} \times R \quad \ldots\ldots(3.18)$$

and

$$\Delta S^* = \text{-intercept} \times R \quad \ldots\ldots(3.19)$$

The excess enthalpy of activation, ΔH^*, excess entropy of activation, ΔS^* and excess free energy of activation, ΔG^* has been calculated as-

$$\Delta H^{*E} = \Delta H^* - (X_1\Delta H_1^* + X_2\Delta H_2^*) \quad \ldots\ldots(3.21)$$

$$\Delta S^{*E} = \Delta S^* - (X_1\, \Delta S_1^* + X_2\Delta S_2^*) \quad \ldots\ldots(3.22)$$

and

$$\Delta G^{*E} = \Delta G^* - (X_1\Delta G_1^* + X_2\Delta G_2^*) \quad \ldots\ldots (3.23)$$

Where the subscript 1 and 2 represent the pure components of the mixture.

3.12 Coefficient Redlich-Kister equation and standard deviation

The experimentally obtained values of excess properties, i.e. excess molar volume (V^E), excess viscosities (η^E) and excess free energy of activation (ΔG^{*E}), excess enthalpy of activation (ΔH^{*E}), excess entropy of activation (ΔS^{*E}) for viscous flow of all compositions for a system were fitted by the least square method of the four coefficient Redlich-Kister equation:

$$\text{PROP}^E = X_1(1-X_1)\sum_{i=0}^{3} a_i(2X_1-1)^i \quad \text{...(3.24)}$$

Where PROP^E represents any excess property (excess molar volume or excess viscosity etc.) for a binary liquid mixture composition and X_1 is the corresponding mole fraction of component one. a_i ($i = 0,1,2,3$) is the coefficient of the Redlich-Kister equation. A computer program was developed in BASIC language to fit the excess property values and the corresponding mole fractions which computes four coefficients of Redlich-Kister equation along with the calculated excess property values.

The standard deviation of all excess properties of each system was calculated by a computer which system was programmed to use the following equation:

$$\text{SD} = \left[\frac{\Sigma(PROP^E_{\exp} - PROP^E_{calcd})^2}{n-p-2}\right]^{1/2} \quad \text{...(3.25)}$$

Where,

$\text{PROP}^E_{\text{exp}}$ = experimental excess property, i.e. excess molar volume or excess viscosity etc.
$\text{PROP}^E_{\text{calcd}}$ = Calculated excess property,
n = Total number of compositions for each system,
p = Number of coefficient of the Redlich-Kister equation,
and SD = Standard deviation.

All the calculated excess properties, their corresponding polynomial coefficients and the standard deviation values have been presented in the tables. In the figures solid lines have been drawn by using the calculated excess property values with the aid of a computer program; whereas, the symbols represent the corresponding experimental excess property values.

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:

1. *n*-Propanol + Acetonitrile
2. *iso*-Propanol + Acetonitrile
3. *n*-Butanol+ Acetonitrile
4. *iso*-Butanol+ Acetonitrile
5. n-Pentanol + Acetonitrile
6. *iso*-Pentanol + Acetonitrile
7. Propylene glycol + Acetonitrile

The above-mentioned systems were studied precisely at six equidistant temperatures ranging from 298.15K to 323.15K at interval of 5K over the entire composition range by volumetric, viscometric and thermodynamic methods. The volumetric properties such as excess molar volume (V^E) are determined from density. Viscometric properties such as excess viscosity (η^E), interaction parameter (ε) and thermodynamic properties such as change of enthalpy (ΔH^*), change of entropy (ΔS^*) and change of free energy (ΔG^*) of activation for viscous flow and their excess quantities, ΔH^{*E}, ΔS^{*E} and ΔG^{*E} are determined from viscosity values. From these studies we obtained various information, which are presented in various section and discussed in the light of theories mentioned in the earlier chapter.

4.1 Volumetric properties:

The densities, ρ of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol in acetonitrile systems were determined at temperatures 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K with an interval of 5K over the entire composition range $0 < x_2 < 1$, where x_2 represents the mole fraction of Alkanols. The densities of the pure components are shown in Table 4.1 together with the literature values, for comparison. The agreement between the measured values and literature values has been found to be almost satisfactory.

The densities of the binary systems have been shown in Table 4.2-4.8 at different temperatures. Figure 4.1- 4.7 shows the plots of densities as a function of mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol, *iso*-Pentanol and Propylene glycol in acetontrile systems. In all the studied system, it shows that density increase almost linearly with composition of alcohols. Density value decreases with increase in the temperature. The experimental density values in pure state of Propylene glycol, *iso*-Pentanol, *n*-Pentanol, *iso*-Butanol, *n*-Butanol, iso-Propanol, *n*-Propanol and acetonitrile at 298.15K are 1.036700, 0.812200, 0.811159, 0.798010, 0.806244, 0.781049, 0.799693, 0.785375, 0.776513 g.cm^{-3} respectively.

The density of Propylene glycol, *n*-Propanol, *n*-Butanol, and *n*-Pentanol of pure solution were found to be order of

Propylene glycol > n-Pentanol> *n*-Butanol > *n*-Propanol

The density of *iso*-Propanol, *iso*-Butanol and iso-Pentanol of pure solution were found to be order of

iso-Pentanol > *iso*-Butanol > *iso*-Propanol

The densities of isomers are found to be order of

n-Butanol> *iso*-Butanol and *n*-Propanol > *iso*-Propanol

The densities of alcohols increase with the increase of carbon number may be depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. As the densities of pure *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol, *iso*-Pentanol and Propylene glycol, are higher than that of pure acetonitrile, with the increase of composition of alcohol, the density of alcohol + acetonitrile system increases and eventually proceeds towards the density of pure alcohol. Increase of density with composition of alcohols indicates the increase in ion-solvent interactions. Increase in density with composition is also due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute (69, 70).

Mixing of alcohols with acetonitrile solutions will induce changes in dipolar interactions. On addition of alcohols to the acetonitrile solutions the self association of acetonitrile will be disrupted partly or fully and new dipolar interactions between acetonitrile and alcohols will be formed. At the same time, segmental inclusion of species into the vacant spaces left in the structural network of solutions may also occur. With the increase of composition of alcohols in acetonitrile solution, the free volume in the solution decreased gradually and the density increased progressively (Figure 4.1-4.7). The dependences of the density with carbon chain length of alcohols with different composition at a fixed temperature are plotted in Figure 4.8-4.10. From the figures, it can be seen that at the same temperature, the density increase with the carbon chain length of the alcohols. The dependences of the density with carbon chain length of alcohols with different temperatures at a fixed mole fraction are plotted Figure 4.11-4.12. It can be also seen that at the same mole fraction, the density increase with the carbon chain length of alcohols. The increasing of density, ρ with the carbon chain length of alcohols (carbon number) can be explained by the increase mass of the alcohols and the degree of solute-solvent interactions with carbon number.

The variation of density, ρ with temperature for n-Propanol, n-Butanol and n-Pentanol are shown in figure 4.13-4.16 at different mole fractions. It is seen that density, ρ decrease linearly with increasing temperature for all alcohols. The densities decrease regularly with the increasing of temperature. This is due to the increase of thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding are occurred. At higher mole fraction of alcohol (Figure 4.14-4.16) the temperature effect is prominent compared with lower mole fraction of alcohols (Figure 4.13). The linear dependence of $\ln\rho$ verses 1/T are plotted in Figures 4.17-4.20.

The density order of alcohols in acetonitrile solution is similar as alcohols in pure solution. The values of densities of alcohols + acetonitrile (equimole fraction) systems has been found to be in the order of,

Propylene glycol > n-Pentanol + acetonitrile > *n*-Butanol + acetonitrile > *n*-Propanol + acetonitrile >

and

iso-Pentanol + acetonitrile > *iso*-Butanol + acetonitrile > *iso*-Propanol + acetonitrile

The density of n-Pentanol + acetonitrile is higher than *n*-Butanol + acetonitrile, *n*-Butanol + acetonitrile is higher than *n*-Propanol + acetonitrile, indicate that the nature of interaction in pure state is similar to the solution (mixture) state.

The excess molar volume, V^E of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-pentanolem and Propylene gcycol in acetonitrile systems have been calculated from density data of these systems using equation 3.8. The values of V^E at different temperatures have been shown in Table 4.2-4.8. For V^E the fitting coefficients (a_i) are shown in Table 4.30 along with standard deviations. Figure 4.21- 4.27 shows the plots of excess molar volume as a function of mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-Pentanol and Propylene glycol in acetonitrile systems.

Examination of Figures 4.21- 4.27 reveals that

(i) At low composition of alcohol in acetonitrile solution, excess molar volumes, V^E are positive and with the increase of alcohol composition, V^E reaches maximum value and then decreases continuously and eventually becomes zero.

(ii) Excess molar volumes, V^E are positive for the whole range of composition for the studied alcohols + acetonitrile systems.

(iii) For all the system dV^E/dT is positive.

(iv) The effect of temperature on V^E shows a definite trend, i.e., the V^E values increase with the increase of temperature.

(v) For all the studied alcohols +acetonitrile system, the maxima appear at ~ 0.3-0.5 mole fraction of alkanols.

(vi) The excess molar volumes, V^E of alcohols or glycols + acetonitrile systems has been found to be in the order of,

Propylene glycol> n-Pentanol + acetonitrile > *n*-Butanol + acetonitrile > *n*-Propanol + acetonitrile

and

iso-Pentanol + acetonitrile > n-pentanole + acetonitrile

and

iso-Butanol + acetonitrile > *n*-Butanol + acetonitrile

and

iso-Propanol + acetonitrile > *n*-Propanol + acetonitrile

vii) The mixing of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso Pentanol and Propylene glycol with acetonitrile systems is accompanied by expansions of volume at all studied temperatures.

Similar behavior was found by Saleh et al (71) in Alkanols + m-xylene systems, excess molar volume were positive in the whole range of composition. But, we have studied similar alcohols with dimethylformamide systems (72) and aqueous SDS systems (73), both the cases the excess molar volumes, V^E show negative value. This indicates that the mode of interactions of alcohols with acetonitrile and dimethylformamide (DMF) or aqueous SDS is not similar.

In general, the sign of V^E depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components.

The factors that cause expansion of volume on mixing of the components are:

a) The dispersive forces which occur predominantly in systems consisting of associated species (formed either by chemical or physical forces) and low-polar components,
b) Dissociation of one component or both of the components,
c) Steric hindrance,
d) Unfavorable Geometrical fitting,
e) Formation of weaker solute- solvent bond than solute – solute and solvent – solvent bonds,
f) Effect due to differences in the chain length of alkanols and
g) Electrostatic repulsive forces.

The factors that cause contraction on mixing are:

a) Strong specific interactions, usually a kind of chemical interaction,
b) Strong dipole-dipole or dipole-induced dipole interactions,
c) Interstitial accommodation of molecules of one component into the structural network of molecules of the other component. This is expected when the molecular sizes of the compounds differ by a large magnitude and
d) Favorable geometrical fitting of component molecules.

Acetonitrile (MeCN) in pure state, no self-association through H-bonding is possible because of the absence of donor/acceptor hydrogen. The attachment of one $-CH_3$ groups at the carbon atom increases electron density on the carbon atom and subsequently on nitrogen atom of the cyanide and so may have the possibility of H-bond formation with alcohol molecules by of the following ways: (i) $-C \equiv N \ldots HO\text{-}R$. At the same time the presence of $-CH_3$ groups of acetonitrile creates a steric hindrance that prevents alcohol molecules from coming sufficiently close to it. On the other hand, alcohol molecules undergo self- and cross-association because of the presence of hydrogen bonds (74, 75).

Mixing of acetonitrile with an alcohol or glycol will induce changes in hydrogen bonding (in the alkanol) and dipolar interactions (in the acetonitrile). On addition of alcohol or glycol to the pure acetonitrile the self association will be disrupted partly or fully and new dispersion force or dipolar interactions or H-bonds between alcohol and acetonitrile may be appeared. At the same time, segmental inclusion of acetonitrile into the vacant spaces left in the structural network of alcohol may also occur. In acetonitrile rich region, disintegration of multimers of alkanols into smaller units through disruption of H-bonding in alkanols takes place. Another important factor that contributes significantly towards volume expansion is the steric hindrance of the long chain or branched chain alkanols. These factors may primarily be responsible for the resultant positive excess molar volume of the mixtures of acetonitrile + Alkanols or glycol.

The dependence of excess molar volume with carbon number of alcohols with different composition at a fixed temperature are plotted in Figures 4.28-4.30. The dependence of excess molar volume with carbon number of alcohols with different temperature at a fixed composition are plotted in Figures 4.31-4.33. From the figures it can be seen that at the same temperatures, the excess molar volume increases with carbon number and the same mole fraction (0.5 and 0.8 mole fraction) the V^E show slightly parabolic curves. The increasing of V^E with the carbon chain length of alcohols may be related to increase of the size of alcohols.

It is observed that the system containing n-Pentanol exhibits the highest positive V^E values and that the positive values generally decrease with a decrease in chain length of alcohols. However, as the chain length of alcohols increases, the steric hindrance increases.

Pikkarainen (76, 77) studied the excess volume of binary solvent mixtures of N,N-diethylmethane sulfonamide with aliphatic alcohols. Garcia et al. (78) carried out volumetric and viscometric measurements on binary liquid mixtures of 2-pyrrolidone with 1-alkanols. Rauf et al. (79) determined the excess molar volumes of N,N-dimethylformamide + n-alkanols (C7–C9). The analysis of the previous works shows that the positive values of V^E decrease with the decrease of the chain length of alkanols. The results of our present investigation of acetonitrile + alkanols (C3–C5) binary mixtures are in conformity with the results of these reported investigations.

From Figs. 4.34 to 4.36, it is seen that the value of excess molar volumes increase with the rise of temperature. It is known that pure components or their mixtures can form either ring- or chain-like complexes, and while temperature increases, the degree of association decreases (80, 81) and hence excess molar volume increases.

The observed V^E of all the studied alcohols +acetonitrile mixtures may be discussed above which may be arbitrarily divided into physical, chemical, and geometrical contributions (82,83). The physical interactions, that is, nonspecific interactions between the real species present in the mixture, involve mainly dispersion force giving a positive contribution. The chemical or specific intermolecular interactions result in a volume decrease and these interactions include formation of hydrogen bonds and other complex-forming interactions. The structural contributions for these systems are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume.

The observed V^E values of the mixtures under investigation also can be explained in terms of the following contributions:

(1) Dispersion force,
(2) Geometric effect due to differences in molar volumes of the component molecules and
(3) Dipole-dipole interaction between the unlike polar molecules.

The positive V^E of the systems, a typical characteristic of hydrophobic solutes, lead to the conviction that the factors causing the volume expansion far outweigh the factor which is to responsible for volume contraction (84). Of the expansion factors, perhaps the dispersion force or steric hindrance is by far the most effective one in volume expansion, as through this process the hydrophobic molecules occupy the spaces inside the so-called cages formed through H-bond is breaking and thus ensure maximum raise of volume. Whereas in other cases, shrinkage takes place through strong interactions or attractive forces whose contribution to volume reduction is only relatively small.

The excess molar volumes of the binary mixtures which are under investigations may be considered to be the resultant of the above-mentioned competing interactions of the component molecules. All the components are polar compounds. The value of dipole moments (μ) are being 1.68D, 1.66 D, 1.66 D, 1.71 D, 1.70 D, 3.60 D and 3.92 D, for n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol, Propylene glycol and acetonitrile, respectively (85).

The value of dipole moment (μ) of acetonitrile is higher than the studied alkanols. Therefore, it has the possibility of the formation of hydrogen bonding through the polar group of the Alkanols and acetonitrile due to the hydrophilic effect. However, if the steric hindrances by the bulky groups or geometrical mismatch of these groups are very strong, then the possibilities of the formation of H-bonding decrease. The strong steric hindrance are existing in the long chain alkanols that affects both hydrogen bonding and electron donar/ acceptor interaction are reported (83, 84). So, if the alkanols are relatively smaller in size and formed H-bonding or associated through strong dipole-dipole interactions between the components small V^E values are generally expected. The experimental results of these mixtures are consistent with this observation.

The molar volumes of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-Pentanol, Propylene glycol and acetonitrile at 298.15K are 75.15, 76.95, 92.38, 92.88, 108.67, 108.6, 73.4 and 52.86 cm^3 $mole^{-1}$ respectively. This shows that a quite large size difference between C3-C5 Alkanols and acetonitrile molecules. The Acetonitrile molecules, being smaller there is possibility of partial accommodation of acetonitrile molecule in the interstices of the alkanols molecules.

The gradual expansion in volume on addition of Alkanols may be explained mainly by taking into account of breaking of the strong network of alcohol-alcohol interactions by the acetonitrile dispersion force with overall raise of space. After attaining the maxima further addition of alkanols acetonitrile composition are decreased and associated forms of alkanols –alkanols through H-bonding are raised resulting the gradual contraction in volume is occurred. The size differences between acetonitrile, n-Pentanol and iso-Pentanol are quite large so the possibility of partial accommodation of acetonitrile in the interstices of n-Pentanol is high but the possibility of making H-bonding cluster for n-Pentanol or iso-Pentanol is lower than the other studied alcohols owing to its higher steric hindrance and hence V^E becomes high. For the increase of temperature (Figure 4.34-4.36), the dissociation of H-bonding or weaker the dipole-dipole interaction are occurred, so the dissociated species in the solution are increased and hence positive V^E are increased (86).

In the case of isomers of *n*-Butanol and *iso*-Butanol and *n*-Propanol and *iso*-Propanol , the V^E becomes higher for branched chain alcohols (*iso*-Butanol and *iso*-Propanol) than linear chain alcohols (*n*-Butanol and *n*-Propanol) throughout the whole composition range. The strength of the intermolecular hydrogen bonding through in acetonitrle and Alkanols, is not the only factor influencing the negative V^E of liquid mixtures, but the orientation of groups, steric hindrance, hydrophobic interaction, molecular sizes and shapes of the components are also equally important. Here steric hindrance may be played important role for providing higher V^E. Larger the branch chain or long chain linear alkanols, the dissociation of H-bonding or weaker the dipole-dipole interaction are occurred as a result more positive V^E is observed.

At higher temperature unfavorable packing may, however, result due to disruption of the closely associated acetonitrile molecules on addition of alkanols and formation of new association between the unlike acetonitrile and an alkanol molecules. Reorganization of the pure components in the mixtures due to formation of different type of weaker bond and geometrical mismatch or steric hindrence may also result unfavorable packing and lead to expansion in volume (Figure 4.34-4.36).

4.2 Viscometric properties

The viscosities, η of n-Propanol, iso-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol, *iso*-Pentanol and Propylene glycol in acetonitrile systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.9-4.15. The viscosities of the pure components are shown in Table 4.1 together with the literature values for *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol wherever possible for comparison. The agreement between the measured values and literature values has been found to be almost satisfactory.

The variation of viscosities at these temperatures as a function of the mole fraction of the alcohols is shown in Figures 4.37-4.43. The following characteristic features of viscosity are observed:

a) The viscosities increase initially slowly up to ~0.6 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol and later on, the viscosity increases sharply until that of pure alcohol is reached specially at lower temperature.

b) At the alcohol rich region rapid change of viscosity are observed for *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol but the change is pronounced for the branched chain alcohols or glycols systems (iso-Propanol, iso-Butanol, Propylene glycols) than the linear alcohol (n-Propanol, n-Butanol) systems.

c) Viscosity decreases with rise of temperature.

The experimental viscosity values in pure state of acetonitrile, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Proylene glycol at 298.15K are 0.3416, 1.9671, 2.0442, 2.5557, 3.3323, 3.4740, 3.1377, 37.5288 mPa.S, respectively.

In pure state the viscosity of alcohols has been found to be in the order of,

Propylene glycole > iso-Pentanol > n-Pentanol> *iso*-Butanol > *n*-Butanol >
iso-Propanol > *n*-Propanol

For dilute solutions in acetonitrile, it is believed that, alcohols which are known to exist in associated forms through H-bonding are dissociated. This explains the low viscosity of the solutions in the acetonitrile rich regions. In alkanol rich region the rapid rise of viscosity is thought to be due to the continuous increase of self association of alkanols. i.e, the concentration of a particular alcohol is increased, multimers are formed, the extent of which increases with the rising concentration of alcohols. This accounts for the sharp rise in viscosity in the alcohol rich regions.

The dependences of the viscosity with carbon chain length of alcohols with different composition at a fixed temperature are plotted in Figures 4.44-4.46. From the figures, it is seen that, at the same temperature, the viscosity increase with the carbon chain length of alcohols. The dependences of the viscosity with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.47-4.48. From the figures, It is seen that at the same mole fraction, the viscosity increase with the carbon chain length of alcohols. The increasing of viscosity with the carbon number of alcohols can be explained by the increase of solution resistance with the increase of carbon number.

Viscosities of the studied alcohols as the function of temperature are represented in Figures 4.49-4.52. There is a marked decrease in the viscosity with increase of temperature for all the studied alcohols.

By using an empirical equation of the form,

$$\ln\eta = A + B/\mathrm{T}$$

the linear dependence of $\ln\eta$ against 1/T shows that at different mole fraction (shown in Figures 4.53-4.56) , the order of viscosity becomes n-Pentanol> n-Butanol> n-Propanol. The above equation is fully valid for all the acetonitrile-alcohols systems. The temperature effect is prominent for branched chain isomer than that of linear chain isomer. This indicates that the branched chain isormers are less stable than linear chain isomer at higher temperature. This is may be due to the maximum geometrical mismatch for the branched alkanols occurred at higher temperature. The viscosity of different isomers of Alkanols in Toluene as reported (87, 88) are in good agreement with our studied isomers.

The excess viscosities, η^{E}, have been calculated from viscosity data according to the equation:

$$\eta^{\mathrm{E}} = \eta_{\mathrm{obs}} - \eta_{\mathrm{id}} \qquad (1)$$

Where, η_{obs} is the experimentally observed viscosity of the mixture and η_{id} is the ideal viscosity of the mixture and

$$\eta_{id} = \exp(X_1 \ln\eta_1 + X_2 \ln\eta_2) \qquad (2)$$

Where, X_1 and η_1 are the mole fraction and viscosity of component 1 (acetonitrile), X_2 and η_2 are the corresponding values of component 2 (Alcohols).

The η^E values are shown in Table 4.9-4.15. The excess viscosities were fitted by least squares method to a polynomial equation 3.13. The values of the fitting parameters along with the standard deviation are presented in Table 4.31. The variation of η^E against mole fraction of alcohol (x_2) is shown in Figure 4.57-4.63. The η^E values are found to be negative, indicating that the acetonitrile solutions of alcohols are non ideal. Figure shows the following features:

i) Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.7-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol and *n*-Pentanol.

ii) The position of maxima and minima virtually does not change remarkably with the variation of temperature.

iii) An increase of temperature decreases the magnitude of negative excess viscosity.

iv) The height of the minima are in the order:

Propylene glycol > iso-pentonol > n-Pentanol> *iso*-Butanol > *n*-Butanol >
iso-Propanol > *n*-Propanol

The excess viscosities are found to be negative for all the studied alcohol systems in acetonitrile solution. The negative excess viscosities (as in Figs. 4.57-4.63) for the systems Acetonitrile + studied alcohol systems indicate the dissociation of components through steric hindrance or dispersive forces.

The value of dipole moments (μ) of all alkanols are almost similar but the size of Propylene glycol is quite smaller than other studied alcohols. The μ of Acetonitrile is much larger than alcohols. Therefore, hydrogen bonding is thought to be formed by the polar group of the Propylene glycol and Acetonitrile due to the hydrophilic effect. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, but the dipole moment of Propylene glycol and its size is noticeable than the other studied alcohols. As the long chain alcohols are more hydrophobic than short chain alcohols and their hydrophobicity decrease with increasing degree of unsaturation. Andini et al (89) showed that hydrophobic interaction varies according to hydrocarbon groups such as CH_3CH_2>CH_3> CH_2> CH.

Therefore, the very negative value of η^E of Propylene glycol can be explained by the higher degree of –OH group and it is possible the H-bond is playing a strong role here.

Acetonitrile and Alkanols molecules form a maximum structural disaggregate around at the 0.6-.7 mole fraction of Alkanols owing to the dissociation of components through dispersive forces or steric hindrance. With a further increase in Alkanols mole fraction, a composition is reached when Alkanols molecules can not find enough Acetonitrile molecules to be disrupted. After attaining the state of minima η^E further addition of alcohol continuously formed the ordered structure and Alkanols- Alkanols cage association, instead of, Acetonitrile-Alkanols dispersion, which result in the continual increase in η^E.

The dependences of excess viscosity with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.64-4.66. The dependences of excess viscosity with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.67-4.69. Both the cases it is seen that the negative excess viscosity value increases with the increasing of carbon number owing to the degree dissociation of components through steric hindrance.

The Figures also reveal that the systems having branched chain alkanols such as iso-Propanol, iso-Butanol, show larger negative excess viscosity, η^E than their straight chain isomers. This is due to the strong steric hindrance for the bulky groups which are existing in the branched chain Alkanols. Ali et al (90), Akhtar et al (91) and Saleh et al (92) observed similar effects for the systems containing branched chain alkanols+ aromatic hydrocarbons and their straight chain isomers + aromatic hydro carbons. Branched chain alkanols are less strongly associated than n-alkanols through H-bonding because of steric hindrance and hence more easily dissociable into smaller units. Thus, the branched chain alkanols cause greater reduction of viscosity from ideal values i.e. larger negative η^E than their straight chain isomers do. In a study of the viscometric properties of different alkanols in toluene, Nikam et al (93) showed the effects of branching and chain length of alkanols, which are consistent with our observation.

The negative excess viscosities are accounted for due to the dissociation of the associated structures of alcohols in Acetonitrile. As pointed out earlier, negative excess viscosity follow the order:

iso-Pentanol > n-Pentanol
iso-Butanol>n-Butanol
iso-Propanol> n-Propanol
n-Pentanol>n-Butanol> n-Propanol,

which in turn reflect the extent of dissociation mainly due to dispersion force. D' Aprano et al. (87) calculated the Kirkwood correlation coefficient, I_k, from the dielectric constant values of pentanol isomers in the temperature range of 303.15 and 323.15K and found that the values of I_k, vary in the order : 1-pentanol>2-pentanol>3-pentanol. Since I_k, is measure of the short range order in polar liquids, it follows that the pentanol whose I_k, is larger i.e. which is more strongly bounded by H-bond, is less likely to be dissociated than the pentanol with smaller I_k, i.e., which is less strongly bound by H-bonds. The relative ease of dissociation of our studied systems: two Butanols and two Propanols isomer either by thermal effect or by the force of dispersion in Acetonitrile should thus follow the order: iso-pentanol > n-pentanol; iso-Butanol>n-Butanol ; and iso-Propanol> n-Propanol.

The strength of H-bonding and dispersive force is not only factor influencing the negative η^E of mixtures, but the orientation of groups, shapes of the components and molecular sizes are also equally important, these later factors may change the order of η^E.

Very high negative excess viscosity showed Propylene glycol with acetonitrile systems. Propylene glycol has higher degree of –OH groups than the simple alcohol systems, so the contribution of hydrophilic interaction of Propylene glycol is higher than normal alcohols. For iso-Pentanol systems, some anomalous behavior is showed for excess viscosity and excess molar volume measurement. Similar behavior was reported (71-73) for iso-Pentanol with DMF systems.

From Figures 4.70-4.72 it is seen that the value of excess viscosity increases with the rise of temperature. The difference in minima of excess viscosity over the temperature range ($\Delta\eta^E_{min}$) of the different systems can be explained in terms of the maximum thermal fragility in the molecular interactions of Acetonitrile and alcohols formed. In comparison with alcohol- Acetonitrile association, the Acetonitrile - Acetonitrile association in the structure is assumed to be more fragile to heat. Examination of excess viscosity curves of different alcohol solutions (Figure 4.57-4.63) shows that $\Delta\eta^E_{min}$ varies in the order,

iso-Butanol (0.26 mPa.S)> *n*-Butanol (0.18 mPa.S)
iso-Propanol (0.23 mPa.S)> *n*-Propanol (0.13 mPa.S)

The values, therefore, indicate the extent of the destruction of the structures by thermal effect. The structure formed by the Acetonitrile - Acetonitrile association around the alcohols through H-bond or dispersion force are also assumed to be thermally unstable than Acetonitrile - Acetonitrile association in pure Acetonitrile (94, 95) that is similar to pure water. The thermal fragility of branched alcohols is higher than the linear chain alcohols.

The volumetric and viscometric properties of some alcohols with acetonitrile systems has reported Nikam et al (45), are partially consistent with our studied alcohols with acetonitrile system. But most of our studied conditions and parameters i.e. mole fraction, temperature, excess viscosity etc. are different, so we can not compare fully with the reported system (45).

4.2.1 Interaction parameter

The interaction parameters (ε) have been calculated by using the equation 3.14. The values of interaction parameters for different systems are shown in Figure 4.73-4.79 and the data are tabulated in Table 4.9-4.15. The values have been found to be negative and quite large in magnitude in alcohol-rich region for all the systems. The ε values are decrease with the increase of temperature.

From the studies of ε and η^E values of a number of binary mixtures of different polar or non-polar liquids, Fort and Moore (96) indicated an approximate idea about the strength of interaction between liquids. They concluded that:

a. If $\varepsilon > 0$ and $\eta^E > 0$ and both are large in magnitudes, then strong specific interaction between the components would be anticipated.
b. If $\varepsilon < 0$ and $\eta^E < 0$ and the magnitude of both parameters are large, then specific interaction would be absent but dispersion force would be dominant.
c. If $\varepsilon > 0$ and $\eta^E < 0$, then weak specific interaction would be present.

In all of our studied systems, both ε and η^E values are negative and large in magnitude. Therefore, the negative interaction parameters indicate that the specific interactions are absent but strong dispersion forces of the mixtures are dominant (96). The interaction parameters, ε decrease with alcohol concentration, showing minima and then increase continuously. In the present investigation at 298.15K, the minima values of ε have been found to be -1.8 (at $x_2 = 0.8$), -2.1 (at $x_2 = 0.8$), -1.3 (at $x_2 = 0.8$), -1.7 (at $x_2 = 0.7$), -1.5 (at $x_2 = 0.8$), -2.4 ($x_2 = 0.8$) for the Acetonitrile + *n*-Propanol, Acetonitrile + *iso*-Propanol and Acetonitrile + *n*-Butanol , Acetonitrile + *iso*-Butanol , and Acetonitrile + n-Pentanol, acetonitrile + Propylene glycol respectively. The height of the minima is higher in branched alcohol than those of linear chain alcohols with some exceptions. These observations accord with the view of Nigam and Mahl (97) that Acetonitrile + all the studied alcohols mixtures have strong dispersion force and geometrical effect. For Propylene glycol systems, strong hydrophilic effect is prominent. The positive excess molar volume V^E, negative η^E values suggest that the geometrical fitting of the molecules is also more important with the interactional factor for these systems.

The positive V^E, negative η^E, and negative ε for the Acetonitrile + studied alcohols systems show agreement with the statements (98-100). On addition of alkanols in acetonitrile solution strong disruptive forces are appeared and H-bonding in alkanols are dissociated causing volume expansion is occurred. For the long chain or branched chain alkanols, maximum geometrical mismatch for the steric factor are occurred causing volume expansion is also seen. From the above discussion, it is seen that the volumetric properties are fully consistent with the viscometric properties.

4.3 Thermodynamic properties

Free energy change (ΔG^*) of activation for the viscous flow of the *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol in acetonitrile solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.16-4.22. The variation of free energy (ΔG^*) at different temperatures as a function of the mole fraction of all the studied alcohols are shown in Figure 4.80-4.86. The following characteristic features of ΔG^* are observed:

i) The change of free energy (ΔG^*) increase slowly up to ~ 0.5-0.6 mole fraction of alcohol concentration for n-Propanol, iso-Propanol, iso-Butanol, iso- Pentanol and Propylene glycol and then, the ΔG^*, increases moderately until that of pure alcohol is reached. For n-Butanol and n-Pentanol systems ΔG^* increases almost linearly with mole fraction of alkanols.

ii) In the acetonitrile rich region (~ 0.0-0.6 mole fraction), the value of free energy ΔG^* is smaller at lower temperature and larger at higher temperature but in the alcohol rich region it is vice versa.

