Studies on Volumetric and Viscometric Properties of Nitrobenzene and Alkanols Mixtures

by

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Declaration

This is to certify that the thesis work entitled "**Studies on Volumetric and Viscometric Properties of Nitrobenzene and Alkanols Mixtures**" has been carried out by **A.K.M Nasimul Islam** 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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A.K.M Nasimul Islam

ABSTRACT

Densities and viscosities of binary mixtures of Ethanol + Nitrobenzene (NB), *n*-Propanol + Nitrobenzene (NB), *iso*-Propanol + Nitrobenzene(NB), *n*-Butanol + Nitrobenzene (NB), *iso*-Butanol + Nitrobenzene (NB), n-Amyl alcohol + Nitrobenzene (NB), *iso*-Amyl alcohol + Nitrobenzene (NB) and Propylene glycol + Nitrobenzene (NB) have been studied over the entire range of composition ($0 < x_2 < 1$) at 298.15- 323.15K with an interval of 5K. The density of alcohols in pure state was found to be in the order of

Propylene glycol > n-Amyl alcohol > n-Butanol > n-Propanol > Ethanol

and

iso-Amyl alcohol > iso-Butanol > iso-Propanol

The values of densities of Alkanols + NB at equi-mole fraction systems has been found to be in the order of

Ethanol+NB > *n*-Propanol+NB > *n*-Butanol+NB > n-Amyl alcohol+NB > Propylene gylcol+NB

and

iso-Propanol+NB > *iso*-Butanol+NB > iso-Amyl alcohol+NB

The value of density of Alkanols in NB decreases with the increasing of composition of the Alkanols. The decrease of density with composition of Alkanols can be attributed to solute-solvent interaction. The densities of all Alkanols in pure state increase with the increasing of carbon number which may depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. 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. At the 0.5 mole fraction, the density of Ethanol+NB is higher than other higher chain or branched chain Alkanols indicating that the nature of association of NB mostly disrupted in higher or branched chain Alkanols.

The excess molar volume, V^E for all the systems are positive over the entire range of composition, showing maxima at 0.5-0.8 mole fraction of Alkanols. The values of maxima of V^E of Alkanols in NB solutions was found to be in the order of

Propylene glycol+NB > n-Amyl alcohol+NB > *n*-Butanol+NB > *n*-Propanol+NB > Ethanol+NB

and

iso-Amyl alcohol+NB > iso-Butanol+NB > iso-Propanol+NB

and

iso-Amyl alcohol+NB > *n*-Amyl alcohol+NB and *iso*-Butanol+NB > *n*-Butanol+NB and *iso*-Propanol+NB > *n*-Propanol+NB

The increasing of V^E with carbon chain length of Alkanols may be related to increase of the size of Alkanols. The values of V^E for the studied Alkanols 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 Alkanols + NB mixtures at six different temperatures have also been determined. The viscosities decrease initially slowly up to ~0.5-0.8 mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol and later on, the viscosity increases sharply until the pure alcohol is reached. The viscosity of NB + Alkanols mixture at 0.5 mole fraction has been found to be in the order of

Propylene glycol + NB > n-Amyl alcohol+ NB > *n*-Butanol >*n*-Propanol+ NB > Ethanol+ NB

and

iso-Amyl alcohol+ NB > iso-Butanol + NB > iso-Propanol+ NB

and

iso- Amyl alcohol + NB > *n*- Amyl alcohol + NB and *iso*-Butanol + NB > *n*-Butanol + NB and *iso*-Propanol + NB > *n*-Propanol + NB

There is a marked decrease in the viscosity with increase of temperature for all the studied alcohols. This ascribed that the Alkanols + NB solutions are less stable at higher temperature. The increasing of viscosity with carbon number of Alkanols or branched chain Alkanols ascribed that the solution resistance increases with the increase of carbon chain length or branched chain. The linear dependence of $\ln\eta$ against 1/T shows for the all studied Alkanols + NB mixtures. 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 Alkanols + NB system 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 fractions. The negative excess viscosity, η^E of all the studied Alkanols + NB 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+NB > n-Amyl alcohol+NB > *n*-Butanol+NB > *n*-Propanol+NB > Ethanol+NB

and

iso-Amyl alcohol+NB > iso-Butanol+NB > iso-Propanol+NB

and

iso-Amyl alcohol+NB > *n*- Amyl alcohol+NB and *iso*-Butanol+NB > *n*-Butanol+NB and *iso*-Propanol+NB > *n*-Propanol+NB

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 interaction parameter (ε) for the studied Alkanols + NB 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.

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 Alkanols+ NB solution is dominant. The ΔH^* values are positive for all the systems indicate that positive work has to be done to overcome the energy barrier for the flow process. The ΔS^* values are found to be very small for all the studied systems indicating that the effects of ΔS^* are negligible. The excess properties (V^E, η^E, ΔG^{*E}) data have been fitted by the least square method to the four parameters 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 liquids resemble gases in their lack of rigidity neither of the two offers permanent resistance to a shearing stress. On the other hand, solids possess a definite geometrical form and offer appreciable resistance to the shearing stress. Therefore, liquid state is an intermediate state between solid and gaseous states, recollects some properties of both the gaseous and solid states. The liquid state can not be effectively defined as the gaseous and the solid states. The macroscopic property of liquids differs from liquid to liquid due to representative intermolecular interactions. The characteristics of multi-component mixtures, on account of molecular connections between dissimilar molecules, become still more challenging to clarify. In view of these facts there are severe complications in design of any general theory of solution (1-3).

It would be possible to calculate theoretically, the properties of solution from the properties of individual components. But there are intrinsic complications generated by liquid state that is not accurately understood. The theoretical behaviors, consequently, 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 suitable to determine experimentally the values of certain macroscopic properties of solutions for proper understanding of the structure of the solution. Some of the experimentally determined macroscopic properties are: density, viscosity, surface tension, etc., which are readily measurable. Experimentally determination of various thermodynamic properties, such as density, viscosity etc. on solutions, undertake significant importance since it is possible to draw conclusions regarding characteristic molecular interactions between constituent molecules of the components (1-5).

The theoretical behaviors need to assume some model for carrying out statistical-mechanical calculations of these properties. The observed inconsistencies 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 basically 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 IR 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 Alcohols with Nitrobenzene in studying the liquid-liquid interaction in binary systems.

1.2 Properties of alcohols

Alcohol is an organic compound in which a hydroxyl group (-OH) is bound to a carbon atom of an alkyl or substituted alkyl group. It is composed of carbon, oxygen and hydrogen and the general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$ where n=1, 2, 3 etc. The properties of any given aliphatic alcohol depend on the nature of the alkyl group in the molecule and on the properties of the hydroxyl group. 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 (9).

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 $78\,^0C$ whereas Propane (MW 44) has boiling point of $-42\,^0C$. 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.

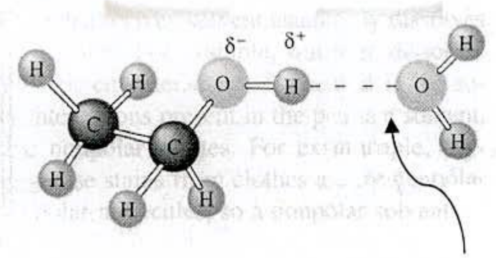

Fig. 1.1

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 Nitrobenzene

Nitrobenzene is an organic compound with the chemical formula $C_6H_5NO_2$. It is a water-insoluble pale yellow oil with an almond-like odor. It freezes to give greenish-yellow crystals. It is produced on a large scale from benzene as a precursor to aniline. In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents. Nitrobenzene is also used to mask unpleasant odors in shoe and floor polishes, leather dressings, paint solvents fuel or fuel additives, and other materials. Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps. A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) (Mannsville 1991). Nitrobenzene is also used in Kerr cells, as it has an unusually large Kerr constant.(10).

1.4 Alcohols Nitrobenzene interactions

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 $-NO_2$ with alcohols, amino acids and their derivatives are of interest. The correlation between solute -solvent interaction is complex (11-21). Nitrobenzene is a dipolar aprotic solvent having an electron-withdrawing tendency. Alkanols are protic, associated solvents. Strong interactions may exist between the hydroxyl group of an Alkanol and the $-NO_2$ group of Nitrobenzene.

In view of the fact that the interactions occurring between Alcohols and Nitrobenzene are different, it would be worthwhile to explore the effect of changing the solvent medium on molecular interactions. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure (16-26). 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 amide solvent on the thermodynamic properties of the Alcohol (16). Zegers and Somsen (27) reported the volumetric properties of binary Alkanols mixtures. In order to give a better description of the solvation of DMF by water and by Alcohol molecules volumetric properties in the ternary mixtures were reported (28-30). The excess molar volumes and viscosity for the ternary mixtures of Alkanols were reported (24-26). Several empirical expressions are used to correlate the ternary excess molar volumes from experimental results on the constituent binaries. In order to obtain some information about the correlation between alcohols + amide interactions with amide solvation, a pseudo binary mixture approach was proposed (28-30). The partial molar volumes of Alkanols at infinite dilution in the mixed solvent at several fixed compositions were evaluated and correlated with the composition of the mixed solvent (27).

Alkanols mixtures has wide application as oxygenated fuels, cosmetics, Pharmaceuticals, electrochemical solvents etc., therefore, several authors reported Ethanol, Propanols, Butanols and Pentanols with different mixtures (31-35).

Nitrobenzene is used as shoe and floor polishes, leather dressings, paint solvents, and other materials. It can also be used as fuel or fuel additives. Some authors (36-39) studied the volumetric and viscometric properties of Nitrobenzene with different solvents.

Alcohols are self-associated liquids through H-bonding. Alcohols possess hydrophilic -OH group as well as hydrophobic group. Nitrobenzene is a dipolar aprotic solvent. The mode of interaction of these two groups towards Nitrobenzene is seems to be different. Alkanols mixtures has wide application in different areas such as oxygenated fuel, cosmetics, pharmaceuticals, electrochemical solvents etc., therefore, it demand detail studies of alkanols in the presence of other mixtures.

In the present investigations, (i) densities and excess molar volumes, (ii) viscosities, excess viscosities and interaction parameters and iii) thermodynamic parameters ($\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$), and excess thermodynamic parameters ($\Delta G^{E\#}$, $\Delta H^{E\#}$, $\Delta S^{E\#}$) of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol with Nitrobenzene at six different temperatures (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K) have been determined. Although in this study, out of eight binary systems few systems are common with Nikam et al reported system at only two temperatures (298.15 and 303.15K) (40). Rest of our studied systems, almost all conditions & parameters i.e. mole fraction, temperature, excess viscosity, interaction parameters, thermodynamic parameters etc. are different from the reported system (40). A noticeable question also raised from their research (40) that both the excess molar volume, V^E and viscosity deviation, $\Delta\eta$ of studied Alkanols in Nitrobenzene mixtures are negative. The negative viscosity deviation, $\Delta\eta$ generally indicate the dissociation of components through steric hindrance or dispersive forces. If the dispersion force or steric hindrance is predominant, the excess molar volume, V^E will be positive. The negative V^E and $\Delta\eta$ of their studied systems seems to depart from general solution structure trend. To clarify this anomalous behavior, further study is necessary. Considering these above issues, we have chosen these systems for the study.

1.5 The object of the present work

The progresses 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. 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 (41-45). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, (46-50) 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-Nitrobenzene solutions are of practical importance. Nitrobenzene is a dipolar aprotic solvent having an electron-withdrawing tendency. Alkanols are protic, associated solvents. Interactions may exist between the hydroxyl group of an Alkanols and the $-NO_2$ group of Nitrobenzene.

A few papers have been published on density and viscosity of mixtures of Nitrobenzene with Alkanols (40). They studied the density and viscosity of the mixtures at low temperature considering limited parameters. However, Alkanols mixtures has wide application as oxygenated fuel, cosmetics, electrochemical solvents etc., therefore, it demands detail studies of Alkanols in the presence of other mixtures. Considering these, we have chosen these systems for the study. In order to understand the issue of solution structure of Alcohols-Nitrobenzene systems a theoretical and experimental aspect of interactions in terms of excess molar volume, viscosity, excess viscosity and 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 Nitrobenzene and Alkanols in different compositions and different temperatures.

(ii) to understand the effect of Nitrobenzenes on Alkanols 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, interaction parameter, thermodynamic parameters data of Nitrobenzenes + some Alkanols 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

Physical properties of a substance depend on the intermolecular forces which originate in the internal structure or the constitution of the molecule. Thus the determination of properties such as viscosity, surface tension, refractive index etc. can give valuable information about the structure of molecules. In the modern times the molecular spectra of substances recorded by spectroscopic techniques have proved extremely helpful in elucidating the structure of organic molecules (51).

(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,

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

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

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 $\mathrm{molL^{-1}}$ (51).

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 (51). Mathematically,

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

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

$$\text{or, } \mathrm{m} = \frac{\frac{\mathrm{a}}{\mathrm{M_2}} \times 1000}{\mathrm{V_1} \times \rho_0}$$

$$\text{or, } \mathrm{m} = \frac{\mathrm{a}}{\mathrm{M_2}} \times \frac{1000}{\mathrm{V_1} \times \rho_0} \quad \text{..(2.2)}$$

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}

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

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

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 (52)

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

where, V is the volume of solution containing n_1 moles of solvent and n_2 moles of solute and $\overline{V}_1^0$ is the molal volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molar volume (φ_v) of an electrolyte in an aqueous solution is given by (52),

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

where, $V = \frac{n_1M_1 + n_2M_2}{\rho}$ and

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molal concentration, $n_2 = m$, the molality and $n_1 = 55.51$, the number of moles of solvent in 1000g of solvent (water), the equation for apparent molal volume takes the form (53, 54),

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

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

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

where, ρ_0 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 (55):

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

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 (55).

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:

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

Similarly for component 2,

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

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,

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

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

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

The partial molar volumes of solute and solvent can be derived using the equation 2.5 as follows (56):

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

and,

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

For solutions of simple electrolytes, the apparent molar volumes (φ_v) vary linearly with √m, even upto moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (52):

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

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

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

and

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

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

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

and

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

For Equation 2.18 and 2.20, it follows that at infinite dilution, (m or c → 0), the partial molar volume and the apprant molar volume are identical. To obtain reliable φ_v values, it is necessary to measure the density ρ, with graet precision because errors in contribute, considerably to the uncertainties φ_v.

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

$$V^0 = \frac{M}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.22)$$

The mixture molar volume is,

$$V_{mix} = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} \quad \text{................................(2.23)}$$

and the ideal molar volume of this system is given by

$$\text{or, } V_{ideal} = \frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2} \quad \text{............................(2.24)}$$

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

$$V^E = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \quad \text{...(2.25)}$$

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,

$$V^E/\mathrm{cm^3mol^{-1}} = X_1X_2\sum_{i=0}^{n} \mathrm{a_i}(1\text{-}2X_1)^{\mathrm{i}} \quad \text{..(2.26)}$$

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 $$f = \eta A \frac{dv}{dx} \qquad \text{...(2.27)}$$

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.

$$\phi = \frac{1}{\eta} \qquad \text{...(2.28)}$$

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 (57). 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 (57):

$$\eta = \frac{\pi \Pr^4 t}{8lV} \qquad \text{...(2.29)}$$

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,

$$\eta = \frac{\pi \mathrm{P} r^4 t}{8lv} - \frac{\rho V}{8\pi l t} \qquad \text{.....(2.30)}$$

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 (2.29) becomes,

$$\eta = \frac{\pi h \rho g r^4 t}{8vl} \qquad \text{.....(2.31)}$$

For a particular viscometer h, l, r and V are fixed, so the equation (2.31) becomes,

$$\eta = A\rho t \qquad \text{.....(2.32)}$$

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

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

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

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 (2.27), 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.

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

Where 'A' and 'E' are constants for the given liquid. It follows from equation (2.35) 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 2.35.

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,

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

$$\text{or } \eta_{id} = \exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \quad \text{...(2.36)}$$

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

$$\eta^E = \eta_{expt.} - \eta_{id} \quad \text{..(2.37)}$$

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

$$\eta^E = X_1X_2 \sum_{i=0}^{n} a_i(1-2X_1)^i \qquad (2.38)$$

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 (58),

$$\varepsilon = \frac{\ln \eta_{\mathrm{expt}} - \ln \eta_{id}}{X_1X_2} \qquad (2.39)$$

Where , ε = Interaction parameter.

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

η_{id} = calculated viscosity

$$=\exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \qquad (2.40)$$

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

$$\eta = \frac{hN}{V_m} e^{\Delta G^* / RT} \qquad \text{.....(2.41)}$$

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 (60):

$$\Delta G^* = RT \ln \left(\frac{\eta V_m}{Nh} \right) \qquad \text{.....(2.42)}$$

The experimental term in equation 2.42 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 (59):

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

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

or, $\ln\frac{\eta V_m}{Nh} = \frac{\Delta G^*}{RT}$ ……………………………………………………………(2.43)

Since,

$\Delta G^* = \Delta H^* - T\Delta S^*$ ……………………………………………………………(2.44)

The Eyring equation takes the form,

$\ln\frac{\eta V_m}{Nh} = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}$ ……………………………………………………………(2.45)

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,

$\Delta H^* = \text{slope} \times R$ ……………………………………………………………(2.46)

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

$\Delta S^* = -\text{ intercept} \times R$ ……………………………………………………………(2.47)

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 :

$$\mathrm{PROP}^E = X_1(1-X_1)\sum_{i=0}^{3} a_i(2X_1-1)^i \quad \ldots\ldots(2.48)$$

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:

$$SD = \left[\frac{\Sigma(PROP^E_{\exp} - PROP^E_{calcd})^2}{n-p-2}\right]^{1/2} \qquad \text{..(2.49)}$$

Where, $PROP^E_{exp}$ = 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 Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Amyl alcohol, iso-Amyl alcohol, Propylene glycol and Nitrobenzene. 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%	E. MERCK India
n-Propanol	$CH_3CH_2CH_2OH$	60.10	99%	MERCK Germany
iso-Propanol	$(CH_3)_2CHOH$	60.10	99%	BDH, England
n-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	99.5%	Scharlau Chemie S.A, Spain
iso-Butanol	$(CH_3)_2CHCH_2OH$	74.12	99%	E. MERCK India
n-Amyl alcohol	$C_5H_{11}OH$	88.15	99 %	MERCK Germany
iso-Amyl alcohol	$C_5H_{11}OH$	88.15	99 %	E. MERCK India
Propylene glycol	C_3H_8O $(CH_3CHOHCH_2OH)$	76.10	99 %	MERCK Germany
Nitrobenzene	$C_6H_5NO_2$	123.06	99 %	LOBA Chemical, India

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 in Nitrobenzene 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^{0}C 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.

$$V^E = \frac{X_1M_1 + X_2M_2}{\rho_{mix}} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \text{...(3.2)}$$

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,

$$V^E = X_1X_2\sum_{i=0}^{n} a_i(1-2X_1)^i \text{...(3.3)}$$

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,

$$\eta = A\rho t \quad \text{...(3.4)}$$

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:

$$\eta^E = \eta_{\text{expt.}} - \eta_{id} \quad \text{...(3.5)}$$

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

$$\ln \eta_{id} = X_1 \ln \eta_1 + X_2 \ln \eta_2 \quad \text{..(3.6)}$$

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

$$\eta^E = X_1 X_2 \sum_{i=0}^{n} a_i(1-2X_1)^i \quad \text{..(3.7)}$$

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.

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 (58),

$$\varepsilon = \frac{\ln \eta_{exptl} - \ln \eta_{id}}{X_1 X_2} \quad \text{..(3.8)}$$

Where, ε = Interaction parameter.

$\eta_{expt.}$ = 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 (60) equation:

$$\Delta G^* = RT \ln \left(\frac{\eta V_m}{Nh}\right) \quad \text{.. (3.9)}$$

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

V_m = Average molar volume of solution (m_l^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 (59):

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

$$\text{or,} \quad \text{In}\ \frac{\eta V_m}{Nh} = \frac{\Delta G^*}{RT} \quad \ldots\ldots(3.10)$$

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

$$\therefore \ln\left(\frac{\eta V_m}{Nh}\right) = \frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R} \quad \ldots\ldots(3.11)$$

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,

$$\Delta H^* = \text{slope} \times R \quad \ldots\ldots(3.12)$$

and

$$\Delta S^* = \text{-intercept} \times R \quad \ldots\ldots(3.13)$$

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

$$\Delta H^{*E} = \Delta H^* - (X_1\Delta H_1^* + X_2\Delta H_2^*) \quad \ldots\ldots(3.14)$$

$$\Delta S^{*E} = \Delta S^* - (X_1\ \Delta S_1^* + X_2\Delta S_2^*) \quad \ldots\ldots(3.15)$$

and

$$\Delta G^{*E} = \Delta G^* - (X_1\Delta G_1^* + X_2\Delta G_2^*) \quad \ldots\ldots(3.16)$$

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:

$$\mathrm{PROP}^E = X_1(1-X_1)\sum_{i=0}^{3} a_i(2X_1-1)^i \quad \text{...(3.17)}$$

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:

$$\mathrm{SD} = \left[\frac{\Sigma(PROP^E_{\mathrm{exp}} - PROP^E_{calcd})^2}{n-p-2}\right]^{1/2} \quad \text{.......................................(3.18)}$$

Where,

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

$\mathrm{PROP}^E_{\mathrm{calcd}}$ = 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. Ethanol+Nitrobenzene
2. *n*-Propanol+Nitrobenzene
3. *iso*-Propanol+Nitrobenzene
4. *n*-Butanol+Nitrobenzene
5. *iso*-Butanol+Nitrobenzene
6. n-Amyl alcohol+Nitrobenzene
7. *iso*-Amyl alcohol+Nitrobenzene
8. Propylene glycol+ Nitrobenzene

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 Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, iso-Amyl alcohol and Propylene glycol in Nitrobenzene (NB) systems were determined at temperatures 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K 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 4.2-4.9 at different temperatures. Figure 4.1- 4.8 shows the plots of densities as a function of mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in Nitrobenzene (NB) systems. In all the studied system, it shows that density decrease almost linearly with composition of alcohols except Propylene glycol. Density value decreases with increase in the temperature. The experimental density values in pure state of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Amyl alcohol, *iso*-Amyl alcohol, Propylene glycol and Nitrobenzene at 298.15K are 0.785683, 0.799695, 0.794580, 0.806262, 0.805908, 0.811181, 0.813120, 1.036698 and 1.198495 g.cm^{-3} respectively.

The density of *n*-Alkanols of pure solution were found to be order of

n-Amyl alcohol l > *n*-Butanol > *n*-Propanol

The density of *iso*-Alkanols of pure solution were found to be order of

iso-Amyl alcohol > *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 depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. As the densities of pure Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol are lower than that of pure Nitrobenzene (NB), with the increase of composition of alcohol, the density of alcohols + NB system decreases and eventually proceeds towards the density of pure alcohol. Decrease 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 (61, 62).

Mixing of alcohols with NB will induce changes in dipolar interactions. On addition of alcohols to the NB solutions the self association of NB will be disrupted partly or fully and new dipolar interactions between NB 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 NB solution, the free volume in the solution increased gradually and the density decreased progressively. The dependences of the density with carbon chain length of alcohols with different composition at a fixed temperature are plotted in Figures 4.9-4.11. From the figures, it is seen that at the same temperature, the density slightly decrease with the carbon chain length of the alcohols at lower composition of alcohols. But in pure state of alcohols, the density increase with the carbon chain length. The dependences of the density with carbon chain length of alcohols with different temperatures at a fixed mole fraction are plotted Figures 4.12-4.13. It is seen that at the 0.5 mole fraction of alcohols, the density decreases with the carbon chain length of alcohols. But in 1.0 mole fraction of alcohols, the density increases 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 of mass of the alcohols and the degree of solute-solvent interactions with carbon number.

The variation of density, ρ with temperature for n-Alkanols are shown in Figures 4.19-4.22 and iso-Alkanols in Figures 4.23-4.26 at different mole fractions. It is seen that density, ρ decrease linearly with increasing temperature for all alcohols. This is due to the increase of thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding are occurred. The linear dependence of $\ln\rho$ verses 1/T are plotted in Figures 4.27-4.30 for n-Alkanols and Figures 4.31-4.34 for iso-Alkanols.

The values of densities of alcohols + NB at 0.5 mole fraction systems has been found to be in the order of,

Ethanol+NB > *n*-Propanol+NB > *n*-Butanol+NB > n-Amyl alcohol+NB > Propylene gylcol+NB

and

iso-Propanol+NB > *iso*-Butanol+NB > iso-Amyl alcohol+NB

At the 0.5 mole fraction, the density of n-Amyl alcohol+NB is higher than Propylene glycol+ NB, *n*-Butanol + NB is higher than n-Amyl alcohol+ NB, *n*-Propanol + NB is higher than *n*-Butanol + NB and similarly *iso*-Butanol + NB is higher than iso-Amyl alcohol +NB and *iso*-Propanol + NB is higher than iso-Butanol+NB indicates that the nature of association of NB mostly disrupted in higher or branched chain alcohols.

The excess molar volume, V^E of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, iso-Amyl alcohol and Propylene glycol in NB systems have been calculated from density data of these systems using equation 3.2. The values of V^E at different temperatures have been shown in Table 4.2-4.9. For V^E the fitting coefficients (a_i) are shown in Table 4.34 along with standard deviations. Figure 4.35- 4.42 shows the plots of excess molar volume as a function of mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in NB systems.

Examination of Figures 4.35-4.42 reveals that

(i) At low composition of Alkanols in NB, 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 Alkanols + NB 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 Alkanols + NB system, the maxima appear at ~ 0.4-0.6 mole fraction of alkanols.

(vi) The excess molar volumes, V^E of Alkanols + NB systems has been found to be in the order of,

Propylene glycol+NB > n-Amyl alcohol+NB > *n*-Butanol+NB > *n*-Propanol+NB > Ethanol+NB

and

iso-Amyl alcohol+NB > *iso*-Butanol+NB > *iso*-Propanol+NB

and

iso-Amyl alcohol+NB > n-Amyl alcohol+NB

and

iso-Butanol+NB > *n*-Butanol+NB

and

iso-Propanol+NB > *n*-Propanol+NB

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

Similar behaviors were found in Alkanols + m-xylene (63) and alkanols+acetonitrile systems (64) where excess molar volumes were positive in the whole range of composition. On the other hand, unlike behaviors were found in Alkanols + dimethylformamide systems (65) and Alkanols + aqueous SDS systems (66), where the excess molar volumes, V^E were found to be negative. This indicates that the mode of interactions of alcohols with NB 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.

Mixing of NB with an alcohol will induce changes in hydrogen bonding (in the alkanols) and dipolar interactions (in the NB). On addition of alcohol to the NB the self association will be disrupted partly or fully and new dispersion force or dipolar interactions or H-bonds between alcohol and NB may be appeared. At the same time, segmental inclusion of small alcohols into the vacant spaces left in the structural network of alcohol may also occur. In NB 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 NB+ Alkanols.

The dependence of excess molar volume with carbon number of n-Alkanols alcohols with different composition at a fixed temperature are plotted in Figures 4.43-4.45 and iso-Alkanols in Figures 4.46-4.48. The dependence of excess molar volume with carbon number of n-Alkanols with different temperature at a fixed composition are plotted in Figures 4.49-4.51 and iso-Alkanols 4.52-4.54. From the figures it can be seen that at the same temperature and mole fraction, the excess molar volume increases with carbon number. 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-Amyl alcohol and *iso*-Amyl alcohol 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 (67, 68) studied the excess molar volume of binary solvent mixtures of N,N-diethylmethane sulfonamide with aliphatic alcohols. Garcia et al. (69) carried out volumetric and viscometric measurements on binary liquid mixtures of 2-pyrrolidone with 1-alkanols. Rauf et al. (70) 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 NB + Alkanols (C2–C5) binary mixtures are in conformity with the results of these reported investigations.

The dependence of excess molar volume with temperature of n-Alkanols are shown in Figures 4.55-4.57 and iso-Alkanols shown in 4.58-4.60. 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 (71, 72) and hence excess molar volume increases.

The observed V^E of all the studied Alcohols + NB mixtures may be discussed above which may be arbitrarily divided into physical, chemical and geometrical contributions (70, 73). 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,
3. Steric hindrance and
4. 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 (74). 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 1.69 D, 1.68 D, 1.66 D, 1.66 D, 1.71 D, 1.70 D, 1.70 D, 2.27 D and 3.95 D for Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Amyl alcohol, iso-Amyl alcohol, Propylene glycol and NB respectively (75).

Therefore, it has the possibility of the formation of hydrogen bonding through the polar group of the Alkanols and NB 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 (70, 74). 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 Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, iso-Amyl alcohol, Propylene glycol and NB at 298.15K are 57.43, 75.15, 76.95, 92.38, 92.88, 108.67, 108.60, 73.4 and 102.67 cm^3mol^{-1} respectively. This shows that a quite large size difference between C2-C4 Alkanols and NB molecules. The Ethanol and Propanol molecules, being smaller there is possibility of partial accommodation of these molecules in the interstices of the NB molecule.

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 NB dispersion force with overall raise of space. After attaining the maxima further addition of alkanols, NB 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 NB and Ethanol & Propanols are quite large so the possibility of partial accommodation of Ethanol and Propanols in the interstices of NB is high but the possibility of making H-bonding cluster for Ethanol and Propanols is higher than the other studied alcohols owing to its lower steric hindrance and hence V^E becomes low. In contrast, the possibility of making H-bonding cluster for Amyl alcohols is lower than other studied alcohols owing to higher steric hindrance and hence V^E become high. For the increase of temperature (Figure 4.53-4.58), 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 (76).

In the case of isomers of *n*-Amyl alcohol and *iso*-Amyl alcohol, *n*-Butanol and *iso*-Butanol and *n*-Propanol and *iso*-Propanol , the V^E becomes higher for branched chain alcohols (*iso*-Amyl alcohol, *iso*-Butanol and *iso*-Propanol) than linear chain alcohols (*n*-Amyl alcohol *n*-Butanol and *n*-Propanol) throughout the whole composition range. The strength of the intermolecular hydrogen bonding through in NB and Alkanols, is not the only factor influencing the 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 NB molecules on addition of Alkanols and formation of new association between the unlike NB 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.

4.2 Viscometric properties

The viscosities, η of Ethanol, n-Propanol, iso-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in NB systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Table 4.10-4.17. The viscosities of the pure components are shown in Table 4.1 together with the literature values for Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol, Propylene glycol and NB 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 4.61-4.68. The following characteristic features of viscosity are observed:

a) The viscosities decrease upto ~ 0.8 mole fraction of Ethanol and show a minima and later on, the viscosity increases sharply until that off pure alcohol is reached.
b) The viscosities decrease slowly upto 0.6-0.7 mole fraction of n-Propanol and iso-Propanol and reaches a minimum value and then the viscosity increases sharply.
c) The viscosities decrease initially and then almost unchanged upto ~0.7 mole fraction of n-Butanol and later on the viscosity increases sharply until the pure alcohol is reached. For iso-Butanol, initially viscosity is almost unchanged, then increases slowly upto 0.9 mole fraction and later on, the viscosity increases sharply until pure alcohol is reached.
d) The change of viscosity of n-Amyl alcohol and iso-Amyl alcohol initially is almost unchanged upto 0.8 mole fraction and later on, the viscosity increases sharply until pure alcohol is reached. For Propylene glycol, the viscosity is unchanged upto ~ 0.5 mole fraction and then the viscosity increases sharply.

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

f) Viscosity decreases with rise of temperature.

The experimental viscosity values in pure state of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol, Propylene glycol and NB at 298.15K are 1.0875, 1.9672, 2.0412, 2.5557, 3.333, 3.4742, 3.6947, 37.5281 and 1.7992 mPa.S, respectively.

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

Propylene glycol> n-Amyl alcohol *n*-Butanol > *n*-Propanol> Ethanol

and

iso-Amyl alcohol > *iso*-Butanol > *iso*-Propanol >

and

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

For dilute alcoholic solutions in NB, it is believed that, alcohols which are known to exist in associated forms through H-bonding are dissociated for the interaction with NB. This explains the low viscosity of the solutions in the NB 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 n-Alkanols and iso-Alkanols with different composition at a fixed temperature are plotted in Figures 4.69-4.74. From the figures, it is seen that, at the same temperature, the viscosity increase with the carbon chain length of alcohols at the higher mole fraction of alcohols. At lower molefraction, the viscosity change is not pronounced. The dependences of the viscosity with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.75-4.78. 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 4.79-4.86. There is a marked decrease in the viscosity with increase of temperature for all the studied alcohols. At lower mole fraction (0.2 mole fraction), the viscosity values are very close to each other but at pure state or higher mole fraction the viscosity change is noticeable.

By using an empirical equation of the form,

$$\ln\eta = A + B/T$$

the linear dependence of $\ln\eta$ against 1/T shows that at different mole fraction (shown in Figures 4.87-4.94), the order of viscosity becomes Propylene glycol > n-Amyl alcohol> n-Butanol> n-Propanol>Ethanol and iso-Amyl alcohol >iso-Butanol >iso-Propanol. The above equation is fully valid for all the NB-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 (77, 78) are in good agreement with our studied isomers.

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

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

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 (NB), X_2 and η_2 are the corresponding values of component 2 (Alcohols).

The η^E values are shown in Table 4.10-4.17. 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 4.35. The variation of η^E against mole fraction of alcohol (x_2) is shown in Figures 4.95-4.102. The η^E values are found to be negative, indicating that the NB solutions of alcohols are non ideal. Figures show 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 0.6-0.8 mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol and *n*-Amyl alcohol, iso-Amyl alcohols and Propylene glycol.

ii) The position of 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 > n-Amyl alcohol > *n*-Butanol > *n*-Propanol > Ethanol

and

iso-Amyl alcohol > *iso*-Butanol > *iso*-Propanol

and

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

The excess viscosities are found to be negative for all the studied alcohol systems in NB. The negative excess viscosities (as in Figs. 4.95-4.102) for the systems in NB+ studied Alkanols indicate the dissociation of components through steric hindrance or dispersive forces.

The value of dipole moments (μ) of all alkanols are almost similar. Therefore, there is a possibility of formation of hydrogen bond by the polar group of the Alkanols and NB due to the hydrophilic effect. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols. The long chain alcohols are more hydrophobic than short chain alcohols. Andini et al. (79) showed that hydrophobic interaction varies according to hydrocarbon groups such as $CH_3CH_2>CH_3>CH_2>CH$. NB and Alkanols molecules form a maximum structural disaggregate around at the 0.6-0.8 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 NB 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 NB -Alkanols dispersion, which result in the continual increase in η^E.

The dependences of excess viscosity with carbon number of n-Alkanols and iso-Aklanols with different composition at a fixed temperature are plotted in Figure 4.103-4.108. The dependences of excess viscosity with carbon number of n-Alkanols and iso-Aklanols with different temperatures at a fixed composition are plotted in Figures 4.109-4.114. 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 or geometrical mismatch. The Figures also reveal that the systems having branched chain alkanols such as iso-Propanol, iso-Butanol, iso-Amyl alcohol 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 (80), Akhtar et al (77) and Saleh et al (81) 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 (82) 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 NB. As pointed out earlier, negative excess viscosity follow the order:

iso-Amyl alcohol ~ n-Amyl alcohol and iso-Butanol > n-Butanol and iso-Propanol > n-Propanol

and

n-Amyl alcohol > n-Butanol > n-Propanol

which in turn reflect the extent of dissociation mainly due to dispersion force. D' Aprano et al. (78) 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 Amyl alcohols, two Butanols and two Propanols isomer either by thermal effect or by the force of dispersion in NB solution should thus follow the order:

iso-Amyl alcohol>n-Amyl alcohol; 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. For iso-Amyl alcohol systems, some anomalous behavior showed for excess viscosity and excess molar volume measurement. Anomalous behavior was reported (63-66) for iso-Amyl alcohol with DMF systems.

Nikam et al. (40) reported that both the excess molar volume, V^E and viscosity deviation, $\Delta\eta$ of studied Alkanols in Nitrobenzene are negative. Our studied Alkanols system in Nitrobenzene shows excess molar volume, V^E are positive and excess viscosity, η^E are negative. The negative excess viscosities, η^E or viscosity deviation, $\Delta\eta$ indicates the dissociation of components through steric hindrance or dispersive forces. If the dispersion force or steric hindrance is predominant, the excess molar volume, V^E will be positive due to the increase of dissociated species in solution and hence the V^E will be positive. This assessment is consistent with our data. At this point the reported V^E (40) is contradictory.

From Figures 4.115-4.120 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 NB and alcohols formed. In comparison with alcohol- NB association, the NB - NB association in the structure is assumed to be more fragile to heat. Examination of excess viscosity curves of different alcohol solutions shows that $\Delta\eta^E_{min}$ varies in the order,

iso-Amyl alcohol (0.50 mPa.S) > n-Amyl alcohol (0.35 mPa.S)
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 NB - NB association around the alcohols through H-bond or dispersion force are also assumed to be thermally unstable than NB - NB association in pure NB (83, 84) that is similar to pure water. The thermal fragility of branched alcohols is higher than the linear chain alcohols.

4.2.1 Interaction parameter

The interaction parameters (ε) have been calculated by using the equation 3.8. The values of interaction parameters for different systems are shown in Figure 4.121-4.128 and the data are tabulated in Table 4.10-4.17. The values have been found to be negative and quite large in magnitude in alcohol-rich region for all the systems. 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 (85) 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 (85). 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 (86) that NB+ all the studied alcohols mixtures have strong dispersion force and geometrical effect. 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 NB+ studied Alkanols show agreement with the reported statements (87-89). On addition of Alkanols in NB 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 Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in NB solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.18-4.25. The variation of free energy (ΔG^*) at different temperatures as a function of the mole fraction of all the studied alcohols are shown in Figures 4.129-4.136. The following characteristic features of ΔG^* are observed:

i) The change of free energy (ΔG^*) decreases almost linearly with mole fraction of for Ethanol, *n*-Propanol and *iso*-Propanol upto 0.8 mole fraction, show a minima and later on the $\Delta G^\#$ increases.

ii) The $\Delta G^\#$ decreases slowly with mole fraction of n-Butanol, iso-Butanol and Propylene glycol, show a minima and then increases sharply.

iii) The $\Delta G^\#$ almost unchanged with mole fraction of n-Amyl alcohol and iso-Amyl alcohol and then increases sharply.

iv) The $\Delta G^\#$ value is positive for all the studied systems.

v) The change of free energy ($\Delta G^\#$) decreases with rise of temperature.

The experimental ΔG^* values in pure state of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol, Propylene glycol and NB at 298.15K are 12.57, 14.66, 14.76, 15.81, 16.46, 16.98, 17.13, 21.91 and 15.21 kJ.mol^{-1}, respectively. The positive free energy change ΔG^* for the studied Alkanols + NB 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 n-Alkanols and iso-Alkanols with different composition at a fixed temperature are plotted in Figure 4.137-4.142. The dependences of ΔG^* with carbon number of alcohols with different temperatures at a fixed mole fraction are plotted in Figures 4.143-4.146. From the figures it is seen that the ΔG^* increase with the carbon number of alcohols. The variation of ΔG^* with temperatures for alcohol - NB solutions are shown in Figures 4.147-4.148. It is seen that the ΔG^* slightly decreases with the increase of temperature. The linear dependence of lnΔG^* vs

1/T are plotted in Figures 4.149-4.150. The variation of lnΔG^* against 1/T is fully valid for all the alcohol- NB systems.

Excess free energy (ΔG^{*E}) change of activation for the viscous flow of the Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in NB solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.18-4.25. Figure 4.151-4.158 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 4.36. The ΔG^{*E} values are found to be negative and large in magnitude, indicating that the NB 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 different position of minima of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, iso-Amyl alcohol 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.

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 NB 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 such as iso-Propanol, iso-Butanol and iso-Amyl alcohol show slightly larger negative excess viscosity, ΔG^{*E} than their straight chain isomers with some exception. 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:

n-Amyl alcohol > n-Butanol > n-Propanol > Ethanol and

iso-Amyl alcohol > iso-Butanol > iso-Propanol

As suggested by the author (90), 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 NB and alcohol systems.

The dependences of excess free energy with carbon number of alcohols with different composition at a fixed temperature are plotted in Figures 4.159-4.164. The dependences of excess ΔG^{*E} with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.165-4.170. The difference in minima of ΔG^{*E} over the temperature range of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol-alcohol association, the NB - NB association in the cage structure is assumed to be more fragile to heat. Therefore, the effect of temperature on ΔG^{*E}, particularly in the region at or around the minima is significant (Tables 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 NB structure (91, 92) i.e The cages formed by the NB - NB association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than NB - NB association in pure NB.

Tables 4.26-4.33 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. All the other studied alkanols in NB solution systems show negative excess entropy, ΔS^{*E}. Saleh et al (63) found that n-Amyl alcohol+ n-Heptane system, excess entropies were negative in the whole range of concentration. 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 NB are supposed to have lesser interactions among themselves. 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 NB molecules are engaged by a network of structured form in pure state. Studies on viscometric properties by Kipkemboi and Easteal (93), Saleh et al. (63) and FTIR spectrophotometric studies by Gojlo et al (94) 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 NB, 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.

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}
Ethanol	298.15	0.7858	0.785683	1.0995	1.0875
	303.15	0.7813	0.781013	1.0606	0.9865
	308.15	0.7761	0.776701	0.9698	0.8884
	313.15	0.7718	0.772079	0.8661	0.8128
	318.15	0.7651	0.766749	0.7841	0.7364
	323.15	0.7605	0.763349	0.7126	0.6413
n-Propanol	298.15	0.79975	0.799695	1.967	1.9672
	303.15	0.79548	0.795573	1.713	1.7193
	308.15	0.79138	0.791441	1.537	1.5315
	313.15	0.7873	0.787419	1.378	1.3763
	318.15	-	0.783225	-	1.2347
	323.15	0.7793	0.779361	1.115	1.1148
iso-Propanol	298.15	0.78123	0.794580	2.045	2.0412
	303.15	0.7766	0.792080	1.763	1.7631
	308.15	0.77246	0.789256	1.5405	1.5401
	313.15	0.7683	0.786296	1.3143	1.3214
	318.15	0.7635	0.782808	1.191	1.1801
	323.15	0.75868	0.779508	1.002	1.0079
n-Butanol	298.15	0.806	0.806262	2.5339	2.5557
	303.15	0.8022	0.802348	2.263	2.2511
	308.15	0.79838	0.798565	1.9778	1.9785
	313.15	0.79432	0.791435	1.7556	1.7506
	318.15	0.7905	0.790339	1.5635	1.5631
	323.15	0.78578	0.785832	1.3971	1.4000
iso-Butanol	298.15	0.7982	0.805908	3.332	3.3313
	303.15	0.79431	0.802872	2.884	2.8431
	308.15	0.7902	0.800712	2.426	2.4306
	313.15	0.78612	0.797624	2.08	2.0901
	318.15	0.7822	0.794976	1.861	1.7994
	323.15	0.7778	0.791072	1.602	1.5981
n-Amyl alcohol	298.15	0.8111	0.811181	3.48	3.4742
	303.15	0.80711	0.807620	2.932	2.9816
	308.15	0.80352	0.803306	2.57	2.5707
	313.15	0.7995	0.799513	2.332	2.2704
	318.15	-	0.795075	-	1.9741
	323.15	0.7905	0.791529	1.765	1.7662
iso-Amyl alcohol	298.15	0.8097	0.813120	3.61	3.6947
	303.15	0.8069	0.811860	3.12	3.1766
	308.15	0.8027	0.807988	2.68	2.7174
	313.15	0.7972	0.804752	2.31	2.3653
	318.15	0.7928	0.801724	-	2.0951
	323.15	0.7881	0.797624	-	1.9337
Propylene glycol	298.15	1.0323	1.036698	39.436	37.5281
	303.15	1.0276	1.032285	28.852	30.1812
	308.15	1.0231	1.029217	22.267	23.6973
	313.15	1.0197	1.024924	17.136	18.5594
	318.15	1.0114	1.019732	13.844	14.5289
	323.15	1.0069	1.015586	10.641	11.7213
Nitrobenzene	298.15	1.1985	1.198495	1.8095	1.7992
	303.15	1.1936	1.194150	1.6190	1.6297
	308.15	1.1911	1.190613	1.5000	1.4802
	313.15		1.187320		1.3661
	318.15		1.184250		1.2924
	323.15		1.181810		1.2082

*All the literature values are cited from the references 37-38, 95-113.

