Studies On Volumetric And Viscometric Properties Of Some Binary And Ternary Liquid Systems

By

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Declaration

This is to certify that the thesis work entitled "Studies on volumetric and viscometric properties of some binary and ternary liquid systems" has been carried out by Md. Fazlul Haque 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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This is to certify that the thesis work submitted by Md. Fazlul Haque entitled " Studies on volumetric and viscometric properties of some binary and ternary liquid systems " has been approved by the board of examiners for the partial fulfillment of the requirements for the degree of M. Phil. in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh in November 19, 2011.

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ABSTRACT

Densities and viscosities of binary mixtures of Methanol +DMF, Ethanol +DMF, *n*-Propanol +DMF, *iso*-Propanol +DMF, *n*-Butanol +DMF, *iso*-Butanol +DMF, *tert*-Butanol +DMF, n-Amyl alcohol +DMF, iso-Amyl alcohol +DMF and ternary mixtures of *n*-Propanol +0.02M SDS in DMF, *n*-Butanol +0.02M SDS in DMF and n-Amyl alcohol +0.02M SDS in DMF have been studied over the entire range of composition $(0 < x_2 < 1)$ at 298.15- 323.15K with an interval of 5K except Methanol. Methanol system was studied at 298.15K, 303.15K and 308.15K owing to its lower boiling point.

The excess molar volumes, V^E were calculated from the densities of the mixtures at different temperatures. The values of V^E for all the systems are negative over the entire range of composition, showing minima at ~ 0.6 mole fraction of Methanol, ~ 0.2-0.3 mole fraction of Ethanol, ~ 0.1-0.2 mole fraction of *n*-Propanol and ~ 0.2 mole fraction of *iso*-Propanol, ~ 0.1-0.2 mole fraction of *n*-Butanol, ~0.2 mole fraction of *iso*-Butanol, ~0.3 mole fraction of *tert*-Butanol, ~0.2 mole fraction of n-Amyl alcohol and ~0.6 mole fraction of *iso*-Amyl alcohol. The values of V^E for the most of studied alcohols are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature, it shows positive throughout the whole range of composition.

The observed values of V^E for the mixtures have been explained in terms of physical, chemical, and geometrical contributions. 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 are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume.

The viscosity coefficients, η of all the above mixtures at all the six different temperatures have also been determined. The viscosities increase initially slowly up to ~0.6 mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohols and later on, the viscosity increases sharply until that of pure alcohol is reached specially at lower temperature. For Methanol, viscosity decrease slowly on continued

addition of Methanol. Viscosity decreases with rise of temperature. In pure state the viscosity of alcohols has been found to be in the order of,

tert-Butanol> n-Amyl alcohol> iso-Amyl alcohol>iso-Butanol>n-Butanol> iso-Propanol> n-Propanol> Ethanol> Methanol

There is a marked decrease in the viscosity with increase of temperature for all the isomeric studied alcohols. At 298.15K, viscosity is found to be in the order:

tert-Butanol> iso-Butanol>n-Butanol

iso-Propanol> n-Propanol, which however changes to

n-Butanol >iso-Butanol> tert-Butanol

n-Propanol> iso-Propanol at 323.15K.

This ascribed that the branched chain isomers are less stable than linear chain isomers at higher temperature and vice versa.

The η^E values are found to be positive or negative, indicating that the DMF solutions of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems except Methanol with minima occurring between 0.6-0.9 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol. Excess viscosity of Methanol is positive at all the temperatures over the entire range of composition and show maxima in the DMF rich region at 0.2-0.4 mole fraction of Methanol. Excess viscosity of Ethanol is negative and show minima at 0.4-0.5 mole fraction of Ethanol. The position of maxima and minima virtually does not change remarkably with the variation of temperature. The heights of the minima are in the order:

tert-Butanol> n-Amyl alcohol> iso-Amyl alcohol~iso-Butanol>n-Butanol> iso-Propanol> n-Propanol> Ethanol.

The negative V^E, positive η^E, and positive interaction parameter ε for the DMF + Methanol system may be ascribed that the interaction is strong, namely formation of H-bonding between DMF and Methanol. The negative V^E, negative η^E, and negative ε for the DMF + rest of the studied alcohols systems indicate that dispersion force is dominant. For the later case, V^E is negative due to the segmental inclusion of DMF in the interstices of polymolecular alkanol aggregates. Some disruptive force causing volume expansion may be present, but it is more than compensated for by volume contraction through the segmental inclusion of DMF.

The thermodynamic parameters such as, free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) change of activation for the viscous flow for these systems were determined for the entire range of composition by using Eyring's equation. The free energy ($\Delta G^{\#}$) 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 excess properties (V^{E}, η^{E}, $\Delta G^{\#E}$) data have been fitted by the least square method to the four parameter Redlich-Kister equation and the values of the parameter a_j have been reported.

Although the value of density and viscosity of the studied systems of 0.02M SDS in DMF solutions are slightly higher than the pure DMF solutions, but no appreciable change in the volumetric and viscometric properties were observed by the addition of the surfactants.

Contents

LIST OF TABLES

LIST OF FIGURES

Nomenclature

SDS	Sodium dodecylsulphate
DMF	Dimethylformamide
CMC	Critical micelle concentration
φ_v	The apparent molar volume
φ_v^0	The limiting apparent molar volume
ρ	Density
ρ_1	Density of solvent
ρ_2	Density of solute
ρ_{mix}	Density of the mixture
V^E	Excess 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 in gram
M_2	Molecular mass of solute in gram
V_o	Molar volume of solvent
V_m	Molar volume of solution
a_i	Fitting coefficient
$\Delta H^{\#}$	Activation Enthalpy
$\Delta G^{\#}$	Activation Free energy
$\Delta S^{\#}$	Activation Entropy
v_1	Volume of solvent in mL.

Nomenclature

v_0	Volume of empty bottle.
w_e	Weight of empty density bottle
w_0	Weight of density bottle with solvent
w	Weight of density bottle with solution
h	Plank's constant
N	Avogadro's number
R	Universal gas constant

CHAPTER I

Introduction

1.1 Properties of solutions

The liquid state, being an intermediate state between gaseous and solid states, retains some characteristics of both the gaseous and solid states. The liquid state, thus, can not be adequately defined as the gaseous and the solid states. The molecular and macroscopic behavior of liquids varies from liquid to liquid due to characteristic intermolecular interactions. The behavior of multi-component mixtures, on account of molecular interactions between dissimilar molecules, becomes still more difficult to interpret. In view of these facts there are serious problems in formulation of any general theory of solution.

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

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

The macroscopic properties of any system have to be interdependent, since these essentially originate from the most probable distribution of energy between the constituent molecules comprising the system. There has, therefore, been interest for seeking interrelations between the macroscopic properties of any system. It should, in principle, 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.

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.

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

Physical properties like density, viscosity, surface tension, conductivity, dielectric constant, refractive index, group frequency shifts in I.R. spectra etc. give 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 a sound information about the structure of some alcohol, N,N'-Dimethylformamide (DMF) and surfactant and in studying the liquid-liquid interaction in binary and ternary systems.

1.2 Properties of alcohols

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

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

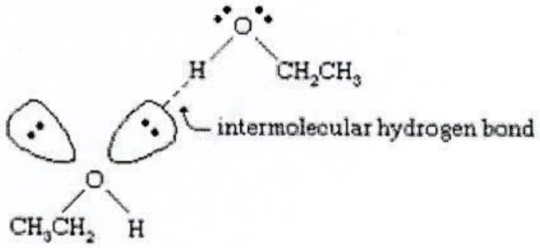

Fig. 1.1

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.

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 DMF

N,N'-Dimethylformamide (DMF) is colourless liquid and miscible with water and most of the organic liquids. DMF is a common solvent for chemical reactions. Pure dimethylformamide is odorless whereas technical grade or degraded dimethylformamide often has a fishy smell due to impurity of dimethylamine. Its name is derived from the fact that it is a derivative of formamide, the amide of formic acid. N,N'-Dimethylformamide is a polar (hydrophilic) aprotic solvent with a high boiling point. It facilitates reactions that follow polar mechanisms, such as SN_2 reactions. Dimethylformamide can be synthesized from methylformate and dimethylamine or reaction of dimethylamine and carbon monoxide. Since the density of DMF is very similar to that of water.

Due to the contribution of the two possible resonance structures of an amide, the bond order of the carbonyl C=O bond is reduced, while that of the carbon-nitrogen bond is increased. Thus the infrared spectrum of DMF shows a lower C=O stretching frequency at 1675 cm^{-1} than an unsubstituted C=O bond. Also, because of the partial double bond character, the rotation about the C-N axis is slow at room temperature, making the two methyl groups inequivalent on the NMR time scale, giving rise to two singlets of 3 protons each at δ 2.97 and 2.88 instead of one singlet of 6 protons in the proton NMR spectrum.The vapour pressure at 20°C is 3.5hPa. The partition coefficient is measured to –0.85. All the DMF physical properties are reported (1-4).

1.4 Surfactants

Surfactant molecules e.g. SDS, CTAB, DTAB, Triton X-100 etc. are a special type of molecules which self-aggregate into super molecular structure when dissolve in water or oil. The simplest aggregate of these Surfactant molecules is called a micelle; and the dispersion of the aggregates in water or oil is referred to as micellar solution. A typical micelle has size of ~ 50A° and is made of about 100 Surfactant molecules. In general, these pseudo-particles could be spherical, cylindrical, ellipsoidal or disk like in shape. It may be mentioned that self aggregation of Surfactant molecules in water/oil arises because of dual affinity of these molecules for water and oil. These consist of two parts name, a polar hydrophilic head group and an apolar hydrophobic tail group (hydrocarbon chain).

Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the change carried by the surface-active part of the molecule. In addition, surfactants are often named in relation to their technological application, hence names such as detergents, wetting agent, emulsifier and dispersant.

Anionic detergents are the most widely used surfactants on account of cost and performance. Cationic are expensive, but their germicidal action makes them useful for some applications. An advantage enjoyed by non ionics is that the lengths of both hydrophilic and hydrophobic groups can be varied.

1.5 Properties of Sodium dodecylsulfate (SDS):

Sodium dodecyl sulfate (SDS) or sodium lauryl sulfate (SLS) is an organic compound with the formula $CH_3(CH_2)_{11}OSO_3Na$. It is an anionic surfactant used in many cleaning and hygiene products. The salt is of an organosulfate consisting of a 12-carbon tail attached to a sulfate group, giving the material the amphiphilic properties required of a detergent. Being derived from inexpensive coconut and palm oils, it is a common component of many domestic cleaning products. The molar mass of SDS is 288.38 g. mol^{-1} and the melting point is 206 ^{0}C.

SDS is mainly used in detergents for laundry and many cleaning applications. SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. For example, it is found in higher concentrations with industrial products including engine degreasers, floor cleaners, and car wash soaps. It is found in toothpastes, shampoos, shaving foams, and bubble bath formulations in part for its thickening effect and its ability to create a lather (25). It can be used to aid in lysing cells during DNA extraction and for unraveling proteins in SDS-PAGE. Sodium dodecyl sulfate (SDS) or Duponol, is commonly used in preparing proteins for electrophoresis in the SDS-PAGE technique(25). This compound works by disrupting non-covalent bonds in the proteins, denaturing them, and causing the molecules to lose their native shape (conformation).This new negative charge is significantly greater than the original charge of that protein. The electrostatic repulsion that is created by binding of SDS causes proteins to unfold into a rod-like shape thereby eliminating differences in shape as a factor for separation in the gel. Sodium lauryl sulfate is probably the most researched anionic surfactant compound.

1.6 Physical Properties of Surfactant Solutions

Solution of highly surface-active materials exhibit unusual physical properties. In dilute solution the surfactant acts as a normal solute. At fairly well defined concentrations, how ever an abrupt change in several physico-chemical properties such as osmotic pressure, turbidity, electrical conductance and surface tension take place. The rate at which osmotic pressure increases with concentration becomes abnormally low and the rate of increase of turbidity with concentration is much enhanced, which suggests that considerable association is taking place. The conductance of ionic surfactant solutions, however, remains relatively high, which shows that ionic dissociation is still in force.

Mc-Bain (26) pointed out that this seemingly anomalous behavior could be explained in terms of organized aggregates or micelle , of the surfactant ions in which the lyphobic hydrocarbon chains are oriented towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. The concentration above which micelle formation becomes appreciable is termed critical micelle concentration (CMC).

The knowledge of densities and viscosities of pure liquids and liquid mixtures is needed for optimal design of many types of equipment in chemical technology. DMF is a versatile solvent, used in the synthesis of pharmaceuticals, in agricultural chemistry, and as a solvent for polymers. A fundamental understanding of the mixture behavior of DMF with polar, nonpolar, associated, and nonassociated solvents is therefore important from the technical and engineering point of view. The density and viscosity data of binary mixtures of DMF with polar, nonpolar, associated, and nonassociated solvents have been reported (1-4).

1.7 DMF-Solvent interaction

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 amides with amino acids, alcohols, and their derivatives are of interest. The correlation between solute -solvent interaction is complex (5-15). In view of the fact that the interactions occurring between solutes in water and in amide solvent are different, it would be worthwhile to explore the effect of changing the solvent medium on molecular interactions. Water + N,N-dimethylformamide (DMF) is a model mixed solvent which represents an environment of the protein's interiors (15). Thermodynamic properties of this solution have been reported (15). Several studies concerning the volumetric properties of DMF + water (7-10) have been published. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure (10-20). Because the environment of the solute affects the thermodynamic properties, it is of interesting to study the effect of the media changing from water to amide solvent on the thermodynamic properties of the alcohol. Zegers and Somsen (21) reported the volumetric properties of DMF + alcohol mixtures. In order to give a better description of the solvation of DMF by water and by alcohol molecules in the ternary mixture DMF + alcohol + water (22-24) published of papers on the excess molar volumes of the ternary mixtures at 313.15 K. The excess molar volumes for the ternary mixture DMF + Methanol + water and for binary constituents DMF + water at 298.15 K are reported (18-20). 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 alcohol + amide interactions with amide solvation, a pseudo binary mixture approach is proposed. The partial molar volumes of Methanol at infinite dilution in DMF + water mixed solvent at several fixed compositions were evaluated and correlated with the composition of the DMF + water mixed solvent.

1.8 The object of the present work

The developments in solution theory are still far from being adequate to account for the properties in terms of the properties of the constituent molecules. Accordingly, it is the experimental data on various macroscopic properties (thermodynamic properties, viscosities, surface tension etc), which provide useful information for proper understanding of specific interaction between the components and structure of the solution. The experimental approach of measurements of various macroscopic properties is also useful in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based. Thermodynamic studies on binary solutions have attracted a great deal of attention and experimental data on a good number of systems are available in a number of review articles (27, 28-31). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, (32-36) 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-amide solutions are of practical importance. DMF to some extent is associated by means of dipole–dipole interactions. Significant structural effects are absent due to the lack of hydrogen bonds. Therefore it acts as an aprotic protophilic solvent of moderately high dielectric constant (ϵ=36.71) of molecules with a large dipolemoment (μ=3.8 D) at 298.15 K [37]. Because of its miscibility with almost all common polar and nonpolar solvents [38–41] it is classified as so-called super solvent. A DMF molecule can interact with an alkanol molecule by virtue of better hydrogen bond acceptor ability of its oxygen atom, resulting in structural and packing effects. Volumetric, viscometric and related thermodynamic properties for the mixtures containing DMF were recently reported in the literature [42–58].

In the present investigations, (i) densities and excess molar volumes, (ii) viscosities and excess viscosities and iii) thermodynamic parameters of ten binary and four ternary mixtures, viz., DMF+ Alcohols and DMF+SDS+ Alcohols at 298.15-323.15K have been determined. In order to understand the issue of solute-solvent interactions in alcohol-DMF and DMF-SDS systems a theoretical and experimental aspect of interactions in terms of excess molar volume and excess viscosity, excess thermodynamic properties analysis is necessary. To our knowledge the studied DMF containing Alcohols or Alcohols +SDS systems interaction with the volumetric, viscometric and thermodynamic properties measurements, has not been analyzed before this work.

We have undertaken a program for studying the volumetric and viscometric properties of binary and ternary liquid mixtures on DMF with Alcohols mixtures. The present thesis presents the density, excess molar volumes, viscosity, excess viscosities, thermodynamic parameters data of DMF + some alcohols or DMF + SDS+ some alcohols over the whole range of compositions at six temperatures from 298.15 K to 323.15 K.

CHAPTER II

Theoretical Background

2.1 Physical Properties and chemical constitutions

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

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

The various physical properties based upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc, have been found to fall into the following four categories (59).

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

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

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

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

2.2 Density

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

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

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

2.3 Density and temperature

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

2.4 Molarity

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

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

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

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 $\mathrm{molL^{-1}}$ (60).

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 (60). 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}

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

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

when two components are mixed together, there may be either a positive or a negative deviation in volume. The positive deviation in volume i.e. volume expansion has been explained by the break down of the mode of association through H-bonding of the associated liquids. The negative deviation in molar volume i.e. volume contraction has been thought of by many observers, as arising from the i) compound formation through association, ii) decrease in the intermolecular distance between the interacting molecules, iii) interstitial accommodation of smaller species in the structural network of the larger species and (iv) change in the bulk structure of either of the substance forming the mixture.

2.6 Apparent/ partial molar volume

The apparent molar volume of a solute in solution, generally denoted by φ_v the relation (61)

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

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 (61),

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

where, $V = \dfrac{n_1M_1 + n_2M_2}{\rho}$ 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 (62,63),

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

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

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

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

If the concentration is expressed in molarity (C), the equation 2.8 takes the form (64):

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

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

is used for inter conversion of the concentration in the two scales (64).

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 (34):

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

and,

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

For solutions of simple electrolytes, the apparent molar volume (φ_v) vary linearly with $\sqrt{m}$, even upto moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (61) :

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

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:

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

and

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

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

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

and

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

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

The concentration dependence of the apparent molar volume of electrolytes have been described by the Masson equation (65), the Redlich-Mayer equation (66) and Owen-Brinkley equation (67). Masson (65) found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

$$\varphi_v = \varphi_v^0 + S_v\sqrt{c} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.22)$$

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

Redlich and Rosenfeld (66) predicated that a constant limiting slope S_v, should be obtained for a given electrolyte charge type if the Debye-Huckel limiting law is obeyed. By differentiating the Debye-Huckel limiting law for activity coefficients with respect to pressure, the theoretical limiting law slope S_v, could be calculated using the equation,

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

where, the terms K and W are given by

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

and $$W = 0.5\sum\gamma_i Z_i^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.25)$$

where, β is the compressibility of the solvent, γ_i is the number of ions of the species i of valency Z_i formed by one molecule of the electrolyte and the other symbols have their usual significance (66). For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

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

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

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

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

2.7 Excess molar volume

For binary systems the molar volumes of pure components, ρ_0 and of mixtures, ρ_{mix} is given by the relation

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

The mixture molar volume is,

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

and the ideal molar volume of this system is given by

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

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

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

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

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

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

2.8 Viscosity

Viscosity means viscous ability. It's more generalized definition is "the internal friction which opposes the relative motion of adjacent layers of a fluid." When a fluid is flowing through a cylindrical tube, layers just touching the sides of the tubes are stationary and velocities of the adjacent layers increases towards the centre of the tube, the layer in the centre of the tube having the maximum velocity. There thus exists a velocity gradient.

In case of liquid, this internal friction arises because of intermolecular friction. Molecules are a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa, with a result that some tangential force is required to maintain uniform flow. This tangential force will depend upon two factors,

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

(ii) velocity gradient $\frac{dv}{dx}$

Thus, $f \propto A \frac{dv}{dx}$

or $f = \eta A \frac{dv}{dx}$ ....(2.33)

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

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

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

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

The C.G.S Unit of viscosity i.e. dynes sec $cm^{-2} = g\ cm^{-1}sec^{-1}$ is called poise, in honor of J.L.M. Poiseuille who is the pioneer in the study of viscosity. Since viscosity of liquid is usually very small, it is usually expressed in millpoise (mP) or centipoise (cP) or mPa.S.

When a liquid flows through a narrow tube it is probable that the thin layer of liquid in contact with the wall is stationary; as a result of viscosity, therefore, the next layer will be slowed down to some extent, and this effect will continue up to the centre of the tube where the flow rate is maximum.

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation (68). 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 (68):

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

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

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

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

The driving pressure P = hρg, where h is the difference in height of the surface of the two reservoirs, since the external pressure is the same at the surface of both reservoirs, g = acceleration due to gravity and ρ = the density of liquid. Thus the equation (2.35) becomes,

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

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

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

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

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

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

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

2.9 Viscosity and temperature

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

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

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

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

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

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

2.10 Viscosity of liquid mixtures

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

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

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

In liquid mixtures, there may be either a positive or a negative deviation in viscosity. The positive deviation from ideal behavior, i.e. higher viscosities than the calculated values indicate that constituents of mixtures 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,

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

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

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

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

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

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

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

2.12 Interaction parameter measurements, (ε)

Interaction parameter, ε for viscosity for all compositions of the mixtures at different temperatures have been calculated by using Grunberg-Nissan equation (69),

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

Where , ε = Interaction parameter.

$\eta_{expt.}$ = observed viscosity

η_{id} = calculated viscosity

$$=\exp(X_1 \ln \eta_1 + X_2 \ln \eta_2) \qquad \ldots\ldots(2.46)$$

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

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

2.13 Viscosity as a rate process

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

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

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

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

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

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

Eyring and his co-workers (70) using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, η as follows:

$$\eta = \frac{hN}{V_m} e^{\Delta G^{\#}/RT} \qquad \ldots\ldots(2.47)$$

Where, $\Delta G^{\#}$ is the free energy of activation per mole for viscous flow, V_m is the molar volume for pure liquids or solutions and h, N, R and T have their meanings. The values of change of free energy of activation ($\Delta G^{\#}$) can be calculated by using the Nightingle and Benck equation (71):

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

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

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

Enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution can be obtained with the help of Eyring equation (70):

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

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

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

Since,

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

The Eyring equation takes the form,

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

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

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

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

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

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

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

2.14 Different thermodynamic parameters

2.14.1 Free energy of activation ($\Delta G^{\#}$) for viscous flow

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

2.14.2 Enthalpy of activation ($\Delta H^{\#}$) for viscous flow

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

2.14.3 Entropy of activation ($\Delta S^{\#}$) for viscous flow

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

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 ($\Delta G^{\#E}$), excess enthalpy of activation ($\Delta H^{\#E}$), excess entropy of activation ($\Delta S^{\#E}$) for viscous flow of all compositions for a system were fitted by the least square method of the four coefficient Redlich-Kister equation :

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

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

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

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

Where, PROPE $_{\exp}$ = 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 of British standard institution form was used for measurement of viscosity. The inside wall of the viscometer was cleaned thoroughly with warm chromic acid so that there was no obstruction in the capillary and the liquid could run clearly without leaving any drop behind. It was then rinsed thoroughly with distilled water followed by rectified spirit and finally with acetone and dried.

3.2 Materials

The chemicals used for study were Methanol, Ethanol, n-Propannol, iso-Propanol, n-Butanol, iso-Butanol, tert-Butanol, n-Amyl alcohol, iso-Amyl alcohol, N.N'-Dimethylformamide, Sodium dodecyl sulphate (SDS). 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**
Methanol	CH_3OH	32.04	99.8%	MERCK Germany
Ethanol	C_2H_5OH	46.07	99%	MERCK Germany
n-Propanol	$CH_3CH_2CH_2OH$	60.10	99%	MERCK Germany
iso-Propanol	$(CH_3)_2CHOH$	60.10	99%	MERCK Germany
n-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	99.5%	Scharlau Chemie U.S.A.
iso-Butanol	$(CH_3)_2CHCH_2OH$	74.12	99.%	MERCK Germany
tert-Butanol	$(CH_3)_3COH$	74.12	99.5.%	BDH, England
n-Amyl alcohol	$C_5H_{11}OH$	88.15	99 %	BDH, England
iso-Amyl alcohol	$C_5H_{11}OH$	88.15	99.5%	MERCK Germany
DMF	C_3H_7NO	73.10	99.5%	Scharlau Chemie, U.S.A.

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 $\pm 0.0001\text{g}$ 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 $\pm 0.05^0\text{C}$. 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-DMF and ternary solution of alcohol-DMF-SDS 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 of solution was determined from the relation.

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

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

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

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

3.7 Apparent/ Partial molar volume measurements

The apparent molar volumes of the solution for binary and ternary systems were determined from density measurement using the following equation. (61,62):

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

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

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

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

where, M_1 and M_2 = the molecular weight of solute and solvent and also from molarity C,

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

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

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

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

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

Molar volume of solvent (pure water) at experimental temperature was calculated using the following equation (61).

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

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

$$\overline{V_2} = \varphi_v + \frac{\sqrt{m}}{2}\left(\frac{\delta\varphi_v}{\delta\sqrt{m}}\right) = \varphi^0{}_v + \frac{3\sqrt{m}}{2}\left(\frac{\delta\varphi_v}{\delta\sqrt{m}}\right) \qquad \text{..(3.6)}$$

Where, $\varphi^0{}_v$ = apparent molar volumes at zero concentration.

and $$\overline{V_1} = V_1^0 - \frac{M_1 m^{3/2}}{2000}\left(\frac{\delta\varphi_v}{\delta\sqrt{m}}\right) \qquad \text{..(3.7)}$$

The values of $\frac{\delta\varphi_v}{\delta\sqrt{m}}$ were obtained from the slope of the plot of φ_v against $\sqrt{C}$ by the use of Masson (65) equation and the apparent molar volume of solutes at infinite dilution ($\varphi_v^0 \approx \overline{V_2}^0$) were determined from the intercept of the plot, at C equal to zero.

3.8 Excess molar volume measurements

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

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

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

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

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

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

3.9 Viscosity measurements

Viscosity of water, SDS and several solutions 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 a 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,

$$\eta = A\rho t \qquad \text{...(3.10)}$$

where, $A = \frac{\eta_{H_2O}}{\rho_{H_2O}.t_{H_2O}}$

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.

3.10 Excess viscosity measurements

The excess viscosities, η^E were calculated using the following equation:

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

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

$$\ln \eta_{id} = X_1 \ln \eta_1 + X_2 \ln \eta_2 \qquad \text{...3.12}$$

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

$$\eta^E = X_1X_2 \sum_{i=0}^{n} \mathrm{a_i}(1\text{-}2X_1)^{\mathrm{i}} \qquad \text{...3.13}$$

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.

3.11 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 (69),

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

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.

3.12 Thermodynamic parametes

The change of free energy of activation ($\Delta G^{\#}$) was calculated by the help of Nightingle and Benck (71) equation:

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

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

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

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

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

T = Absolute temperature (K)

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

Energy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution were determined y using the Eyring equation (70):

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

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

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

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

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

$$\Delta H^{\#} = \text{slope} \times R \qquad (3.18)$$

and

$$\Delta S^{\#} = -\text{intercept} \times R \qquad (3.19)$$

The excess enthalpy of activation, $\Delta H^{\#}$, excess entropy of activation, $\Delta S^{\#}$ and excess free energy of activation, $\Delta G^{\#}$ has been calculated as-

$$\Delta H^{\#E} = \Delta H^{\#} - (X_1\Delta H_1^{\#} + X_2\Delta H_2^{\#}) \qquad (3.21)$$

$$\Delta S^{\#E} = \Delta S^{\#} - (X_1\,\Delta S_1^{\#} + X_2\Delta S_2^{\#}) \qquad (3.22)$$

and

$$\Delta G^{\#E} = \Delta G^{\#} - (X_1\Delta G_1^{\#} + X_2\Delta G_2^{\#}) \qquad (3.23)$$

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

3.13 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 ($\Delta G^{\#E}$), excess enthalpy of activation ($\Delta H^{\#E}$), excess entropy of activation ($\Delta S^{\#E}$) for viscous flow of all compositions for a system were fitted by the least square method of the four coefficient Redlich-Kister equation :

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

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

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

$$\mathrm{SD} = \left[\frac{\Sigma(PROP_{\exp}^{E} - PROP_{calcd}E)^2}{n-p-2}\right]^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.25)$$

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. Methanol + *N,N'*-Dimethylformamide (DMF)
2. Ethanol + DMF
3. *n*-Propanol + DMF
4. *iso*-Propanol + DMF
5. *n*-Butanol+ DMF
6. *iso*-Butanol+ DMF
7. *tert*-Butanol+ DMF
8. n-Amyl alcohol + DMF
9. iso-Amyl alcohol + DMF
10. Sodium Dodecyl Sulfate (SDS) + DMF
11. *n*-Propanol + SDS + DMF
12. *n*-Butanol+ SDS+ DMF
13. *n*-Amyl alchol+SDS+DMF

The above-mentioned systems were studied precisely at six equidistant temperatures ranging from 298.15K to 323.15K except Methanol at interval of 5K by volumetric and viscometric methods. Methanol system was studied at 298.15, 303.15 and 308.15K owing to its lower boiling point. The volumetric properties such as partial molar volume ($\overline{V}_2$), excess molar volume V^E are determined from density. Viscometric properties like excess viscosity (η^E), interaction parameter (ε) and thermodynamic properties like enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) of activation for viscous flow and their excess quantities, $\Delta H^{\#E}$, $\Delta S^{\#E}$ and $\Delta G^{\#E}$ 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 Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol in DMF systems were determined at temperatures ranging from 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K (except Methanol) with an interval of 5K over the entire composition range $0 < x_2 < 1$, where x_2 represents the mole fraction of Alkanols. Methanol system was studied at 298.15, 303.15 and 308.15K owing to its low boiling point. 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 4.2-4.10 at different temperatures. Figure 4.1- 4.9 shows the plots of densities as a function of mole fraction of Methanol, Ethanol and *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF systems. For Methanol, Ethanol, it shows continuous decrease in density with different temperature. In Methanol and Ethanol systems the decrease in density is found firstly slowly and beyond the 0.5 mole fraction it shows slight rapidly on addition of Alkanols. Rest of the systems, shows that density decrease linearly with concentration. Density value decreases with increase in the temperature.

The experimental density values in pure state of DMF, *iso*-Amyl alcohol , n-Amyl alcohol, Ethanol, *n*-Butanol, n-Propanol, *iso*-Butanol, Methanol, *tert*-Butanol, iso-Propanol at 303.15K are 0.939263 , 0.806953, 0.805203, 0.804509, 0.802915, 0.796323, 0.795634, 0.782764, 0.778467, 0.774467, g.cm^{-3}, respectively. As the densities of pure Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol are less than that of pure DMF, with the increase of concentration of alcohol the density of alcohol + DMF system decreases and eventually proceeds towards the density of pure alcohol.

The excess molar volume, V^E of Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF systems have been calculated from density data of these systems using equation 3.8. The values of V^E at different temperatures have been shown in Table 4.2-4.10. For V^E the fitting coefficients (a_i) are shown in Table 4.38-4.39 along with standard deviations. Figure 4.10- 4.18 shows the plots of excess molar volume as a function of mole fraction of Methanol, Ethanol, *n*-

Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF systems.

Examination of Figures 4.10- 4.18 reveals that

(i) For DMF + Methanol system (Fig. 4.10) the excess molar volumes V^E are negative throughout the whole range of composition with minima at ~ 0.6 mole fractions of Methanol. The effect of temperature on V^E shows a definite trend, i.e., the negative values increase with the decrease of temperature.

(ii) On addition of DMF to Ethanol (Fig. 4.11) the excess molar volumes V^E are negative with minima at ~ 0.2 -0.3 mole fraction of Ethanol. The values of V^E are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature it shows positive in Ethanol rich region.

(iii) For n-Propanol, the values of V^E are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature it shows positive in both DMF rich and n-Propanol rich region. The minima appear at ~ 0.1-0.2 mole fraction and maxima at ~0.8 mole fraction of n-Propanol.

(iv) For iso-Propanol, the values of V^E are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature (323.15K), it shows positive throughout the whole range of composition. The very broad minima appear at lower temperature and maxima appear at higher temperature.

(v) For *n*-Butanol, *iso*-Butanol and *tert*-Butanol, the values of V^E are very slightly negative at lower temperature (298.15K-303.15K), but at higher temperature (323.15K), it shows positive.

(vi) For n-Amyl alcohol and iso-Amyl alcohols, the values of V^E are negative throughout the whole range of composition. The minima appear at ~ 0.6-0.7 mole fraction of iso-Amyl alcohol.

Similar behavior was found by Saleh et al (72) in Alkanols + n-Heptane system, excess molar volume were small negative in the whole range of concentration, except at ~0.8-0.9 mole fraction of Alkanols for which the values are positive at higher temperatue.

Examination of the excess molar volume curves in the Figures of 4.10- 4.18 reveals the following characteristics:

a) The mixing of Methanol with DMF is accompanied by contractions of volume i.e V^E are slightly negative.
b) The mixing of Ethanol, n-Propanol and iso-Propanol with DMF is accompanied by contractions of volume at lower temperature but expansions of volume at higher temperature.
c) For *n*-Butanol, *iso*-Butanol and *tert*-Butanol, the mixing are associated with both contractions and expansions of volume.
d) For n-Amyl alcohol and iso-Amyl alcohols, the mixing shows contractions of volume throughout the whole range of composition.
e) n-Propanol, iso-Propanol, *n*-Butanol, and *iso*-Butanol systems showed extrema. Broad minima and broad maxima are observed.

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 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,
d) Favorable geometrical fitting of component molecules,

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 non-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,
g) Electrostatic repulsive forces.

DMF results from the replacement of aminic hydrogens of formamide by two $-CH_3$ groups. Therefore, no self-association of DMF through H-bonding is possible because of the absence of aminic hydrogen. The attachment of two $-CH_3$ groups at the nitrogen atom increases electron density on the nitrogen atom and carbonyl oxygen of the amide and consequently favors the possibility of H-bond formation with alcohol molecules by one or more of the following ways: (i)> C =O…HO, (ii) $(CH_3)_2N$…HO. At the same time the presence of two $-CH_3$ groups on the nitrogen atom of DMF creates a steric hindrance that prevents alcohol molecules from coming sufficiently close to it. On the other hand, alcohol molecules undergo self- and cross-association because of the presence of hydrogen bonds (73,74).

Mixing of DMF with an alcohol will induce changes in hydrogen bonding (in the alkanol) and dipolar interactions (in the DMF). On addition of alcohol to the pure DMF the self association will be disrupted partly or fully and new H-bonds between alcohol and DMF will be formed. At the same time, segmental inclusion of DMF into the vacant spaces left in the structural network of alcohol may also occur. The two factors may primarily be responsible for the resultant negative excess molar volume of the mixtures: DMF + Alkanols.

It is observed from Figs. of 4.10 that the system containing Methanol exhibits the highest negative V^E values and that the negative values generally decrease with an increase in chain length of alcohols. The chemical contraction through H-bonding and the size effect of Methanol is greatest considering all the alcohols. Therefore, volume contraction of DMF + Methanol is expected to be greater than the systems containing other alcohols. However, as the chain length of alcohols increases, the size effect consequently decreases. The negative contribution to V^E due to this effect is therefore expected to be in the order: DMF+Methanol > +Ethanol> +n-Propanol> +n-Butanol

Pikkarainen (75,76) studied the excess volume of binary solvent mixtures of N,N-diethylmethane sulfonamide with aliphatic alcohols. Garcia et al. (77) carried out volumetric and viscometric measurements on binary liquid mixtures of 2-pyrrolidone with 1-alkanols. Sandhu et al. (78) determined the excess molar volumes of 1-alkanols (C1– C5) binary mixtures with acetonitrile. Rauf et al. (79) determined the excess molar volumes of N,N-dimethylformamide + n-alkanols (C7–C9). The analysis of the previous works shows that the negative values of V^E decrease with the increase of the chain length of alkanol. The results of our present investigation of DMF + alkanols (C1–C5) binary mixtures were in conformity with the results of these reported investigations.

From Figs. 4.10 to 4.18, it is seen that the value of excess molar volumes increases with the rise of temperature. This may be accounted for in the following manner. It is known that pure alkanols can form either ring- or chain-like complexes, and while temperature increases, the degree of association decreases (80, 81) and hence excess molar volume increases.

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

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

(1) Dipole-dipole interaction between the unlike polar molecules and

(2) Geometric effect due to differences in molar volumes of the component molecules.

The negative V^E of the systems, a typical characteristic of hydrophobic solutes, lead to the conviction that the factors causing the volume contraction far outweigh the factor which is to responsible for volume expansion (84). Of the contractive factors, perhaps the hydrophobic interaction is by far the most effective one in volume reduction, as through this process the hydrophobic molecules occupy the spaces inside the so-called cages formed and thus ensure maximum economy 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 1.71D, 1.69D, 1.68D, 1.66 D, 1.66 D, 1.71 D, 1.70 D and 3.86D for Methanol, Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanlo, tert-Butanol and DMF, respectively. The μ of n-Amyl alcohol and iso-Amyl alcohol is not found in the literature.The value of dipole moment (μ) of DMF is higher than the rest of the studied alkanols. Therefore, it has the possibility of the formation of hydrogen bonding through the polar group of the Alkanols and DMF 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 higher alkanols that affects both hydrogen bonding and electron donar acceptor interaction are reported (83, 84). So, if the alkanols are relatively smaller in size and formed H-bonding or associated through strong dipole-dipole interactions between the components negative V^E values are generally expected. The experimental results of these mixtures are consistent with this observation.

The molar volumes of Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol and DMF at 298.15K are 40.70, 56.95, 74.96, 77.21, 91.80, 92.78, 94.63, 108.92, 109.55 and 77.57 cm^3 $mole^{-1}$ respectively. This shows that a quite large size difference between Methanol and DMF molecules. The Methanol molecules, being smaller there is possibility of partial accommodation of Methanol molecule in the interstices of the DMF molecules. Large and negative V^E value of DMF + Methanol mixtures may be attributed to the occupation of void spaces of one component by other i.e. the probability is high for the smaller Methanol molecules , either in segregated or monomeric forms to occupy the vacant spaces offered by the structural network of larger DMF molecules. In view of the present state of our knowledge about the structure and the related properties of DMF and Methanol, one can easily visualize that factors such as chemical contraction through hydrogen bonding between DMF and Methanol, the other forces such as strong dipole-dipole interaction and the size difference between DMF and Methanol, these factors are all the important causes for volume contraction. For these particular systems the factors causing volume expansion are of little or no significance. The contractive forces thus predominate far more than the expansive forces, if any. The overall effect for Methanol +DMF systems is thus contraction of volume.

The gradual contraction in volume on addition of Alkanols may be explained mainly by taking into account of formation of strong alcohol-DMF interactions due to H-bonds and by the hydrophobic interaction with overall economy of space. After attaining the minima further addition of alkanols associated forms of DMF and alkanols through H-bonding are dissociated resulting the gradual expansion in volume is occurred. The molar volume of DMF, Propanols and Butanols are quite similar, so there is less possibility of partial accommodation of DMF or alkanols in the interstices and hence V^E becomes less negative as has been observed in the present systems: more negative V^E has been observed with Methanol+ DMF systems than with Ethanol+ DMF and n-Propanol + DMF and n-Butanol + DMF systems. The size differences between DMF and Amyl alcohols are quite large so the possibility of partial accommodation of DMF in the interstices of Amyl alcohols is high and hence V^E becomes negative for Amyl alcohols. As the temperature increase (318.15 or more), positive V^E is obtained for Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol and iso-Butanol. Alkanols are thought to form multimers through self-association in the liquid phase via hydrogen bonding (85). For the increase of temperature, the dissociation of H-bonding or wearker the dipole-dipole interaction are occurred, so the dissociated species in the solution are increased and hence positive V^E are observed.

In the case of n-Amyl alcohol and iso-Amyl alcohol + DMF systems, the V^E becomes also slightly negative throughout the whole composition range. The strength of the intermolecular hydrogen bonding through in DMF and Alkanols, is not the only factor influencing the negative V^E of liquid mixtures, but the orientation of groups, hydrophobic interaction, molecular sizes and shapes of the components are also equally important. Here size differences may be played important role for providing negative V^E. Larger the branch or chain length of alkanols, the DMF structure around the hydrocarbon moieties of aliphatic alcohol is highly promoted leading to the formation of cages surrounding the alcohol molecules as a result more negative V^E is observed. Such results can also be seen in the work of Aminabhavi et al. (82) for methyl acetoacetate + Alkanols mixtures.

In highly alcohol rich region of alkanols, where smaller units of alkanols are believed to be reformed into larger units, negative V^E are observed for the alkanols at lower temperature. *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol shows such type of behavior at lower temperatue.

At higher temperature unfavorable packing may, however, result due to disruption of the closely associated DMF molecules on addition of alkanols and formation of new association between the unlike DMF 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 Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K (except Methanol) over the entire composition range are shown in Tables 4.11-4.19. Methanol system was studied at 298.15, 303.15 and 308.15K. The viscosities of the pure components are shown in Table 4.1 together with the literature values for Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol , 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 4.19-4.27. The following characteristic features of viscosity are observed:

a) The viscosities increase initially slowly up to ~0.6 mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohols and later on, the viscosity increases sharply until that of pure alcohol is reached specially at lower temperature.
b) For Methanol, viscosity decrease slowly on continued addition of Methanol.
c) At the alcohol rich region rapid change of viscosity are observed for Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohols but the change is pronounced for the branched alcohol systems (iso-Propanol, iso-Butanol, tert-Butanol, iso-Amyl alcohol) than the linear alcohol (Ethanol, n-Propanol, n-Butanol) systems.
d) Viscosity decreases with rise of temperature.