The experimental ΔG^* values in pure state of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol at 298.15K are 14.66, 14.81, 15.81, 16.49, 16.98, 16.73 and 22.28 kJ.mol^{-1}, respectively. The positive free energy change ΔG^* for the studied alcohols + acetonitrile systems with the concentration indicate that the species formed in the solutions have to surmount a large additional energy barrier in order to flow. This implies that the species experience enhanced resistance to flow.

The dependences of the free energy (ΔG^*) with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.87-4.89. The dependences of ΔG^* with carbon number of alcohols with different temperatures at a fixed mole fraction are plotted in Figure 4.90-4.91. From the figures it is seen that the ΔG^* increase with the carbon number of alcohols. The variation of ΔG^* with temperatures for alcohol-acetonitrile solutions are shown in Figure 4.92-4.95. It is seen that the ΔG^* slightly decreases with the increase of temperature except 0.2 mole fraction. The linear dependence of $\ln\Delta G^*$ vs 1/T are plotted in Figures 4.96-4.99. The variation of $\ln\Delta G^*$ against 1/T is fully valid for all the alcohol-acetonitrile systems.

Excess free energy (ΔG^{*E}) change of activation for the viscous flow of the *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol in acetonitrile solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.16-4.22. Figure 4.100-4.106 represent the variation of ΔG^{*E} of the systems against the mole fraction of the alcohols at different temperatures. The excess free energy (ΔG^{*E}) was fitted by least squares method to a polynomial equation. The values of the fitting parameters along with the standard deviation of alcohol systems are presented in Table 4.32. The ΔG^{*E} values are found to be negative and large in magnitude, indicating that the acetonitrile solutions of alcohols are non ideal. Figure shows the following features:

i) Excess free energies ΔG^{*E} are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.5-0.7

mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-Pentanol and Propylene glycol.

ii) The position of maxima and minima virtually does not change remarkably with the variation of temperature.

iii) An increase of temperature decreases the magnitude of negative excess ΔG^{*E}.

iv) Variation of ΔG^{*E} with composition for all the systems under investigation are more or less similar in nature, all being associated with minima.

v) The effect of temperature on ΔG^{*E} is seen to be significant, particularly in the region at or around the minima, though the positions of minima apparently remain almost unchanged with the variation of temperature.

The negative excess free energy, ΔG^{*E} throughout the whole range of composition indicates the formation of smaller units of alkanols in different proportions or strong disruptive force or segmental inclusion of acetonitrile in the interstices of alkanols depending upon the concentration of alkanols in solution systems. The figures also reveal that the systems having branched chain alkanols, iso-Propanol and iso-Butanol, show slightly larger negative excess viscosity, ΔG^{*E} than their straight chain isomers. Branched chain alkanols are less strongly associated than n-alkanols through H-bonding because of steric hindrance and hence more easily dissociable into smaller units. Thus, the branched chain alkanols has the possibility of reduction of viscous free energy from ideal values. The negative excess free energy, ΔG^{*E} follows the order:

iso-pentanol>n-Pentnol
iso-Butanol>n-Butanol
iso-Propanol> n-Propanol

This is of course as expected in terms of the branching of the hydrocarbon moieties in the isomeric alkanols.

As suggested by the author (101), a large negative excess free energy, ΔG^{*E} indicates the presence of dispersion force, whereas a large positive excess free energy, ΔG^{*E} suggests a specific association between the molecules in the solvent mixture. The negative ΔG^{*E} values in our studied systems are also indicative of the dispersion force containing molecular interaction among the Acetonitrile and alcohol systems.

The dependences of excess free energy with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.107-4.109. The dependences of excess ΔG^{*E} with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figure 4.110-4.112.

The difference in minima of ΔG^{*E} over the temperature range are shown in Figure 4.100-4.106 of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol- Acetonitrile association, the Acetonitrile - Acetonitrile association in the cage structure is assumed to be more fragile to heat.

This indicates that the extent of the destruction of the cages structures by thermal effect which, in turn, reflects the extent of cage formation. Therefore, the effect of temperature on ΔG^{*E}, particularly in the region at or around the minima is significant (Table 4.16-4.22). This may be due to the structures formed by hydrophilic or hydrophobic interaction that are considered to be much more labile and thermally less stable than the normal Acetonitrile structure (102, 103) i.e The cages formed by the Acetonitrile - Acetonitrile association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than Acetonitrile - Acetonitrile association in pure Acetonitrile.

Table 4.23-4.29 lists enthalpy ΔH^{*}, entropy ΔS^{*}, excess enthalpy ΔH^{*E} and excess entropy ΔS^{*E} values for the studied system for different molar ratios. The entropies of the systems increase almost linearly with composition of alkanols. All studied alcohols show negative entropy change, however for branched alkanols at alkanol rich region the change of entropy is pronounced.

All the other studied alkanols in Acetonitrile solution systems show negative excee entropy, ΔS^{*E} with distinct minima. Also the values are more negative for the branched alkanols than the linear system in the whole range of composition. Saleh et al (71) found that n-Pentanol + n-Heptane system, excess entropies were negative in the whole range of concentration.

On examination of the values of ΔS^{*} and ΔS^{*E}, it is evident that the systems with larger values of ΔS^{*} show smaller values of ΔS^{*E}. ΔS^{*} measure the randomness or disorderness of the system. ΔS^{*} values are negative for all the studied alcohol systems. This is believed to be due to more severe the segregated species in alkanols producing greater population of smaller species in their activated states. The segregated species so formed in Acetonitrile are supposed to have lesser interactions among themselves. In this state the complexes themselves can reorient in the flow process, and thereby, reduce their motional degrees of freedom. This brings about relative decrease in the randomness of overall structures of the activated complex, and hence smaller entropy values. The net result is, therefore, the negative excess entropy of the systems, which explains qualitatively the entropy-excess entropy correlation of the systems. This also attribute that the structural factor dominates over the interacional one, as in the case of the mixing properties.

In order to explain ΔH^* and ΔH^{*E} behavior similar to ΔG^* and ΔG^{*E} hydrophobic interaction, structural effect and hydrophilic interaction may be considered as the major cause in which it is assumed that both alcohols and Acetonitrile molecules are engaged by a network of highly structured form in pure state. Studies on viscometric properties by Kipkemboi and Easteal (104), Saleh et al. (71) and FTIR spectrophotometric studies by

Gojlo et al (105) of some alcohols indicated that the alcohols are hydrophobic in nature. The bulkier species so formed by hydrophobic interaction may be supposed to use large energy for their passage to activated state and hence the large positive ΔH^*. An investigation of the ΔH^* values of alcohols indicate that the ΔH^* of iso-Butanol is higher than that of studied other alcohol systems. It might be due to the structure of branched alkanols in Acetonitrile, is much bulkier and more rigid than that of or n-Propanol or n-Butanol requiring greater energy during the viscous flow. The ΔH^* values are positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. All these concepts can equally be applied to explain the positive values of free energy and enthalpy functions in the Acetonitrile systems (71).

The structural rearrangement that takes place in the activation process for the viscous flow in this region is believed to be associated with either loss or gain of some degree of structural order, resulting in a small increase or decrease of entropies as observed experimentally. The values of ΔH^* are positive and of ΔS^* are negative, so the entropy change of activation from the initial state to the transition state at a given composition is significant during an activated viscous flow process, therefore, this process is entropy controlled for Acetonitrile +Alkanols mixtures.

Table 4.1: Comparison of experimental and literature values of density, ρ (g.cm^{-3}) and viscosity, η (mPa.s) of pure components at different temperatures.

Component	Temperature (K)	Density (g.cm^{-3})		Viscosity (mPa.s)	
		ρ_{lit*}	ρ_{exp}	η_{lit*}	η_{exp}
n-Propanol	298.15	0.79975	0.799693	1.967	1.9671
	303.15	0.79548	0.795537	1.713	1.7192
	308.15	0.79138	0.791481	1.537	1.5310
	313.15	0.7873	0.787403	1.378	1.3760
	318.15	-	0.783213	-	1.2345
	323.15	0.7793	0.779364	1.115	1.1149
iso-Propanol	298.15	0.78123	0.781049	2.045	2.0442
	303.15	0.7766	0.776715	1.763	1.7630
	308.15	0.77246	0.772308	1.5405	1.5405
	313.15	0.7683	0.768101	1.3143	1.3224
	318.15	0.7635	0.763112	1.191	1.1806
	323.15	0.75868	0.757709	1.002	1.0084
n-Butanol	298.15	0.806	0.806244	2.5339	2.5557
	303.15	0.8022	0.802327	2.263	2.2515
	308.15	0.79838	0.798562	1.9778	1.9788
	313.15	0.79432	0.794338	1.7556	1.7502
	318.15	0.7905	0.790333	1.5635	1.5631
	323.15	0.78578	0.785853	1.3971	1.3990
iso-Butanol	298.15	0.7982	0.798010	3.332	3.3323
	303.15	0.79431	0.794211	2.884	2.8435
	308.15	0.7902	0.790210	2.426	2.4211
	313.15	0.78612	0.786116	2.08	2.0908
	318.15	0.7822	0.782130	1.861	1.7999
	323.15	0.7778	0.777865	1.602	1.5938
n-Pentanol	298.15	0.8111	0.811159	3.48	3.4740
	303.15	0.80711	0.807038	2.932	2.9817
	308.15	0.80352	0.803361	2.57	2.5702
	313.15	0.7995	0.799562	2.332	2.2702
	318.15	-	0.795605	-	1.9744
	323.15	0.7905	0.791408	1.765	1.7661
iso-Pentanol	298.15	0.8097	0.812200	3.61	3.1377
	303.15	0.8069	0.809256	3.12	2.9540
	308.15	0.8027	0.806700	2.68	2.6880
	313.15	0.7972	0.802400	2.31	2.3690
	318.15	0.7928	0.798279	-	2.0967
	323.15	0.7881	0.794047	-	1.9378
Propylene glycol	298.15	-	1.036700	-	37.5288
	303.15	-	1.032300	-	30.1815
	308.15	-	1.029200	-	23.6979
	313.15	-	1.024900	-	18.5595
	318.15	-	1.019733	-	14.5290
	323.15	-	1.015588	-	11.7216
Acetonitrile	298.15	0.7765	0.776513	0.341	0.3416
	303.15	0.7715	0.771401	0.328	0.3291
	308.15	0.76586	0.765936	0.314	0.3154
	313.15	0.7607	0.760667	0.3042	0.3029
	318.15	0.7552	0.755370	0.2918	0.2908
	323.15	0.7495	0.749410	0.2746	0.2751

*All the literature values are cited from the references 106-120.

Table-4.2: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+ n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.1007	0.778408	0.0912	0.773282	0.1025	0.767766	0.1213	0.762406	0.1413	0.757079	0.1564	0.751213	0.1728
0.2006	0.780996	0.1183	0.775853	0.1404	0.770550	0.1572	0.765402	0.1732	0.760206	0.1895	0.754505	0.2140
0.3007	0.783634	0.1272	0.778715	0.1412	0.773579	0.1581	0.768574	0.1740	0.763520	0.1895	0.758099	0.2114
0.3999	0.786314	0.1159	0.781445	0.1343	0.776524	0.1463	0.771712	0.1571	0.766735	0.1761	0.761645	0.1894
0.4994	0.788991	0.0906	0.784302	0.1022	0.779438	0.1211	0.774753	0.1312	0.769921	0.1474	0.765047	0.1602
0.6012	0.791532	0.0658	0.786950	0.0763	0.782280	0.0904	0.777637	0.1066	0.772942	0.1203	0.768298	0.1307
0.6994	0.793834	0.0412	0.789365	0.0491	0.784853	0.0602	0.780384	0.0703	0.775773	0.0851	0.771320	0.0947
0.8014	0.796114	0.0123	0.791735	0.0193	0.787398	0.0254	0.783044	0.0342	0.778601	0.0422	0.774342	0.0505
0.9008	0.798065	-0.0035	0.793789	0.0009	0.789605	0.0031	0.785388	0.0079	0.781040	0.0151	0.776972	0.0211
1.0000	0.799693	0.0000	0.795537	0.0000	0.791481	0.0000	0.787403	0.0000	0.783213	0.0000	0.779364	0.0000

Table-4.3: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+ n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.0998	0.780059	0.0916	0.775113	0.0943	0.769763	0.1066	0.764448	0.1238	0.759117	0.1434	0.753108	0.1672
0.1991	0.783445	0.1580	0.778639	0.1634	0.773438	0.1839	0.768259	0.2035	0.763176	0.2193	0.757480	0.2360
0.3008	0.786963	0.1867	0.782300	0.1930	0.777231	0.2216	0.772196	0.2414	0.767193	0.2653	0.761725	0.2795
0.4006	0.790147	0.2034	0.785548	0.2161	0.780706	0.2426	0.775860	0.2568	0.771023	0.2796	0.765650	0.3006
0.5003	0.793268	0.1944	0.788830	0.2032	0.784132	0.2331	0.779363	0.2501	0.774725	0.2668	0.769474	0.2907
0.6005	0.796429	0.1522	0.792022	0.1683	0.787595	0.1873	0.782961	0.2004	0.778380	0.2230	0.773241	0.2493
0.6996	0.799197	0.1163	0.794956	0.1255	0.790717	0.1396	0.786157	0.1537	0.781673	0.1775	0.776675	0.2021
0.7989	0.801923	0.0589	0.797799	0.0648	0.793678	0.0796	0.789236	0.0891	0.784899	0.1075	0.779988	0.1348
0.9006	0.804326	0.0157	0.800285	0.0214	0.796297	0.0346	0.791987	0.0373	0.787821	0.04670	0.783109	0.0634
1.0000	0.806244	0.0000	0.802327	0.0000	0.798562	0.0000	0.794338	0.0000	0.790333	0.0000	0.785853	0.0000

Table-4.4: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+ n-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.1023	0.781306	0.1336	0.776205	0.1482	0.770843	0.1672	0.765603	0.1879	0.760132	0.2233	0.753819	0.2806
0.1949	0.785704	0.1883	0.780739	0.2047	0.775593	0.2284	0.770565	0.2505	0.765354	0.2828	0.759349	0.3393
0.3056	0.790503	0.2181	0.785698	0.2342	0.780810	0.2595	0.776054	0.2776	0.771067	0.3093	0.765091	0.3912
0.3923	0.793954	0.2181	0.789189	0.2402	0.784538	0.2605	0.779933	0.2784	0.774998	0.3193	0.769344	0.3906
0.4919	0.797402	0.2185	0.792773	0.2379	0.788333	0.2552	0.783844	0.2767	0.779095	0.3141	0.773766	0.3731
0.6077	0.801207	0.1811	0.796772	0.1905	0.792473	0.2121	0.788103	0.2371	0.783612	0.2621	0.778550	0.3135
0.7077	0.804055	0.1501	0.799665	0.1629	0.795534	0.1811	0.791348	0.1983	0.786837	0.2385	0.782073	0.2721
0.7818	0.806002	0.1215	0.801611	0.1405	0.797580	0.1578	0.793483	0.1733	0.789145	0.2016	0.784569	0.2234
0.9064	0.809111	0.0499	0.804824	0.0655	0.801009	0.0724	0.797049	0.0845	0.792923	0.0988	0.788515	0.1161
1.0000	0.811159	0.0000	0.807038	0.0000	0.803361	0.0000	0.799562	0.0000	0.795605	0.0000	0.791408	0.0000

Table-4.5: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+ iso-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.1007	0.776546	0.0429	0.771480	0.0480	0.766030	0.0583	0.760850	0.0634	0.755481	0.0729	0.749473	0.0836
0.1994	0.776543	0.0874	0.771526	0.0969	0.766223	0.1071	0.761108	0.1183	0.755629	0.1406	0.749492	0.1686
0.3007	0.776597	0.1286	0.771620	0.1431	0.766442	0.1543	0.761402	0.1706	0.755916	0.1980	0.749783	0.2331
0.3996	0.776874	0.1505	0.772036	0.1611	0.766917	0.1774	0.761968	0.1963	0.756581	0.2194	0.750565	0.2511
0.4993	0.777462	0.1449	0.772689	0.1569	0.767691	0.1723	0.762826	0.1937	0.757497	0.2151	0.751584	0.2434
0.5990	0.778123	0.1294	0.773461	0.1382	0.768527	0.1569	0.763823	0.1731	0.758551	0.1923	0.752755	0.2151
0.7008	0.779063	0.0857	0.774448	0.0961	0.769682	0.1080	0.764997	0.1311	0.759753	0.1502	0.754024	0.1714
0.8012	0.779758	0.0583	0.775186	0.0706	0.770564	0.0771	0.766133	0.0845	0.760861	0.1087	0.755241	0.1236
0.899	0.780471	0.0241	0.776042	0.0282	0.771464	0.0377	0.767053	0.0507	0.761955	0.0601	0.756531	0.0590
1.0000	0.781049	0.0000	0.776715	0.0000	0.772308	0.0000	0.768101	0.0000	0.763112	0.0000	0.757709	0.0000

Table-4.6: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+ iso-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.1002	0.778425	0.1173	0.773443	0.1247	0.768131	0.1323	0.762990	0.1385	0.757775	0.1500	0.751807	0.1738
0.2007	0.780617	0.1932	0.775761	0.2064	0.770652	0.2156	0.765580	0.2308	0.760513	0.2469	0.754581	0.2901
0.3003	0.782804	0.2445	0.778087	0.2608	0.773079	0.2777	0.768254	0.2854	0.763257	0.3108	0.757653	0.3464
0.3999	0.784869	0.2841	0.780314	0.2999	0.775605	0.3054	0.770906	0.3138	0.766109	0.3354	0.760746	0.3677
0.4997	0.787190	0.2792	0.782710	0.3006	0.778127	0.3077	0.773570	0.3138	0.769015	0.3252	0.763820	0.3585
0.6004	0.789547	0.2490	0.785201	0.2692	0.780771	0.2739	0.776239	0.2877	0.771800	0.2993	0.766814	0.3277
0.7002	0.791816	0.2024	0.787618	0.2185	0.783283	0.2250	0.778819	0.2415	0.774551	0.2458	0.769723	0.2724
0.8004	0.794118	0.1304	0.790011	0.1469	0.785790	0.1520	0.781431	0.1662	0.777210	0.1754	0.772511	0.2016
0.8995	0.796118	0.0677	0.792206	0.0720	0.788058	0.0792	0.783864	0.0831	0.779738	0.0908	0.775285	0.1015
1.0000	0.798010	0.0000	0.794211	0.0000	0.790210	0.0000	0.786116	0.0000	0.782130	0.0000	0.777865	0.0000

Table-4.7: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+iso-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.0996	0.781900	0.0909	0.778000	0.0295	0.771800	0.1255	0.765400	0.2284	0.760100	0.2479	0.754400	0.2549
0.1996	0.786600	0.1624	0.782700	0.1228	0.777000	0.2228	0.770100	0.3906	0.764600	0.4458	0.759100	0.4604
0.3004	0.791600	0.1436	0.787600	0.1340	0.781300	0.3298	0.775100	0.4593	0.769800	0.5145	0.764600	0.5230
0.4007	0.796000	0.1095	0.792094	0.1125	0.786300	0.3041	0.779600	0.5020	0.774478	0.5563	0.769400	0.5721
0.5002	0.799300	0.1229	0.795773	0.1086	0.790270	0.3115	0.784500	0.4344	0.778900	0.5537	0.774100	0.5577
0.6000	0.802600	0.0916	0.799150	0.0874	0.794291	0.2590	0.788300	0.4223	0.783200	0.5032	0.778700	0.4886
0.6998	0.805800	0.0264	0.802120	0.0663	0.797500	0.2454	0.792000	0.3686	0.786800	0.4757	0.782500	0.4510
0.7999	0.808000	0.0390	0.804811	0.0392	0.800700	0.1894	0.795500	0.2894	0.791200	0.2978	0.787000	0.2716
0.8982	0.810500	-0.0212	0.807300	-0.0038	0.803700	0.1100	0.799300	0.1172	0.795000	0.1333	0.791000	0.0909
1.0000	0.812200	0.0000	0.809256	0.0000	0.806700	0.0000	0.802400	0.0000	0.798279	0.0000	0.794047	0.0000

Table-4.8: Density (ρ) and Excess molar volume (V^E) of Acetonitrile+Propylene glycol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.776513	0.0000	0.771401	0.0000	0.765936	0.0000	0.760667	0.0000	0.755370	0.0000	0.749410	0.0000
0.0995	0.810736	0.3485	0.807500	0.2231	0.801866	0.2535	0.795700	0.3255	0.790000	0.3561	0.783600	0.4046
0.2005	0.842743	0.6021	0.839365	0.4905	0.833637	0.5487	0.827900	0.5996	0.823597	0.5283	0.816900	0.6146
0.3008	0.873685	0.6612	0.871100	0.4948	0.866000	0.5252	0.859639	0.6293	0.854200	0.6427	0.848700	0.6533
0.3992	0.900417	0.7670	0.897400	0.6353	0.893698	0.5808	0.888300	0.6213	0.881517	0.7384	0.877867	0.6202
0.5006	0.927200	0.7363	0.924000	0.6213	0.919519	0.6438	0.914600	0.6565	0.908300	0.7395	0.903600	0.7172
0.6005	0.952700	0.5963	0.950188	0.4311	0.946400	0.4170	0.940000	0.5517	0.935800	0.4699	0.930300	0.5234
0.7003	0.976600	0.4184	0.972700	0.3636	0.969776	0.2991	0.964533	0.3512	0.959400	0.3433	0.954099	0.3954
0.7993	0.998200	0.2650	0.996144	0.0677	0.992473	0.0782	0.987624	0.1057	0.981629	0.1681	0.976033	0.2590
0.8993	1.017800	0.1579	1.013900	0.1119	1.010800	0.0947	1.006400	0.0949	1.001700	0.0537	0.997800	0.0184
1.0000	1.036700	0.0000	1.032300	0.0000	1.029200	0.0000	1.024900	0.0000	1.019733	0.0000	1.015588	0.0000

Table-4.9: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+ n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.1007	0.3545	-0.0530	-1.5382	0.3374	-0.0513	-1.5633	0.3221	-0.0477	-1.5246	0.3063	-0.0465	-1.5598	0.2964	-0.0400	-1.3971	0.2849	-0.0318	-1.1687
0.2006	0.3911	-0.0943	-1.3465	0.3712	-0.0873	-1.3174	0.3522	-0.0808	-1.2881	0.3341	-0.0763	-1.2820	0.3181	-0.0705	-1.2490	0.3060	-0.0582	-1.0863
0.3007	0.4399	-0.1384	-1.3010	0.4128	-0.1282	-1.2865	0.3885	-0.1187	-1.2679	0.3688	-0.1087	-1.2282	0.3475	-0.1017	-1.2204	0.3357	-0.0833	-1.0541
0.3999	0.5042	-0.1838	-1.2952	0.4661	-0.1714	-1.3047	0.4351	-0.1582	-1.2919	0.4145	-0.1403	-1.2151	0.3882	-0.1302	-1.2055	0.3742	-0.1072	-1.0497
0.4994	0.5910	-0.2279	-1.3046	0.5449	-0.2065	-1.2856	0.5040	-0.1902	-1.2809	0.4742	-0.1708	-1.2305	0.4402	-0.1584	-1.2297	0.4237	-0.1296	-1.0677
0.6012	0.7221	-0.2566	-1.2680	0.6623	-0.2269	-1.2286	0.6063	-0.2091	-1.2357	0.5571	-0.1954	-1.2537	0.5171	-0.1765	-1.2246	0.4935	-0.1445	-1.0714
0.6994	0.8761	-0.2861	-1.3442	0.7869	-0.2590	-1.3534	0.7248	-0.2274	-1.2980	0.6694	-0.2036	-1.2633	0.6157	-0.1837	-1.2417	0.5777	-0.1543	-1.1263
0.8014	1.1063	-0.2831	-1.4317	0.9951	-0.2429	-1.3724	0.9072	-0.2115	-1.3167	0.8291	-0.1897	-1.2944	0.7561	-0.1703	-1.2762	0.7034	-0.1410	-1.1477
0.9008	1.4061	-0.2474	-1.8138	1.2660	-0.1932	-1.5890	1.1388	-0.1701	-1.5581	1.0336	-0.1506	-1.5218	0.9388	-0.1308	-1.4592	0.8597	-0.1107	-1.3553
1.0000	1.9671	0.0000	0.0000	1.7192	0.0000	0.0000	1.5310	0.0000	0.0000	1.3760	0.0000	0.0000	1.2345	0.0000	0.0000	1.1149	0.0000	0.0000

Table-4.10: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+ n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.0998	0.3793	-0.0383	-1.0711	0.3574	-0.0413	-1.2179	0.3411	-0.0377	-1.1680	0.3238	-0.0370	-1.2058	0.3089	-0.0350	-1.1961	0.2975	-0.0261	-0.9344
0.1991	0.4301	-0.0799	-1.0684	0.4092	-0.0734	-1.0349	0.3874	-0.0672	-1.0034	0.3682	-0.0613	-0.9658	0.3491	-0.0574	-0.9540	0.3346	-0.0457	-0.8023
0.3008	0.5063	-0.1195	-1.0076	0.4801	-0.1068	-0.9547	0.4509	-0.0971	-0.9271	0.4231	-0.0903	-0.9196	0.3996	-0.0827	-0.8941	0.3822	-0.0665	-0.7623
0.4006	0.6008	-0.1642	-1.0062	0.5644	-0.1466	-0.9618	0.5316	-0.1266	-0.8896	0.4991	-0.1125	-0.8465	0.4661	-0.1043	-0.8411	0.4391	-0.0886	-0.7657
0.5003	0.7351	-0.1999	-0.9620	0.6851	-0.1762	-0.9154	0.6432	-0.1472	-0.8245	0.5932	-0.1353	-0.8217	0.5522	-0.1223	-0.8005	0.5142	-0.1064	-0.7526
0.6005	0.9004	-0.2434	-0.9975	0.8362	-0.2081	-0.9264	0.7734	-0.1767	-0.8578	0.7145	-0.1540	-0.8134	0.6642	-0.1342	-0.7669	0.6105	-0.1200	-0.7480
0.6996	1.1007	-0.2956	-1.1318	1.0283	-0.2352	-0.9802	0.9409	-0.1989	-0.9124	0.8616	-0.1717	-0.8648	0.7944	-0.1487	-0.8167	0.7314	-0.1269	-0.7611
0.7989	1.4042	-0.3009	-1.2086	1.2917	-0.2377	-1.0513	1.1711	-0.1967	-0.9662	1.0651	-0.1648	-0.8957	0.9654	-0.1492	-0.8943	0.8861	-0.1226	-0.8066
0.9006	1.8641	-0.2283	-1.2904	1.6845	-0.1752	-1.1055	1.5082	-0.1404	-0.9944	1.3453	-0.1248	-0.9913	1.2081	-0.1144	-1.0104	1.0952	-0.0949	-0.9286
1.0000	2.5557	0.0000	0.0000	2.2515	0.0000	0.0000	1.9788	0.0000	0.0000	1.7502	0.0000	0.0000	1.5631	0.0000	0.0000	1.3990	0.0000	0.0000

Table-4.11: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+ n-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.1023	0.4011	-0.0320	-0.8361	0.3776	-0.0347	-0.9581	0.3586	-0.0323	-0.9392	0.3417	-0.0305	-0.9313	0.3284	-0.0253	-0.8096	0.3128	-0.0199	-0.6719
0.1949	0.4682	-0.0687	-0.8722	0.4392	-0.0665	-0.8982	0.4113	-0.0634	-0.9139	0.3903	-0.0582	-0.8862	0.3691	-0.0533	-0.8596	0.3518	-0.0434	-0.7418
0.3056	0.5726	-0.1214	-0.9063	0.5322	-0.1132	-0.9088	0.4921	-0.1067	-0.9249	0.4591	-0.1015	-0.9410	0.4330	-0.0892	-0.8823	0.4024	-0.0832	-0.8853
0.3923	0.6901	-0.1585	-0.8673	0.6384	-0.1429	-0.8472	0.5842	-0.1341	-0.8666	0.5414	-0.1261	-0.8784	0.5003	-0.1162	-0.8760	0.4663	-0.1042	-0.8460
0.4919	0.8633	-0.2058	-0.8556	0.7971	-0.1760	-0.7981	0.7281	-0.1571	-0.7816	0.6712	-0.1446	-0.7807	0.6102	-0.1359	-0.8043	0.5634	-0.1232	-0.7912
0.6077	1.0977	-0.3008	-1.0160	0.9911	-0.2649	-0.9935	0.9083	-0.2203	-0.9109	0.8351	-0.1950	-0.8804	0.7661	-0.1652	-0.8192	0.7006	-0.1510	-0.8185
0.7077	1.3591	-0.4045	-1.2595	1.2108	-0.3548	-1.2424	1.1027	-0.2893	-1.1264	1.0092	-0.2508	-1.0730	0.9244	-0.2035	-0.9620	0.8391	-0.1865	-0.9701
0.7818	1.6522	-0.4421	-1.3900	1.4871	-0.3563	-1.2590	1.3453	-0.2809	-1.1115	1.2083	-0.2545	-1.1205	1.1002	-0.1998	-0.9780	0.9942	-0.1829	-0.9899
0.9064	2.4492	-0.3469	-1.5612	2.2216	-0.2043	-1.0370	1.9925	-0.1195	-0.6864	1.7776	-0.1025	-0.6609	1.5711	-0.0792	-0.5800	1.4066	-0.0774	-0.6314
1.0000	3.4740	0.0000	0.0000	2.9817	0.0000	0.0000	2.5702	0.0000	0.0000	2.2702	0.0000	0.0000	1.9744	0.0000	0.0000	1.7661	0.0000	0.0000

Table-4.12: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+ iso-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.1007	0.3595	-0.0496	-1.4263	0.3403	-0.0494	-1.4968	0.3217	-0.0483	-1.5452	0.3072	-0.0442	-1.4831	0.2936	-0.0413	-1.4522	0.2845	-0.0290	-1.0725
0.1994	0.3871	-0.1010	-1.4518	0.3615	-0.0984	-1.5082	0.3434	-0.0893	-1.4483	0.3241	-0.0823	-1.4171	0.3119	-0.0726	-1.3113	0.3027	-0.0537	-1.0232
0.3007	0.4316	-0.1534	-1.4466	0.4029	-0.1422	-1.4379	0.3791	-0.1290	-1.3932	0.3581	-0.1137	-1.3114	0.3383	-0.1049	-1.2841	0.3232	-0.0833	-1.0910
0.3996	0.4926	-0.2057	-1.4543	0.4582	-0.1854	-1.4161	0.4287	-0.1657	-1.3624	0.4022	-0.1436	-1.2728	0.3766	-0.1324	-1.2560	0.3578	-0.1045	-1.0678
0.4993	0.5733	-0.2613	-1.5023	0.5256	-0.2352	-1.4794	0.4882	-0.2081	-1.4201	0.4548	-0.1774	-1.3175	0.4228	-0.1626	-1.3013	0.3973	-0.1289	-1.1239
0.5990	0.6845	-0.3131	-1.5681	0.6211	-0.2783	-1.5414	0.5722	-0.2434	-1.4754	0.5273	-0.2050	-1.3673	0.4873	-0.1858	-1.3449	0.4547	-0.1443	-1.1472
0.7008	0.8372	-0.3597	-1.7045	0.7623	-0.3047	-1.6036	0.6938	-0.2647	-1.5411	0.6335	-0.2173	-1.4067	0.5759	-0.2004	-1.4242	0.5331	-0.1505	-1.1862
0.8012	1.0472	-0.3852	-1.9664	0.9502	-0.3126	-1.7857	0.8562	-0.2677	-1.7081	0.7702	-0.2163	-1.5541	0.6942	-0.1994	-1.5851	0.6383	-0.1406	-1.2497
0.899	1.4003	-0.3059	-2.1763	1.2311	-0.2570	-2.0880	1.0962	-0.2163	-1.9832	0.9805	-0.1590	-1.6548	0.8861	-0.1387	-1.6017	0.7924	-0.0920	-1.2098
1.0000	2.0442	0.0000	0.0000	1.7630	0.0000	0.0000	1.5405	0.0000	0.0000	1.3224	0.0000	0.0000	1.1806	0.0000	0.0000	1.0084	0.0000	0.0000

