Physico-Chemical Properties of Some Alcohols in SDS-Acetonitrile Containing Ternary Systems

by

Biswajit Kumar Das

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Declaration

This is to certify that the thesis work entitled “Physico-Chemical Properties of Some Alcohols in SDS-Acetonitrile Containing Ternary Systems” has been carried out by Biswajit Kumar Das in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work has not been submitted anywhere for the award of any degree or diploma.

Signature of Supervisor

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Abstract

The critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in 80% acetonitrile + 20% water was determined from the conductance and viscosity measurement. They shows a sharp break in their values where micelle starts to form. The estimated CMC of SDS was found to be 0.02 mol. L^{-1}.

Densities and viscosities of ternary mixtures of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS), n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS), iso-Propanol +(80% acetonitrile + 20% water + 0.02M SDS),n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS), iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS), n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) and iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) have been studied over the entire range of composition ($0 < X_2 < 1$) at 298.15-323.15K with an interval of 5K. In pure state the density of alcohol has been found to be in the order of:

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

The values of densities of Alkanols + (80% acetonitrile + 20% water + 0.02M SDS) at equimole fraction solvent systems has been found to be

n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)
and
iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)

The value of the density of alcohols in 80% acetonitrile + 20% water + 0.02M SDS increases with increasing of composition of the alcohols. The densities of all alcohols

increase with carbon number which may be depend on the molecular weight of alcohols and structural formula. The densities decrease regularly with increasing of temperature. This is due to the thermal agitation and hence the dipole-dipole interaction or the 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 negative over the entire range of composition, showing minima at ~ 0.5 mole fraction of Ethanol, ~ 0.8 mole fraction of n-Propanol, ~ 0.8 mole fraction of iso-Propanol, ~ 0.7-0.8 mole fraction of n-Butanol, ~ 0.8 mole fraction of iso-Butanol, ~ 0.7 mole fraction of n-Pentanol, ~ 0.7 mole fraction of iso-Pentanol.

The increasing of V^E with carbon chain length of alcohols may be related to increase of the size of alcohols. The values of V^E for the studied alcohols increase with 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 different temperatures have also been determined. The viscosities increase initially slowly up to ~ 0.8 mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in 80% acetonitrile + 20% Water + 0.02M SDS systems and later on, the viscosities increases sharply until the pure alcohol is reached specially at lower temperature. In the pure state the viscosity of the alcohols has been found to be in the order of

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

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

The excess viscosities, η^E values are found to be negative, indicating that the (80% acetonitrile + 20% water + 0.02M SDS) solutions of alcohols are non-ideal. Excess viscosities are negative at all the temperature over the entire range of composition for all the systems with minima occurring between 0.7-0.8 mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol. The negative excess viscosities, η^E of the systems indicate that the dissociation of component through dispersion force or steric hindrance. The position of minima virtually does not change remarkably with the variation of temperature.

The negative V^E, negative η^E and negative ε for the systems indicate the segmental inclusion of Acetonitrile in the interstices of polymolecular alkanols aggregate; these will be fewer surfaces available for friction that may results in a reduction of viscosity. For long chain or branched chain alkanols, maximum geometrical for the steric hindrance are occurred.

The thermodynamic parameters such as free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) change of activation for the viscous flow for these systems were examined for the entire range of composition. The free energy ($\Delta G^{\#}$) were found to be positive in magnitude indicating that the kinetic species involved in forming cavities or holes in the liquid medium is giving by the work required in forming the hole against surface tension of the solution. The excess properties (V^E, η^E, $\Delta G^{\#E}$) data have been fitted by the least square method to the four parameter Redlich-kister equation and the values of the parameter a_i and standard deviation have been reported.

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Nomenclature

SDS	Sodium dodecyl sulphate
CMC	Critical micelle concentration
ρ	Density
ρ_1	Density of solvent
ρ_2	Density of solute
ρ_{mix}	Density of the mixture
V^E	Excess molar volume
η	Viscosity
η^E	Excess viscosity
η_{expt}	Observed viscosity
η_{id}	Ideal viscosity
σ	Standard deviation
ε	Interaction parameter
c	Molarity
X_1	Mole fraction of solvent
X_2	Mole fraction of solute
M_1	Molecular mass of solvent in gram
M_2	Molecular mass of solute in gram
V_o	Molar volume of solvent
V_m	Molar volume of solution
a_i	Fitting coefficient
$\Delta H^\#$	Enthalpy
$\Delta G^\#$	Free energy
$\Delta S^\#$	Entropy
v_1	Volume of solvent in mL.
v_0	Volume of bottle.

Nomenclature

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

A solution is a homogenous mixture of substances with variable composition. The substance present in the major proportion is called the solvent, whereas the substance present in the minor proportion is called the solute. The majority of chemical processes are reactions that occur in solution. The liquid state, being an intermediate state between gaseous and solid states, retains some characteristics of both the gaseous and solid states. The liquid state, thus, cannot be adequately defined as the gaseous and the solid states. The molecular and macroscopic behavior of liquids varies from liquid to liquid due to characteristic intermolecular interactions. The behavior of multi-component mixtures, on account of molecular interactions between dissimilar molecules, becomes still more difficult to interpret. In view of these facts there are serious problems in formulation of any general theory of solution [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 properties of any system have to be interdependent, since these essentially originate from the most probable distribution of energy between the constituent molecules comprising the system. There has, therefore, been interest for seeking interrelations between the macroscopic properties of any system. It should, in principle, be possible to express the value of any macroscopic property in terms of the known values of the other. Since viscosity coefficient is a macroscopic property under non equilibrium condition, there has been a considerable effort for establishing its relationship with thermodynamic properties of a system [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.

For example due to the mixing of liquids their may be either positive or negative deviation of volume and thus different from additively 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 breakdown of association of the species formed either by chemical forces such as H-bonding or by physical forces such as dipole-dipole and dipole-induced dipole interaction.

Physical properties like density, viscosity, surface tension, conductivity, dielectric constant, refractive index, group frequency shifts in I.R. spectra etc. give an indication about the molecular structure as well as the molecular interactions that occur when liquids are mixed together. The density and viscosity are two fundamental physico-chemical properties of which are easy, simple, inexpensive and precise tools, by which one can get the valuable information about the molecular interactions in liquids and liquid mixture correlated with equilibrium and transport properties. The thermodynamic and excess thermodynamic data are used subsequently by a variety of physical scientists including chemical kineticists and spectroscopists involved in reaction occurring in solution and by chemical engineers engaged in the operation and design of chemical reactor, distillation columns or other type of separation devices. From the above mentioned properties, quantitative conclusion can hardly be drawn about the molecular interactions even in simple liquids or their mixtures.

Our present investigation is based on the methods of physico-chemical analysis, which is a useful tool in getting sound information about the structure of some alcohols, water and surfactant and in studying the liquid-liquid interaction in binary and ternary systems.

1.2 Physical 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 [9]. For example Ethanol with a MW of 46 has a b.p 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.

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).

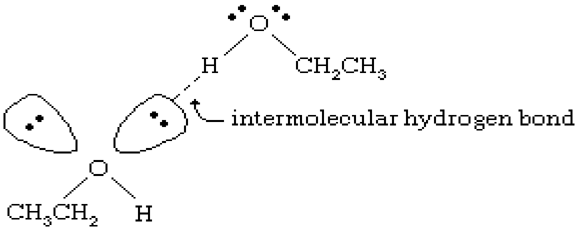

Fig. 1.1

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 [10]. 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 [11].

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[12].

Alcohols are self-associated liquids through H-bonding. Alcohols have a wide use in industry and certain alcohols are solvents for fats, oils, resins, drugs, paints, varnish, perfumes, cosmetics and nitrocellulose [13-14]. Alcohols can also be used in the synthesis of many other organic compounds. Mixtures of alcohols can be used as oxygenates in fuels [14]. Oxygenated compounds are important materials in the oil industry because of their application in enhancing octane number in gasoline as additives and pollution reducing properties. Binary and ternary mixtures of alcohols 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 molecular interaction.

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^o 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 a polar 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-1.1. 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 1.1: 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, however 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(1) pointed out that this seemingly anomalous behavior could be explained in terms of organized aggregates or micelle , of the surfactant ions in which the lyophobic 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. Micellization 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 micellization 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 breakdown 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. can fit the apparent molar quantities of monomeric surfactant over a wide concentration range below and above the CMC, Recently this model has been extending by Caron et al. 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 Factors affecting critical micelle concentrations

(a) Increasing the hydrophobic part of the surfactant molecules favors micelle formation (see Table 1.2), in aqueous medium, the CMC of ionic surfactants is approximately halved by the addition of each CH_2-group. For non-ionic surfactants this effects is usually even more pronounced. This trend usually continues up to about the C_{16} member. Above the C_{18} member the CMC tends to be approximately constant.

Table 1.2: Critical micelle concentrations for a homologous series of sodium alkyl sulfate in water at 40 ^{0}C

Number of carbon atoms	8	10	12	14	16	18
CMC/10^{-3}mol dm^{-3}	140	33	8.6	2.2	0.58	0.23

(b) Micelle formation is opposed by thermal agitation and CMC’s would thus be expected to increase with increasing temperature. This is usually, but not always true.

(c) With ionic micelles, the addition of simple electrolyte reduces the repulsion between the charged groups at the surface of the micelle by the screening action of the added ions. The CMC is therefore, lowered, as illustrated in table 1.3.

Table 1.3: Critical micelle concentrations of sodium dodecyl sulfate in aqueous sodium chloride solutions at 25^0C.

Concentration of NaCl/ mol dm^3	0	0.01	0.03	0.1	0.3
CMC/10^{-3}mol dm^{-3}	8.1	5.6	3.1	1.5	0.7

The addition of organic molecules can affect CMC's in a variety of ways. The pronounced changes are affected by those molecules (e.g. medium chain-length alcohols) which can be into the outer regions of the micelle. Therefore, they can reduce electrostatic repulsion and steric hindrance, thus lowering the CMC. Micelles containing more than one surfactant often form readily with a CMC lower than any of the CMC's of the pure constituents.

Organic molecules may influence CMC's at higher additive concentration by virtue if their influence of water structuring. Sugars are structure-makers and such cause a lowering of CMC's whereas urea and formamide are structure-breaker and their addition cause an increase in CMC.

1.7 Structure of micelle

Micellar theory has developed in a somewhat uncertain fashion and is still in many respects open to discussion. Possible micelle structures include the spherical, lamellar and cylindrical arrangements illustrated schematically in Figure 1.2 Living Cells can be considered as micellar-type arrangements with a vesicular structure.

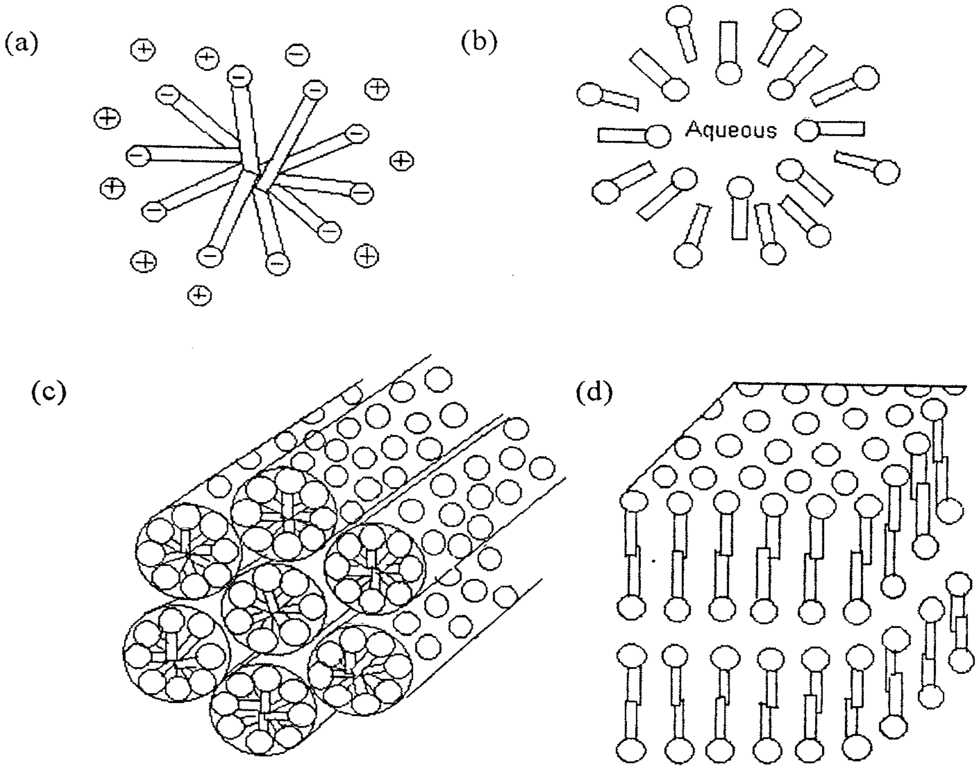

Figure 1.2: Micellar structures: (a) Spherical (anionic) micelle. This is the usual shape at surfactant concentrations below about 40 percent. (b) Spherical vesicle bilayer structures, which is representative of the living cell. (c) and (d) Hexagonal and lamellar phase formed cylindrical and lamellar micelles, respectively. These, and other structures, exist in highly concentrated surfactant solutions.

Typically, micelles tend to be approximately spherical over a fairly wide range of concentration above the CMC, but there are marked transitions to larger, non-spherical liquid-crystal structures at high concentrations. Systems containing spherical micelles tend to have low viscosities, whereas liquid-crystal phases tend to have high viscosities. The free energy of transition between miceller phases tend to be small and, consequently, the phase diagrams of these systems tend to be quite complicated and sensitive to additive.

Some of experimental evidence favoring the existence of spherical, liquid-like micelles is summarized, as follows:

1. Critical micelle concentrations depend almost entirely on the nature of the lyophobic part of the surfactant. If micelle structure involved some kind of crystal lattice arrangement, the nature of the lyophilic head group would also be expected to be important.

2. The micelle of a given surfactant is of approximately mono-dispersed and their size depends predominantly on the nature of the lyophobic part of the surfactant molecules. One would expect the radius of spherical micelle to be slightly less than the length of the constituents units; otherwise the hydrocarbon chains would be considerably buckled or the micelle would have either a hole or ionic groups in the center. The radii of micelles calculated from diffusion and light scattering data support this expectation. For straight-chain ionic surfactants the number of monomer units per micelle, m, and the number of carbon atoms per hydrocarbon chain, n, are approximately related as follows:

N	12	14	16	18
m	33	46	60	78

Laminar and cylindrical models, in contrast, provide no satisfactory mechanism by which the size of the micelles might be limited.

Earlier Mc Bain assumed two kinds of micelles: one is a spherical ionic micelle of not more than ten monomers formed in dilute solution before the CMC and the second kind of micelle formed is lamellar in shape consisting of hydrocarbon chain arranged parallel to each other. The basic feature of roughly spherical micelles is worked out by G.S. Hartly (figure 1.3). He suggested that the surfactant molecules are completely dissociated and unaggregated below the CMC while at CMC the aggregation of the amphiphiles occurs to give, initially, relatively small micelles. These micelles then rapidly over a narrow concentration rang to a size which then becomes independent of concentration. Further addition of surfactant causes only an increase in the number of micelles. Thus Harley,s model predicts only one type of micelle, which above the CMC remain constant in aggregation number. The classical Hartley model assumes a liquid-like interior of the micelle approximating in structure to that of liquid paraffin surrounded by a polar layer of head groups, counter ions and water. The major features to the Hartley model have been verified through many experimental studies. However a number of workers [15-16] did not accord with the view of spherical structure of the aggregates the results of angular light scattering studies by debye and anqcker [16] indicated that neither a sphere nor a disc-shaped micelle is formed but rather a rod like micelle having the general shape of a stock of coins may be formed. This model also fill reasonably well into the kind of structure suggested by x ray measurement of more concentrated solutions surfactant having long alkyl chains may upon sonifications in aqueous media, form vesicles, this type of micelle formation depends upon the length of alkyl chains and the nature of the hydrophilic groups.

In 1955 Tartar [17] described an ellipsoidal model for aggregated surfactants, which due to constraint introduced by the length incapable of aggregating to form a sphere; this model was subsequently adopted and refined by others [18-19]. The smell angle x-ray scattering studied by Reiss Husson and Luzzlatil showed different surfactant system classified the ionic micelles as being either:

(a) Spherical at all concentration,
(b) Rod shaped at all concentration,
(c) Spherical at low concentration and rod shaped at high concentration.

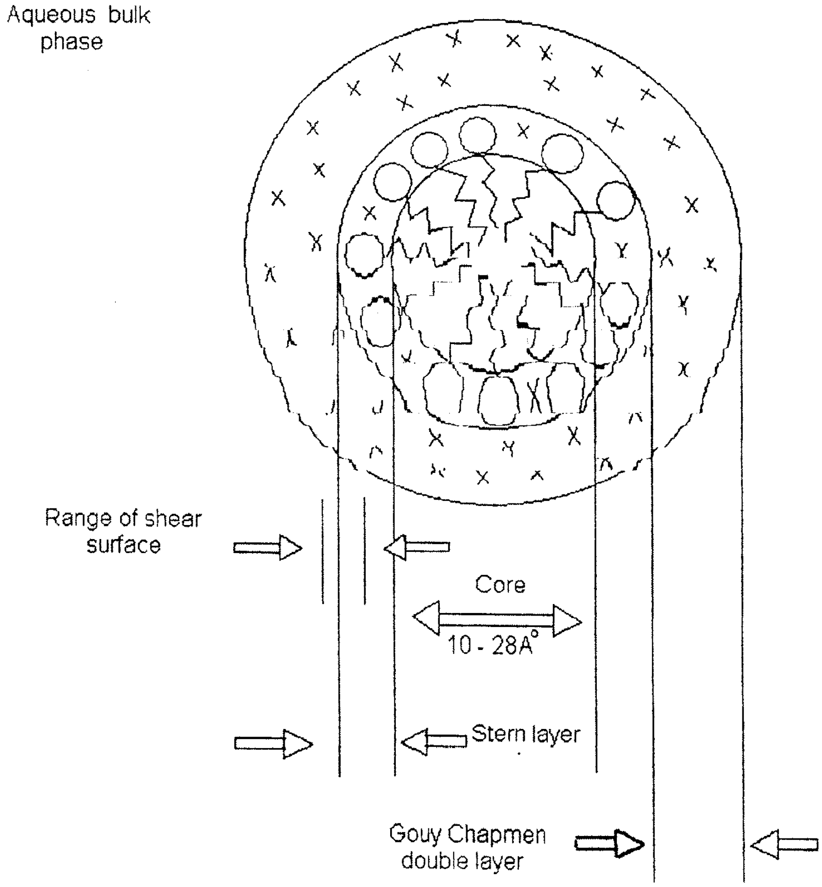

Figure 1.3: A two-dimensional schematic representation of a model of an ionic micelle, x the counter ions. (Adapted from “Solution Chemistry” Ed.K I. Mittal, Planum press, New York 1979)

In an attempt to develop a consistent interpretation of the result of a variety of experimental studies, stigter [20] introduced a rather detailed model for an ionic micelle. According to these model three regions, (Figure 1.3) can be identified; (a) a spherical micelle cores (b) an aqueous stern layer and (c) the Gouy Chapman diffuse double layer. The spherical core of the micelle is formed from hydrocarbon part of the surfactants molecules with radius equal to the length of the hydrocarbon chain of the surfactants molecule. The ionic head of the micellized surfactants and a fraction of the counter ions form the stern layer and outside the sphere surface is the Gouy Chapman diffuse double layer.

1.8 Physical properties of water

Water has a very simple atomic structure. The nature of the atomic structure of water causes its molecules to have unique electrochemical properties. The hydrogen side of the water molecule has a slight positive charge. On the other side of the molecule a negative charge exists. This molecular polarity causes water to be a powerful solvent and is responsible for its strong surface tension.

When the water molecule makes a physical phase change its molecules arrange themselves in distinctly different patterns. The molecular arrangement taken by ice (the solid form of the water molecule) leads to an increase in volume and a decrease in density. Expansion of the water molecule at freezing allows ice to float on top of liquid water.

1.9 Structure of water

It has been recognized that water is an 'anomalous' liquid many of its properties is differ essentially from normal liquids of simple structures [21]. The deviations from regularity indicate some kind of association of water molecules. The notable unique physical properties exhibited by liquid water are [22] : 1) negative volume of melting ii) density maximum in normal liquid range (at 4^{0}C) iii) isothermal compressibility minimum in the normal liquid range at (46^{0}C) iv) numerous crystalline polymorphs v) high dielectric constant vi) abnormally high melting, boiling and critical temperatures for such a low molecular weight substance that is neither ionic nor metallic vii) increasing liquid fluidity with increasing pressure and viii) high mobility transport for H^{+} and OH^{-} ions pure water has a unique molecular structure. The O-H bond length is 0.096 nm and the H-O-H angle 104.5^{0}. For a very long time the physical and the chemist have pondered over the possible structural arrangements that may be responsible for imparting very unusual properties to water. To understand the solute water interaction the most fundamental problem in solution chemistry the knowledge of water structure is a prerequisite. The physico-chemical properties of aqueous solution in most of the cares are interpreted in terms of the structural change produced by solute molecules. It is recognized that an understating of the structural changes in the solvent may be crucial to study of the role of water in biological systems.

Various structural models that have been developed to describe the properties of water may generally be grouped into two categories, namely the continumm model and the mixture models. The continumm models [23-24] treat liquid water as a uniform dielectric medium, and when averaged over a large number of molecules the environment about a particular molecules is considered to be the same as about any other molecules that is the behavior of all the molecules is equivalent.

The mixture model theories [25-27] depict the water as being a mixture of short lived liquid clusters of varying extents consisting of highly hydrogen bonded molecules which are mixed with and which alternates role with non-bonded monomers.

Among the mixture models, the flickering cluster of Frank and Wen [28], latter developed by Nemethy and scherage [23], is commonly adopted in solution chemistry. Properties of dilute aqueous solutions in terms of structural changes brought about by the solutes can be explained more satisfactorily using this model than any other model. According to this model the tetrahedraly hydrogen bonded clusters, referred to as bulky water $(H_2O)_b$, are in dynamic equilibrium with the monomers, referred to as dense water, $(H_2O)_d$ as represented by [16].

$$(H_2O)_b \rightleftharpoons (H_2O)_d$$

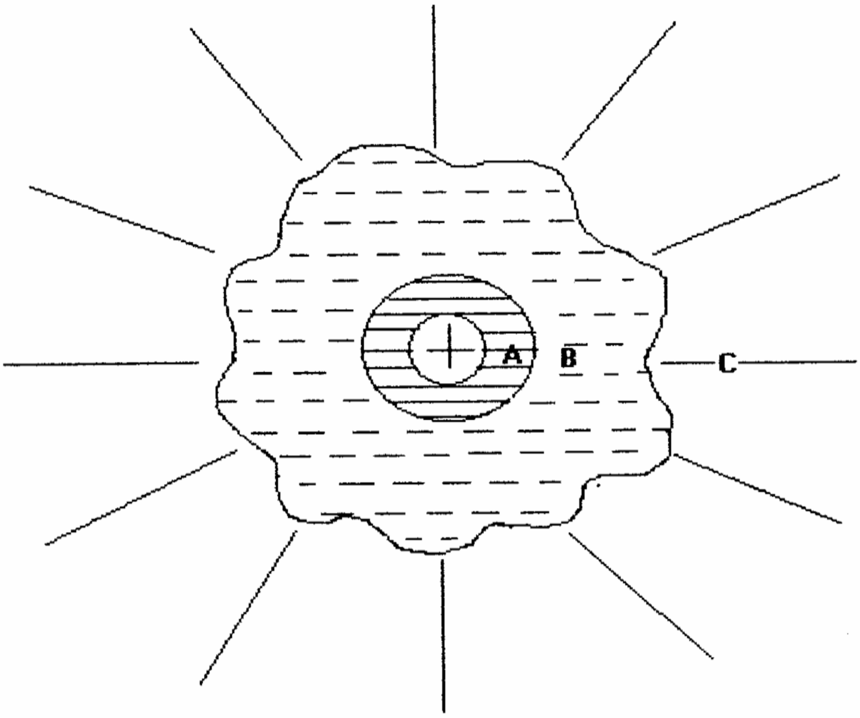

Fig 1.4: Frank and Wen model for the structure modification produce by an ion

The hydrogen bonding in the clusters is postulated to be cooperative phenomenon [29]. So that when one bond forms several other also come into existence will be dissolved. The properties of solution can be accounted for in terms of solvent-solvent, solvent-solute and solute-solute interaction. In terms of thermodynamics, the concentration dependence of a given property extrapolated to the limit of infinite dilution provides a measure of solute-solvent interactions. Solute-water interaction or hydration phenomenon can be conveniently classified into three basic types:

i. Hydrophilic Hydration
ii. Ionic hydration
iii. Hydrophobic hydration

The introduction of a solute into liquid water produces changes in the properties of the solvent which are analogous to these brought about by temperature or pressure. The solute that shifts the equilibrium to the left and increase the average half-life of the clusters is termed as structure maker whereas that which has an effect in the opposite direction is called 'Structure breaker'.

The experimental result on various macroscopic properties provides useful information for proper understanding of specific interactions between the components and the structure of the solution. The thermodynamic and transport properties are sensitive to the solute-solvent, solute-solute, and solvent-solvent interaction. In solution systems these three types of interaction are possible but solute-solute interaction are negligible at dilute solutions. The concentration dependencies of the thermodynamic properties are a measure of solute-solute interaction and in the limit of infinite dilutions these parameters serve as a measure of solute-solvent interactions. The solute induced changes in water structure also result in a change in solution viscosity.

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1.10 Hydrophilic hydration

Solvation occurs as the consequences of solute-solvent interactions different from those between solvent molecules themselves. The solubilization of a solute molecule in water is characterized by changes in the water structure that depend on the nature of the solute. Dissolution of any solute will disrupt the arrangement of water molecules in the liquid state and create a hydration shell around the solute molecule. If the solute is an ionic species, then this hydration shell is characterized to extend from an inner layer where water molecules near the charge species are strongly polarized and oriented by the electrostatic field, through an intermediate region where water molecules are significantly polarized but not strongly oriented, to an outer solvent region of bulk water where the water molecules are only slightly polarized by the electric field of the ion [19].

1.11 Hydrophobic hydration and hydrophobic interaction

The hydrophobic effect refers to the combined phenomena of low solubility and the entropy dominated character of the solvation energy of non-polar substances in aqueous media [31]. It is also reflected by anomalous behavior in other thermodynamic properties, such as the partial molar enthalpies, heat capacities, and volumes of the nonpolar solutes in water. This effect originated from much stronger attractive interaction energy between the nonpolar solutes merged in water than their vander Waals interaction in free space [32]. The tendency of relativity nonpolar molecules to “stick together” in aqueous solution is denoted as the hydrophobic interaction [33]. It results from hydrophobic hydration of a nonpolar molecule. Because hydrophobic hydration plays an important role in facilitating amphiphiles to aggregates in the aqueous bulk phase and to absorb, excessively, at the aqueous solution/air interface, it has been an on going objective of chemists working in these areas to seek a clearer understanding of the molecular nature behind the subtle hydration phenomenon occurring between nonpolar solutes and water. A brief but detailed account of the general aspects of hydrophobic hydration, which is essential to the rationalization of the results obtained in this work, is given at this point.

1.12 Properties of Acetonitrile

Acetonitrile is the chemical compound with the formula, CH_3CN. This colorless liquid is the simplest organic nitrile. It is produced mainly as a byproduct of acrylonitrile manufacture. It is used as a polar aprotic solvent in organic synthesis and in the purification of butadiene. It is widely used as an electrochemical solvent. In the laboratory, it is used as a medium-polarity solvent that is miscible with water and has a convenient liquid range. With a dipole moment of 3.92D, acetonitrile dissolves a wide range of ionic and non-polar compounds (e.g. Wohl-Ziegler reaction) and is useful as a mobile phase in HPLC and LCMS [34-36].

It is widely used in battery applications because of its relatively high dielectric constant and ability to dissolve electrolytes. For similar reasons it is a popular solvent in cyclic voltammetry. Its low viscosity and low chemical reactivity make it a popular choice for liquid chromatography. Acetonitrile plays a significant role as the dominant solvent used in the manufacture of DNA oligonucleotides from monomers. Industrially, it is used as a solvent for the manufacture of pharmaceuticals and photographic film [37].

Acetronitrile is a dipolar aprotic solvent lacking strong specific intermolecular forces, where dipole-dipole forces predominate. It is an archetype solvent with simple molecular structure and high solvation power for many solutes [38]. Consequently, the association or dissociation of solute in acetonitrile has attracted considerable interest. Acetonitrile, a relatively inert and inexpensive solvent, with a high density and low viscosity is also an important solvent with liquid-liquid extraction potential capabilities. It has important technological applications, namely, in battery industry and plating techniques [39, 40].

The mode of interactions of alcohols and acetonitrile is of vital importance in the field of solution chemistry as it can provide with important information regarding hydrophilic and hydrophobic interactions. Binary mixtures of acetonitrile and alkanols are widely used as solvents in chemistry and modern chemical technology. Acetonitrile and alkanol mixtures are also used as very powerful cosolvents of polymers [41]. Acetonitriles and alchohols are versatile solvents used in the separation of saturated and unsaturated hydrocarbons, in pharmaceutical synthesis, and serve as solvents for many polymers.

1.13 Acetonitrile-Solvent systems

The experimental data on macroscopic properties provide valuable information for proper understanding the nature of interaction between the components of the solution. The thermodynamic properties of solution containing acetonitrile and alcohols are of interest.
The correlation between solute -solvent interaction is complex. Thermodynamic properties of the solution have been reported [42]. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure [43]. Because the environment of the solute affects the thermodynamic properties, it is of interesting to study the effect of the media changing from water to acetonitrile solvent on the thermodynamic properties of the alcohol.

Acetonitrile, alkanols, and their binary mixtures are used as solvents in chemistry and modern chemical engineering. Acetonitrile and alkanol mixtures are also used as very powerful cosolvents of polymers. Excess molar enthalpies have been measured for the binary mixtures methanol-acetonitrile and ethanol-acetonitrile and for the ternary mixtures methanol-acetonitrile-benzene and ethanol-acetonitrile-benzene [44]. The excess molar enthalpies of (propan-1-ol + acetonitrile), (propan-2-ol + acetonitrile), (propan-1-ol + chlorobenzene), and (propan-2-ol + chlorobenzene), and of (propan-1-ol + acetonitrile + chlorobenzene) and (propan-2-ol + acetonitrile + chlorobenzene) have been reported previously [45]. Surface tension and density of {acetonitrile + methanol, ethanol, 1-

propanol, 1-butanol, or 1-pentanol} at the temperature 293.15 K and normal atmospheric pressure have been measured as a function of mole fraction [46].

The excess molar enthalpy H_m^E as a function of composition of acetonitrile + 1-pentanol and acetonitrile + 1-hexanol mixtures are reported [47]. Excess Gibbs free energies, excess enthalpies, and volumes were also measured for butanenitrile + 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol [48]. Excess functions for binary mixtures of butanenitrile + methanol, 1-pentanol, 1-heptanol, 1-nonanol, or 1-decanol have been measured at 298.15 K [49]. Densities and viscosities of butanenitrile + 1-butanol, + 2-methyl-1-propanol, + 2-butanol, or + 2-methyl-2-propanol were measured at several temperatures [50]. Excess molar enthalpies and volumes of butanenitrile +2-methyl-1-propanol or +2-methyl-2-propanol at several temperatures were also measured [51].

