Studies on Volumetric and Viscometric Properties of Some iso-meric Alcohols in Surfactant Containing Ethanol Systems

by

Md. Atiar Rahman

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Philosophy (M. Phil.) in Chemistry

Khulna University of Engineering & Technology
Khulna 9203, Bangladesh.
December, 2015

Declaration

This is to certify that the thesis work entitled "**Studies on Volumetric and Viscometric Properties of Some iso-meric Alcohols in Surfactant Containing Ethanol Systems.**" has been carried out by Md. Atiar Rahman 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.

Signature of Supervisor

Signature of Candidate

Approval

This is to certify that the thesis work submitted by Md. Atiar Rahman entitled " **Studies on Volumetric and Viscometric Properties of Some iso-meric Alcohols in Surfactant Containing Ethanol 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 December, 2015.

BOARD OF EXAMINERS

05.12.15

1. ______________________

Dr. Md. Abdul Motin
Professor, Department of Chemistry
Khulna University of Engineering & Technology
Chairman
(Supervisor)

05.12.15

2. ______________________

Head
Department of Chemistry
Khulna University of Engineering & Technology
Member

05/12/2015

3. ______________________

Dr. Md. Abdul Aziz
Professor, Department of Chemistry
Khulna University of Engineering & Technology
Member

05.12.15

4. ______________________

Dr. Mohammad Hasan Morshed
Professor, Department of Chemistry
Khulna University of Engineering & Technology
Member

5. ______________________

Dr. Md. Abdur Rahim Khan
Professor
Department of Analytical and Environmental Chemistry
Bangabandhu Sheikh Mujibur Rahman Science & Technology
Member
(External)

Acknowledgement

I would like to express my deepest sense of gratitude and sincere thanks to my respected supervisor **Dr. Md. Abdul Motin**, Professor, Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh for his proper guidance, co-operation, invaluable suggestions and constant encouragement throughout this research work. I will remember his inspiring guidance and cordial behavior forever in my future life.

I am pleased to express my gratitude to the Departmental Head Professor **Dr. Md. Abdul Motin**, for providing me necessary laboratory facilities and proper guidance for the research. I should take this opportunity to express my sincere thanks to **Md. Abdul Hafiz Mia,** Lecturer, Department of Chemistry and **all teachers** of this department for their valuable advice and moral support in my research work. I am also like to express my thanks to all the stuffs of this department.

I wish to convey my hearty thanks to **Parvez Zaman** and all my friends and class fellows. All of them helped me according to their ability.

I wish to thank my **mother**, **wife, son** and **daughter** for their sincere understanding and support.

Md. Atiar Rahman

ABSTRACT

The critical micelle concentration (CMC) of Sodium Dodecyl Sulfate (SDS) in Ethanol was determined from the conductance, density and viscosity measurement. The estimated value of CMC was found to be 0.015 mol.L^{-1}. The micellar concentration of SDS in Ethanol was used for the volumetric and viscometric measurements of *n*-Propanol, iso-Propanol, *n*-Butanol, iso-Butanol, n-Pentanol and *iso*-Pentanol at different temperatures.

Densities and viscosities of ternary mixtures of *n*-Propanol in 0.015M SDS+Ethanol, *iso*-Propanol in 0.015M SDS+Ethanol, *n*-Butanol in 0.015M SDS+Ethanol, *iso*-Butanol in 0.015M SDS+Ethanol, n-Pentanol in 0.015M SDS+Ethanol and *iso*-Pentanol in 0.015M SDS+Ethanol have been studied over the entire range of composition $(0 < x_2 < 1)$ at 298.15-323.15K with an interval of 5K. The density of alcohols in equi-molefraction of 0.015M SDS+Ethanol was found to be order of

n-Pentanol > *n*-Butanol > *n*-Propanol

and

iso-Pentanol > iso-Butanol > iso-Propanol.

The value of density of alcohols in 0.015M SDS+Ethanol decreases with the increasing of composition of the alcohols. The decrease of density with composition of alcohols can be attributed to dissociation of components. The densities of all alcohols increase with the increase of carbon number which may be depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. The densities decrease regularly with the increasing of temperature. This is due to the thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding are occurred.

The excess molar volumes, V^E were calculated from the densities of the mixtures at different temperatures. The values of V^E for all the systems are positive over the entire range of composition, showing maxima ~ 0.5 mole fraction of *n*-Propanol and ~ 0.5-0.6 mole fraction of *iso*-Propanol, ~ 0.5-0.6 mole fraction of *n*-Butanol, ~0.6 mole fraction of *iso*-Butanol, ~ 0.7-0.8 mole fraction of n-Pentanol and ~0.8 mole fraction of iso-Pentanol. The excess molar volume, V^E of alcohols in 0.015M SDS+Ethanol solutions was found to be order of

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

and

iso-Pentanol > *n*-Pentanol, *iso*-Butanol > *n*-Butanol and *iso*-Propanol > *n*-Propanol.

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

The viscosity coefficients, η of all the above mixtures at all the six different temperatures have also been determined. The viscosities increase slowly up to entire mole fraction of *n*-Propanol, *iso*-Propanol. For *n*-Butanol and *iso*-Butanol, the viscosities increase initially slowly up to ~0.6 mole fraction and later on, the viscosity increases sharply until the pure alcohol is reached. . For *n*-Pentanol and *iso*-Pentanol, the viscosities increase initially slowly up to ~0.8 mole fraction and later on, the viscosity increases very sharply until the pure alcohol is reached. In pure state the viscosity of alcohols has been found to be in the order of,

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

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

The excess viscosity, η^E values are found to be negative, indicating that the 0.015M SDS + Ethanol solution of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.6-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and iso-Pentanol. The negative excess viscosity, η^E of 0.015M SDS+Ethanol + all the studied alcohols indicate that the dissociation of components through dispersive forces or steric hindrance. The position of minima virtually does not change remarkably with the variation of temperature. The values of the minima are in the order:

n-Pentanol>n-Butanol > n-Propanol and iso-Pentanol > iso-Butanol > iso-Propanol

The hydrophobic effect increases with the increasing of carbon chain length of alcohols. This indicates that the η^E decreases with the decrease of carbon number. The positive V^E, negative η^E, and negative ε for the 0.015M SDS+Ethanol + studied alcohols systems indicate that dispersion force is dominant.

The thermodynamic parameters such as free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) change of activation for the viscous flow for these systems were examined for the entire range of composition. The free energy (ΔG^*) were found to be positive in magnitude indicating that the kinetic species involved in forming cavities or holes in the liquid medium is given by the work required in forming the hole against surface tension of the solution. The negative excess free energy, ΔG^{*E} indicate that the strong dispersion force in alcohols+ 0.015M SDS+Ethanol solution is dominant. The excess properties (V^E, η^E, ΔG^{*E}) data have been fitted by the least square method to the four parameter Redlich-Kister equation and the values of the parameter a_i and standard deviation have been reported. The volumetric properties are fully consistent with viscometric and thermodynamic properties.

Contents

LIST OF TABLES

LIST OF FIGURES

Nomenclature

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

Nomenclature

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

CHAPTER I

Introduction

1.1 Properties of solutions

The science of solution chemistry is very complex. It needs for its clarifications of many branches of science namely chemistry, physics, mathematics, statistical thermodynamics, hydrodynamics etc. The liquid state, is an intermediate state between solid and gaseous states, retains some properties of both the gaseous and solid states. Therefore, the liquid state can not be adequately defined as the gaseous and the solid states. The molecular and macroscopic property of liquids varies from liquid to liquid due to characteristic intermolecular interactions. The properties of multi-component mixtures, on account of molecular interactions between dissimilar molecules, become still more difficult to explain. Considering these facts there are serious difficulties in formulation of any general theory of solution (1-3).

It should, in principle, be possible to calculate theoretically, the properties of solution from the properties of individual components. But there are inherent difficulties created by liquid state that is not properly understood. The theoretical treatments, therefore, have to assume some model (e.g., lattice model, cell model etc.) for the structure of the components and their solution. Alternatively, it is considered convenient and useful to determine experimentally the values of certain macroscopic properties of solutions for proper understanding of the structure of the solution. Some of the usually experimentally determined macroscopic properties are: density, viscosity, thermodynamic properties, surface tension, etc., which are readily measurable. Investigations, comprising experimental determination of various thermodynamic properties, viscosity etc. on solutions, assume significant importance since it is possible to draw conclusions regarding characteristic molecular interactions between constituent molecules of the components from purely thermodynamic reasoning (1-5).

The theoretical treatments need to assume some model for carrying out statistical-mechanical calculations of these properties. The observed discrepancies between theoretically calculated and experimentally determined values are naturally on account of the inadequacies in the theoretical models. Such a comparison often suggests appropriate refinements of the assumed model.
The macroscopic behaviors of any system have to be interdependent, since these essentially originate from the most probable distribution of energy between the constituent molecules comprising the system. Therefore, there has been interest for seeking interrelations between the macroscopic properties of any system. It should be possible to express the value of any macroscopic property in terms of the known values of the other. Since viscosity coefficient is a macroscopic property under non equilibrium condition, there has been a considerable effort for establishing its relationship with thermodynamic properties of a system (6-8).

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

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

Physical properties like density, viscosity, surface tension, conductivity, dielectric constant, refractive index, group frequency shifts in I.R. spectra etc. provide an indication about the molecular structure as well as the molecular interactions that occur when liquids are mixed together. The density and viscosity are two fundamental physico-chemical properties of which are easy, simple, inexpensive and precise tools, by which one can get the valuable information about the molecular interactions in liquids and liquid mixture correlated with equilibrium and transport properties. The thermodynamic and excess thermodynamic data are used subsequently by a variety of physical scientists including chemical kineticists and spectroscopists involved in reaction occurring in solution and by chemical engineers engaged in the operation and design of chemical reactor, distillation columns or other type of separation devices. Liquid mixtures frequently appear in chemical research. Most of the mixtures are nonideal and show peculiar behavior. The interpretation of nonideality is a fascinating area and a large number of contributions were made over the last decade. Solution theory is still far from adequate to account for solution non idealities in terms of the properties of the constituent molecules.

From the above mentioned properties, quantitative conclusion can be drawn about the molecular interactions even in simple liquids or their mixtures.

Our present investigation is based on the methods of physico-chemical analysis, which is a useful tool in getting sound information about the structure of some alcohol with SDS in studying the liquid-liquid interaction in binary systems.

1.2 Properties of alcohols

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

The boiling point of an alcohol is always much higher than that of the alkane with the same number of carbon atoms. The boiling point of the alcohols increases as the number of carbon atoms increase. For example Ethanol (MW 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.

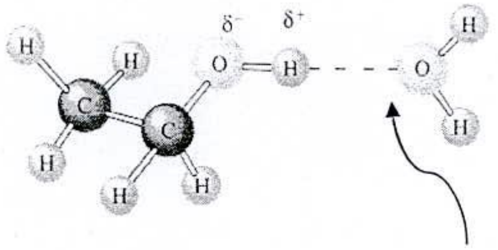

Fig. 1.1

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 (9).

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

1.3 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 ~ $50A^0$ 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).

1.4 Classification of surfactants

The hydrophilic part of the most effective soluble surfactants (e.g soap, synthetic detergents and dyestuffs) is often an ionic group. Ions have a strong affinity for water owing to their electrostatic attraction to the water dipoles and are capable of pulling fairly long hydrocarbon chain into solution with them.

Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the change carried by the surface-active part of the molecule. Some common examples are given in table-1.2. 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 one 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.

Table 1.2: Surface active agents

Anionic	
Sodium Stearate	$CH_3(CH_2)_{16}COO^-Na^+$
Sodium oleate	$CH_3(CH_2)_7CH=CH(CH_2)_7COO^-Na^+$
Sodium dodecyl sulphate	$CH_3(CH_2)_{11}SO_4^-Na^+$
sodium dodecyl benzene sulphate	$CH_3(CH_2)_{11}C_2H_4SO_4^-Na^+$
Cationic	
Dodecyl trimethyl ammonium bromide	$CH_3(CH_2)_{11}N^+(CH_3)_2\,CH_3Br$
Dodecylamine hydrocloride	$CH_3(CH_2)_{11}NH_3^+Cl$
Non-ionic	
Polyethylene oxices	$CH_3(CH_2)_{11}(O\,CH_2CH_2)_6OH$
Ampholytic	
Dodecyl betain	$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$

1.5 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(10) 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).

Micellization is, therefore, an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution might decrease when one considers the energetic of micellization in terms of the hydrocarbon chain of the surface font molecules, the following factors are among those which must be taken into account:

1. The intermolecular attractions between the hydrocarbon chains in the interior of the micelle represent an energetically favorable situation but it is not one which is significantly more favorable than that which results from the alternative hydrocarbon water attraction in the case of single dissolved surfactant molecules. Comparison of the surface tension of typical hydrocarbon oil with the dispersion component of surface tension of water illustrates this point.

2. Micellisation permits strong water-water interaction (hydrogen bonding) which would have otherwise prevented if the surfactant was in solution as single molecules wedged between the solvent water molecules. This is a most important in micelle formation and also of course, in any adsorption process at an aqueous interface. It is often referred to as the hydrophobic effect.

Micelle formation is a typical hydrophobic process in water. In aqueous medium surfactant molecules with their long hydrophobic tails undergo hydrophobic hydration. As the surfactant concentration increase the association of surfactant molecules occurs by hydrophobic interaction and this result in the removal of the non polar portion of the molecules from the external aqueous environment to form the interior of the micelle while the hydrophilic groups are exposed to the aqueous environment.

The decrease in the Gibbs free energy of the system, which results from the preferential self-association of the hydrophobic hydrocarbon chain of monomeric surfactants molecules, is the primary reason for the formation of micelle. The Gibbs free energy of micelle formation in aqueous medium has been found to be more dependents on entropy than on enthalpy factors. The enthalpy of micellisation is often positive and, even when negative, is much smaller than the entropy contribution. The large positive entropy change in the formation of micelles results from the break down of the water structure around the hydrocarbon part of the monomer surfactant species.

Two main approaches namely the phase-separation model and the mass-separation model to the thermodynamic analysis of the micellization process have gained wide acceptance. In the phase separation approach the micelles are considered to form a separate phase at the CMC. While in the mass-separation approach micelles and unassociated monomers are considered to be in association dissociation equilibrium. The mass action model developed by Desnoyers et al.(11) can fit the apparent molar quantities of monomeric surfactant over a wide concentration range below and above the CMC, Recently this model has been extendent by Caron et al.(12) to ionic surfactants by taking into account the long range coulombic force between the monomer and interactions between micelle. Both these models have proved to be very useful in defining the CMC and in defining the thermodynamic relations describing micellization. This model can also fit quantitatively the thermodynamic properties of surfactant and water.

1.6 Alcohol SDS interactions

The experimental data on macroscopic properties provide valuable information for proper understanding the nature of interaction between the components of the solution. The thermodynamic properties of solution containing SDS + Ethanol and alcohols are of interest. The correlation between solute-solvent interactions is complex. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure.

Alcohols are self-associated liquids through H-bonding. Alcohols possess hydrophilic – OH group as well as hydrophobic group. Alcohols have a wide use in industry, and certain alcohols are solvents for fats, oils, resins, paints, and nitrocellulose; others find use in the manufacture of perfumes and brake fluids (13). Mixtures of ethanol with 1-propanol, 1-butanol, or 1-pentanol can be used as oxygenates in fuels. Also, these mixtures can be used as cryogenic fluids as a heat reservoir in cryogenic power generation systems (14). The thermodynamic properties for mixtures of alcohols at various temperatures are important for their use as refrigerants in the design of cryogenic systems. Dizechi and Marschall (15) have reported experimental density and viscosity measurements for ethanol + 1-propanol.

Mixtures containing oxygenated compounds such as alkanols are also important materials in the oil industry because of their application in enhancing octane number in gasoline as additives and pollution reducing properties. Binary mixtures of alkanols are interesting due to their self-association between like molecules and capability of forming intermolecular hydrogen bonds created between unlike molecules upon mixing. So, the treatment of this class of mixtures could be helpful in examination of theoretical models. Interactions between SDS and alcohols are extremely complex. The mode of interaction of these two groups towards SDS is completely different. The hydrophilic -OH group of an alcohol forms H-bond with SDS through hydrophilic interactions and disrupts the SDS structure, while the alkyl group promotes the structure of SDS molecules surrounding this group through hydrophobic hydration. Recently, we have reported the densities and excess molar volumes of alcohols in water Surf Excel solution, the volumetric and viscometric properties of carbohydrates in water Surf Excel, the electrolytes in water SDS systems, density and viscosity of Methanol, Ethanol n-Propanol and iso-Propanol in SDS solution, thermodynamic properties of Methanol, Ethanol n-Propanol and iso-Propanol in aqueous SDS systems etc. (2,4,7,8,16-20). The density of the binary mixtures of cetyltrimethylammonium bromide and sodium dodecyl sulphate in pure water and in methanol(1) + water (2) mixed solvent media containing (0.10, 0.20, and 0.30) volume fractions of methanol at 308.15, 318.15, and 323.15 K were also reported (21). As the mixtures of Ethanol with alkanols can be used as oxygenates in fuels and mixtures containing oxygenated compounds are also important materials in the oil industry because of their application in enhancing octane number in gasoline as additives. Surfactants are usually used as the solution stabilizer for additives. Considering these, we have undertaken the volumetric, viscometric and thermodynamic studies of surfactant (used as stabilizer) containing Ethanol with isomeric alkanols in terms of solute solvent interactions.

1.7 The object of the present work

The developments in solution theory are still far from being adequate to account for the properties of the constituent molecules. Accordingly, it is the experimental data on various macroscopic properties (thermodynamic properties, viscosities, surface tension etc), which provide useful information for proper understanding of specific interaction between the components and structure of the solution. The experimental approach of measurements of various macroscopic properties is also useful in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based. Thermodynamic studies on binary solutions have attracted a great deal of attention and experimental data on a good number of systems are available in a number of review articles (22-26). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications (27-31) 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 physic-chemical 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 informations 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.

In the present investigations, (i) densities and excess molar volumes, (ii) viscosities and excess viscosities and iii) thermodynamic parameters of mixtures, viz., *n*-Propanol + 0.015M SDS + Ethanol, n-Butanol+ 0.015M SDS + Ethanol, n-Pentanol+ 0.015M SDS + Ethanol, *iso*-Propanol+ 0.015M SDS + Ethanol, *iso*-Butanol+ 0.015M SDS + Ethanol, *iso*-Pentanol+ 0.015M SDS + Ethanol at 298.15-323.15K have been determined. In order to understand the issue of solute-solvent interactions in alcohols + 0.015M SDS + Ethanol 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 ternary systems (alcohol+0.015M SDS+Ethanol) interaction with the volumetric, viscometric and thermodynamic properties measurements, has not been analyzed before this work.

The specific aims of this study are-

(i) to examine the volumetric, viscometric and thermodynamic properties of the mixture of SDS containing Ethanol and isomeric-alcohols in different compositions and different temperatures.

(ii) to understand the effect of SDS containing Ethanol on isomeric-alcohols solutions to generalize the type of interactions among them.

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

(iv) to examine the effect of SDS on the unlike alcohol mixtures.

The thesis presents the density, excess molar volumes, viscosity, excess viscosities, thermodynamic parameters data of 0.015M SDS + Ethanol + 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

Physical properties of a substance depend on the intermolecular forces which originate in the internal structure or the constitution of the molecule. Thus the determination of properties such as viscosity, surface tension, refractive index etc. can give valuable information about the structure of molecules. In the modern times the molecular spectra of substances recorded by spectroscopic techniques have proved extremely helpful in elucidating the structure of organic molecules (32).

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

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

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

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

2.2 Density

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

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

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

2.3 Density and Temperature

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

2.4 Molarity

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

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

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

For one mole of solute dissolved in one liter of solution, C=1 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 $\mathrm{molL^{-1}}$ (32).

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 (32). Mathematically,

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

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

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

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

Where, a = Weight of solute in gram

M_2 = Molecular weight of solute in gram

V_1 = Volume of solvent in mL

ρ_0 = Density of solvent in g cm^{-3}

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

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

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

2.6 Apparent/ Partial Molar Volume

The apparent molar volume of a solute in solution, generally denoted by φ_v the relation (33)

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

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 (33),

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

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

n_1 and n_2 are the number of moles, M_1 and M_2 are molar masses of the solvent and solute respectively and ρ is the density of the solution. For molal concentration, $n_2 = m$, the molality and $n_1 = 55.51$, the number of moles of solvent in 1000g of solvent (water), the equation for apparent molal volume takes the form (34, 35),

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

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

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

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 (36):

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

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 (36).

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:

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

Similarly for component 2,

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

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

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

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

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

The partial molar volumes of solute and solvent can be derived using the equation 2.5 as follows (37):

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

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 volumes (φ_v) vary linearly with $\sqrt{m}$, even upto moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (33):

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

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:

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

and

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

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

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

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

and

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

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

2.7 Excess Molar Volume

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

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

The mixture molar volume is,

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

and the ideal molar volume of this system is given by

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

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

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

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

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

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

2.8 Viscosity

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

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

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

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

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

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

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

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

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

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

The C.G.S Unit of viscosity i.e. dynes sec cm^{-2} = g $cm^{-1}sec^{-1}$ is called poise, in honor of J.L.M. Poiseuille who is the pioneer in the study of viscosity. Since viscosity of liquid is usually very small, it is usually expressed in millpoise (mP) or centipoise (cP) or mPa.S.
When a liquid flows through a narrow tube it is probable that the thin layer of liquid in contact with the wall is stationary; as a result of viscosity, therefore, the next layer will be slowed down to some extent, and this effect will continue up to the centre of the tube where the flow rate is maximum.

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation (38). 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 (38):

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

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

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

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

The driving pressure P = hρg, where h is the difference in height of the surface of the two reservoirs, since the external pressure is the same at the surface of both reservoirs, g = acceleration due to gravity and ρ = the density of liquid. Thus the equation (2.29) becomes,

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

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

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

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

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

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

knowing the value of η_{H_2O} and ρ_{H_2O} at the experimental temperature and measuring the time of flow for water, the calibration constant A for a particular viscometer can be determined. Putting the value of and of the experimental liquid/solution and the value of viscometer constant A in equation (2.27), the coefficient of viscosity can be obtained for a liquid at a definite temperature.

2.9 Viscosity and Temperature

The viscosity of a liquid is generally decrease with the increase of temperature, i.e., a liquid becomes more free moving at higher temperatures. This in sharp contrast with the gas behavior, viscosity of gases increases with the increase of temperature. Numerous equations, connecting viscosity and temperature, have been proposed, but those of the exponential type, first derived due to their theoretical practical importance.

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

Where 'A' and 'E' are constants for the given liquid. It follows from equation (2.35) that the plot of log η versus 1/T will be a straight line. By analogy with the Arrhenius theory of reaction rates, 'E' has the dimension of work and can be regarded as the activation energy of viscous flow. It is probably related to the work needed to form 'holes' in the liquid, into which molecules can move, thus permitting relative motion to take place.

It has been suggested that before a molecule can take part in liquid flow, it must acquire sufficient energy 'B' to push aside the molecules which surround it. As the temperature increases, the number of such molecules increases in proportion to the Boltzmann factor $e^{-E/RT}$ as in equation 2.35.

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

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

2.10 Viscosity of Liquid Mixtures

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

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

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

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

2.11 Excess Viscosity Measurements

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

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

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

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

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

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

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

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

2.12 Interaction Parameter Measurements (ε)

Interaction parameter, ε for viscosity for all compositions of the mixtures at different temperatures have been calculated by using Grunberg-Nissan equation (39),

$$\varepsilon = \frac{\ln\eta_{exptl} - \ln\eta_{id}}{X_1X_2} \qquad\text{……………………………………………………(2.39)}$$

Where , ε = Interaction parameter.

$\eta_{exptl.}$ = observed viscosity

η_{id} = calculated viscosity

$$=\exp(X_1\ln\eta_1 + X_2\ln\eta_2) \qquad\text{…………………………………………(2.40)}$$

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

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

2.13 Viscosity as a Rate Process

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

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

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

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

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

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

Eyring and his co-workers (40) using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, η as follows:

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

Where, ΔG^* is the change of free energy of activation per mole for viscous flow, V_m is the molar volume for pure liquids or solutions and h, N, R and T have their meanings. The values of change of free energy of activation (ΔG^*) can be calculated by using the Nightingle and Benck equation (41):

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

The experimental term in equation 2.42 depends on the temperature and is typical for the processes which require activation energy. The activation process to which ΔG^* refers can not be precisely described but in general terms, it corresponds to the passes of the system into some relatively favorable configuration, from which it can then easily go to the final state of the molecular process. For example, in normal liquids the activation step may be the creation in the body of the liquid of a vacancy or holes into which an adjacent molecule can move. For associated liquids, it might be the breaking of enough intermolecular bonds to permit a molecule to move into available vacancy.

2.13.1 Enthalpy (ΔH^*) and Entropy (ΔS^*) of activation for viscous flow:

Change of enthalpy of activation (ΔH^*) and change of entropy of activation (ΔS^*) for viscous flow for the solution can be obtained with the help of Eyring equation (40):

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

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

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

Since,

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \text{……(2.44)}$$

The Eyring equation takes the form,

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

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

From the slope of this straight line, ΔH^* can be calculated as,

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

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

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

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

2.14 Different Thermodynamic Parameters

2.14.1 Change of free energy of activation (ΔG^*) for viscous flow

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

2.14.2 Change of enthalpy of activation (ΔH^*) for viscous flow

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

2.14.3 Change of entropy of activation (ΔS^*) for viscous flow

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

2.15 Redlich-Kister Equation

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

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

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

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

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

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

$PROP^E_{calcd}$ = calculated excess property,

n = total number of compositions for each system,

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

and SD = standard deviation.

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

CHAPTER III

Experimental

3.1 General Techniques

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

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

Ostwald viscometer (British standard) was used for measurement of viscosity. The inside wall of the viscometer was cleaned thoroughly with warm chromic acid so that there was no obstruction in the capillary and the liquid could run clearly without leaving any drop behind. It was then rinsed thoroughly with distilled water followed by rectified spirit and finally with acetone and dried.

3.2 Materials

The chemicals used for study were n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol, iso-Pentanol and 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**
Ethanol	C_2H_5OH	46.07	99%	E. MERCK India
n-Propanol	$CH_3CH_2CH_2OH$	60.10	99%	MERCK Germany
iso-Propanol	$(CH_3)_2CHOH$	60.10	99%	BDH, England
n-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	99.5%	Scharlau Chemie U.S.A.
iso-Butanol	$(CH_3)_2CHCH_2OH$	74.12	99.%	E. MERCK India
n-Pentanol	$C_5H_{11}OH$	88.15	99 %	MERCK Germany
iso-Pentanol	$C_5H_{11}OH$	88.15	99 %	E. MERCK India
SDS	$C_{12}H_{25}NaO_4S$	288.38	99.0%	LOBA Chemical, India

3.3 Preparation and Purification of Solvent

Ordinary distilled water was purified by a quick-fit glass made distillation apparatus. About 1.5L water was taken in a round bottom flux of which the capacity was 2L. Then it was distilled in presence of $KMnO_4$. Distilled water was collected at only 100°C. Other liquids of which the temperatures were below and above the mentioned boiling point were discarded. In all the experiments double distilled and deionized water was used. Conductivity of this redistilled water was found to be less than 1×10^{-6} $S.cm^{-1}$. This redistilled water was used for the calibaration of viscometer and density bottle.

3.4 Apparatus

The glass-ware used for the measurement for density of solvents and solutions were of the density bottle. Viscosities of various liquids were measured using the calibrated ostwald type viscometer. A & D company, HR 200 electronic balance with an accuracy of $\pm$ 0.0001g was used for weighting. The flow time of liquids were recorded by a stop-watch capable to read up to 0.01 seconds. The temperature was controlled by water thermostat with an accuracy of ± 0.05^{0}C. The experimental temperatures were 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K respectively. Both the density bottle and viscometer were calibrated with doubly distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

3.5 Methods (preparation of solution)

The binary solution of alcohol in 0.015M SDS+Etahnol 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 Conductance measurements

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

3.7 Density measurements

The densities of the solutions were determined by weighing a definite volume of the solution in a density bottle at specified temperature. The volumes were obtained by measuring the weight of water at that temperature and using the density of water from literature. The density (g.cm^{-3}) of solution was determined from the relation.

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

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

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

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

3.8 Excess molar volume measurements

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

$$V^E = \frac{X_1 M_1 + X_2 M_2}{\rho_{mix}} - \left(\frac{X_1 M_1}{\rho_1} + \frac{X_2 M_2}{\rho_2} \right) \text{..} (3.8)$$

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,

$$V^E = X_1 X_2 \sum_{i=0}^{n} a_i (1-2X_1)^i \text{..} (3.9)$$

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 (mPa.S) of water, acetonitrile, alcohols and their mixtures were measured by using the British standard Ostwald U-type viscometer. The interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind. It was then rinsed with acetone and dried in and oven at about 75^0C. The viscometer was then clamped vertically in the thermostatic water bath such that the upper mark of the top bulb was well below the water level. 10 mL of doubly distilled water was poured into the viscometer. Then it was allowed to keep in the thermostatic bath for about 30 minutes to attain the bath temperature. With the help of pipette filler attached to the narrower limb of the viscometer, the water was sucked up above the upper mark of the bulb. The water of bulb was then allowed to fall into the capillary and the time of fall between the two marks was noted with the help of stop-watch capable of reading up to 0.01 second. The reading at each temperature was repeated three or four times, in order to check the reproducibility of the flow time, the temperature being maintained at the same value. Since the accurate viscosity and density of water at different temperatures are known (from literature) calibration constant A of the viscometer for different temperature were obtained by using equation,

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

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

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

3.10 Excess viscosity measurements

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

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

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

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

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

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

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 (39),

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

Where, ε = Interaction parameter.

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

η_{id} = calculated viscosity

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

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

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

3.12 Thermodynamic parametes

The change of free energy of activation (ΔG^*/ kJ mol^{-1}) was calculated by the help of Nightingle and Benck (41) equation:

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

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

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

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

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

T = Absolute temperature (K)

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

Enthalpy of activation (ΔH^* /kJ mol^{-1}) and entropy of activation (ΔS^* /J mol^{-1}) for viscous flow for the solution was determined y using the Eyring equation (40):

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

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

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

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

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

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

and

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

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

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

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

and

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

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

3.13 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 (ΔG^{*E}), excess enthalpy of activation (ΔH^{*E}), excess entropy of activation (ΔS^{*E}) for viscous flow of all compositions for a system were fitted by the least square method of the four coefficient Redlich-Kister equation:

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

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

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

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

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.

CHAPTER IV

Results and Discussion

The CMC of Sodium Dodecyl Sulfate (SDS) in ethanol was determined from the conductance, density and viscosity measurement. Densities vs. concentration of SDS in Ethanol are shown in Figure 4.1. The densities increases very slowly upto 0.015 mol.L^{-1} SDS and then increases sharply with increasing SDS concentration. Viscosities vs. concentration of SDS in Ethanol are shown in Figure 4.2. The viscosities are almost unchanged with increasing SDS concentration upto 0.015 mol.L^{-1} and then increase very sharply. The concentration dependence of molar conductivity of SDS in Ethanol data are shown in Figure 4.3. The conductivity increases with increasing SDS concentration and then shows a maxima at 0.015 mol.L^{-1} and finally decreases again. It shows a sharp break in its value where micelle starts to form and it is determined by extrapolating the conductivity data in the pre-micellar region to intersect with a straight line drawn through the data in the post-micellar region. The maxima of conductivity express the

CMC of SDS. The estimated value of CMC was found to be 0.015 mol.L^{-1}.The conductance data is in good agreement with the viscosity and density data. The data are presented in Table 4.1-4.3. The effect of surfactant (SDS) in ethanol to alcohols system has been studied in terms of volumetric, viscometric and thermodynamic properties measurement. The CMC of SDS in Ethanol of 0.015 mol.L^{-1} was used for these measurements.

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

1. *n*-Propanol in 0.015M SDS + Ethanol
2. *iso*-Propanol in 0.015M SDS + Ethanol
3. *n*-Butanol in 0.015M SDS + Ethanol
4. *iso*-Butanol in 0.015M SDS + Ethanol
5. n-Pentanol in 0.015M SDS + Ethanol
6. *iso*-Pentanol in 0.015M SDS + Ethanol

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

4.1 Volumetric properties:

The densities, ρ of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in 0.015M SDS+Ethanol systems were determined at temperatures 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K with an interval of 5K over the entire composition range $0 < x_2 < 1$, where x_2 represents the mole fraction of Alkanols. The densities of the pure components are shown in Table 4.4 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 studied systems have been shown in Table 4.5-4.10 at different temperatures. Figure 4.4-4.9 shows the plots of densities as a function of mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in 0.015M SDS+Ethanol systems. In all the studied system, it shows that density decrease with the composition of alcohols. Density value decreases with increase in the temperature. The experimental density values in pure state of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol at 298.15K are 0.799693, 0.781049, 0.806244, 0.798010, 0.811159, 0.812200 g.cm^{-3} respectively.

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

n-Pentanol> *n*-Butanol > *n*-Propanol

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

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

The densities of isomers are found to be order of iso-Pentanol > n-Pentanol> *n*-Butanol > *iso*-Butanol and *n*-Propanol > *iso*-Propanol

The densities of alcohols increase with the increase of carbon number may be depend on the molecular weight of alcohols, structural formula and H-bonding of alcohols. As the densities of pure *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol and *iso*-Pentanol are lower than that of pure 0.015M SDS+Ethanol, with the increase of composition of alcohol, the density of alcohol in 0.015M SDS+Ethanol system decreases and eventually proceeds towards the density of pure alkanols. Decrease of density with composition of alcohols indicates the decrease in solute-solvent interactions. Decrease in density with composition is also due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute (42, 43).

Mixing of alcohols with in 0.015M SDS+Ethanol will induce changes in dipolar interactions. On addition of alcohols to the in 0.015M SDS+Ethanol solutions the self association of SDS will be disrupted partly or fully and new dipolar interactions between SDS and alcohols will be formed. At the same time, segmental inclusion of species into the vacant spaces left in the structural network of solutions may also occur. With the increase of composition of alcohols in 0.015M SDS+Ethanol solution, the free volume in the solution increased gradually and the density decreased progressively (Figure 4.4-4.9). The dependences of the density with carbon chain length of alcohols with different composition at a fixed temperature are plotted in Figure 4.10-4.12. From the figures, it can be seen that at the same temperature, the density increase with the carbon chain length of the alcohols. The dependences of the density with carbon chain length of alcohols with different temperatures at a fixed mole fraction are plotted Figure 4.13-4.14. It can be also seen that at the same mole fraction, the density increase with the carbon chain length of alcohols. The increasing of density, ρ with the carbon chain length of alcohols (carbon number) can be explained by the increase mass of the alcohols and the degree of solute-solvent interactions with carbon number.

The variation of density, ρ with temperature for n-Propanol, n-Butanol and n-Pentanol are shown in Figures 4.20-4.23 at different mole fractions. It is seen that density, ρ decrease linearly with increasing temperature for all alcohols. The densities decrease regularly with the increasing of temperature. This is due to the increase of thermal agitation and hence the weaker the dipole-dipole interaction or dissociation of H-bonding are occurred. At higher mole fraction of alcohol (Figure 4.22-4.23) the temperature effect is prominent compared with lower mole fraction of alcohols (Figure 4.20). The linear dependence of lnρ verses 1/T are plotted in Figures 4.24-4.27.

The density order of alcohols in 0.015M SDS+Ethanol is similar as alcohols in pure solution.

The values of densities of alcohols in 0.015M SDS+Ethanol (equimole fraction) systems has been found to be in the order of,

n-Pentanol in 0.015M SDS+Ethanol > *n*-Butanol in0.015M SDS+Ethanol > *n*-Propanol in 0.015M SDS+Ethanol >

and

iso-Pentanol in 0.015M SDS+Ethanol > *iso*-Butanol in 0.015M SDS+Ethanol > *iso*-Propanol in 0.015M SDS+Ethanol

The density of n-Pentanol is higher than *n*-Butanol, *n*-Butanol is higher than *n*-Propanol in 0.015M SDS+Ethanol, indicate that the nature of interaction in pure state is similar to the solution (mixture) state.

The excess molar volume, V^E of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and iso-pentanol in 0.015M SDS+Ethanol 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 4.5-4.10. For V^E the fitting coefficients (a_i) are shown in Table 4.29 along with standard deviations. Figure 4.28- 4.33 shows the plots of excess molar volume as a function of mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and iso-pentanol in 0.015M SDS+Ethanol systems.

Examination of Figures 4.28- 4.33 reveals that

(i) At low composition of alcohol in 0.015M SDS+Ethanol, excess molar volumes, V^E are positive and with the increase of alcohol composition, V^E reaches maximum value and then decreases continuously and eventually becomes zero.

(ii) Excess molar volumes, V^E are positive for the whole range of composition for the studied alcohols in 0.015M SDS+Ethanol systems.

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

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

(v) For all the studied alcohols in 0.015M SDS+Ethanol system, the maxima appear at ~ 0.5-0.8 mole fraction of alkanols.

(vi) The excess molar volumes, V^E of alcohols in 0.015M SDS+Ethanol systems has been found to be in the order of,

n-Pentanol in 0.015M SDS+Ethanol > *n*-Butanol in 0.015M SDS+Ethanol > *n*-Propanol in 0.015M SDS+Ethanol

and

iso-Pentanol in 0.015M SDS+Ethanol > *iso*-Butanol in 0.015M SDS+Ethanol > *iso*-Propanol in 0.015M SDS+Ethanol

and

iso-Pentanol in 0.015M SDS+Ethanol > n-pentanole in 0.015M SDS+Ethanol

and

iso-Butanol in 0.015M SDS+Ethanol > *n*-Butanol in 0.015M SDS+Ethanol

and

iso-Propanol in 0.015M SDS+Ethanol > *n*-Propanol in 0.015M SDS+Ethanol

vii) The mixing of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and iso Pentanol with 0.015M SDS+Ethanol systems is accompanied by expansions of volume at all studied temperatures.

Similar behavior was found in Alkanols + m-xylene (44) systems, alkanols+acetonitrile (45) excess molar volume were positive in the whole range of composition. In contrast, similar alcohols with dimethylformamide systems (46) and aqueous SDS systems (47), both the cases the excess molar volumes, V^E show negative value. This indicates that the mode of interactions of alcohols with 0.015M SDS+Ethanol and dimethylformamide (DMF) or aqueous SDS is not similar.

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

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

a) The dispersive forces which occur predominantly in systems consisting of associated species (formed either by chemical or physical forces) and low-polar components,

b) Dissociation of one component or both of the components,
c) Steric hindrance,
d) Unfavorable Geometrical fitting,
e) Formation of weaker solute- solvent bond than solute – solute and solvent – solvent bonds,
f) Effect due to differences in the chain length of alkanols and
g) Electrostatic repulsive forces.

The factors that cause contraction on mixing are:

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

Mixing of 0.015M SDS+Ethanol with an alcohol will induce changes in hydrogen bonding (in the alkanol) and dipolar interactions (in the 0.015M SDS+Ethanol solution). On addition of alcohol to the 0.015M SDS+Ethanol the self association will be disrupted partly or fully and new dispersion force or dipolar interactions or H-bonds between alcohol and 0.015M SDS+Ethanol may be appeared. At the same time, segmental inclusion of 0.015M SDS+Ethanol into the vacant spaces left in the structural network of alcohol may also occur. In SDS+Ethanol rich region, disintegration of multimers of alkanols into smaller units through disruption of H-bonding in alkanols takes place. Another important factor that contributes significantly towards volume expansion is the steric hindrance of the long chain or branched chain alkanols. These factors may primarily be responsible for the resultant positive excess molar volume of the mixtures of 0.015M SDS+Ethanol + Alkanols.

The dependence of excess molar volume with carbon number of alcohols with different composition at a fixed temperature are plotted in Figures 4.34-4.36. The dependence of excess molar volume with carbon number of alcohols with different temperature at a fixed composition are plotted in Figures 4.37-4.39. From the figures it can be seen that at the same temperatures, the excess molar volume increases with carbon number and the lower mole fraction (0.2), the V^E show slightly parabolic curves. The increasing of V^E with the carbon chain length of alcohols may be related to increase of the size of alcohols.

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

Pikkarainen (48, 49) studied the excess volume of binary solvent mixtures of N,N-diethylmethane sulfonamide with aliphatic alcohols. Garcia et al. (50) carried out volumetric and viscometric measurements on binary liquid mixtures of 2-pyrrolidone with 1-alkanols. Rauf et al. (51) determined the excess molar volumes of N,N-dimethylformamide + n-alkanols (C7–C9). The analysis of the previous works shows that the positive values of V^E decrease with the decrease of the chain length of alkanols. The results of our present investigation of 0.015M SDS+Ethanol + alkanols (C3–C5) mixtures are in conformity with the results of these reported investigations.

From Figs. 4.46 to 4.48, it is seen that the value of excess molar volumes increase with the rise of temperature. It is known that pure components or their mixtures can form either ring- or chain-like complexes, and while temperature increases, the degree of association decreases (52, 53) and hence excess molar volume increases.

The observed V^E of all the studied alcohols + 0.015M SDS+Ethanol mixtures may be discussed above which may be arbitrarily divided into physical, chemical, and geometrical contributions (51, 54). 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 observed V^E values of the mixtures under investigation also can be explained in terms of the following contributions:

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

The positive V^E of the systems, a typical characteristic of hydrophobic solutes, lead to the conviction that the factors causing the volume expansion far outweigh the factor which is to responsible for volume contraction (55). Of the expansion factors, perhaps the dispersion force or steric hindrance is by far the most effective one in volume expansion, as through this process the hydrophobic molecules occupy the spaces inside the so-called cages formed through H-bond is breaking and thus ensure maximum raise of volume. Whereas in other cases, shrinkage takes place through strong interactions or attractive forces whose contribution to volume reduction is only relatively small.

The excess molar volumes of the mixtures which are under investigations may be considered to be the resultant of the above-mentioned competing interactions of the component molecules. All the components are polar compounds. The value of dipole moments (μ) are being 1.68D, 1.66 D, 1.66 D, 1.71 D, 1.70 D and 1.70 D for n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol respectively (56).

Therefore, it has the possibility of the formation of hydrogen bonding through the polar group of the Alkanols and 0.015M SDS+Ethanol due to the hydrophilic effect. However, if the steric hindrances by the bulky groups or geometrical mismatch of these groups are very strong, then the possibilities of the formation of H-bonding decrease. The strong steric hindrance are existing in the long chain alkanols that affects both hydrogen bonding and electron donar/ acceptor interaction are reported (57, 58). So, if the alkanols are relatively smaller in size and formed H-bonding or associated through strong dipole-dipole interactions between the components small V^E values are generally expected. The experimental results of these mixtures are consistent with this observation.

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

The gradual expansion in volume on addition of Alkanols may be explained mainly by taking into account of breaking of the strong network of alcohol-alcohol interactions by the SDS+Ethanol dispersion force with overall raise of space. After attaining the maxima further addition of alkanols SDS+Ethanol composition are decreased and associated forms of alkanols –alkanols through H-bonding are raised resulting the gradual contraction in volume is occurred. The size differences between SDS, n-Pentanol and iso-Pentanol are quite large so the possibility of partial accommodation of SDS in the interstices of n-Pentanol is high but the possibility of making H-bonding cluster for n-Pentanol or iso-Pentanol is lower than the other studied alcohols owing to its higher steric hindrance and hence V^E becomes high. For the increase of temperature (Figure 4.46-4.48), the dissociation of H-bonding or weaker the dipole-dipole interaction are occurred, so the dissociated species in the solution are increased and hence positive V^E are increased (57).

In the case of isomers of n-Pentanol and iso-Pentanol, *n*-Butanol and *iso*-Butanol and *n*-Propanol and *iso*-Propanol the V^E becomes higher for branched chain alcohols (iso-Pentanol, *iso*-Butanol and *iso*-Propanol) than linear chain alcohols (n-Pentanol, *n*-Butanol and *n*-Propanol) throughout the whole composition range. The dispersion force in 0.015M SDS+Ethanol and Alkanols, is not the only factor influencing the positive V^E of liquid mixtures, but the orientation of groups, steric hindrance, hydrophobic interaction, molecular sizes and shapes of the components are also equally important. Here steric hindrance may be played important role for providing higher V^E. Larger the branch chain or long chain linear alkanols, the dissociation of H-bonding or weaker the dipole-dipole interaction are occurred as a result more positive V^E is observed.

At higher temperature unfavorable packing may, however, result due to disruption of the closely associated SDS molecules on addition of alkanols and formation of new association between the unlike SDS and an alkanol molecules. Reorganization of the pure components in the mixtures due to formation of different type of weaker bond and geometrical mismatch or steric hindrence may also result unfavorable packing and lead to expansion in volume (Figure 4.46-4.48).

4.2 Viscometric properties

The viscosities, η of n-Propanol, iso-Propanol, *n*-Butanol, *iso*-Butanol, *n*-Pentanol and *iso*-Pentanol in SDS+Ethanol systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.11-4.16. The viscosities of the pure components are shown in Table 4.1 together with the literature values for *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol 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 4.49-4.54. The following characteristic features of viscosity are observed:

a) The viscosities increase slowly up to entire mole fraction of *n*-Propanol and *iso*-Propanol.

b) For n-Butanol and iso-Butanol, the viscosities increase initially slowly upto 0.5 mole fraction and latter on, the viscosity increases sharply until the pure alcohol is reached.

c) For n-Pentanol and iso-Pentanol, the viscositiy increase initially slowly upto 0.8 mole fraction and latter on, the viscosity increases very sharply until the pure alcohol is reached.

d) At the alcohol rich region rapid change of viscosity are observed for *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol but the change is pronounced for the n-Pentanol and iso-Pentanol systems.

e) Viscosity decreases with rise of temperature.