Table-4.13: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+ iso-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.1002	0.3757	-0.0535	-1.4769	0.3573	-0.0512	-1.4847	0.3393	-0.0476	-1.4549	0.3229	-0.0447	-1.4378	0.3075	-0.0416	-1.4065	0.2980	-0.0300	-1.0646
0.2007	0.4324	-0.1072	-1.3808	0.4072	-0.1001	-1.3705	0.3851	-0.0897	-1.3053	0.3651	-0.0813	-1.2527	0.3453	-0.0740	-1.2098	0.3314	-0.0600	-1.0367
0.3003	0.5111	-0.1659	-1.3381	0.4752	-0.1537	-1.3335	0.4461	-0.1356	-1.2629	0.4211	-0.1200	-1.1930	0.3955	-0.1072	-1.1417	0.3760	-0.0902	-1.0234
0.3999	0.6225	-0.2269	-1.2953	0.5736	-0.2060	-1.2784	0.5336	-0.1790	-1.2053	0.4976	-0.1583	-1.1508	0.4663	-0.1365	-1.0699	0.4379	-0.1175	-0.9901
0.4997	0.7667	-0.2995	-1.3192	0.6929	-0.2738	-1.3322	0.6404	-0.2329	-1.2408	0.5914	-0.2039	-1.1851	0.5471	-0.1760	-1.1155	0.5131	-0.1487	-1.0178
0.6004	0.9678	-0.3733	-1.3598	0.8701	-0.3311	-1.3441	0.7931	-0.2792	-1.2570	0.7242	-0.2419	-1.2014	0.6652	-0.2036	-1.1128	0.6172	-0.1727	-1.0281
0.7002	1.2547	-0.4287	-1.4002	1.1205	-0.3692	-1.3566	1.0062	-0.3079	-1.2720	0.9093	-0.2623	-1.2073	0.8240	-0.2181	-1.1186	0.7547	-0.1865	-1.0521
0.8004	1.6640	-0.4510	-1.5011	1.4751	-0.3739	-1.4140	1.3091	-0.3028	-1.3024	1.1562	-0.2656	-1.2944	1.0461	-0.2048	-1.1193	0.9494	-0.1730	-1.0477
0.8995	2.2594	-0.3911	-1.7662	1.9762	-0.3133	-1.6278	1.7501	-0.2226	-1.3243	1.5481	-0.1737	-1.1766	1.3653	-0.1333	-1.0305	1.2121	-0.1237	-1.0753
1.0000	3.3323	0.0000	0.0000	2.8435	0.0000	0.0000	2.4211	0.0000	0.0000	2.0908	0.0000	0.0000	1.7999	0.0000	0.0000	1.5938	0.0000	0.0000

Table-4.14: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+iso-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.0996	0.4020	-0.0241	-0.6483	0.3807	-0.0288	-0.8132	0.3610	-0.0294	-0.8740	0.3395	-0.0323	-1.0124	0.3211	-0.0329	-1.0888	0.3077	-0.0264	-0.9184
0.1996	0.4840	-0.0478	-0.5900	0.4570	-0.0530	-0.6867	0.4260	-0.0577	-0.7955	0.4000	-0.0567	-0.8292	0.3699	-0.0615	-0.9621	0.3507	-0.0554	-0.9188
0.3004	0.6030	-0.0621	-0.4661	0.5685	-0.0678	-0.5358	0.5242	-0.0761	-0.6454	0.4814	-0.0805	-0.7355	0.4494	-0.0770	-0.7526	0.4230	-0.0715	-0.7429
0.4007	0.7450	-0.0857	-0.4535	0.6974	-0.0955	-0.5345	0.6476	-0.0967	-0.5795	0.5987	-0.0919	-0.5947	0.5492	-0.0926	-0.6486	0.5116	-0.0898	-0.6737
0.5002	0.9180	-0.1178	-0.4829	0.8520	-0.1344	-0.5860	0.7900	-0.1312	-0.6144	0.7190	-0.1284	-0.6575	0.6650	-0.1162	-0.6439	0.6120	-0.1184	-0.7073
0.6000	1.1270	-0.1654	-0.5705	1.0380	-0.1899	-0.7002	0.9580	-0.1828	-0.7276	0.8740	-0.1665	-0.7267	0.8030	-0.1484	-0.7065	0.7410	-0.1465	-0.7517
0.6998	1.4330	-0.1795	-0.5618	1.2860	-0.2426	-0.8226	1.1710	-0.2418	-0.8935	1.0762	-0.2014	-0.8167	0.9673	-0.1914	-0.8595	0.9009	-0.1775	-0.8561
0.7999	1.9224	-0.0909	-0.2886	1.6962	-0.2079	-0.7225	1.5094	-0.2413	-0.9267	1.3537	-0.2160	-0.9250	1.2240	-0.1881	-0.8931	1.1050	-0.2062	-1.0687
0.8982	2.5272	0.0236	0.1024	2.3200	-0.0426	-0.1989	2.0670	-0.0942	-0.4875	1.8230	-0.0985	-0.5753	1.6240	-0.0907	-0.5946	1.4677	-0.1208	-0.8653
1.0000	3.1377	0.0000	0.0000	2.9540	0.0000	0.0000	2.6880	0.0000	0.0000	2.3690	0.0000	0.0000	2.0967	0.0000	0.0000	1.9378	0.0000	0.0000

Table-4.15: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Acetonitrile+Propylene glycol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.3416	0.0000	0.0000	0.3291	0.0000	0.0000	0.3154	0.0000	0.0000	0.3029	0.0000	0.0000	0.2908	0.0000	0.0000	0.2751	0.0000	0.0000
0.0995	0.4473	-0.0980	-2.2105	0.4201	-0.0958	-2.2932	0.3966	-0.0881	-2.2398	0.3745	-0.0817	-2.2019	0.3545	-0.0747	-2.1328	0.3377	-0.0619	-1.8775
0.2005	0.5686	-0.3079	-2.6995	0.5595	-0.2548	-2.3413	0.5272	-0.2226	-2.1976	0.4928	-0.1985	-2.1112	0.4736	-0.1634	-1.8495	0.4586	-0.1251	-1.5045
0.3008	0.9025	-0.5017	-2.1018	0.8237	-0.4575	-2.1004	0.7512	-0.4052	-2.0512	0.6877	-0.3568	-1.9872	0.6353	-0.3078	-1.8783	0.6183	-0.2321	-1.5154
0.3992	1.3375	-0.8922	-2.1309	1.1876	-0.8110	-2.1702	1.0865	-0.6824	-2.0321	0.9821	-0.5838	-1.9453	0.8890	-0.4968	-1.8509	0.8202	-0.4100	-1.6901
0.5006	2.1300	-1.4607	-2.0889	1.9300	-1.2302	-1.9724	1.7675	-0.9735	-1.7551	1.5650	-0.8119	-1.6716	1.3931	-0.6672	-1.5653	1.2570	-0.5427	-1.4355
0.6005	3.2400	-2.5020	-2.3853	2.9400	-2.0231	-2.1827	2.4950	-1.7250	-2.1907	2.1950	-1.3905	-2.0455	1.9272	-1.1181	-1.9072	1.7367	-0.8814	-1.7110
0.7003	5.8300	-3.3477	-2.1620	4.9500	-2.8412	-2.1613	4.2300	-2.2641	-2.0426	3.7373	-1.6693	-1.7594	3.1958	-1.3036	-1.6300	2.7886	-1.0187	-1.4836
0.7993	10.7166	-3.8976	-1.9337	8.7475	-3.4392	-2.0669	7.1667	-2.7926	-2.0512	5.9551	-2.1706	-1.9373	4.9741	-1.6529	-1.7885	4.2448	-1.2752	-1.6375
0.8993	19.5444	-3.8362	-1.9790	15.4895	-3.6586	-2.3415	12.4078	-2.9317	-2.3422	10.0706	-2.1922	-2.1748	8.2270	-1.5720	-1.9309	6.8219	-1.2114	-1.8049
1.0000	37.5288	0.0000	0.0000	30.1815	0.0000	0.0000	23.6979	0.0000	0.0000	18.5595	0.0000	0.0000	14.5290	0.0000	0.0000	11.7216	0.0000	0.0000

Table-4.16: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ n-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1007	9.6491	9.7029	9.7624	9.8081	9.8964	9.9665	-0.3260	-0.3368	-0.3327	-0.3457	-0.3117	-0.2606
0.2006	9.9919	10.0444	10.0931	10.1369	10.1870	10.2631	-0.5038	-0.4998	-0.4956	-0.5007	-0.4943	-0.4314
0.3007	10.3781	10.4078	10.4410	10.4918	10.5194	10.6111	-0.6392	-0.6420	-0.6422	-0.6307	-0.6361	-0.5518
0.3999	10.8060	10.8049	10.8229	10.8885	10.9060	10.9966	-0.7283	-0.7459	-0.7503	-0.7145	-0.7194	-0.6304
0.4994	11.2861	11.2857	11.2879	11.3280	11.3286	11.4211	-0.7668	-0.7676	-0.7770	-0.7568	-0.7681	-0.6715
0.6012	11.8681	11.8638	11.8484	11.8358	11.8437	11.9206	-0.7154	-0.7035	-0.7193	-0.7420	-0.7352	-0.6484
0.6994	12.4269	12.3788	12.3871	12.3959	12.3883	12.4273	-0.6684	-0.6844	-0.6658	-0.6576	-0.6558	-0.6011
0.8014	13.0851	13.0515	13.0438	13.0355	13.0149	13.0401	-0.5417	-0.5270	-0.5130	-0.5119	-0.5124	-0.4656
0.9008	13.7555	13.7351	13.7039	13.6879	13.6666	13.6590	-0.3894	-0.3453	-0.3439	-0.3410	-0.3316	-0.3118
1.0000	14.6619	14.5814	14.5379	14.5094	14.4681	14.4349	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.17: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ n-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0998	9.8899	9.9219	9.9837	10.0282	10.0823	10.1610	-0.1950	-0.2317	-0.2239	-0.2359	-0.2368	-0.1767
0.1991	10.3678	10.4317	10.4806	10.5358	10.5807	10.6531	-0.3487	-0.3413	-0.3339	-0.3234	-0.3235	-0.2635
0.3008	10.9302	10.9945	11.0318	11.0620	11.1047	11.1788	-0.4331	-0.4128	-0.4044	-0.4066	-0.3987	-0.3308
0.4006	11.4999	11.5499	11.6028	11.6431	11.6646	11.7063	-0.4982	-0.4799	-0.4433	-0.4237	-0.4268	-0.3850
0.5003	12.1363	12.1764	12.2309	12.2345	12.2562	12.2755	-0.4959	-0.4752	-0.4246	-0.4296	-0.4226	-0.3971
0.6005	12.7679	12.8096	12.8352	12.8526	12.8802	12.8739	-0.5015	-0.4669	-0.4327	-0.4120	-0.3890	-0.3828
0.6996	13.3872	13.4536	13.4616	13.4659	13.4812	13.4883	-0.5126	-0.4410	-0.4120	-0.3927	-0.3719	-0.3462
0.7989	14.1061	14.1452	14.1406	14.1376	14.1180	14.1264	-0.4252	-0.3688	-0.3399	-0.3159	-0.3202	-0.2870
0.9006	14.9216	14.9291	14.9049	14.8633	14.8300	14.8156	-0.2566	-0.2192	-0.1972	-0.1997	-0.2074	-0.1907
1.0000	15.8103	15.7683	15.7096	15.6587	15.6231	15.5858	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.18: Change of Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ n-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^{*}}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1023	10.1079	10.1418	10.1945	10.2520	10.3297	10.3837	-0.1132	-0.1431	-0.1408	-0.1408	-0.1125	-0.0784
0.1949	10.7026	10.7369	10.7628	10.8179	10.8609	10.9238	-0.2163	-0.2301	-0.2402	-0.2328	-0.2249	-0.1775
0.3056	11.4313	11.4540	11.4582	11.4793	11.5248	11.5299	-0.3218	-0.3286	-0.3431	-0.3578	-0.3304	-0.3355
0.3923	12.0594	12.0805	12.0676	12.0807	12.0815	12.1019	-0.3471	-0.3408	-0.3588	-0.3724	-0.3764	-0.3620
0.4919	12.7918	12.8199	12.8137	12.8247	12.7935	12.7986	-0.3653	-0.3353	-0.3309	-0.3360	-0.3567	-0.3529
0.6077	13.5775	13.5617	13.5757	13.5917	13.5957	13.5866	-0.4522	-0.4466	-0.4039	-0.3917	-0.3595	-0.3642
0.7077	14.2604	14.2221	14.2304	14.2443	14.2547	14.2349	-0.5229	-0.5229	-0.4704	-0.4495	-0.3955	-0.4062
0.7818	14.8521	14.8496	14.8507	14.8255	14.8288	14.8052	-0.4895	-0.4413	-0.3843	-0.3947	-0.3365	-0.3474
0.9064	15.9985	16.0344	16.0322	16.0081	15.9508	15.9193	-0.2820	-0.1745	-0.1013	-0.0973	-0.0806	-0.0935
1.0000	16.9859	16.8985	16.8084	16.7703	16.6819	16.6588	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.19: Change of Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ iso-Propanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^{*}}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1007	9.6897	9.7304	9.7650	9.8211	9.8768	9.9689	-0.3008	-0.3218	-0.3380	-0.3288	-0.3263	-0.2386
0.1994	9.9793	9.9905	10.0414	10.0711	10.1496	10.2505	-0.5408	-0.5724	-0.5571	-0.5529	-0.5162	-0.3997
0.3007	10.3533	10.3697	10.4020	10.4396	10.4749	10.5387	-0.7103	-0.7173	-0.7049	-0.6712	-0.6658	-0.5658
0.3996	10.7780	10.7920	10.8166	10.8428	10.8607	10.9153	-0.8162	-0.8067	-0.7867	-0.7431	-0.7436	-0.6328
0.4993	11.2471	11.2323	11.2451	11.2596	11.2649	11.2959	-0.8821	-0.8822	-0.8586	-0.8053	-0.8067	-0.6994
0.5990	11.7759	11.7435	11.7435	11.7373	11.7343	11.7533	-0.8882	-0.8869	-0.8605	-0.8066	-0.8047	-0.6891
0.7008	12.3621	12.3481	12.3264	12.3055	12.2680	12.2737	-0.8482	-0.8090	-0.7886	-0.7274	-0.7482	-0.6253
0.8012	13.0003	12.9881	12.9508	12.9004	12.8498	12.8461	-0.7487	-0.6884	-0.6680	-0.6150	-0.6371	-0.5032
0.899	13.7990	13.7202	13.6643	13.6105	13.5777	13.5100	-0.4747	-0.4624	-0.4454	-0.3747	-0.3676	-0.2779
1.0000	14.8156	14.7051	14.6166	14.4704	14.4188	14.2409	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.20: Change of Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ iso-Butanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^{*}}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1002	9.8722	9.9274	9.9764	10.0267	10.0757	10.1710	-0.2837	-0.2903	-0.2882	-0.2889	-0.2859	-0.2069
0.2007	10.3928	10.4314	10.4775	10.5258	10.5639	10.6406	-0.4710	-0.4748	-0.4560	-0.4414	-0.4301	-0.3612
0.3003	10.9659	10.9815	11.0172	11.0622	11.0901	11.1484	-0.5994	-0.6071	-0.5791	-0.5507	-0.5306	-0.4717
0.3999	11.6034	11.6064	11.6282	11.6508	11.6815	11.7151	-0.6635	-0.6645	-0.6311	-0.6077	-0.5660	-0.5233
0.4997	12.2589	12.2237	12.2385	12.2452	12.2503	12.2887	-0.7109	-0.7310	-0.6850	-0.6603	-0.6252	-0.5692
0.6004	12.9683	12.9314	12.9218	12.9100	12.9065	12.9256	-0.7108	-0.7132	-0.6720	-0.6483	-0.6027	-0.5575
0.7002	13.7355	13.6942	13.6585	13.6314	13.6030	13.5975	-0.6464	-0.6342	-0.5995	-0.5739	-0.5342	-0.5050
0.8004	14.5530	14.5064	14.4535	14.3791	14.3583	14.3397	-0.5347	-0.5085	-0.4715	-0.4757	-0.4094	-0.3849
0.8995	15.4225	15.3560	15.3114	15.2544	15.1795	15.1137	-0.3632	-0.3378	-0.2732	-0.2429	-0.2118	-0.2260
1.0000	16.4935	16.3823	16.2534	16.1488	16.0238	15.9636	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.21: Change of Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ iso-Pentanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^{*}}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0996	10.1047	10.1496	10.2013	10.2287	10.2630	10.3300	-0.0706	-0.1124	-0.1249	-0.1551	-0.1754	-0.1374
0.1996	10.7930	10.8418	10.8594	10.8949	10.8808	10.9280	-0.1104	-0.1538	-0.1983	-0.2095	-0.2676	-0.2537
0.3004	11.5452	11.6030	11.6071	11.5945	11.6158	11.6539	-0.0920	-0.1321	-0.1879	-0.2363	-0.2484	-0.2478
0.4007	12.2592	12.3108	12.3428	12.3609	12.3475	12.3686	-0.1082	-0.1603	-0.1860	-0.1926	-0.2290	-0.2495
0.5002	12.9532	12.9935	13.0321	13.0174	13.0377	13.0360	-0.1385	-0.2075	-0.2245	-0.2531	-0.2453	-0.2929
0.6000	13.6256	13.6576	13.6930	13.6960	13.7077	13.7227	-0.1928	-0.2757	-0.2936	-0.2937	-0.2840	-0.3191
0.6998	14.3738	14.3536	14.3651	14.3965	14.3615	14.4109	-0.1711	-0.3119	-0.3515	-0.3123	-0.3388	-0.3438
0.7999	15.2485	15.1986	15.1635	15.1430	15.1328	15.1101	-0.0251	-0.2013	-0.2854	-0.2871	-0.2784	-0.3597
0.8982	16.0606	16.1242	16.1058	16.0544	16.0192	16.0126	0.0713	0.0031	-0.0621	-0.0841	-0.0899	-0.1593
1.0000	16.7304	16.8680	16.9126	16.8720	16.8320	16.8991	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.22: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Acetonitrile+ Propylene glycol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	9.4502	9.5312	9.5977	9.6661	9.7311	9.7559	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0995	10.2794	10.3037	10.3441	10.3828	10.4224	10.4776	-0.4471	-0.4793	-0.4742	-0.4702	-0.4603	-0.4044
0.2005	11.0235	11.1778	11.2274	11.2518	11.3402	11.4538	-0.9985	-0.8759	-0.8299	-0.8059	-0.7115	-0.5713
0.3008	12.3011	12.2845	12.2661	12.2544	12.2572	12.3943	-1.0075	-1.0310	-1.0216	-0.9997	-0.9553	-0.7660
0.3992	13.4013	13.3349	13.3375	13.3066	13.2759	13.2793	-1.1694	-1.2186	-1.1573	-1.1212	-1.0754	-0.9947
0.5006	14.6724	14.6787	14.7079	14.6437	14.5880	14.5550	-1.1989	-1.1506	-1.0308	-0.9937	-0.9369	-0.8666
0.6005	15.8192	15.8462	15.6973	15.6362	15.5535	15.5341	-1.3336	-1.2399	-1.2669	-1.1929	-1.1277	-1.0182
0.7003	17.3766	17.2657	17.1554	17.1255	16.9990	16.9148	-1.0563	-1.0761	-1.0331	-0.8940	-0.8373	-0.7670
0.7993	18.9829	18.7947	18.6035	18.4359	18.2702	18.1467	-0.7199	-0.7925	-0.7995	-0.7645	-0.7118	-0.6556
0.8993	20.5683	20.3369	20.1118	19.9061	19.7014	19.5184	-0.4171	-0.5085	-0.5180	-0.4871	-0.4380	-0.4157
1.0000	22.2771	22.1123	21.8651	21.5944	21.3049	21.0738	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.23: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy(ΔS^{*E}) of Acetonitrile + n-Propanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.1007	5.8844	-0.9769	-50.8856	-2.1179
0.2006	6.8839	-1.1280	-48.7041	-2.0615
0.3007	7.7447	-1.4202	-47.0773	-2.5640
0.3999	8.5591	-1.7484	-45.7302	-3.3271
0.4994	9.8590	-1.5945	-43.0009	-2.7143
0.6012	11.5641	-1.0620	-39.2521	-1.1310
0.6994	12.3590	-1.3982	-38.4231	-2.3909
0.8014	13.6722	-1.2599	-36.2702	-2.4076
0.9008	14.9589	-1.1181	-34.2406	-2.4924
1.0000	17.2196	0.0000	-29.6380	0.0000

Table 4.24: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy(ΔS^{*E}) of Acetonitrile + n-Butanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.0998	6.6875	-0.2969	-48.9878	-0.2580
0.1991	7.0861	-1.1749	-49.3052	-2.7444
0.3008	8.2085	-1.3599	-47.4367	-3.0974
0.4006	9.0834	-1.7681	-46.4254	-4.2660
0.5003	10.5332	-1.6000	-43.7133	-3.7316
0.6005	11.4711	-1.9504	-42.6845	-4.8915
0.6996	12.3833	-2.3122	-41.7429	-6.1145
0.7989	14.0816	-1.8905	-38.4412	-4.9819
0.9006	16.4075	-0.8720	-33.3633	-2.1253
1.0000	18.5574	0.0000	-29.0667	0.0000

Table 4.25: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy (ΔS^{*E}) of Acetonitrile + n-Pentanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.1023	6.7006	-0.5607	-49.6661	-1.4138
0.1949	8.0963	-0.5769	-46.9947	-1.1478
0.3056	10.1961	-0.1651	-42.4204	0.5508
0.3923	11.6763	-0.0069	-39.5837	1.1353
0.4919	12.8512	-0.3508	-38.1465	-0.0148
0.6077	13.2916	-1.6761	-39.2218	-4.0982
0.7077	14.2773	-2.2152	-38.1722	-5.6462
0.7818	15.4002	-2.2222	-36.4703	-5.8693
0.9064	17.1395	-2.3829	-34.5904	-7.2260
1.0000	20.9496	0.0000	-24.9329	0.0000

Table 4.26: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy (ΔS^{*E}) of Acetonitrile + iso-Propanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.1007	6.4772	-0.8066	-49.0128	-1.6014
0.1994	6.8156	-2.0193	-48.7984	-4.8159
0.3007	8.1756	-2.2512	-45.5449	-5.0816
0.3996	9.2166	-2.7643	-43.4960	-6.4686
0.4993	10.6407	-2.9069	-40.2741	-6.7102
0.5990	12.0269	-3.0875	-37.3908	-7.2906
0.7008	13.5638	-3.1503	-34.2654	-7.7017
0.8012	15.1163	-3.1756	-31.2272	-8.1515
0.8990	17.0781	-2.7507	-27.2436	-7.5654
1.0000	21.4160	0.0000	-16.1693	0.0000

Table 4.27: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy (ΔS^{*E}) of Acetonitrile + iso-Butanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.1002	6.4923	-0.9454	-49.6069	-2.1612
0.2007	7.5261	-1.6530	-47.8790	-3.9078
0.3003	8.7803	-2.1248	-45.5765	-5.0485
0.3999	10.2303	-2.4007	-42.8510	-5.7664
0.4997	11.8581	-2.5023	-39.5531	-5.9187
0.6004	13.4830	-2.6224	-36.4998	-6.3468
0.7002	15.4278	-2.4069	-32.5767	-5.8739
0.8004	17.2651	-2.3059	-29.1676	-5.9289
0.8995	19.0451	-2.2432	-26.1460	-6.3332
1.0000	23.0298	0.0000	-16.3383	0.0000

Table 4.28: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy (ΔS^{*E}) of Acetonitrile + iso-Pentanol system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.0996	7.5640	0.8804	-46.8156	3.2502
0.1996	9.3862	1.7163	-43.0535	6.1651
0.3004	10.5898	1.9258	-41.5512	6.8133
0.4007	11.1066	1.4534	-42.2322	5.2825
0.5002	12.0458	1.4112	-41.3981	5.2735
0.6000	12.5357	0.9169	-41.9846	3.8415
0.6998	13.9624	1.3594	-39.6230	5.3575
0.7999	16.7998	3.2095	-33.0298	11.1025
0.8982	17.1057	2.5459	-34.9318	8.3676
1.0000	15.5638	0.0000	-42.4369	0.0000

Table 4.29: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy (ΔS^{*E}) of Acetonitrile + Propylene glycol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	5.7013	0.0000	-50.9097	0.0000
0.0995	7.9198	-0.9082	-46.1706	-1.4558
0.2005	6.5129	-5.4890	-53.5242	-15.0978
0.3008	11.6951	-3.4585	-40.2131	-8.0315
0.3992	14.7909	-3.4549	-33.5623	-7.5072
0.5006	16.2386	-5.1935	-33.1458	-13.4039
0.6005	19.8798	-4.6916	-24.7729	-11.2509
0.7003	22.7171	-4.9904	-20.3341	-13.0257
0.7993	29.0831	-1.7353	-4.3465	-3.2019
0.8993	33.1168	-0.8441	3.8582	-1.2233
1.0000	37.1253	0.0000	11.3512	0.0000

Table 4.30: Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol, iso-Pentanol and Propylene glycol +Acetonitrile systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Acetonitrile+ n-Propanol	298.15	0.3694	-0.4734	0.1537	-0.2581	0.0026
	303.15	0.4203	0.5336	0.2287	-0.2562	0.0028
	308.15	0.4792	-0.5255	0.2875	-0.4459	0.0023
	313.15	0.5245	-0.5039	0.4048	-0.6387	0.0035
	318.15	0.5879	-0.5183	0.4688	-0.7015	0.0049
	323.15	0.6368	-0.5807	0.6051	-0.7335	0.0038
Acetonitrile+n-Butanol	298.15	0.7613	-0.4473	-0.2485	-0.1387	0.0042
	303.15	0.8092	-0.4295	-0.2703	-0.1501	0.0039
	308.15	0.9097	-0.5308	-0.2319	0.0248	0.0043
	313.15	0.9708	-0.5382	-0.1481	-0.1154	0.0045
	318.15	1.0552	-0.5098	-0.0420	-0.2334	0.0037
	323.15	1.1402	-0.4115	0.1226	-0.4267	0.0064
Acetonitrile+n-Pentanol	298.15	0.8405	-0.3236	0.2824	-0.3069	0.0042
	303.15	0.9011	-0.3845	0.4233	-0.1585	0.0072
	308.15	0.9810	-0.3901	0.5436	-0.2698	0.0061
	313.15	1.0597	-0.3620	0.6637	-0.4209	0.0066
	318.15	1.1965	-0.3450	0.8467	-0.6040	0.0106
	323.15	1.4377	-0.5827	0.9972	-0.5994	0.0139
Acetonitrile+iso-Propanol	298.15	0.5843	-0.2583	-0.3578	0.2261	0.0036
	303.15	0.6302	-0.2761	-0.3182	0.2650	0.0039
	308.15	0.6927	-0.2677	-0.3027	0.2244	0.0047
	313.15	0.7731	-0.2727	-0.3057	0.2813	0.0039
	318.15	0.8631	-0.3202	-0.2132	0.3796	0.0018
	323.15	0.9857	-0.4025	-0.2378	0.3936	0.0043
Acetonitrile+ iso-Butanol	298.15	1.1109	-0.2742	-0.2163	-0.1084	0.0051
	303.15	1.1903	-0.2464	-0.2136	-0.1739	0.0038
	308.15	1.2167	-0.3000	-0.1309	-0.0967	0.0033
	313.15	1.2567	-0.2378	-0.0416	-0.2378	0.0013
	318.15	1.3152	-0.3665	0.0281	-0.0512	0.0023
	323.15	1.4417	-0.4121	0.1959	-0.1371	0.0032
Acetonitrile+ iso-Pentanol	298.15	0.4370	-0.4770	0.1592	-0.5107	0.0208
	303.15	0.4567	-0.4274	-0.1429	0.1858	0.0180
	308.15	1.2312	-0.5386	0.2212	0.7520	0.0176
	313.15	1.8708	-0.5434	0.4302	-0.2321	0.0239
	318.15	2.2507	-0.2799	0.0737	-0.9733	0.0228
	323.15	2.2645	-0.4703	-0.1738	-1.1432	0.0250
Acetonitrile+ Propylene glycol	298.15	2.8162	-1.6787	-0.3451	0.3211	0.0334
	303.15	2.3066	-1.6449	-1.2168	0.5577	0.0687
	308.15	2.2298	-1.8652	-0.7992	0.3308	0.0672
	313.15	2.4931	-1.6103	-0.6033	-0.9049	0.0545
	318.15	2.6503	-2.0232	-1.1181	0.1113	0.0491
	323.15	2.5661	-1.0114	-0.0724	-2.5669	0.0453

Table 4.31: Coefficient, a_i, of Redlich- Kister Eq expressing η^E and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol, iso-Pentanol and Propylene glycol +Acetonitrile systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Acetonitrile+ n-Propanol	298.15	-0.8711	-0.6924	-1.0285	-0.9724	0.0115
	303.15	-0.8032	-0.6411	-0.7508	-0.5404	0.0072
	308.15	-0.7384	-0.5406	-0.6028	-0.4701	0.0070
	313.15	-0.6695	-0.5160	-0.5474	-0.2936	0.0061
	318.15	-0.6191	-0.4417	-0.4355	-0.2778	0.0043
	323.15	-0.5084	-0.3664	-0.3781	-0.2592	0.0037
Acetonitrile+n-Butanol	298.15	-0.8064	-0.9009	-1.0743	-0.6816	0.0038
	303.15	-0.7022	-0.6868	-0.7608	-0.4157	0.0028
	308.15	-0.6012	-0.5569	-0.6220	-0.2756	0.0023
	313.15	-0.5353	-0.4355	-0.5277	-0.2799	0.0025
	318.15	-0.4766	-0.3307	-0.5059	-0.3692	0.0029
	323.15	-0.4161	-0.3162	-0.3443	-0.2478	0.0030
Acetonitrile+n-Pentanol	298.15	-0.8700	-1.4170	-2.0787	-1.4042	0.0059
	303.15	-0.8175	-1.4405	-1.2116	0.1543	0.0213
	308.15	-0.7404	-1.1808	-0.6349	0.6236	0.0253
	313.15	-0.6730	-0.9903	-0.5398	0.4745	0.0240
	318.15	-0.5995	-0.7410	-0.2875	0.3574	0.0171
	323.15	-0.5449	-0.6654	-0.2650	0.2165	0.0151
Acetonitrile+iso-Propanol	298.15	-1.0228	-1.0646	-1.3999	-1.1164	0.0049
	303.15	-0.9164	-0.8398	-1.0921	-0.8687	0.0074
	308.15	-0.8118	-0.7148	-0.9108	-0.6577	0.0059
	313.15	-0.6995	-0.5845	-0.6415	-0.3170	0.0027
	318.15	-0.6437	-0.5537	-0.5548	-0.2190	0.0025
	323.15	-0.5129	-0.4085	-0.2551	-0.0648	0.0019
Acetonitrile+ iso-Butanol	298.15	-1.1639	-1.3316	-1.7880	-1.4710	0.0130
	303.15	-1.0606	-1.1357	-1.3072	-0.9727	0.0107
	308.15	-0.9215	-0.9883	-0.8669	-0.3421	0.0023
	313.15	-0.8101	-0.8713	-0.6812	-0.0981	0.0053
	318.15	-0.6982	-0.6895	-0.4524	0.0678	0.0024
	323.15	-0.5917	-0.5511	-0.3947	-0.1370	0.0013
Acetonitrile+ iso-Pentanol	298.15	-0.5622	-0.9890	0.5258	2.0816	0.0203
	303.15	-0.6213	-1.3062	-0.1687	1.7268	0.0283
	308.15	-0.5887	-1.1491	-0.6114	0.9180	0.0253
	313.15	-0.5399	-0.8716	-0.5997	0.4932	0.0180
	318.15	-0.5014	-0.7479	-0.5668	0.4489	0.0154
	323.15	-0.4768	-0.6569	-0.7281	-0.0989	0.0122
Acetonitrile+ Propylene glycol	298.15	-5.8345	-14.0736	-22.4542	-16.5695	0.1614
	303.15	-4.7102	-10.4715	-21.8123	-20.5160	0.1835
	308.15	-3.9157	-8.4767	-17.4331	-16.1829	0.1527
	313.15	-3.2346	-6.2153	-12.7547	-12.3783	0.1199
	318.15	-2.7280	-5.0040	-8.8582	-8.0274	0.0795
	323.15	-2.1953	-3.9294	-6.6104	-6.0385	0.0645

Table 4.32: Coefficient, a_i, of Redlich- Kister Eq expressing ΔG^{*E} and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol, iso-Pentanol and Propylene glycol +Acetonitrile systems.