Excess molar enthalpies and volumes of butanenitrile + 2-butanol are measured previously [52]. Vapour pressures of butanenitrile + 2-methyl-1-propanol or + 2-methyl-2-propanol at several temperatures have been reported [53].

1.14 The object of the present work

The developments in solution theory are still far from being adequate to account for the properties in terms of the properties of the constituent molecules. Accordingly, it is the experimental data on various macroscopic properties (thermodynamic properties, viscosities, surface tension etc.), which provide useful information for proper understanding of specific interaction between the components and structure of the solution. The experimental approach of measurements of various macroscopic properties is also useful in providing guidance to theoretical approaches, since the experimentally determined values of solution properties may bring to light certain inadequacies in the proposed model on which theoretical treatments may be based. Thermodynamic studies on binary solutions have attracted a great deal of attention and experimental data on a good number of systems are available in a number of review articles [42, 47]. There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, [48, 53] of particular interest has been the determination of densities and viscosities of mixtures.

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

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

In the present investigations, (i) densities and excess molar volumes, (ii) viscosities and excess viscosities and iii) thermodynamic parameters of seven ternary mixtures, viz.,

Ethanol + 0.02M Sodium Dodecyl Sulfate (SDS) +20% Water + 80% Acetonitrile; n-Propanol + 0.02M SDS + 20% Water + 80% Acetonitrile; n-Butanol + 0.02M SDS+20% Water + 80% Acetonitrile; n-Pentanol + 0.02M SDS+20% Water + 80% Acetonitrile; iso-Propanol + 0.02M SDS + 20% Water + 80% Acetonitrile; iso- Butanol + 0.02M SDS+20% Water + 80% Acetonitrile and iso- Pentanol + 0.02M SDS+20% Water + 80% Acetonitrile at 298.15-323.15K have been determined. . In order to understand the issue of solute-solvent interactions in acetonitrile-alcohol-water-SDS systems a theoretical and experimental aspect of interactions in terms of excess molar volume and excess viscosity, excess thermodynamic properties analysis is necessary. To our knowledge the studied ternary systems (acetonitrile-alcohol-SDS-water) interaction with the volumetric, viscometric and thermodynamic properties measurements, has not been analyzed before this work. The objectives of the present work have been to:

The specific aims are:

i) to examine the volumetric, viscometric and thermodynamic properties of alcohols in the SDS containing acetonitrile + water mixtures in different compositions and different temperatures.

ii) to understand the effect of aqueous SDS containing acetonitrile on alcohols solutions to generalize the type of interactions among them.

iii) to understand the deviation of excess properties with the experimental values.

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

CHAPTER II

Theoretical Background

2.1 Physical Properties and chemical constitutions

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

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

The various physical properties based upon the measurement of density, viscosity, surface tension, refractive index, dielectric constant etc., have been found to fall into the following four categories [54].

(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 kenotic group (=CO) it is 12.2. The parachor, molar refraction, molecular viscosity etc. are the other example of this type.

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

2.2 Density

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

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

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

2.3 Density and temperature

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

2.4 Molarity

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

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

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

For one mole of solute dissolved in one liter of solution, C=l i.e. molarity is one. Such a solution is called 1 molar. A solution containing two moles of solute in one liter is 2 molar and so on. As evident from expression (2.1), unit of molarity is $molL^{-1}$ [55].

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, ifρ 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 [55]. 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}

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

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

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 breakdown 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 Excess molar volume

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

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

The mixture molar volume is,

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

and the ideal molar volume of this system is given by

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

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

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

Where X_1, M_1 and ρ_1 are the mole fraction, molar mass and density of component 1(solvent); X_2, M_2,andρ_2 are the corresponding values of component 2 (organic solutes); and ρ_{mix} is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich Kister polynomial equation of the form,

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

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

2.7 Viscosity

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

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

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

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

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

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

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

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

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

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

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

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation [56]. 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 [56]:

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

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

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

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

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

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

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

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

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

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

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

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

2.8 Viscosity and temperature

The viscosity of a liquid is generally decrease with the increase of temperature, i.e., a liquid becomes more free moving at 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 independently by S. Arrhenius (1912) and J. De Guzmann(1913), are preferred due to their theoretical practical importance.

$$\eta = Ae^{E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (2.41)$$

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

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

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

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

2.9 Viscosity of liquid mixtures

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

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

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

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

2.10 Excess viscosity measurements

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

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

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

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

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

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

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

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

2.11 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 [57],

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

Where, ε = Interaction parameter.

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

η_{id} = calculated viscosity

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

η_1 and η_2 are the viscosities of the pure component 1 and 2 respectively and x_1 and x_2 are there 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 η indicates there is no specific interaction between the components present in the mixture and the positive value of η indicates the presence of strong interaction.

2.12 Viscosity as a rate process

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

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

i) The motion of one layer with respect to another is assumed to involve the passes of a molecule from one equilibrium position to another is the same layer.
ii) In order to move a molecule from one equilibrium position to another, a suitable ‘hole’ or site should be available.

iii) The production of 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 [58] using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, ηas follows:

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

Where, $\Delta G^{\#}$ is the free energy of activation per mole for viscous flow, V_m is the molar volume for pure liquids or solutions and h, N, R and T have their meanings. The values of change of free energy of activation ($\Delta G^{\#}$) can be calculated by using the Nightingle and Benck equation [59]:

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

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

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

Enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution can be obtained with the help of Eyring equation [58]:

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

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

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

Since,

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

The Eyring equation takes the form,

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

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

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

$\Delta H^{\#}$ = slope × R ……………………………….…………………….(2.52)

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

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

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

2.13 Different thermodynamic parameters

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

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

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

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

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

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

2.14 Redlich-Kister equation

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

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

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

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

$$\mathrm{SD} = \left[\frac{\sum(PROP_{\exp}^{E} - PROP_{calcd}E)^2}{n-p-2}\right]^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.55)$$

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

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

n = total number of compositions for each system

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

and SD = standard deviation

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

CHAPTER III

Experimental

3.1 General Techniques

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

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

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

3.2 Materials

The chemicals used for study were Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol, iso-Pentanol and Sodium dodecyl sulphate (SDS). All chemicals were of analytical reagent (A.R) grade. Specifications and structural formula for all of them are given below: grade. Specifications and structural formula for all of them are given below:

Chemicals	**Molecular formula**	**Molar mass**	**Reported purity**	**Producer**
Ethanol	C_2H_5OH	46.07	99%	MERCK Germany
n-Propanol	$CH_3CH_2CH_2OH$	60.10	99%	E. MERCK India
iso-Propanol	$(CH_3)_2CHOH$	60.10	99%	MERCK Germany
n-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	99.5%	Scharlau Chemie U.S.A.
iso-Butanol	$(CH_3)_2CHCH_2OH$	74.12	99.%	E. MERCK India
n-Pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88.15	99 %	BDH, England
iso-Pentanol	$(CH_3)_2CHCH_2CH_2OH$	88.15	99 %	LOBA Chemical, India
Acetonitrile	CH_3CN	41.05	99.8%	MERCK Germany
SDS	$C_{12}H_{25}OSO_3Na$	288.38	99.0%	E. MERCK 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 preparation of 0.02M SDS solutions for volumetric and viscometric studies.

3.4 Apparatus

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

3.5 Methods (preparation of solution)

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

3.6 Conductance measurements

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

3.7 Density measurements

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

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

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

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

The solution under investigation was taken in a density bottle up to the mark. The density bottle was clamped carefully with stand in the thermostatic water bath maintained at the desired temperature. As the solution started to gain the temperature of the bath excess liquid overflowed through the capillary. Then it was allowed to keep in the bath for about 30 minutes to attain the thermal equilibrium. When no overflowed observed through the capillary the density bottle was taken out from the thermostatic water bath, wiped with tissue-paper, dried and weighed in the analytical balance. The difference between the two weights (weight with solution and without solution) gave the weight of the solution in the density bottle. The density measurement was performed for each of the solutions at the temperature 298, 303, 308, 313, 318 and 323K respectively in this way using equation 3.1.

3.8 Excess molar volume measurements

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

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

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,

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

Where a_i is the i^{th} fitting coefficient. Using $n = 3$ four a_i coefficient and the standard deviation σ were obtained through the least square method.

3.9 Viscosity measurements

Viscosity of water, SDS and several solutions were measured by using the British standard Ostwald U-type viscometer. The interior of the viscometer was cleaned thoroughly with warm chromic acid and then with distilled water, so that there was no obstruction in the capillary and the liquid could run freely without leaving any drop behind. It was then rinsed with acetone and dried in and oven at about 75^0C. 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,

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

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

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

3.10 Excess viscosity measurements

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

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

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

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

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

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

Where, a_i is the i^th^ fitting coefficient. Using $n = 3$, four $\mathrm{a_i}$ 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 [57],

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

Where**,** ε = Interaction parameter.

$\eta_{\text{expt.}}$ = 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 there 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 η indicates there is no specific interaction between the components present in the mixture and the positive value of η indicates the presence of strong interaction.

3.12 Thermodynamic parameters

The change of free energy of activation ($\Delta G^{\#}$) was calculated by the help of Nightingle and Benck [59] equation:

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

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

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

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

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

T = Absolute temperature (K)

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

Energy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) for viscous flow for the solution were determined y using the Eyring equation [58]:

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

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

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

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

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

$\Delta H^{\#}$ = slope × R ………………………………..………………(3.18)

and $\Delta S^{\#}$ = -intercept × R ………………………………………………...(3.19)

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

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

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

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

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

3.13 Coefficient Redlich-Kister equation and standard deviation

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

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

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:

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

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 IV

Results and Discussion

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

1. **Ethanol + 80% acetonitrile + 20% water + 0.02M SDS**
2. **n-Propanol + 80% acetonitrile + 20% water + 0.02M SDS**
3. **iso-Propanol + 80% acetonitrile + 20% water + 0.02M SDS**
4. **n-Butanol + 80% acetonitrile + 20% water + 0.02M SDS**
5. **iso-Butanol + 80% acetonitrile + 20% water + 0.02M SDS**
6. **n-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS**
7. **iso-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS**

The above-mention systems were studied precisely at six equidistant temperatures ranging from 298.15K to 323.15K at interval of 5K by volumetric and viscometric methods. The volumetric properties excess molar volume (V^E) is determined from density. Viscometric properties like excess viscosity (η^E), interaction parameter (ε) and thermodynamic properties like enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy (($\Delta G^{\#}$) of activation for viscous flow and their excess quantities, $\Delta H^{\#E}$, $\Delta S^{\#E}$ and $\Delta G^{\#E}$ are determined from viscosity values. From these studies, we obtained various information which are presented in various sections and discussed in the light of theories mentioned in the earlier chapter.

4.1 Conductance and viscosity studies of SDS:

In this research the critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in (80% acetonitrile + 20% water) was determine from the conductance and viscosity measurement. The concentration dependence of molar conductivity of (80% acetonitrile + 20% water) solution of SDS is shown in Figure 4.1 and data is presented in Table 4.1. The molar conductivity at first decreases with increasing SDS concentration and then increases and finally decreases again. It shows a sharp break in its value where micelle starts to form and it is determined by extrapolating the molar conductivity data in the pre-micelle region to intersect with a straight line drawn through the data in the post micelle region. Viscosities vs. concentration of SDS in (80% acetonitrile + 20% water) are plotted in Figure 4.2 and the data is presented in Table 4.2 The viscosities increase with increasing SDS concentration and then decrease and eventually increase again. The minima of viscosity express the CMC of SDS. The estimated value of CMC was found to be 0.02M at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively. The conductance data is in good agreement with viscosity data. The effect of surfactant in 0.02M SDS + 80% acetonitrile + 20% water to alcohol systems has been studied in terms of volumetric, viscometric and thermodynamic properties. The concentration of SDS 0.02M was used for these measurements.

4.2 Volumetric Properties

The densities, ρ of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems were determined at temperatures ranging from (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15)K with an interval of 5K over the entire composition range $0 < X_2 < 1$, where x_2 represents the mole fraction of Alcohols. The densities of the pure components are shown in Table 4.3 together with the literature values, for possible of comparison. The agreement between the measured values and literature values has been found to be almost satisfactory. The concentration of SDS in micelle region of 0.02M was used. The densities of the ternary systems have been shown in Tables 4.4-4.10 at different temperatures. Figures 4.3-4.9 show the plots of densities as a function of mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems. For Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol systems, it shows continuous decrease in density with the composition of alcohols. The density value decreases with increase in the temperature. The experimental density value in pure state of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol iso-Pentanol and acetonitrile at 298.15K are

0.808823, 0.800209, 0.778313, 0.806312, 0.798895, 0.810852, 0.813120, 0.783584 g.cm^{-3} respectively.

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

n-Pentanol > Ethanol > n-Butanol > n-Propanol

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

iso-Pentanol > iso-Butanol > iso-Propanol

The densities of isomers are found to be order of

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

Most of the cases, the densities of alcohols increase with increase of carbon number may be depending on the molecular weight of alcohols, structural formula and H-bonding of alcohols. As the density of (80% acetonitrile + 20% water + 0.02M SDS) is higher than that of pure Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol, with the increase of the composition of alcohols, the density of alcohol + (80% acetonitrile + 20% water + 0.02M SDS) system decreases and eventually proceeds towards the density of pure alcohol.

The dependences of density with carbon chain length of n-Alcohols and iso-Alkanols with different composition at a fixed temperature are plotted in Figures 4.10-4.12 and Figures 4.13-4.15 respectively. From the figures, it can be seen that at the same temperature, the density increase with the carbon chain length of the alcohols. In pure state of alcohols, the density increase with carbon chain length. The dependences of density with carbon chain length of n-Alcohols and iso-Alkanols with different temperatures at a fixed mole fraction are plotted in Figures 4.16-4.17 and Figures 4.18-4.19 respectively. It can be seen that at the same mole fraction, the density increase with 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-Alkanols and iso-Alkanols are shown in Figures 4.20-4.23 and Figures 4.24-4.27 respectively at different mole fractions. It can be seen that density, ρ decrease almost linearly with increasing temperature for all alcohols. This is due to the increase of thermal agitation and hence the weaker dipole-dipole interaction or dissociation of H-bonding is occurred. The linear dependence of $\ln\rho$ verses 1/T is plotted in Figures 4.28-4.31 for n-Alkanols and Figures 4.32-4.35 respectively for iso-Alkanols respectively.

The density order of alcohols in (80% acetonitrile + 20% water + 0.02M SDS) solution is similar as alcohols in pure solution. The values of densities of alcohols + (80% acetonitrile + 20% water + 0.02M SDS) systems have been found to be in the order of,

n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)

and

iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)

The density of n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) is higher than n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS), n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) is higher than n-Propanol, indicates that the nature of interaction in pure state is similar to the solution (mixture) state. Here, the density of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) is higher than n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) and n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS). This is due to the small size of Ethanol which causes higher interstitial accommodation.

The excess molar volume, V^E of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M) 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 4.4-4.10. For V^E the fitting coefficients (a_i) are shown in Table 4.32 along with standard deviations. Figures 4.36-4.42 shows the plots of excess molar volume as a function of mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems.

Figure 4.36 shows the plots of excess molar volume as a function of mole fraction of Ethanol at different temperatures. The values have been found to be negative throughout the whole range of composition, showing minima at ~ 0.5 mole fraction of Ethanol. The excess molar volumes of n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems are shown in Figures 4.37-4.42 respectively.

For n-Propanol, the values of V^E are negative throughout the whole range of composition. The minima appear at ~ 0.8 mole fraction of n-Propanol. For iso-Propanol, V^E are negative and with increasing of alcohol concentration, V^E reaches minimum value at ~ 0.8 mole fraction of iso-Propanol and increase continuously. And for n-Butanol, V^E are negative and with increase of alcohol concentration, V^E reaches minimum value at ~ 0.79 mole fraction of n-Butanol and increases continuously. Similarly iso-Butanol, V^E are negative and with increase of alcohol concentration, V^E reaches minimum value at ~ 0.82 mole fraction of iso-Butanol and increases continuously. The values of excess molar volume of n-Pentanol, V^E have been found to be negative throughout the whole range of composition, showing minima at ~ 0.7 mole fraction of n-Pentanol. At lower concentration of iso-Pentanol, V^E are negative and with increase of alcohol concentration, V^E reaches minimum value at ~ 0.69 mole fraction of iso-Pentanol and increases continuously. In the present investigation at 298.15K, the minimum values V^E have been found to be -1.4790 (at X_2 = 0.8991), -1.4666 (at X_2 = 0.8004), -1.3096 (at X_2 = 0.7003), -0.9989 (at X_2 = 0.7990), -0.8077 (at X_2 = 0.7011), -0.3568 (at X_2 = 0.4997) and -0.2120 (at X_2 = 0.5997) for iso-Butanol + 80% acetonitrile + 20% water + 0.02M SDS, iso-Propanol + 80% acetonitrile + 20% water + 0.02M SDS, n-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS, n-Butanol + 80% acetonitrile + 20% water + 0.02M SDS, n-Propanol + 80% acetonitrile + 20% water + 0.02M SDS, Ethanol + 80% acetonitrile + 20% water + 0.02M SDS and iso-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS mixtures respectively. The negative excess molar volume has found to be in the orders:

iso-Butanol > iso-Propanol > n-Pentanol > n-Butanol > n-Propanol > Ethanol > iso-Pentanol

Examination of Figures 4.36-4.42 reveals that

(i) At low composition of alcohol in (80% acetonitrile + 20% water + 0.02M SDS) solution, excess molar volumes, V^E are negative and with the increase of alcohol composition, V^E reaches minima value and then decreases continuously and eventually becomes zero.

(ii) Excess molar volumes, V^E are negative for the whole range of composition for the studied alcohol + (80% acetonitrile + 20% water + 0.02M SDS) systems.

(iii) For all the systems $d V^E / dT$ is negative.

(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 + (80% acetonitrile + 20% water + 0.02M SDS) systems, the minima appear at ~ 0.6 - 0.8 mole fraction of alkanols.

(vi) The excess molar volumes, V^E of alcohols + (80% acetonitrile + 20% water + 0.02M SDS) systems have been to be in the order of,

n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)> Ethanol + (80% acetonitrile + 20% water + 0.02M)

and

n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso- Pentanol + (80% acetonitrile + 20% water + 0.02M SDS)

and

iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS)

and

iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)

(Vii) The mixing of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol with (80% acetonitrile + 20% water + 0.02M SDS) systems is accomplished by contraction of volume at all studied temperatures.

Similar behavior was found by Dikko. A.B. et. al. [60] in ternary mixture of (Water + Methanol + Ethanol) systems, excess molar volume were negative in the whole range of composition. We have studied similar alcohols with dimethylformamide systems [61]. The acetonitrile + alcohol system shows negative excess molar volume, V^E [62].

In general, the sign of V^E depends upon the relative magnitude of contractive and expansive effects that arise on mixing of the components. The factors that cause contraction on mixing are:

a) Strong specific interactions, usually a kind of chemical interaction,
b) Strong physical interactions, such as dipole-dipole or dipole-induced dipole interactions or Vander Waals forces that operate between component molecules,
c) Interstitial accommodation of molecules of one component into the structural network of molecules of the other component. This is expected when the molecular sizes of the compounds differ by a large magnitude,
d) Favorable geometrical fitting of component molecules,
e) The water structure around the hydrocarbon moieties of aliphatic alcohol is highly promoted leading to the formation of cages surrounding the alcohol molecules. This is a special type of interactions, which occurs in water rich region when an organic solute molecule is surrounded by a network of highly ordered water molecules.

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

a) The dispersive forces which occur predominantly in systems consisting of associated species (formed either by chemical or physical forces) and non-polar components,
b) Dissociation of one component or both of the components,
c) Steric hindrance,

d) Geometrical mismatch of the molecules,
e) Formation of weaker solute- solvent bond than solute – solute and solvent – solvent bonds,
f) Effect due to differences in the chain length of alkanols,
g) Electrostatic repulsive forces.

Acetonitrile (MeCN) in pure state, no self-association through H-bonding is possible because of the absence of donor/acceptor hydrogen. The attachment of one $–CH_3$ groups at the carbon atom increases electron density on the carbon atom and subsequently on nitrogen atom of the cyanide and so may have the possibility of H-bond formation with alcohol molecules by the following ways (i) -C≡N…HO-R. At the same time the presence of $–CH_3$ groups of acetonitrile creates a steric hindrance that prevents alcohol molecules from coming sufficiently close to it. On the other hand, alcohols molecules undergo self-association and cross-association because of the presence of hydrogen bonds [63, 64].

Mixing of (80% acetonitrile + 20% water + 0.02M SDS) with an alcohol will induce strong specific interaction. On the addition of alcohol to the (80% acetonitrile + 20% water + 0.02M SDS) solution undergo self-association among alcohol, water, SDS and acetonitrile.

The dependence of excess molar volume with temperature of n-Alkanols and iso-Alkanols are shown in Figures 4.43-4.45 and in Figures 4.46-4.48 respectively. It is known that pure compounds or their mixtures can form either ring or chain-like complexes, and while temperature increases, the degree of association decrease [65, 66] and hence the negative excess molar volume increases.

The observed V^E may be discussed above which may be arbitrarily divided into physical, chemical, and geometrical contributions [63,67]. The physical interactions, that is, nonspecific interactions between the real species present in the mixture, involve mainly dispersion force giving a positive contribution. The chemical or specific intermolecular interactions result in a volume decrease and these interactions include formation of hydrogen bonds and other complex-forming interactions. The structural contributions for these systems are mostly negative and arise from several effects, especially from hydrogen bonding interstitial accommodation and changes of free volume. Structural contributions arising from geometrical fitting (interstitially accommodated) of one component into another due to the differences in the free volume and molar volume between components lead to a negative contribution to V^E.

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

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

The large negative V^E of the systems, a typical characteristic of hydrophobic solutes, lead to the conviction that the factors causing the volume contraction far outweigh the factor which is to responsible for volume expansion [68]. Of the contractive factors, perhaps the hydrophobic hydration is by far the most effective one in volume reduction, as through this process the hydrophobic molecules occupy the spaces inside the so-called cages formed by the highly structured water molecules, and thus ensure maximum economy of volume. Whereas in other cases, shrinkage takes place through strong interactions or attractive forces whose contribution to volume reduction is only relatively small.

The excess molar volumes of ternary mixtures which are under investigation may be considered to be the resultant of the above-mentioned competing interaction of the component molecules. All the components are polar compounds: the value of dipole moment (μ) being 1.85D for Water, 1.69D for Ethanol, 1.68D for n-Propanol, 1.68D for iso-Propanol , 1.66D for n-Butanol, 1.66D for iso-Butanol, 1.71D for n-Pentanol, 1.70D for iso-Pentanol and 3.44D for acetonitrile respectively. Due to the dipole-dipole interaction between the components negative V^E values are generally expected.

The value of dipole moment (μ) of acetonitrile is higher than the studied alkanols. Therefore, it has been the possibility of the formation of hydrogen bonding through the polar group of the Alkanols, water and acetonitrile due to the hydrophilic effect. However, if the steric hindrance by the bulky groups or geometrical mismatch of these groups is 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 donor/acceptor interaction are reported [69, 70]. So, if the alkanols are relatively smaller in size and formed H-bonding or association through dipole-dipole interactions between the components small V^E values generally expected. The experimental results of these mixtures are consistent with this observation.

The molar volume of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol at 298.15K are respectively 46.07, 60.10, 60.10, 74.12, 74.12, 88.15 and 88.15 cm^3mole^{-1}. The negative V^E of the systems under investigation indicates that the factors leading to contraction on mixing of the components dominate over the factors responsible for volume expansion. In view of the present state of our knowledge about the structure and the related properties of water, acetonitrile, aliphatic alcohol, one can easily visualize that factors such as chemical through hydrogen bonding among water, acetonitrile and alcohol, the hydrophobic hydration are all important causes for volume contraction. The contractive forces thus predominate far more than the expansive forces, if any. The overall effect is thus contraction of volume.

The gradual contraction in volume on addition of aliphatic alcohol may be explained mainly by taking into account of formation of strong alcohol-water, alcohol-acetonitrile, SDS-water, SDS-alcohol and water-acetonitrile interaction due to H-bonds and by hydrophobic hydration with overall economy of space. When hydrogen bonded tetrahedral structure of liquid water and acetonitrile are formed near a hydrophobic part of the solute the inert part (alkyl group of alcohol) of the fills the interstitial cavities of the structures. This loss of free during hydrophobic hydration is larger than the increase in volume accompanying the increase of ice-likeness. As the hydrocarbon part of alcohol increased, fewer sites are available to accommodate it, and the fraction of solute enclosed in interstitial spaces of cluster decreases and hence V^E becomes less negative less negative as has been observed in the present systems. The strength of the intermolecular hydrogen bonding through alcohol-water, alcohol-acetonitrile, SDS-water, SDS-alcohol and water-acetonitrile are not the only factor influencing the negative V^E of liquid mixtures but the orientation of groups, molecular sizes and shapes of the components are also equally important.

The size differences between water and acetonitrile of n-Pentanol and iso-Pentanol are quite large so the possibility of partial accommodation of water or acetonitrile in the interstices of n-Pentanol is high but the possibility of making H-bonding cluster for n-Pentanol or iso-Pentanol is lower than other studied alcohols owing to its higher steric hindrance and hence V^E becomes high.

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

4.3 Viscometric properties

The viscosities, η of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over entire composition range are shown in Tables 4.11-4.17. The viscosities of the pure components are shown in Table 4.3 together with the literature values for Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol, iso-Pentanol and acetonitrile wherever possible for composition. The agreement between the measured values and literature values has been found to be almost satisfactory.

The variation of viscosities at these temperatures as function of the alcohols is shown in Figures 4.49-4.55 respectively. The following characteristics features of viscosity are observed

a) The viscosities increase initially slowly up to ~ 0.8 mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems and later on, the viscosities increases sharply until the pure alcohol is reached specially at lower temperature.
b) Viscosity decreases with rise of temperature.

The experimental viscosity values in pure state of acetonitrile, Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol at 298.15K are 0.3495, 1.1856, 1.9480, 2.0259, 2.5778, 3.3493, 3.5403, 3.6947 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 > Ethanol
and
iso-Pentanol > iso-Butanol > iso-Propanol
and
iso-Pentanol > n-Pentanol and iso-Butanol > n-Butanol and iso-Propanol > n-Propanol

In dilute solutions of alcohols in acetonitrile + water + SDS, it is believed that alcohols which are known to exist in associated form through H-bonding are dissociated. This explains the low viscosity of the solutions in the acetonitrile rich regions. In alkanols rich region the rapid rise of viscosity is through 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 increase with raising concentration of alcohol. This accounts for the sharp rise in viscosity in the alcohol rich regions.

The dependence of the viscosity with carbon chain length of n-alcohols and iso-Alkanols with different composition at a fixed temperature is plotted in Figures 4.56-4.58 and Figures 4.59-4.61 respectively. From the figures, it is seen that, at the same temperature, the viscosity increase with carbon chain length of alcohols.

The dependence of viscosity with carbon number of n-Alkanols and iso-Alkanols with different temperatures at a fixed composition are plotted in Figures 4.62-4.63 and Figures

4.64-4.65 respectively. From the figures, it is seen that at the same mole fraction, the viscosity increase with carbon number of alcohols can be explained by the increase of solution resistance with the increase of carbon number.

The dependence of viscosity with temperature of n-Alkanols are shown in Figures 4.66-4.69 respectively and iso-Alkanols are shown in Figures 4.70-4.73 respectively at different mole fractions. It is seen that viscosity, η decreases with increasing temperature for all alcohols. The linear dependence of $\ln\eta$ verses $1/T$ of n-Alkanols and iso-Alkanols are plotted in Figures 4.74-4.77 and Figures 4.78-4.81 respectively.

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 4.74-4.81), the order of viscosity becomes n-Pentanol > n-Butanol > n-Propanol > Ethanol. The above equation is valid for all the (80% acetonitrile + 20% water + 0.02M SDS)-alcohols systems. The temperature effect is prominent for branch chain isomer than that linear chain isomer. This indicates that the branched chain isomers 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 viscosities of different isomers of Alkanols in Toluene as reported [70] are in good agreement with our studied isomers.

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

$$\eta^E = \eta_{obs} - \eta_{id} \tag{1}$$

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

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

where, X_1 and η_1 are the mole fraction and viscosity of component 1 (80% acetonitrile + 20% water + 0.02M SDS), X_2 and η_2 are the mole fraction and viscosity of component 2 (Alcohols).

The η^E values are shown in Tables 4.11-4.17. The excess viscosities were fitted by least squares method to a polynomial equation 3.11. The values of the fitting parameters along with the standard deviation are present in Tables 4.33.The variation of η^E against mole fraction of alcohol (X_2) is shown in Figures 4.82-4.88 respectively. The values are found to be negative and large in magnitude, indicating the (80% acetonitrile + 20% water + 0.02M SDS) solution of alcohols are non-ideal. Figures show the following features:

i. Excess viscosities are negative at all the temperatures over entire range of composition for all the systems with minima occurring between 0.7-0.8 mole fraction of Ethanol, 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 viscosity.
iv. iso-Propanol, n-Butanol, n-Pentanol and iso-Pentanol, η^E are being slightly positive at lower mole fractions.
v. The height of the minima are in the order:

n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol+(80% acetonitrile + 20% water + 0.02M SDS)
and
iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Propanol +(80% acetonitrile + 20% water + 0.02M SDS) > iso-Pentanol +(80% acetonitrile + 20% water + 0.02M SDS)
and

iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) and n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) > iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) and iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) > n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS)

The negative V^E and negative η^E for the systems present an apparent discrepancy but show agreement with the statements Bhuiyan el at. [71]. If V^E is negative due to the segmental inclusion of acetonitrile in the interstices of polymmolecular alkanol aggregate, these will be fewer surfaces available for fiction that may result in a reduction of viscosity. Some disruptive force causing volume expansion may be present, but it is more than compensated for by volume contraction through inclusion of acetonitrile.

The excess viscosities are found to be negative for all the studied alcohol systems in (80% acetonitrile + 20% water + 0.02M SDS) solution. The negative excess viscosities (as in Figure 4.82-4.88) for the systems (80% acetonitrile + 20% water + 0.02M SDS) + studied alcohol systems indicate the dissociation of compounds through steric hindrance or dispersive force.

The values of dipole moments (μ) of all alcohols are almost similar. The dipole moment (μ) of acetonitrile is much larger than alcohols. Therefore hydrogen bonding is thought to be form by the polar group of alcohols with acetonitrile and water due to the hydrophilic effect. The hydrophobic effect obviously increases with the size of the hydrocarbon 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 at. [72] showed that hydrophobic interaction varies according to hydrocarbon groups such as

$$CH_3CH_2 > CH_3 > CH_2 > CH$$

Acetonitrile, water and alcohols molecules form a maximum structural disaggregate around at 0.7-0.8 mole fraction alcohols owing to the dissociation of components through dispersive force or Steric hindrance. With a further increase in Alcohols mole fraction a composition is reached when alcohols molecules cannot find enough acetonitrile molecules to be disrupted. After attaining the state of minima η^E further addition of alcohol continuously formed the ordered structure and alkanols-alkanols cage association, instead of acetonitrile-alkanols dispersion, which result in the continual increase in η^E.