Table-4.2: Density (ρ) and Excess molar volume (V^E) of Ethanol+Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.1002	1.172748	0.089	1.168266	0.095	1.164382	0.116	1.160732	0.134	1.157374	0.139	1.154642	0.155
0.1992	1.142688	0.368	1.137620	0.419	1.132949	0.499	1.129134	0.520	1.125257	0.551	1.122196	0.587
0.2993	1.112287	0.426	1.107254	0.468	1.102464	0.548	1.098576	0.562	1.094400	0.597	1.091172	0.637
0.3990	1.079556	0.434	1.074439	0.477	1.069689	0.544	1.065617	0.560	1.061051	0.606	1.057749	0.642
0.4996	1.043481	0.398	1.038357	0.436	1.033161	0.529	1.029078	0.533	1.024299	0.575	1.020763	0.620
0.6200	0.995758	0.278	0.990341	0.332	0.985542	0.383	0.980551	0.443	0.975394	0.490	0.971627	0.542
0.6992	0.960456	0.197	0.955005	0.251	0.950102	0.304	0.945038	0.360	0.939641	0.410	0.935784	0.462
0.8006	0.909552	0.112	0.904474	0.136	0.899688	0.174	0.894481	0.230	0.889241	0.249	0.885280	0.301
0.8996	0.852697	0.039	0.847741	0.055	0.842994	0.087	0.838028	0.117	0.832620	0.134	0.828986	0.155
1.0000	0.785683	0.000	0.781013	0.000	0.776701	0.000	0.772079	0.000	0.766749	0.000	0.763349	0.000

Table-4.3: Density (ρ) and Excess molar volume (V^E) of n-Propanol+Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.0992	1.165968	0.240	1.161214	0.275	1.157281	0.302	1.153479	0.338	1.149795	0.380	1.146781	0.416
0.1990	1.132664	0.387	1.127698	0.440	1.123472	0.485	1.119458	0.531	1.115476	0.587	1.112103	0.640
0.2988	1.096871	0.590	1.091916	0.643	1.087355	0.711	1.082884	0.790	1.078777	0.846	1.075183	0.905
0.4008	1.059736	0.669	1.055130	0.692	1.049927	0.810	1.046075	0.826	1.041179	0.941	1.037865	0.960
0.4991	1.023024	0.636	1.018131	0.685	1.013479	0.748	1.009136	0.800	1.004627	0.869	1.000653	0.934
0.6008	0.983570	0.518	0.978611	0.574	0.974047	0.623	0.969621	0.675	0.965024	0.741	0.960822	0.813
0.7004	0.942711	0.364	0.938000	0.400	0.933477	0.440	0.929034	0.487	0.924188	0.566	0.919831	0.640
0.7996	0.898800	0.236	0.894310	0.256	0.889902	0.282	0.885454	0.325	0.880846	0.374	0.876533	0.433
0.8998	0.850870	0.138	0.846522	0.151	0.842105	0.177	0.837879	0.197	0.833456	0.223	0.829398	0.249
1.0000	0.799695	0.000	0.795573	0.000	0.791441	0.000	0.787419	0.000	0.783225	0.000	0.779361	0.000

Table-4.4: Density (ρ) and Excess molar volume (V^E) of n-Butanol+ Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.1003	1.158221	0.308	1.153525	0.342	1.148891	0.435	1.144400	0.495	1.140859	0.561	1.137533	0.615
0.2009	1.119711	0.604	1.115090	0.634	1.110645	0.708	1.105623	0.774	1.102635	0.811	1.099152	0.857
0.2994	1.081602	0.769	1.077145	0.788	1.072233	0.903	1.066874	0.960	1.063858	1.021	1.059778	1.102
0.4007	1.042318	0.880	1.037984	0.891	1.033180	0.996	1.027401	1.052	1.024460	1.128	1.020780	1.148
0.4998	1.004246	0.881	0.999919	0.895	0.995619	0.949	0.988837	1.067	0.985770	1.178	0.981706	1.216
0.5990	0.966257	0.783	0.961457	0.849	0.956855	0.933	0.950698	0.952	0.946890	1.163	0.942859	1.178
0.7005	0.926983	0.623	0.922149	0.699	0.917684	0.769	0.910436	0.868	0.908453	0.909	0.904182	0.930
0.7998	0.887932	0.432	0.883429	0.480	0.879131	0.533	0.872061	0.581	0.869742	0.680	0.864912	0.746
0.9011	0.847828	0.142	0.843481	0.181	0.839387	0.213	0.832412	0.219	0.830921	0.246	0.825754	0.335
1.0000	0.806262	0.000	0.802348	0.000	0.798565	0.000	0.791435	0.000	0.790339	0.000	0.785832	0.000

Table-4.5: Density (ρ) and Excess molar volume (V^E) of n-Amyl alcohol+ Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.0979	1.156483	0.188	1.152140	0.194	1.147878	0.246	1.144064	0.284	1.140208	0.335	1.137366	0.355
0.1984	1.112242	0.548	1.107453	0.605	1.102902	0.676	1.099019	0.715	1.094643	0.800	1.090936	0.890
0.2992	1.068851	0.895	1.064113	0.959	1.059379	1.042	1.054869	1.140	1.049762	1.287	1.046165	1.357
0.4060	1.026917	1.033	1.022172	1.109	1.017257	1.205	1.012455	1.331	1.007937	1.405	1.003977	1.503
0.4997	0.988289	1.200	0.983629	1.280	0.978978	1.344	0.975034	1.377	0.970341	1.459	0.965935	1.600
0.6004	0.950037	1.197	0.945463	1.280	0.940254	1.404	0.935575	1.520	0.930682	1.617	0.926468	1.732
0.7002	0.916374	0.747	0.911930	0.824	0.906588	0.959	0.901192	1.160	0.895696	1.320	0.890929	1.497
0.7999	0.882354	0.355	0.878362	0.387	0.873314	0.483	0.868763	0.580	0.864500	0.574	0.861055	0.574
0.9005	0.846798	0.131	0.842859	0.168	0.838108	0.226	0.834070	0.258	0.829368	0.300	0.825983	0.284
1.0000	0.811181	0.000	0.807620	0.000	0.803306	0.000	0.799513	0.000	0.795075	0.000	0.791529	0.000

Table-4.6: Density (ρ) and Excess molar volume (V^E) of iso-Propanol+Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.0991	1.166236	0.171	1.161814	0.192	1.158051	0.216	1.154632	0.228	1.151289	0.246	1.148465	0.270
0.1944	1.132104	0.469	1.127649	0.508	1.123736	0.551	1.120369	0.561	1.116804	0.594	1.113738	0.631
0.2992	1.095724	0.532	1.091281	0.586	1.087550	0.618	1.083834	0.660	1.080138	0.699	1.076785	0.752
0.3993	1.056602	0.797	1.052413	0.846	1.048642	0.888	1.044961	0.930	1.041197	0.972	1.037434	1.054
0.5001	1.017488	0.848	1.013546	0.892	1.009806	0.938	1.006107	0.985	1.002108	1.043	0.998149	1.136
0.5993	0.975582	0.995	0.971749	1.047	0.968104	1.092	0.964547	1.131	0.960376	1.203	0.956475	1.285
0.7003	0.934182	0.795	0.930394	0.860	0.926868	0.901	0.923209	0.952	0.919211	1.005	0.914793	1.128
0.8005	0.891256	0.497	0.887604	0.566	0.884146	0.608	0.880659	0.647	0.876538	0.709	0.872271	0.811
0.8995	0.845074	0.252	0.841857	0.300	0.838711	0.321	0.835412	0.347	0.831423	0.395	0.827518	0.459
1.0000	0.794580	0.000	0.792080	0.000	0.789256	0.000	0.786296	0.000	0.782808	0.000	0.779508	0.000

Table-4.7: Density (ρ) and Excess molar volume (V^E) of iso-Butanol+Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.1004	1.159323	0.307	1.154581	0.355	1.150604	0.408	1.147023	0.435	1.143488	0.481	1.140382	0.523
0.1992	1.121639	0.479	1.117020	0.529	1.112939	0.606	1.109145	0.653	1.105379	0.725	1.101209	0.849
0.3001	1.084026	0.511	1.078710	0.637	1.074358	0.755	1.069968	0.861	1.065793	0.977	1.061836	1.068
0.3992	1.043138	0.842	1.038308	0.940	1.034381	1.035	1.030104	1.136	1.025864	1.266	1.021439	1.391
0.5004	1.002948	0.964	0.998361	1.055	0.994078	1.203	0.989981	1.291	0.986060	1.398	0.981269	1.548
0.5997	0.961974	1.162	0.957346	1.275	0.953501	1.398	0.949689	1.462	0.945913	1.563	0.940999	1.719
0.7010	0.920963	1.201	0.916622	1.302	0.913010	1.419	0.908759	1.537	0.905125	1.632	0.900173	1.784
0.8048	0.882209	0.787	0.878203	0.867	0.875030	0.952	0.870628	1.091	0.866964	1.195	0.861156	1.435
0.9143	0.844914	-0.198	0.841176	-0.136	0.838089	-0.047	0.834297	0.025	0.830738	0.121	0.824357	0.412
1.0000	0.805908	0.000	0.802872	0.000	0.800712	0.000	0.797624	0.000	0.794976	0.000	0.791072	0.000

Table-4.8: Density (ρ) and Excess molar volume (V^E) of iso-Amyl alcohol+ Nitrobenzene 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	1.198495	0.000	1.194150	0.000	1.190613	0.000	1.187320	0.000	1.184250	0.000	1.181810	0.000
0.1005	1.151514	0.568	1.146798	0.642	1.141906	0.761	1.138005	0.818	1.134880	0.824	1.131585	0.881
0.2002	1.107122	1.017	1.102961	1.080	1.098379	1.170	1.094443	1.233	1.090744	1.295	1.087426	1.335
0.2993	1.066221	1.227	1.062277	1.307	1.057506	1.415	1.053489	1.489	1.049923	1.540	1.046037	1.619
0.3996	1.025667	1.415	1.021991	1.506	1.016908	1.648	1.012930	1.722	1.008916	1.824	1.004832	1.909
0.4990	0.986874	1.511	0.983437	1.614	0.978228	1.773	0.974246	1.852	0.970175	1.966	0.965763	2.074
0.5997	0.948133	1.600	0.944822	1.727	0.939610	1.892	0.935481	1.994	0.931474	2.108	0.926776	2.239
0.6996	0.910556	1.642	0.907307	1.800	0.902146	1.966	0.897982	2.080	0.894050	2.193	0.889152	2.341
0.8016	0.872919	1.648	0.870163	1.784	0.865388	1.909	0.861253	2.028	0.856892	2.205	0.851866	2.364
0.9008	0.843533	0.767	0.841189	0.881	0.835962	1.063	0.831247	1.261	0.826632	1.477	0.819890	1.858
1.0000	0.813120	0.000	0.811860	0.000	0.807988	0.000	0.804752	0.000	0.801724	0.000	0.797624	0.000

Table-4.9: Density (ρ) and Excess molar volume (V^E) of Propylene glycol+ Nitrobenzene 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	1.198495	0.000	1.194152	0.000	1.190613	0.000	1.187321	0.000	1.184250	0.000	1.181810	0.000
0.0995	1.129178	5.080	1.117459	5.812	1.107961	6.423	1.097513	7.152	1.088444	7.771	1.082929	8.102
0.2005	1.079272	8.491	1.067702	9.271	1.051607	10.612	1.041104	11.411	1.028854	12.420	1.019137	13.241
0.3008	1.040928	10.782	1.027542	11.790	1.011588	13.182	0.996926	14.473	0.984675	15.531	0.977590	16.092
0.3992	1.006694	12.632	0.991674	13.852	0.977157	15.143	0.965360	16.152	0.953256	17.212	0.941047	18.382
0.5006	0.971888	14.411	0.957654	15.590	0.944086	16.822	0.929219	18.211	0.914994	19.554	0.900771	21.012
0.6005	0.945606	15.221	0.925053	17.113	0.904991	19.132	0.894062	20.113	0.881325	21.312	0.869463	22.512
0.7003	0.933596	14.412	0.922424	15.250	0.909663	16.376	0.897372	17.431	0.885000	18.491	0.872607	19.661
0.7993	0.967569	9.112	0.957443	9.721	0.946033	10.562	0.934831	11.340	0.922755	12.181	0.907896	13.412
0.8993	1.004899	4.082	0.995361	4.533	0.987820	4.924	0.982255	5.080	0.971897	5.590	0.958907	6.421
1.0000	1.036698	0.000	1.032285	0.000	1.029217	0.000	1.024924	0.000	1.019732	0.000	1.015586	0.000

Table-4.10: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Ethanol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.1002	1.5761	-0.1345	-0.9082	1.4305	-0.1192	-0.8873	1.3075	-0.0989	-0.8083	1.2222	-0.0746	-0.6571	1.1431	-0.0785	-0.7360	1.0651	-0.0688	-0.6940
0.1992	1.3962	-0.2313	-0.9610	1.2861	-0.1885	-0.8575	1.1788	-0.1582	-0.7896	1.0902	-0.1416	-0.7658	1.0242	-0.1312	-0.7558	0.9554	-0.1096	-0.6809
0.2993	1.2401	-0.3074	-1.0561	1.1491	-0.2533	-0.9498	1.0512	-0.2193	-0.9036	0.9762	-0.1933	-0.8614	0.9143	-0.1779	-0.8478	0.8453	-0.1544	-0.7998
0.3990	1.1203	-0.3515	-1.1380	1.0332	-0.3007	-1.0654	0.9473	-0.2602	-1.0119	0.8781	-0.2324	-0.9791	0.8161	-0.2165	-0.9814	0.7601	-0.1784	-0.8791
0.4996	1.0162	-0.3829	-1.2790	0.9270	-0.3412	-1.2537	0.8470	-0.3000	-1.2127	0.7826	-0.2713	-1.0125	0.7340	-0.2418	-1.1390	0.6693	-0.2112	-1.0970
0.6200	0.9312	-0.3856	-1.4706	0.8289	-0.3650	-1.5487	0.7631	-0.3155	-1.4687	0.7071	-0.2829	-1.4285	0.6531	-0.2588	-1.4168	0.5914	-0.2245	-1.3657
0.6992	0.8781	-0.3872	-1.7370	0.7762	-0.3711	-1.8580	0.6984	-0.3375	-1.8743	0.6411	-0.3091	-1.8707	0.5882	-0.2840	-1.8730	0.5311	-0.2448	-1.8026
0.8006	0.8691	-0.3332	-2.0334	0.7604	-0.3300	-2.2581	0.6732	-0.3104	-2.3755	0.6003	-0.3011	-2.5469	0.5433	-0.2805	-2.6079	0.4940	-0.2337	-2.4264
0.8996	0.9271	-0.2168	-2.3258	0.8121	-0.2255	-2.7114	0.7221	-0.2131	-2.8614	0.6451	-0.2112	-3.1339	0.5672	-0.2120	-3.5147	0.5103	-0.1732	-3.2337
1.0000	1.0875	0.0000	0.0000	0.9865	0.0000	0.0000	0.8884	0.0000	0.0000	0.8128	0.0000	0.0000	0.7364	0.0000	0.0000	0.6413	0.0000	0.0000

Table-4.11: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Propanol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.0992	1.6251	-0.1901	-1.2383	1.4864	-0.1520	-1.0897	1.3691	-0.1161	-0.9111	1.2582	-0.1089	-0.9292	1.1832	-0.1034	-0.9376	1.0823	-0.1163	-1.1427
0.1990	1.5283	-0.3031	-1.1354	1.4141	-0.2331	-0.9572	1.3002	-0.1901	-0.8561	1.1923	-0.1758	-0.8631	1.1061	-0.1746	-0.9198	1.0114	-0.1776	-1.0153
0.2988	1.4690	-0.3788	-1.0951	1.3573	-0.2987	-0.9493	1.2472	-0.2481	-0.8661	1.1441	-0.2250	-0.8570	1.0642	-0.2107	-0.8622	0.9604	-0.2191	-0.9810
0.4008	1.4301	-0.4347	-1.1051	1.3142	-0.3508	-0.9853	1.2041	-0.2964	-0.9165	1.1112	-0.2590	-0.8723	1.0201	-0.2489	-0.9090	0.9291	-0.2408	-0.9596
0.4991	1.4082	-0.4730	-1.1584	1.2861	-0.3877	-1.0540	1.1752	-0.3304	-0.9909	1.0824	-0.2888	-0.9652	0.9943	-0.2689	-0.9576	0.9093	-0.2513	-0.9762
0.6008	1.4123	-0.4861	-1.2333	1.2940	-0.3890	-1.0959	1.1721	-0.3387	-1.0584	1.0750	-0.2972	-1.0178	0.9861	-0.2713	-1.0134	0.9001	-0.2511	-1.0260
0.7004	1.4551	-0.4602	-1.3097	1.3361	-0.3558	-1.1252	1.2184	-0.2975	-1.0412	1.1082	-0.2650	-1.0219	1.0071	-0.2446	-1.0362	0.9022	-0.2398	-1.1234
0.7996	1.5330	-0.3994	-1.4451	1.4154	-0.2856	-1.1474	1.2892	-0.2318	-1.0322	1.1752	-0.1990	-0.9765	1.0452	-0.2008	-1.0970	0.9412	-0.1917	-1.1573
0.8998	1.7093	-0.2405	-1.4599	1.5355	-0.1746	-1.1945	1.3848	-0.1415	-1.0789	1.2671	-0.1082	-0.9085	1.1251	-0.1152	-1.0814	1.0058	-0.1180	-1.2309
1.0000	1.9672	0.0000	0.0000	1.7193	0.0000	0.0000	1.5315	0.0000	0.0000	1.3763	0.0000	0.0000	1.2347	0.0000	0.0000	1.1148	0.0000	0.0000

Table-4.12: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Butanol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.1003	1.6501	-0.2136	-1.3497	1.5171	-0.1664	-1.1534	1.3751	-0.1489	-1.1397	1.2501	-0.1505	-1.2602	1.1582	-0.1593	-1.4288	1.0503	-0.1762	-1.7198
0.2009	1.5940	-0.3366	-1.1932	1.4580	-0.2810	-1.0976	1.3330	-0.2361	-1.0155	1.2170	-0.2189	-1.0301	1.1080	-0.2348	-1.1969	1.0080	-0.2365	-1.3128
0.2994	1.5517	-0.4469	-1.2065	1.4229	-0.3723	-1.1081	1.3084	-0.3062	-1.0025	1.1914	-0.2800	-1.0062	1.1003	-0.2678	-1.0385	0.9921	-0.2707	-1.1503
0.4007	1.5502	-0.5209	-1.2065	1.4173	-0.4379	-1.1214	1.3157	-0.3470	-0.9746	1.1922	-0.3168	-0.9815	1.0919	-0.3028	-1.0193	0.9920	-0.2897	-1.0669
0.4998	1.5480	-0.5962	-1.3031	1.4250	-0.4902	-1.1826	1.3226	-0.3886	-1.0303	1.1928	-0.3536	-1.0214	1.0831	-0.3383	-1.0872	0.9832	-0.3175	-1.1197
0.5990	1.5502	-0.6701	-1.4958	1.4332	-0.5446	-1.3410	1.3108	-0.4503	-1.2294	1.1851	-0.3998	-1.2102	1.0850	-0.3633	-1.2024	0.9750	-0.3447	-1.2602
0.7005	1.6003	-0.7007	-1.7313	1.4636	-0.5799	-1.5910	1.3420	-0.4718	-1.4361	1.2196	-0.4057	-1.3688	1.1092	-0.3676	-1.3645	1.0034	-0.3366	-1.3793
0.7998	1.7581	-0.6242	-1.8973	1.5947	-0.5154	-1.7487	1.4696	-0.3972	-1.4940	1.3330	-0.3328	-1.3916	1.2003	-0.3047	-1.4128	1.0831	-0.2763	-1.4189
0.9011	2.0252	-0.4434	-2.2213	1.8444	-0.3359	-1.8766	1.6437	-0.2788	-1.7577	1.5005	-0.2076	-1.4538	1.3670	-0.1669	-1.2925	1.2330	-0.1467	-1.2613
1.0000	2.5557	0.0000	0.0000	2.2511	0.0000	0.0000	1.9785	0.0000	0.0000	1.7506	0.0000	0.0000	1.5631	0.0000	0.0000	1.4001	0.0000	0.0000

Table-4.13: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Amyl alcohol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.0979	1.6684	-0.2506	-1.5837	1.5231	-0.2060	-1.4361	1.3861	-0.1764	-1.3562	1.2571	-0.1788	-1.5052	1.1452	-0.2022	-1.8404	1.0513	-0.2030	-1.9988
0.1984	1.5940	-0.4561	-1.5820	1.4460	-0.3913	-1.5055	1.3260	-0.3256	-1.3803	1.2140	-0.2970	-1.3759	1.1110	-0.2948	-1.4794	1.0160	-0.2868	-1.5631
0.2992	1.5628	-0.6278	-1.6106	1.4229	-0.5296	-1.5092	1.3084	-0.4376	-1.3763	1.1914	-0.3989	-1.3774	1.0851	-0.3820	-1.4388	0.9823	-0.3716	-1.5306
0.4060	1.5660	-0.7842	-1.6834	1.4290	-0.6537	-1.5619	1.3003	-0.5521	-1.4676	1.1793	-0.5000	-1.4660	1.0850	-0.4500	-1.4386	0.9651	-0.4446	-1.5713
0.4997	1.5508	-0.9488	-1.9095	1.4203	-0.7839	-1.7583	1.3080	-0.6424	-1.5981	1.1790	-0.5819	-1.6351	1.0590	-0.5381	-1.6435	0.9390	-0.5216	-1.7673
0.6004	1.5581	-1.1130	-2.2468	1.4370	-0.9052	-2.0363	1.3108	-0.7511	-1.8881	1.1851	-0.6682	-1.8639	1.0510	-0.6157	-1.9221	0.9132	-0.6046	-2.1181
0.7002	1.6350	-1.2171	-2.6506	1.4636	-1.0241	-2.5268	1.3262	-0.8526	-2.3652	1.2196	-0.7301	-2.2348	1.0763	-0.6627	-2.2859	0.9470	-0.6292	-2.4269
0.7999	1.8933	-1.1525	-2.9702	1.6431	-0.9990	-2.9673	1.4460	-0.8558	-2.9041	1.3002	-0.7509	-2.8480	1.1579	-0.6557	-2.8030	1.0081	-0.6290	-3.0288
0.9005	2.6660	-0.5879	-2.2232	2.1070	-0.7006	-3.2026	1.7550	-0.6783	-3.6457	1.5490	-0.6095	-3.7016	1.3771	-0.5156	-3.5484	1.1925	-0.5082	-3.9605
1.0000	3.4742	0.0000	0.0000	2.9816	0.0000	0.0000	2.5707	0.0000	0.0000	2.2704	0.0000	0.0000	1.9741	0.0000	0.0000	1.7662	0.0000	0.0000

Table-4.14: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Propanol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.0991	1.6303	-0.1918	-1.2463	1.5003	-0.1425	-1.0163	1.3813	-0.1050	-0.8210	1.2611	-0.1006	-0.8598	1.1753	-0.1058	-0.9660	1.0803	-0.1067	-1.0555
0.1944	1.5321	-0.3118	-1.1828	1.4240	-0.2308	-0.9592	1.2960	-0.1957	-0.8978	1.1900	-0.1673	-0.8399	1.0970	-0.1728	-0.9340	1.0090	-0.1574	-0.9256
0.2992	1.4629	-0.4055	-1.1669	1.3489	-0.3196	-1.0142	1.2291	-0.2689	-0.9436	1.1219	-0.2307	-0.8918	1.0334	-0.2243	-0.9370	0.9521	-0.1924	-0.8780
0.3993	1.4072	-0.4850	-1.2346	1.2987	-0.3830	-1.0775	1.1830	-0.3208	-1.0004	1.0830	-0.2651	-0.9128	0.9941	-0.2523	-0.9432	0.9055	-0.2184	-0.9007
0.5001	1.3671	-0.5494	-1.3513	1.2541	-0.4411	-1.2056	1.1512	-0.3589	-1.0855	1.0442	-0.2996	- 1.0574	0.9590	-0.2760	-1.0117	0.8771	-0.2265	-0.9190
0.5993	1.3530	-0.5875	-1.5018	1.2430	-0.4654	-1.3243	1.1430	-0.3728	-1.1755	1.0260	-0.3131	-1.1092	0.9343	-0.2896	-1.1243	0.8562	-0.2278	-0.9827
0.7003	1.3712	-0.5944	-1.7161	1.2542	-0.4680	-1.5111	1.1403	-0.3819	-1.3766	1.0263	-0.3086	-1.2531	0.9302	-0.2827	-1.2646	0.8380	-0.2262	-1.1385
0.8005	1.4200	-0.5705	-2.1146	1.2890	-0.4466	-1.8629	1.1720	-0.3560	-1.6608	1.0500	-0.2802	-1.4811	0.9450	-0.2567	-1.5048	0.8543	-0.1910	-1.2640
0.8995	1.5944	-0.4215	-2.5952	1.4313	-0.3182	-2.2212	1.2891	-0.2450	-1.9247	1.1380	-0.1878	-1.6899	1.0261	-0.1649	-1.6490	0.9131	-0.1134	-1.2954
1.0000	2.0412	0.0000	0.0000	1.7631	0.0000	0.0000	1.5401	0.0000	0.0000	1.3214	0.0000	0.0000	1.1801	0.0000	0.0000	1.0079	0.0000	0.0000

Table-4.15: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Butanol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.1004	1.7400	-0.1740	-1.0552	1.5731	-0.1504	-1.0107	1.4251	-0.1308	-0.9721	1.3062	-0.1197	-0.9708	1.2072	-0.1291	-1.1250	1.1171	-0.1256	-1.1801
0.1992	1.7150	-0.3191	-1.0697	1.5490	-0.2718	-1.0133	1.3920	-0.2419	-1.0045	1.2771	-0.2099	-0.9538	1.1771	-0.2035	-0.9997	1.0820	-0.1955	-1.0410
0.3001	1.7080	-0.4565	-1.1278	1.5412	-0.3849	-1.0616	1.3893	-0.3284	-1.0104	1.2662	-0.2859	-0.9691	1.1708	-0.2566	-0.9434	1.0733	-0.2407	-0.9634
0.3992	1.7435	-0.5573	-1.1564	1.5670	-0.4681	-1.0899	1.4061	-0.3983	-1.0399	1.2771	-0.3419	-0.9890	1.1671	-0.3080	-0.9765	1.0722	-0.2789	-0.9643
0.5004	1.7994	-0.6494	-1.2326	1.6031	-0.5499	-1.1797	1.4300	-0.4672	-1.1307	1.2822	-0.4080	-1.6580	1.1820	-0.3432	-1.0197	1.0823	-0.3077	-1.0012
0.5997	1.8470	-0.7563	-1.4297	1.6448	-0.6305	-1.3518	1.4633	-0.5299	-1.2877	1.3150	-0.4479	-1.2211	1.1962	-0.3801	-1.1497	1.0912	-0.3378	-1.1238
0.7010	1.9516	-0.8193	-1.6723	1.7191	-0.6882	-1.6064	1.5272	-0.5686	-1.5102	1.3632	-0.4775	-1.4331	1.2340	-0.3959	-1.3275	1.1200	-0.3499	-1.2971
0.8048	2.0690	-0.8849	-2.2664	1.8262	-0.7244	-2.1270	1.6110	-0.5953	-2.0018	1.4300	-0.4936	-1.8875	1.2952	-0.3916	-1.6817	1.1649	-0.3483	-1.6652
0.9143	2.3338	-0.8262	-3.8679	2.0450	-0.6657	-3.5965	1.7767	-0.5528	-3.4570	1.5734	-0.4419	-3.1590	1.4052	-0.3439	-2.7938	1.2611	-0.2993	-2.7177
1.0000	3.3313	0.0000	0.0000	2.8431	0.0000	0.0000	2.4306	0.0000	0.0000	2.0901	0.0000	0.0000	1.7994	0.0000	0.0000	1.5981	0.0000	0.0000

Table-4.16: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Amyl alcohol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.1005	1.7382	-0.1961	-1.1828	1.5681	-0.1748	-1.1690	1.4393	-0.1344	-0.9876	1.3231	-0.1206	-0.9649	1.2411	-0.1157	-0.9862	1.1531	-0.1137	-1.0404
0.2002	1.7241	-0.3540	-1.1663	1.5542	-0.3087	-1.1316	1.4322	-0.2396	-0.9663	1.3160	-0.2088	-0.9197	1.2212	-0.2027	-0.9591	1.1321	-0.1955	-0.9950
0.2993	1.7450	-0.4866	-1.1728	1.5610	-0.4290	-1.1579	1.4391	-0.3364	-1.0016	1.3232	-0.2870	-0.9363	1.2211	-0.2725	-0.9605	1.1262	-0.2648	-1.0073
0.3996	1.8283	-0.5703	-1.1316	1.6192	-0.5086	-1.1386	1.4662	-0.4209	-1.0520	1.3433	-0.3582	-0.9854	1.2342	-0.3336	-0.9974	1.1463	-0.3120	-1.0037
0.4990	1.9150	-0.6614	-1.1867	1.6899	-0.5839	-1.1871	1.5101	-0.4942	-1.1326	1.3910	-0.4056	-1.0021	1.2750	-0.3697	-1.0185	1.1661	-0.3618	-1.0810
0.5997	2.0332	-0.7368	-1.2882	1.8069	-0.6249	-1.2373	1.5980	-0.5328	-1.1986	1.4361	-0.4627	-1.1635	1.3163	-0.4107	-1.1315	1.2211	-0.3809	-1.1310
0.6996	2.1582	-0.8183	-1.5296	1.9142	-0.6853	-1.4561	1.6903	-0.5738	-1.3907	1.5256	-0.4801	-1.3019	1.3910	-0.4211	-1.2584	1.2752	-0.4039	-1.3096
0.8016	2.3301	-0.8732	-2.0012	2.0710	-0.7116	-1.8572	1.8201	-0.5888	-1.7625	1.6332	-0.4880	-1.6440	1.4861	-0.4176	-1.5573	1.3503	-0.4114	-1.6727
0.9008	2.6561	-0.7841	-2.8946	2.3346	-0.6385	-2.7055	2.0446	-0.5139	-2.5091	1.8075	-0.4324	-2.4005	1.6501	-0.3471	-2.1364	1.5130	-0.3326	-2.2235
1.0000	3.6947	0.0000	0.0000	3.1766	0.0000	0.0000	2.7174	0.0000	0.0000	2.3653	0.0000	0.0000	2.0951	0.0000	0.0000	1.9337	0.0000	0.0000

Table-4.17: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Propylene glycol+Nitrobenzene 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	1.7992	0.0000	0.0000	1.6297	0.0000	0.0000	1.4802	0.0000	0.0000	1.3661	0.0000	0.0000	1.2924	0.0000	0.0000	1.2082	0.0000	0.0000
0.0995	1.8511	-0.5830	-3.0560	1.7205	-0.4584	-2.6363	1.5502	-0.4003	-2.5639	1.3204	-0.4506	-3.2770	1.1801	-0.4641	-3.7018	1.0012	-0.5135	-4.6211
0.2005	1.9802	-1.3280	-3.2016	1.7713	-1.1547	-3.1311	1.5211	-1.0600	-3.2986	1.3207	-0.9843	-3.4742	1.1808	-0.9186	-3.5899	0.9302	-0.9753	-4.4735
0.3008	2.2205	-2.2661	-3.3443	1.9421	-1.9790	-3.3407	1.6609	-1.7479	-3.4186	1.4311	-1.5633	-3.5104	1.2111	-1.4650	-3.7696	0.9808	-1.4124	-4.2414
0.3992	2.6212	-3.4285	-3.4872	2.2806	-2.9451	-3.4571	1.9706	-2.5076	-3.4227	1.7208	-2.1501	-3.3801	1.4607	-1.9347	-3.5170	1.1809	-1.8120	-3.8774
0.5006	3.2310	-5.0011	-3.7410	2.7821	-4.2435	-3.7054	2.3315	-3.6009	-3.7357	2.1109	-2.9323	-3.4250	1.8309	-2.5087	-3.4519	1.5211	-2.2473	-3.6289
0.6005	4.2801	-6.8707	-3.9914	3.7412	-5.6630	-3.8422	3.2121	-4.6141	-3.7122	2.8421	-3.7027	-3.4770	2.5615	-2.9647	-3.2051	2.1415	-2.5872	-3.3020
0.7003	6.2421	-8.8576	-4.2089	5.4609	-7.1234	-3.9777	4.6422	-5.6794	-3.8072	4.0816	-4.4098	-3.4904	3.6819	-3.3537	-3.0853	3.2313	-2.7010	-2.8947
0.7993	10.8315	-9.5660	-3.9456	8.9222	-7.8784	-3.9451	7.2617	-6.3208	-3.9033	6.0524	-4.9416	-3.7208	5.4321	-3.5078	-3.1056	4.9815	-2.4473	-2.4912
0.8993	19.7212	-7.9167	-3.7268	15.7201	-6.7749	-3.9571	12.6225	-5.3008	-3.8717	10.2128	-4.0585	-3.6949	8.5227	-2.8644	-3.1996	7.5116	-1.8124	-2.3868
1.0000	37.5281	0.0000	0.0000	30.1812	0.0000	0.0000	23.6973	0.0000	0.0000	18.5594	0.0000	0.0000	14.5289	0.0000	0.0000	11.7213	0.0000	0.0000

Table-4.18: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Ethanol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1002	14.78	14.79	14.81	14.88	14.95	15.00	-0.1705	-0.1687	-0.1530	-0.1198	-0.1409	-0.1328
0.1992	14.37	14.42	14.44	14.48	14.56	14.60	-0.3150	-0.2778	-0.2530	-0.2473	-0.2471	-0.2184
0.2993	13.96	14.01	14.03	14.07	14.13	14.15	-0.4621	-0.4131	-0.3936	-0.3774	-0.3761	-0.3545
0.3990	13.58	13.62	13.63	13.67	13.70	13.74	-0.5749	-0.5402	-0.5151	-0.5036	-0.5132	-0.4550
0.4996	13.21	13.21	13.21	13.23	13.28	13.25	-0.6843	-0.6795	-0.6625	-0.6600	-0.6366	-0.6179
0.6200	12.82	12.76	12.77	12.79	12.80	12.74	-0.7550	-0.8130	-0.7774	-0.7645	-0.7695	-0.7483
0.6992	12.55	12.47	12.42	12.41	12.40	12.33	-0.8115	-0.8882	-0.9106	-0.9225	-0.9382	-0.9122
0.8006	12.37	12.25	12.16	12.07	12.01	11.96	-0.7313	-0.8337	-0.8948	-0.9793	-1.0212	-0.9581
0.8996	12.36	12.25	12.16	12.08	11.95	11.87	-0.4786	-0.5741	-0.6175	-0.6909	-0.7930	-0.7368
1.0000	12.57	12.55	12.51	12.49	12.45	12.29	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 n-Propanol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0992	14.90	14.93	14.98	15.01	15.09	15.10	-0.2583	-0.2285	-0.1908	-0.1974	-0.2016	-0.2533
0.1990	14.68	14.74	14.78	14.80	14.85	14.85	-0.4206	-0.3550	-0.3186	-0.3258	-0.3538	-0.3992
0.2988	14.52	14.57	14.61	14.63	14.68	14.65	-0.5291	-0.4599	-0.4213	-0.4216	-0.4301	-0.5026
0.4008	14.38	14.42	14.44	14.48	14.49	14.48	-0.6115	-0.5490	-0.5129	-0.4937	-0.5222	-0.5632
0.4991	14.26	14.29	14.30	14.33	14.35	14.34	-0.6701	-0.6146	-0.5830	-0.5623	-0.5776	-0.5979
0.6008	14.19	14.22	14.21	14.23	14.24	14.23	-0.6888	-0.6161	-0.6023	-0.5857	-0.5909	-0.6067
0.7004	14.18	14.21	14.22	14.22	14.21	14.15	-0.6440	-0.5565	-0.5198	-0.5167	-0.5310	-0.5867
0.7996	14.22	14.27	14.28	14.28	14.22	14.17	-0.5461	-0.4346	-0.3941	-0.3763	-0.4322	-0.4635
0.8998	14.40	14.39	14.37	14.39	14.32	14.25	-0.3100	-0.2547	-0.2315	-0.1948	-0.2386	-0.2779
1.0000	14.66	14.58	14.53	14.50	14.46	14.43	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 n-Butanol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1003	14.98	15.03	15.04	15.04	15.09	15.07	-0.2904	-0.2499	-0.2486	-0.2796	-0.3226	-0.3969
0.2009	14.87	14.91	14.93	14.95	14.95	14.94	-0.4577	-0.4260	-0.3975	-0.4088	-0.4852	-0.5418
0.2994	14.78	14.82	14.86	14.88	14.91	14.88	-0.6052	-0.5629	-0.5127	-0.5221	-0.5468	-0.6165
0.4007	14.76	14.79	14.85	14.85	14.87	14.85	-0.6925	-0.6525	-0.5705	-0.5831	-0.6144	-0.6546
0.4998	14.73	14.78	14.84	14.83	14.82	14.80	-0.7814	-0.7184	-0.6315	-0.6446	-0.6842	0.0000
0.5990	14.70	14.76	14.79	14.78	14.80	14.75	-0.8669	-0.7861	-0.7285	-0.7283	-0.7294	-0.7781
0.7005	14.75	14.78	14.82	14.83	14.82	14.80	-0.8809	-0.8197	-0.7482	-0.7215	-0.7295	-0.7490
0.7998	14.95	14.96	15.01	15.03	14.99	14.97	-0.7394	-0.6906	-0.5962	-0.5623	-0.5775	-0.5876
0.9011	15.26	15.29	15.26	15.30	15.30	15.28	-0.4857	-0.4154	-0.3943	-0.3302	-0.2966	-0.2914
1.0000	15.81	15.76	15.70	15.66	15.62	15.58	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 n-Amyl alcohol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0979	15.04	15.07	15.09	15.09	15.09	15.11	-0.3420	-0.3147	-0.3005	-0.3387	-0.4212	-0.4649
0.1984	14.95	14.97	15.00	15.03	15.04	15.05	-0.6101	-0.5883	-0.5453	-0.5513	-0.6016	-0.6445
0.2992	14.92	14.95	14.99	15.00	15.01	14.99	-0.8151	-0.7737	-0.7131	-0.7229	-0.7649	-0.8269
0.4060	14.95	14.98	14.99	15.00	15.03	14.96	-0.9837	-0.9246	-0.8793	-0.8895	-0.8845	-0.9819
0.4997	14.94	14.98	15.03	15.01	14.98	14.91	-1.1544	-1.0767	-0.9903	-1.0099	-1.0498	-1.1460
0.6004	14.97	15.03	15.05	15.05	14.98	14.85	-1.3075	-1.2003	-1.1261	-1.1266	-1.1792	-1.3213
0.7002	15.09	15.08	15.09	15.13	15.06	14.96	-1.3612	-1.3168	-1.2485	-1.1927	-1.2363	-1.3310
0.7999	15.46	15.37	15.31	15.30	15.25	15.13	-1.1699	-1.1876	-1.1790	-1.1725	-1.1723	-1.2878
0.9005	16.31	16.01	15.82	15.76	15.72	15.59	-0.4906	-0.7193	-0.8315	-0.8573	-0.8336	-0.9464
1.0000	16.98	16.89	16.80	16.77	16.68	16.65	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 iso-Propanol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0991	14.90	14.95	15.00	15.01	15.07	15.09	-0.2620	-0.2141	-0.1724	-0.1840	-0.2117	-0.2360
0.1944	14.69	14.77	14.78	14.80	14.83	14.85	-0.4302	-0.3482	-0.3283	-0.3099	-0.3532	-0.3545
0.2992	14.51	14.56	14.57	14.58	14.60	14.62	-0.5693	-0.4967	-0.4663	-0.4446	-0.4761	-0.4493
0.3993	14.35	14.40	14.40	14.42	14.43	14.41	-0.6855	-0.6007	-0.5622	-0.5157	-0.5425	-0.5218
0.5001	14.20	14.23	14.26	14.24	14.26	14.25	-0.7851	-0.7052	-0.6388	-0.5983	-0.6084	-0.5535
0.5993	14.11	14.14	14.17	14.13	14.11	14.11	-0.8373	-0.7424	-0.6620	-0.6305	-0.6485	-0.5654
0.7003	14.05	14.08	14.07	14.04	14.01	13.97	-0.8441	-0.7479	-0.6869	-0.6292	-0.6445	-0.5801
0.8005	14.05	14.05	14.05	14.00	13.96	13.92	-0.8023	-0.7123	-0.6402	-0.5748	-0.5924	-0.4955
0.8995	14.25	14.22	14.20	14.12	14.08	14.00	-0.5622	-0.4849	-0.4236	-0.3745	-0.3693	-0.2873
1.0000	14.76	14.65	14.56	14.40	14.35	14.16	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.23: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso-Butanol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1004	15.11	15.12	15.12	15.15	15.19	15.23	-0.2274	-0.2200	-0.2134	-0.2159	-0.2551	-0.2715
0.1992	15.05	15.06	15.04	15.07	15.10	15.13	-0.4088	-0.3919	-0.3928	-0.3770	-0.4006	-0.4215
0.3001	15.01	15.02	15.01	15.03	15.07	15.08	-0.5714	-0.5428	-0.5212	-0.5045	-0.4954	-0.5123
0.3992	15.05	15.04	15.02	15.03	15.04	15.06	-0.6628	-0.6313	-0.6087	-0.5843	-0.5824	-0.5807
0.5004	15.10	15.08	15.04	15.01	15.05	15.06	-0.7356	-0.7125	-0.6891	-0.6816	-0.6331	-0.6270
0.5997	15.14	15.12	15.08	15.06	15.06	15.06	-0.8174	-0.7812	-0.7515	-0.7206	-0.6842	-0.6744
0.7010	15.25	15.20	15.16	15.12	15.11	15.10	-0.8346	-0.8113	-0.7700	-0.7374	-0.6883	-0.6782
0.8048	15.36	15.31	15.25	15.20	15.20	15.17	-0.8595	-0.8167	-0.7775	-0.7398	-0.6633	-0.6605
0.9143	15.60	15.54	15.45	15.39	15.35	15.32	-0.7554	-0.7127	-0.6940	-0.6425	-0.5744	-0.5592
1.0000	16.46	16.35	16.22	16.11	15.98	15.92	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.24: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso-Amyl alcohol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1005	15.15	15.16	15.20	15.23	15.32	15.37	-0.2511	-0.2505	-0.2097	-0.2064	-0.2147	-0.2298
0.2002	15.16	15.16	15.21	15.25	15.30	15.35	-0.4382	-0.4301	-0.3673	-0.3523	-0.3732	-0.3935
0.2993	15.20	15.19	15.24	15.28	15.32	15.35	-0.5800	-0.5801	-0.5031	-0.4739	-0.4937	-0.5259
0.3996	15.34	15.30	15.31	15.34	15.37	15.42	-0.6389	-0.6519	-0.6061	-0.5726	-0.5870	-0.5982
0.4990	15.47	15.42	15.40	15.45	15.47	15.49	-0.6993	-0.7090	-0.6821	-0.6203	-0.6243	-0.6735
0.5997	15.63	15.61	15.56	15.55	15.58	15.63	-0.7286	-0.7073	-0.6913	-0.6783	-0.6662	-0.6732
0.6996	15.79	15.77	15.72	15.72	15.74	15.77	-0.7583	-0.7285	-0.7016	-0.6618	-0.6456	-0.6812
0.8016	16.00	15.98	15.92	15.91	15.93	15.94	-0.7506	-0.7024	-0.6727	-0.6318	-0.6014	-0.6565
0.9008	16.31	16.27	16.21	16.17	16.20	16.25	-0.6233	-0.5886	-0.5491	-0.5282	-0.4691	-0.4884
1.0000	17.13	17.04	16.93	16.86	16.81	16.88	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.25: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Propylene glycol+Nitrobenzene 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	15.21	15.23	15.24	15.28	15.39	15.45	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0995	15.33	15.43	15.44	15.30	15.27	15.08	-0.5442	-0.4416	-0.4180	-0.5740	-0.6694	-0.8937
0.2005	15.51	15.52	15.42	15.33	15.31	14.94	-1.0429	-1.0142	-1.0685	-1.1409	-1.1850	-1.5653
0.3008	15.78	15.74	15.64	15.54	15.38	15.08	-1.4461	-1.4454	-1.4788	-1.5234	-1.6680	-1.9485
0.3992	16.17	16.12	16.05	15.99	15.85	15.56	-1.7185	-1.7010	-1.6777	-1.6554	-1.7448	-1.9775
0.5006	16.66	16.59	16.45	16.50	16.43	16.23	-1.9078	-1.8901	-1.9118	-1.7465	-1.7227	-1.8348
0.6005	17.30	17.31	17.26	17.25	17.29	17.12	-1.9316	-1.8285	-1.7302	-1.5892	-1.4149	-1.4719
0.7003	18.14	18.14	18.06	18.05	18.10	18.08	-1.7587	-1.6458	-1.5532	-1.3796	-1.1515	-1.0335
0.7993	19.29	19.15	18.97	18.83	18.88	18.99	-1.2754	-1.2805	-1.2614	-1.1847	-0.9203	-0.6362
0.8993	20.54	20.34	20.13	19.92	19.79	19.79	-0.6937	-0.7444	-0.7250	-0.6909	-0.5680	-0.3534
1.0000	21.91	21.74	21.48	21.21	20.91	20.67	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

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

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.1002	11.87	-0.6982	-47.93	-1.7725
0.1992	11.60	-1.3026	-47.56	-3.3569
0.2993	11.63	-1.5932	-46.09	-3.8533
0.3990	11.81	-1.7481	-44.23	-3.9630
0.4996	12.42	-1.4720	-40.91	-2.6244
0.6200	13.22	-1.0673	-36.86	-0.9527
0.6992	14.88	0.3259	-30.41	3.9374
0.8006	17.21	2.3260	-21.95	10.3947
0.8996	18.19	2.9787	-18.72	11.6762
1.0000	15.54	0.0000	-28.41	0.0000

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

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.0992	12.29	-0.4415	-47.01	-0.7076
0.1990	12.62	-0.6080	-45.24	-0.7913
0.2988	12.80	-0.9219	-44.09	-1.4847
0.4008	13.03	-1.2064	-42.86	-2.1387
0.4991	13.21	-1.5187	-41.85	-2.9543
0.6008	13.68	-1.5468	-40.01	-2.9993
0.7004	14.45	-1.2794	-37.49	-2.3188
0.7996	14.92	-1.3035	-36.11	-2.7763
0.8998	15.98	-0.7433	-33.06	-1.5839
1.0000	17.22	0.0000	-29.63	0.0000

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

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.1003	13.90	1.0312	-41.96	4.2788
0.2009	14.06	0.5629	-41.06	3.2697
0.2994	13.52	-0.5955	-42.57	-0.1112
0.4007	13.54	-1.2094	-42.42	-1.8719
0.4998	13.86	-1.5106	-41.29	-2.6222
0.5990	14.07	-1.9280	-40.52	-3.7291
0.7005	14.11	-2.5278	-40.51	-5.6429
0.7998	14.57	-2.6906	-39.64	-6.6476
0.9011	15.03	-2.8598	-39.09	-8.0184
1.0000	18.51	0.0000	-29.20	0.0000

Table 4.29: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of n-Amyl alcohol+Nitrobenzene system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.0979	14.40	1.3047	-40.50	5.3706
0.1984	13.71	-0.2570	-42.47	1.0727
0.2992	14.07	-0.7655	-41.19	0.0126
0.4060	14.56	-1.2063	-39.64	-0.9090
0.4997	15.22	-1.3595	-37.49	-0.9282
0.6004	16.13	-1.3328	-34.62	-0.3949
0.7002	16.16	-2.1637	-34.76	-2.8414
0.7999	18.91	-0.2804	-26.67	2.9435
0.9005	24.07	4.0080	-11.87	15.4121
1.0000	20.93	0.0000	-24.97	0.0000

Table 4.30: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Propanol+Nitrobenzene system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.0991	12.70	-0.4856	-45.72	-0.8762
0.1944	13.00	-1.0839	-44.02	-2.3495
0.2992	13.35	-1.7345	-42.22	-4.0264
0.3993	13.57	-2.4616	-40.95	-6.0847
0.5001	13.67	-3.3244	-40.13	-8.6147
0.5993	14.25	-3.6863	-37.89	-9.6743
0.7003	15.17	-3.7209	-34.62	-9.7607
0.8005	15.71	-4.1398	-32.81	-11.2782
0.8995	17.21	-3.5755	-28.41	-10.1676
1.0000	21.74	0.0000	-14.91	0.0000

Table 4.31: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Butanol+Nitrobenzene system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.1004	13.67	0.3252	-43.07	1.7998
0.1992	14.14	-0.2886	-41.30	0.3546
0.3001	14.18	-1.3523	-41.04	-2.6645
0.3992	14.96	-1.6591	-38.53	-3.3825
0.5004	15.65	-2.0788	-36.36	-4.5034
0.5997	16.24	-2.5862	-34.58	-5.9489
0.7010	17.08	-2.8566	-32.10	-6.7707
0.8048	17.67	-3.4070	-30.50	-8.5437
0.9143	19.06	-3.2203	-26.65	-8.2536
1.0000	23.22	0.0000	-15.61	0.0000

Table 4.32: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy(ΔS^{*E}) of iso-Amyl alcohol+Nitrobenzene system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.1005	12.44	-0.6336	-47.28	-1.3088
0.2002	12.75	-1.1550	-46.27	-2.4548
0.2993	13.18	-1.5590	-45.01	-3.3250
0.3996	14.18	-1.3927	-42.04	-2.5223
0.4990	14.92	-1.4811	-39.99	-2.6171
0.5997	15.80	-1.4367	-37.61	-2.4010
0.6996	16.15	-1.9206	-36.99	-3.9414
0.8016	16.77	-2.1536	-35.63	-4.7783
0.9008	17.32	-2.4264	-34.78	-6.0688
1.0000	20.58	0.0000	-26.57	0.0000

Table 4.33: Change of Enthalpy (ΔH^{*}), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^{*}) and Excess entropy(ΔS^{*E}) of Propylene glycol+Nitrobenzene system.

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*}}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	12.24	0.0000	-48.13	0.0000
0.0995	18.56	3.8404	-27.83	14.2619
0.2005	21.58	4.3546	-18.18	17.7822
0.3008	23.72	3.9993	-11.90	17.9762
0.3992	22.79	0.6193	-16.28	7.6133
0.5006	20.99	-3.7022	-23.75	-6.0087
0.6005	18.95	-8.2306	-32.82	-21.1478
0.7003	18.91	-10.7526	-35.66	-30.0409
0.7993	23.49	-8.6365	-23.89	-24.2826
0.8993	30.10	-4.5171	-6.05	-12.5150
1.0000	37.12	0.0000	12.57	0.0000

Table 4.34: Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol, iso-Propanol, iso-Butanol and iso-Amyl alcohol+Nitrobenzene systems.