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

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

n-Pentanol> *n*-Butanol > *n*-Propanol

and

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

For dilute alcoholic solutions in SDS+Ethanol, 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 SDS+Ethanol rich regions. In alkanol rich region the rapid rise of viscosity is thought to be due to the continuous increase of self association of alkanols. i.e, the concentration of a particular alcohol is increased, multimers are formed, the extent of which increases with the rising concentration of alcohols. This accounts for the sharp rise in viscosity in the alcohol rich regions.

The dependences of the viscosity with carbon chain length of alcohols with different composition at a fixed temperature are plotted in Figures 4.55-4.60. From the figures, it is seen that, at the same temperature, the viscosity increase with the carbon chain length of alcohols. The dependences of the viscosity with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.61-4.64. From the figures, it is seen that at the same mole fraction, the viscosity increase with the carbon chain length of alcohols. The increasing of viscosity with the carbon number of alcohols can be explained by the increase of solution resistance with the increase of carbon number.

Viscosities of the studied alcohols as the function of temperature are represented in Figures 4.65-4.68. There is a marked decrease in the viscosity with increase of temperature for all the studied alcohols.

By using an empirical equation of the form,

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

the linear dependence of $\ln\eta$ against 1/T shows that at different mole fraction (shown in Figures 4.69-4.72) , the order of viscosity becomes n-Pentanol> n-Butanol> n-Propanol and iso-Pentanol >*iso*-Butanol > *iso*-Propanol. The above equation is fully valid for all the SDS-alcohols systems. The temperature effect is prominent for branched chain isomer than that of linear chain isomer. This indicates that the branched chain isormers are less stable than linear chain isomer at higher temperature. This is may be due to the maximum geometrical mismatch for the branched alkanols occurred at higher temperature. The viscosity of different isomers of Alkanols in Toluene as reported (59, 60) 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 (SDS+Ethanol), X_2 and η_2 are the corresponding values of component 2 (Alcohols).

The η^E values are shown in Table 4.11-4.16. 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 4.30. The variation of η^E against mole fraction of alcohol (x_2) is shown in Figure 4.73-4.78. The η^E values are found to be negative, indicating that the SDS+Ethanol solutions of alcohols are non ideal. Figure shows the following features:

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

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

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

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

iso-pentonol > *iso*-Butanol > *iso*-Propanol

and

n-Pentanol> *n*-Butanol > *n*-Propanol

The excess viscosities are found to be negative for all the studied alcohol systems in 0.015M SDS+Ethanol. The negative excess viscosities (as in Figs. 4.73-4.76) for the systems 0.015M SDS+Ethanol + studied alcohols system indicate the dissociation of components through steric hindrance or dispersive forces.

The value of dipole moments (μ) of all alkanols are almost similar. Therefore, hydrogen bonding is thought to be formed by the polar group of the alcohol and SDS due to the hydrophilic effect. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of 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. (58) showed that hydrophobic interaction varies according to hydrocarbon groups such as CH_3CH_2>CH_3> CH_2> CH.

Alkanols and SDS in Ethanol form a maximum structural disaggregate around at the 0.6-0.7 mole fraction of Alkanols owing to the dissociation of components through dispersive forces or steric hindrance. With a further increase in Alkanols mole fraction, a composition is reached when Alkanols molecules can not find enough SDS molecules to be disrupted. After attaining the state of minima η^E further addition of alcohol continuously formed the ordered structure and Alkanols-Alkanols cage association, instead of, SDS-Alkanols dispersion, which result in the continual increase in η^E.

The dependences of excess viscosity with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.79-4.81. The dependences of excess viscosity with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figures 4.82-4.84. It is seen that the negative excess viscosity value increases with the increasing of carbon number at higher mole fraction owing to the degree dissociation of components through steric hindrance. But at lower mole fraction the change is parabolic.

The Figures also reveal that the systems having branched chain alkanols such as iso-Propanol, iso-Butanol, iso-Pentanol 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. (61), Akhtar et al. (60) and Saleh et al. (62) 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. (63) 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 SDS+Ethanol. As pointed out earlier, negative excess viscosity follow the order:

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

which in turn reflect the extent of dissociation mainly due to dispersion force. D' Aprano et al. (59) calculated the Kirkwood correlation coefficient, I_k, from the dielectric constant values of pentanol isomers in the temperature range of 303.15 and 323.15K and found that the values of I_k, vary in the order : 1-pentanol>2-pentanol>3-pentanol. Since I_k, is measure of the short range order in polar liquids, it follows that the pentanol whose I_k, is larger i.e. which is more strongly bounded by H-bond, is less likely to be dissociated than the pentanol with smaller I_k, i.e., which is less strongly bound by H-bonds. The relative ease of dissociation of our studied systems: two Butanols and two Propanols isomer either by thermal effect or by the force of dispersion in SDS+Ethanol solution should thus follow the order:

iso-pentanol > n-pentanol; iso-Butanol>n-Butanol ; and iso-Propanol> n-Propanol.

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

For iso-Pentanol systems, some anomalous behavior is showed for excess viscosity and excess molar volume measurement. Similar behavior was reported (44, 46, 47) for iso-Pentanol with DMF systems.

From Figures 4.85-4.87 it is seen that the value of excess viscosity increases with the rise of temperature. The difference in minima of excess viscosity over the temperature range ($\Delta\eta^E_{min}$) of the different systems can be explained in terms of the maximum thermal fragility in the molecular interactions of Ethanol (SDS) and alcohols formed. In comparison with alcohol- Ethanol (SDS) association, the Ethanol (SDS) – Ethanol (SDS) association in the structure is assumed to be more fragile to heat. Examination of excess viscosity curves of different alcohol solutions (Figure 4.73-4.78) shows that $\Delta\eta^E_{min}$ varies in the order,

iso-Pentanol (0.53 mPa.S)> *n*-Pentanol (0.25 mPa.S)
iso-Butanol (0.35 mPa.S)> *n*-Butanol (0.11 mPa.S)
iso-Propanol (0.05 mPa.S)> *n*-Propanol (0.03 mPa.S)

The values, therefore, indicate the extent of the destruction of the structures by thermal effect. The structure formed by the Ethanol (SDS) – Ethanol (SDS) association around the alcohols through H-bond or dispersion force are also assumed to be thermally unstable than Ethanol (SDS) – Ethanol (SDS) association in pure Ethanol (SDS) (20, 64) that is similar to pure water. The thermal fragility of branched alcohols is higher than the linear chain alcohols.

4.2.1 Interaction parameter

The interaction parameters (ε) have been calculated by using the equation 3.14. The values of interaction parameters for different systems are shown in Figure 4.88-4.93 and the data are tabulated in Table 4.11-4.16. The values have been found to be negative and quite large in magnitude for all the systems.

From the studies of ε and η^E values of a number of binary mixtures of different polar or non-polar liquids, Fort and Moore (65) indicated an approximate idea about the strength of interaction between liquids. They concluded that:

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

In all of our studied systems, both ε and η^E values are negative and large in magnitude. Therefore, the negative interaction parameters indicate that the specific interactions are absent but strong dispersion forces of the mixtures are dominant (65). The interaction parameters, ε decrease with alcohol concentration, showing minima and then increase continuously. 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 (66) that SDS+Ethanol + all the studied alcohols mixtures have strong dispersion force and geometrical effect. The positive excess molar volume V^E, negative η^E values suggest that the geometrical fitting of the molecules is also more important with the interactional factor for these systems.

The positive V^E, negative η^E, and negative ε for the SDS+Ethanol + studied alcohols systems show agreement with the statements (65-67). On addition of alkanols in SDS+Ethanol solution strong disruptive forces are appeared and H-bonding in alkanols are dissociated causing volume expansion is occurred. For the long chain or branched chain alkanols, maximum geometrical mismatch for the steric factor are occurred causing volume expansion is also seen. From the above discussion, it is seen that the volumetric properties are fully consistent with the viscometric properties.

4.3 Thermodynamic properties

Free energy change (ΔG^*) of activation for the viscous flow of the *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in SDS+Ethanol solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.17-4.22. The variation of free energy (ΔG^*) at different temperatures as a function of the mole fraction of all the studied alcohols are shown in Figure 4.94-4.99. The following characteristic features of ΔG^* are observed:

i) The change of free energy (ΔG^*) increases almost linearly with mole fraction of alkanols for *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in solutions.

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

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

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

The dependences of the free energy (ΔG^*) with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.100-4.102. The dependences of ΔG^* with carbon number of alcohols with different temperatures at a fixed mole fraction are plotted in Figure 4.103-4.104. From the figures it is seen that the ΔG^* increase with the carbon number of alcohols. The variation of ΔG^* with temperatures for alcohol-SDS+Ethanol solutions are shown in Figure 4.110-4.113. It is seen that the ΔG^* slightly decreases with the increase of temperature. The linear dependence of lnΔG^* vs 1/T are plotted in Figures 4.114-4.117. The variation of lnΔG^* against 1/T is fully valid for all the alcohol- SDS+Ethanol systems.

Excess free energy (ΔG^{*E}) change of activation for the viscous flow of the *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in SDS+Ethanol solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over the entire composition range are shown in Tables 4.17-4.22. Figure 4.118-4.123 represent the variation of ΔG^{*E} of the systems against the mole fraction of the alcohols at different temperatures. The excess free energy (ΔG^{*E}) was fitted by least squares method to a polynomial equation. The values of the fitting parameters along with the standard deviation of alcohol systems are presented in Table 4.31. The ΔG^{*E} values are found to be negative and large in magnitude, indicating that the SDS+Ethanol solutions of alcohols are non ideal. Figure shows the following features:

i) Excess free energies ΔG^{*E} are negative with some exception at all the temperatures over the entire range of composition for all the systems with different position of minima of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and iso-Pentanol .

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

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

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

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

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

iso-Pentanol>n-Pentnol
iso-Butanol>n-Butanol
iso-Propanol> n-Propanol

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

As suggested by the author (1), a large negative excess free energy, ΔG^{*E} indicates the presence of dispersion force, whereas a large positive excess free energy, ΔG^{*E} suggests a specific association between the molecules in the solvent mixture. The negative ΔG^{*E} values in our studied systems are also indicative of the dispersion force containing molecular interaction among the SDS+Ethanol and alcohol systems.

The dependences of excess free energy with carbon number of alcohols with different composition at a fixed temperature are plotted in Figure 4.124-4.126. The dependences of excess ΔG^{*E} with carbon number of alcohols with different temperatures at a fixed composition are plotted in Figure 4.127-4.129.

The difference in minima of ΔG^{*E} over the temperature range are shown in Figure 4.118-4.123 of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol- association, the Ethanol (SDS) – Ethanol (SDS) association in the cage structure is assumed to be more fragile to heat.

This indicates that the extent of the destruction of the cages structures by thermal effect which, in turn, reflects the extent of cage formation. Therefore, the effect of temperature on ΔG^{*E}, particularly in the region at or around the minima is significant (Table 4.17-4.22). This may be due to the structures formed by hydrophilic or hydrophobic interaction that are considered to be much more labile and thermally less stable than the normal Ethanol (SDS) structure (64, 68) i.e The cages formed by the Ethanol (SDS) – Ethanol (SDS) association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than SDS - SDS association in SDS.

Table 4.23-4.28 lists enthalpy ΔH^{*}, entropy ΔS^{*}, excess enthalpy ΔH^{*E} and excess entropy ΔS^{*E} values for the studied system for different molar ratios. The entropies of the systems increase almost linearly with composition of alkanols. All studied alcohols show negative entropy change, however for branched alkanols at alkanol rich region the change of entropy is pronounced.

All the other studied alkanols in SDS+Ethanol solution systems show negative excees entropy, ΔS^{*E} with distinct minima. Also the values are more negative for the branched alkanols than the linear system in the whole range of composition. Saleh et al. (44) found that n-Pentanol + n-Heptane system, excess entropies were negative in the whole range of concentration.

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

In order to explain ΔH^{*} and ΔH^{*E} behavior similar to ΔG^{*} and ΔG^{*E} hydrophobic interaction, structural effect and hydrophilic interaction may be considered as the major cause in which it is assumed that both alcohols and SDS molecules are engaged by a network of highly structured form in pure state. Studies on viscometric properties by Kipkemboi and Easteal (69), Saleh et al. (44) and FTIR spectrophotometric studies by

Gojlo et al. (70) of some alcohols indicated that the alcohols are hydrophobic in nature. The bulkier species so formed by hydrophobic interaction may be supposed to use large energy for their passage to activated state and hence the large positive ΔH^{*}. An investigation of the ΔH^{*} values of alcohols indicate that the ΔH^{*} of iso-Butanol is higher than that of studied other alcohol systems. It might be due to the structure of branched alkanols in SDS, is much bulkier and more rigid than that of or n-Propanol or n-Butanol requiring greater energy during the viscous flow. The ΔH^{*} values are positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. All these concepts can equally be applied to explain the positive values of free energy and enthalpy functions in the SDS systems (44).

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

Table 4.1: Density, ρ (g.cm^{-3}) of sodium dodecyl sulfate (SDS) in Ethanol at different temperatures.

c/ mol.L^{-1}	**Density (g.cm^{-3})**					
	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
0.001	0.833052	0.828840	0.826468	0.823116	0.818360	0.814088
0.005	0.833424	0.829264	0.826804	0.823620	0.818732	0.814460
0.010	0.833888	0.829648	0.827264	0.824092	0.819136	0.814820
0.015	0.834108	0.830080	0.827868	0.824412	0.819508	0.815380
0.020	0.842300	0.837640	0.833800	0.829948	0.825800	0.821300
0.025	0.850000	0.845200	0.841100	0.836700	0.832100	0.827400

Table 4.2: Viscosity, η (mPa.s) of sodium dodecyl sulfate (SDS) in Ethanol at different temperatures.

c/ mol.L^{-1}	**Viscosity, η (mPa.s)**					
	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
0.0010	1.1455	1.0287	0.9247	0.8387	0.7662	0.7015
0.0050	1.1499	1.0295	0.9252	0.8400	0.7686	0.7048
0.0100	1.1510	1.0297	0.9249	0.8419	0.7694	0.7048
0.0150	1.1620	1.0425	0.9322	0.8525	0.7765	0.7109
0.0199	1.2255	1.0861	0.9694	0.8908	0.8061	0.7337
0.0250	1.3000	1.1600	1.0400	0.9528	0.8629	0.8000

Table 4.3: Conductivity(μs/cm) of sodium dodecyl sulfate (SDS) in Ethanol at different temperatures.

c/ mol.L^{-1}	**Conductivity(μs/cm)**					
	298.15K	**303.15K**	**308.15K**	**313.15K**	**318.15K**	**323.15K**
0.0010	80	100	120	140	160	180
0.0050	185	216	234	259	287	326
0.0100	350	390	430	460	470	540
0.0150	490	510	550	590	630	700
0.0200	500	525	560	610	650	710
0.0250	495	515	550	595	635	690

Table 4.4: Comparison of experimental and literature values of density, ρ (g.cm^{-3}) and viscosity, η (mPa.s) of pure components at different temperatures.

Component	Temperature (K)	Density (g.cm^{-3})		Viscosity (mPa.s)	
		ρ_{lit*}	ρ_{exp}	η_{lit*}	η_{exp}
n-Propanol	298.15	0.79975	0.799694	1.967	1.9671
	303.15	0.79548	0.795537	1.713	1.7192
	308.15	0.79138	0.791461	1.537	1.5312
	313.15	0.7873	0.787411	1.378	1.3761
	318.15	-	0.783219	-	1.2346
	323.15	0.7793	0.779362	1.115	1.1148
iso-Propanol	298.15	0.78123	0.781122	2.045	2.0427
	303.15	0.7766	0.776690	1.763	1.7633
	308.15	0.77246	0.772253	1.5405	1.5403
	313.15	0.7683	0.768209	1.3143	1.3219
	318.15	0.7635	0.763311	1.191	1.1803
	323.15	0.75868	0.758510	1.002	1.0082
n-Butanol	298.15	0.806	0.806253	2.5339	2.5554
	303.15	0.8022	0.802337	2.263	2.2513
	308.15	0.79838	0.798563	1.9778	1.9787
	313.15	0.79432	0.792886	1.7556	1.7504
	318.15	0.7905	0.790336	1.5635	1.5631
	323.15	0.78578	0.785832	1.3971	1.3995
iso-Butanol	298.15	0.7982	0.798111	3.332	3.3318
	303.15	0.79431	0.794250	2.884	2.8433
	308.15	0.7902	0.790212	2.426	2.4258
	313.15	0.78612	0.786120	2.08	2.0905
	318.15	0.7822	0.782163	1.861	1.7997
	323.15	0.7778	0.777832	1.602	1.5959
n-Pentanol	298.15	0.8111	0.811170	3.48	3.4741
	303.15	0.80711	0.807329	2.932	2.9816
	308.15	0.80352	0.803333	2.57	2.5704
	313.15	0.7995	0.799537	2.332	2.2703
	318.15	-	0.795340	-	1.9743
	323.15	0.7905	0.791468	1.765	1.7661
iso-Pentanol	298.15	0.8097	0.812660	3.61	3.4162
	303.15	0.8069	0.810558	3.12	3.0653
	308.15	0.8027	0.807344	2.68	2.7027
	313.15	0.7972	0.803576	2.31	2.3672
	318.15	0.7928	0.800001	-	2.0960
	323.15	0.7881	0.795835	-	1.9355

*All the literature values are cited from the references 71-85.

Table-4.5: Density (ρ) and Excess molar volume (V^E) of n-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.1007	0.829326	0.0160	0.825249	0.0183	0.822152	0.0223	0.819163	0.0240	0.814288	0.0292	0.810163	0.0320
0.2006	0.824631	0.0515	0.820512	0.0561	0.817241	0.0624	0.814057	0.0669	0.809266	0.0732	0.805114	0.0812
0.3007	0.820247	0.0864	0.816082	0.0938	0.812644	0.1030	0.809292	0.1093	0.804527	0.1207	0.800337	0.1350
0.3999	0.815962	0.1379	0.811822	0.1430	0.808232	0.1550	0.804715	0.1642	0.800039	0.1756	0.795848	0.1934
0.4994	0.812232	0.1653	0.808000	0.1773	0.804328	0.1871	0.800739	0.1922	0.796168	0.2014	0.792071	0.2145
0.6012	0.809230	0.1447	0.804986	0.1568	0.801247	0.1630	0.797500	0.1711	0.793000	0.1800	0.788864	0.1991
0.6994	0.806613	0.1150	0.802414	0.1224	0.798538	0.1316	0.794700	0.1379	0.790245	0.1482	0.786138	0.1670
0.8014	0.804155	0.0744	0.799929	0.0830	0.796006	0.0875	0.792059	0.0938	0.787630	0.107	0.783658	0.1156
0.9008	0.801781	0.0446	0.797607	0.0475	0.793598	0.0515	0.789574	0.0555	0.785267	0.0624	0.781357	0.0669
1.0000	0.799694	0.0000	0.795537	0.0000	0.791461	0.0000	0.787411	0.0000	0.783219	0.0000	0.779362	0.0000

Table-4.6: Density (ρ) and Excess molar volume (V^E) of n-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.0998	0.828929	0.0573	0.824787	0.0673	0.822176	0.0783	0.818575	0.0814	0.813722	0.0884	0.809522	0.0904
0.1991	0.824450	0.1110	0.820299	0.1240	0.817408	0.1411	0.813616	0.1521	0.808894	0.1591	0.804529	0.1711
0.3008	0.820330	0.1739	0.816149	0.1919	0.813025	0.2139	0.809079	0.2319	0.804461	0.2399	0.800036	0.2549
0.4006	0.816628	0.2412	0.812443	0.2622	0.809159	0.2851	0.805180	0.3011	0.800541	0.3201	0.795953	0.3480
0.5003	0.813444	0.2947	0.809189	0.3247	0.805666	0.3576	0.801582	0.3786	0.796989	0.4026	0.792370	0.4325
0.6005	0.811120	0.2931	0.806807	0.3311	0.803235	0.3572	0.799088	0.3792	0.794529	0.4082	0.789894	0.4383
0.6996	0.809620	0.2337	0.805338	0.2707	0.801650	0.2966	0.797473	0.3166	0.793079	0.3356	0.788335	0.3746
0.7989	0.808327	0.1644	0.804278	0.1785	0.800591	0.1927	0.796462	0.2019	0.792087	0.2248	0.787384	0.2570
0.9006	0.807260	0.0784	0.803270	0.0864	0.799534	0.0944	0.795407	0.0974	0.791182	0.1094	0.786465	0.1404
1.0000	0.806253	0.0000	0.802337	0.0000	0.798563	0.0000	0.792886	0.0000	0.790336	0.0000	0.785832	0.0000

Table-4.7: Density (ρ) and Excess molar volume (V^E) of n-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.0998	0.829257	0.0338	0.825232	0.0468	0.822331	0.0619	0.818740	0.0720	0.814105	0.0739	0.810245	0.0789
0.1966	0.825228	0.0890	0.821329	0.1040	0.817907	0.1328	0.814267	0.1478	0.809882	0.1479	0.806135	0.1649
0.2920	0.821232	0.1628	0.817362	0.1887	0.813551	0.2243	0.809860	0.2457	0.805565	0.2572	0.802013	0.2808
0.4007	0.818002	0.2399	0.814301	0.2610	0.810128	0.3078	0.806332	0.3405	0.801892	0.3826	0.798185	0.4408
0.5001	0.815078	0.3184	0.811427	0.3455	0.806833	0.4141	0.802928	0.4607	0.798586	0.5119	0.794873	0.5930
0.6006	0.812037	0.4427	0.808418	0.4786	0.803798	0.5318	0.799893	0.5832	0.795647	0.6439	0.792213	0.7187
0.7003	0.810129	0.4881	0.806496	0.5360	0.801702	0.5914	0.797723	0.6548	0.793596	0.7185	0.790384	0.7862
0.7996	0.809512	0.3991	0.805944	0.4464	0.801006	0.5008	0.797057	0.5609	0.792947	0.6344	0.789805	0.7074
0.9000	0.809558	0.2347	0.806221	0.2615	0.801323	0.2918	0.797481	0.3401	0.792935	0.4880	0.789467	0.6239
1.0000	0.811170	0.0000	0.807329	0.0000	0.803333	0.0000	0.799537	0.0000	0.795340	0.0000	0.791468	0.0000

Table-4.8: Density (ρ) and Excess molar volume (V^E) of iso-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\,mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.1007	0.825768	0.0820	0.821649	0.0860	0.818988	0.0960	0.815321	0.1040	0.810420	0.1040	0.805929	0.1180
0.1994	0.818393	0.1490	0.814177	0.1580	0.811274	0.1660	0.807497	0.1760	0.802475	0.1850	0.797839	0.1990
0.3007	0.811589	0.2010	0.807296	0.2140	0.804050	0.2290	0.800119	0.2450	0.795038	0.2590	0.790204	0.2780
0.3996	0.805580	0.2380	0.801252	0.2520	0.797734	0.2710	0.793747	0.2860	0.788693	0.2980	0.783725	0.3180
0.4993	0.800228	0.2500	0.795842	0.2670	0.792057	0.2910	0.787957	0.3100	0.782915	0.3210	0.777821	0.3420
0.59900	0.795379	0.2480	0.790949	0.2670	0.786927	0.2950	0.782807	0.3105	0.777697	0.3272	0.772552	0.3432
0.7008	0.791069	0.2160	0.786660	0.2310	0.782500	0.2550	0.778203	0.2810	0.773043	0.302	0.767778	0.3191
0.8012	0.787422	0.1520	0.783019	0.1640	0.778729	0.1840	0.774353	0.2120	0.769226	0.229	0.763763	0.2554
0.8990	0.784137	0.0830	0.779771	0.0890	0.775475	0.0940	0.771269	0.1000	0.766237	0.106	0.760775	0.1222
1.0000	0.781122	0.0000	0.776690	0.0000	0.772253	0.0000	0.768209	0.0000	0.763311	0.0000	0.758510	0.0000

Table-4.9: Density (ρ) and Excess molar volume (V^E) of iso-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K. 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.1002	0.826833	0.1112	0.822690	0.1232	0.820042	0.1343	0.816373	0.1433	0.811493	0.1543	0.807096	0.1743
0.2050	0.820772	0.1968	0.816653	0.2110	0.813692	0.2277	0.809875	0.2426	0.805098	0.2576	0.800700	0.2784
0.3020	0.815846	0.2524	0.811787	0.2654	0.808466	0.2953	0.804563	0.3122	0.799860	0.3322	0.795456	0.3542
0.3999	0.811408	0.3140	0.807354	0.3300	0.803842	0.3620	0.799877	0.3800	0.795270	0.4020	0.790861	0.4250
0.4997	0.807196	0.3934	0.803149	0.4124	0.799544	0.4394	0.795545	0.4564	0.791162	0.4674	0.786697	0.4964
0.6004	0.803875	0.4227	0.799880	0.4397	0.796164	0.4638	0.791949	0.4978	0.787675	0.5068	0.783118	0.5459
0.7002	0.801486	0.3922	0.797484	0.4122	0.793639	0.4361	0.789397	0.4690	0.785118	0.4860	0.780667	0.5140
0.8070	0.799949	0.2748	0.795961	0.2947	0.792006	0.3159	0.787766	0.3434	0.783548	0.3606	0.778971	0.4012
0.8995	0.799242	0.1131	0.795350	0.1232	0.791394	0.1313	0.787244	0.1434	0.783173	0.1484	0.778504	0.1985
1.0000	0.798111	0.0000	0.794250	0.0000	0.790212	0.0000	0.786120	0.0000	0.782163	0.0000	0.777832	0.0000

Table-4.10: Density (ρ) and Excess molar volume (V^E) of iso-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K		303.15K		308.15K		313.15K		318.15K		323.15K	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3\ mol^{-1}}$
0.0000	0.834108	0.0000	0.830080	0.0000	0.827868	0.0000	0.824412	0.0000	0.819508	0.0000	0.815380	0.0000
0.1010	0.829725	0.0404	0.825922	0.0484	0.823402	0.0624	0.819941	0.0664	0.815315	0.0724	0.811278	0.0665
0.1966	0.825900	0.1141	0.822200	0.1351	0.819510	0.1570	0.815749	0.1890	0.811227	0.2100	0.806941	0.2260
0.3070	0.822345	0.1759	0.818741	0.2129	0.815782	0.2528	0.812105	0.2838	0.807889	0.3039	0.803249	0.3548
0.4007	0.819459	0.2627	0.815929	0.3119	0.812848	0.3604	0.809160	0.3972	0.805033	0.4285	0.800484	0.4752
0.5001	0.816654	0.3593	0.813244	0.4176	0.810132	0.4670	0.806235	0.5307	0.802260	0.5681	0.797787	0.6118
0.6006	0.814102	0.4626	0.811035	0.5063	0.807725	0.5759	0.803899	0.6401	0.800123	0.6777	0.795599	0.7320
0.7003	0.812421	0.5079	0.809471	0.5555	0.806169	0.6231	0.802437	0.6823	0.798723	0.7308	0.794130	0.7972
0.7996	0.811500	0.4776	0.808478	0.5476	0.805177	0.6121	0.801516	0.6656	0.797772	0.7327	0.793197	0.7989
0.9000	0.810720	0.4502	0.807866	0.5178	0.804623	0.5743	0.800832	0.6505	0.797281	0.7120	0.792570	0.8014
1.0000	0.812660	0.0000	0.810558	0.0000	0.807344	0.0000	0.803576	0.0000	0.800001	0.0000	0.795835	0.0000

Table-4.11: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.1007	1.2180	-0.0073	-0.0656	1.0930	-0.0056	-0.0562	0.9770	-0.0052	-0.0585	0.8920	-0.0040	-0.0491	0.8080	-0.0077	-0.1053	0.7360	-0.0094	-0.1400
0.2006	1.2760	-0.0154	-0.0749	1.1420	-0.0152	-0.0824	1.0220	-0.0124	-0.0754	0.9280	-0.0133	-0.0887	0.8430	-0.0136	-0.1001	0.7720	-0.0093	-0.0744
0.3007	1.3300	-0.0313	-0.1106	1.1870	-0.0320	-0.1267	1.0670	-0.0226	-0.0995	0.9680	-0.0210	-0.1021	0.8790	-0.0207	-0.1105	0.8030	-0.0159	-0.0935
0.3999	1.3830	-0.0513	-0.1517	1.2410	-0.0426	-0.1407	1.1160	-0.0311	-0.1145	1.0130	-0.0257	-0.1042	0.9190	-0.0254	-0.1138	0.8390	-0.0191	-0.0936
0.4994	1.4460	-0.0654	-0.1769	1.3030	-0.0488	-0.1471	1.1740	-0.0339	-0.1137	1.0620	-0.0290	-0.1053	0.9640	-0.0276	-0.1129	0.8750	-0.0242	-0.1091
0.6012	1.5310	-0.0636	-0.1698	1.3740	-0.0513	-0.1530	1.2410	-0.0324	-0.1073	1.1200	-0.0272	-0.1002	1.0170	-0.0253	-0.1023	0.9190	-0.0243	-0.1089
0.6994	1.6240	-0.0552	-0.1590	1.4640	-0.0361	-0.1157	1.3080	-0.0319	-0.1146	1.1830	-0.0213	-0.0847	1.0710	-0.0226	-0.0993	0.9680	-0.0199	-0.0969
0.8014	1.7270	-0.0448	-0.1610	1.5530	-0.0288	-0.1155	1.3920	-0.0207	-0.0928	1.2540	-0.0125	-0.0622	1.1380	-0.0116	-0.0637	1.0260	-0.0105	-0.0639
0.9008	1.8430	-0.0240	-0.1449	1.6560	-0.0098	-0.0658	1.4820	-0.0055	-0.0411	1.3250	-0.0052	-0.0439	1.2000	-0.0069	-0.0645	1.0795	-0.0066	-0.0683
1.0000	1.9671	0.0000	0.0000	1.7192	0.0000	0.0000	1.5312	0.0000	0.0000	1.3761	0.0000	0.0000	1.2346	0.0000	0.0000	1.1148	0.0000	0.0000

Table-4.12: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.0998	1.2000	-0.0571	-0.5174	1.0700	-0.0558	-0.5655	0.9498	-0.0551	-0.6279	0.8545	-0.0614	-0.7729	0.7700	-0.0627	-0.8708	0.6950	-0.0656	-1.0038
0.1991	1.2380	-0.1214	-0.5868	1.1000	-0.1152	-0.6247	0.9690	-0.1139	-0.6970	0.8830	-0.1008	-0.6777	0.7650	-0.1276	-0.9671	0.7000	-0.1135	-0.9421
0.3008	1.2760	-0.1969	-0.6823	1.1310	-0.1832	-0.7138	1.0000	-0.1691	-0.7427	0.9000	-0.1584	-0.7709	0.7920	-0.1664	-0.9066	0.7220	-0.1495	-0.8945
0.4006	1.3350	-0.2584	-0.7370	1.1950	-0.2242	-0.7160	1.0550	-0.2053	-0.7404	0.9480	-0.1892	-0.7578	0.8350	-0.1927	-0.8647	0.7430	-0.1894	-0.9455
0.5003	1.4320	-0.2917	-0.7416	1.2820	-0.2504	-0.7136	1.1360	-0.2225	-0.7154	1.0120	-0.2097	-0.7601	0.9050	-0.1969	-0.7875	0.8000	-0.1975	-0.8824
0.6005	1.5670	-0.2983	-0.7265	1.3780	-0.2773	-0.7643	1.2220	-0.2429	-0.7557	1.0930	-0.2200	-0.7646	0.9750	-0.2070	-0.8024	0.8853	-0.1822	-0.7800
0.6996	1.7340	-0.2829	-0.7191	1.5350	-0.2515	-0.7221	1.3520	-0.2263	-0.7365	1.2000	-0.2101	-0.7676	1.0820	-0.1848	-0.7503	0.9920	-0.1495	-0.6681
0.7989	1.9404	-0.2407	-0.7278	1.7230	-0.2055	-0.7013	1.5240	-0.1768	-0.6833	1.3520	-0.1625	-0.7063	1.2120	-0.1459	-0.7077	1.1019	-0.1190	-0.6384
0.9006	2.1994	-0.1637	-0.8020	1.9840	-0.1016	-0.5577	1.7418	-0.0943	-0.5891	1.5290	-0.1004	-0.7104	1.3810	-0.0771	-0.6068	1.2490	-0.0589	-0.5150
1.0000	2.5554	0.0000	0.0000	2.2513	0.0000	0.0000	1.9787	0.0000	0.0000	1.7504	0.0000	0.0000	1.5631	0.0000	0.0000	1.3995	0.0000	0.0000

Table-4.13: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.0998	1.3100	0.0198	0.1698	1.1440	-0.0122	-0.1182	1.0420	0.0098	0.1047	0.9320	-0.0070	-0.0836	0.8500	-0.0025	-0.0327	0.7581	-0.0203	-0.2938
0.1966	1.4240	-0.0040	-0.0177	1.2470	-0.0314	-0.1572	1.1310	-0.0085	-0.0476	1.0210	-0.0103	-0.0637	0.9320	-0.0013	-0.0089	0.8370	-0.0129	-0.0972
0.2920	1.5310	-0.0472	-0.1468	1.3570	-0.0543	-0.1899	1.2130	-0.0432	-0.1691	1.1100	-0.0212	-0.0914	1.0210	0.0005	0.0026	0.9250	-0.0019	-0.0100
0.4007	1.6690	-0.0997	-0.2416	1.4730	-0.1068	-0.2915	1.3360	-0.0677	-0.2058	1.2060	-0.0508	-0.1717	1.1100	-0.0197	-0.0733	1.0210	-0.0021	-0.0087
0.5001	1.7760	-0.1870	-0.4003	1.5890	-0.1624	-0.3893	1.4250	-0.1287	-0.3458	1.3090	-0.0748	-0.1917	1.1920	-0.0478	-0.1573	1.0970	-0.0228	-0.0824
0.6006	1.9140	-0.2671	-0.5445	1.7000	-0.2439	-0.5588	1.5210	-0.2007	-0.5166	1.3840	-0.1413	-0.4051	1.2810	-0.0811	-0.2558	1.1650	-0.0619	-0.2159
0.7003	2.0610	-0.3604	-0.7678	1.8430	-0.3127	-0.7467	1.6370	-0.2692	-0.7255	1.4940	-0.1859	-0.5588	1.3700	-0.1252	-0.4167	1.2553	-0.0880	-0.3227
0.7996	2.2650	-0.4221	-1.0664	1.9860	-0.4036	-1.1545	1.7740	-0.3357	-1.0817	1.5960	-0.2535	-0.9199	1.4460	-0.1948	-0.7887	1.3160	-0.1541	-0.6910
0.9000	2.5849	-0.4004	-1.6002	2.3140	-0.3379	-1.5145	2.0340	-0.3036	-1.5458	1.7579	-0.2805	-1.6449	1.5691	-0.2333	-1.5403	1.4137	-0.1968	-1.4482
1.0000	3.4741	0.0000	0.0000	2.9816	0.0000	0.0000	2.5704	0.0000	0.0000	2.2703	0.0000	0.0000	1.9743	0.0000	0.0000	1.7661	0.0000	0.0000

Table-4.14: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.1007	1.2180	-0.0101	-0.0913	1.0950	-0.0041	-0.0417	0.9770	-0.0036	-0.0402	0.8890	-0.0020	-0.0252	0.8000	-0.0100	-0.1367	0.7320	-0.0044	-0.0658
0.1994	1.3310	-0.0246	-0.1198	1.1390	-0.0186	-0.1017	1.0170	-0.0134	-0.0820	0.9180	-0.0125	-0.0846	0.8250	-0.0192	-0.1438	0.7560	-0.0062	-0.0514
0.3007	1.3900	-0.0398	-0.1400	1.1830	-0.0379	-0.1501	1.0560	-0.0282	-0.1253	0.9480	-0.0248	-0.1228	0.8400	-0.0408	-0.2253	0.7660	-0.0237	-0.1449
0.3996	1.4540	-0.0573	-0.1684	1.2330	-0.0530	-0.1756	1.0950	-0.0444	-0.1657	0.9770	-0.0390	-0.1630	0.8690	-0.0490	-0.2287	0.7810	-0.0365	-0.1903
0.4993	1.5310	-0.0748	-0.2007	1.2960	-0.0592	-0.1787	1.1390	-0.0589	-0.2018	1.0120	-0.0494	-0.1930	0.9000	-0.0572	-0.2464	0.7960	-0.0505	-0.2459
0.5990	1.6270	-0.0839	-0.2222	1.3550	-0.0731	-0.2187	1.2000	-0.0595	-0.2013	1.0510	-0.0579	-0.2233	0.9480	-0.0500	-0.2140	0.8250	-0.0515	-0.2521
0.7008	1.7430	-0.0808	-0.2312	1.4340	-0.0725	-0.2354	1.2570	-0.0685	-0.2532	1.1050	-0.0546	-0.2300	0.9970	-0.0445	-0.2083	0.8640	-0.0443	-0.2382
0.8012	1.8650	-0.0617	-0.2184	1.5220	-0.0661	-0.2671	1.3410	-0.0531	-0.2438	1.1690	-0.0428	-0.2260	1.0510	-0.0352	-0.2071	0.9180	-0.0227	-0.1533
0.8990	1.9234	-0.0393	-0.2298	1.6325	-0.0394	-0.2626	1.4390	-0.0253	-0.1919	1.2443	-0.0207	-0.1817	1.1152	-0.0165	-0.1616	0.9670	-0.0064	-0.0728
1.0000	2.0427	0.0000	0.0000	1.7633	0.0000	0.0000	1.5403	0.0000	0.0000	1.3219	0.0000	0.0000	1.1803	0.0000	0.0000	1.0082	0.0000	0.0000

Table-4.15: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.1002	1.1850	-0.1064	-0.9535	1.0260	-0.1268	-1.2921	0.9280	-0.0978	-1.1108	0.8340	-0.0987	-1.2404	0.7400	-0.1047	-1.4683	0.6720	-0.0988	-1.5214
0.2050	1.2110	-0.2311	-1.0718	1.0550	-0.2256	-1.1890	0.9360	-0.1977	-1.1756	0.8340	-0.1906	-1.2631	0.7400	-0.1825	-1.3529	0.6550	-0.1839	-1.5180
0.3020	1.2810	-0.3163	-1.0468	1.1230	-0.2885	-1.0847	0.9960	-0.2476	-1.0533	0.8770	-0.2408	-1.1509	0.7740	-0.2269	-1.2197	0.6810	-0.2262	-1.3605
0.3999	1.3770	-0.3938	-1.0482	1.2170	-0.3402	-1.0272	1.0810	-0.2844	-0.9733	0.9530	-0.2674	-1.0306	0.8600	-0.2268	-0.9753	0.7570	-0.2248	-1.0835
0.4997	1.4920	-0.4752	-1.1059	1.3280	-0.3932	-1.0374	1.2000	-0.3019	-0.8976	1.0625	-0.2722	-1.0106	0.9592	-0.2227	-0.8352	0.8424	-0.2218	-0.9348
0.6004	1.6380	-0.5493	-1.2054	1.4775	-0.4267	-1.0575	1.3370	-0.3164	-0.8853	1.2340	-0.2269	-0.7035	1.1000	-0.1863	-0.6522	0.9540	-0.2003	-0.7944
0.7002	1.8810	-0.5488	-1.2196	1.6510	-0.4538	-1.1568	1.5000	-0.3186	-0.9176	1.3715	-0.2262	-0.7273	1.2201	-0.1788	-0.6515	1.0941	-0.1571	-0.6390
0.8070	2.2630	-0.4562	-1.1791	1.9375	-0.4054	-1.2198	1.7620	-0.2518	-0.8576	1.5740	-0.1844	-0.7113	1.4000	-0.1303	-0.5715	1.2510	-0.1128	-0.5545
0.8995	2.6970	-0.3005	-1.1687	2.3877	-0.1831	-0.8172	2.0658	-0.1339	-0.6945	1.7958	-0.1147	-0.6851	1.5805	-0.0736	-0.5033	1.3960	-0.0736	-0.5683
1.0000	3.3318	0.0000	0.0000	3.3318	0.0000	0.0000	2.4258	0.0000	0.0000	2.0905	0.0000	0.0000	1.7997	0.0000	0.0000	1.5959	0.0000	0.0000

Table-4.16: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε	$\frac{\eta}{mPa.s}$	$\frac{\eta^E}{mPa.s}$	ε
0.0000	1.1620	0.0000	0.0000	1.0425	0.0000	0.0000	0.9322	0.0000	0.0000	0.8525	0.0000	0.0000	0.7765	0.0000	0.0000	0.7109	0.0000	0.0000
0.1010	1.3160	0.0100	0.0839	1.1900	0.0233	0.2180	1.0630	0.0244	0.2560	0.9510	0.0059	0.0691	0.8765	0.0188	0.2384	0.7954	0.0171	0.2389
0.1966	1.4620	0.0033	0.0142	1.3160	0.0182	0.0882	1.1700	0.0196	0.1068	1.0570	0.0151	0.0911	0.9700	0.0276	0.1825	0.8770	0.0290	0.2126
0.3070	1.6150	-0.0424	-0.1219	1.4490	-0.0187	-0.0602	1.2890	-0.0057	-0.0206	1.1630	-0.0031	-0.0127	1.0570	0.0063	0.0281	0.9657	0.0294	0.1451
0.4007	1.7492	-0.0980	-0.2269	1.5664	-0.0628	-0.1636	1.3837	-0.0475	-0.1405	1.2480	-0.0352	-0.1157	1.1301	-0.0222	-0.0810	1.0278	0.0093	0.0380
0.5001	1.8884	-0.1839	-0.3716	1.6887	-0.1313	-0.2995	1.5045	-0.0873	-0.2255	1.3475	-0.0727	-0.2057	1.2105	-0.0603	-0.1946	1.0881	-0.0254	-0.0922
0.6006	2.0117	-0.3160	-0.6083	1.8210	-0.2146	-0.4645	1.6302	-0.1423	-0.3488	1.4496	-0.1239	-0.3420	1.2992	-0.1039	-0.3207	1.1709	-0.0476	-0.1663
0.7003	2.1705	-0.4418	-0.8827	1.9619	-0.3129	-0.7050	1.7413	-0.2307	-0.5927	1.5493	-0.1928	-0.5587	1.3859	-0.1620	-0.5267	1.2381	-0.0945	-0.3503
0.7996	2.3435	-0.5867	-1.3944	2.1055	-0.4354	-1.1731	1.8616	-0.3314	-1.0224	1.6701	-0.2577	-0.8956	1.4892	-0.2178	-0.8517	1.3135	-0.1432	-0.6460
0.9000	2.5440	-0.7471	-2.8610	2.2814	-0.5603	-2.4400	2.0017	-0.4400	-2.2077	1.7750	-0.3608	-2.0562	1.5698	-0.3146	-2.0297	1.4027	-0.1914	-1.4210
1.0000	3.4162	0.0000	0.0000	3.0653	0.0000	0.0000	2.7027	0.0000	0.0000	2.3672	0.0000	0.0000	2.0960	0.0000	0.0000	1.9355	0.0000	0.0000