The negative excess viscosities are accounted for due to the dissociation of the associated structures of alcohols in (80% acetonitrile + 20% water + 0.02M SDS). As pointed out earlier, negative excess viscosity

iso-Pentanol > n-Pentanol
n-Butanol > iso-Butanol
iso-Propanol > n-Propanol
n-Butanol > n-Pentanol > Ethanol > n-Propanol

The relative case of dissociation of dissociation of our studied systems: two Propanol, two Butanols and two Pentanols isomer either by thermal effect or by the force of dispersion in (80% acetonitrile + 20% water + 0.02M SDS) should thus follow the order:

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

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

The dependence of excess viscosity with temperature of n-Alkanols and iso-Alkanols are shown in Figures 4.89-4.91 and Figures 4.92-4.94 respectively. From figures 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 ($\Delta\eta_{min}$) of the different systems can be explained in terms of the maximum thermal fragility in the molecular interaction of (80% acetonitrile + 20% water + 0.02M SDS) and alcohols formed. In comparison with alcohol-(80% acetonitrile + 20% water + 0.02M SDS) association in the structure is assumed to be more fragile to heat. Examination of excess viscosity curves of different alcohol solution Figures 4.82-4.88 shows that $\Delta\eta_{min}$ varies in the order:

iso-Propanol (0.1575 mPa.S) > n-Propanol (0.0276 mPa.S) iso-Pentanol (0.1402mPa.S) > n-Pentanol (0.0909 mPa.S)

The values, therefore, indicate the extent of the destruction of the structures by thermal effect. The structure formed by the (80% acetonitrile + 20% water + 0.02M SDS) - (80% acetonitrile + 20% water + 0.02M SDS) association around alcohols through H-bond or dispersion force are also assumed to be thermally unstable than (80% acetonitrile + 20% water + 0.02M SDS)-(80% acetonitrile + 20% water + 0.02M SDS) in pure (80% acetonitrile + 20% water + 0.02M SDS) that is similar to water [73,74]. The thermal fragility of branched alcohols is higher than the linear chain alcohols.

4.3.1 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 Figures 4.95-4.101 respectively. The values have been found to be negative and quite large in magnitude of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) for all the systems. The ε values are decrease with the increase of temperature.

From the studies of ε and η^E values of a number of binary mixtures of different polar or non-polar liquids, Fort and Moore [75] 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 both are not that much large in magnitudes, then weak interaction would be present between the components.
c. If $\varepsilon < 0$ and $\eta^E < 0$ and the magnitude of both parameters are large, then specific interaction would be absent and dispersion force would be dominant.

In all our studied systems, both ε and η^E values are negative and large in magnitude. Therefore the negative interaction parameters indicate that the specific interaction is absent but strong dispersion force of the mixtures is dominant [76]. The interaction parameters, ε decrease with alcohol concentration, showing minima. In the present investigation at 298.15K, the minima values of ε have been found to be -1.19 (at X_2= 0.9), -0.27 (at X_2 = 0.9), -1.67 (at X_2 = 0.9), -2.51(at X_2 =0.9), -1.25 (at X_2 = 0.9), -0.67 (at X_2 = 0.9) and -0.94 (at X_2 = 0.9) for the Ethanol +(80% acetonitrile + 20% water + 0.02M SDS) , n-Propanol +(80% acetonitrile + 20% water + 0.02M SDS), iso-Propanol +(80% acetonitrile + 20% water + 0.02M SDS), n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS), iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS), n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) and iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) respectively.

The height of the minima is higher in branched alcohol than those of linear chain alcohols with some exceptions. These observation accord with the view of Nigam and Mahl [76] that (80% acetonitrile + 20% water + 0.02M SDS) and all studied alcohols mixtures have strong dispersion force and geometric effect.

4.4 Thermodynamic properties

The free energy change ($\Delta G^{\#}$) of activation for the viscous flow of the Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over entire composition range are shown in Tables 4.18-4.24. The variations of free energy ($\Delta G^{\#}$) at different temperatures as a function of the mole fraction of all the studied alcohols are shown in Figures 4.102-4.108 respectively. The following characteristic features of $\Delta G^{\#}$ are observed:

a. The change of free energy ($\Delta G^{\#}$) increase almost linearly with mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol and then the $\Delta G^{\#}$ increases moderately until that of pure alcohol is reached.

b. In the 80% acetonitrile + 20% water + 0.02M SDS rich region (~0.0-0.6 mole fraction) the value of free energy $\Delta G^{\#}$ is smaller at low temperature and larger at higher temperature but in alcohol rich region it is vice versa.

The experimental $\Delta G^{\#}$ values in the pure state of Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol at 298.15K are 12.71, 14.63, 14.80, 15.83, 16.50, 17.03 and 17.13KJ mole^{-1} respectively. The positive free energy change $\Delta G^{\#}$ for the studied alcohols + (80% acetonitrile + 20% water + 0.02M SDS) systems indicate that the species formed in the solutions have to surmount a large addition energy barrier in order to flow. This implies that the species experience enhanced resistance to flow.

The dependence of the free energy, $\Delta G^{\#}$ with carbon number of n-Alkanols and iso-Alkanols with different composition at a fixed temperature are plotted in Figures 4.109-4.111 and Figures 4.112-4.114 respectively. The dependence of the free energy, $\Delta G^{\#}$ with carbon number of n-Alkanols and iso-Alkanols with different temperatures at a fixed mole fraction are plotted in Figures 4.115-4.116 and Figures 4.117-4.118 respectively. From the figures, it is seen that $\Delta G^{\#}$ increase with carbon number of alcohols.

The excess free energy ($\Delta G^{\#E}$) change of activation for the viscous flow of the Ethanol n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) solutions at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K over entire composition range are shown in Tables 4.18-4.24. Figures 4.119-4.125 represents the variation of ($\Delta G^{\#E}$) of the systems against the mole fraction of alcohols at different temperatures. The excess free energy ($\Delta G^{\#E}$) was fitted by least squares method to a polynomial equation. The values of the fitting parameters along with the standard deviation of alcohol systems are represented in Table 4.34 .The $\Delta G^{\#E}$ values are negative in magnitude, indicating that Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) solutions are non-ideal. Figures show the following features

i. Excess free energy $\Delta G^{\#E}$ are negative at all temperatures over the entire range of composition for Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) systems with minima occurring between 0.6 - 0.8 mole fraction of Ethanol, n-Propanol, iso-Propanol, n-Butanol, and iso-Butanol.

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 free energy ($\Delta G^{\#E}$).

iv. Variation of $\Delta G^{\#E}$ with composition for Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) systems under investigation are more or less similar in nature all being associated with minima.

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

vi. iso-Propanol and n-Butanol the $\Delta G^{\#E}$ are being slightly positive at lower mole fractions.

The negative excess free energy, $\Delta G^{\#E}$ throughout the whole range of composition indicates the formation of smaller units of alcohols in different proportion or strong disruptive force or segmental inclusion of (80% acetonitrile + 20% water + 0.02M SDS) in the interstices of alkanols depending upon the concentration of Ethanol, n-Propanol, iso-Propanol, n-Butanol and iso-Butanol in solution systems.

The $\Delta G^{\#E}$ values are positive in magnitude, indicating that n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) solutions are highly non-ideal. Figures show the following features:

i. Excess free energy $\Delta G^{\#E}$ are positive at all temperatures over the entire range of composition for n-Pentanol and iso-Pentanol (80% acetonitrile + 20% water + 0.02M SDS) systems with maxima occurring between 0.2 - 0.3 mole fraction of 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 increases the magnitude of positive excess $\Delta G^{\#E}$.

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

v. n-Pentanol and iso-Pentanol the $\Delta G^{\#E}$ are being slightly negative at higher mole fractions.

The systems having branched chain alkanols, iso-Propanol and iso-Butanol show slightly larger negative excess viscosity, $\Delta G^{\#E}$ than the 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 small units. Thus, the branched chain alkanols has the possibility of reduction of viscous free energy from ideal values. The negative excess free energy, $\Delta G^{\#E}$ follows the order:

iso-Pentanol > n-Pentanol
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 [77], a large negative excess free energy $\Delta G^{\#E}$ indicates the presence of dispersion force, whereas a large positive excess free energy $\Delta G^{\#E}$ suggests a specific association between the molecules in the solvent mixtures. The negative values of Ethanol, n-Propanol, iso-Propanol, n-Butanol and iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) systems are also indicative of the dispersion force containing molecular interaction among (80% acetonitrile + 20% water + 0.02M SDS) and alcohol systems. The positive values of n-Pentanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) systems are also indicative a specific association among containing molecule (80% acetonitrile + 20% water + 0.02M SDS) and alcohol systems.

The difference in minima of $\Delta G^{\#E}$ over the temperature range are shown in Figures 4.119-4.125 respectively of the different systems can be explained in terms of the thermal fragility of the cages formed. This indicates that the extent of the destruction of the cages structures by thermal effect which, in turn, reflect the extent of cage formation. Therefore, the effect of temperature on $\Delta G^{\#E}$, particularly in the region at or around the minima is significant (Table 4.18-4.24). This may be due to the structures formed by hydrophilic or hydrophobic interaction that are considered to be much more liable and thermally less stable than the normal acetonitrile structure [78, 74].

Table 4.25-4.31 shows enthalpy $\Delta H^{\#}$, entropy $\Delta S^{\#}$, excess enthalpy $\Delta H^{\#E}$ and excess entropy $\Delta S^{\#E}$ values for the studied system for different molar ratios. The entropies of the system increase almost linearly with composition of alkanols. All studied alcohols show negative entropy change with some exception, however for branched alkanols at alkanols rich region the change of entropy is pronounced.

All the other studied alkanols in (80% acetonitrile + 20% water + 0.02M SDS) solution systems show negative excess entropy $\Delta S^{\#E}$. Also the values are more negative for the branched alkanols than the linear system in the whole range of composition. Saleh et al. [79] found that n-Propanol + n-Heptane system, excess entropies were negative in the whole range of concentration.

$\Delta S^{\#}$ measure the randomness or disorderness to the system. $\Delta S^{\#}$ values are negative at lower concentration and $\Delta S^{\#}$ values are positive at higher concentration. This is believed to be due to more severe the segregated species in alkanols producing greater population of the smaller species in their activated states. The segregated species so formed in (80% acetonitrile + 20% water + 0.02M SDS) solution are supposed to have lesser interactions among 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 at lower concentration. The net result is therefore, the negative excess entropy of the systems. This also attribute that the structural factor dominates over the interactional one, as in the case of the mixing properties.

In order to explain $\Delta H^{\#}$ and $\Delta H^{\#E}$ behavior similar to $\Delta G^{\#}$ and $\Delta G^{\#E}$ hydrophobic interaction, structural effect and hydrophobic interaction may be consider as the major cause in which it is assumed that alcohols, acetonitrile, SDS and water molecules are engaged by a network of highly structured form in pure state. Studies on viscometric properties by kipkemboi and Easteal [80], Saleh el at. [77] and FTIR spectrophotometric studied by Gojlo el at [81] of some alcohols indicated that the alcohols are hydrophobic in nature. The bulkier species so formed by hydrophobic interaction may be supposed to use large energy for their passage to activated state and hence the large positive $\Delta H^{\#}$. The $\Delta H^{\#}$ values are positive all the studied systems indicate the positive work has to be done to overcome the energy barrier for flow process. All these concepts can equally be applied the positive values of free energy and enthalpy functions in the acetonitrile systems [77].

Table 4.1: Molar conductance of sodium dodecyl sulfate (SDS) in 80% acetonitrile + 20% water at 298.15K 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

Concentration (mol.L^{-1})	Molar conductance (ohm^{-1}cm^{2}mol^{-1})					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.005	148.24	152.73	157.23	166.21	175.20	193.16
0.01	130.27	132.52	134.77	139.26	150.49	159.47
0.02	172.95	174.07	176.32	178.56	179.69	181.93
0.03	89.84	94.64	96.36	97.48	98.83	100.10
0.04	85.35	85.91	87.04	87.60	88.72	89.84
0.05	67.83	69.18	69.63	70.53	70.98	72.32
0.06	57.28	57.65	58.40	59.15	59.90	61.02

Table 4.2: Viscosity of sodium dodecyl sulfate (SDS) in 80% acetonitrile + 20% water at 298.15K 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

Concentration (mol.L^{-1})	Viscosity (mPa.s)					
	298.15K	303.15K	308.15K	313.15K	318.15K	323.15K
0.005	0.5146	0.4814	0.4504	0.4210	0.3909	0.3697
0.01	0.5192	0.4880	0.4565	0.4271	0.3967	0.3737
0.02	0.5136	0.4777	0.4480	0.4188	0.3912	0.3703
0.03	0.5308	0.4933	0.4630	0.4333	0.4030	0.3799
0.04	0.5392	0.4980	0.4661	0.4330	0.4047	0.3818
0.05	0.5436	0.5024	0.4711	0.4403	0.4100	0.3857
0.06	0.5540	0.5118	0.4816	0.4511	0.4206	0.3949

Table 4.3: Comparison of experimental and literature values of density, ρ (g.cm^{-3}) and viscosity, η (mPa.s) of pure components at different temperatures.

Component	Temperature(K)	Density (g.cm^{-3})		viscosity (mPa.s)	
		ρ_{lit}	ρ_{exp}	η_{lit}	η_{exp}
Ethanol	298.15	0.801900	0.808823	1.0900	1.1856
	303.15	0.798255	0.804254	1.1808	1.1381
	308.15	0.794517	0.799218	1.0638	1.0865
	313.15	0.780157	0.793756	0.9646	0.9645
	318.15	0.785760	0.788145	0.8714	0.8707
	323.15	0.771336	0.783336	0.8010	0.7945
n-Propanol	298.15	0.799692	0.800209	1.9340	1.9480
	303.15	0.795840	0.796412	1.6626	1.7265
	308.15	0.797499	0.792324	1.5422	1.5420
	313.15	0.787500	0.788513	1.3000	1.3790
	318.15	0.789183	0.784317	1.2440	1.2358
	323.15	0.778500	0.781032	1.1091	1.1100
iso- Propanol	298.15	0.780000	0.778313	2.0360	2.0259
	303.15	0.777100	0.774452	1.7732	1.7627
	308.15	0.772460	0.771182	1.5420	1.5213
	313.15	0.768300	0.766973	1.3143	1.3179
	318.15	0.763500	0.762582	1.1910	1.1516
	323.15	0.75868	0.758127	1.0020	1.0075
n-Butanol	298.15	0.806000	0.806312	2.5339	2.5778
	303.15	0.802200	0.802091	2.2630	2.2710
	308.15	0.798360	0.798223	1.9778	1.9975
	313.15	0.794320	0.794370	1.7556	1.7734
	318.15	0.790500	0.789910	1.5635	1.5269
	323.15	0.785780	0.786431	1.3971	1.3631
iso-Butanol	298.15	0.7982	0.798895	3.3320	3.3493
	303.15	0.79431	0.795624	2.8840	2.8267
	308.15	0.7902	0.790135	2.4260	2.3934
	313.15	0.78612	0.786143	2.0800	2.1545
	318.15	0.7822	0.782037	1.8610	1.8675
	323.15	0.7778	0.777935	1.6020	1.6283
n-Pentanol	298.15	0.8111	0.810852	3.4800	3.5403
	303.15	0.80711	0.807124	2.9320	3.0265
	308.15	0.80352	0.803453	2.5700	2.6581
	313.15	0.7995	0.799981	2.3320	2.3143
	318.15	-	0.795903	-	2.1508
	323.15	0.7905	0.792235	1.7650	1.8012
iso-Pentanol	298.15	0.8097	0.813120	3.6100	3.6947
	303.15	0.8069	0.811860	3.1200	3.1766
	308.15	0.8027	0.807988	2.6800	2.7174
	313.15	0.7972	0.804752	2.3100	2.3653
	318.15	0.7928	0.801724	-	2.0795
	323.15	0.7881	0.797624	-	1.7437

Component	Temperature(K)	Density (g.cm^{-3})		viscosity (mPa.s)	
		ρ_{lit}	ρ_{exp}	ρ_{lit}	ρ_{exp}
Acetonitrile	298.15	0.7765	0.783584	0.341	0.3495
	303.15	0.7715	0.77938	0.328	0.3331
	308.15	0.76586	0.77406	0.314	0.3161
	313.15	0.7607	0.768948	0.3042	0.303
	318.15	0.7552	0.762628	0.2918	0.2879
	323.15	0.7495	0.758472	0.2746	0.2774

- All the literature values are cited from the reference 66-81.

Table 4.4: Density (ρ) and Excess molar volume (V^E) of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.1001	0.837512	-0.0853	0.834688	-0.1055	0.830636	-0.1441	0.827208	-0.1841	0.823504	-0.1978	0.819032	-0.2043
0.2006	0.835508	-0.1733	0.832636	-0.2029	0.829014	-0.2725	0.825528	-0.3223	0.821624	-0.3392	0.817528	-0.3733
0.2995	0.833584	-0.2594	0.830552	-0.2911	0.827864	-0.4238	0.824004	-0.4634	0.820076	-0.4941	0.815768	-0.5192
0.4005	0.831632	-0.3448	0.828506	-0.3827	0.824830	-0.4591	0.821236	-0.5278	0.816832	-0.5427	0.812884	-0.5943
0.4997	0.828632	-0.3568	0.825320	-0.3941	0.821380	-0.4577	0.817192	-0.4995	0.813048	-0.5446	0.809276	-0.6110
0.5990	0.823636	-0.2338	0.820576	-0.2975	0.816744	-0.3712	0.812912	-0.4470	0.808524	-0.4887	0.804720	-0.5558
0.7004	0.819535	-0.1630	0.816614	-0.2470	0.812136	-0.2805	0.808715	-0.3954	0.804502	-0.4622	0.800825	-0.5411
0.7997	0.815525	-0.0854	0.812619	-0.1812	0.808021	-0.2089	0.803625	-0.2672	0.800126	-0.3966	0.796621	-0.4905
0.9010	0.812132	-0.0455	0.808525	-0.1039	0.803715	-0.1187	0.798741	-0.1459	0.795415	-0.3014	0.791258	-0.3508
1.0000	0.808823	0.0000	0.804254	0.0000	0.799218	0.0000	0.793756	0.0000	0.788145	0.0000	0.783336	0.0000

Table 4.5: Density (ρ) and Excess molar volume (V^E) of n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.0993	0.835308	-0.0869	0.832872	-0.1279	0.829208	-0.1842	0.826128	-0.2353	0.823664	-0.3187	0.820922	-0.4228
0.2002	0.832984	-0.2810	0.831128	-0.3707	0.827684	-0.4420	0.824788	-0.5096	0.821828	-0.5714	0.818992	-0.6656
0.3003	0.831332	-0.5041	0.828768	-0.5586	0.824864	-0.5992	0.821648	-0.6488	0.818480	-0.7050	0.815588	-0.7905
0.4015	0.828280	-0.6222	0.825152	-0.6466	0.821272	-0.6872	0.817816	-0.7219	0.814992	-0.8111	0.811816	-0.8704
0.4997	0.824840	-0.6832	0.821668	-0.7120	0.817996	-0.7666	0.814704	-0.8155	0.811272	-0.8668	0.808236	-0.9305
0.5989	0.821472	-0.7318	0.818648	-0.7953	0.815104	-0.8592	0.811472	-0.8832	0.808108	-0.9467	0.805068	-1.0042
0.7011	0.818592	-0.8077	0.815248	-0.8378	0.811828	-0.9111	0.808456	-0.9576	0.804824	-1.0056	0.801880	-1.0651
0.8010	0.814520	-0.7576	0.811580	-0.8284	0.808420	-0.9233	0.805148	-0.9798	0.801684	-1.0481	0.798816	-1.1085
0.8999	0.807030	-0.3739	0.804196	-0.4593	0.800756	-0.5261	0.797884	-0.6175	0.796104	-0.8434	0.793860	-0.9542
1.0000	0.800209	0.0000	0.796412	0.0000	0.792324	0.0000	0.788513	0.0000	0.784317	0.0000	0.781032	0.0000

Table 4.6: Density (ρ) and Excess molar volume (V^E) of n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.0997	0.837544	-0.2334	0.834748	-0.2600	0.830576	-0.2832	0.827228	-0.3197	0.823828	-0.3493	0.819884	-0.3779
0.2002	0.835152	-0.4271	0.832176	-0.4581	0.828788	-0.5316	0.825796	-0.5979	0.822116	-0.6211	0.818452	-0.6633
0.3001	0.832192	-0.5533	0.829120	-0.5926	0.825896	-0.6777	0.822732	-0.7370	0.819060	-0.7715	0.815616	-0.8246
0.4002	0.829728	-0.6894	0.826528	-0.7334	0.823068	-0.8000	0.819872	-0.8615	0.816316	-0.9161	0.812852	-0.9628
0.5003	0.827064	-0.7838	0.823768	-0.8336	0.820468	-0.9126	0.817464	-0.9953	0.813920	-1.0621	0.810340	-1.0938
0.6005	0.824872	-0.8934	0.821408	-0.9417	0.818208	-1.0294	0.815376	-1.1335	0.811512	-1.1822	0.807868	-1.2021
0.6989	0.822716	-0.9790	0.819296	-1.0437	0.816016	-1.1239	0.813136	-1.2297	0.809220	-1.2823	0.805588	-1.2973
0.7990	0.820076	-0.9989	0.816820	-1.0922	0.813444	-1.1620	0.810156	-1.2316	0.806328	-1.3014	0.802808	-1.3211
0.8998	0.816698	-0.9146	0.813312	-1.0063	0.809568	-1.0339	0.806116	-1.0877	0.802052	-1.1388	0.798502	-1.1471
1.0000	0.806312	0.0000	0.802091	0.0000	0.798223	0.0000	0.794370	0.0000	0.789910	0.0000	0.786431	0.0000

Table 4.7: Density (ρ) and Excess molar volume (V^E) of n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.0998	0.837503	-0.2348	0.835780	-0.3280	0.830648	-0.2850	0.827248	-0.3138	0.823036	-0.2855	0.819964	-0.3745
0.2000	0.835472	-0.4473	0.832860	-0.4966	0.828472	-0.4936	0.825040	-0.5200	0.821832	-0.5703	0.818672	-0.6545
0.2992	0.832964	-0.5904	0.829972	-0.6232	0.826328	-0.6706	0.822884	-0.6954	0.819532	-0.7446	0.816860	-0.8695
0.3993	0.831597	-0.8002	0.828628	-0.8467	0.824908	-0.8840	0.821904	-0.9475	0.818536	-1.0056	0.815632	-1.1142
0.5008	0.829872	-0.9619	0.826764	-1.0069	0.823180	-1.0525	0.819912	-1.0931	0.816716	-1.1773	0.813999	-1.3064
0.6006	0.828588	-1.1381	0.825300	-1.1754	0.821404	-1.1855	0.818312	-1.2446	0.814360	-1.2605	0.811868	-1.4163
0.7003	0.827428	-1.3096	0.823652	-1.3029	0.819788	-1.3103	0.816088	-1.3035	0.812060	-1.3149	0.809569	-1.4754
0.8003	0.824788	-1.2949	0.821100	-1.3025	0.817588	-1.3443	0.814144	-1.3640	0.810096	-1.3766	0.806904	-1.4570
0.8985	0.820536	-1.0375	0.817068	-1.0749	0.814012	-1.1679	0.810084	-1.1225	0.806118	-1.1458	0.802596	-1.1805
1.0000	0.839608	0.0000	0.807124	0.0000	0.803453	0.0000	0.799981	0.0000	0.795903	0.0000	0.792235	0.0000

Table 4.8: Density (ρ) and Excess molar volume (V^E) of iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.839608	0.0000	0.839608	0.0000	0.839608	0.0000	0.839608	0.0000	0.839608	0.0000
0.1004	0.832124	-0.1062	0.832124	-0.1525	0.832124	-0.2594	0.832124	-0.3657	0.832124	-0.4459	0.832124	-0.5961
0.2007	0.828696	-0.4281	0.828696	-0.5357	0.828696	-0.6276	0.828696	-0.7255	0.828696	-0.8248	0.828696	-0.9532
0.2994	0.824276	-0.6528	0.824276	-0.7538	0.824276	-0.8061	0.824276	-0.9310	0.824276	-1.0177	0.824276	-1.2244
0.3991	0.820300	-0.8863	0.820300	-0.9443	0.820300	-1.0067	0.820300	-1.0957	0.820300	-1.2311	0.820300	-1.3994
0.5008	0.815980	-1.0790	0.815980	-1.1446	0.815980	-1.2108	0.815980	-1.2751	0.815980	-1.3863	0.815980	-1.5646
0.5997	0.811260	-1.1973	0.811260	-1.3119	0.811260	-1.3775	0.811260	-1.4345	0.811260	-1.5862	0.811260	-1.7584
0.6989	0.807216	-1.3424	0.807216	-1.4543	0.807216	-1.5358	0.807216	-1.6204	0.807216	-1.7732	0.807216	-1.8907
0.8004	0.803124	-1.4666	0.803124	-1.5735	0.803124	-1.6670	0.803124	-1.7452	0.803124	-1.9284	0.803124	-2.0029
0.9011	0.790536	-0.7759	0.790536	-0.9130	0.790536	-1.0858	0.790536	-1.3635	0.790536	-1.5356	0.790536	-1.8157
1.0000	0.778313	0.0000	0.778313	0.0000	0.778313	0.0000	0.778313	0.0000	0.778313	0.0000	0.778313	0.0000

Table 4.9: Density (ρ) and Excess molar volume (V^E) of iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.1004	0.834008	-0.0970	0.831724	-0.1448	0.827428	-0.1780	0.823848	-0.2003	0.820588	-0.2342	0.816512	-0.2605
0.2005	0.830268	-0.2635	0.828164	-0.3323	0.824160	-0.4003	0.820748	-0.4398	0.817572	-0.4894	0.813592	-0.5230
0.3002	0.827484	-0.4615	0.825736	-0.5666	0.821812	-0.6569	0.818372	-0.7006	0.815152	-0.7573	0.811392	-0.8088
0.4003	0.825204	-0.6729	0.823628	-0.8034	0.819604	-0.9023	0.816400	-0.9714	0.813260	-1.0449	0.809288	-1.0813
0.5006	0.823156	-0.8812	0.821520	-1.0192	0.817616	-1.1444	0.814480	-1.2268	0.811360	-1.3127	0.807332	-1.3452
0.6011	0.821268	-1.0841	0.819768	-1.2466	0.815824	-1.3850	0.812568	-1.4641	0.809564	-1.5713	0.805616	-1.6120
0.6999	0.819288	-1.2529	0.817960	-1.4446	0.814140	-1.6111	0.810952	-1.7038	0.807940	-1.8212	0.804104	-1.8740
0.8007	0.817040	-1.3809	0.815940	-1.6093	0.812256	-1.8065	0.809064	-1.9059	0.806268	-2.0567	0.802432	-2.1109
0.8991	0.8148072	-1.4790	0.813772	-1.7289	0.810048	-1.9383	0.80684	-2.0425	0.803914	-2.1905	0.800318	-2.2718
1.0000	0.798895	0.0000	0.795624	0.0000	0.790135	0.0000	0.786143	0.0000	0.782037	0.0000	0.777935	0.0000

Table 4.10: Density (ρ) and Excess molar volume (V^E) of iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	
	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$	$\frac{\rho}{gcm^{-3}}$	$\frac{V^E}{cm^3mol^{-1}}$
0.0000	0.839608	0.0000	0.836648	0.0000	0.832025	0.0000	0.828152	0.0000	0.824488	0.0000	0.819984	0.0000
0.0995	0.834043	0.0229	0.831759	0.0010	0.827460	-0.0106	0.823878	-0.0217	0.820623	-0.0410	0.816542	-0.0649
0.1994	0.830303	-0.0092	0.828199	-0.0268	0.824192	-0.0527	0.820778	-0.0703	0.817607	-0.0908	0.813622	-0.1203
0.3001	0.827519	-0.0667	0.825771	-0.0970	0.821844	-0.1246	0.818402	-0.1354	0.815187	-0.1477	0.811422	-0.1946
0.4004	0.825239	-0.1275	0.823663	-0.1596	0.819636	-0.1740	0.816430	-0.2010	0.813295	-0.2158	0.809318	-0.2441
0.4999	0.823191	-0.1759	0.821555	-0.1902	0.817648	-0.2110	0.814510	-0.2413	0.811395	-0.2538	0.807362	-0.2754
0.5997	0.821303	-0.2120	0.819803	-0.2277	0.815856	-0.2399	0.812598	-0.2548	0.809599	-0.2752	0.805646	-0.3036
0.6995	0.819323	-0.2107	0.817995	-0.2337	0.814172	-0.2548	0.810982	-0.2735	0.807975	-0.2895	0.804134	-0.3296
0.7997	0.817075	-0.1499	0.815975	-0.1892	0.812288	-0.2220	0.809094	-0.2365	0.806303	-0.2747	0.802462	-0.3142
0.9018	0.814842	-0.0609	0.813807	-0.0992	0.810080	-0.1230	0.806870	-0.1311	0.803949	-0.1497	0.800348	-0.2188
1.0000	0.813120	0.0000	0.811860	0.0000	0.807988	0.0000	0.804752	0.0000	0.801724	0.0000	0.797624	0.0000

Table 4.11: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) 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		
	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.4777	0.0000	0.0000	0.4480	0.0000	0.0000	0.4188	0.0000	0.0000	0.3912	0.0000	0.0000	0.3703	0.0000	0.0000
0.1001	0.5317	-0.0268	-0.5452	0.5095	-0.0116	-0.2502	0.4812	-0.0083	-0.1898	0.4506	-0.0047	-0.1898	0.4190	-0.0048	-0.1271	0.3952	-0.0045	-0.1259
0.2006	0.5545	-0.0529	-0.5681	0.5423	-0.0262	-0.2947	0.5131	-0.0220	-0.2622	0.4788	-0.0163	-0.2622	0.4485	-0.0109	-0.1491	0.4225	-0.0091	-0.1325
0.2995	0.5833	-0.0766	-0.5880	0.5776	-0.0420	-0.3343	0.5499	-0.0342	-0.2877	0.5088	-0.0289	-0.2877	0.4741	-0.0230	-0.2261	0.4487	-0.0167	-0.1746
0.4005	0.6144	-0.1036	-0.6487	0.6134	-0.0629	-0.4068	0.5848	-0.0540	-0.3678	0.5396	-0.0453	-0.3678	0.5042	-0.0348	-0.2778	0.4761	-0.0266	-0.2266
0.4997	0.6605	-0.1197	-0.6661	0.6539	-0.0832	-0.4793	0.6240	-0.0735	-0.4452	0.5736	-0.0618	-0.4452	0.5374	-0.0461	-0.3293	0.5022	-0.0401	-0.3074
0.5990	0.7132	-0.1346	-0.7196	0.6982	-0.1053	-0.5848	0.6716	-0.0901	-0.5240	0.6171	-0.0732	-0.5240	0.5767	-0.0551	-0.3797	0.5399	-0.0451	-0.3337
0.7004	0.7783	-0.1444	-0.8113	0.7599	-0.1175	-0.6853	0.7292	-0.1040	-0.6352	0.6655	-0.0858	-0.6352	0.6209	-0.0642	-0.4689	0.5854	-0.0467	-0.3655
0.7997	0.8695	-0.1332	-0.8896	0.8412	-0.1152	-0.8014	0.8125	-0.0973	-0.7062	0.7352	-0.0809	-0.7062	0.6854	-0.0564	-0.4933	0.6521	-0.0297	-0.2783
0.9010	0.9812	-0.1102	-1.1930	0.9525	-0.0919	-1.0324	0.9225	-0.0728	-0.8512	0.8425	-0.0455	-0.8512	0.7721	-0.0323	-0.4594	0.7225	-0.0142	-0.2177
1.0000	1.1856	0.0000	0.0000	1.1381	0.0000	0.0000	1.0865	0.0000	0.0000	0.9645	0.0000	0.0000	0.8707	0.0000	0.0000	0.7945	0.0000	0.0000

Table 4.12: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K to 323.15K respectively.