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
Acetonitrile+ n-Propanol	298.15	-2.9689	0.0259	-1.1568	-0.7546	0.0216
	303.15	-3.0034	-0.0511	-0.9064	-0.1855	0.0237
	308.15	-3.0315	0.0117	-0.7076	-0.2630	0.0233
	313.15	-2.9740	-0.2424	-0.8845	0.4195	0.0206
	318.15	-3.0087	-0.1170	-0.6045	-0.0413	0.0141
	323.15	-2.6460	-0.1993	-0.6339	-0.1942	0.0117
Acetonitrile+n-Butanol	298.15	-2.0473	-0.3160	-0.9373	-0.2228	0.0155
	303.15	-1.9139	-0.1480	-0.8745	0.2326	0.0107
	308.15	-1.7632	-0.0699	-0.9645	0.2952	0.0103
	313.15	-1.7114	0.0255	-0.9866	0.2515	0.0103
	318.15	-1.6596	0.1854	-1.1181	-0.1409	0.0122
	323.15	-1.5597	-0.0568	-0.5669	-0.1060	0.0102
Acetonitrile+n-Pentanol	298.15	-1.6276	-1.1749	-1.4156	-0.2795	0.0285
	303.15	-1.6220	-1.4187	-0.9982	1.5240	0.0477
	308.15	-1.6073	-1.0185	-0.4873	1.5958	0.0542
	313.15	-1.6155	-0.8232	-0.4461	1.1784	0.0566
	318.15	-1.5885	-0.4767	0.0669	0.6466	0.0431
	323.15	-1.5951	-0.5364	0.2670	0.1580	0.0471
Acetonitrile+iso-Propanol	298.15	-3.5122	-0.7397	-1.3136	-0.7920	0.0083
	303.15	-3.4802	-0.5138	-1.2620	-0.5404	0.0137
	308.15	-3.3818	-0.5325	-1.3277	-0.2385	0.0116
	313.15	-3.1882	-0.4581	-1.1493	0.2936	0.0110
	318.15	-3.2028	-0.6643	-1.0490	0.4461	0.0110
	323.15	-2.7790	-0.5250	-0.1500	0.2766	0.0115
Acetonitrile+ iso-Butanol	298.15	-2.8173	-0.2746	-1.0328	-0.3279	0.0107
	303.15	-2.8551	-0.2292	-0.7604	-0.0340	0.0152
	308.15	-2.7093	-0.3037	-0.5736	0.6493	0.0073
	313.15	-2.6073	-0.4217	-0.5917	1.0202	0.0122
	318.15	-2.4507	-0.3107	-0.4756	1.2661	0.0092
	323.15	-2.2643	-0.2607	-0.2166	0.2652	0.0061
Acetonitrile+ iso-Pentanol	298.15	-0.6580	-0.8860	0.7542	3.1751	0.0226
	303.15	-0.9378	-1.5725	-0.0718	3.6933	0.0309
	308.15	-1.0193	-1.3988	-0.8114	2.7982	0.0396
	313.15	-1.0456	-0.9975	-0.9957	2.1683	0.0324
	318.15	-1.0719	-0.8326	-1.2919	2.2082	0.0338
	323.15	-1.1802	-0.7795	-1.3698	0.9013	0.0329
Acetonitrile+ Propylene glycol	298.15	-5.0350	-0.4699	-0.1670	2.5197	0.0924
	303.15	-4.8948	-0.0888	-0.9268	0.3576	0.0493
	308.15	-4.6696	-0.2964	-1.3484	0.5054	0.0790
	313.15	-4.4262	0.2981	-1.3304	-0.3636	0.0764
	318.15	-4.2071	0.2582	-0.9535	-0.1946	0.0769
	323.15	-3.8033	-0.2007	-0.4978	-0.0225	0.0752

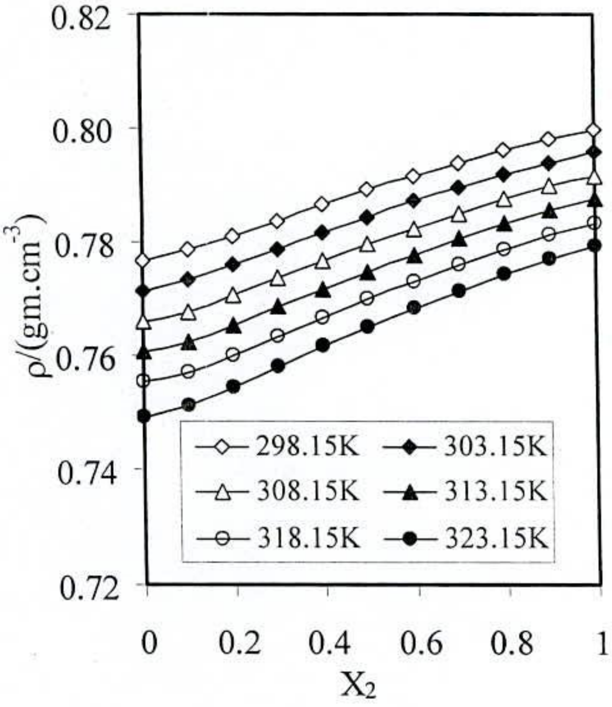

Figure 4.1: Plots of density (ρ) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

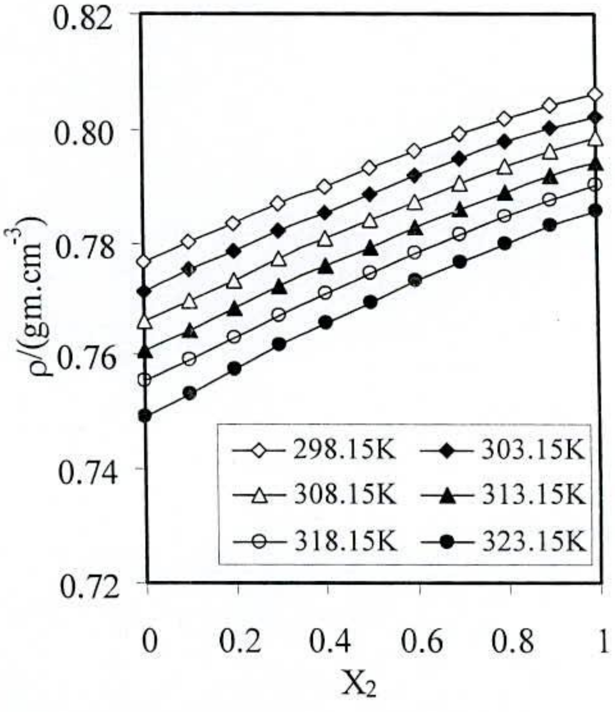

Figure 4.2: Plots of density (ρ) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

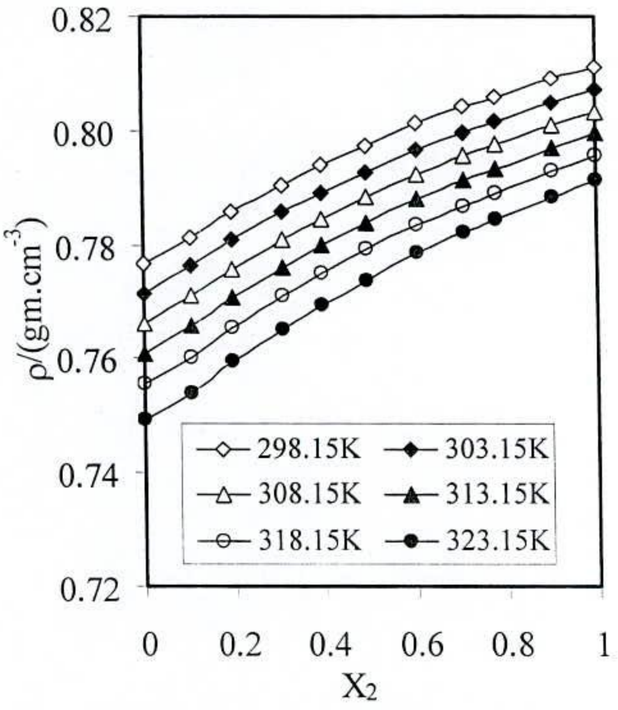

Figure 4.3: Plots of density (ρ) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

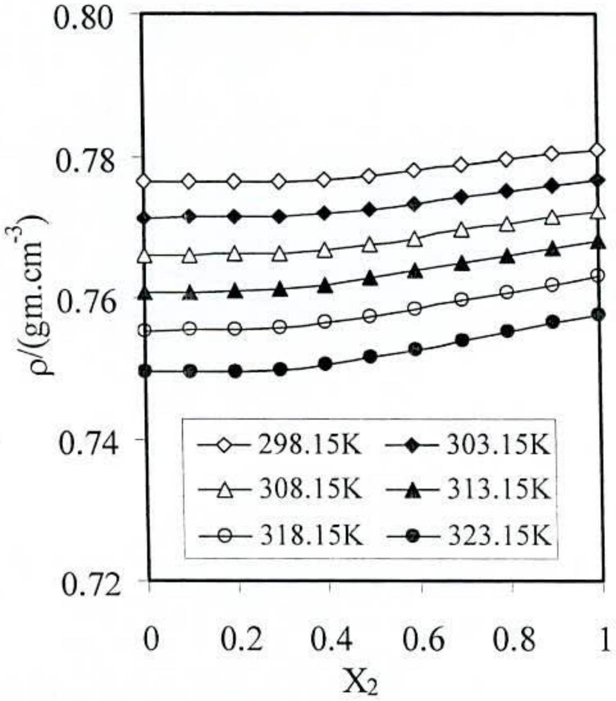

Figure 4.4: Plots of density (ρ) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

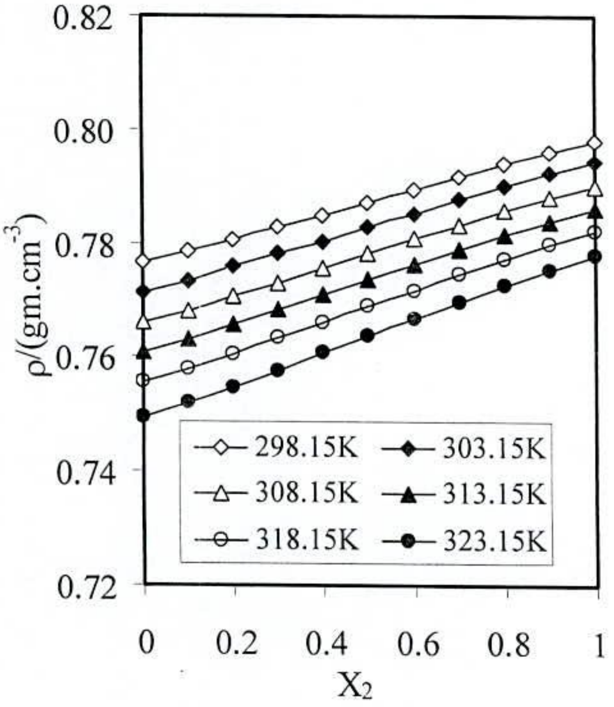

Figure 4.5: Plots of density (ρ) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

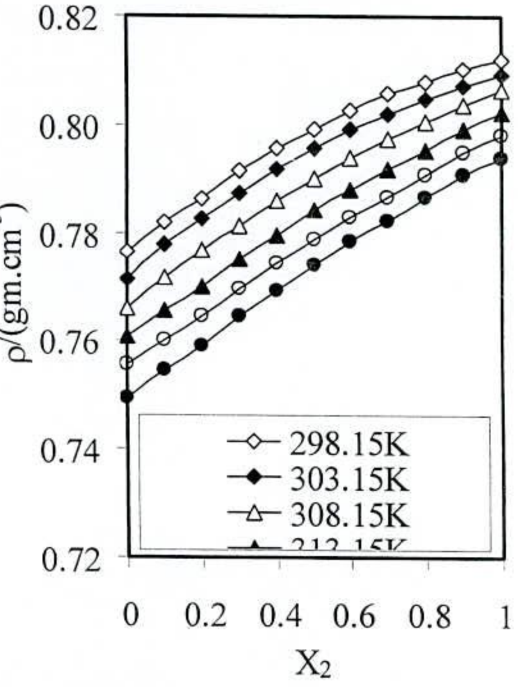

Figure 4.6: Plots of density (ρ) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

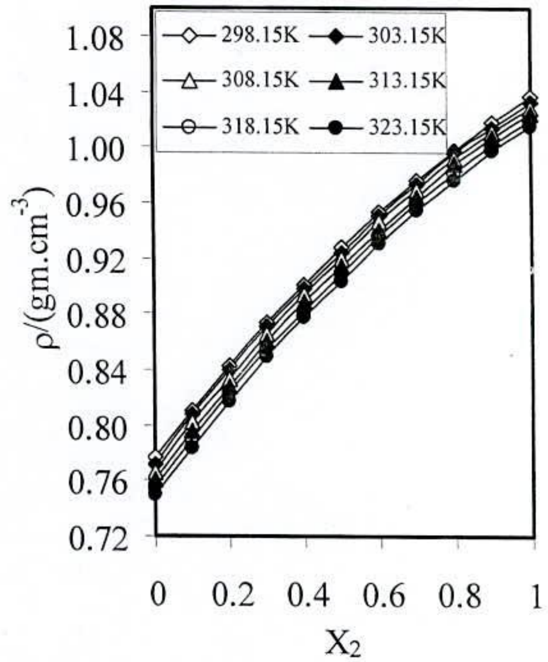

Figure 4.7: Plots of density (ρ) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

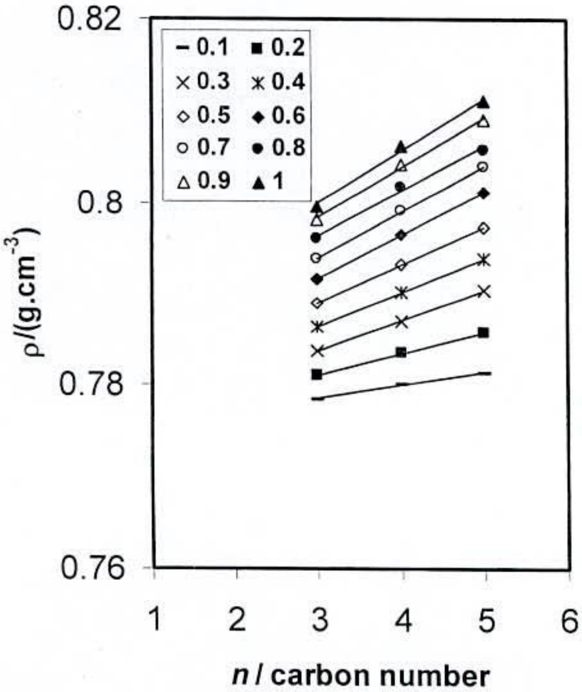

Figure 4.8: Dependence of the density (ρ) with carbon number (n) of alcohols with different mole fraction at 298.15K.

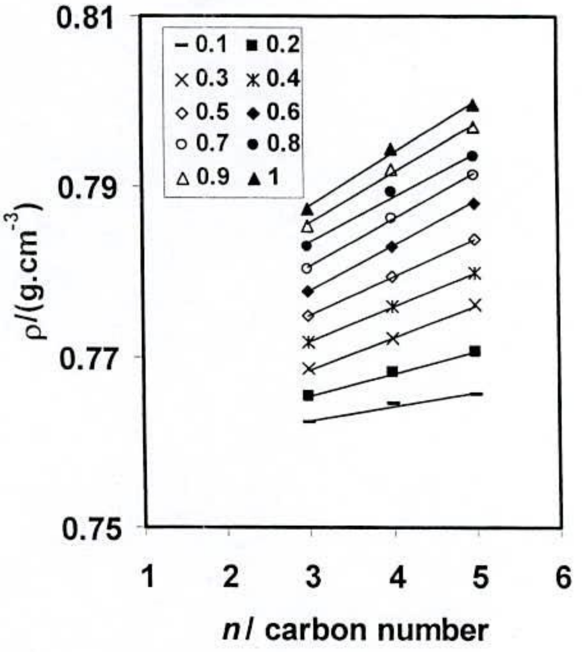

Figure 4.9: Dependence of the density (ρ) with carbon number (n) of alcohols with different mole fraction at 313.15K.

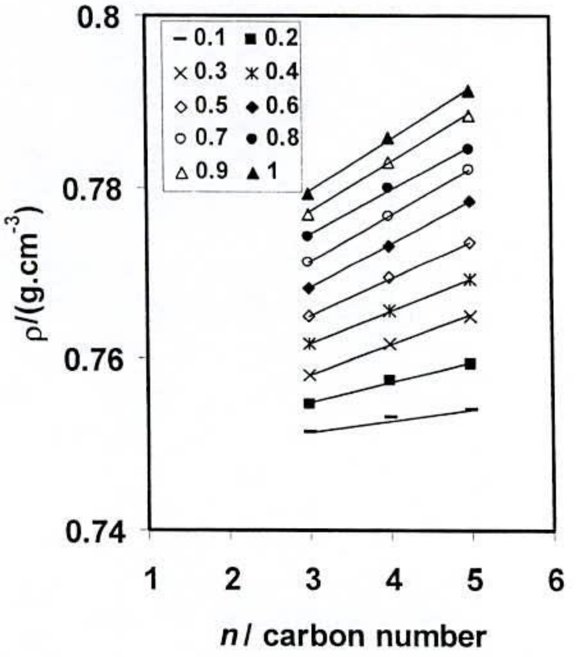

Figure 4.10: Dependence of the density (ρ) with carbon number (n) of alcohols with different mole fraction at 323.15K.

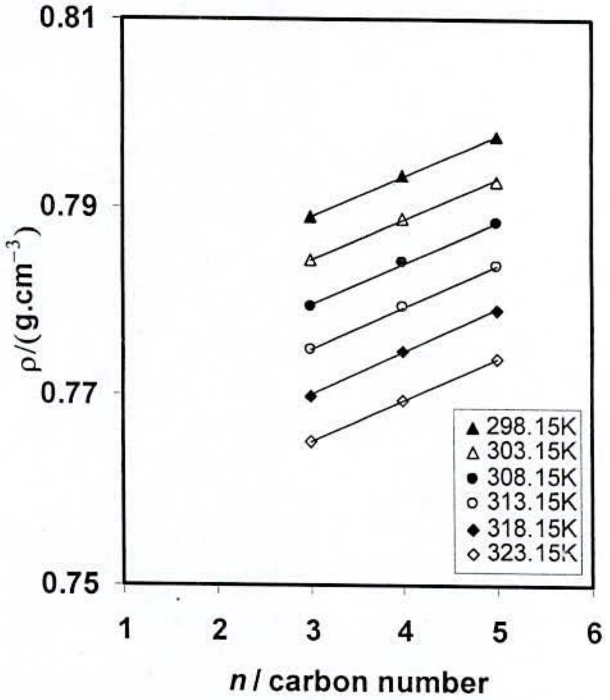

Figure 4.11: Dependence of the density (ρ) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

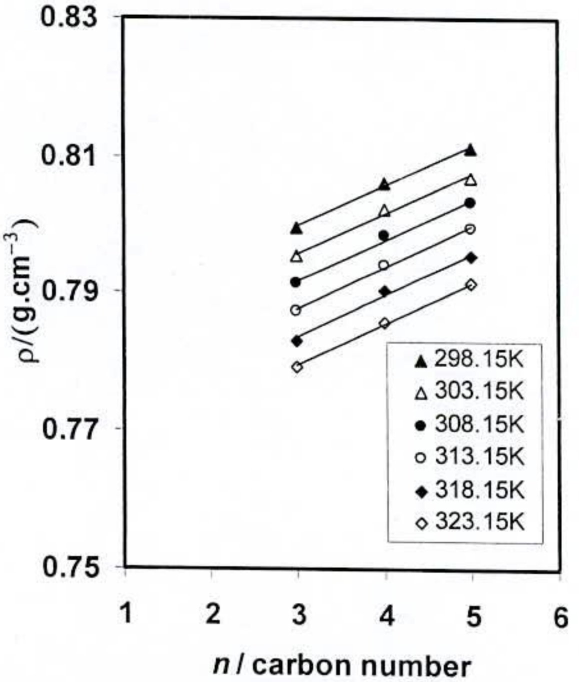

Figure 4.12: Dependence of the density (ρ) with carbon number (n) of alcohols with different temperature at 1.0 mole fraction.

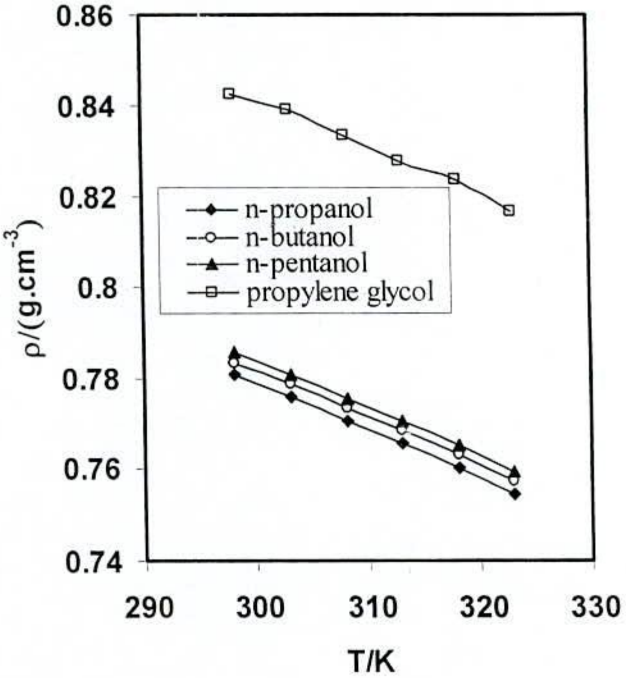

Figure 4.13: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

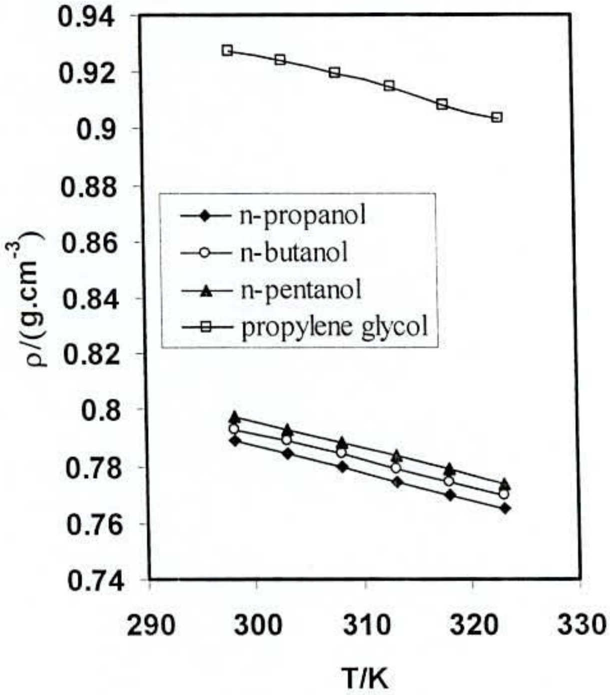

Figure 4.14: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

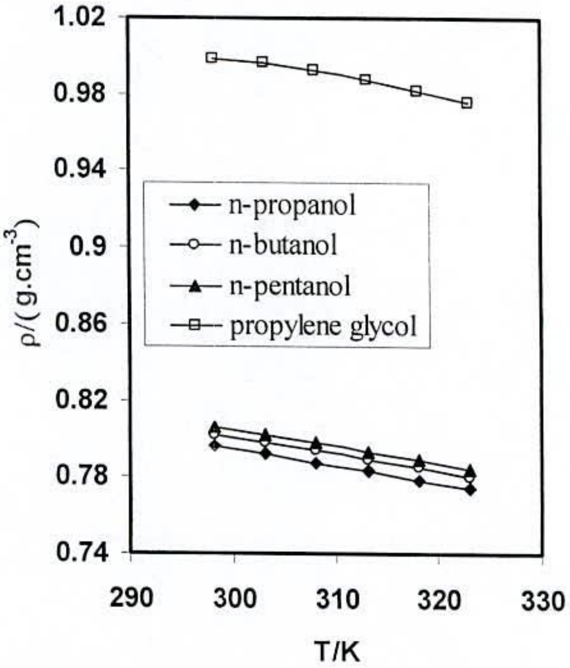

Figure 4.15: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

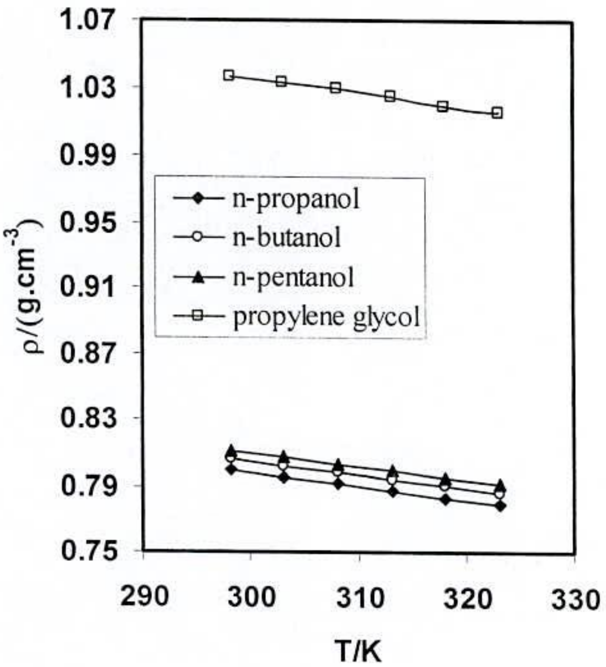

Figure 4.16: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

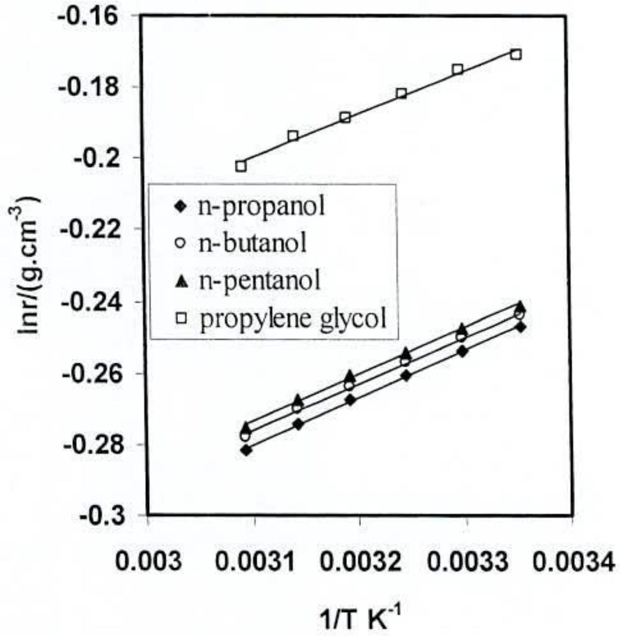

Figure 4.17: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile 0at 0.2 mole fraction.