Table-4.17: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.59	12.54	12.47	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1007	12.79	12.75	12.68	12.66	12.62	12.58	-0.0025	-0.0002	-0.0005	0.0020	-0.0113	-0.0198
0.2006	13.00	12.95	12.89	12.85	12.82	12.80	-0.0076	-0.0105	-0.0073	-0.0126	-0.0174	-0.0063
0.3007	13.18	13.13	13.08	13.05	13.02	13.00	-0.0285	-0.0371	-0.0225	-0.0236	-0.0284	-0.0186
0.3999	13.36	13.32	13.28	13.26	13.23	13.20	-0.0561	-0.0502	-0.0342	-0.0276	-0.0338	-0.0206
0.4994	13.55	13.53	13.49	13.46	13.44	13.40	-0.0741	-0.0560	-0.0349	-0.0310	-0.0347	-0.0323
0.6012	13.76	13.74	13.71	13.68	13.66	13.62	-0.0681	-0.0586	-0.0310	-0.0264	-0.0280	-0.0320
0.6994	13.98	13.97	13.92	13.90	13.87	13.83	-0.0551	-0.0328	-0.0321	-0.0158	-0.0239	-0.0223
0.8014	14.20	14.19	14.15	14.12	14.11	14.06	-0.0434	-0.0255	-0.0163	-0.0035	-0.0038	-0.0037
0.9008	14.43	14.42	14.38	14.34	14.32	14.27	-0.0209	-0.0033	0.0025	0.0021	-0.0025	-0.0033
1.0000	14.66	14.63	14.59	14.54	14.53	14.49	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.18: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.59	12.54	12.4	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0998	12.83	12.77	12.68	12.62	12.57	12.50	-0.0796	-0.0914	-0.1065	-0.1419	-0.1673	-0.2018
0.1991	13.06	12.99	12.89	12.87	12.71	12.69	-0.1709	-0.1885	-0.2200	-0.2148	-0.3403	-0.3343
0.3008	13.28	13.21	13.12	13.07	12.96	12.93	-0.2775	-0.2981	-0.3172	-0.3369	-0.4177	-0.4167
0.4006	13.53	13.49	13.40	13.35	13.25	13.16	-0.3511	-0.3435	-0.3628	-0.3787	-0.4523	-0.5103
0.5003	13.83	13.79	13.72	13.66	13.60	13.49	-0.3701	-0.3577	-0.3630	-0.3927	-0.4210	-0.4901
0.6005	14.17	14.10	14.03	13.99	13.92	13.90	-0.3487	-0.3762	-0.3758	-0.3865	-0.4159	-0.4069
0.6996	14.53	14.48	14.41	14.35	14.32	14.32	-0.3047	-0.3103	-0.3219	-0.3433	-0.3389	-0.2964
0.7989	14.92	14.88	14.83	14.77	14.73	14.72	-0.2385	-0.2314	-0.2270	-0.2399	-0.2438	-0.2166
0.9006	15.34	15.34	15.28	15.20	15.19	15.17	-0.1506	-0.0978	-0.1062	-0.1360	-0.1134	-0.0921
1.0000	15.81	15.76	15.70	15.65	15.62	15.5858	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.19: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of n-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.59	12.54	12.47	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0998	13.12	13.01	12.99	12.92	12.90	12.81	0.1008	0.0376	0.0908	0.0487	0.0613	-0.0010
0.1966	13.53	13.43	13.42	13.38	13.36	13.30	0.0986	0.0449	0.0922	0.0877	0.1113	0.0756
0.2920	13.90	13.84	13.79	13.80	13.81	13.77	0.0586	0.0375	0.0518	0.0953	0.1478	0.1431
0.4007	14.31	14.24	14.24	14.22	14.24	14.25	0.0041	-0.0258	0.0294	0.0524	0.1164	0.1610
0.5001	14.63	14.61	14.58	14.61	14.61	14.63	-0.0989	-0.0931	-0.0634	0.0175	0.0615	0.1145
0.6006	14.98	14.94	14.92	14.93	14.97	14.96	-0.1827	-0.1939	-0.1684	-0.1000	-0.0058	0.0212
0.7003	15.31	15.29	15.26	15.28	15.31	15.33	-0.2785	-0.2711	-0.2617	-0.1731	-0.0959	-0.0432
0.7996	15.68	15.62	15.60	15.59	15.60	15.60	-0.3342	-0.3744	-0.3486	-0.2852	-0.2326	-0.1927
0.9000	16.13	16.13	16.09	15.98	15.95	15.93	-0.3085	-0.2937	-0.3047	-0.3317	-0.3086	-0.2881
1.0000	16.87	16.86	16.83	16.74	16.68	16.65	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.20: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso-Propanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.59	12.54	12.47	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1007	12.80	12.76	12.69	12.66	12.60	12.58	-0.0035	0.0080	0.0092	0.0133	-0.0131	0.0047
0.1994	13.12	12.96	12.89	12.85	12.79	12.77	0.0944	-0.0106	-0.0019	-0.0025	-0.0271	0.0131
0.3007	13.32	13.15	13.08	13.03	12.93	12.91	0.0724	-0.0404	-0.0266	-0.0248	-0.0815	-0.0362
0.3996	13.52	13.34	13.27	13.20	13.12	13.05	0.0539	-0.0623	-0.0560	-0.0543	-0.0964	-0.0719
0.4993	13.73	13.55	13.45	13.38	13.30	13.20	0.0468	-0.0678	-0.0823	-0.0754	-0.1130	-0.1132
0.5990	13.96	13.74	13.67	13.56	13.52	13.38	0.0594	-0.0901	-0.0793	-0.0935	-0.0884	-0.1134
0.7008	14.20	13.97	13.87	13.78	13.74	13.59	0.0854	-0.0884	-0.0981	-0.0859	-0.0744	-0.0915
0.8012	14.45	14.19	14.11	14.00	13.96	13.83	0.1069	-0.0809	-0.0717	-0.0643	-0.0568	-0.0335
0.8990	14.70	14.44	14.37	14.23	14.19	14.05	0.1517	-0.0455	-0.0295	-0.0273	-0.0227	-0.0007
1.0000	14.77	14.70	14.61	14.47	14.41	14.24	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.21: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso-Butanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.59	12.54	12.47	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1002	12.81	12.67	12.63	12.57	12.47	12.42	-0.1737	-0.2531	-0.2146	-0.2479	-0.3059	-0.3227
0.2050	13.02	12.91	12.82	12.74	12.64	12.53	-0.3656	-0.4194	-0.4195	-0.4626	-0.5084	-0.5877
0.3020	13.30	13.21	13.13	13.02	12.92	12.79	-0.4628	-0.4903	-0.4796	-0.5400	-0.5866	-0.6746
0.3999	13.62	13.55	13.48	13.38	13.34	13.22	-0.5302	-0.5259	-0.4996	-0.5425	-0.5157	-0.5926
0.4997	13.95	13.90	13.88	13.80	13.77	13.65	-0.5894	-0.5556	-0.4736	-0.4900	-0.4468	-0.5197
0.6004	14.30	14.30	14.29	14.32	14.26	14.12	-0.6266	-0.5473	-0.4490	-0.3414	-0.3143	-0.4096
0.7002	14.76	14.69	14.70	14.72	14.66	14.61	-0.5577	-0.5333	-0.4121	-0.3136	-0.2763	-0.2727
0.8070	15.34	15.21	15.23	15.20	15.15	15.10	-0.4006	-0.4228	-0.2842	-0.2285	-0.1743	-0.1686
0.8995	15.86	15.84	15.74	15.64	15.57	15.50	-0.2324	-0.1559	-0.1296	-0.1291	-0.0876	-0.1033
1.0000	16.49	16.38	16.25	16.14	16.02	15.96	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table-4.22: Change of Free energy (ΔG^*) and Excess Free energy (ΔG^{*E}) of iso-Pentanol+0.015M SDS+Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

X_2	$\frac{\Delta G^*}{kJ.mol^{-1}}$						$\frac{\Delta G^{*E}}{kJ.mol^{-1}}$					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.0000	12.593	12.54	12.47	12.45	12.41	12.39	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1010	13.13	13.11	13.04	12.97	12.98	12.94	0.0819	0.1138	0.1253	0.0833	0.1250	0.1269
0.1966	13.59	13.57	13.50	13.46	13.47	13.42	0.1108	0.1423	0.1533	0.1505	0.1911	0.2075
0.3070	14.05	14.03	13.97	13.94	13.92	13.91	0.0705	0.1052	0.1303	0.1377	0.1627	0.2340
0.4007	14.42	14.39	14.32	14.30	14.28	14.26	0.0121	0.0514	0.0684	0.0862	0.1096	0.1897
0.5001	14.78	14.75	14.71	14.68	14.64	14.60	-0.0812	-0.0362	0.0124	0.0246	0.0354	0.1061
0.6006	15.09	15.11	15.08	15.03	15.00	14.97	-0.2214	-0.1378	-0.0666	-0.0617	-0.0491	0.0513
0.7003	15.43	15.44	15.40	15.36	15.32	15.28	-0.3388	-0.2499	-0.1916	-0.1746	-0.1591	-0.0604
0.7996	15.75	15.76	15.71	15.70	15.66	15.58	-0.4632	-0.3802	-0.3228	-0.2738	-0.2583	-0.1721
0.9000	16.09	16.09	16.03	15.99	15.94	15.90	-0.5850	-0.4980	-0.4512	-0.4212	-0.4204	-0.2777
1.0000	17.13	17.04	16.93	16.86	16.79	16.60	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.23: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of n-Propanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.15	0.0000
0.1007	15.36	0.1951	-29.64	0.6452
0.2006	15.37	0.0271	-30.30	0.1204
0.3007	15.35	-0.1572	-30.97	-0.4209
0.3999	15.22	-0.4553	-32.03	-1.3463
0.4994	15.29	-0.5487	-32.44	-1.6252
0.6012	15.47	-0.5456	-32.57	-1.6255
0.6994	15.77	-0.4085	-32.29	-1.2172
0.8014	15.84	-0.5165	-32.82	-1.6110
0.9008	16.35	-0.1745	-31.89	-0.5482
1.0000	16.69	0.0000	-31.47	0.0000

Table 4.24: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of n-Butanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.16	0.0000
0.0998	16.76	1.4082	-25.10	4.9561
0.1991	17.69	1.9850	-22.77	7.1780
0.3008	17.62	1.5528	-23.73	6.1058
0.4006	18.00	1.5790	-23.35	6.3696
0.5003	17.79	1.0176	-25.05	4.5605
0.6005	17.50	0.3665	-27.08	2.4193
0.6996	17.30	-0.1807	-28.95	0.4462
0.7989	17.50	-0.3333	-29.61	-0.3232
0.9006	17.70	-0.5025	-30.41	-1.2440
1.0000	18.55	0.0000	-29.06	0.0000

Table 4.25: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of n-Pentanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.16	0.0000
0.0998	16.37	0.8974	-27.29	2.7072
0.1966	15.89	-0.0567	-30.29	-0.4562
0.292	15.10	-1.3070	-34.16	-4.4938
0.4007	14.83	-2.1020	-36.43	-6.9474
0.5001	14.56	-2.8485	-38.45	-9.1363
0.6006	14.89	-3.0012	-38.47	-9.3231
0.7003	15.05	-3.3272	-39.09	-10.1074
0.7996	16.47	-2.3782	-35.52	-6.7072
0.9000	18.99	-0.3475	-28.78	-0.1340
1.0000	19.82	0.0000	-28.47	0.0000

Table 4.26: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Propanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.16	0.0000
0.1007	15.64	0.0295	-28.78	0.0850
0.1994	17.07	0.8670	-24.84	2.7559
0.3007	18.01	1.1967	-22.37	3.9260
0.3996	18.70	1.2869	-20.73	4.2967
0.4993	19.64	1.6185	-18.31	5.4272
0.599	20.15	1.5298	-17.32	5.1422
0.7008	20.72	1.4832	-16.18	4.9640
0.8012	21.00	1.1532	-16.04	3.8198
0.8990	21.75	1.3123	-14.39	4.2105
1.0000	21.05	0.0000	-17.30	0.0000

Table 4.27: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Butanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.16	0.0000
0.1002	17.21	1.4053	-23.44	5.3380
0.2050	18.68	2.0383	-19.28	8.0437
0.3020	19.34	1.9206	-18.07	7.9175
0.3999	18.22	0.0110	-22.88	1.7556
0.4997	17.27	-1.7338	-27.18	-3.9314
0.6004	15.92	-3.8927	-32.95	-11.0886
0.7002	16.12	-4.4996	-33.69	-13.2153
0.8070	17.70	-3.7749	-30.25	-11.2509
0.8995	20.54	-1.6805	-22.68	-4.9601
1.0000	23.02	0.0000	-16.33	0.0000

Table 4.28: Change of Enthalpy (ΔH^*), Excess enthalpy (ΔH^{*E}), Change of Entropy (ΔS^*) and Excess entropy(ΔS^{*E}) of iso-Pentanol+0.015M SDS+Ethanol system.

X_2	$\frac{\Delta H^*}{kJ.mol^{-1}}$	$\frac{\Delta H^{*E}}{kJ.mol^{-1}}$	$\frac{\Delta S^*}{J.mol^{-1}}$	$\frac{\Delta S^{*E}}{J.mol^{-1}}$
0.0000	15.00	0.0000	-30.16	0.0000
0.1010	15.53	-0.2779	-30.24	-1.2466
0.1966	15.62	-0.9512	-31.46	-3.5747
0.3070	15.84	-1.6172	-32.26	-5.6565
0.4007	16.39	-1.8150	-31.64	-6.1203
0.5001	16.95	-2.0577	-31.02	-6.6567
0.6006	16.82	-2.9946	-32.58	-9.3793
0.7003	17.42	-3.1918	-31.69	-9.6443
0.7996	17.76	-3.6440	-31.62	-10.7266
0.9000	18.58	-3.6308	-30.00	-10.2641
1.0000	23.01	0.0000	-18.57	0.0000

Table 4.29: Coefficient, a_i, of Redlich- Kister Eq expressing V^E and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Propanol +0.015M SDS+Ethanol systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
n-Propanol+0.015M SDS+Ethanol	298.15	0.6111	0.1118	-0.5605	0.1149	0.0091
	303.15	0.6512	0.1411	-0.5719	0.0756	0.0094
	308.15	0.6906	0.1178	-0.5717	0.1178	0.0094
	313.15	0.7204	0.1107	-0.5639	0.1577	0.0088
	318.15	0.7607	0.1029	-0.5110	0.2185	0.0082
	323.15	0.8335	0.1241	-0.5502	0.1948	0.0065
n-Butanol+0.015M SDS+Ethanol	298.15	1.1341	0.4728	-0.7256	-0.5337	0.0095
	303.15	1.2605	0.6228	-0.7894	-0.8372	0.0098
	308.15	1.3750	0.6544	-0.8187	-0.9340	0.0112
	313.15	1.4624	0.6819	-0.8823	-1.0001	0.0112
	318.15	1.5520	0.7770	-0.8872	-1.0784	0.0126
	323.15	1.6687	0.8463	-0.8057	-0.8967	0.0134
n-Pentanol+0.015M SDS+Ethanol	298.15	1.3965	2.0769	0.3792	-1.1544	0.0202
	303.15	1.5152	2.2389	0.5884	-1.2232	0.0231
	308.15	1.7432	2.3437	0.6291	-1.1961	0.0194
	313.15	1.9154	2.5612	0.8322	-1.1268	0.0182
	318.15	2.0698	2.5829	1.4119	0.2503	0.0191
	323.15	2.3094	2.5732	1.8150	1.4950	0.0389
iso-Propanol +0.015M SDS+Ethanol	298.15	1.0135	0.1070	-0.1688	-0.1857	0.0025
	303.15	1.0827	0.1333	-0.1845	-0.2115	0.0026
	308.15	1.1804	0.2361	-0.2100	-0.3958	0.0023
	313.15	1.2544	0.3139	-0.1349	-0.4751	0.0052
	318.15	1.3163	0.3584	-0.1126	-0.4812	0.0084
	323.15	1.3883	0.3484	0.0272	-0.3881	0.0092
iso-Butanol +0.015M SDS+Ethanol	298.15	1.5717	1.1368	-0.3533	-1.7887	0.0085
	303.15	1.6398	1.1845	-0.2618	-1.8644	0.0088
	308.15	1.7570	1.1458	-0.2579	-1.7846	0.0097
	313.15	1.8532	1.2846	-0.1759	-1.9748	0.0117
	318.15	1.9137	1.2432	-0.0842	-1.9182	0.0147
	323.15	2.0140	1.2822	0.2368	-1.6962	0.0086
iso-Pentanol +0.015M SDS+Ethanol	298.15	1.4039	1.6883	1.6243	1.3910	0.0311
	303.15	1.5914	1.6382	1.9067	2.1541	0.0328
	308.15	1.8113	1.7919	2.1183	2.3586	0.0354
	313.15	2.0160	1.8648	2.3625	2.8351	0.0475
	318.15	2.1440	1.9406	2.7358	3.3118	0.0489
	323.15	2.3375	1.8687	3.0708	4.3798	0.0538

Table 4.30: Coefficient, a_i, of Redlich- Kister Eq expressing η^E and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Propanol +0.015M SDS+Ethanol systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
n-Propanol+0.015M SDS+Ethanol	298.15	-0.2450	-0.1502	0.1497	0.0292	0.0031
	303.15	-0.1976	-0.0589	0.1762	0.0243	0.0025
	308.15	-0.1393	-0.0572	0.1050	0.0653	0.0019
	313.15	-0.1153	-0.0026	0.0974	-0.0007	0.0006
	318.15	-0.1092	-0.0072	0.0607	0.0263	0.0012
	323.15	-0.0921	-0.0451	0.0438	0.1035	0.0020
n-Butanol+0.015M SDS+Ethanol	298.15	-1.1521	-0.4256	-0.0203	-0.5093	0.0050
	303.15	-1.0419	-0.5069	0.1623	0.2474	0.0074
	308.15	-0.9293	-0.3785	0.0773	0.1631	0.0057
	313.15	-0.8502	-0.3283	-0.0254	0.0694	0.0050
	318.15	-0.8221	-0.1218	-0.0248	0.0515	0.0055
	323.15	-0.7717	0.0006	0.1583	0.0207	0.0059
n-Pentanol+0.015M SDS+Ethanol	298.15	-0.6879	-1.5028	-1.9855	-2.0889	0.0142
	303.15	-0.6269	-1.3342	-1.9884	-1.5108	0.0104
	308.15	-0.4909	-1.1424	-1.6952	-1.5732	0.0075
	313.15	-0.2839	-0.7020	-1.7260	-1.7629	0.0179
	318.15	-0.1276	-0.4647	-1.5264	-1.6893	0.0175
	323.15	-0.0436	-0.3512	-1.5051	-1.2555	0.0179
iso-Propanol +0.015M SDS+Ethanol	298.15	-0.2967	-0.2577	0.0559	0.1176	0.0018
	303.15	-0.2561	-0.2058	-0.0079	-0.0760	0.0028
	308.15	-0.2310	-0.2363	0.0787	0.1101	0.0035
	313.15	-0.2044	-0.1971	0.1032	0.1076	0.0012
	318.15	-0.2186	-0.0277	0.1216	-0.0672	0.0028
	323.15	-0.1966	-0.1649	0.2494	0.2311	0.0021
iso-Butanol +0.015M SDS+Ethanol	298.15	-1.9386	-1.4468	-0.5782	0.3058	0.0100
	303.15	-1.6098	-1.1695	-0.6497	0.9639	0.0264
	308.15	-1.2536	-0.4287	-0.2876	0.2668	0.0126
	313.15	-1.0528	0.2461	-0.2684	-0.6225	0.0096
	318.15	-0.8827	0.3437	-0.2491	-0.2348	0.0080
	323.15	-0.8861	0.4204	-0.1161	-0.3172	0.0054
iso-Pentanol +0.015M SDS+Ethanol	298.15	-0.6041	-1.4816	-4.3087	-5.3878	0.0617
	303.15	-0.3978	-1.0232	-3.1791	-4.3823	0.0458
	308.15	-0.2505	-0.6660	-2.5363	-3.7447	0.0356
	313.15	-0.2068	-0.6200	-2.0854	-2.7521	0.0349
	318.15	-0.1610	-0.5465	-1.7084	-2.5201	0.0318
	323.15	-0.0259	-0.4724	-1.1443	-1.4123	0.0178

Table 4.31: Coefficient, a_i, of Redlich- Kister Eq expressing ΔG^{*E} and standard deviation, σ for the n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Propanol +0.015M SDS+Ethanol systems.

Systems	T/K	a_0	a_1	a_2	a_3	σ
n-Propanol+0.015M SDS+Ethanol	298.15	-0.2694	-0.1664	0.2864	0.0175	0.0053
	303.15	-0.2305	-0.0263	0.3360	-0.0329	0.0046
	308.15	-0.1489	-0.0522	0.2143	0.0728	0.0038
	313.15	-0.1241	0.0514	0.2144	-0.0560	0.0017
	318.15	-0.1368	0.0379	0.1358	0.0487	0.0030
	323.15	-0.1135	-0.0954	0.1016	0.3238	0.0063
n-Butanol+0.015M SDS+Ethanol	298.15	-1.4657	-0.0301	0.4137	-0.7800	0.0069
	303.15	-1.5039	-0.2171	0.5748	0.2065	0.0126
	308.15	-1.5371	-0.0767	0.4119	0.1328	0.0119
	313.15	-1.5999	-0.1056	0.2304	0.1421	0.0134
	318.15	-1.7848	0.4843	0.0772	-0.0863	0.0165
	323.15	-1.9023	0.7938	0.5695	-0.2086	0.0199
n-Pentanol+0.015M SDS+Ethanol	298.15	-0.3458	-1.7272	-1.1708	-1.6383	0.0095
	303.15	-0.3629	-1.7237	-1.6865	-1.0154	0.0129
	308.15	-0.2436	-1.7170	-1.5308	-1.5696	0.0106
	313.15	0.0660	-1.3014	-2.1543	-1.9850	0.0235
	318.15	0.3526	-1.0733	-2.2314	-2.2356	0.0266
	323.15	0.5498	-0.9977	-2.8083	-1.3939	0.0329
iso-Propanol +0.015M SDS+Ethanol	298.15	0.1972	-0.3007	1.0869	1.7780	0.0212
	303.15	-0.3095	-0.2802	0.0951	-0.1690	0.0054
	308.15	-0.3162	-0.4051	0.2623	0.1664	0.0072
	313.15	-0.3164	-0.3994	0.3333	0.1964	0.0026
	318.15	-0.4216	0.0390	0.3897	-0.2826	0.0083
	323.15	-0.4292	-0.4502	0.8497	0.6256	0.0079
iso-Butanol +0.015M SDS+Ethanol	298.15	-2.4107	-0.7005	0.0962	0.7142	0.0172
	303.15	-2.2659	-0.5339	-0.5990	1.6435	0.0313
	308.15	-1.9847	0.4432	-0.3294	0.3018	0.0238
	313.15	-1.8985	1.7412	-0.5253	-1.5434	0.0218
	318.15	-1.7808	2.0086	-0.9039	-0.8261	0.0223
	323.15	-2.0976	2.4636	-0.6149	-1.2636	0.0210
iso-Pentanol +0.015M SDS+Ethanol	298.15	-0.2388	-1.7919	-3.1179	-4.0456	0.0473
	303.15	-0.0337	-1.4608	-2.5440	-4.0546	0.0394
	308.15	0.1449	-1.1410	-2.3895	-4.2305	0.0350
	313.15	0.2011	-1.2453	-2.3670	-3.2554	0.0444
	318.15	0.2561	-1.2626	-2.0628	-3.6305	0.0461
	323.15	0.5747	-1.3233	-1.6457	-2.1651	0.0311

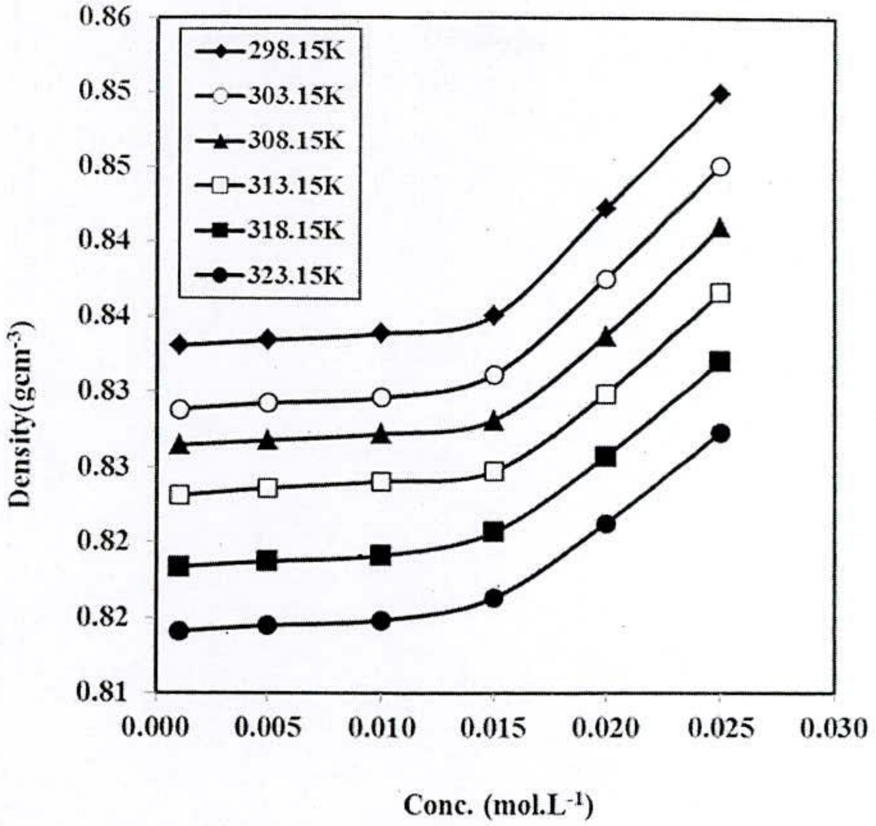

Figure 4.1: Plots of density (ρ) vs concentration of SDS in Ethanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

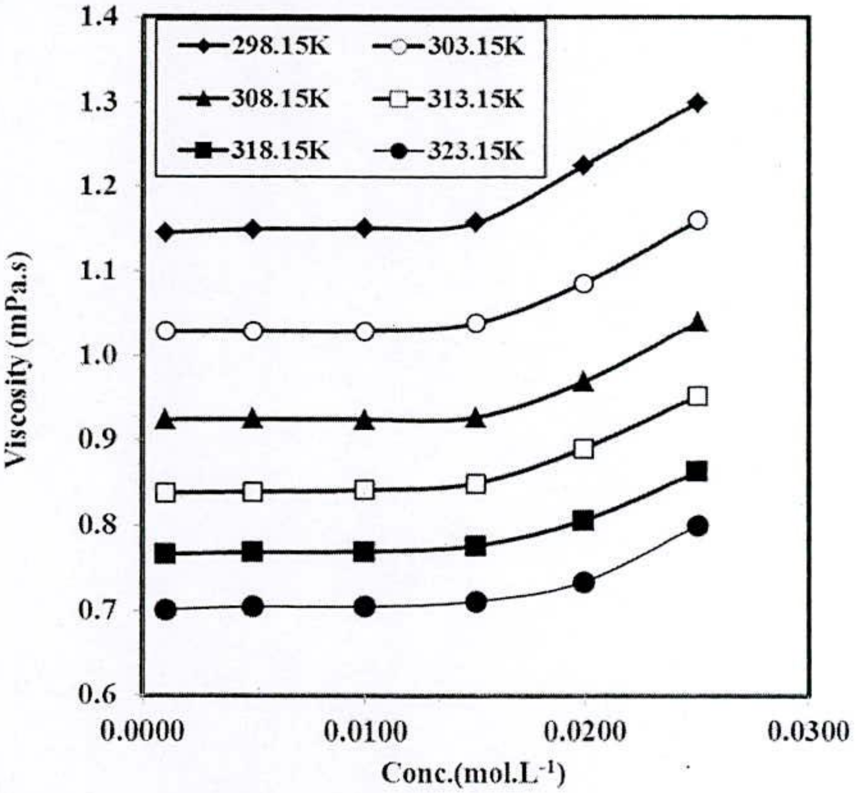

Figure 4.2: Plots of viscosity vs concentration of SDS in Ethanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

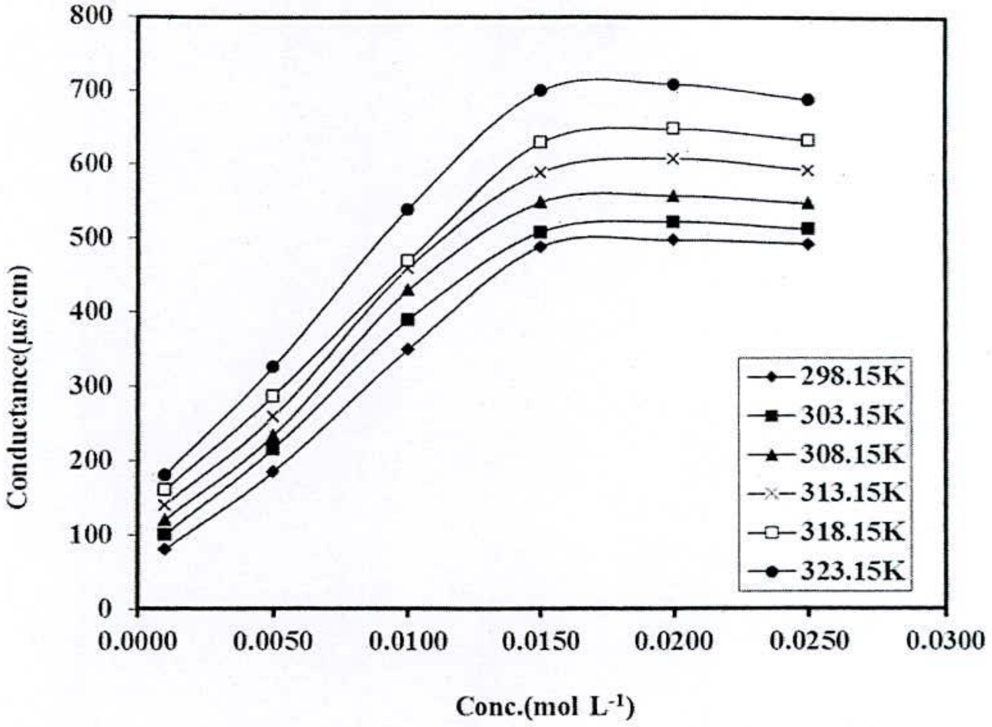

Figure 4.3: Plots of conductance vs concentration of SDS in Ethanol at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

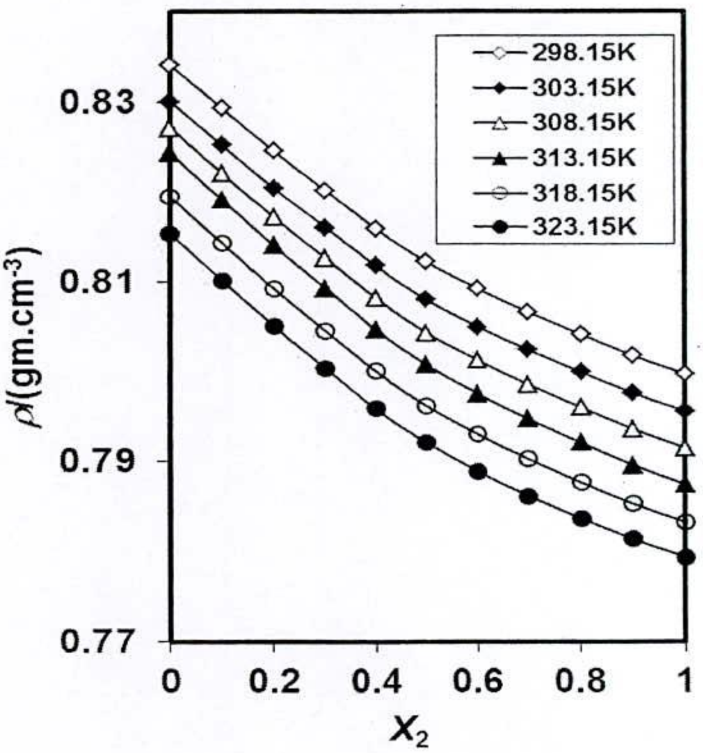

Figure 4.4: Plots of density (ρ) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

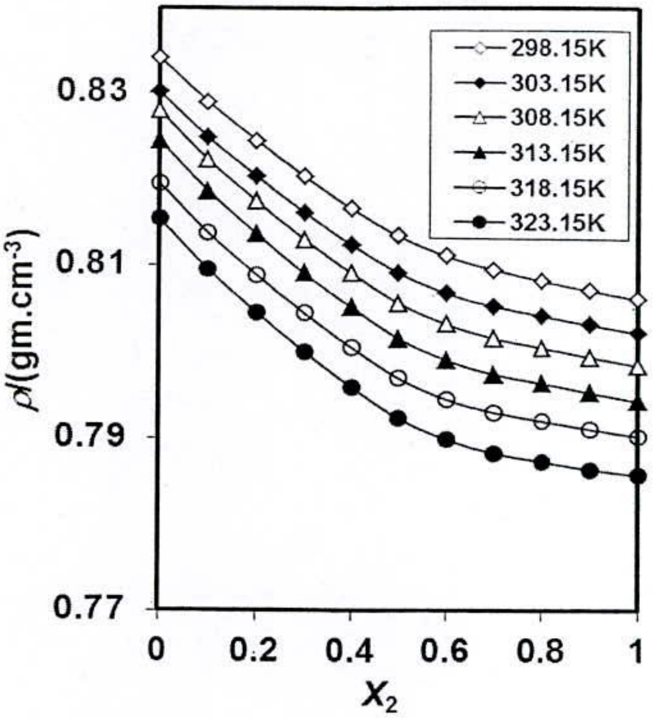

Figure 4.5: Plots of density (ρ) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

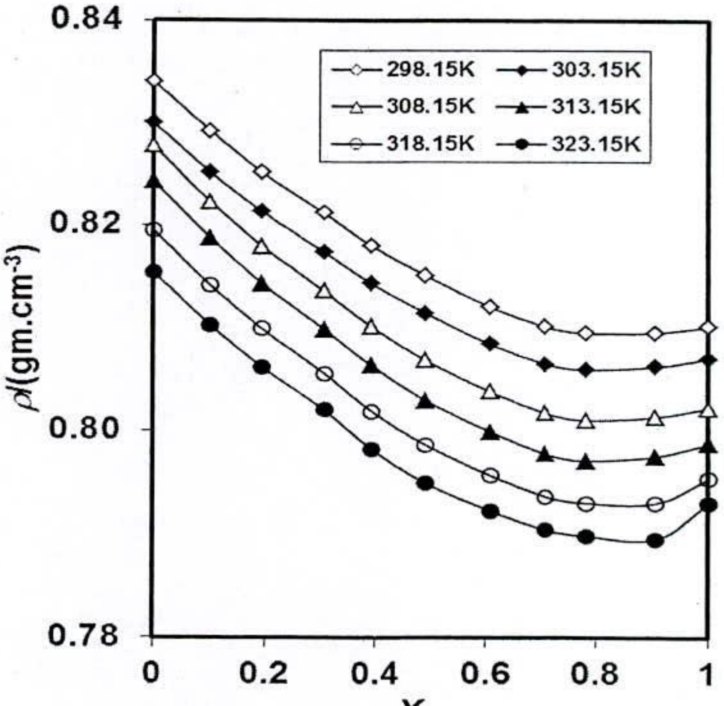

Figure 4.6: Plots of density (ρ) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

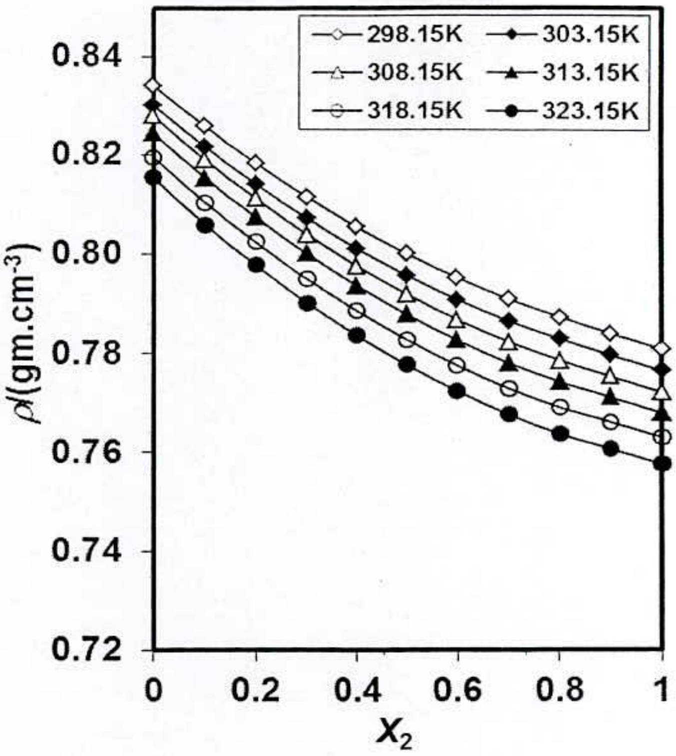

Figure 4.7: Plots of density (ρ) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

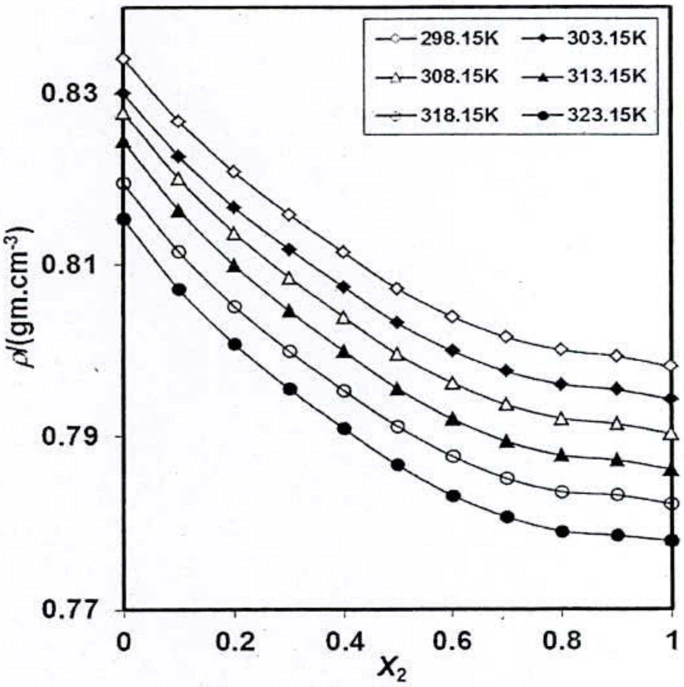

Figure 4.8: Plots of density (ρ) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

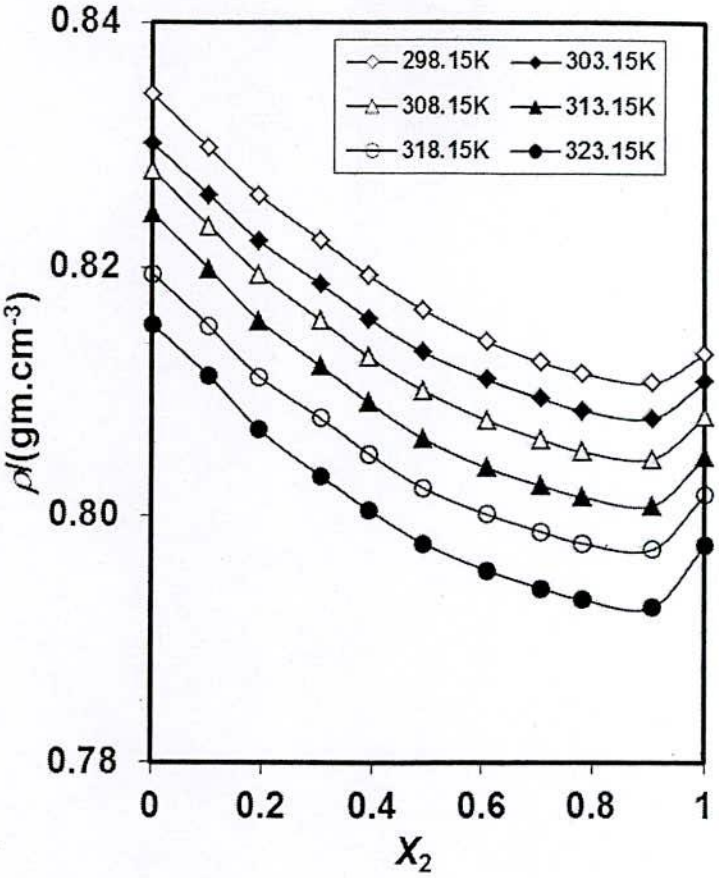

Figure 4.9: Plots of density (ρ) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

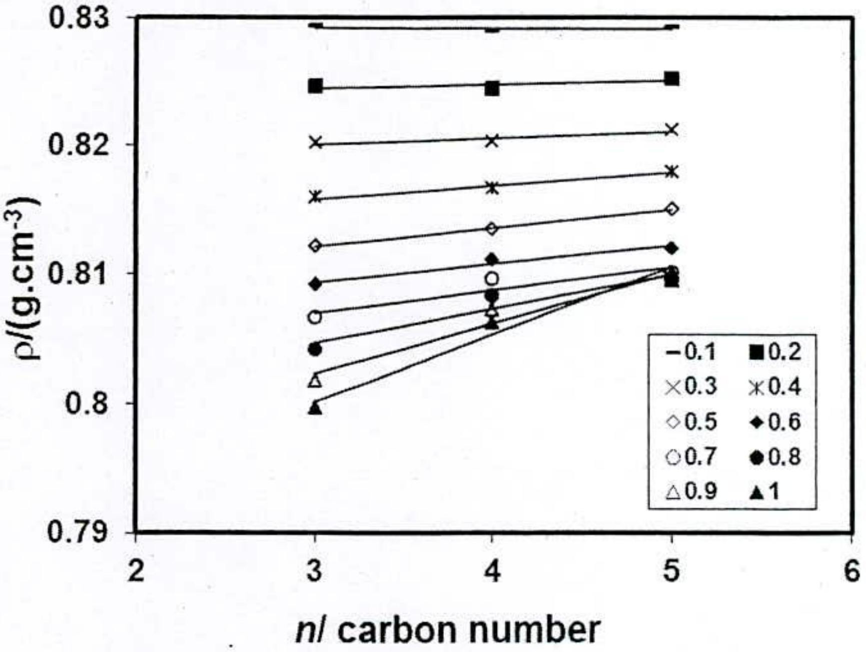

Figure 4.10: Dependence of the density (ρ) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

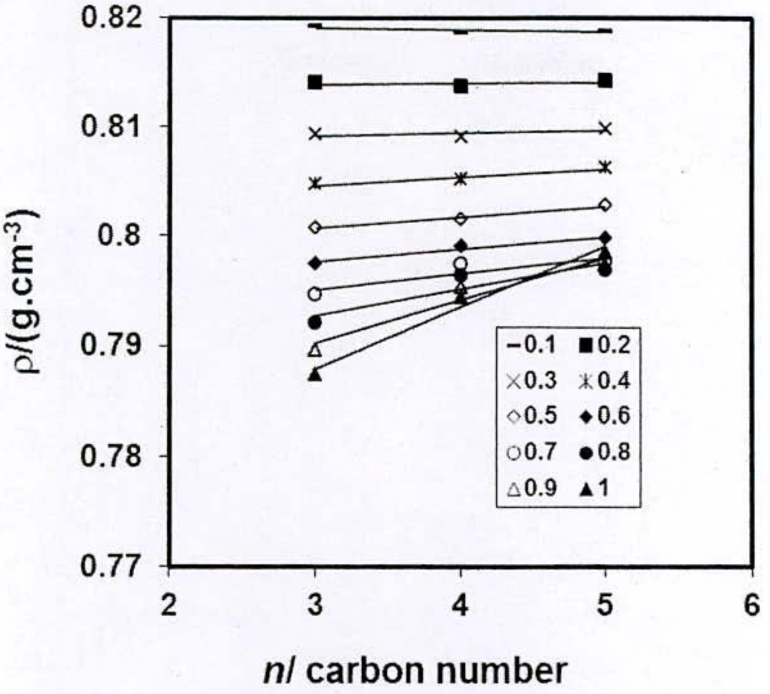

Figure 4.11: Dependence of the density (ρ) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

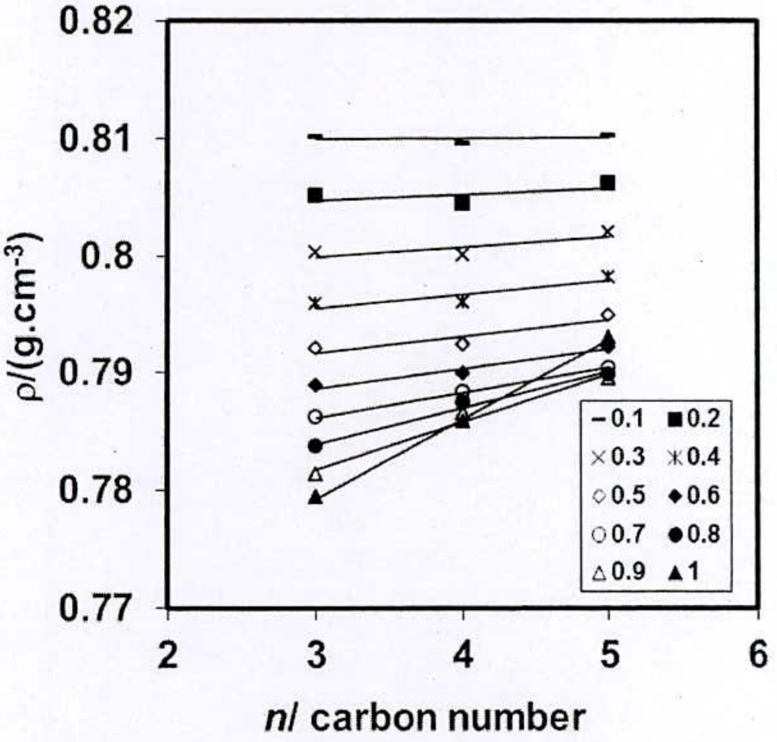

Figure 4.12: Dependence of the density (ρ) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

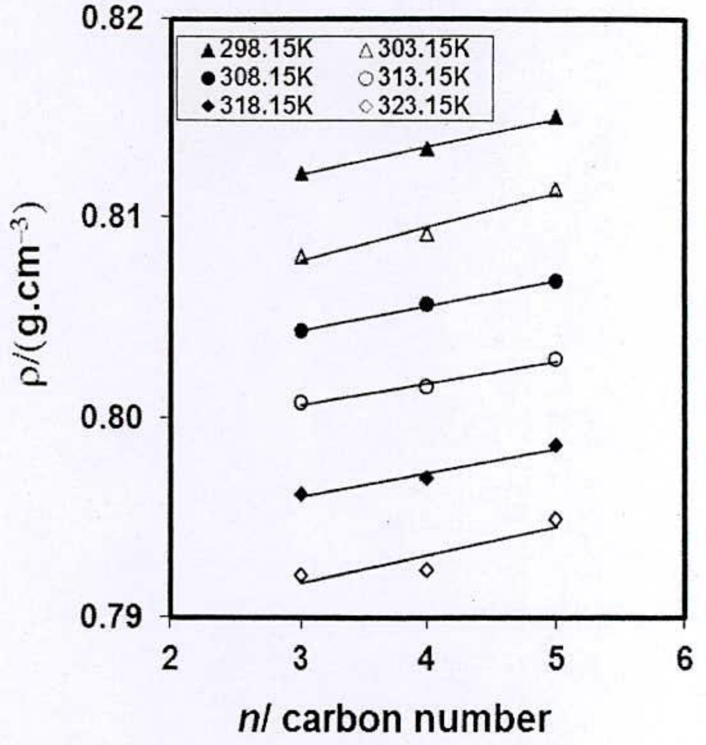

Figure 4.13: Dependence of the density (ρ) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

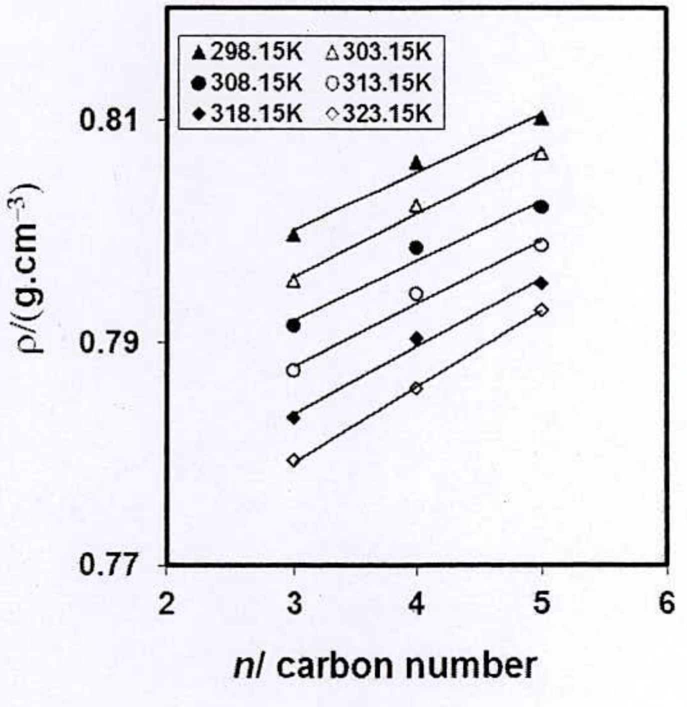

Figure 4.14: Dependence of the density (ρ) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 1.0 mole fraction.