X_2	298.15K			303.15K			308.15K			313.15K			318.15K			323.15K		
	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.4777	0.0000	0.0000	0.4480	0.0000	0.0000	0.4188	0.0000	0.0000	0.3912	0.0000	0.0000	0.3703	0.0000	0.0000
0.0993	0.5801	-0.0062	-0.1188	0.5372	-0.0055	-0.1140	0.5015	-0.0050	-0.1110	0.4697	-0.0017	-0.0407	0.4381	-0.0004	-0.0111	0.4153	0.0024	0.0635
0.2002	0.6578	-0.0129	-0.1214	0.6035	-0.0143	-0.1466	0.5646	-0.0092	-0.1007	0.5260	-0.0056	-0.0667	0.4894	-0.0031	-0.0395	0.4619	0.0006	0.0078
0.3003	0.7343	-0.0322	-0.2040	0.6781	-0.0245	-0.1691	0.6331	-0.0163	-0.1206	0.5887	-0.0103	-0.0826	0.5449	-0.0077	-0.0668	0.5106	-0.0043	-0.0400
0.4015	0.8281	-0.0491	-0.2395	0.7604	-0.0398	-0.2123	0.7029	-0.0330	-0.1908	0.6511	-0.0247	-0.1548	0.5997	-0.0211	-0.1441	0.5601	-0.0153	-0.1122
0.4997	0.9387	-0.0611	-0.2524	0.8567	-0.0511	-0.2318	0.7849	-0.0459	-0.2275	0.7195	-0.0402	-0.2174	0.6589	-0.0362	-0.2137	0.6089	-0.0320	-0.2049
0.5989	1.0653	-0.0759	-0.2866	0.9602	-0.0710	-0.2970	0.8778	-0.0614	-0.2816	0.7978	-0.0572	-0.2883	0.7256	-0.0535	-0.2960	0.6651	-0.0495	-0.2991
0.7011	1.2119	-0.0959	-0.3634	1.0877	-0.0882	-0.3721	0.9846	-0.0811	-0.3777	0.8906	-0.0752	-0.3866	0.8063	-0.0700	-0.3971	0.7345	-0.0650	-0.4046
0.8010	1.4276	-0.0665	-0.2856	1.2856	-0.0514	-0.2458	1.1722	-0.0336	-0.1771	1.0667	-0.0212	-0.1232	0.9694	-0.0136	-0.0872	0.8854	-0.0068	-0.0478
0.8999	1.6633	-0.0413	-0.2726	1.4915	-0.0266	-0.1965	1.3538	-0.0087	-0.0715	1.2200	-0.0039	-0.0357	1.0995	-0.0019	-0.0191	0.9943	-0.0002	-0.0021
1.0000	1.9480	0.0000	0.0000	1.7265	0.0000	0.0000	1.5420	0.0000	0.0000	1.3790	0.0000	0.0000	1.2358	0.0000	0.0000	1.1100	0.0000	0.0000

Table 4.13: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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		
	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000
0.0997	0.6552	0.0520	0.9208	0.6552	0.0520	0.9208	0.6552	0.0520	0.9208	0.6552	0.0520	0.9208	0.6552	0.0520	0.9208	0.6552	0.0520	0.9208
0.2002	0.7342	0.0248	0.2146	0.7342	0.0248	0.2146	0.7342	0.0248	0.2146	0.7342	0.0248	0.2146	0.7342	0.0248	0.2146	0.7342	0.0248	0.2146
0.3001	0.8015	-0.0320	-0.1861	0.8015	-0.0320	-0.1861	0.8015	-0.0320	-0.1861	0.8015	-0.0320	-0.1861	0.8015	-0.0320	-0.1861	0.8015	-0.0320	-0.1861
0.4002	0.8903	-0.0892	-0.3979	0.8903	-0.0892	-0.3979	0.8903	-0.0892	-0.3979	0.8903	-0.0892	-0.3979	0.8903	-0.0892	-0.3979	0.8903	-0.0892	-0.3979
0.5003	0.9675	-0.1837	-0.6953	0.9675	-0.1837	-0.6953	0.9675	-0.1837	-0.6953	0.9675	-0.1837	-0.6953	0.9675	-0.1837	-0.6953	0.9675	-0.1837	-0.6953
0.6005	1.1016	-0.2516	-0.8574	1.1016	-0.2516	-0.8574	1.1016	-0.2516	-0.8574	1.1016	-0.2516	-0.8574	1.1016	-0.2516	-0.8574	1.1016	-0.2516	-0.8574
0.6989	1.2505	-0.3355	-1.1293	1.2505	-0.3355	-1.1293	1.2505	-0.3355	-1.1293	1.2505	-0.3355	-1.1293	1.2505	-0.3355	-1.1293	1.2505	-0.3355	-1.1293
0.7990	1.4566	-0.4073	-1.5353	1.4566	-0.4073	-1.5353	1.4566	-0.4073	-1.5353	1.4566	-0.4073	-1.5353	1.4566	-0.4073	-1.5353	1.4566	-0.4073	-1.5353
0.8998	1.7485	-0.4445	-2.5125	1.7485	-0.4445	-2.5125	1.7485	-0.4445	-2.5125	1.7485	-0.4445	-2.5125	1.7485	-0.4445	-2.5125	1.7485	-0.4445	-2.5125
1.0000	2.5778	0.0000	0.0000	2.5778	0.0000	0.0000	2.5778	0.0000	0.0000	2.5778	0.0000	0.0000	2.5778	0.0000	0.0000	2.5778	0.0000	0.0000

Table 4.14: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) 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		
	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε	η / mPa.s	η^E / mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000
0.0998	0.6293	0.0065	0.1160	0.6293	0.0065	0.1160	0.6293	0.0065	0.1160	0.6293	0.0065	0.1160	0.6293	0.0065	0.1160	0.6293	0.0065	0.1160
0.2000	0.7480	-0.0076	-0.0635	0.7480	-0.0076	-0.0635	0.7480	-0.0076	-0.0635	0.7480	-0.0076	-0.0635	0.7480	-0.0076	-0.0635	0.7480	-0.0076	-0.0635
0.2992	0.8828	-0.0323	-0.1716	0.8828	-0.0323	-0.1716	0.8828	-0.0323	-0.1716	0.8828	-0.0323	-0.1716	0.8828	-0.0323	-0.1716	0.8828	-0.0323	-0.1716
0.3993	1.0498	-0.0604	-0.2331	1.0498	-0.0604	-0.2331	1.0498	-0.0604	-0.2331	1.0498	-0.0604	-0.2331	1.0498	-0.0604	-0.2331	1.0498	-0.0604	-0.2331
0.5008	1.2582	-0.0924	-0.2835	1.2582	-0.0924	-0.2835	1.2582	-0.0924	-0.2835	1.2582	-0.0924	-0.2835	1.2582	-0.0924	-0.2835	1.2582	-0.0924	-0.2835
0.6006	1.5083	-0.1291	-0.3424	1.5083	-0.1291	-0.3424	1.5083	-0.1291	-0.3424	1.5083	-0.1291	-0.3424	1.5083	-0.1291	-0.3424	1.5083	-0.1291	-0.3424
0.7003	1.8187	-0.1662	-0.4166	1.8187	-0.1662	-0.4166	1.8187	-0.1662	-0.4166	1.8187	-0.1662	-0.4166	1.8187	-0.1662	-0.4166	1.8187	-0.1662	-0.4166
0.8003	2.2003	-0.2075	-0.5640	2.2003	-0.2075	-0.5640	2.2003	-0.2075	-0.5640	2.2003	-0.2075	-0.5640	2.2003	-0.2075	-0.5640	2.2003	-0.2075	-0.5640
0.8985	2.7373	-0.1728	-0.6710	2.7373	-0.1728	-0.6710	2.7373	-0.1728	-0.6710	2.7373	-0.1728	-0.6710	2.7373	-0.1728	-0.6710	2.7373	-0.1728	-0.6710
1.0000	3.5403	0.0000	0.0000	3.5403	0.0000	0.0000	3.5403	0.0000	0.0000	3.5403	0.0000	0.0000	3.5403	0.0000	0.0000	3.5403	0.0000	0.0000

Table 4.15: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) 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		
	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000
0.1004	0.6131	0.0236	0.4351	0.6131	0.0236	0.4351	0.6131	0.0236	0.4351	0.6131	0.0236	0.4351	0.6131	0.0236	0.4351	0.6131	0.0236	0.4351
0.2007	0.6911	0.0146	0.1335	0.6911	0.0146	0.1335	0.6911	0.0146	0.1335	0.6911	0.0146	0.1335	0.6911	0.0146	0.1335	0.6911	0.0146	0.1335
0.2994	0.7478	-0.0268	-0.1679	0.7478	-0.0268	-0.1679	0.7478	-0.0268	-0.1679	0.7478	-0.0268	-0.1679	0.7478	-0.0268	-0.1679	0.7478	-0.0268	-0.1679
0.3991	0.8164	-0.0717	-0.3510	0.8164	-0.0717	-0.3510	0.8164	-0.0717	-0.3510	0.8164	-0.0717	-0.3510	0.8164	-0.0717	-0.3510	0.8164	-0.0717	-0.3510
0.5008	0.9037	-0.1175	-0.4888	0.9037	-0.1175	-0.4888	0.9037	-0.1175	-0.4888	0.9037	-0.1175	-0.4888	0.9037	-0.1175	-0.4888	0.9037	-0.1175	-0.4888
0.5997	1.0083	-0.1612	-0.6179	1.0083	-0.1612	-0.6179	1.0083	-0.1612	-0.6179	1.0083	-0.1612	-0.6179	1.0083	-0.1612	-0.6179	1.0083	-0.1612	-0.6179
0.6989	1.1452	-0.1950	-0.7473	1.1452	-0.1950	-0.7473	1.1452	-0.1950	-0.7473	1.1452	-0.1950	-0.7473	1.1452	-0.1950	-0.7473	1.1452	-0.1950	-0.7473
0.8004	1.2856	-0.2549	-1.1323	1.2856	-0.2549	-1.1323	1.2856	-0.2549	-1.1323	1.2856	-0.2549	-1.1323	1.2856	-0.2549	-1.1323	1.2856	-0.2549	-1.1323
0.9011	1.5234	-0.2453	-1.6751	1.5234	-0.2453	-1.6751	1.5234	-0.2453	-1.6751	1.5234	-0.2453	-1.6751	1.5234	-0.2453	-1.6751	1.5234	-0.2453	-1.6751
1.0000	2.0259	0.0000	0.0000	2.0259	0.0000	0.0000	2.0259	0.0000	0.0000	2.0259	0.0000	0.0000	2.0259	0.0000	0.0000	2.0259	0.0000	0.0000

Table 4.16: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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		
	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε	η/mPa.s	η^E/mPa.s	ε
0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000
0.1004	0.5990	-0.0209	-0.3798	0.5990	-0.0209	-0.3798	0.5990	-0.0209	-0.3798	0.5990	-0.0209	-0.3798	0.5990	-0.0209	-0.3798	0.5990	-0.0209	-0.3798
0.2005	0.6843	-0.0636	-0.5546	0.6843	-0.0636	-0.5546	0.6843	-0.0636	-0.5546	0.6843	-0.0636	-0.5546	0.6843	-0.0636	-0.5546	0.6843	-0.0636	-0.5546
0.3002	0.8127	-0.0891	-0.4951	0.8127	-0.0891	-0.4951	0.8127	-0.0891	-0.4951	0.8127	-0.0891	-0.4951	0.8127	-0.0891	-0.4951	0.8127	-0.0891	-0.4951
0.4003	0.9525	-0.1355	-0.5539	0.9525	-0.1355	-0.5539	0.9525	-0.1355	-0.5539	0.9525	-0.1355	-0.5539	0.9525	-0.1355	-0.5539	0.9525	-0.1355	-0.5539
0.5006	1.1153	-0.1976	-0.6526	1.1153	-0.1976	-0.6526	1.1153	-0.1976	-0.6526	1.1153	-0.1976	-0.6526	1.1153	-0.1976	-0.6526	1.1153	-0.1976	-0.6526
0.6011	1.3392	-0.2461	-0.7035	1.3392	-0.2461	-0.7035	1.3392	-0.2461	-0.7035	1.3392	-0.2461	-0.7035	1.3392	-0.2461	-0.7035	1.3392	-0.2461	-0.7035
0.6999	1.6084	-0.2997	-0.8137	1.6084	-0.2997	-0.8137	1.6084	-0.2997	-0.8137	1.6084	-0.2997	-0.8137	1.6084	-0.2997	-0.8137	1.6084	-0.2997	-0.8137
0.8007	1.9692	-0.3358	-0.9866	1.9692	-0.3358	-0.9866	1.9692	-0.3358	-0.9866	1.9692	-0.3358	-0.9866	1.9692	-0.3358	-0.9866	1.9692	-0.3358	-0.9866
0.8991	2.4725	-0.2994	-1.2598	2.4725	-0.2994	-1.2598	2.4725	-0.2994	-1.2598	2.4725	-0.2994	-1.2598	2.4725	-0.2994	-1.2598	2.4725	-0.2994	-1.2598
1.0000	3.3493	0.0000	0.0000	3.3493	0.0000	0.0000	3.3493	0.0000	0.0000	3.3493	0.0000	0.0000	3.3493	0.0000	0.0000	3.3493	0.0000	0.0000

Table 4.17: Viscosity (η), Excess viscosity (η^E) and Interaction parameter (ε) of iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) system 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		
	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε	$\frac{\eta}{\text{mPa.s}}$	$\frac{\eta^E}{\text{mPa.s}}$	ε
0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000	0.5136	0.0000	0.0000
0.0995	0.6249	-0.0001	-0.0024	0.6249	-0.0001	-0.0024	0.6249	-0.0001	-0.0024	0.6249	-0.0001	-0.0024	0.6249	-0.0001	-0.0024	0.6249	-0.0001	-0.0024
0.1994	0.7559	-0.0053	-0.0439	0.7559	-0.0053	-0.0439	0.7559	-0.0053	-0.0439	0.7559	-0.0053	-0.0439	0.7559	-0.0053	-0.0439	0.7559	-0.0053	-0.0439
0.3001	0.9203	-0.0083	-0.0425	0.9203	-0.0083	-0.0425	0.9203	-0.0083	-0.0425	0.9203	-0.0083	-0.0425	0.9203	-0.0083	-0.0425	0.9203	-0.0083	-0.0425
0.4004	1.1046	-0.0271	-0.1010	1.1046	-0.0271	-0.1010	1.1046	-0.0271	-0.1010	1.1046	-0.0271	-0.1010	1.1046	-0.0271	-0.1010	1.1046	-0.0271	-0.1010
0.4999	1.3306	-0.0467	-0.1381	1.3306	-0.0467	-0.1381	1.3306	-0.0467	-0.1381	1.3306	-0.0467	-0.1381	1.3306	-0.0467	-0.1381	1.3306	-0.0467	-0.1381
0.5997	1.5792	-0.0978	-0.2503	1.5792	-0.0978	-0.2503	1.5792	-0.0978	-0.2503	1.5792	-0.0978	-0.2503	1.5792	-0.0978	-0.2503	1.5792	-0.0978	-0.2503
0.6995	1.8802	-0.1618	-0.3927	1.8802	-0.1618	-0.3927	1.8802	-0.1618	-0.3927	1.8802	-0.1618	-0.3927	1.8802	-0.1618	-0.3927	1.8802	-0.1618	-0.3927
0.7997	2.2568	-0.2318	-0.6106	2.2568	-0.2318	-0.6106	2.2568	-0.2318	-0.6106	2.2568	-0.2318	-0.6106	2.2568	-0.2318	-0.6106	2.2568	-0.2318	-0.6106
0.9018	2.8010	-0.2431	-0.9402	2.8010	-0.2431	-0.9402	2.8010	-0.2431	-0.9402	2.8010	-0.2431	-0.9402	2.8010	-0.2431	-0.9402	2.8010	-0.2431	-0.9402
1.0000	3.6947	0.0000	0.0000	3.6947	0.0000	0.0000	3.6947	0.0000	0.0000	3.6947	0.0000	0.0000	3.6947	0.0000	0.0000	3.6947	0.0000	0.0000

Table 4.18: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1001	10.3870	10.4621	10.5011	10.5107	10.3334	10.5209	-0.1233	-0.0593	-0.0482	-0.0336	-0.0368	-0.0379
0.2006	10.5274	10.6565	10.7015	10.7061	10.5479	10.7380	-0.2295	-0.1242	-0.1163	-0.0980	-0.0738	-0.0707
0.2995	10.6876	10.8514	10.9129	10.8997	10.7283	10.9370	-0.3121	-0.1845	-0.1689	-0.1600	-0.1409	-0.1175
0.4005	10.8522	11.0393	11.1106	11.0930	10.9300	11.1381	-0.3955	-0.2573	-0.2411	-0.2279	-0.1921	-0.1676
0.4997	11.0690	11.2395	11.3173	11.2951	11.1383	11.3244	-0.4222	-0.3131	-0.2993	-0.2823	-0.2322	-0.2280
0.5990	11.3026	11.4482	11.5493	11.5288	11.3664	11.5652	-0.4323	-0.3607	-0.3326	-0.3053	-0.2527	-0.2341
0.7004	11.5604	11.7030	11.8045	11.7687	11.6020	11.8266	-0.4234	-0.3675	-0.3481	-0.3275	-0.2709	-0.2248
0.7997	11.8750	11.9997	12.1233	12.0739	11.9026	12.1607	-0.3525	-0.3270	-0.2945	-0.2790	-0.2187	-0.1375
0.9010	12.2130	12.3542	12.4912	12.4739	12.2576	12.4847	-0.2633	-0.2341	-0.1972	-0.1409	-0.1175	-0.0655
1.0000	12.7192	12.8438	12.9528	12.8708	12.6228	12.7963	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.19: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n- Propanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0993	10.6911	10.6841	10.6955	10.7081	10.5346	10.7364	-0.0075	-0.0084	-0.0106	0.0031	0.0059	0.0186
0.2002	11.1185	11.0934	11.1163	11.1214	10.9430	11.1464	-0.0212	-0.0356	-0.0208	-0.0100	-0.0013	0.0143
0.3003	11.4996	11.4995	11.5254	11.5332	11.3420	11.5390	-0.0776	-0.0625	-0.0392	-0.0212	-0.0147	-0.0042
0.4015	11.9071	11.9013	11.9082	11.9131	11.7081	11.9089	-0.1125	-0.0985	-0.0886	-0.0689	-0.0656	-0.0500
0.4997	12.3218	12.3078	12.2980	12.2815	12.0635	12.2467	-0.1270	-0.1168	-0.1183	-0.1154	-0.1148	-0.1154
0.5989	12.7367	12.6972	12.6879	12.6566	12.4204	12.5933	-0.1457	-0.1565	-0.1521	-0.1595	-0.1665	-0.1763
0.7011	13.1556	13.1140	13.0859	13.0479	12.8007	12.9687	-0.1735	-0.1818	-0.1905	-0.2001	-0.2073	-0.2206
0.8010	13.6594	13.6335	13.6318	13.6180	13.3802	13.5736	-0.1064	-0.0945	-0.0713	-0.0521	-0.0393	-0.0260
0.8999	14.1429	14.1141	14.1097	14.0771	13.8121	13.9906	-0.0552	-0.0417	-0.0158	-0.0109	-0.0148	-0.0152
1.0000	14.6356	14.5888	14.5531	14.5109	14.2394	14.4169	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.20: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0997	11.0662	11.1275	11.2140	11.2787	11.1246	11.3861	0.2466	0.3134	0.3884	0.4542	0.4868	0.5574
0.2002	11.5349	11.6233	11.7062	11.7415	11.6185	11.8997	0.1560	0.2537	0.3327	0.3736	0.4583	0.5481
0.3001	11.9275	12.0102	12.0847	12.1397	11.9779	12.2447	-0.0075	0.0884	0.1665	0.2316	0.2984	0.3731
0.4002	12.3516	12.3929	12.4159	12.4593	12.2729	12.5648	-0.1407	-0.0821	-0.0481	0.0099	0.0732	0.1724
0.5003	12.7126	12.8008	12.8455	12.8818	12.6445	12.9085	-0.3368	-0.2275	-0.1643	-0.1088	-0.0756	-0.0048
0.6005	13.1798	13.2091	13.2814	13.2939	13.0801	13.3521	-0.4273	-0.3730	-0.2748	-0.2384	-0.1608	-0.0826
0.6989	13.6298	13.6612	13.6828	13.7050	13.4834	13.7406	-0.5251	-0.4648	-0.4099	-0.3594	-0.2690	-0.2062
0.7990	14.1408	14.1195	14.0872	14.1262	13.8551	14.1748	-0.5713	-0.5598	-0.5512	-0.4794	-0.4175	-0.2929
0.8998	14.7235	14.7180	14.7223	14.6935	14.3241	14.6230	-0.5497	-0.5185	-0.4657	-0.4572	-0.4725	-0.3691
1.0000	15.8310	15.7903	15.7344	15.6924	15.3175	15.5136	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.21: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0998	11.0436	11.0628	11.1064	11.0987	10.9491	11.1747	0.1033	0.1338	0.1644	0.1611	0.1785	0.2261
0.2000	11.7217	11.7219	11.7582	11.7728	11.6431	11.8492	0.1033	0.1244	0.1539	0.1807	0.2193	0.2596
0.2992	12.3596	12.3543	12.3919	12.4007	12.2642	12.4454	0.0699	0.0950	0.1317	0.1606	0.1935	0.2211
0.3993	12.9969	12.9742	13.0078	13.0013	12.8441	13.0104	0.0296	0.0470	0.0857	0.1072	0.1206	0.1457
0.5008	13.6416	13.6150	13.6297	13.5997	13.4440	13.6052	-0.0130	0.0103	0.0363	0.0422	0.0582	0.0907
0.6006	14.2690	14.2324	14.2297	14.1916	14.0412	14.1726	-0.0607	-0.0378	-0.0232	-0.0175	0.0049	0.0199
0.7003	14.8989	14.8355	14.8266	14.7733	14.6171	14.7396	-0.1055	-0.0998	-0.0854	-0.0870	-0.0692	-0.0508
0.8003	15.5322	15.4320	15.3905	15.3187	15.1498	15.2572	-0.1496	-0.1710	-0.1831	-0.1954	-0.1892	-0.1736
0.8985	16.2277	16.1400	16.1088	16.0297	15.8599	15.9541	-0.1182	-0.1177	-0.1135	-0.1255	-0.1189	-0.1045
1.0000	17.0332	16.9353	16.8937	16.8185	16.6411	16.7083	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.22: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1004	10.8389	10.8402	10.8252	10.8069	10.6202	10.8175	0.1189	0.1306	0.1109	0.1018	0.0982	0.1134
0.2007	11.2542	11.2708	11.2532	11.2299	11.0140	11.1459	0.0791	0.1150	0.1070	0.1056	0.0898	0.0479
0.2994	11.5650	11.5402	11.5232	11.4823	11.2626	11.4505	-0.0581	-0.0549	-0.0481	-0.0547	-0.0575	-0.0352
0.3991	11.8934	11.8544	11.8369	11.8130	11.5889	11.7555	-0.1817	-0.1838	-0.1633	-0.1403	-0.1305	-0.1214
0.5008	12.2554	12.2159	12.1753	12.1286	11.8919	12.0593	-0.2813	-0.2749	-0.2629	-0.2499	-0.2354	-0.2170
0.5997	12.6322	12.5758	12.5323	12.4698	12.2214	12.3817	-0.3531	-0.3549	-0.3317	-0.3221	-0.3024	-0.2830
0.6989	13.0481	12.9847	12.9377	12.8635	12.6061	12.7567	-0.3875	-0.3876	-0.3537	-0.3433	-0.3156	-0.2977
0.8004	13.4342	13.3484	13.3009	13.2197	12.9379	13.0825	-0.4619	-0.4753	-0.4275	-0.4111	-0.3908	-0.3704
0.9011	13.9772	13.8919	13.8099	13.7291	13.4234	13.5707	-0.3756	-0.3797	-0.3520	-0.3225	-0.3088	-0.2774
1.0000	14.8016	14.7116	14.5878	14.4650	14.1288	14.2366	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.23: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1004	10.8558	10.8847	10.8918	10.9316	10.7609	10.9900	-0.0349	0.0096	0.0134	0.0498	0.0645	0.1069
0.2005	11.3756	11.4046	11.4051	11.4359	11.2296	11.4758	-0.1396	-0.0812	-0.0681	-0.0406	-0.0424	0.0211
0.3002	11.9762	11.9625	11.9693	11.9795	11.7564	11.9943	-0.1612	-0.1316	-0.0965	-0.0896	-0.0888	-0.0300
0.4003	12.5328	12.5021	12.4827	12.4751	12.2430	12.4767	-0.2292	-0.2026	-0.1779	-0.1887	-0.1778	-0.1193
0.5006	13.0772	13.0374	12.9892	13.0269	12.7708	12.9707	-0.3101	-0.2787	-0.2670	-0.2324	-0.2262	-0.1977
0.6011	13.6756	13.5832	13.5174	13.5364	13.2580	13.4445	-0.3387	-0.3460	-0.3361	-0.3200	-0.3168	-0.2979
0.6999	14.2654	14.1609	14.0344	14.0792	13.7865	13.9601	-0.3656	-0.3713	-0.4064	-0.3646	-0.3565	-0.3468
0.8007	14.8994	14.7724	14.6474	14.6295	14.3226	14.5064	-0.3601	-0.3744	-0.3921	-0.4128	-0.3996	-0.3759
0.8991	15.5872	15.4873	15.3716	15.3838	15.0310	15.1858	-0.2861	-0.2596	-0.2525	-0.2430	-0.2567	-0.2583
1.0000	16.5029	16.3624	16.2237	16.2263	15.8678	16.0204	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.24: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) 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	10.2646	10.2630	10.2820	10.2855	10.1195	10.3099	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0995	11.0356	11.0552	11.0718	11.0786	10.9355	11.1309	0.0877	0.1178	0.1277	0.1390	0.1777	0.1949
0.1994	11.7618	11.7683	11.8126	11.8286	11.6601	11.8788	0.1277	0.1534	0.2037	0.2321	0.2613	0.3139
0.3001	12.4809	12.4748	12.4968	12.5197	12.3557	12.5555	0.1554	0.1773	0.2180	0.2612	0.3110	0.3571
0.4004	13.1440	13.1440	13.1558	13.1596	12.9736	13.1931	0.1298	0.1666	0.2098	0.2419	0.2857	0.3636
0.4999	13.7986	13.7798	13.7695	13.7796	13.5601	13.7454	0.1008	0.1276	0.1611	0.2075	0.2337	0.2894
0.5997	14.4033	14.3609	14.3231	14.3197	14.0798	14.2333	0.0203	0.0323	0.0508	0.0916	0.1133	0.1495
0.6995	15.0045	14.9621	14.9108	14.8673	14.6080	14.7316	-0.0638	-0.0431	-0.0255	-0.0169	0.0013	0.0198
0.7997	15.6174	15.5369	15.4432	15.4253	15.1394	15.2233	-0.1394	-0.1479	-0.1602	-0.1179	-0.1103	-0.1194
0.9018	16.3067	16.2384	16.1734	16.1366	15.8372	15.9459	-0.1512	-0.1386	-0.1093	-0.0778	-0.0674	-0.0393
1.0000	17.1321	17.0425	16.9358	16.8598	16.5343	16.6029	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4.25: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Ethanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7856	0.0000	-1.5797	0.0000
0.1001	9.0539	-0.9830	-4.5893	-2.9972
0.2006	8.4304	-1.8588	-7.2082	-5.6036
0.2995	8.3556	-2.1819	-8.0729	-6.4559
0.4005	8.1303	-2.6609	-9.4114	-7.7818
0.4997	8.5468	-2.4935	-8.7214	-7.0794
0.5990	8.5967	-2.6929	-9.3034	-7.6490
0.7004	8.9292	-2.6149	-9.0290	-7.3620
0.7997	9.0623	-2.7312	-9.6193	-7.9399
0.9010	9.4198	-2.6281	-9.6276	-7.9356
1.0000	12.2964	0.0000	-1.7044	0.0000

Table 4.26: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy (($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7856	0.0000	-1.5797	0.0000
0.0993	10.1930	-0.3290	-1.6129	-1.0462
0.2002	10.7500	-0.5203	-1.1640	-1.6266
0.3003	11.0327	-0.9800	-1.5547	-3.0385
0.4015	11.9223	-0.8409	0.0582	-2.4580
0.4997	13.2608	-0.2306	3.1510	-0.3669
0.5989	14.4913	0.2642	5.6535	1.1236
0.7011	15.3809	0.3959	7.4577	1.8852
0.8010	14.6243	-1.1015	3.2341	-3.3574
0.8999	15.9130	-0.5463	5.9196	-1.6809
1.0000	17.2017	0.0000	8.6216	0.0000

Table 4.27: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7898	0.0000	-1.5805	0.0000
0.0997	7.3403	-3.4462	-12.5176	-12.4105
0.2002	7.4584	-4.3329	-13.7123	-15.0905
0.3001	8.3281	-4.4619	-12.1276	-14.9823
0.4002	10.0949	-3.6959	-7.5566	-11.8906
0.5003	10.7616	-4.0298	-6.6645	-12.4779
0.6005	11.2912	-4.5020	-6.3610	-13.6553
0.6989	12.4710	-4.3060	-3.9101	-12.6586
0.7990	14.0349	-3.7428	-0.2760	-10.5039
0.8998	16.4958	-2.2896	5.8697	-5.8479
1.0000	19.7872	0.0000	13.1985	0.0000

Table 4.28: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7898	0.0000	-1.5805	0.0000
0.0998	9.6417	-1.1744	-4.6991	-4.3011
0.2000	10.0699	-1.7762	-5.4889	-6.2776
0.2992	11.0751	-1.7909	-4.2709	-6.2346
0.3993	12.5084	-1.3867	-1.6029	-4.7524
0.5008	13.7854	-1.1537	0.5171	-3.8352
0.6006	14.9901	-0.9745	2.4584	-3.0755
0.7003	16.2722	-0.7173	4.6733	-2.0414
0.8003	18.2093	0.1910	9.0847	1.1846
0.8985	18.8329	-0.1943	8.8120	-0.2504
1.0000	20.0712	0.0000	10.2653	0.0000

Table 4.29: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Propanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7898	0.0000	-1.5805	0.0000
0.1004	11.3314	0.3483	1.6478	0.7590
0.2007	12.6390	0.4638	4.5552	1.1996
0.2994	13.1282	-0.2205	5.2403	-0.5436
0.3991	13.5303	-1.0024	5.5022	-2.7319
0.5008	14.7094	-1.0324	8.2309	-2.5051
0.5997	15.7048	-1.2123	10.3127	-2.8554
0.6989	16.5803	-1.5166	11.8491	-3.7604
0.8004	17.6245	-1.6785	14.0665	-4.0390
0.9011	18.8967	-1.6027	16.5058	-4.0753
1.0000	21.6751	0.0000	23.0140	0.0000

Table 4.30: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Butanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7898	0.0000	-1.5805	0.0000
0.1004	9.4114	-1.5890	-4.8221	-5.2127
0.2005	10.4673	-1.7408	-3.0512	-5.4080
0.3002	11.9056	-1.5055	-0.1829	-4.4984
0.4003	13.3689	-1.2499	2.8434	-3.4384
0.5006	14.2502	-1.5777	3.9824	-4.2679
0.6011	16.1957	-0.8448	8.5717	-1.6527
0.6999	17.5924	-0.6406	11.2904	-0.8756
0.8007	19.4298	-0.0184	15.3310	1.1864
0.8991	20.0949	-0.5401	13.5269	-2.5501
1.0000	21.8524	0.0000	18.0588	0.0000

Table 4.31: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) system.