In pure state the viscosity of alcohols has been found to be in the order of,
tert-Butanol> n-Amyl alcohol> iso-Amyl alcohol>iso-Butanol>n-Butanol> iso-Propanol> n-Propanol> Ethanol> Methanol

The experimental viscosity values in pure state of DMF, Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol at 303.15K are 0.5108, 1.2060, 1.6951, 1.7639, 2.2458, 2.8400, 3.3071, 3.2290, 3.1289, mPa.S, respectively.

For dilute solutions in DMF it is believed that, alcohols which are known to exist in associated forms through H-bonding, are dissociated. This explains the low viscosity of the solutions in the DMF 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.

Viscosities of the isomeric alcohols as the function of temperature are represented in Figure 4.28.

There is a marked decrease in the viscosity with increase of temperature for all the isomeric studied alcohols. At 298.15K, viscosity is found to be in the order:

tert-Butanol> iso-Butanol>n-Butanol >iso-Propanol> n-Propanol, which however changes to

n-Butanol >iso-Butanol> tert-Butanol >n-Propanol> iso-Propanol at 323.15K.

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 298.15K (shown in Figure 4.29) , the order of viscosity becomes tert-Butanol> iso-Butanol> n-Butanol> iso-Propanol> n-Propanol, but is reversed at 323.15K. This change of order arises from the difference of temperature dependence of viscosity of isomers as can be seen in Figure 4.28. 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 (86,87) 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 (DMF), X_2 and η_2 are the corresponding values of component 2 (Alcohols).

The η^E values are shown in Table 4.11-4.19. 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 4.40-4.41. The variation of η^E against mole fraction of alcohol (x_2) is shown in Figure 4.30-4.38. The η^E values are found to be positive or negative, indicating that the DMF solutions of alcohols are non ideal. Figure shows the following features:

i) Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems except Methanol with minima occurring between 0.6-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol and *tert*-Butanol. n-Amyl alcohol and iso-Amyl alcohol show minima at 0.8-0.9 mole fraction.

ii) Excess viscosity of Methanol is positive at all the temperatures over the entire range of composition and show maxima in the DMF rich region at 0.2-0.4 mole fraction of Methanol.

iii) Excess viscosity of Ethanol is negative and show minima at 0.4-0.5 mole fraction of Ethanol.

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

v) An increase of temperature decreases the magnitude of negative excess viscosity. The order of the temperature dependence of negative excess viscosity is the same as in (vi).

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

tert-Butanol> n-Amyl alcohol> iso-Amyl alcohol~iso-Butanol>n-Butanol> iso-Propanol> n-Propanol> Ethanol

A fundamental difference in the behavior of excess viscosities observed is that the values are found to be positive for DMF + Methanol, whereas they are negative for systems consisting of DMF+ rest of the studied alcohol systems. The positive excess viscosities (as in Fig. 4.30) for the DMF + Methanol system indicate long range structural aggregates through H-bonding or dipole –dipole interaction and the negative excess viscosities (as in

Figs. 4.31-38 and Tables 4.12-4.19) for the systems DMF + rest of the studied alcohol systems indicate the dissociation of components through steric hindrance or dispersive forces.

In the case of Methanol, excess viscosity is positive at all the temperatures over the entire range of composition and show maxima in the DMF rich region at 0.2-0.4 mole fraction of Methanol. On addition of Methanol to DMF, the hydroxyl groups of Methanol may form hydrogen bonds with the surrounding DMF molecules.

The value of dipole moments (μ) of all alkanols are almost similar but the size of Methanol is quite smaller than other studied alcohols . The μ of DMF is much larger than alcohols. Therefore, hydrogen bonding is thought to be formed by the polar group of the Methanols and DMF due to the hydrophilic effect. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, but the dipole moment of Methanol and its size is noticeable than the other studied alcohols. As the long chain alcohols are more hydrophobic than short chain alcohols and their hydrophobicity decrease with increasing degree of unsaturation. Andini et al (88) showed that hydrophobic interaction varies according to hydrocarbon groups such as CH_3CH_2>CH_3> CH_2> CH.

Therefore, the large positive η^E of Methanol can be explained by hydrophilic effect only and it is possible the H-bond is playing a strong role here. According to hydrophilic effect, DMF and Methanol molecules form a long range structural aggregate around at the 0.2-0.3 mole fraction of Methanol. With a further increase in Methanol mole fraction, a composition is reached when Methanol molecules can not find enough DMF molecules to be surrounded. After attaining the state of maximum η^E further addition of alcohol continuously breaks down both the ordered structure and Methanol-DMF association, and instead, Methanol-Methanol association are inequitably formed, which result in the continual decrease in η^E.

The negative excess viscosities are showed Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, and *tert*-Butanol throughout the whole range of composition at lower temperatue (Figure 4.31-4.38). The figure also reveals that the systems having branched chain alkanols, iso-Propanol, iso-Butanol, and tert-Butanol show larger negative excess viscosity, η^E than their straight chain isomers. This is due to the strong steric hindrance for the bulky groups which are existing in the branched chain Alkanols. Ali et al (89), Akhtar et al (90) and Saleh et al (91) 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 (92) 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 DMF. As pointed out earlier, negative excess viscosity follow the order :
tert-Butanol> iso-Butanol>n-Butanol
iso-Propanol> n-Propanol
n-Amyl alcohol>n-Butanol> n-Propanol > Ethanol,
which in turn reflect the extent of dissociation mainly due to dispersion force. D' Aprano et al. (86) 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: three Butanols and two Propanols isomer either by thermal effect or by the force of dispersion in DMF should thus follow the order: tert-Butanol>iso-Butanol>n-Butanol ; and iso-Propanol> n-Propanol.

In the case of n-Amyl alcohol and iso –Amyl alcohol , the η^E should be follow the order: iso –Amyl alcohol >n-Amyl alcohol. But the η^E of n-Amyl alcohol +DMF is slightly higher than iso-Amyl alcohol +DMF. 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.

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 DMF and alcohols formed. In comparison with alcohol-DMF association, the DMF-DMF association in the structure is assumed to be more fragile to heat. Examination of excess viscosity curves of different alcohol solutions (Figure 4.31-4.38) shows that $\Delta\eta^{E}{}_{\min}$ varies in the order,

tert-Butanol (0.6 mPa.S)> *iso*-Butanol (0.3 mPa.S)> *n*-Butanol (0.29 mPa.S)
> *iso*-Propanol (0.28 mPa.S)> *n*-Propanol (0.16 mPa.S) >Ethanol (0.05 mPa.S)

The values, therefore, indicate the extent of the destruction of the structures by thermal effect. The structure formed by the DMF-DMF association around the alcohols through H-bond or dispersion force are also assumed to be thermally unstable than DMF-DMF association in pure DMF (93,94) that is similar to pure water. The thermal fragility of branched alcohols are higher than the linear chain alcohols.

4.2.1 Interaction parameter

The interaction parameters (ε) have been calculated by using the equation 3.14. The values of interaction parameters for different systems are shown in Figure 4.39-4.47 and the data are tabulated in Table 4.11-4.19. The values have been found to be negative and quite large in magnitude in alcohol-rich region for all the systems except Methanol. The ε values are decrease with the increase of temperature.

From the studies of ε and η^E values of a number of binary mixtures of different polar or non-polar liquids, Fort and Moore (95) 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 If $\varepsilon > 0$ and $\eta^E < 0$, then weak specific interaction would be present.

In Methanol both ε and η^E values are positive and large in magnitude. Therefore, the positve interaction parameters indicate that strong interactions between the components of the mixtures (95) are occurred. In Methanol, the interaction parameters increase with concentration, showing maxima at alcohol reach region. Rest 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 (95). The interaction parameters, ε decrease with alcohol concentration, showing minima at ~ 0.6-0.8 mole fraction of alcohol and then increase continuously. The position of minima virtually does not change remarkably with the variation of temperature. In the present investigation at 298.15K, the minima values of ε have been found to be -0.25 (at $x_2 = 0.6$), -1.3 (at $x_2 = 0.8$), -1.8 (at $x_2 = 0.8$), -1.5 (at $x_2 = 0.8$), -1.1 (at $x_2 = 0.7$), -1.6 (at $x_2 = 0.8$), -1.4 (at $x_2 = 0.8$), -1.2 (at $x_2 = 0.8$) for the DMF + Ethanol, DMF + *n*-Propanol, DMF + *iso*-Propanol and DMF + *n*-Butanol , DMF + *iso*-Butanol , DMF + *tert*-Butanol , DMF + n-Amyl alcohol , DMF + iso-Amyl alcohol mixtures, respectively. The height of the minima is higher in branched alcohol than those of linear chain alcohols with some exceptions. These observations accord with the view of Nigam and Mahl (96) that DMF + all the studied alcohols mixtures except Methanol have strong dispersion force and geometrical effect.The negative excess molar volume, negative η^E values suggest that the geometrical fitting of the molecules is more important than interactional factor for these systems.

The negative V^E , positive η^E, and positive ε for the DMF + Methanol system confirm well to the correlation stated above (97–99). This leads us to believe that the interaction is strong, namely formation of H-bonding between DMF and Methanol. The negative V^E , negative η^E, and negative ε for the DMF + Rest of the studied alcohols systems present an apparent discrepancy in the above correlation (97) but show agreement with the statements (98,99). If V^E is negative due to the segmental inclusion of DMF in the interstices of polymolecular alkanol aggregates, there will be fewer surfaces available for friction that may result in a reduction of viscosity. Some disruptive force causing volume expansion may be present, but it is more than compensated for by volume contraction through the segmental inclusion of DMF.

4.3 Thermodynamic properties

Free energy change ($\Delta G^{\#}$) of activation for the viscous flow of the Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K except Methanol over the entire composition range are shown in Tables 4.20-4.28. Methanol system was studied at 298.15, 303.15 and 308.15K. The variation of free energy ($\Delta G^{\#}$) at different temperatures as a function of the mole fraction of all the studied alcohols are shown in Figure 4.48-4.56. The following characteristic features of $\Delta G^{\#}$ are observed:

i) The change of free energy ($\Delta G^{\#}$) increase slowly up to ~ 0.6-0.8 mole fraction of alcohol concentration and then, the $\Delta G^{\#}$, increases moderately until that of pure alcohol is reached.

ii) For Methanol, $\Delta G^{\#}$ decrease slowly on addition of Methanol.

iii) In the DMF rich region (~ 0.0-0.6 mole fraction), the value of free energy $\Delta G^{\#}$ is smaller at lower temperature and larger at higher temperature but in the alcohol rich region it is vice versa.

The experimental $\Delta G^{\#}$ values in pure state of Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol at 303.15K are 10.01, 12.99, 14.54, 14.71, 15.76, 16.37, 16.81, 17.11, 17.02 kJ.mol^{-1}, respectively. The positive free energy change $\Delta G^{\#}$ for the studied alcohols +DMF 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.

Excess free energy ($\Delta G^{\#E}$) change of activation for the viscous flow of the Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol in DMF solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K except Methanol over the entire composition range are shown in Tables 4.20-4.28. Figure 4.57-4.65 represents the variation of $\Delta G^{\#E}$ of the systems against the mole fraction of the alcohols at 303.15K. The excess free energy ($\Delta G^{\#E}$) 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 4.42-4.43. The $\Delta G^{\#E}$ values are found to be positive or negative and large in magnitude, indicating that the DMF solutions of alcohols are non ideal. Figure shows the following features:

i) Excess free energies $\Delta G^{\#E}$ are negative at all the temperatures over the entire range of composition for all the systems except Methanol with minima occurring between 0.5-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohol.

ii) The $\Delta G^{\#E}$ of Methanol is positive in the both DMF rich region and in alcohol rich region.

iii) The $\Delta G^{\#E}$ of Ethanol is negative and show minima at 0.4-0.5 mole fraction of Ethanol.

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

v) An increase of temperature decreases the magnitude of negative excess $\Delta G^{\#}$.

vi) Variation of $\Delta G^{\#E}$ with composition for all the systems under investigation are more or less similar in nature, all being associated with minima or maxima.

vii) The effect of temperature on $\Delta G^{\#E}$ is seen to be significant, particularly in the region at or around the minima, through the positions of minima apparently remain almost unchanged with the variation of temperature.

The negative excess free energy, $\Delta G^{\#E}$ throughout the whole range of composition indicates the formation of smaller units of alkanols in different proportions or segmental inclusion of DMF in the interstices of alkanols depending upon the concentration of alkanols in solution systems. The figure also reveals that the systems having branched chain alkanols, iso-Butanol, iso-Propanol, iso-Amyl alcohol and tert-Butanol show larger negative excess viscosity, $\Delta G^{\#E}$ than their straight chain isomers. Branched chain alkanols are less strongly associated than n-alkanols through H-bonding because of steric hindrance and hence more easily dissociable into smaller units. Thus, the branched chain alkanols has the possibility of reduction of viscosity or viscous free energy from ideal values. The negative excess free energy, $\Delta G^{\#E}$ follows the order:

tert-Butanol> iso-Butanol>n-Butanol
iso-Amyl alcohol> n-Amyl alcohol >iso-Propanol> n-Propanol

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

In the case of Methanol, $\Delta G^{\#E}$ is positive in DMF rich region and show maxima in the DMF rich region and in the alcohol rich region. On addition of Methanol to DMF, the hydroxyl groups of Methanol form hydrogen bonds with the surrounding DMF molecules.

As suggested by the author (101), a large negative excess free energy, $\Delta G^{\#E}$ indicates the presence of dispersion force, whereas a large positive excess free energy, $\Delta G^{\#E}$ suggests a specific association between the molecules in the solvent mixture. The negative $\Delta G^{\#E}$ values in our studied systems except Methanol are also indicative of the dispersion force containg molecular interaction among the DMF and alcohol systems.

The difference in minima of $\Delta G^{\#E}$ over the temperature range ($\Delta\Delta G^{\#E}{}_{\min}$) of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol- DMF association, the DMF - DMF association in the cage structure is assumed to be more fragile to heat. Examination of $\Delta G^{\#}$ curves of different alcohol solutions shows that $\Delta\Delta G^{\#E}{}_{\min}$ varies in the order,

iso-Propanol (0.37 kJ $\mathrm{mol^{-1}}$) > *n*-Propanol (0.16 kJ $\mathrm{mol^{-1}}$)

tert-Butanol (0.55 kJ $\mathrm{mol^{-1}}$) > iso-Butanol (0.38 kJ $\mathrm{mol^{-1}}$)>n-Butanol (0.18 kJ $\mathrm{mol^{-1}}$)

n-Amyl alcohol (0.20 kJ $\mathrm{mol^{-1}}$) > iso-Amyl alcohol (0.15 kJ $\mathrm{mol^{-1}}$).

The values, therefore, indicate the extent of the destruction of the cages structures by thermal effect which, in turn, reflects the extent of cage formation. Therefore, the effect of temperature on $\Delta G^{\#E}$, particularly in the region at or around the minima is significant (Table 4.21-4.28). 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 DMF structure (102, 103) i.e The cages formed by the DMF - DMF association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than DMF - DMF association in pure DMF.

Table 4.29-4.37 lists enthalpy $\Delta H^{\#}$, entropy $\Delta S^{\#}$, excess enthalpy $\Delta H^{\#E}$ and excess entropy $\Delta S^{\#E}$ values for the studied system for different molar ratios. Figure 4.66 - 4.69 shows the plots of $\Delta H^{\#}$, $\Delta S^{\#}$ and its excess values as a mole fraction of alcohols, respectively. The $\Delta H^{\#}$ curves show that, on addition of alcohols to DMF, $\Delta H^{\#}$ rise up regularly except Methanol. For Methanol, $\Delta H^{\#}$ is almost unchanged with the mole fraction of alcohols.

Figure 4.67 shows the variation of entropy of activation for viscous flow, $\Delta S^{\#}$ against mole fraction of Alkanols. The entropies of the systems increase almost linearly and at similar rate up to about 0.6 mole fraction of the Alkanols. Beyond this concentration, the system of all studied alkanols follows the linear trend, while Methanol, Ethanol and n-Propanol show little divergences. Except t-Butanol, all studied alcohols show negative entropy change, however for branched alkanols at alkanol rich region the change of entropy is pronounced.

The excess entropies, $\Delta S^{\#E}$ of the systems are plotted as the function of mole fraction of Alkanols in Figure 4.69.The value of Methanol +DMF is slightly positive and show broad maxima at alkanol rich region. For Ethanol, n-Propanol and n-Butanol, excess entropies are negative in the whole range of composition except at ~0.9 mole fraction of alkanols the values are slightly positive. Unlike Methanol, Ethanol, n-Propanol and n-Butanol, all the other studied alkanols +DMF systems show large negative $\Delta S^{\#E}$ with distinct minima. Also the values are more negative for the branched alkanols than the linear system in the whole range of composition. Saleh et al (72) found that n-Pentanol + n-Heptane system, excess entropies were negative in the whole range of concentration, except at 0.9 mole fraction of n-Pentanol for which the values are slightly positive.

On examination of curves for $\Delta S^{\#}$ and $\Delta S^{\#E}$ versus composition (Figure 4.67 and 4.69) , it is evident that the systems with larger values of $\Delta S^{\#}$ show smaller values of $\Delta S^{\#E}$. $\Delta S^{\#}$ measure the randomness or disorderness of the system. $\Delta S^{\#}$ values are negative all the studied alcohol systems except t-Butanol. The positive $\Delta S^{\#}$ apparently indicates more random orientation of the complexes formed in the activated state. 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 DMF are supposed to have lesser interactions among themselves. In this state the complexes themselves can reorient in the flow process, and thereby, reduce their motional degrees of freedom. This brings about relative decrease in the randomness of overall structures of the activated complex, and hence smaller entropy values. The net result, is, therefore, the negative excess entropy of the systems, which explains qualitatively the entropy-excess entropy correlation of the systems. This also attribute that the structural factor dominates over the interacional one, as in the case of the mixing properties.

In order to explain $\Delta H^{\#}$ and $\Delta H^{\#E}$ (Figure 4.66 - 4.68) behavior similar to $\Delta G^{\#}$ and $\Delta G^{\#E}$ hydrophobic interaction, structural effect and hydrophilic interaction may be considered as the major cause in which it is assumed that both alcohols and DMF molecules are encaged by a network of highly structured form in pure state. Recent studies on viscometric properties by Kipkemboi and Easteal (104), Saleh et al. (72), and FTIR spectrophotometric studies by Gojlo et al (105) of some alcohols indicated that the alcohols are hydrophobic in nature. The bulkier species so formed by hydrophobic interaction may be supposed to use large energy for their passage to activated state and hence the large positive $\Delta H^{\#}$. An investigation of the $\Delta H^{\#}$ values of alcohols indicate that the $\Delta H^{\#}$ of t-Butanol is higher than that of studied other alcohol systems. It might be due to the structure of branched alkanols in DMF, is much bulkier and more rigid than that of Methanol, Ethanol or n-Propanol or n-Butanol requiring greater energy during the viscous flow. The $\Delta H^{\#}$ 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. That is, the viscous flow is not thermodynamically favored for the systems studied. All these concepts can equally be applied to explain the positive values of free energy and enthalpy functions in the DMF systems (72).

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

4.4 Ternary systems:

The effect of addition of surfactant, Sodium Dodecyl sulfate (SDS) in DMF systems has also been studied. The highest solubility of SDS in DMF is 0.04M. The densities and viscosities vs. concentration of DMF solution of SDS are plotted in Figure 4.70-4.71 and the data is presented in Table 4.44. The viscosities increase with increasing SDS concentration and then decreases and eventually increases again. The minima of viscosity may express the CMC at 0.02M of SDS solutions. The density data also shows a break point at 0.02M SDS. This SDS concentration (0.02M) in DMF was used for the determination of volumetric, viscometric and thermodynamic measurements for *n*-Propanol, *n*-Butanol and n-Amyl alcohol. Rests of the studied alcohols are less soluble in SDS containing DMF systems except Methanol.

The densities of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in DMF + 0.02M SDS systems have been shown in Table 4.45-4.47 at different temperatures. Figure 4.72- 4.74 shows the plots of densities as a function of mole fraction of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in DMF + 0.02M SDS systems. The density decreases linearly with the mole fraction of alkanols. Density value decreases with increase in the temperature. From these Figures, it is seen that the basic pattern of density behavior of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS + DMF solution is very similar to Alkanols + DMF systems. In SDS systems, density increases in comparison to corresponding systems without SDS. The density of alcohol in DMF and SDS systems has been found to be in the order of,

Alcohol - 0.02M SDS +DMF > Alcohol - DMF

The values of Excess molar volume, V^E for the systems of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS + DMF solution systems are given in the Tables 4.45-4.47. The plots of V^E of alcohol and SDS+DMF mixture systems against mole fraction of alcohols are shown in Figures 4.75-4.77, respectively. The lines are generated by the polynomial equation 3.9. For V^E the fitting coefficients (a_i) are shown in Table 4.57 along with standard deviations.

Examination of Figs. 4.75-4.77 reveals that

i) For *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS + DMF solution, the values of V^E are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature it shows positive in both 0.02M SDS containing DMF rich and alkanols rich region.

ii) The effect of temperatue on V^E shows a definite trend i.e. the negative values increase with the decrease of temperatue.

The values of viscosity at different temperatures have been shown in Table 4.48-4.50. Figures 4.78-4.80 show the plots of viscosities as a function of mole fraction of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS containing DMF solutions. From these Figures, it is seen that the basic pattern of viscosity behavior of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS is very similar to pure DMF systems. In the presence of SDS solution the viscosity of solution increases with the mole fraction of Alcohols similarly of DMF systems. In SDS systems, viscosity increases slightly in comparison to corresponding systems without SDS. This indicate that the SDS solution may be reorganized the alcohol and DMF structure again so that the viscosity increasing are observed. The viscosity of alcohol in DMF and SDS systems has been found to be in the order of,

Alcohol - 0.02M SDS +DMF > Alcohol – DMF

The variation of viscosities at these temperatures as a function of the mole fraction of the alcohols is shown in Figures 4.78 and 4.80. The following characteristic features of viscosity are observed:

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

ii) The viscosities of alcohols in SDS containing DMF systems are higher than pure DMF systems.

iii) Viscosity decreases with rise of temperature.

In SDS -DMF state the viscosity of alcohols at 0.5 mole fraction has been found to be in the order of,

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

The values of Excess viscosity, η^E for the systems of *n*-Propanol, *n*-Butanol and n-Amyl alcohol in 0.02M SDS in DMF systems are given in the Tables 4.48-4.50. The plots of η^E of alcohol + SDS in DMF systems against mole fraction of alcohols are shown in Figures 4.83-4.85, respectively. The lines are generated by the polynomial equation 3.13. For η^E the fitting coefficients (a_i) are shown in Table 4.58 along with standard deviations. The η^E values are found to be negative and large in magnitude, indicating that the DMF in SDS solutions of alcohols are also non ideal. All the curves pass through minima in DMF SDS-rich region. Figure shows the following features:

i) Excess viscosities are negative at all the temperatures over the entire range of composition for all the ternary systems with minima occurring between 0.6-0.8 mole fraction of Alkanols.

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

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

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

In the present investigation at 298.15K, the minima values of η^E have been found to be -0.34 (at $x_2 = 0.75$), -0.56 (at $x_2 = 0.8$) for the 0.02M SDS -DMF + n-Propanol, 0.02M SDS -DMF + n-Butanol, 0.02M SDS -DMF + n-Amyl alcohol mixtures, respectively. The heights of the minima are in the order has been found to be slightly higher than pure DMF systems

From these Figures 4.86-4.88, it is seen that the basic pattern of interaction parameter behavior of n-Propanol, n-Butanol and n-Amyl alcohol in 0.02M SDS containing DMF is very similar to Alcohols + DMF systems. But it is seen that there is no appreciable change of ε after adding SDS to the systems observed.

The effect of addition of surfactant, SDS containing DMF to alcohol systems has also been studied for free energy ($\Delta G^{\#}$) change. The values of viscous free energy ($\Delta G^{\#}$) at different temperatures have been shown in Table 4.51-4.53. Figures 4.90-4.92 show the plots of

($\Delta G^{\#}$) as a function of mole fraction of n-Propanol, n-Butanol and n-Amyl alcohol in 0.02M SDS containing DMF solutions.

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

i) The change of free energy ($\Delta G^{\#}$) increase slowly up to ~ 0.6-0.8 mole fraction of alcohol concentration and then, the $\Delta G^{\#}$, increases moderately until that of pure alcohol is reached.

ii) In the DMF rich region (~ 0.0-0.6 mole fraction), the value of free energy $\Delta G^{\#}$ is smaller at lower temperature and larger at higher temperature but in the alcohol rich region it is vice versa.

From these Figures, it is seen that the basic pattern of ($\Delta G^{\#}$) behavior of n-Propanol, n-Butanol and n-Amyl alcohol in 0.02M SDS is very similar to pure DMF systems. In SDS systems, $\Delta G^{\#}$ increases in comparison to corresponding systems without SDS. This indicates that the SDS solution are reorganized the alcohol structure again so that the $\Delta G^{\#}$ increasing are observed. The $\Delta G^{\#}$ of alcohol in DMF and SDS systems has been found to be in the order of,

Alcohol - 0.02M SDS +DMF > Alcohol – DMF

Excess free energy ($\Delta G^{\#E}$) change of activation for the viscous flow of the n-Propanol, n-Butanol and n-Amyl alcohol in 0.02M SDS containing DMF solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.51-4.53. The plots of ($\Delta G^{\#E}$) of alcohol + SDS containing DMF systems against mole fraction of alcohols are shown in Figures 4.93-4.95, respectively. The excess free energy ($\Delta G^{\#E}$) 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 4.59. The $\Delta G^{\#E}$ values are found to be positive or negative and large in magnitude, indicating that the SDS containing DMF solutions of alcohols are non ideal. Figure shows the following features:

i) Excess free energies $\Delta G^{\#E}$ are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.5-0.8 mole fraction of n-Propanol, n-Butanol and n-Amyl alcohol.

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

iii) Variation of $\Delta G^{\#E}$ with composition for all the systems under investigation are more or less similar in nature, all being associated with minima or maxima.

Table 4.54-4.56 lists enthalpy $\Delta H^{\#}$, entropy $\Delta S^{\#}$, excess enthalpy $\Delta H^{\#E}$ and excess entropy $\Delta S^{\#E}$ values for the studied system for different molar ratios. The plots of enthalpy $\Delta H^{\#}$, entropy $\Delta S^{\#}$, excess enthalpy $\Delta H^{\#E}$ and excess entropy $\Delta S^{\#E}$ of alcohols + SDS containing DMF systems against mole fraction of alcohols are shown in Figures 4.95-4.97.On addition of alcohols to SDS containing DMF, $\Delta H^{\#}$ rise up regularly. For Ethanol, $\Delta H^{\#}$ is almost unchanged with the mole fraction of alcohols. As it is found that $\Delta H^{\#}$ values are quite large in magnitude for all the alkanols, and vary as,

n-Amyl alcohol >n-Butanol> n-Propanol > Ethanol, indicating that the order is related to the chain length of alkanols. This seems to be generally true for other alkanols as revealed by different studies notably by the works of D'Aprano et al (86).

Figure 4.96 shows the variation of entropy of activation for viscous flow, $\Delta S^{\#}$ against mole fraction of Alkanols. The entropies of the systems increase with the mole fraction of the Alkanols except Ethanol.

The excess entropies, $\Delta S^{\#E}$ of the systems are plotted as the function of mole fraction of Alkanols in Figure 4.98. For n-Propanol, n-Butanol and n-Amyl alcohol, excess entropies are negative in the whole range of composition. n-Propanol and n-Butanol show large negative $\Delta S^{\#E}$ with distinct minima at 0.6-0.8 mole fraction of alkanols.

On examination of curves for $\Delta S^{\#}$ and $\Delta S^{\#E}$ versus composition (Figure 4.96 and 4.98) , it is evident that the systems with larger values of $\Delta S^{\#}$ show smaller values of $\Delta S^{\#E}$. $\Delta S^{\#}$ measure the randomness or disorderness of the system. $\Delta S^{\#}$ values are negative all the studied alcohol systems. The negative $\Delta S^{\#}$ apparently indicates more ordered orientation of the complexes formed in the activated state. In this state the complexes themselves can reorient in the flow process, and thereby, reduce their motional degrees of freedom. This brings about relative decrease in the randomness of overall structures of the activated complex, and hence negative entropy values. This also attribute that the SDS containing DMF is more structural than without SDS.

In order to explain $\Delta H^{\#}$ and $\Delta H^{\#E}$ behavior similar to $\Delta G^{\#}$ and $\Delta G^{\#E}$ hydrophobic interaction, structural effect and hydrophilic interaction may be considered as the major cause in which it is assumed that both alcohols and SDS containing DMF molecules are encaged by a network of highly structured form in pure state. 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 $\Delta H^{\#}$. The $\Delta H^{\#}$ values are positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. All these concepts can equally be applied to explain the positive values of free energy and enthalpy functions in the SDS containing DMF systems.

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}
Methanol	298.15	0.787200(106)	0.787323	0.553 0(111)	0.5523
	303.15	0.782420(107)	0.782764	0.5100(112)	0.5108
	308.15	0.777100(108)	0.777426	0.4837(113)	0.4902
	313.15	0.772500(109)	0.772540	0.4542(113)	0.4577
	318.15	0.769285(110)	0.766700	0.4256(113)	0.4280
	323.15	0.762800(109)	0.758600	0.4000(111)	0.4055
Ethanol	298.15	0.801900(114)	0.808867	1.1000(111)	1.1355
	303.15	0.798255(110)	0.804509	1.1908(113)	1.2060
	308.15	0.794517(110)	0.799029	1.0738(113)	1.0871
	313.15	0.780157(110)	0.793200	0.9646(113)	0.9655
	318.15	0.785760(115)	0.788300	0.8714(113)	0.8708
	323.15	0.771336(110)	0.783558	0.8010(113)	0.7952
n-Propanol	298.15	0.799692(116)	0.800501	1.9340(117)	1.9233
	303.15	0.795840(107)	0.796323	1.6826(107)	1.6951
	308.15	0.797499(110)	0.791910	1.5422(113)	1.5234
	313.15	0.787500(109)	0.787892	1.3200(111)	1.3430
	318.15	0.789183(110)	0.782407	1.2140(113)	1.2060
	323.15	0.778500(109)	0.779224	1.0891(113)	1.0690
iso-Propanol	298.15	0.780000(118)	0.778306	2.0360(121)	2.0257
	303.15	0.777100(119)	0.774467	1.7732(122)	1.7639
	308.15	0.772460(120)	0.771190	1.5320(120)	1.5220
	313.15		0.766972		1.3179
	318.15		0.762585		1.1516
	323.15		0.758129		1.0075
n-Butanol	298.15	0.80234 (123)	0.798876	2.600 (127)	2.5965
	303.15	0.80203(124)	0.802914	2.257(128)	2.2458
	308.15	0.79959 (125)	0.797100		1.9898
	313.15	0.79432 (126)	0.791728	1.75656(129)	1.7463
	318.15		0.787800		1.5454
	323.15	0.773559(125)	0.782337		1.3639
iso-Butanol	298.15	0.80234(123)	0.798876	3.274(128)	3.2929
	303.15	0.7943(130)	0.795634	2.842(131)	2.8400
	308.15	0.79026 (131)	0.791921	2.379(133)	2.3988
	313.15	0.78613(131)	0.787821	2.080(131)	2.0534
	318.15	0.78220(132)	0.783464	1.722(133)	1.7702
	323.15	0.77793 (133)	0.777979	1.502(133)	1.5330
tert-Butanol	298.15	0.781626(134)	0.783219	4.2719(135)	4.2357
	303.15		0.778467		3.3071
	308.15	0.76975(131)	0.773783	2.609(131)	2.6277
	313.15	0.76507(133)	0.768484	2.142(133)	2.1027
	318.15	0.75967(133)	0.762976	1.736(133)	1.7123
	323.15	0.75419(133)	0.757378	1.409(135)	1.4165

Component	Temperature (K)	Density (g.cm^{-3})		Viscosity (mPa.s)	
		ρ_{lit}	ρ_{exp}	ρ_{lit}	ρ_{exp}
n-Amyl alcohol	298.15	0.8110(136)	0.809300	3.510(138)	3.7352
	303.15	0.8105(137)	0.805203	3.121(139)	3.2290
	308.15	0.8071(137)	0.801484		2.7723
	313.15	0.8036(137)	0.796924		2.3876
	318.15	0.8001(137)	0.791358		2.0568
	323.15	0.7966(137)	0.786230		1.7865
iso-Amyl alcohol	298.15	0.8046(137)	0.809766		3.6140
	303.15	0.8032(140)	0.806953	3.1111(140)	3.1289
	308.15	0.7971(137)	0.802770		2.6860
	313.15	0.7964(141)	0.797268	2.4409(141)	2.3112
	318.15	0.7895(137)	0.792871		2.0149
	323.15	0.7898(141)	0.788113	1.8396(141)	1.7610
DMF	298.15	0.942915	0.942291	0.803(142)	0.7932
	303.15	0.9398(142)	0.939263	0.756(142)	0.7547
	308.15	0.9344(143)	0.934500	0.710(142)	0.7091
	313.15	0.9298(144)	0.929810	0.6683(143)	0.6675
	318.15	0.9251(143)	0.925000		0.6315
	323.15	0.9204(143)	0.920069	0.6004(143)	0.5975

Table-4.2: Density (ρ) and Excess molar volume (V^E) of Methanol +DMF system at 298.15K, 303.15K, 308.15K respectively

X_2	298.15K		303.15K		308.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000
0.1000	0.937627	-0.3049	0.933801	-0.2522	0.928600	-0.2235
0.1983	0.929213	-0.3569	0.925079	-0.2921	0.920000	-0.2781
0.3009	0.919865	-0.4422	0.915821	-0.3968	0.910847	-0.3964
0.3989	0.909515	-0.5004	0.905535	-0.4713	0.899698	-0.4154
0.5001	0.897284	-0.5489	0.893432	-0.5399	0.887693	-0.4983
0.5992	0.883223	-0.5682	0.878662	-0.5255	0.872426	-0.4583
0.7009	0.864800	-0.4762	0.860000	-0.4311	0.854430	-0.4108
0.8002	0.843619	-0.3602	0.839670	-0.3754	0.833199	-0.3074
0.8997	0.818947	-0.2412	0.814478	-0.2373	0.808890	-0.2233
1.0000	0.787323	0.0000	0.782764	0.0000	0.777425	0.0000

Table-4.3: Density (ρ) and Excess molar volume (V^E) of DMF-Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.0994	0.935800	-0.2833	0.932019	-0.2340	0.926741	-0.2000	0.921653	-0.1685	0.916611	-0.1530	0.911362	-0.1360
0.1997	0.927000	-0.4253	0.922338	-0.3180	0.916700	-0.2624	0.911469	-0.2200	0.906168	-0.1860	0.900620	-0.1530
0.3060	0.915281	-0.4375	0.910454	-0.3300	0.904491	-0.2560	0.899304	-0.2170	0.894007	-0.1860	0.888453	-0.1620
0.4009	0.903600	-0.4038	0.898821	-0.3110	0.892800	-0.2389	0.887531	-0.1930	0.882247	-0.1650	0.876582	-0.1400
0.5010	0.890600	-0.3719	0.885524	-0.2680	0.879539	-0.2050	0.874469	-0.1740	0.869212	-0.1500	0.863402	-0.1220
0.6015	0.876900	-0.3526	0.871884	-0.2650	0.865800	-0.2011	0.860400	-0.1440	0.855000	-0.1105	0.848867	-0.0651
0.7002	0.862608	-0.3361	0.857403	-0.2460	0.851200	-0.1794	0.845674	-0.1120	0.840000	-0.0589	0.833800	-0.0162
0.8006	0.846300	-0.2623	0.841400	-0.2051	0.834500	-0.0929	0.829232	-0.0430	0.823703	-0.0020	0.817335	0.0460
0.8996	0.828293	-0.1297	0.822908	-0.0470	0.816707	0.0100	0.811100	0.0876	0.806200	0.0817	0.800212	0.0940
1.0000	0.808867	0.0000	0.804509	0.0000	0.799029	0.0000	0.794500	0.0000	0.789500	0.0000	0.783558	0.0000

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

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.1006	0.931332	-0.2400	0.927406	-0.1782	0.922313	-0.1498	0.917281	-0.1166	0.912519	-0.1296	0.907378	-0.0964
0.2007	0.917435	-0.2406	0.913422	-0.1820	0.908051	-0.1270	0.902909	-0.0780	0.897563	-0.0470	0.892900	-0.0384
0.3001	0.903412	-0.2298	0.899114	-0.1570	0.893612	-0.0870	0.888548	-0.0380	0.883031	0.0020	0.878470	0.0182
0.3987	0.889433	-0.2207	0.884991	-0.1450	0.879181	-0.0440	0.874161	0.0080	0.868683	0.0390	0.863945	0.0880
0.5015	0.874863	-0.2197	0.870099	-0.1253	0.864563	-0.0440	0.859521	0.0170	0.853910	0.0540	0.849558	0.0850
0.5988	0.859804	-0.2205	0.855100	-0.1420	0.849750	-0.0740	0.845000	-0.0332	0.839267	0.0080	0.835027	0.0450
0.7002	0.845727	-0.1556	0.841465	-0.1232	0.835886	-0.0290	0.831257	0.0080	0.825660	0.0330	0.821294	0.0983
0.8008	0.830431	-0.0853	0.826154	-0.0597	0.820718	0.0270	0.816086	0.0720	0.810477	0.0940	0.806200	0.1687
0.8961	0.816725	-0.0971	0.812355	-0.0714	0.806500	0.0596	0.802400	0.0611	0.796725	0.0850	0.793300	0.0928
1.0000	0.800501	0.0000	0.796323	0.0000	0.791910	0.0000	0.787892	0.0000	0.782407	0.0000	0.779224	0.0000

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

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.0987	0.928880	-0.2260	0.924960	-0.1614	0.919294	-0.0730	0.913100	0.0590	0.907900	0.0965	0.902100	0.1776
0.1996	0.913003	-0.2820	0.908666	-0.1900	0.903307	-0.1130	0.897300	0.0081	0.891600	0.0932	0.885330	0.2218
0.3002	0.896776	-0.3070	0.892430	-0.2211	0.886800	-0.1054	0.881083	-0.0040	0.875200	0.1025	0.869000	0.2311
0.4006	0.881237	-0.3140	0.876172	-0.1720	0.870786	-0.0633	0.865330	0.0200	0.859789	0.1000	0.853600	0.2326
0.5008	0.863700	-0.2995	0.858665	-0.1640	0.853184	-0.0290	0.847412	0.0910	0.842100	0.1568	0.836400	0.2523
0.6006	0.847269	-0.3000	0.842353	-0.1800	0.836842	-0.0260	0.830867	0.1200	0.825800	0.1681	0.820000	0.2800
0.7003	0.830792	-0.2960	0.825818	-0.1750	0.820347	-0.0080	0.814599	0.1240	0.809097	0.2200	0.804103	0.2600
0.7996	0.813870	-0.2450	0.809028	-0.1400	0.804200	-0.0178	0.798510	0.1160	0.793523	0.1670	0.788400	0.2252
0.9012	0.796478	-0.1845	0.792098	-0.1280	0.788088	-0.070	0.783100	0.0008	0.777800	0.0882	0.772600	0.1601
1.0000	0.778306	0.0000	0.774467	0.0000	0.771190	0.0000	0.766972	0.0000	0.762585	0.0000	0.758129	0.0000

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

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.1009	0.928278	-0.1530	0.924727	-0.1270	0.919135	-0.0700	0.914691	-0.1014	0.909541	-0.0630	0.904226	-0.0370
0.1990	0.912343	-0.0610	0.908627	-0.0353	0.902900	0.0245	0.898000	0.0259	0.893400	0.0259	0.887709	0.0820
0.2982	0.898266	-0.1000	0.894258	-0.0630	0.888852	-0.0430	0.883598	-0.0170	0.878800	0.0104	0.873100	0.0626
0.4008	0.883799	-0.1030	0.879626	-0.0650	0.874035	-0.0380	0.868795	-0.0200	0.864147	0.0030	0.858287	0.0666
0.4999	0.870525	-0.1280	0.866316	-0.1000	0.860664	-0.0770	0.855168	-0.0400	0.850500	-0.0054	0.844687	0.0500
0.5997	0.857489	-0.1430	0.853123	-0.1124	0.847287	-0.0800	0.841808	-0.0500	0.837213	-0.0130	0.831270	0.0530
0.7003	0.844683	-0.1490	0.840174	-0.1160	0.834225	-0.0800	0.828727	-0.0530	0.824200	-0.0132	0.818500	0.0234
0.7989	0.832364	-0.1370	0.827776	-0.1070	0.821997	-0.0970	0.816600	-0.0860	0.812212	-0.0522	0.806635	-0.0330
0.9006	0.819371	-0.0485	0.815184	-0.0737	0.809500	-0.0821	0.804200	-0.0869	0.799700	-0.0300	0.794227	-0.0260
1.0000	0.807425	0.0000	0.802915	0.0000	0.797100	0.0000	0.791729	0.0000	0.787800	0.0000	0.782338	0.0000