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
Ethanol+ Nitrobenzene	298.15	1.6043	-1.7412	-0.8379	1.8320	0.0331
	303.15	1.8026	-1.7084	-0.8152	1.7174	0.0435
	308.15	2.1038	-1.9688	-0.7430	2.1083	0.0528
	313.15	2.2018	-1.6110	-0.3841	1.6517	0.0556
	318.15	2.3969	-1.5866	-0.4706	1.6450	0.0602
	323.15	2.5832	-1.4680	-0.3256	1.5174	0.0639
n-Propanol + Nitrobenzene	298.15	2.4911	-1.4954	-1.0837	1.4375	0.0261
	303.15	2.6675	-1.4453	-0.9344	0.9922	0.0256
	308.15	2.9696	-1.8395	-1.0582	1.7004	0.0306
	313.15	3.1540	-1.8154	-0.7721	1.4722	0.0305
	318.15	3.4858	-1.8576	-0.7415	1.4554	0.0318
	323.15	3.7126	-1.5683	-0.4493	0.8114	0.0273
n-Butanol + Nitrobenzene	298.15	3.5299	-0.8279	-1.2318	-0.3620	0.0194
	303.15	3.6497	-0.3681	-0.7895	-1.1423	0.0175
	308.15	3.9717	-0.5151	-0.3269	-1.4071	0.0243
	313.15	4.2617	-0.3558	-0.1633	-2.1315	0.0295
	318.15	4.7347	0.2316	-0.3630	-3.4022	0.0297
	323.15	4.8101	-0.1091	0.5846	-2.4294	0.0401
n-Amyl alcohol + Nitrobenzene	298.15	4.7782	-0.1875	-5.0439	-1.2120	0.0728
	303.15	5.1147	-0.2220	-5.1742	-1.0331	0.0787
	308.15	5.5059	0.1347	-4.7390	-1.5649	0.0806
	313.15	5.9481	0.6624	-4.5334	-2.3064	0.0865
	318.15	6.3729	0.6846	-4.4194	-2.8403	0.1244
	323.15	6.9253	1.1783	-5.0835	-4.4227	0.1460
iso-Propanol + Nitrobenzene	298.15	3.6091	1.6944	-1.8386	-2.6540	0.0619
	303.15	3.8090	1.7301	-1.4703	-2.3893	0.0609
	308.15	3.9819	1.7888	-1.3070	-2.5297	0.0630
	313.15	4.1664	1.8185	-1.2964	-2.3483	0.0572
	318.15	4.3867	1.9573	-1.1046	-2.2907	0.0595
	323.15	4.7430	2.2591	-0.8691	-2.2587	0.0550
iso-Butanol + Nitrobenzene	298.15	4.3044	5.8422	-2.6918	-12.8757	0.1394
	303.15	4.7287	5.7736	-2.4605	-12.4809	0.1362
	308.15	5.2229	5.7694	-2.1788	-12.1470	0.1206
	313.15	5.5885	5.6984	-1.6250	-11.1640	0.1376
	318.15	6.0284	5.4015	-1.1777	-10.0120	0.1347
	323.15	6.4969	5.2670	0.6849	-7.3120	0.1039
iso-Amyl alcohol + Nitrobenzene	298.15	6.1949	2.8929	3.9441	-1.1301	0.1147
	303.15	6.6113	3.3706	4.7481	-1.4134	0.1076
	308.15	7.1701	3.5979	5.7241	-1.2139	0.0769
	313.15	7.4512	3.5971	6.9835	0.0765	0.0523
	318.15	7.8196	3.5444	8.0403	2.2679	0.0492
	323.15	8.1239	3.3622	10.0665	5.5353	0.0590
Propylene glycol + Nitrobenzene	298.15	59.0317	28.7756	-9.7718	-60.8023	0.4564
	303.15	64.4759	30.9055	-10.9744	-68.4549	0.4548
	308.15	70.6177	32.1502	-10.4933	-75.5107	0.6642
	313.15	75.4977	32.4730	-10.0142	-80.6028	0.5908
	318.15	80.3541	33.0228	-7.8842	-83.3808	0.5878
	323.15	85.2339	35.1644	-5.7351	-81.7344	0.4904

Table 4.35: Coefficient, a_i, of Redlich- Kister Eq expressing η^E and standard deviation, σ for the Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol, iso-Propanol, iso-Butanol and iso-Amyl alcohol+Nitrobenzene systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
Ethanol + Nitrobenzene	298.15	-1.5257	-0.4085	-0.6785	-0.2840	0.0042
	303.15	-1.3536	-0.6716	-0.8109	-0.1286	0.0037
	308.15	-1.1784	-0.6316	-0.8360	-0.3200	0.0062
	313.15	-1.0553	-0.5560	-0.8636	-0.6666	0.0065
	318.15	-0.9482	-0.4777	-0.9807	-0.7517	0.0053
	323.15	-0.8188	-0.4624	-0.7656	-0.4423	0.0050
n-Propanol + Nitrobenzene	298.15	-1.8843	-0.5571	-0.8180	0.2907	0.0041
	303.15	-1.5250	-0.4082	-0.3435	0.4020	0.0058
	308.15	-1.3085	-0.3656	-0.0929	0.3530	0.0062
	313.15	-1.1555	-0.3490	-0.0667	0.5965	0.0028
	318.15	-1.0687	-0.2385	-0.2407	0.2671	0.0034
	323.15	-1.0094	-0.1452	-0.4454	0.2120	0.0024
n-Butanol + Nitrobenzene	298.15	-2.4030	-1.4833	-1.8519	-0.1593	0.0096
	303.15	-2.0007	-1.2054	-1.3527	-0.0184	0.0087
	308.15	-1.6065	-1.0001	-1.1866	0.2297	0.0118
	313.15	-1.4548	-0.8690	-0.8438	0.7324	0.0076
	318.15	-1.3649	-0.7360	-0.8153	1.0337	0.0055
	323.15	-1.2896	-0.6175	-0.8533	1.2284	0.0044
n-Amyl alcohol+ Nitrobenzene	298.15	-3.9085	-3.9792	-2.2838	2.0734	0.0568
	303.15	-3.1386	-2.7369	-3.2319	-1.1056	0.0117
	308.15	-2.5584	-2.0600	-3.3068	-2.1258	0.0095
	313.15	-2.2772	-1.6468	-2.9947	-2.0399	0.0169
	318.15	-2.0962	-1.5748	-2.6812	-0.8758	0.0160
	323.15	-2.0371	-1.4458	-2.6042	-0.9733	0.0218
iso-Propanol + Nitrobenzene	298.15	-2.1518	-0.9903	-1.7954	-0.9078	0.0104
	303.15	-1.7214	-0.8139	-1.1908	-0.6638	0.0082
	308.15	-1.4206	-0.5597	-0.8445	-0.6534	0.0031
	313.15	-1.1855	-0.4558	-0.6345	-0.2449	0.0030
	318.15	-1.1045	-0.3616	-0.6557	-0.0902	0.0028
	323.15	-0.9107	-0.2134	-0.5084	0.2190	0.0040
iso-Butanol + Nitrobenzene	298.15	-2.4876	-1.3023	-4.2881	-5.2836	0.0543
	303.15	-2.1030	-1.1244	-3.4177	-4.0381	0.0426
	308.15	-1.7782	-0.8529	-2.8206	-3.3591	0.0377
	313.15	-1.5368	-0.7211	-2.2228	-2.5150	0.0292
	318.15	-1.3250	-0.5220	-1.8214	-1.6357	0.0236
	323.15	-1.1898	-0.4047	-1.6794	-1.3737	0.0190
iso-Amyl alcohol + Nitrobenzene	298.15	-2.5471	-1.3159	-3.9858	-4.1867	0.0291
	303.15	-2.2320	-0.9503	-3.0536	-3.4532	0.0268
	308.15	-1.8845	-0.9873	-2.2500	-2.5111	0.0228
	313.15	-1.5901	-0.8363	-1.9203	-1.9688	0.0213
	318.15	-1.4610	-0.6528	-1.4956	-1.4406	0.0131
	323.15	-1.3874	-0.6150	-1.5239	-1.4272	0.0107
Propylene glycol + Nitrobenzene	298.15	-19.8143	-34.8653	-41.1083	-24.0717	0.0884
	303.15	-16.4811	-26.2636	-34.3981	-26.2732	0.1301
	308.15	-13.8291	-20.1807	-26.2746	-20.9192	0.0949
	313.15	-11.3441	-14.7860	-20.2219	-15.8758	0.0750
	318.15	-9.7032	-9.7487	-12.3255	-10.5254	0.0698
	323.15	-8.9211	-7.3359	-5.5308	-1.9694	0.0443

Table 4.36: Coefficient, a_i, of Redlich- Kister Eq expressing ΔG^{*E} and standard deviation, σ for the Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol, iso-Propanol, iso-Butanol and iso-Amyl alcohol+ Nitrobenzene systems.

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
Ethanol+ Nitrobenzene	298.15	-2.7362	-1.9581	-1.4668	-0.3900	0.0136
	303.15	-2.7145	-2.7722	-2.1842	-0.1581	0.0088
	308.15	-2.6088	-2.8707	-2.6981	-0.8206	0.0227
	313.15	-2.5485	-2.8346	-3.2880	-2.0977	0.0298
	318.15	-2.4786	-2.7413	-4.1432	-3.0796	0.0226
	323.15	-2.3747	-2.9287	-3.7355	-2.1760	0.0213
n-Propanol + Nitrobenzene	298.15	-2.6767	-0.8375	-0.8437	0.7032	0.0068
	303.15	-2.4147	-0.7162	-0.2564	0.8598	0.0091
	308.15	-2.3073	-0.7607	0.1154	0.8738	0.0123
	313.15	-2.2526	-0.8290	0.1277	1.4403	0.0071
	318.15	-2.2957	-0.7121	-0.2950	0.7764	0.0089
	323.15	-2.4126	-0.5593	-0.8660	0.6250	0.0071
n-Butanol + Nitrobenzene	298.15	-3.1798	-1.7470	-1.7561	0.6329	0.0139
	303.15	-2.9584	-1.5711	-1.4287	0.5683	0.0185
	308.15	-2.6381	-1.5152	-1.5185	0.9363	0.0229
	313.15	-2.6757	-1.4874	-1.1712	1.7969	0.0173
	318.15	-2.6757	-1.4874	-1.1712	1.7969	0.0173
	323.15	-1.9848	-1.3597	-4.4648	3.2061	0.2475
n-Amyl alcohol + Nitrobenzene	298.15	-4.7949	-4.0567	-1.1666	4.2572	0.0706
	303.15	-4.3722	-3.2644	-2.8861	0.6235	0.0354
	308.15	-4.0144	-2.8520	-3.7879	-1.2817	0.0137
	313.15	-3.9985	-2.5398	-3.9773	-1.7088	0.0140
	318.15	-4.1220	-2.9470	-4.2146	0.1318	0.0183
	323.15	-4.5227	-3.1859	-4.6413	-0.2172	0.0355
iso-Propanol + Nitrobenzene	298.15	-3.0805	-1.5304	-2.2142	-0.8790	0.0116
	303.15	-2.7474	-1.4518	-1.6578	-0.7827	0.0137
	308.15	-2.5272	-1.1416	-1.3414	-1.0219	0.0099
	313.15	-2.3648	-1.1219	-1.1656	-0.3786	0.0083
	318.15	-2.4399	-1.0668	-1.3717	-0.1247	0.0102
	323.15	-2.2324	-0.8050	-1.1743	0.5520	0.0137
iso-Butanol + Nitrobenzene	298.15	-2.8646	-0.8621	-3.7058	-4.6872	0.0457
	303.15	-2.7569	-0.9285	-3.4702	-4.1740	0.0426
	308.15	-2.6472	-0.7937	-3.3906	-4.1395	0.0456
	313.15	-2.5743	-0.8146	-3.0904	-3.5856	0.0427
	318.15	-2.4531	-0.6533	-2.9956	-2.6373	0.0410
	323.15	-2.4344	-0.5538	-3.1300	-2.4804	0.0361
iso-Amyl alcohol + Nitrobenzene	298.15	-2.7323	-0.6101	-3.0058	-3.0173	0.0176
	303.15	-2.7387	-0.3832	-2.5818	-3.0365	0.0220
	308.15	-2.6179	-0.7553	-2.0551	-2.4775	0.0235
	313.15	-2.4602	-0.7897	-2.0619	-2.1403	0.0258
	318.15	-2.4931	-0.6325	-1.7510	-1.7214	0.0164
	323.15	-2.5959	-0.6723	-1.9995	-1.8389	0.0142
Propylene glycol + Nitrobenzene	298.15	-7.6885	-2.1244	1.1649	2.0239	0.0226
	303.15	-7.4910	-0.9898	1.1596	-1.4639	0.0223
	308.15	-7.3673	-0.0515	1.0138	-2.9749	0.0540
	313.15	-6.8397	1.0679	-0.6434	-3.0479	0.0350
	318.15	-6.6949	3.5436	0.0518	-4.8629	0.0423
	323.15	-7.2470	5.7938	0.8034	-2.9313	0.0232

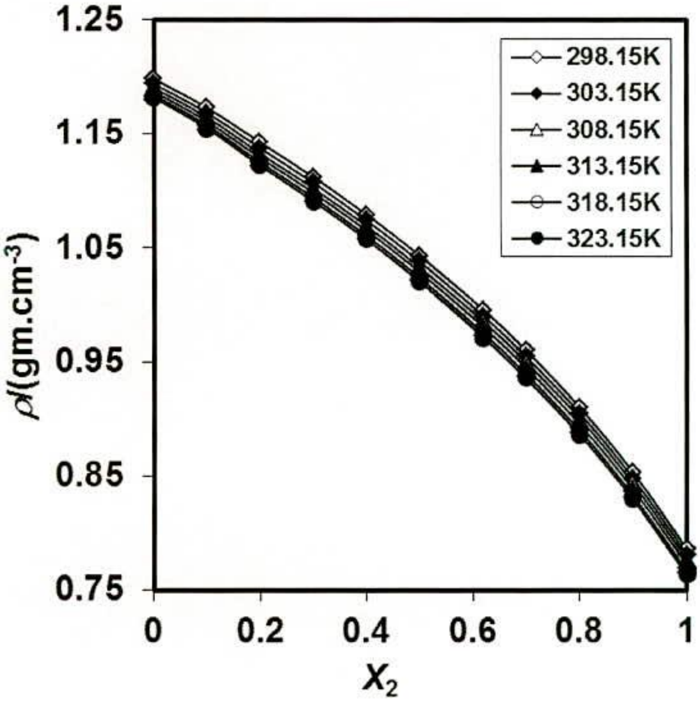

Figure 4.1: Plots of density (ρ) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

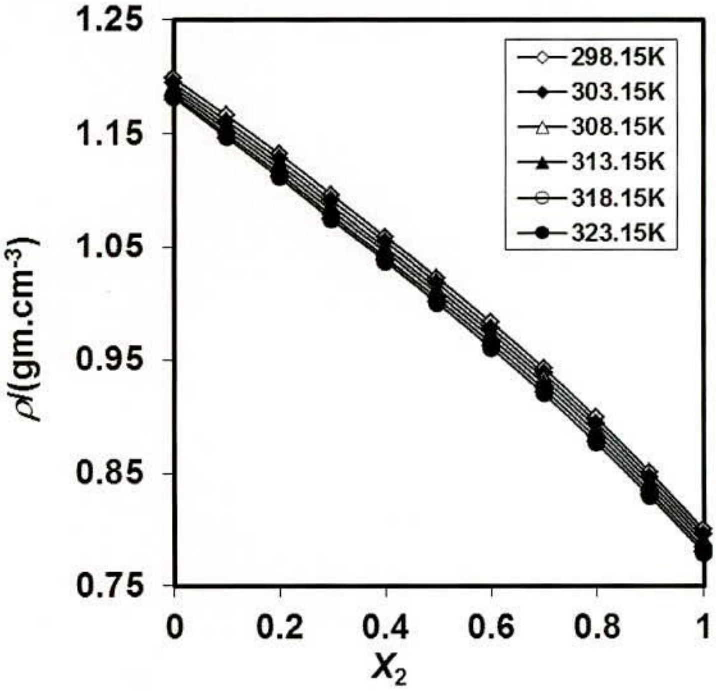

Figure 4.2: Plots of density (ρ) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

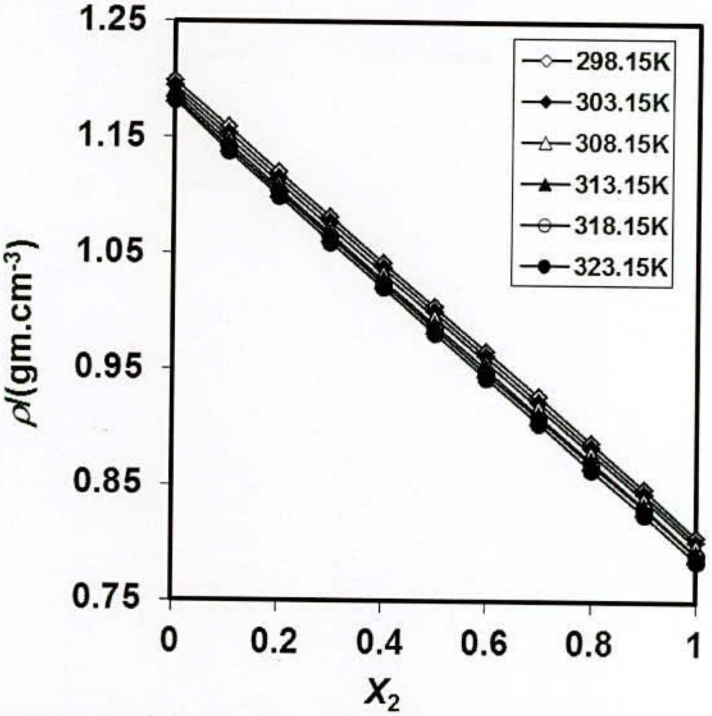

Figure 4.3: Plots of density (ρ) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

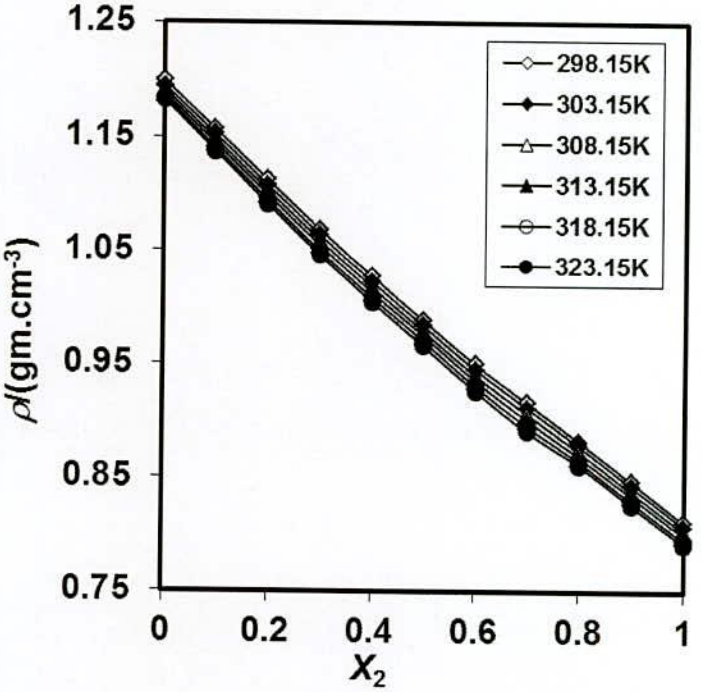

Figure 4.4: Plots of density (ρ) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

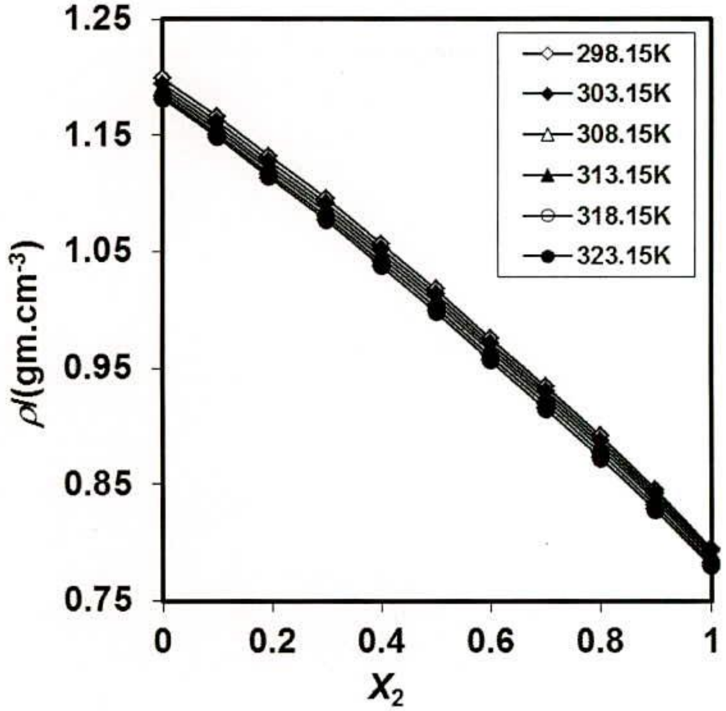

Figure 4.5: Plots of density (ρ) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

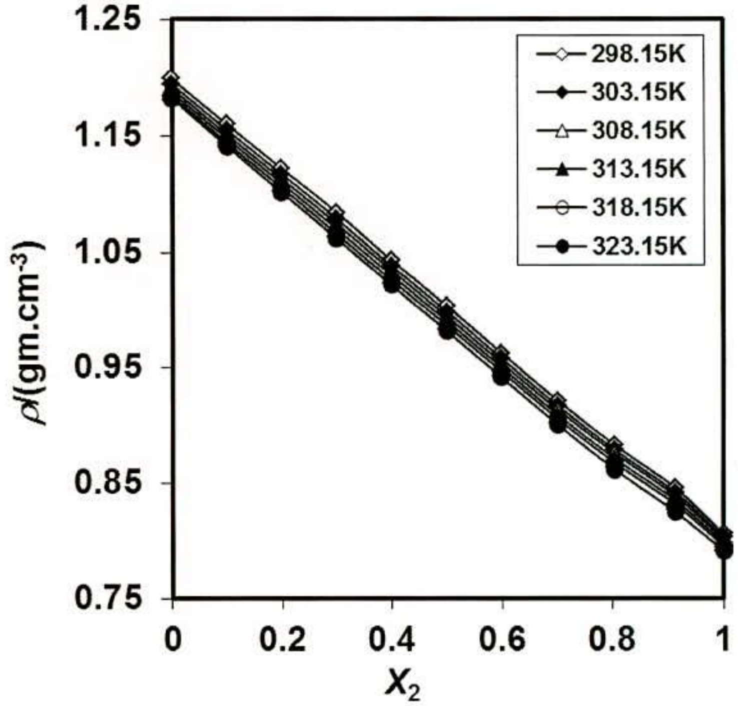

Figure 4.6: Plots of density (ρ) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

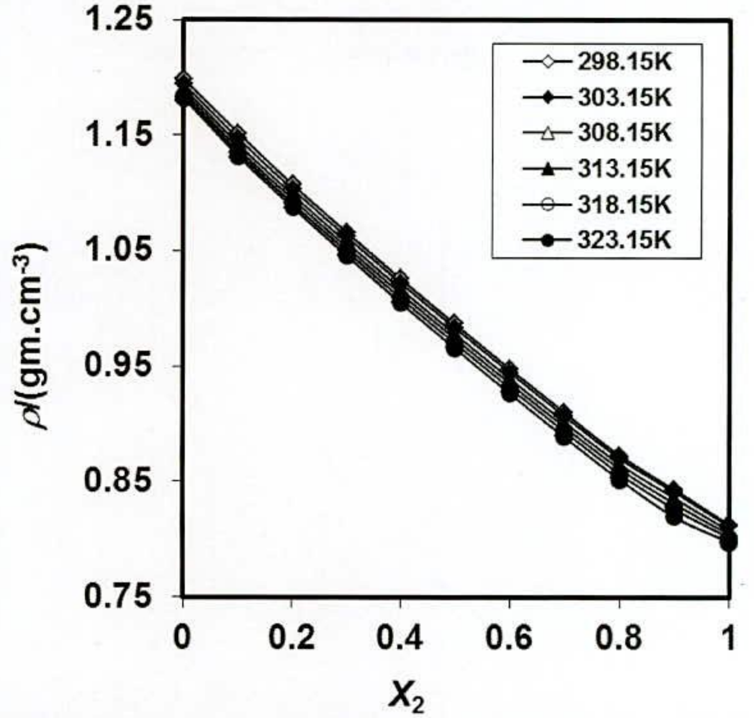

Figure 4.7: Plots of density (ρ) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

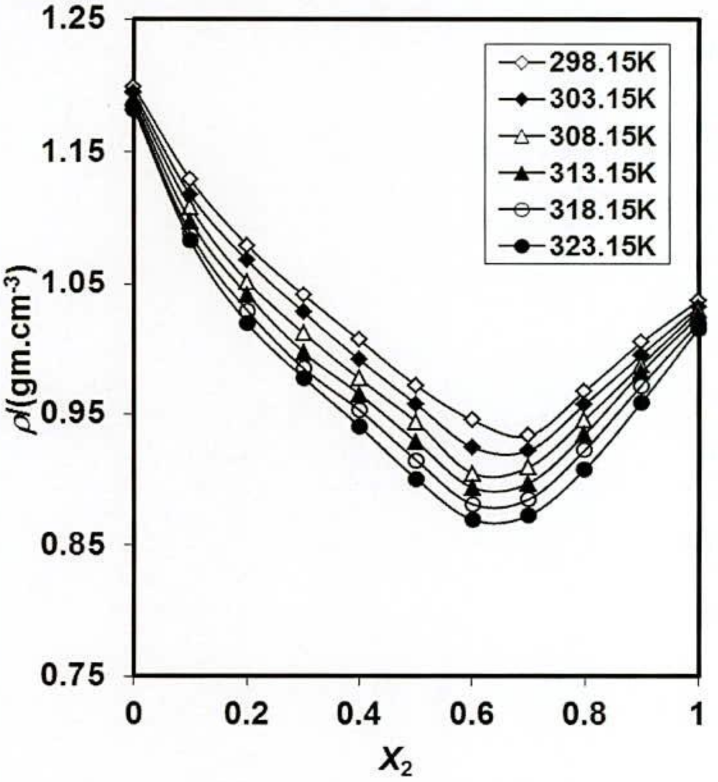

Figure 4.8: Plots of density (ρ) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

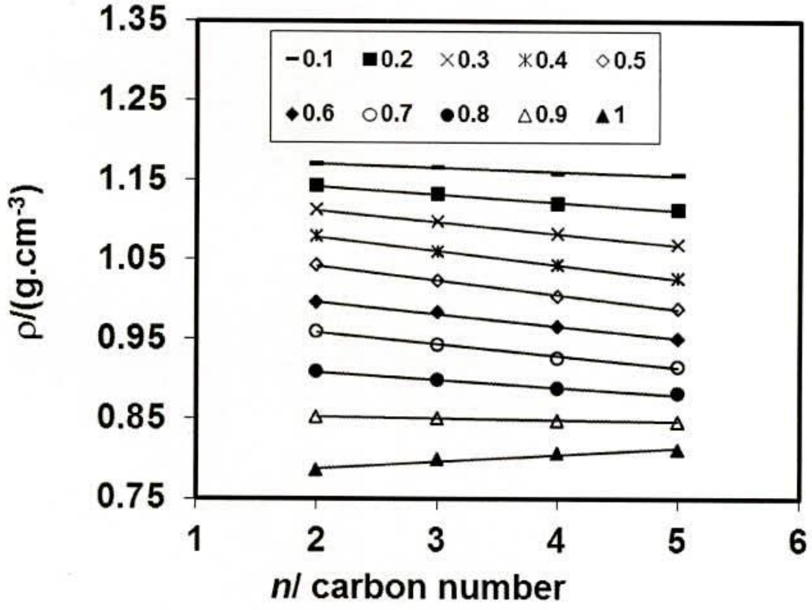

Figure 4.9: Dependence of the density (ρ) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

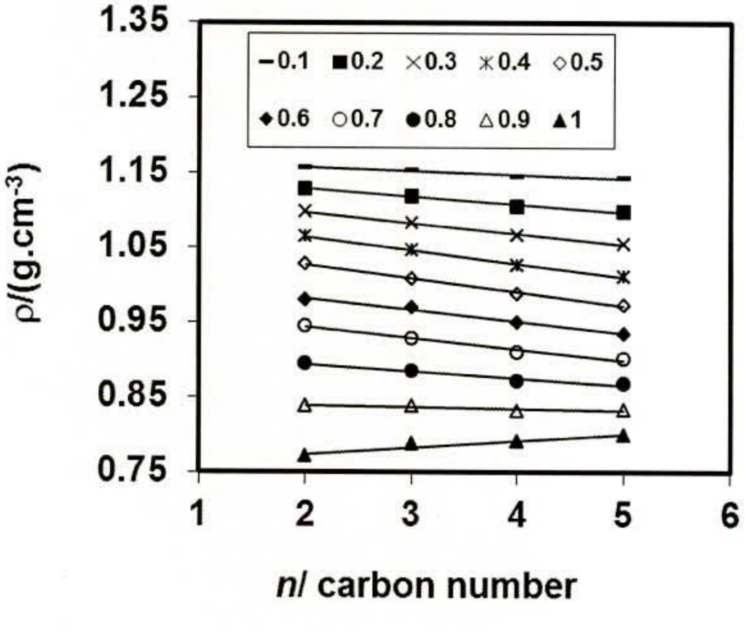

Figure 4.10: Dependence of the density (ρ) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

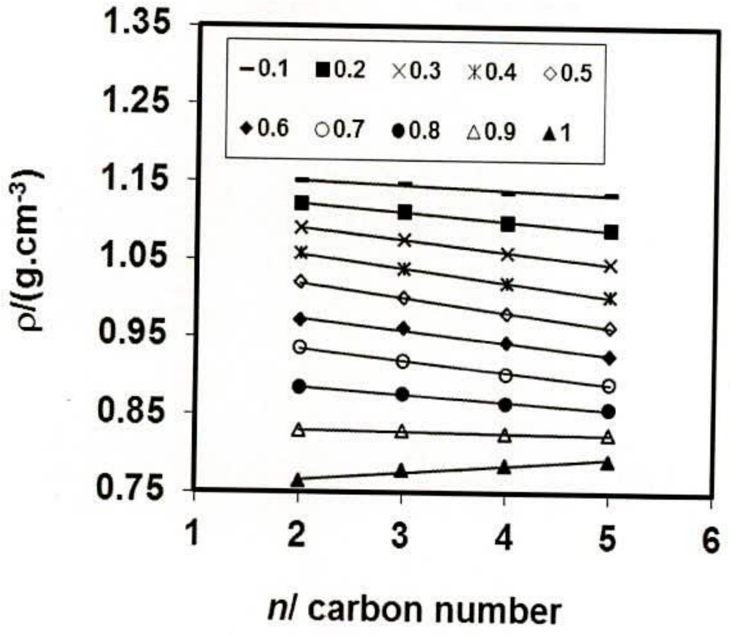

Figure 4.11: Dependence of the density (ρ) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

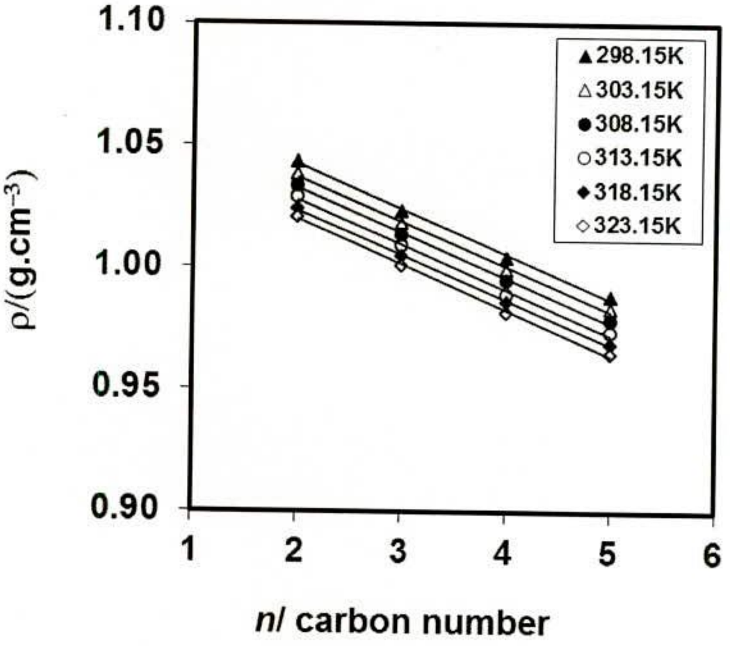

Figure 4.12: Dependence of the density (ρ) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

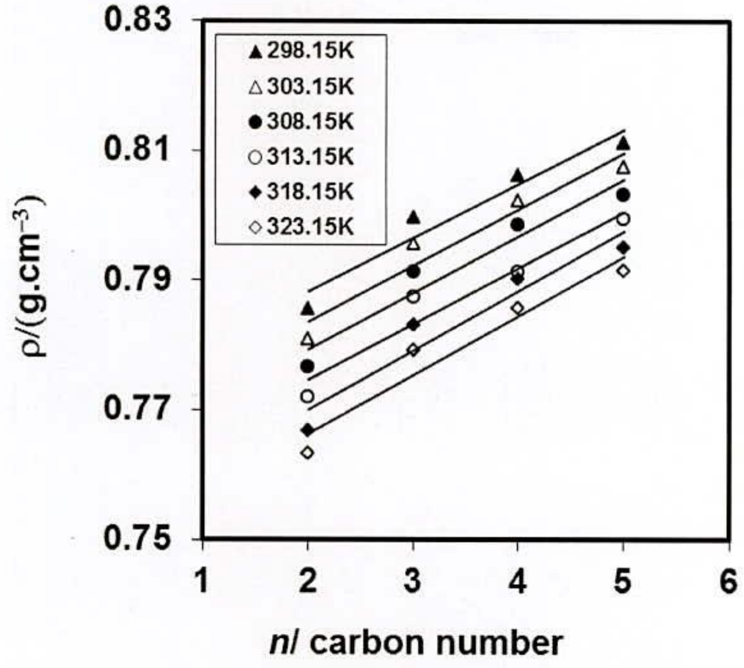

Figure 4.13: Dependence of the density (ρ) with carbon number (n) of n-alcohols with different temperature at 1.0 mole fraction.

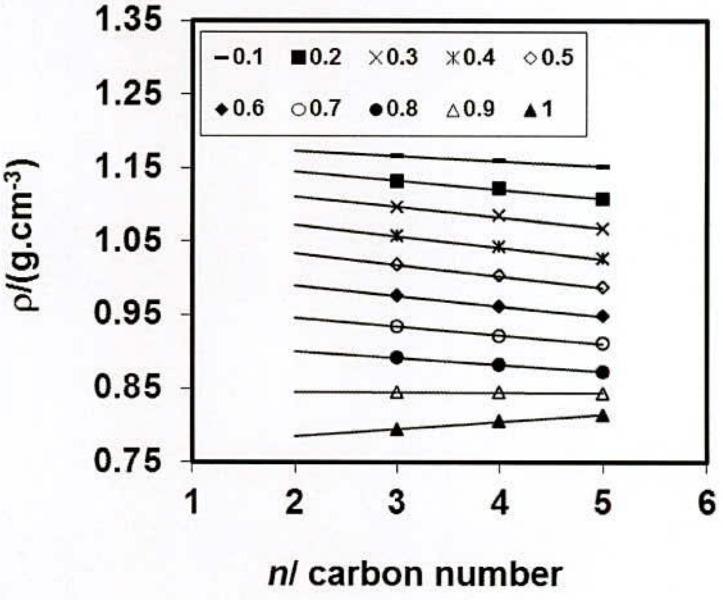

Figure 4.14: Dependence of the density (ρ) with carbon number (n) of iso-alcohols with different mole fraction at 298.15K.

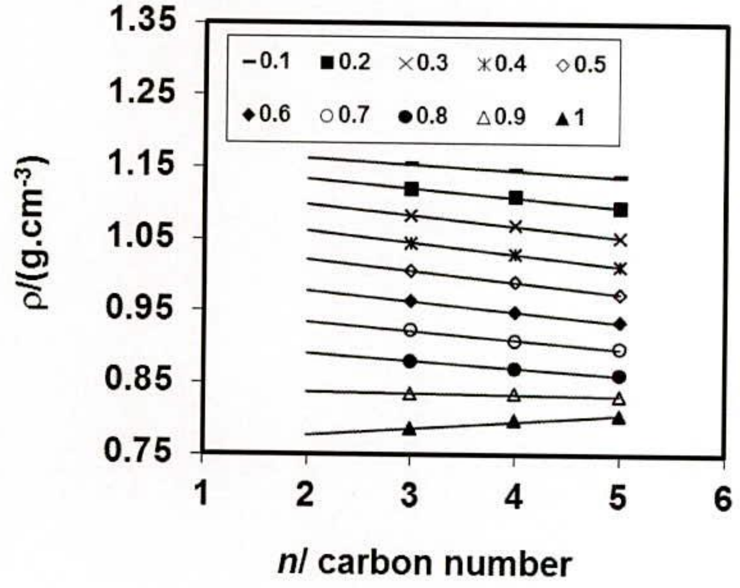

Figure 4.15: Dependence of the density (ρ) with carbon number (n) of iso -alcohols with different mole fraction at 313.15K.

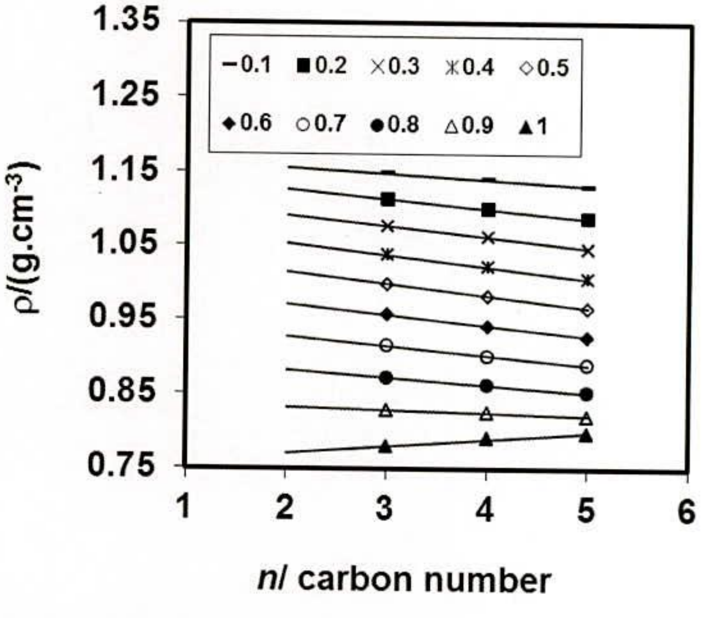

Figure 4.16: Dependence of the density (ρ) with carbon number (n) of iso -alcohols with different mole fraction at 323.15K.

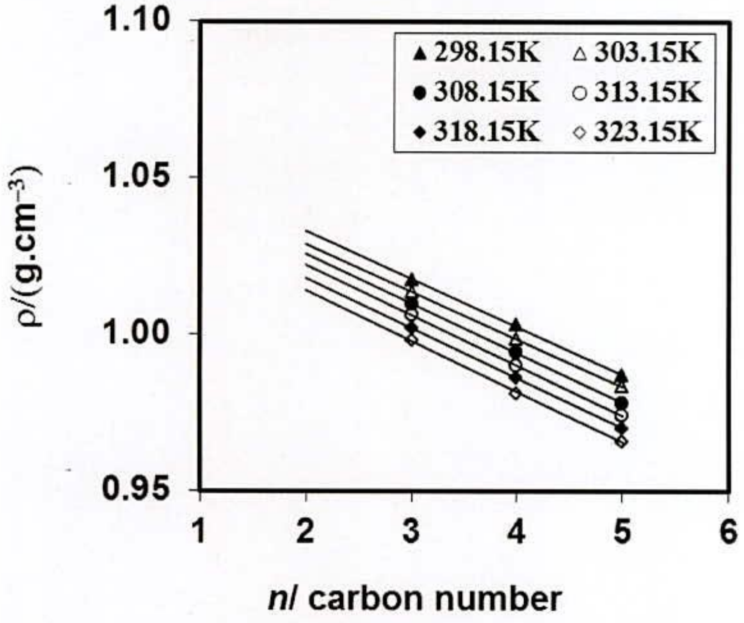

Figure 4.17: Dependence of the density (ρ) with carbon number (n) of iso -alcohols with different temperature at 0.5 mole fraction.

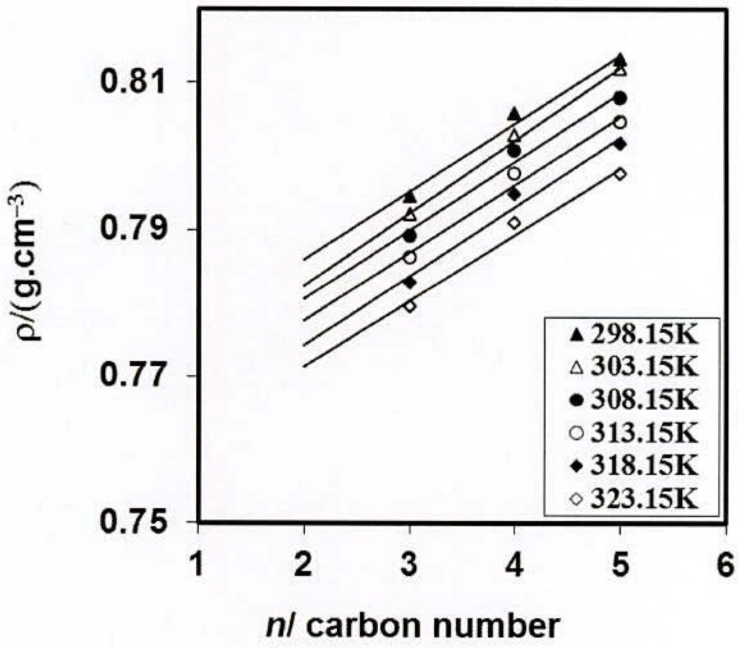

Figure 4.18: Dependence of the density (ρ) with carbon number (n) of iso -alcohols with different temperature at 1.0 mole fraction.

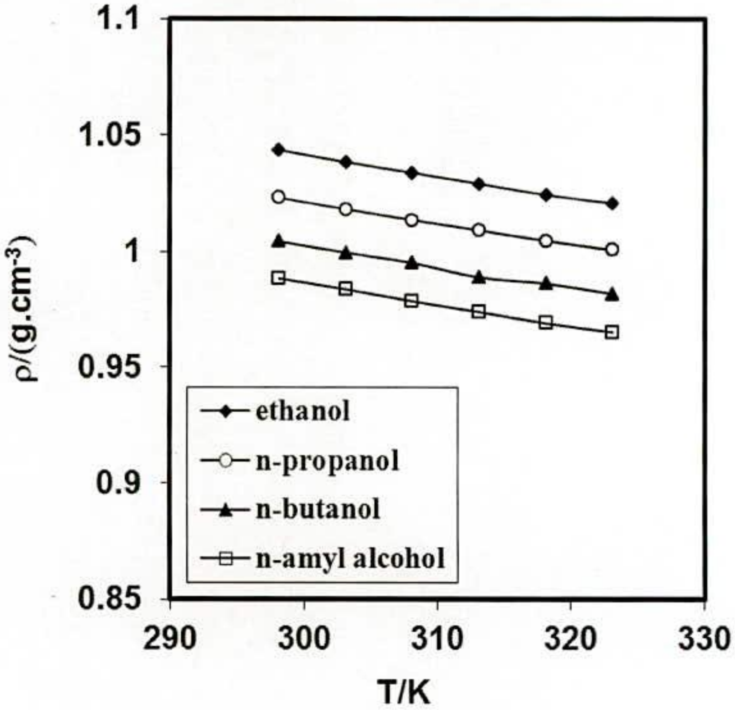

Figure 4.19: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

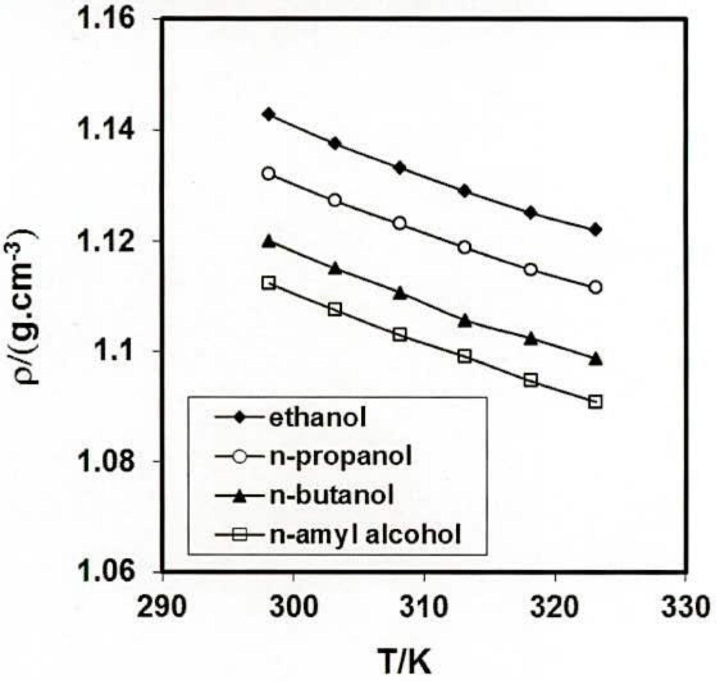

Figure 4.20: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

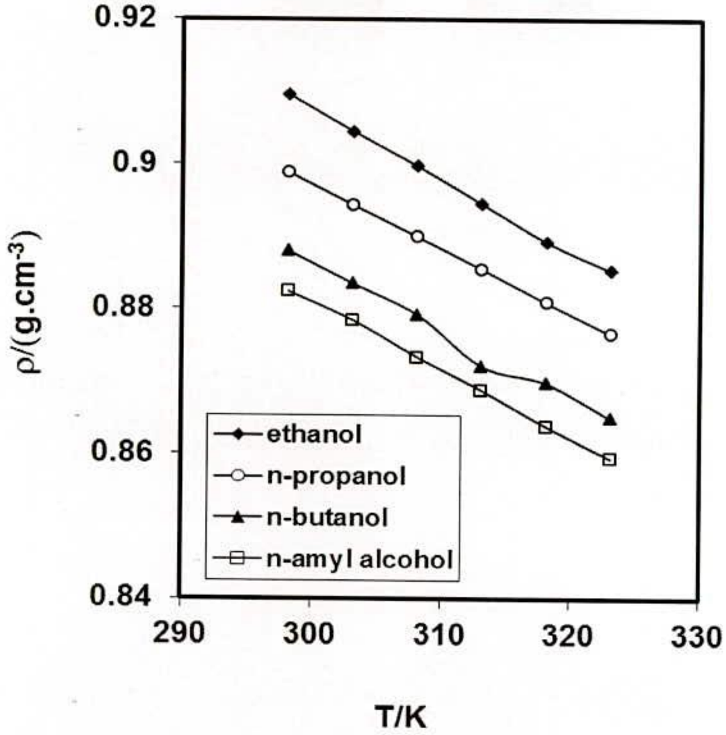

Figure 4.21: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

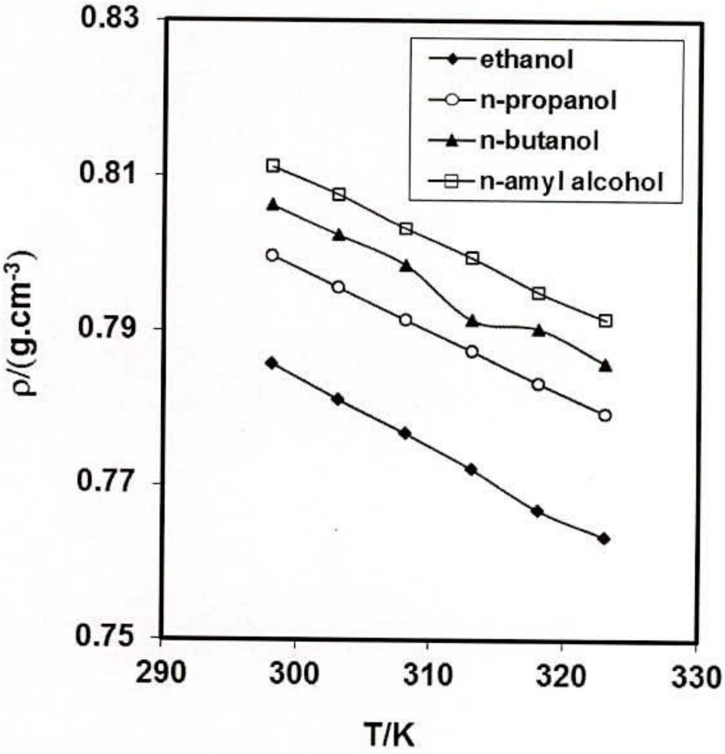

Figure 4.22: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

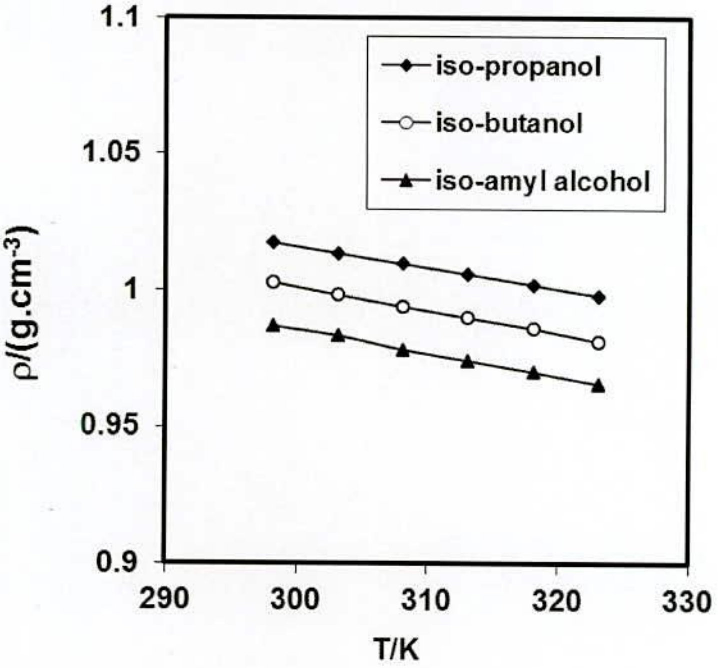

Figure 4.23: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

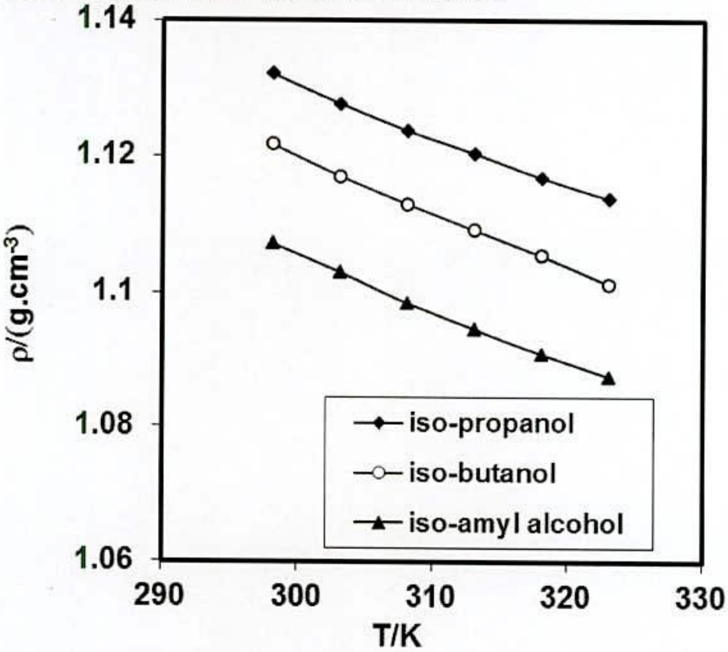

Figure 4.24: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

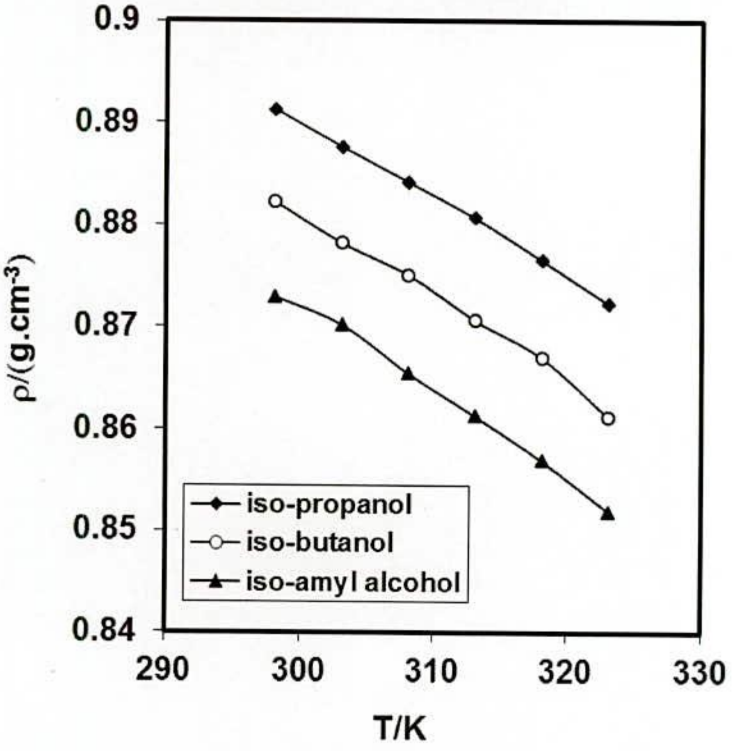

Figure 4.25 Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

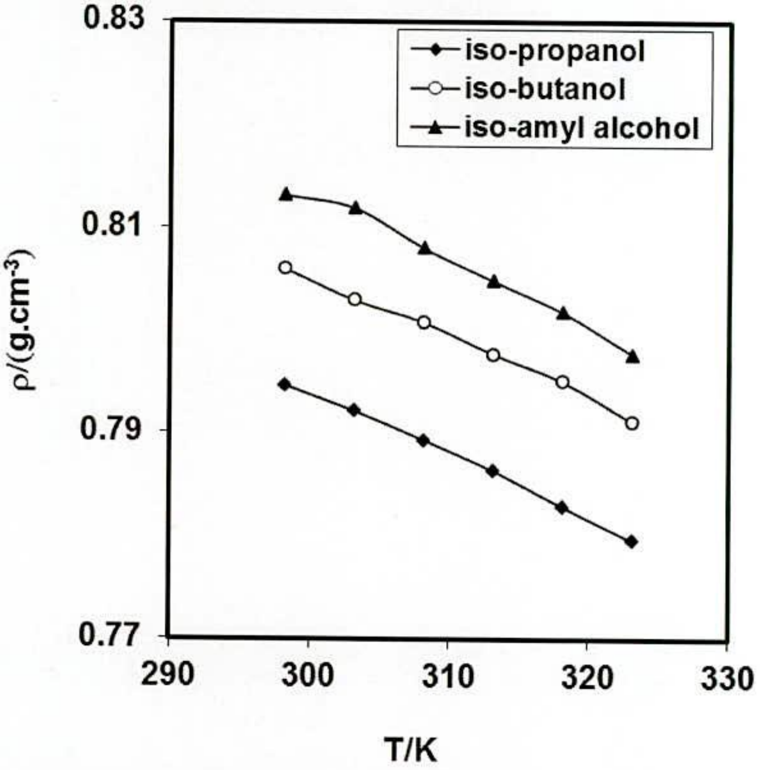

Figure 4.26: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

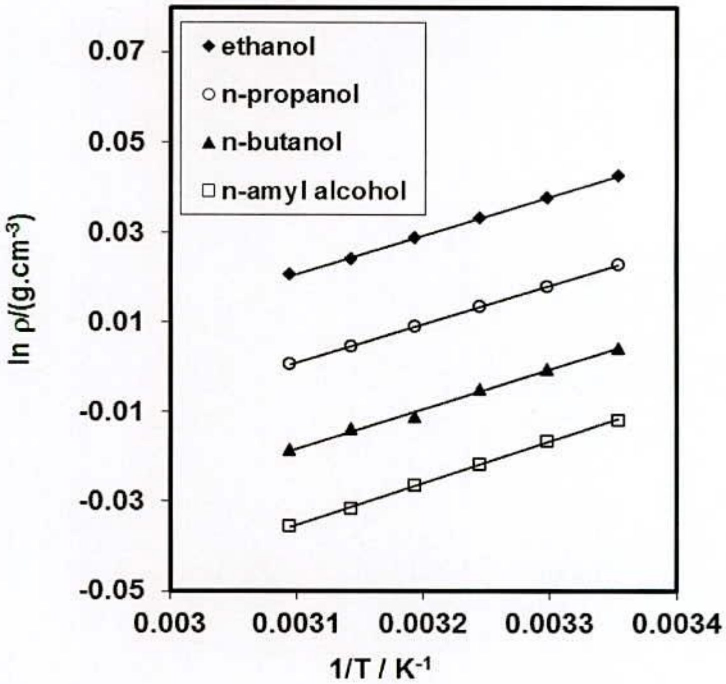

Figure 4.27: Comparison of $\ln\rho$ vs 1/T Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