X_2	$\frac{\Delta H^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta H^{\#E}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#}}{KJ.mol^{-1}}$	$\frac{\Delta S^{\#E}}{KJ.mol^{-1}}$
0.0000	9.7898	0.0000	-1.5805	0.0000
0.0995	9.9445	-1.1618	-3.6565	-4.1956
0.1994	10.3465	-2.0820	-4.7307	-7.3985
0.3001	11.4125	-2.3483	-3.5434	-8.3563
0.4004	12.5446	-2.5431	-1.9904	-8.9395
0.4999	14.2582	-2.1466	1.5555	-7.5142
0.5997	16.1502	-1.5749	5.8788	-5.3166
0.6995	18.0286	-1.0168	10.1156	-3.2056
0.7997	19.8011	-0.5709	14.0465	-1.4105
0.9018	20.2022	-1.5207	13.0497	-4.5824
1.0000	23.0218	0.0000	19.7233	0.0000

Table 4.32: Coefficient, a_o of Redlich-Kisher Equation express in V^E and Standard deviation, σ for the Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) systems.

Systems	T/K	a_o	a_1	a_2	a_3	σ
Ethanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-1.2776	0.8523	1.1805	-1.0071	0.0248
	303.15	-1.4617	0.5290	0.6786	-0.9698	0.0214
	308.15	-1.7763	0.9771	0.6306	-1.4215	0.0136
	313.15	-2.0425	0.5757	0.3729	-0.6280	0.0152
	318.15	-2.1347	0.5167	-0.7492	2.0638	0.0158
	323.15	-2.3794	0.2455	-0.9791	-2.1430	0.0132
n-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-2.8725	-1.7229	-0.4492	-0.9934	0.0563
	303.15	-2.9890	-1.6101	-1.3826	-1.4046	0.0491
	308.15	-3.1755	-1.8453	-2.1870	-1.1301	0.0494
	313.15	-3.2878	-1.6725	-3.0655	-1.7152	0.0395
	318.15	-3.4387	-1.1904	-4.5320	-3.7341	0.0153
	323.15	-3.6291	-1.0013	-5.6924	-3.9801	0.0324
iso-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-4.3471	-3.9595	-2.5981	-2.1198	0.0978
	303.15	-4.6501	-3.9755	-3.7020	-2.7200	0.0868
	308.15	-4.8182	-3.9503	-5.2639	-3.2798	0.0600
	313.15	-5.0019	-3.1957	-7.2966	-5.9212	0.0169
	318.15	-5.4716	-3.4327	-8.5270	-6.5480	0.0261
	323.15	-6.0648	-2.6428	-9.9531	-8.7447	0.0810
n-Butanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-3.0534	-1.7211	-4.4454	-4.3099	0.0417
	303.15	-3.2194	-1.7769	-5.1126	-4.9710	0.0452
	308.15	-3.5564	-1.8134	-5.2513	-4.8939	0.0376
	313.15	-3.8937	-2.1290	-5.5136	-4.4148	0.0434
	318.15	-4.1037	-3.7020	-2.7200	0.0868	0.0445
	323.15	-4.2376	-1.9592	-5.9080	-4.8738	0.0413
iso-Butanol + 80%acetonitrile + 20% water + 0.02M SDS systems	298.15	-3.2727	-3.1041	-6.6170	-9.2444	0.1014
	303.15	-3.7959	-3.3239	-8.0238	-11.0387	0.1174
	308.15	-4.2442	-3.5448	-9.2190	-12.4933	0.1288
	313.15	-4.5292	-3.6775	-9.7099	-13.1249	0.1370
	318.15	-4.8472	-3.9257	-10.6293	-13.9411	0.1452
	323.15	-4.9813	-3.8379	-11.2087	-14.6039	0.1520
n-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-3.8186	-3.5928	-4.7217	-2.8128	0.0219
	303.15	-3.9239	-3.4701	-5.1970	-2.4363	0.0416
	308.15	-4.0434	-2.9179	-5.3073	-4.7052	0.0474
	313.15	-4.2478	-2.9425	-4.9110	-4.0671	0.0495
	318.15	-4.4740	-2.4382	-4.6146	-5.2676	0.0523
	323.15	-5.0346	-2.8983	-4.7463	-3.9348	0.0449
iso-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.7386	-0.9270	0.7053	0.5273	0.0067
	303.15	-0.8101	-0.8270	0.3477	0.1055	0.0083
	308.15	-0.8747	-0.7698	0.0766	-0.1249	0.0087
	313.15	-0.9671	-0.7642	0.0788	-0.1146	0.0087
	318.15	-1.0177	-0.8288	-0.2057	-0.0626	0.0111
	323.15	-1.1124	-0.6976	-0.7356	-0.6921	0.0058

Table 4.33: Coefficient, a_o of Redlich-Kisher Equation express in η^E and Standard deviation, σ for the Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) systems.

Systems	T/K	a_o	a_1	a_2	a_3	σ
Ethanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.4744	-0.3139	-0.3694	0.3840	0.0047
	303.15	-0.3315	-0.4099	-0.3405	-0.2083	0.0027
	308.15	-0.2913	-0.3825	-0.2385	-0.0850	0.0017
	313.15	-0.2493	-0.3417	-0.1052	0.0600	0.0032
	318.15	-0.1891	-0.2511	-0.0530	0.0713	0.0021
	323.15	-0.1577	-0.2034	0.0861	0.2271	0.0017
n-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.2656	-0.3688	-0.0129	0.2011	0.0063
	303.15	-0.2358	-0.3954	0.0447	0.4328	0.0073
	308.15	-0.2118	-0.4160	0.1659	0.6542	0.0087
	313.15	-0.1883	-0.4216	0.2165	0.7187	0.0098
	318.15	-0.1727	-0.4040	0.2396	0.7139	0.0103
	323.15	-0.1543	-0.3958	0.2628	0.7062	0.0109
iso-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.4245	-0.7735	-1.0312	-1.7206	0.0131
	303.15	-0.3734	-0.6900	-0.8363	-1.5444	0.0119
	308.15	-0.3095	-0.5612	-0.5978	-1.1694	0.0106
	313.15	-0.2647	-0.5136	-0.4281	-0.8087	0.0077
	318.15	-0.2216	-0.4080	-0.3409	-0.7093	0.0067
	323.15	-0.1805	-0.4957	-0.2316	-0.4957	0.0042
n-Butanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.6282	-1.2968	-1.9388	-3.1211	0.0274
	303.15	-0.4533	-1.1821	-1.5874	-2.7128	0.0181
	308.15	-0.3238	-1.0089	-1.2099	-2.4506	0.0104
	313.15	-0.2277	-0.8458	-0.9155	-2.2487	0.0108
	318.15	-0.1253	-0.6230	-0.7080	-2.3026	0.0166
	323.15	-0.0481	-0.5829	-0.2655	-1.6752	0.0125
iso-Butanol + 80% acetonitrile +20% water + 0.02M SDS systems	298.15	-0.7347	-1.0184	-1.4743	-1.3184	0.0108
	303.15	-0.6278	-1.0227	-1.0593	-0.7199	0.0041
	308.15	-0.5379	-1.0248	-0.8902	-0.2814	0.0068
	313.15	-0.4617	-0.8342	-0.7710	-0.4588	0.0125
	318.15	-0.4029	-0.6884	-0.6639	-0.5028	0.0083
	323.15	-0.3228	-0.6442	-0.5052	-0.3739	0.0048
n-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.3564	-0.6749	-0.8559	-0.9183	0.0040
	303.15	-0.2797	-0.5995	-0.7941	-0.8976	0.0085
	308.15	-0.2105	-0.5857	-0.7136	-0.7371	0.0118
	313.15	-0.1681	-0.5646	-0.6890	-0.6635	0.0104
	318.15	-0.1284	-0.5238	-0.6102	-0.6370	0.0112
	323.15	-0.0872	-0.4423	-0.4070	-0.5342	0.0098
iso-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.1717	-0.6430	-1.6893	-1.5997	0.0091
	303.15	-0.1117	-0.6008	-1.4334	-1.2779	0.0063
	308.15	-0.0572	-0.6505	-1.1727	-0.7542	0.0116
	313.15	-0.0040	-0.6100	-0.9031	-0.3484	0.0085
	318.15	0.0388	-0.5900	-0.7719	-0.2294	0.0085
	323.15	0.0882	-0.6122	-0.6623	0.0631	0.0131

Table 4.34: Coefficient, a_o of Redlich-Kisher Equation express in $\Delta G^{\#E}$ and Standard deviation, σ for the Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol + (80% acetonitrile + 20% water + 0.02M SDS) systems.

Systems	T/K	a_o	a_1	a_2	a_3	σ
Ethanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-1.6826	-0.4416	-0.5441	-0.7748	0.0117
	303.15	-1.2518	-1.0260	-0.5056	-0.2400	0.0064
	308.15	-1.1887	-0.9964	-0.2705	-0.0040	0.0056
	313.15	-1.1383	-1.0072	0.0487	0.3083	0.0119
	318.15	-0.9458	-0.7968	0.0671	0.2679	0.0088
	323.15	-0.8815	-0.7357	0.5441	0.9093	0.0080
n-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.5604	-0.5513	0.3004	0.3065	0.0142
	303.15	-0.5450	-0.7400	0.3068	0.9019	0.0165
	308.15	-0.5360	-0.9611	0.5449	1.5595	0.0201
	313.15	-0.5242	-1.1444	0.7126	1.8931	0.0255
	318.15	-0.5291	-1.2188	0.7984	2.0068	0.0300
	323.15	-0.5326	-1.3845	0.9574	2.2278	0.0365
iso-Propanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-1.0783	-1.5988	-0.3719	-3.0329	0.0161
	303.15	-1.0774	-1.6459	-0.2606	-3.2804	0.0226
	308.15	-0.9961	-1.5552	-0.2165	-2.8424	0.0236
	313.15	-0.9506	-1.6008	-0.1965	-2.3684	0.0237
	318.15	-0.8893	-1.4222	-0.2564	-2.4154	0.0225
	323.15	-0.8296	-1.3519	-0.2406	-2.1649	0.0164
n-Butanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-1.2141	-2.3565	-0.4475	-4.6166	0.0276
	303.15	-0.9068	-2.5679	-0.2151	-4.8731	0.0129
	308.15	-0.6640	-2.4920	0.2056	-5.5645	0.0178
	313.15	-0.4611	-2.4391	0.5812	-5.9443	0.0166
	318.15	-0.1892	-2.1974	0.7799	-6.8687	0.0245
	323.15	0.0869	-2.3536	1.7728	-6.1592	0.0209
iso-Butanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-1.1617	-0.9807	-0.9612	-0.9581	0.0174
	303.15	-1.1196	-1.3191	-0.6042	-0.7529	0.0121
	308.15	-1.0698	-1.7338	-0.7103	-0.0900	0.0171
	313.15	-1.0113	-1.4871	-0.5863	-0.9849	0.0276
	318.15	-0.9838	-1.3878	-0.5965	-1.3089	0.0249
	323.15	-0.8452	-1.6925	-0.3532	-1.2152	0.0193
n-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	-0.0621	-0.9028	-0.1286	-1.0347	0.0058
	303.15	0.0175	-0.9539	-0.1656	-1.3627	0.0156
	308.15	0.1236	-1.1318	-0.1532	-1.3921	0.0221
	313.15	0.1831	-1.3587	-0.2603	-1.1956	0.0205
	318.15	0.2590	-1.4131	-0.1076	-1.3315	0.0235
	323.15	0.3411	-1.4402	0.1986	-1.6324	0.0243
iso-Pentanol + 80% acetonitrile + 20% water + 0.02M SDS systems	298.15	0.3812	-1.1436	-1.1443	-0.7857	0.0054
	303.15	0.4749	-1.2448	-1.0870	-0.8520	0.0106
	308.15	0.6006	-1.5788	-1.0214	-0.3368	0.0202
	313.15	0.7480	-1.7311	-0.8942	0.1427	0.0177
	318.15	0.8697	-1.9093	-0.7614	0.1829	0.0192
	323.15	1.0835	-2.3008	-0.8738	0.7619	0.0303

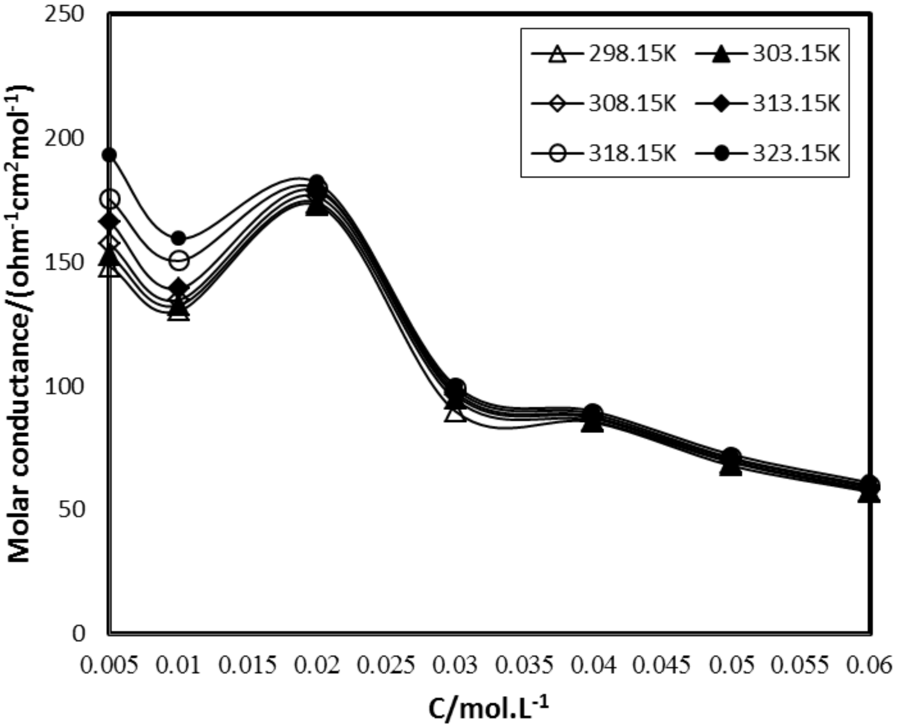

Figure 4.1: Plots of Molar conductance vs concentration of SDS in 80% acetonitrile + 20% water systems at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

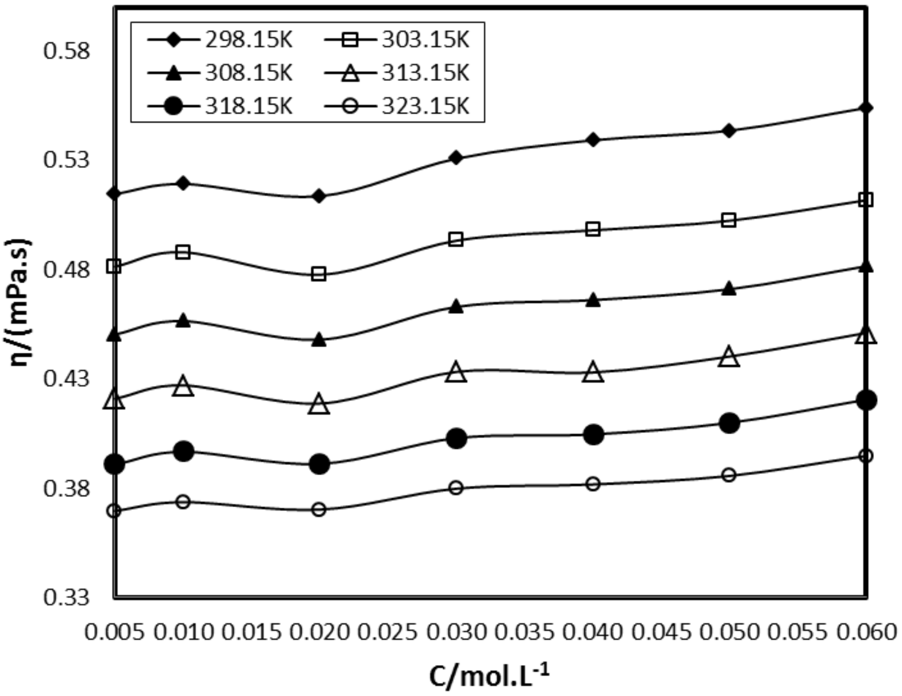

Figure 4.2: Plots of viscosity vs concentration of SDS in 80% acetonitrile + 20% water systems at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

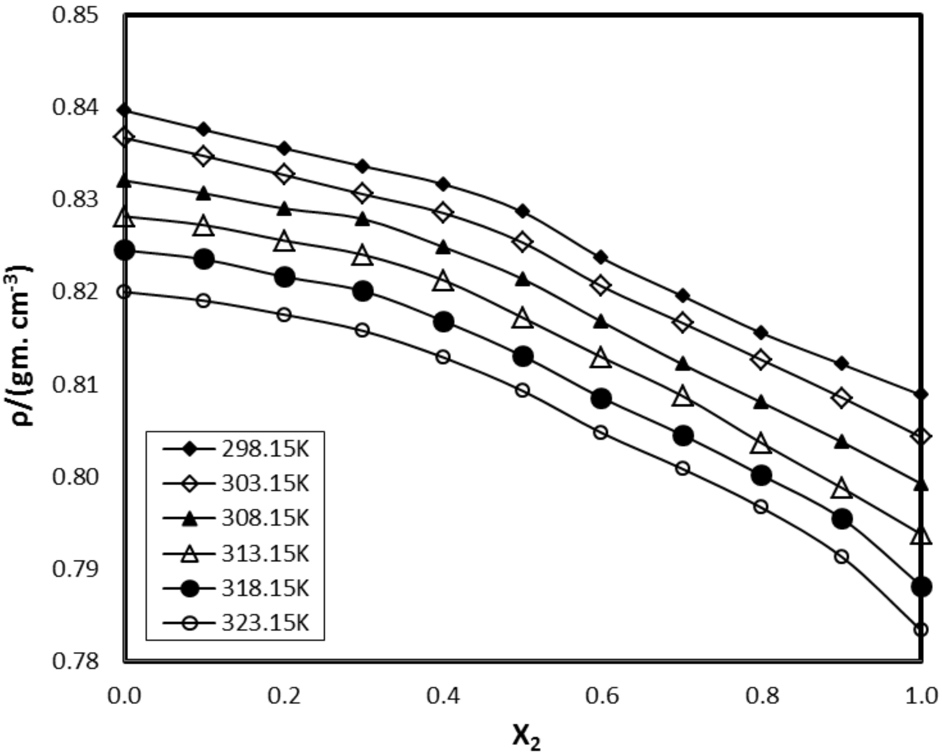

Figure 4.3: Plots of density vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

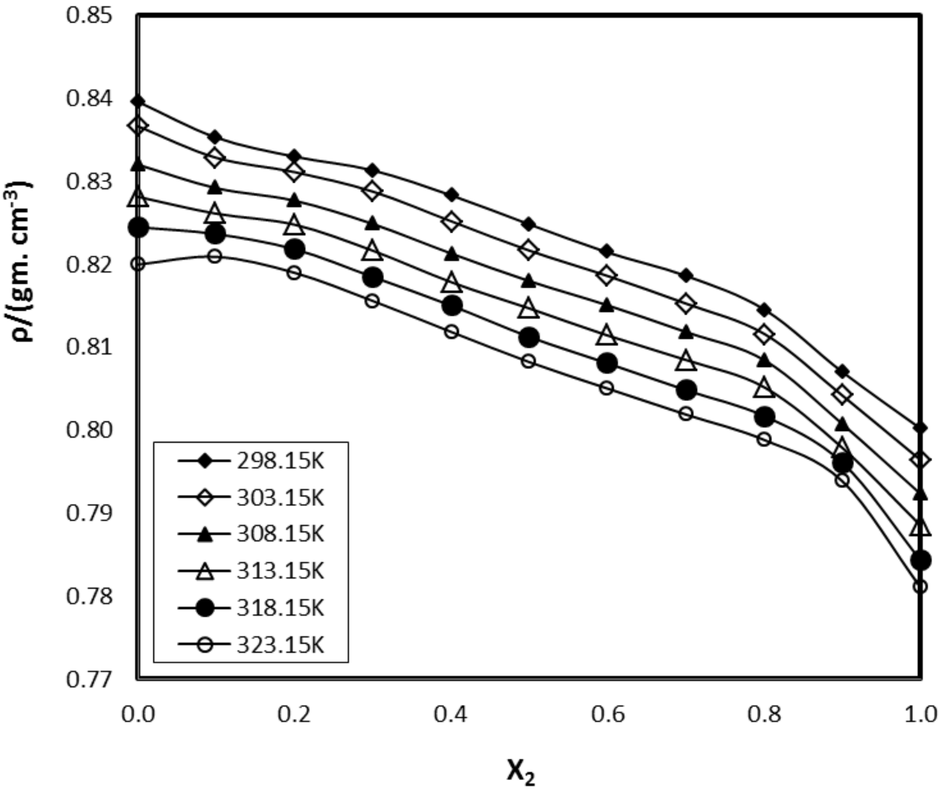

Figure 4.4: Plots of density vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

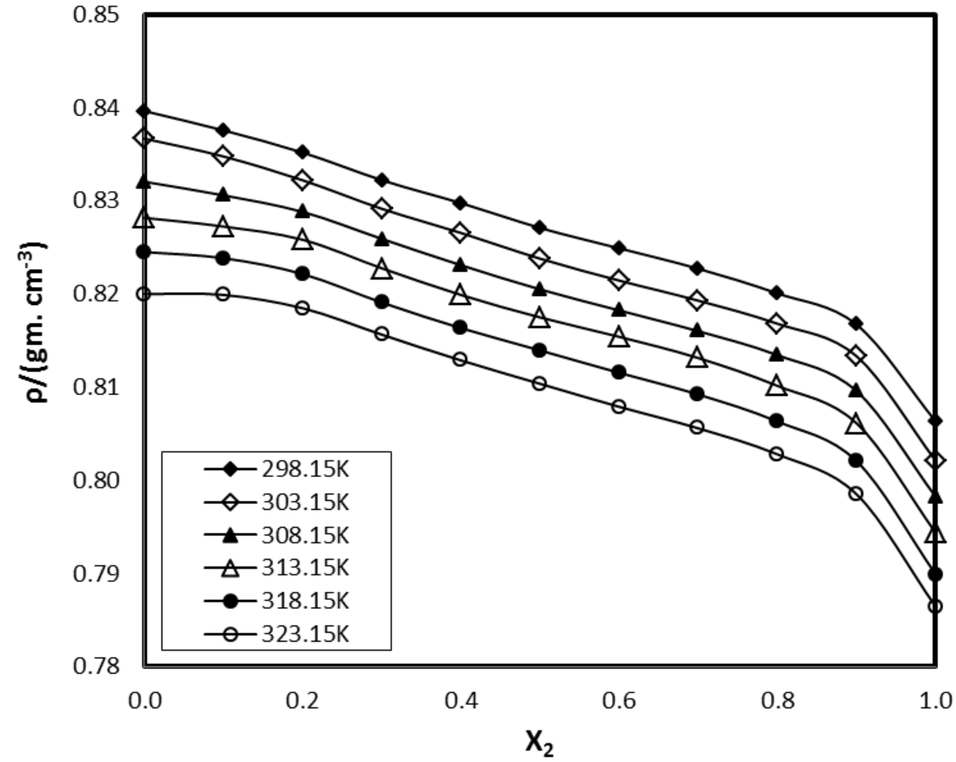

Figure 4.5: Plots of density vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

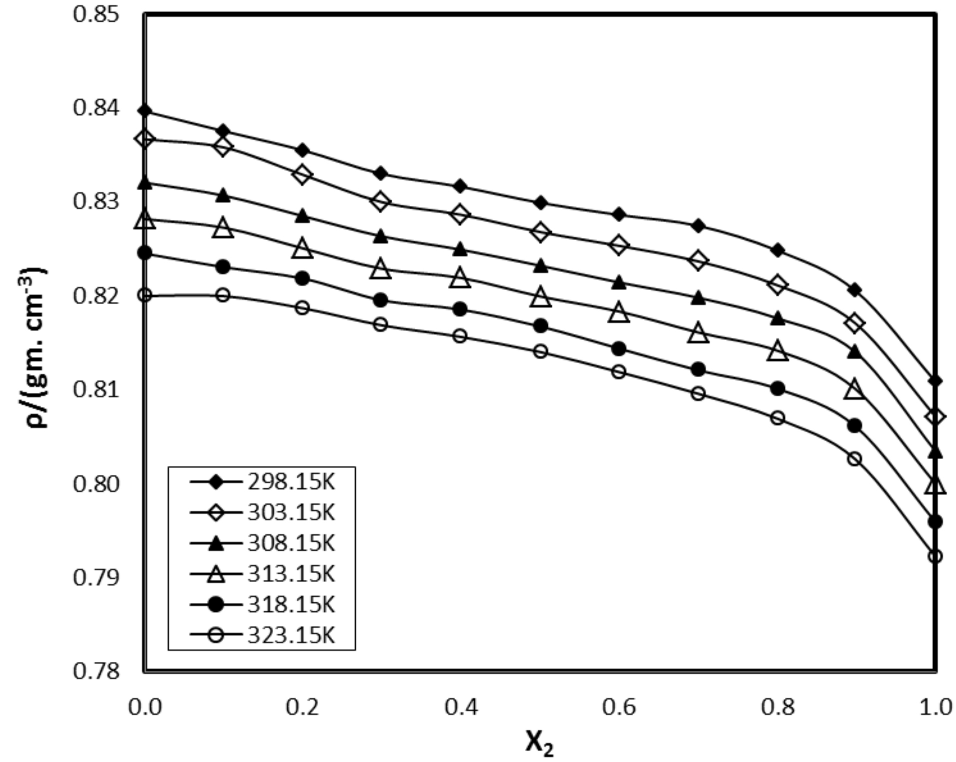

Figure 4.6: Plots of density vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

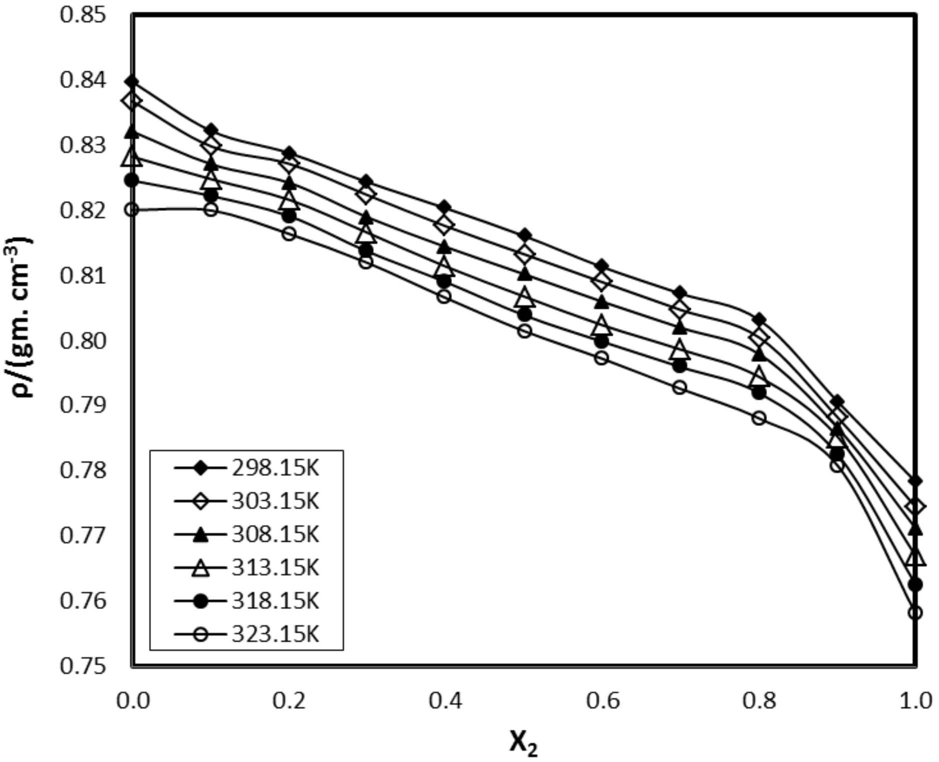

Figure 4.7: Plots of density vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

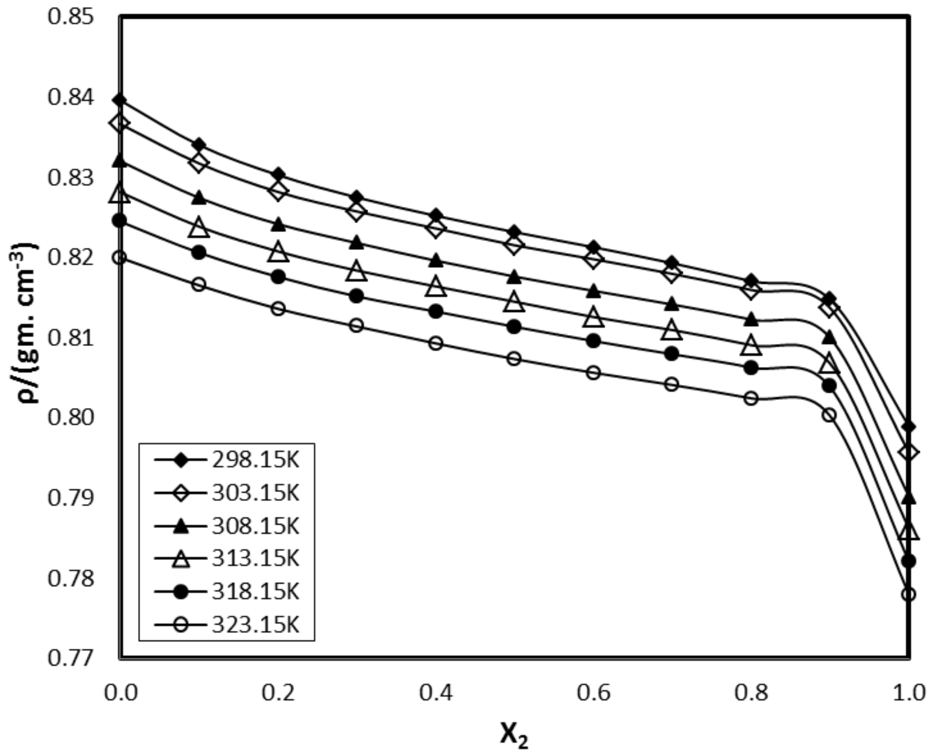

Figure 4.8: Plots of density vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