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

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.1009	0.931371	-0.5140	0.927947	-0.4870	0.922780	-0.4460	0.917692	-0.4100	0.912676	-0.3920	0.907246	-0.3600
0.1997	0.914809	-0.4830	0.911356	-0.4550	0.906547	-0.4330	0.901700	-0.4113	0.896429	-0.3650	0.890146	-0.2600
0.3003	0.897284	-0.3330	0.893978	-0.3190	0.889119	-0.2790	0.884199	-0.2420	0.879125	-0.2060	0.873272	-0.1430
0.4005	0.881483	-0.2740	0.877743	-0.2200	0.872868	-0.1650	0.868160	-0.1400	0.863047	-0.0930	0.857470	-0.0600
0.4995	0.866727	-0.2429	0.862837	-0.1740	0.858192	-0.1290	0.853626	-0.1110	0.848539	-0.0600	0.842815	-0.0160
0.5995	0.852616	-0.2380	0.848837	-0.1800	0.844512	-0.1560	0.839836	-0.1200	0.834840	-0.0721	0.829134	-0.0340
0.7006	0.839100	-0.2596	0.835497	-0.2200	0.831152	-0.1830	0.826542	-0.1470	0.821584	-0.0970	0.815456	-0.0160
0.7998	0.826516	-0.3060	0.822520	-0.2240	0.818451	-0.2060	0.813823	-0.1610	0.808639	-0.0790	0.803040	-0.0600
0.8996	0.813792	-0.3000	0.809669	-0.2020	0.805573	-0.1700	0.801172	-0.1430	0.796390	-0.1000	0.790482	-0.0480
1.0000	0.798876	0.0000	0.795634	0.0000	0.791921	0.0000	0.787821	0.0000	0.783464	0.0000	0.777979	0.0000

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

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.0997	0.924712	-0.1160	0.920830	-0.0650	0.916053	-0.0650	0.910741	-0.0200	0.905329	0.0230	0.899655	0.0800
0.2017	0.907580	-0.2470	0.903295	-0.1800	0.897743	-0.1110	0.892114	-0.0440	0.886356	0.0230	0.880544	0.0860
0.2995	0.890716	-0.2740	0.886111	-0.1940	0.880505	-0.1170	0.874815	-0.0490	0.868944	0.0230	0.862981	0.0950
0.3990	0.873439	-0.2250	0.869042	-0.180	0.863718	-0.1270	0.857995	-0.0600	0.851993	0.0200	0.845953	0.0950
0.5004	0.856485	-0.1680	0.852073	-0.1370	0.846647	-0.0700	0.841059	-0.0200	0.835327	0.0280	0.829463	0.0800
0.6010	0.840735	-0.1519	0.836177	-0.1210	0.830892	-0.0650	0.825686	-0.0600	0.819977	-0.0200	0.813663	0.0770
0.7004	0.826256	-0.1884	0.821401	-0.1400	0.816201	-0.0900	0.810770	-0.0650	0.805004	-0.0230	0.799114	0.0230
0.8011	0.812363	-0.2520	0.807477	-0.2138	0.802197	-0.1520	0.796770	-0.1320	0.791183	-0.1160	0.785170	-0.0600
0.9001	0.797996	-0.1759	0.793263	-0.1675	0.788372	-0.1470	0.782827	-0.1160	0.777209	-0.1000	0.771308	-0.0600
1.0000	0.783219	0.0000	0.778467	0.0000	0.773783	0.0000	0.768484	0.0000	0.762976	0.0000	0.757378	0.0000

Table-4.9: Density (ρ) and Excess molar volume (V^E) of n-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.1009	0.928500	-0.3749	0.924671	-0.3229	0.919817	-0.3050	0.914740	-0.2730	0.909621	-0.2600	0.904460	-0.2460
0.2002	0.912000	-0.3947	0.907800	-0.3196	0.902904	-0.2840	0.898030	-0.2680	0.892599	-0.2350	0.887280	-0.2080
0.2990	0.896300	-0.3707	0.892200	-0.3139	0.887396	-0.2730	0.882574	-0.2600	0.876996	-0.2200	0.871705	-0.1970
0.4007	0.880457	-0.2621	0.876360	-0.2140	0.871887	-0.1920	0.866961	-0.1650	0.861499	-0.1430	0.855908	-0.0880
0.5001	0.867220	-0.2810	0.862921	-0.2200	0.858398	-0.1800	0.853410	-0.1430	0.847985	-0.1320	0.842790	-0.1210
0.5988	0.854800	-0.2860	0.850618	-0.2460	0.846084	-0.1920	0.841159	-0.1590	0.835537	-0.1320	0.830114	-0.0950
0.7013	0.842889	-0.2970	0.838704	-0.2650	0.834213	-0.2030	0.829225	-0.1590	0.823555	-0.1320	0.817878	-0.0630
0.7990	0.831953	-0.2690	0.827800	-0.2485	0.823454	-0.1920	0.818455	-0.1430	0.812660	-0.1050	0.807160	-0.0570
0.8997	0.820362	-0.1595	0.816164	-0.1400	0.812179	-0.1160	0.807306	-0.0780	0.801578	-0.0520	0.796162	-0.0130
1.0000	0.809300	0.0000	0.805203	0.0000	0.801484	0.0000	0.796924	0.0000	0.791358	0.0000	0.786230	0.0000

Table-4.10: Density (ρ) and Excess molar volume (V^E) of iso-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.942291	0.0000	0.939263	0.0000	0.934500	0.0000	0.929810	0.0000	0.925000	0.0000	0.920069	0.0000
0.1009	0.926300	-0.1777	0.922740	-0.1300	0.917816	-0.1103	0.913383	-0.1469	0.908181	-0.1084	0.903027	-0.0880
0.2002	0.910800	-0.2722	0.907388	-0.2340	0.902447	-0.2060	0.897242	-0.1840	0.892000	-0.1352	0.887059	-0.1330
0.2990	0.896416	-0.3631	0.893115	-0.3320	0.888235	-0.3030	0.882888	-0.2770	0.877900	-0.2475	0.872401	-0.1880
0.4007	0.882939	-0.4897	0.879341	-0.4250	0.874552	-0.3980	0.868800	-0.3390	0.863800	-0.3025	0.858400	-0.2490
0.5001	0.870045	-0.5514	0.866517	-0.4890	0.861738	-0.4560	0.856000	-0.4049	0.851100	-0.3737	0.845600	-0.3050
0.5988	0.857285	-0.5270	0.854123	-0.5000	0.849493	-0.4760	0.843800	-0.4359	0.838900	-0.3986	0.833691	-0.3590
0.7013	0.844771	-0.4883	0.841658	-0.4630	0.837146	-0.4450	0.831593	-0.4270	0.826833	-0.4000	0.821593	-0.3520
0.7990	0.833377	-0.4263	0.830289	-0.4000	0.825822	-0.3800	0.820270	-0.3670	0.815640	-0.3500	0.810573	-0.3190
0.8997	0.821900	-0.3061	0.818695	-0.2600	0.814722	-0.2957	0.809090	-0.2770	0.804465	-0.2540	0.799563	-0.2400
1.0000	0.809766	0.0000	0.806953	0.0000	0.802770	0.0000	0.797268	0.0000	0.792871	0.0000	0.788113	0.0000

Table-4.11: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Methanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K respectively

X_2	298.15K			303.15K			308.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000
0.1000	0.7868	0.0217	0.3114	0.7490	0.0223	0.3358	0.7033	0.0200	0.3204
0.1983	0.7722	0.0339	0.2825	0.7310	0.0308	0.2710	0.6883	0.0293	0.2736
0.3009	0.7460	0.0346	0.2260	0.7030	0.0295	0.2037	0.6625	0.0280	0.2049
0.3989	0.7180	0.0314	0.1866	0.6750	0.0260	0.1638	0.6350	0.0230	0.1542
0.5001	0.6870	0.0251	0.1490	0.6460	0.0214	0.1346	0.6090	0.0195	0.1301
0.5992	0.6600	0.0214	0.1375	0.6190	0.0174	0.1184	0.5820	0.0137	0.0989
0.7009	0.6330	0.0175	0.1339	0.5920	0.0131	0.1064	0.5600	0.0126	0.1086
0.8002	0.6060	0.0122	0.1277	0.5660	0.0084	0.0936	0.5360	0.0083	0.0978
0.8997	0.5800	0.0072	0.1391	0.5430	0.0060	0.1230	0.5130	0.0043	0.0940
1.0000	0.5523	0.0000	0.0000	0.5170	0.0000	0.0000	0.4902	0.0000	0.0000

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

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.0994	0.8210	-0.0144	-0.1938	0.7705	-0.0203	-0.2899	0.7321	-0.0077	-0.1165	0.6906	-0.0029	-0.0471	0.6475	-0.0045	-0.0778	0.6127	-0.0020	-0.0370
0.1997	0.8550	-0.0252	-0.1816	0.7941	-0.0347	-0.2674	0.7497	-0.0225	-0.1848	0.7060	-0.0149	-0.1304	0.6620	-0.0114	-0.1066	0.6196	-0.0130	-0.1301
0.3060	0.8900	-0.0403	-0.2085	0.8184	-0.0528	-0.2942	0.7732	-0.0349	-0.2078	0.7220	-0.0290	-0.1853	0.6762	-0.0206	-0.1414	0.6300	-0.0221	-0.1627
0.4009	0.9269	-0.0506	-0.2211	0.8474	-0.0634	-0.3003	0.7955	-0.0461	-0.2343	0.7402	-0.0388	-0.2126	0.6888	-0.0296	-0.1750	0.6412	-0.0289	-0.1833
0.5010	0.9730	-0.0568	-0.2268	0.8880	-0.0665	-0.2888	0.8209	-0.0574	-0.2705	0.7623	-0.0472	-0.2404	0.7045	-0.0373	-0.2064	0.6579	-0.0316	-0.1875
0.6015	1.0270	-0.0581	-0.2297	0.9420	-0.0585	-0.2515	0.8659	-0.0509	-0.2385	0.7926	-0.0489	-0.2495	0.7319	-0.0343	-0.1912	0.6763	-0.0333	-0.2004
0.7002	1.1033	-0.0391	-0.1659	0.9994	-0.0485	-0.2256	0.9160	-0.0403	-0.2053	0.8350	-0.0391	-0.2178	0.7610	-0.0299	-0.1833	0.7020	-0.0279	-0.1858
0.8006	1.1820	-0.0217	-0.1140	1.0714	-0.0270	-0.1557	0.9750	-0.0233	-0.1477	0.8780	-0.0305	-0.2140	0.7970	-0.0198	-0.1536	0.7320	-0.0192	-0.1619
0.8996	1.2630	-0.0044	-0.0385	1.1369	-0.0137	-0.1322	1.0303	-0.0111	-0.1186	0.9300	-0.0138	-0.1631	0.8330	-0.0102	-0.1346	0.7610	-0.0117	-0.1692
1.0000	1.3355	0.0000	0.0000	1.2060	0.0000	0.0000	1.0871	0.0000	0.0000	0.9810	0.0000	0.0000	0.8708	0.0000	0.0000	0.7952	0.0000	0.0000

Table-13: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.1006	0.8309	-0.0362	-0.4715	0.7740	-0.0447	-0.6204	0.7354	-0.0303	-0.4468	0.6941	-0.0234	-0.3667	0.6516	-0.0227	-0.3790	0.6162	-0.0185	-0.3275
0.2007	0.8730	-0.0745	-0.5106	0.8090	-0.0788	-0.5794	0.7630	-0.0637	-0.4997	0.7170	-0.0540	-0.4528	0.6710	-0.0488	-0.4374	0.6300	-0.0441	-0.4221
0.3001	0.9100	-0.1247	-0.6115	0.8440	-0.1182	-0.6238	0.7890	-0.1030	-0.5841	0.7400	-0.0881	-0.5354	0.6880	-0.0799	-0.5233	0.6450	-0.0706	-0.4948
0.3987	0.9540	-0.1751	-0.7031	0.8820	-0.1601	-0.6956	0.8210	-0.1408	-0.6604	0.7660	-0.1228	-0.6204	0.7140	-0.1049	-0.5718	0.6650	-0.0943	-0.5533
0.5015	1.0090	-0.2278	-0.8142	0.9243	-0.2082	-0.8125	0.8610	-0.1795	-0.7575	0.7956	-0.1613	-0.7385	0.7392	-0.1364	-0.6776	0.6850	-0.1227	-0.6592
0.5988	1.0810	-0.2671	-0.9191	0.9913	-0.2340	-0.8820	0.9160	-0.2049	-0.8403	0.8410	-0.1852	-0.8285	0.7860	-0.1470	-0.7135	0.7200	-0.1364	-0.7220
0.7002	1.1713	-0.3034	-1.0974	1.0621	-0.2679	-1.0716	0.9817	-0.2296	-1.0012	0.9054	-0.1984	-0.9438	0.8422	-0.1545	-0.8023	0.7694	-0.1408	-0.8007
0.8008	1.3338	-0.2784	-1.1884	1.1950	-0.2477	-1.1810	1.1016	-0.2065	-1.0773	0.9997	-0.1868	-1.0737	0.9129	-0.1513	-0.9613	0.8341	-0.1328	-0.9265
0.8961	1.5594	-0.1948	-1.2642	1.3851	-0.1734	-1.2665	1.2718	-0.1353	-1.0856	1.1356	-0.1349	-1.2059	1.0132	-0.1192	-1.1946	0.9206	-0.1034	-1.1429
1.0000	1.9233	0.0000	0.0000	1.6951	0.0000	0.0000	1.5234	0.0000	0.0000	1.3689	0.0000	0.0000	1.2118	0.0000	0.0000	1.0899	0.0000	0.0000

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

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.0987	0.8196	-0.0505	-0.6724	0.7647	-0.0560	-0.7946	0.7248	-0.0398	-0.6010	0.6843	-0.0296	-0.4758	0.6422	-0.0279	-0.4777	0.6034	-0.0258	-0.4703
0.1996	0.8467	-0.1098	-0.7630	0.7853	-0.1088	-0.8123	0.7413	-0.0845	-0.6759	0.7030	-0.0616	-0.5257	0.6580	-0.0540	-0.4935	0.6168	-0.0464	-0.4538
0.3002	0.8820	-0.1691	-0.8347	0.8170	-0.1568	-0.8356	0.7680	-0.1238	-0.7114	0.7257	-0.0931	-0.5744	0.6793	-0.0771	-0.5116	0.6354	-0.0636	-0.4538
0.4006	0.9182	-0.2366	-0.9550	0.8477	-0.2127	-0.9323	0.7973	-0.1656	-0.7858	0.7424	-0.1342	-0.6920	0.7000	-0.1034	-0.5736	0.6489	-0.0878	-0.5283
0.5008	0.9712	-0.2974	-1.0685	0.8910	-0.2636	-1.0366	0.8263	-0.2132	-0.9182	0.7700	-0.1685	-0.7914	0.7180	-0.1352	-0.6901	0.6670	-0.1092	-0.6066
0.6006	1.0430	-0.3500	-1.2062	0.9513	-0.3053	-1.1605	0.8730	-0.2488	-1.0454	0.8030	-0.2014	-0.9328	0.7480	-0.1579	-0.7985	0.6940	-0.1238	-0.6842
0.7003	1.1300	-0.3995	-1.4423	1.0409	-0.3267	-1.3007	0.9271	-0.2835	-1.2713	0.8501	-0.2248	-1.1177	0.7825	-0.1793	-0.9833	0.7270	-0.1345	-0.8088
0.7996	1.2789	-0.3998	-1.6975	1.1609	-0.3270	-1.5489	1.0492	-0.2568	-1.3662	0.9480	-0.2020	-1.2054	0.8594	-0.1615	-1.0749	0.7770	-0.1303	-0.9677
0.9012	1.5547	-0.2918	-1.9318	1.3918	-0.2301	-1.7186	1.2355	-0.1759	-1.4946	1.0925	-0.1397	-1.3515	0.9642	-0.1210	-1.3280	0.8672	-0.0896	-1.1048
1.0000	2.0257	0.0000	0.0000	1.7639	0.0000	0.0000	1.5220	0.0000	0.0000	1.3179	0.0000	0.0000	1.1516	0.0000	0.0000	1.0075	0.0000	0.0000

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

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0
0.1009	0.8571	-0.0369	-0.4651	0.7980	-0.0445	-0.5980	0.7596	-0.0272	-0.3877	0.7159	-0.0196	-0.2981	0.6694	-0.0218	-0.3536	0.6330	-0.0164	-0.2818
0.1990	0.9150	-0.0893	-0.5844	0.8580	-0.0797	-0.5570	0.8084	-0.0622	-0.4653	0.7517	-0.0566	-0.4552	0.7062	-0.0484	-0.4162	0.6624	-0.0418	-0.3834
0.2982	0.9758	-0.1539	-0.6997	0.9090	-0.1357	-0.6650	0.8517	-0.1127	-0.5938	0.7960	-0.0932	-0.5292	0.7438	-0.0809	-0.4935	0.6972	-0.0671	-0.4389
0.4008	1.0510	-0.2249	-0.8073	0.9800	-0.1884	-0.7322	0.9090	-0.1630	-0.6869	0.8502	-0.1313	-0.5979	0.7914	-0.1126	-0.5538	0.7369	-0.0949	-0.5043
0.4999	1.1515	-0.2835	-0.8805	1.0533	-0.2485	-0.8473	0.9821	-0.2053	-0.7592	0.9098	-0.1698	-0.6846	0.8384	-0.1495	-0.6562	0.7817	-0.1210	-0.5757
0.5997	1.2710	-0.3442	-0.9984	1.1632	-0.2883	-0.9223	1.0801	-0.2361	-0.8234	0.9846	-0.2038	-0.7836	0.9061	-0.1740	-0.7317	0.8350	-0.1452	-0.6680
0.7003	1.4326	-0.3873	-1.1401	1.2935	-0.3262	-1.0716	1.1939	-0.2661	-0.9588	1.0958	-0.2133	-0.8473	0.9986	-0.1832	-0.8026	0.9206	-0.1444	-0.6943
0.7989	1.6639	-0.3818	-1.2857	1.4841	-0.3195	-1.2135	1.3566	-0.2596	-1.0900	1.2182	-0.2210	-1.0379	1.1118	-0.1791	-0.9295	1.0081	-0.1472	-0.8484
0.9006	1.9984	-0.3095	-1.6083	1.7646	-0.2505	-1.4828	1.6116	-0.1834	-1.2038	1.4384	-0.1488	-1.0994	1.2888	-0.1250	-1.0342	1.1643	-0.0922	-0.8516
1.0000	2.5965	0.0000	0.0000	2.2458	0.0000	0.0000	1.9888	0.0000	0.0000	1.7463	0.0000	0.0000	1.5454	0.0000	0.0000	1.3639	0.0000	0

Table-4.16: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0
0.1009	0.8419	-0.0739	-0.9269	0.7975	-0.0652	-0.8657	0.7510	-0.0508	-0.7220	0.7022	-0.0455	-0.6921	0.6629	-0.0378	-0.6115	0.6200	-0.0371	-0.6405
0.1997	0.9202	-0.1338	-0.8498	0.8648	-0.1185	-0.8038	0.8063	-0.0981	-0.7187	0.7529	-0.0826	-0.6510	0.7110	-0.0649	-0.5462	0.6648	-0.0564	-0.5094
0.3003	1.0130	-0.2033	-0.8704	0.9500	-0.1736	-0.7988	0.8879	-0.1345	-0.6715	0.8231	-0.1124	-0.6090	0.7630	-0.0976	-0.5730	0.7187	-0.0742	-0.4678
0.4005	1.1273	-0.2755	-0.9105	1.0597	-0.2235	-0.7971	0.9843	-0.1709	-0.6669	0.8997	-0.1472	-0.6312	0.8369	-0.1173	-0.5464	0.7715	-0.0999	-0.5073
0.4995	1.2520	-0.3630	-1.0184	1.1765	-0.2865	-0.8719	1.0849	-0.2185	-0.7339	0.9881	-0.1820	-0.6762	0.9136	-0.1431	-0.5821	0.8420	-0.1146	-0.5106
0.5995	1.4324	-0.4296	-1.0925	1.3260	-0.3444	-0.9616	1.2248	-0.2476	-0.7668	1.0947	-0.2146	-0.7455	1.0130	-0.1585	-0.6054	0.9220	-0.1292	-0.5460
0.7006	1.7360	-0.4143	-1.0203	1.5881	-0.3218	-0.8796	1.4169	-0.2485	-0.7705	1.2704	-0.1964	-0.6852	1.1270	-0.1731	-0.6814	1.0190	-0.1372	-0.6022
0.7998	2.1630	-0.3134	-0.8450	1.9290	-0.2492	-0.7588	1.7130	-0.1664	-0.5791	1.4680	-0.1717	-0.6909	1.2750	-0.1651	-0.7605	1.1350	-0.1344	-0.6991
0.8996	2.6557	-0.1987	-0.7989	2.3849	-0.1013	-0.4606	2.0370	-0.0855	-0.4554	1.7470	-0.0873	-0.5401	1.4850	-0.1111	-0.7991	1.3074	-0.0872	-0.7151
1.0000	3.2929	0.0000	0.0000	2.8400	0.0000	0.0000	2.3988	0.0000	0.0000	2.0534	0.0000	0.0000	1.7702	0.0000	0.0000	1.5330	0.0000	0

Table-4.17: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of tert-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.0997	0.8716	-0.0658	-0.8108	0.8211	-0.0534	-0.7022	0.7803	-0.0276	-0.3879	0.7168	-0.0316	-0.4812	0.6726	-0.0249	-0.4055	0.6351	-0.0161	-0.2794
0.2017	0.9524	-0.1597	-0.9628	0.8915	-0.1252	-0.8163	0.8316	-0.0919	-0.6511	0.7732	-0.0681	-0.5244	0.7192	-0.0531	-0.4421	0.6738	-0.0374	-0.3352
0.2995	1.0710	-0.2391	-0.9603	0.9900	-0.1848	-0.8157	0.9100	-0.1397	-0.6807	0.8450	-0.0963	-0.5142	0.7730	-0.0784	-0.4604	0.7160	-0.0578	-0.3701
0.3990	1.2080	-0.3397	-1.0333	1.0950	-0.2658	-0.9064	1.0000	-0.1958	-0.7458	0.9180	-0.1371	-0.5804	0.8450	-0.0952	-0.4453	0.7730	-0.0702	-0.3625
0.5004	1.3572	-0.4771	-1.2049	1.2333	-0.3475	-0.9930	1.1101	-0.2556	-0.8287	1.0067	-0.1785	-0.6530	0.9172	-0.1230	-0.5035	0.8367	-0.0836	-0.3809
0.6010	1.5885	-0.5824	-1.3026	1.4240	-0.4101	-1.0555	1.2724	-0.2857	-0.8446	1.1346	-0.1957	-0.6635	1.0178	-0.1323	-0.5095	0.9133	-0.0905	-0.3940
0.7004	1.9057	-0.6585	-1.4144	1.6758	-0.4485	-1.1301	1.4636	-0.3111	-0.9185	1.2854	-0.2056	-0.7073	1.1404	-0.1296	-0.5128	1.0145	-0.0792	-0.3583
0.8011	2.3681	-0.6673	-1.5580	2.0278	-0.4372	-1.2254	1.7404	-0.2846	-0.9507	1.4935	-0.1801	-0.7146	1.2925	-0.1116	-0.5198	1.1220	-0.0710	-0.3853
0.9001	3.1646	-0.4184	-1.3809	2.5535	-0.2998	-1.2345	2.1061	-0.1993	-1.0056	1.7699	-0.1051	-0.6415	1.4866	-0.0632	-0.4632	1.2713	-0.0282	-0.2441
1.0000	4.2357	0.0000	0.0000	3.3071	0.0000	0.0000	2.6277	0.0000	0.0000	2.1027	0.0000	0.0000	1.7123	0.0000	0.0000	1.4165	0.0000	0.0000

Table-4.18: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.1009	0.9160	-0.0114	-0.1369	0.8510	-0.0229	-0.2932	0.8100	-0.0036	-0.0493	0.7530	-0.0061	-0.0893	0.7120	0.0006	0.0088	0.6710	0.0037	0.0601
0.2002	1.0220	-0.0597	-0.3546	0.9570	-0.0526	-0.3344	0.8920	-0.0396	-0.2713	0.8260	-0.0355	-0.2631	0.7850	-0.0149	-0.1177	0.7280	-0.0160	-0.1359
0.2990	1.1450	-0.1156	-0.4591	1.0550	-0.1106	-0.4755	0.9704	-0.0956	-0.4481	0.9005	-0.0766	-0.3897	0.8424	-0.0565	-0.3096	0.7775	-0.0515	-0.3059
0.4007	1.2552	-0.2206	-0.6741	1.1508	-0.2005	-0.6688	1.0622	-0.1623	-0.5921	0.9762	-0.1362	-0.5439	0.8957	-0.1179	-0.5149	0.8305	-0.0962	-0.4564
0.5001	1.3961	-0.3254	-0.8382	1.2817	-0.2796	-0.7894	1.1686	-0.2336	-0.7290	1.0718	-0.1908	-0.6552	0.9893	-0.1505	-0.5666	0.9080	-0.1253	-0.5171
0.5988	1.5735	-0.4326	-1.0110	1.4394	-0.3628	-0.9356	1.3175	-0.2867	-0.8197	1.1946	-0.2372	-0.7541	1.0842	-0.1965	-0.6935	0.9900	-0.1612	-0.6281
0.7013	1.8730	-0.4783	-1.0857	1.6930	-0.3987	-1.0096	1.5460	-0.2989	-0.8437	1.3740	-0.2577	-0.8205	1.2600	-0.1855	-0.6557	1.1290	-0.1590	-0.6291
0.7990	2.2250	-0.5106	-1.2864	1.9880	-0.4229	-1.2010	1.7830	-0.3247	-1.0418	1.5790	-0.2690	-0.9797	1.4340	-0.1883	-0.7683	1.2833	-0.1502	-0.6891
0.8997	2.7292	-0.4683	-1.7549	2.4178	-0.3732	-1.5907	2.1191	-0.2988	-1.4620	1.8631	-0.2381	-1.3326	1.6540	-0.1731	-1.1029	1.4723	-0.1283	-0.9262
1.0000	3.7352	0.0000	0.0000	3.2290	0.0000	0.0000	2.7723	0.0000	0.0000	2.3876	0.0000	0.0000	2.0568	0.0000	0.0000	1.7865	0.0000	0.0000

Table-4.19: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.7932	0.0000	0.0000	0.7547	0.0000	0.0000	0.7091	0.0000	0.0000	0.6675	0.0000	0.0000	0.6315	0.0000	0.0000	0.5975	0.0000	0.0000
0.1009	0.8872	-0.0371	-0.4518	0.8268	-0.0443	-0.5757	0.7844	-0.0266	-0.3682	0.7360	-0.0207	-0.3053	0.6875	-0.0224	-0.3537	0.6489	-0.0175	-0.2927
0.2002	0.9970	-0.0776	-0.4680	0.9220	-0.0813	-0.5278	0.8629	-0.0628	-0.4390	0.8003	-0.0557	-0.4199	0.7487	-0.0480	-0.3879	0.7084	-0.0334	-0.2880
0.2990	1.1150	-0.1333	-0.5387	1.0293	-0.1253	-0.5481	0.9553	-0.1006	-0.4778	0.8790	-0.0887	-0.4587	0.8230	-0.0704	-0.3916	0.7726	-0.0529	-0.3162
0.4007	1.2710	-0.1854	-0.5670	1.1675	-0.1668	-0.5563	1.0709	-0.1382	-0.5055	0.9812	-0.1168	-0.4683	0.9070	-0.0983	-0.4285	0.8518	-0.0696	-0.3269
0.5001	1.4450	-0.2484	-0.6345	1.3145	-0.2224	-0.6252	1.2084	-0.1718	-0.5318	1.0970	-0.1452	-0.4974	0.9970	-0.1312	-0.4944	0.9324	-0.0935	-0.3822
0.5988	1.6450	-0.3218	-0.7437	1.4988	-0.2697	-0.6888	1.3511	-0.2230	-0.6358	1.2238	-0.1805	-0.5726	1.1080	-0.1570	-0.5517	1.0143	-0.1271	-0.4913
0.7013	1.9248	-0.3727	-0.8450	1.7045	-0.3416	-0.8719	1.5459	-0.2585	-0.7382	1.3963	-0.1986	-0.6347	1.2562	-0.1686	-0.6010	1.1415	-0.1336	-0.5282
0.7990	2.2402	-0.4243	-1.0801	1.9880	-0.3630	-1.0443	1.7779	-0.2772	-0.9022	1.5817	-0.2189	-0.8072	1.4134	-0.1824	-0.7558	1.2704	-0.1468	-0.6807
0.8997	2.7673	-0.3368	-1.2727	2.4023	-0.3107	-1.3478	2.1322	-0.2179	-1.0785	1.8808	-0.1597	-0.9033	1.6545	-0.1390	-0.8941	1.4762	-0.1039	-0.7538
1.0000	3.6140	0.0000	0.0000	3.1289	0.0000	0.0000	2.6860	0.0000	0.0000	2.3112	0.0000	0.0000	2.0149	0.0000	0.0000	1.7610	0.0000	0.0000

Table 4.20: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Methanol + DMF system at 298.15K, 303.15K, 308.15K, respectively

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$			$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.0000	12.49	12.58	12.64	0.0000	0.0000	0.0000
0.1000	12.34	12.43	12.49	0.0984	0.1071	0.1062
0.1983	12.16	12.24	12.30	0.1704	0.1705	0.1745
0.3009	11.94	12.00	12.06	0.1998	0.1924	0.1958
0.3989	11.70	11.75	11.81	0.2078	0.1978	0.1969
0.5001	11.44	11.48	11.54	0.1960	0.1897	0.1912
0.5992	11.18	11.22	11.26	0.1835	0.1760	0.1695
0.7009	10.90	10.93	10.98	0.1629	0.1525	0.1566
0.8002	10.62	10.63	10.69	0.1250	0.1118	0.1186
0.8997	10.32	10.34	10.38	0.0729	0.0703	0.0653
1.0000	9.99	10.01	10.05	0.0000	0.0000	0.0000

Table 4.21: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0994	12.50	12.56	12.65	12.72	12.76	12.83	-0.0426	-0.0634	-0.0236	-0.0067	-0.0136	-0.0036
0.1997	12.53	12.56	12.64	12.70	12.75	12.79	-0.0686	-0.1008	-0.0669	-0.0438	-0.0334	-0.0430
0.3060	12.55	12.56	12.64	12.68	12.73	12.75	-0.1010	-0.1450	-0.0979	-0.0857	-0.0614	-0.0740
0.4009	12.58	12.58	12.64	12.68	12.70	12.73	-0.1184	-0.1652	-0.1250	-0.1118	-0.0888	-0.0950
0.5010	12.63	12.62	12.65	12.68	12.68	12.72	-0.1248	-0.1625	-0.1513	-0.1330	-0.1120	-0.1004
0.6015	12.68	12.69	12.71	12.70	12.71	12.71	-0.1211	-0.1332	-0.1253	-0.1320	-0.0960	-0.1020
0.7002	12.78	12.76	12.77	12.75	12.73	12.73	-0.0738	-0.1033	-0.0917	-0.0973	-0.0777	-0.0789
0.8006	12.87	12.86	12.85	12.80	12.77	12.76	-0.0357	-0.0510	-0.0441	-0.0703	-0.0444	-0.0468
0.8996	12.96	12.93	12.91	12.87	12.80	12.78	-0.0025	-0.0205	-0.0153	-0.0227	-0.0167	-0.0250
1.0000	13.01	12.99	12.96	12.91	12.82	12.80	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.22: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1006	12.59	12.63	12.72	12.79	12.84	12.91	-0.1133	-0.1472	-0.1084	-0.0902	-0.0950	-0.0828
0.2007	12.70	12.74	12.81	12.87	12.92	12.96	-0.2106	-0.2400	-0.2094	-0.1915	-0.1870	-0.1831
0.3001	12.80	12.83	12.89	12.95	12.98	13.02	-0.3255	-0.3351	-0.3169	-0.2938	-0.2905	-0.2784
0.3987	12.91	12.94	12.99	13.03	13.07	13.10	-0.4247	-0.4248	-0.4068	-0.3867	-0.3610	-0.3531
0.5015	13.04	13.05	13.10	13.12	13.15	13.17	-0.5114	-0.5158	-0.4864	-0.4798	-0.4460	-0.4396
0.6130	13.20	13.21	13.25	13.25	13.30	13.29	-0.5878	-0.5699	-0.5497	-0.5481	-0.4799	-0.4896
0.7002	13.39	13.38	13.42	13.44	13.48	13.47	-0.5759	-0.5708	-0.5392	-0.5153	-0.4442	-0.4480
0.8008	13.71	13.68	13.71	13.69	13.69	13.68	-0.4725	-0.4766	-0.4392	-0.4433	-0.4022	-0.3911
0.8961	14.09	14.04	14.07	14.02	13.96	13.93	-0.2949	-0.2995	-0.2568	-0.2901	-0.2912	-0.2826
1.0000	14.60	14.54	14.52	14.49	14.42	14.37	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.23: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso- Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0987	12.56	12.61	12.69	12.77	12.82	12.87	-0.1555	-0.1834	-0.1394	-0.1082	-0.1092	-0.1064
0.1996	12.64	12.67	12.75	12.84	12.88	12.93	-0.3112	-0.3333	-0.2803	-0.2184	-0.2054	-0.1873
0.3002	12.74	12.77	12.84	12.92	12.97	13.01	-0.4445	-0.4497	-0.3864	-0.3143	-0.2809	-0.2483
0.4006	12.83	12.86	12.93	12.97	13.04	13.06	-0.5810	-0.5723	-0.4880	-0.4345	-0.3635	-0.3355
0.5008	12.98	12.99	13.03	13.07	13.11	13.14	-0.6718	-0.6585	-0.5891	-0.5121	-0.4511	-0.3989
0.6006	13.15	13.15	13.17	13.18	13.22	13.25	-0.7269	-0.7075	-0.6434	-0.5786	-0.5011	-0.4315
0.7003	13.35	13.38	13.32	13.33	13.34	13.37	-0.7599	-0.6937	-0.6838	-0.6067	-0.5385	-0.4473
0.7996	13.66	13.66	13.64	13.61	13.59	13.55	-0.6822	-0.6301	-0.5615	-0.4990	-0.4500	-0.4090
0.9012	14.14	14.11	14.05	13.98	13.89	13.84	-0.4323	-0.3899	-0.3433	-0.3133	-0.3098	-0.2589
1.0000	14.80	14.71	14.59	14.47	14.35	14.24	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.24: Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of n-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.72	12.76	12.86	12.93	12.98	13.04	-0.1061	-0.1373	-0.0887	-0.0699	-0.0831	-0.0660
0.1990	12.93	13.00	13.07	13.11	13.17	13.22	-0.2270	-0.2189	-0.1829	-0.1815	-0.1680	-0.1547
0.2982	13.13	13.18	13.25	13.30	13.35	13.41	-0.3585	-0.3449	-0.3115	-0.2804	-0.2643	-0.2359
0.4008	13.36	13.42	13.46	13.52	13.56	13.60	-0.4752	-0.4363	-0.4145	-0.3648	-0.3420	-0.3132
0.4999	13.63	13.64	13.71	13.75	13.76	13.81	-0.5406	-0.5277	-0.4790	-0.4369	-0.4241	-0.3747
0.5997	13.91	13.93	13.99	14.00	14.01	14.03	-0.5900	-0.5526	-0.4997	-0.4818	-0.4555	-0.4194
0.7003	14.25	14.24	14.29	14.32	14.32	14.34	-0.5902	-0.5627	-0.5100	-0.4564	-0.4377	-0.3823
0.7989	14.66	14.63	14.66	14.64	14.64	14.63	-0.5104	-0.4887	-0.4455	-0.4305	-0.3903	-0.3607
0.9006	15.16	15.11	15.15	15.11	15.08	15.06	-0.3552	-0.3335	-0.2751	-0.2553	-0.2423	-0.2020
1.0000	15.85	15.76	15.73	15.66	15.60	15.53	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.25: Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of iso-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.67	12.75	12.83	12.87	12.94	12.98	-0.2208	-0.2096	-0.1783	-0.1728	-0.1556	-0.1638
0.1997	12.94	13.01	13.06	13.10	13.18	13.22	-0.3450	-0.3312	-0.3012	-0.2771	-0.2356	-0.2199
0.3003	13.23	13.30	13.36	13.39	13.42	13.49	-0.4549	-0.4241	-0.3613	-0.3317	-0.3158	-0.2592
0.4005	13.54	13.62	13.67	13.67	13.72	13.73	-0.5404	-0.4791	-0.4052	-0.3887	-0.3395	-0.3184
0.4995	13.84	13.93	13.97	13.96	14.00	14.02	-0.6283	-0.5443	-0.4636	-0.4330	-0.3761	-0.3324
0.5995	14.22	14.28	14.32	14.28	14.32	14.31	-0.6477	-0.5775	-0.4665	-0.4596	-0.3765	-0.3428
0.7006	14.74	14.78	14.74	14.71	14.64	14.62	-0.5297	-0.4630	-0.4109	-0.3699	-0.3721	-0.3308
0.7998	15.33	15.31	15.27	15.13	15.02	14.96	-0.3377	-0.3062	-0.2370	-0.2862	-0.3178	-0.2957
0.8996	15.88	15.89	15.76	15.63	15.46	15.38	-0.1836	-0.1069	-0.1066	-0.1274	-0.1901	-0.1711
1.0000	16.46	16.37	16.22	16.10	15.98	15.86	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.26: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of tert-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	0.0000
0.0000	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0997	12.77	12.85	12.94	12.95	13.00	13.07	-0.1794	-0.1561	-0.0863	-0.1079	-0.0902	-0.0592
0.2017	13.04	13.11	13.16	13.20	13.24	13.29	-0.3837	-0.3283	-0.2633	-0.2121	-0.1781	-0.1325
0.2995	13.38	13.42	13.44	13.49	13.48	13.51	-0.4971	-0.4262	-0.3582	-0.2707	-0.2426	-0.1930
0.3990	13.73	13.73	13.74	13.76	13.78	13.77	-0.6090	-0.5407	-0.4493	-0.3510	-0.2682	-0.2165
0.5004	14.07	14.08	14.06	14.05	14.05	14.04	-0.7393	-0.6169	-0.5197	-0.4121	-0.3181	-0.2389
0.6010	14.51	14.50	14.46	14.42	14.38	14.33	-0.7670	-0.6293	-0.5084	-0.4032	-0.3105	-0.2378
0.7004	15.01	14.95	14.87	14.79	14.73	14.67	-0.7310	-0.5912	-0.4856	-0.3772	-0.2738	-0.1895
0.8011	15.60	15.48	15.36	15.23	15.11	14.99	-0.6147	-0.4902	-0.3843	-0.2919	-0.2138	-0.1577
0.9001	16.36	16.11	15.90	15.72	15.53	15.38	-0.3083	-0.2800	-0.2312	-0.1487	-0.1082	-0.0557
1.0000	17.13	16.81	16.52	16.22	15.96	15.72	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.27: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.93	12.98	13.08	13.11	13.19	13.25	-0.0281	-0.0625	-0.0063	-0.0147	0.0092	0.0225
0.2002	13.30	13.37	13.42	13.45	13.55	13.58	-0.1280	-0.1195	-0.0945	-0.0920	-0.0305	-0.0377
0.2990	13.67	13.71	13.73	13.77	13.83	13.85	-0.2179	-0.2282	-0.2161	-0.1872	-0.1442	-0.1434
0.4007	13.99	14.02	14.06	14.08	14.10	14.13	-0.3736	-0.3749	-0.3333	-0.3076	-0.2931	-0.2581
0.5001	14.34	14.38	14.39	14.41	14.45	14.46	-0.4914	-0.4668	-0.4348	-0.3927	-0.3396	-0.3111
0.5988	14.72	14.75	14.78	14.78	14.78	14.78	-0.5761	-0.5386	-0.4748	-0.4404	-0.4078	-0.3707
0.7013	15.23	15.24	15.28	15.23	15.26	15.23	-0.5431	-0.5109	-0.4287	-0.4217	-0.3361	-0.3243
0.7990	15.73	15.72	15.72	15.67	15.69	15.65	-0.4980	-0.4711	-0.4119	-0.3913	-0.3065	-0.2758
0.8997	16.32	16.30	16.24	16.19	16.15	16.11	-0.3847	-0.3532	-0.3287	-0.3026	-0.2518	-0.2119
1.0000	17.17	17.11	17.01	16.91	16.80	16.71	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.28: Free energy (ΔG^{*}) and Excess Free energy (ΔG^{*E}) of iso-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.49	12.58	12.64	12.70	12.77	12.84	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.86	12.91	13.00	13.06	13.10	13.17	-0.0930	-0.1213	-0.0744	-0.0617	-0.0731	-0.0586
0.2002	13.24	13.27	13.34	13.37	13.43	13.50	-0.1695	-0.1952	-0.1612	-0.1548	-0.1421	-0.1012
0.2990	13.61	13.64	13.69	13.71	13.77	13.83	-0.2592	-0.2675	-0.2333	-0.2254	-0.1908	-0.1494
0.4007	14.02	14.05	14.07	14.09	14.12	14.19	-0.3163	-0.3131	-0.2862	-0.2654	-0.2433	-0.1797
0.5001	14.42	14.43	14.47	14.47	14.46	14.52	-0.3725	-0.3711	-0.3164	-0.2973	-0.2990	-0.2262
0.5988	14.82	14.84	14.84	14.84	14.83	14.84	-0.4232	-0.3963	-0.3695	-0.3344	-0.3253	-0.2901
0.7013	15.29	15.25	15.27	15.27	15.25	15.25	-0.4226	-0.4432	-0.3782	-0.3270	-0.3127	-0.2752
0.7990	15.74	15.72	15.70	15.67	15.64	15.62	-0.4190	-0.4108	-0.3586	-0.3241	-0.3068	-0.2783
0.8997	16.35	16.27	16.25	16.20	16.14	16.10	-0.2802	-0.3008	-0.2443	-0.2065	-0.2069	-0.1758
1.0000	17.09	17.02	16.92	16.82	16.74	16.66	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.29: Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of Methanol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1000	8.45	0.0255	-51.37	-0.2629
0.1983	8.57	0.1417	-50.38	-0.1014
0.3009	8.82	0.3865	-48.78	0.6256
0.3989	8.85	0.4154	-47.87	0.7029
0.5001	9.01	0.5721	-46.47	1.2497
0.5992	9.11	0.6735	-45.25	1.6339
0.7009	9.12	0.6834	-44.29	1.7322
0.8002	9.01	0.5739	-43.68	1.4978
0.8996	8.99	0.5484	-42.76	1.5757
1.0000	8.44	0.0000	-43.49	0.0000