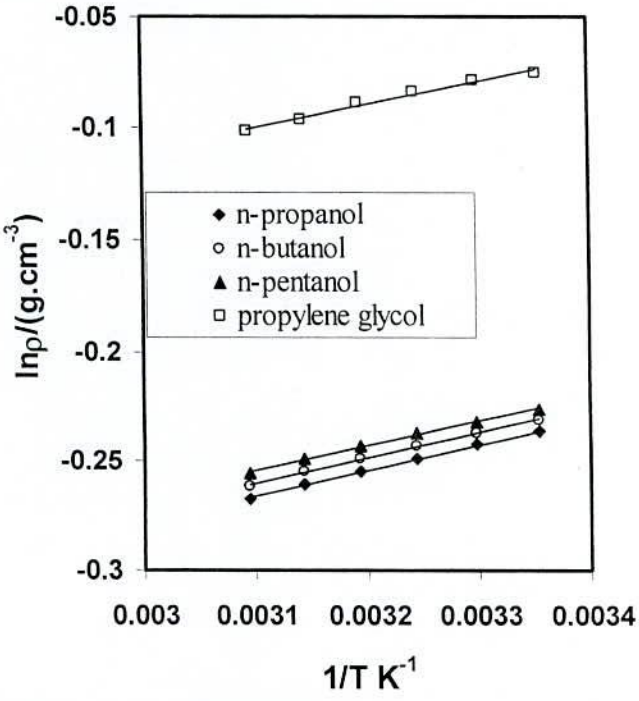

Figure 4.18: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

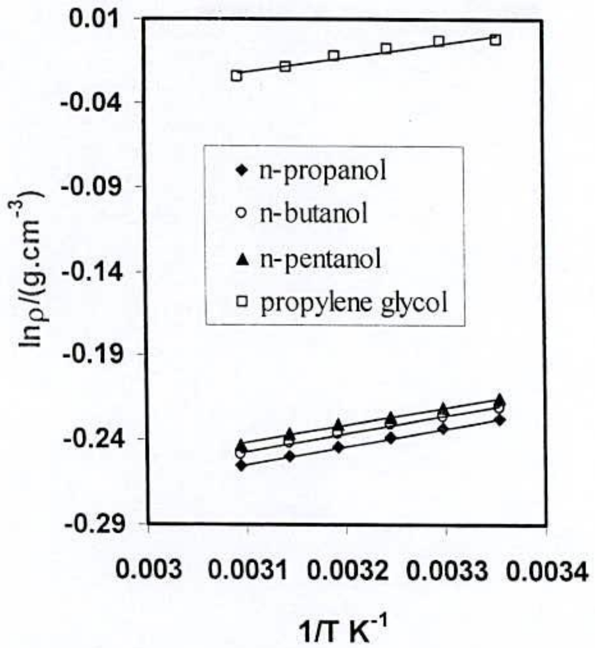

Figure 4.19: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

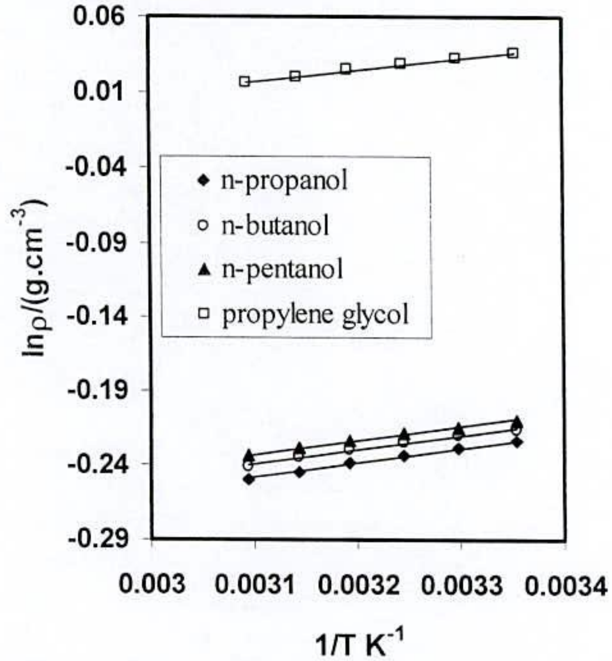

Figure 4.20: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

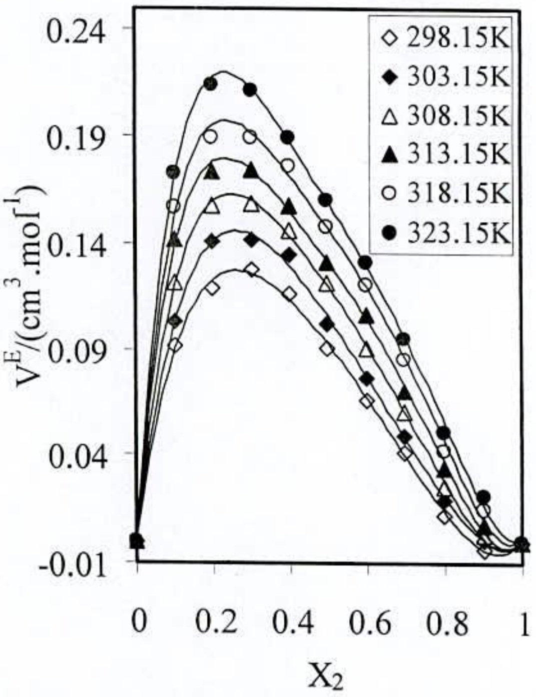

Figure 4.21: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

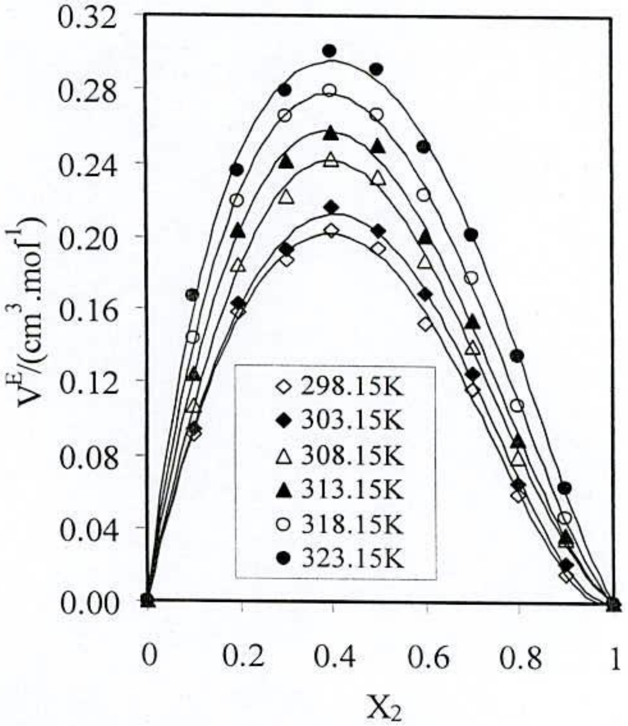

Figure 4.22: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

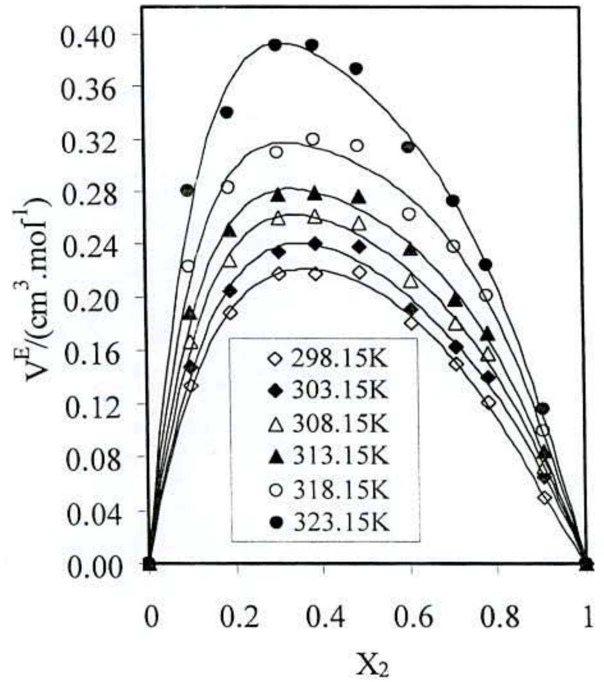

Figure 4.23: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

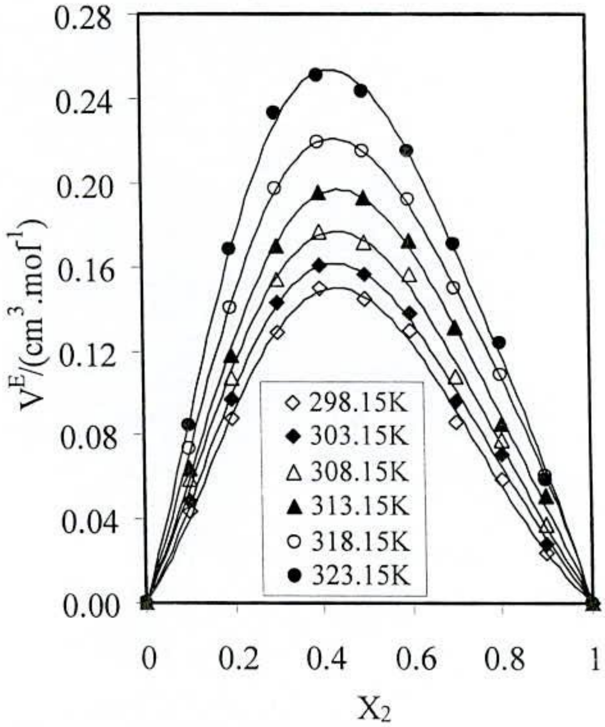

Figure 4.24: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

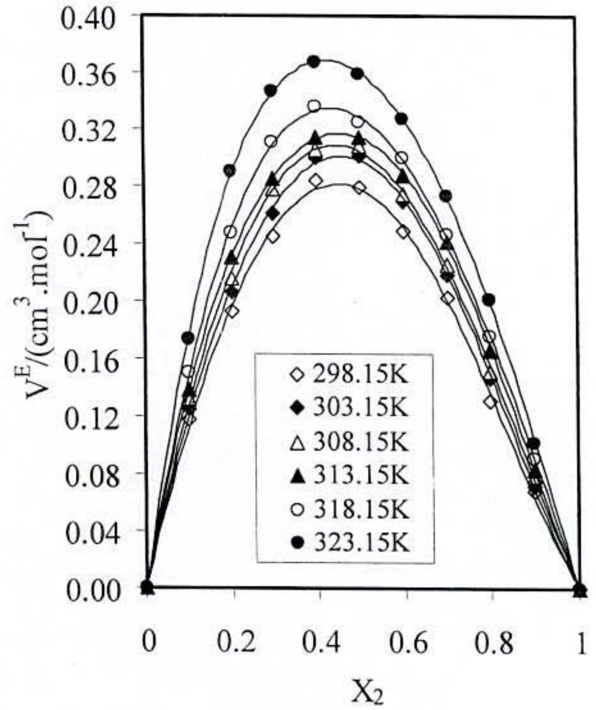

Figure 4.25: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

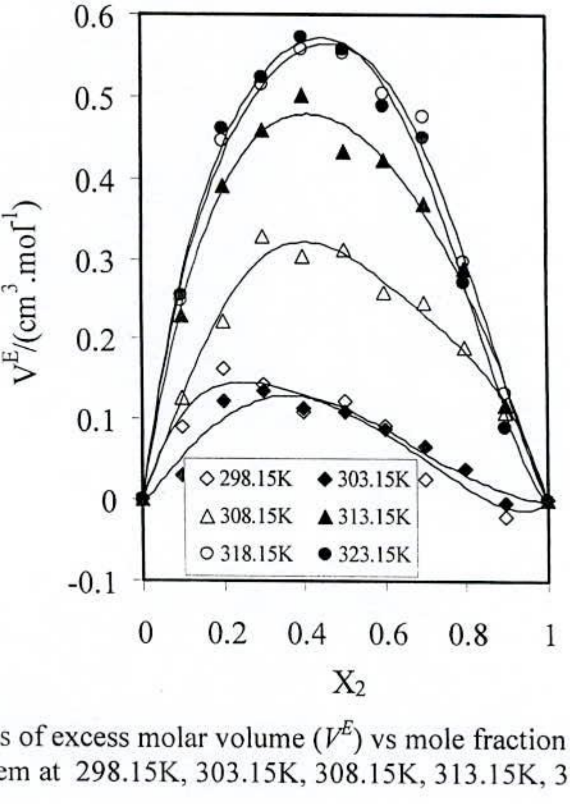

Figure 4.26: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

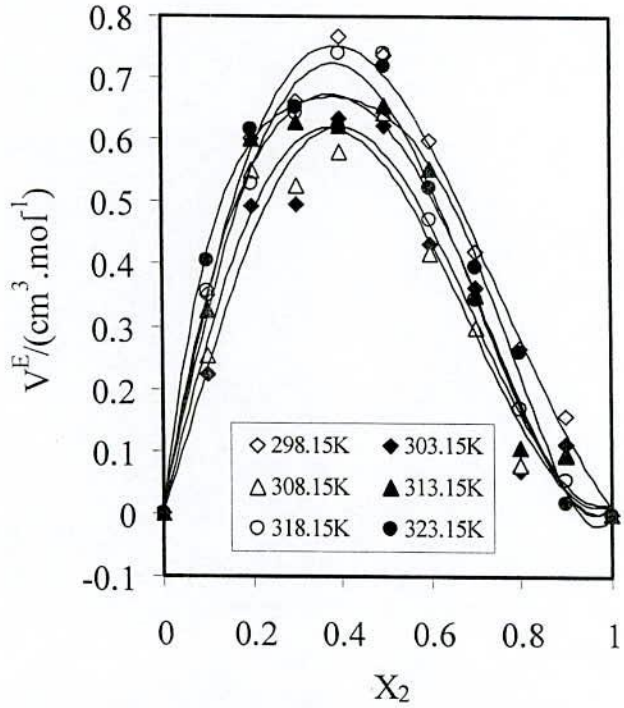

Figure 4.27: Plots of excess molar volume (V^E) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

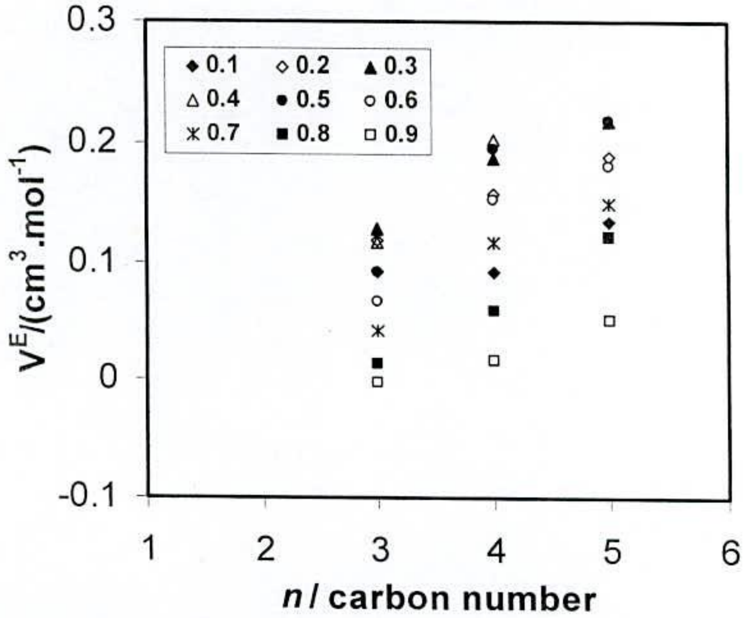

Figure 4.28: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different mole fraction at 298.15K.

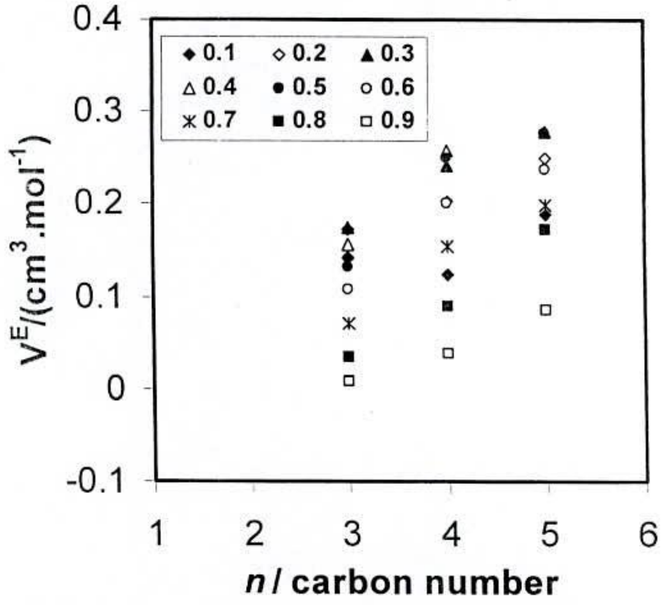

Figure 4.29: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different mole fraction at 313.15K.

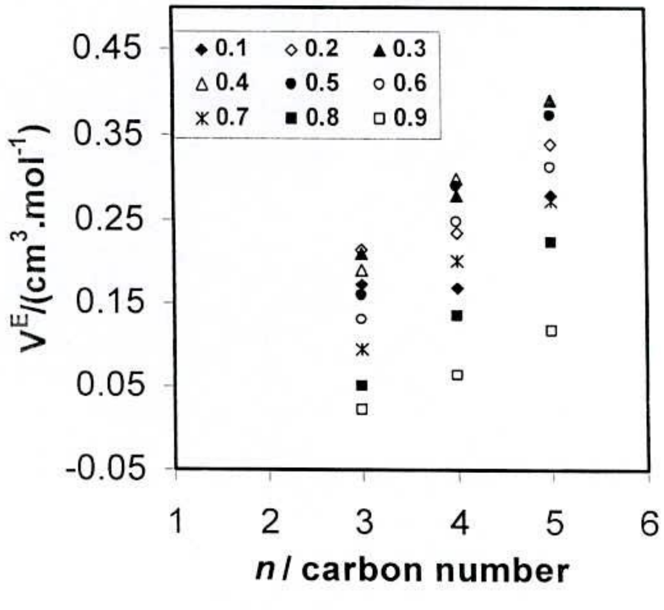

Figure 4.30: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different mole fraction at 323.15K.

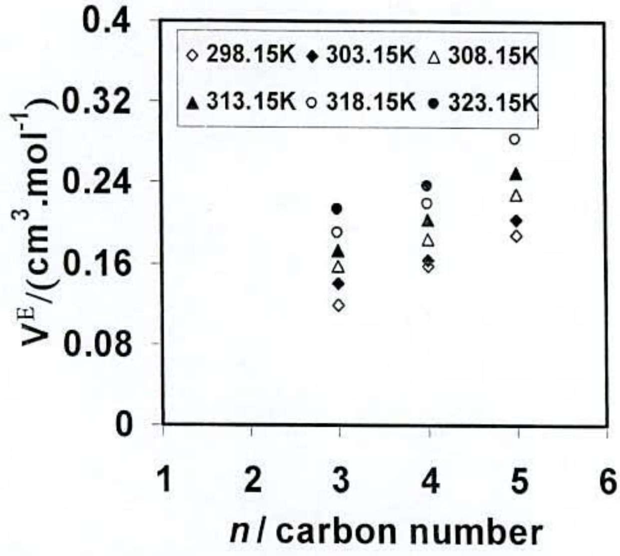

Figure 4.31: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different temperature at 0.2 mole fraction.

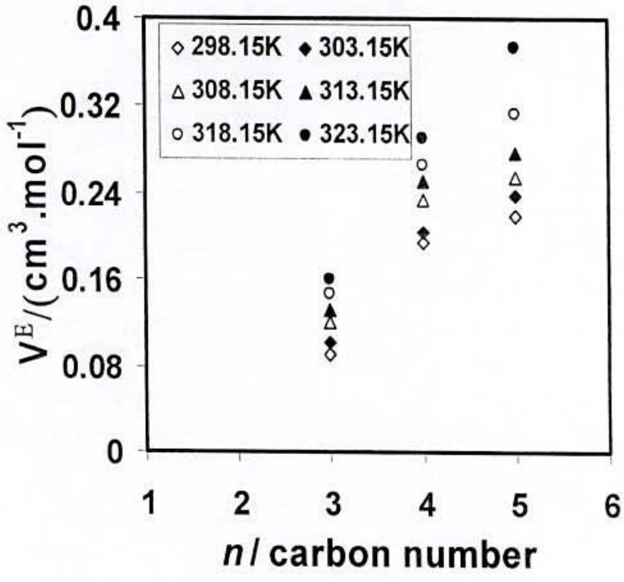

Figure 4.32: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

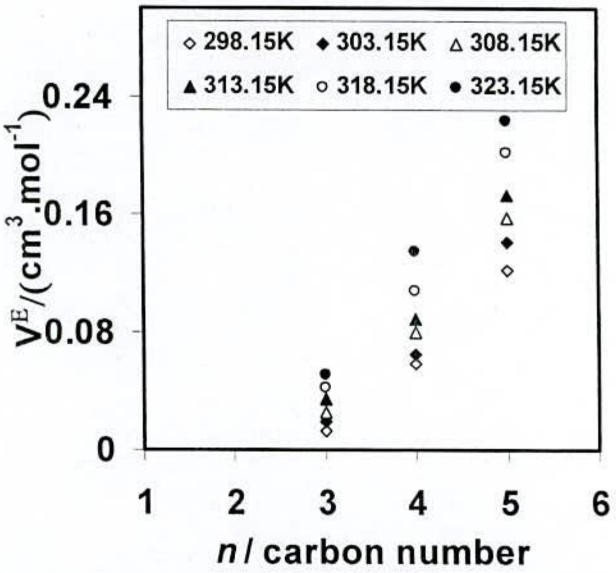

Figure 4.33: Dependence of the excess molar volume (V^E) with carbon number (n) of alcohols with different temperature at 0.8 mole fraction.

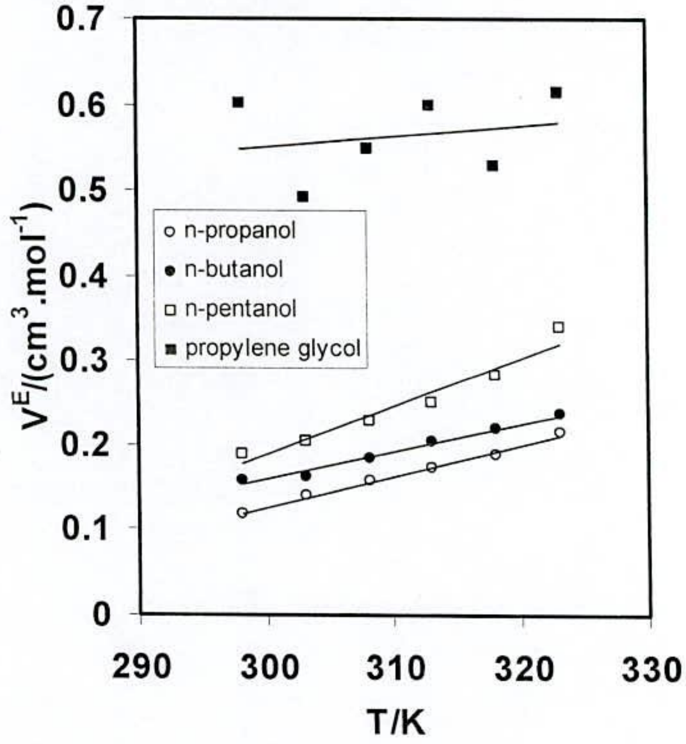

Figure 4.34: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

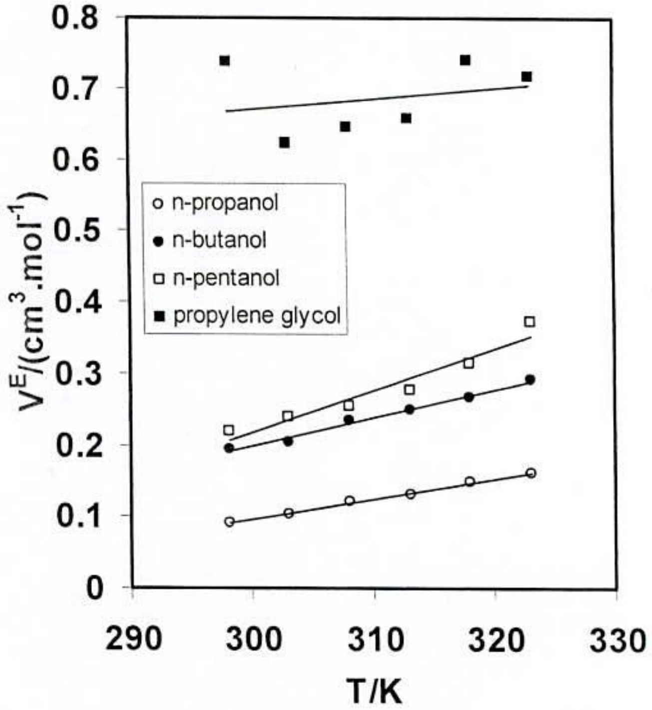

Figure 4.35: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

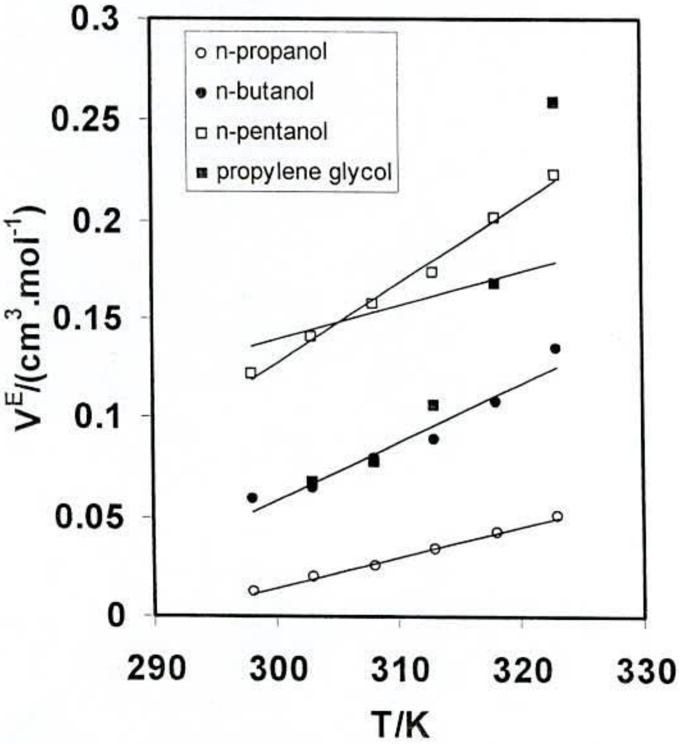

Figure 4.36: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

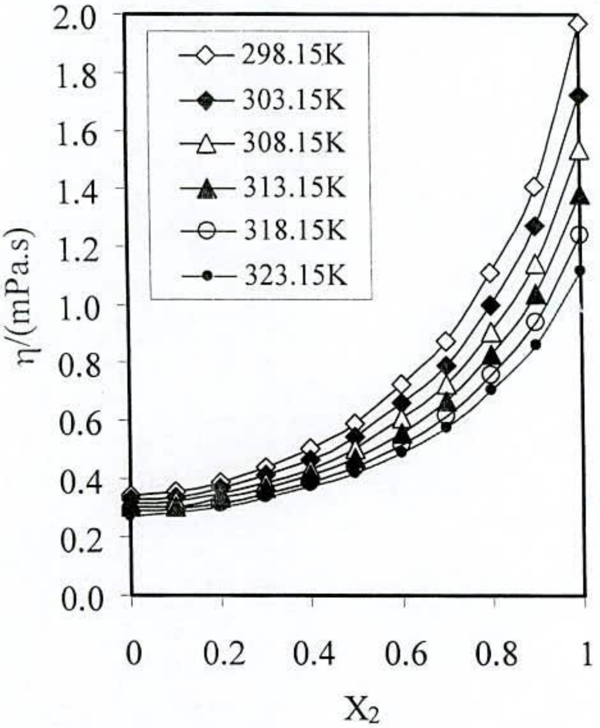

Figure 4.37: Plots of viscosity (η) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

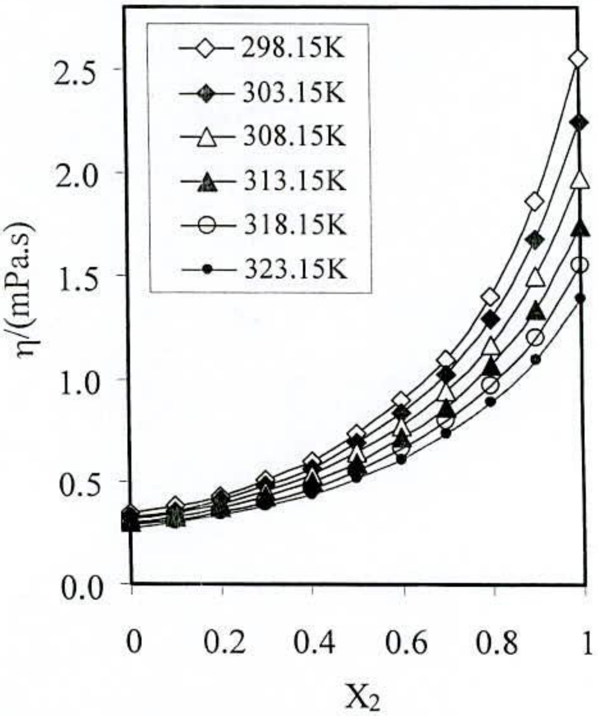

Figure 4.38: Plots of viscosity (η) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

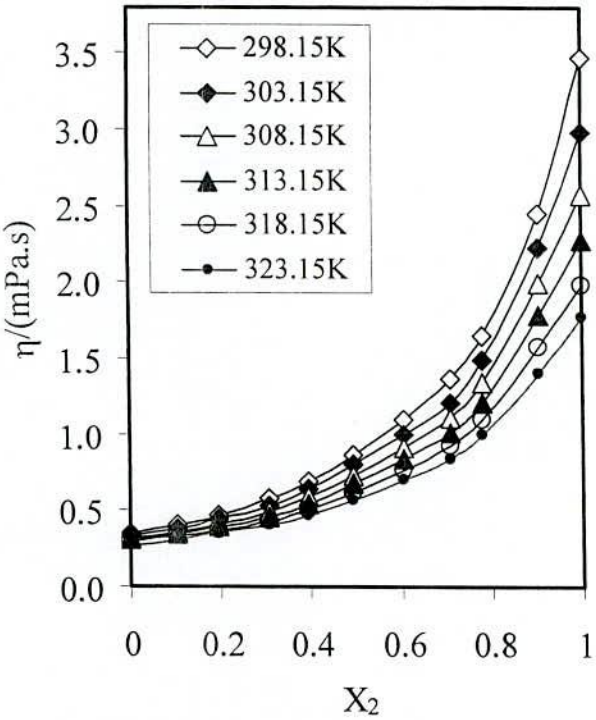

Figure 4.39: Plots of viscosity (η) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

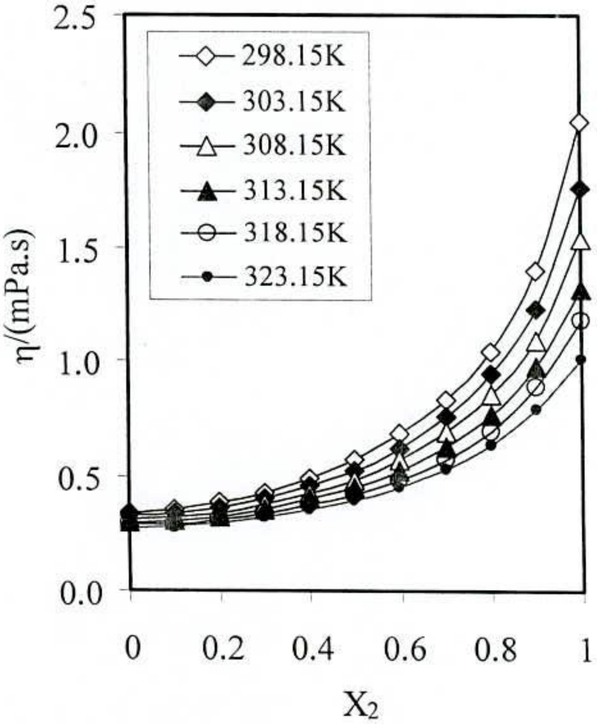

Figure 4.40: Plots of viscosity (η) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

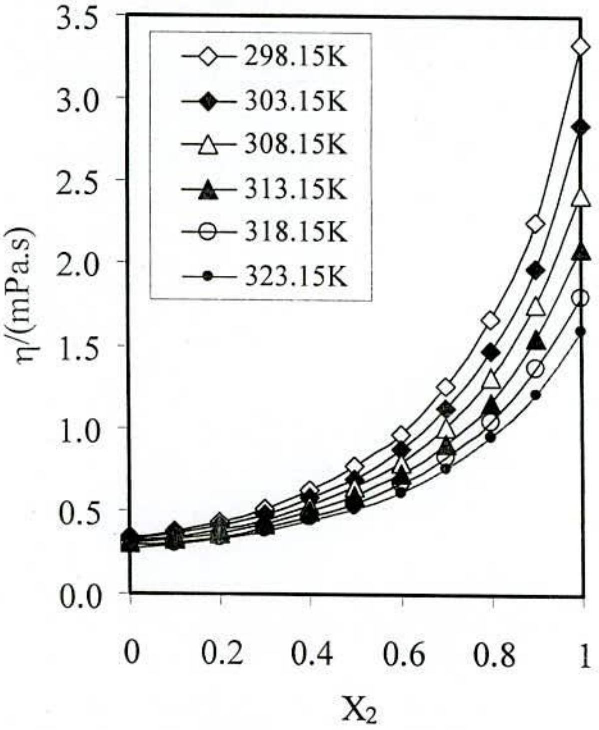

Figure 4.41: Plots of viscosity (η) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

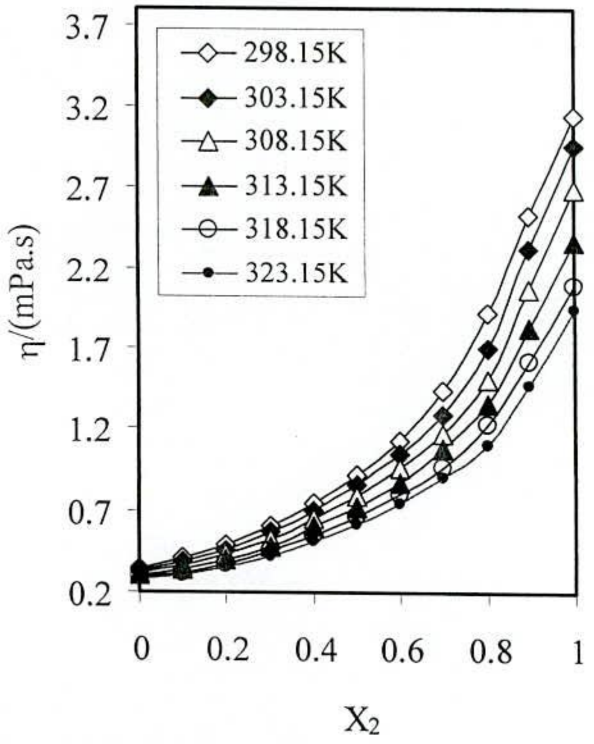

Figure 4.42: Plots of viscosity (η) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

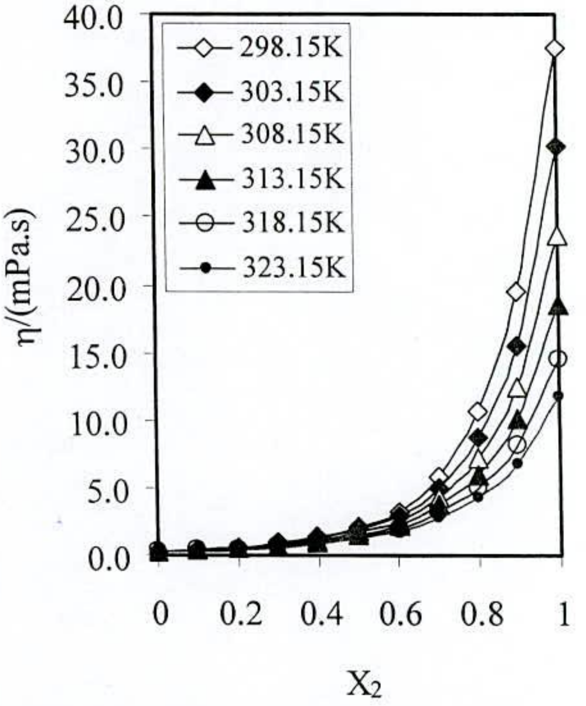

Figure 4.43: Plots of viscosity (η) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

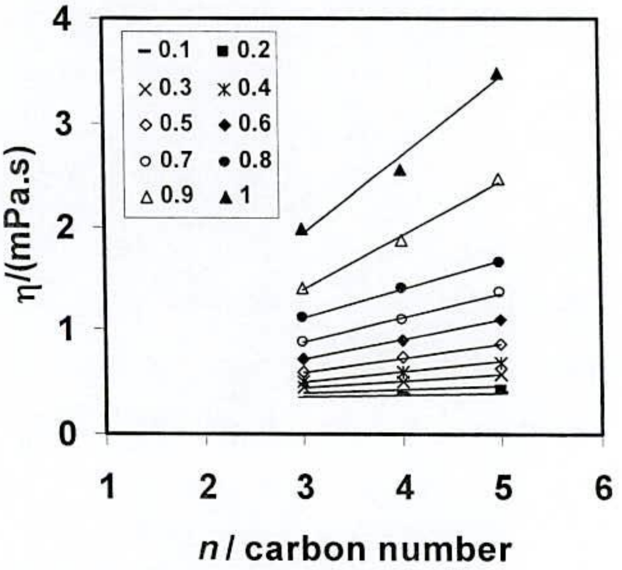

Figure 4.44: Dependence of the viscosity (η) with carbon number (n) of alcohols with different mole fraction at 298.15K.