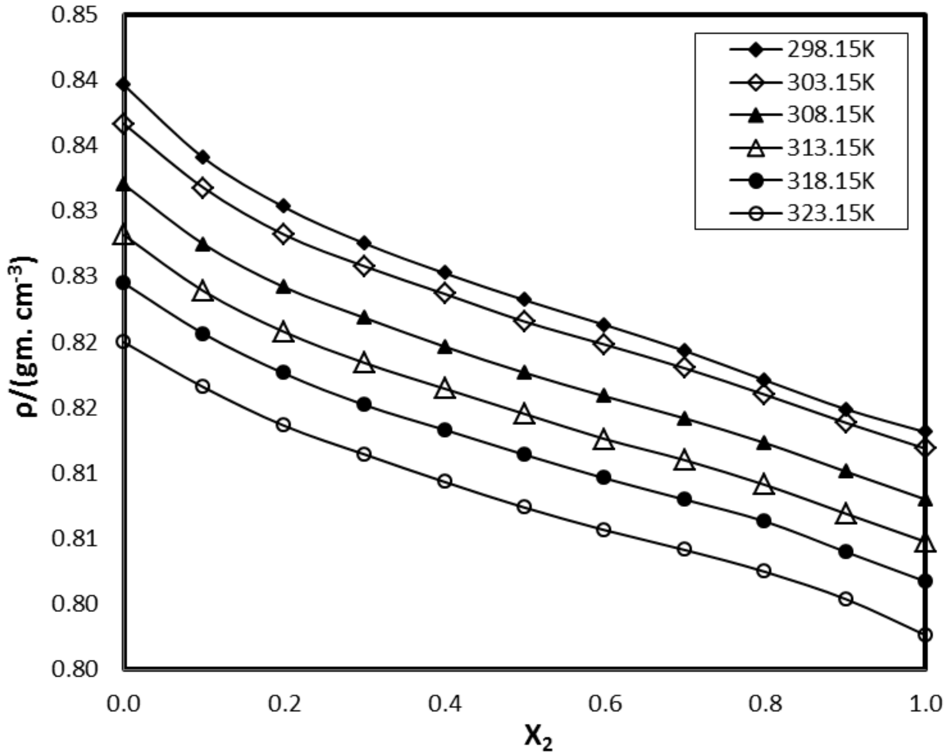

Figure 4.9: Plots of density vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

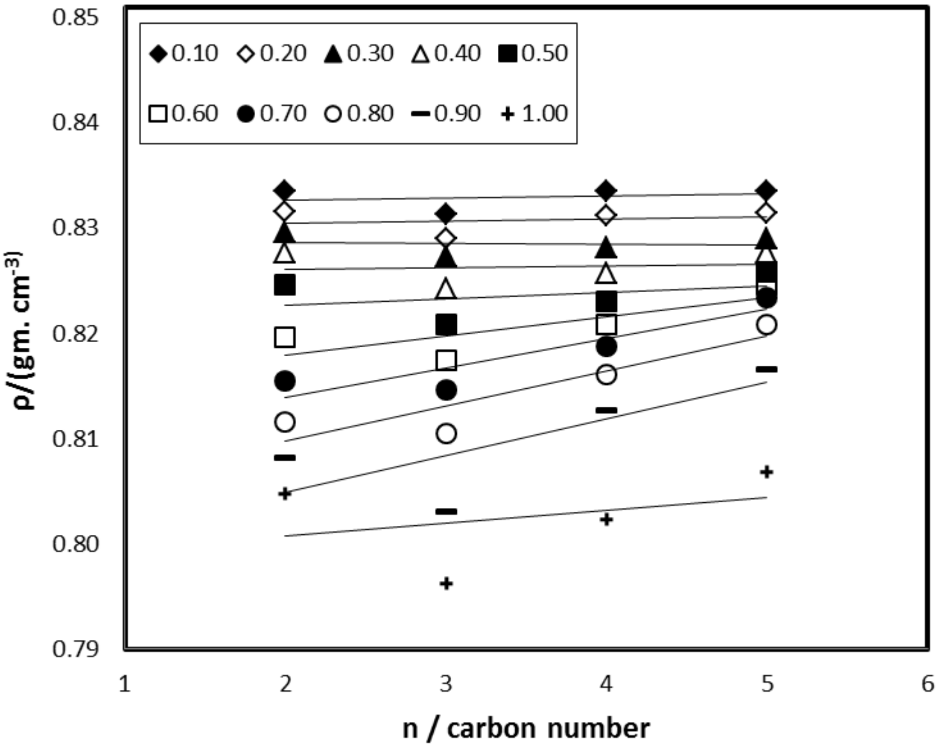

Figure 4.10: Dependence of the density (ρ) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

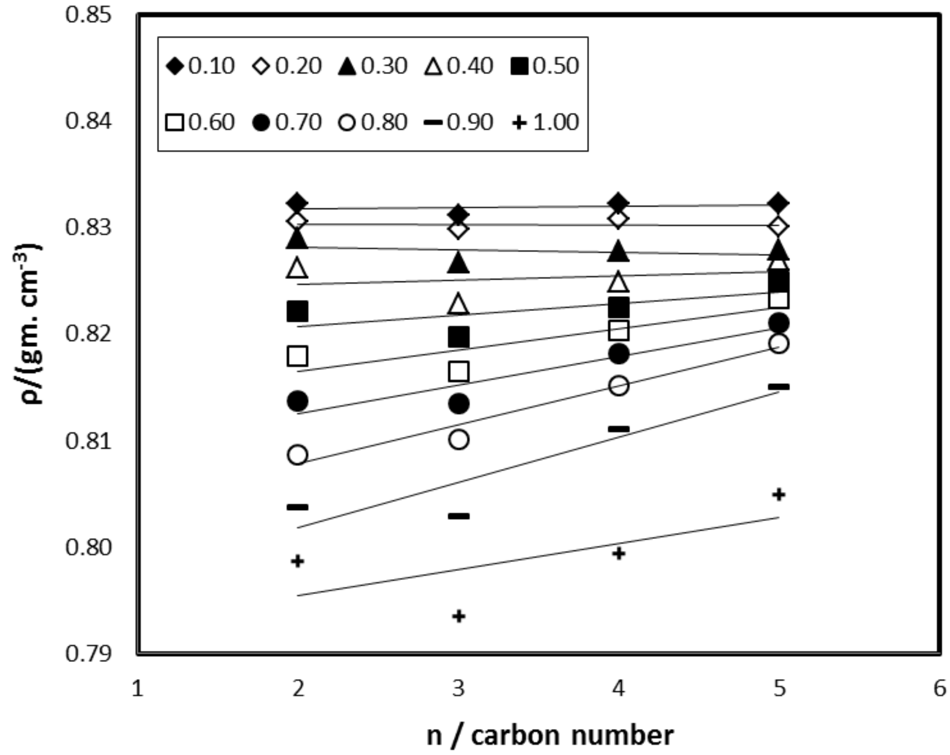

Figure 4.11: Dependence of the density (ρ) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

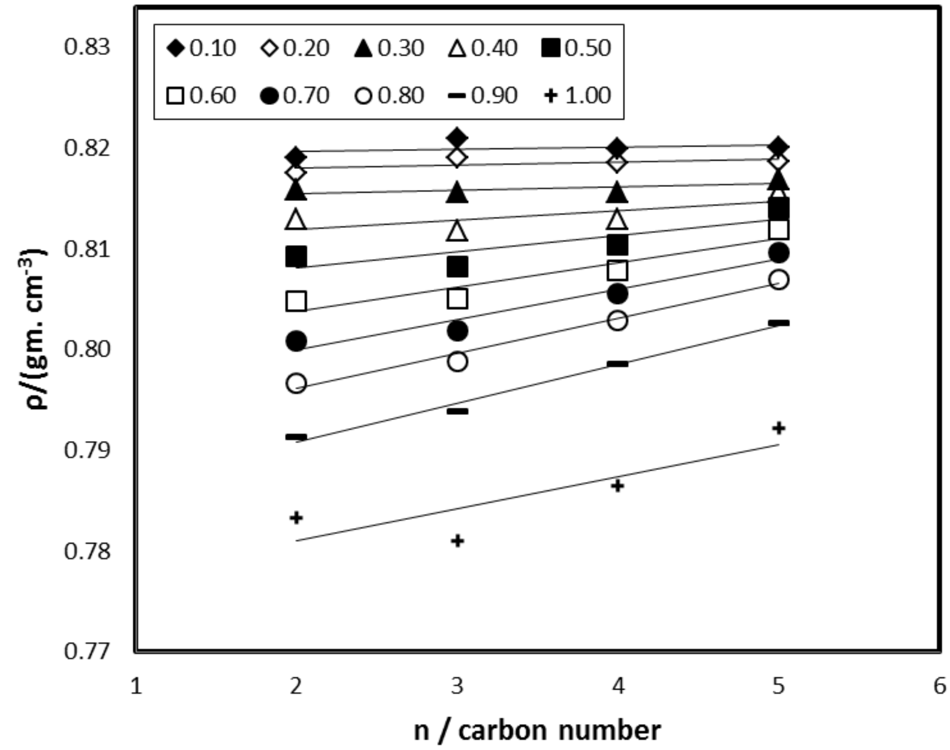

Figure 4.12: Dependence of the density (ρ) with carbon number (n) of n- alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

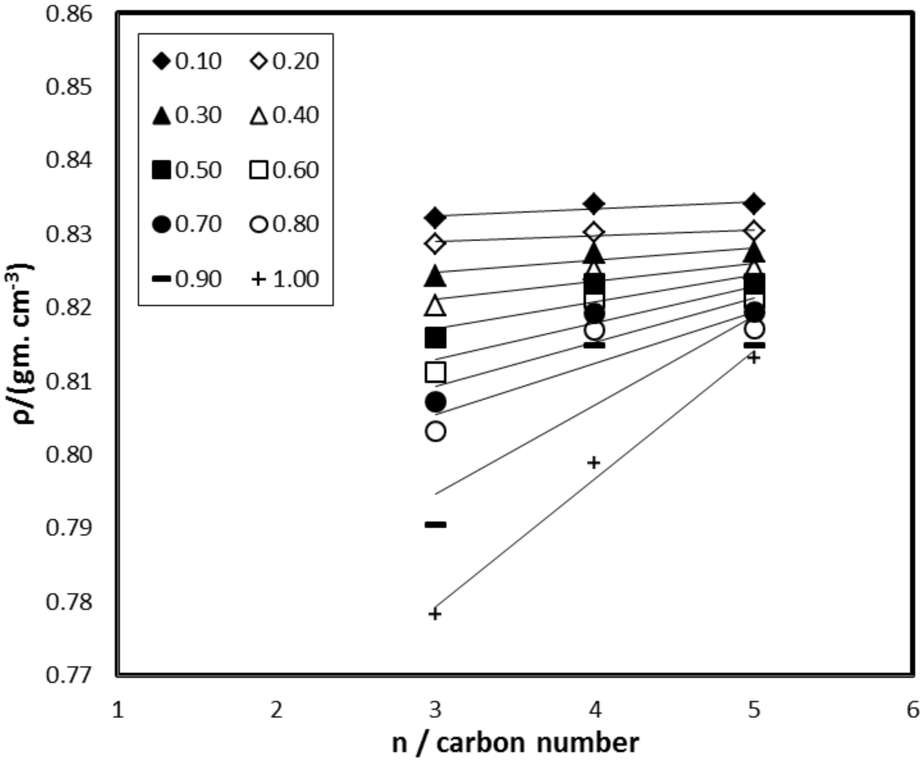

Figure 4.13: Dependence of the density (ρ) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

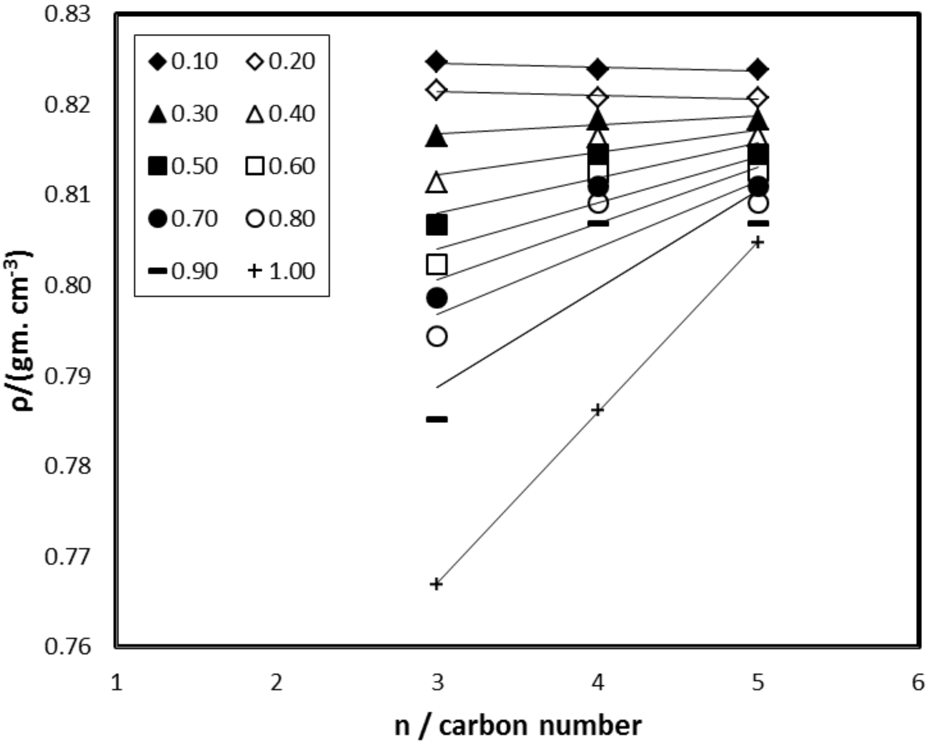

Figure 4.14: Dependence of the density (ρ) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

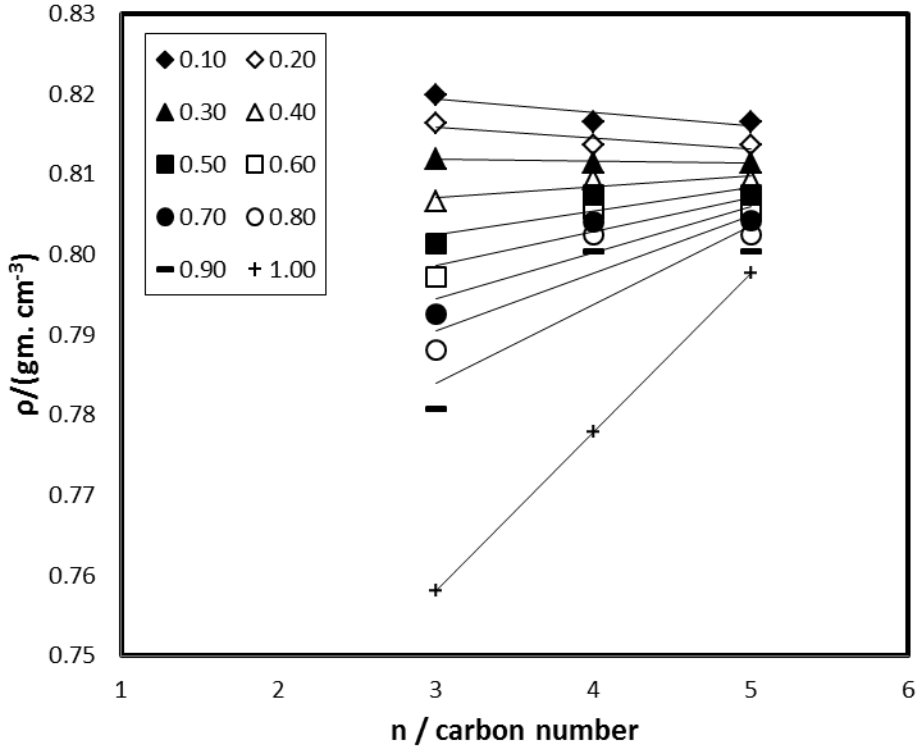

Figure 4.15: Dependence of the density (ρ) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

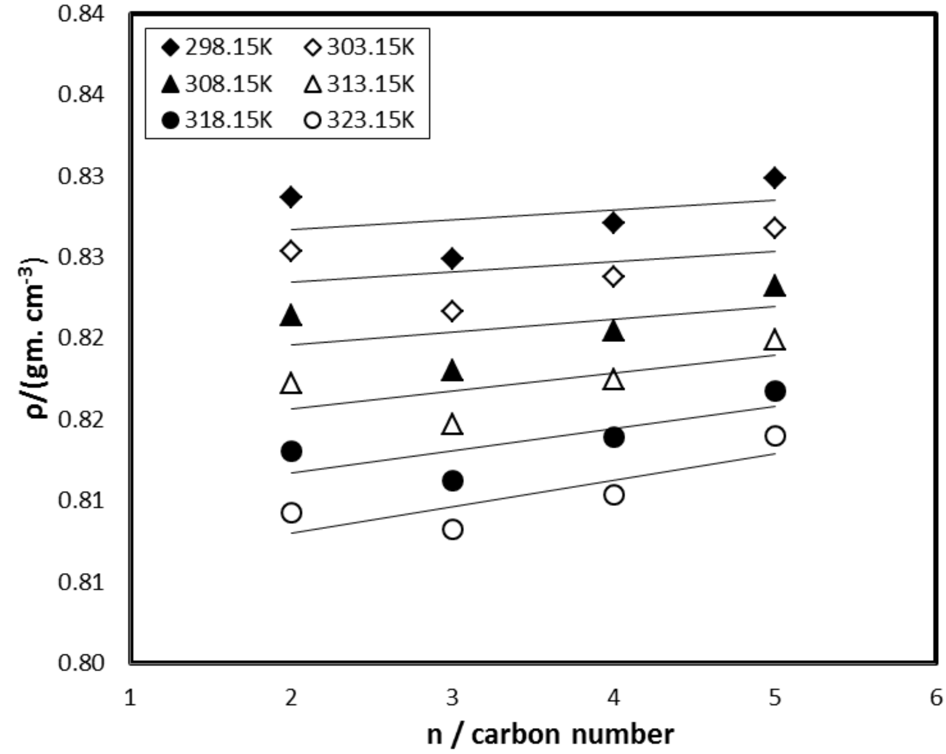

Figure 4.16: Dependence of the density (ρ) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

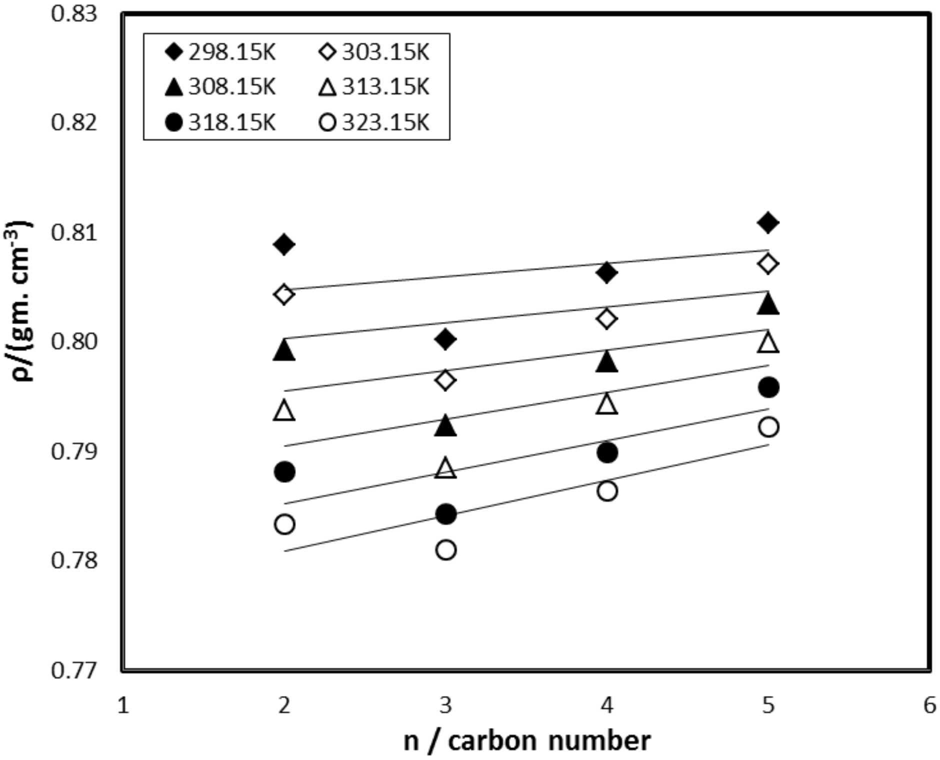

Figure 4.17: Dependence of the density (ρ) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

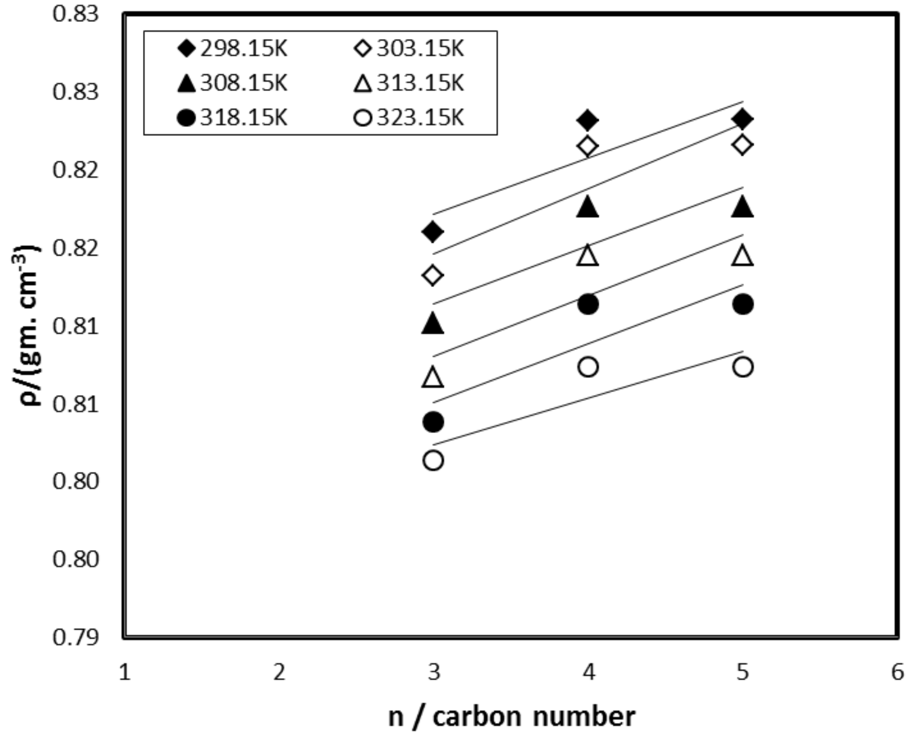

Figure 4.18: Dependence of the density (ρ) with carbon number (n) of iso- alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

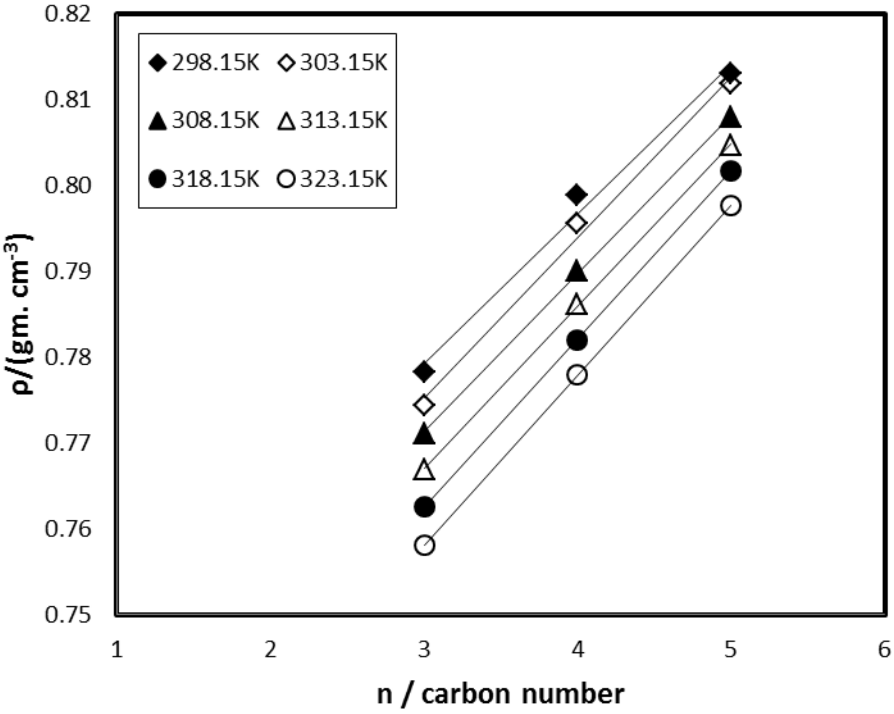

Figure 4.19: Dependence of the density (ρ) with carbon number (n) of iso- alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

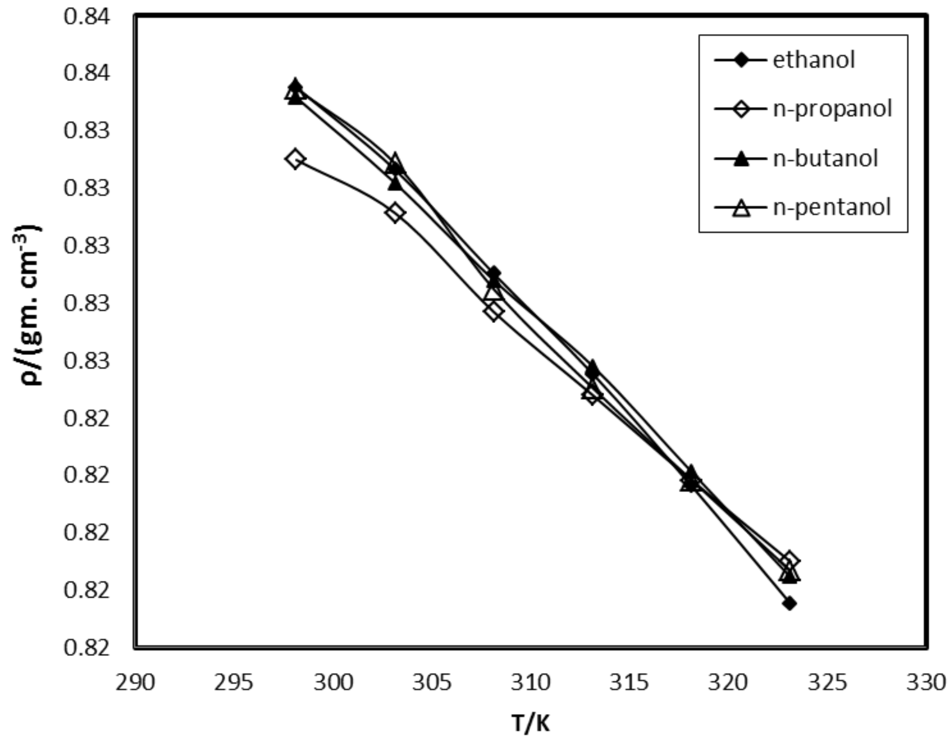

Figure 4.20: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

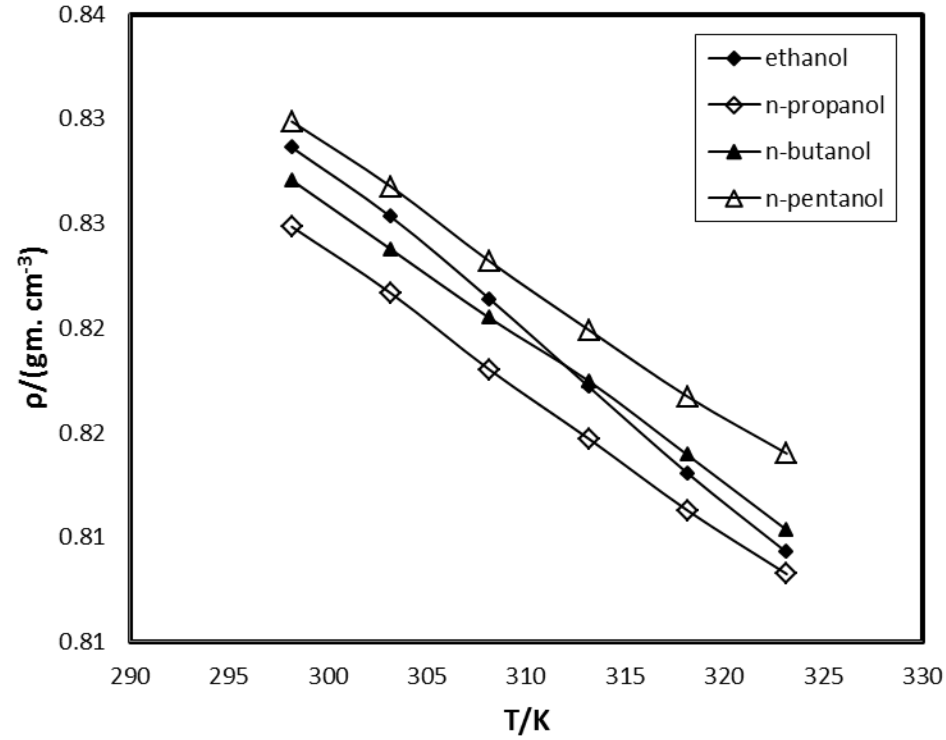

Figure 4.21: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

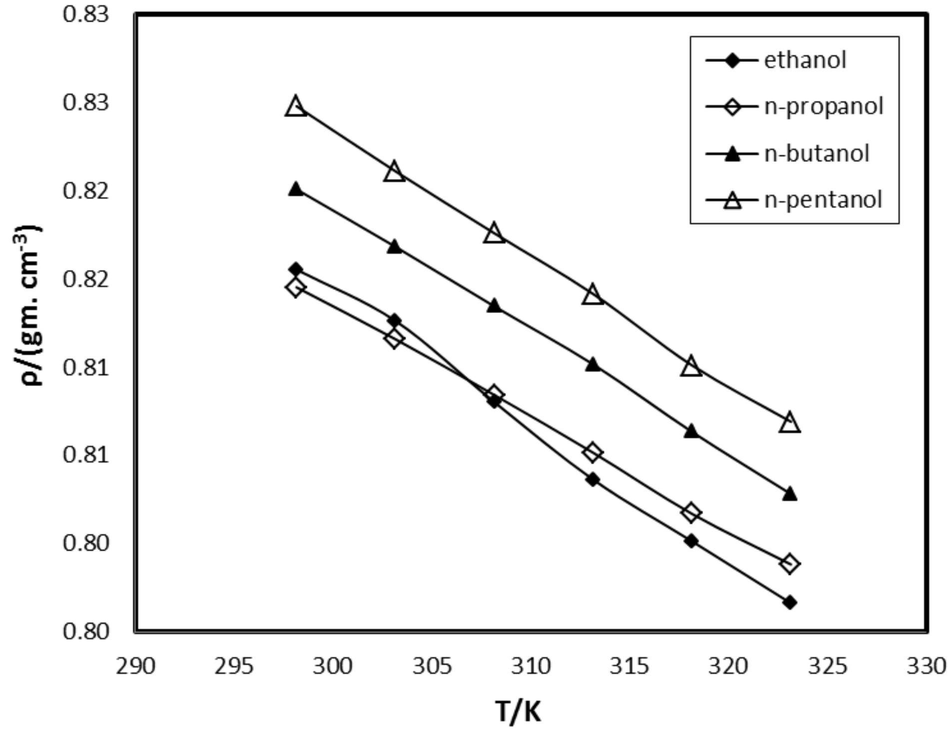

Figure 4.22: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

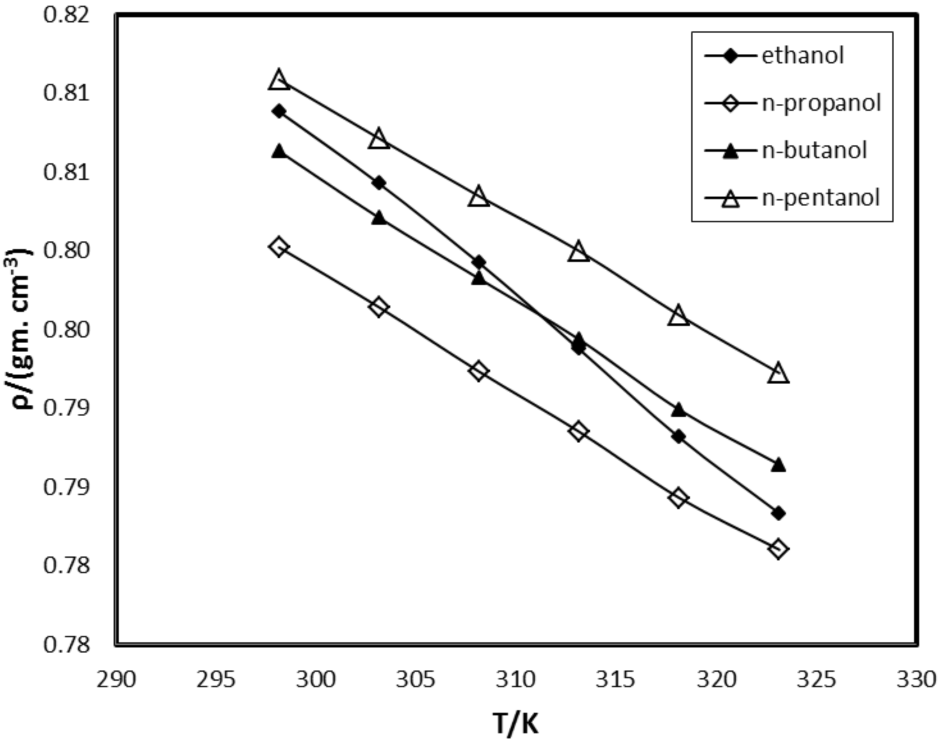

Figure 4.23: Comparison of density (ρ) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