Table 4.30: Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of Ethanol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.0994	8.49	-0.6690	-51.75	-2.0712
0.1997	9.21	-0.6841	-49.39	-2.0109
0.3060	9.89	-0.7943	-47.19	-2.2539
0.4009	10.63	-0.7443	-44.78	-2.0181
0.5010	11.49	-0.6267	-42.07	-1.5967
0.6015	12.39	-0.4629	-39.28	-1.1095
0.7002	13.43	-0.1544	-36.12	-0.2165
0.8006	14.39	0.0720	-33.21	0.3886
0.8996	15.23	0.1797	-30.70	0.6337
1.0000	15.79	0.0000	-29.03	0.0000

Table 4.31 Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of n-Propanol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1009	9.06	-0.8214	-51.26	-2.6013
0.2002	9.95	-1.3585	-49.53	-4.1036
0.2990	11.40	-1.3359	-45.90	-3.6902
0.4007	12.37	-1.8243	-43.72	-4.8313
0.5001	12.88	-2.7510	-43.20	-7.5484
0.5988	13.99	-3.0576	-40.77	-8.3359
0.7013	15.21	-3.3187	-38.40	-9.3070
0.7990	16.67	-3.2690	-35.17	-9.2597
0.8997	18.97	-2.4138	-29.42	-6.7868
1.0000	22.83	0.0000	-19.36	0.0000

Table 4.32: Enthalpy(ΔH^{*}), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^{*}) and Excess entropy(ΔS^{*E}) of iso-Propanol + DMF system

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.0987	8.71	-1.0214	-51.19	-2.8575
0.1996	8.93	-2.1425	-50.71	-6.0727
0.3002	9.28	-3.1163	-49.85	-8.8919
0.4006	9.88	-3.8444	-48.16	-10.8866
0.5008	10.86	-4.1965	-45.35	-11.7482
0.6006	11.97	-4.4106	-42.22	-12.2726
0.7003	13.36	-4.3327	-38.24	-11.9459
0.7996	14.97	-4.0431	-33.94	-11.2812
0.9012	17.99	-2.3703	-25.47	-6.5317
1.0000	21.66	0.0000	-15.32	0.0000

Table 4.33: Enthalpy(ΔH^{*}), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^{*}) and Excess entropy(ΔS^{*E}) of n-Butanol + DMF system

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1009	8.77	-0.7696	-51.53	-2.1818
0.1990	9.51	-1.1089	-49.78	-2.9617
0.2982	9.84	-1.8720	-49.33	-5.0627
0.4008	10.42	-2.4223	-48.16	-6.5388
0.4999	11.38	-2.5599	-45.81	-6.7473
0.5997	12.47	-2.5712	-43.16	-6.6679
0.7003	13.05	-3.0954	-42.28	-8.3872
0.7989	14.92	-2.3150	-37.39	-6.0431
0.9006	16.19	-2.1645	-34.80	-6.0750
1.0000	19.45	0.0000	-26.16	0.0000

Table 4.34: Enthalpy(ΔH^{*}), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^{*}) and Excess entropy(ΔS^{*E}) of iso-Butanol + DMF system

X_2	$\frac{\Delta H^{*}}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*}}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1009	8.99	-0.9981	-50.69	-2.6223
0.1997	9.57	-1.9432	-49.61	-5.3377
0.3003	10.33	-2.7287	-48.04	-7.6319
0.4005	11.43	-3.1788	-45.46	-8.9069
0.4995	12.08	-4.0624	-44.33	-11.5869
0.5995	13.39	-4.2897	-41.17	-12.2688
0.7006	16.48	-2.7609	-32.57	-7.5589
0.7998	20.22	-0.5562	-22.03	-0.8350
0.8996	22.49	0.1788	-16.31	1.0505
1.0000	23.87	0.0000	-13.50	0.0000

Table 4.35: Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of tert-Butanol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.0997	9.48	-1.5060	-49.40	-4.4835
0.2017	10.22	-3.3832	-47.80	-10.0872
0.2995	11.93	-4.1833	-43.20	-12.3999
0.3990	13.14	-5.5240	-40.25	-16.4759
0.5004	14.55	-6.7161	-36.71	-20.0932
0.6010	16.76	-7.0916	-30.81	-21.2959
0.7004	19.25	-7.1521	-24.10	-21.6022
0.8011	22.90	-6.0858	-13.82	-18.4357
0.9001	28.04	-3.4851	0.99	-10.6113
1.0000	34.08	0.0000	18.66	0.0000

Table 4.36: Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of n-Amyl alcohol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1009	9.06	-0.8214	-51.26	-2.6013
0.2002	9.95	-1.3585	-49.53	-4.1036
0.2990	11.40	-1.3359	-45.90	-3.6902
0.4007	12.37	-1.8243	-43.72	-4.8313
0.5001	12.88	-2.7510	-43.20	-7.5484
0.5988	13.99	-3.0576	-40.77	-8.3359
0.7013	15.21	-3.3187	-38.40	-9.3070
0.7990	16.67	-3.2690	-35.17	-9.2597
0.8997	18.97	-2.4138	-29.42	-6.7868
1.0000	22.83	0.0000	-19.36	0.0000

Table 4.37: Enthalpy(ΔH^*), Excess enthalpy(ΔH^{*E}), Entropy(ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Amyl alcohol + DMF system

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{kJ.mol^{-1}}$	$\frac{\Delta S^{*E}}{kJ.mol^{-1}}$
0.0000	8.43	0.0000	-51.95	0.0000
0.1009	9.16	-0.6659	-50.70	-1.8850
0.2002	10.17	-1.0357	-48.56	-2.8381
0.2990	10.98	-1.5988	-47.08	-4.4353
0.4007	12.12	-1.8668	-44.63	-5.1488
0.5001	13.34	-2.0208	-41.88	-5.4951
0.5988	14.75	-1.9804	-38.55	-5.2277
0.7013	15.71	-2.4460	-36.84	-6.7156
0.7990	17.30	-2.2157	-33.10	-6.0071
0.8997	19.18	-1.7265	-28.75	-4.7987
1.0000	22.30	0.0000	-20.83	0.0000

Table 4.38. Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the DMF +Methanol, +Ethanol, + n-Propanol, +iso-Propanol systems

Systems	T/K	a_0	a_1	a_2	a_3	σ
DMF+Methanol systems	298.15	-2.1429	-0.5600	-0.7700	1.5825	0.0302
	303.15	-2.0281	-0.5080	-0.4910	0.7539	0.0342
	308.15	-1.8496	-0.2618	-0.4546	0.4116	0.0299
DMF+Ethanol systems	298.15	-1.8496	-0.2618	-0.4546	0.4116	0.0299
	303.15	-1.1611	0.2259	-1.0242	1.4585	0.0233
	308.15	-0.8995	0.1900	-0.4841	1.9520	0.0146
	313.15	-0.7387	0.2484	0.0597	2.2167	0.0211
	318.15	-0.6005	0.4282	0.1689	1.7516	0.0104
	323.15	-0.4664	0.6177	0.3532	1.4104	0.0081
DMF+*n*-Propanol systems	298.15	-0.8287	0.1826	-1.0097	1.4507	0.0298
	303.15	-0.5169	0.0615	-1.0063	1.2432	0.0191
	308.15	-0.2083	-0.1584	-0.3875	2.5991	0.0105
	313.15	0.0022	-0.1757	-0.3146	2.3811	0.0186
	318.15	0.1602	-0.3125	-0.3777	2.8601	0.0172
	323.15	0.3190	0.0244	-0.1786	2.3471	0.0292
DMF+*iso*-Propanol systems	298.15	-1.1988	0.0476	-1.4880	0.3770	0.0119
	303.15	-0.6791	0.1567	-1.2845	0.2027	0.0166
	308.15	-0.1260	0.6822	-0.9207	-0.8413	0.0134
	313.15	0.3114	1.2141	0.0776	-2.2966	0.0151
	318.15	0.5895	0.8807	0.7075	-1.4184	0.0128
	323.15	0.9999	0.3424	1.2263	-0.7982	0.0102

Table 4.39. Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the DMF+n-Butanol, +iso-Butanol, +tert-Butanol, +n-Amyl alcohol, +iso-Amyl alcohol systems

Systems	T/K	a_0	a_1	a_2	a_3	σ
DMF+n-Butanol systems	298.15	-0.2247	0.2691	-0.6893	0.2763	0.0381
	303.15	-0.3770	-0.2279	-0.7431	0.7207	0.0442
	308.15	-0.3836	-1.2974	-1.0359	1.8105	0.0495
	313.15	-0.3767	-0.8338	-0.3978	1.1470	0.0479
	318.15	-0.0064	-0.3838	-0.6157	0.9346	0.0395
	323.15	0.2139	-0.5138	-1.0761	-0.0593	0.0685
DMF+iso-Butanol systems	298.15	-0.3030	-0.7225	-6.9703	3.7401	0.0865
	303.15	-0.1349	-0.8753	-5.5388	3.0892	0.0505
	308.15	0.0312	0.2237	-5.7556	2.2581	0.0747
	313.15	0.1648	-0.9475	-6.0573	4.3080	0.0508
	318.15	0.0186	-0.9958	-5.4275	5.8775	0.0755
	323.15	-0.3628	-0.4787	-6.0249	2.1472	0.0699
DMF+tert-Butanol systems	298.15	-0.9583	0.4600	-0.0463	-2.6635	0.0491
	303.15	-1.2894	0.8701	-0.6370	-1.7106	0.0390
	308.15	-1.1396.	1.1040	-0.2778	-1.2591	0.0288
	313.15	-1.4096	0.7147	-0.0529	0.9476	0.0183
	318.15	-1.8413	1.2322	0.3687	-1.9465	0.0340
	323.15	-1.9273	0.9571	-0.8832	-1.4537	0.0366
DMF+Amyl alcohol systems	298.15	-1.0866	-0.3403	-2.9331	2.8876	0.0212
	303.15	-0.7885	0.2274	-2.9061	1.0761	0.0222
	308.15	-0.8905	0.3914	-2.7049	1.1686	0.0308
	313.15	-1.1399	0.7316	-2.3521	-0.0000	0.0414
	318.15	-1.7202	0.3336	-4.2639	-0.9080	0.0591
	323.15	-1.9781	0.5742	-5.0567	-2.6781	0.0696
DMF+iso-Amyl alcohol systems	298.15	-2.0606	-0.5211	-0.5253	-0.6826	0.0281
	303.15	-1.4894	-0.8276	-0.4510	-0.1400	0.0298
	308.15	-1.5271	-0.1743	-0.5636	-1.8137	0.0423
	313.15	-1.5990	-1.0889	-1.1601	-0.3084	0.0258
	318.15	-1.4629	-0.9474	0.1407	0.7720	0.0278
	323.15	-1.2081	-1.6349	-1.0471	1.4092	0.0229

Table 4.40. Coefficient, a_i, of Redlich- Kister Eq express in η^E and standard deviation, σ for the DMF + Methanol, +Ethanol, +n-Propanol, +iso-Propanol systems

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
DMF+Methanol systems	298.15	0.1054	-0.1061	0.1010	-0.0005	0.0010
	303.15	0.0852	-0.0948	0.1076	-0.0395	0.0006
	308.15	0.0760	-0.0921	0.1064	-0.0322	0.0010
DMF+Ethanol systems	298.15	-0.2289	-0.0468	0.2162	0.1868	0.0021
	303.15	-0.2611	0.0258	0.1493	0.0324	0.0020
	308.15	-0.2144	-0.0390	0.1926	0.0485	0.0023
	313.15	-0.1873	-0.0802	0.1410	0.0079	0.0013
	318.15	-0.1398	-0.0591	0.1086	0.0341	0.0013
	323.15	-0.1305	-0.0285	0.0822	-0.0429	0.0011
DMF+n-Propanol systems	298.15	-0.9240	-1.0686	-0.5207	0.0057	0.0024
	303.15	-0.8256	-0.8912	-0.5546	0.0348	0.0013
	308.15	-0.7297	-0.7712	-0.3045	0.0933	0.0027
	313.15	-0.6407	-0.6575	-0.3187	-0.1257	0.0027
	318.15	-0.5247	-0.4168	-0.3164	-0.3477	0.0047
	323.15	-0.4792	-0.4022	-0.2346	-0.2285	0.0041
DMF+iso-Propanol systems	298.15	-1.1769	-1.2306	-1.1478	-0.7383	0.0030
	303.15	-1.0384	-0.9565	-0.8654	-0.4333	0.0041
	308.15	-0.8518	-0.9061	-0.5966	-0.0466	0.0044
	313.15	-0.6807	-0.7448	-0.4180	-0.0215	0.0030
	318.15	-0.5321	-0.5650	-0.4391	-0.0903	0.0037
	323.15	-0.4272	-0.4017	-0.3351	-0.0813	0.0018

Table 4.41: Coefficient, a_i, of Redlich- Kister Eq expressing η^E and standard deviation, σ for the DMF, +n-Butanol, +iso-Butanol, +tert-Butanol, +n-Amyl alcohol, +iso-Amyl alcohol systems

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
DMF+n-Butanol systems	298.15	-1.1275	-1.1829	-1.0972	-1.0662	0.0081
	303.15	-0.9614	-1.0176	-0.9201	-0.6515	0.0072
	308.15	-0.8138	-0.8251	-0.5479	-0.4664	0.0033
	313.15	-0.6765	-0.6978	-0.4518	-0.3465	0.0048
	318.15	-0.5848	-0.5960	-0.3458	-0.2001	0.0025
	323.15	-0.4854	-0.4805	-0.2236	-0.1038	0.0044
DMF+iso-Butanol systems	298.15	-1.4625	-1.4299	0.0376	1.0554	0.0119
	303.15	-1.1921	-1.1888	0.2447	1.4688	0.0105
	308.15	-0.8927	-0.7898	0.1579	0.9675	0.0090
	313.15	-0.7414	-0.6376	-0.0553	0.5365	0.0059
	318.15	-0.5674	-0.4423	-0.4183	-0.1406	0.0028
	323.15	-0.4578	-0.3704	-0.3611	-0.0125	0.0033
DMF+tert-Butanol systems	298.15	-1.8908	-2.5583	-1.5729	0.0317	0.0183
	303.15	-1.3734	-1.5060	-0.9708	-0.3360	0.0047
	308.15	-1.0017	-0.9210	-0.4410	-0.3749	0.0048
	313.15	-0.6992	-0.6679	-0.1468	0.2314	0.0040
	318.15	-0.4829	-0.3465	-0.0506	0.1244	0.0030
	323.15	-0.3397	-0.1859	0.0756	0.1218	0.0046
DMF+Amyl alcohol systems	298.15	-1.2410	-1.8541	-1.7598	-1.8204	0.0275
	303.15	-1.0762	-1.5023	-1.3693	-1.3547	0.0203
	308.15	-0.8724	-1.0072	-0.9200	-1.5111	0.0196
	313.15	-0.7277	-0.9112	-0.7511	-1.0066	0.0127
	318.15	-0.5955	-0.6616	-0.2837	-0.7807	0.0158
	323.15	-0.5046	-0.5669	-0.1459	-0.4809	0.0086
DMF+iso-Amyl alcohol systems	298.15	-0.9785	-1.2915	-1.6381	-1.2783	0.0079
	303.15	-0.8556	-1.0570	-1.6036	-1.2129	0.0074
	308.15	-0.7003	-0.8277	-1.0104	-0.7837	0.0027
	313.15	-0.5864	-0.5989	-0.6875	-0.6036	0.0045
	318.15	-0.5052	-0.5437	-0.5728	-0.4136	0.0047
	323.15	-0.3817	-0.5082	-0.4680	-0.1563	0.0046

Table 4.42. Coefficient, a_i, of Redlich- Kister Eq express in ΔG^E and standard deviation, σ for the DMF +Methanol, +Ethanol, + n-Propanol, +iso-Propanol systems

Systems	T/ K	a_o	a_1	a_2	a_3	σ
DMF+Methanol systems	298.15	0.8029	-0.2506	0.3000	0.0887	0.0040
	303.15	0.7632	-0.2457	0.3451	-0.0667	0.0028
	308.15	0.7630	-0.2482	0.3752	-0.0745	0.0048
DMF+Ethanol systems	298.15	-0.5025	0.0469	0.4531	0.3703	0.0051
	303.15	-0.6393	0.2510	0.3570	0.0529	0.0052
	308.15	-0.5596	0.0261	0.5863	0.1184	0.0068
	313.15	-0.5283	0.1344	0.5342	0.0343	0.0043
	318.15	-0.4124	-0.1162	0.4428	0.1514	0.0049
	323.15	-0.4186	-0.0076	0.3869	-0.1565	0.0040
DMF+ n-Propanol Systems	298.15	-2.0842	-1.6205	-0.2081	0.6719	0.0066
	303.15	-2.0533	-1.5252	-0.5625	0.8101	0.0028
	308.15	-1.9857	-1.4609	-0.0930	0.7459	0.0075
	313.15	-1.9190	-1.4284	-0.1878	0.2208	0.0084
	318.15	-1.7292	-0.9369	-0.4031	-0.5419	0.0134
	323.15	-1.7280	-1.0514	-0.2597	-0.3088	0.0140
DMF+ iso-Propanol Systems	298.15	-2.6897	-1.7513	-1.0572	-0.3752	0.0096
	303.15	-2.6152	-1.4698	-0.9710	-0.0357	0.0087
	308.15	-2.3660	-1.7569	-0.6972	0.5925	0.0141
	313.15	-2.0843	-1.6912	-0.4750	0.4524	0.0105
	318.15	-1.7867	-1.4718	0.8292	0.2363	0.0109
	323.15	-1.5675	-1.1569	-0.7525	0.0856	0.0073

Table 4.43. Coefficient, a_i, of Redlich- Kister Eq expressing ΔG^E and standard deviation, σ for the DMF+n-Butanol, +iso-Butanol, +tert-Butanol, +n-Amyl alcohol, +iso-Amyl alcohol systems

Systems	T/K	a_0	a_1	a_2	a_3	σ
DMF+n-Butanol systems	298.15	-2.1809	-1.1977	-0.4842	-0.8277	0.0073
	303.15	-2.0534	-1.2582	-0.6591	-0.2517	0.0128
	308.15	-1.9105	-1.0788	-0.1803	-0.5055	0.0093
	313.15	-1.7496	-1.0781	-0.2419	-0.3979	0.0118
	318.15	-1.6619	-1.0807	-0.2060	-0.0831	0.0068
	323.15	-1.5056	-0.9730	-0.0914	-0.0378	0.0127
DMF+iso-Butanol systems	298.15	-2.4836	-0.7970	0.7024	1.8935	0.0215
	303.15	-2.2133	-0.7489	0.6616	2.3754	0.0134
	308.15	-1.8566	-0.5248	0.4198	1.8504	0.0161
	313.15	-1.8566	-0.5248	0.4198	1.8504	0.0161
	318.15	-1.4918	-0.4149	-0.6867	0.1782	0.0082
	323.15	-1.3247	-0.4976	-0.7715	0.5490	0.0110
DMF+tert-Butanol systems	298.15	-2.9181	-1.6061	-0.0944	1.1001	0.0225
	303.15	-2.4434	-0.9668	-0.1021	0.1956	0.0101
	308.15	-2.0454	-0.5826	0.2584	-0.5214	0.0139
	313.15	-1.6022	-0.6696	0.2083	0.6090	0.0090
	318.15	-1.2418	-0.2975	0.1325	0.2922	0.0085
	323.15	-0.9670	-0.1089	0.3427	0.1353	0.0114
DMF+Amyl alcohol systems	298.15	-1.9112	-1.7907	-0.2278	-0.8281	0.0265
	303.15	-1.8273	-1.6073	-0.2936	-0.6227	0.0240
	308.15	-1.6558	-1.0865	0.0569	-1.6923	0.0236
	313.15	-1.5224	-1.2140	-0.0843	-1.1300	0.0169
	318.15	-1.3705	-0.9953	0.5698	-1.2417	0.0308
	323.15	-1.2706	-0.9516	0.6186	-0.9557	0.0173
DMF+iso-Amyl alcohol systems	298.15	-1.4952	-0.9935	-0.9063	-0.5735	0.0091
	303.15	-1.4531	-0.9309	-1.3211	-0.5154	0.0077
	308.15	-1.3169	-0.7937	-0.7932	-0.6103	0.0074
	313.15	-1.2212	-0.5749	-0.5875	-0.7099	0.0107
	318.15	-1.1578	-0.7318	-0.5891	-0.3062	0.0091
	323.15	-0.9322	-0.9124	-0.6212	0.1340	0.0118

Table-4.44: Density and viscosity of Sodium dodecyl sulfate (SDS) in DMF solution at 298.15K, 303.15K and 308.15K

Concentration ($mol.L^{-1}$)	Density ($gm\ cm^{-3}$)			Viscosity (cP)		
	298.15K	303.15K	308.15K	298.15K	303.15K	308.15K
0.001	0.942833	0.939706	0.935822	0.8098	0.7733	0.7163
0.005	0.943101	0.940003	0.936010	0.8770	0.8351	0.7750
0.01	0.943605	0.940572	0.936601	0.9568	0.9150	0.8439
0.015	0.943900	0.940901	0.936801	0.7213	0.6891	0.6355
0.02	0.944802	0.941902	0.938198	0.8489	0.8008	0.7486
0.025	0.945501	0.942700	0.939228	0.9438	0.8826	0.8036
0.03	0.946205	0.943403	0.940100	0.9421	0.8840	0.8091
0.04	0.947300	0.944702	0.941600	0.9601	0.8931	0.8270

Table-4.45: Density (ρ) and Excess molar volume (V^E) of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942894	0.0000	0.940604	0.0000	0.936416	0.0000	0.931546	0.0000	0.925339	0.0000	0.919122	0.0000
0.1004	0.929375	-0.0307	0.927081	-0.0489	0.923000	-0.0615	0.917800	-0.0268	0.910900	0.0386	0.904300	0.1017
0.2001	0.916400	-0.1071	0.914034	-0.1378	0.909085	-0.0801	0.903600	-0.0133	0.897000	0.0328	0.890800	0.0896
0.2991	0.902521	-0.1076	0.899036	-0.0604	0.894900	-0.0741	0.889335	0.0081	0.883047	0.0335	0.877300	0.0785
0.3999	0.887594	-0.0474	0.884500	-0.0506	0.880000	-0.0348	0.875500	-0.0379	0.868900	0.0216	0.862789	0.1289
0.5002	0.872652	0.0140	0.869784	-0.0258	0.865205	-0.0046	0.860738	-0.0027	0.854000	0.0772	0.848441	0.1641
0.5995	0.858214	0.0370	0.855695	-0.0508	0.850940	-0.0157	0.845718	0.0627	0.840000	0.0570	0.834300	0.1860
0.7007	0.843978	-0.0477	0.841616	-0.1678	0.837090	-0.1562	0.831800	-0.0643	0.824760	0.0587	0.819000	0.2241
0.8011	0.829632	-0.0067	0.827570	-0.1715	0.822786	-0.1372	0.817300	-0.0170	0.810003	0.1409	0.803700	0.3902
0.8985	0.814800	0.0533	0.811925	-0.0529	0.807421	-0.0441	0.802860	-0.0011	0.796500	0.0759	0.790200	0.3545
1.0000	0.800501	0.0000	0.796323	0.0000	0.791910	0.0000	0.787892	0.0000	0.782407	0.0000	0.779224	0.0000

Table-4.46: Density (ρ) and Excess molar volume (V^E) of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942894	0.0000	0.940604	0.0000	0.936416	0.0000	0.931546	0.0000	0.925339	0.0000	0.919122	0.0000
0.1009	0.928511	-0.1281	0.926096	-0.1317	0.921295	-0.0893	0.916019	-0.0659	0.909700	-0.0510	0.903700	-0.0634
0.1989	0.912750	-0.0558	0.910581	-0.0934	0.906400	-0.1131	0.901481	-0.1312	0.895082	-0.1036	0.888482	-0.0540
0.2982	0.898451	-0.0820	0.895900	-0.0984	0.891700	-0.1250	0.886900	-0.1647	0.880300	-0.1115	0.874000	-0.0813
0.4008	0.883600	-0.0546	0.881036	-0.0823	0.876516	-0.0869	0.871900	-0.1545	0.866200	-0.1812	0.858972	-0.0506
0.4998	0.869762	-0.0277	0.867700	-0.1164	0.862900	-0.1009	0.858000	-0.1509	0.852000	-0.1419	0.845100	-0.0321
0.5997	0.855691	0.0574	0.853873	-0.0691	0.849548	-0.1079	0.845192	-0.2237	0.838800	-0.1680	0.832800	-0.1427
0.7003	0.843034	-0.0431	0.841273	-0.1901	0.836867	-0.2292	0.832853	-0.3932	0.826659	-0.3530	0.820158	-0.2668
0.7989	0.830575	0.1051	0.828505	-0.0227	0.824513	-0.1120	0.820533	-0.2915	0.814291	-0.2367	0.807219	-0.0728
0.9006	0.818974	0.0001	0.816500	-0.0969	0.812100	-0.1494	0.806700	-0.1800	0.801300	-0.2120	0.794900	-0.1130
1.0000	0.807425	0.0000	0.804000	0.0000	0.799100	0.0000	0.793400	0.0000	0.787800	0.0000	0.782338	0.0000

Table-4.47: Density (ρ) and Excess molar volume (V^E) of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.942894	0.0000	0.940604	0.0000	0.936416	0.0000	0.931546	0.0000	0.925339	0.0000	0.919122	0.0000
0.1009	0.926545	-0.1800	0.923767	-0.1442	0.919076	-0.0956	0.913900	-0.0663	0.909006	-0.1784	0.902647	-0.1539
0.2002	0.908477	-0.0696	0.906001	-0.0644	0.902057	-0.0768	0.897100	-0.0630	0.890800	-0.0396	0.884724	-0.0257
0.2990	0.893354	-0.1076	0.890913	-0.1105	0.887141	-0.1357	0.881900	-0.0901	0.875700	-0.0687	0.869389	-0.0173
0.4007	0.878473	-0.1060	0.875519	-0.0607	0.871732	-0.0800	0.866400	-0.0181	0.860249	0.0078	0.854179	0.0501
0.5001	0.864841	-0.0959	0.862513	-0.1203	0.858568	-0.1186	0.852900	-0.0133	0.847236	-0.0335	0.840781	0.0666
0.5988	0.853361	-0.2185	0.849985	-0.1296	0.845689	-0.0825	0.840855	-0.0649	0.834800	-0.0336	0.828900	0.0171
0.7013	0.840700	-0.1719	0.838100	-0.1744	0.833877	-0.1290	0.829258	-0.1335	0.823693	-0.1547	0.817300	-0.0294
0.7990	0.829028	-0.0832	0.826551	-0.1037	0.822623	-0.0877	0.819006	-0.2156	0.813400	-0.2266	0.807227	-0.1142
0.8997	0.818020	-0.0293	0.816000	-0.1130	0.812460	-0.1422	0.807800	-0.1342	0.802200	-0.1382	0.796600	-0.0862
1.0000	0.807884	0.0000	0.805203	0.0000	0.801484	0.0000	0.796924	0.0000	0.791358	0.0000	0.786230	0.0000

Table-4.48: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.8361	0.0000	0.0000	0.7956	0.0000	0.0000	0.7429	0.0000	0.0000	0.6955	0.0000	0.0000	0.6560	0.0000	0.0000	0.6169	0.0000	0.0000
0.1004	0.8705	-0.0385	-0.4791	0.8168	-0.0416	-0.5500	0.7630	-0.0354	-0.5025	0.7233	-0.0212	-0.3193	0.6730	-0.0247	-0.3991	0.6323	-0.0209	-0.3601
0.2001	0.9002	-0.0875	-0.5795	0.8500	-0.0756	-0.5323	0.7866	-0.0710	-0.5402	0.7409	-0.0556	-0.4517	0.6850	-0.0567	-0.4972	0.6450	-0.0463	-0.4335
0.2991	0.9420	-0.1306	-0.6195	0.8820	-0.1156	-0.5875	0.8150	-0.1059	-0.5827	0.7600	-0.0917	-0.5433	0.7016	-0.0865	-0.5549	0.6628	-0.0687	-0.4702
0.3999	0.9873	-0.1793	-0.6953	0.9250	-0.1516	-0.6325	0.8470	-0.1430	-0.6502	0.7933	-0.1185	-0.5801	0.7340	-0.1045	-0.5545	0.6850	-0.0896	-0.5122
0.5002	1.0359	-0.2324	-0.8096	0.9688	-0.1927	-0.7257	0.8870	-0.1770	-0.7277	0.8270	-0.1489	-0.6622	0.7660	-0.1257	-0.6078	0.7093	-0.1108	-0.5804
0.5995	1.1139	-0.2637	-0.8850	1.0396	-0.2125	-0.7746	0.9391	-0.2035	-0.8170	0.8747	-0.1691	-0.7361	0.8150	-0.1327	-0.6284	0.7526	-0.1152	-0.5931
0.7007	1.2149	-0.2918	-1.0391	1.1345	-0.2237	-0.8687	1.0087	-0.2256	-0.9744	0.9445	-0.1781	-0.8338	0.8760	-0.1363	-0.6983	0.8030	-0.1195	-0.6698
0.8011	1.3571	-0.2724	-1.1481	1.2544	-0.2040	-0.9455	1.1230	-0.1976	-1.0172	1.0248	-0.1716	-0.9717	0.9399	-0.1326	-0.8283	0.8591	-0.1141	-0.7828
0.8985	1.5640	-0.2033	-1.3401	1.4297	-0.1401	-1.0253	1.2739	-0.1425	-1.1623	1.1585	-0.1195	-1.0763	1.0375	-0.1011	-1.0192	0.9478	-0.0810	-0.8987
1.0000	1.9233	0.0000	0.0000	1.6951	0.0000	0.0000	1.5234	0.0000	0.0000	1.3689	0.0000	0.0000	1.2118	0.0000	0.0000	1.0899	0.0000	0.0000

Table-4.49: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.8361	0.0000	0.0000	0.7956	0.0000	0.0000	0.7429	0.0000	0.0000	0.6955	0.0000	0.0000	0.6560	0.0000	0.0000	0.6169	0.0000	0.0000
0.1009	0.9230	-0.0143	-0.1699	0.8610	-0.0224	-0.2832	0.7830	-0.0375	-0.5155	0.7410	-0.0222	-0.3261	0.6940	-0.0213	-0.3326	0.6520	-0.0163	-0.2730
0.1989	0.9910	-0.0564	-0.3476	0.9229	-0.0551	-0.3639	0.8338	-0.0698	-0.5048	0.7819	-0.0534	-0.4150	0.7338	-0.0441	-0.3663	0.6854	-0.0370	-0.3300
0.2982	1.0590	-0.1132	-0.4852	0.9816	-0.1025	-0.4747	0.8973	-0.0992	-0.5009	0.8303	-0.0850	-0.4658	0.7817	-0.0653	-0.3832	0.7295	-0.0521	-0.3299
0.4008	1.1574	-0.1593	-0.5369	1.0700	-0.1359	-0.4979	0.9785	-0.1239	-0.4965	0.8969	-0.1090	-0.4776	0.8350	-0.0898	-0.4254	0.7770	-0.0709	-0.3635
0.4998	1.2520	-0.2210	-0.6504	1.1630	-0.1734	-0.5559	1.0635	-0.1518	-0.5336	0.9721	-0.1298	-0.5013	0.8882	-0.1185	-0.5010	0.8309	-0.0862	-0.3950
0.5997	1.3830	-0.2666	-0.7344	1.2765	-0.2059	-0.6228	1.1553	-0.1856	-0.6205	1.0430	-0.1651	-0.6120	0.9600	-0.1367	-0.5544	0.8931	-0.0997	-0.4410
0.7003	1.5130	-0.3541	-1.0194	1.4140	-0.2464	-0.7787	1.2730	-0.2203	-0.7736	1.1430	-0.1929	-0.7560	1.0380	-0.1663	-0.7204	0.9700	-0.1127	-0.5329
0.7989	1.7110	-0.3473	-1.1339	1.5810	-0.2344	-0.8484	1.4190	-0.2063	-0.8327	1.2630	-0.1830	-0.8303	1.1530	-0.1434	-0.7194	1.0360	-0.1232	-0.6896
0.9006	2.1230	-0.1969	-0.9908	1.9034	-0.1223	-0.6957	1.6856	-0.1178	-0.7547	1.4997	-0.0939	-0.6784	1.3393	-0.0799	-0.6471	1.2000	-0.0605	-0.5494
1.0000	2.5965	0.0000	0.0000	2.2458	0.0000	0.0000	1.9888	0.0000	0.0000	1.7463	0.0000	0.0000	1.5454	0.0000	0.0000	1.3639	0.0000	0.0000

Table-4.50: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	0.8361	0.0000	0.0000	0.7956	0.0000	0.0000	0.7429	0.0000	0.0000	0.6955	0.0000	0.0000	0.6560	0.0000	0.0000	0.6169	0.0000	0.0000
0.1009	0.9330	-0.0394	-0.4555	0.8850	-0.0314	-0.3840	0.8257	-0.0227	-0.2993	0.7752	-0.0125	-0.1770	0.7140	-0.0222	-0.3374	0.6560	-0.0308	-0.5057
0.2002	1.0260	-0.1022	-0.5929	0.9720	-0.0811	-0.5007	0.9040	-0.0630	-0.4206	0.8410	-0.0494	-0.3561	0.7780	-0.0467	-0.3637	0.7114	-0.0519	-0.4397
0.2990	1.1370	-0.1710	-0.6685	1.0640	-0.1455	-0.6114	0.9820	-0.1193	-0.5472	0.9140	-0.0917	-0.4563	0.8510	-0.0722	-0.3886	0.7680	-0.0798	-0.4717
0.4007	1.2640	-0.2591	-0.7764	1.1670	-0.2277	-0.7421	1.0712	-0.1880	-0.6734	0.9870	-0.1531	-0.6006	0.9190	-0.1180	-0.5030	0.8210	-0.1236	-0.5841
0.5001	1.4290	-0.3384	-0.8502	1.3183	-0.2847	-0.7821	1.1980	-0.2373	-0.7227	1.0790	-0.2098	-0.7108	1.0000	-0.1617	-0.5996	0.8915	-0.1584	-0.6542
0.5988	1.6210	-0.4278	-0.9748	1.4952	-0.3455	-0.8653	1.3314	-0.3031	-0.8537	1.1922	-0.2634	-0.8310	1.0988	-0.2016	-0.7013	0.9670	-0.1991	-0.7793
0.7013	1.8710	-0.5175	-1.1658	1.7250	-0.3999	-0.9954	1.5430	-0.3278	-0.9195	1.3585	-0.2933	-0.9333	1.2350	-0.2270	-0.8056	1.0863	-0.2141	-0.8586
0.799	2.1883	-0.5764	-1.4559	1.9910	-0.4457	-1.2577	1.7790	-0.3486	-1.1141	1.5873	-0.2760	-0.9984	1.4135	-0.2213	-0.9056	1.2745	-0.1682	-0.7718
0.8997	2.7445	-0.4700	-1.7516	2.4749	-0.3309	-1.3906	2.1513	-0.2780	-1.3468	1.9054	-0.2044	-1.1293	1.6978	-0.1363	-0.8557	1.5084	-0.0974	-0.6933
1.0000	3.7352	0.0000	0.0000	3.2290	0.0000	0.0000	2.7723	0.0000	0.0000	2.3876	0.0000	0.0000	2.0568	0.0000	0.0000	1.7865	0.0000	0.0000

Table 4.51: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.62	12.71	12.76	12.81	12.87	12.93	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1004	12.71	12.77	12.82	12.90	12.93	12.99	-0.1081	-0.1267	-0.1182	-0.0759	-0.0940	-0.0838
0.2001	12.78	12.86	12.89	12.95	12.97	13.03	-0.2332	-0.2191	-0.2240	-0.1885	-0.2092	-0.1832
0.2991	12.89	12.95	12.97	13.01	13.03	13.10	-0.3251	-0.3122	-0.3152	-0.2960	-0.3063	-0.2619
0.3999	13.00	13.06	13.06	13.12	13.14	13.18	-0.4148	-0.3840	-0.4007	-0.3635	-0.3510	-0.3255
0.5002	13.11	13.17	13.17	13.22	13.25	13.27	-0.5010	-0.4579	-0.4660	-0.4309	-0.3990	-0.3839
0.5995	13.28	13.34	13.31	13.36	13.40	13.42	-0.5253	-0.4702	-0.5029	-0.4578	-0.3969	-0.3759
0.7007	13.49	13.55	13.48	13.55	13.59	13.59	-0.5357	-0.4598	-0.5231	-0.4525	-0.3813	-0.3656
0.8011	13.76	13.79	13.75	13.75	13.77	13.77	-0.4535	-0.3852	-0.4197	-0.4035	-0.3441	-0.3215
0.8985	14.10	14.12	14.07	14.07	14.02	14.02	-0.3011	-0.2373	-0.2730	-0.2555	-0.2432	-0.2078
1.0000	14.60	14.54	14.52	14.49	14.42	14.37	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.52: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.62	12.71	12.76	12.81	12.87	12.93	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.90	12.95	12.94	13.02	13.07	13.13	-0.0389	-0.0655	-0.1191	-0.0754	-0.0776	-0.0647
0.1989	13.13	13.17	13.14	13.20	13.26	13.31	-0.1332	-0.1430	-0.2034	-0.1698	-0.1511	-0.1362
0.2982	13.33	13.37	13.38	13.40	13.48	13.52	-0.2466	-0.2456	-0.2643	-0.2505	-0.2070	-0.1793
0.4008	13.60	13.64	13.65	13.65	13.70	13.74	-0.3127	-0.2950	-0.2989	-0.2938	-0.2661	-0.2262
0.4998	13.84	13.89	13.90	13.91	13.91	13.97	-0.3950	-0.3446	-0.3353	-0.3210	-0.3256	-0.2561
0.5997	14.13	14.17	14.16	14.14	14.16	14.21	-0.4270	-0.3701	-0.3758	-0.3798	-0.3475	-0.2790
0.7003	14.39	14.47	14.45	14.42	14.41	14.48	-0.5164	-0.4040	-0.4089	-0.4108	-0.3966	-0.2962
0.7989	14.73	14.79	14.77	14.72	14.73	14.70	-0.4493	-0.3430	-0.3446	-0.3541	-0.3103	-0.2973
0.9006	15.31	15.30	15.25	15.21	15.17	15.14	-0.2168	-0.1565	-0.1740	-0.1598	-0.1558	-0.1319
1.0000	15.85	15.76	15.72	15.66	15.60	15.53	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.53: Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 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	12.62	12.71	12.76	12.81	12.87	12.93	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1009	12.98	13.08	13.13	13.19	13.20	13.20	-0.0936	-0.0776	-0.0576	-0.0287	-0.0712	-0.1125
0.2002	13.32	13.41	13.46	13.50	13.53	13.52	-0.2127	-0.1787	-0.1491	-0.1241	-0.1285	-0.1628
0.2990	13.66	13.73	13.76	13.81	13.86	13.83	-0.3187	-0.2938	-0.2649	-0.2181	-0.1834	-0.2315
0.4007	14.01	14.06	14.08	14.11	14.17	14.11	-0.4297	-0.4147	-0.3798	-0.3385	-0.2811	-0.3367
0.5001	14.40	14.45	14.45	14.43	14.48	14.42	-0.4934	-0.4592	-0.4287	-0.4249	-0.3586	-0.3981
0.5988	14.79	14.85	14.81	14.78	14.82	14.73	-0.5523	-0.4927	-0.4924	-0.4857	-0.4100	-0.4655
0.7013	15.23	15.29	15.27	15.20	15.21	15.13	-0.5808	-0.5005	-0.4668	-0.4819	-0.4193	-0.4524
0.799	15.70	15.73	15.72	15.69	15.65	15.64	-0.5599	-0.4895	-0.4381	-0.3999	-0.3670	-0.3122
0.8997	16.34	16.36	16.28	16.24	16.22	16.17	-0.3806	-0.3068	-0.3024	-0.2559	-0.1948	-0.1572
1.0000	17.18	17.11	17.01	16.91	16.80	16.71	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.54: Enthalpy($\Delta H^{\#}$), Excess enthalpy($\Delta H^{\#E}$), Entropy($\Delta S^{\#}$) and Excess entropy($\Delta S^{\#E}$) of n-Propanol +SDS+DMF system.

X_2	$\frac{\Delta H^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{kJ.mol^{-1}}$
0.0000	9.07	0.0000	-50.23	0.0000
0.1004	9.33	-0.5629	-49.64	-1.4866
0.2001	9.93	-0.7691	-47.89	-1.8014
0.2991	10.59	-0.9200	-46.02	-1.9867
0.3999	10.93	-1.4007	-45.26	-3.3074
0.5002	11.29	-1.8526	-44.42	-4.5481
0.5995	11.72	-2.2353	-43.55	-5.7315
0.7070	12.34	-2.4876	-42.14	-6.5497
0.8011	13.80	-1.7968	-38.18	-4.5354
0.8985	15.31	-1.0779	-34.28	-2.6554
1.0000	17.22	0.0000	-29.52	0.0000

Table 4.55: Enthalpy($\Delta H^{\#}$), Excess enthalpy($\Delta H^{\#E}$), Entropy($\Delta S^{\#}$) and Excess entropy($\Delta S^{\#E}$) of n-Butanol +SDS+DMF system.