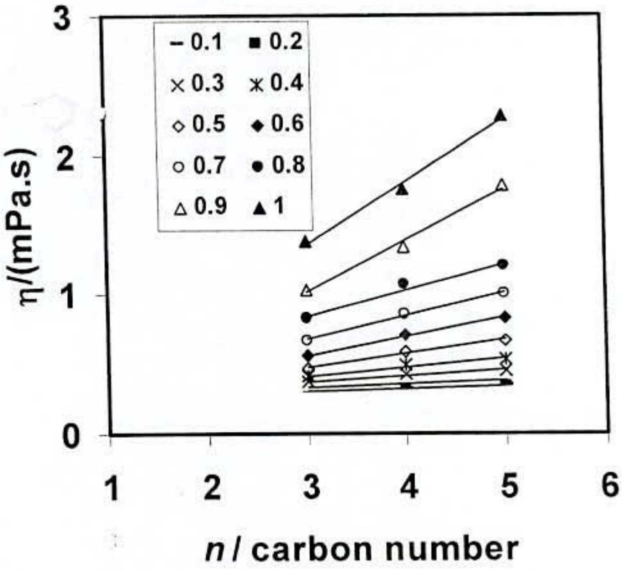

Figure 4.45: Dependence of the viscosity (η) with carbon number (n) of alcohols with different mole fraction at 313.15K.

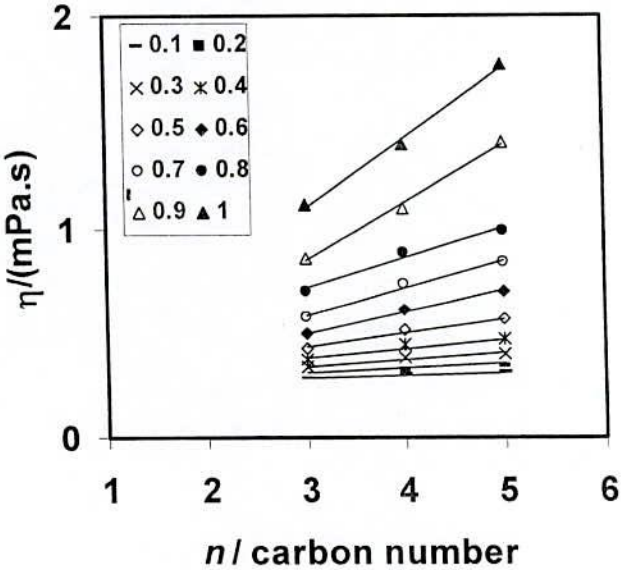

Figure 4.46: Dependence of the viscosity (η) with carbon number (n) of alcohols with different mole fraction at 323.15K.

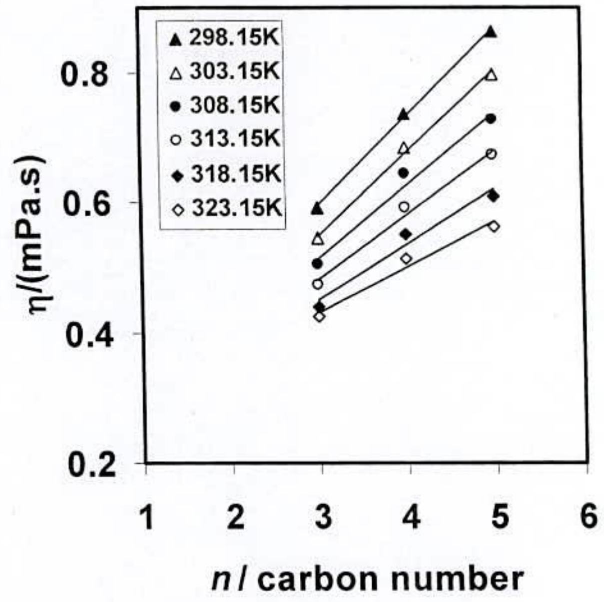

Figure 4.47: Dependence of the viscosity (η) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

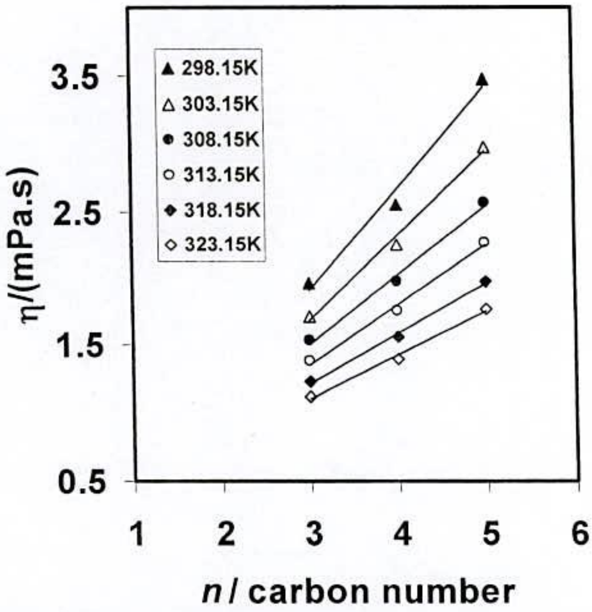

Figure 4.48: Dependence of the viscosity (η) with carbon number (n) of alcohols with different temperature at 1.0 mole fraction.

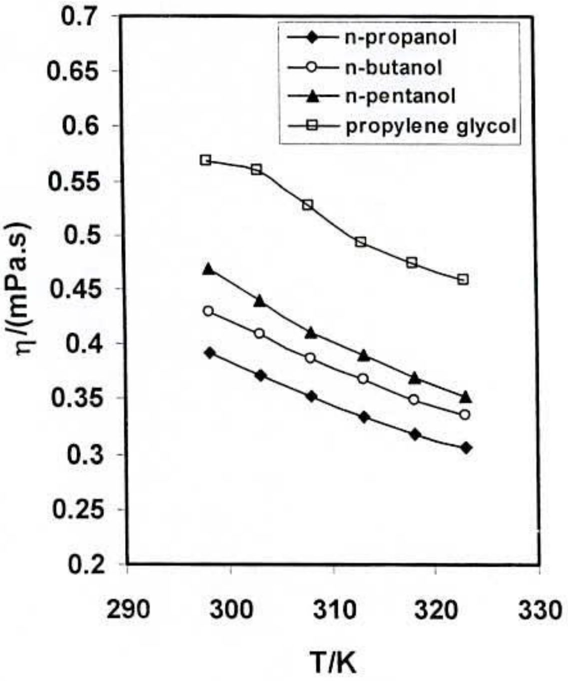

Figure 4.49: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

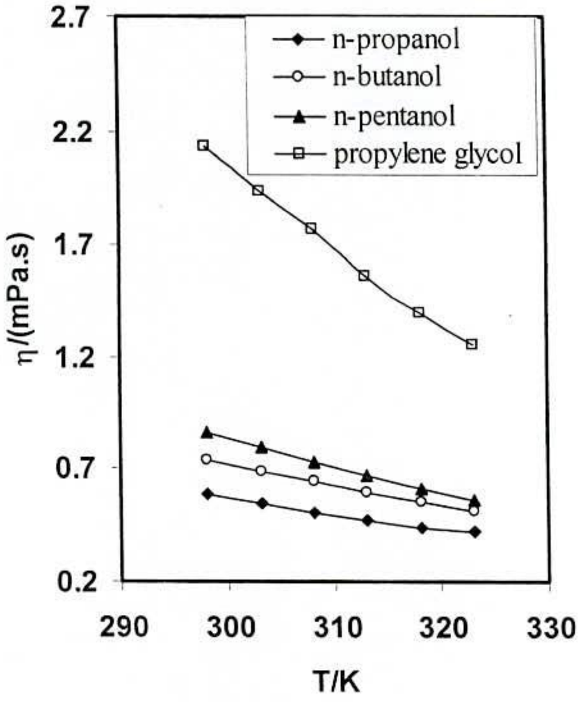

Figure 4.50: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

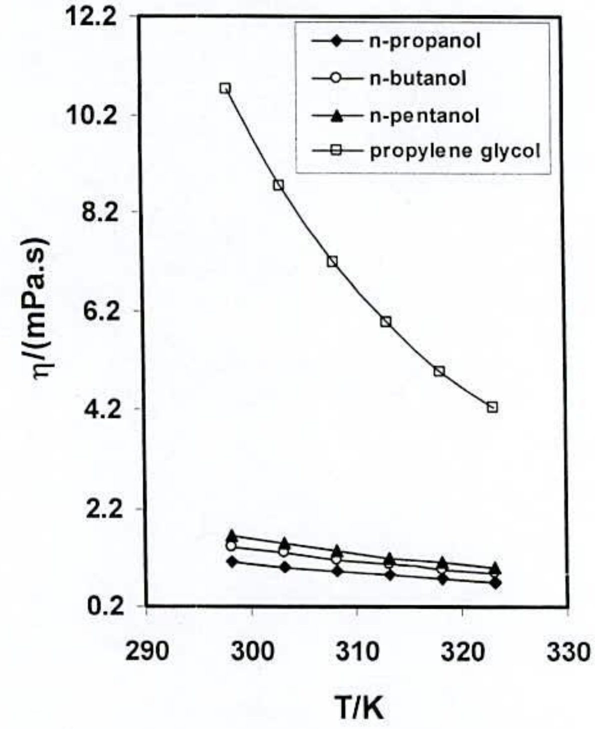

Figure 4.51: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

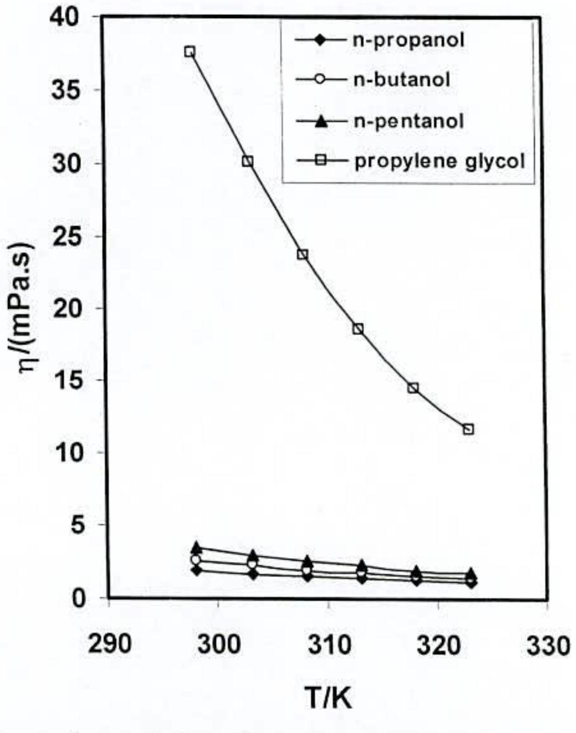

Figure 4.52: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

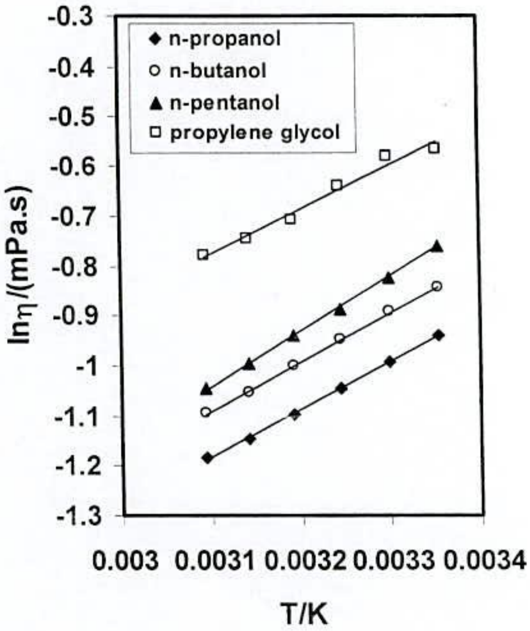

Figure 4.53: Comparison of lnη vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

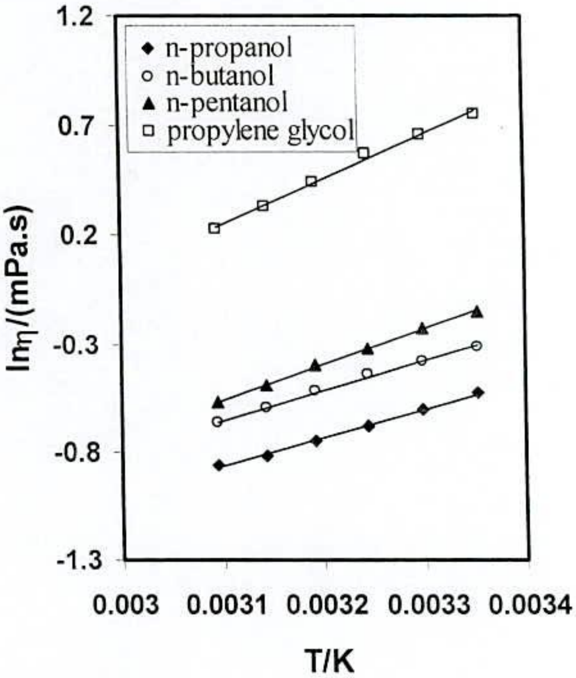

Figure 4.54: Comparison of lnη vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

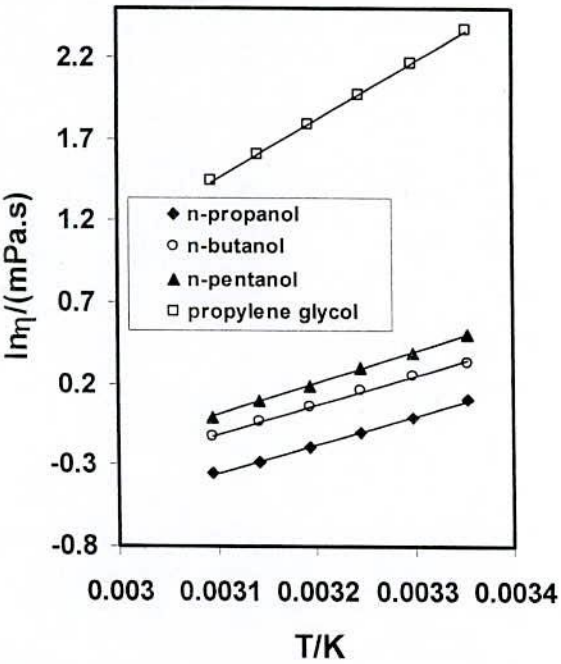

Figure 4.55: Comparison of lnη vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

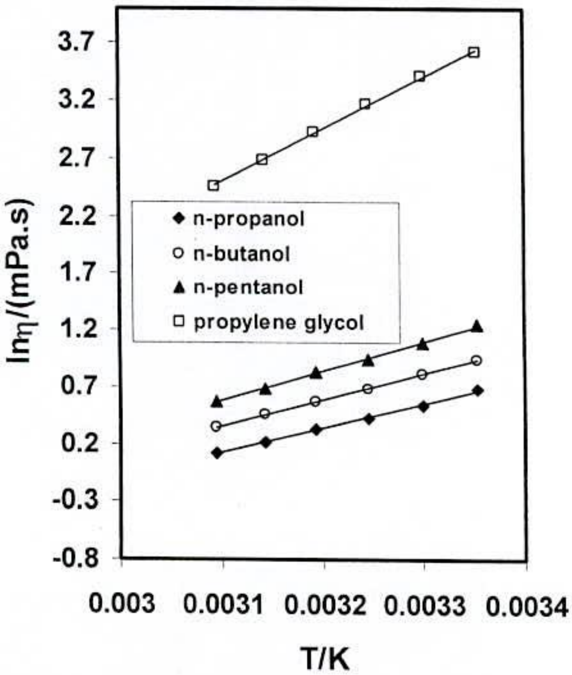

Figure 4.56: Comparison of lnη vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

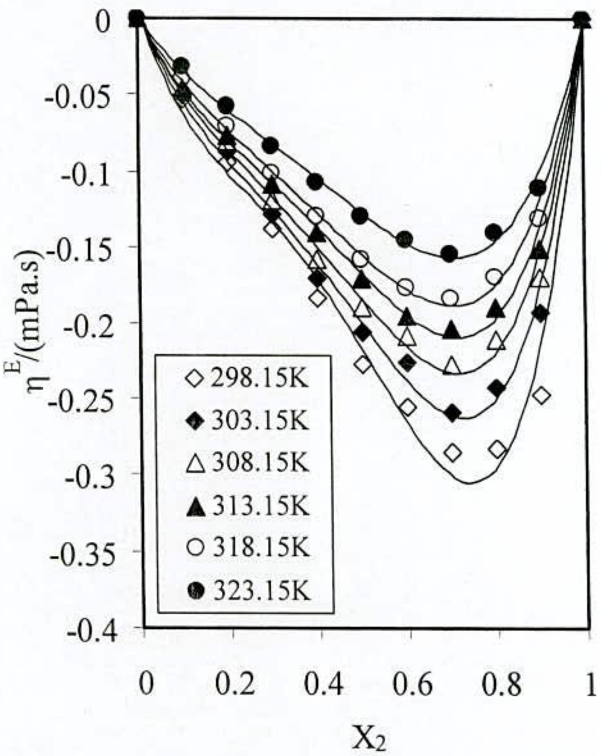

Figure 4.57: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

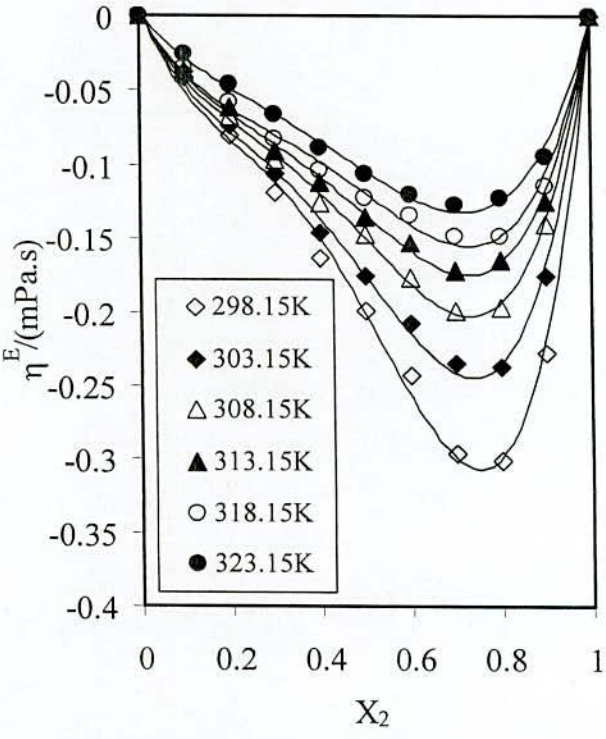

Figure 4.58: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

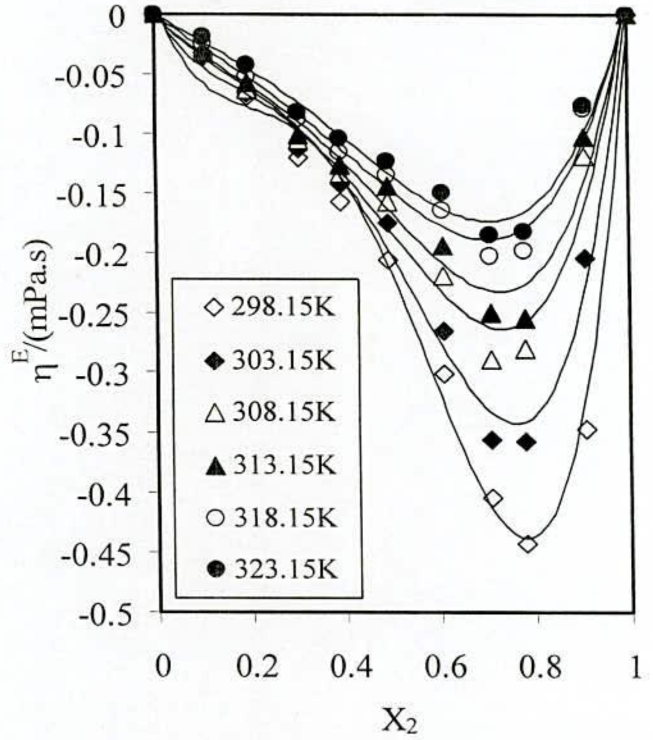

Figure 4.59: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

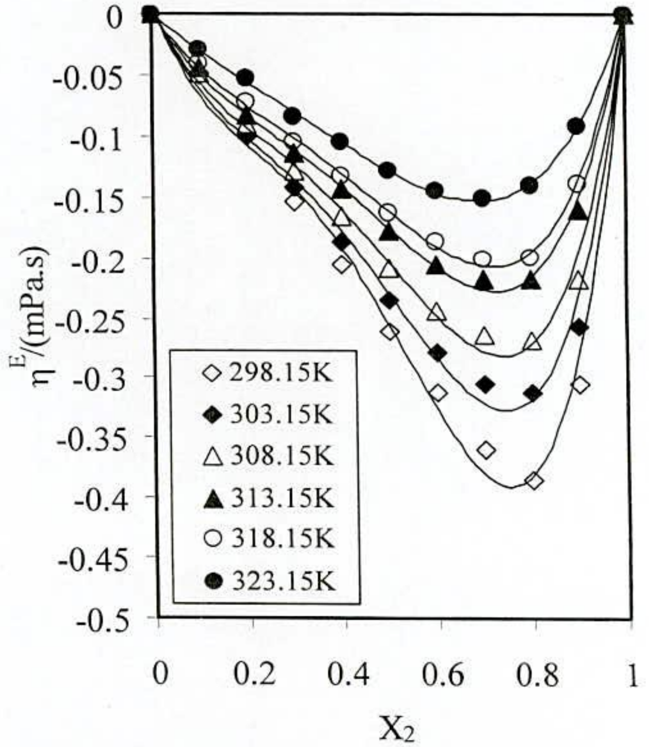

Figure 4.60: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

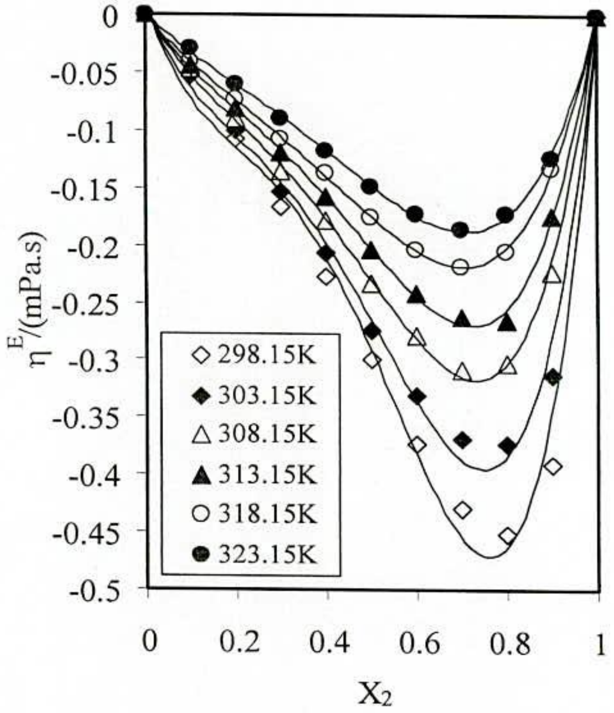

Figure 4.61: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

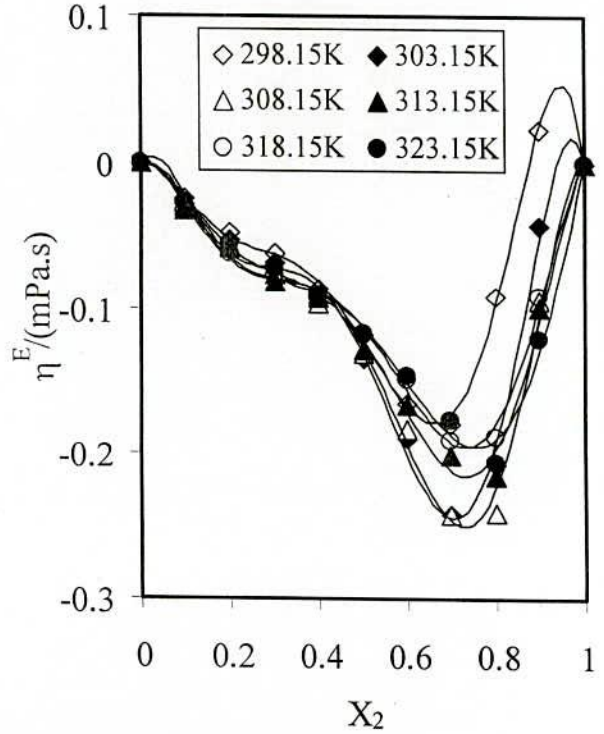

Figure 4.62: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

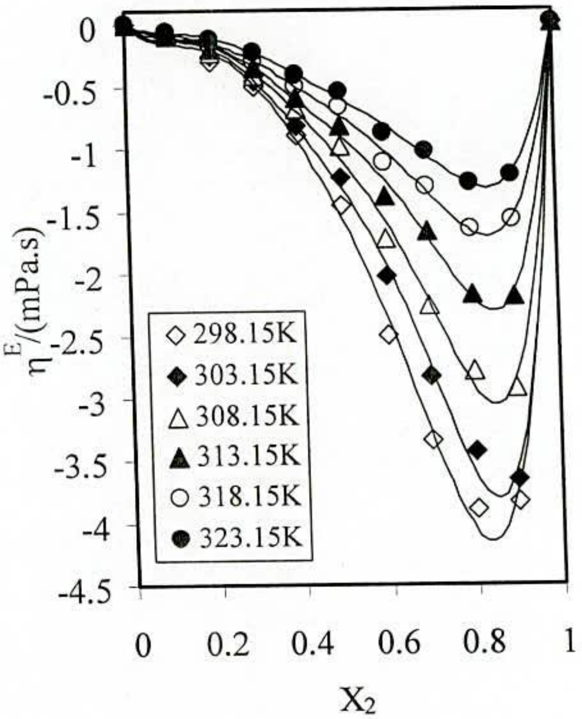

Figure 4.63: Plots of excess viscosity (η^E) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

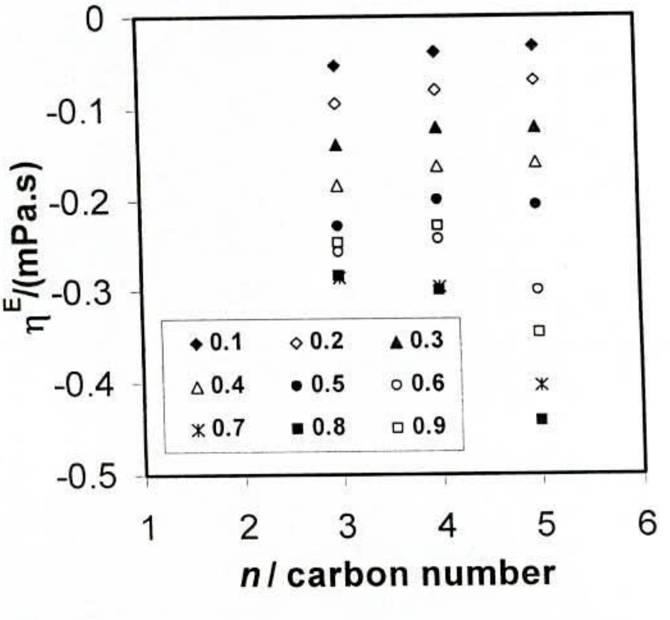

Figure 4.64: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different mole fraction at 298.15K.

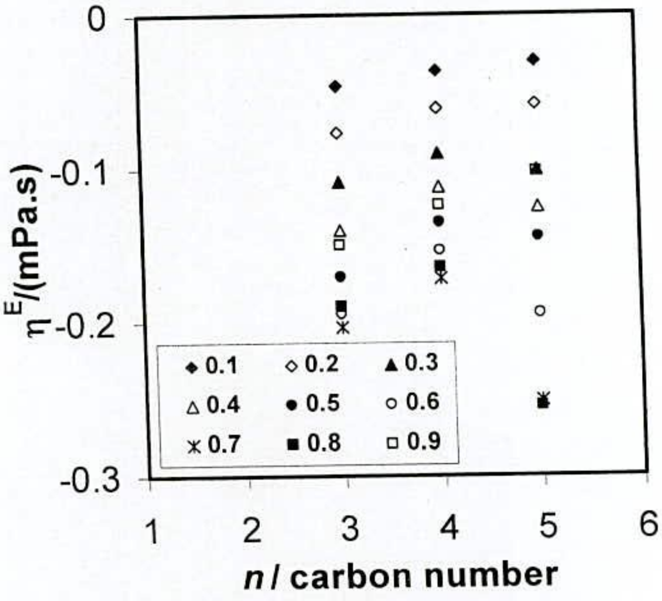

Figure 4.65: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different mole fraction at 313.15K.

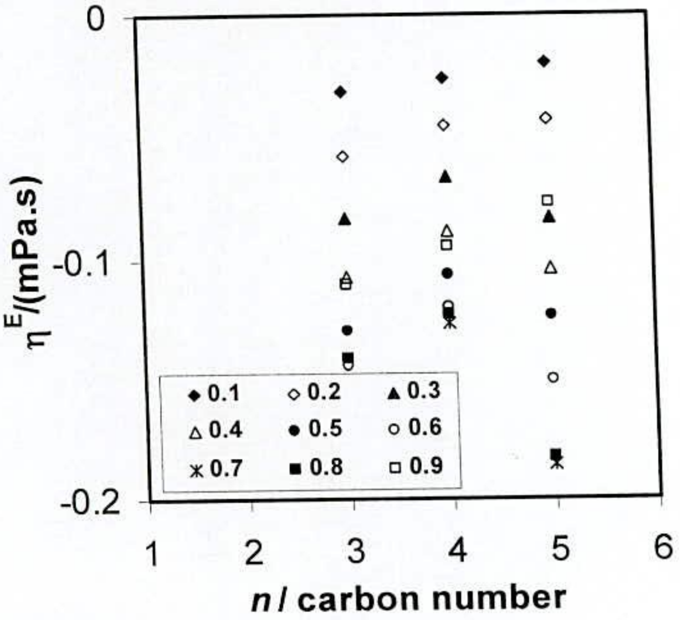

Figure 4.66: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different mole fraction at 323.15K.