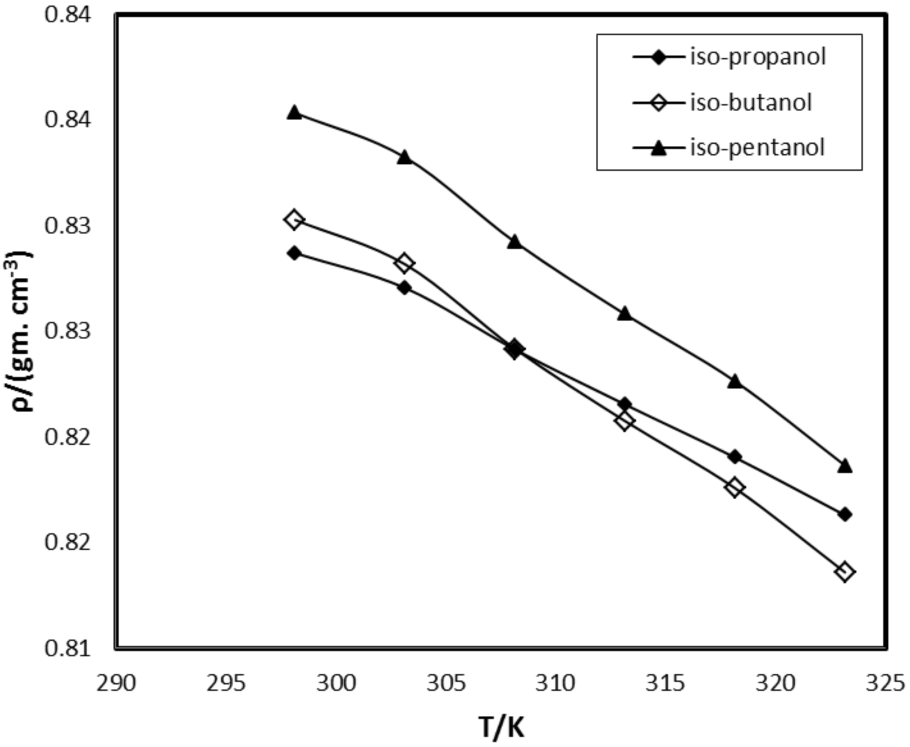

Figure 4.24: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

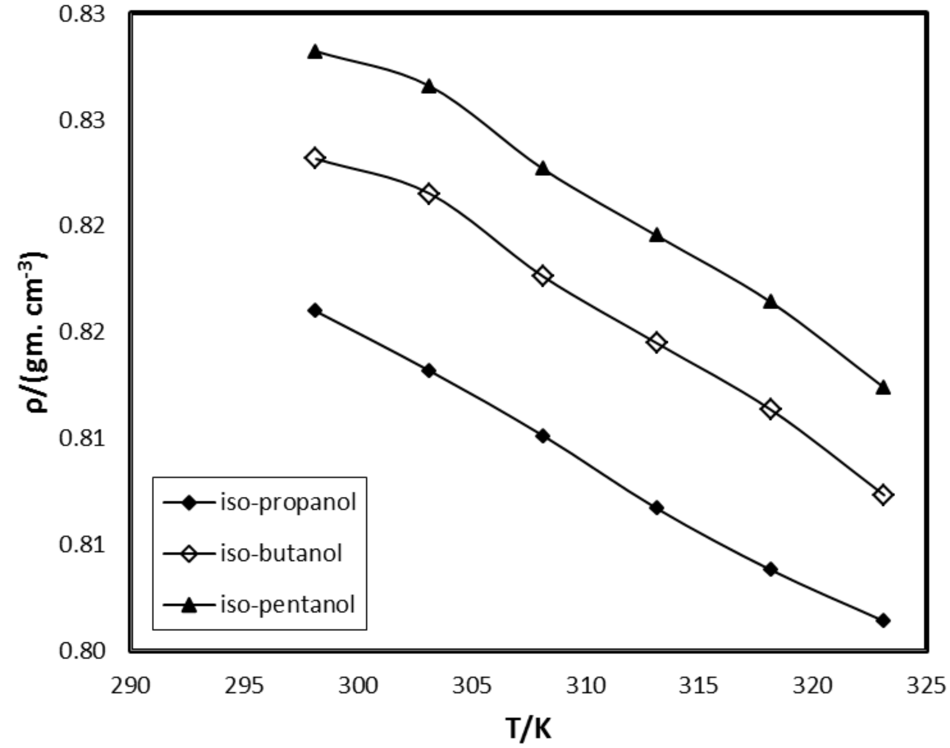

Figure 4.25: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

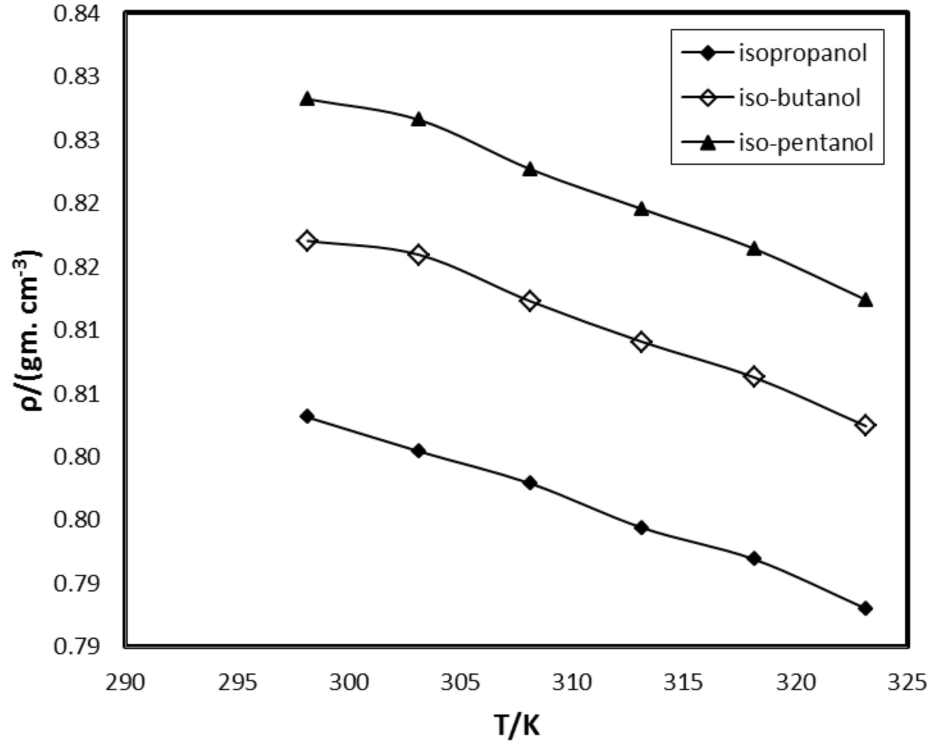

Figure 4.26: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

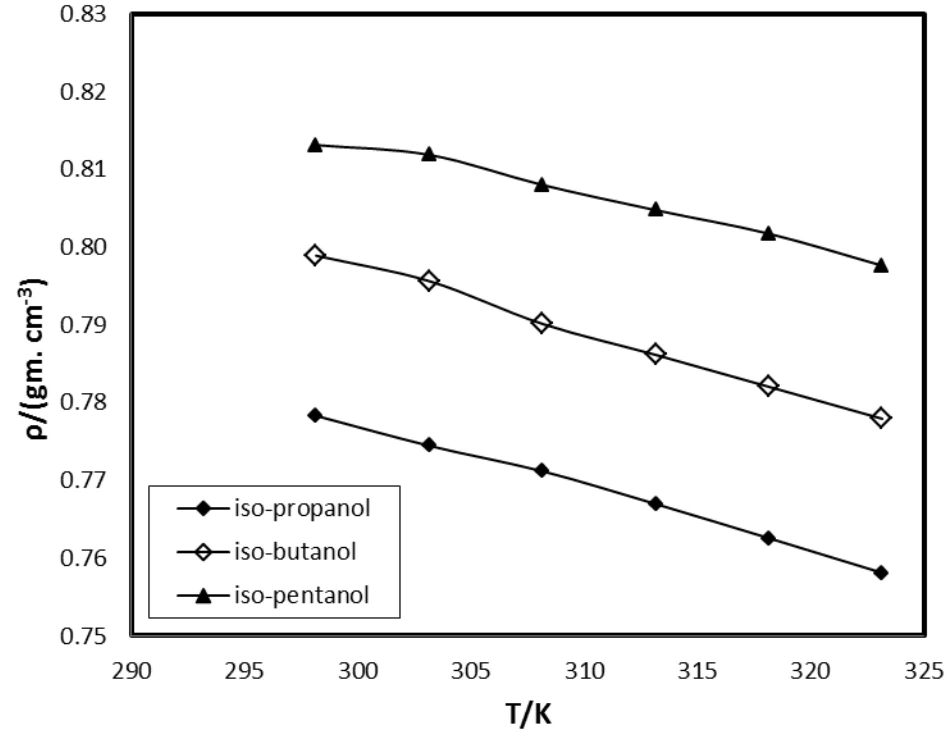

Figure 4.27: Comparison of density (ρ) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

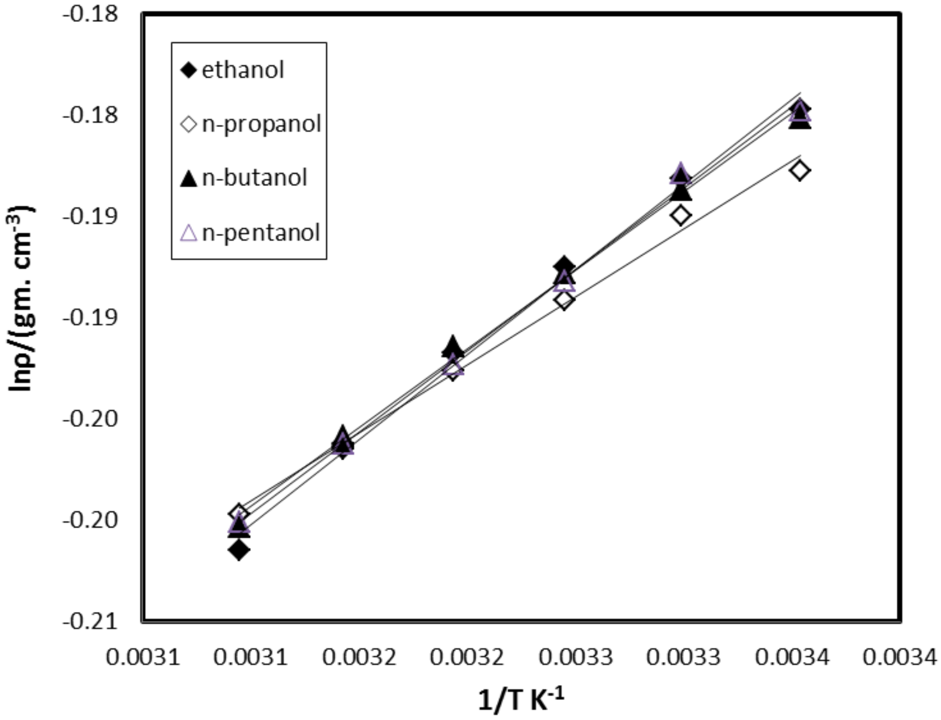

Figure 4.28: Comparison of lnρ vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

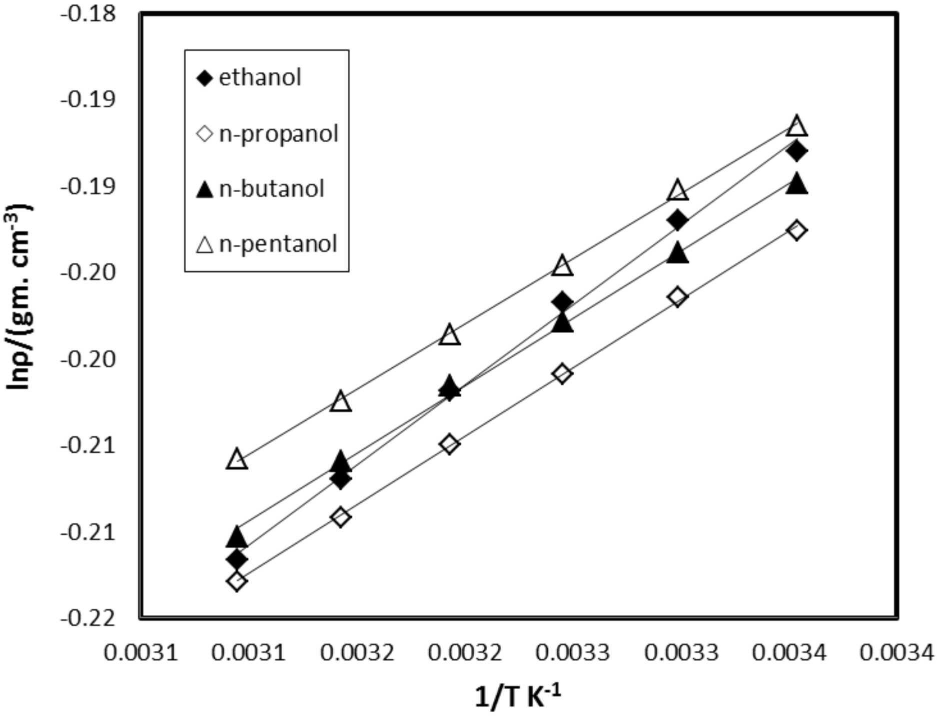

Figure 4.29: Comparison of lnρ vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

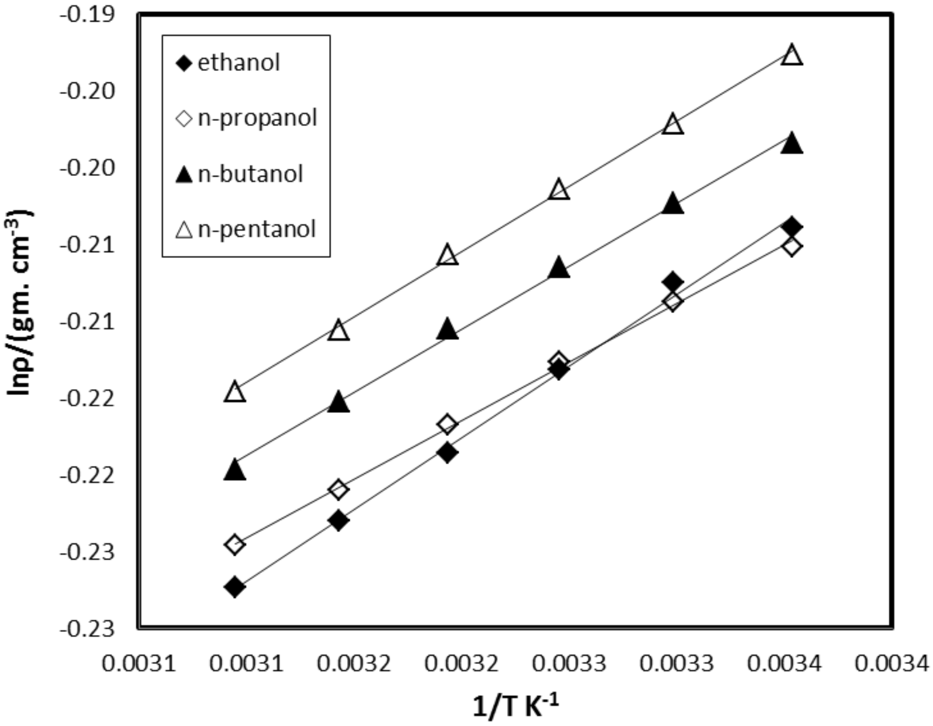

Figure 4.30: Comparison of lnρ vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

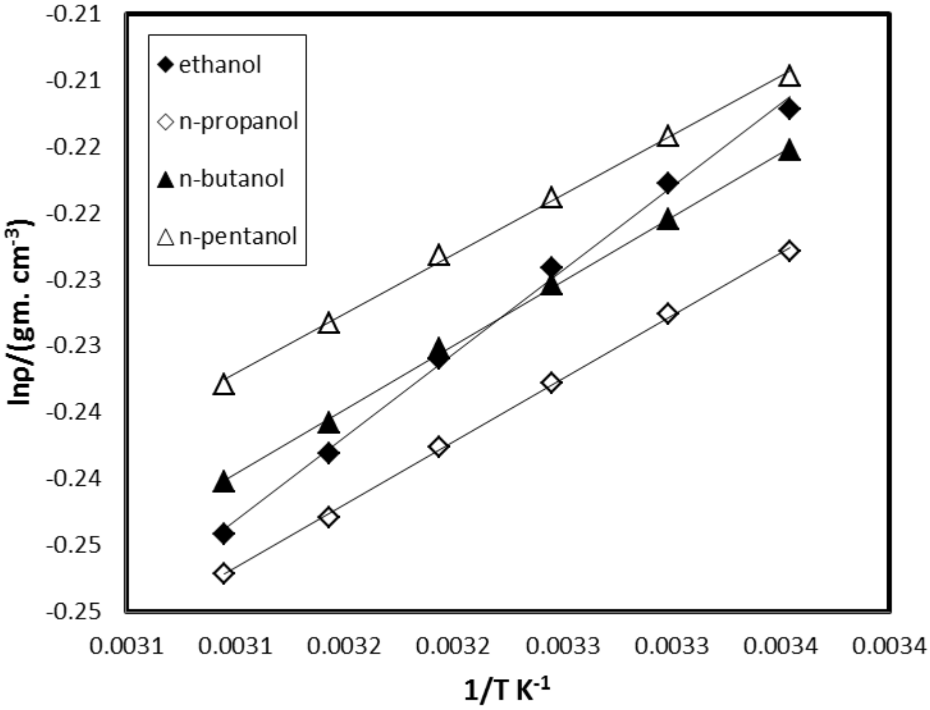

Figure 4.31: Comparison of lnρ vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

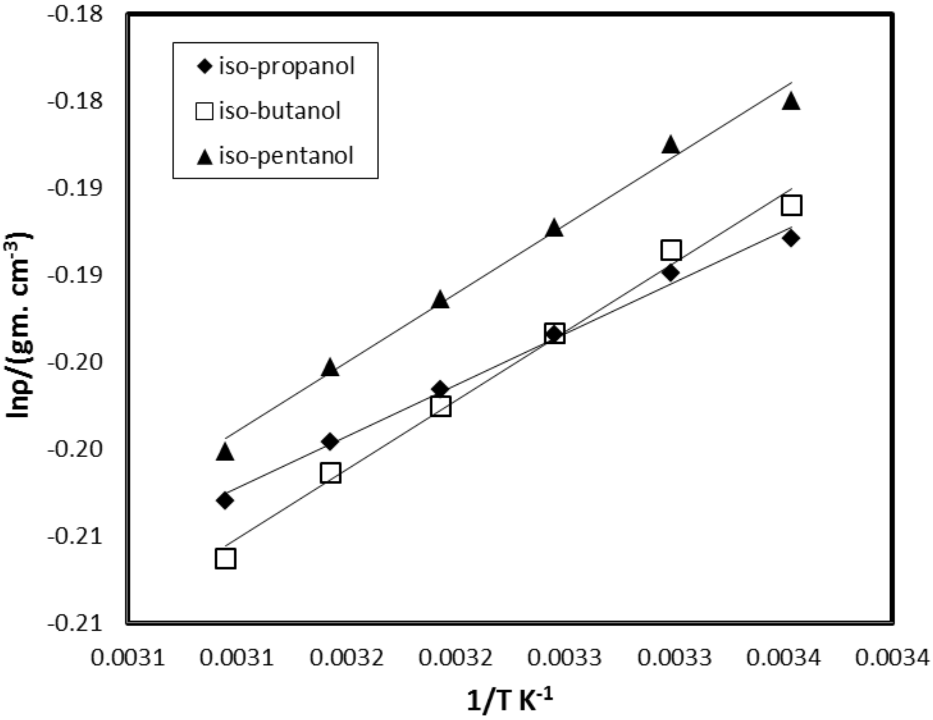

Figure 4.32: Comparison of lnρ vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

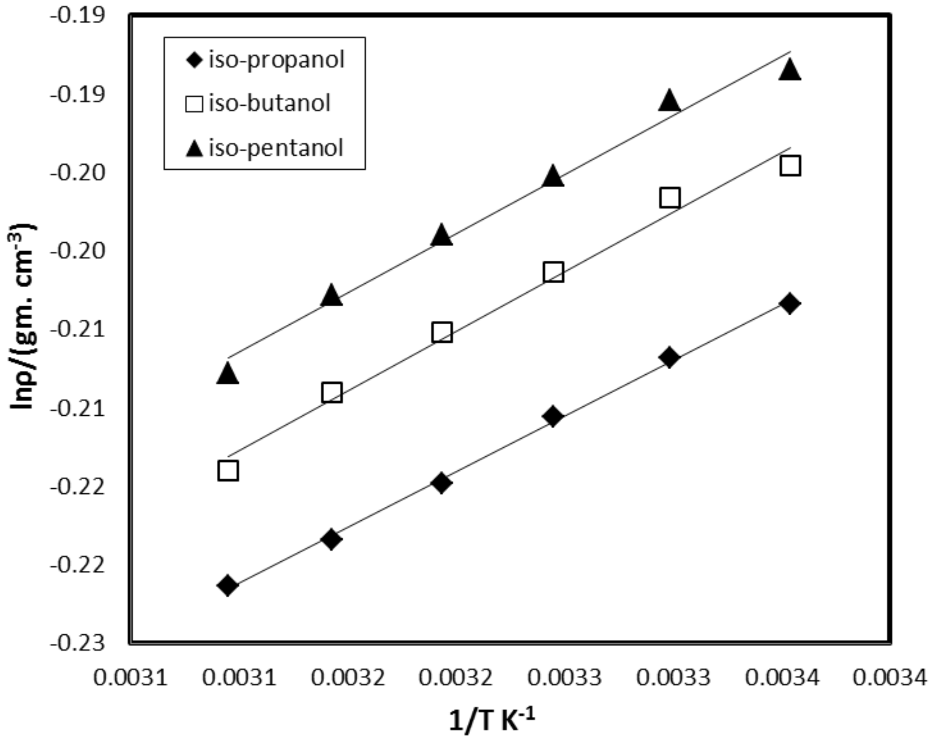

Figure 4.33: Comparison of lnρ vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

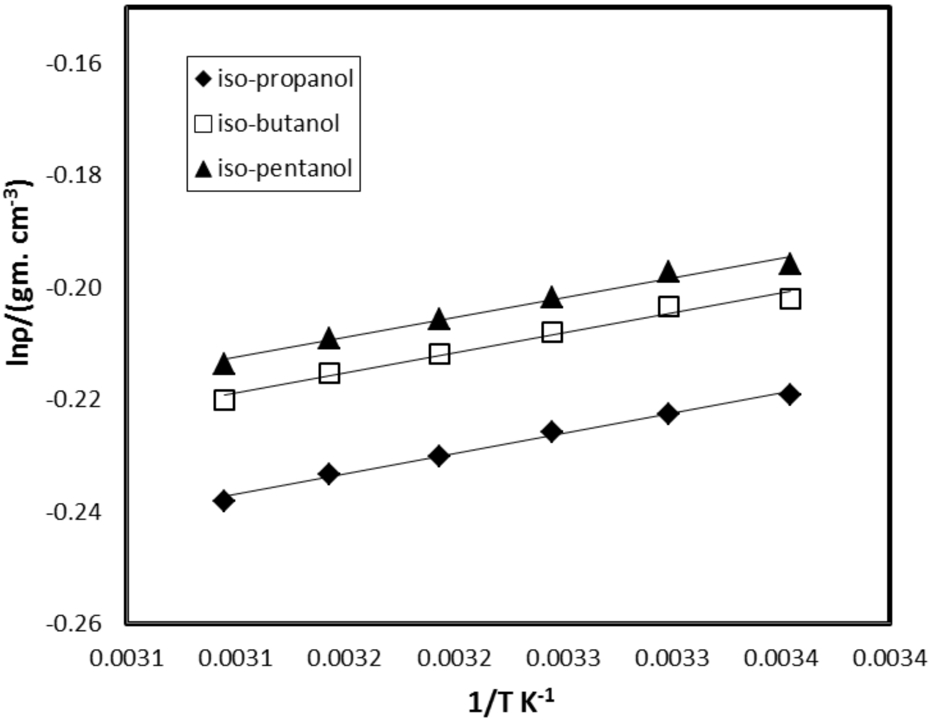

Figure 4.34: Comparison of lnρ vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

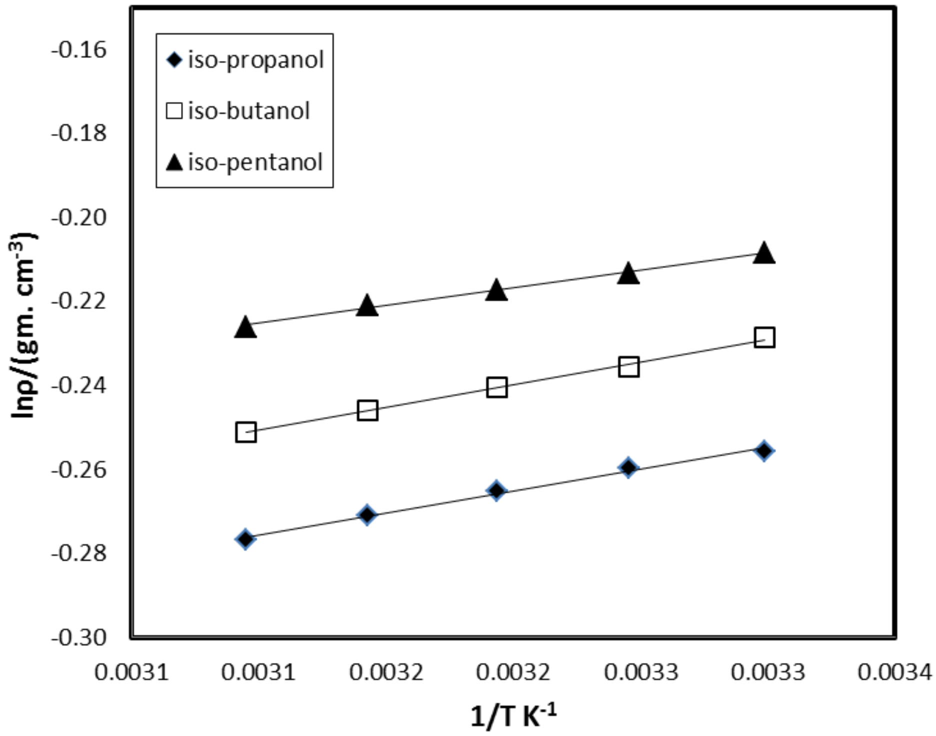

Figure 4.35: Comparison of lnρ vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

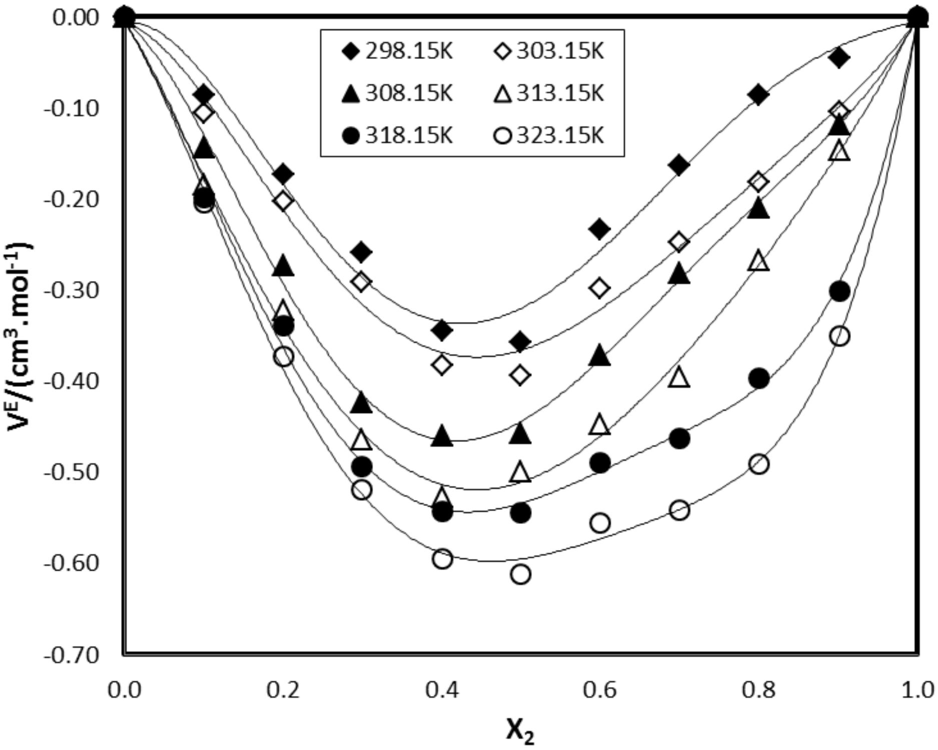

Figure 4.36: Plots of excess molar volume vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