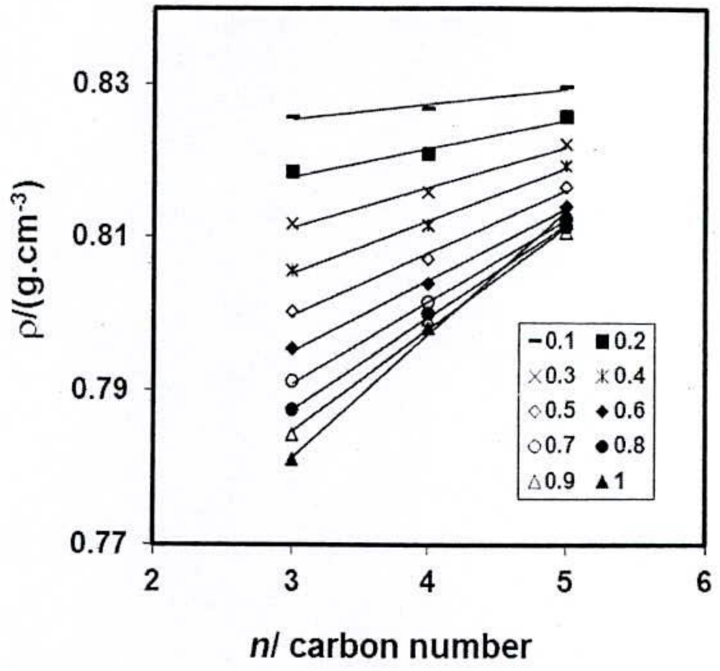

Figure 4.15: Dependence of the density (ρ) with carbon number (n) of iso-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

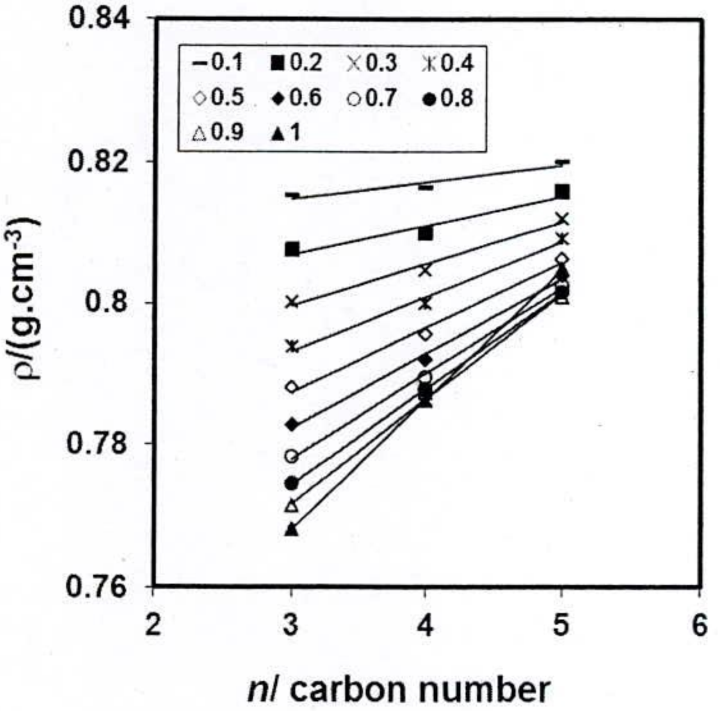

Figure 4.16: Dependence of the density (ρ) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

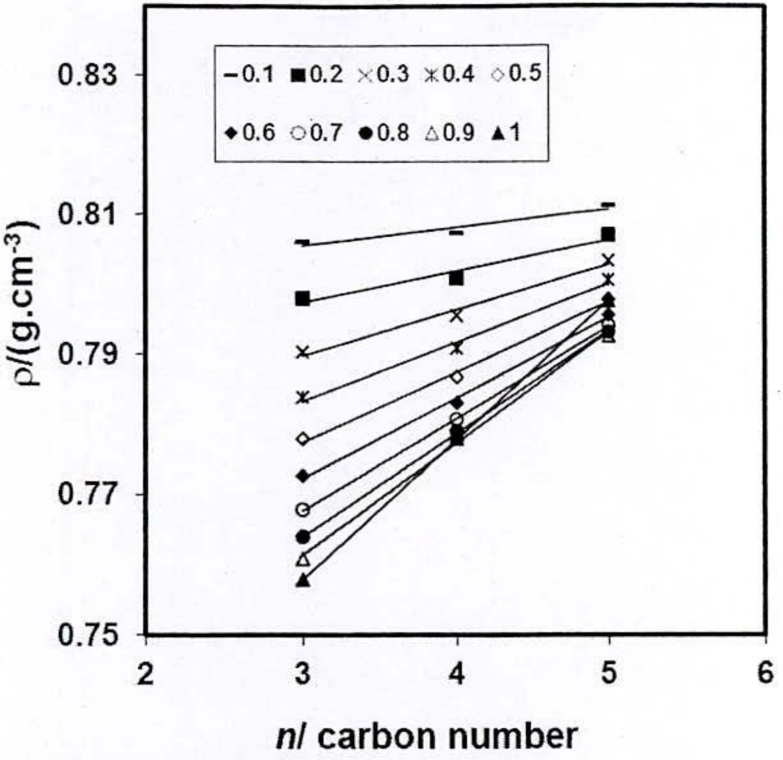

Figure 4.17: Dependence of the density (ρ) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

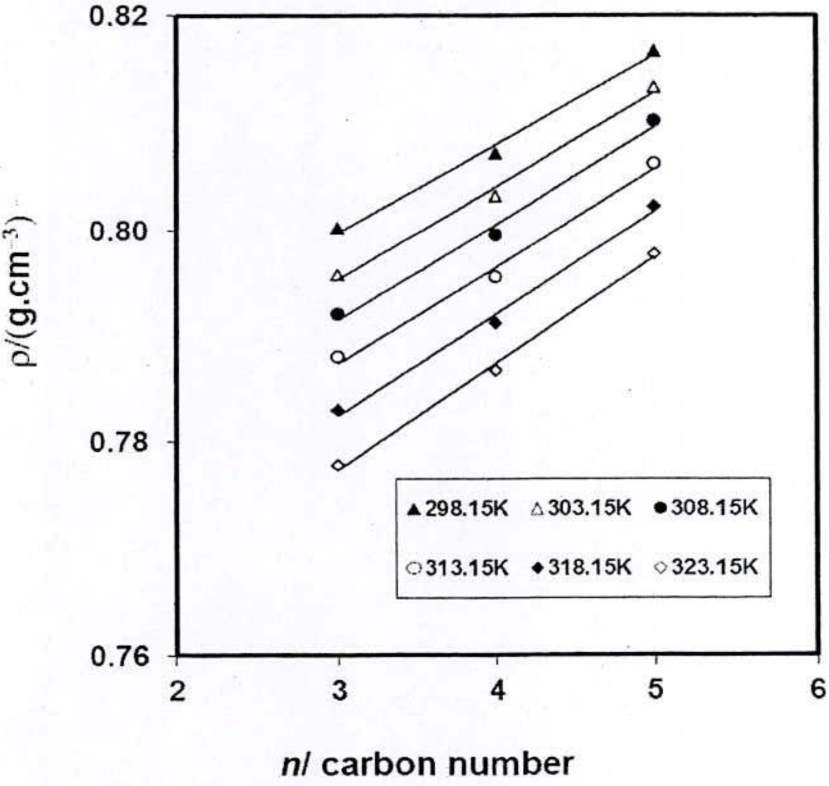

Figure 4.18: Dependence of the density (ρ) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

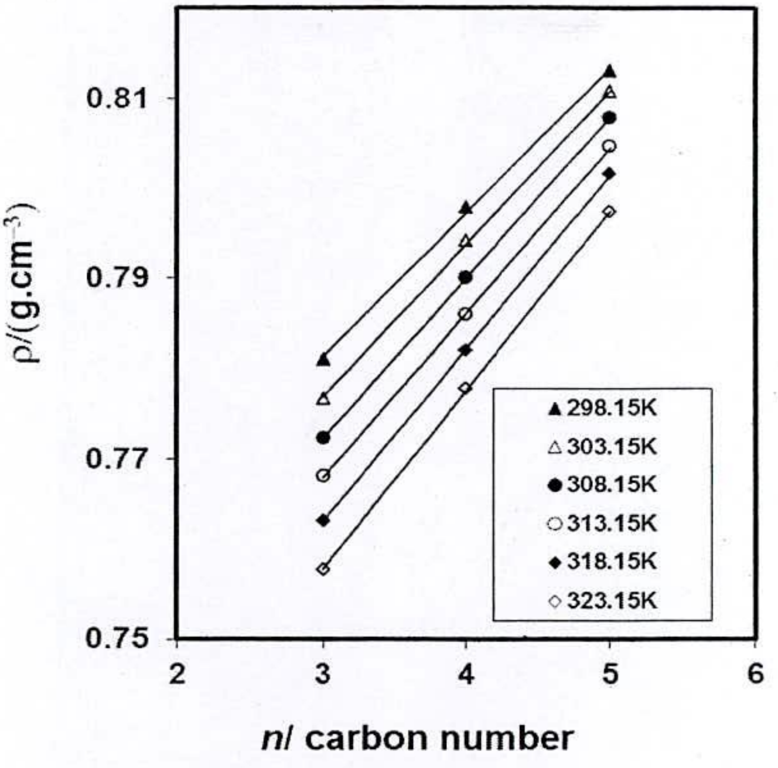

Figure 4.19: Dependence of the density (ρ) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different temperature at 1.0 mole fraction.

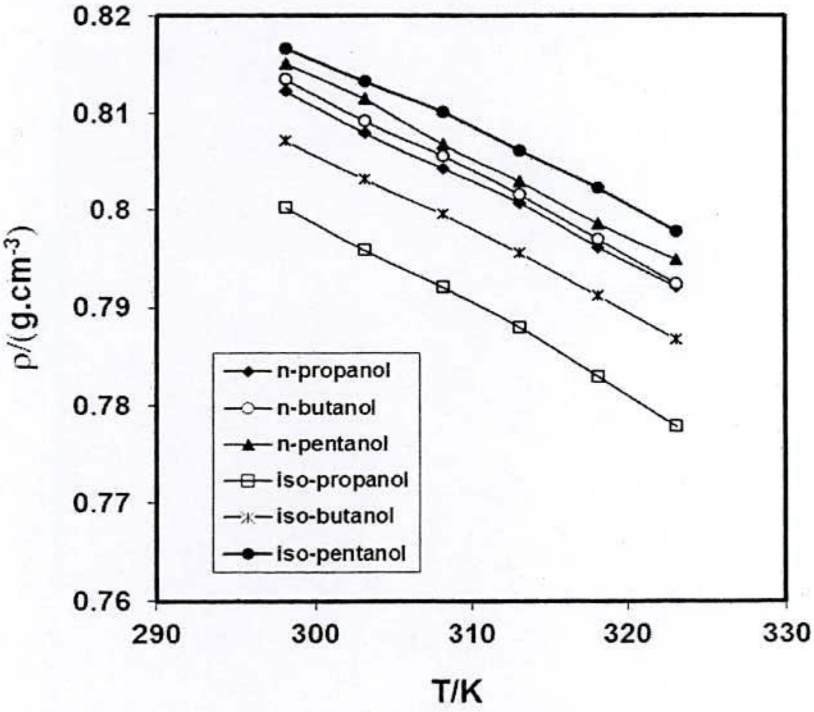

Figure 4.20: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

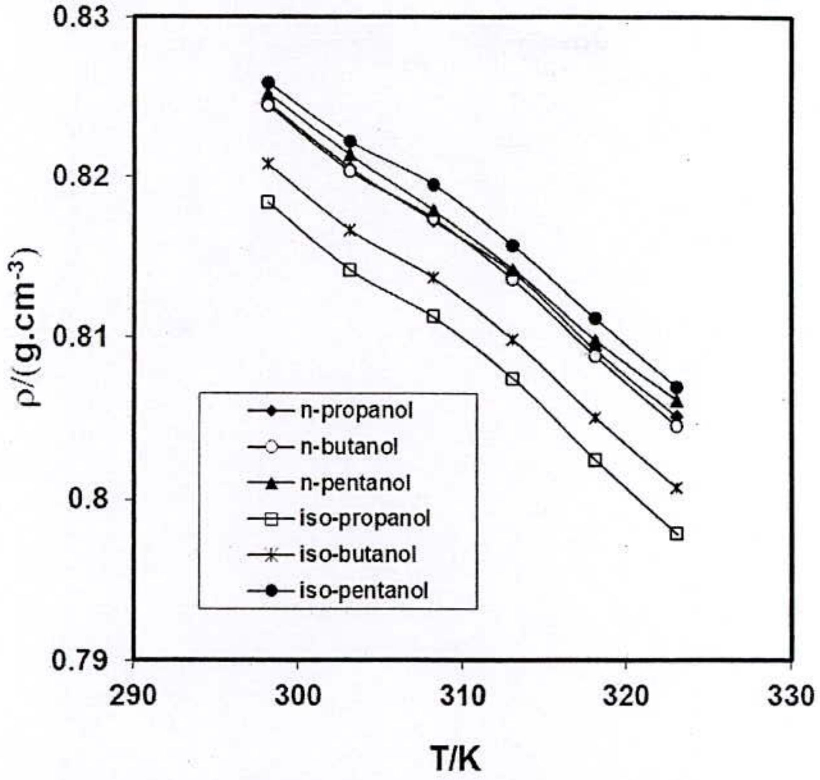

Figure 4.21: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

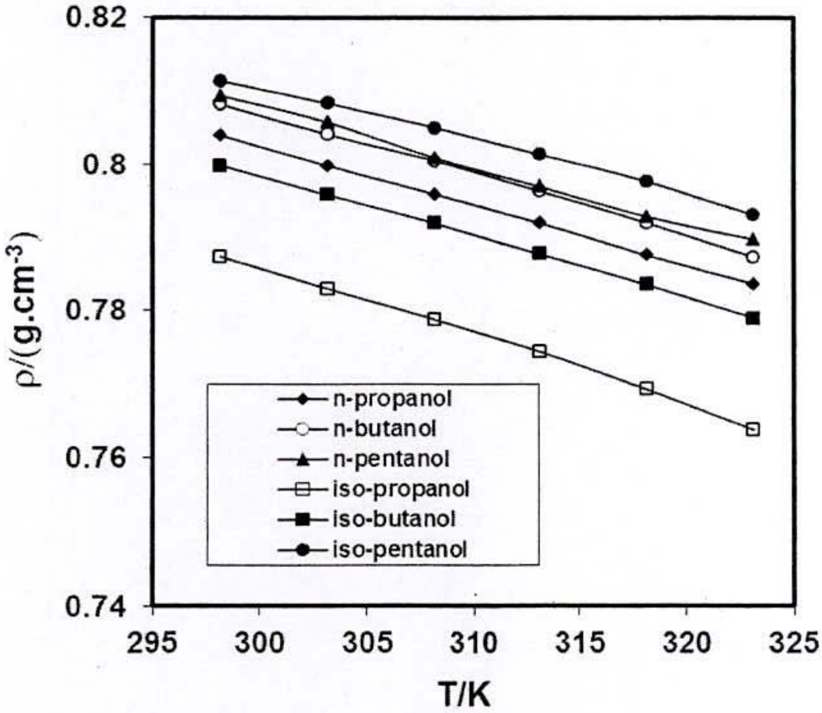

Figure 4.22: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

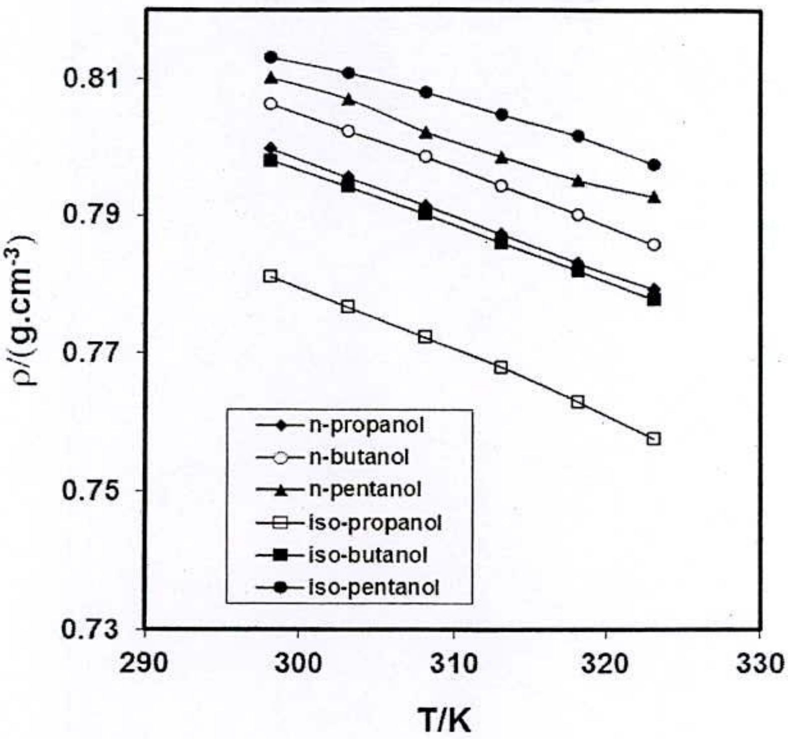

Figure 4.23: Comparison of density (ρ) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

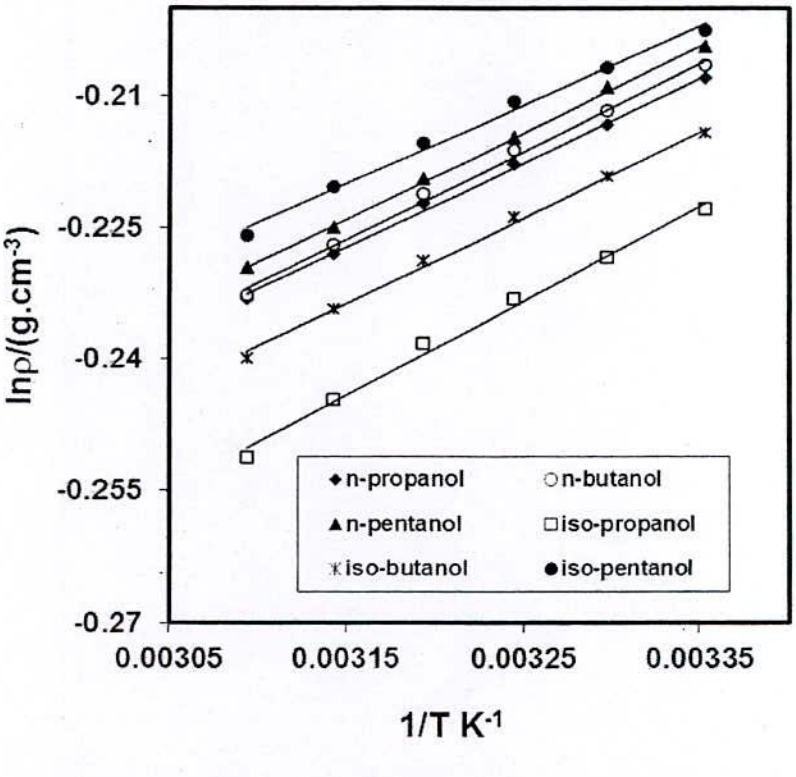

Figure 4.24: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

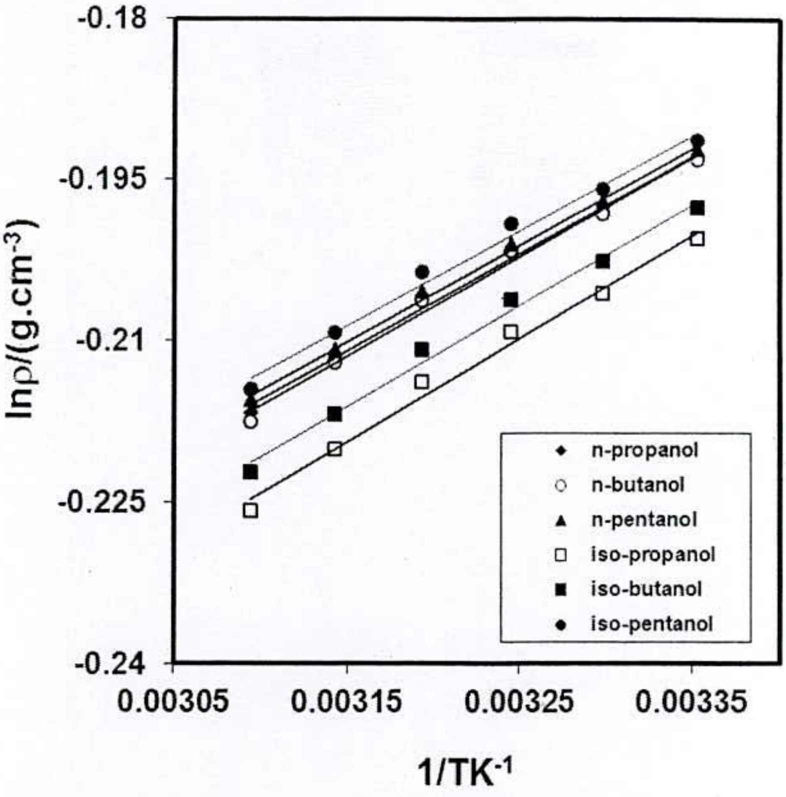

Figure 4.25: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

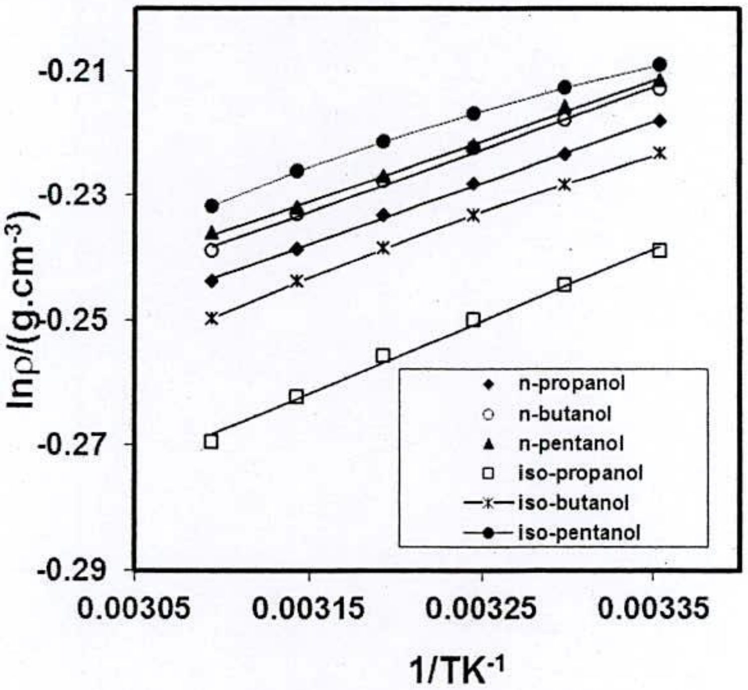

Figure 4.26: Comparison of lnρ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

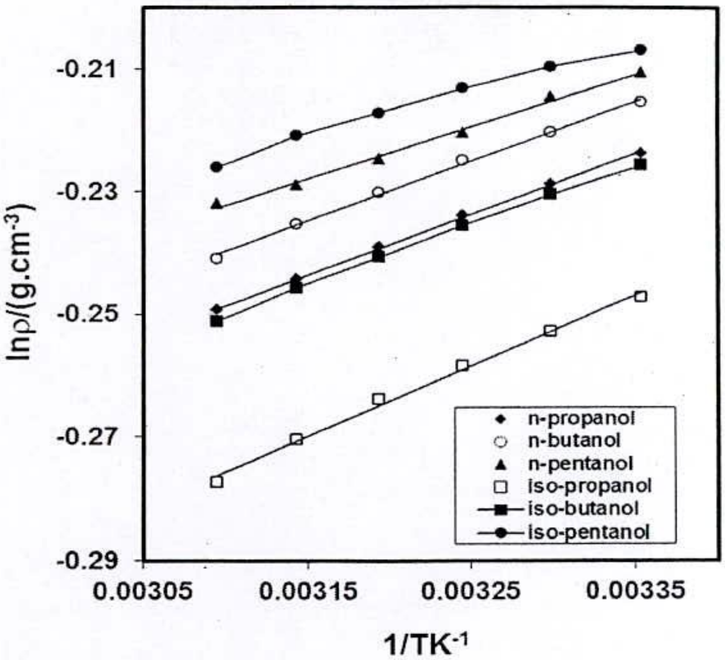

Figure 4.27: Comparison of $\ln\rho$ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

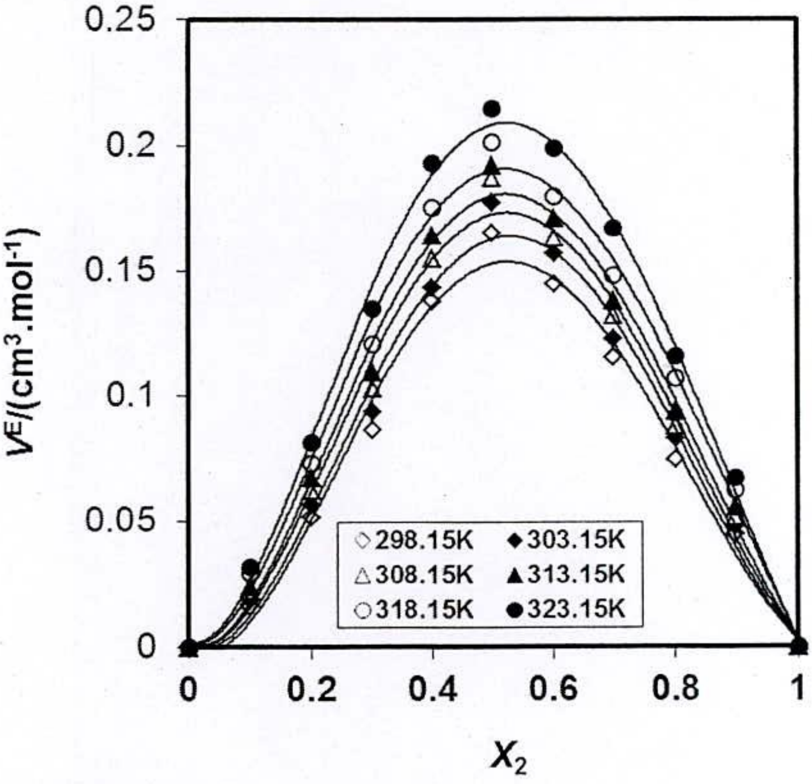

Figure 4.28: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

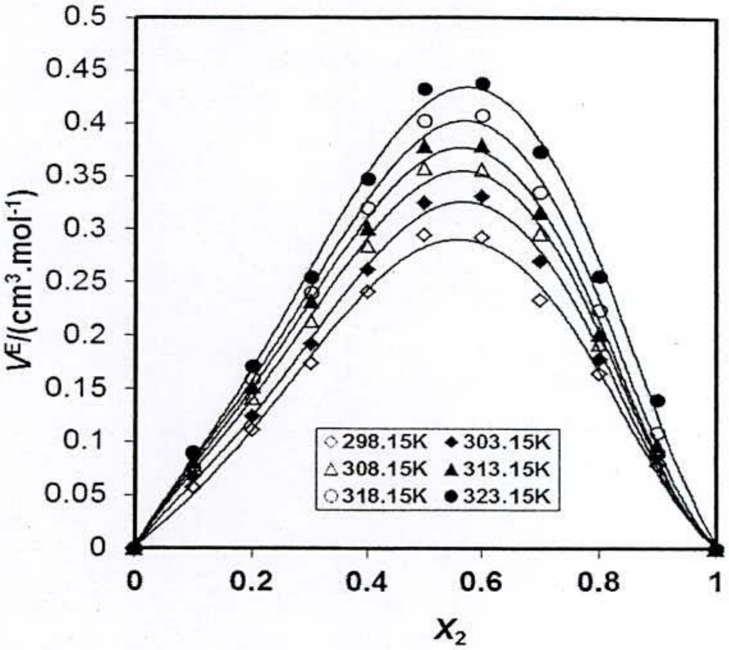

Figure 4.29: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

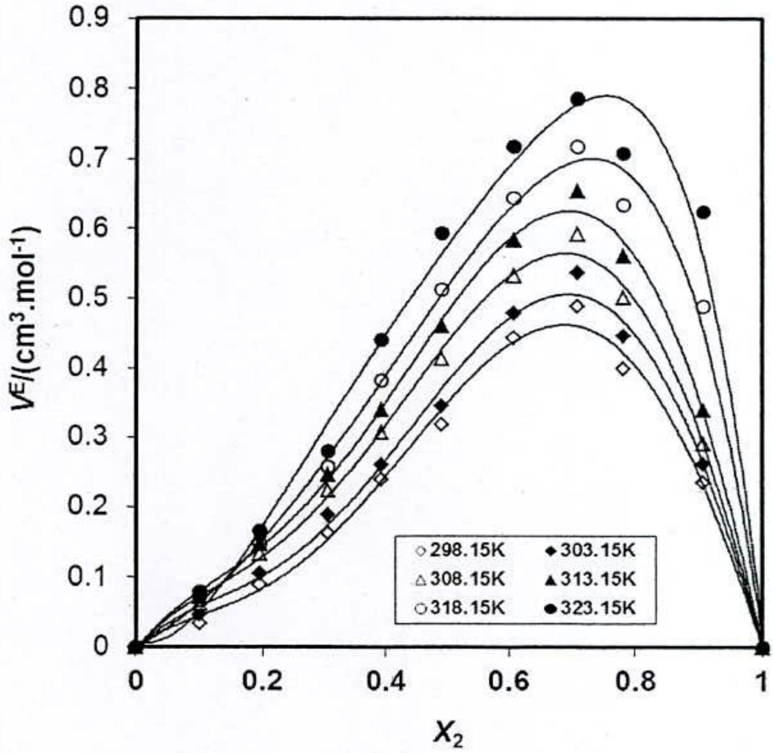

Figure 4.30: Plots of excess molar volume (V^E) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

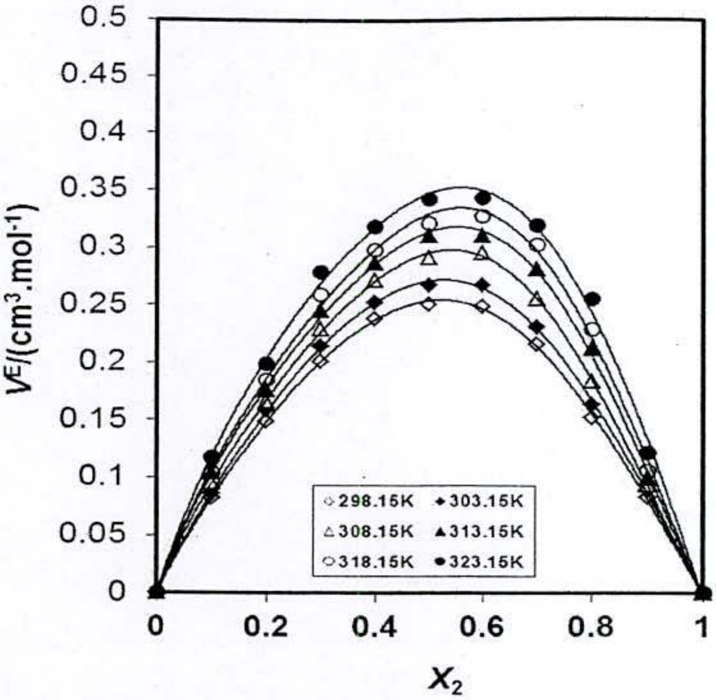

Figure 4.31: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

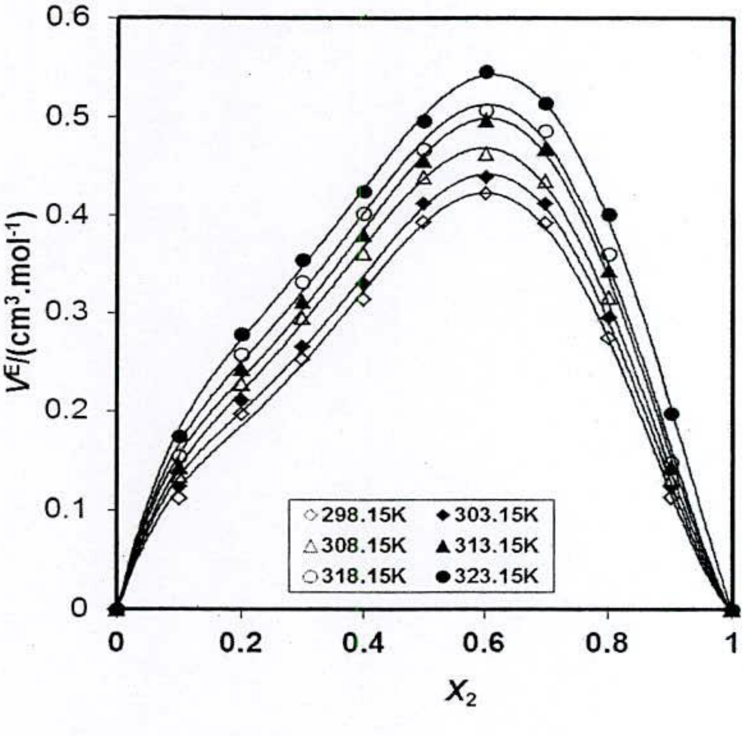

Figure 4.32: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

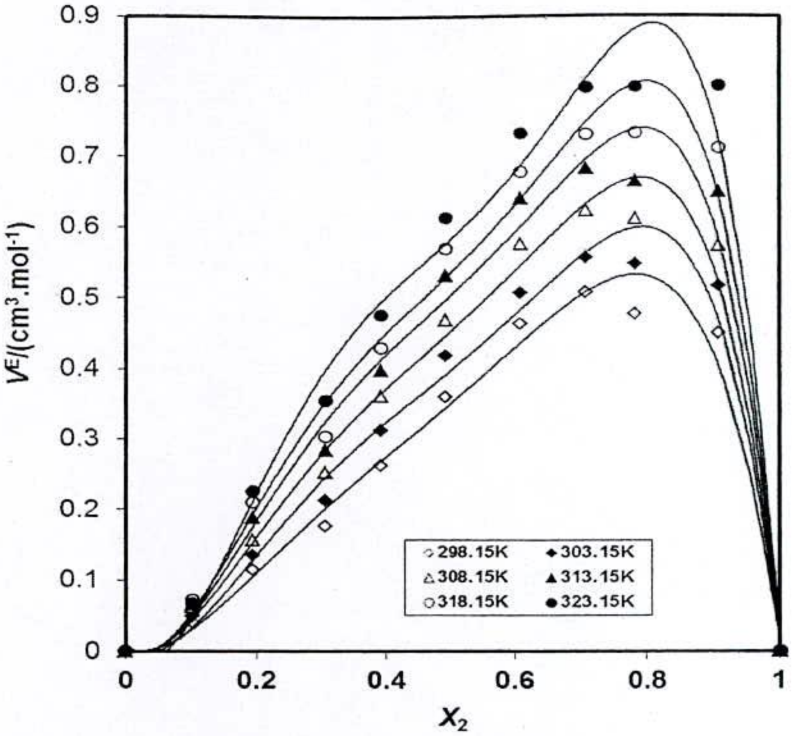

Figure 4.33: Plots of excess molar volume (V^E) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

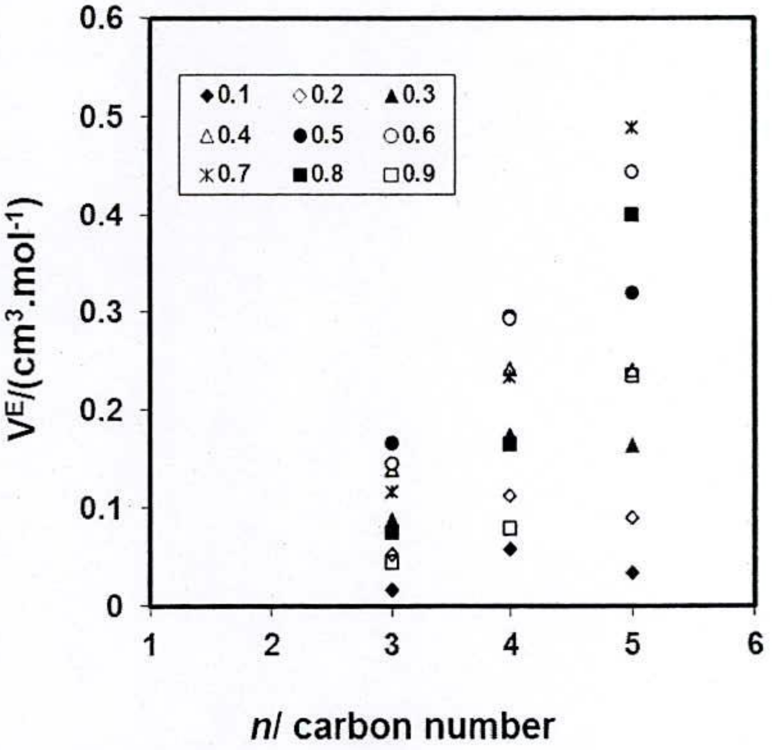

Figure 4.34: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

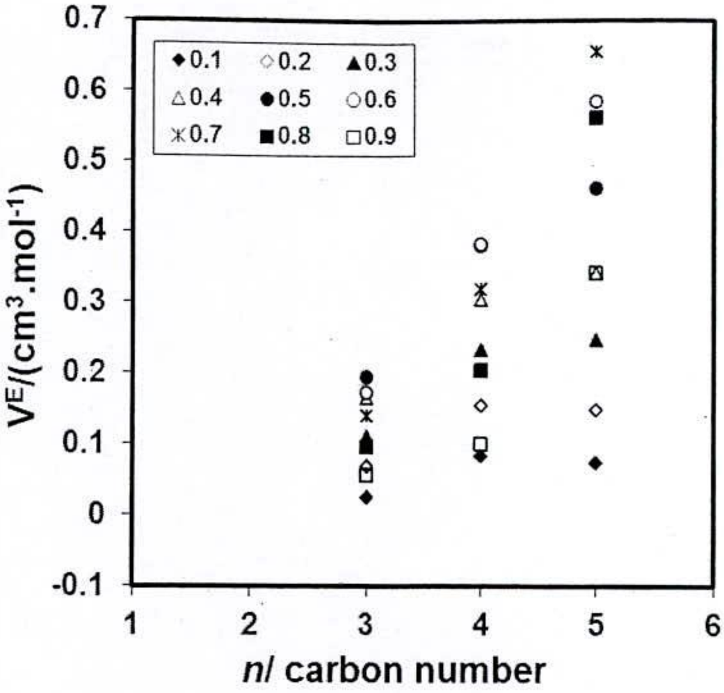

Figure 4.35: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

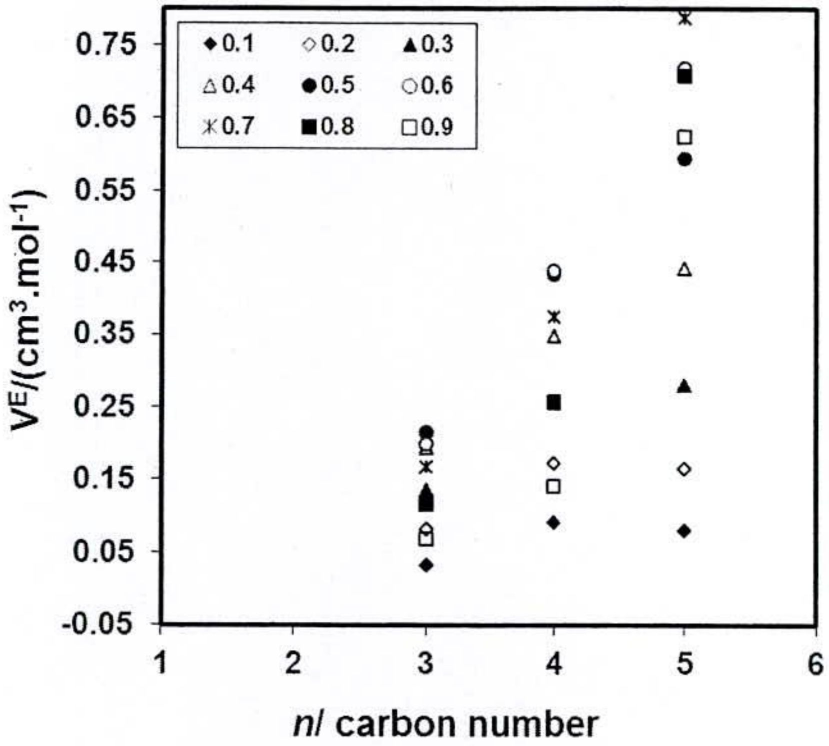

Figure 4.36: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

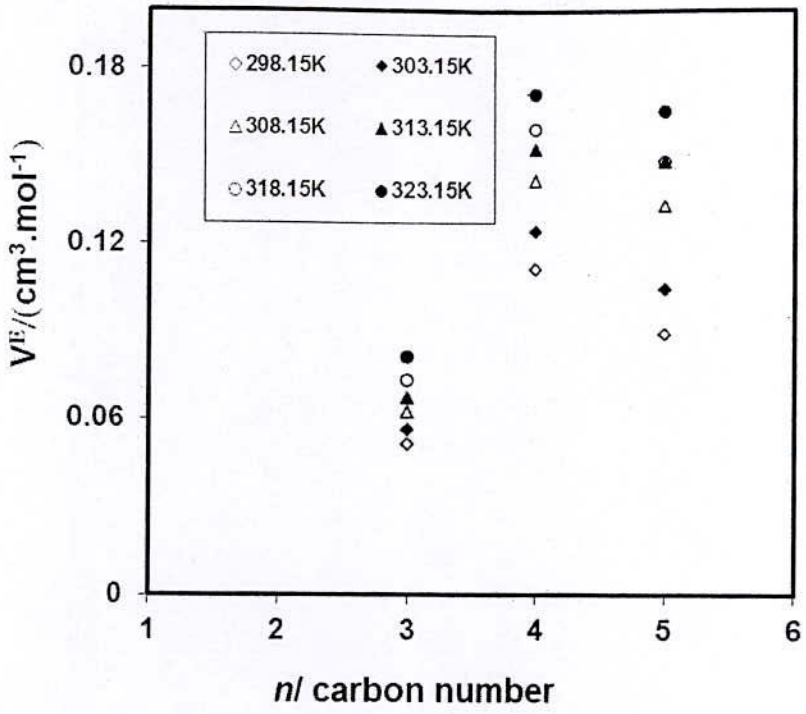

Figure 4.37: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.2 mole fraction.

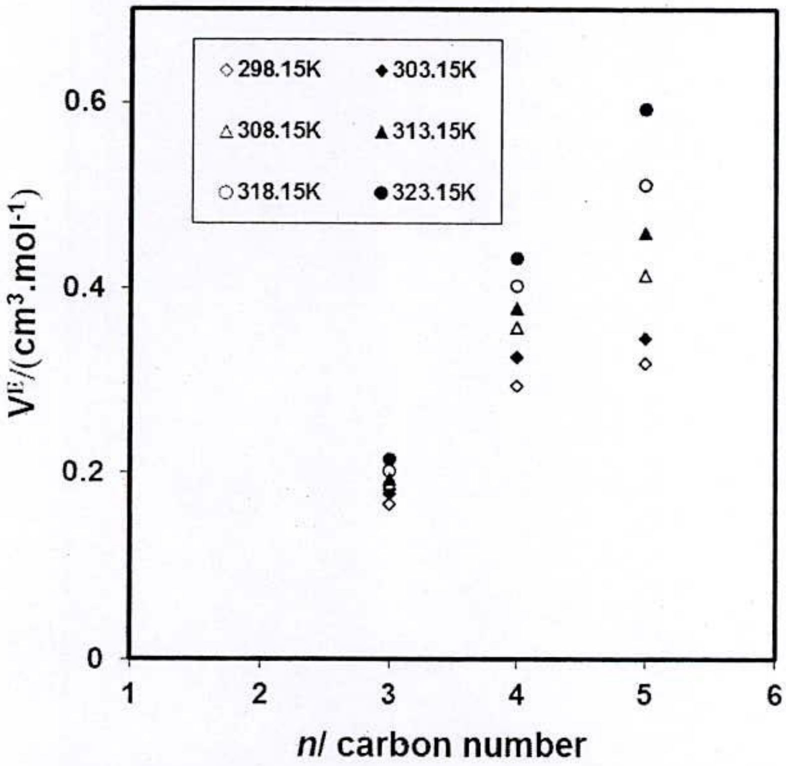

Figure 4.38: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

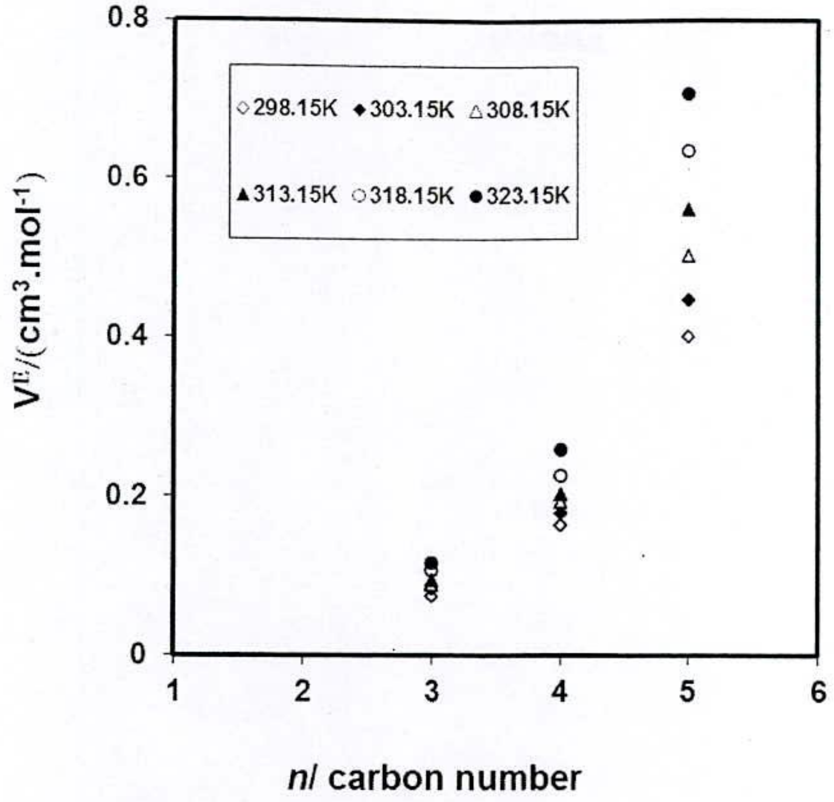

Figure 4.39: Dependence of the excess molar volume (V^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.8 mole fraction.