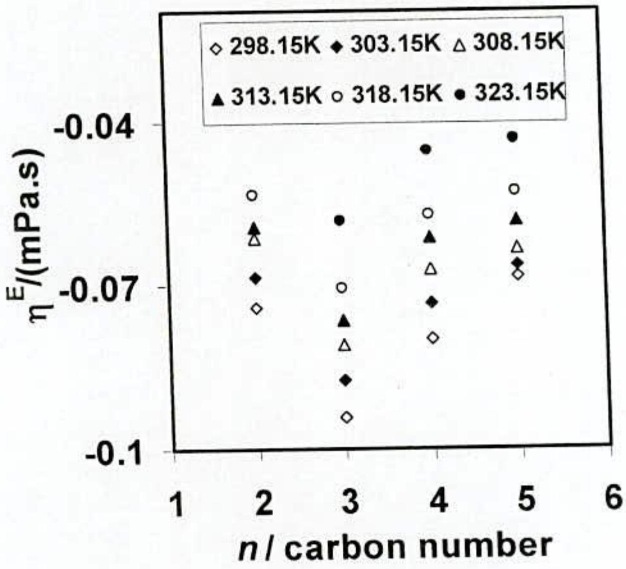

Figure 4.67: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different temperature at 0.2 mole fraction.

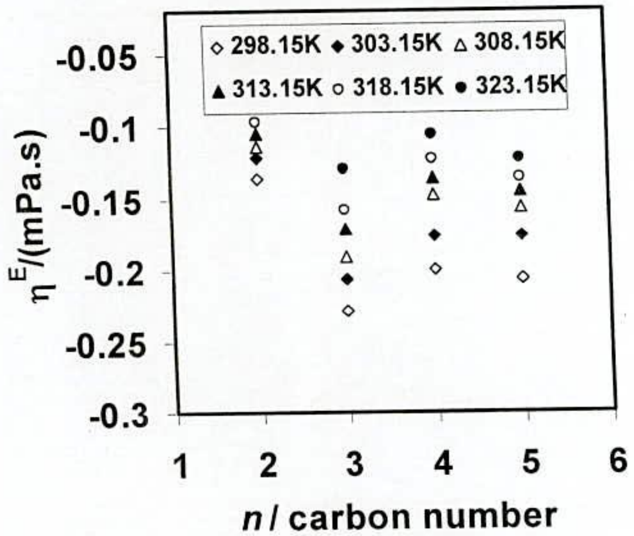

Figure 4.68: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

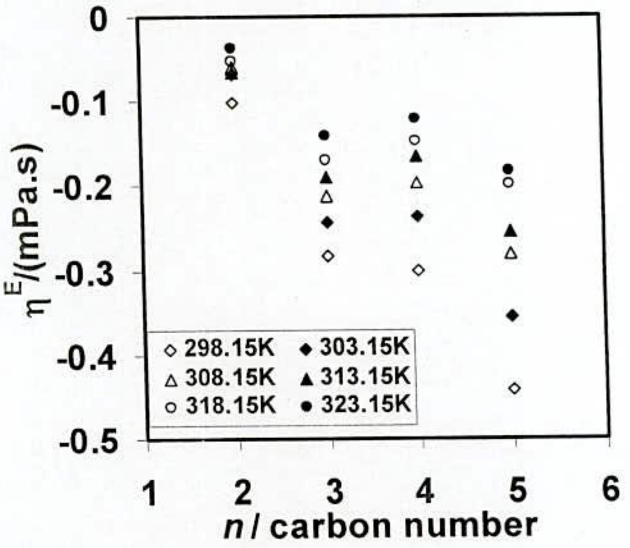

Figure 4.69: Dependence of the excess viscosity (η^E) with carbon number (n) of alcohols with different temperature at 0.8 mole fraction.

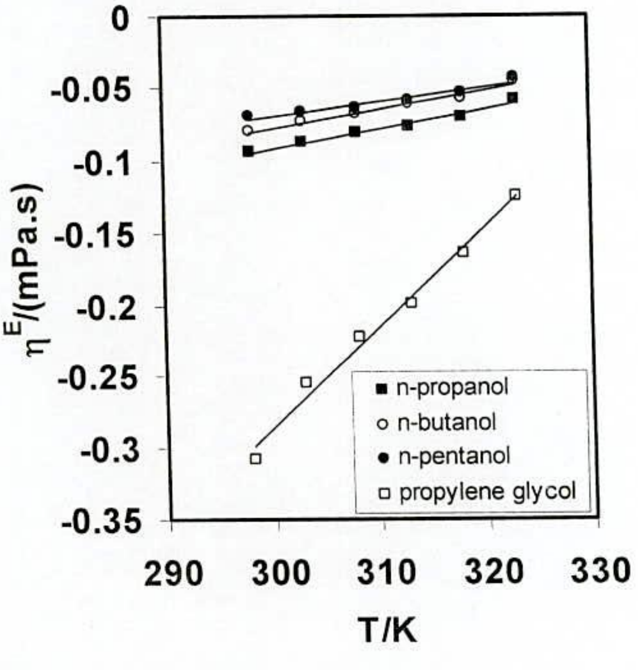

Figure 4.70: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

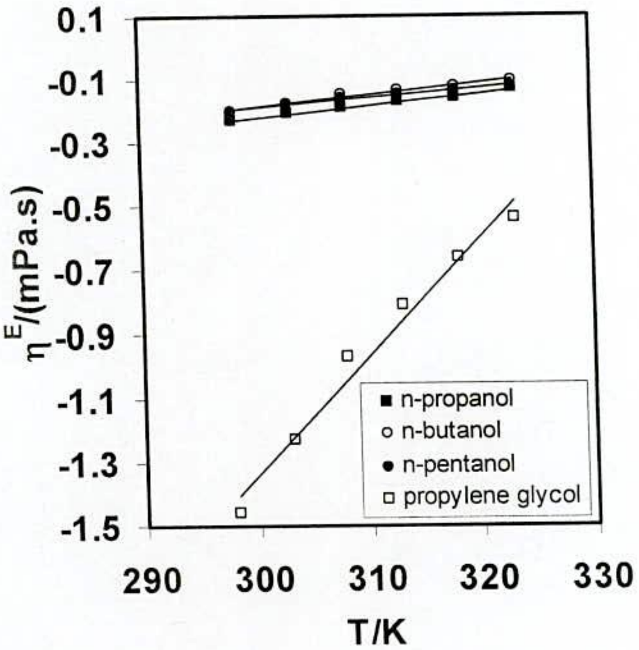

Figure 4.71: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

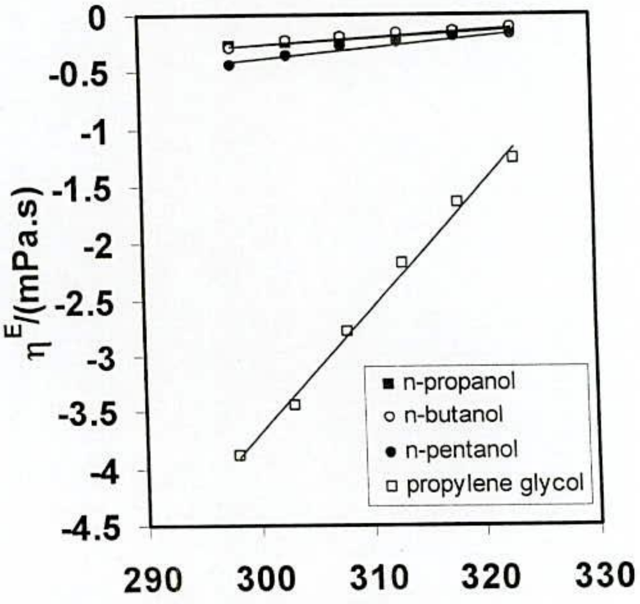

Figure 4.72: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

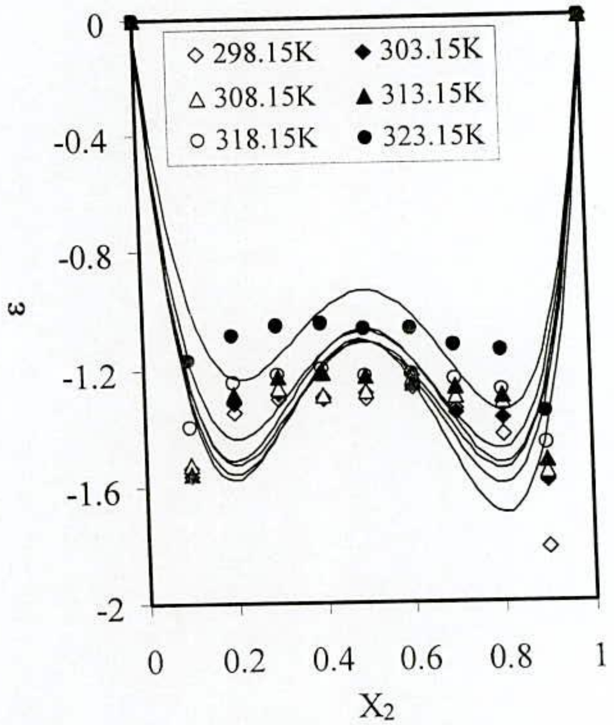

Figure 4.73: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

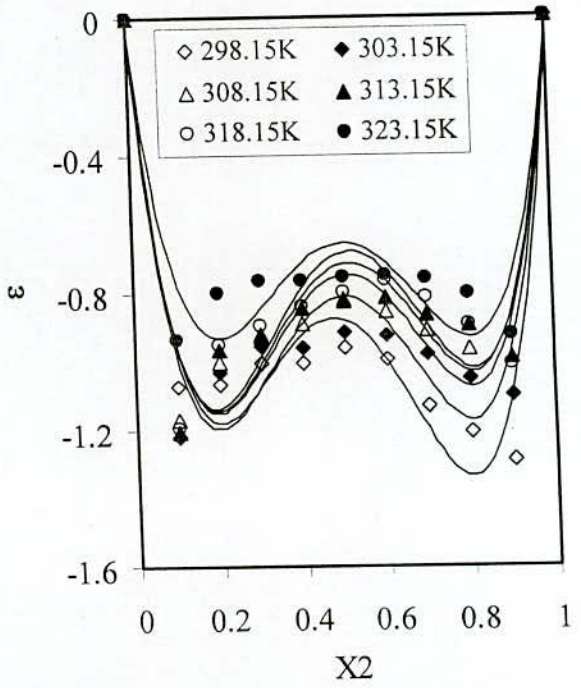

Figure 4.74: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

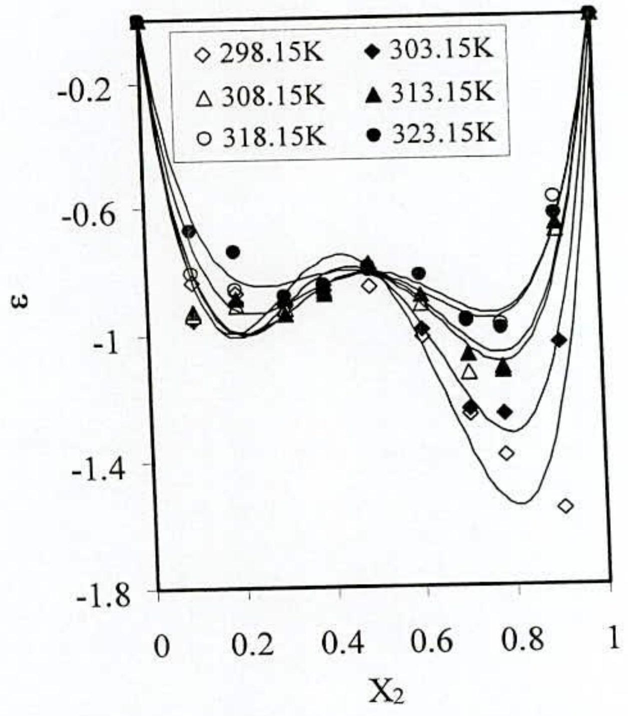

Figure 4.75: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

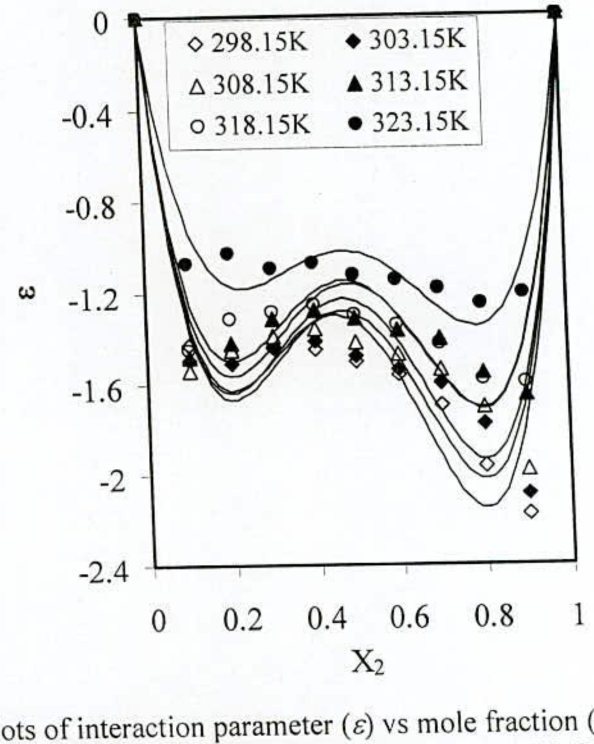

Figure 4.76: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

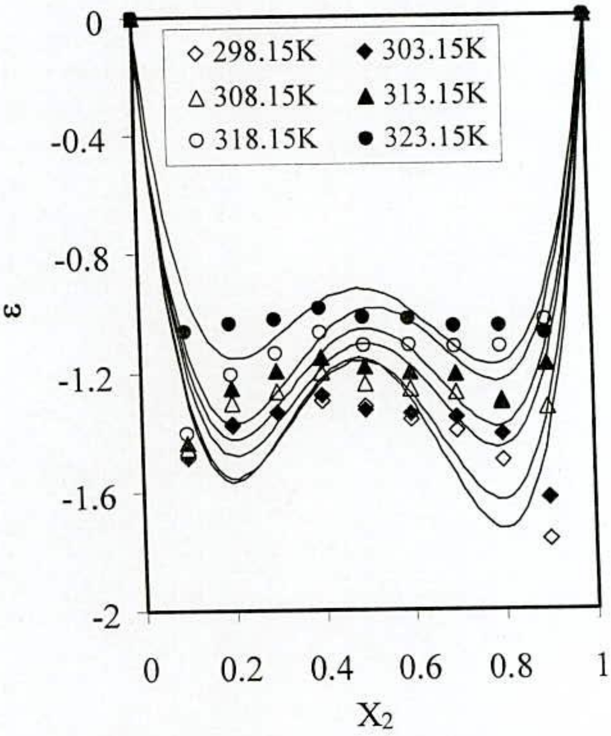

Figure 4.77: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

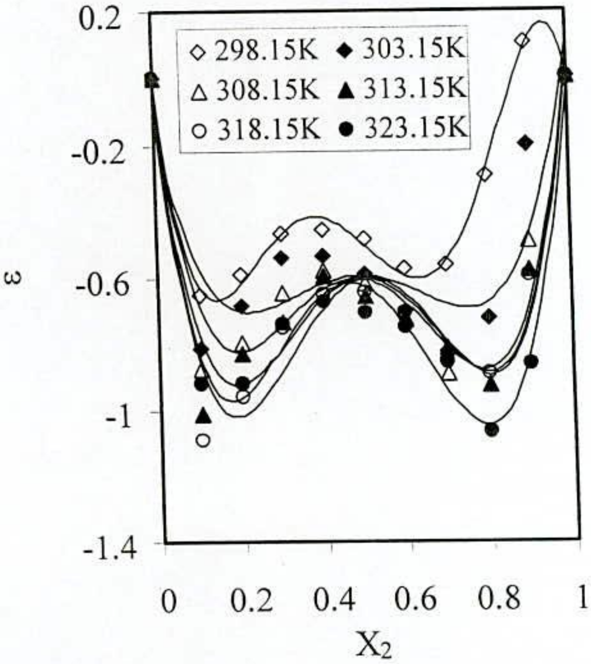

Figure 4.78: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

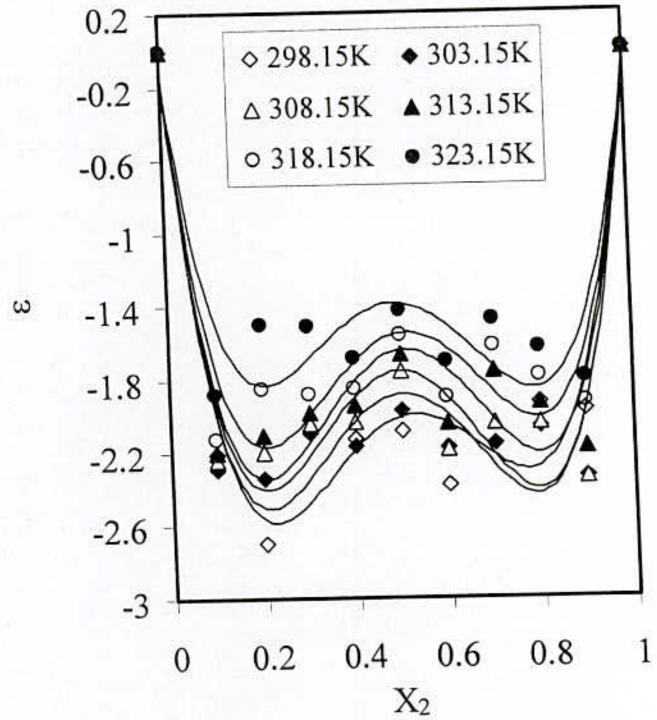

Figure 4.79: Plots of interaction parameter (ε) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

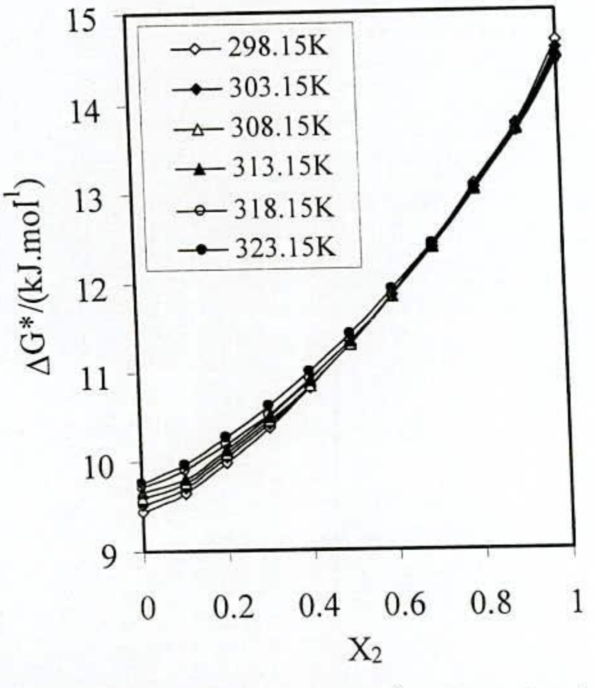

Figure 4.80: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

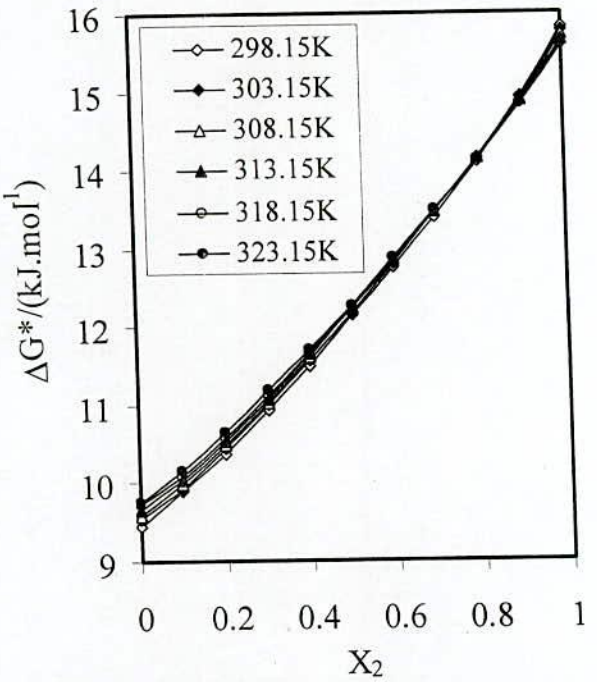

Figure 4.81: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

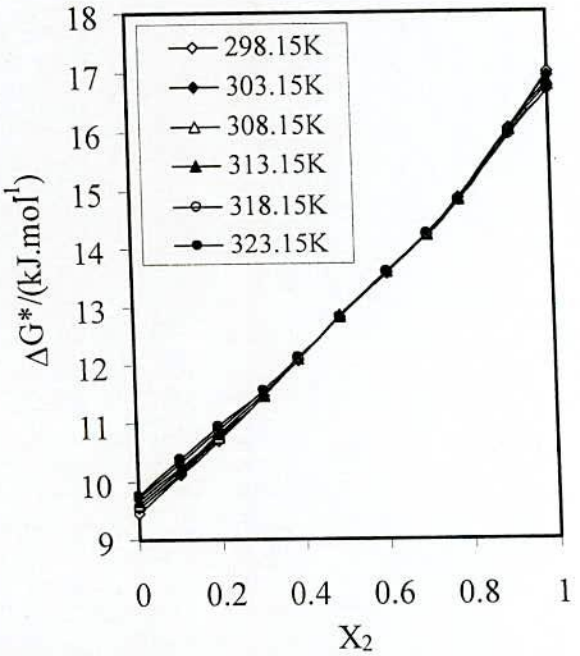

Figure 4.82: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

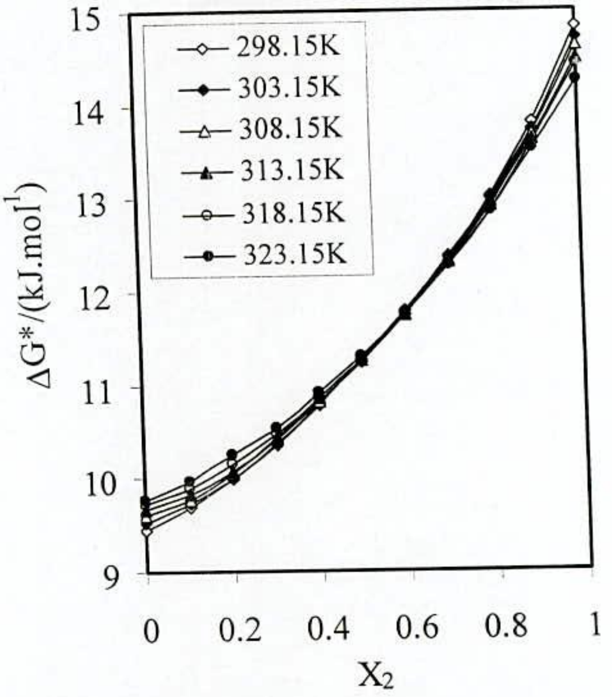

Figure 4.83: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

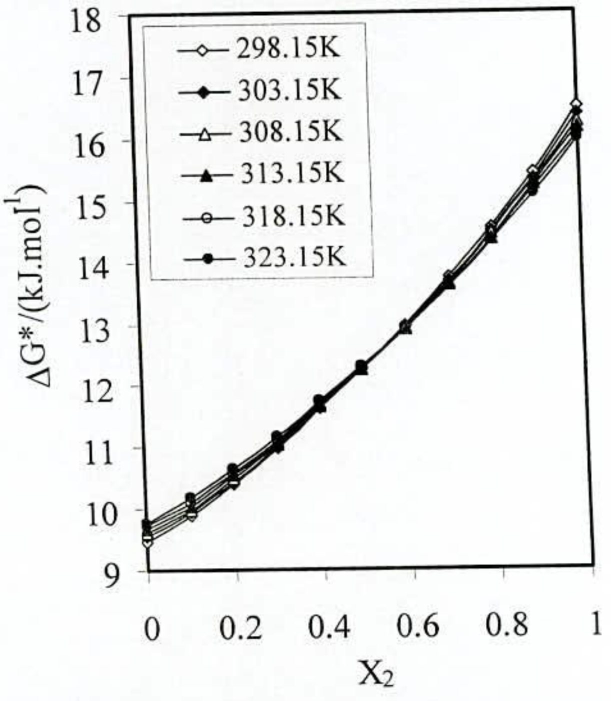

Figure 4.84: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

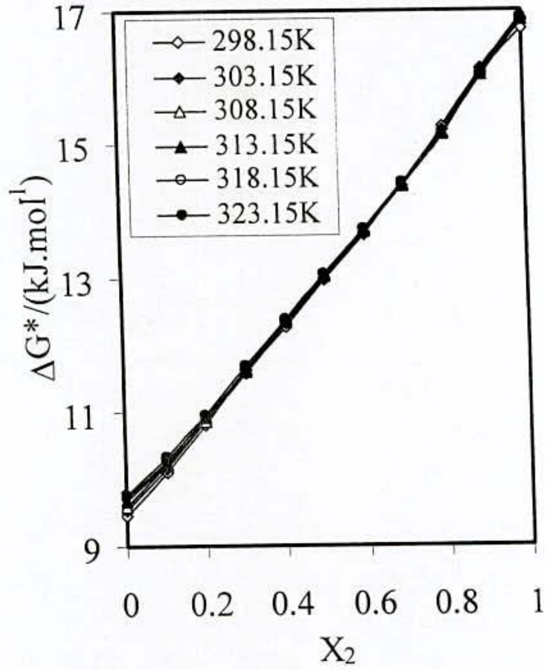

Figure 4.85: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

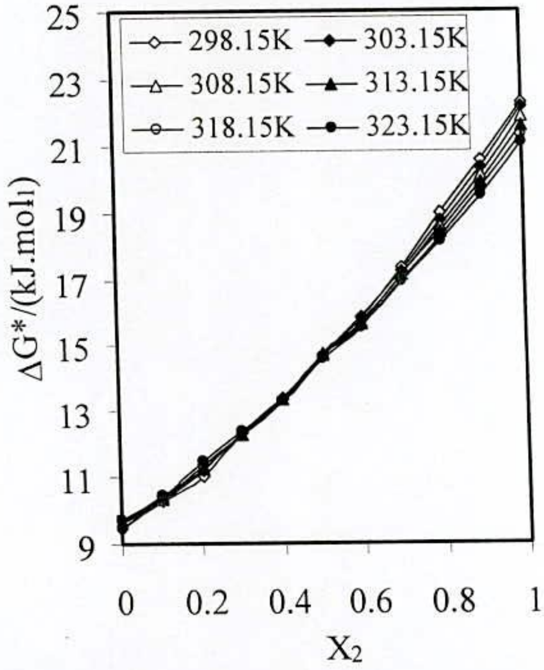

Figure 4.86: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

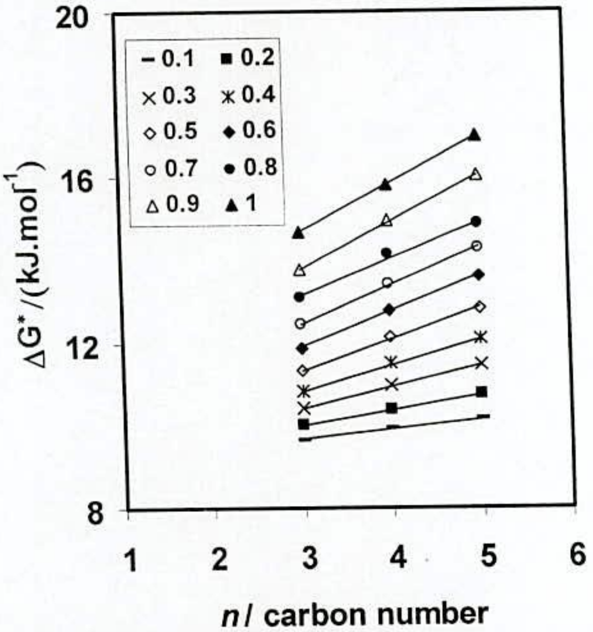

Figure 4.87: Dependence of the change of free energy (ΔG^*) with carbon number (n) of alcohols with different mole fraction at 298.15K.

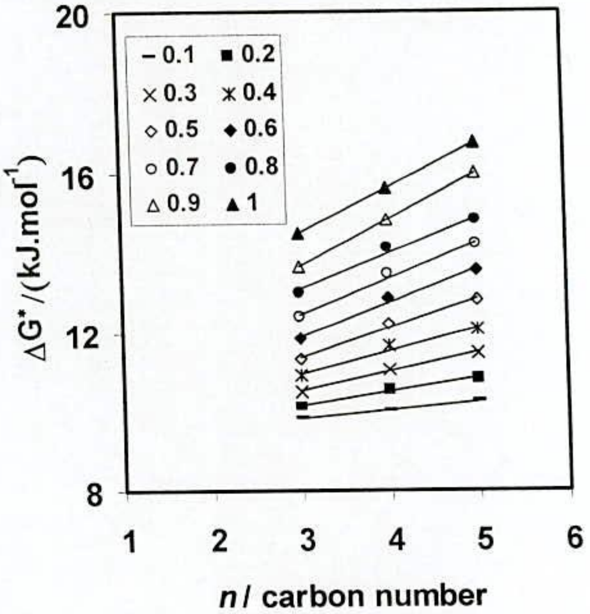

Figure 4.88: Dependence of the change of free energy (ΔG^*) with carbon number (n) of alcohols with different mole fraction at 313.15K.

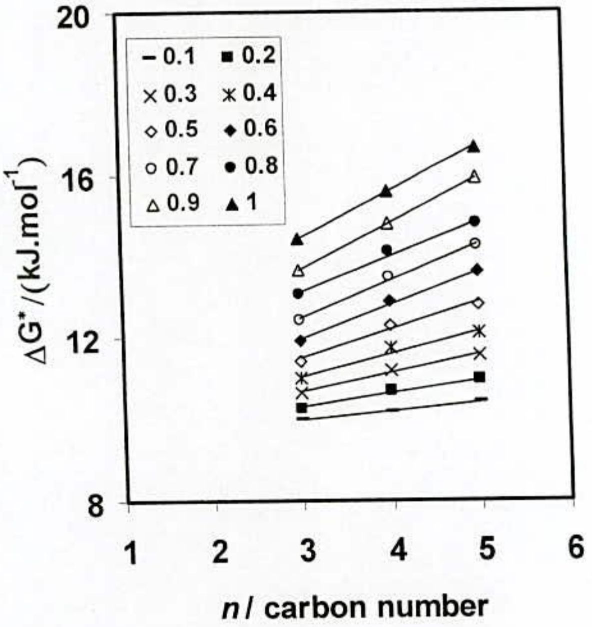

Figure 4.89: Dependence of the change of free energy (ΔG^*) with carbon number (n) of alcohols with different mole fraction at 323.15K.

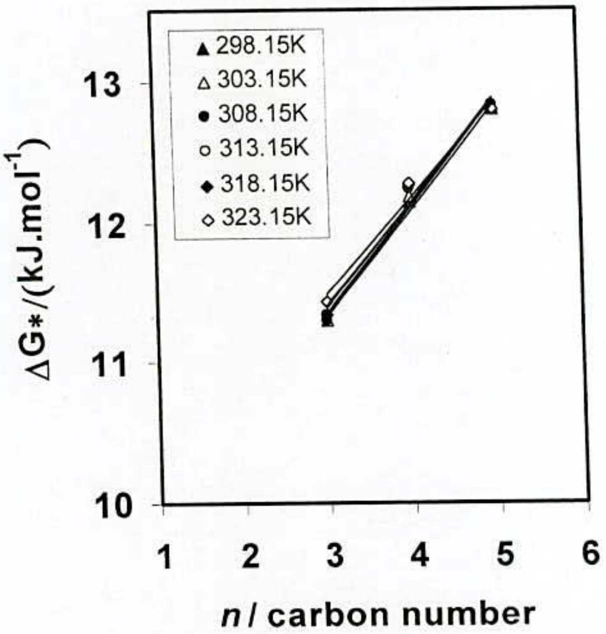

Figure 4.90: Dependence of the change of free energy (ΔG^*) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

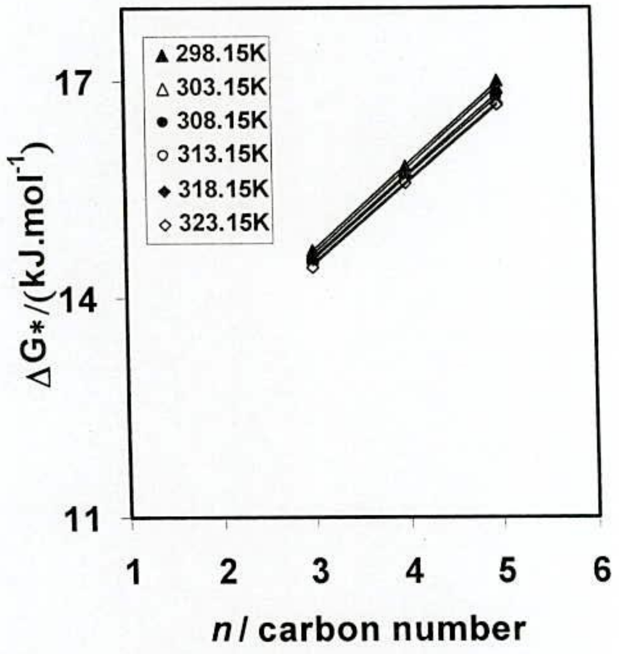

Figure 4.91: Dependence of the change of free energy (ΔG^*) with carbon number (n) of alcohols with different temperature at 1.0 mole fraction.