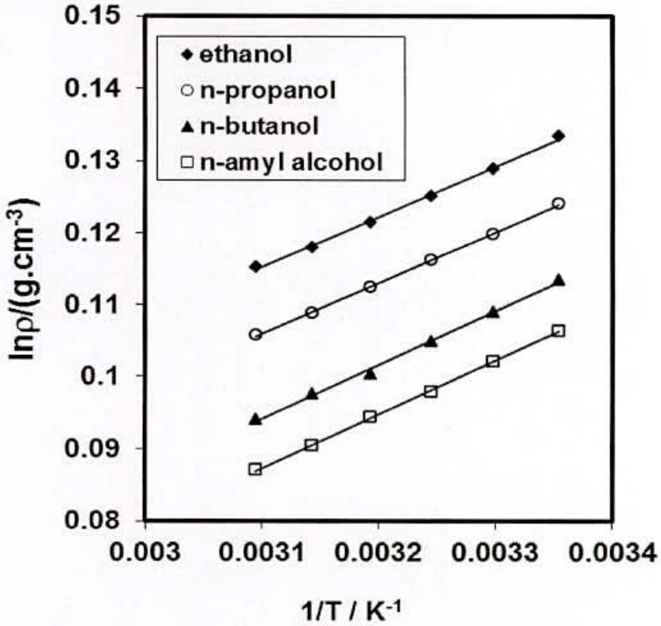

Figure 4.28: Comparison of $\ln\rho$ vs 1/T Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

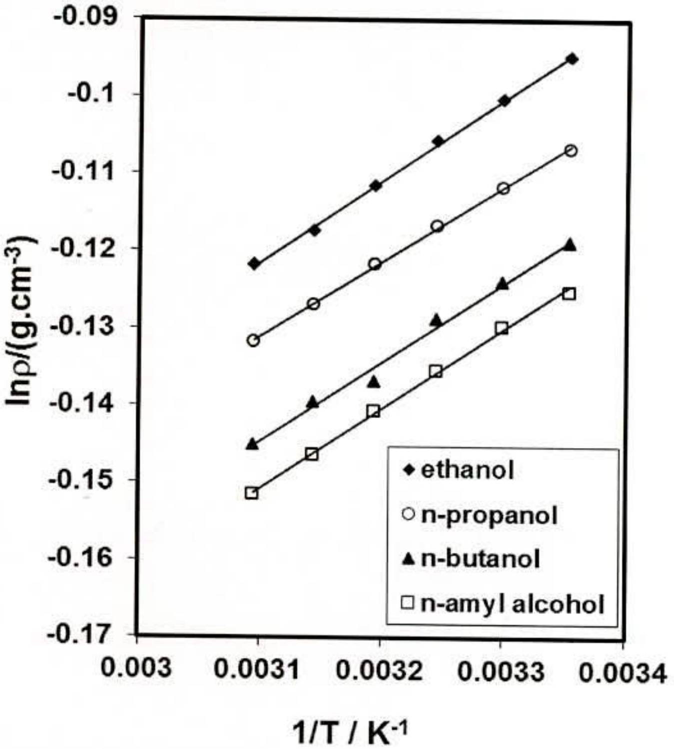

Figure 4.29: Comparison of $\ln\rho$ vs 1/T Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

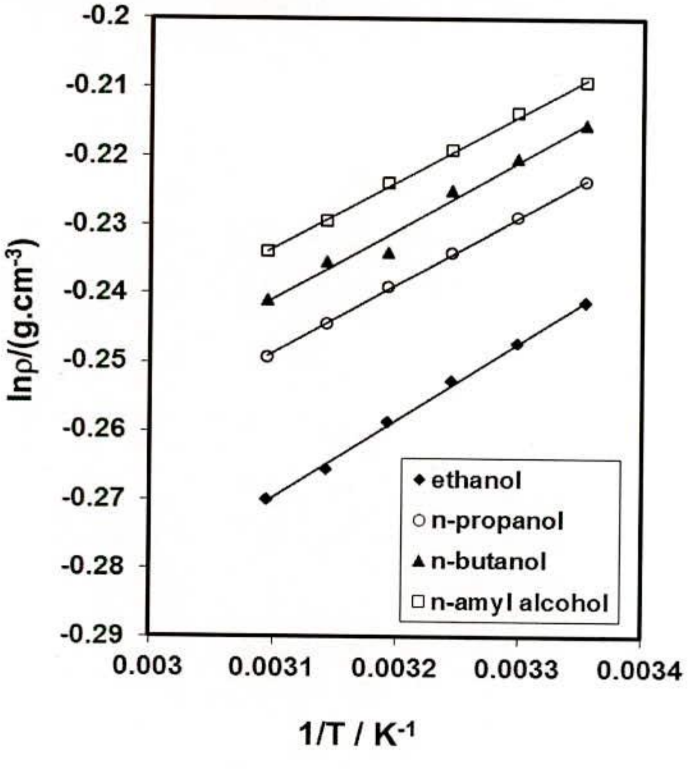

Figure 4.30: Comparison of $\ln\rho$ vs 1/T Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

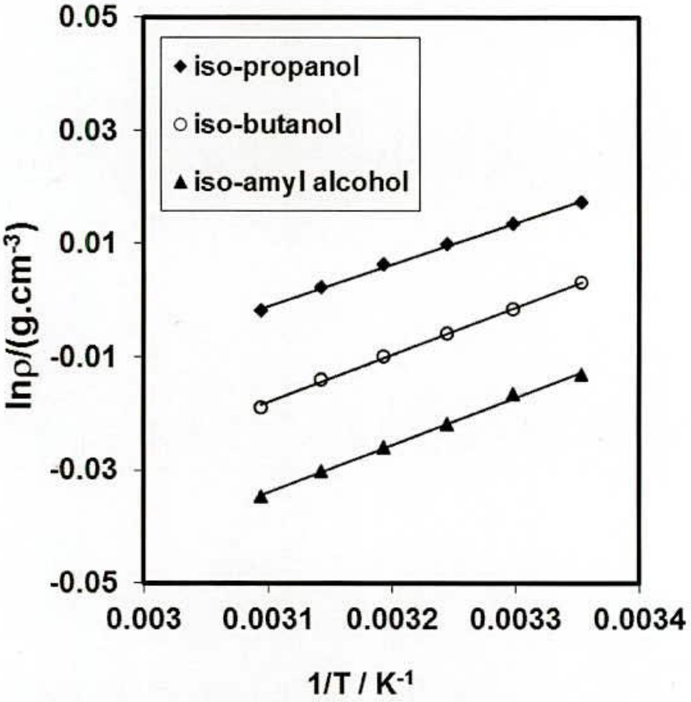

Figure 4.31: Comparison of $\ln\rho$ vs 1/T iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

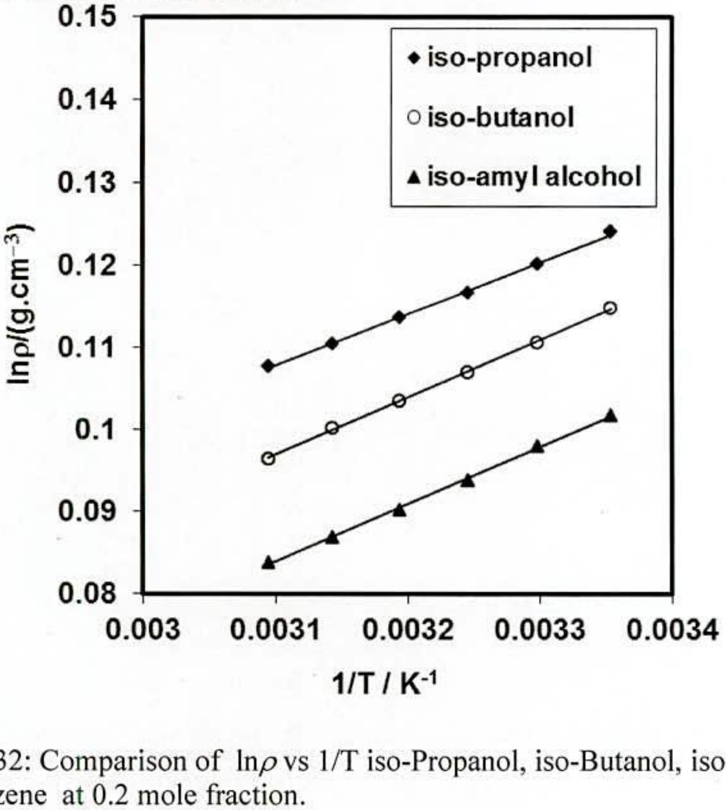

Figure 4.32: Comparison of $\ln\rho$ vs 1/T iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

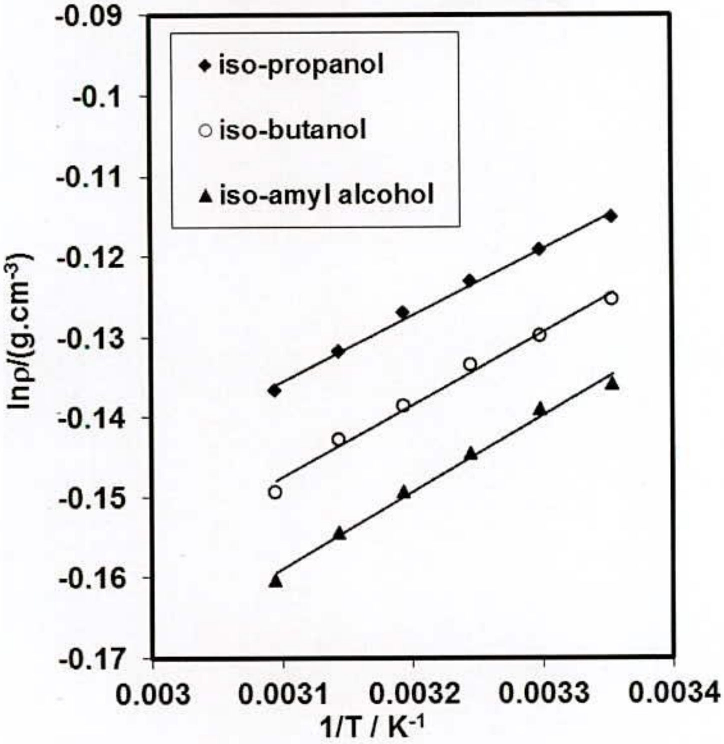

Figure 4.33: Comparison of $\ln\rho$ vs 1/T iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

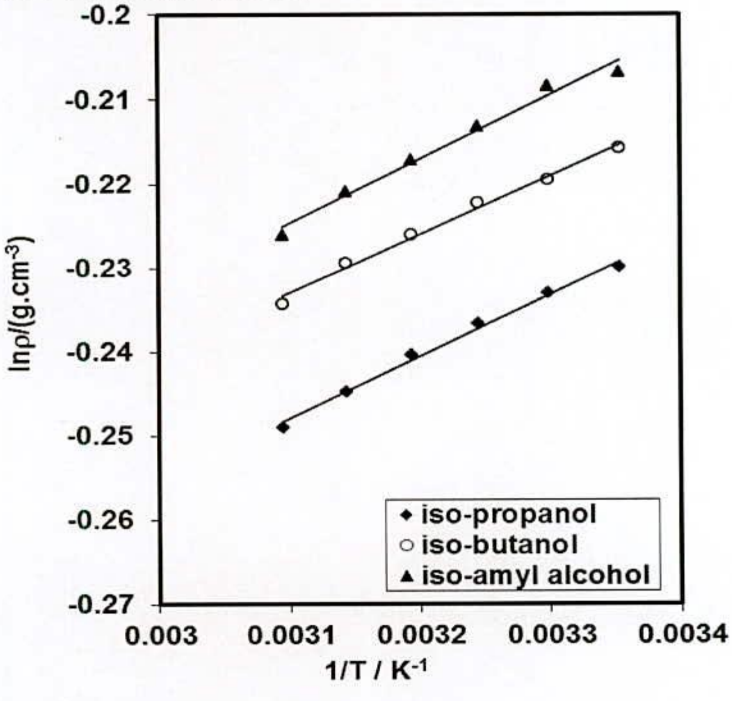

Figure 4.34: Comparison of $\ln\rho$ vs 1/T iso-Propanol, iso-Butanol, iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

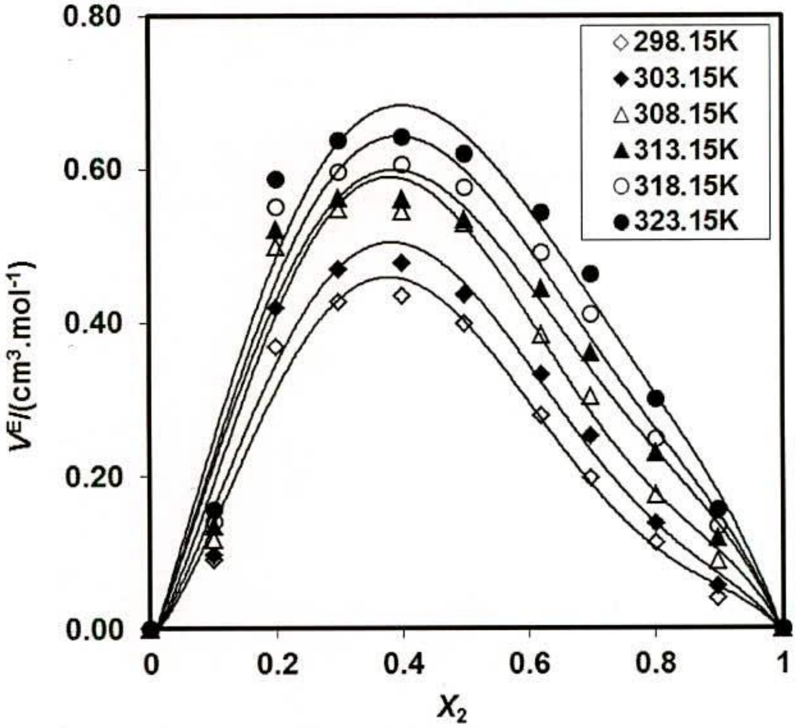

Figure 4.35: Plots of excess molar volume (V^E) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

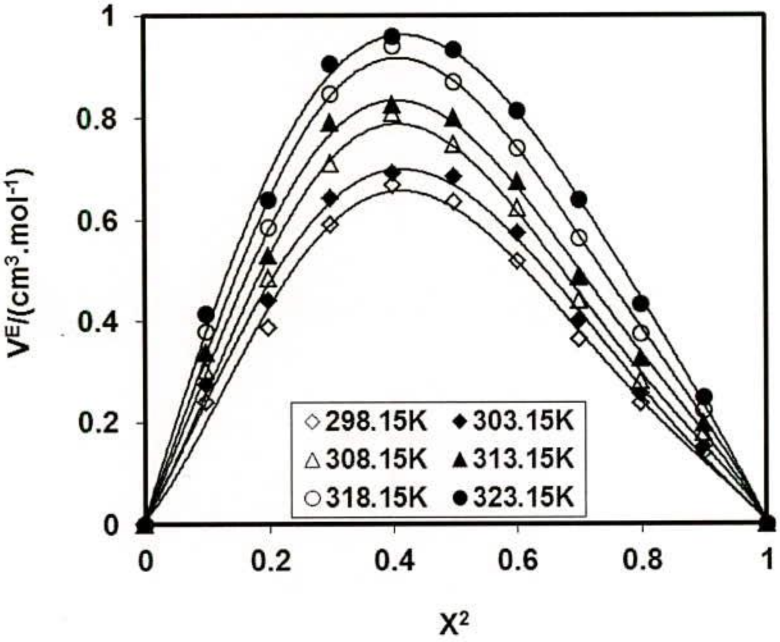

Figure 4.36: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

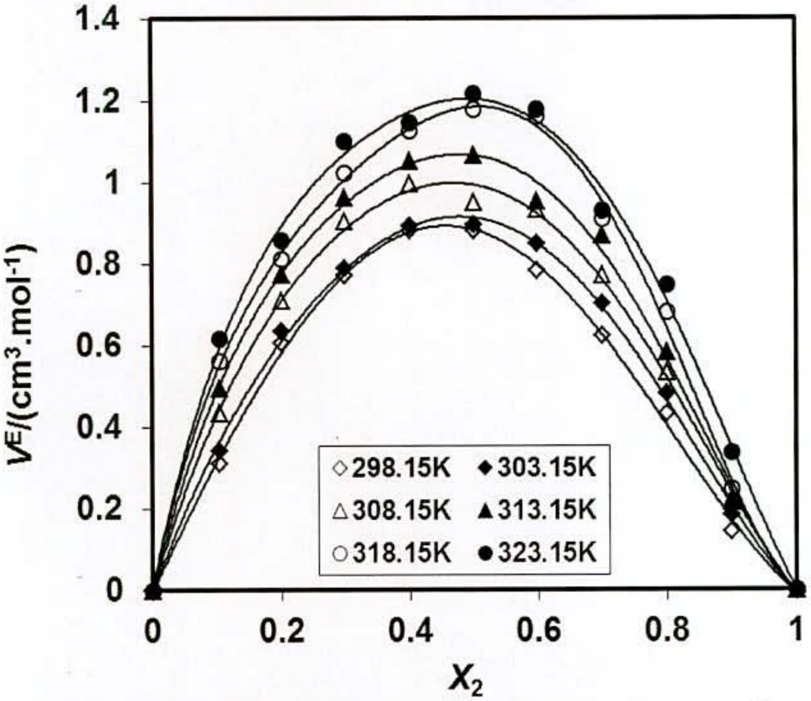

Figure 4.37: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

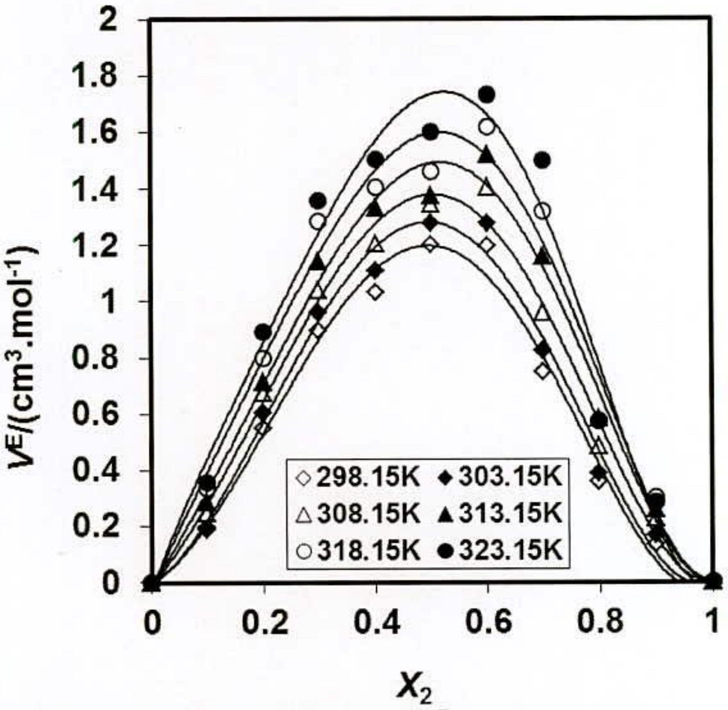

Figure 4.38: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

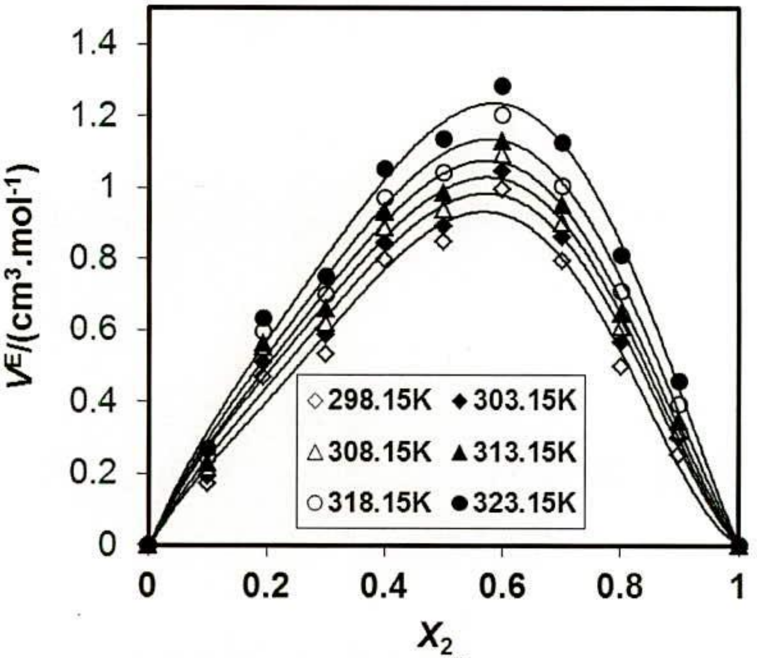

Figure 4.39: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

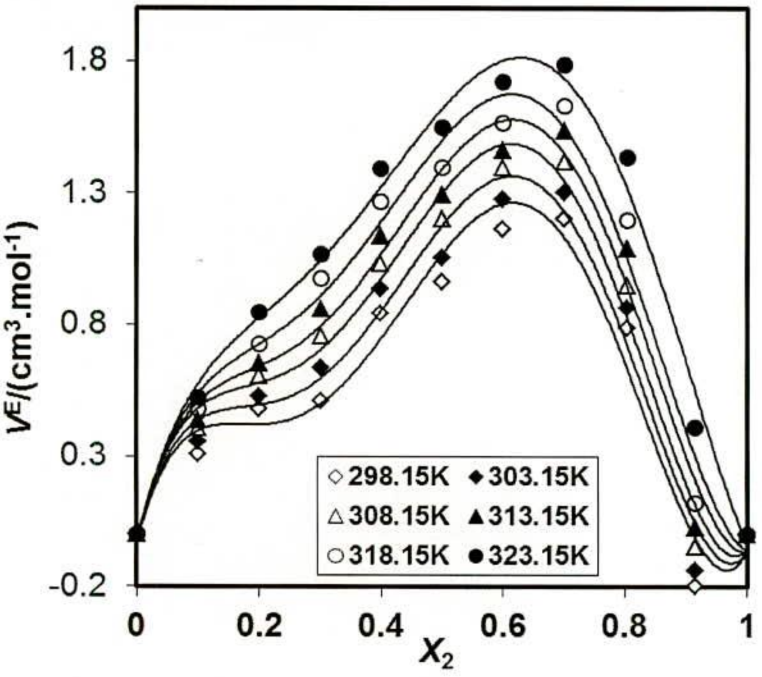

Figure 4.40: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

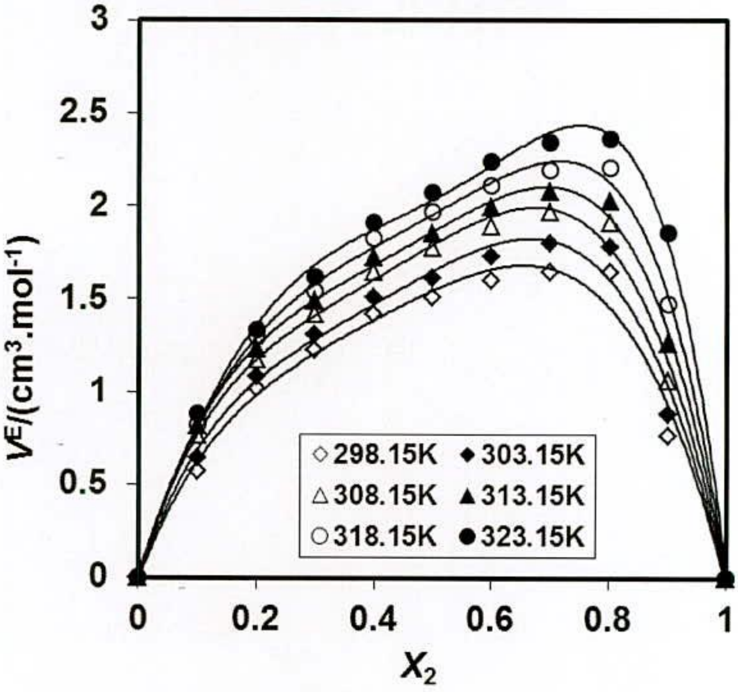

Figure 4.41: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

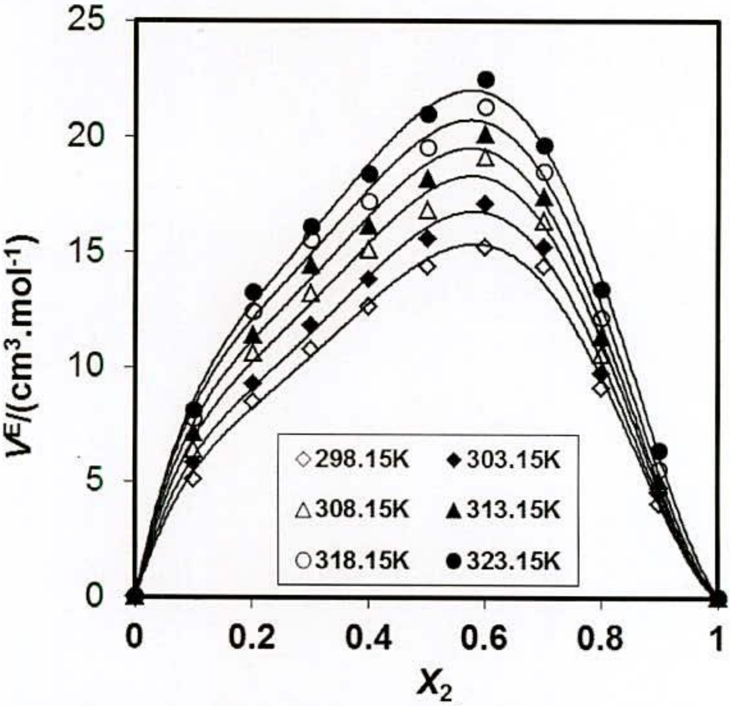

Figure 4.42: Plots of excess molar volume (V^E) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

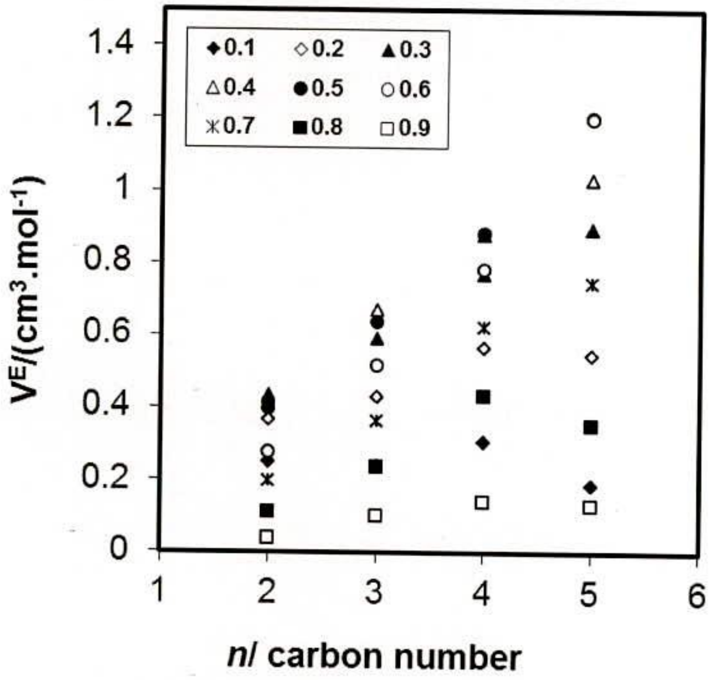

Figure 4.43: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

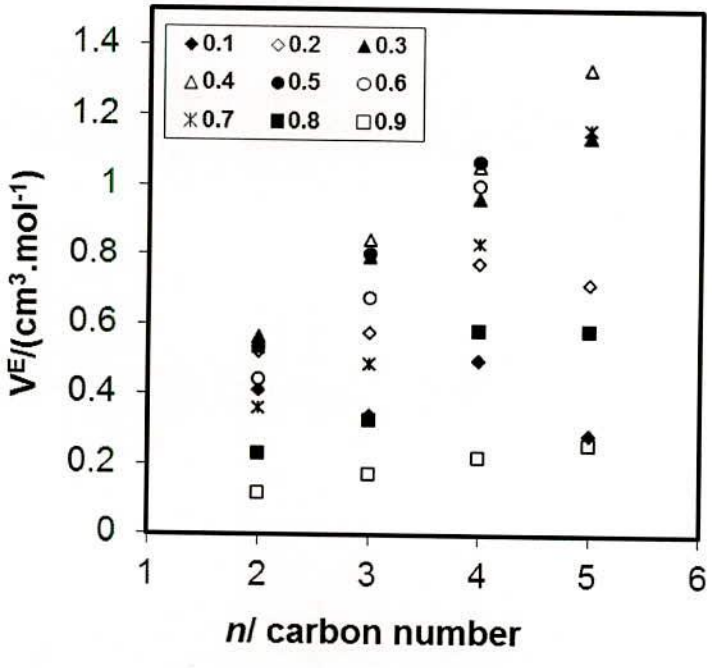

Figure 4.44: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

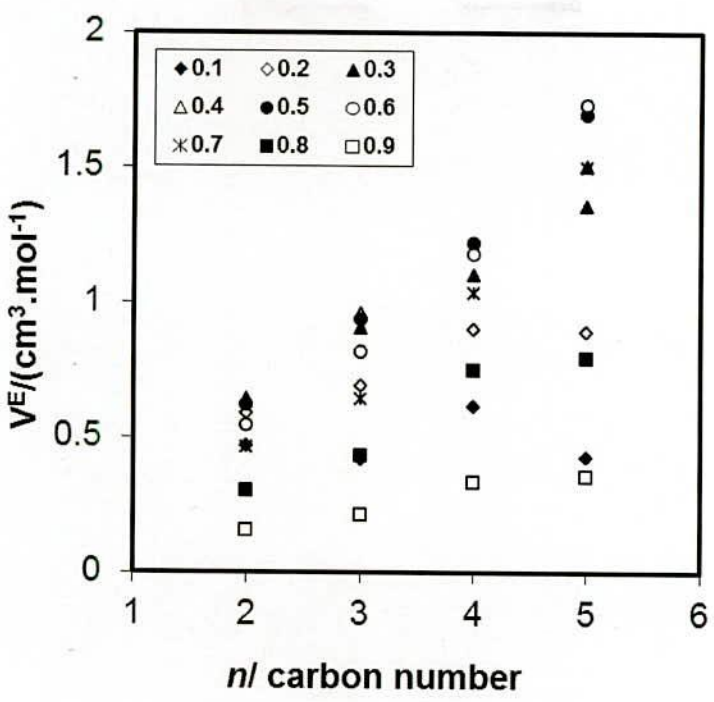

Figure 4.45: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

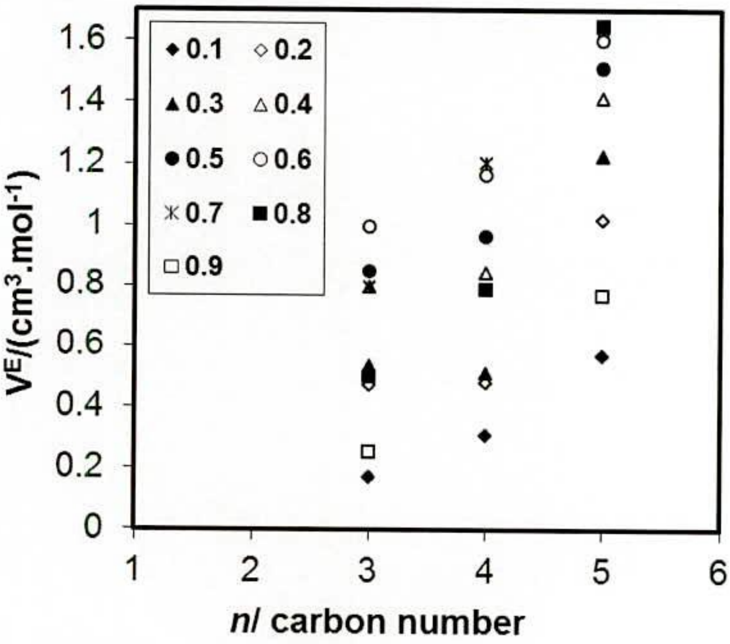

Figure 4.46: Dependence of the excess molar volume (V^E) with carbon number (n) of iso-alcohols with different mole fraction at 298.15K.

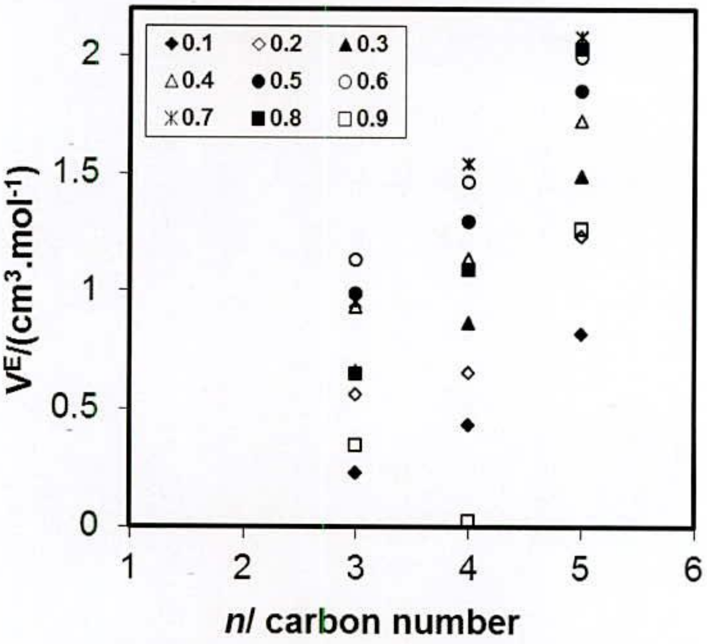

Figure 4.47: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols with different mole fraction at 313.15K.

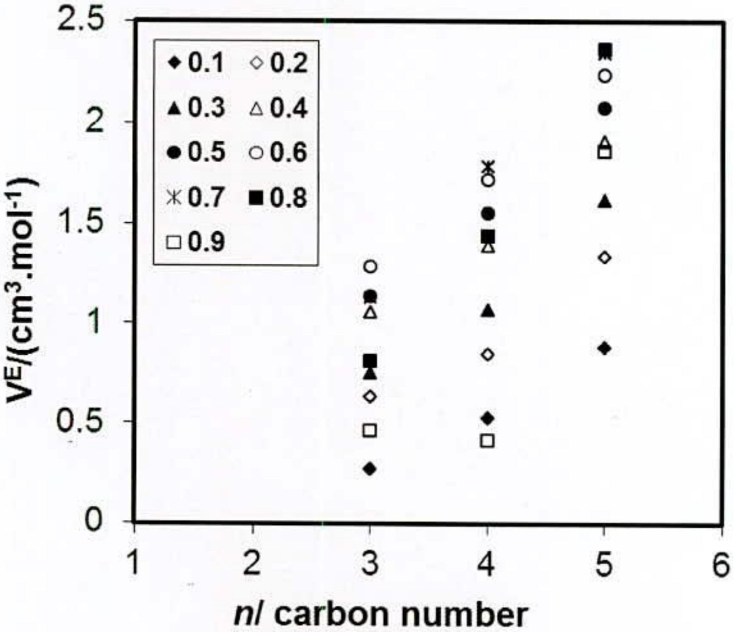

Figure 4.48: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols with different mole fraction at 323.15K.

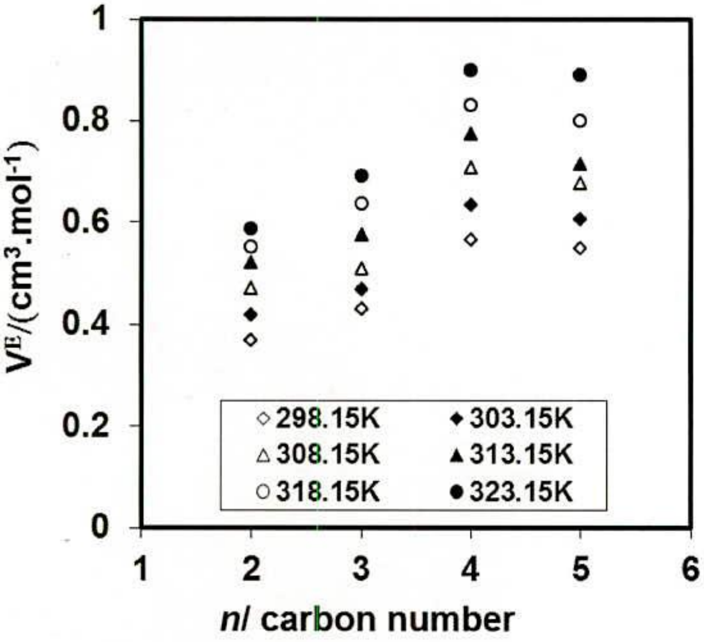

Figure 4.49: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different temperature at 0.2 mole fraction.

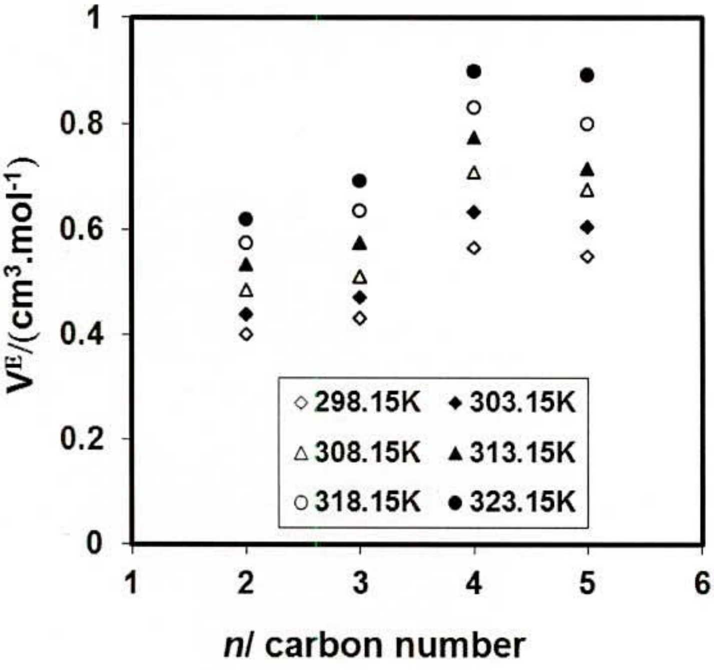

Figure 4.50: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

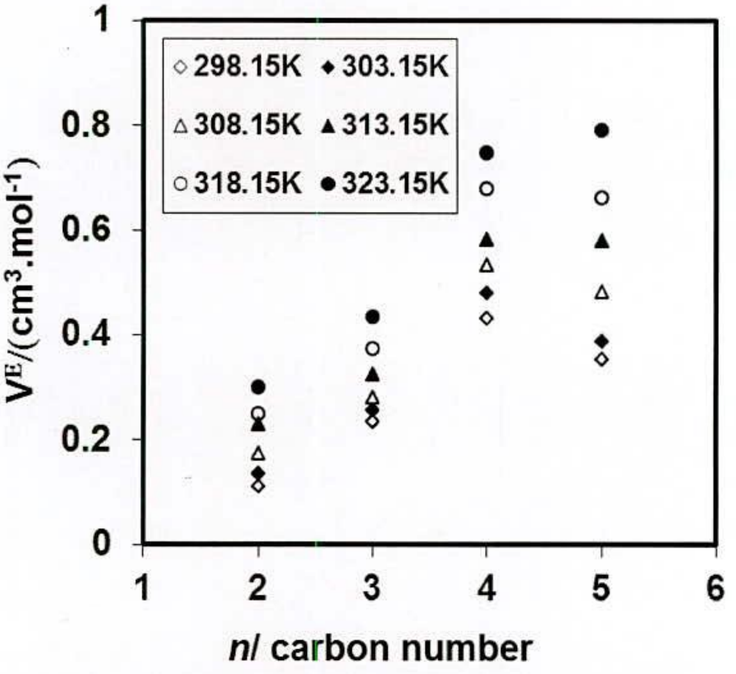

Figure 4.51: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols with different temperature at 0.8 mole fraction.

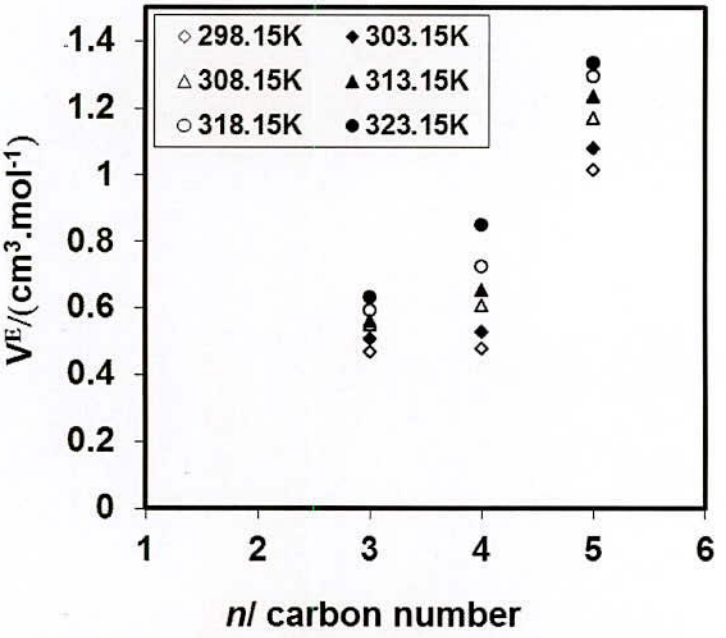

Figure 4.52: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols with different temperature at 0.2 mole fraction.

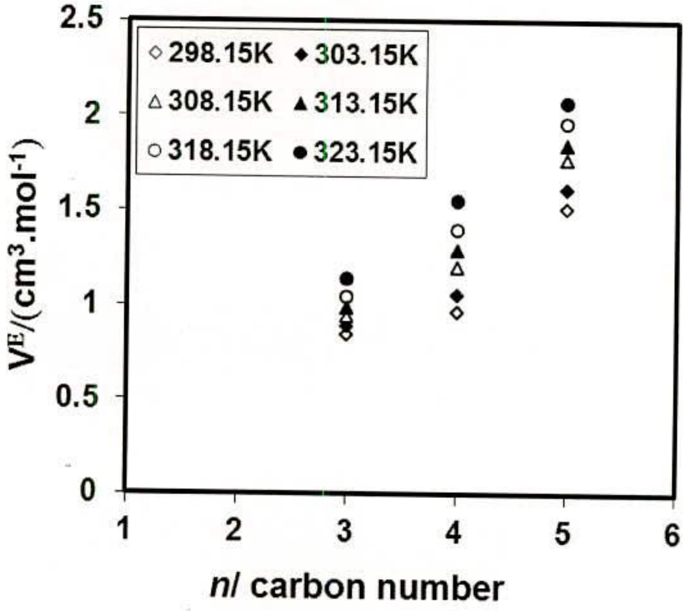

Figure 4.53: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols with different temperature at 0.5 mole fraction.

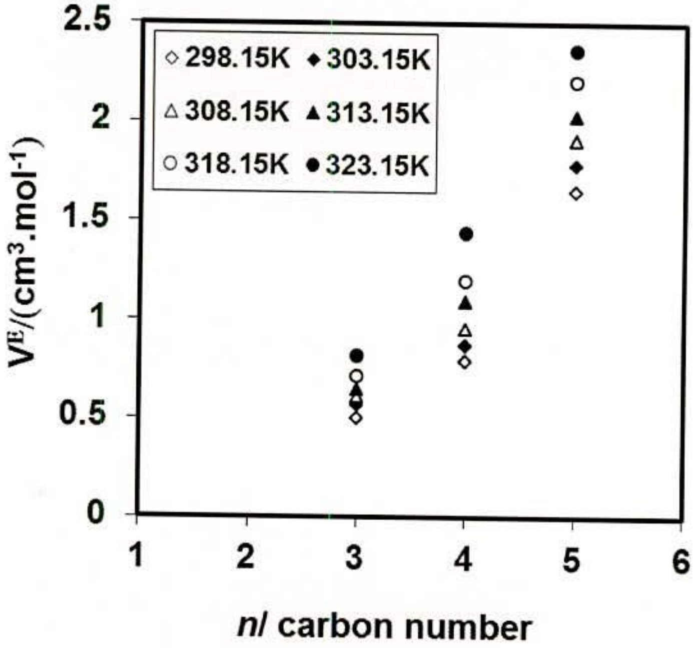

Figure 4.54: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols with different temperature at 0.8 mole fraction.