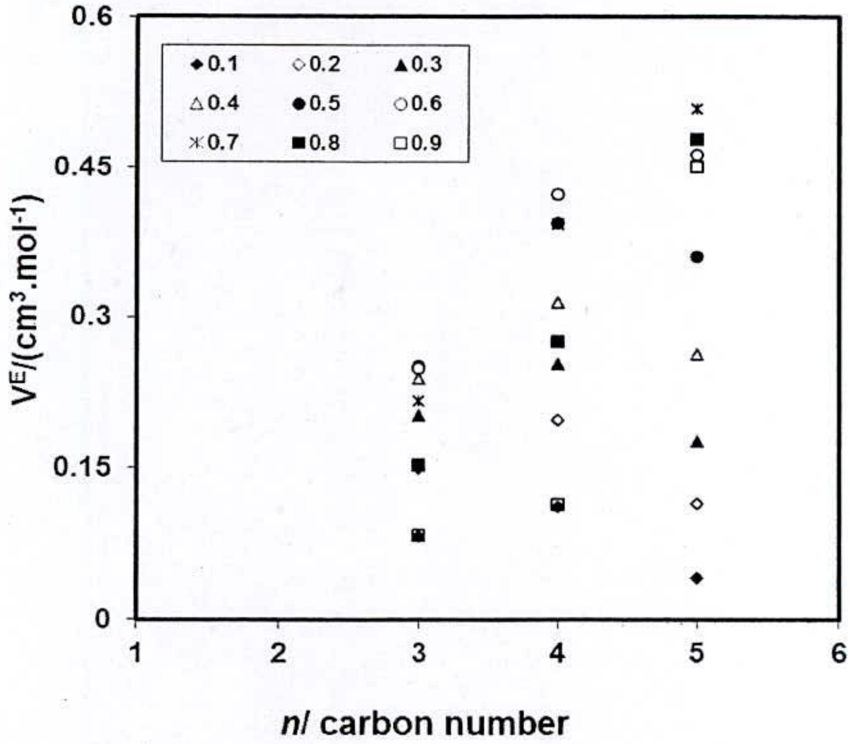

Figure 4.40: Dependence of the excess molar volume (V^E) with carbon number (n) of iso-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

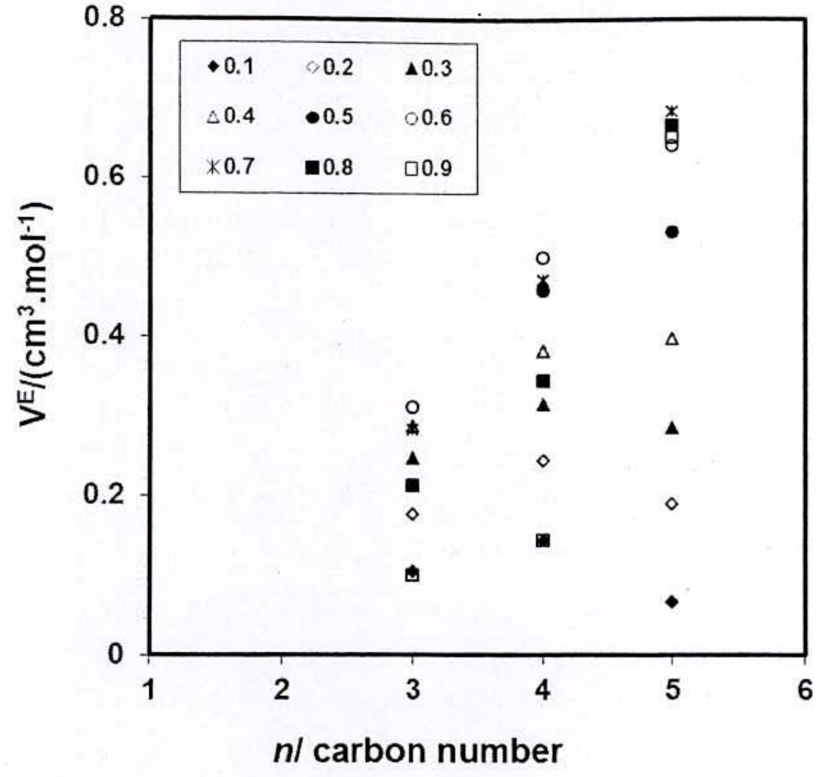

Figure 4.41: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

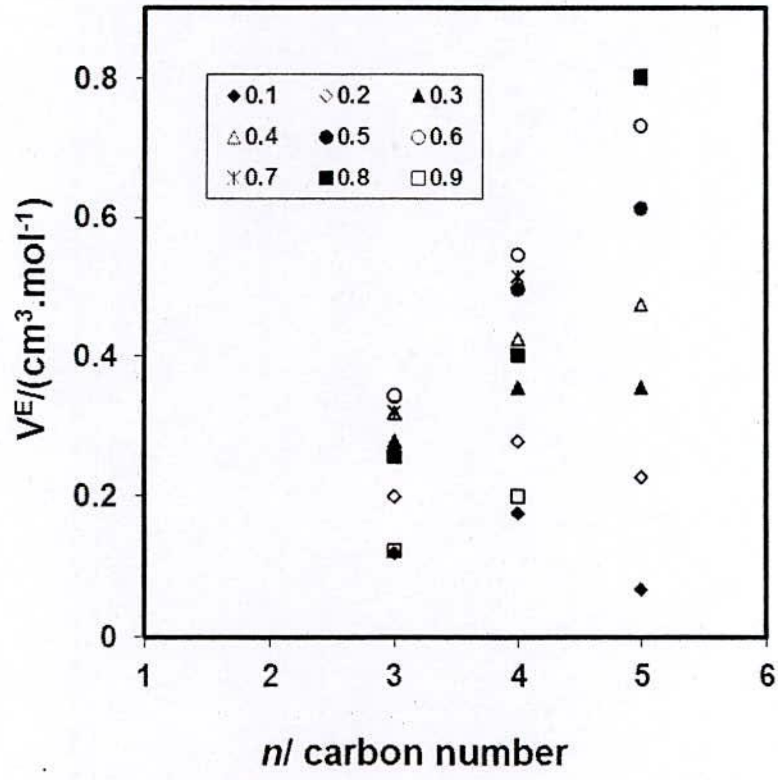

Figure 4.42: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

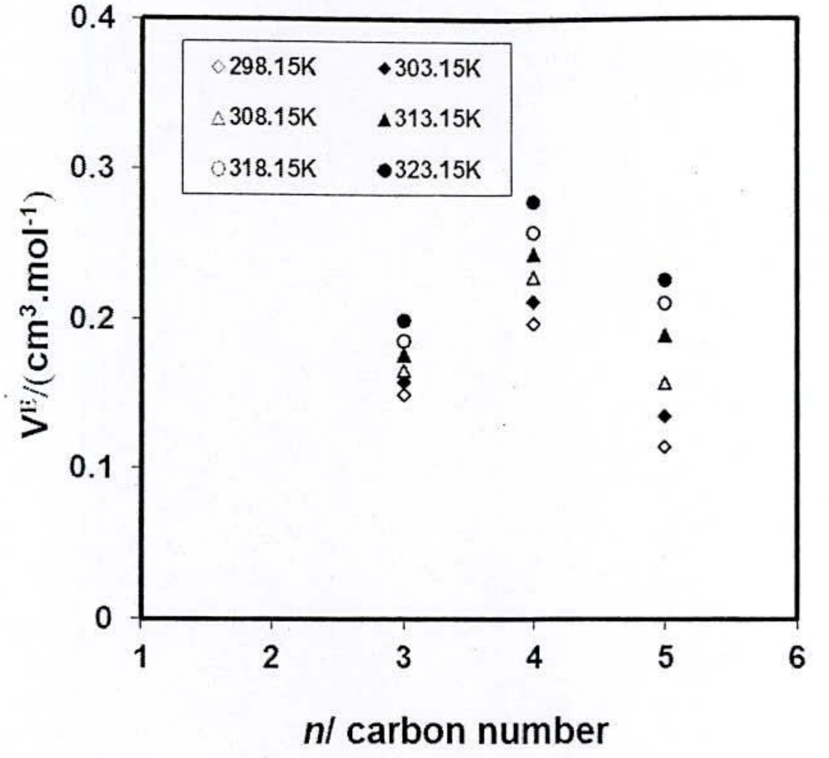

Figure 4.43: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different temperature at 0.2 mole fraction.

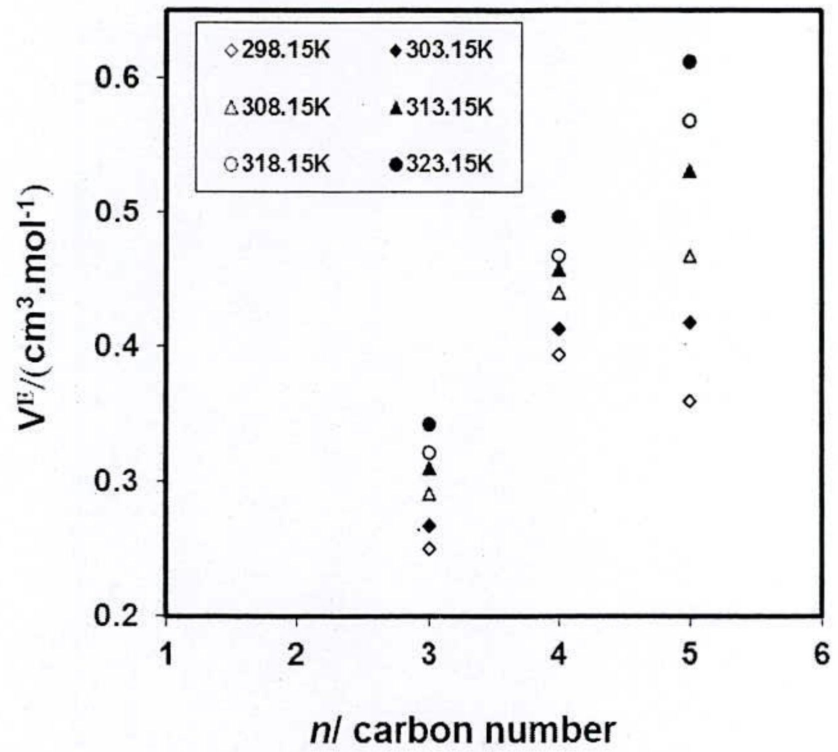

Figure 4.44: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

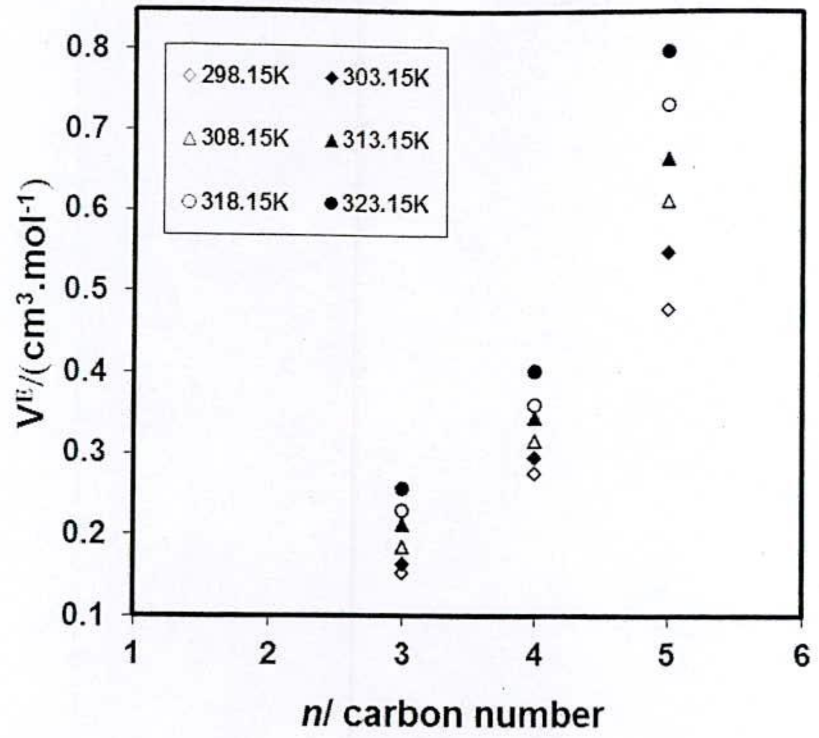

Figure 4.45: Dependence of the excess molar volume (V^E) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different temperature at 0.8 mole fraction.

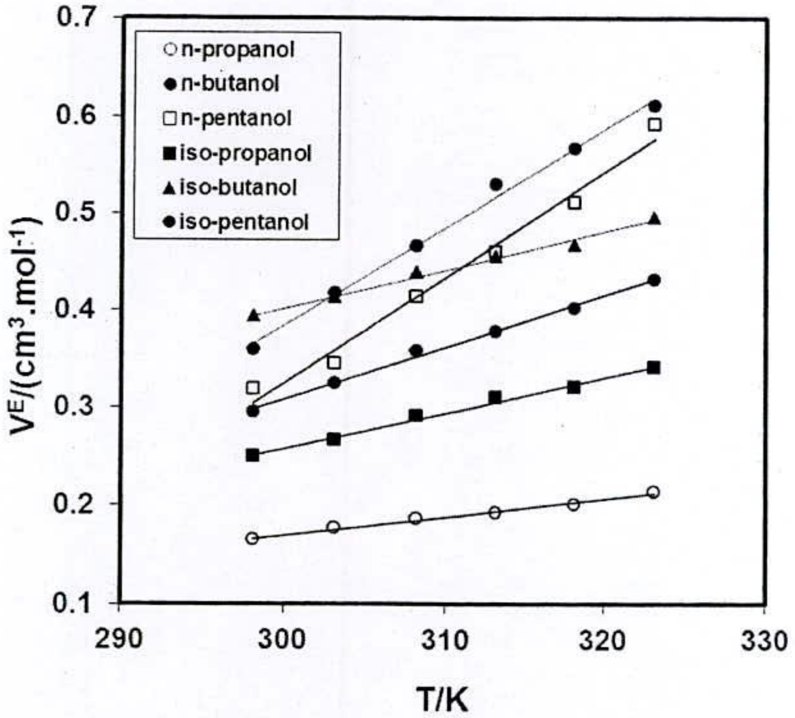

Figure 4.46: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

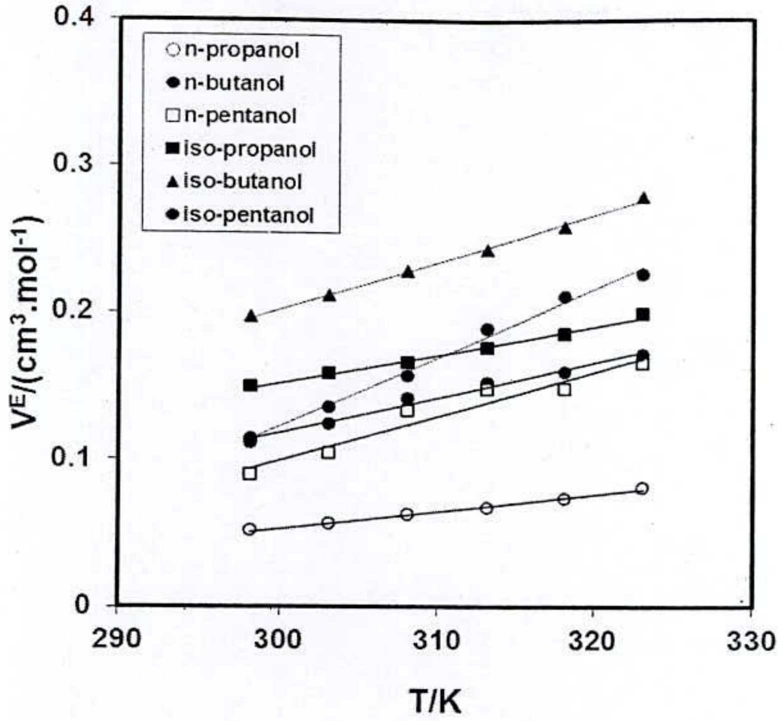

Figure 4.47: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

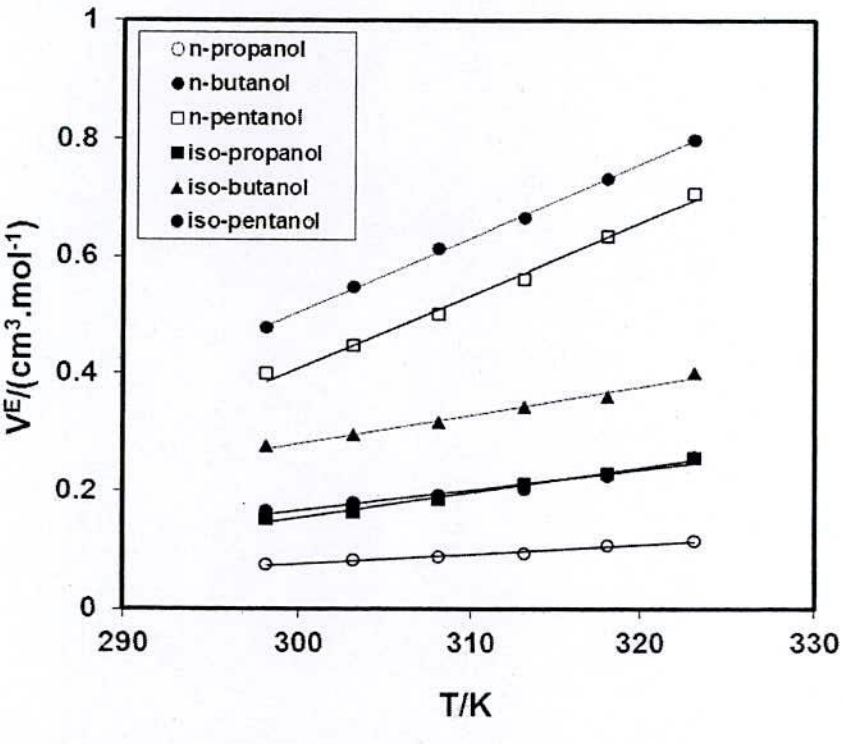

Figure 4.48: Comparison of excess molar volume (V^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

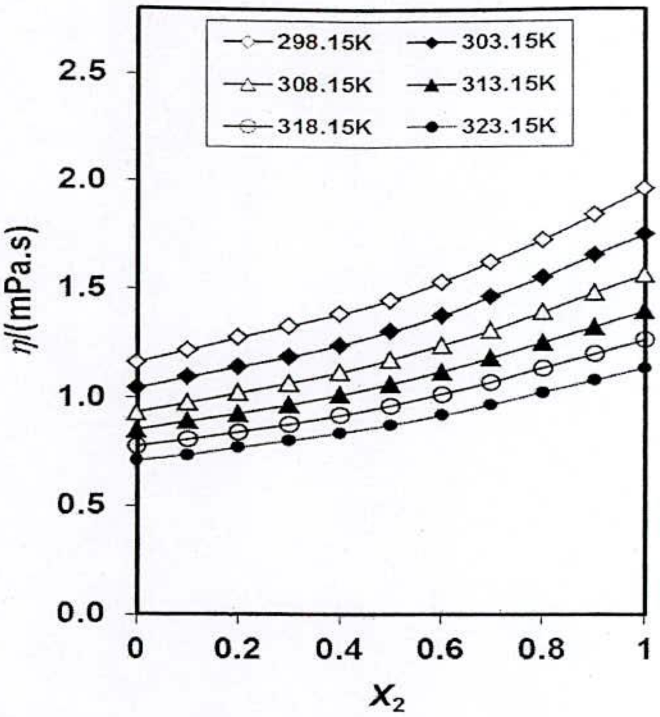

Figure 4.49: Plots of viscosity (η) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

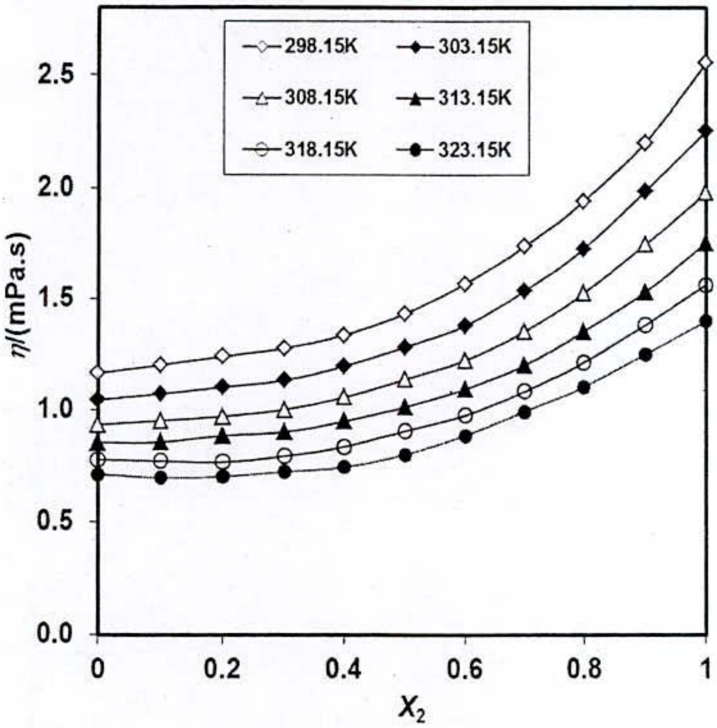

Figure 4.50: Plots of viscosity (η) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

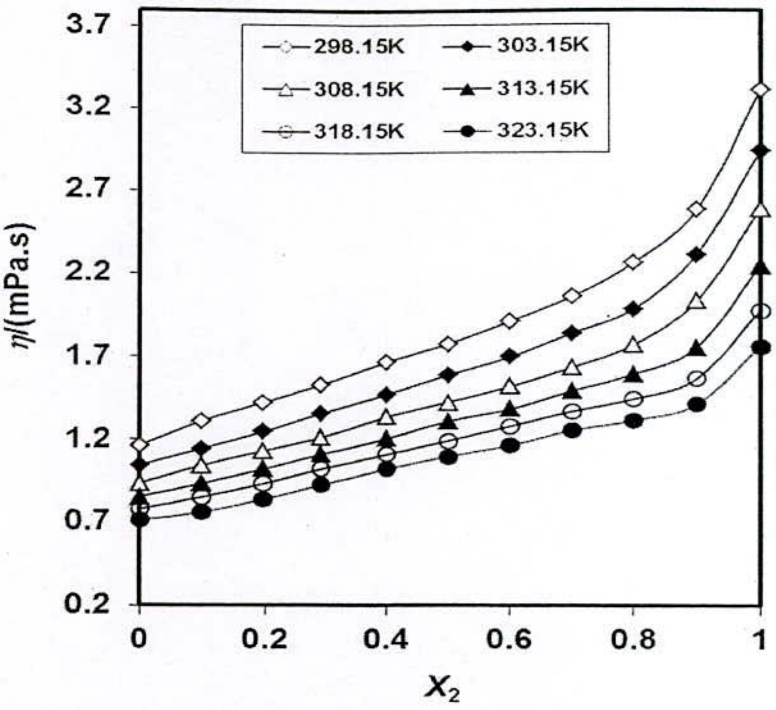

Figure 4.51: Plots of viscosity (η) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

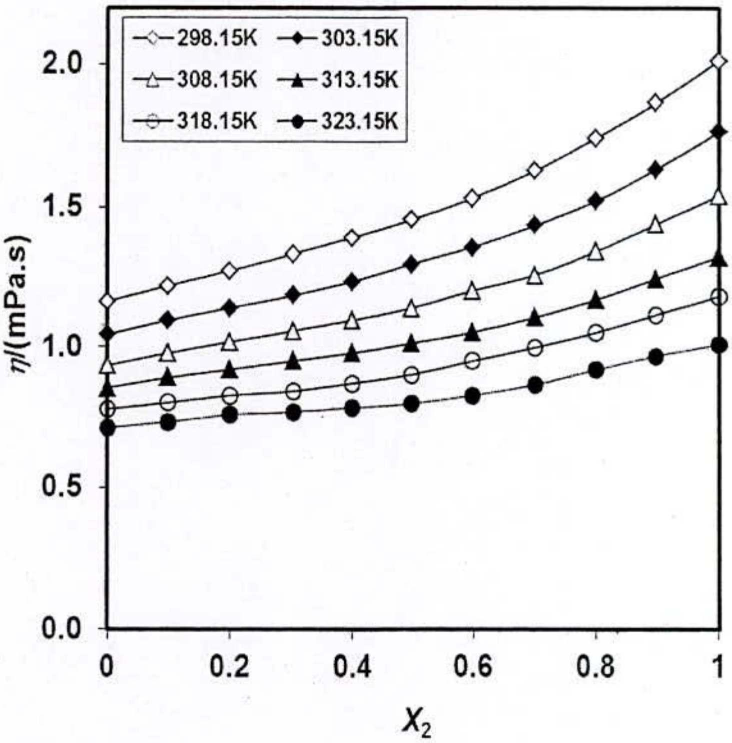

Figure 4.52: Plots of viscosity (η) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

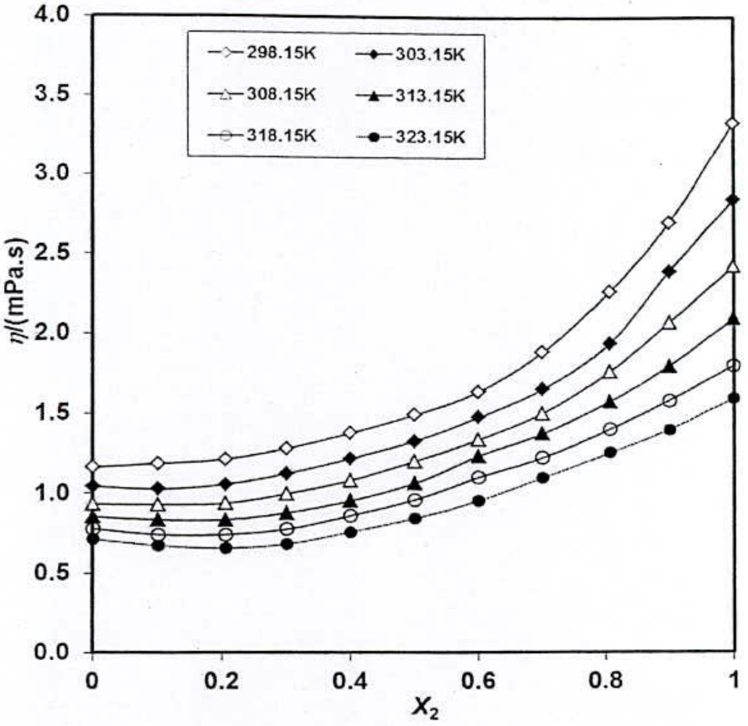

Figure 4.53: Plots of viscosity (η) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

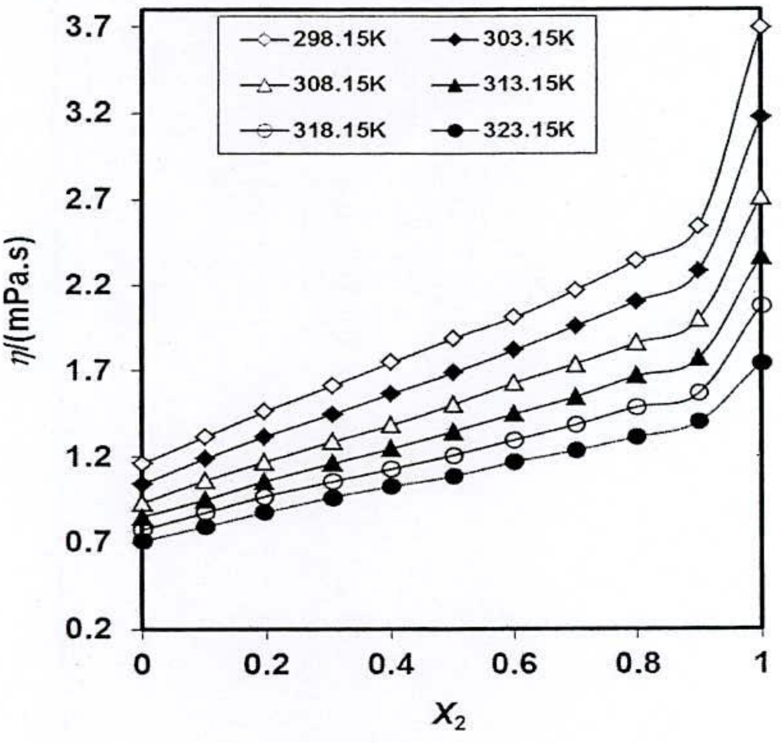

Figure 4.54: Plots of viscosity (η) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

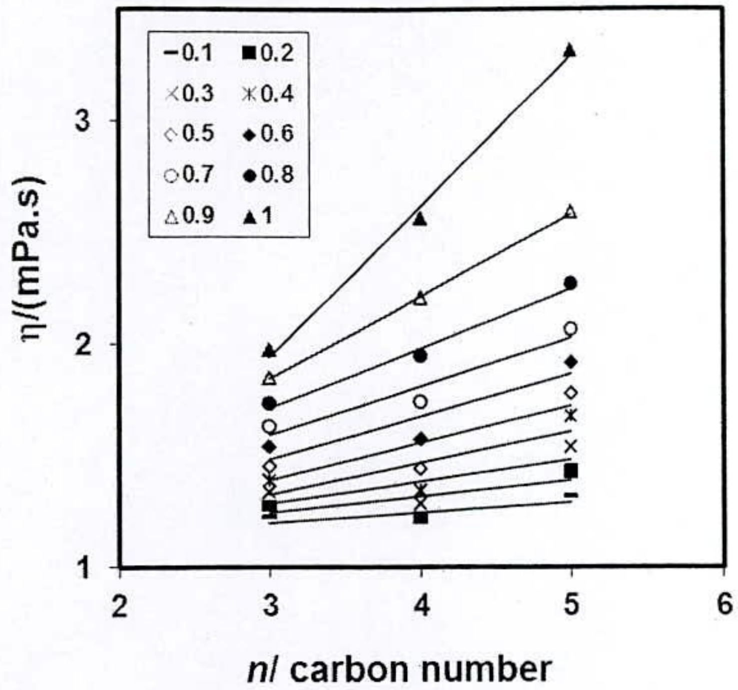

Figure 4.55: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

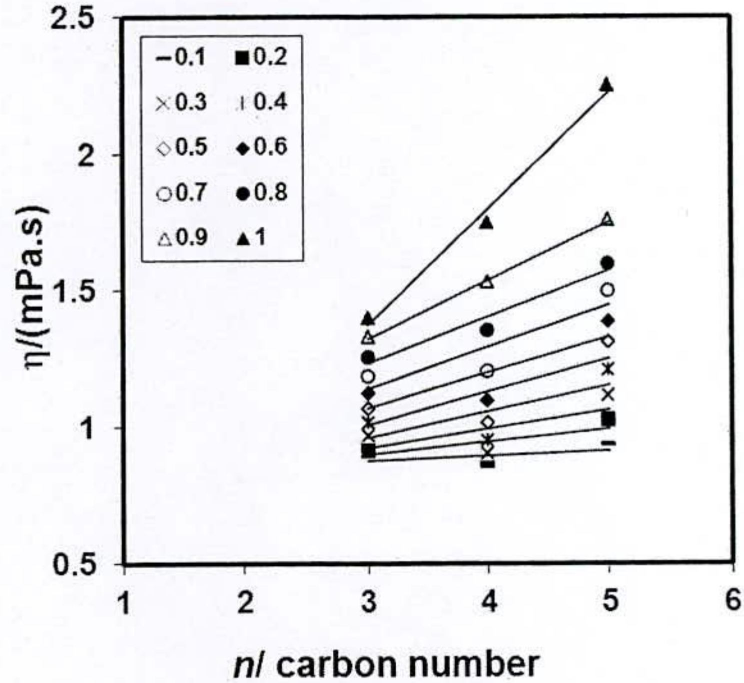

Figure 4.56: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

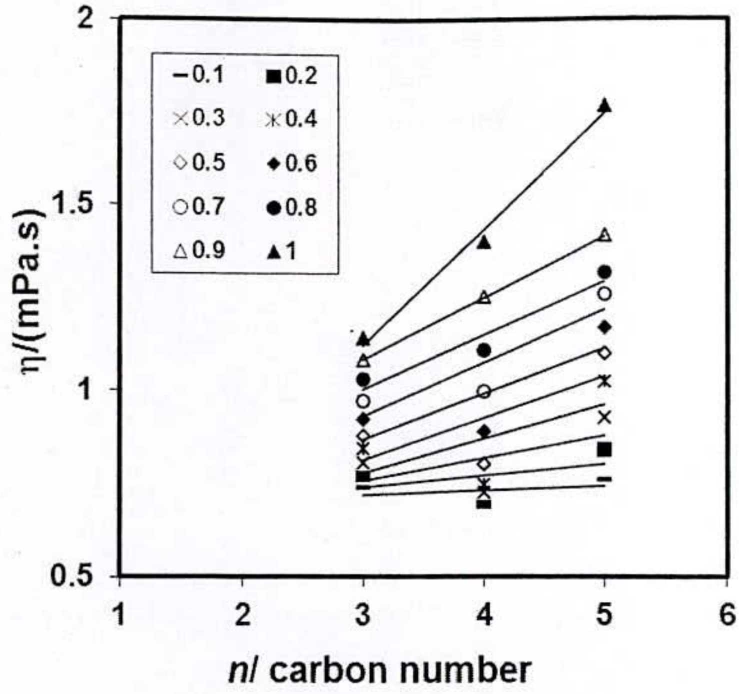

Figure 4.57: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

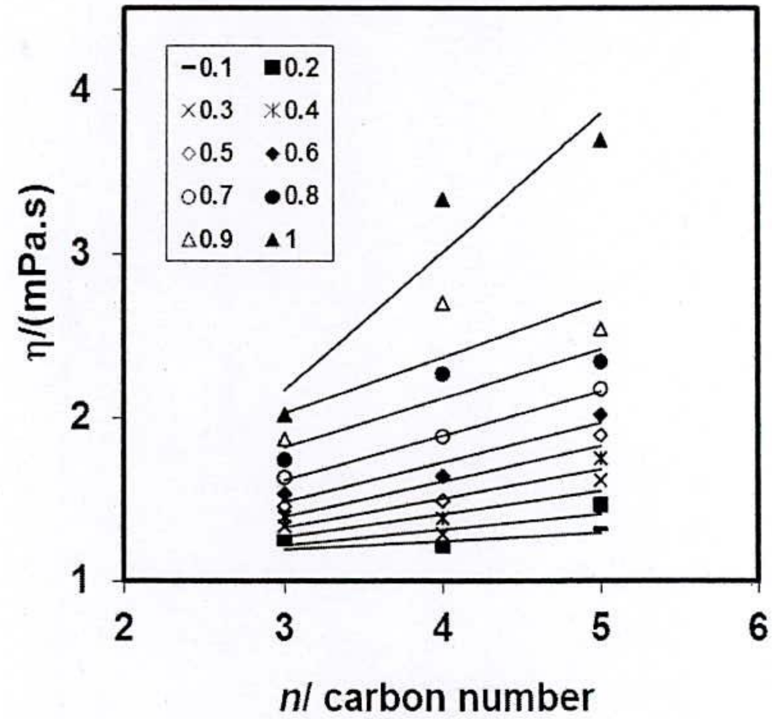

Figure 4.58: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

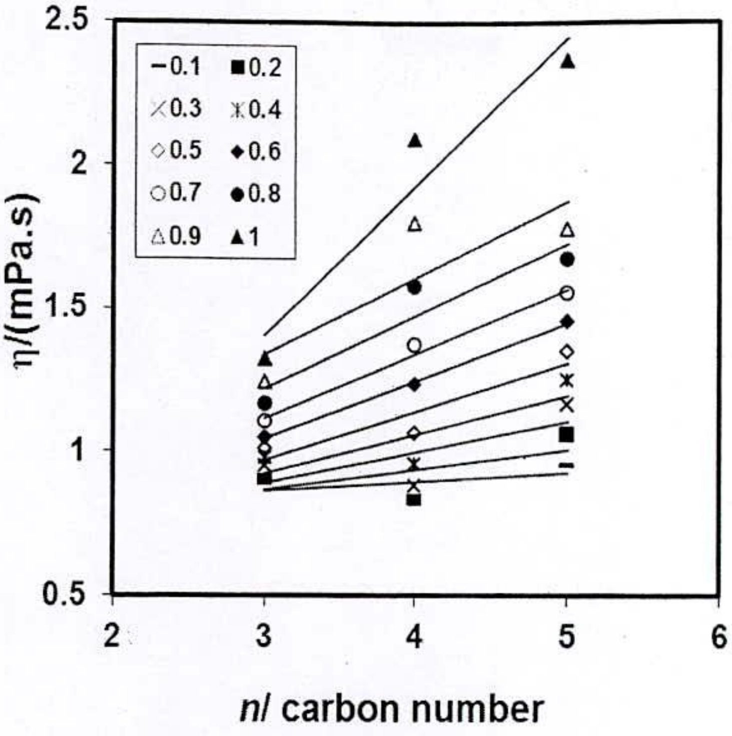

Figure 4.59: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

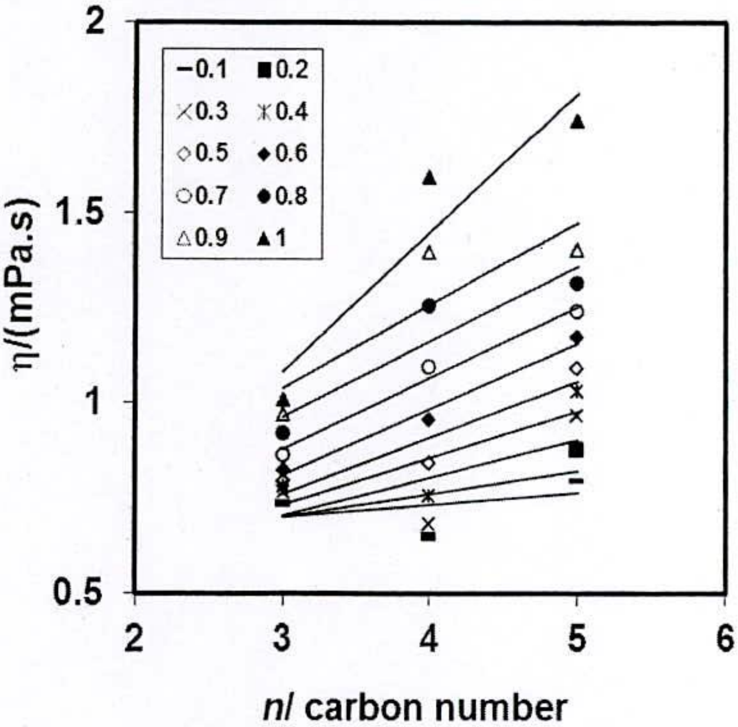

Figure 4.60: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

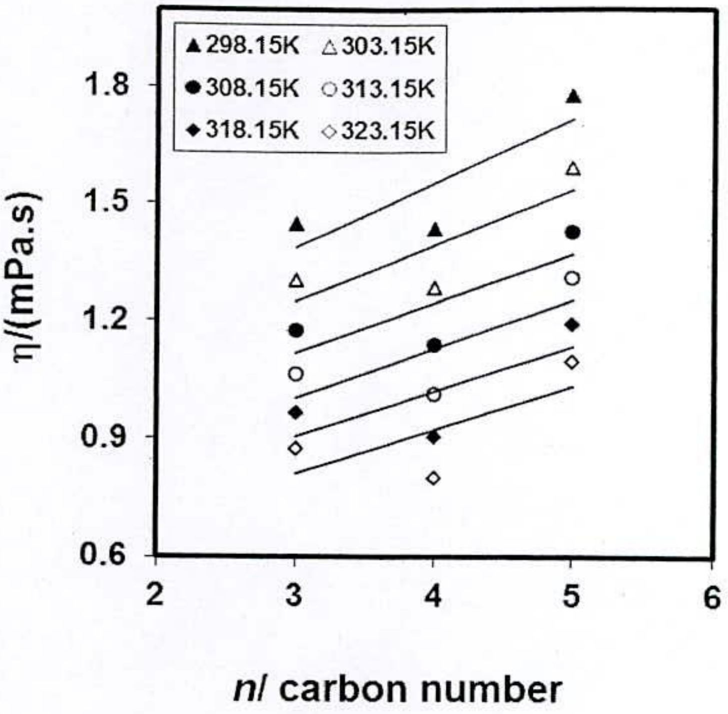

Figure 4.61: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

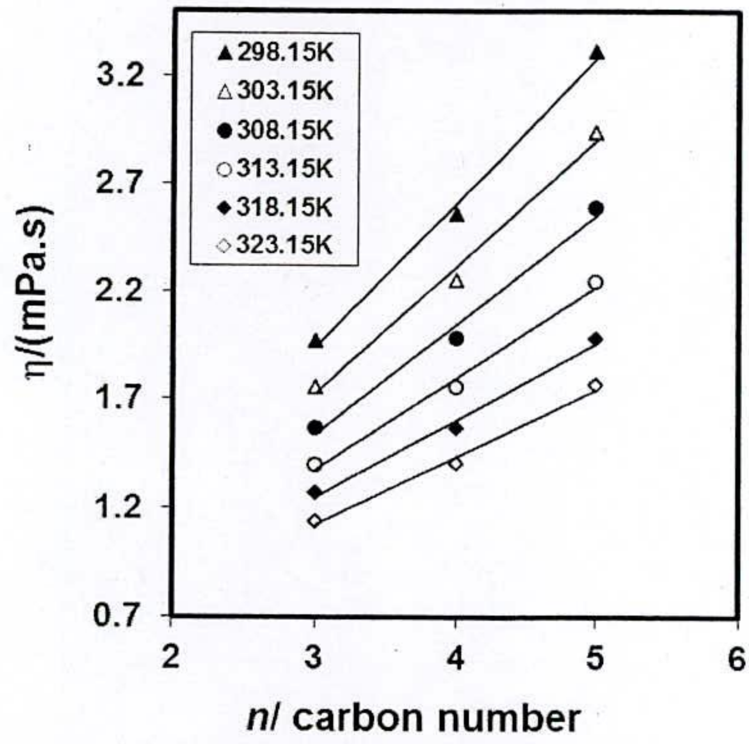

Figure 4.62: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 1.0 mole fraction.

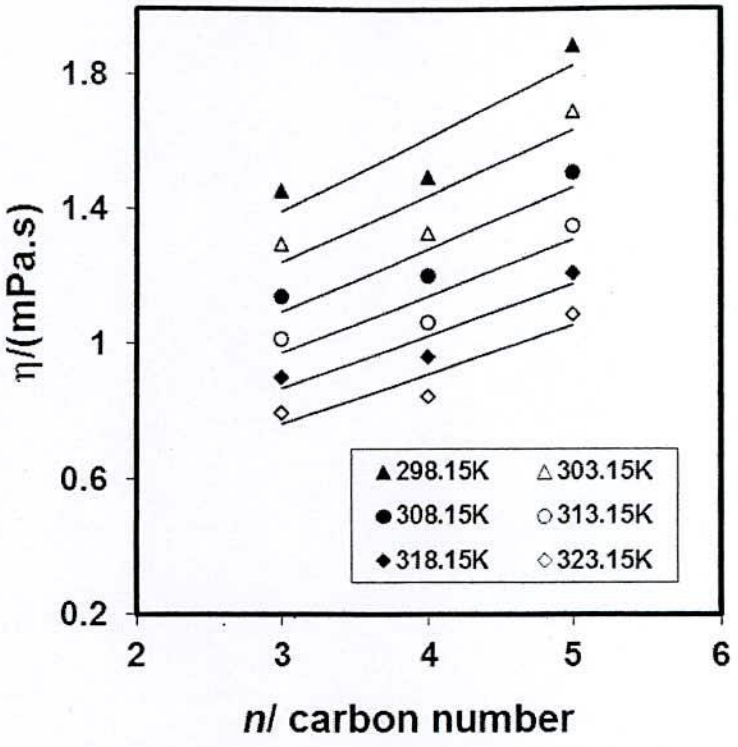

Figure 4.63: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanol with different temperature at 0.5 mole fraction.