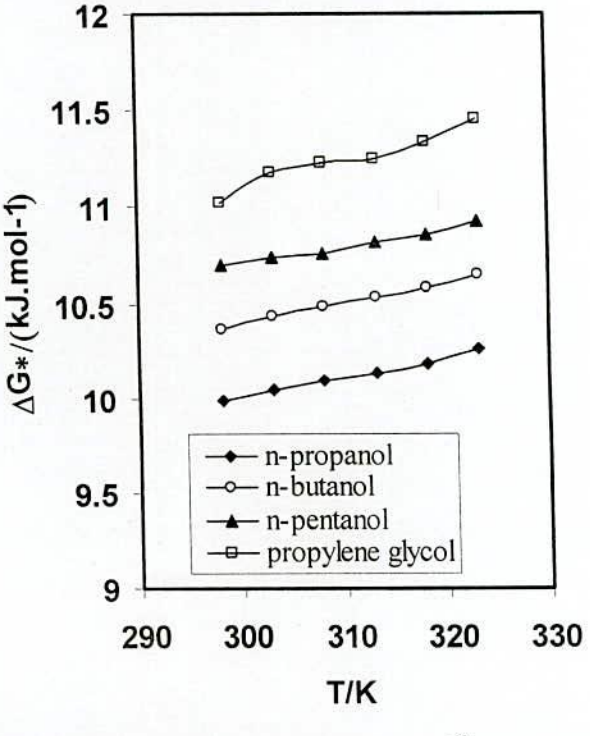

Figure 4.92: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

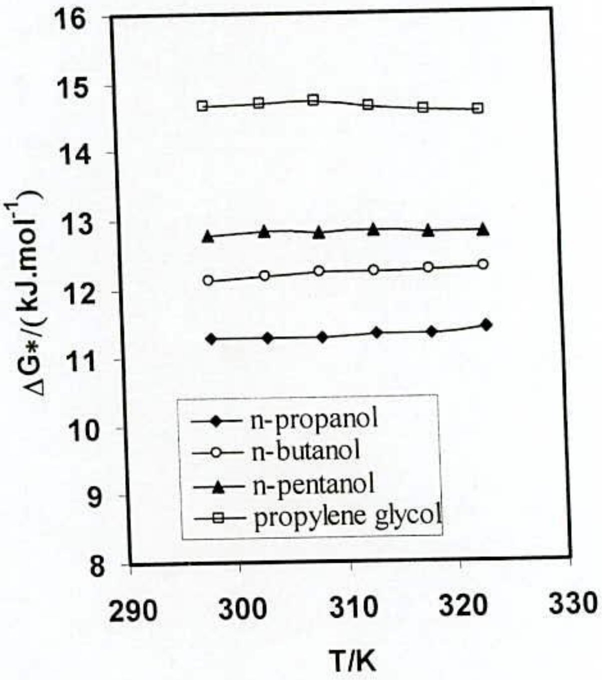

Figure 4.93: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

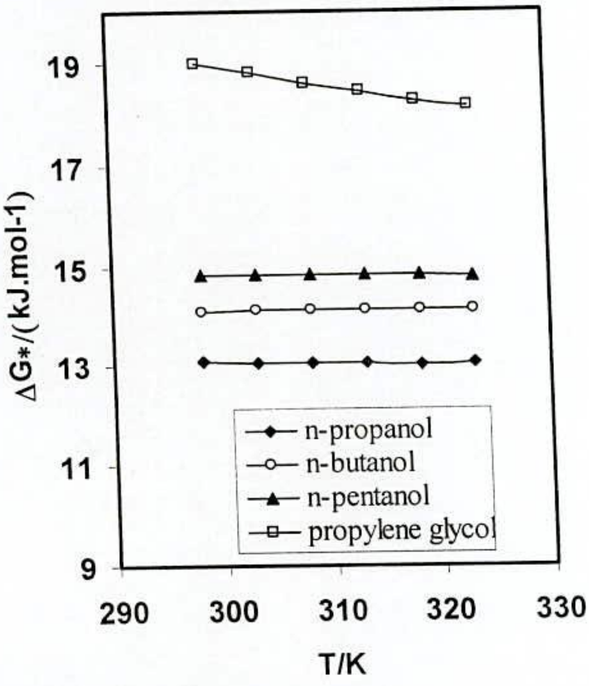

Figure 4.94: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

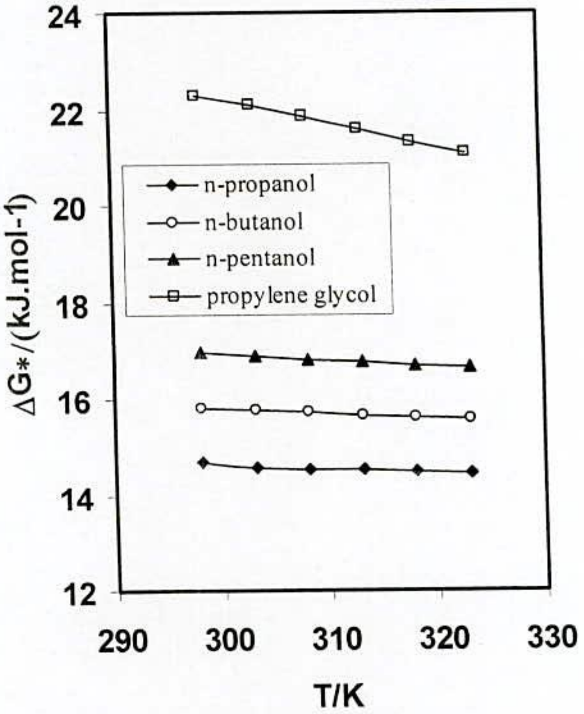

Figure 4.95: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

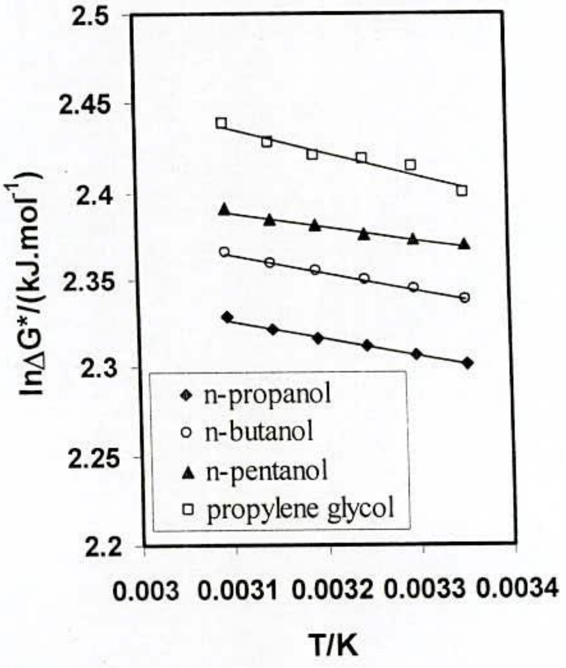

Figure 4.96: Comparison of $\ln\Delta G^*$ vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.2 mole fraction.

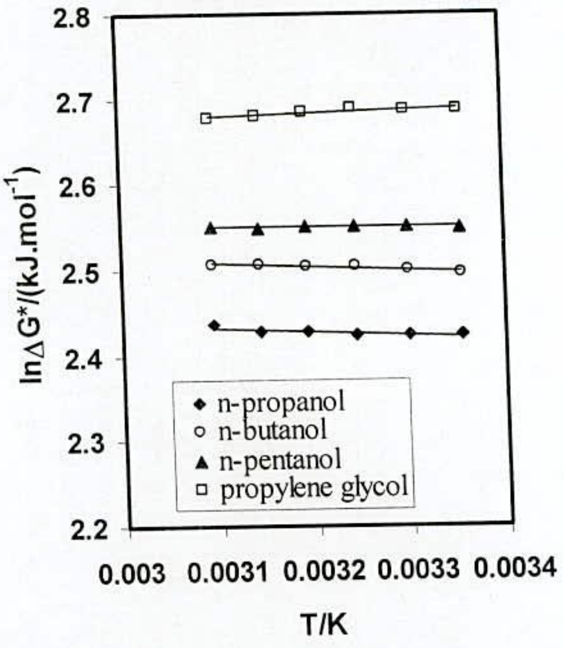

Figure 4.97: Comparison of lnΔG* vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.5 mole fraction.

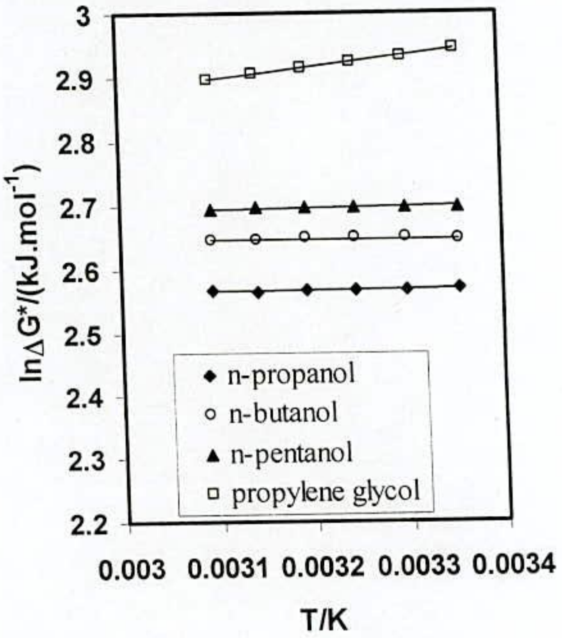

Figure 4.98: Comparison of lnΔG* vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 0.8 mole fraction.

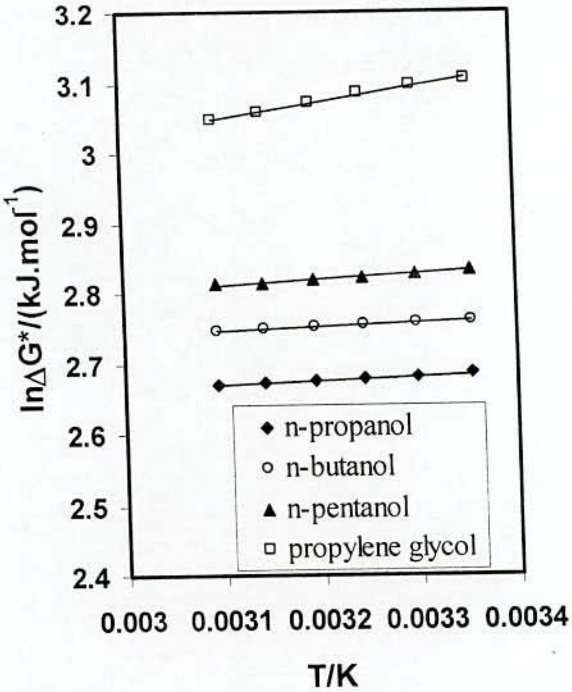

Figure 4.99: Comparison of lnΔG* vs 1/T of n-Propanol, n-Butanol, n-Pentanol and Propylene glycol in Acetonitrile at 1.0 mole fraction.

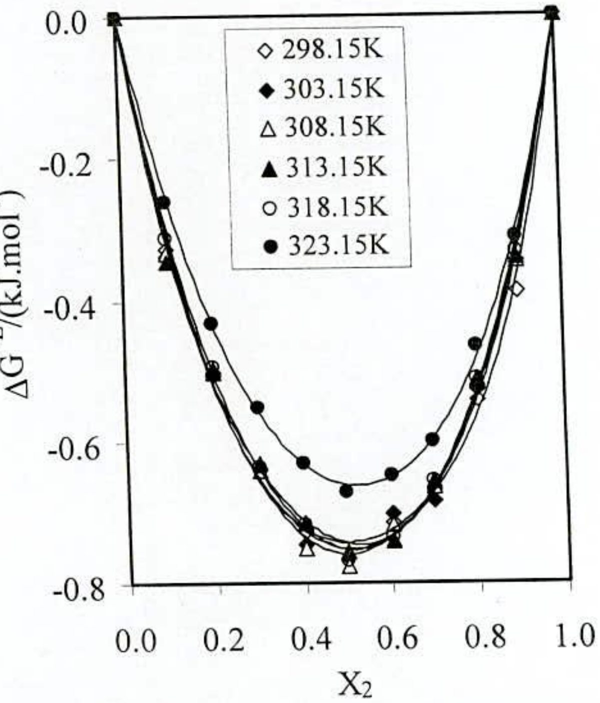

Figure 4.100: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

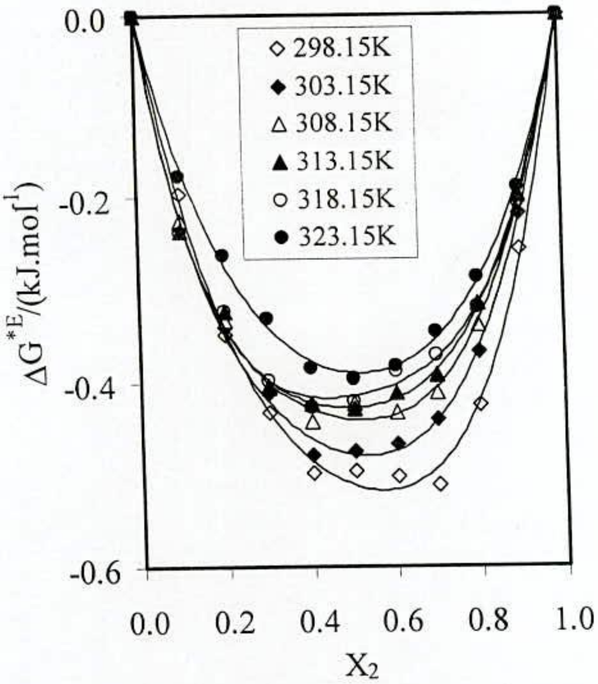

Figure 4.101: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

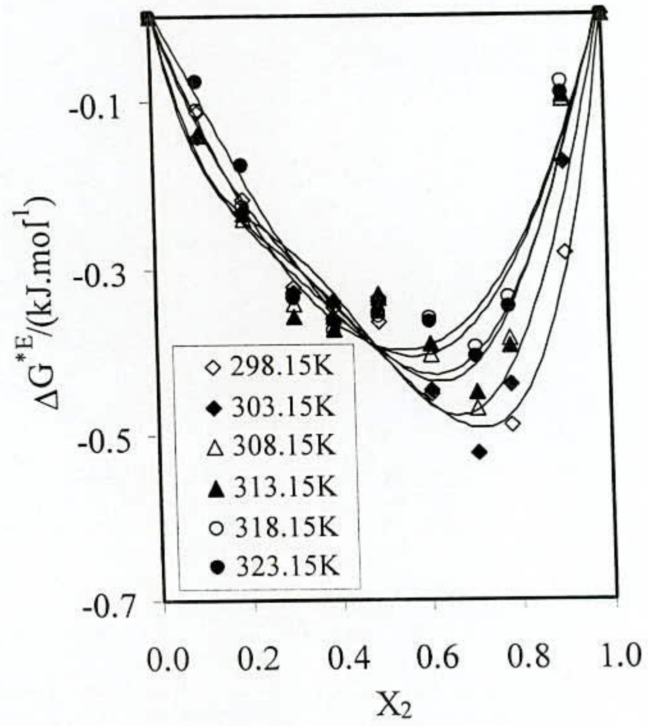

Figure 4.102: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

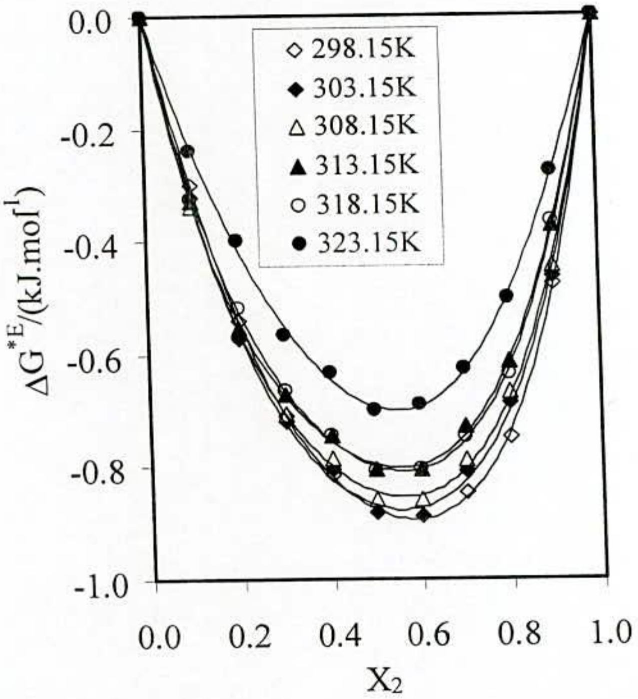

Figure 4.103: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Propanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

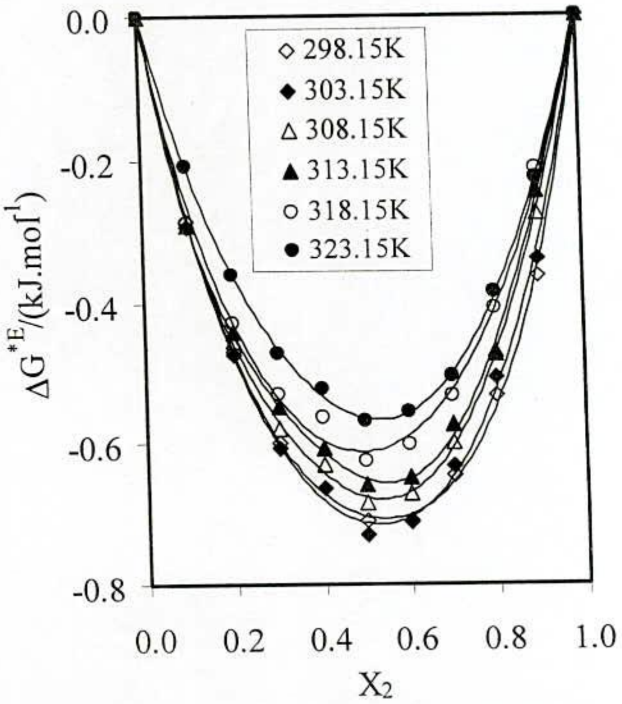

Figure 4.104: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Butanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

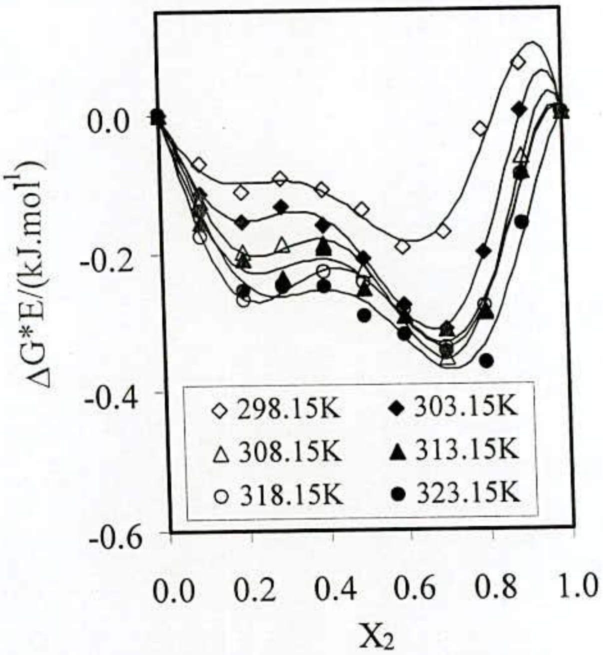

Figure 4.105: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Pentanol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

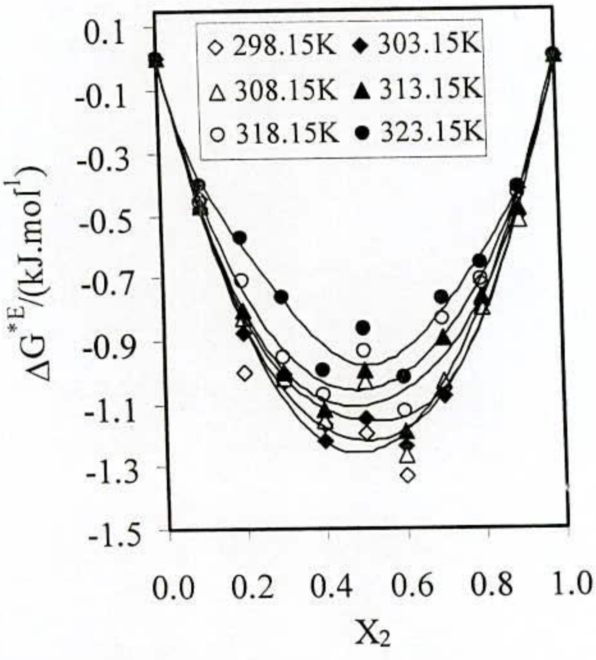

Figure 4.106: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of Propylene glycol + Acetonitrile system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

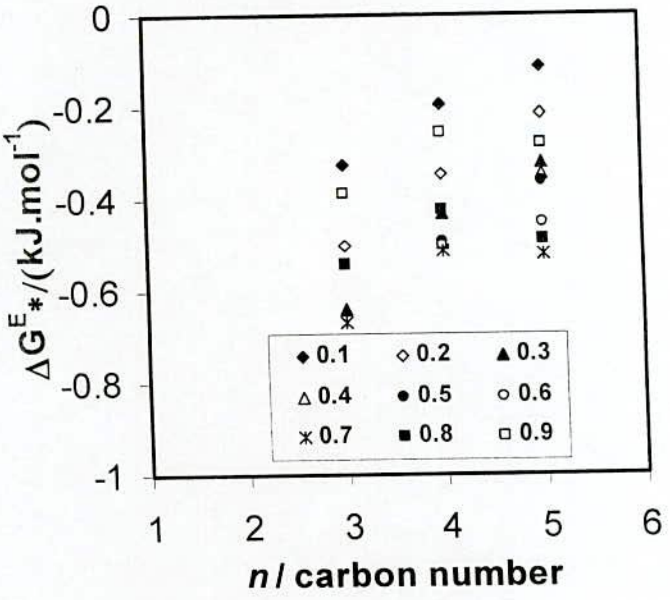

Figure 4.107: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different mole fraction at 298.15K.

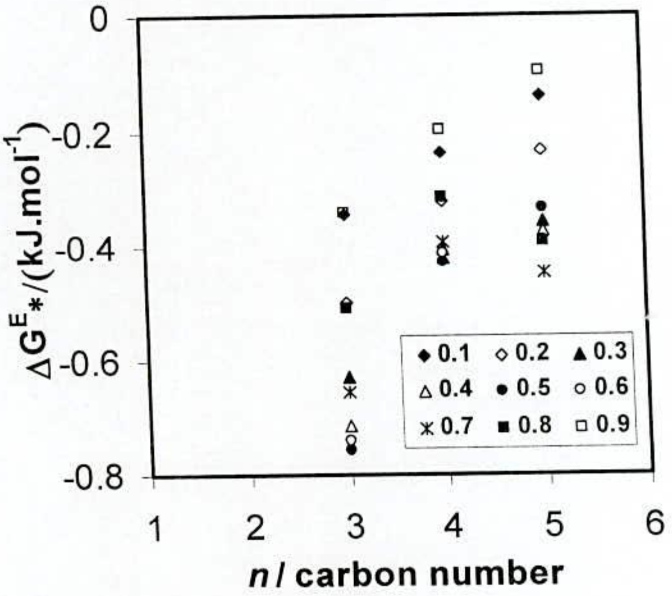

Figure 4.108: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different mole fraction at 313.15K.

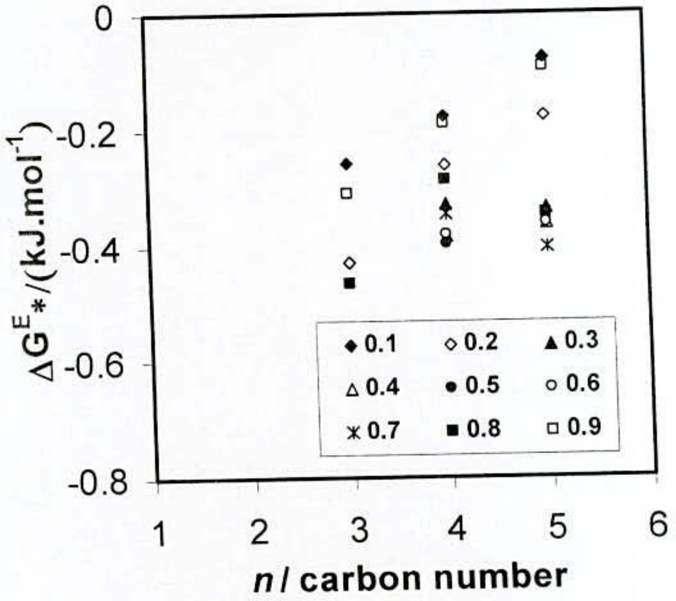

Figure 4.109: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different mole fraction at 323.15K.

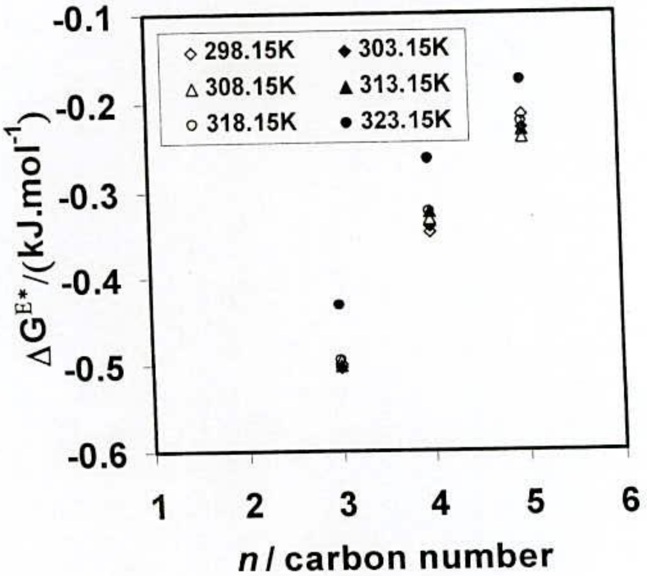

Figure 4.110: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different temperature at 0.2 mole fraction.

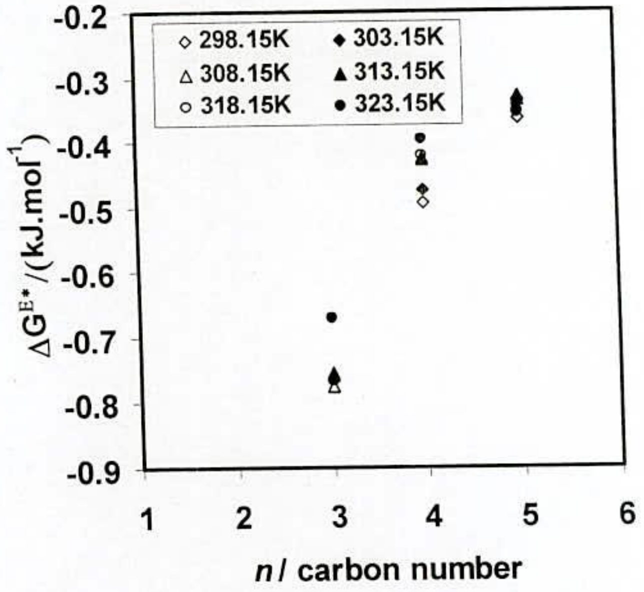

Figure 4.111: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different temperature at 0.5 mole fraction.

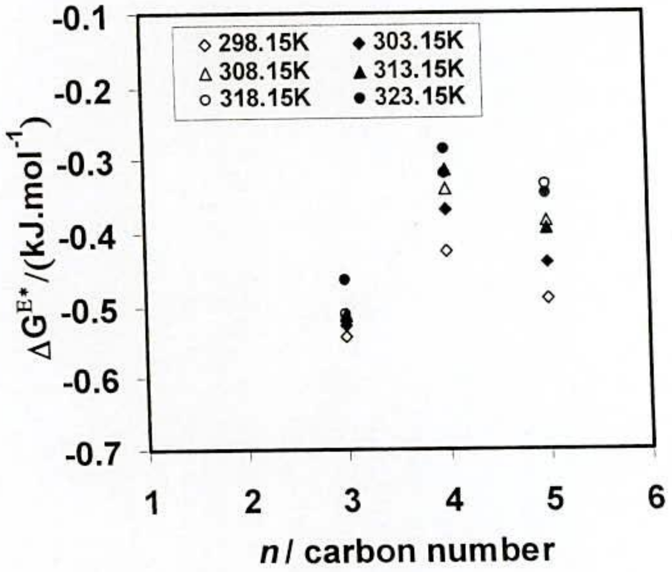

Figure 4.112: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of alcohols with different temperature at 0.8 mole fraction.

CHAPTER V

Conclusion

The studies presented in this thesis are based on simple binary (alcohols+acetonitrile) systems. The studies on the solution properties of binary mixtures of *n*-Propanol + acetonitrile, *iso*-Propanol + acetonitrile, *n*-Butanol + acetonitrile, *iso*-Butanol + acetonitrile, n-Pentanol + acetonitrile, *iso*-Pentanol + acetonitrile and Propylene glycol + acetonitrile show strong solute–solvent interactions. The values of V^E for the studied alcohols are positive throughout the whole range of composition at all the studied temperature. The observed values of V^E for the mixtures have been explained in terms of specific intermolecular interactions and structural contributions.

The viscosities increase initially slowly up to ~0.6 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol and later on, the viscosity increases sharply until that of pure alcohol is reached specially at lower temperature. The excess viscosity, η^E values are found to be negative, indicating that the acetonitrile solutions of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.6-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, iso-pentanol and Propylene glycol. The interaction parameters, ε have been found to be negative and quite large in magnitude for all the systems. The negative ε of all the studied alcohols indicate that dispersion force is occurred.

The positive V^E, negative η^E, and negative ε for the Acetonitrile + studied alcohols or glycol systems show agreement with the statements. On addition of alkanols in acetonitrile solution strong disruptive forces are appeared and H-bonding in alkanols is dissociated causing volume expansion is occurred. For the long chain or branched chain alkanols, maximum geometrical mismatch for the steric factor are occurred causing volume expansion is also seen. The volumetric properties are fully consistent with the viscometric properties.

The free energy, ΔG^{*} is found to be positive in magnitude indicating that the kinetic species involved in forming cavities or holes in liquid is given by the work required in forming the hole against surface tension of the solution.

For n-Propanol, iso-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol, *iso*-Pentanol and Propylene glycol in Acetonitrile systems, ΔG^{*E} are negative over the entire composition range. The negative excess free energy, ΔG^{*E} indicates the presence of dispersion force, whereas positive excess free energy, ΔG^{*E} suggests a specific association in the mixtures.

The entropy change, ΔS^{*} is found to be negative for all the studied alcohol systems. The negative ΔS^{*} apparently indicates more ordered orientation of the complexes formed in the activated state and thereby reduce their motional degrees of freedom.

The enthalpy change, ΔH^{*} is positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process.

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