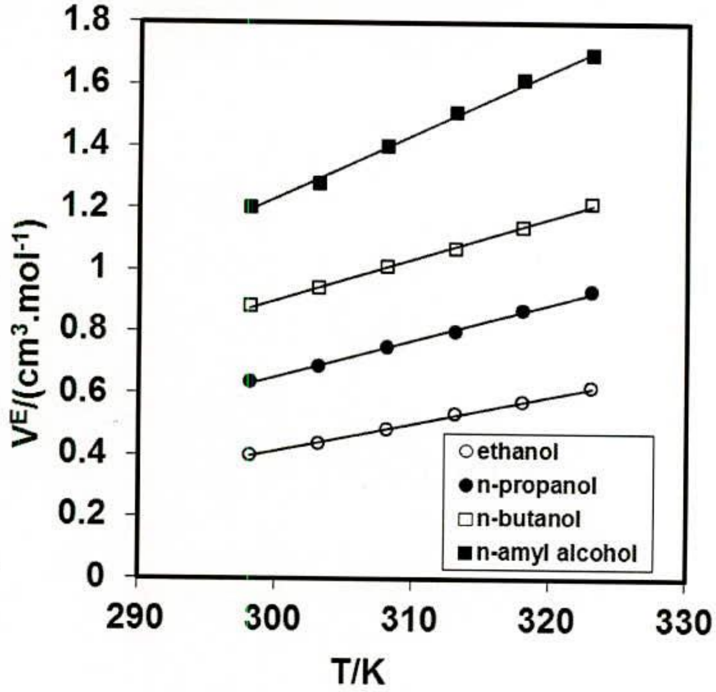

Figure 4.55: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

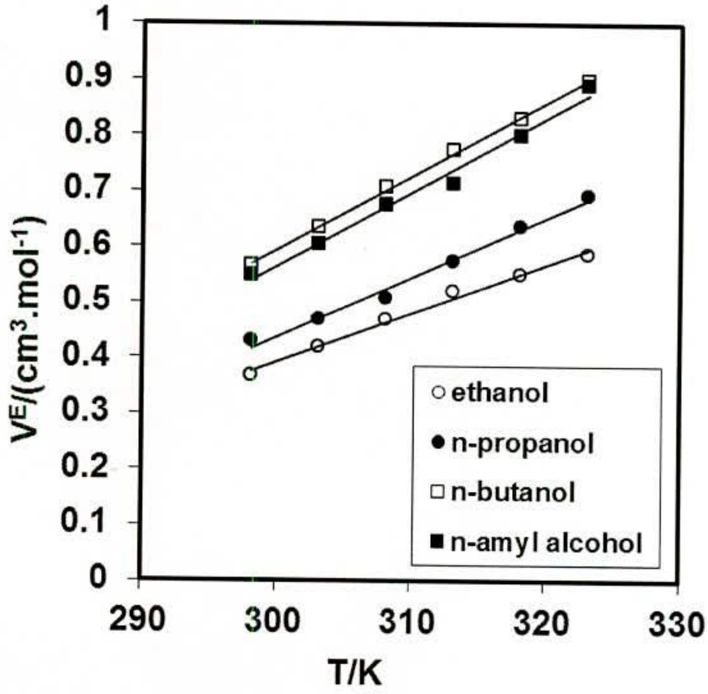

Figure 4.56: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

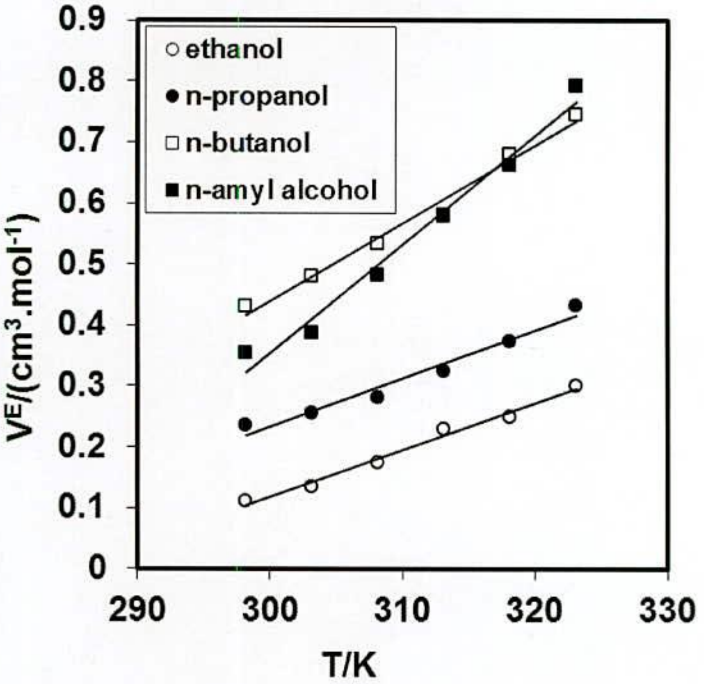

Figure 4.57: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

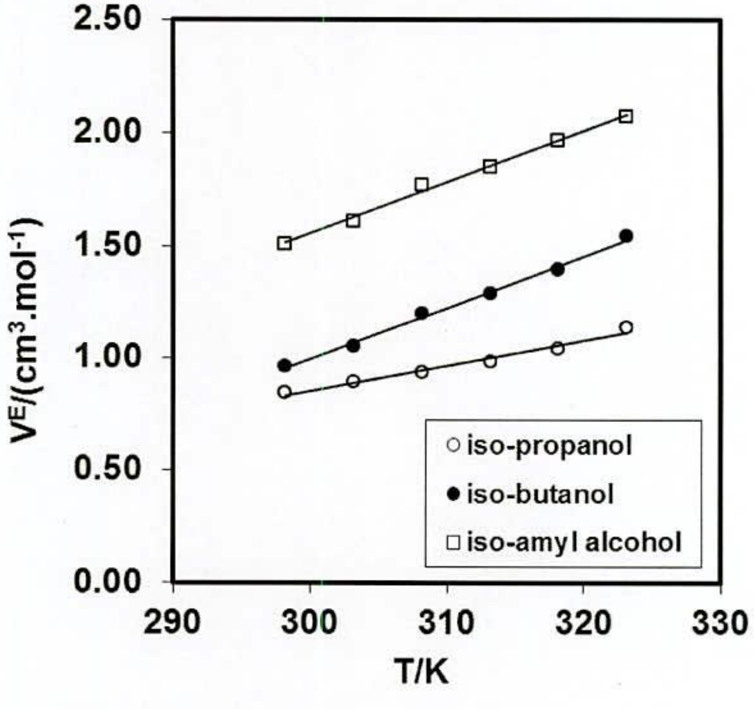

Figure 4.58: Comparison of excess molar volume (V^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

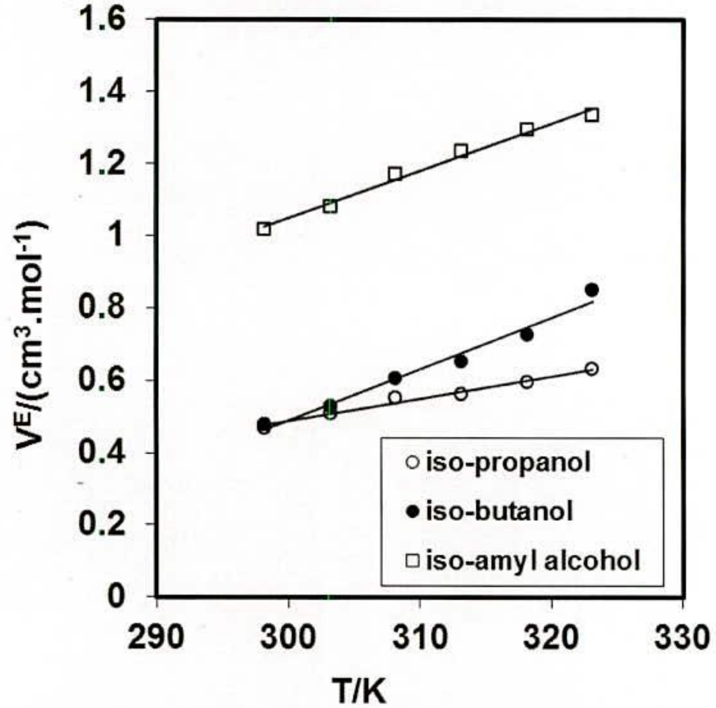

Figure 4.59: Comparison of excess molar volume (V^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

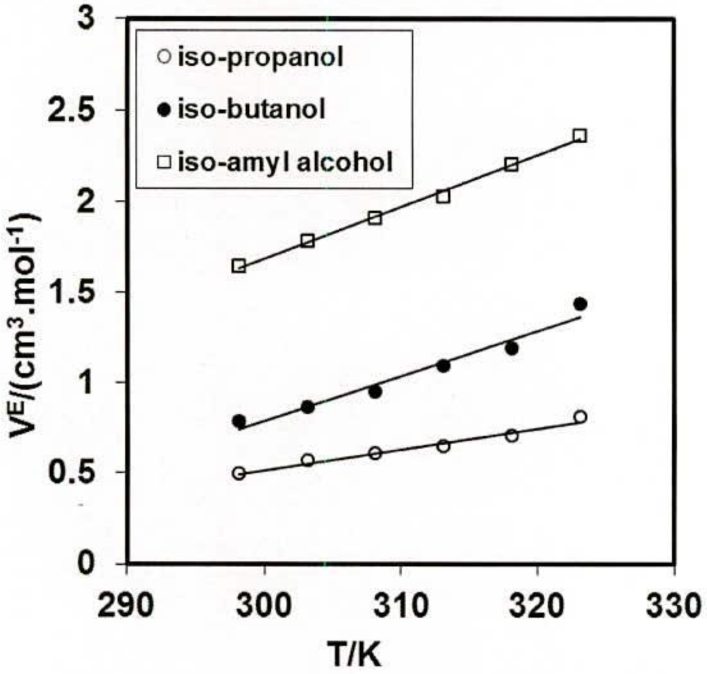

Figure 4.60: Comparison of excess molar volume (V^E) vs temperature (T) iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

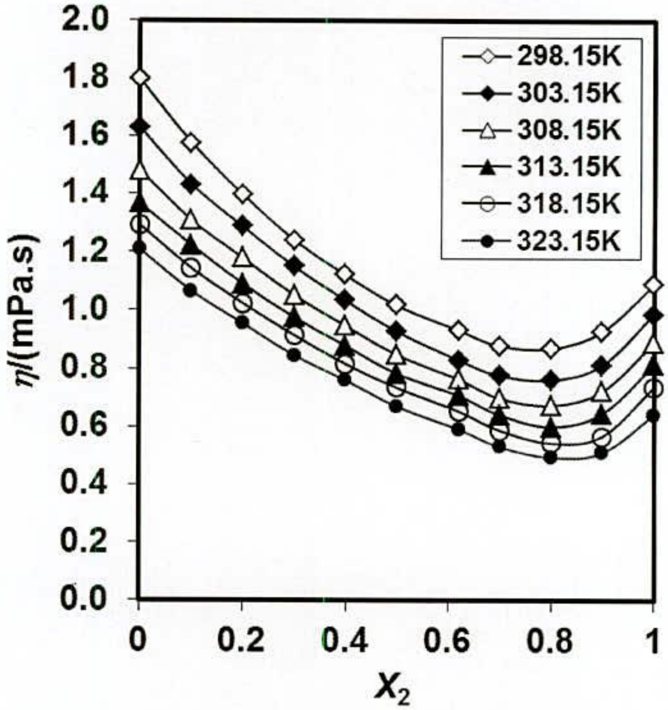

Figure 4.61: Plots of viscosity (*η*) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

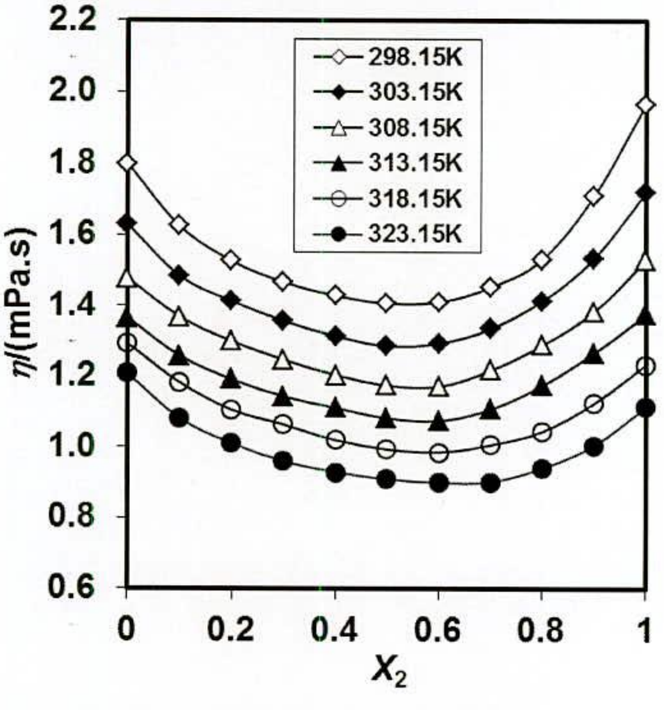

Figure 4.62: Plots of viscosity (*η*) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

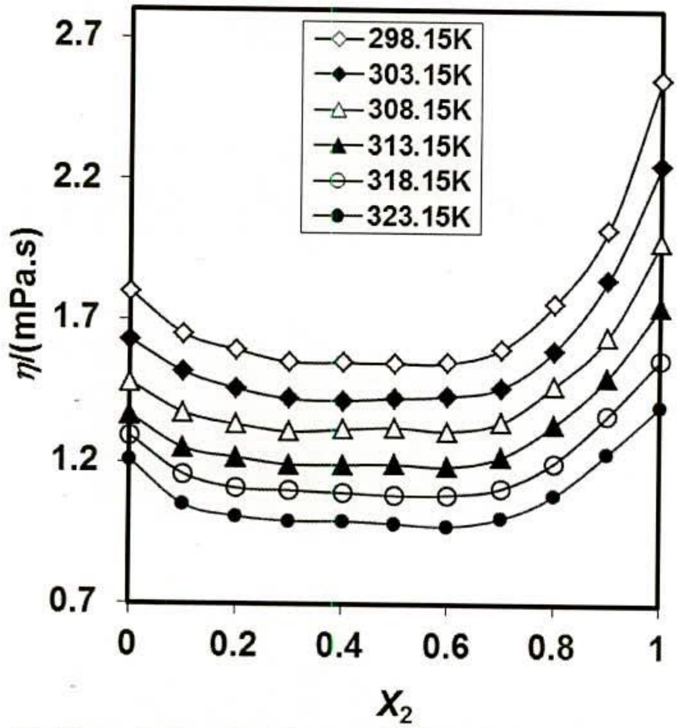

Figure 4.63: Plots of viscosity (*η*) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

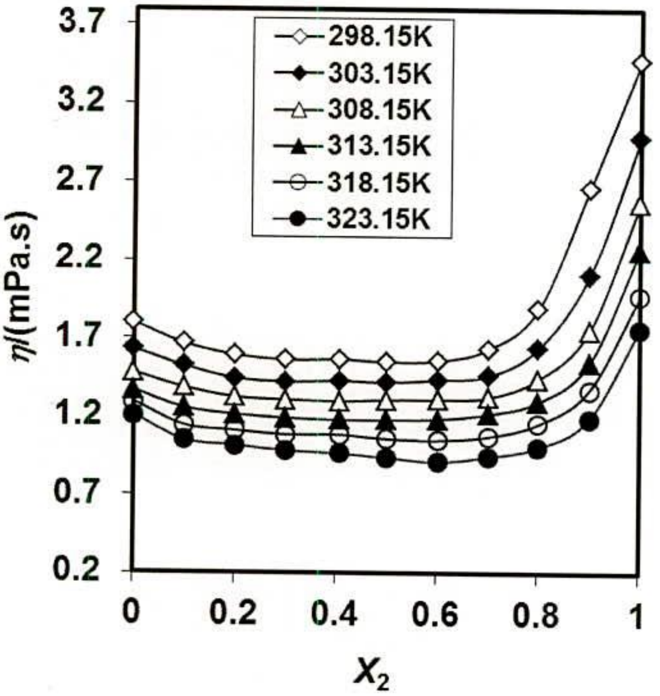

Figure 4.64: Plots of viscosity (*η*) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

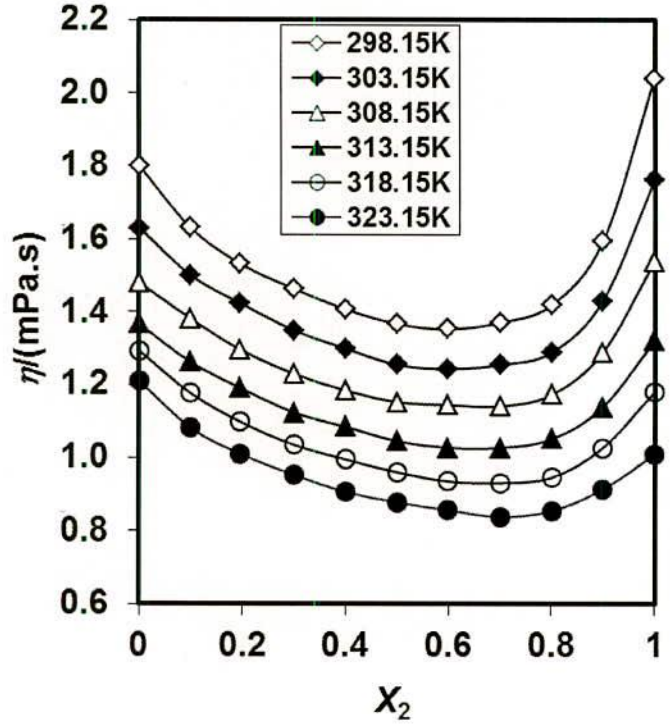

Figure 4.65: Plots of viscosity (η) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

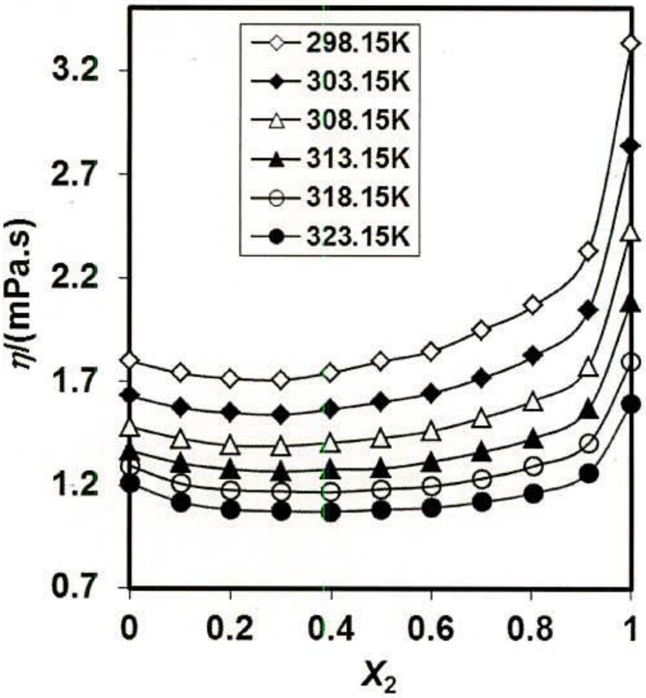

Figure 4.66: Plots of viscosity (η) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

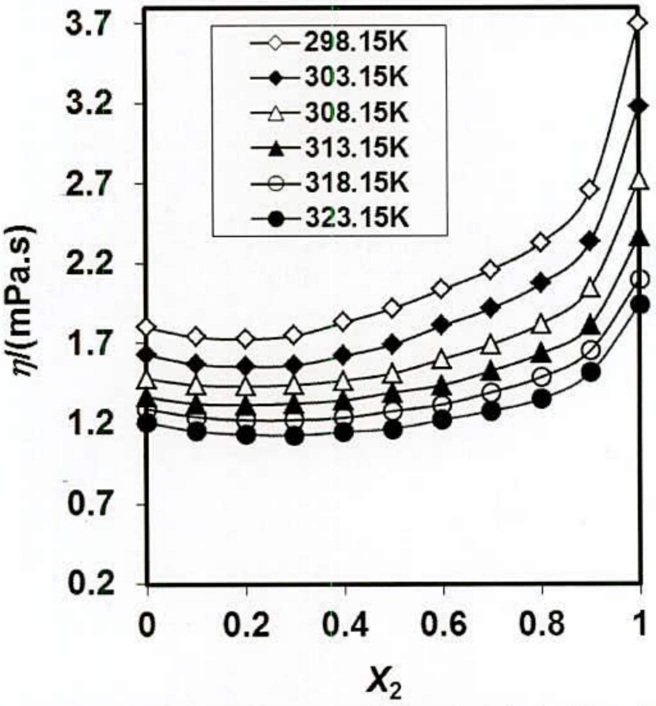

Figure 4.67: Plots of viscosity (*η*)vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

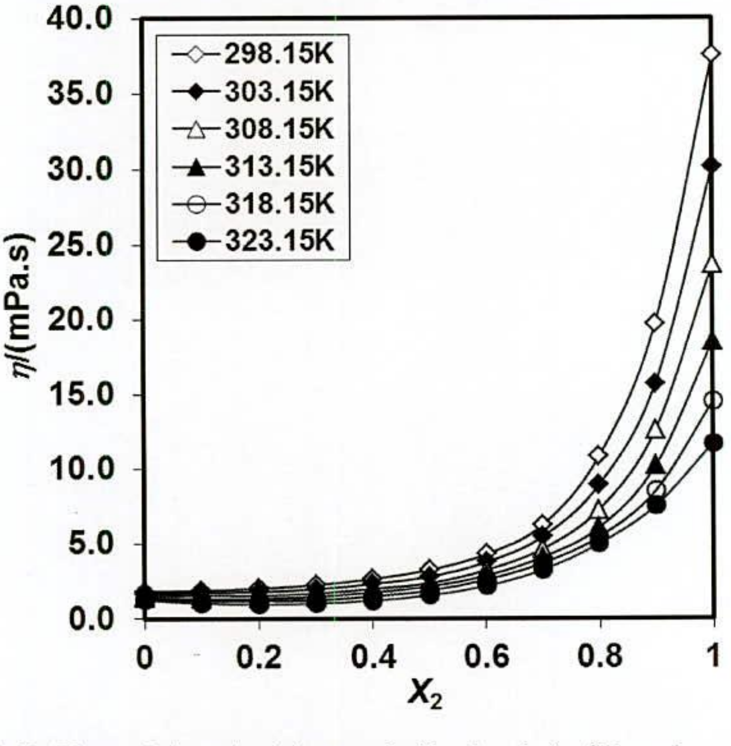

Figure 4.68: Plots of viscosity (*η*) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

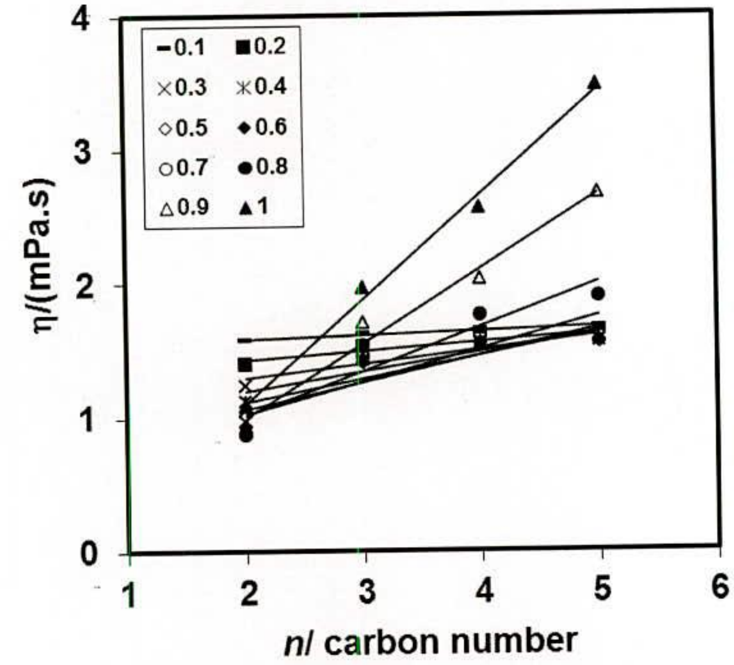

Figure 4.69: Dependence of the viscosity (η) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

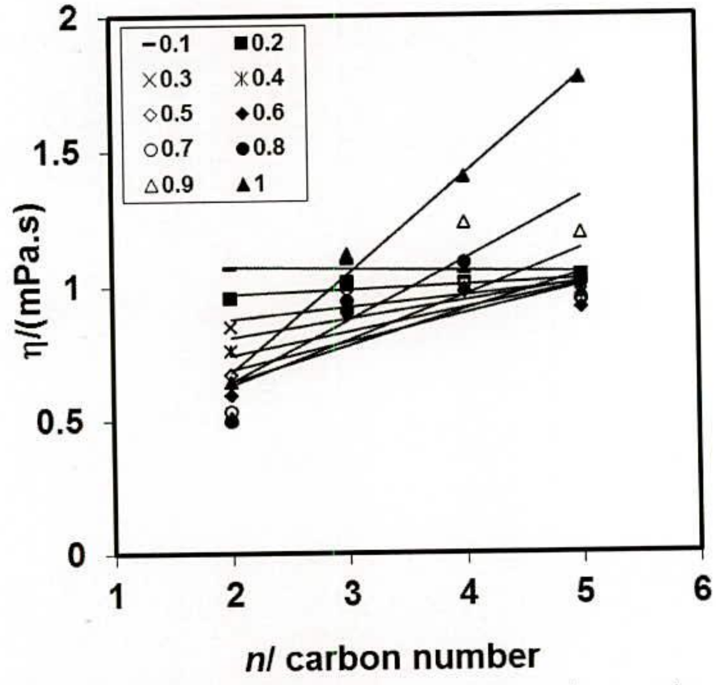

Figure 4.70: Dependence of the viscosity (η) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

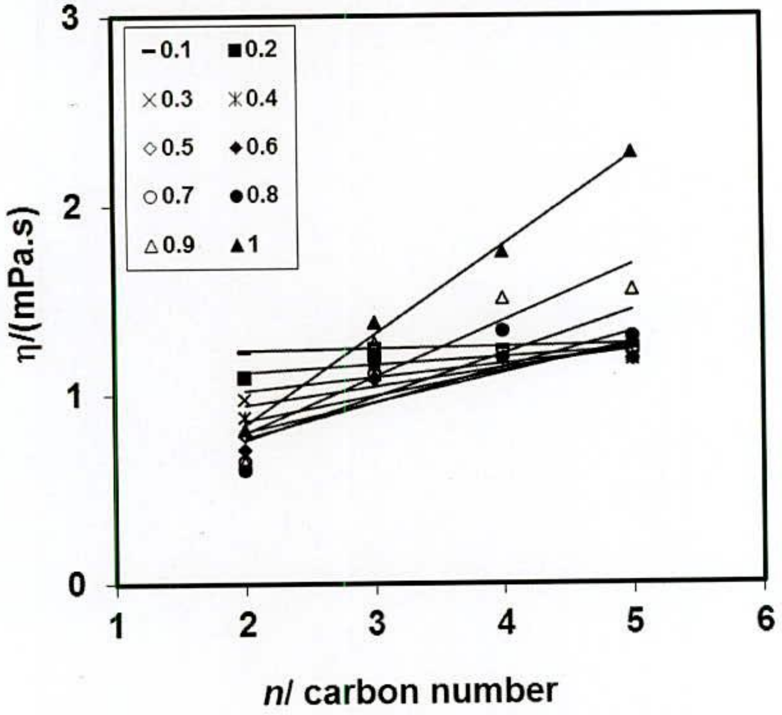

Figure 4.71: Dependence of the viscosity (η) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

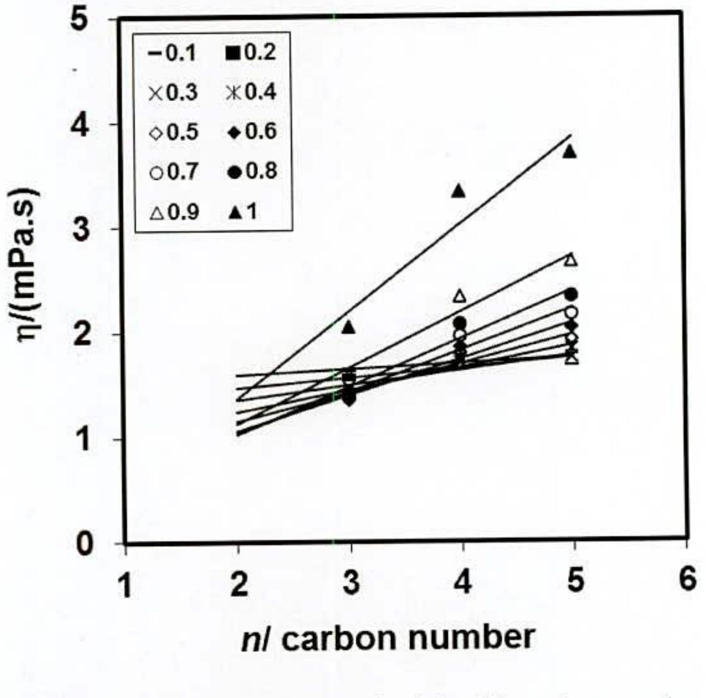

Figure 4.72: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols with different mole fraction at 298.15K.

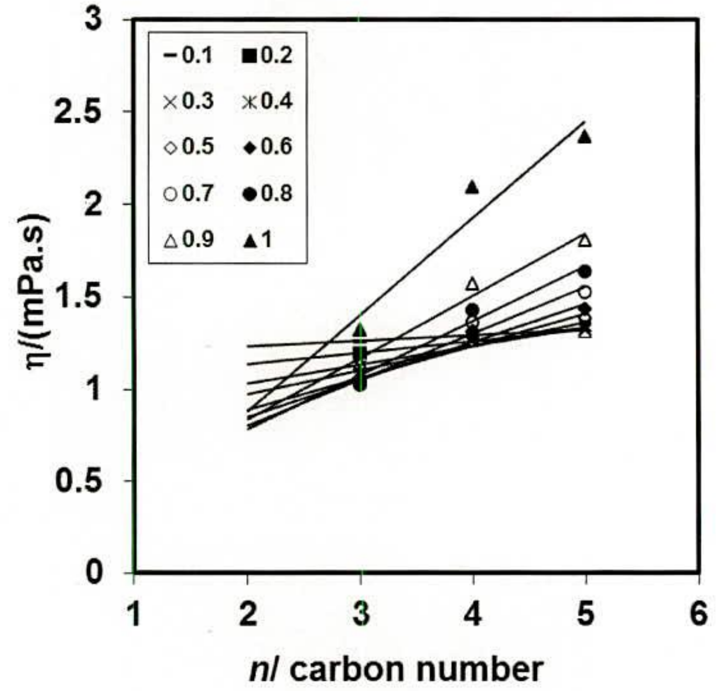

Figure 4.73: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols with different mole fraction at 313.15K.

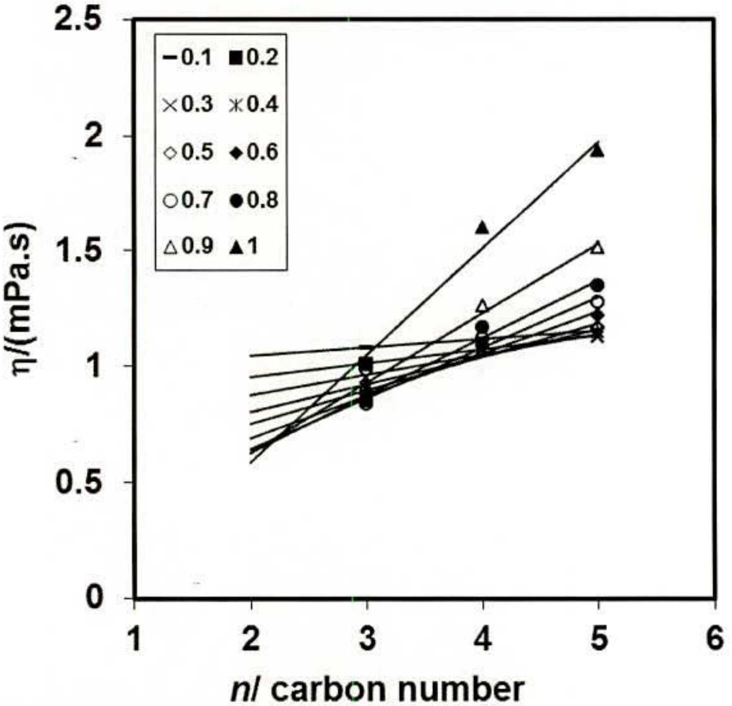

Figure 4.74: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols with different mole fraction at 323.15K.

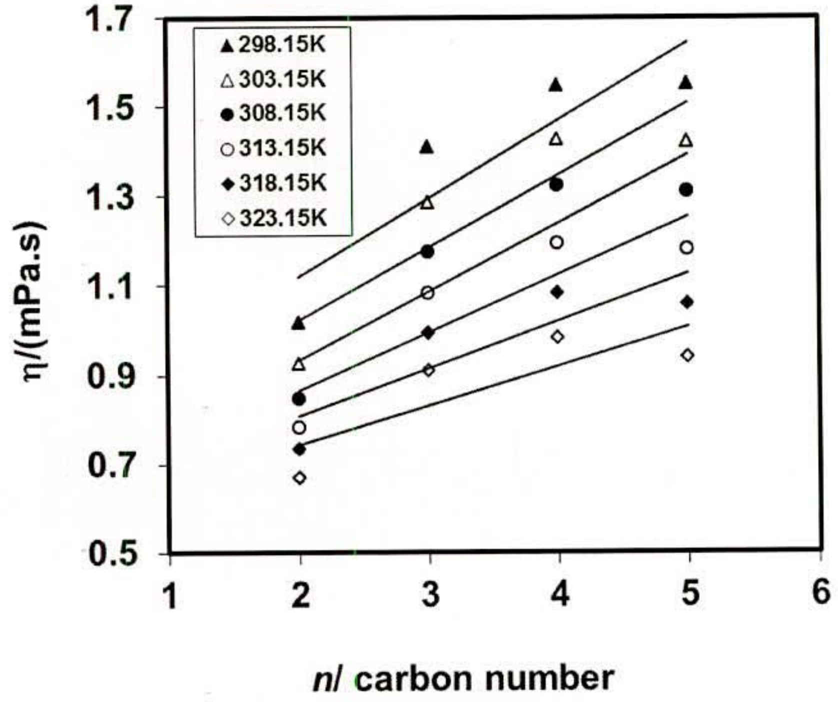

Figure 4.75: Dependence of the viscosity (*η*) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

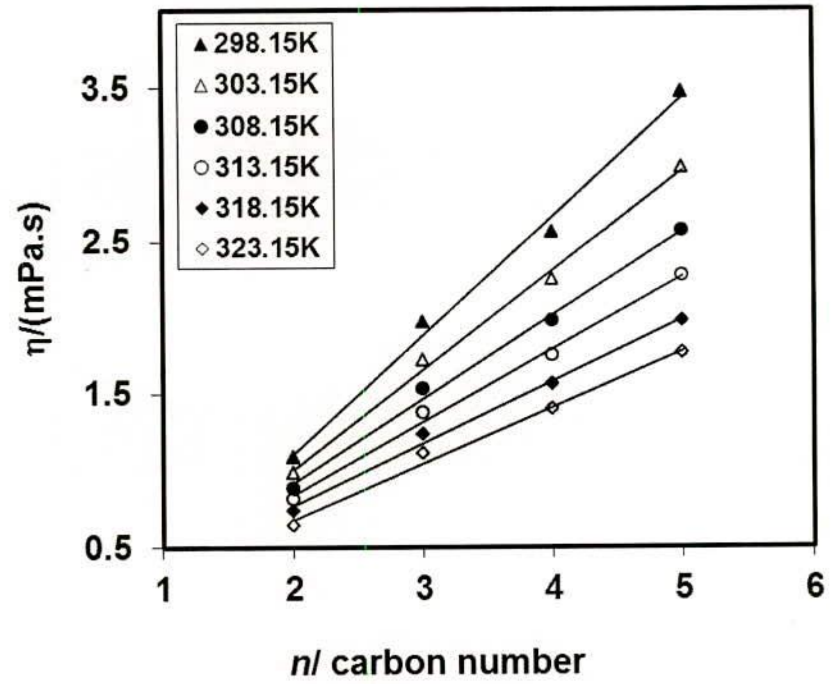

Figure 4.76: Dependence of the viscosity (*η*) with carbon number (n) of n-alcohols with different temperature at 1.0 mole fraction.

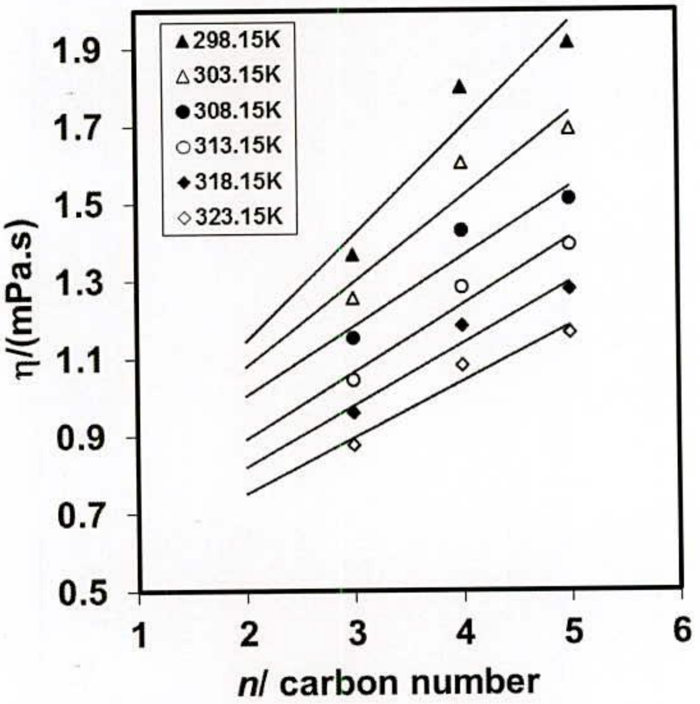

Figure 4.77: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols with different temperature at 0.5 mole fraction.

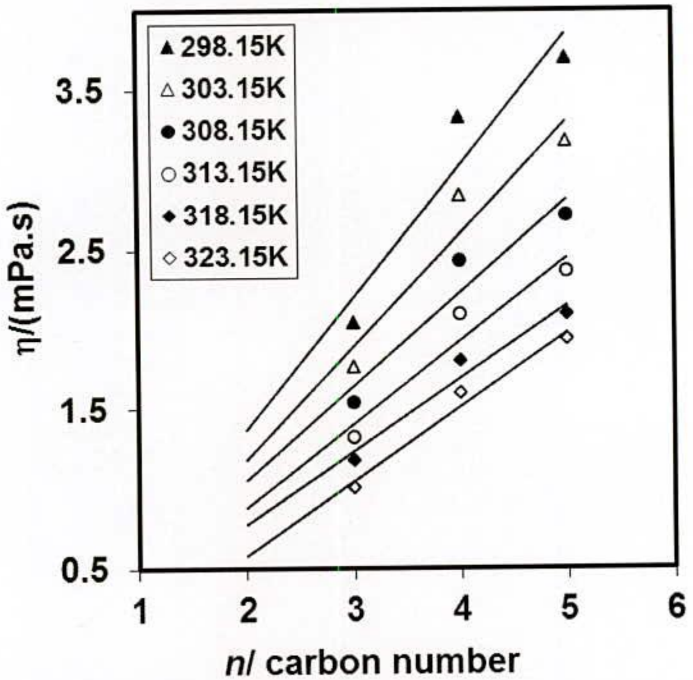

Figure 4.78: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols with different temperature at 1.0 mole fraction.

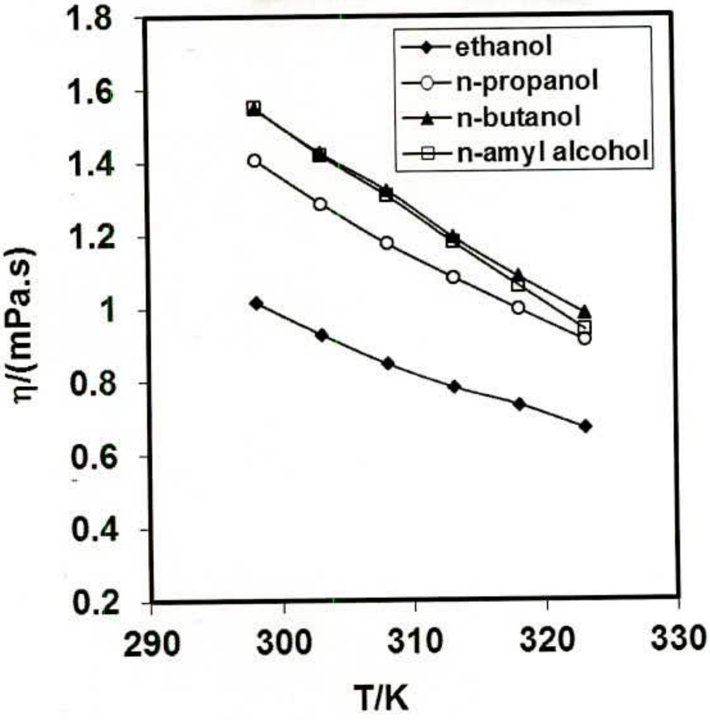

Figure 4.79: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

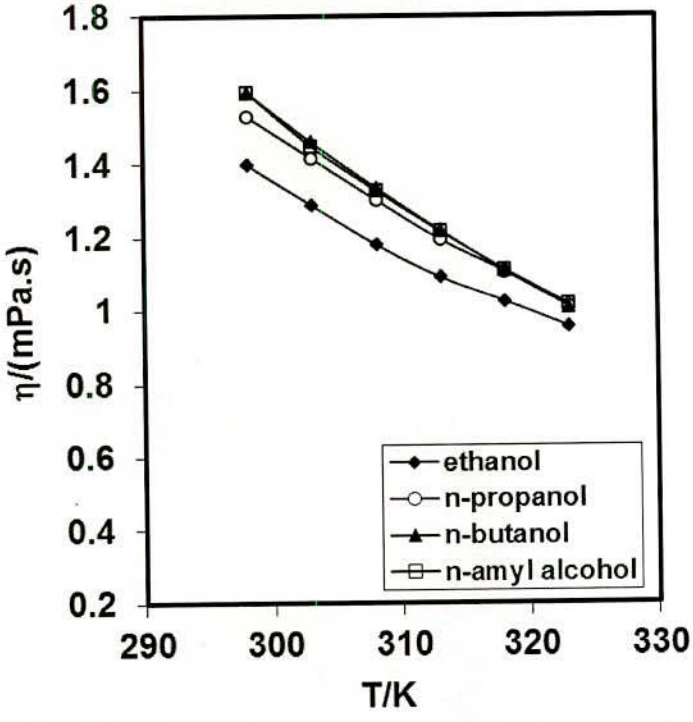

Figure 4.80: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

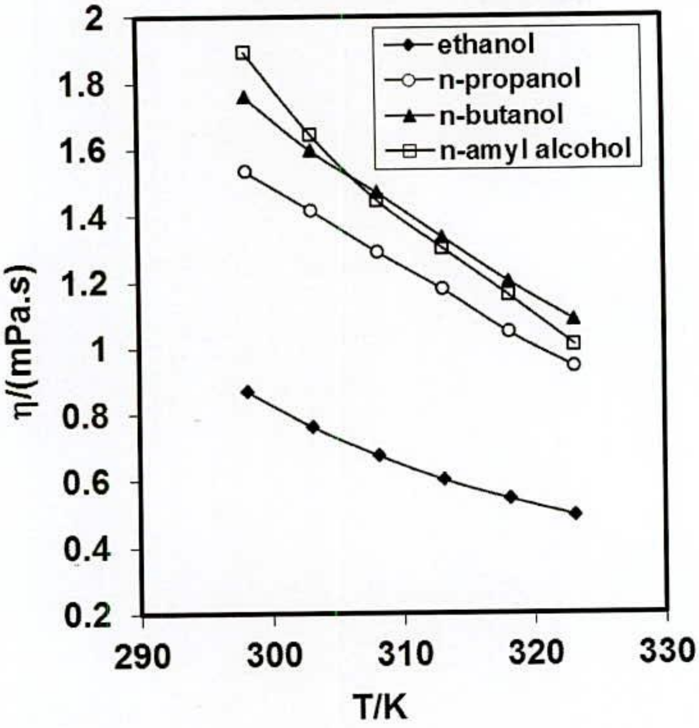

Figure 4.81: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

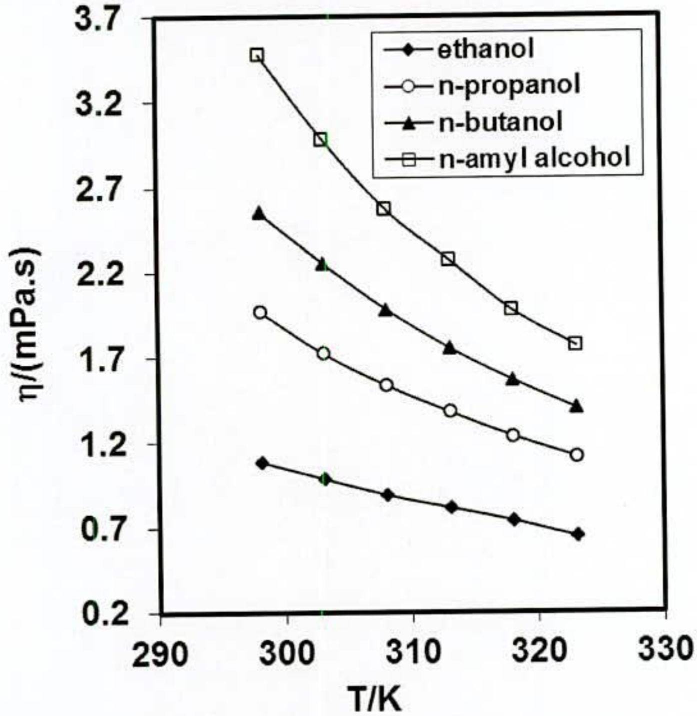

Figure 4.82: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

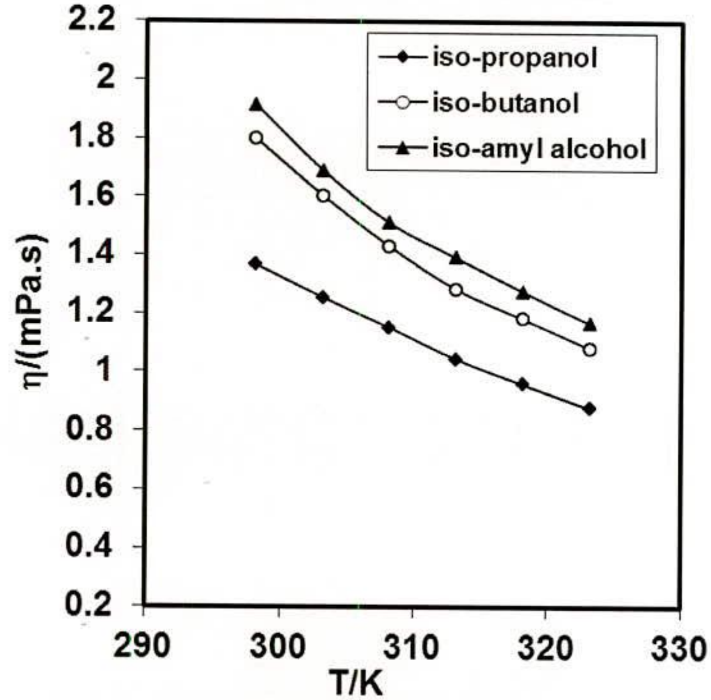

Figure 4.83: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

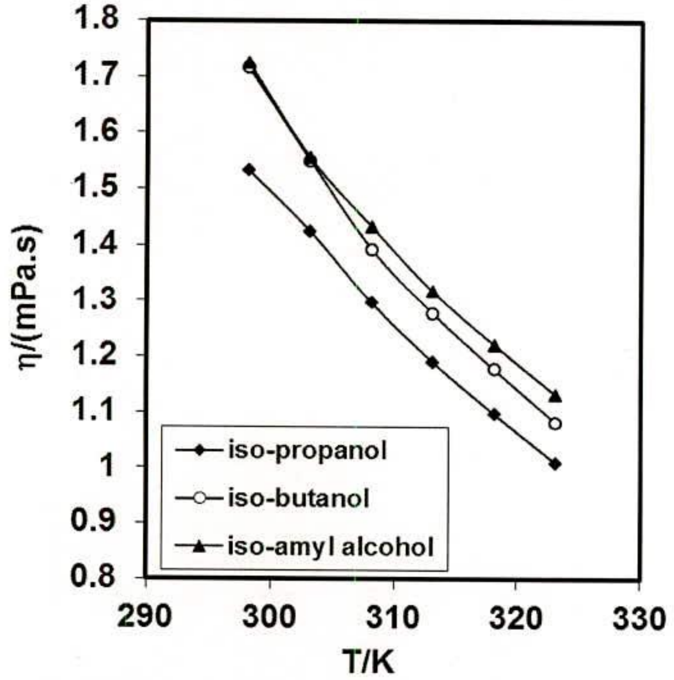

Figure 4.84: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

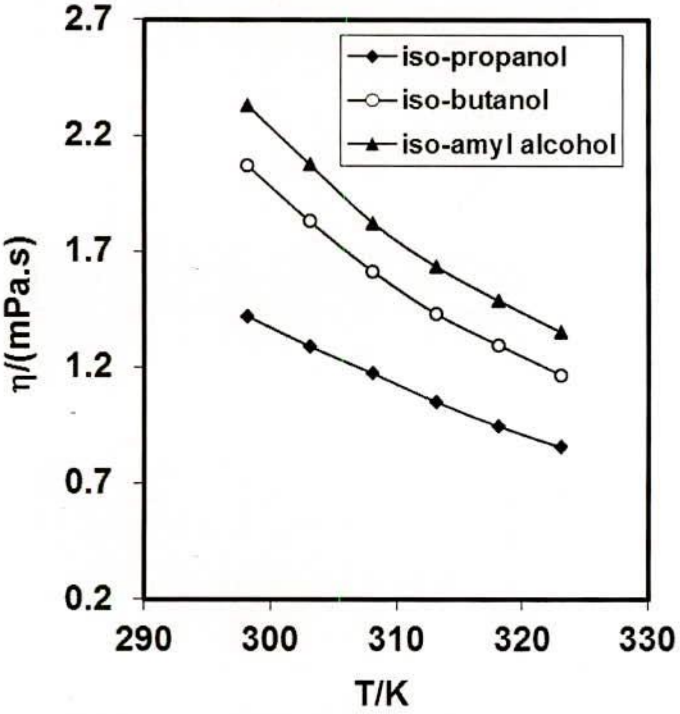

Figure 4.85: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

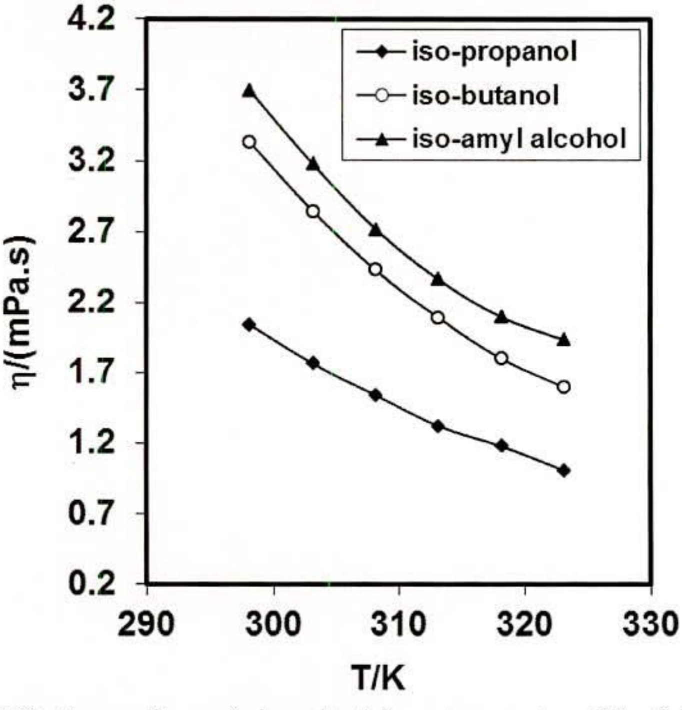

Figure 4.86: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

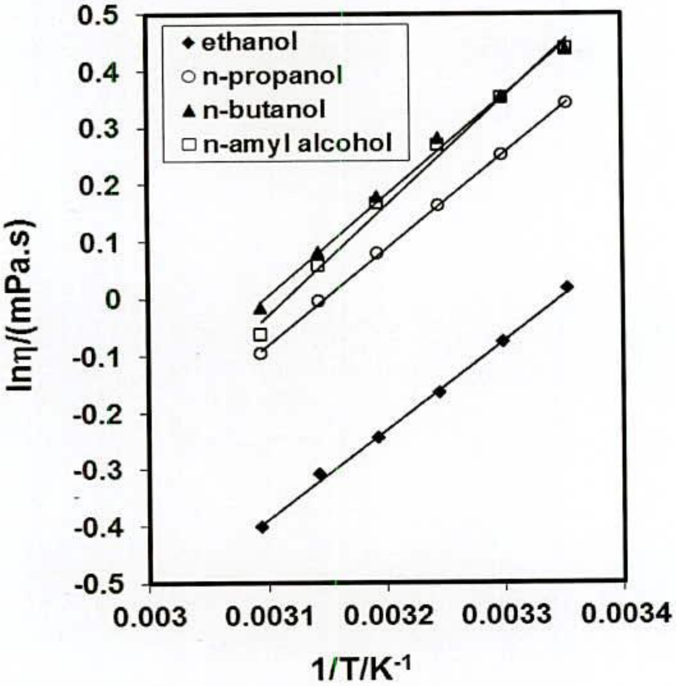

Figure 4.87: Comparison of ln η vs 1/T of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