X_2	$\frac{\Delta H^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{kJ.mol^{-1}}$
0.0000	9.07	0.0000	-50.23	0.0000
0.1009	10.29	0.1745	-47.01	0.7983
0.1989	11.02	-0.1119	-45.31	0.1425
0.2982	11.13	-1.0308	-45.64	-2.5708
0.4008	12.03	-1.1954	-43.54	-2.9399
0.4998	12.56	-1.6873	-42.60	-4.3706
0.5997	13.51	-1.7744	-40.37	-4.5425
0.7090	14.02	-2.3963	-39.61	-6.4085
0.7950	15.43	-1.8791	-36.06	-4.9231
0.9006	17.45	-0.9565	-31.15	-2.5453
1.0000	19.44	0.0000	-26.22	0.0000

Table 4.56: Enthalpy($\Delta H^{\#}$), Excess enthalpy($\Delta H^{\#E}$), Entropy($\Delta S^{\#}$) and Excess entropy($\Delta S^{\#E}$) of n-Amyl alcohol+SDS+DMF system.

X_2	$\frac{\Delta H^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{kJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{kJ.mol^{-1}}$
0.0000	9.07	0.0000	-50.23	0.0000
0.1009	10.43	-0.0315	-46.97	0.1351
0.2002	10.89	-0.9488	-46.56	-2.5413
0.2990	11.48	-1.7222	-45.69	-4.7334
0.4007	12.61	-1.9925	-43.05	-5.2441
0.5001	14.14	-1.8323	-39.25	-4.5231
0.5988	15.61	-1.7263	-35.67	-4.0018
0.7013	16.69	-2.0632	-33.57	-5.0849
0.7990	16.74	-3.3582	-34.89	-9.4333
0.8997	18.56	-2.9248	-30.90	-8.5580
1.0000	22.87	0.0000	-19.23	0.0000

Table 4.57. Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the n-Propanol, n-Butanol, Amyl alcohol in SDS containing DMF systems

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
DMF+SDS+n-Propanol	298.15	-0.0826	0.5020	-0.4227	0.0572	0.0440
	303.15	-0.2087	-0.5126	-1.4212	0.7550	0.0451
	308.15	-0.1303	-0.4229	-1.3089	0.6332	0.0417
	313.15	0.0068	-0.0306	-0.3384	0.1070	0.0390
	318.15	0.1783	0.3045	0.7591	0.1494	0.0251
	323.15	0.5027	0.6500	2.7370	1.9669	0.0376
DMF+SDS+n-Butanol	298.15	-0.0515	0.4890	-0.3961	0.6387	0.0528
	303.15	-0.3761	-0.3317	-0.8341	1.1419	0.0522
	308.15	-0.4286	-0.3722	-1.2811	0.2324	0.0401
	313.15	-0.7971	-1.1979	-1.4667	0.6837	0.0501
	318.15	-0.6987	-0.7969	-1.3078	-0.3952	0.0504
	323.15	-0.3673	-1.0406	-0.8638	1.5293	0.0606
DMF+SDS+Amyl alcohol	298.15	-0.5434	-1.0903	-0.4763	3.2212	0.0386
	303.15	-0.4062	-0.6642	-1.0542	1.3611	0.0345
	308.15	-0.3703	0.1266	-1.0201	-0.6354	0.0321
	313.15	-0.1280	-0.4146	-1.8957	-0.3644	0.0275
	318.15	-0.0402	-0.9135	-2.5063	1.2180	0.0421
	323.15	0.2527	-0.4801	-2.2139	1.0546	0.0293

Table 4.58: Coefficient, a_i, of Redlich- Kister Eq expressing η^E and standard deviation, σ for the n-Propanol, n-Butanol, *n*- Amyl alcohol in SDS containing DMF systems

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
DMF+SDS+n-Propanol	298.15	-0.9075	-0.8663	-0.6291	-0.3752	0.0039
	303.15	-0.7527	-0.6364	-0.3594	-0.0714	0.0025
	308.15	-0.7101	-0.6603	-0.4069	-0.0874	0.0036
	313.15	-0.5919	-0.4840	-0.3073	-0.3069	0.0020
	318.15	-0.4877	-0.2391	-0.2985	-0.4385	0.0023
	323.15	-0.4249	-0.2645	-0.2020	-0.2369	0.0024
DMF+SDS+n-Butanol	298.15	-0.9071	-1.3987	-0.7668	0.0196	0.0211
	303.15	-0.7225	-0.8911	-0.3592	0.1697	0.0139
	308.15	-0.6372	-0.7455	-0.5236	0.2270	0.0095
	313.15	-0.5657	-0.6823	-0.3412	0.2036	0.0118
	318.15	-0.4814	-0.6062	-0.2345	0.2808	0.0072
	323.15	-0.3523	-0.3856	-0.2575	0.0309	0.0086
DMF+SDS+n-Amyl alcohol	298.15	-1.3284	-1.7330	-2.2228	-1.9924	0.0077
	303.15	-1.1257	-1.3190	-1.3657	-1.3267	0.0101
	308.15	-0.9514	-1.1004	-0.9855	-1.0482	0.0089
	313.15	-0.8403	-1.1280	-0.5216	-0.2637	0.0038
	318.15	-0.6501	-0.9494	-0.4293	0.2012	0.0047
	323.15	-0.6629	-0.8634	-0.0948	0.6497	0.0051

Table 4.59. Coefficient, a_i, of Redlich- Kister Eq expressing ΔG^{*E} and standard deviation, σ for the n-Propanol, n-Butanol, *n*-Amyl alcohol in SDS containing DMF systems

Systems	*T/K*	a_0	a_1	a_2	a_3	σ
DMF+SDS+n-Propanol	298.15	1.9690	-1.1720	-0.4761	-0.1540	0.0080
	303.15	-1.7922	-0.9408	-0.3031	0.2607	0.0058
	308.15	-1.8800	-1.1916	-0.4536	0.2673	0.0102
	313.15	-1.7214	-0.8997	-0.2795	-0.5425	0.0072
	318.15	-1.5630	-0.3243	-0.4615	-1.0689	0.0060
	323.15	-1.4811	-0.5387	-0.2093	-0.4976	0.0074
DMF+SDS+n-Butanol	298.15	-1.6229	-1.6078	-0.2484	0.3406	0.0348
	303.15	-1.4323	-1.0334	-0.0590	0.4187	0.0238
	308.15	-1.4074	-0.9792	-0.6753	0.8474	0.0190
	313.15	-1.4082	-1.0731	-0.3482	0.6220	0.0279
	318.15	-1.3194	-1.1595	-0.2222	0.9213	0.0188
	323.15	-1.0540	-0.7769	-0.4420	0.2814	0.0213
DMF+SDS+n-Amyl alcohol	298.15	-1.9906	-1.3741	-1.0652	-1.0520	0.0074
	303.15	-1.8501	-1.0656	-0.5084	-1.0653	0.0158
	308.15	-1.7516	-1.0939	-0.2652	-0.9964	0.0118
	313.15	-1.7129	-1.5144	0.2218	0.0007	0.0064
	318.15	-1.4323	-1.5393	-0.1645	0.9812	0.0085
	323.15	-1.6542	-1.5396	0.3264	1.9692	0.0121

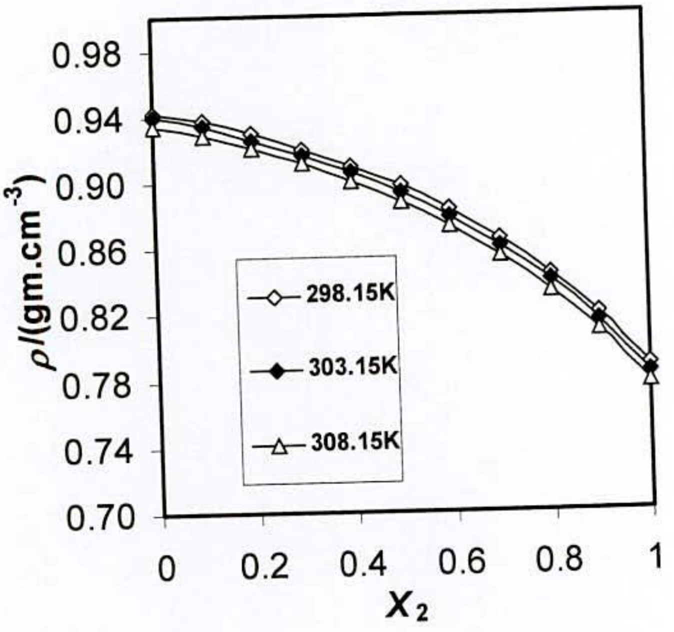

Figure 4.1. Plots of density vs mole fraction of Methanol + DMF system at 298.15K, 303.15K and 308.15K respectively

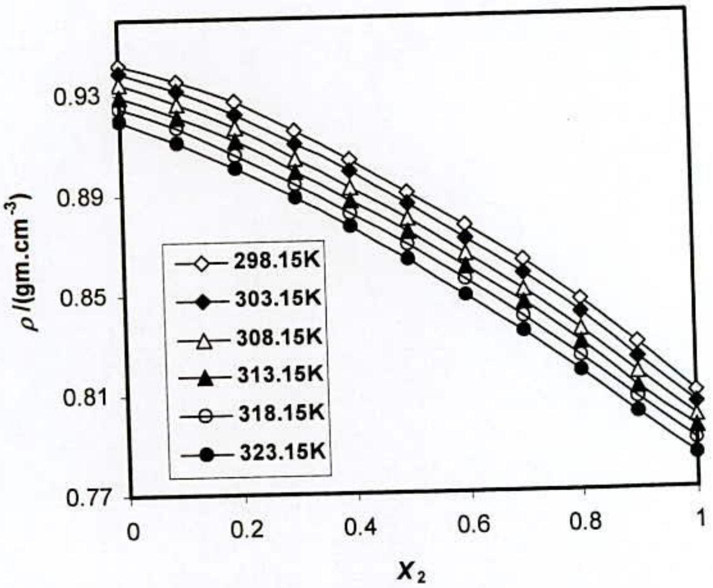

Figure 4.2. Plots of density vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

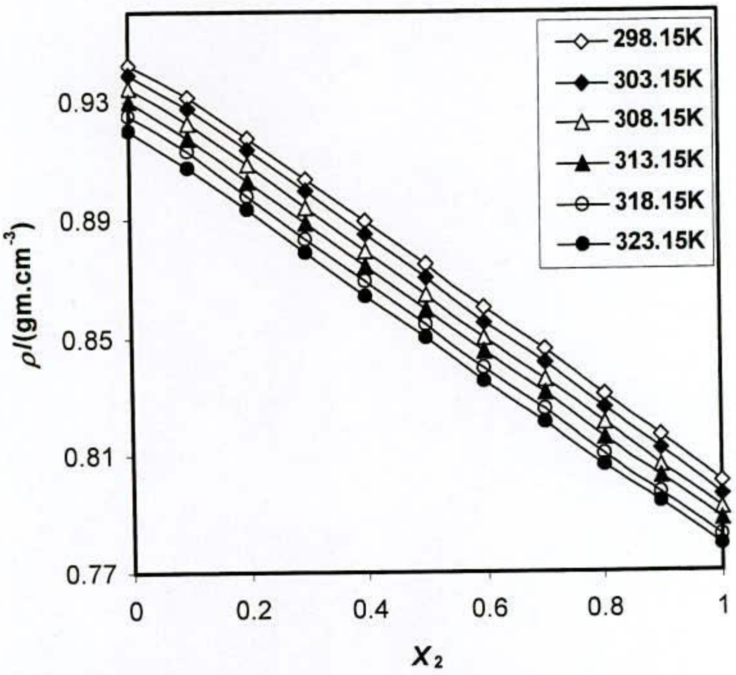

Figure 4.3. Plots of density vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

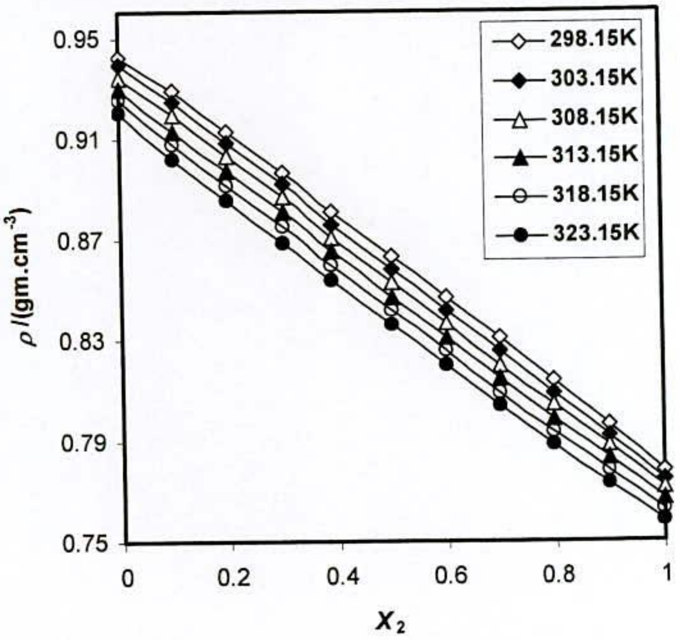

Figure 4.4. Plots of density vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

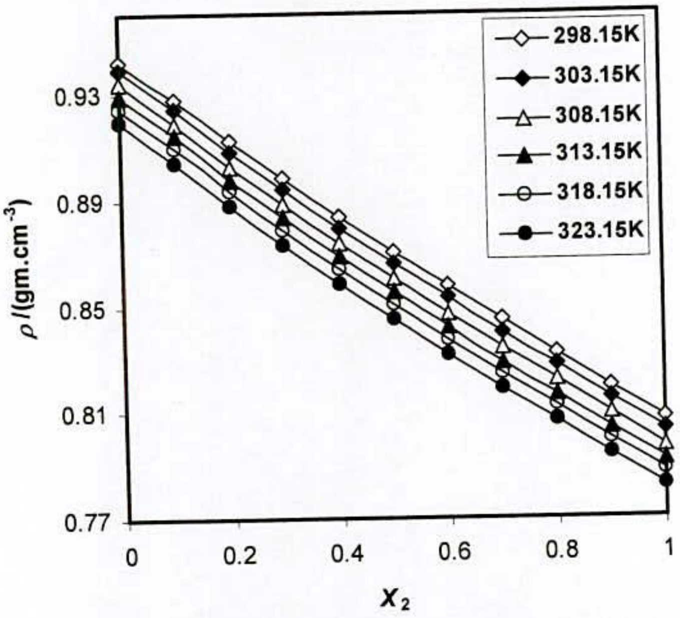

Figure 4.5. Plots of density vs mole fraction of n-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

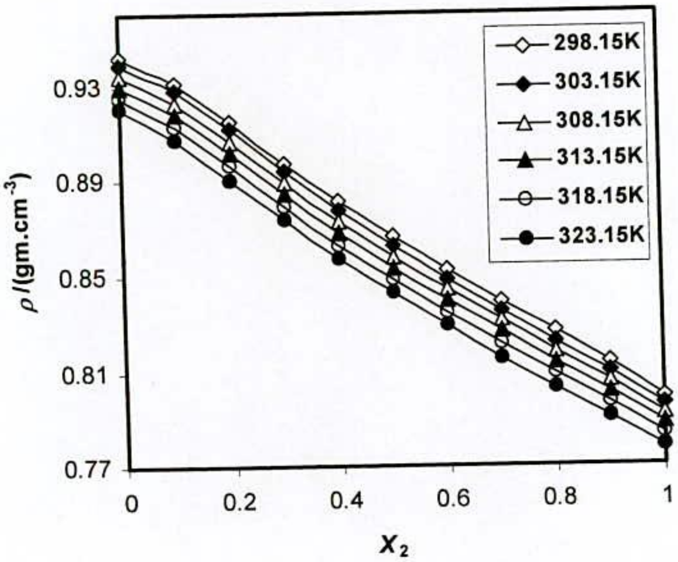

Figure 4.6. Plots of density vs mole fraction of iso-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

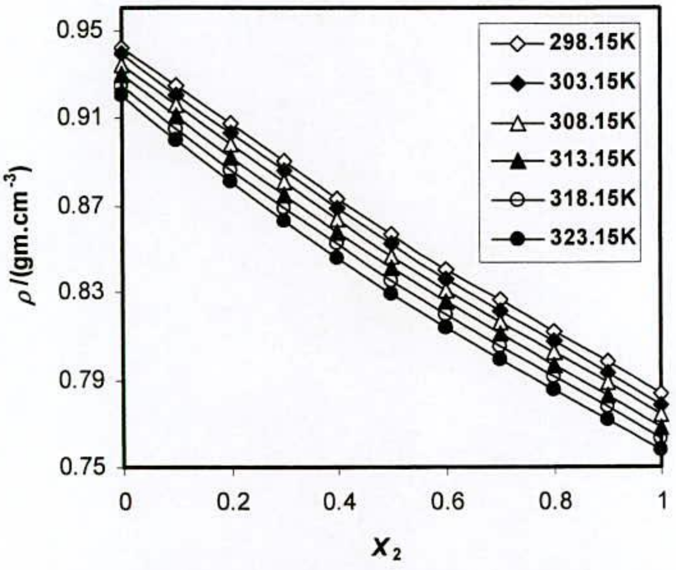

Figure 4.7. Plots of density vs mole fraction of tert-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

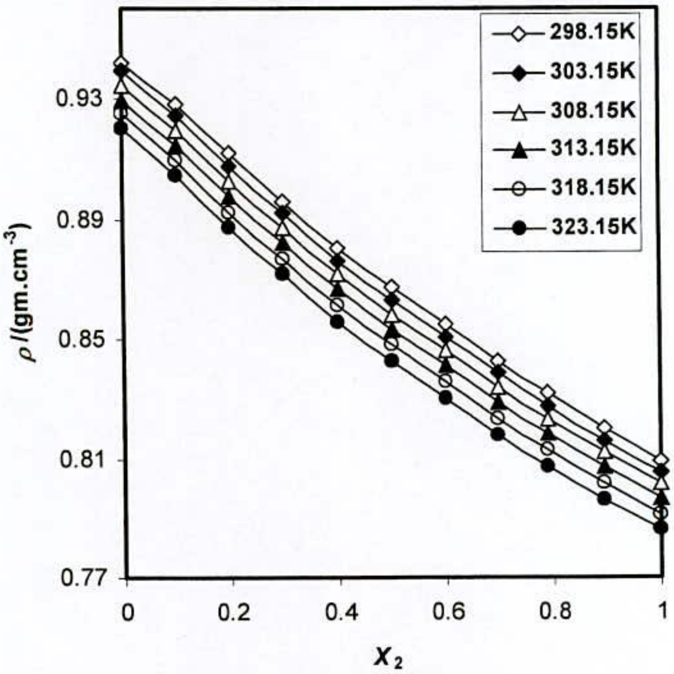

Figure 4.8. Plots of density vs mole fraction of n-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

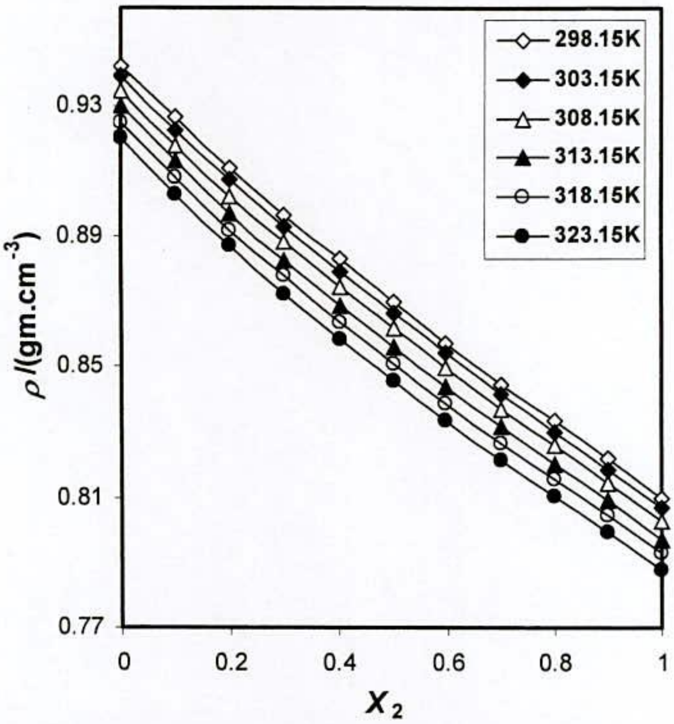

Figure 4.9. Plots of density vs mole fraction of iso-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

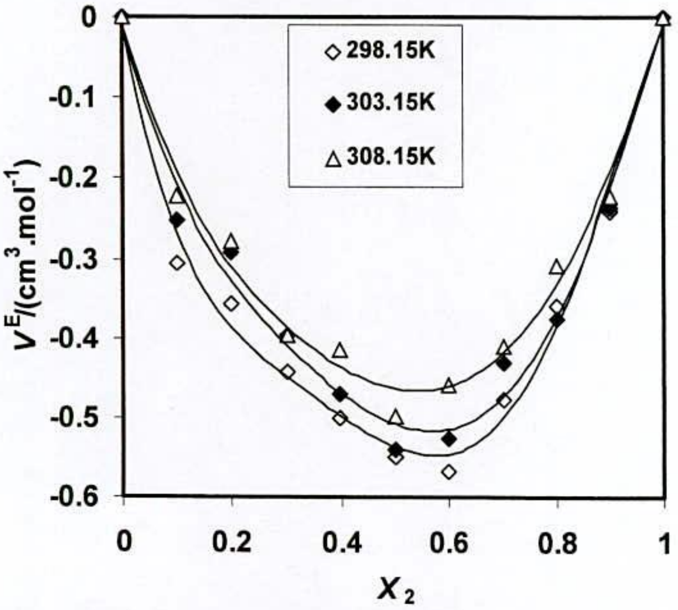

Figure 4.10. Plots of excess molar volume vs mole fraction of Methanol + DMF system at 298.15K, 303.15K, and 308.15K respectively

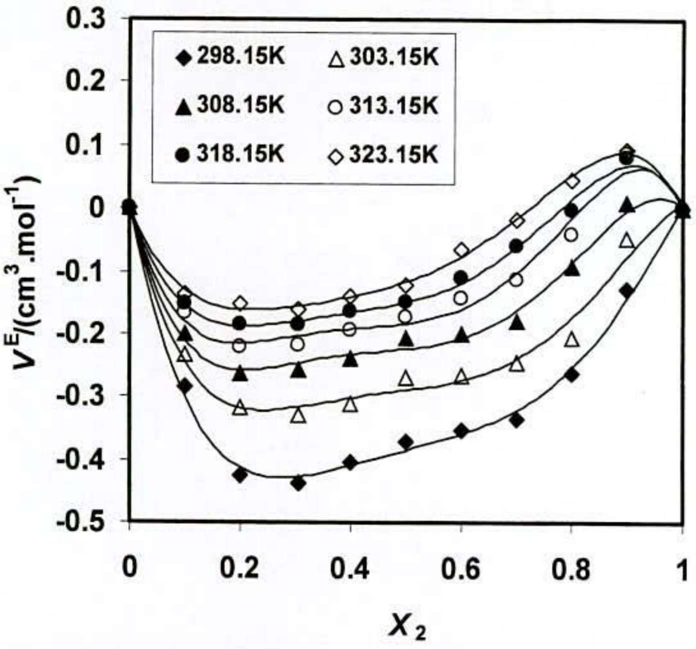

Figure 4.11. Plots of excess molar volume vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

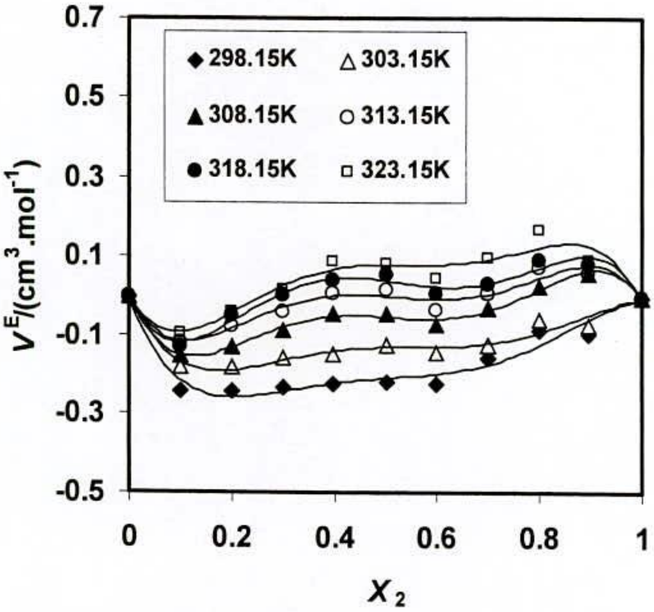

Figure 4.12. Plots of excess molar volume vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

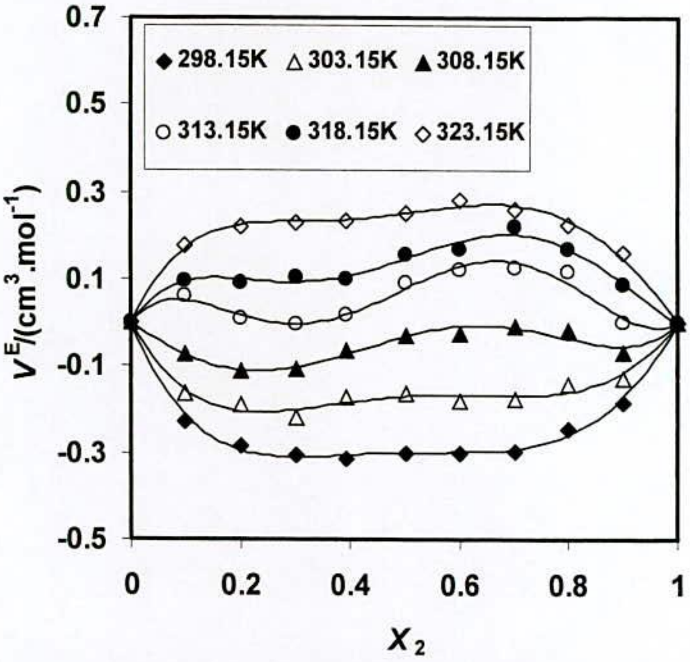

Figure 4.13. Plots of excess molar volume vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

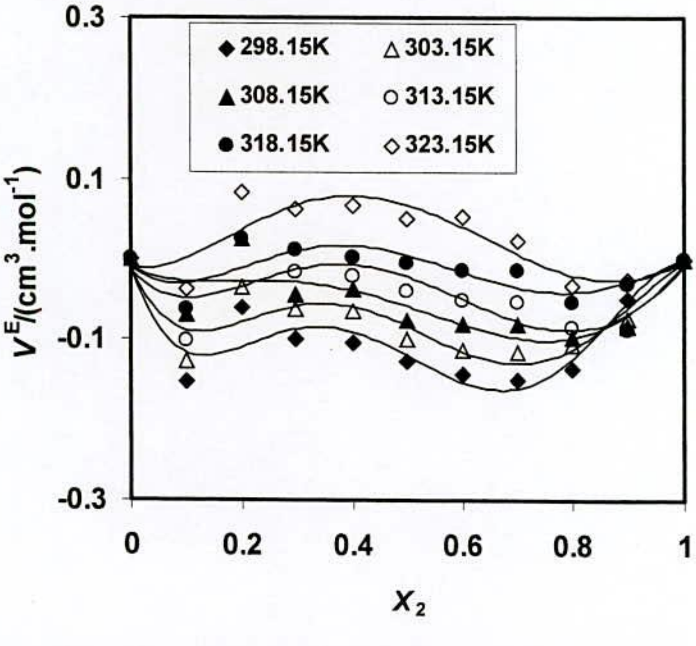

Figure 4.14. Plots of excess molar volume vs mole fraction of n-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

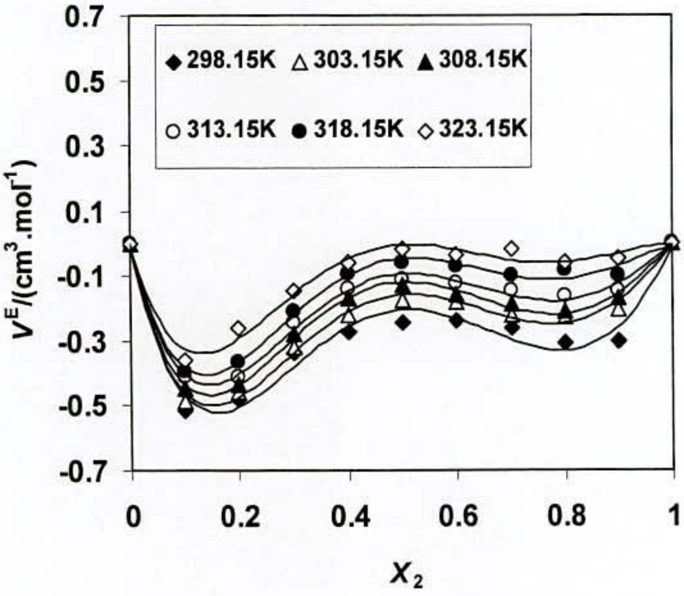

Figure 4.15. Plots of excess molar volume vs mole fraction of iso-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

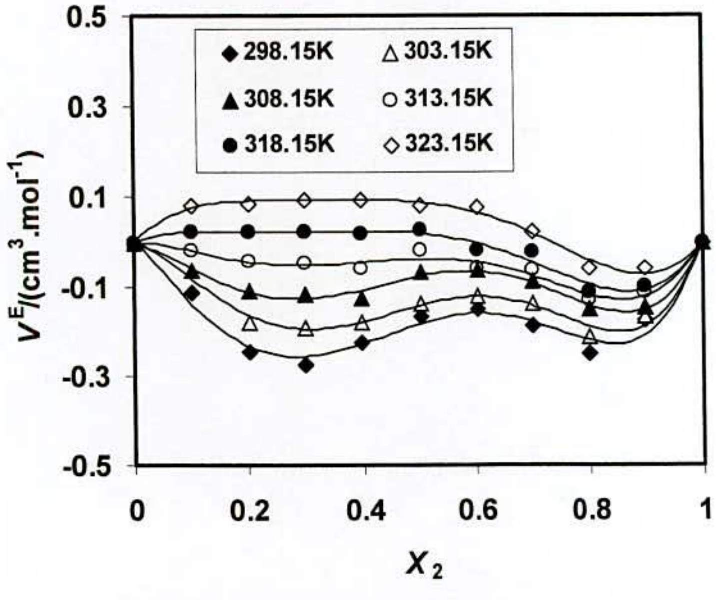

Figure 4.16. Plots of excess molar volume vs mole fraction of tert-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

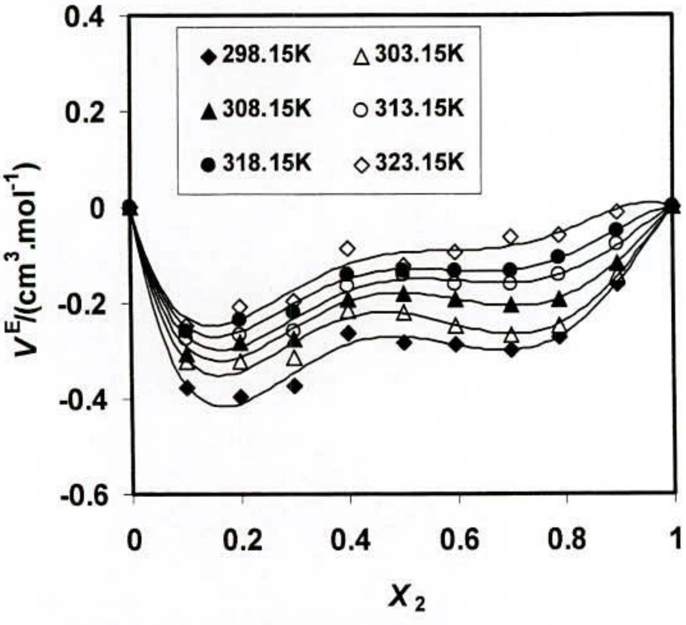

Figure 4.17. Plots of excess molar volume vs mole fraction of n-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

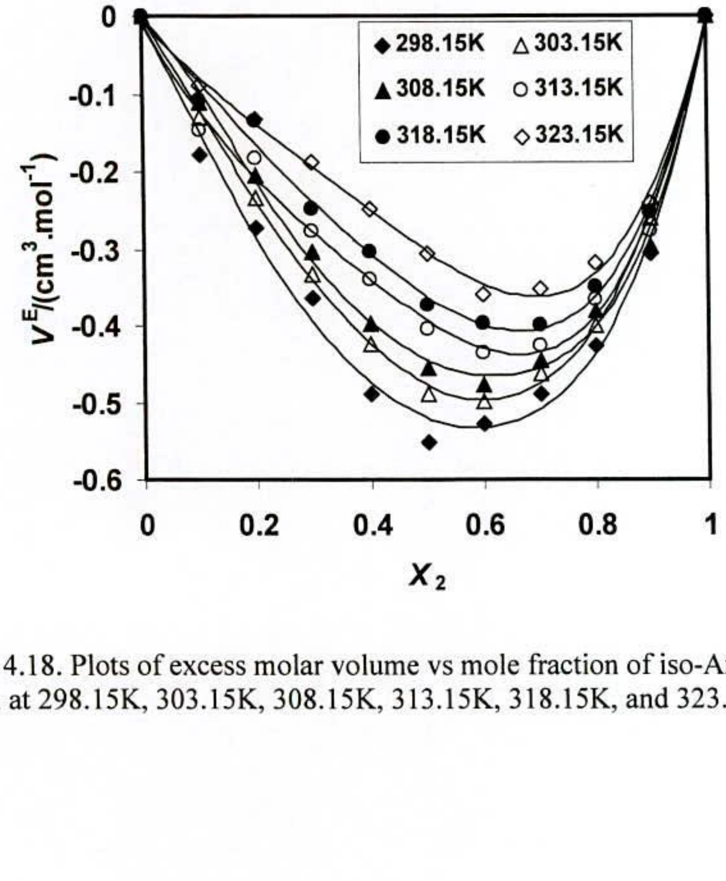

Figure 4.18. Plots of excess molar volume vs mole fraction of iso-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

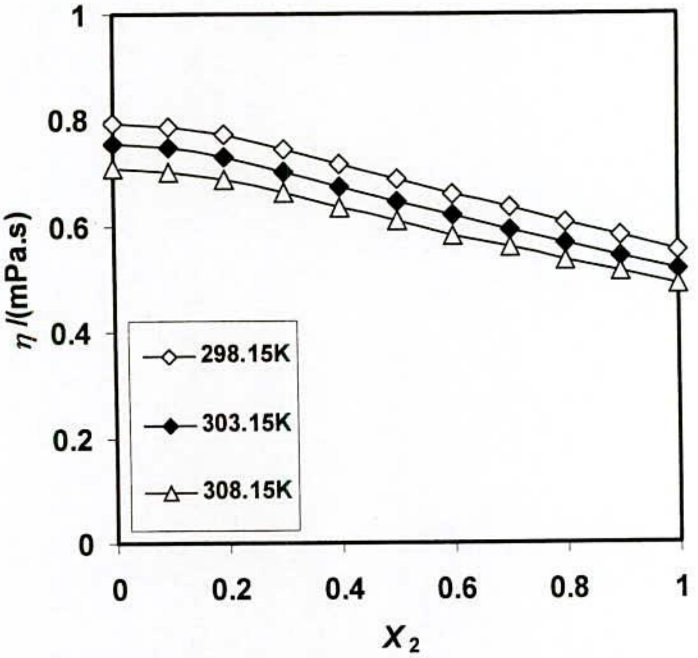

Figure 4.19. Plots of viscosity vs mole fraction of Methanol + DMF system at 298.15K, 303.15K, and 308.15K respectively

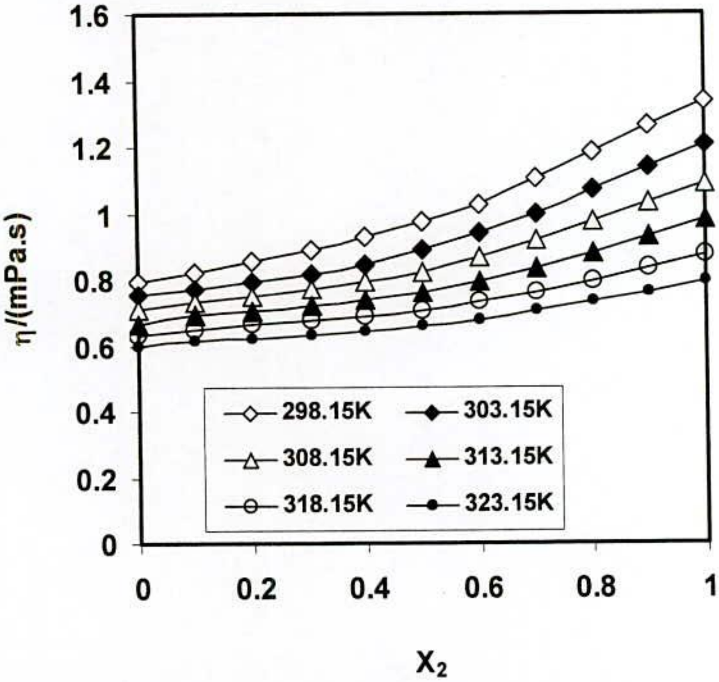

Figure 4.20. Plots of viscosity vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

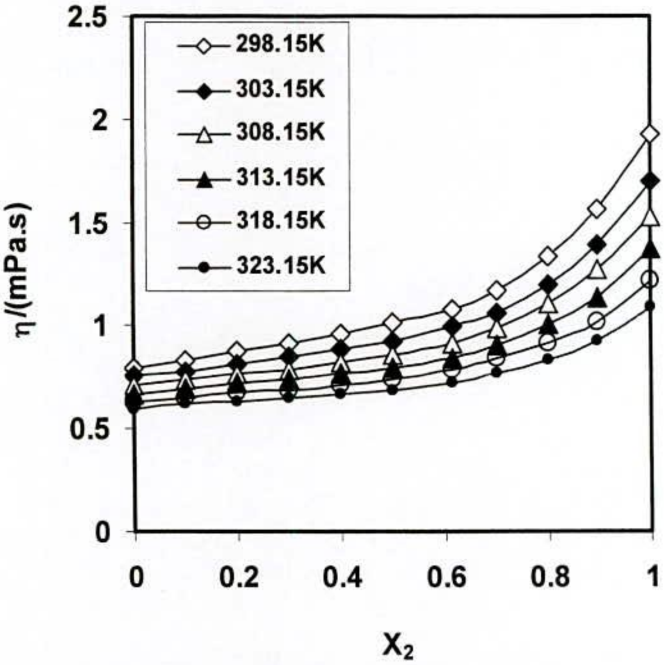

Figure 4.21. Plots of viscosity vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

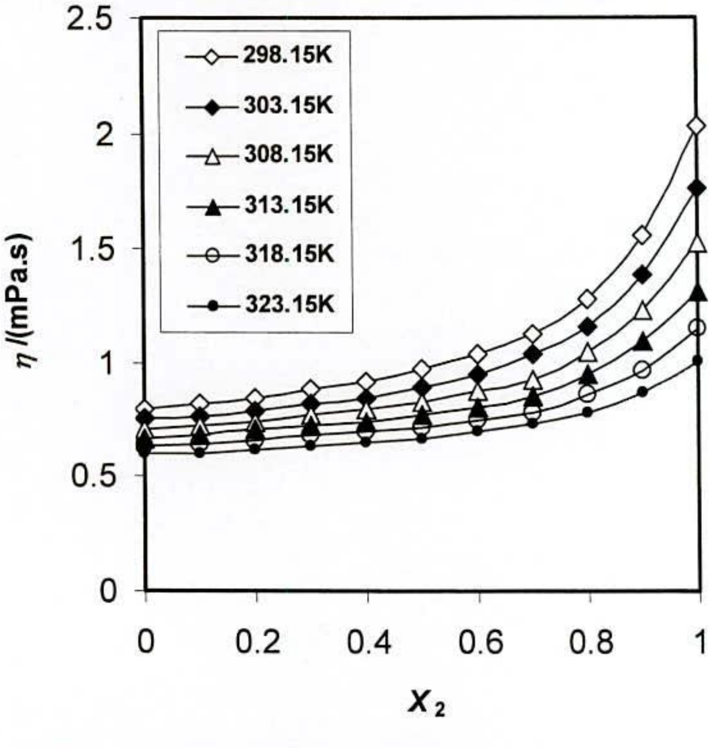

Figure 4.22. Plots of viscosity vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

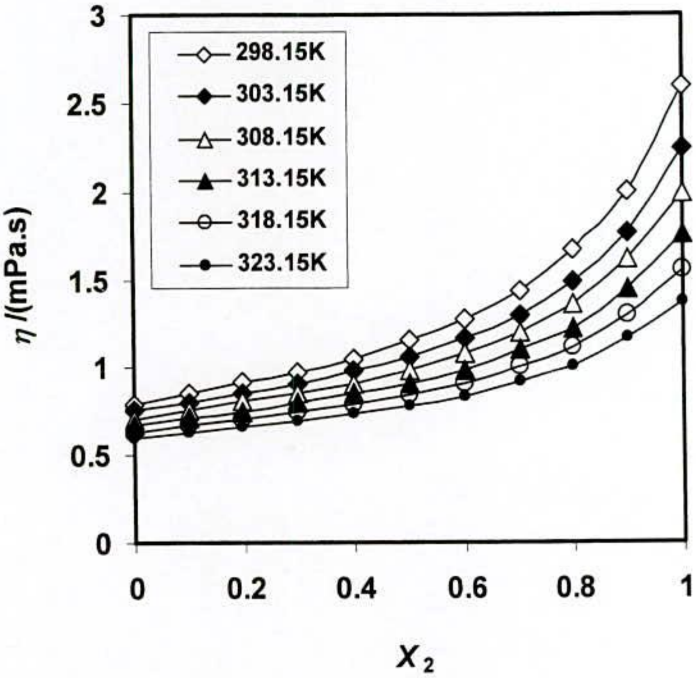

Figure 4.23. Plots of viscosity vs mole fraction of n-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