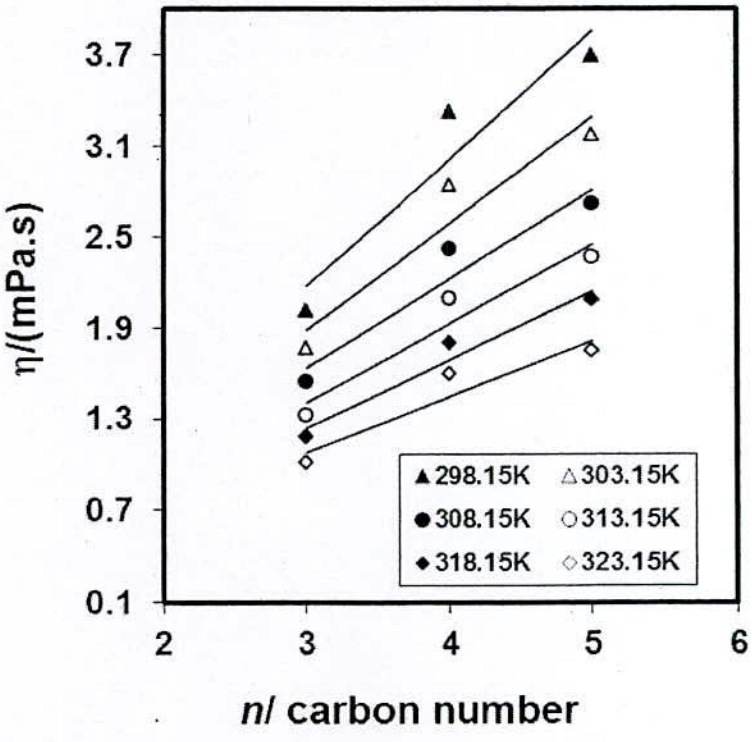

Figure 4.64: Dependence of the viscosity (η) with carbon number (n) of iso -alcohols in 0.015M SDS + Ethanol with different temperature at 1.0 mole fraction.

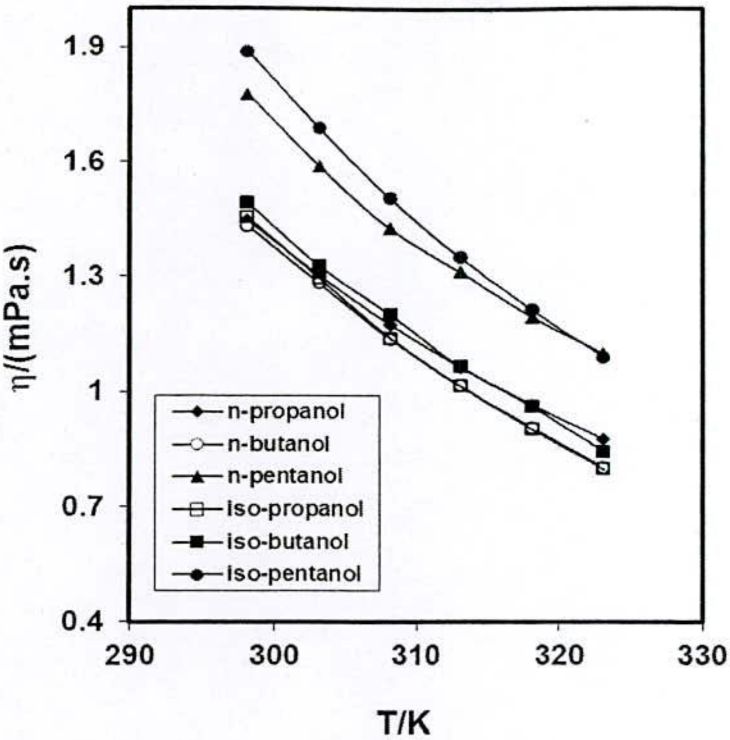

Figure 4.65: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

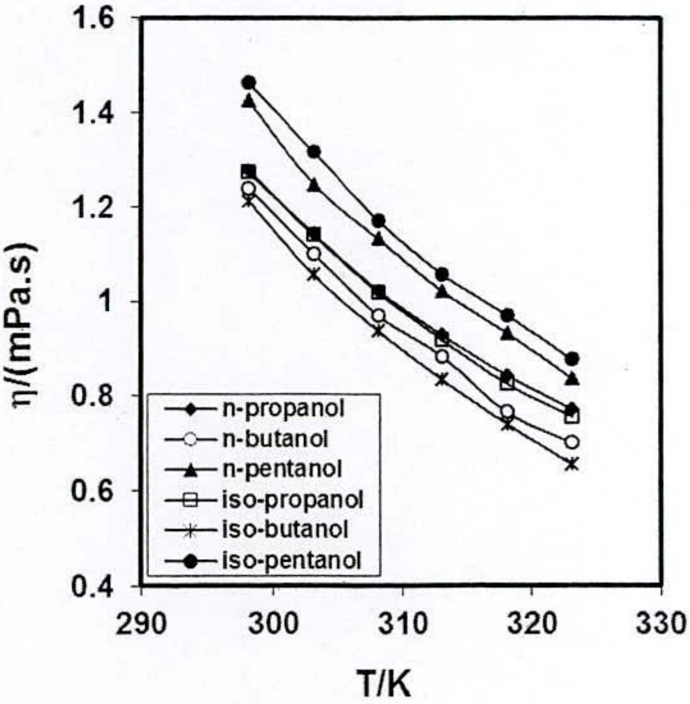

Figure 4.66: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

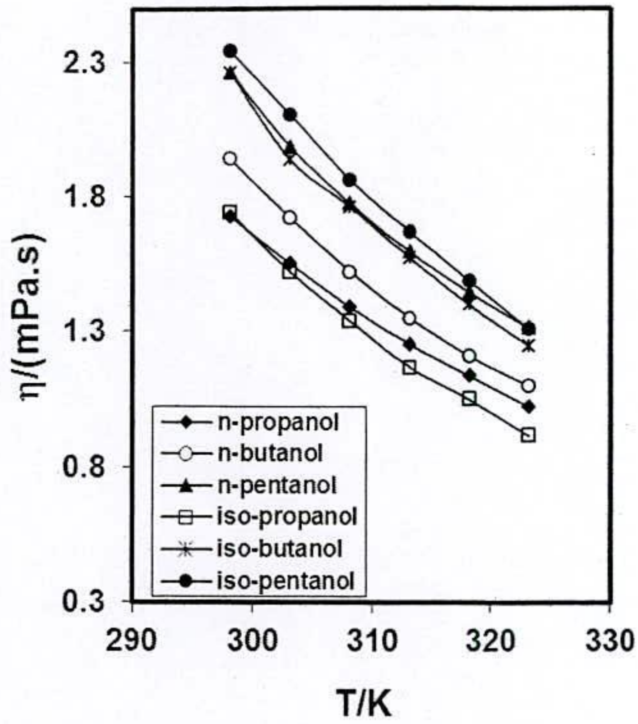

Figure 4.67: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

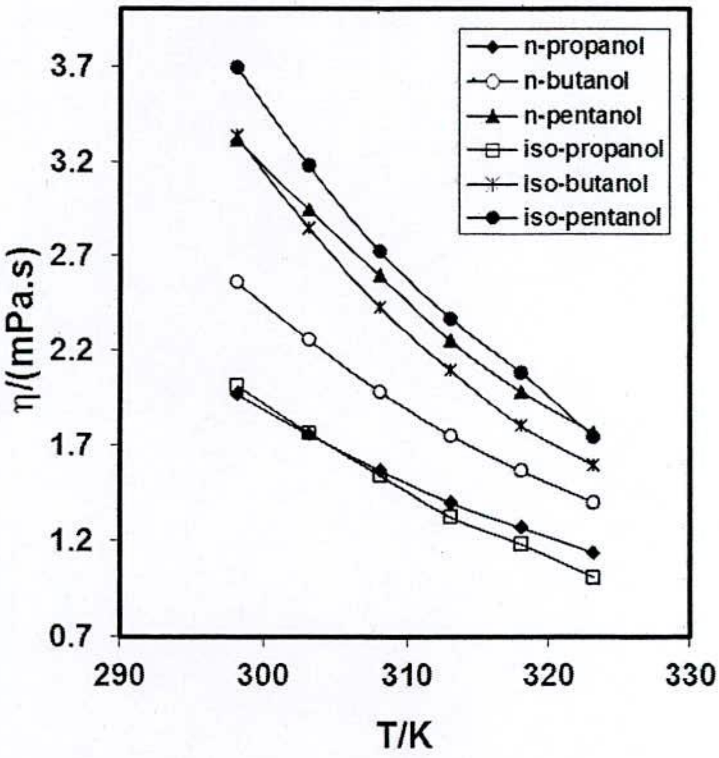

Figure 4.68: Comparison of viscosity (η) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

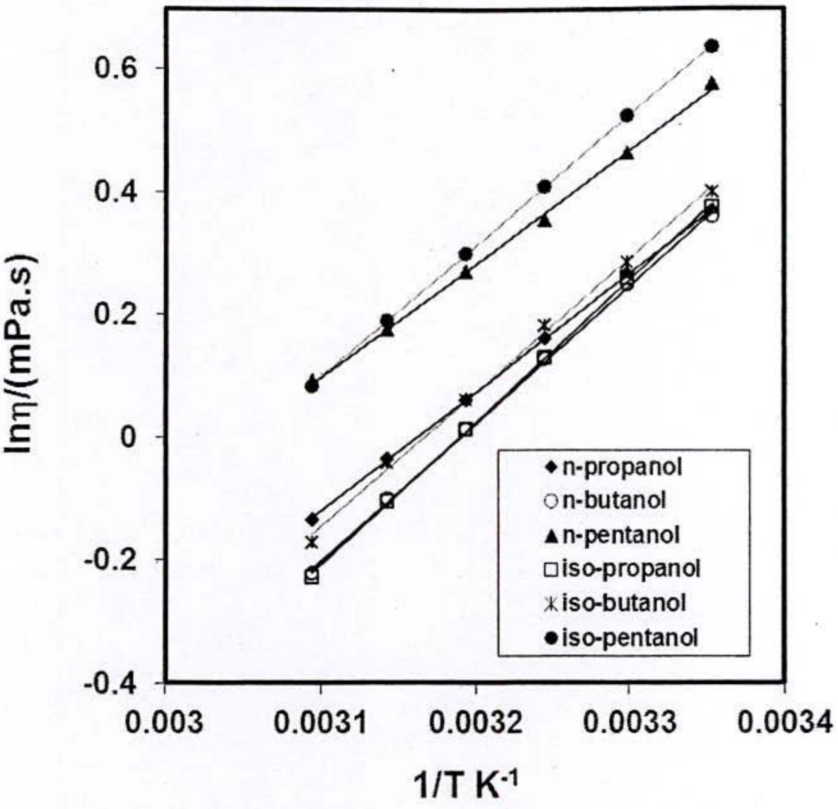

Figure 4.69: Comparison of ln η vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

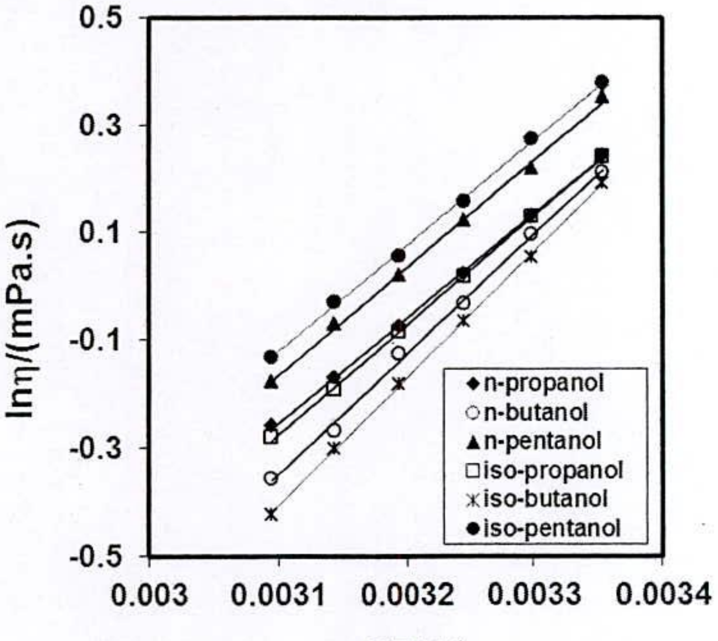

Figure 4.70: Comparison of ln η vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

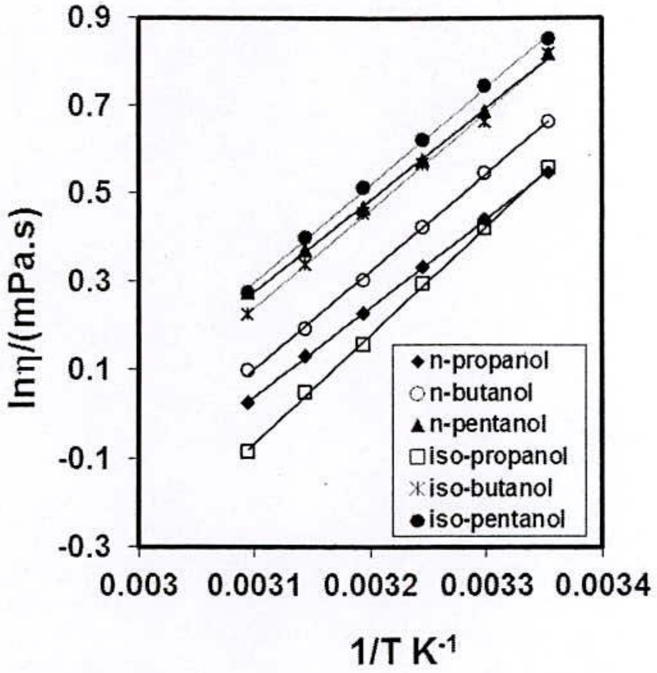

Figure 4.71: Comparison of ln η vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

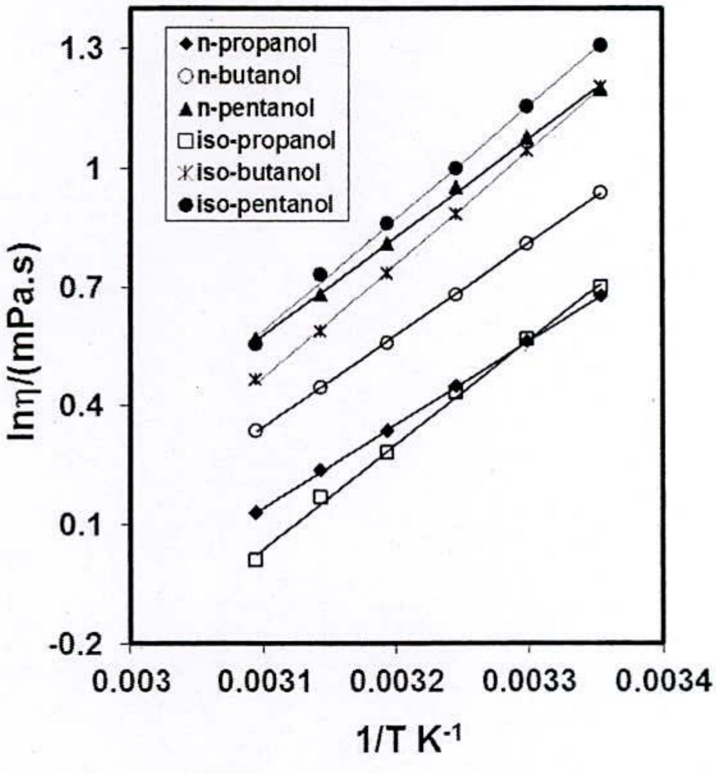

Figure 4.72: Comparison of ln η vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

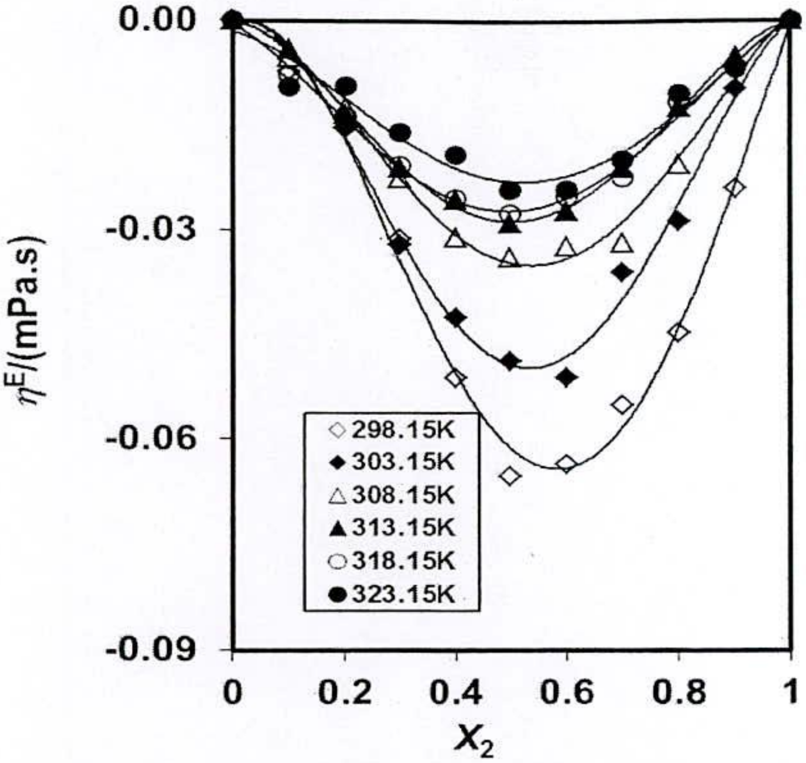

Figure 4.73: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

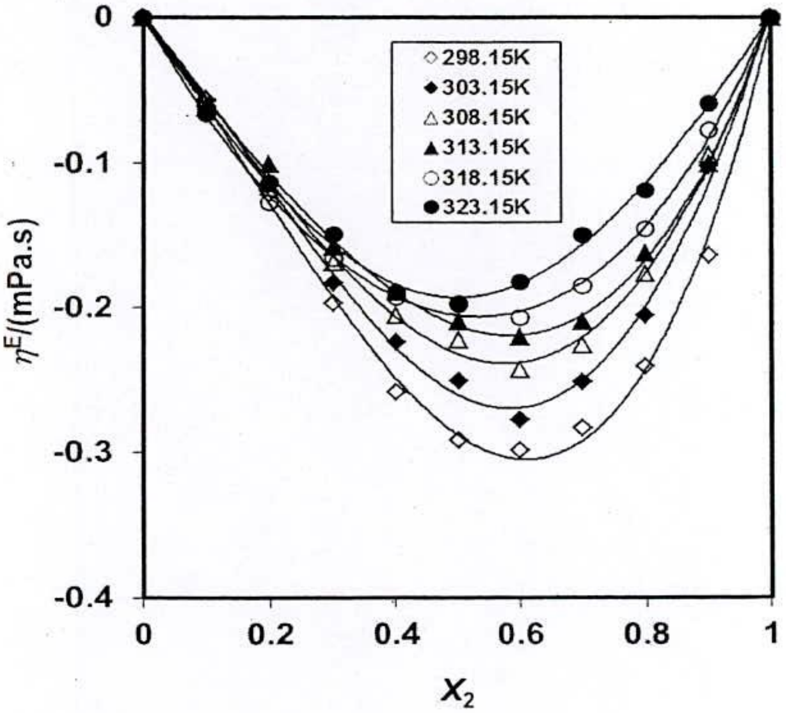

Figure 4.74: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

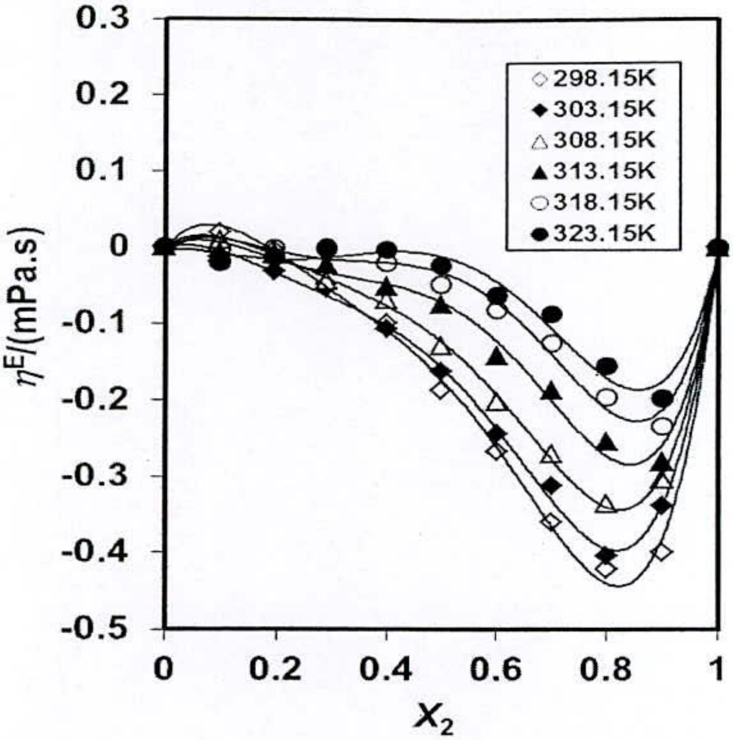

Figure 4.75: Plots of excess viscosity (η^E) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

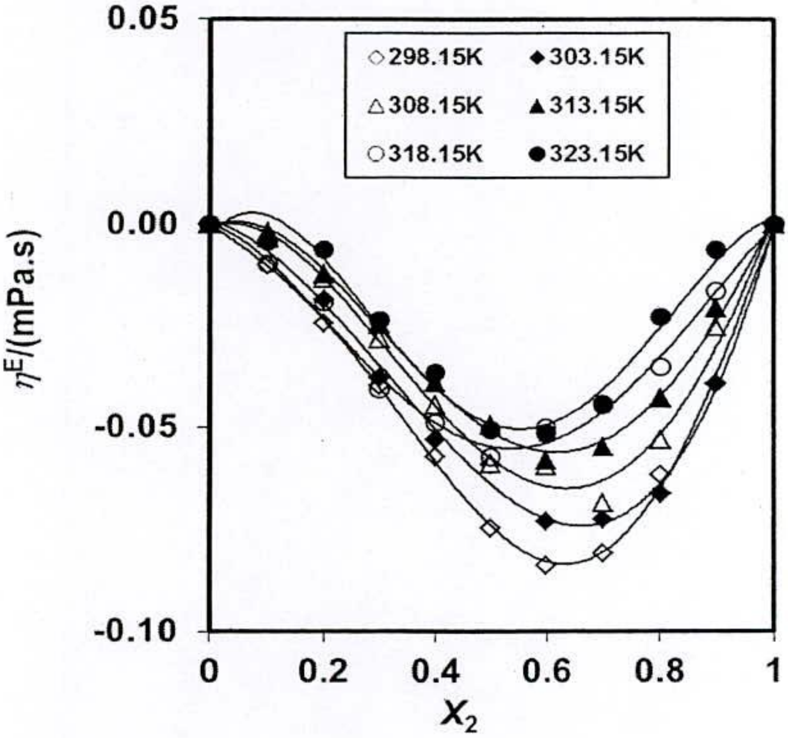

Figure 4.76: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

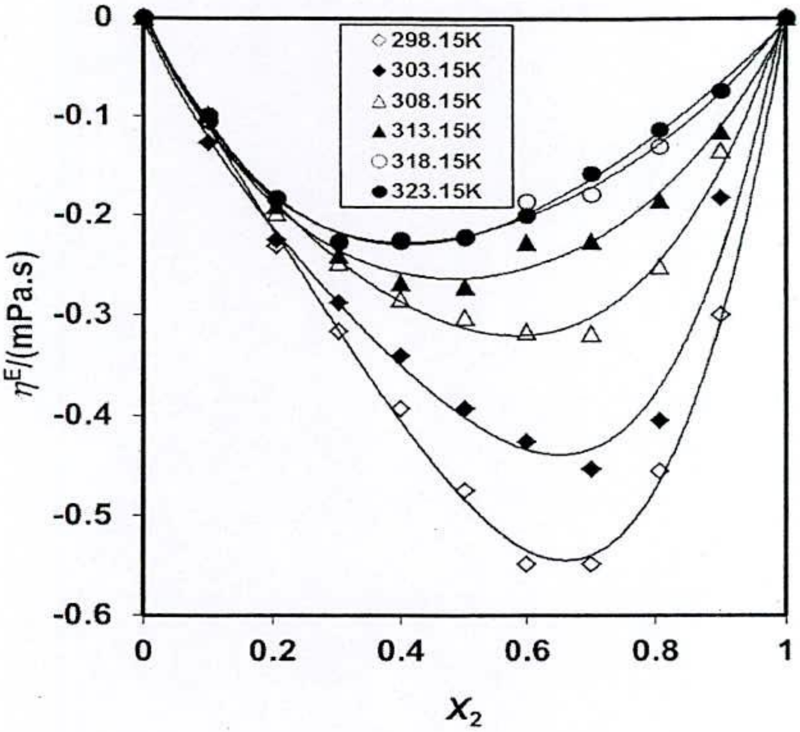

Figure 4.77: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

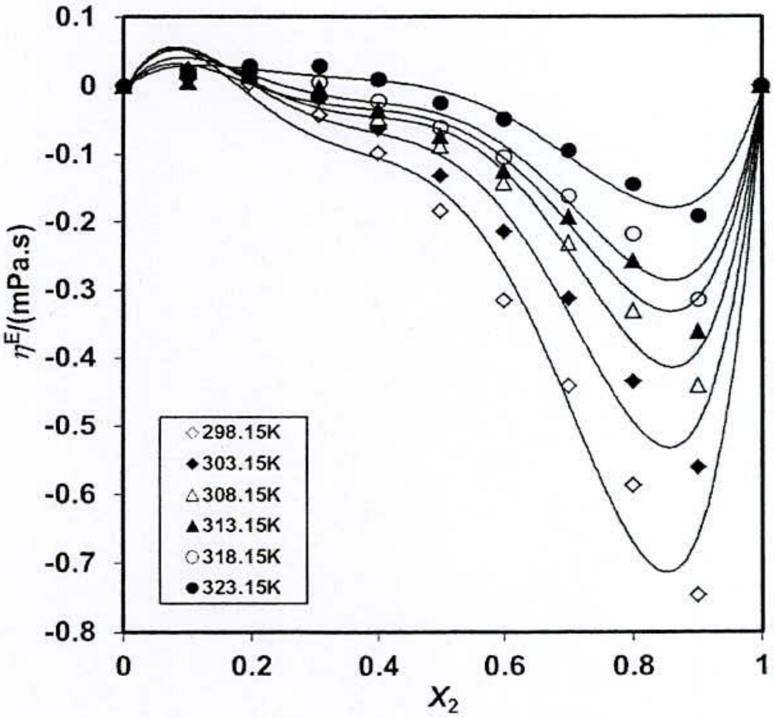

Figure 4.78: Plots of excess viscosity (η^E) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

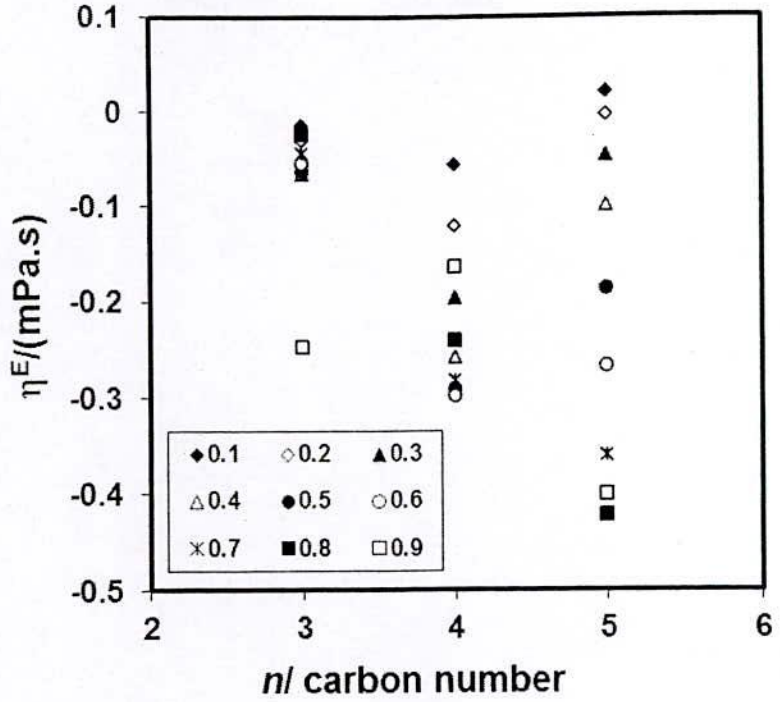

Figure 4.79: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

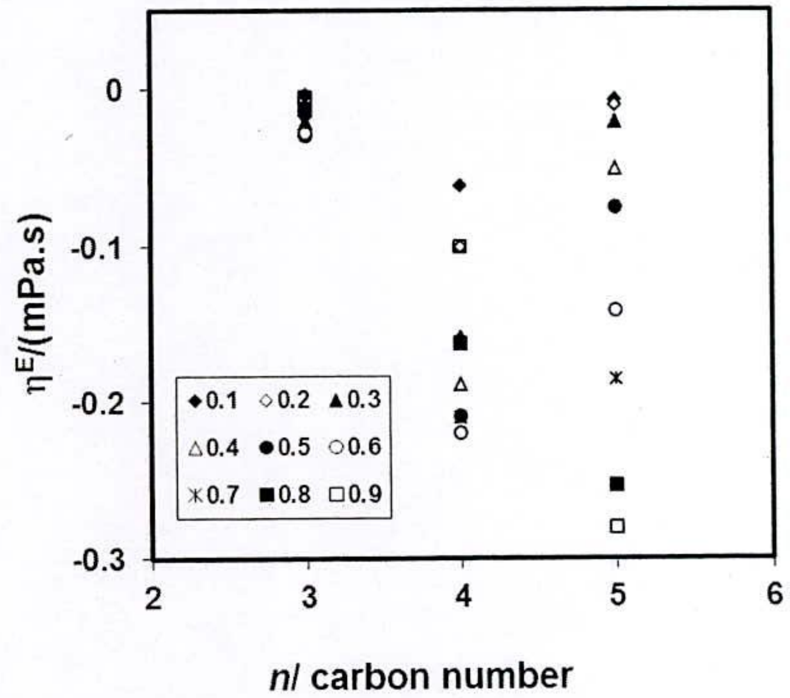

Figure 4.80: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

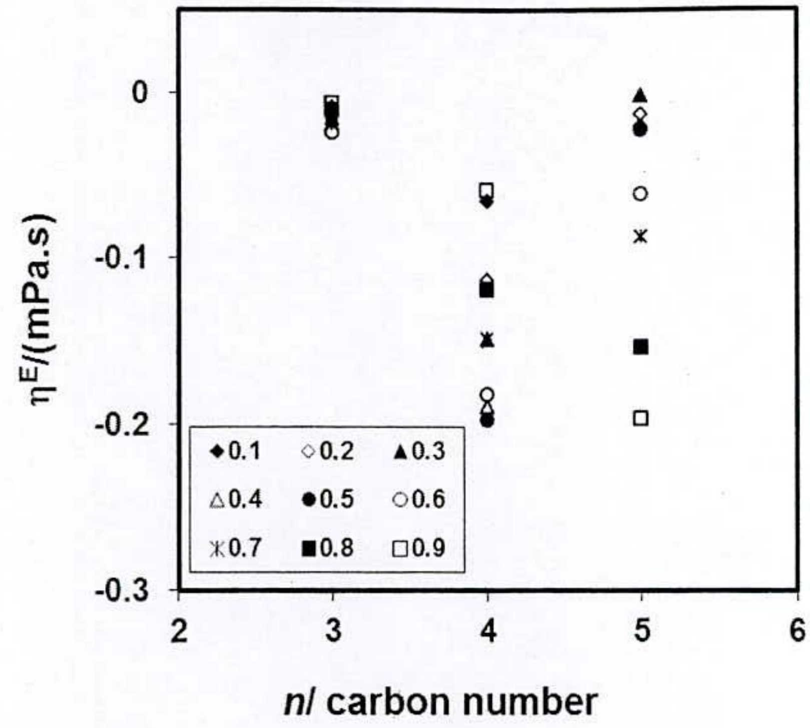

Figure 4.81: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

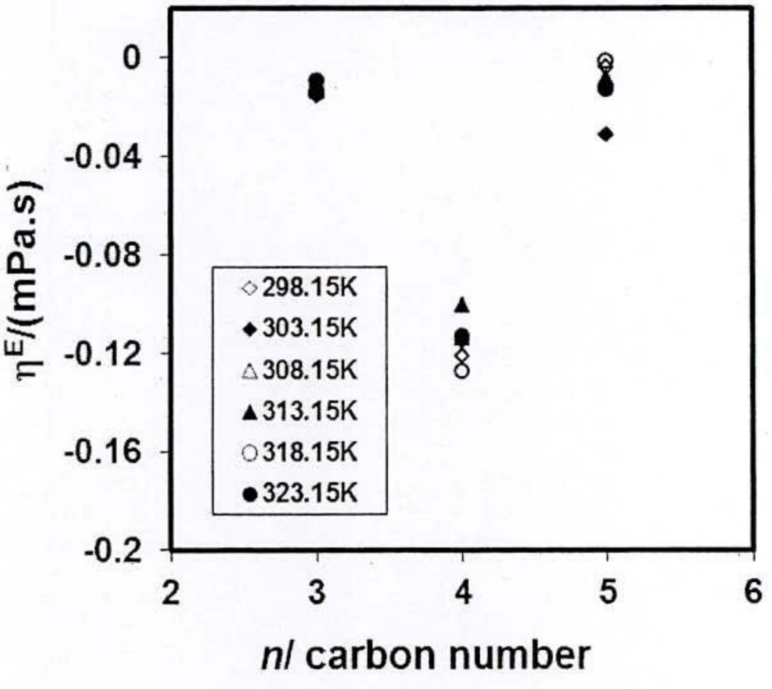

Figure 4.82: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.2 mole fraction. .

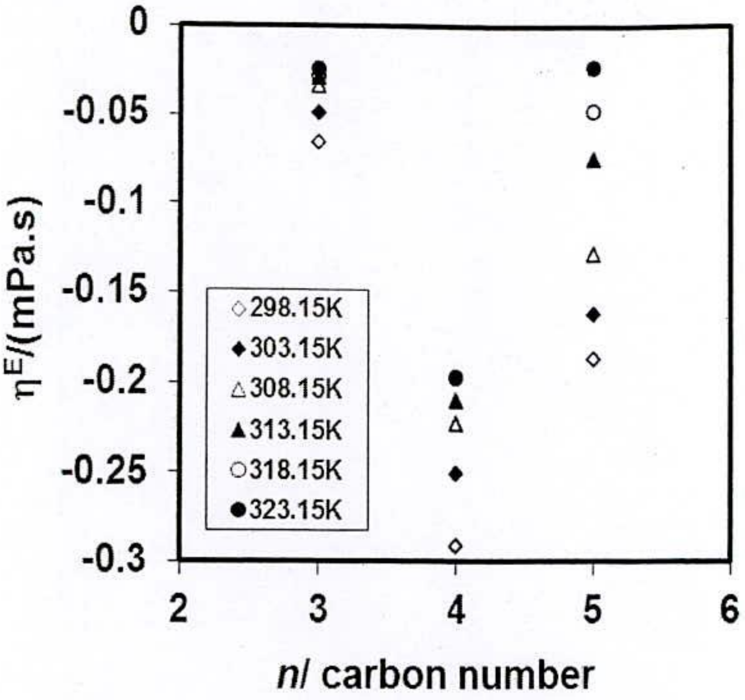

Figure 4.83: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

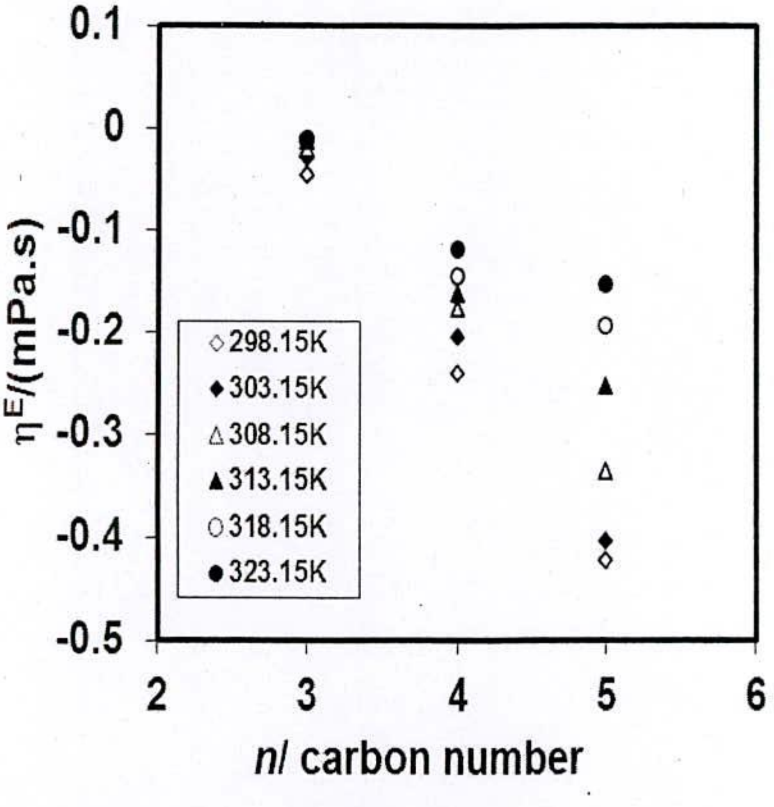

Figure 4.84: Dependence of the excess viscosity (η^E) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.8 mole fraction.

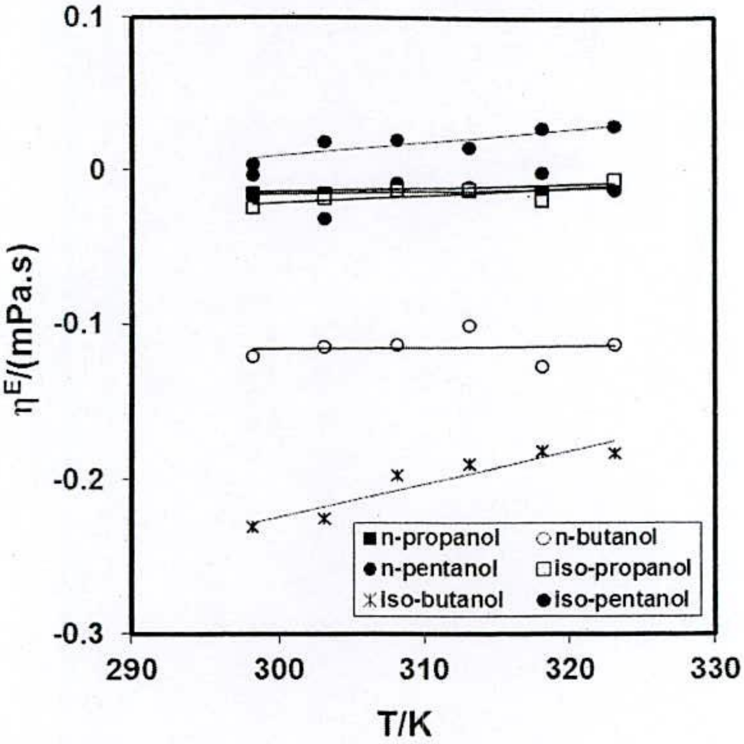

Figure 4.85: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

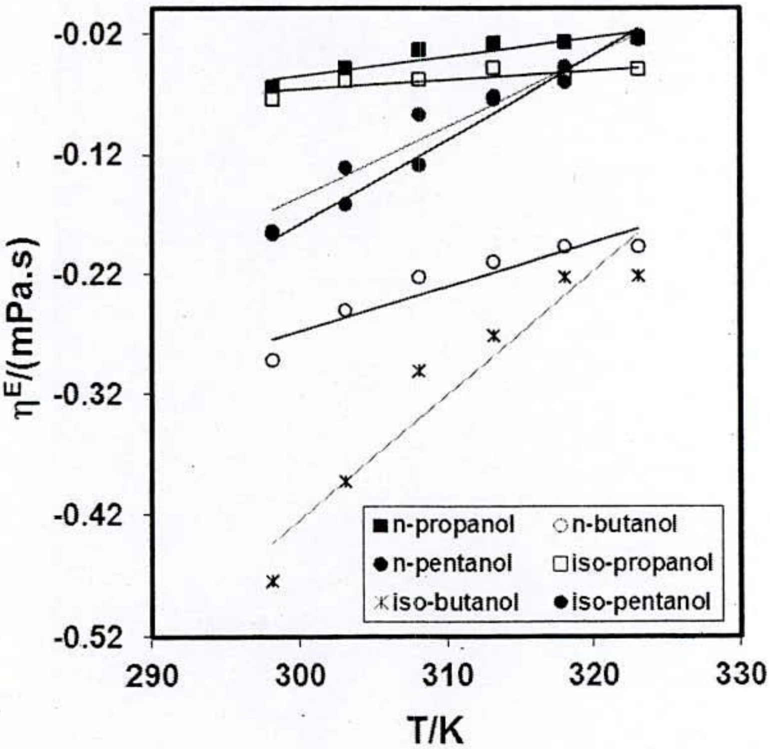

Figure 4.86: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

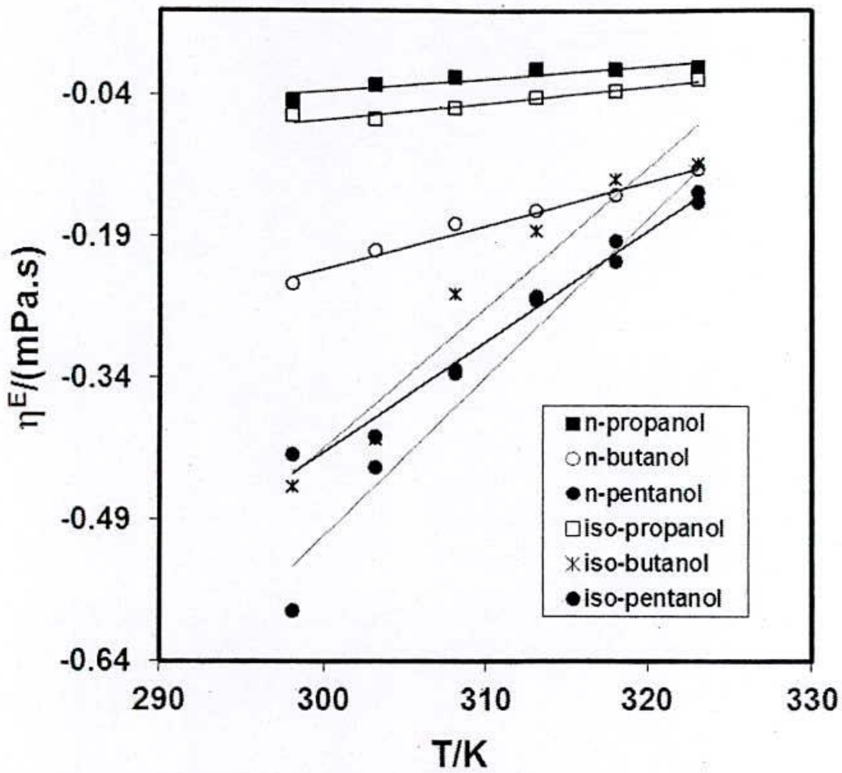

Figure 4.87: Comparison of excess viscosity (η^E) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

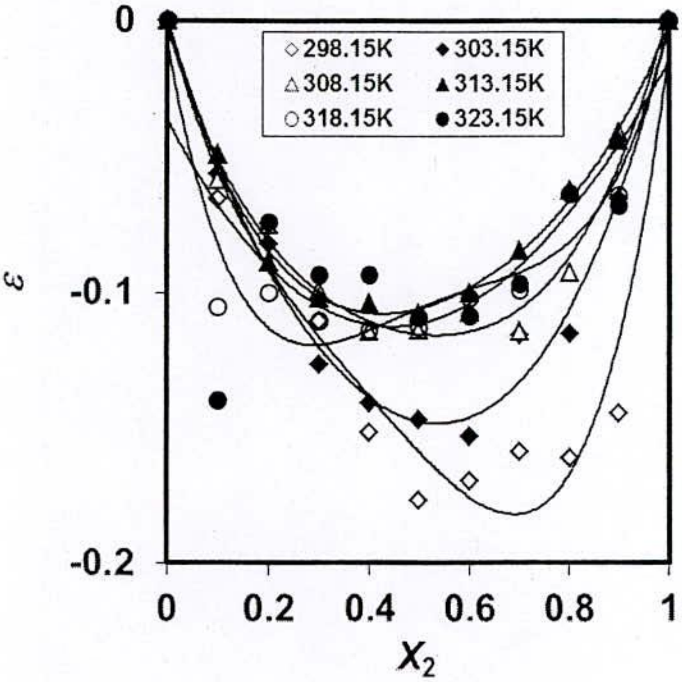

Figure 4.88: Plots of interaction parameter (ε) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

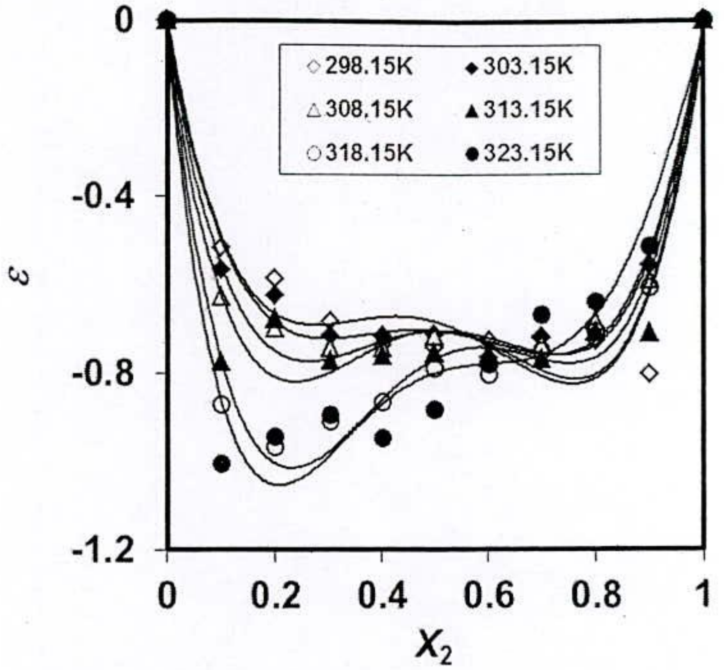

Figure 4.89: Plots of interaction parameter (*ε*) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