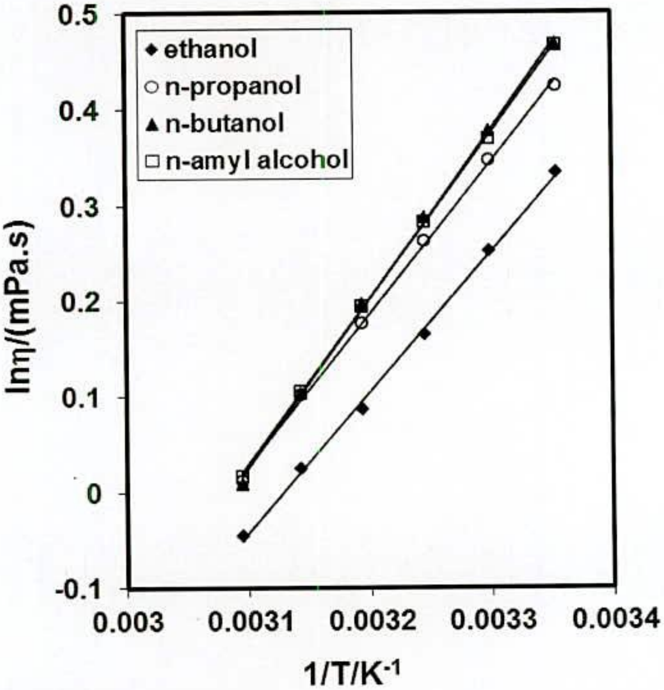

Figure 4.88: Comparison of ln η vs 1/T of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

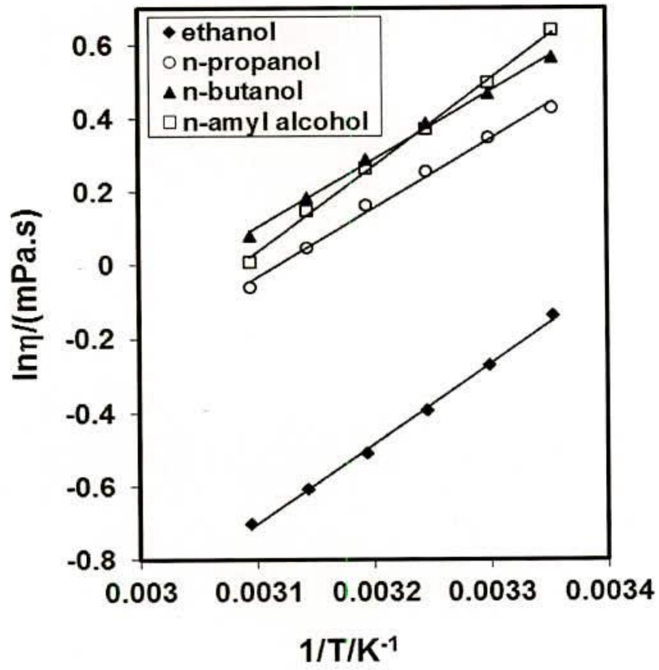

Figure 4.89: Comparison of ln η vs 1/T of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

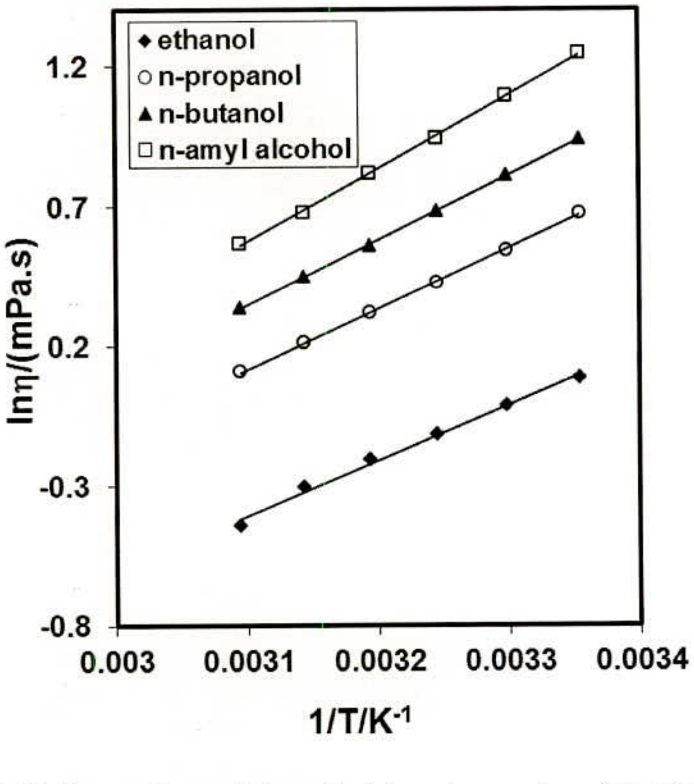

Figure 4.90: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

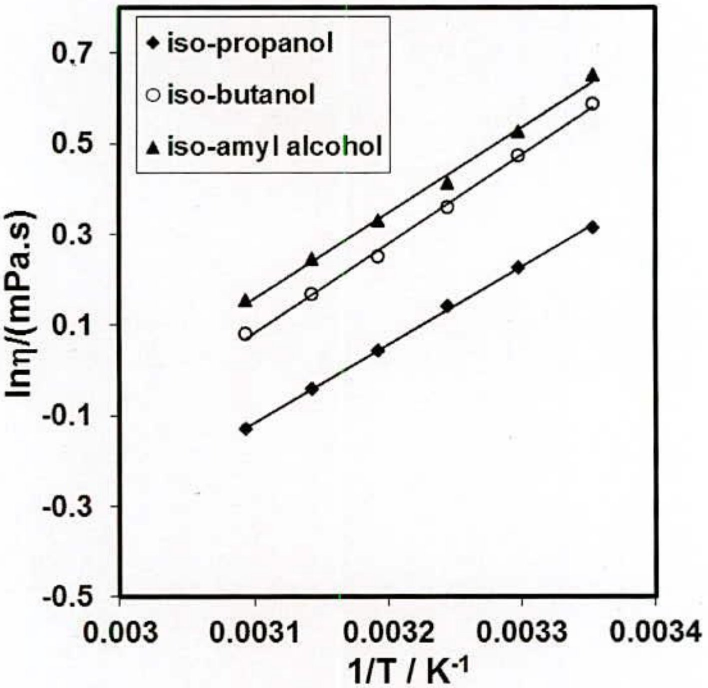

Figure 4.91: Comparison of ln *η* vs 1/T of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

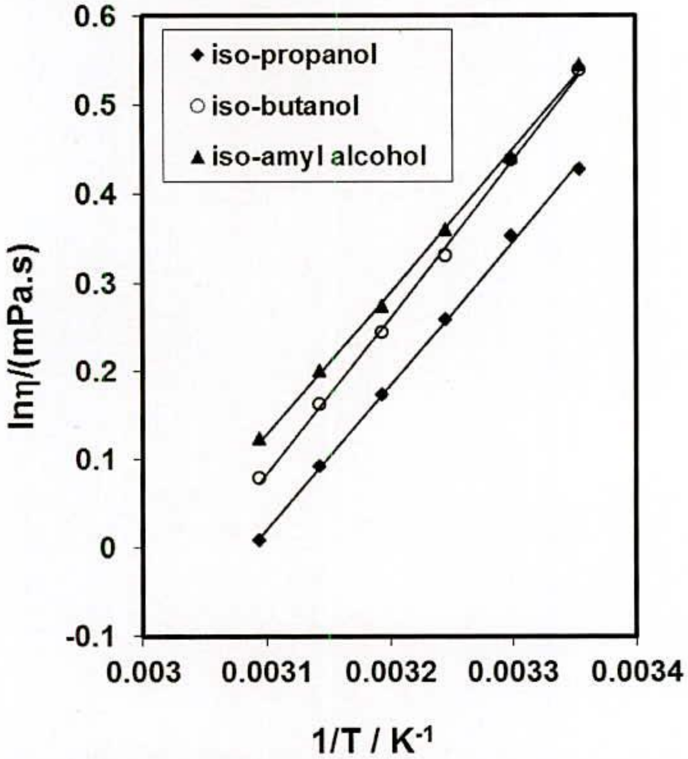

Figure 4.92: Comparison of ln *η* vs 1/T of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

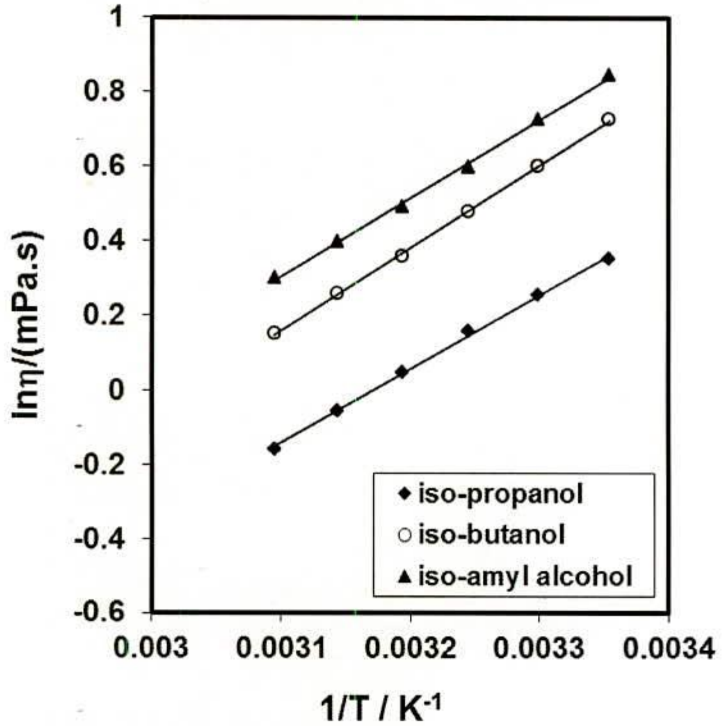

Figure 4.93: Comparison of ln η vs 1/T of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

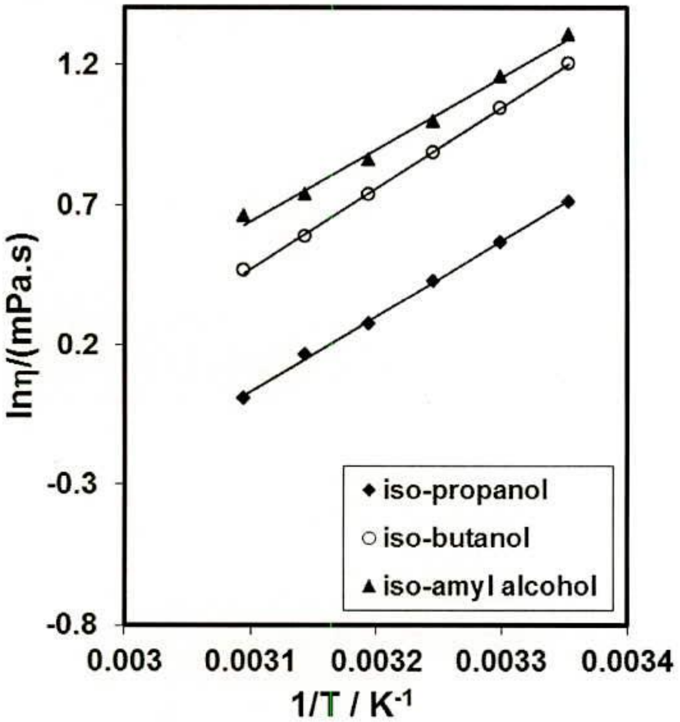

Figure 4.94: Comparison of ln η vs 1/T of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

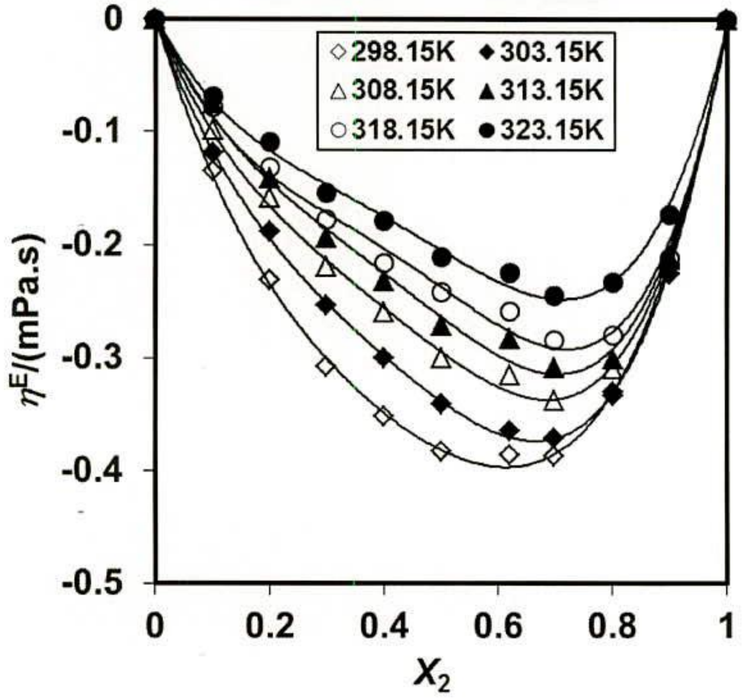

Figure 4.95: Plots of excess viscosity (η^E) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

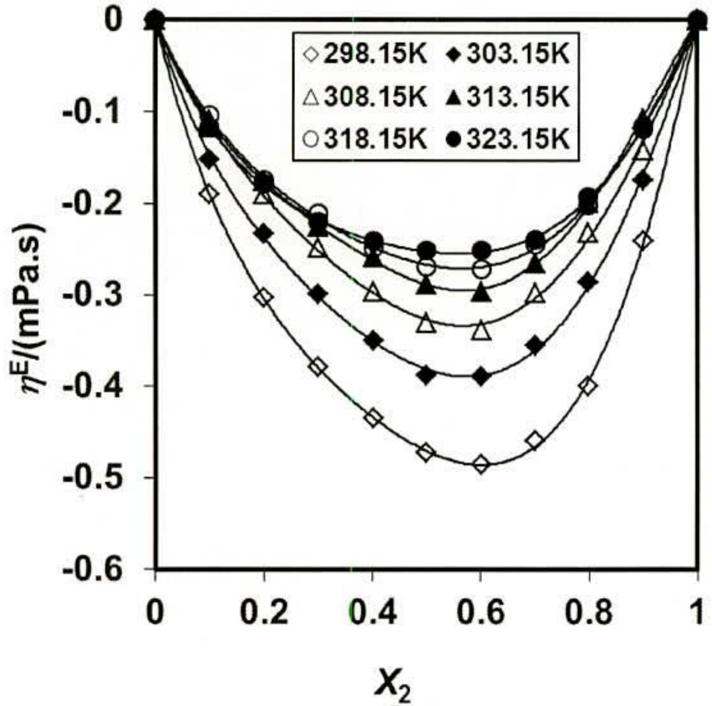

Figure 4.96: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

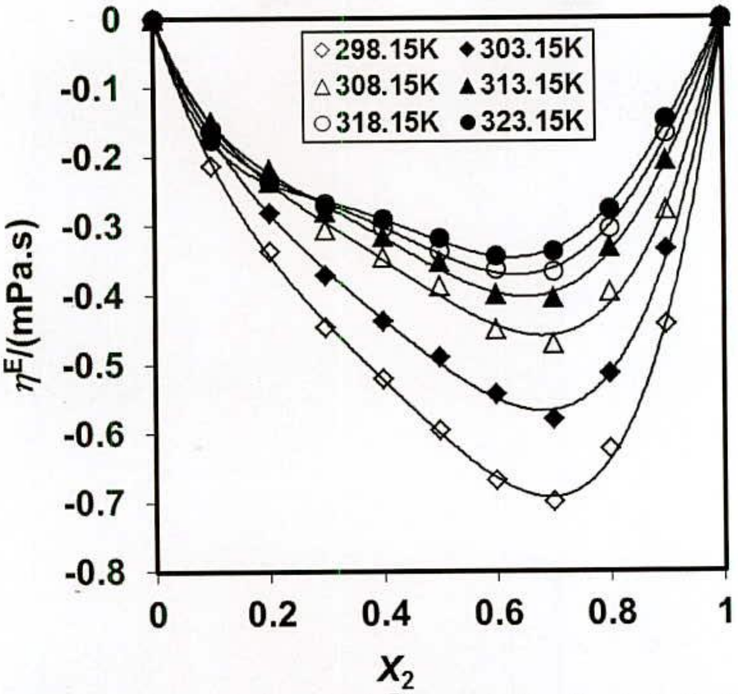

Figure 4.97: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

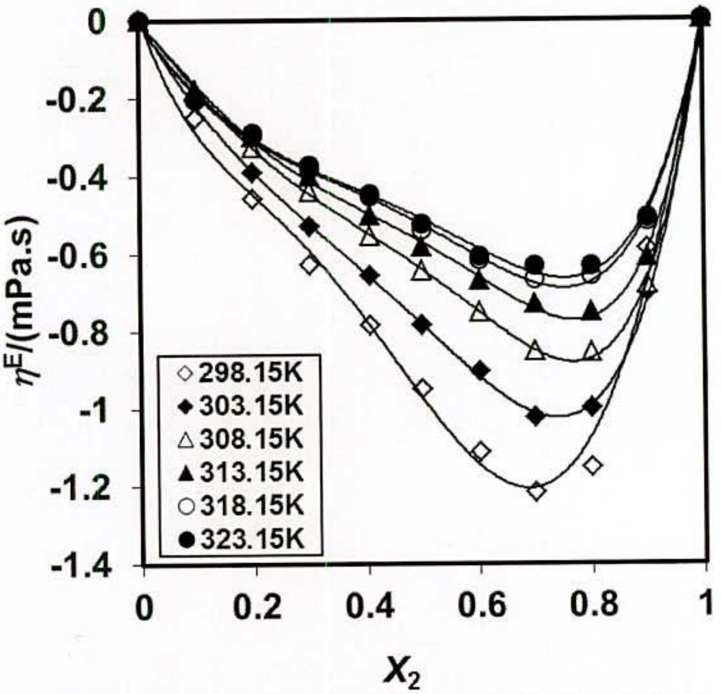

Figure 4.98: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

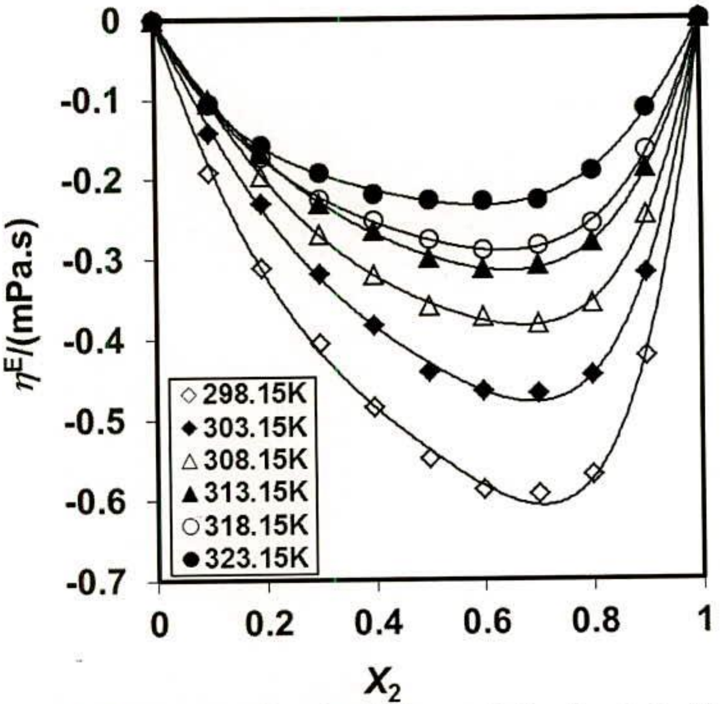

Figure 4.99: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

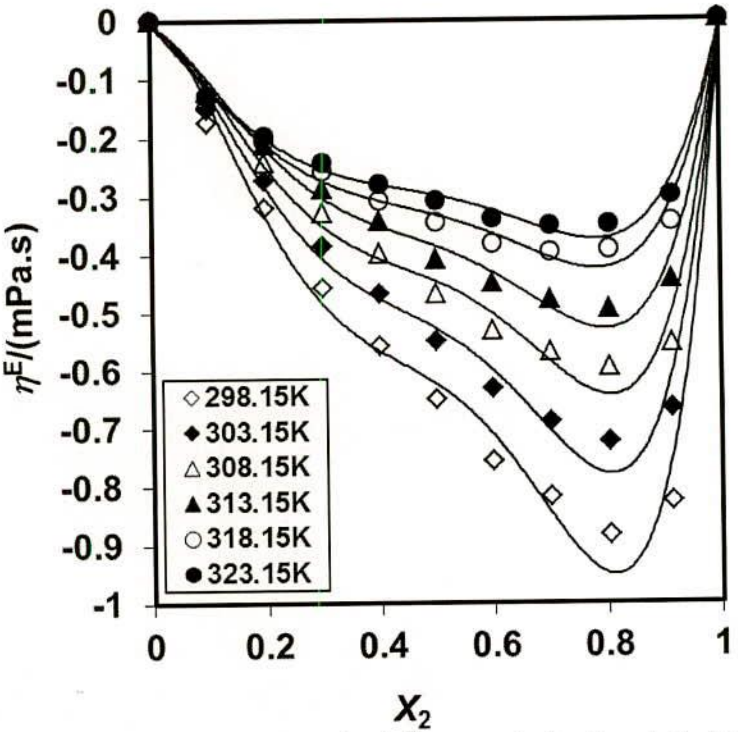

Figure 4.100: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Butanol+ Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

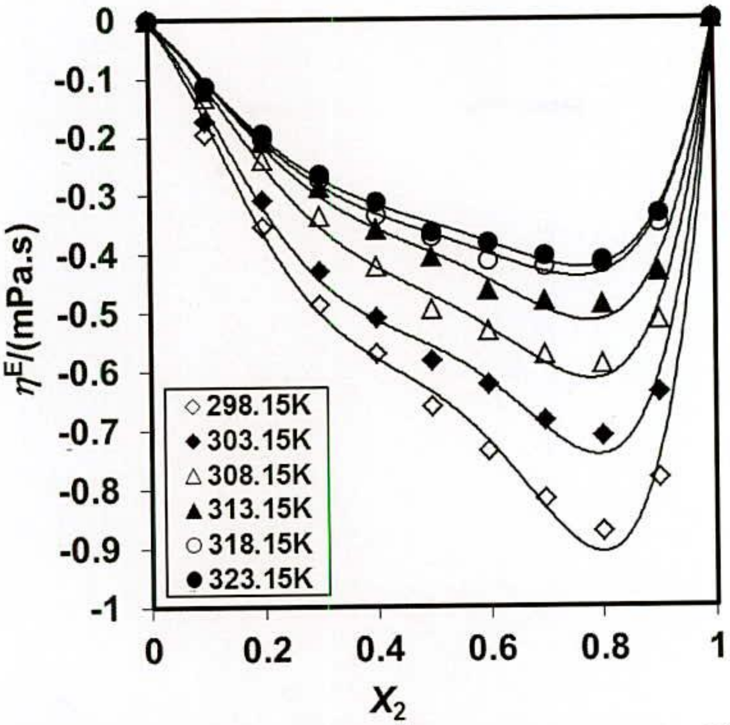

Figure 4.101: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

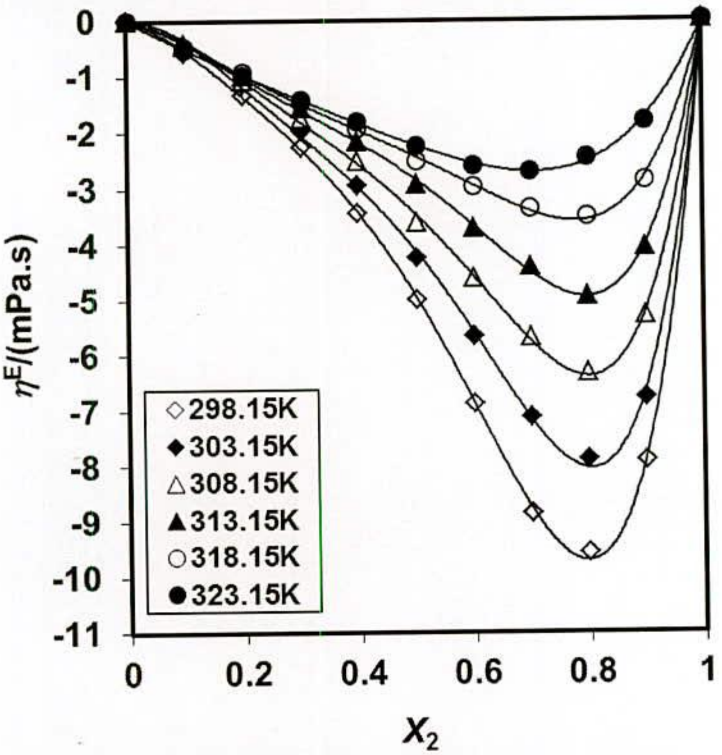

Figure 4.102: Plots of excess viscosity (η^E) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

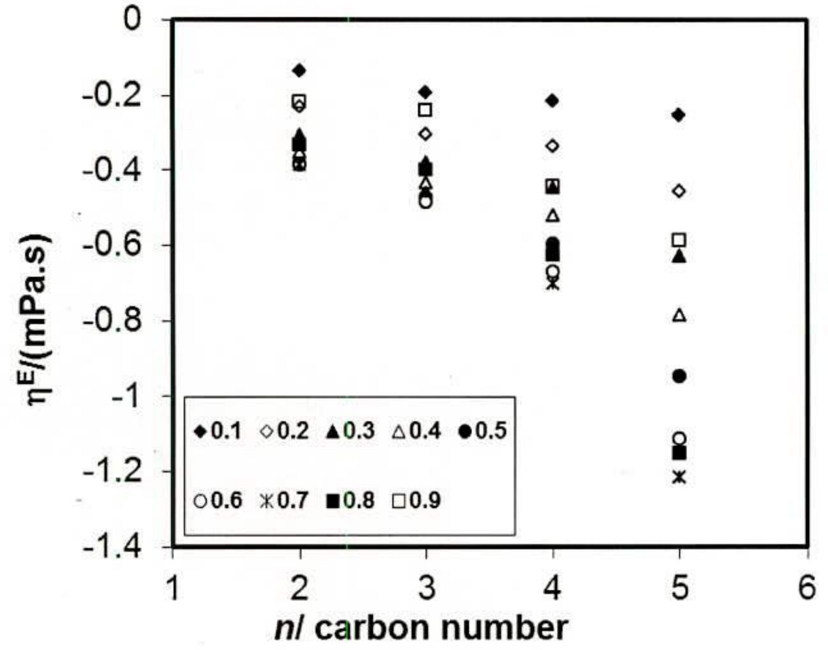

Figure 4.103: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

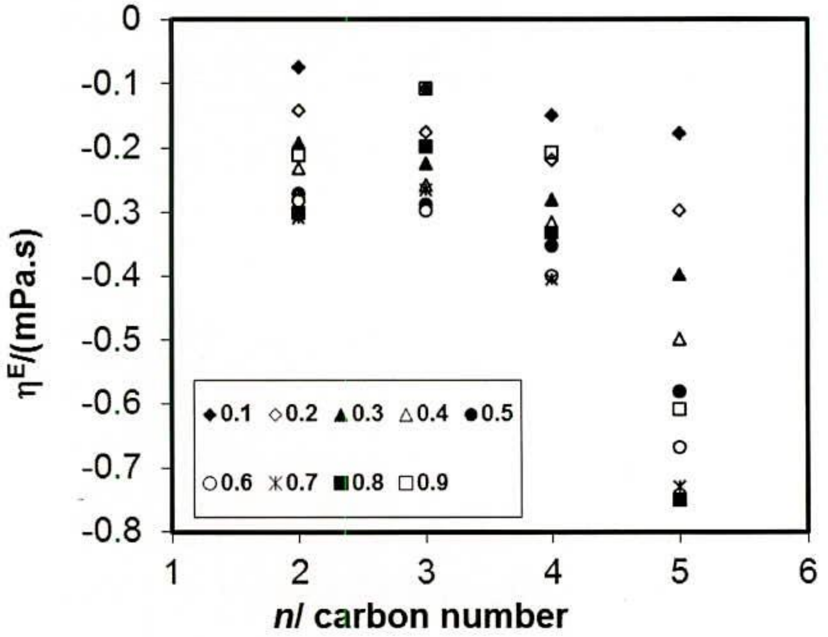

Figure 4.104: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

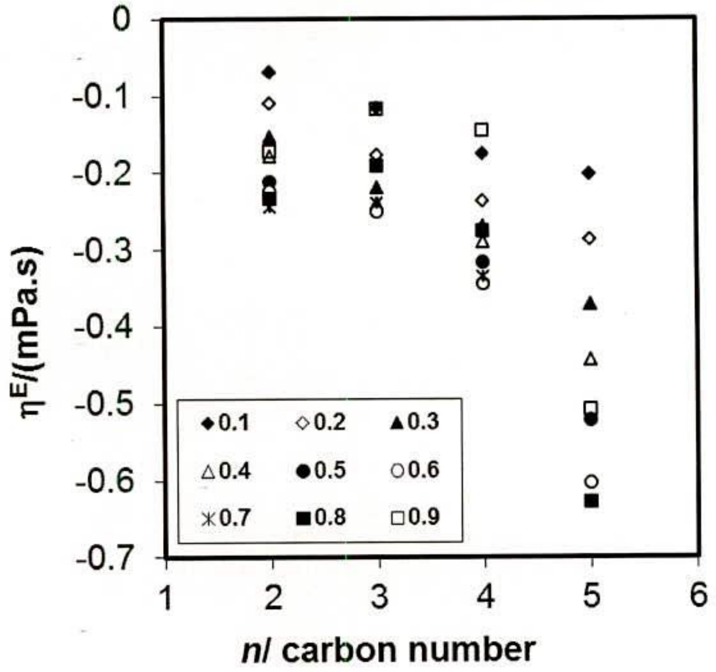

Figure 4.105: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

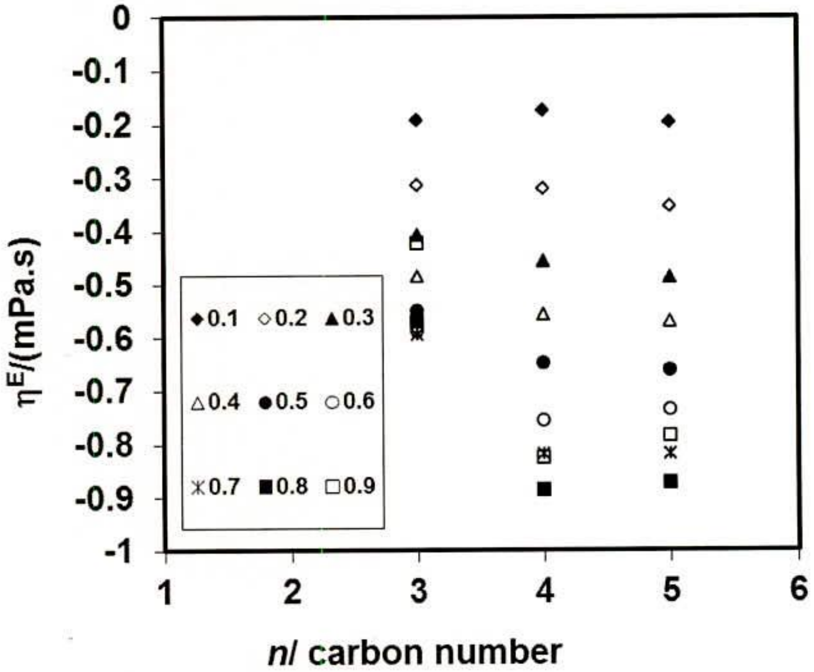

Figure 4.106: Dependence of the excess viscosity (η^E) with carbon number (n) of iso-alcohols with different mole fraction at 298.15K.

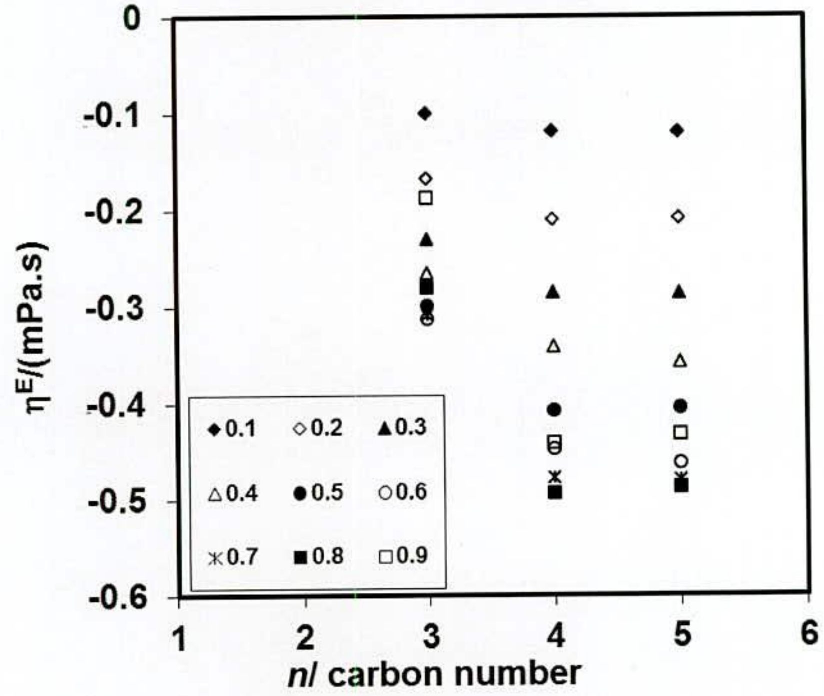

Figure 4.107: Dependence of the excess viscosity (η^E) with carbon number (n) of iso-alcohols with different mole fraction at 313.15K.

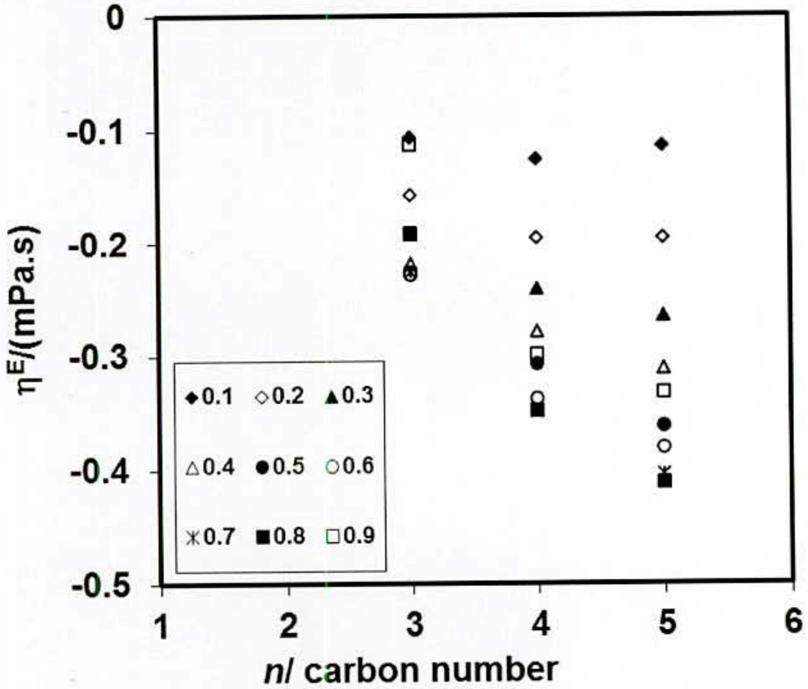

Figure 4.108: Dependence of the excess viscosity (η^E) with carbon number (n) of iso-alcohols with different mole fraction at 323.15K.

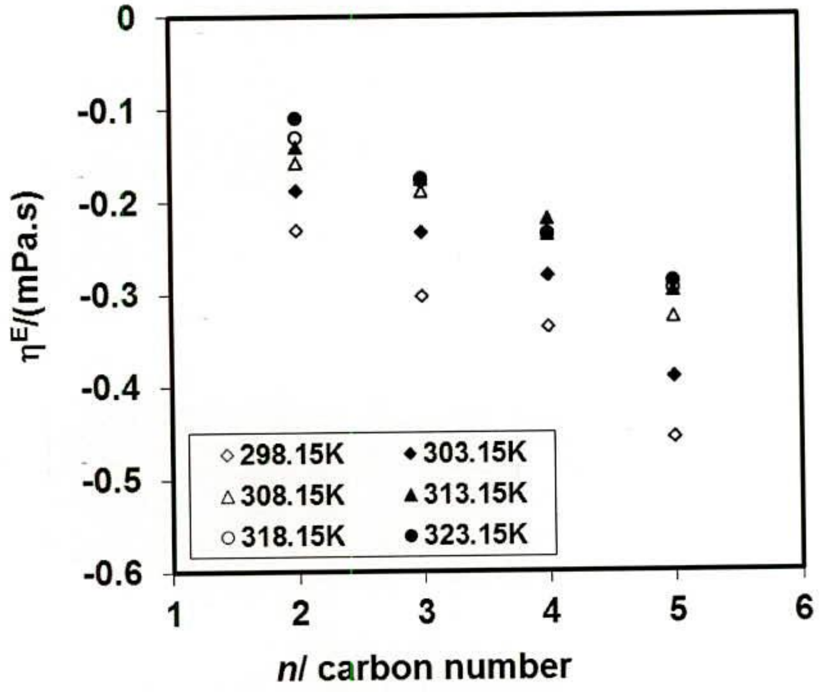

Figure 4.109: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different temperature at 0.2 mole fraction.

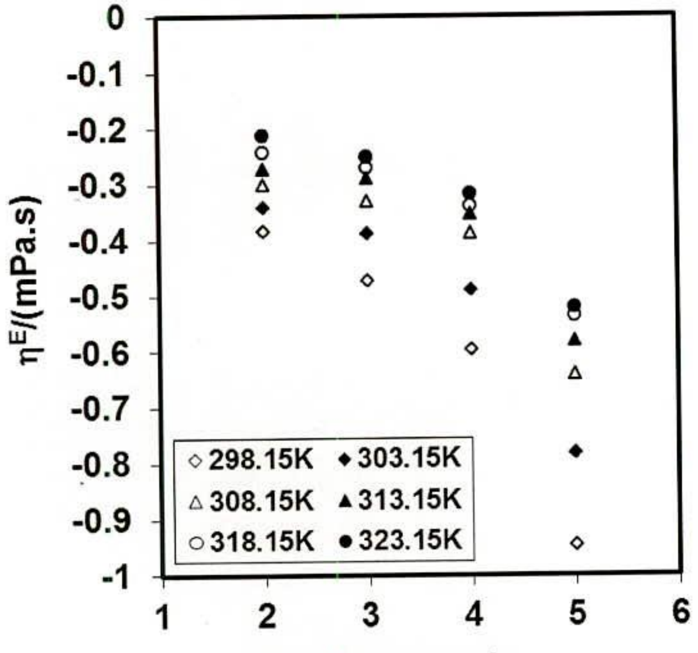

Figure 4.110: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

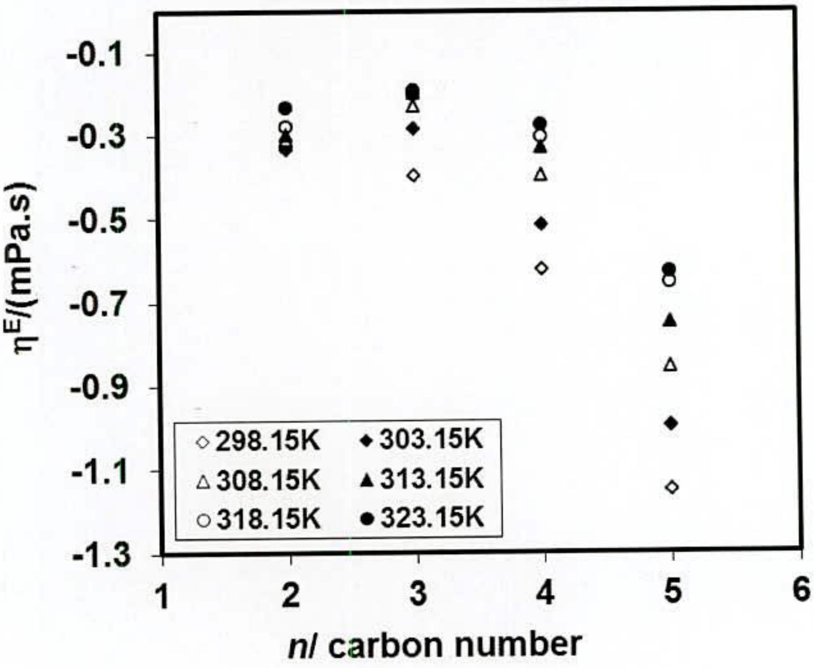

Figure 4.111: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols with different temperature at 0.8 mole fraction.

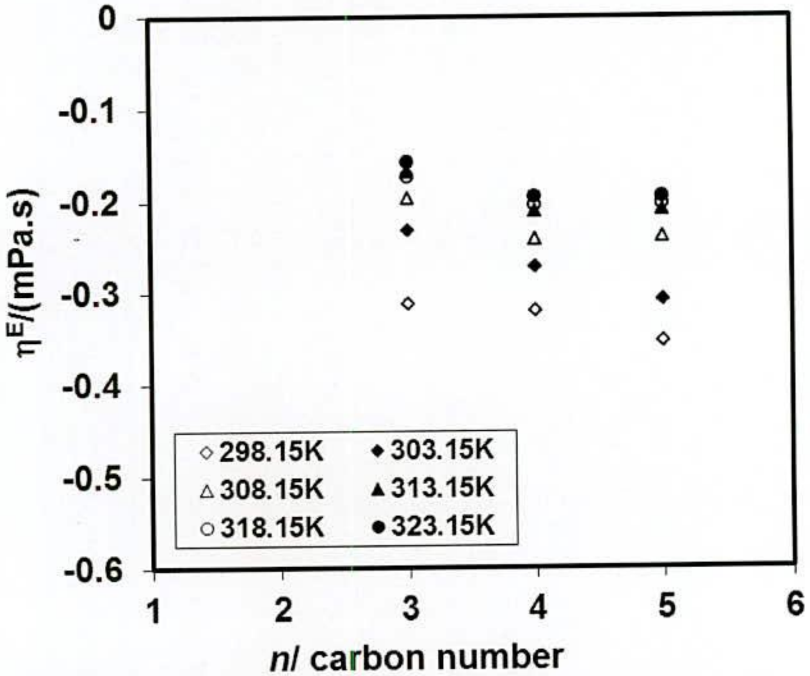

Figure 4.112: Dependence of the excess viscosity (η^E) with carbon number (n) of iso - alcohols with different temperature at 0.2 mole fraction.

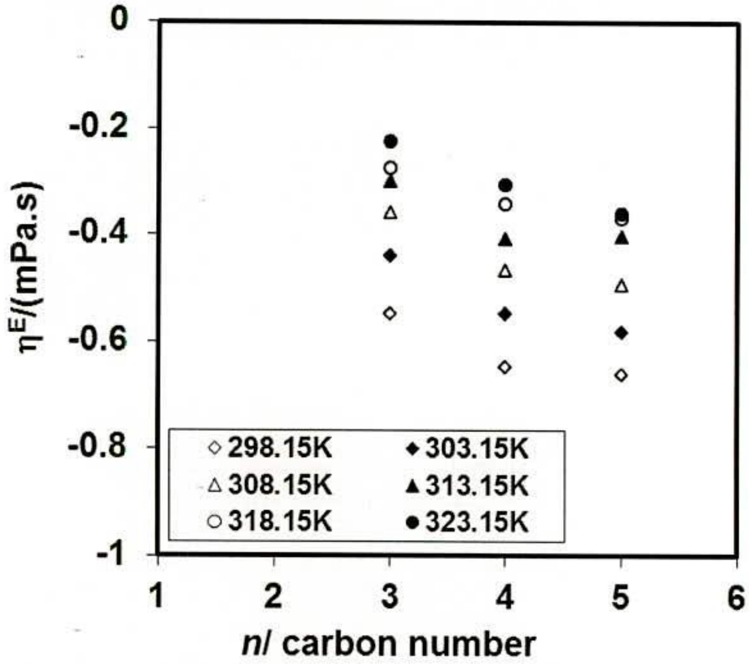

Figure 4.113: Dependence of the excess viscosity (η^E) with carbon number (n) of iso-alcohols with different temperature at 0.5 mole fraction.