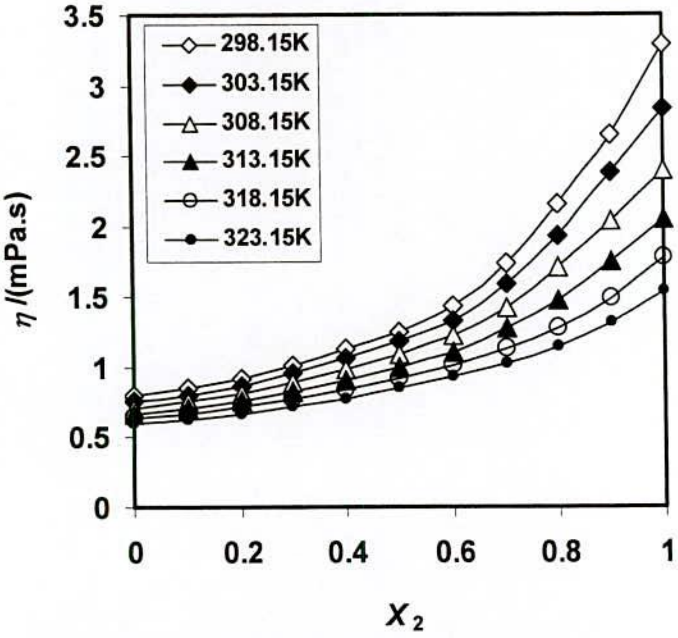

Figure 4.24. Plots of viscosity vs mole fraction of iso-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

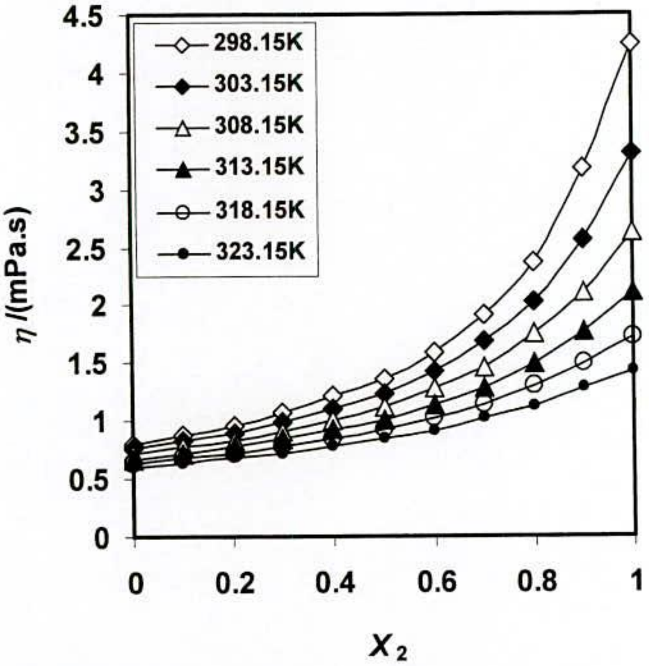

Figure 4.25. Plots of viscosity vs mole fraction of tert-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

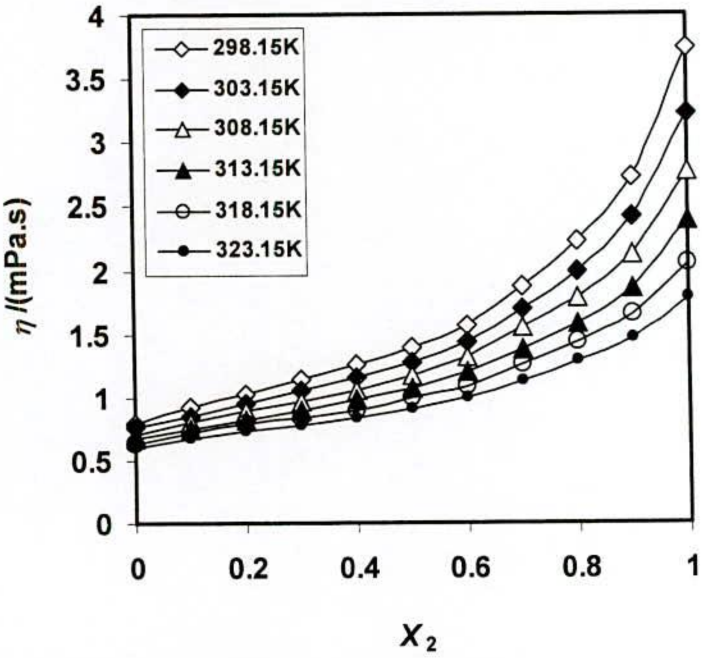

Figure 4.26. Plots of viscosity vs mole fraction of n-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

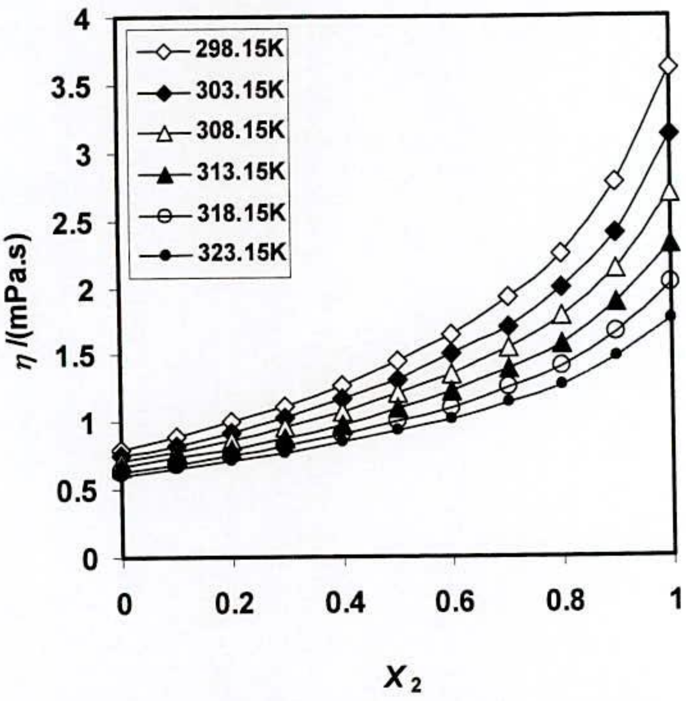

Figure 4.27. Plots of viscosity vs mole fraction of iso-Amyl alcohol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

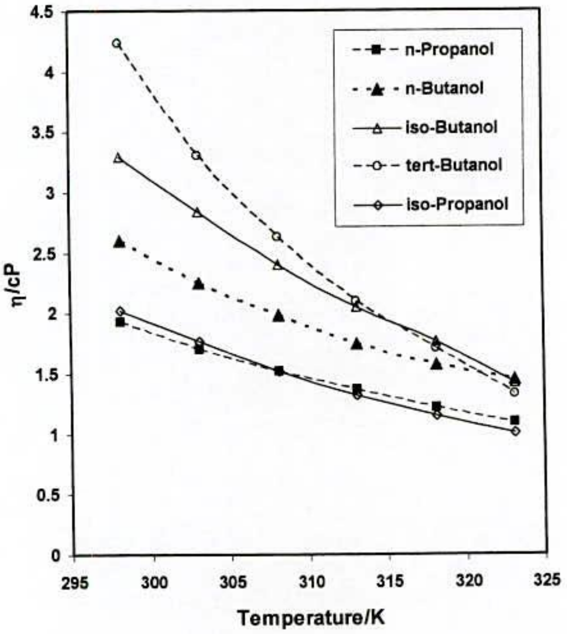

Figure 4.28. Plots of viscosity vs temperature of n-Propanol, *iso*-propanol, n-Butanol, iso-Butanol, tert-Butanol in DMF system.

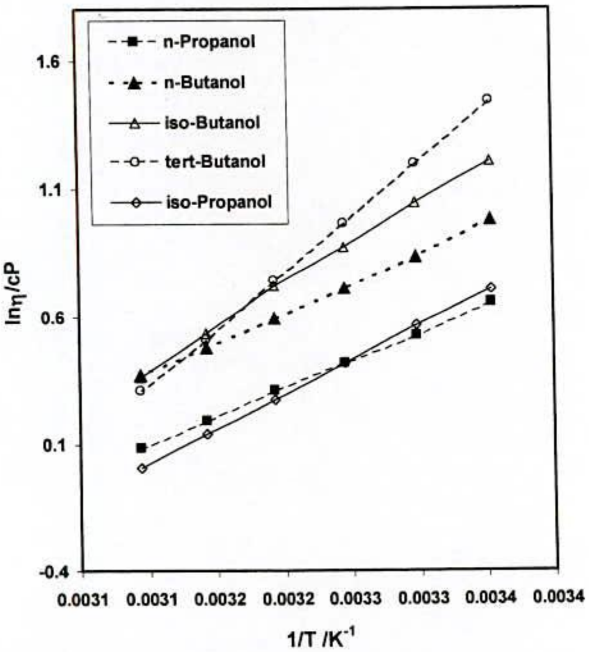

Figure 4.29. Plots of lnη vs 1/T of n-Propanol, *iso*-propanol, n-Butanol, iso-Butanol, tert-Butanol in DMF system.

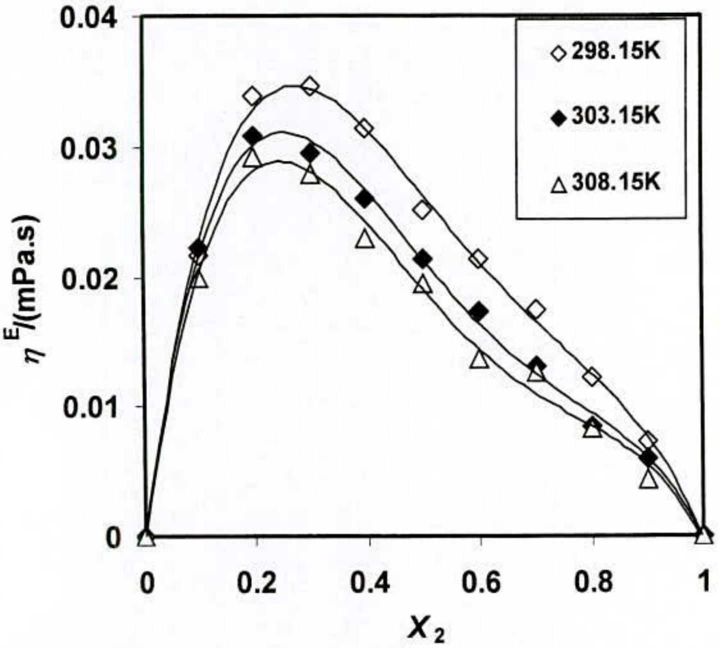

Figure 4.30. Plots of excess viscosity vs mole fraction of Methanol + DMF system at 298.15K, 303.15K, and 308.15K respectively

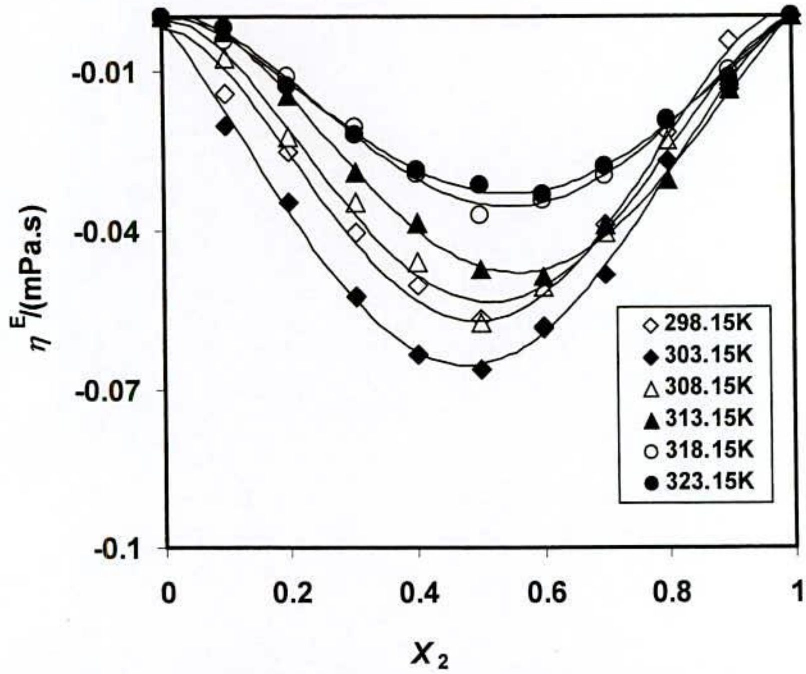

Figure 4.31. Plots of excess viscosity vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

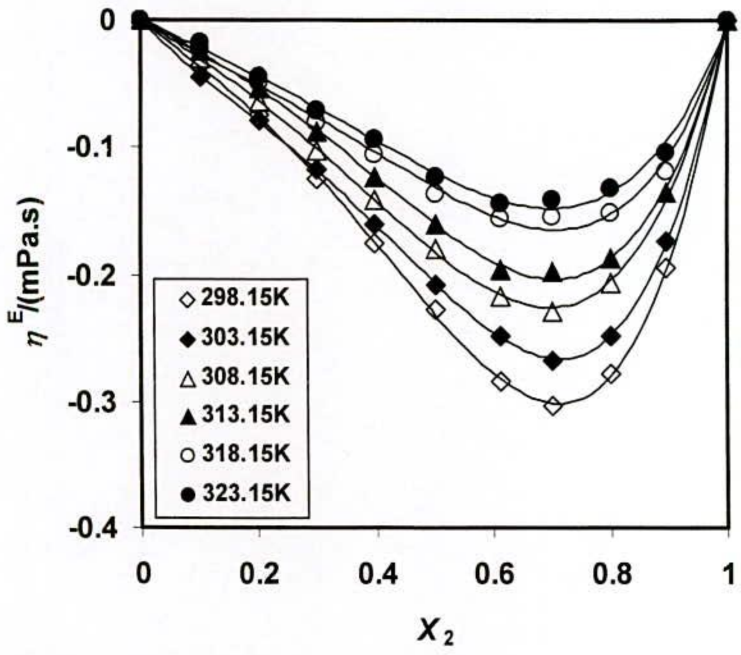

Figure 4.32. Plots of excess viscosity vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

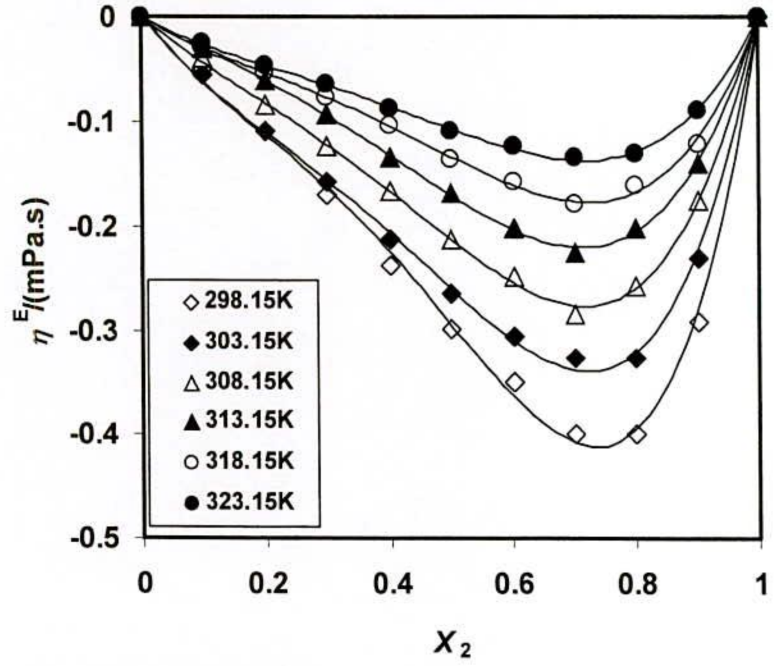

Figure 4.33. Plots of excess viscosity vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

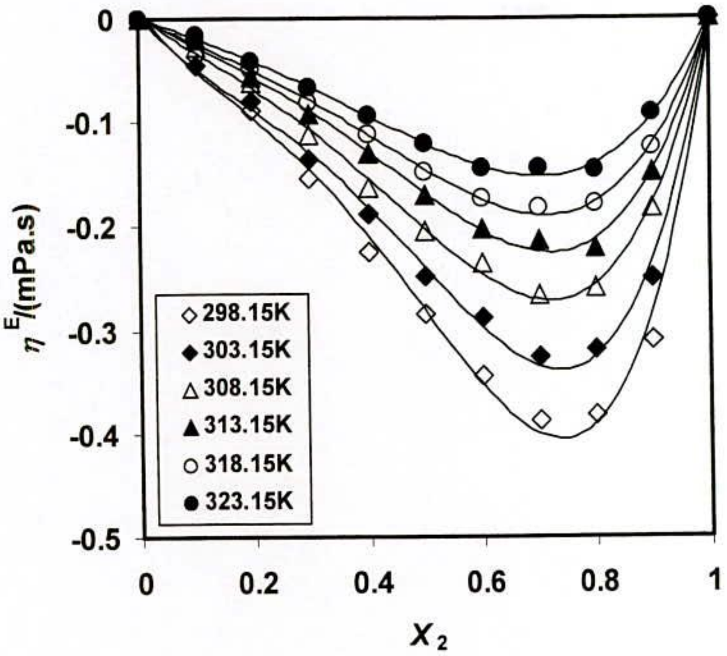

Figure 4.34. Plots of excess viscosity vs mole fraction of n-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

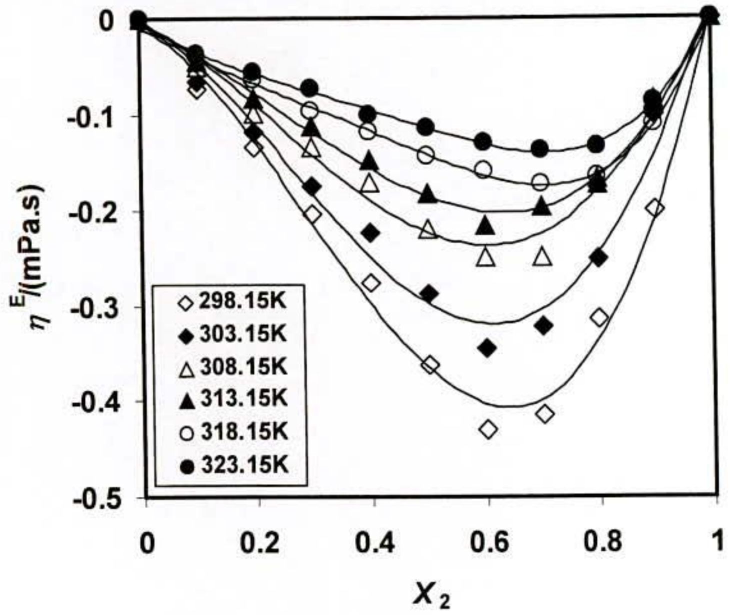

Figure 4.35. Plots of excess viscosity vs mole fraction of iso-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

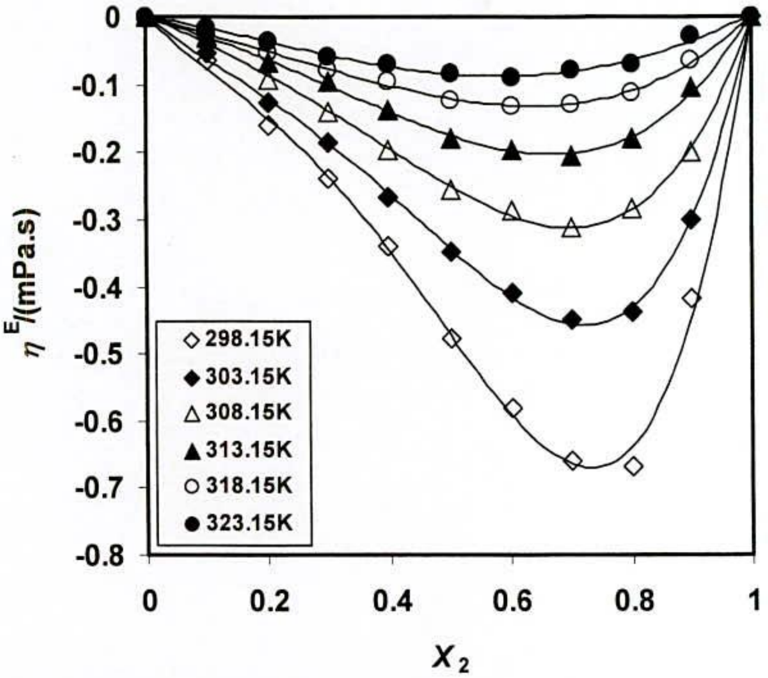

Figure 4.36. Plots of excess viscosity vs mole fraction of tert-Butanol+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

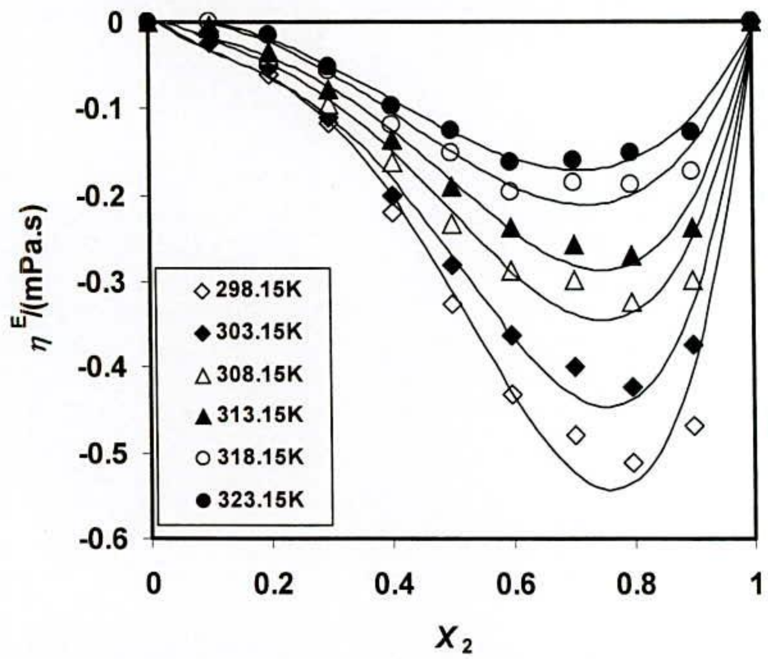

Figure 4.37. Plots of excess viscosity vs mole fraction of n-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

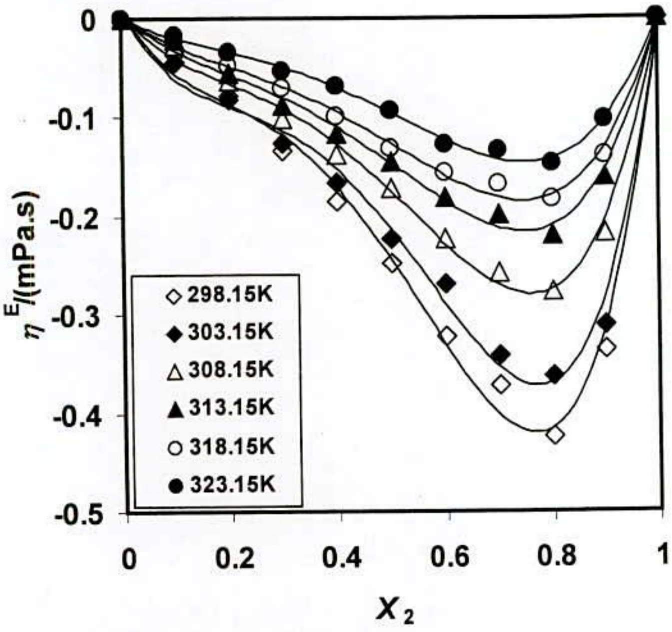

Figure 4.38. Plots of excess viscosity vs mole fraction of iso-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

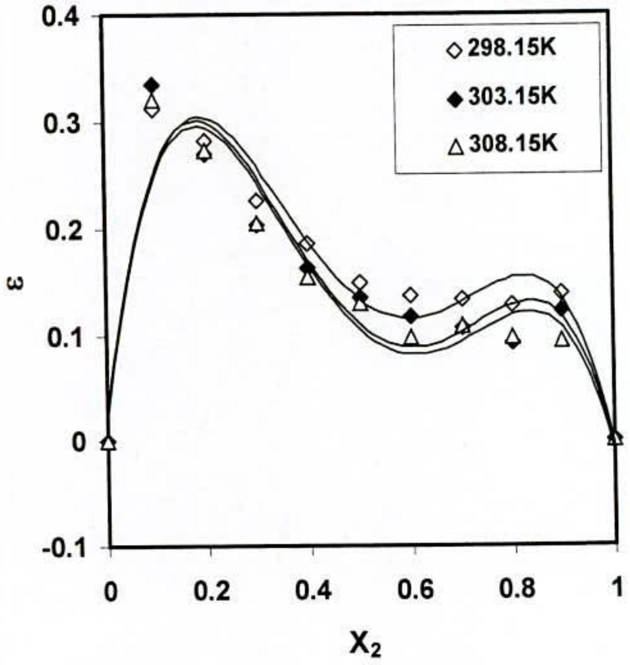

Figure 4.39. Plots of interaction parameter vs mole fraction of Methanol + DMF system at 298.15K, 303.15K, and 308.15K respectively

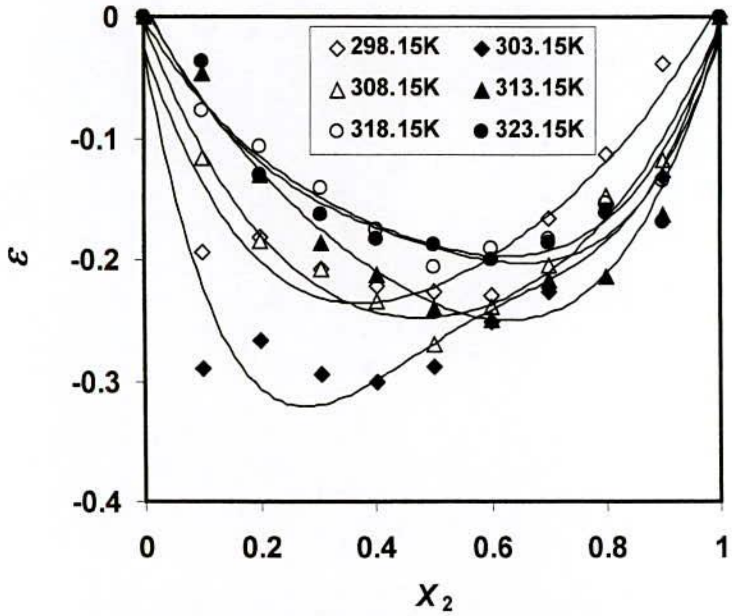

Figure 4.40. Plots of interaction parameter vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

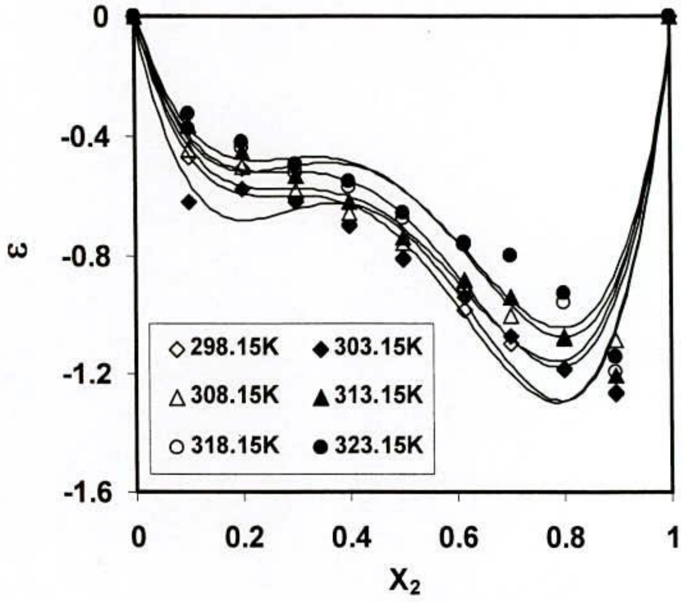

Figure 4.41. Plots of interaction parameter vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

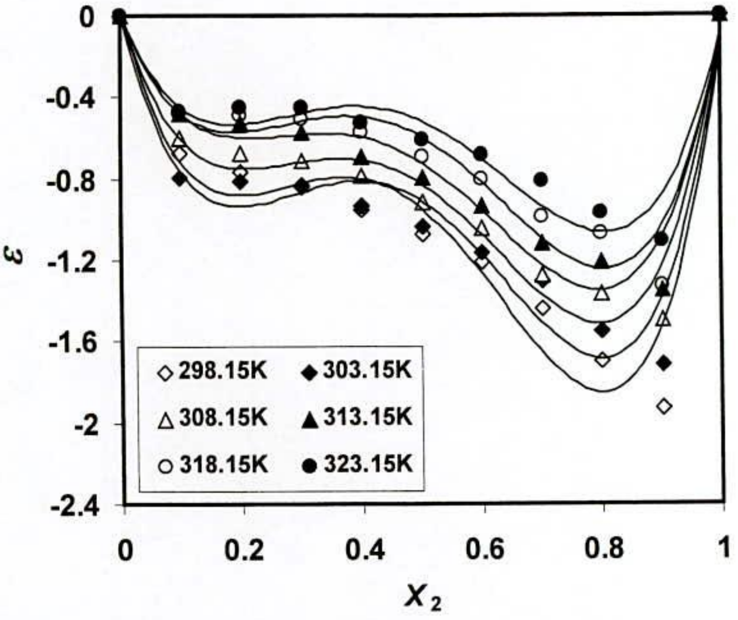

Figure 4.42. Plots of interaction parameter vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

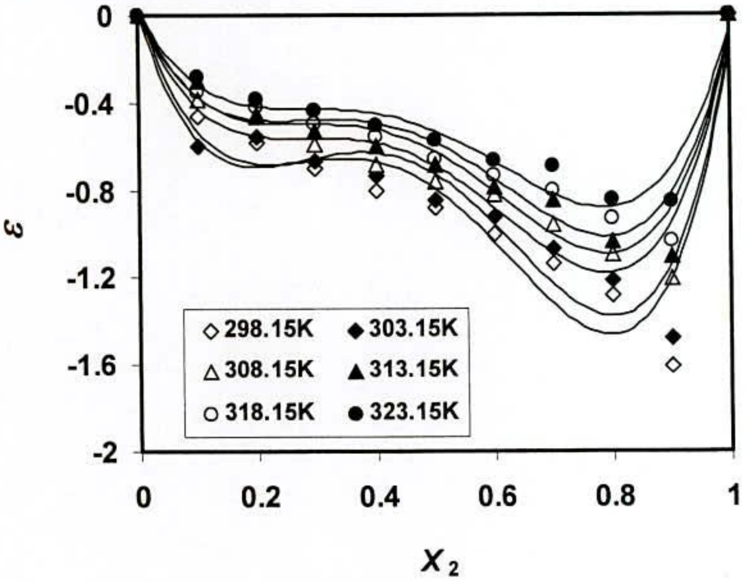

Figure 4.43. Plots of interaction parameter vs mole fraction of n-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

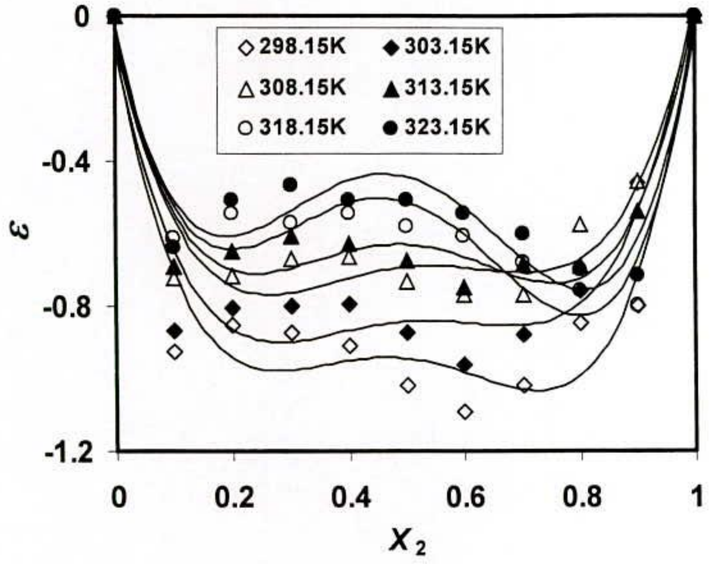

Figure 4.44. Plots of interaction parameter vs mole fraction of iso-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

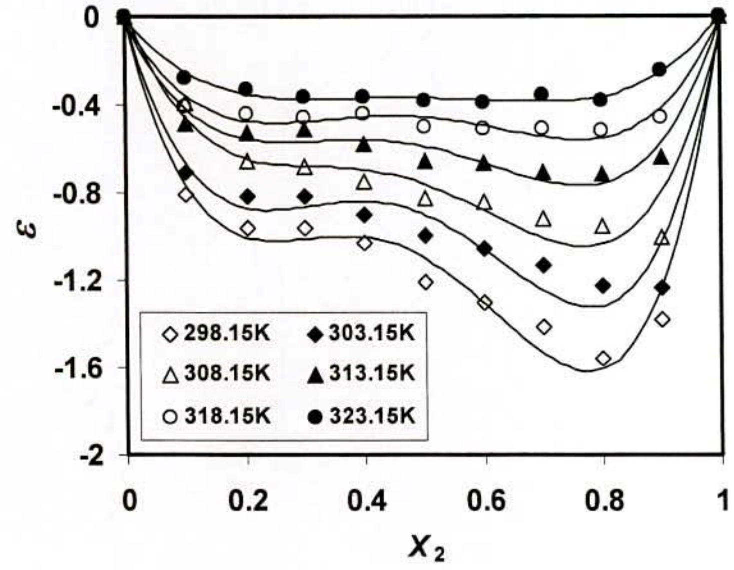

Figure 4.45. Plots of interaction parameter vs mole fraction of tert-Butanol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

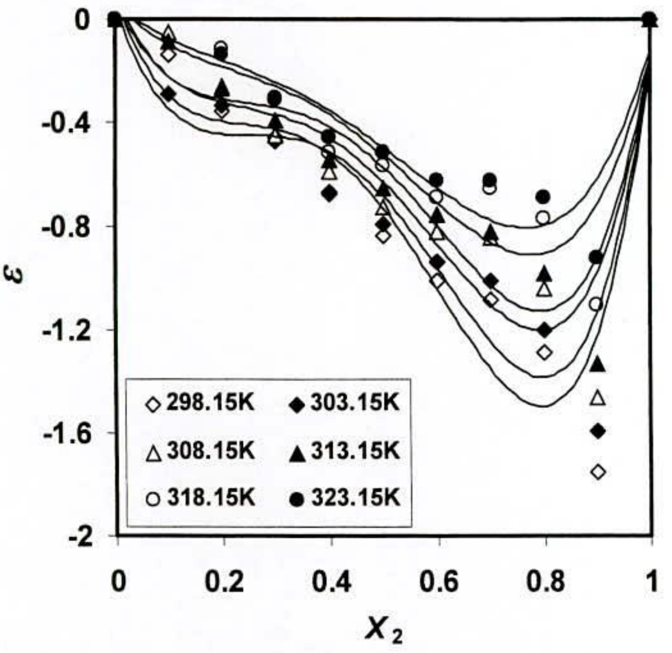

Figure 4.46. Plots of interaction parameter vs mole fraction of n-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

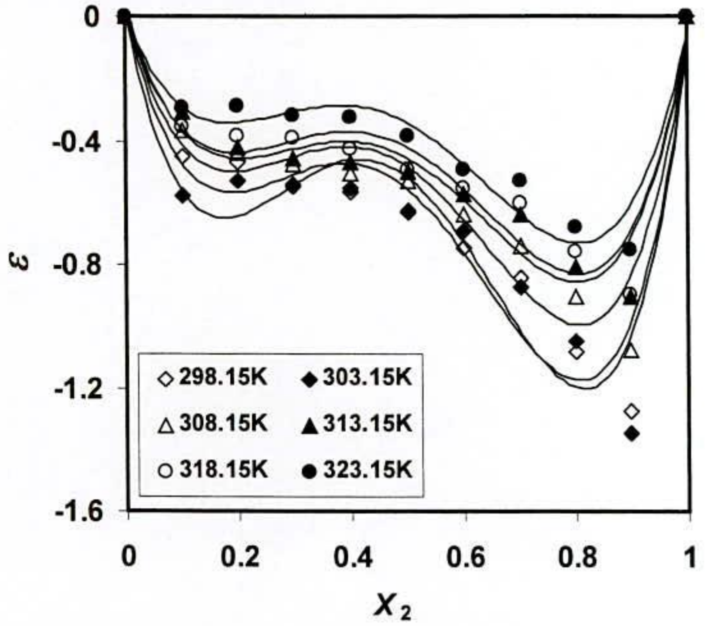

Figure 4.47. Plots of interaction parameter vs mole fraction of iso-Amyl alcohol + DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively.