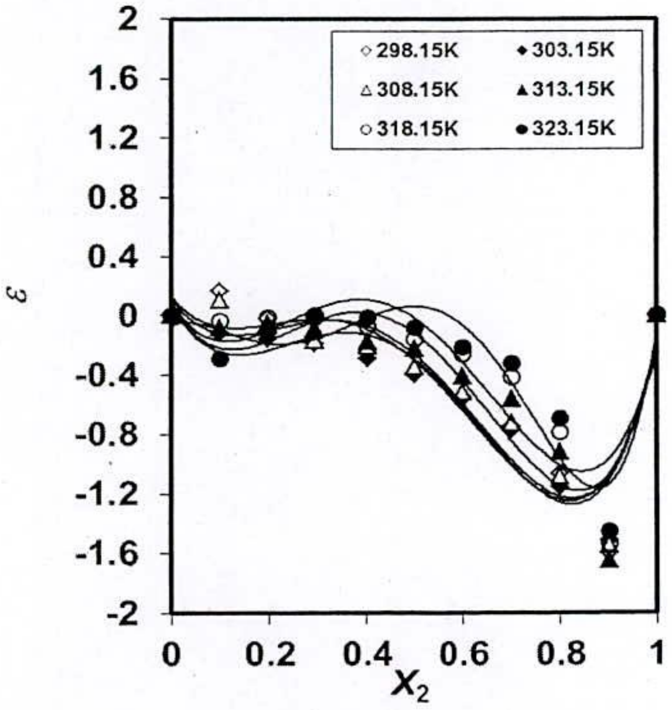

Figure 4.90: Plots of interaction parameter (*ε*) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

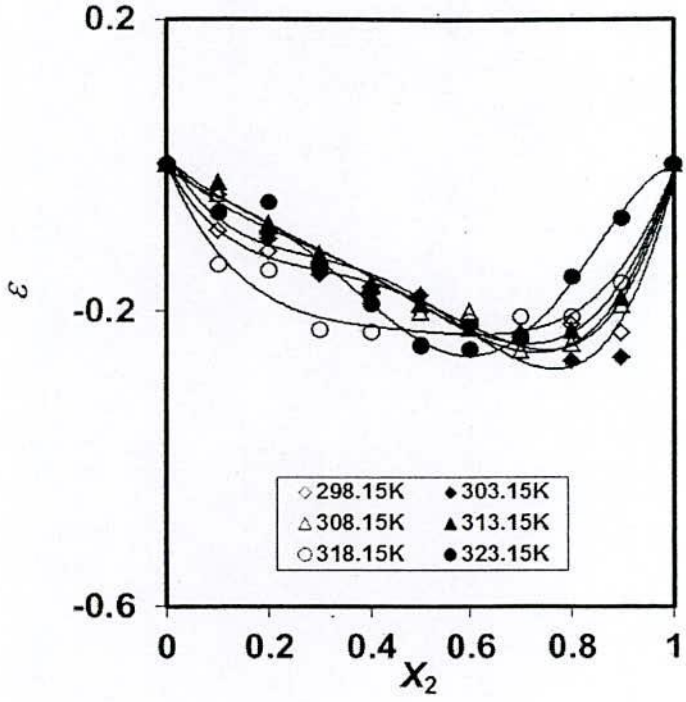

Figure 4.91: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

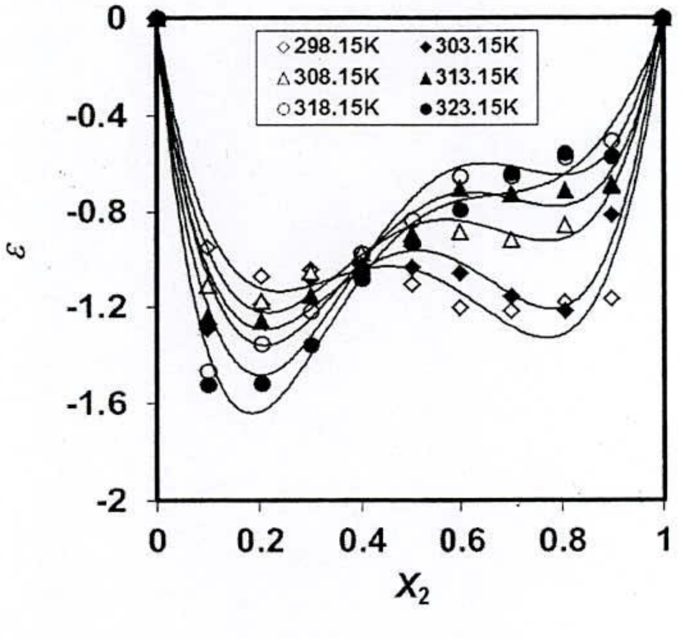

Figure 4.92: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

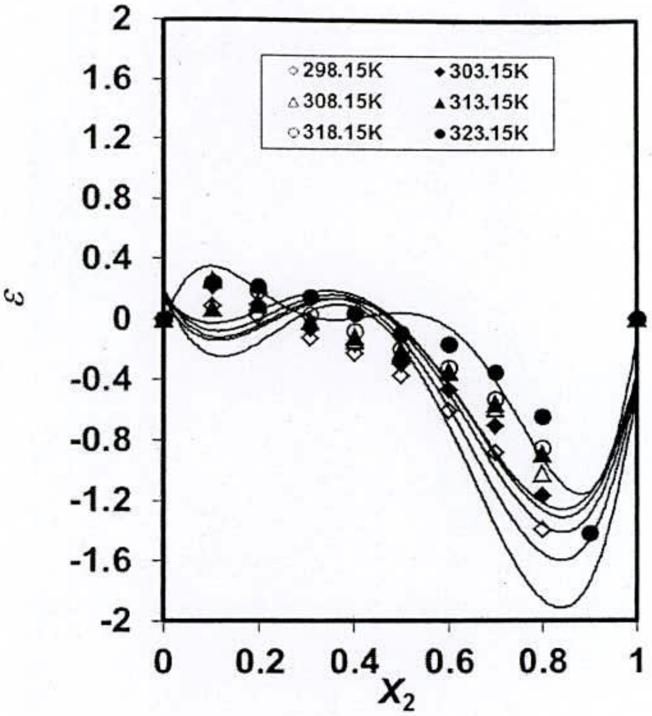

Figure 4.93: Plots of interaction parameter (ε) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

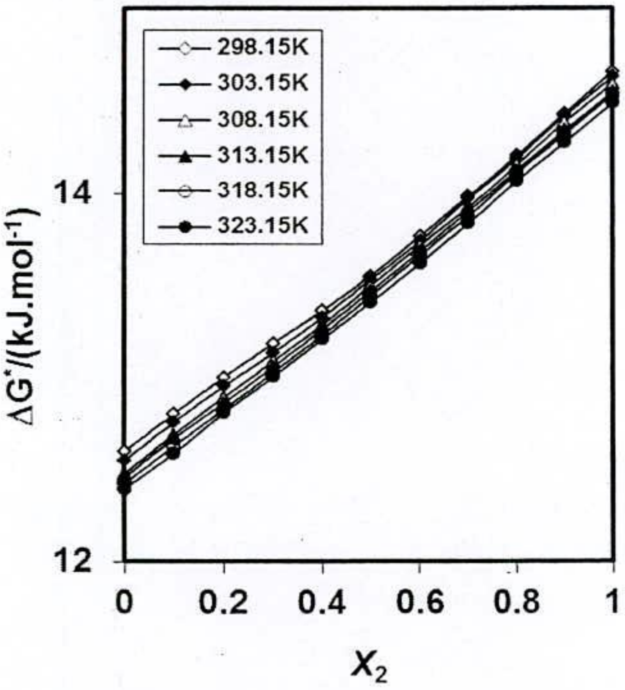

Figure 4.94: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

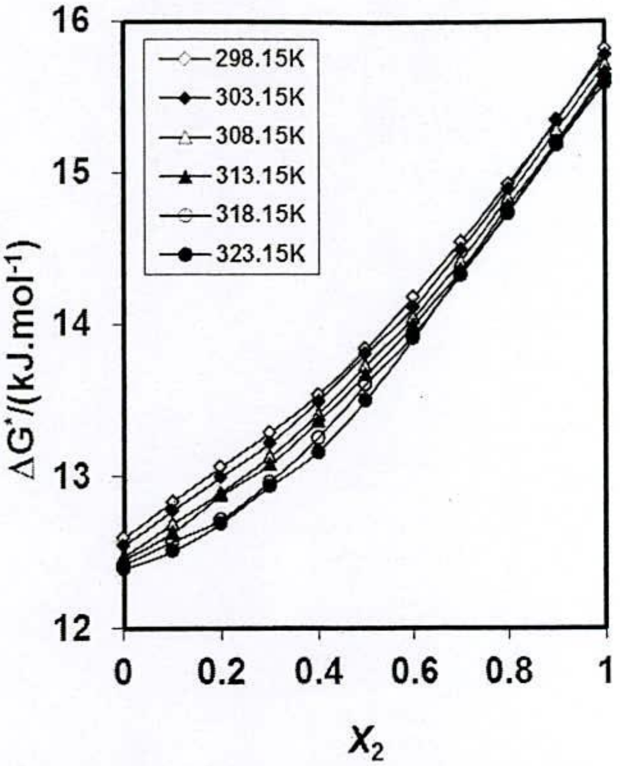

Figure 4.95: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

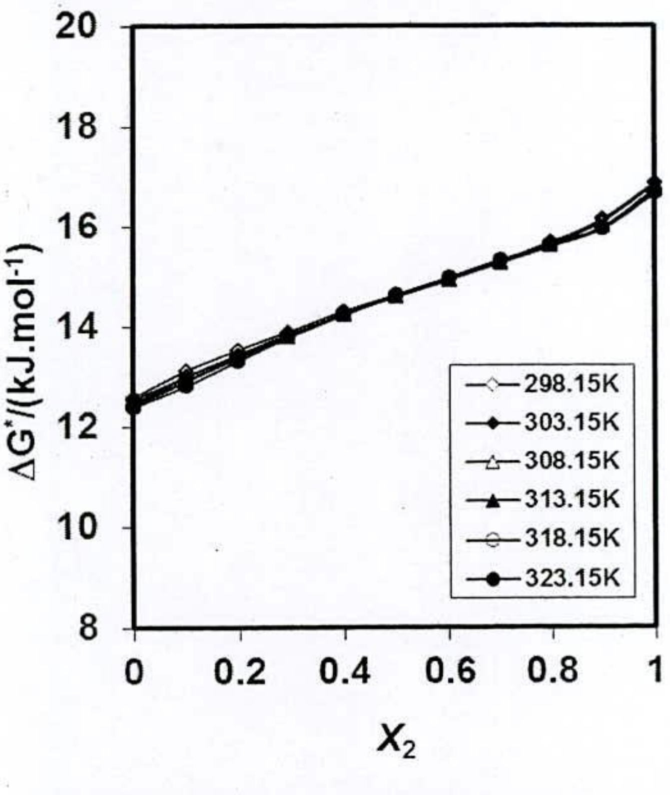

Figure 4.96: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

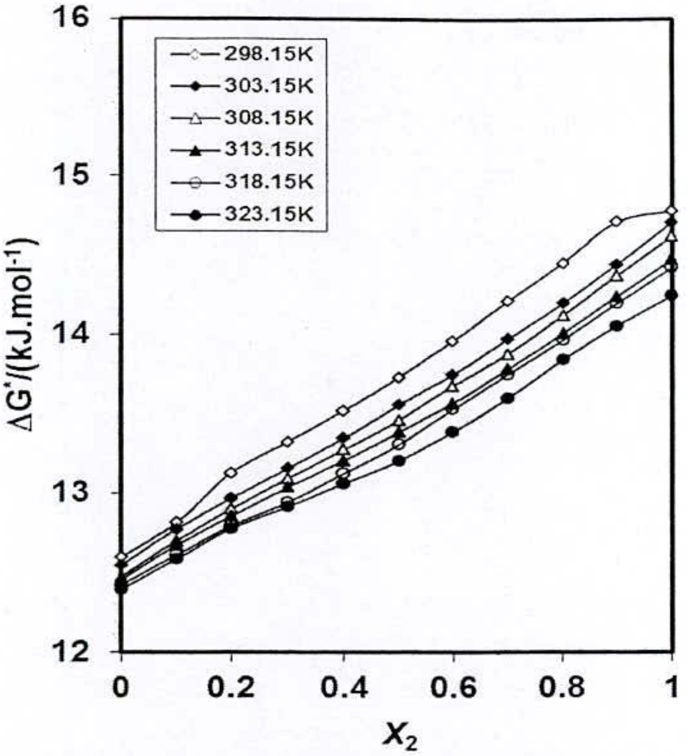

Figure 4.97: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

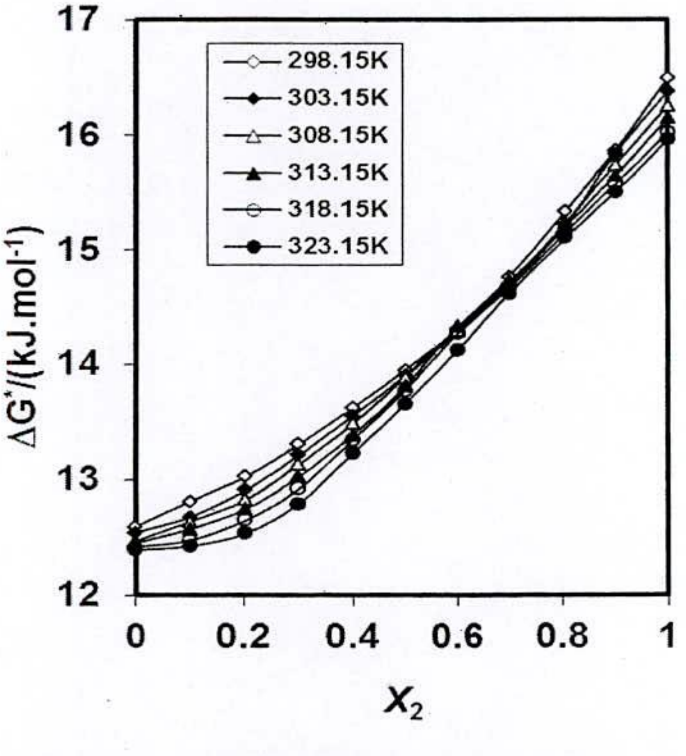

Figure 4.98: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

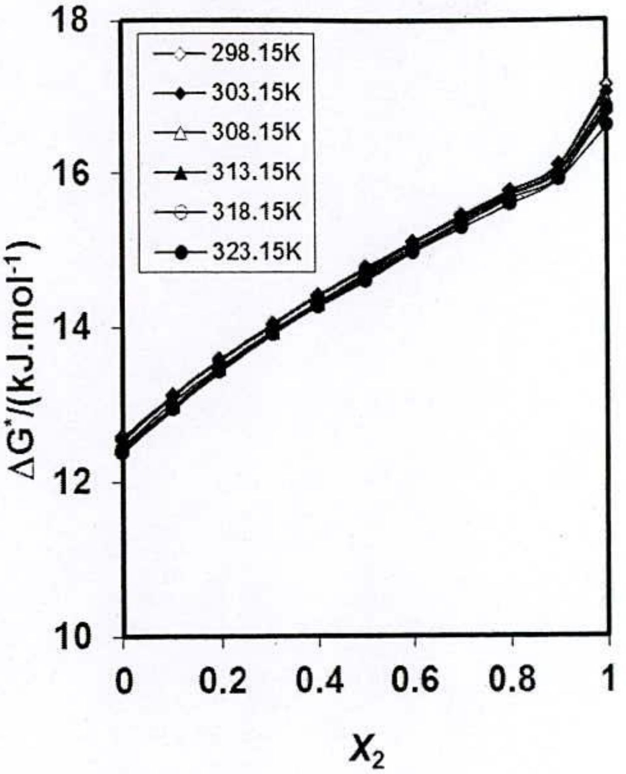

Figure 4.99: Plots of change of free energy (ΔG^*) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

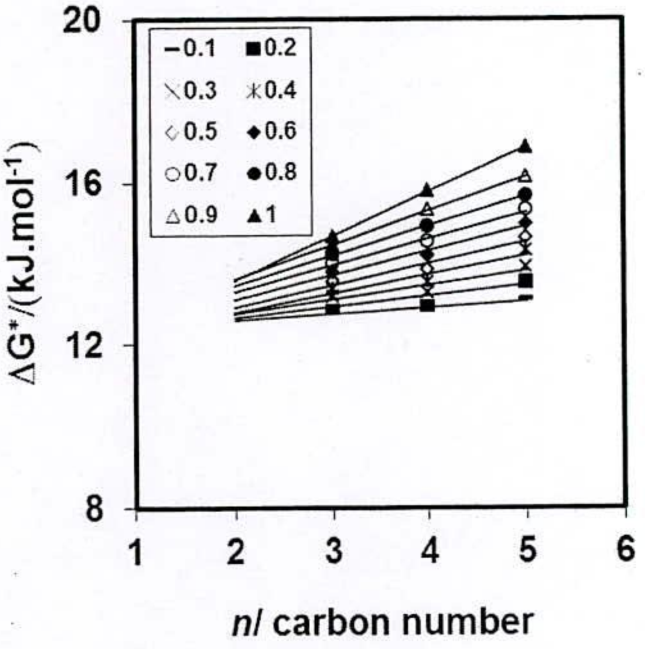

Figure 4.100: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

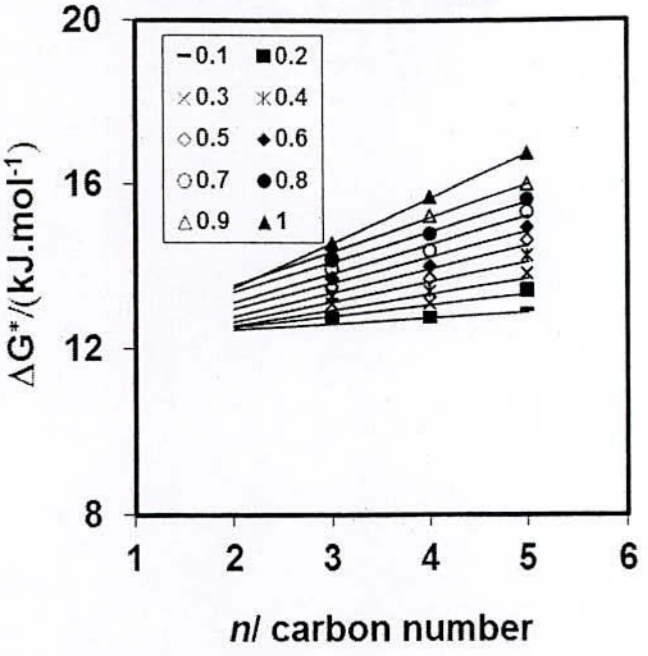

Figure 4.101: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

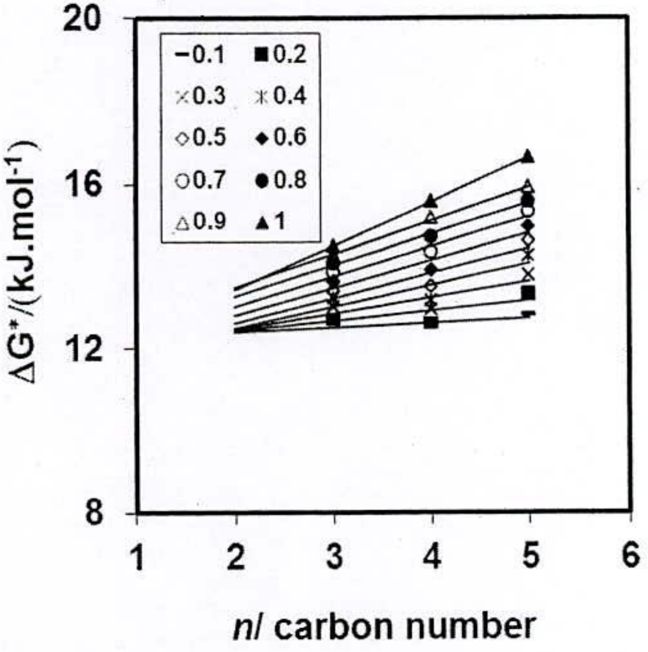

Figure 4.102: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

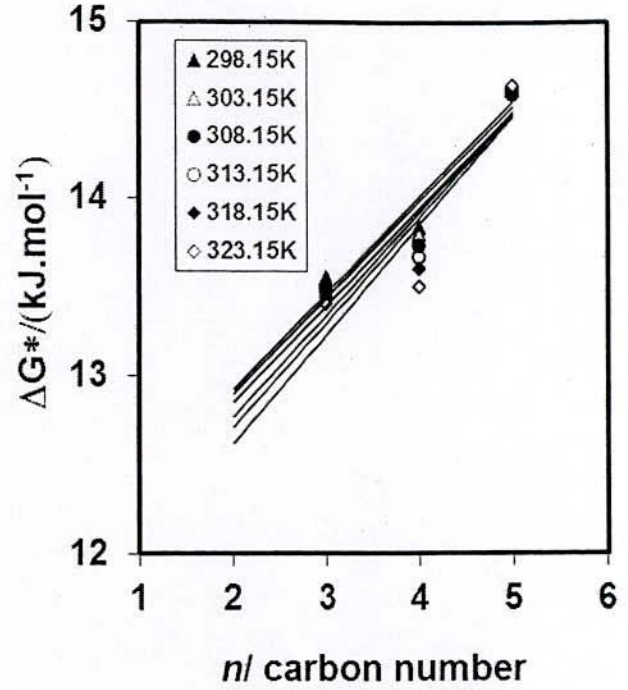

Figure 4.103: Dependence of the change of free energy (ΔG^*) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

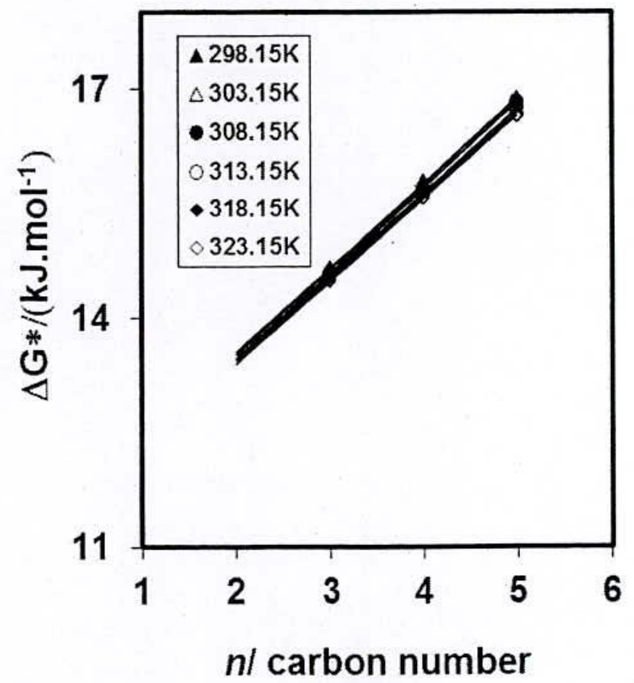

Figure 4.104: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso-alcohols in 0.015M SDS + Ethanolwith different temperature at 1.0 mole fraction.

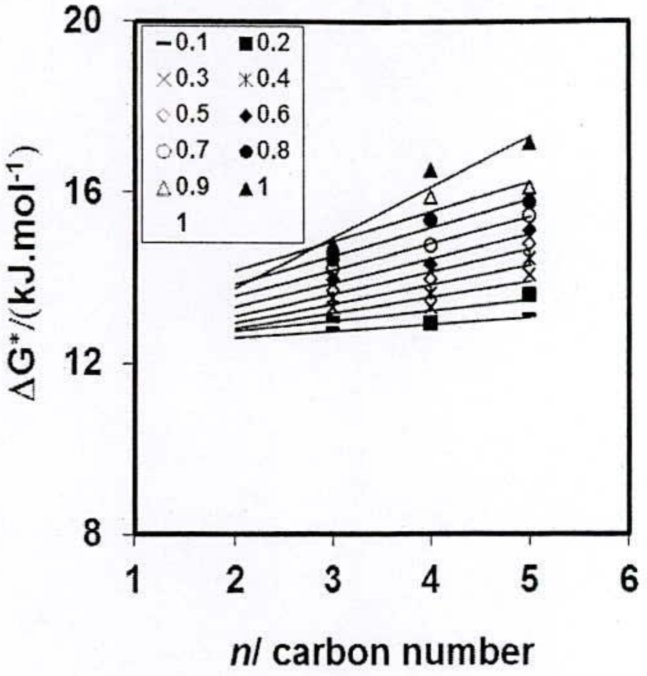

Figure 4.105: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different mole fraction at 298.15K.

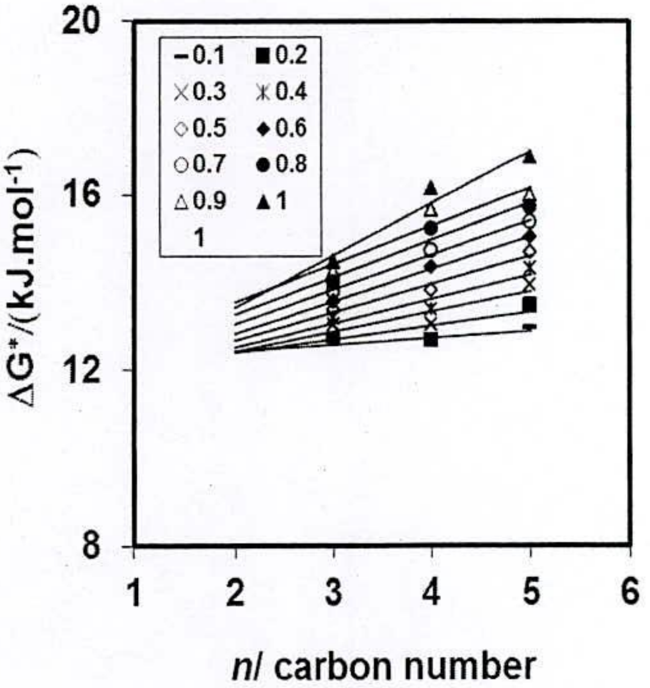

Figure 4.106: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different mole fraction at 313.15K.

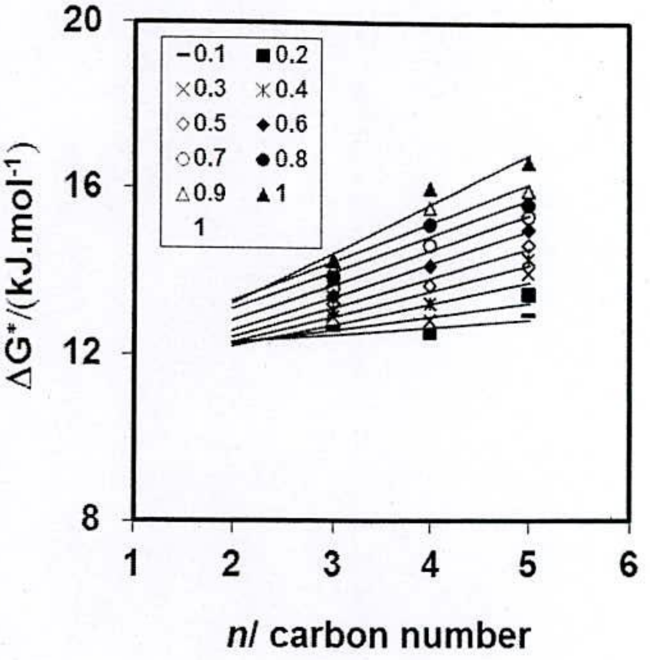

Figure 4.107: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different mole fraction at 323.15K.

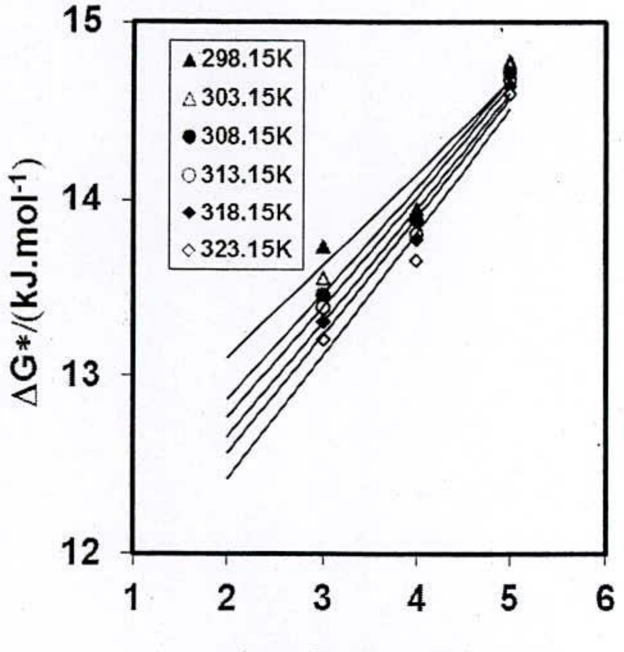

Figure 4.108: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different temperature at 0.5 mole fraction.

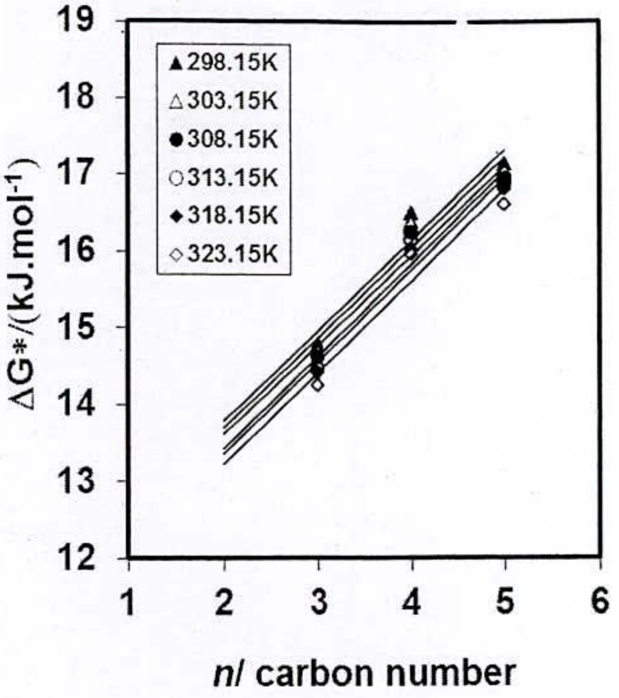

Figure 4.109: Dependence of the change of free energy (ΔG^*) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanolwith different temperature at 1.0 mole fraction.

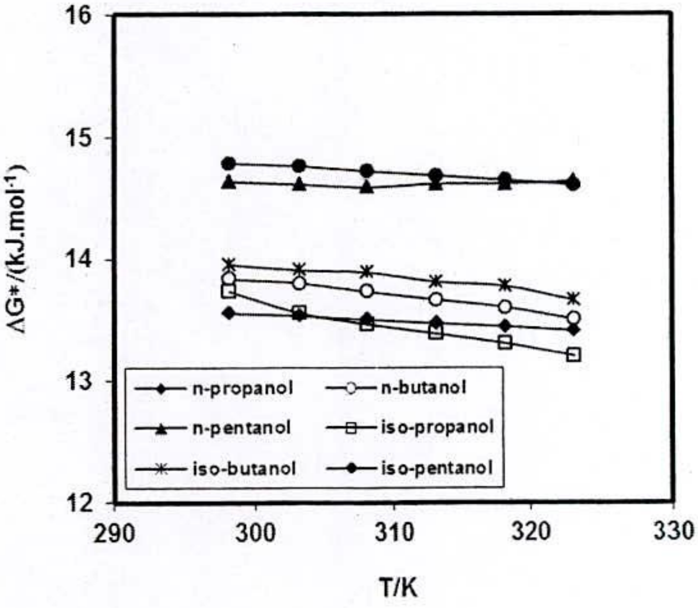

Figure 4.110: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

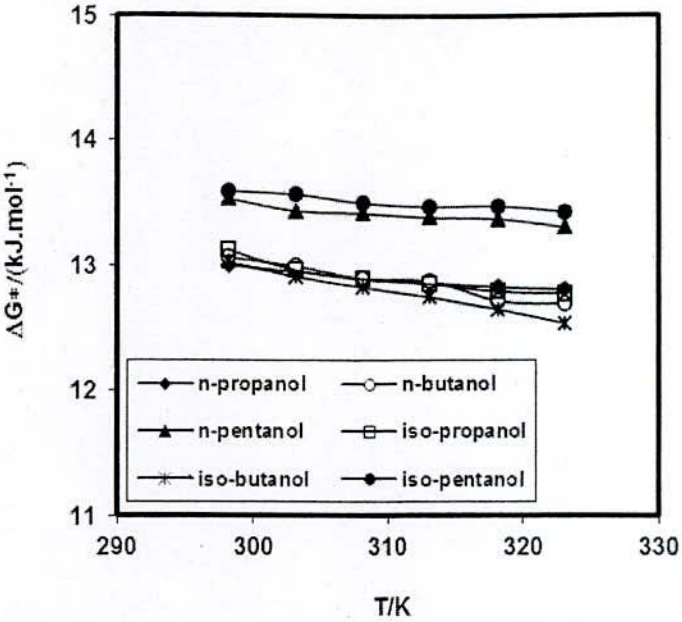

Figure 4.111: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

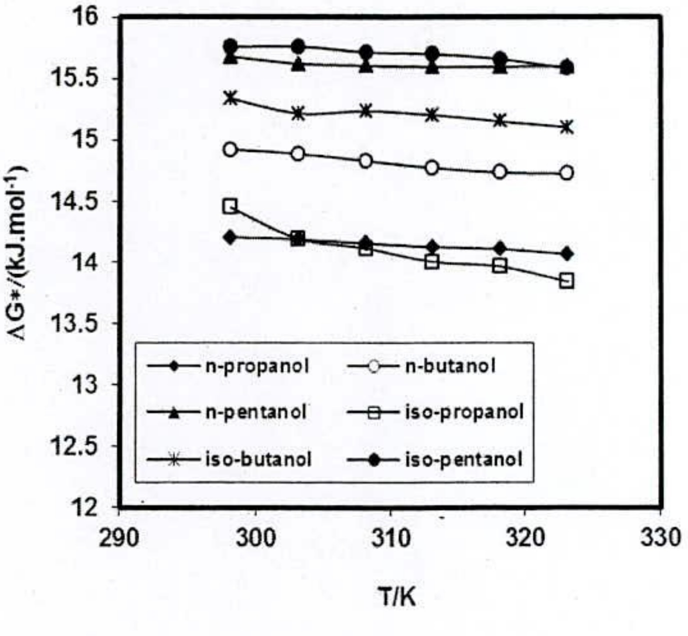

Figure 4.112: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

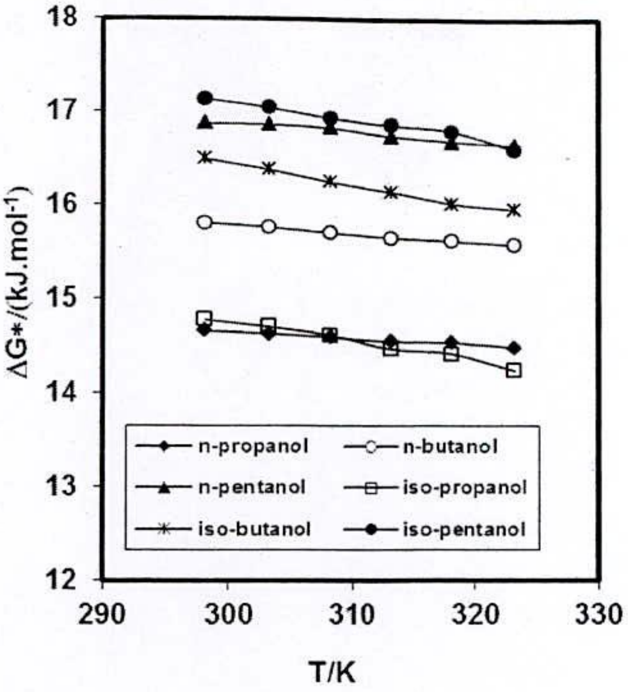

Figure 4.113: Comparison of change of free energy (ΔG^*) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

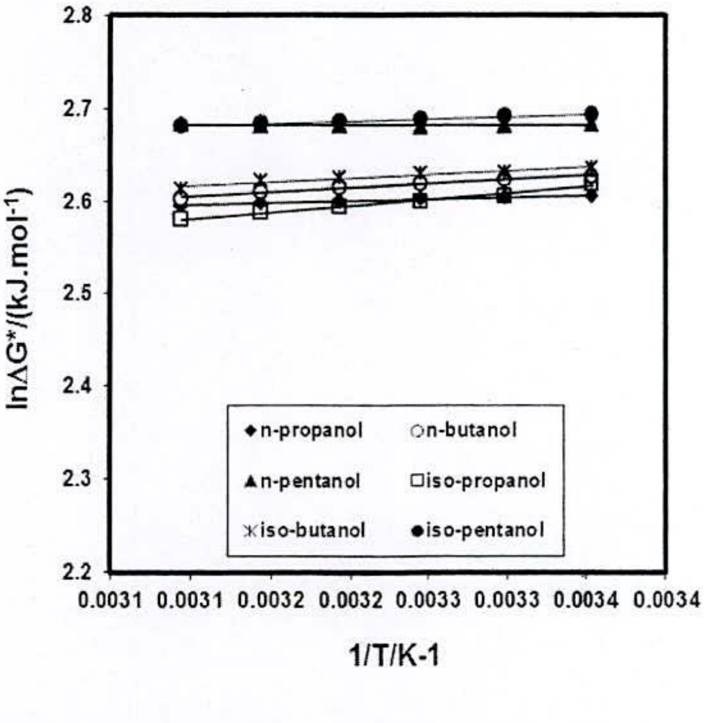

Figure 4.114: Comparison of $\ln\Delta G^*$ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.5 mole fraction.

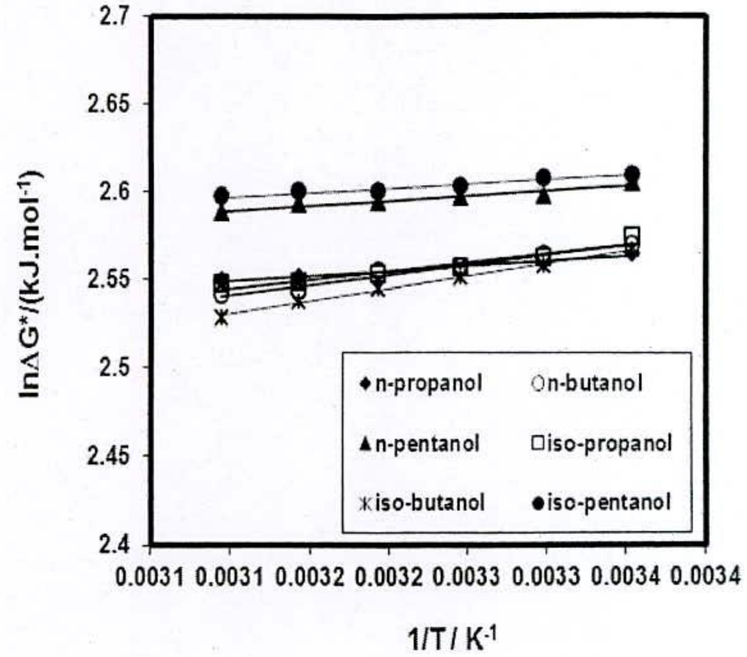

Figure 4.115: Comparison of $\ln\Delta G^*$ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

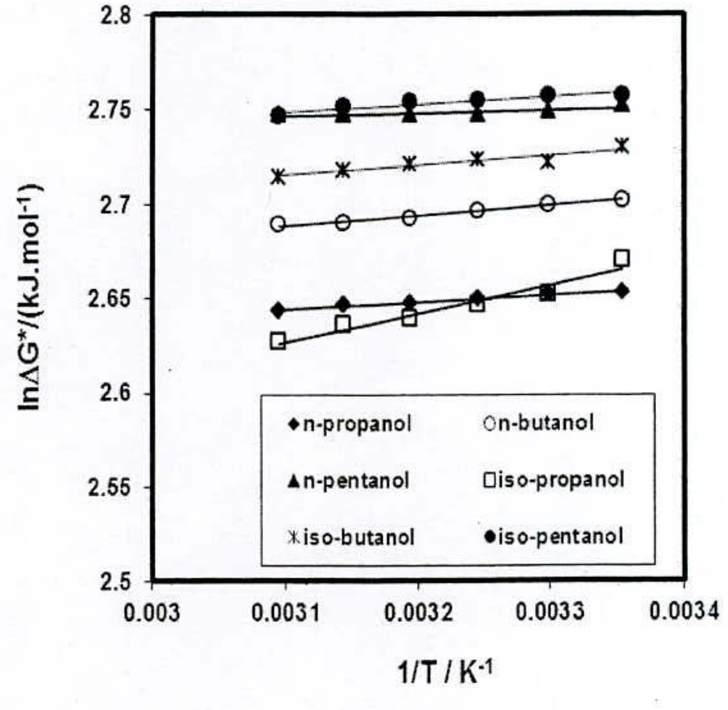

Figure 4.116: Comparison of $\ln\Delta G^*$ vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.8 mole fraction.

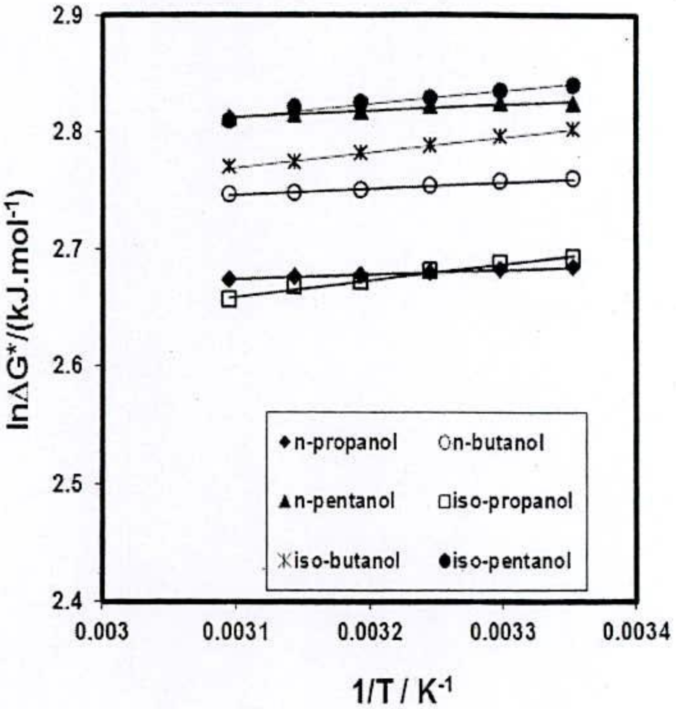

Figure 4.117: Comparison of lnΔG* vs 1/T of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 1.0 mole fraction.