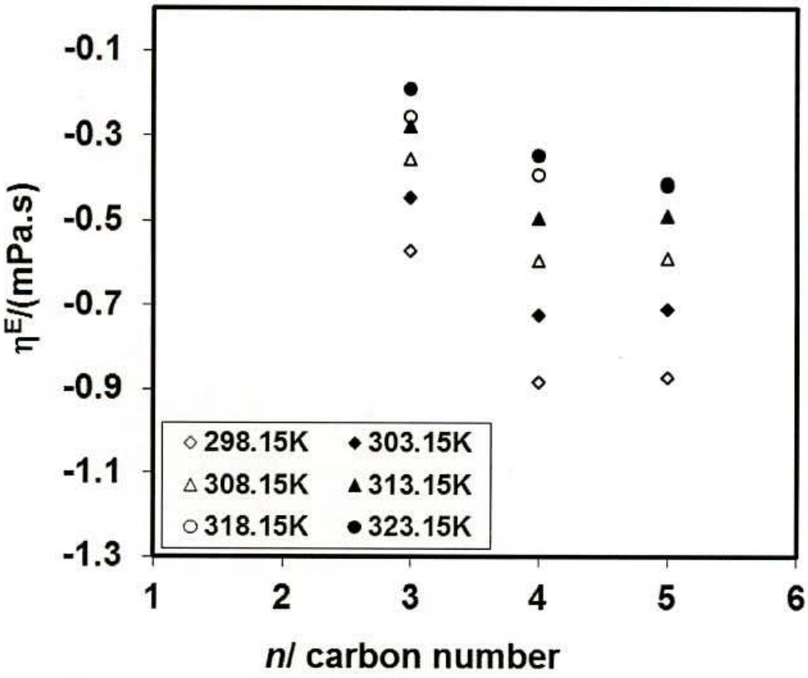

Figure 4.114: Dependence of the excess viscosity (η^E) with carbon number (n) of iso-alcohols with different temperature at 0.8 mole fraction.

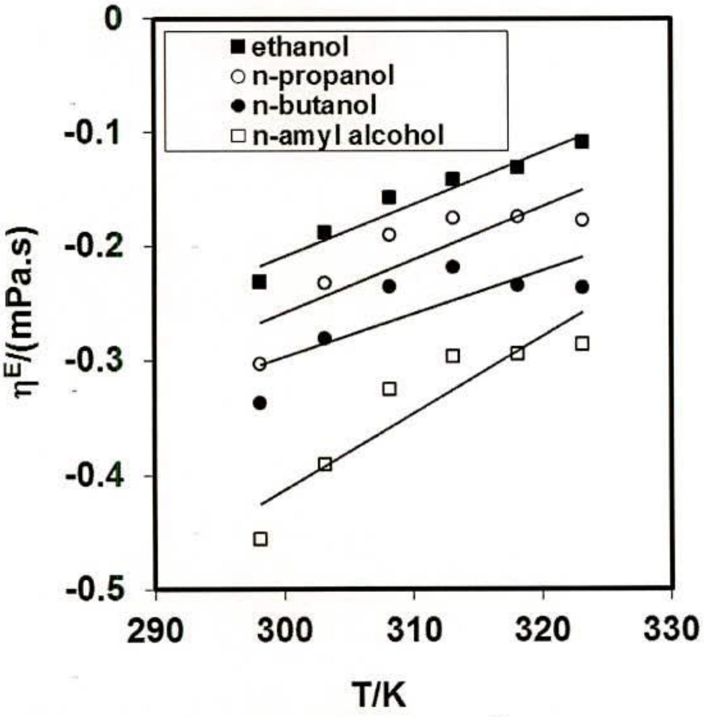

Figure 4.115: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

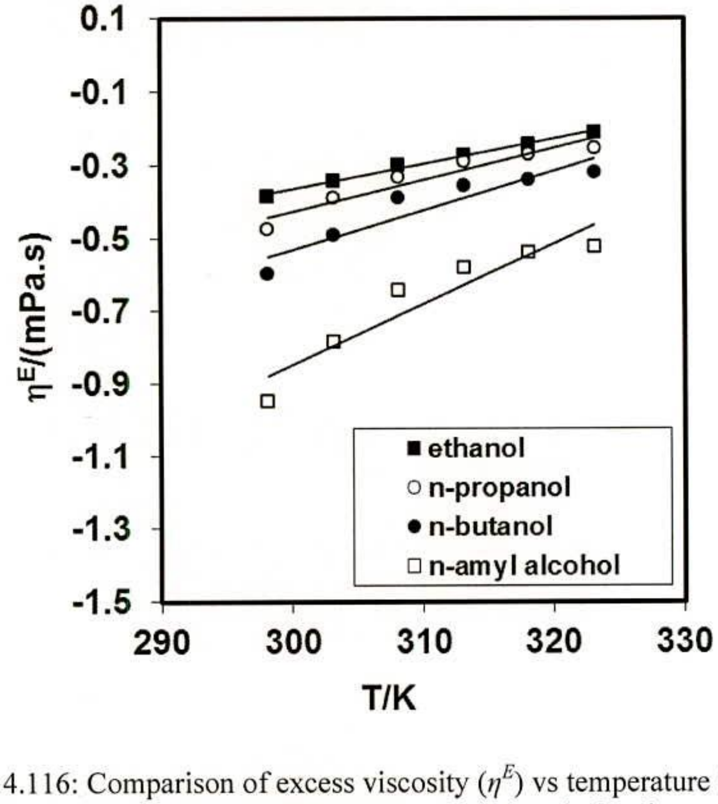

Figure 4.116: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

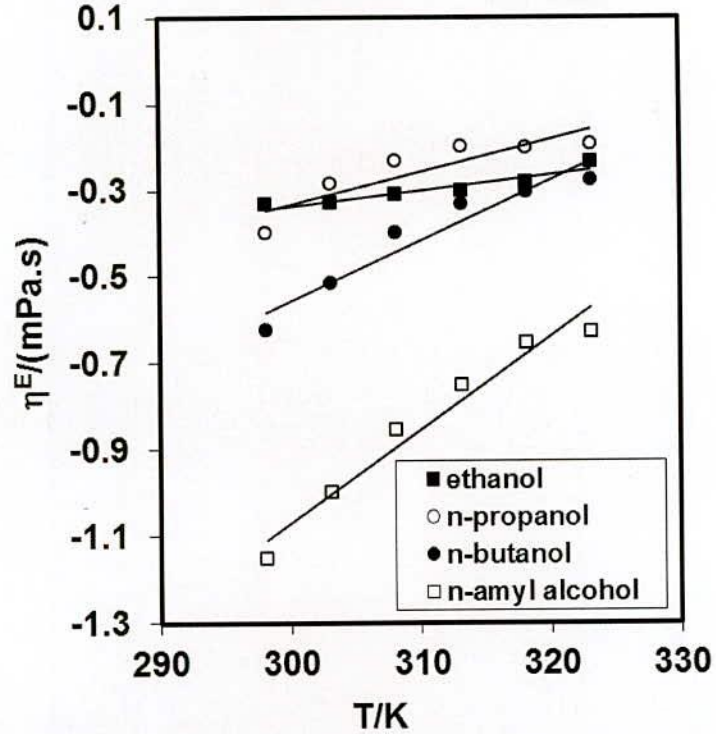

Figure 4.117: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

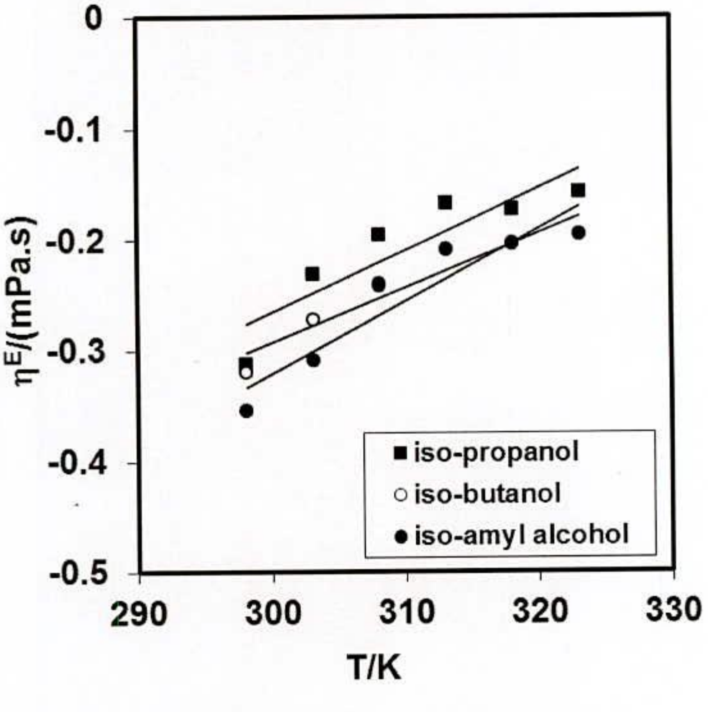

Figure 4.118: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.2 mole fraction.

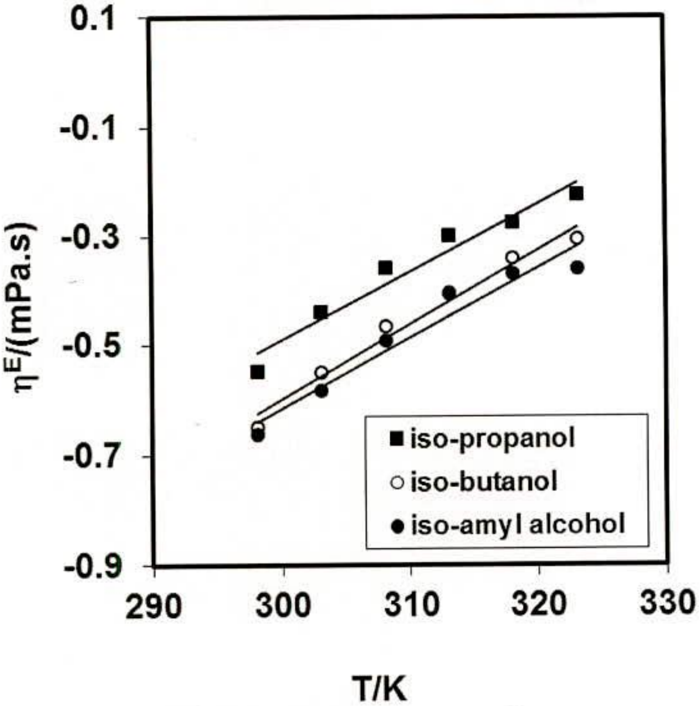

Figure 4.119: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.5 mole fraction.

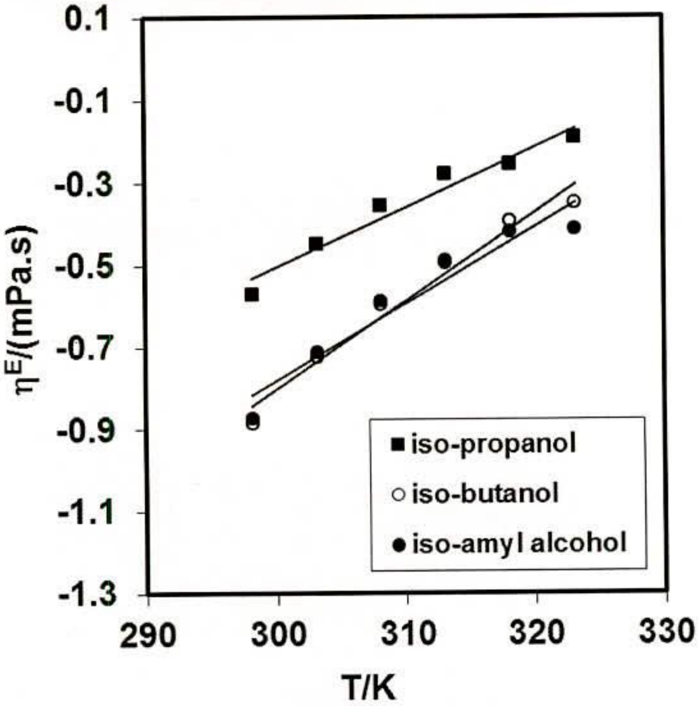

Figure 4.120: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 0.8 mole fraction.

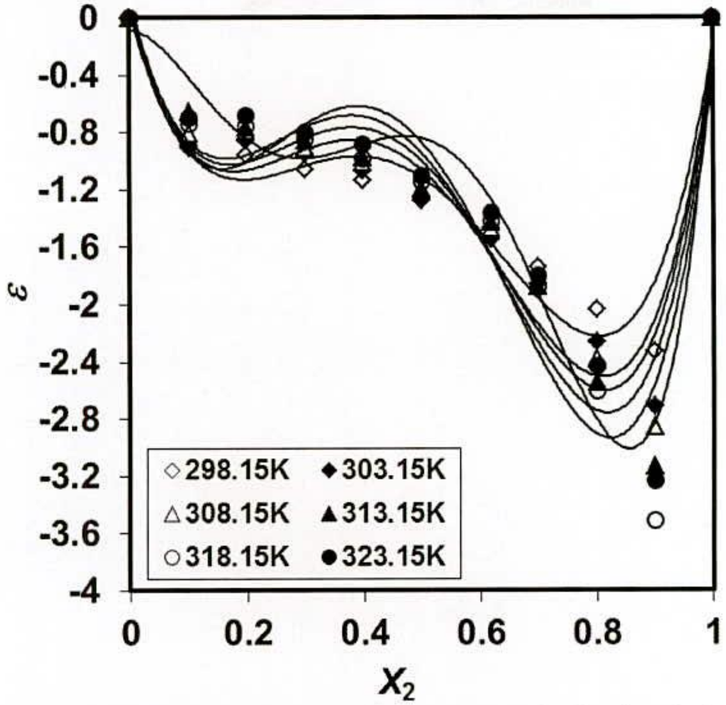

Figure 4.121: Plots of interaction parameter (ε) vs mole fraction (x_2) of Ethanol +Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

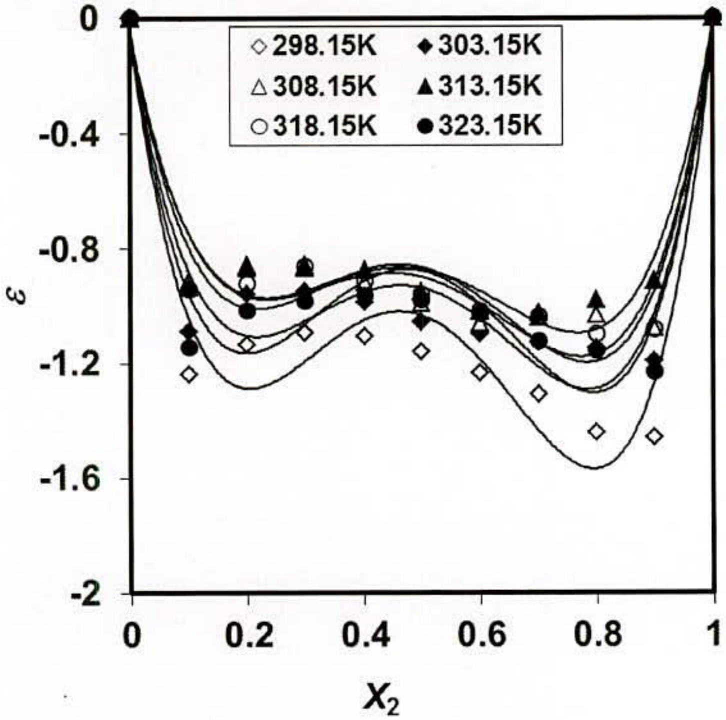

Figure 4.122: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

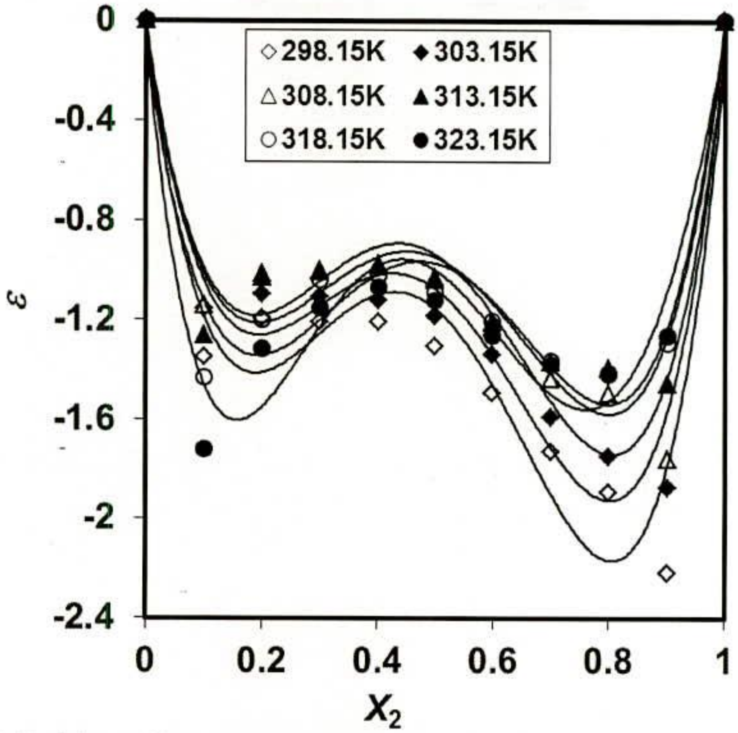

Figure 4.123: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

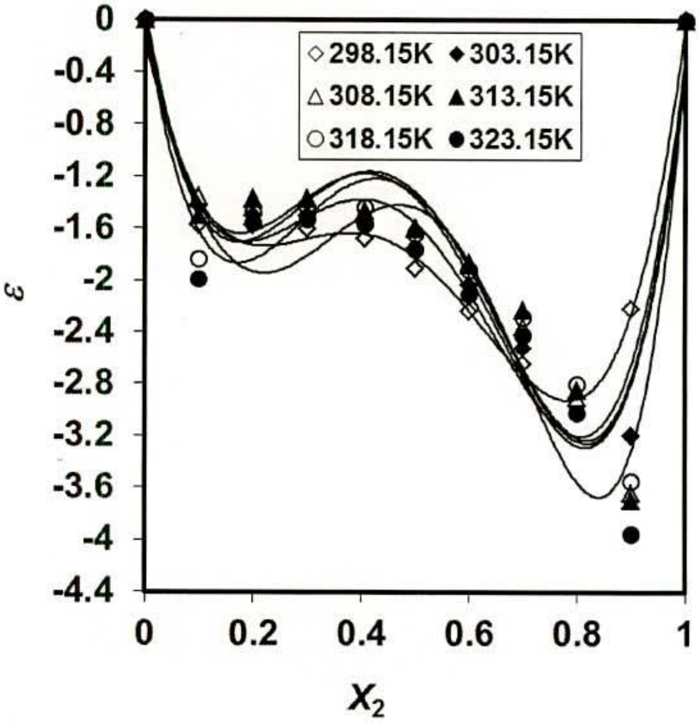

Figure 4.124: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

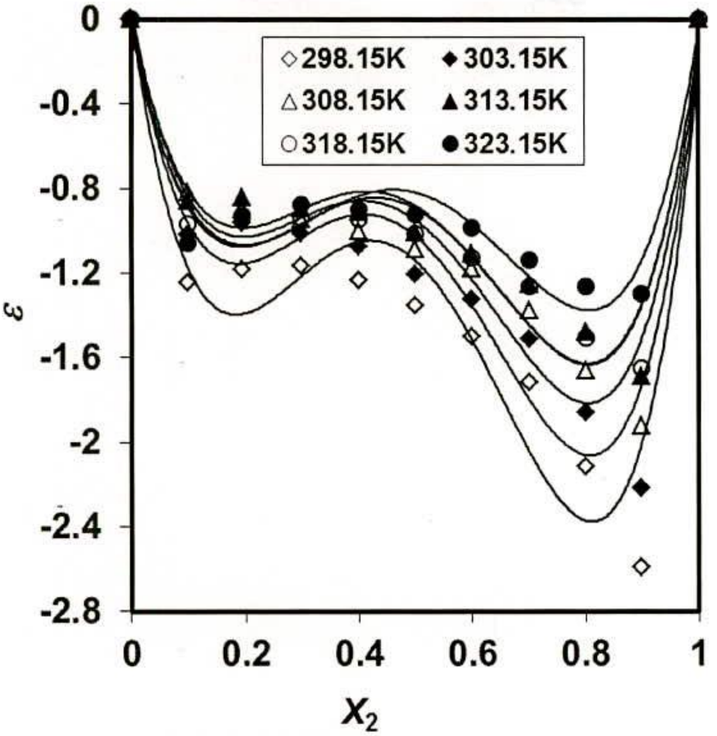

Figure 4.125: Plots of interaction parameter (*ε*) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

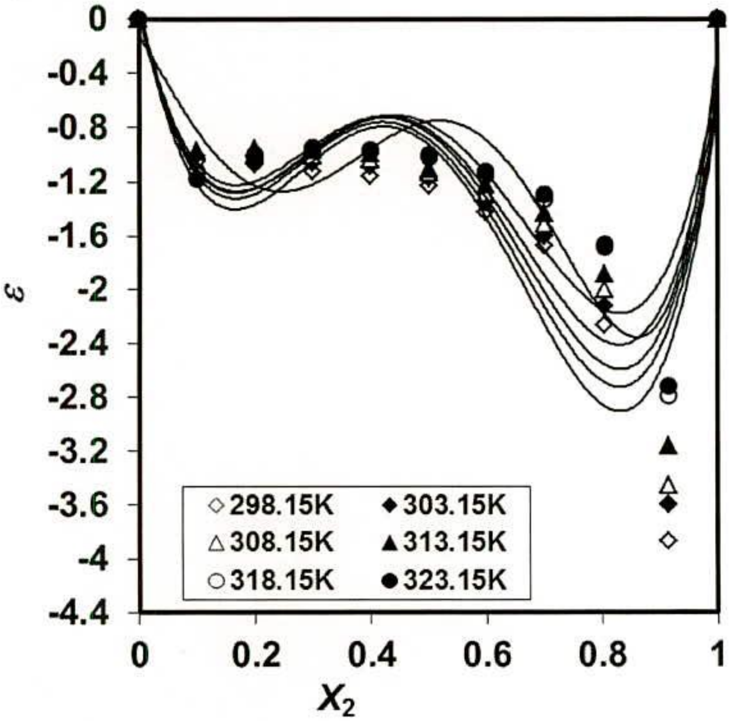

Figure 4.126: Plots of interaction parameter (*ε*) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

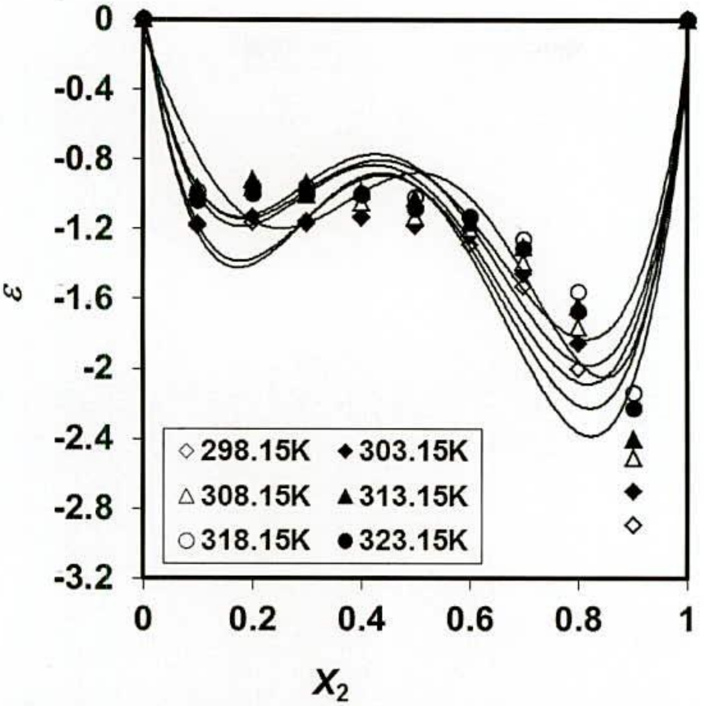

Figure 4.127: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

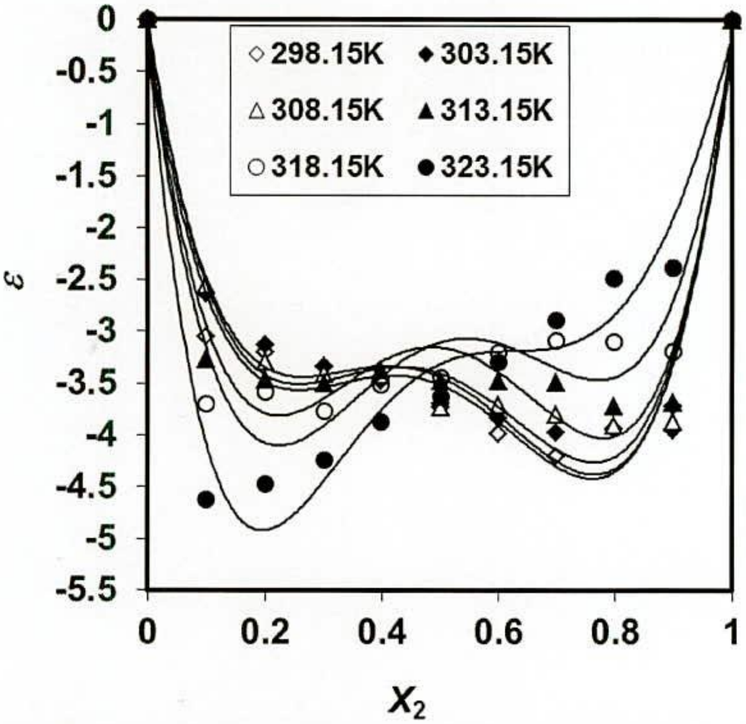

Figure 4.128: Plots of interaction parameter (ε) vs mole fraction (x_2) of Propylene glycol +Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

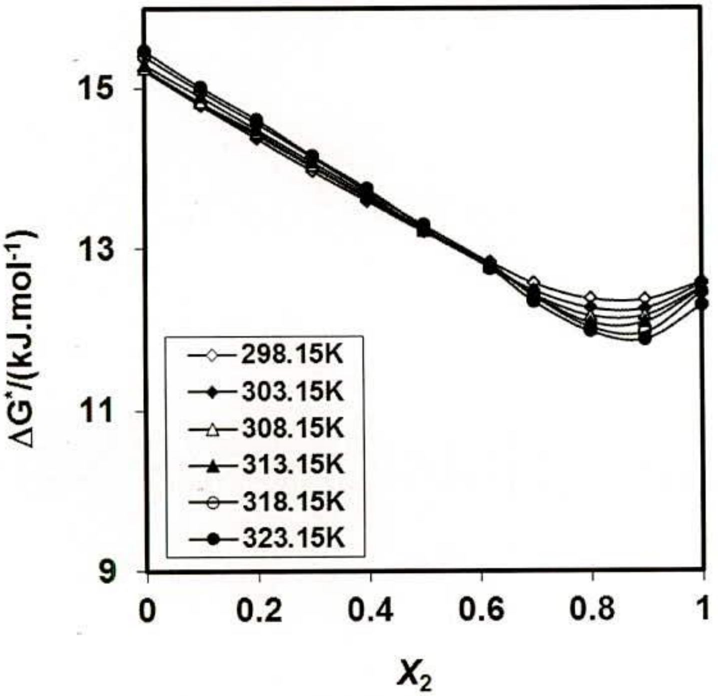

Figure 4.129: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

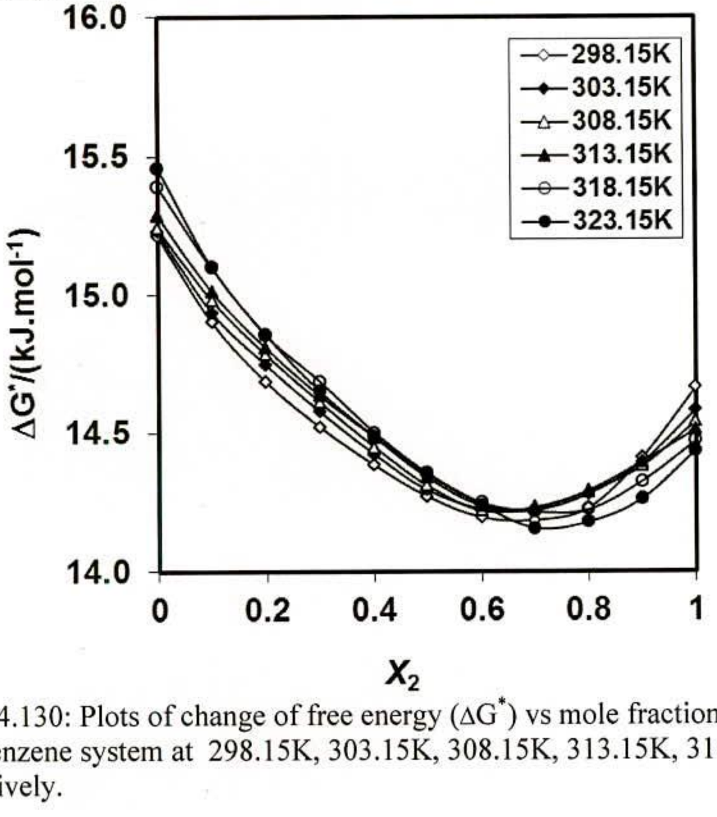

Figure 4.130: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

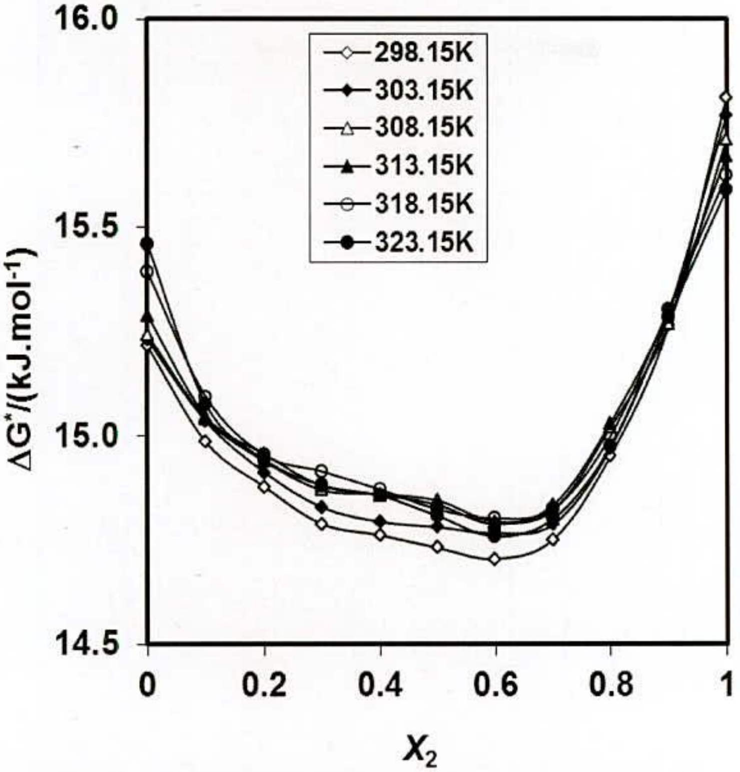

Figure 4.131: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

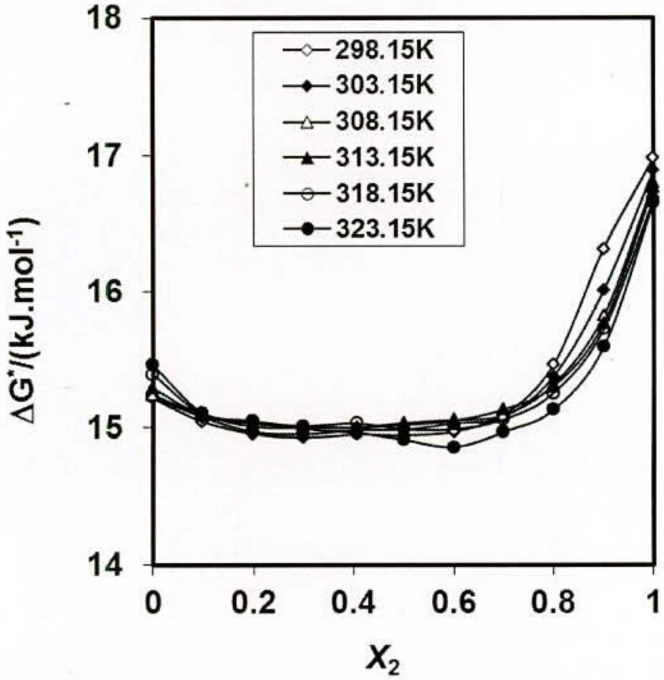

Figure 4.132: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

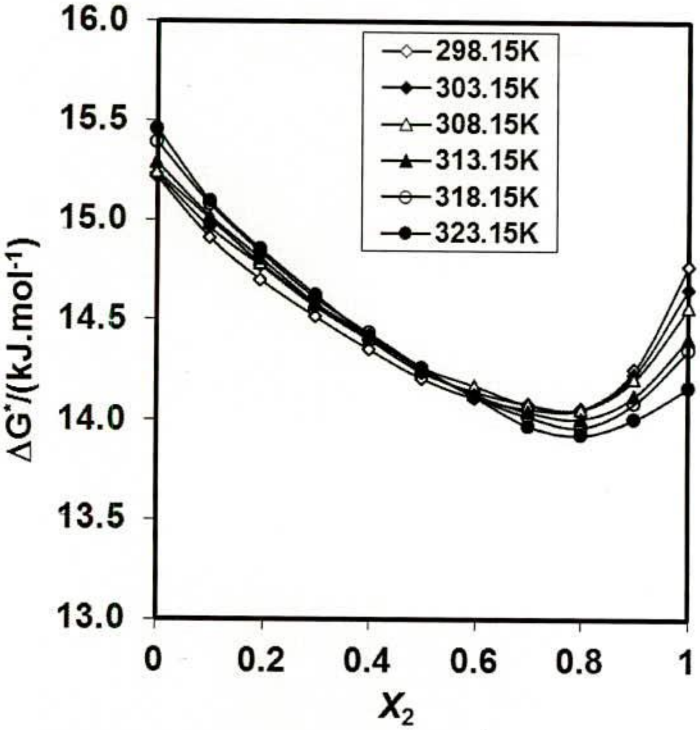

Figure 4.133: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

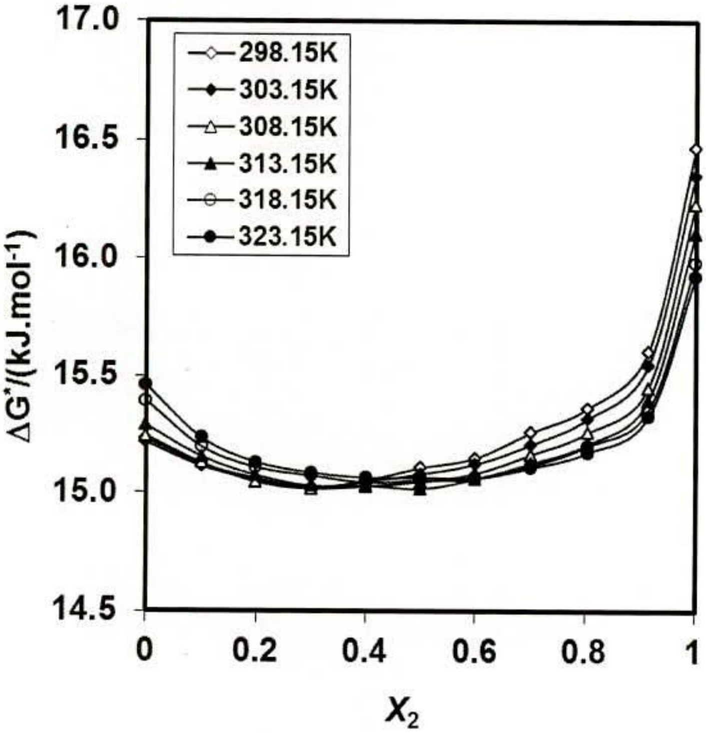

Figure 4.134: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

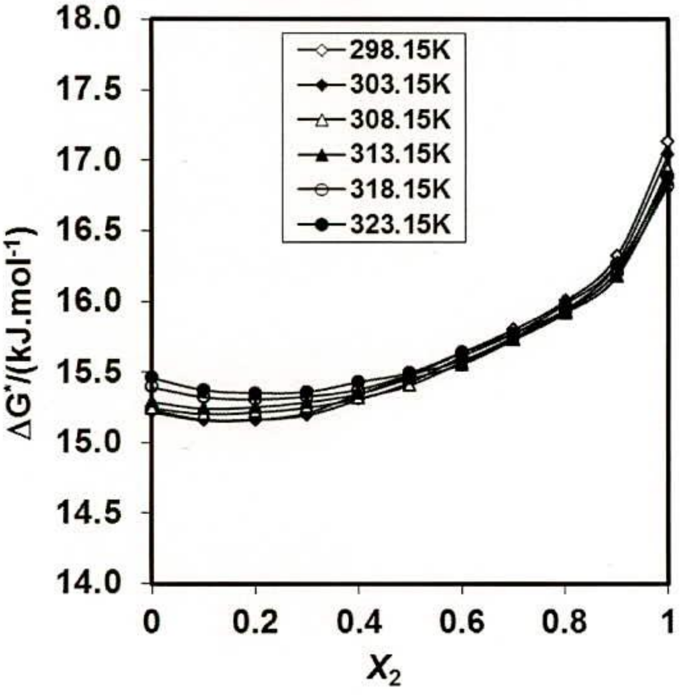

Figure 4.135: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

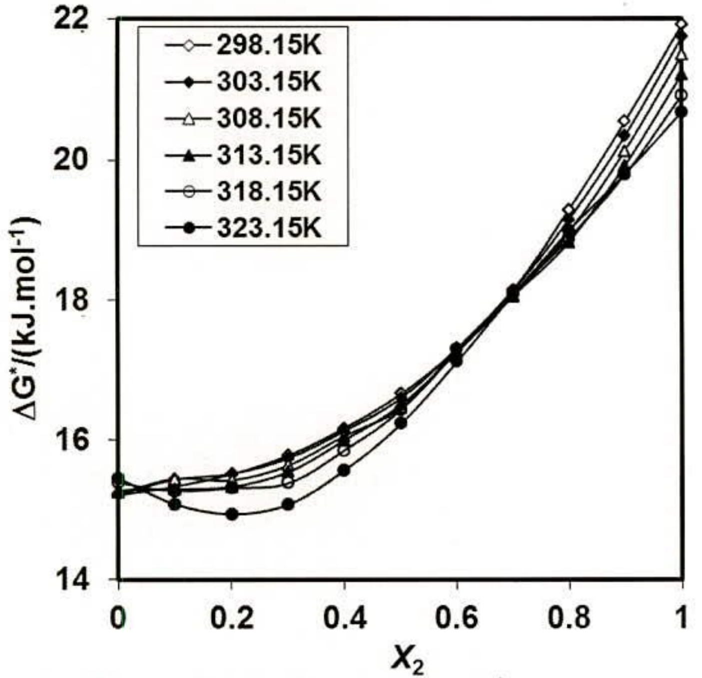

Figure 4.136: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

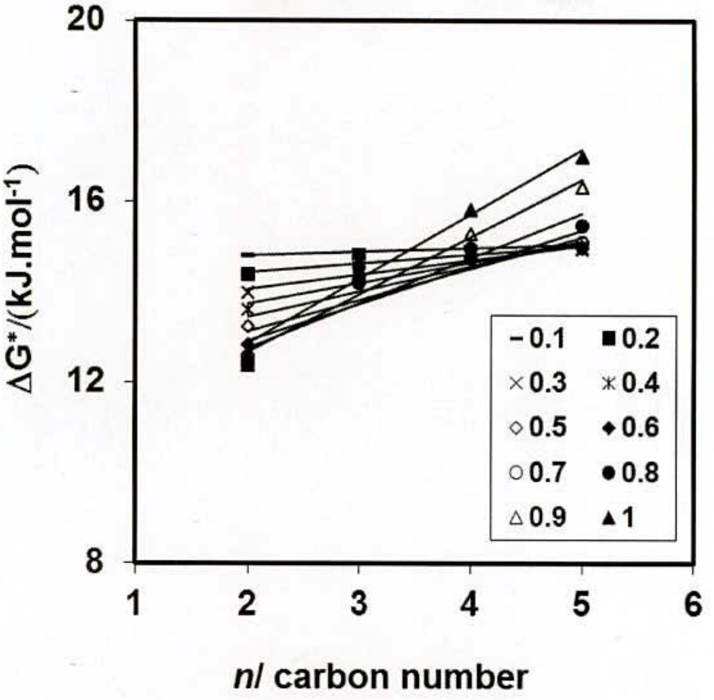

Figure 4.137: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

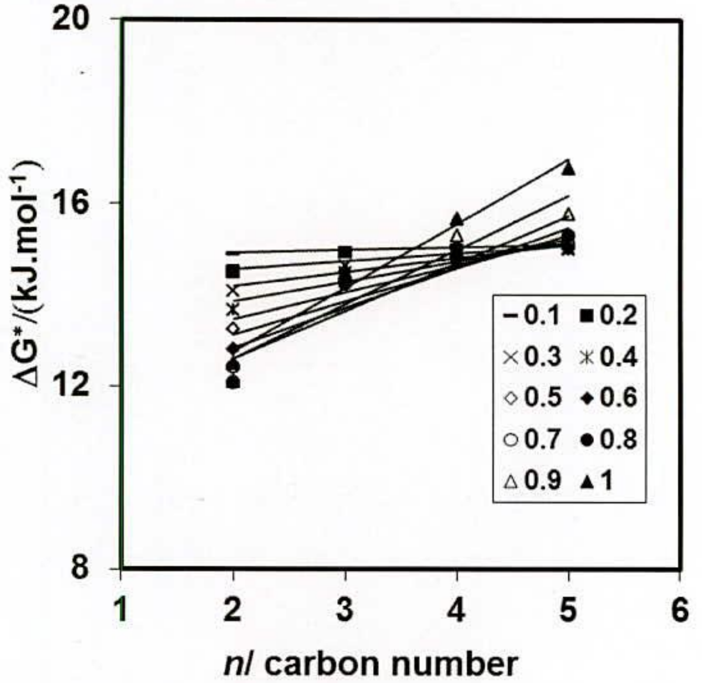

Figure 4.138: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

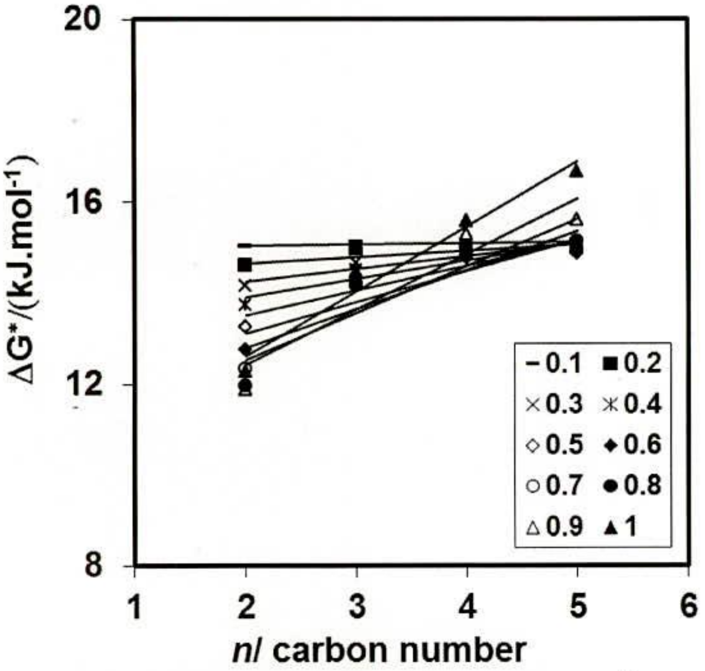

Figure 4.139: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

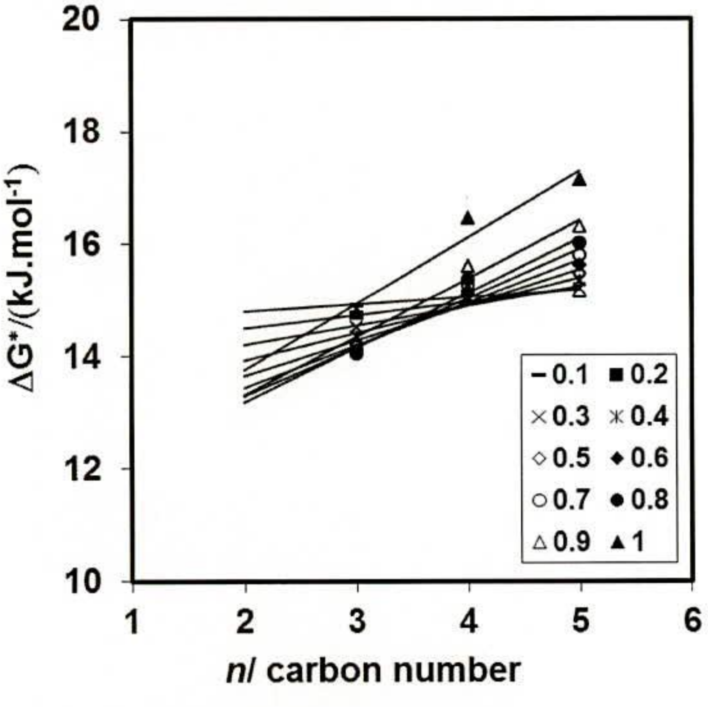

Figure 4.140: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols with different mole fraction at 298.15K.

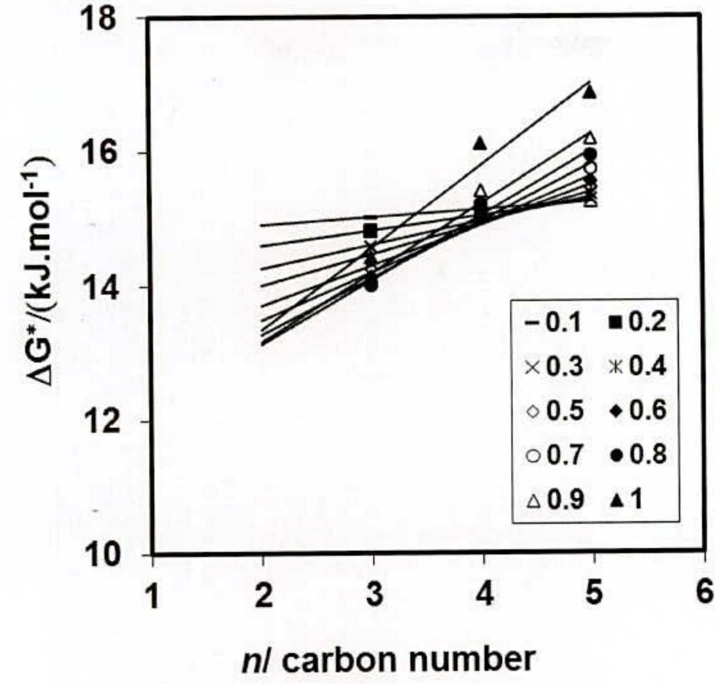

Figure 4.141: Dependence of the change of free energy (ΔG^{*}) with carbon number (n) of iso - alcohols with different mole fraction at 313.15K.

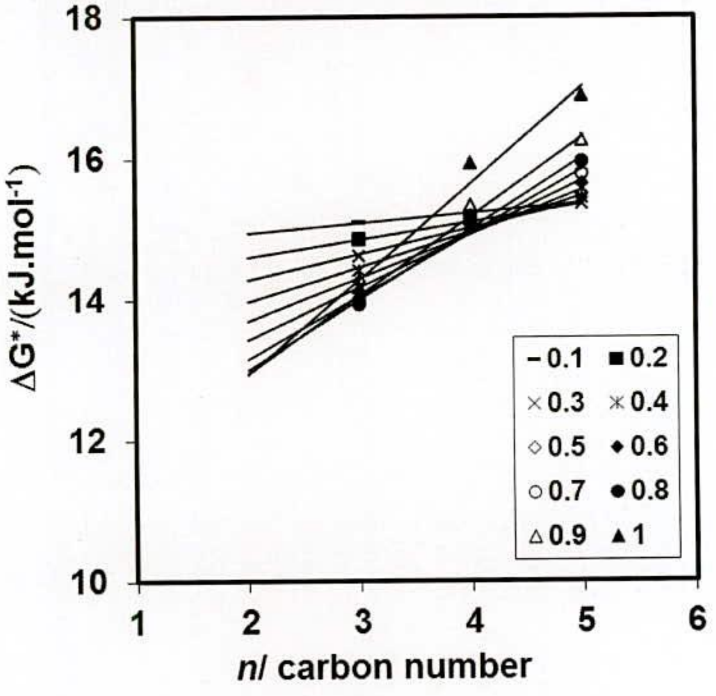

Figure 4.142: Dependence of the change of free energy (ΔG^{*}) with carbon number (n) of iso - alcohols with different mole fraction at 323.15K.