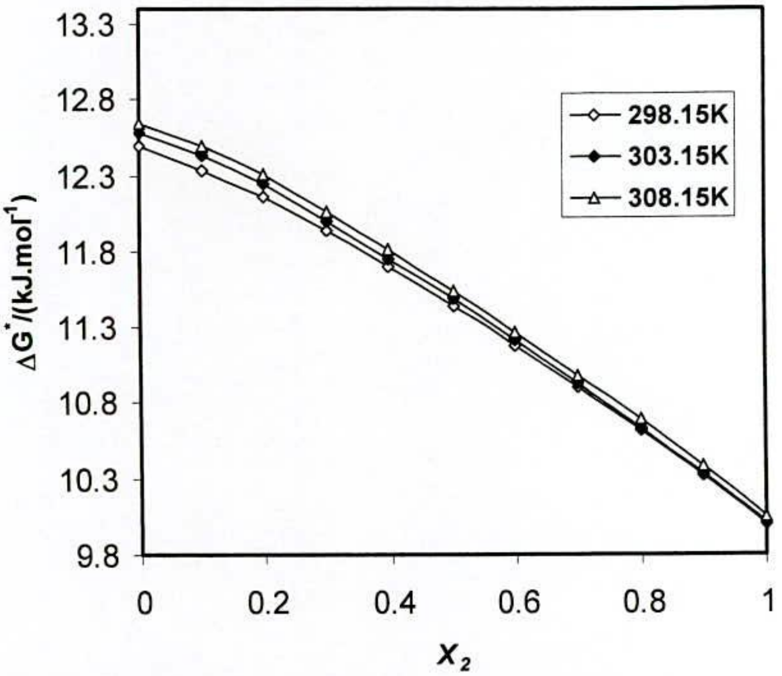

Figure 4.48. Plots of free energy vs mole fraction of Methanol + DMF system at 298.15K, 303.15K and 308.15K respectively

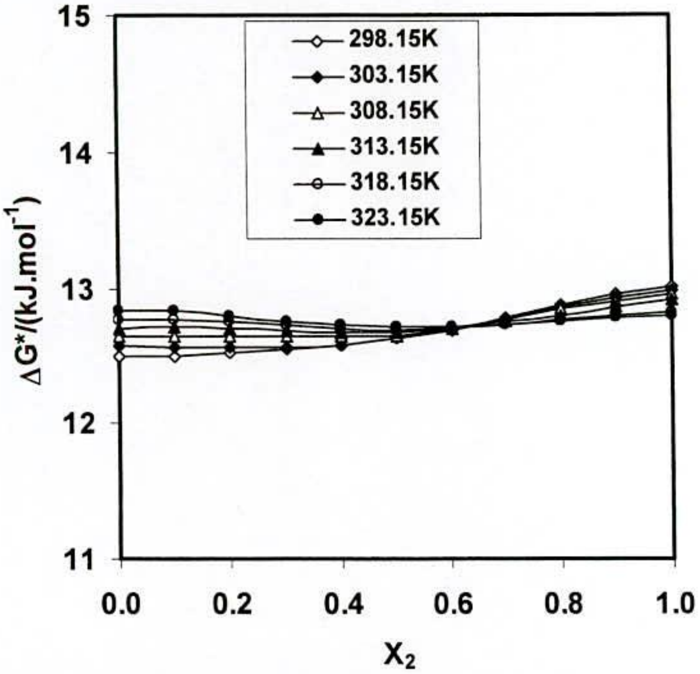

Figure 4.49. Plots of free energy vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K and 308.15K respectively

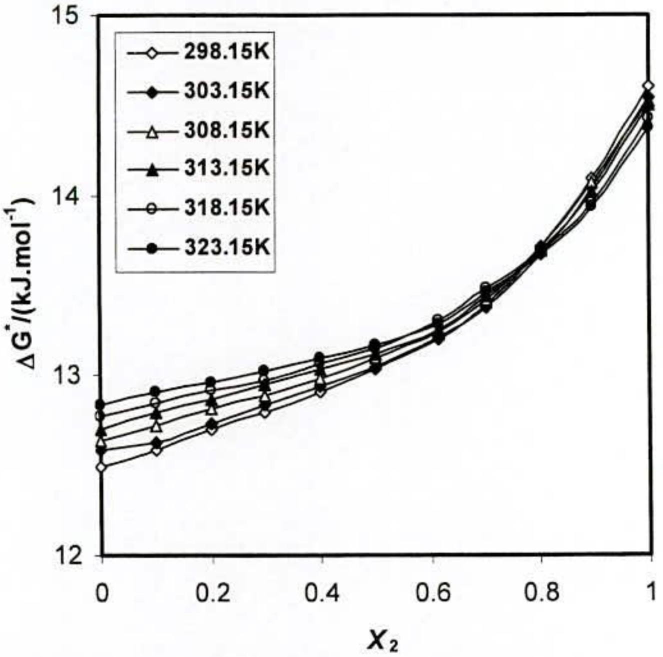

Figure 4.50. Plots of free energy vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K and 308.15K respectively

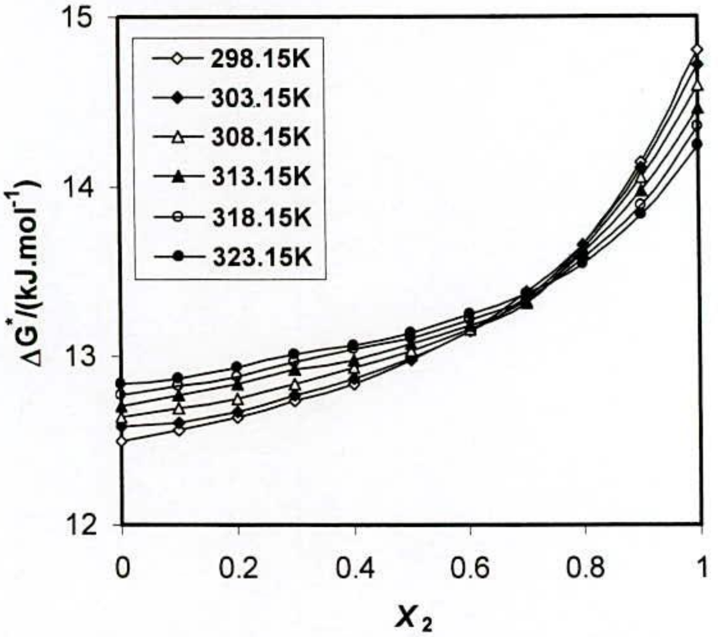

Figure 4.51. Plots of free energy vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K and 308.15K respectively

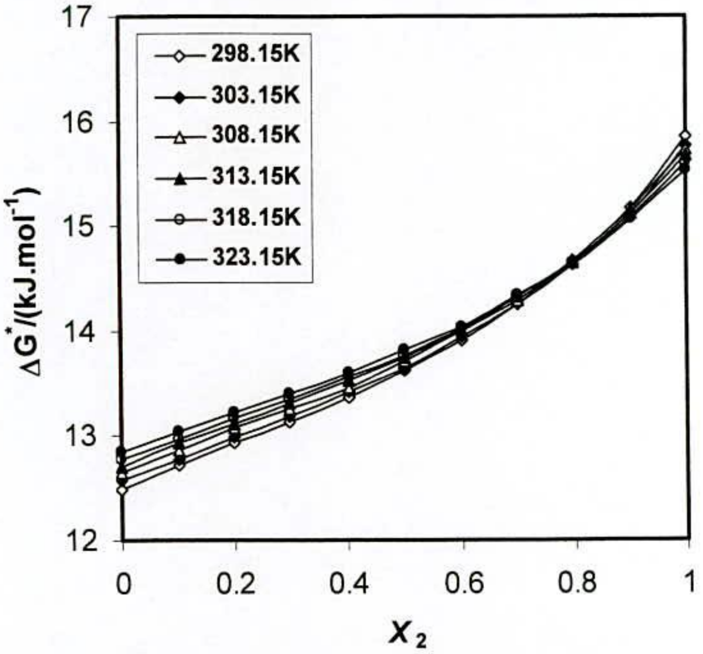

Figure 4.52. Plots of free energy vs mole fraction of n-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

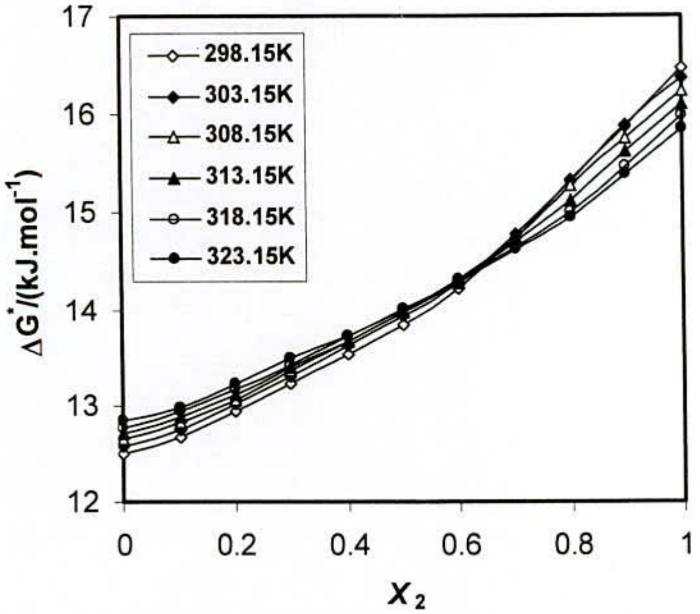

Figure 4.53. Plots of free energy vs mole fraction of iso-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

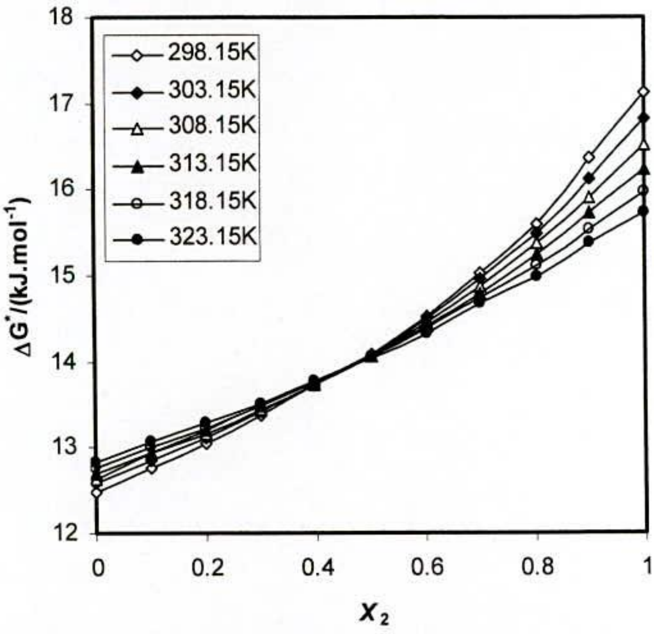

Figure 4.54: Plots of free energy vs mole fraction of t-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

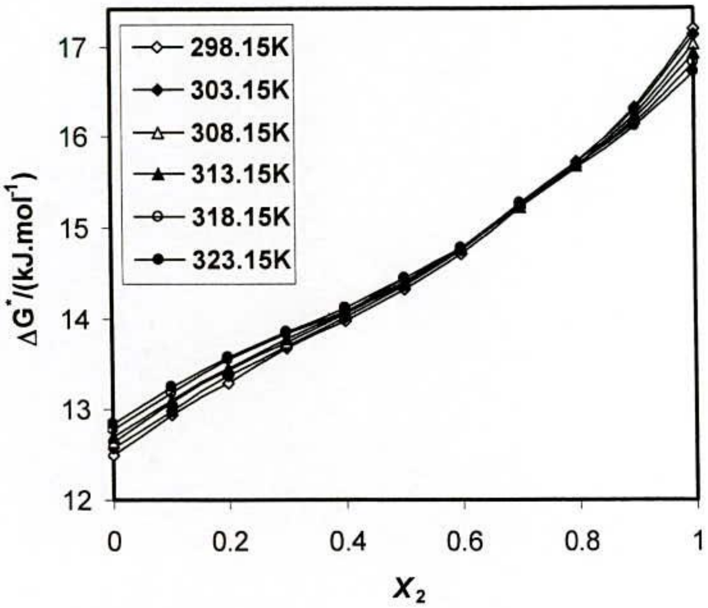

Figure 4.55. Plots of free energy vs mole fraction of n-Amyl alcohol + DMF system at 298.15K, 303.15K and 308.15K respectively

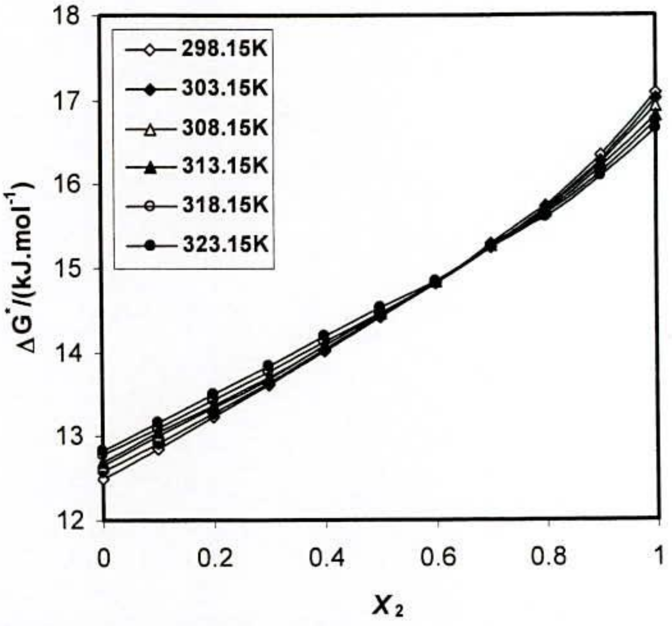

Figure 4.56. Plots of free energy vs mole fraction of iso-Amyl alcohol + DMF system at 298.15K, 303.15K and 308.15K respectively

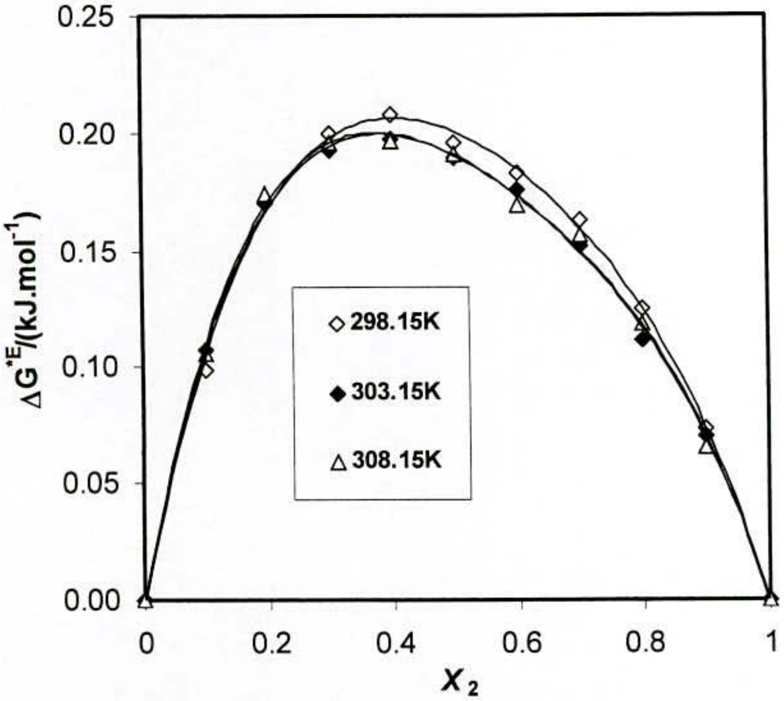

Figure 4.57. Plots of excess free energy vs mole fraction of Methanol + DMF system at 298.15K, 303.15K and 308.15K respectively

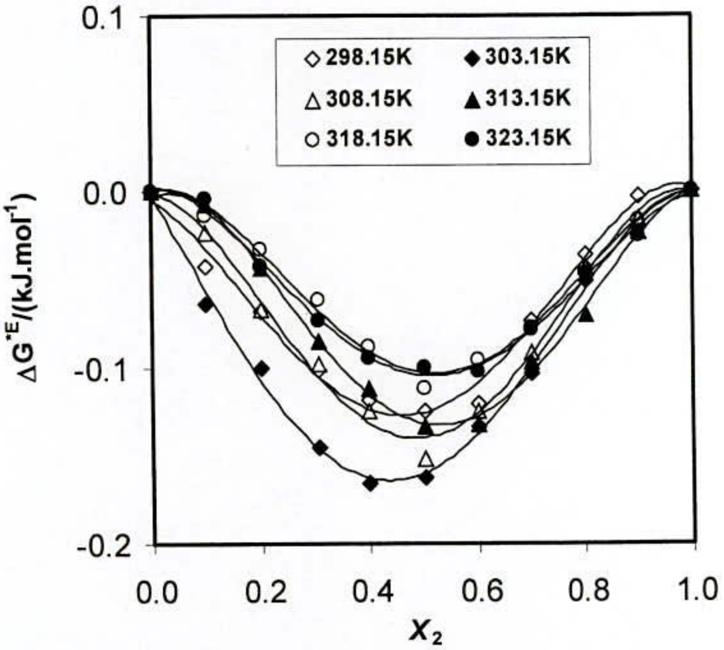

Figure 4.58. Plots of excess free energy vs mole fraction of Ethanol + DMF system at 298.15K, 303.15K and 308.15K respectively

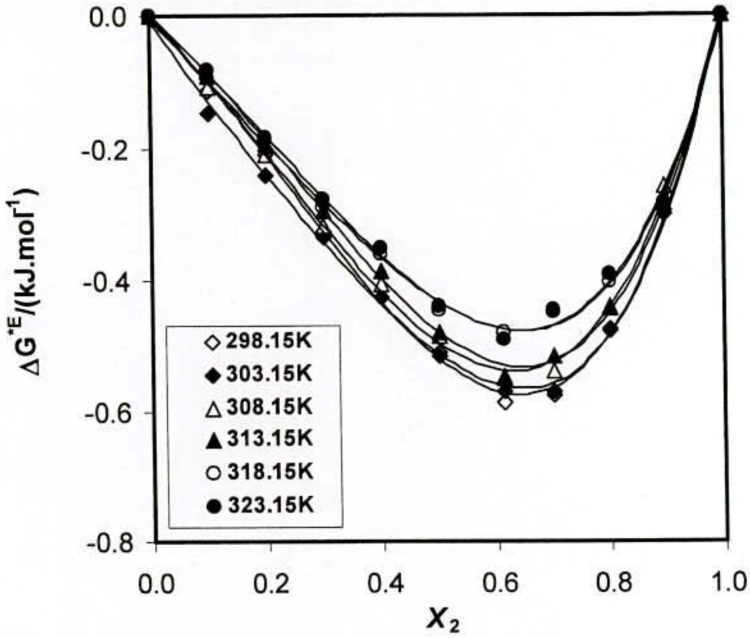

Figure 4.59. Plots of excess free energy vs mole fraction of n-Propanol + DMF system at 298.15K, 303.15K and 308.15K respectively

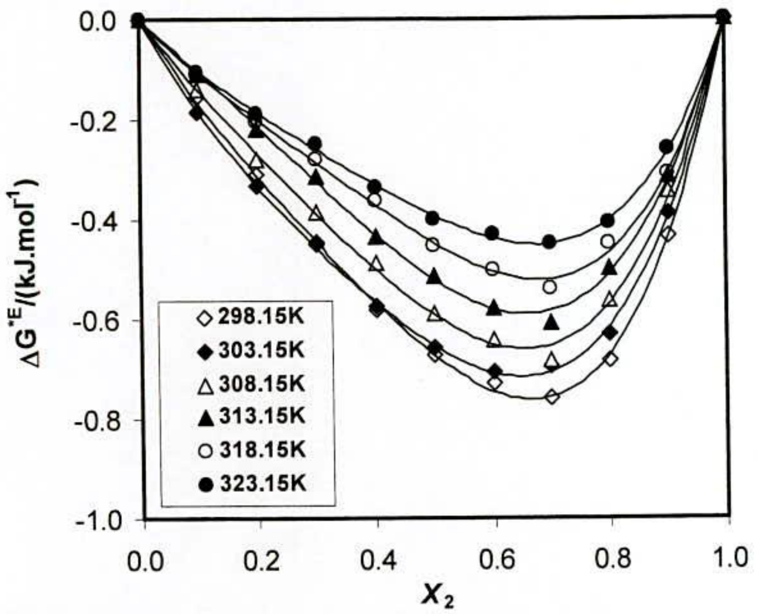

Figure 4.60. Plots of excess free energy vs mole fraction of iso-Propanol + DMF system at 298.15K, 303.15K and 308.15K respectively

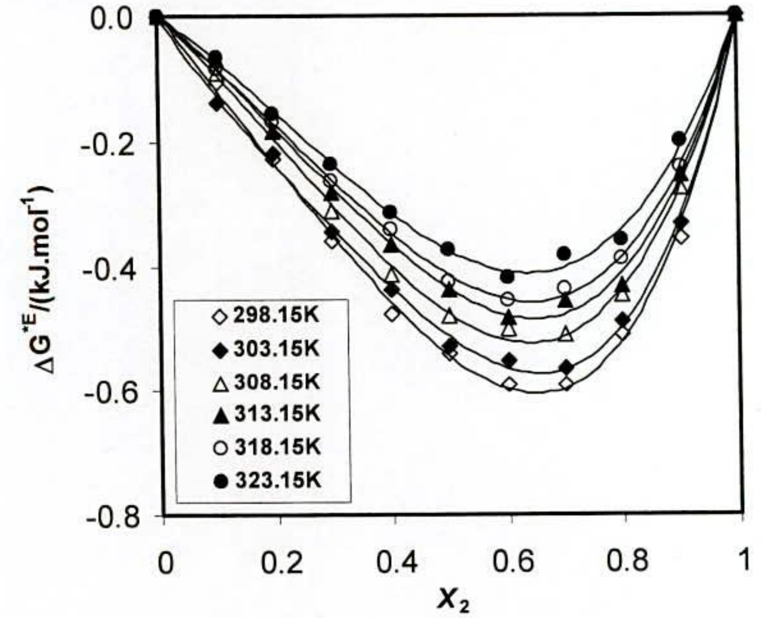

Figure 4.61. Plots of excess free energy vs mole fraction of n-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

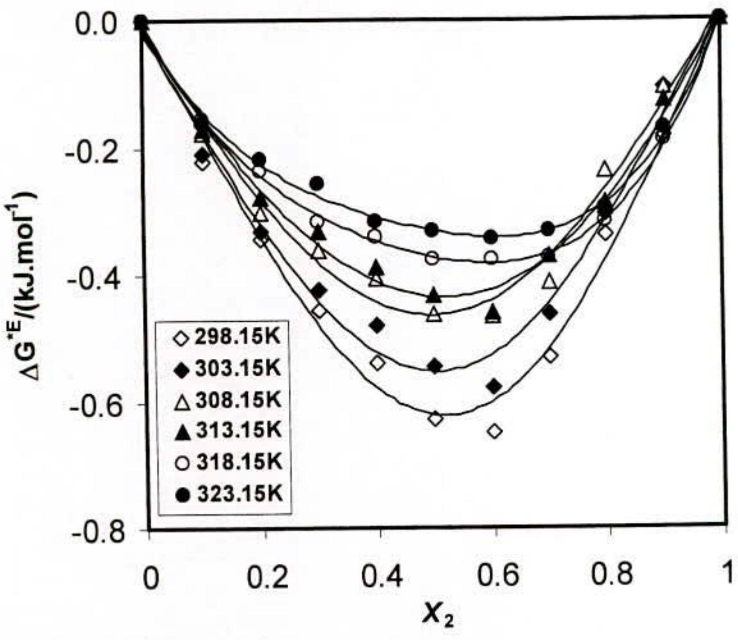

Figure 4.62. Plots of excess free energy vs mole fraction of iso-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

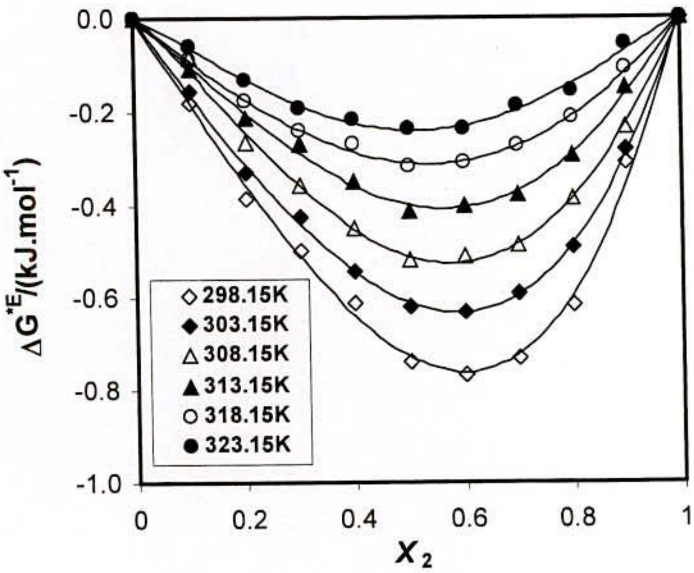

Figure 4.63. Plots of excess free energy vs mole fraction of t-Butanol + DMF system at 298.15K, 303.15K and 308.15K respectively

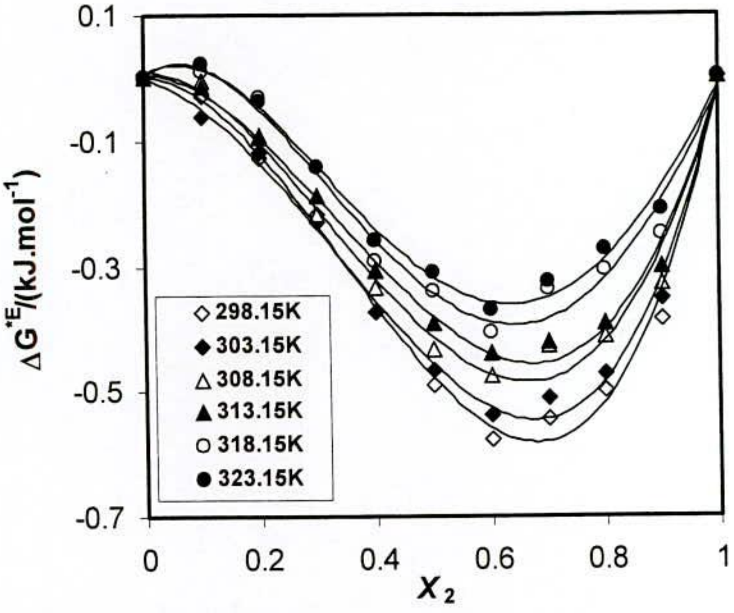

Figure 4.64. Plots of excess free energy vs mole fraction of n-Amyl alcohol + DMF system at 298.15K, 303.15K and 308.15K respectively

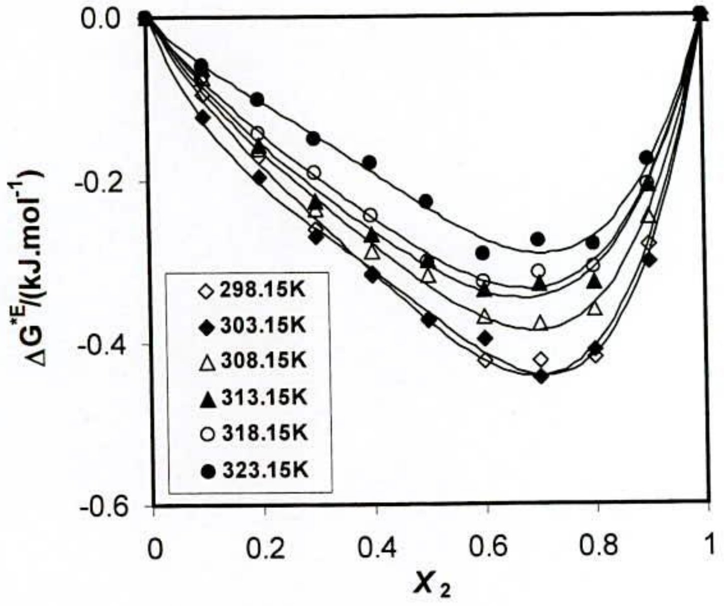

Figure 4.65. Plots of excess free energy vs mole fraction of iso-Amyl alcohol + DMF system at 298.15K, 303.15K and 308.15K respectively

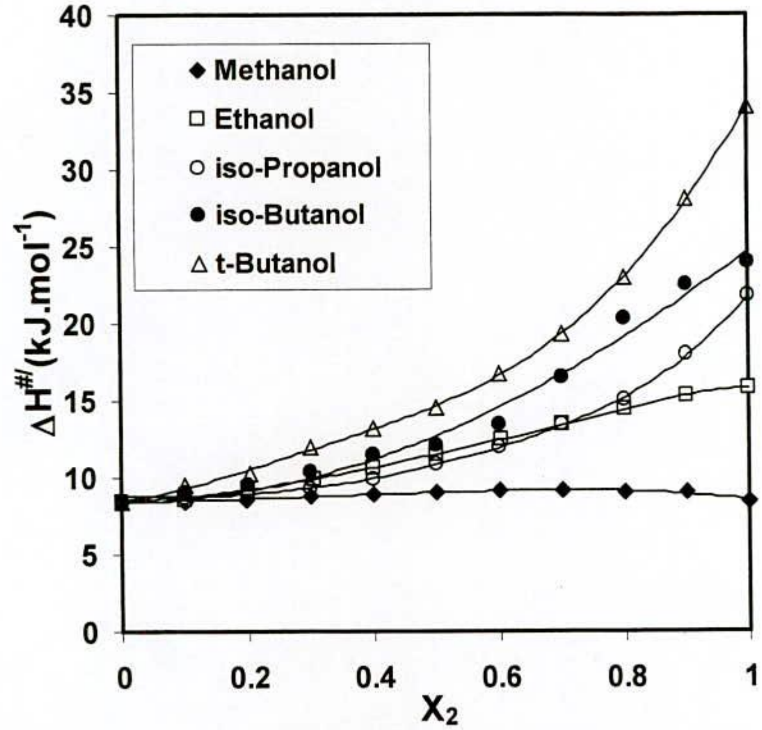

Figure 4.66. Plots of viscous enthalpy vs mole fraction of Methanol, Ethanol, iso-Propanol, iso-Butanol, t-Butanol + DMF system respectively.

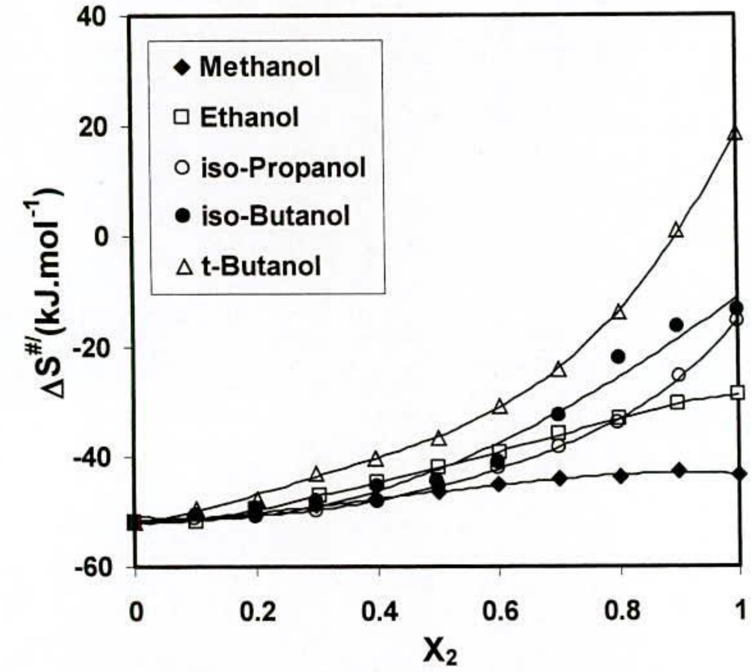

Figure 4.67. Plots of viscous entropy vs mole fraction of Methanol, Ethanol, iso-Propanol, iso-Butanol, t-Butanol + DMF system respectively.

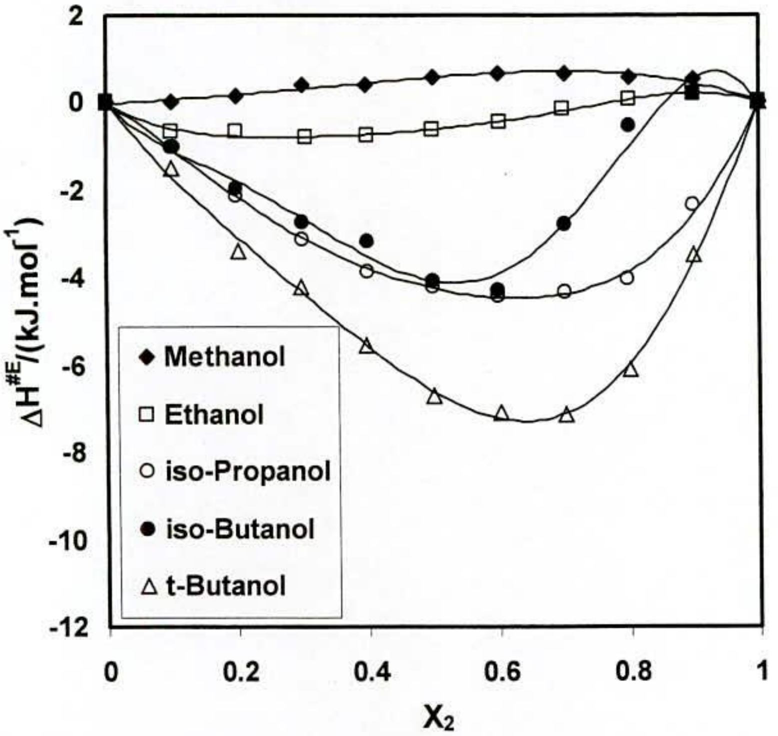

Figure 4.68. Plots of excess enthalpy vs mole fraction of Methanol, Ethanol, iso-Propanol, iso-Butanol, t-Butanol + DMF system respectively.

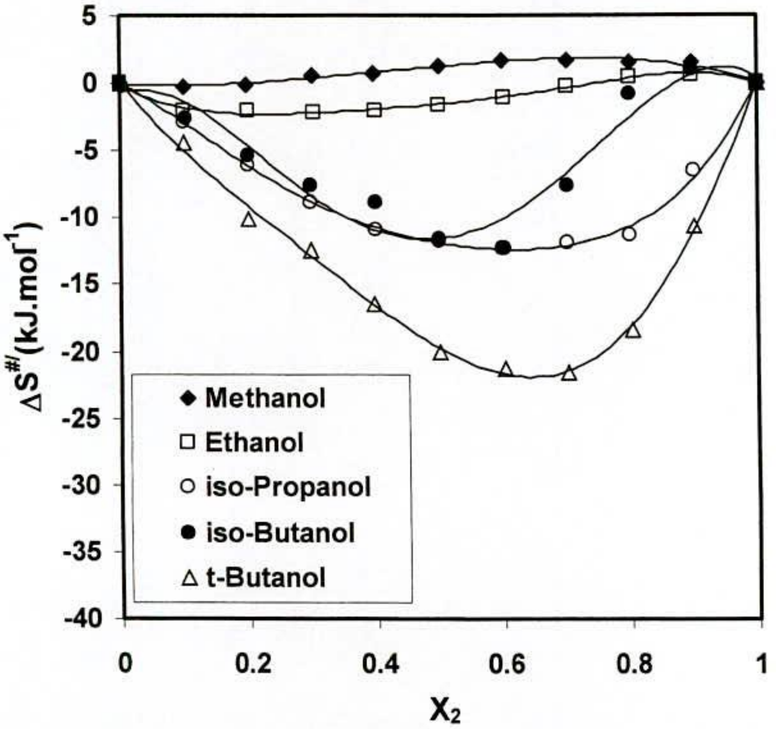

Figure 4.69. Plots of excess entropy vs mole fraction of Methanol, Ethanol, iso-Propanol, iso-Butanol, t-Butanol + DMF system respectively.

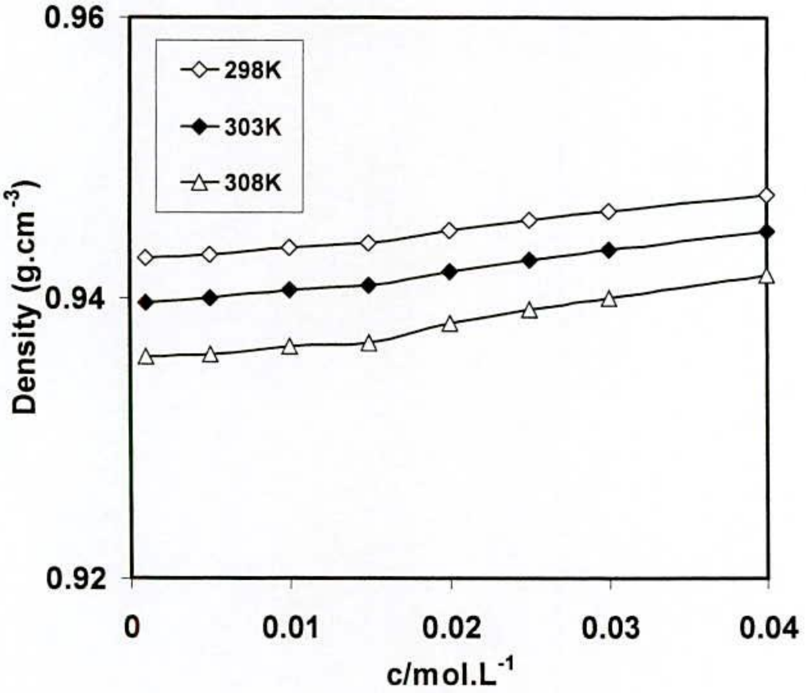

Figure 4.70. Plots of density vs concentration of SDS at 298.15K, 303.15K, and 308.15K respectively

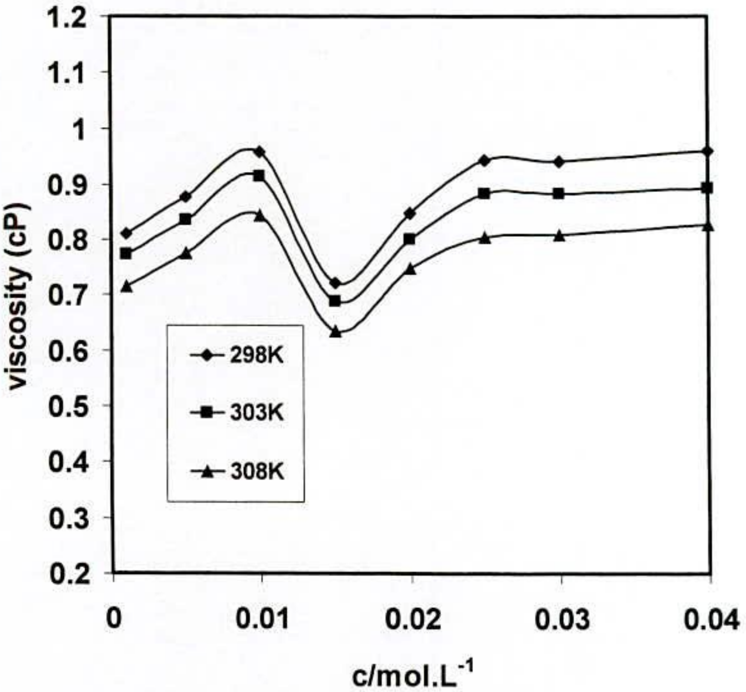

Figure 4.71. Plots of viscosity vs concentration of SDS at 298.15K, 303.15K, and 308.15K respectively

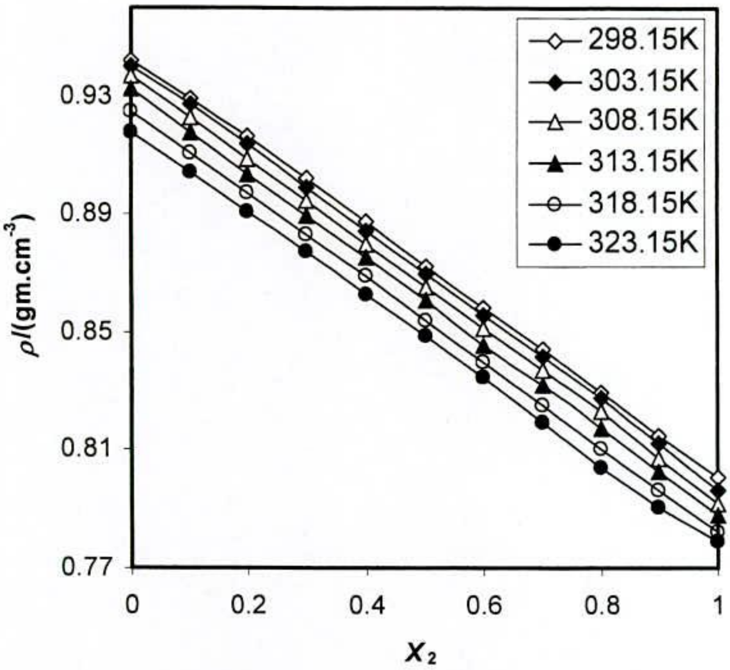

Figure 4.72. Plots of density vs mole fraction of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

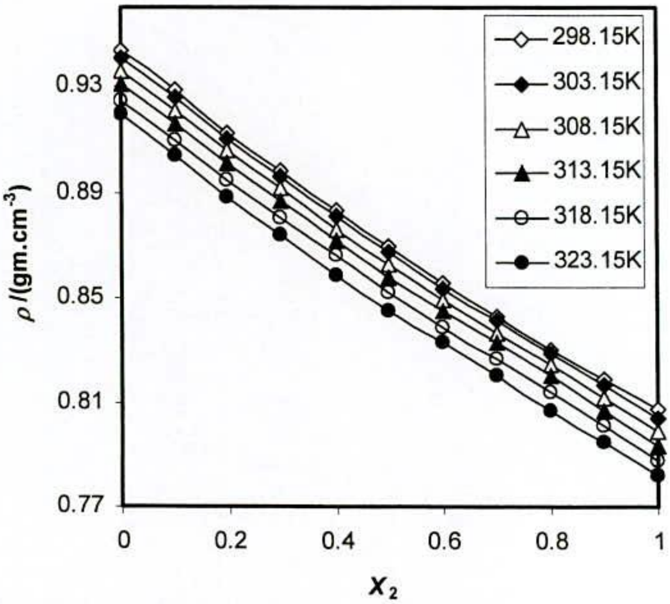

Figure 4.73. Plots of density vs mole fraction of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

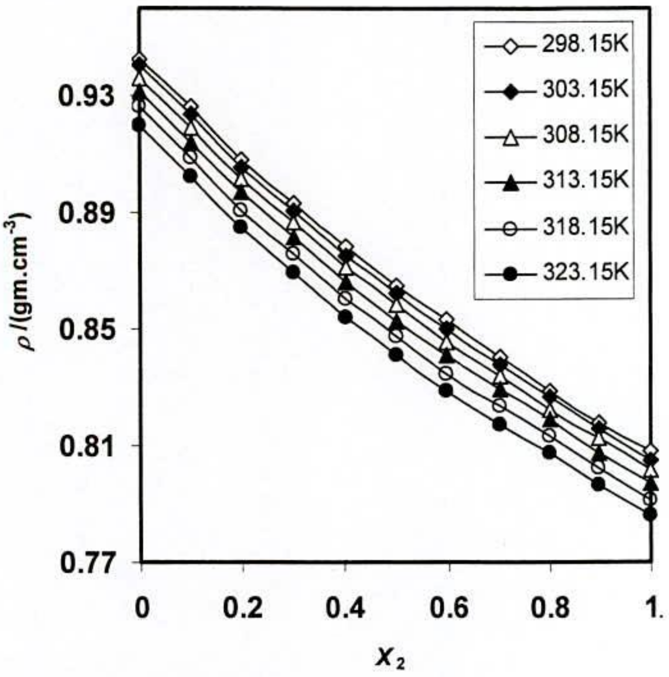

Figure 4.74. Plots of density vs mole fraction of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

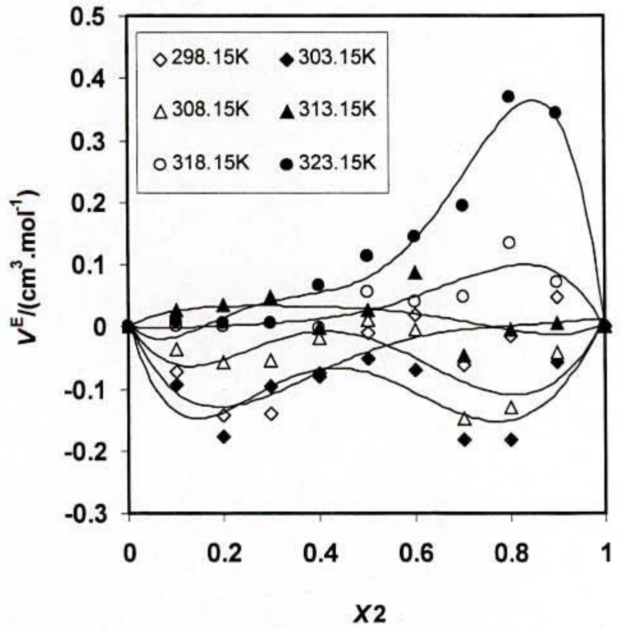

Figure 4.75. Plots of excess molar volume vs mole fraction of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