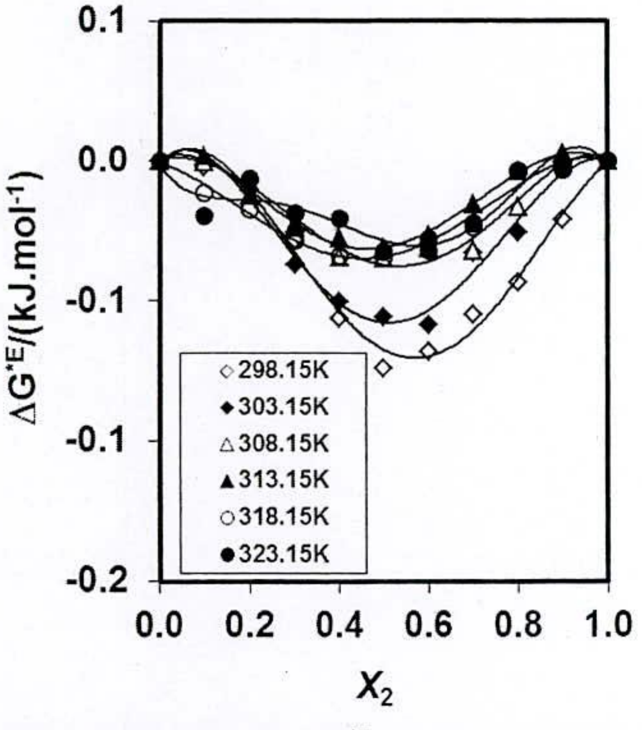

Figure 4.118: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

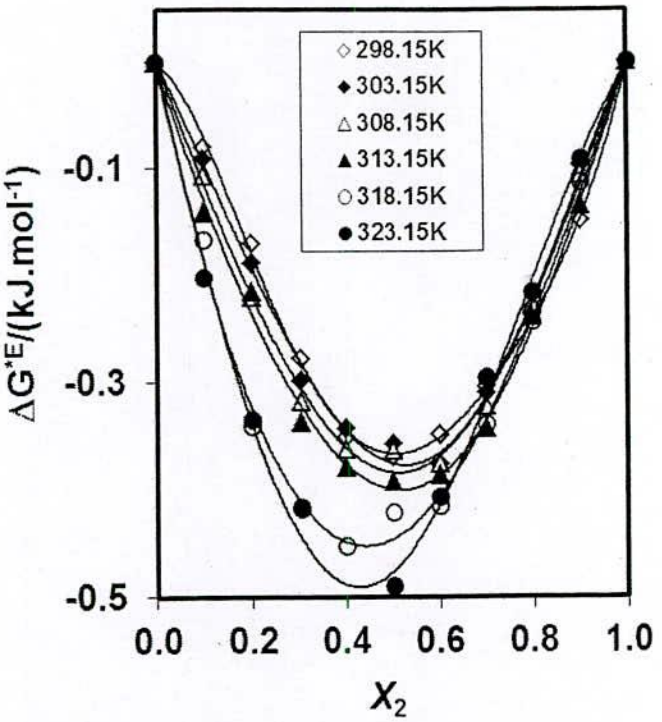

Figure 4.119: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

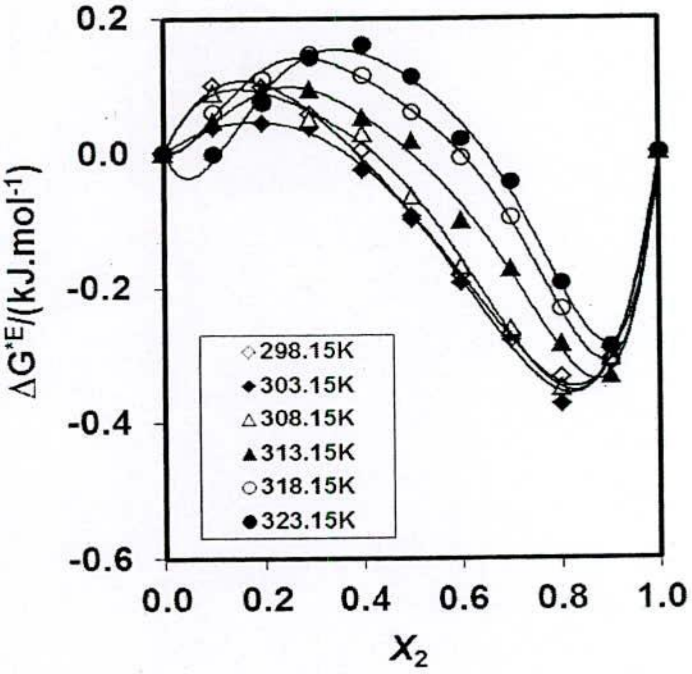

Figure 4.120: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of n-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

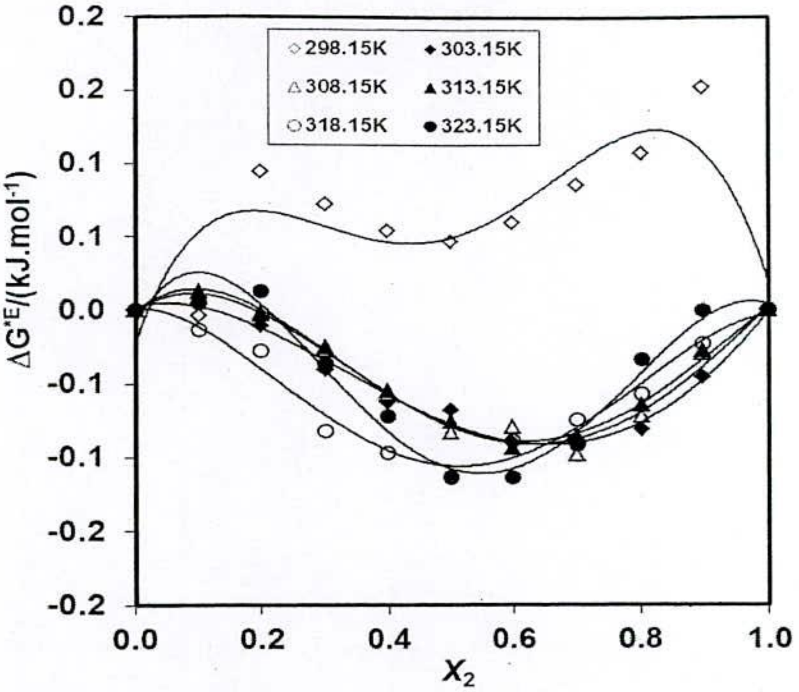

Figure 4.121: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Propanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

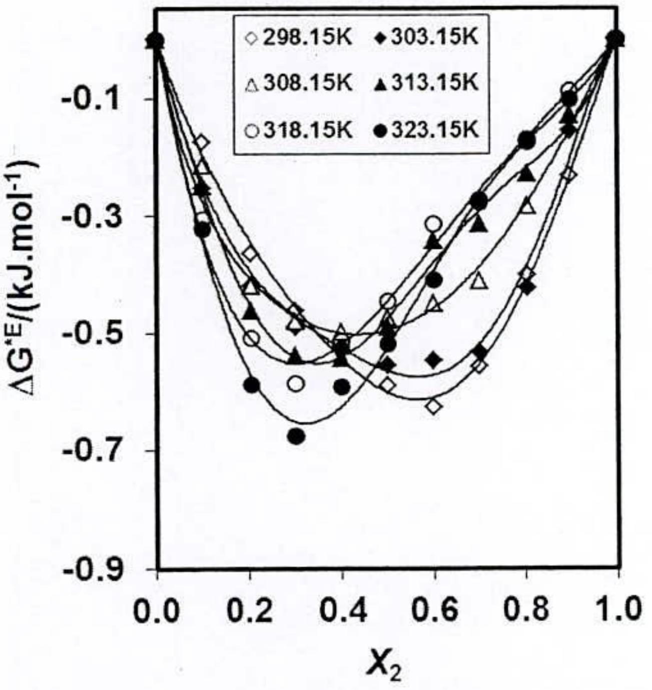

Figure 4.122: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Butanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

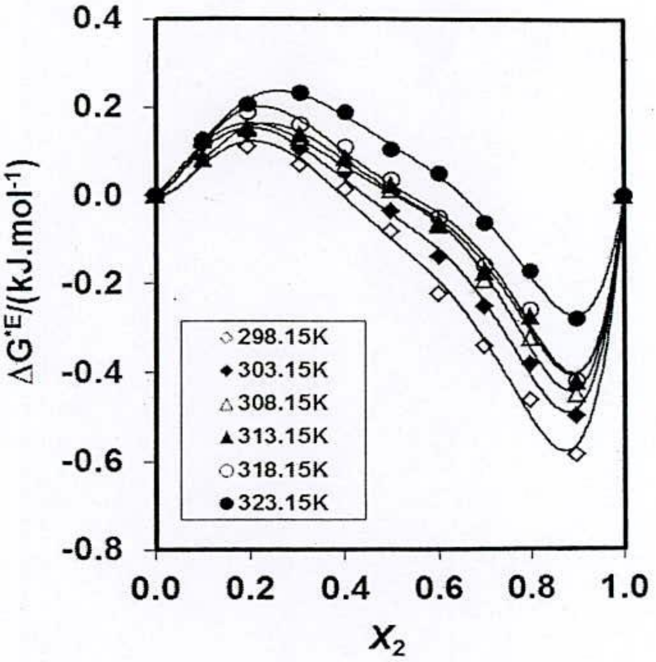

Figure 4.123: Plots of excess free energy (ΔG^{*E}) vs mole fraction (x_2) of iso-Pentanol in 0.015M SDS+ Ethanol system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

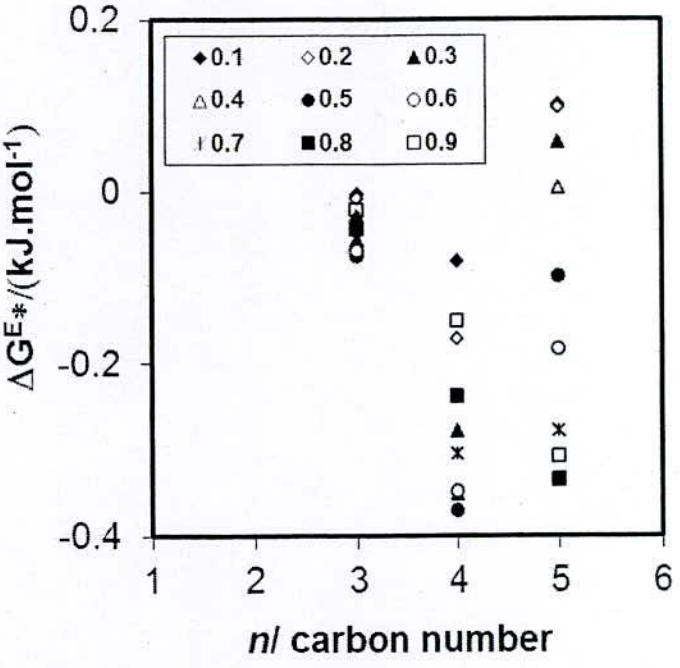

Figure 4.124: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different mole fraction at 298.15K.

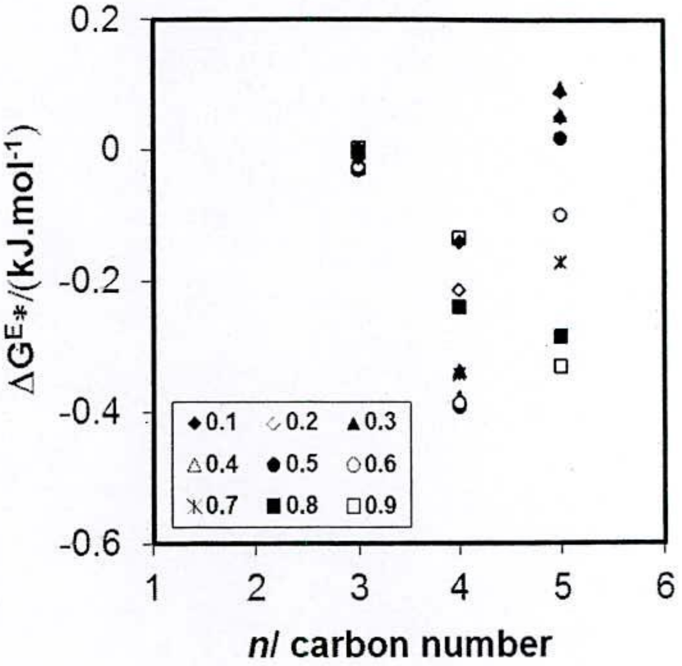

Figure 4.125: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different mole fraction at 313.15K.

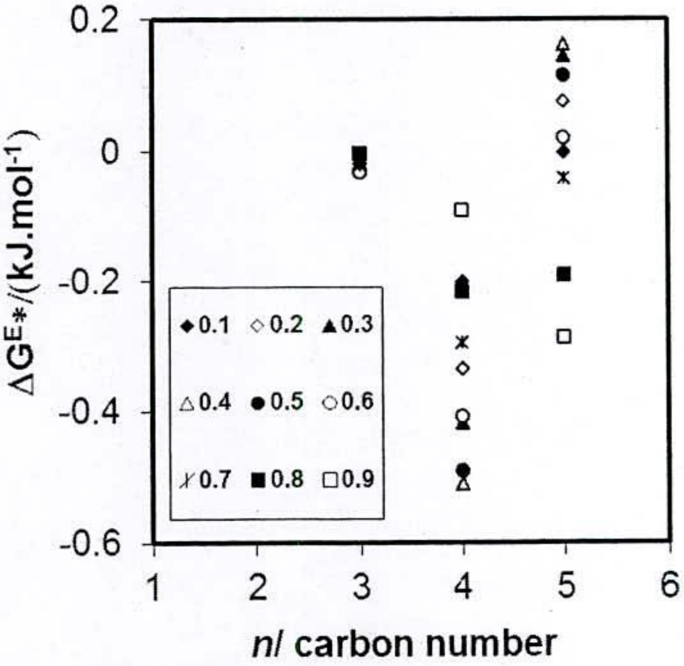

Figure 4.126: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different mole fraction at 323.15K.

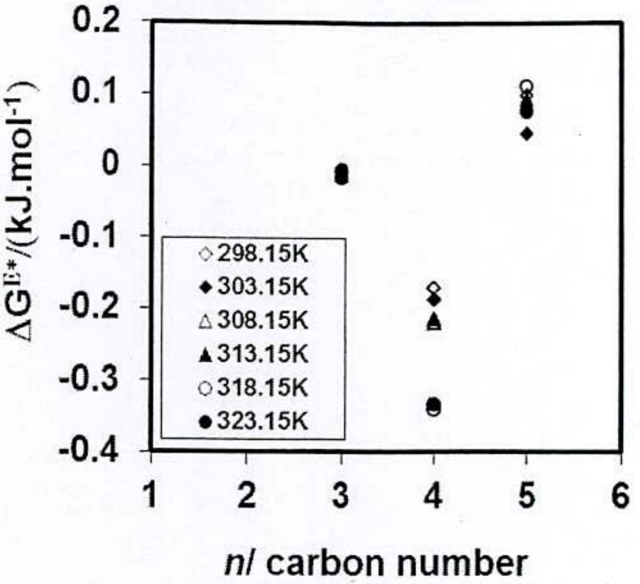

Figure 4.127: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different temperature at 0.2 mole fraction.

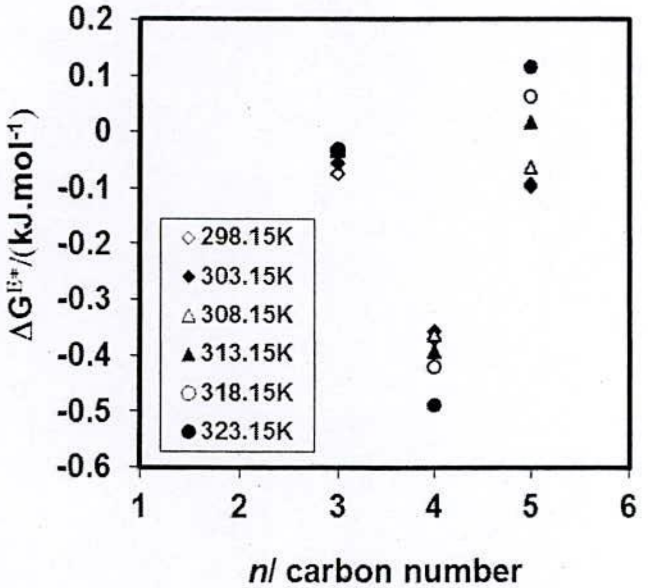

Figure 4.128: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different temperature at 0.5 mole fraction.

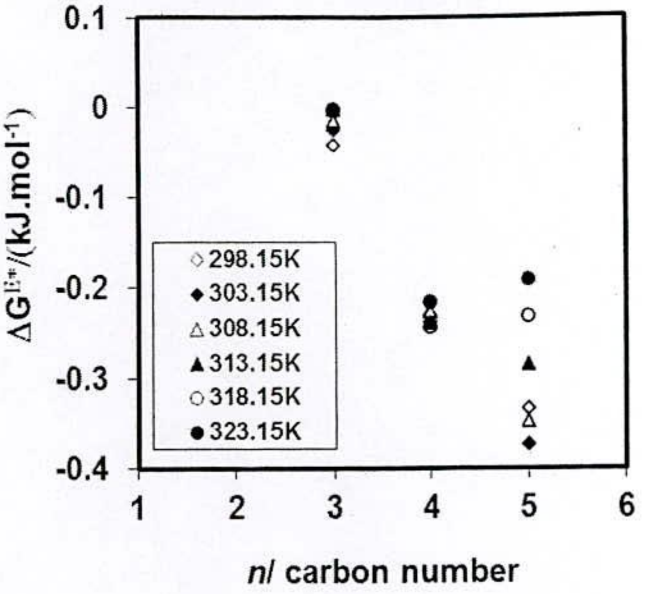

Figure 4.129: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of n-alcohols in 0.015M SDS + Ethanol with different temperature at 0.8 mole fraction.

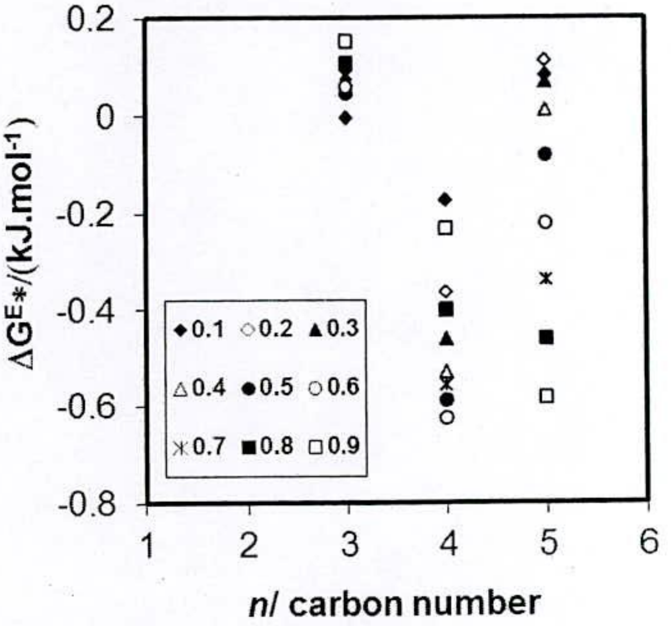

Figure 4.130: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanol with different mole fraction at 298.15K.

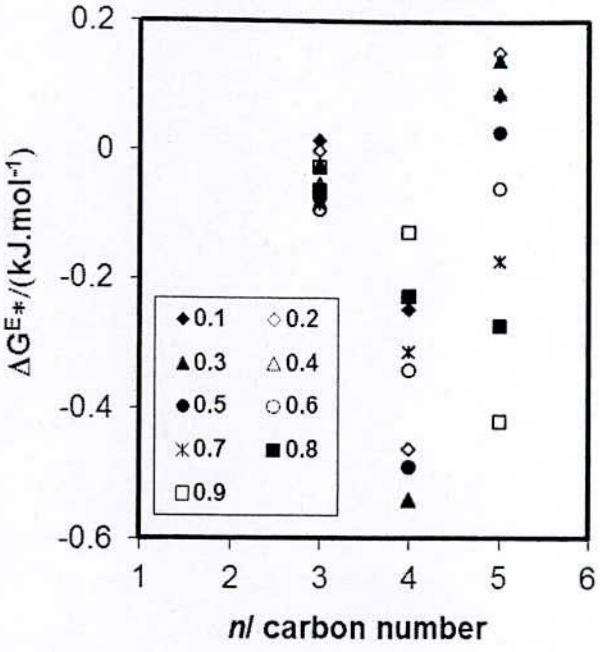

Figure 4.131: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanol with different mole fraction at 313.15K.

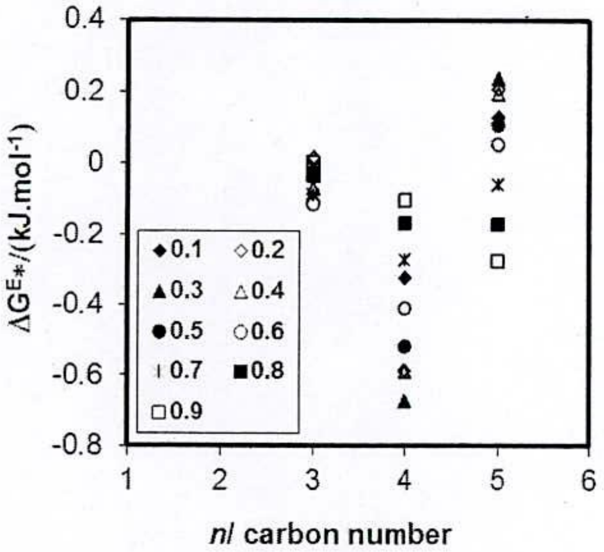

Figure 4.132: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanol with different mole fraction at 323.15K.

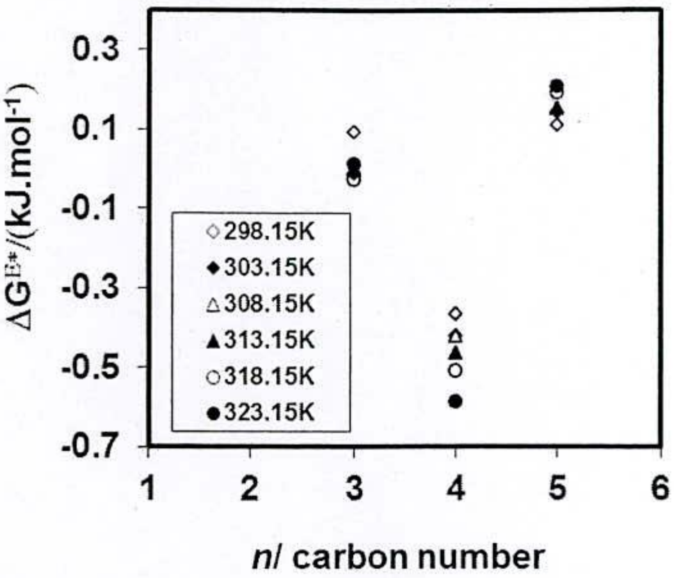

Figure 4.133: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanol with different temperature at 0.2 mole fraction.

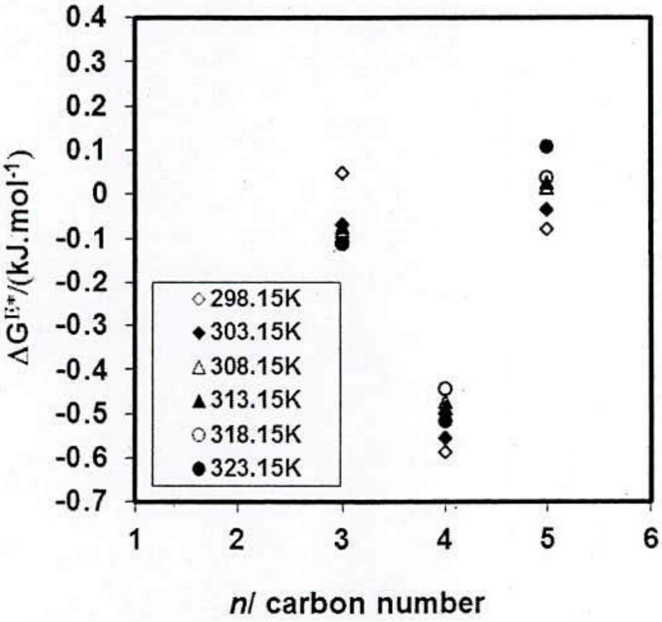

Figure 4.134: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso - alcohols in 0.015M SDS + Ethanol with different temperature at 0.5 mole fraction.

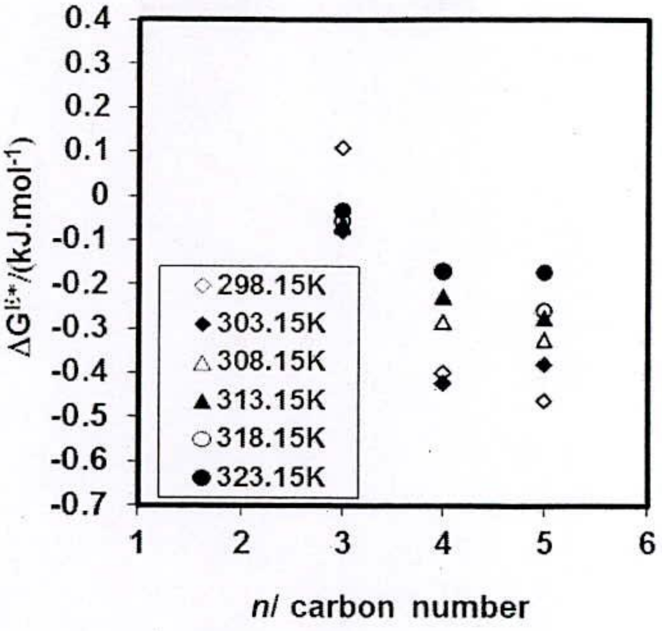

Figure 4.135: Dependence of the excess free energy (ΔG^{*E}) with carbon number (n) of iso-alcohols in 0.015M SDS + Ethanol with different temperature at 0.8 mole fraction.

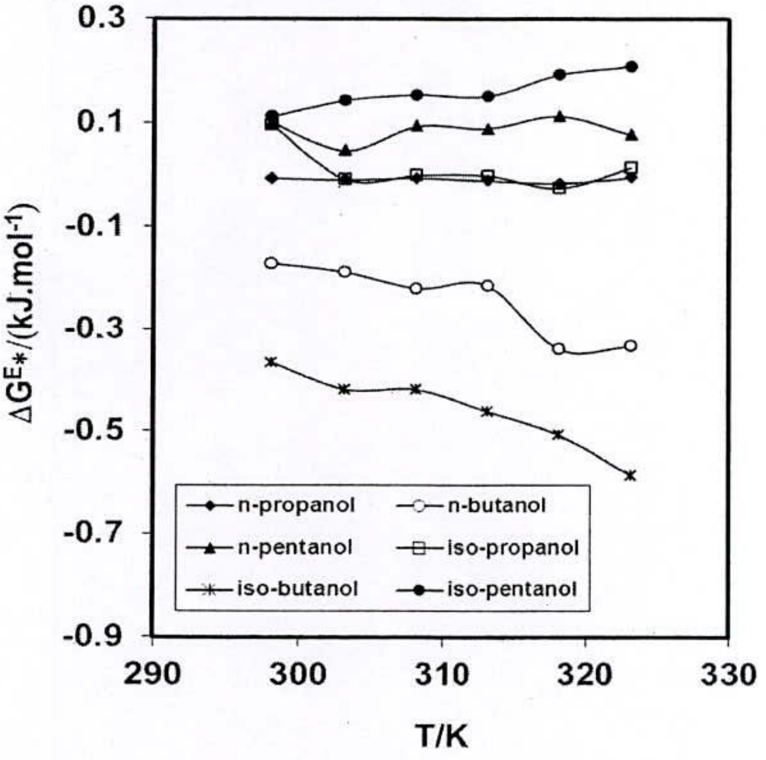

Figure 4.136: Comparison of change of excess free energy (ΔG^{E*}) vs temperature (T) of n-Propanol, n-Butanol, n-Pentanol, iso-Propanol, iso-Butanol and iso-Pentanol in 0.015M SDS+Ethanol at 0.2 mole fraction.

CHAPTER V

Conclusion

The critical micelle concentration (CMC) of Sodium Dodecyl Sulfate (SDS) in Ethanol was determined from the conductance, density and viscosity measurement. The estimated value of CMC was found to be 0.015 mol.L^{-1}.

The studies presented in this thesis are based on ternary (alcohols + 0.015M SDS + Ethanol) systems. The solution properties of ternary mixtures of *n*-Propanol + 0.015M SDS + Ethanol, *iso*-Propanol + 0.015M SDS + Ethanol, *n*-Butanol + 0.015M SDS + Ethanol, *iso*-Butanol + 0.015M SDS + Ethanol, n-Pentanol + 0.015M SDS + Ethanol and *iso*-Pentanol + 0.015M SDS + Ethanol show strong solute–solvent interactions. The values of V^E for the studied alcohols are positive throughout the whole range of composition at all the studied temperature. The observed values of V^E for the mixtures have been explained in terms of specific intermolecular interactions and structural contributions.

The viscosities increase slowly up to entire mole fraction of *n*-Propanol and *iso*-Propanol. For *n*-Butanol and *iso*-Butanol, the viscosities increase initially slowly up to ~0.6 mole fraction and later on, the viscosity increases sharply until the pure alcohol is reached. . For *n*-Pentanol and *iso*-Pentanol, the viscosities increase initially slowly up to ~0.8 mole fraction and later on, the viscosity increases very sharply until the pure alcohol is reached.

The excess viscosity, η^E values are found to be negative, indicating that the 0.015M SDS + Ethanol solutions of alcohols are non ideal. Excess viscosities are negative at all the temperatures over the entire range of composition for all the systems with minima occurring between 0.6-0.8 mole fraction of *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol. The interaction parameters, ε have been found to be negative and quite large in magnitude for all the systems. The negative ε of all the studied alcohols indicate that dispersion force is occurred.

The positive V^E, negative η^E, and negative ε for the 0.015M SDS+Ethanol + studied alcohols systems show agreement with the statements. On addition of alkanols in 0.015M SDS+Ethanol solution strong disruptive forces are appeared and H-bonding in alkanols is dissociated causing volume expansion is occurred. For the long chain or branched chain alkanols, maximum geometrical mismatch for the steric factor are occurred causing volume expansion is also seen. The volumetric properties are fully consistent with the viscometric properties.

The free energy, ΔG^* is found to be positive in magnitude indicating that the kinetic species involved in forming cavities or holes in liquid is given by the work required in forming the hole against surface tension of the solution. For *n*-Propanol, *iso*-Propanol, *n*-Butanol, *iso*-Butanol, n-Pentanol and *iso*-Pentanol in 0.015M SDS+Ethanol systems, ΔG^{*E} are negative over the entire composition range. The negative excess free energy, ΔG^{*E} indicates the presence of dispersion force. The entropy change, ΔS^* is found to be negative for all the studied alcohol systems. The negative ΔS^* apparently indicates more ordered orientation of the complexes formed in the activated state and thereby reduce their motional degrees of freedom. The enthalpy change, ΔH^* is positive for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process.

References

1. Timmermans, J., 1950, "Physico-chemical constants of pure organic compounds" Elsevier Publishing co. New York, 304-457.

2. Al-Azzawi, S.F, Awwad, A.M., 1990, "Excess Molar Volumes Excess Logarithmic Viscosities, and Excess Activation Energies of Viscous Flow for 2-Ethoxyethanol + γ-Butyrolactone and + Sulfolane at 303.15 K", J. Chem. Eng. Data, Vol. 35, pp. 411-414

3. Gong, Y-h., Shen, C., Lu Y-z., Meng, H and Li, C., 2012, "Viscosity and Density Measurements for Six Binary Mixtures of Water (Methanol or Ethanol) with an Ionic Liquid at Atmospheric Pressure in the Temperature Range of (293.15 to 333.15) K", J. Chem. Eng. Data, Vol. 57, pp. 33–39.

4. Awwad, A.M, Al-Dujaili, A.H and Salman, T.A., 2001, "Excess Molar Volumes and Viscosities of Binary and Ternary Mixture of Sulfolane + Benzene + 1-Alkanol at 303.15K", Iraqi J. Chem. Vol. 27, pp. 121-125.

5. Awwad, A.M, Al-Dujaili, A.H and Salman, H.E., 2001, "Refractive Index, Relative Permittivity and Excess Properties of Substituted Benzenes+ Sulfolane at 303.15 K", Iraqi J. Chem. Vol. 27, pp. 115-120.

6. Awwad, A.M, Al-Dujaili, A.H and Alian, N.R., 2000, "Dielectric Constants of the Binary Mixtures of 2-Ethoxyethanol + γ-Butyrolactone and + Sulfolane at 303.15 K Comparison with Theory", Iraqi J. Chem. Vol. 26, pp. 94-100.

7. Sacco, A. and Rakshit, A. K., 1975, "Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. III. Excess Volumes of Sulfolane with Each of Nine Alcohols". J. Chem. Thermodyn. **7**, pp.257-261.

8. Karvo, M., 1980, "Thermodynamic Properties of Binary and Ternary Mixtures Containing Sulfolane. V. Excess Enthalpies of Cyclohexane + Benzene, Cyclohexane + Toluene, Benzene + Sulfolane and Toluene + Sulfolane", J. Chem. Thermodyn. Vol. 12, pp. 635-639.

9. http://en.wikipedia.org/wiki/Alcohol.

10. Mc Bain, J. and Martin, J., 1914, J. Chem. Soc., Vol. 105, pp. 957.

11. Desnoyers, J.E, Caron, G., DeLisi, R., Roberts, D., Roux, A. and Perron, G., 1983, J. Phys. Chem., Vol. 87, pp. 1397.

12. Caron, G., Lindhemer, M., Perron, G., and Desnoyers, J. E., 1985, J. Coll. Inter. Sci., Vol. 106, pp. 324.

13. Cano-Gomez J., Iglesias-Silva, G.A., Ramos-Estrada, M. and Hall, K.R., 2012, "Densities and Viscosities for Binary Liquid Mixtures of Ethanol + 1-Propanol, 1-Butanol, and 1-Pentanol from (293.15 to 328.15) K at 0.1 MPa", J. Chem. Eng. Data, Vol. 57, pp. 2560−2567

14 Kumagai, A. and Yokoyama, C., 1998, "Liquid Viscosity of Binary Mixtures of Methanol with Ethanol and 1-Propanol from 273.15 K to 333.15", Int. J. Thermophys. Vol. 19, pp. 3−13.

15 Dizechi, M. and Marschall, E., 1982, "Viscosity of some binary and ternary liquid mixtures", J. Chem. Eng. Data, Vol. 27, pp. 358−363.

16. Karvo, M., 1982, J. Chem. Thermodyn., Vol. 15, p. 821.

17. Jannelli, L., Pansini, M. and Jalenti, R., 1984, J. Chem. Eng. Data, Vol. **29**, p. 263.

18. Motin, M.A, Hafiz Mia, M.A, Salim Reza, K.M, Yousuf, M.A. Nasimul Islam, A.K.M. Salam, M.A., 2012, "Effect of Sodium Dodecyl Sulfate on Volumetric Properties of Methanol Ethanol n-Propanol and iso-Propanol at (298.15 - 323.15)K", Dhaka Univ. J. Sci,. Vol. 60, pp.129-136.

19. Motin M.A, Hafiz Mia M.A, Nasimul Islam A.K.M, 2015,"Thermodynamic properties of Sodium Dodecyl Sulfate aqueous solutions with Methanol, Ethanol, n-Propanol and iso-Propanol at different temperatures" Journal of Saudi Chemical Society", Vol. 19, pp. 172–180.

20. Kabir M.H, Motin M.A. and Huque M.E. 2004, "Densities and excess molar volumes of Methanol, Ethanol and N-Propanol in pure Water and in Water + Surf Excel solutions at different temperatures", Physics and Chemistry of Liquids, Vol. 42, pp. 279-290.

21. Bhattarai, A., Chatterjee, S.K. and Niraula T.P., 2013, "Effects of concentration, temperature and solvent composition on density and apparent molar volume of the binary mixtures of cationic-anionic surfactants in methanol–water mixed solvent media", Springerplus, Vol. 2, pp. 280.

22. Hildebrand, J.H., 1949, Chemical Reviews; Vol. 44, pp. 37.

23. Battino, R., 1971, Chemical Reviews; Vol. 71, pp. 5.

24. Rice, O.K., 1949, Chemical Reviews; Vol. 44, pp. 69.

25. Scatchard, G., 1949, Chemical Reviews; Vol. 44, pp. 7.

26. McGlashan, M.L., 1962, Ann. Rev. Phys. Chem., Vol. 13, pp. 409.

27. Nothnagel, K.H, Abrams, D.S. and Pransnitz, J.M., 1973, Industr. Engg. Chem. Process Des. Develop., Vol. 12, p. 25.

28. Cruickshank, J.B. and Everett, D.H., 1953, Chem. Soc. Ann. Rep. Vol. 50, p. 80.

29. Parsonage, N.G. 1967, Chem. Soc. Ann. Rep., A 64, 57; A65, 33.

30. Toulon Kian, Y.S, Gerritaan, J.K. and Noore, N.Y., 1967, "Thermophysical Properties Research Literature Retrieval Guide", N. Y., Plenum Press.

31. Irving, J.B., 1967, NEL Report No. 630, East Kilbridge, Glasgo,w., No. 631, East.

32. Bahl, B.H, Tuli, G.D. and Bahl, A., 1994, "Essential of physical chemistry". S. Chand and company Ltd., pp. 380-381.

33. D.P. Shoemaker, C.W. Garland, J.J. Stein field and J.W. Nibler, 1981, "Experiments in physical chemistry", pp. 162-165, USA Mc-Graw-Hill, Fourth edition,

34. Wilson, J.M. Newcombl, R.J. Denaro A.R. and W Rickett, R.M., 1962, "Experimental in physical chemistry" Pergamon press, New York, 162-163.

35. Marignac, C., 1871, Ann. Chem. (Paris), Vol. 22, p. 415.

36. H.L. Friedman and C.V. Krishnan, 1973, "Water: A comprehensive Treatise", Vol. 3. Ch. 1, Ed. F. Frank, Plenum press, New York,

37. Garriga, R., Perez, P. and Gracia, M., 1995, "Vapour pressures at several temperatures T and excess functions at T) 298.15 K of (butanenitrile + hexan-1-ol or octan-1-ol)", J. Chem. Thermodyn. Vol. 27, pp. 1057- 1066.

38. S. Glasstone, 1948, "Text book of Physical chemistry" 2nd edition, 524, 496.

39. L. Grumberg and A.H. Nissan, 1949, Nature, 164, 799.

40. Eyring, H., 1931, J. Phys. Chem., Vol. 4, p. 283.

41. Nightingale, E.R. and Benck, R.F., 1959, "Viscosity of aqueous fluoride and sodium periodate solutions ionic energies and entropies of activation for viscous flow", J. Phys. Chem., Vol. 63, pp. 1777-1781.

42. Thirumaran, S. and Job Sabu. K., 2012, "Ultrasonic studies on interionic interactions of some alkali metal halides in aqueous d-glucose solution at varying molalities and temperatures, Journal of Experimental Sciences", Vol. 3, pp. 33-39.

43. Thirumaran, S. and Job Sabu. K. 2009. "Ultrasonic investigation of amino acids in aqueous sodium acetate medium", Ind. J. Pure Appl. Phys., Vol. 47, pp. 87-96.

44. Saleh M. A, Habibullah M. and Khan N.U.A., 1995, Chittagong Univ. Stud. Part II: Sci., Vol. 19, pp. 191.

45. Monoranjan Mondal, 2013, "Study of the effects of Aceotonitrile on the Alcohol solutions by Volumetric and Viscometric measurements", M.Phil Thesis, Dept. of chemistry, KUET.

46. Md. Fazlul Haque, 2011, "Studies on Volumetric and Viscometric Properties of some binary and ternary liquid systems", M.Phil Thesis, Dept. of chemistry, KUET.

47. Md. Abdul Hafiz Mia, 2010, "Volumetric and Viscometric Studies of some binary and ternary Sodium Dodecyl Sulfate (SDS) containing Alcohol system" M.Phil Thesis, Dept. of chemistry, KUET.

48. Pikkarainen L., 1987, J. Chem. Eng. Data, Vol. 32, p. 429.

49. Pikkarainen L., 1983, J. Chem. Eng. Data, Vol. 23, p. 344.

50. Garcia, B, Herrera C. and Leal L.M., 1991, J. Chem. Eng. Data, Vol. 36, p. 269.

51. Treszczanowicz, A.J. Kiyohara, O. and Benson, G.C., 1981, "Excess Molar Volumes for *n* -Alkanes Binary Mixtures of Decan-1-ol + *n* -Pentane, + *n* -Hexane, + *n* -Octane, + n -Decane, and + n-Hexadecane", J. Chem. Thermodyn., Vol. 13 , pp. 253-260.

52. Ratkovics, F, Salamon, T, Domonkos L., 1974, Acta Chim. Acad. Sci. Hung. Vol. 83, p. 71.

53. Costas, M., Patterson, D., 1985, J. Chem. Soc., Farady Trans., I Vol. 88, p.635.

54. Aminabhavi, T.M. and Gopalakrishna, B., 1996, J. Chem. Eng. Data . Vol. 40, p.452.

55. Saleh, M.A., Akhtar, S. Ahmed, M.S, Uddin, M.H., 2002, "Excess molar volumes and thermal expansivities of aqueous solutions of dimethylsulfoxide, tetrehydrofuran and 1,4- dioxane". Phys . Chem. Liq., Vol. 40, pp. 621-635.

56. www.ncbi.nlm.nih.gov/pmc/articles/PMC2826382

57. Larsen G., Ismail Z.K., Herreros B. and Parra R.D., 1998, J. Phys. Chem., Vol. 102,p. 4734.

58. Andini S., Castronuovo G., Elia V. and Fasano L., 1990, J. Chem. Soc. Farday Trans. Vol. 86, p. 3567.

59. D'Aprano A., Donato I.D. and Liveri V.T., 1990, J. Soln. Chem., Vol. 19, p. 711

60. Akhtar S., Hossain K.M.S. and Saleh M.A., 2002, Phys. Chem. Liq., Vol. 40, p. 435.

61. Ali A., Nain A.K., Lal B. and Chand D., 2004, Int. J. Themophys. Vol. 25, p.1835.

62. Saleh M.A., Habibullah M., Ahmed M.S., Ashraf Uddin M., Uddin S.M.H., Uddin M.A., Khan F.M., 2005, Phys. Chem. Liq. Vol. 43, p. 485.

63. Nikam P.S., Jagdale B.S., Sawant A.B. and Hasan M., 2000, J. Chem. Eng. Data, Vol. 45, p. 559.

64 F. Franks, 1983, Water, The Royal Society of Chemistry, London.

65. Fort, R.J. and Moore, W.R., 1966, Trans. Farad. Soc. Vol. 62, pp. 112-1119.

66. Nigam, R.K. and Mahl B.S., 1972, Indian J. Chem., Vol. 9, p.1255.

67. Chowdhury, M.A., Majid, M.A. and Saleh, M.A., 2001, J. Chem. Thermodyn., Vol. 33, p. 347.

68. Covington, A.K. and Jones P., 1968, Hydrogen Bonded Solvent Systems, Taylor & Francis Ltd., London.

69. Kipkemboi, P.K. and Easteal, A.J., 1994, Can. J. Chem. Vol. 72, p.1937.

70. Gojlo, M., Smiechoeski J. and Stangret J., 2005, J. Mol. Sturcture, Vol. 744, pp. 809

71. Djojoputro, H. and Ismadji, S., 2005, "Density and Viscosity of Several Aldehydes Fragrance Compounds in Their Binary Mixtures with Ethanol at (298.15 K, 308.15 K, and 318.15 K)", J. Chem. Eng. Data. Vol. 50, pp. 2003-2007.

72. Zarei, H.A. Mirhidari N. and Zangeneh Z., 2009, "Densities, Excess Molar Volumes, Viscosity, and Refractive Indices of Binary and Ternary Liquid Mixtures of Methanol (1) + Ethanol (2) + 1,2-Propanediol (3) at 81.5 kPa", J. Chem. Eng. Data. Vol. 54, pp. 847–854.

73. lvarez, E. A., Cancela, A. N. Maceiras, R., Navaza, J. M. and Taboas, R., 2006, "Density, Viscosity, Excess Molar Volume, and Viscosity Deviation of Three Amyl Alcohols + Ethanol Binary Mixtures from 293.15 to 323.15 K". J. Chem. Eng. Data. Vol. 51, 940-945.

74. Djojoputro, H. and Ismadji, S., 2005, "Density and Viscosity of Binary Mixtures of Ethyl-2-methylbutyrate and Ethyl Hexanoate with Methanol, Ethanol, and 1-Propanol at (293.15, 303.15, and 313.15) K", J. Chem. Eng. Data. Vol. 50, pp. 1343-1347.

75. Lee M-J, Lin T-K, Pai Y-H and Lin K-S, 1997, "Density and Viscosity for Monoethanolamine + 1-Propanol, + 1-Hexanol, and + 1-Octanol", J. Chem. Eng. Data. Vol. 42, pp. 854-857.

76. Zarei, H.A. and Shahvarpour, S., 2008, "Volumetric Properties of Binary and Ternary Liquid Mixtures of 1-Propanol (1) + 2-Propanol (2) + Water (3) at Different Temperatures and Ambient Pressure(81.5 kPa)", J. Chem. Eng. Data. Vol. 53, pp. 1660–1668.

77. Zafarani-Moattar M.T. and Majdan-Cegincara R., 2008, "Density, Speed of Sound, and Viscosity of Binary Mixtures of Poly(propyleneglycol) 400 + Ethanol and + 2-Propanol at Different Temperatures", J. Chem. Eng. Data. Vol. 53, pp. 2211–2216.

78. Weng W-L, 1999, "Viscosities and Densities for Binary Mixtures of Anisole with 1-Butanol, 1-Pentanol, 1-Hexanol, 1-Heptanol, and 1-Octanol", J. Chem. Eng. Data. Vol. 44, pp. 63-66.

79. Chen, J-T, Weng W-L and Chu H-P, 2006, "Densities and Viscosities of Binary Mixtures of 1-Butanol with Methacrylic Acid, Benzyl Methacrylate, and 2-Hydroxyethyl Methacrylate between 288.15 K and 318.15 K", J. Chem. Eng. Data. Vol. 51, pp. 1441-1445.

80. Jose J. Cano-Gómez and Gustavo A. Iglesias-Silva, 2012, "Densities and Viscosities for Binary Liquid Mixtures of Ethanol + 1-Propanol, 1-Butanol, and 1-Pentanol from (293.15 to 328.15) K at 0.1 MPa", J. Chem. Eng. Data. Vol. 57, pp. 2560−2567.

81. Micael G. Sanchez B., Gustavo A. Silva I. and Estrada-Baltazar, A., 2010, "Densities and Viscosities of Binary Mixtures of *n*-Butanol with 2-Butanol, Isobutanol, and tert-Butanol from (303.15 to 343.15) K", J. Chem. Eng. Data. Vol. 55, pp. 2310–2315.

82. Indraswati, N., Mudjijati, Wicaksana, F. and Hindarso, H., 2001, "Measurements of Density and Viscosity of Binary Mixtures of Several Flavor Compounds with 1-Butanol and 1-Pentanol at 293.15K, 303.15 K, 313.15 K, and 323.15 K", J. Chem. Eng. Data. Vol. 46, pp. 696-702.

83. Pai Y-H and Chen, L-J., 1998, "Viscosity and Density of Dilute Aqueous Solutions of 1-Pentanol and 2-Methyl-2-butanol", J. Chem. Eng. Data. Vol. 43, pp. 665-667.

84. Tahery, R. Modarress, H. and Satherley, J., "Density and Surface Tension of Binary Mixtures of Acetonitrile + 1-Alkanol at 293.15 K".

85. Saleh, M.A., Akhtar S. and Ahmed, M.S., 2006, "Density, viscosity and thermodynamic activation of viscous flow of water/acetonitrile", Physics and Chemistry of Liquids, Vol. 44, pp.551–562.