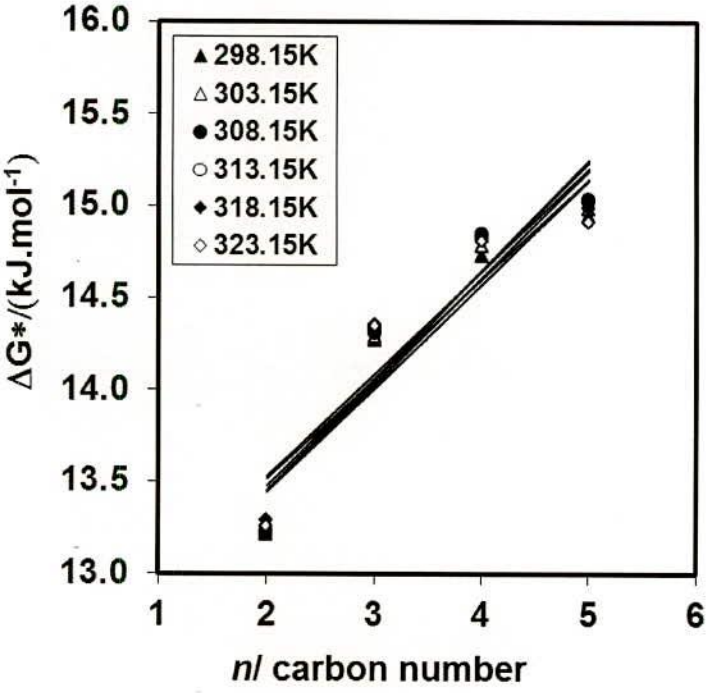

Figure 4.143: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

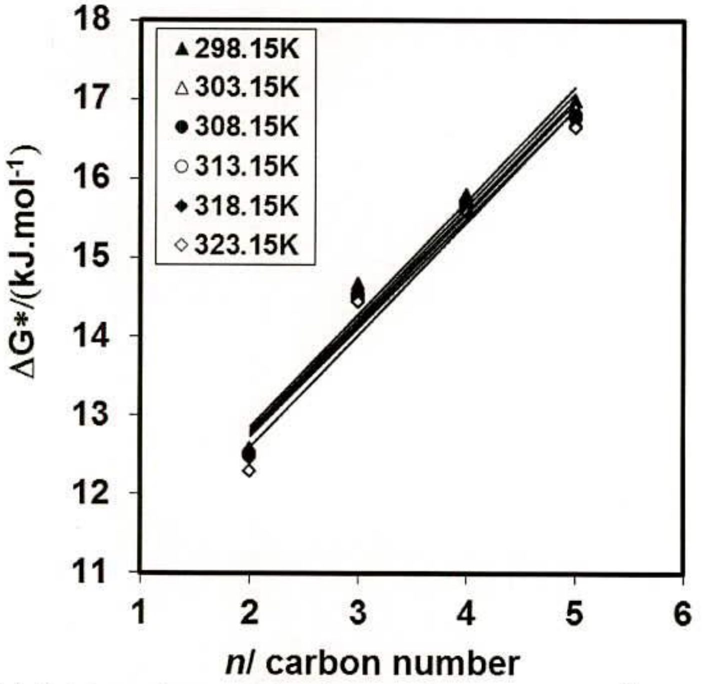

Figure 4.144: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols with different temperature at 1.0 mole fraction.

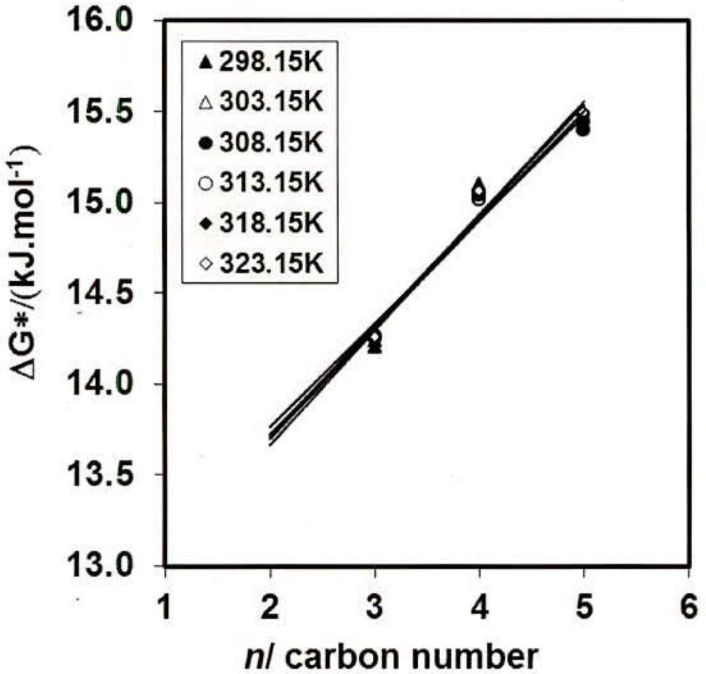

Figure 4.145: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols with different temperature at 0.5 mole fraction.

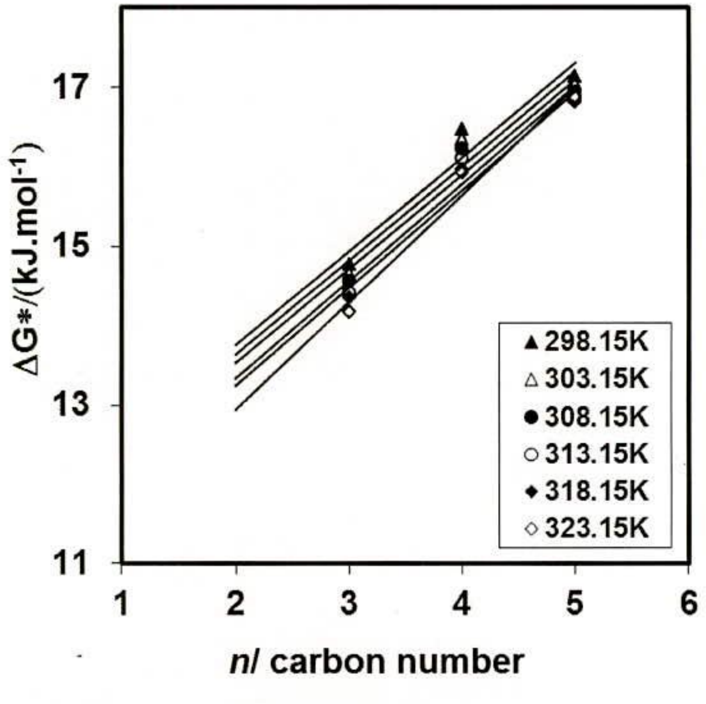

Figure 4.146: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols with different temperature at 1.0 mole fraction.

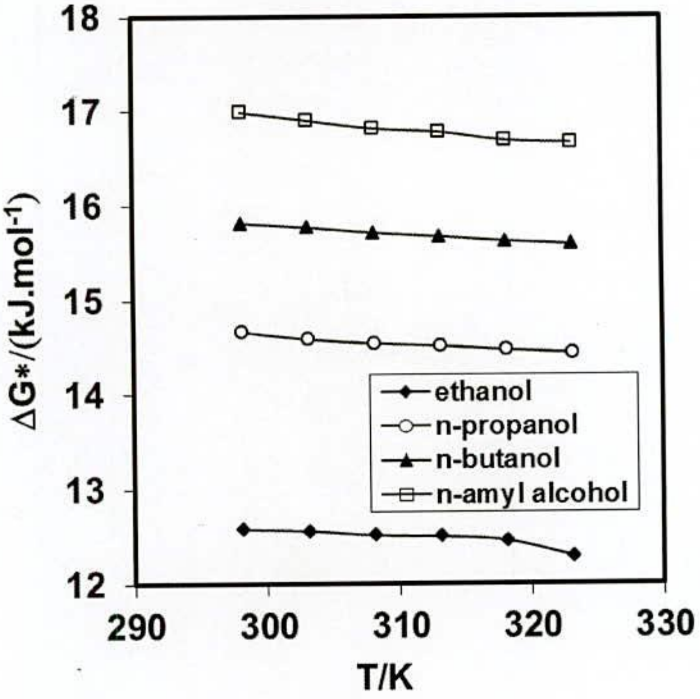

Figure 4.147: Comparison of change of free energy (ΔG^*) vs temperature (T) of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

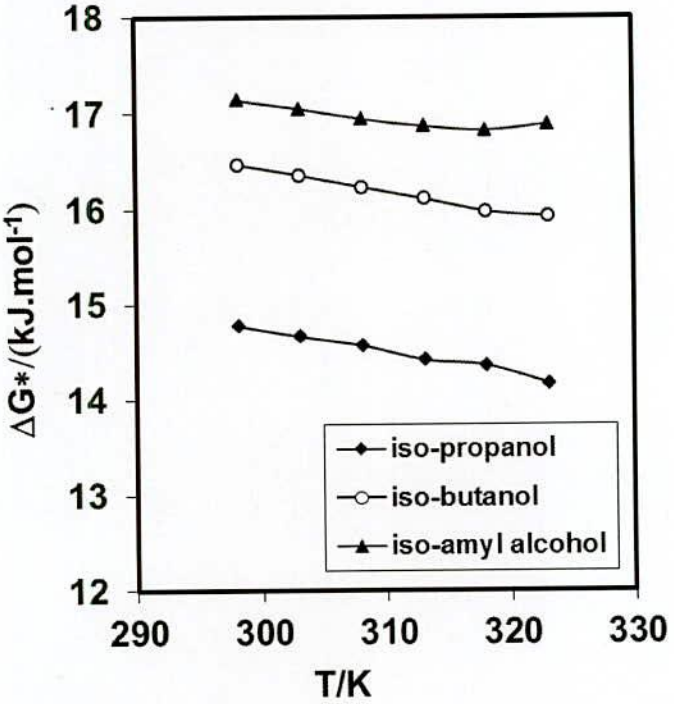

Figure 4.148: Comparison of change of free energy (ΔG^*) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

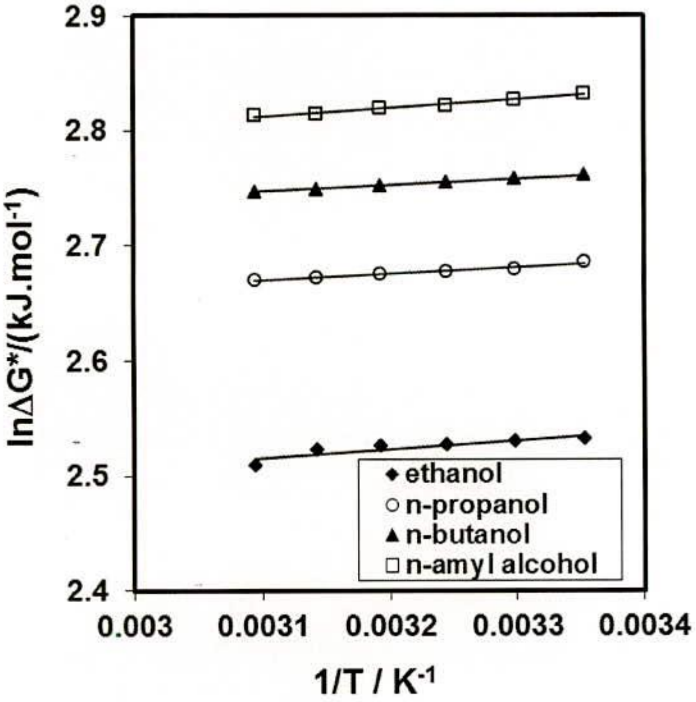

Figure 4.149: Comparison of lnΔG* vs 1/T of Ethanol, n-Propanol, n-Butanol, n-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

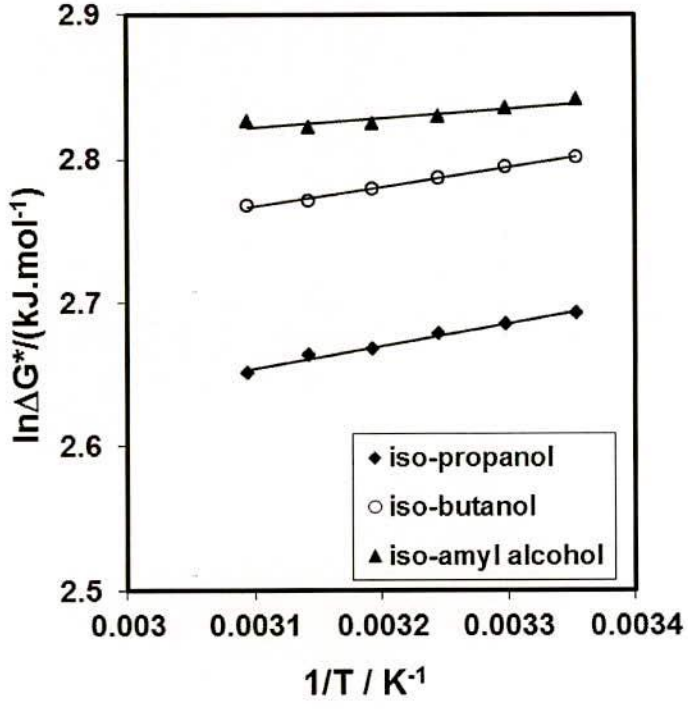

Figure 4.150: Comparison of lnΔG* vs 1/T of iso-Propanol, iso-Butanol and iso-Amyl alcohol in Nitrobenzene at 1.0 mole fraction.

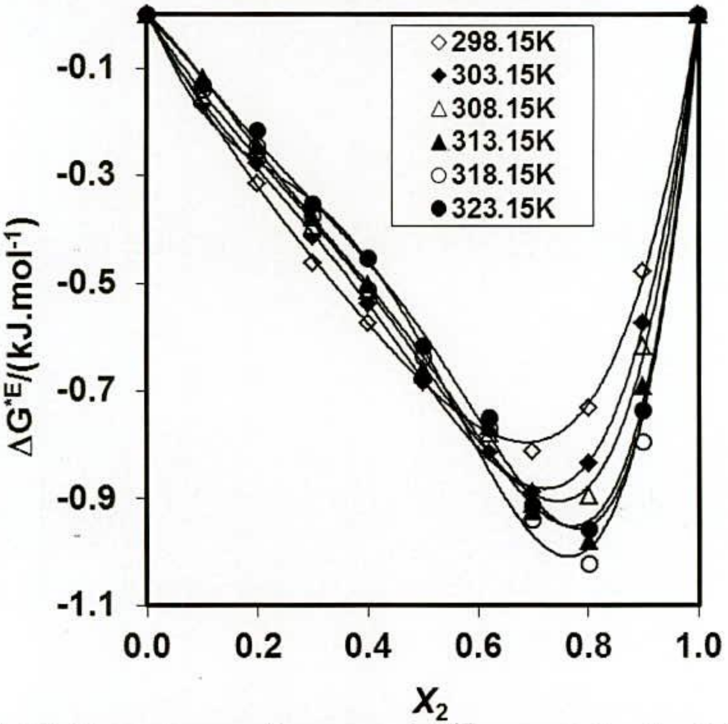

Figure 4.151: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of Ethanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

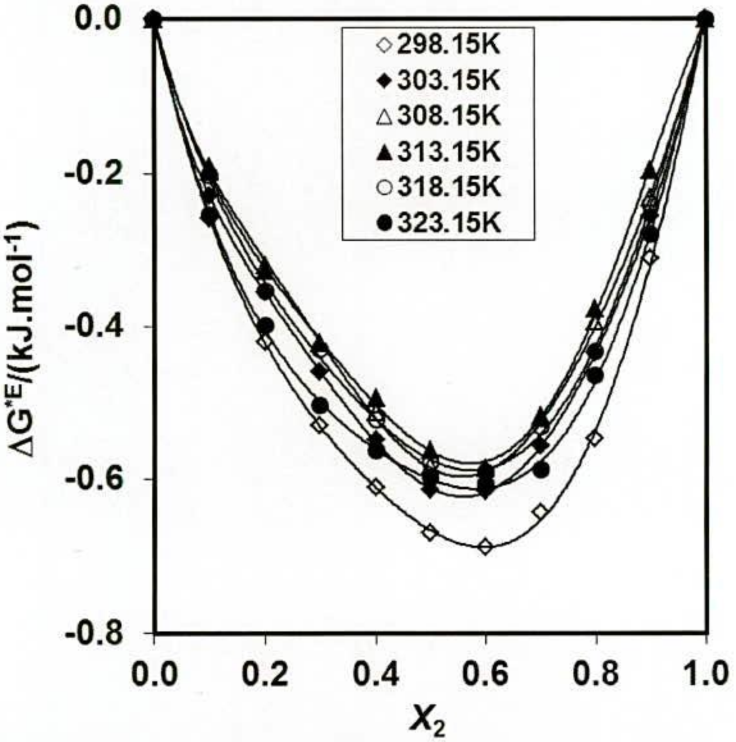

Figure 4.152: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

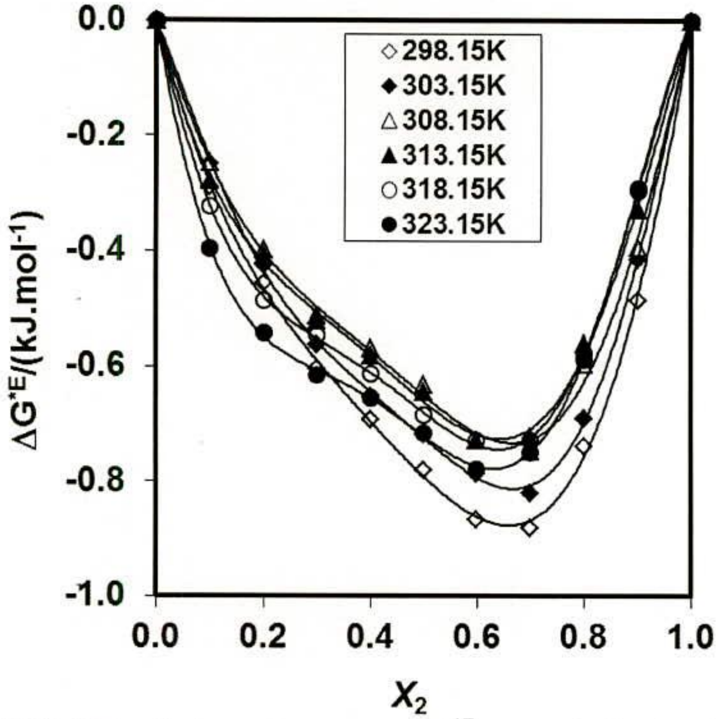

Figure 4.153: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

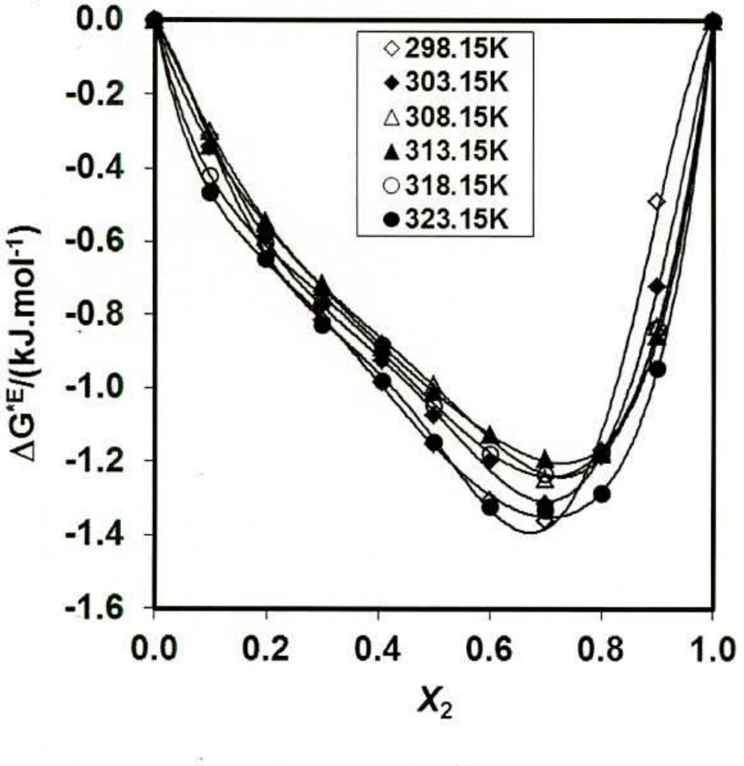

Figure 4.154: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

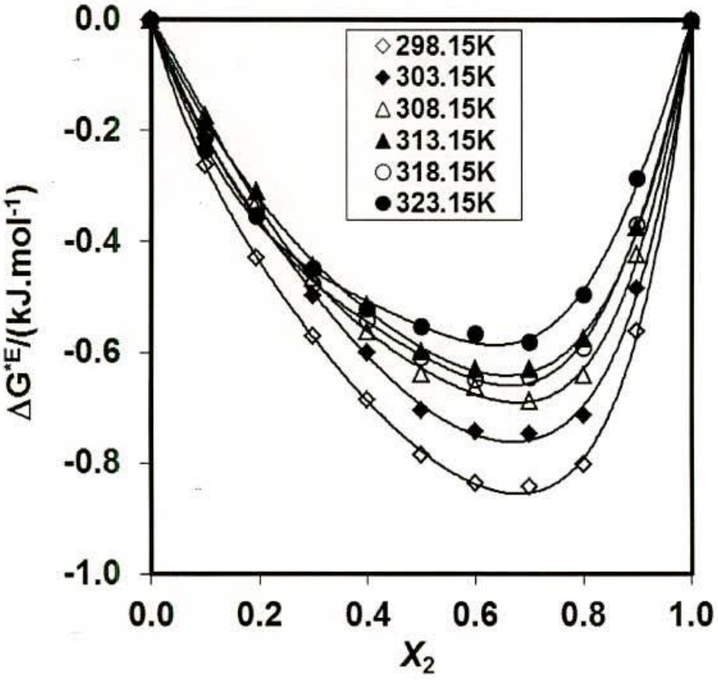

Figure 4.155: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Propanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

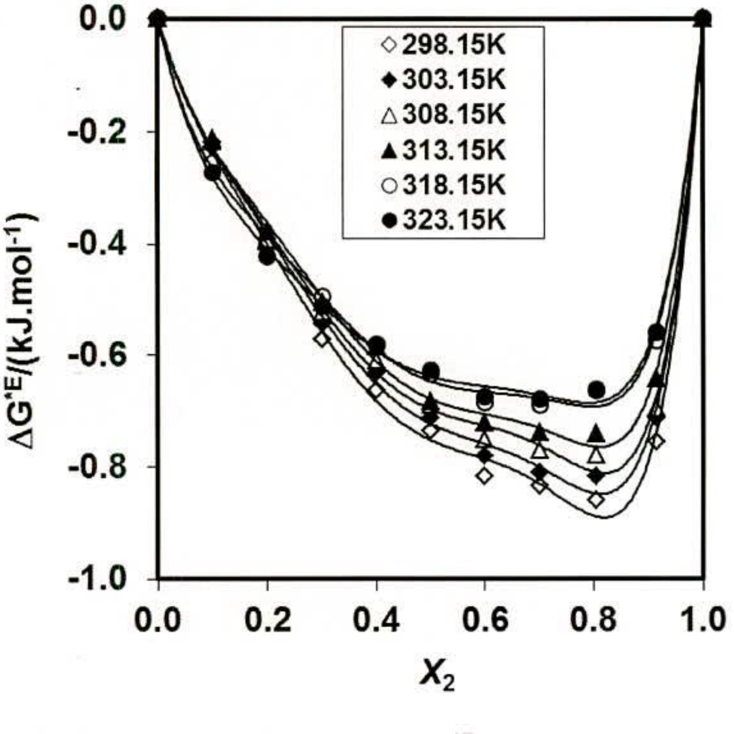

Figure 4.156: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Butanol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

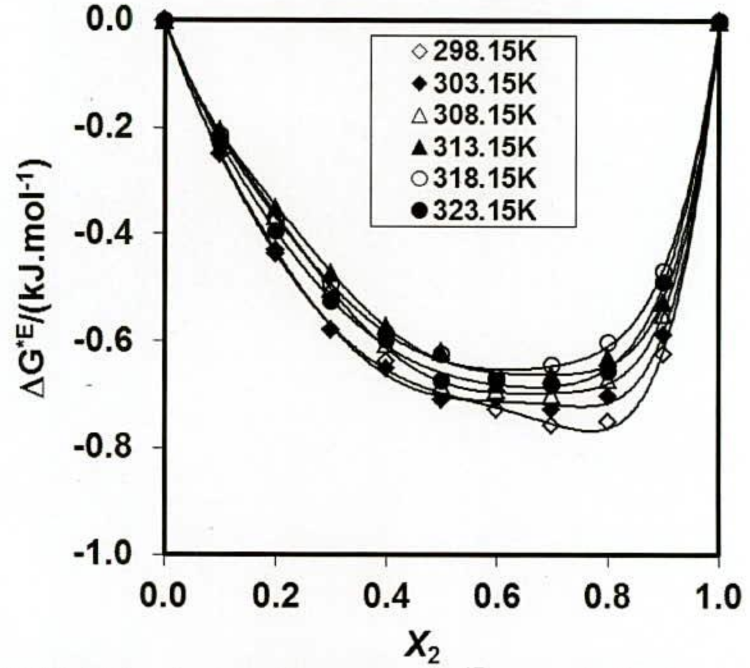

Figure 4.157: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Amyl alcohol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

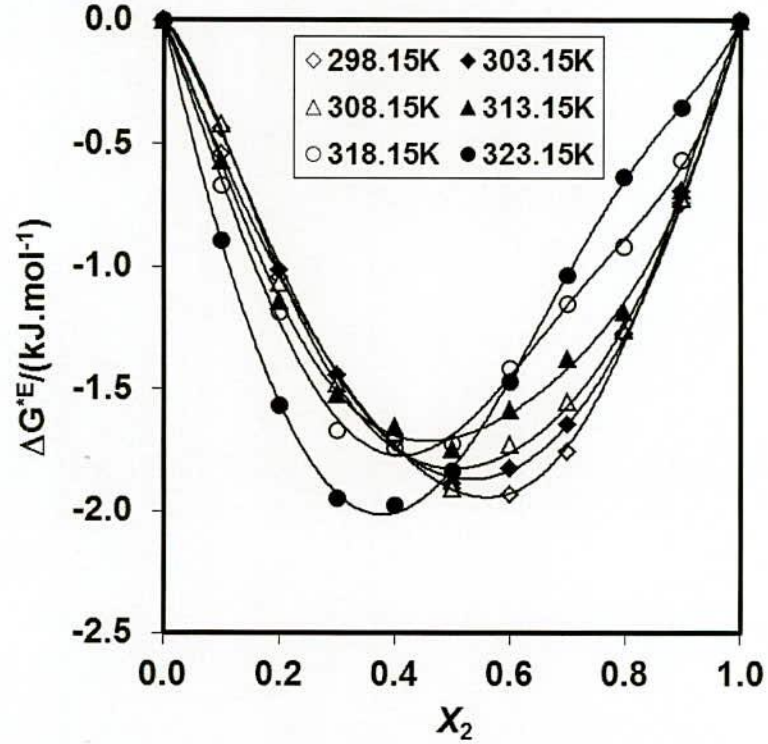

Figure 4.158: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of Propylene glycol + Nitrobenzene system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

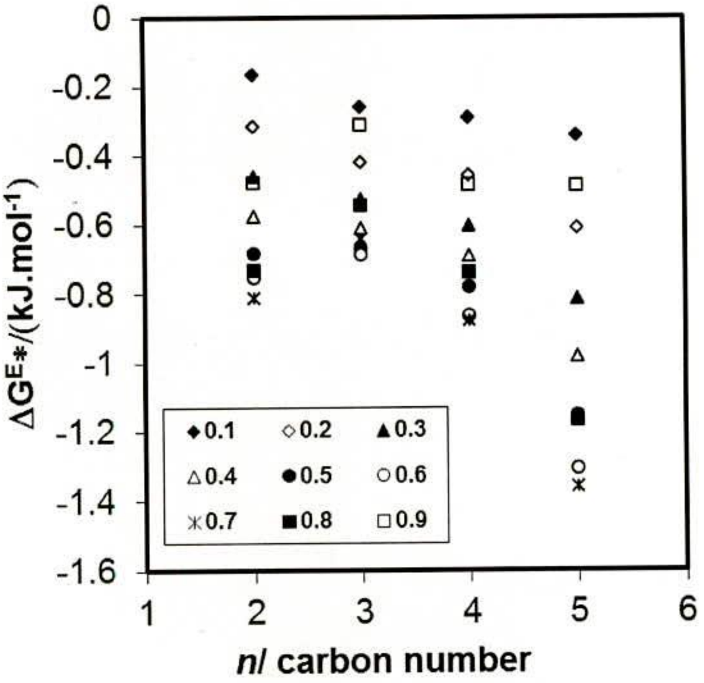

Figure 4.159: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different mole fraction at 298.15K.

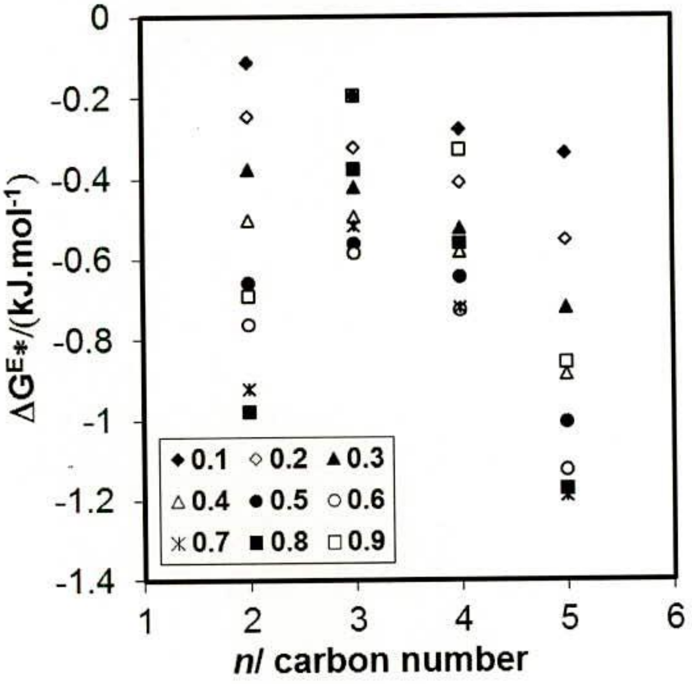

Figure 4.160: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different mole fraction at 313.15K.

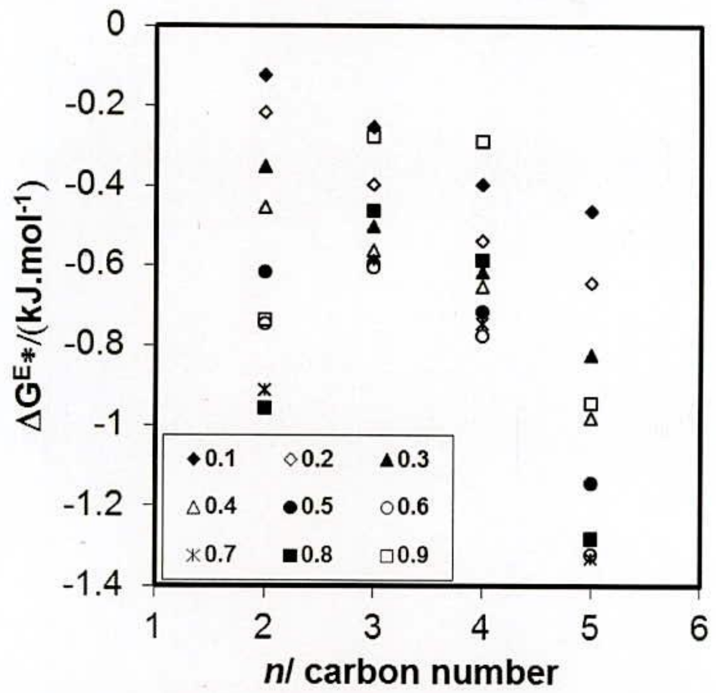

Figure 4.161: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different mole fraction at 323.15K.

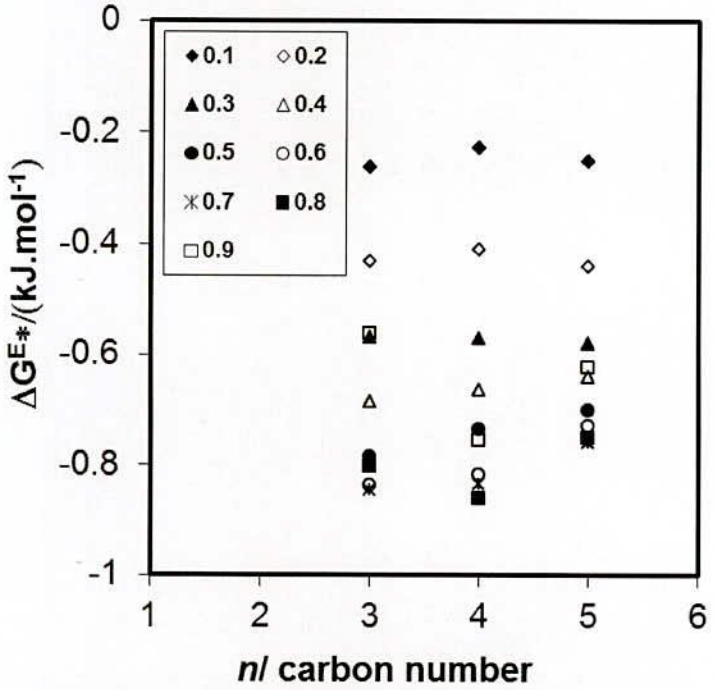

Figure 4.162: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols with different mole fraction at 298.15K.

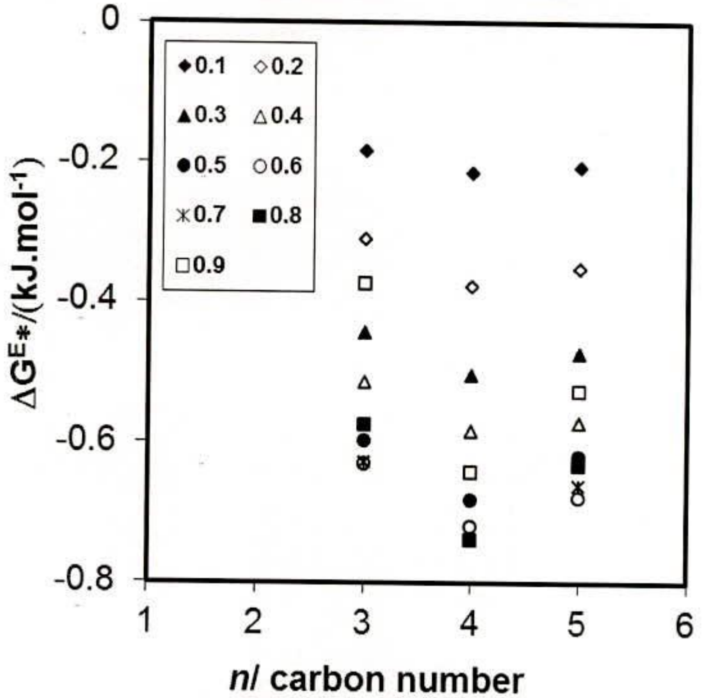

Figure 4.163: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols with different mole fraction at 313.15K.

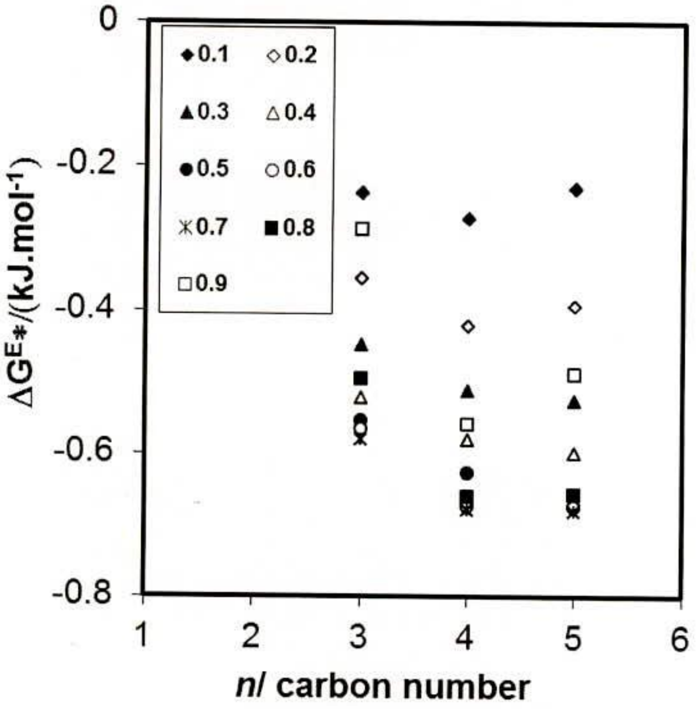

Figure 4.164: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols with different mole fraction at 323.15K.

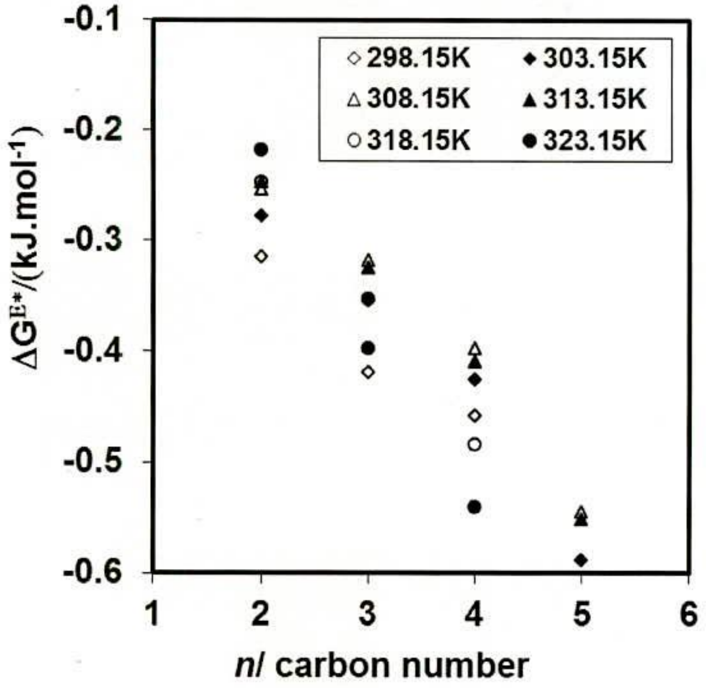

Figure 4.165: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different temperature at 0.2 mole fraction.

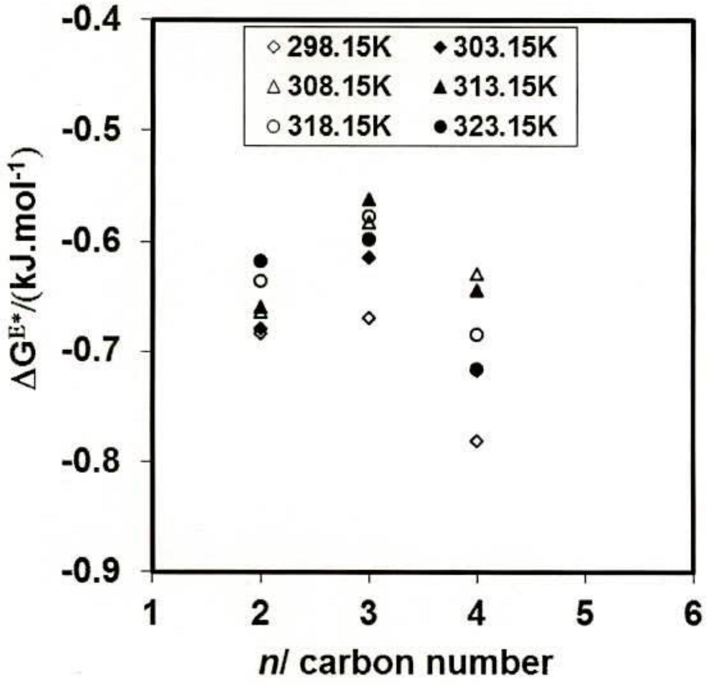

Figure 4.166: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different temperature at 0.5 mole fraction.

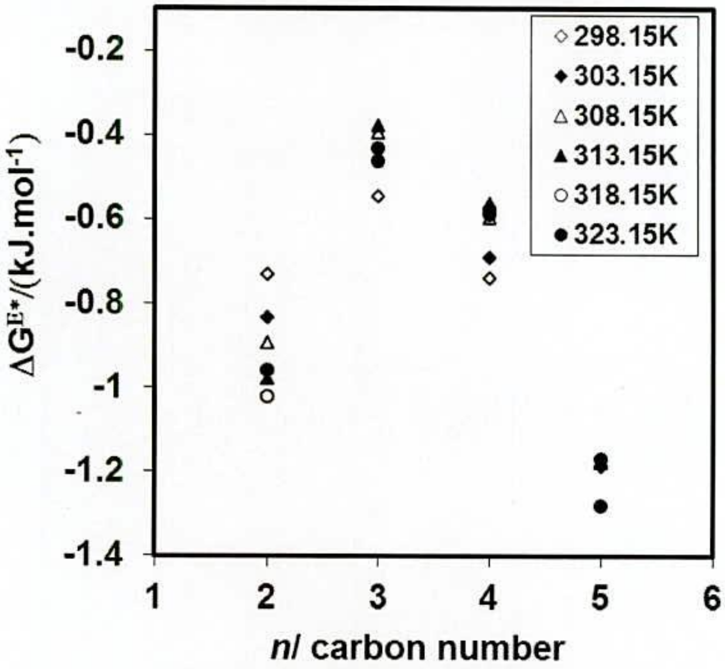

Figure 4.167: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols with different temperature at 0.8 mole fraction.

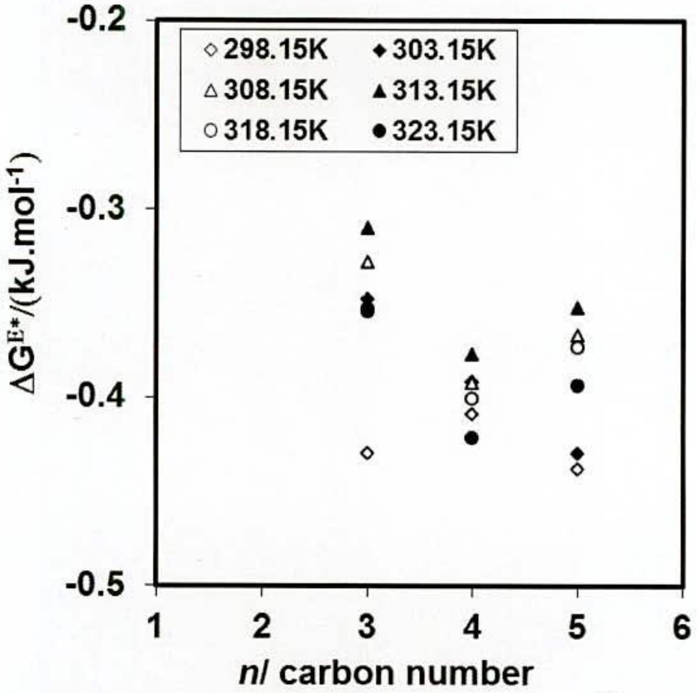

Figure 4.168: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols with different temperature at 0.2 mole fraction.

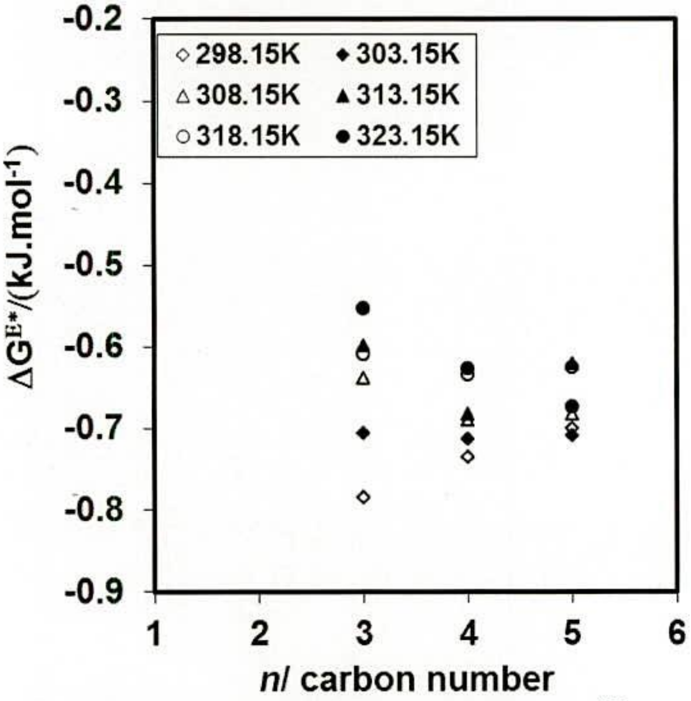

Figure 4.169: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols with different temperature at 0.5 mole fraction.

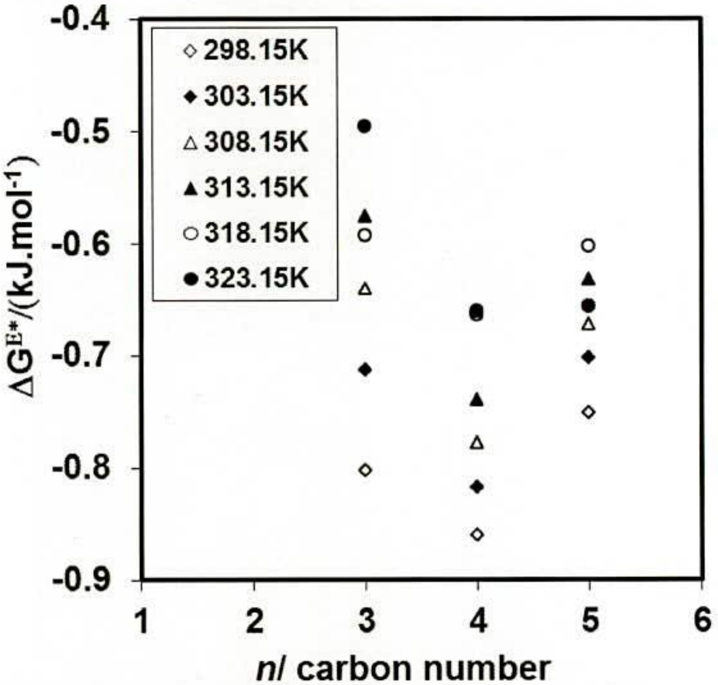

Figure 4.170: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso-alcohols with different temperature at 0.8 mole fraction.

CHAPTER V

Conclusions

The solution properties of binary mixtures of Ethanol + Nitrobenzene (NB), *n*-Propanol + NB, *iso*-Propanol + NB, *n*-Butanol + NB, *iso*-Butanol + NB, n-Amyl alcohol + NB, *iso*-Amyl alcohol + NB and Propylene glycol + NB show strong solute–solvent interactions. The value of density of alcohols in NB decreases with the increasing of composition of the alcohols. The decrease of density with composition of alcohols can be attributed to solute-solvent interaction. The densities of all alcohols in pure state increase with the increasing of carbon number. 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 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 decrease upto ~ 0.8 mole fraction of Ethanol and show a minima later on, the viscosity increase sharply until that of pure alcohol is reached. The viscosities decrease slowly upto 0.6-0.7 mole fraction of n-Propanol and iso-Propanol reaches a minimum value and then the viscosity increase sharply. The viscosities decrease initially and then almost unchanged upto ~0.7 mole fraction of n-Butanol and later on the viscosity increase sharply until the pure alcohol is reached. For iso-Butanol, initially viscosity is almost unchanged, then increase slowly upto 0.9 mole fraction of Alkanol and later on, the viscosity increase sharply until pure alcohol is reached. The change of viscosity of n-Amyl alcohol and iso-Amyl alcohol initially is almost unchanged upto 0.8 mole fraction and later on, the viscosity increase sharply until pure alcohol is reached. For Propylene glycol, the viscosity is unchanged upto ~ 0.5 mole fraction and then the viscosity increases sharply. At the alcohol rich region rapid change of viscosity are observed for *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol and *iso*-Amyl alcohol but the change is pronounced for the branched chain alcohols systems (iso-Propanol, iso-Butanol, *iso*-Amyl alcohol) than the linear alcohol (n-Propanol, n-Butanol, n-Amyl alcohol) systems. The increasing of viscosity with carbon number of alcohols or branched chain alcohols ascribed that the solution resistance increases with the increase of carbon chain length.

The excess viscosity, η^E values are found to be negative, indicating that the Nitrobenzene 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 Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol 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 Nitrobenzene + studied alcohols systems show agreement with the statements. On addition of alkanols in Nitrobenzene 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 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 Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Amyl alcohol, *iso*-Amyl alcohol and Propylene glycol in Nitrobenzene systems, ΔG^{*E} are negative over the entire composition range. The negative excess free energy, ΔG^{*E} indicates the presence of dispersion force. The ΔS^* values are found to be very small for all the studied systems indicating that the effects of ΔS^* are negligible. 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.

The volumetric properties are fully consistent with the viscometric and thermodynamic properties.

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