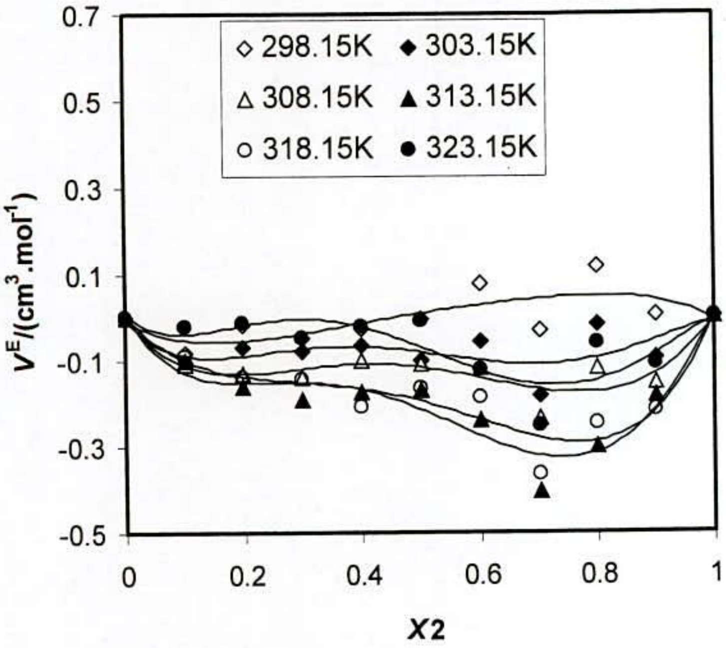

Figure 4.76. Plots of excess molar volume vs mole fraction of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

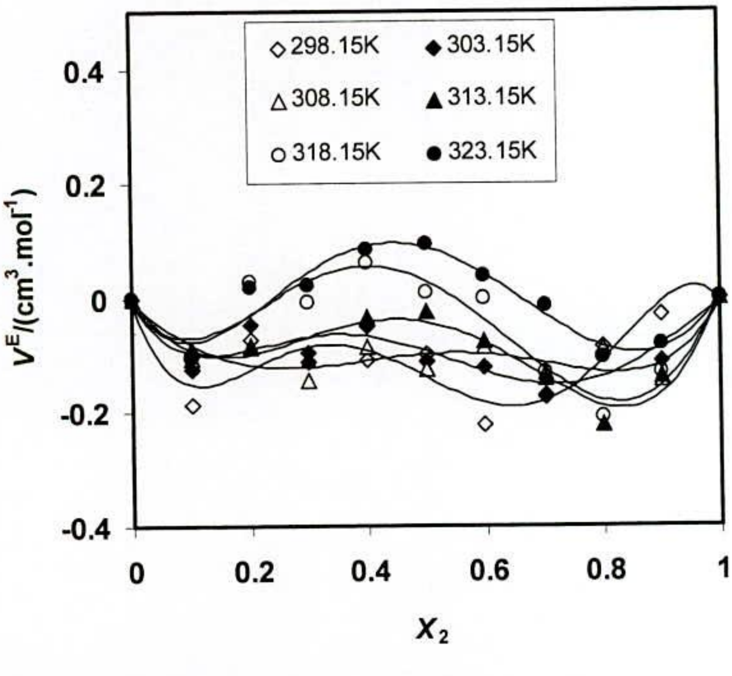

Figure 4.77. Plots of excess molar volume vs mole fraction of n-Amyl alcohol+SDS+ DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

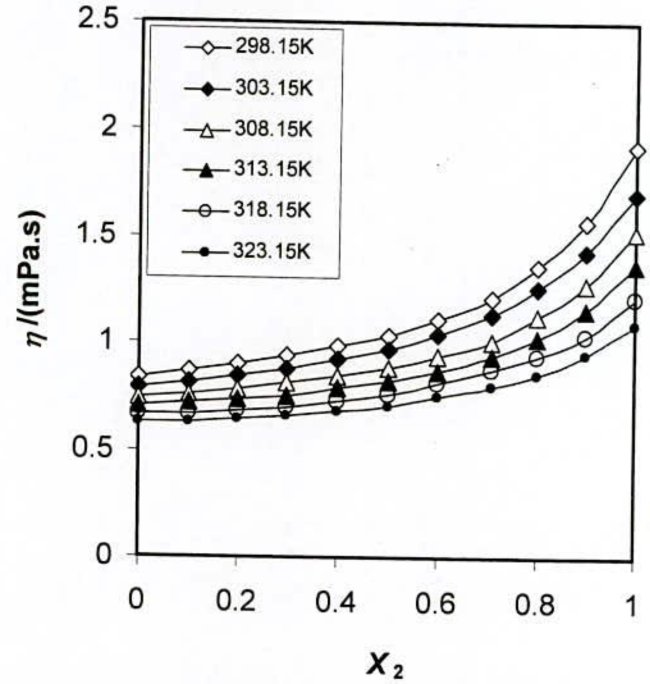

Figure 4.78: Plots of viscosity vs mole fraction of n-Propanol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

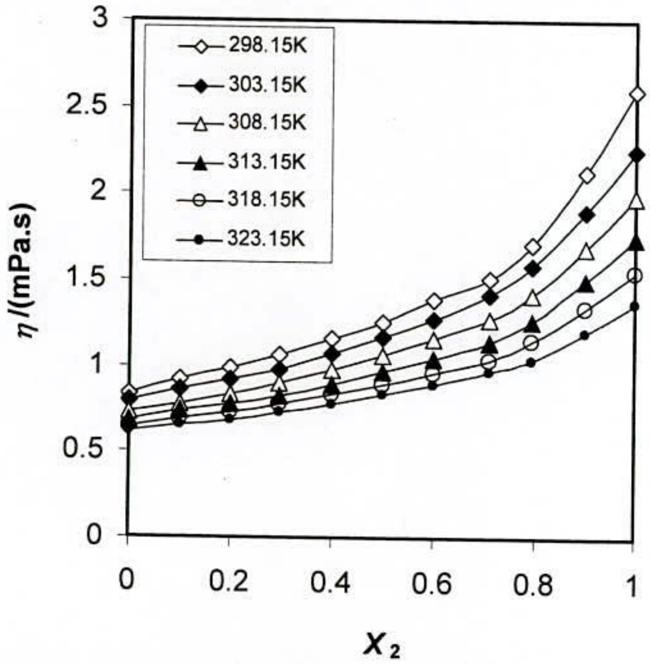

Figure 4.79. Plots of viscosity vs mole fraction of n-Butanol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

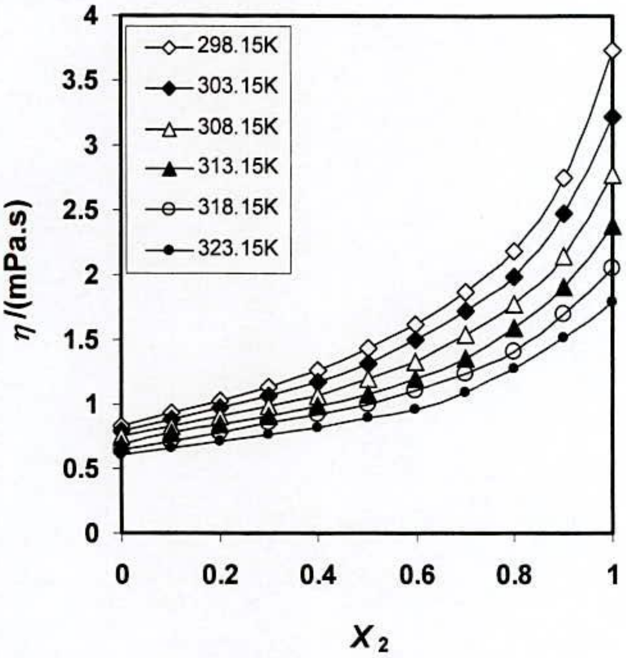

Figure 4.80. Plots of viscosity vs mole fraction of Amyl alcohol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

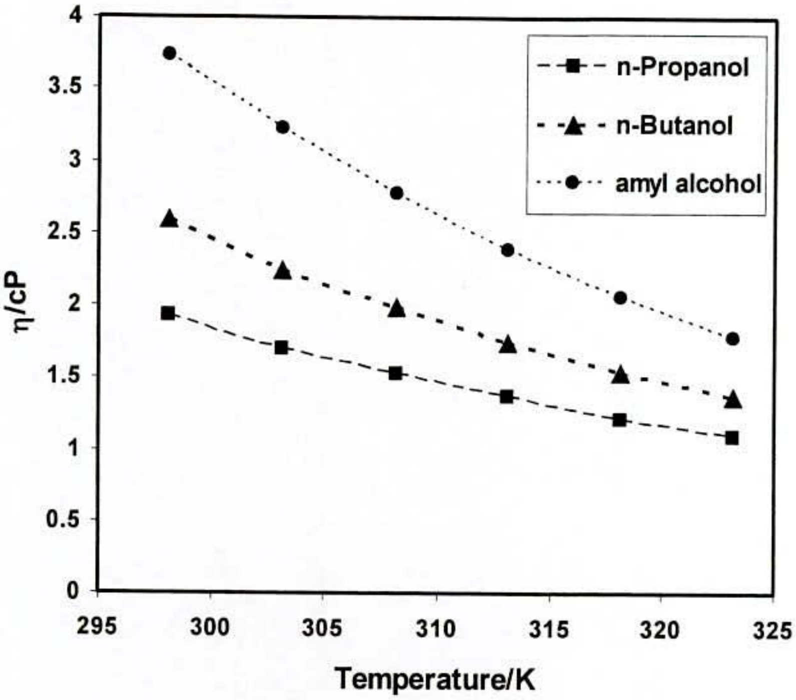

Figure 4.81: Plots of viscosity vs temperature of n-Propanol, n-Butanol and n-Amyl alcohol in SDS containing DMF system.

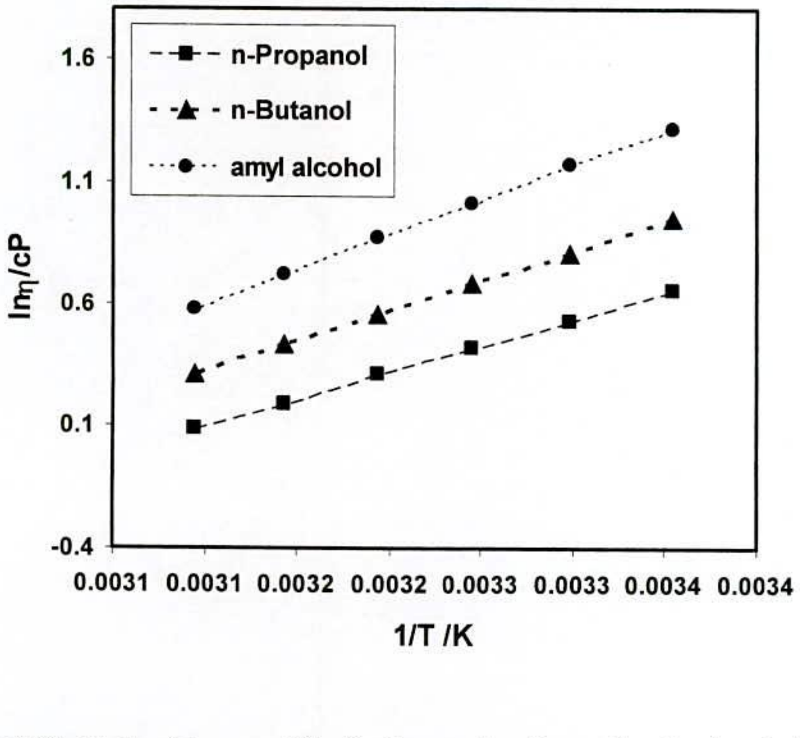

Figure 4.82: Plots of lnη vs 1/T of n-Propanol, n-Butanol and n-Amyl alcohol in SDS containing DMF system.

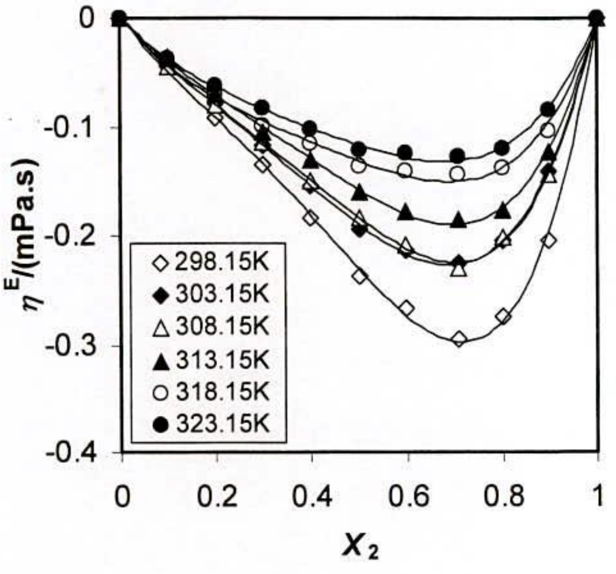

Figure 4.83. Plots of excess viscosity vs mole fraction of n-Propanol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

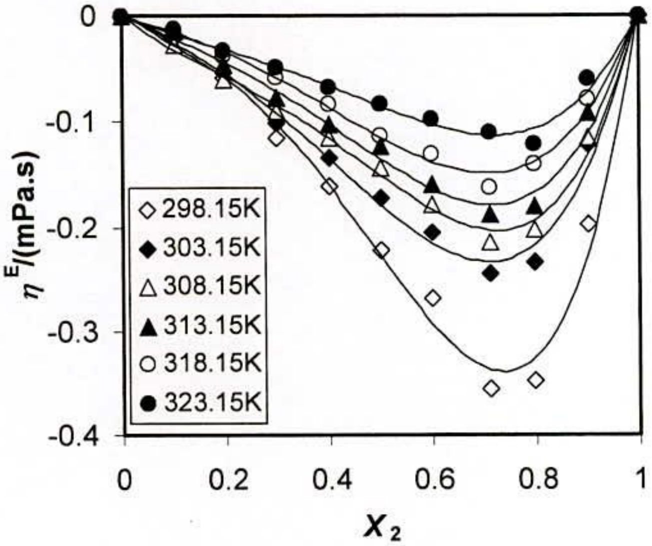

Figure 4.84. Plots of excess viscosity vs mole fraction of n-Butanol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

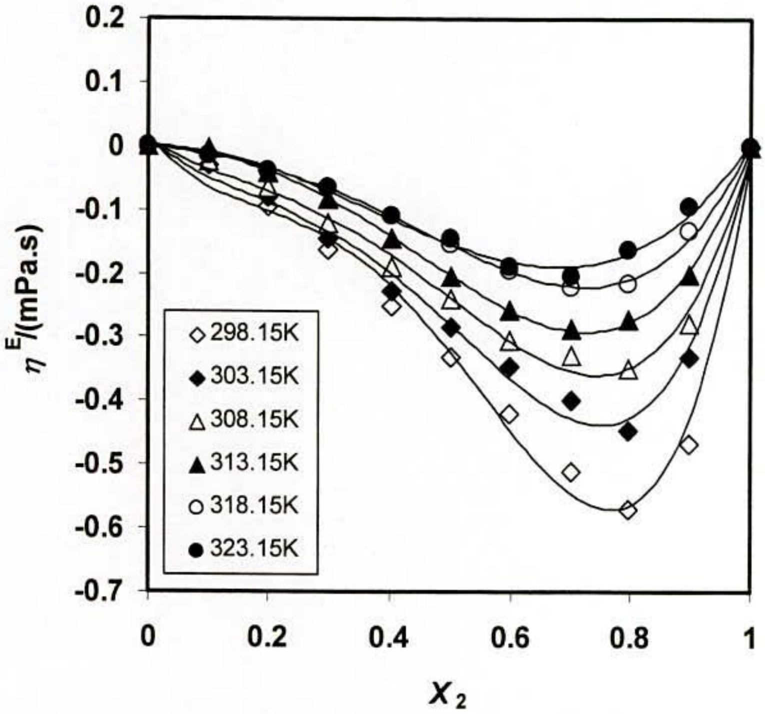

Figure 4.85. Plots of excess viscosity vs mole fraction of Amyl alcohol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

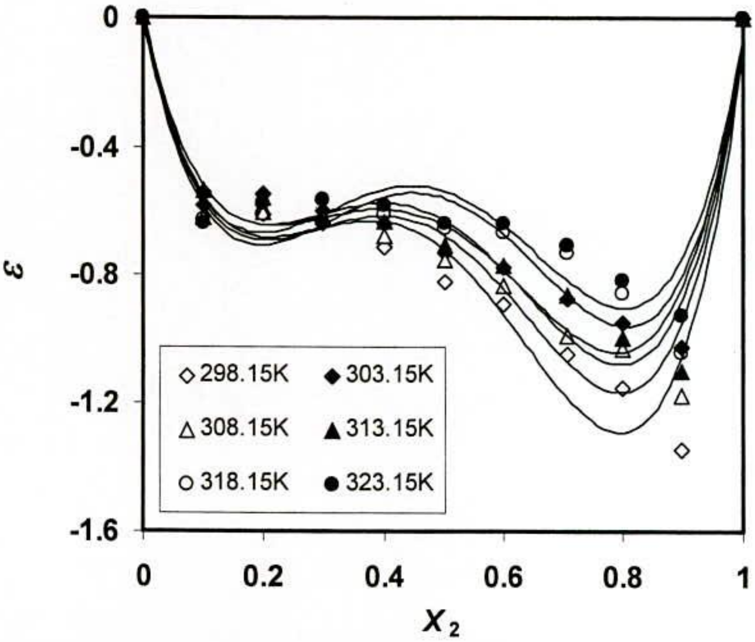

Figure 4.86. Plots of interaction parameter vs mole fraction of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

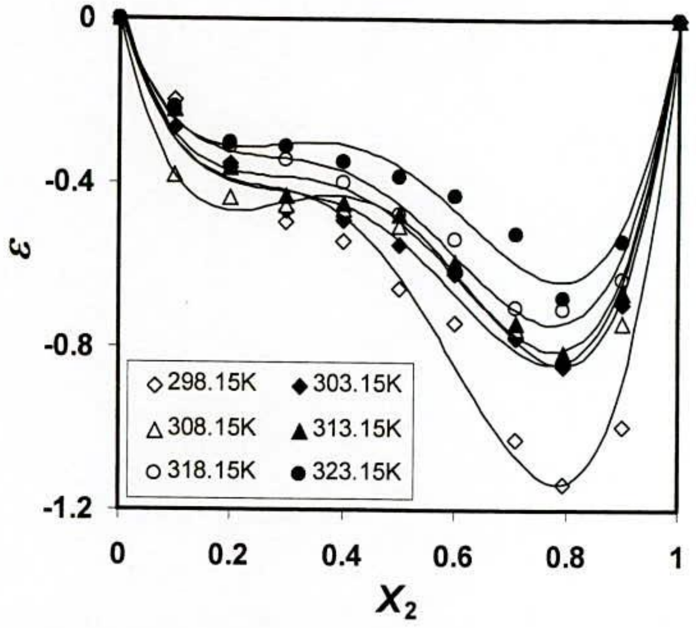

Figure 4.87. Plots of interaction parameter vs mole fraction of n-Butanol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

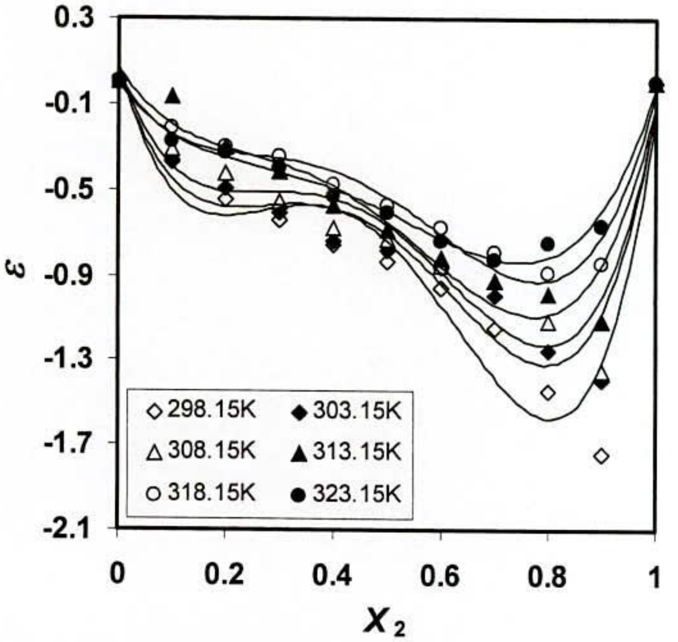

Figure 4.88. Plots of interaction parameter vs mole fraction of n-Amyl alcohol +SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

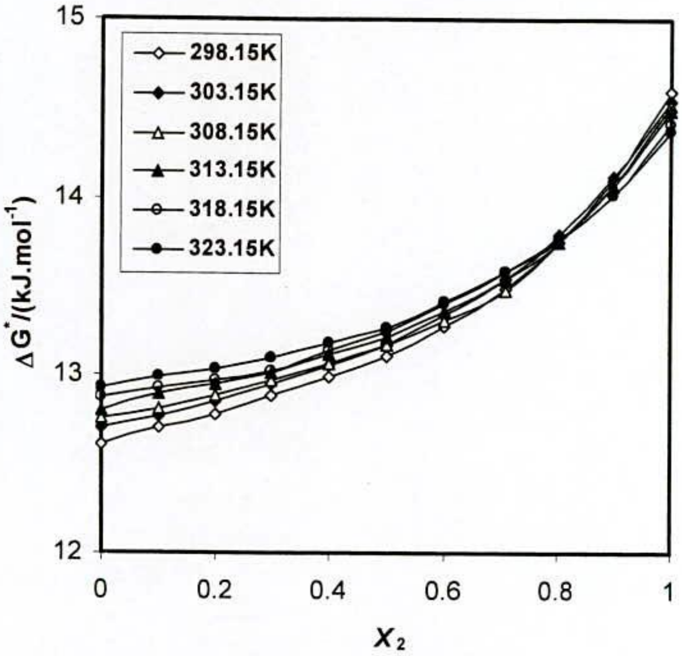

Figure 4.89. Plots of viscous free energy vs mole fraction of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

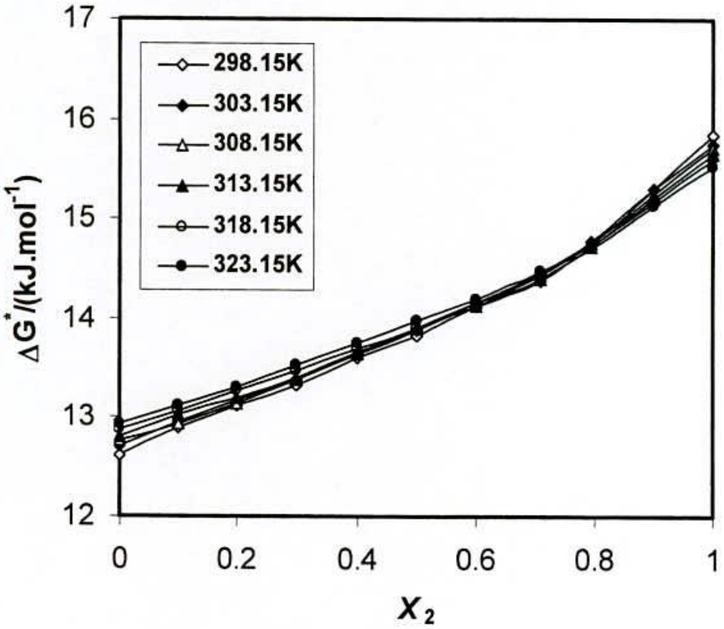

Figure 4.90. Plots of viscous free energy vs mole fraction of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

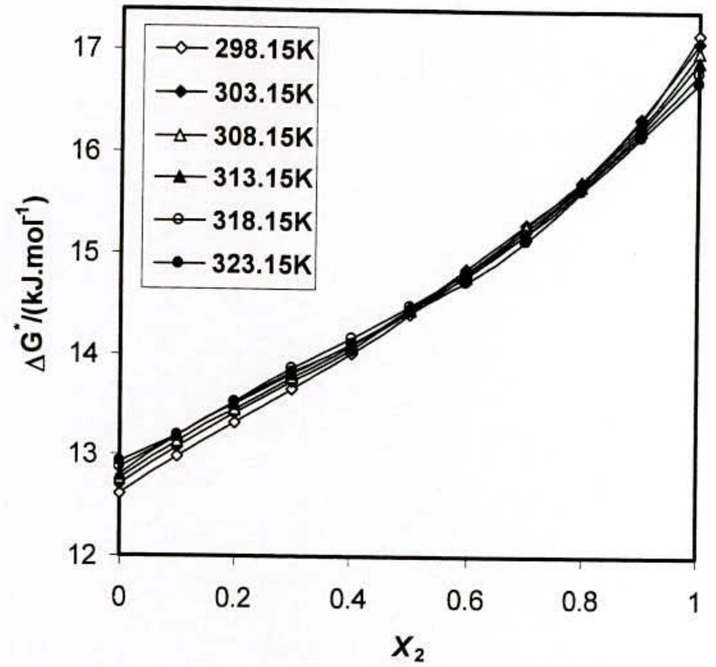

Figure 4.91. Plots of viscous free energy vs mole fraction of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

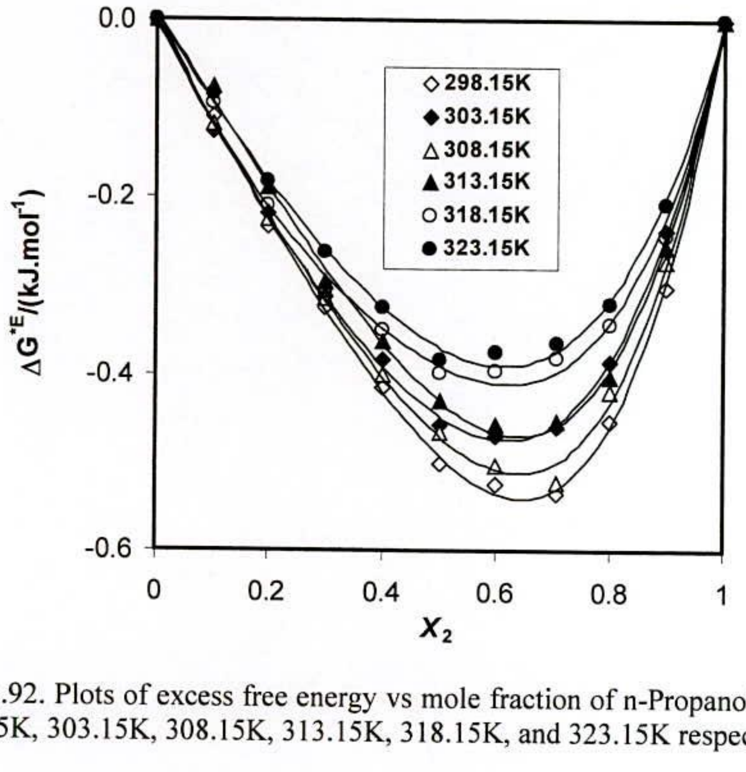

Figure 4.92. Plots of excess free energy vs mole fraction of n-Propanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

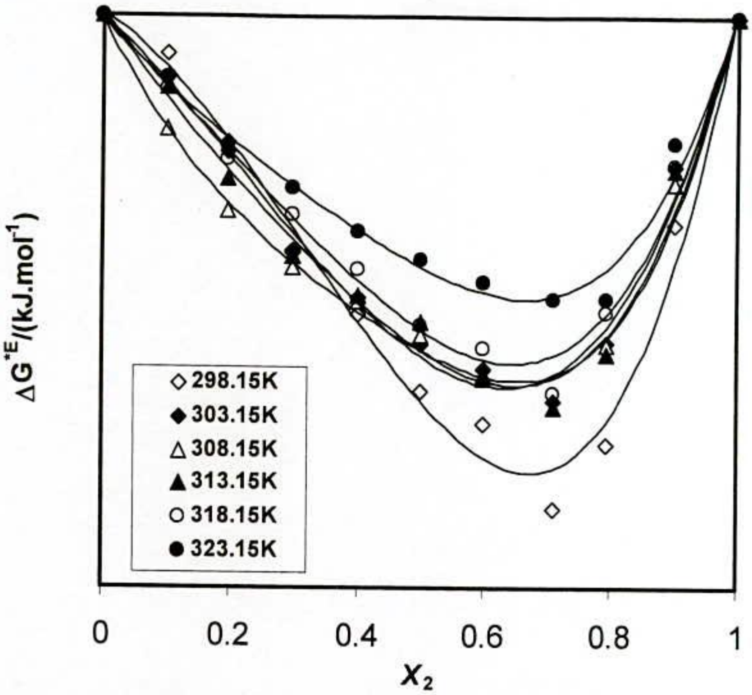

Figure 4.93. Plots of excess free energy vs mole fraction of n-Butanol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

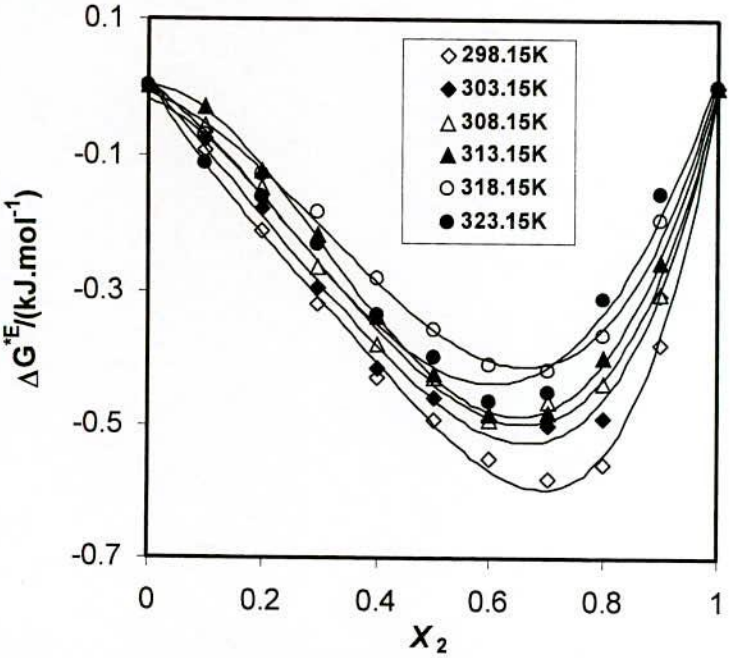

Figure 4.94. Plots of excess free energy vs mole fraction of n-Amyl alcohol+SDS+DMF system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, and 323.15K respectively

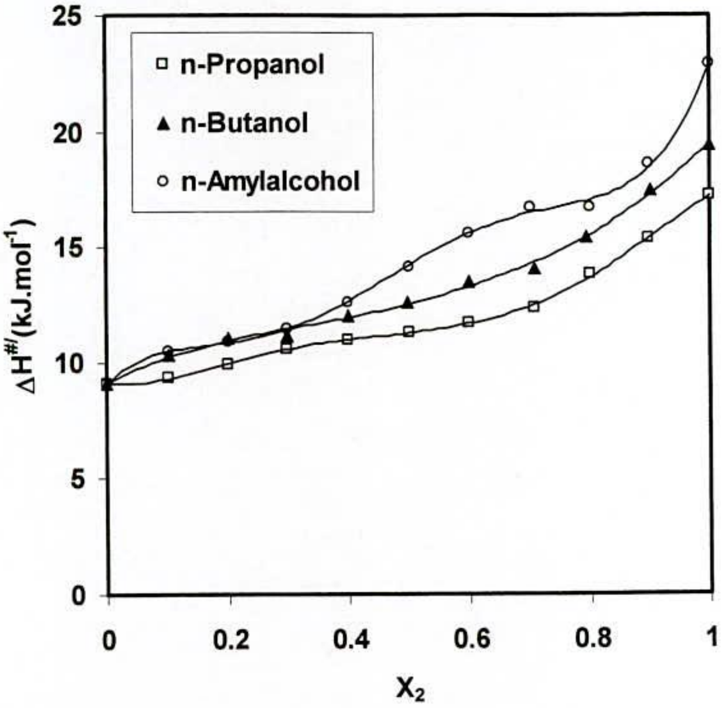

Figure 4.95. Plots of viscous enthalpy vs mole fraction of n-Propanol, n-Butanol, n-Amyl alcohol in SDS containimg DMF system.

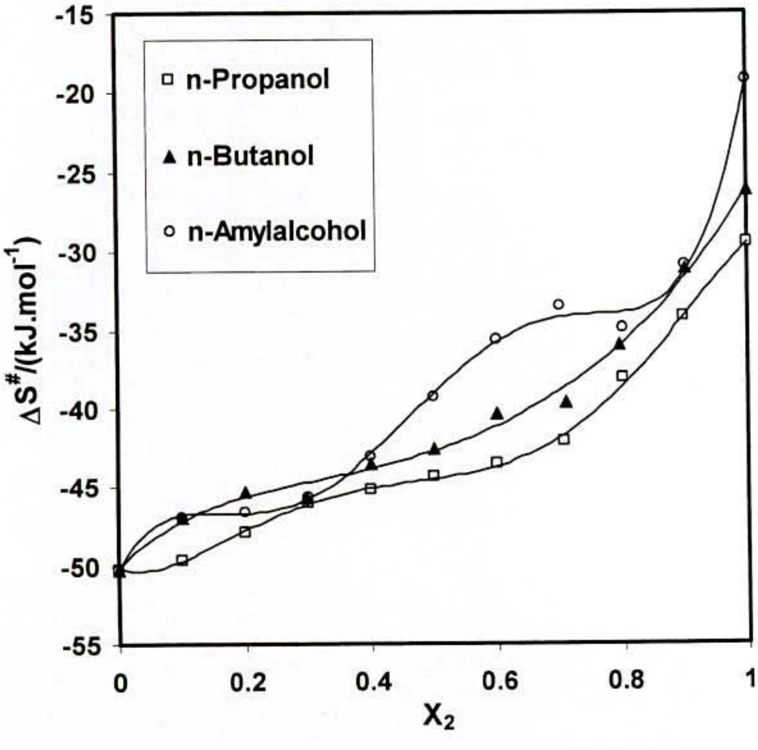

Figure 4.96. Plots of viscous entropy vs mole fraction of n-Propanol, n-Butanol, n-Amyl alcohol in SDS containimg DMF system.

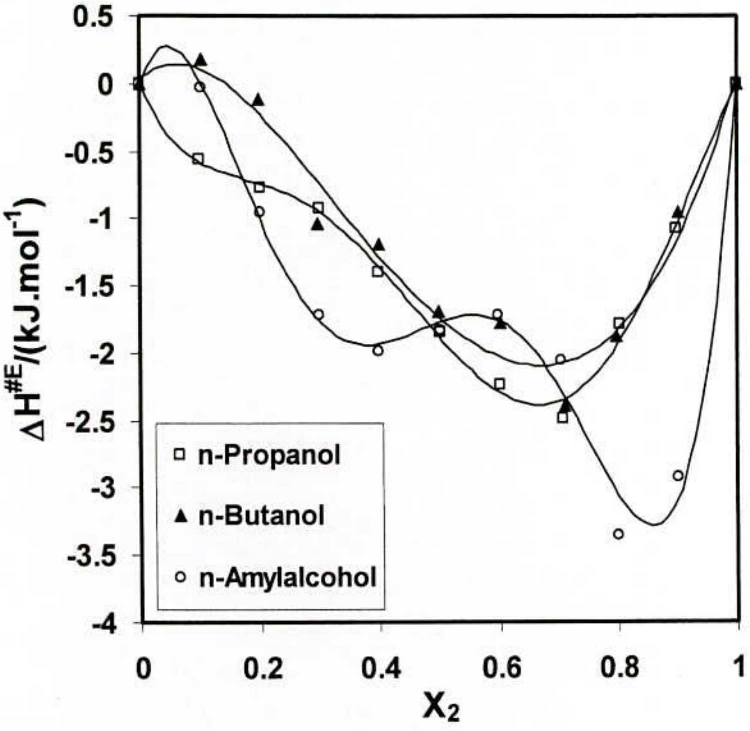

Figure 4.97. Plots of excess enthalpy vs mole fraction of n-Propanol, n-Butanol, n-Amyl alcohol in SDS containimg DMF system.

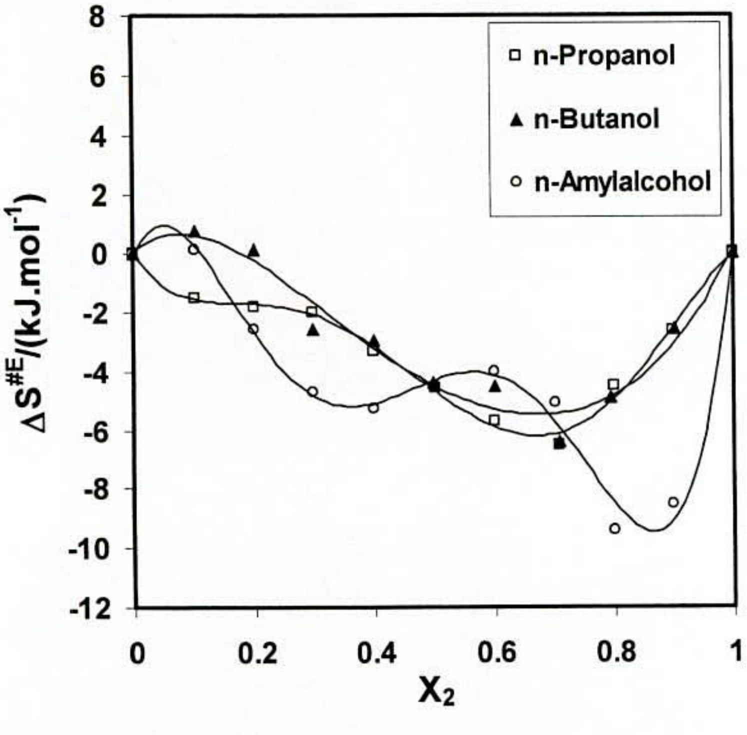

Figure 4.98. Plots of excess entropy vs mole fraction of n-Propanol, n-Butanol, n-Amyl alcohol in SDS containimg DMF system.

CHAPTER V

Conclusion

The studies presented in this thesis are based on simple binary (alcohols+DMF) and ternary systems (alcohols+DMF+SDS). The studies on the solution properties of binary mixtures of Methanol +DMF, Ethanol +DMF, *n*-Propanol +DMF, *iso*-Propanol +DMF, *n*-Butanol +DMF, *iso*-Butanol +DMF, *tert*-Butanol +DMF, n-Amyl alcohol +DMF, iso-Amyl alcohol +DMF and ternary mixtures of *n*-Propanol +0.02M SDS in DMF, *n*-Butanol +0.02M SDS in DMF and n-Amyl alcohol +0.02M SDS in DMF, show strong solute–solvent interactions in DMF and SDS containing DMF solutions. The values of V^E for the most of studied alcohols are negative throughout the whole range of composition at lower temperature (298.15K-303.15K), but at higher temperature, it shows positive. For Methanol +DMF, n-Amyl alcohol + DMF and iso-Amyl alcohol +DMF systems, the excess molar volumes are negative throughout the whole range of composition. Methanol shows the highest negative V^E values. The observed values of V^E for the mixtures have been explained in terms of specific intermolecular interactions and structural contributions.

The viscosities increase initially slowly up to ~0.6 mole fraction of Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol and iso-Amyl alcohols and later on, the viscosity increases sharply until that of pure alcohol is reached specially at lower temperature. For Methanol, viscosity decrease slowly on continued addition of Methanol.

The excess viscosity, η^E values are found to be positive or negative, indicating that the DMF solutions of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems except Methanol with minima occurring between 0.6-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol and *tert*-Butanol. n-Amyl alcohol and iso-Amyl alcohol show minima at 0.8-0.9 mole fraction. Excess viscosity of Methanol is positive at all the temperatures over the entire range of composition and show maxima in the DMF rich region at 0.2-0.4 mole fraction of Methanol.

The interaction parameters, ε have been found to be negative and quite large in magnitude except Methanol +DMF systems. The negative ε of all the studied alcohols indicate that dispersion force is occurred. The positive ε of Methanol +DMF system indicate that strong specific interaction.

The negative V^E , positive η^E, and positive ε for the DMF + Methanol system may be ascribed that the interaction is strong, namely formation of H-bonding between DMF and Methanol. The negative V^E , negative η^E, and negative ε for the DMF + rest of the studied alcohols systems may be indicate that dispersion force is dominant.

The free energy, $\Delta G^{\#}$ 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.

The $\Delta G^{\#E}$ of Methanol +DMF is positive in the DMF rich region but negative in alcohol rich region. For Ethanol, *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *tert*-Butanol, n-Amyl alcohol, iso-Amyl alcohol in DMF systems, $\Delta G^{\#E}$ are negative over the entire composition range. The negative excess free energy, $\Delta G^{\#E}$ indicates the presence of dispersion force, whereas positive excess free energy, $\Delta G^{\#E}$ suggests a specific association in the mixtures.

The entropy change, $\Delta S^{\#}$ is found to be negative for all the studied alcohol systems except t-Butanol. The positive $\Delta S^{\#}$ apparently indicates more random orientation of the complexes formed in the activated state.

The enthalpy change, $\Delta H^{\#}$ is positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process.

Although the value of density and viscosity of the studied systems in SDS containing DMF solutions are higher than the pure DMF solutions, but no appreciable change in the volumetric and viscometric properties are observed by the addition of the surfactants.

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