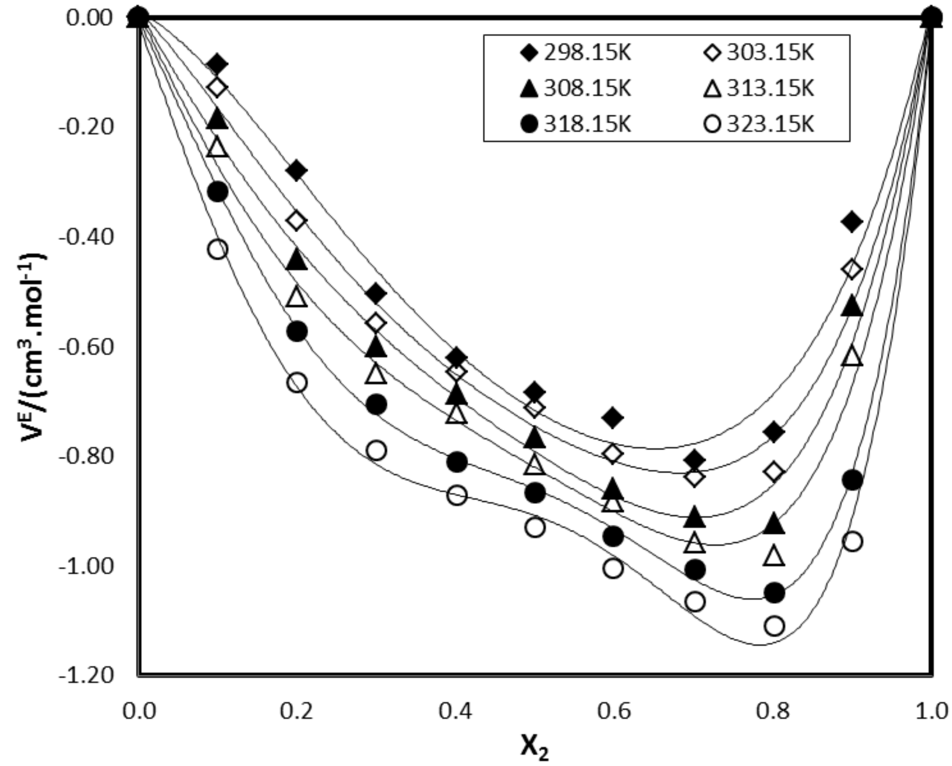

Figure 4.37: Plots of excess molar volume vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

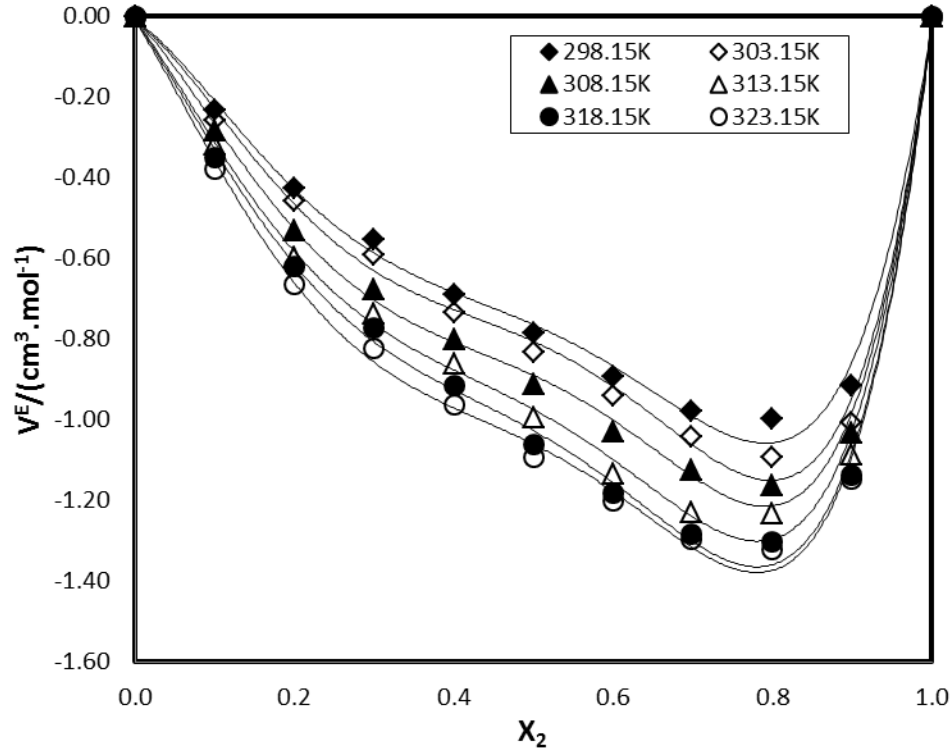

Figure 4.38: Plots of excess molar volume vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

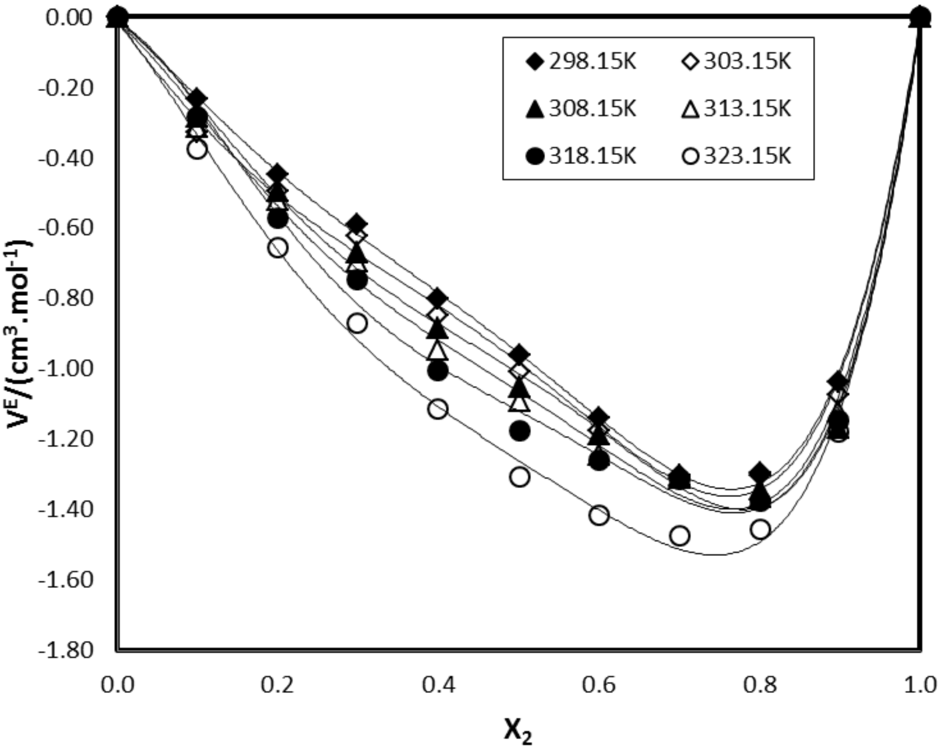

Figure 4.39: Plots of excess molar volume vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

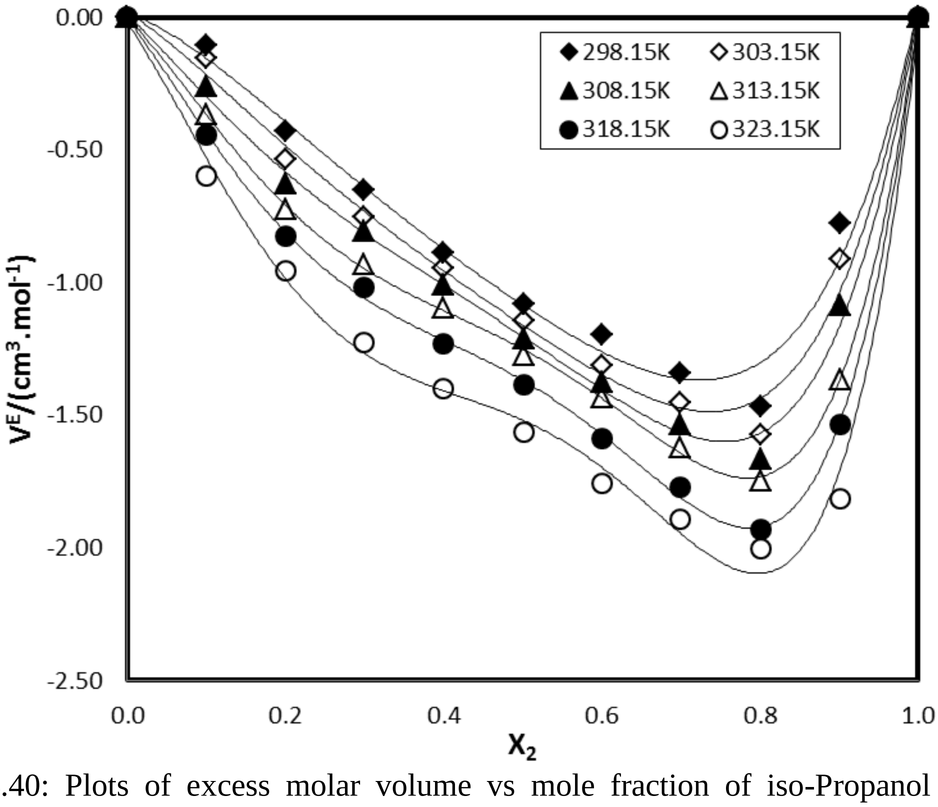

Figure 4.40: Plots of excess molar volume vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

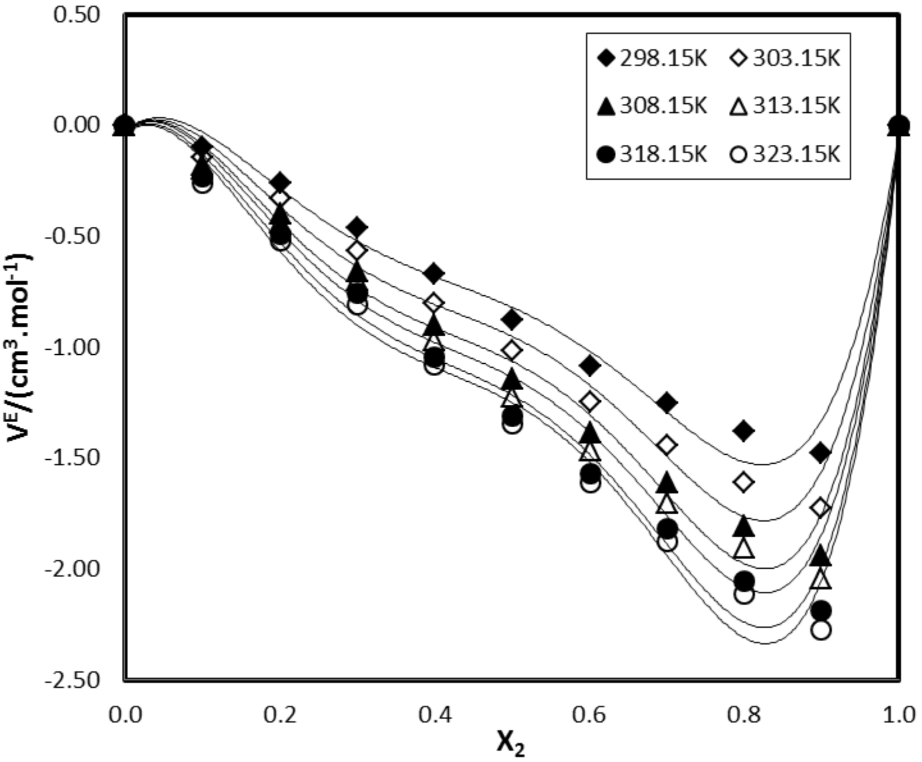

Figure 4.41: Plots of excess molar volume vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

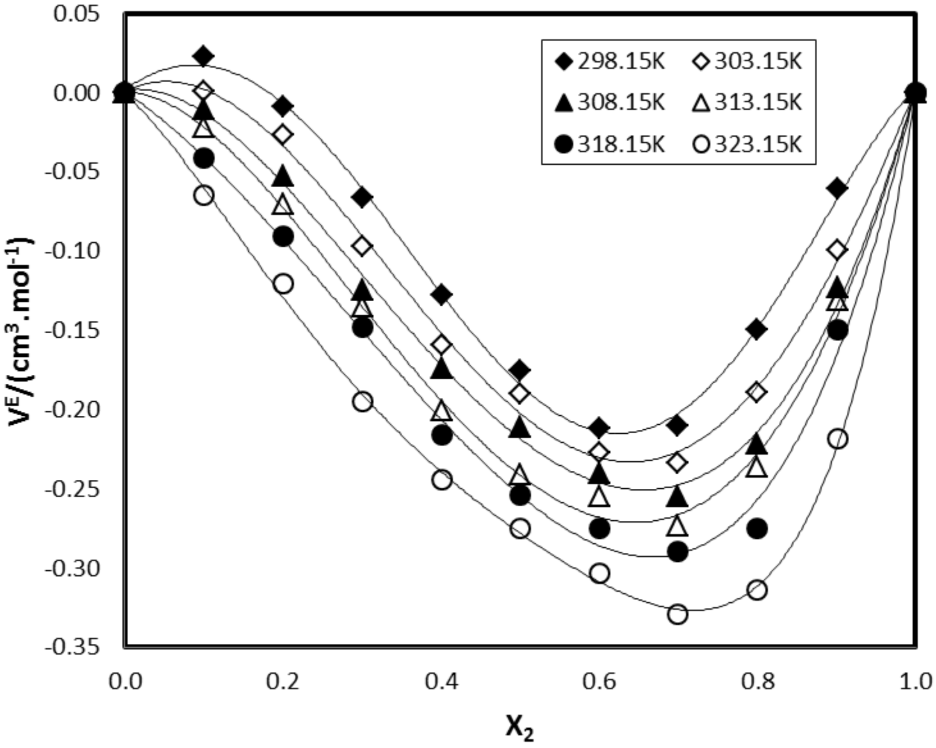

Figure 4.42: Plots of excess molar volume vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

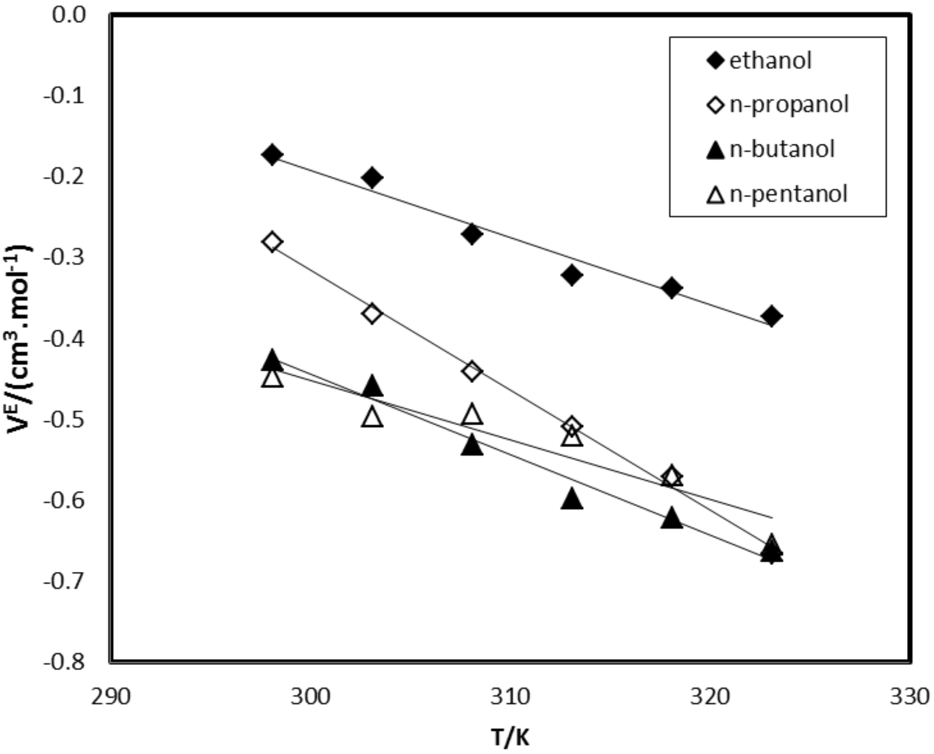

Figure 4.43: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

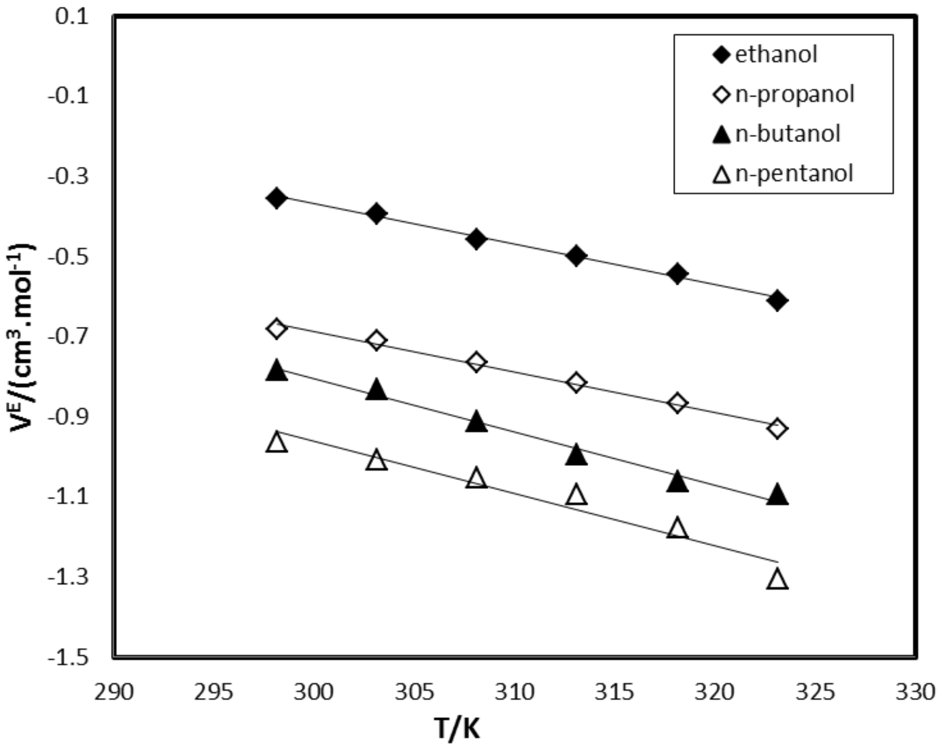

Figure 4.44: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

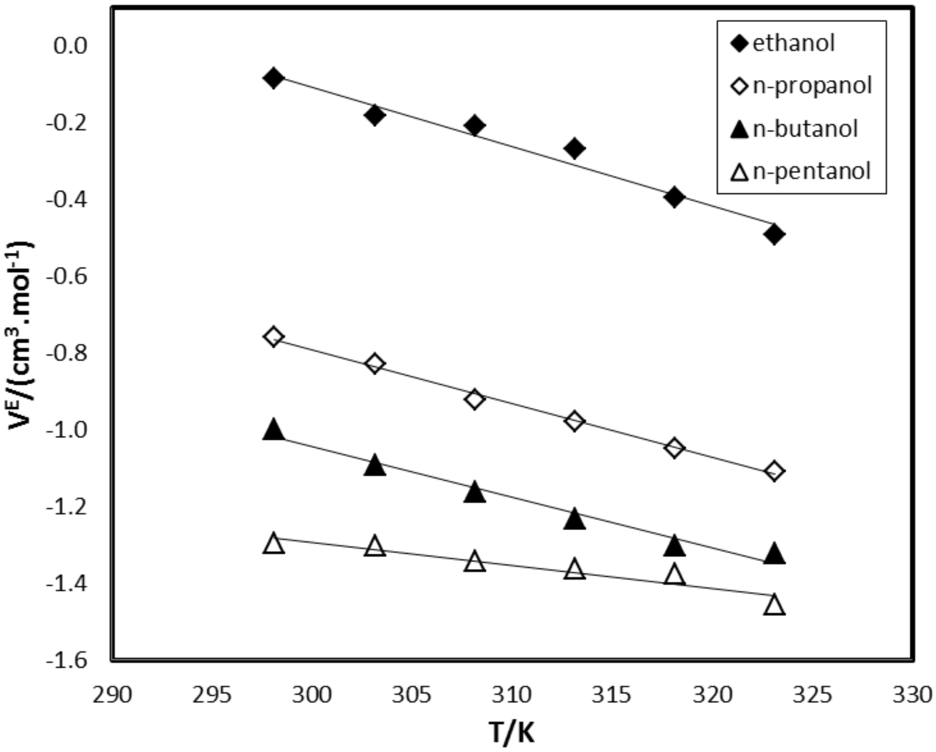

Figure 4.45: Comparison of excess molar volume (V^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

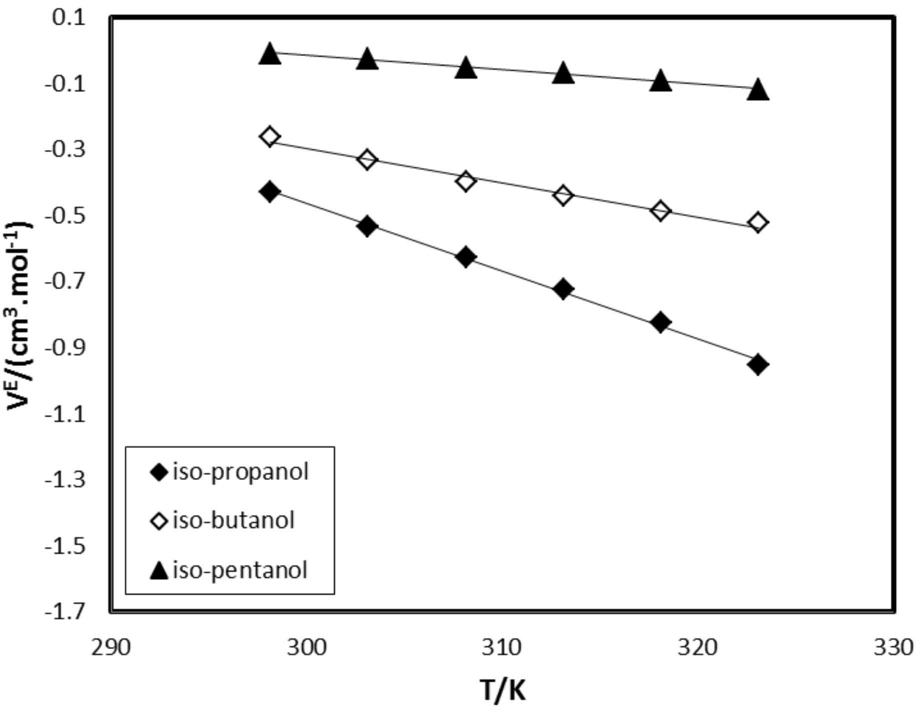

Figure 4.46: Comparison of excess molar volume (V^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

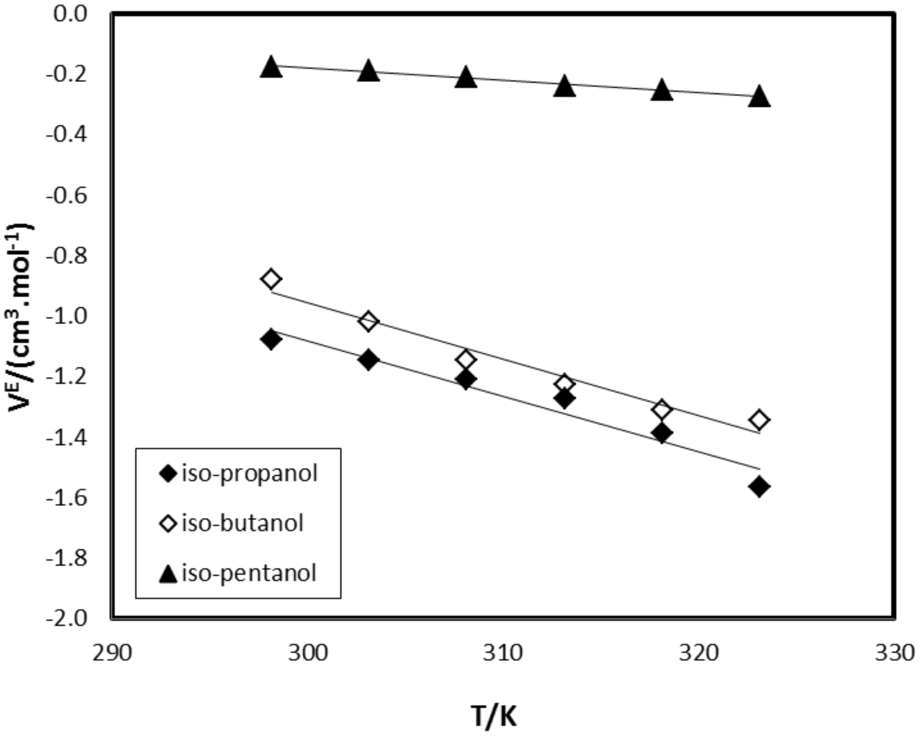

Figure 4.47: Comparison of excess molar volume (V^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

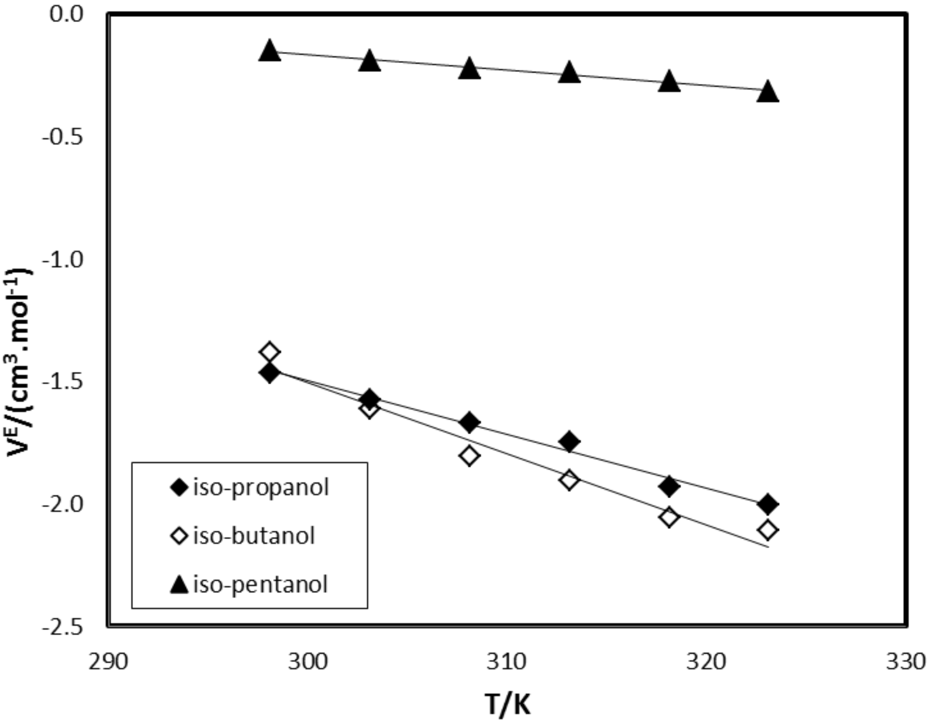

Figure 4.48: Comparison of excess molar volume (V^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

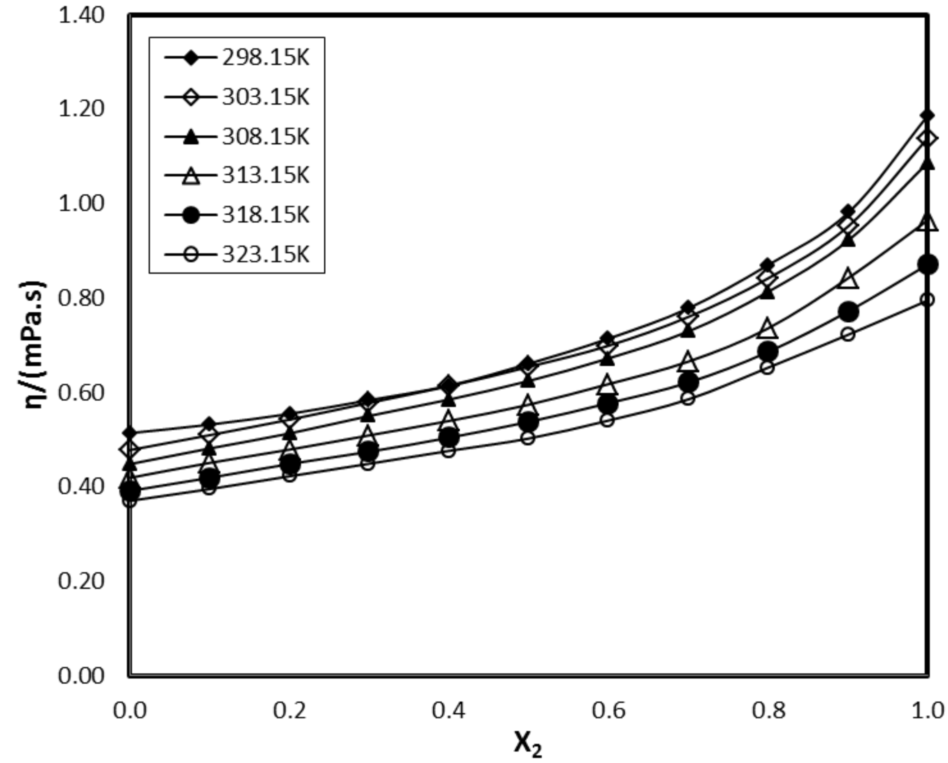

Figure 4.49: Plots of viscosity vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

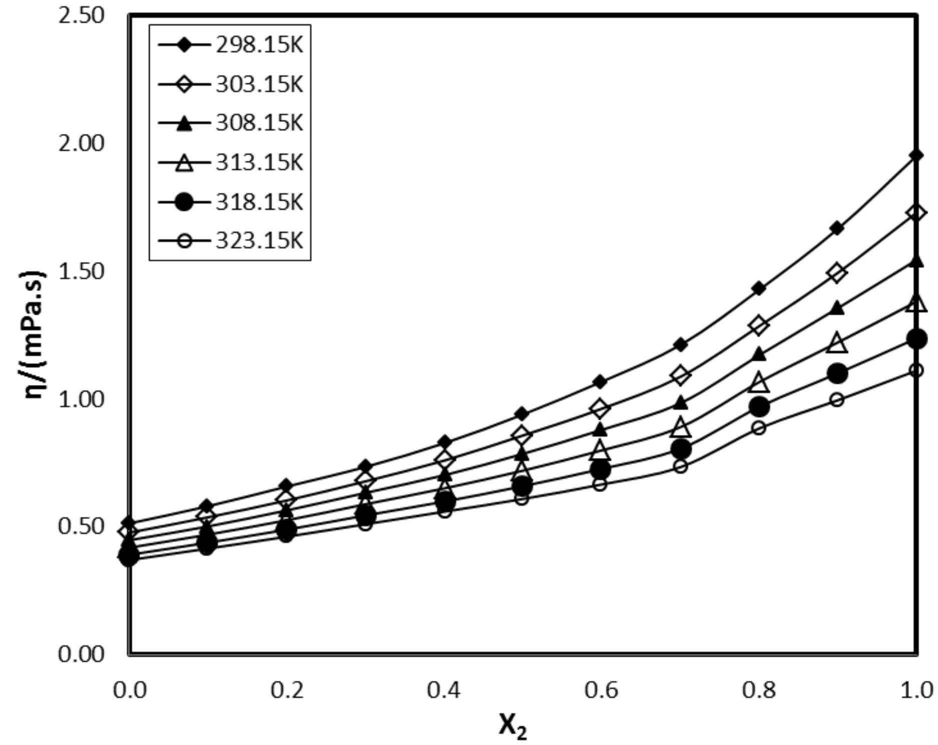

Figure 4.50: Plots of viscosity vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

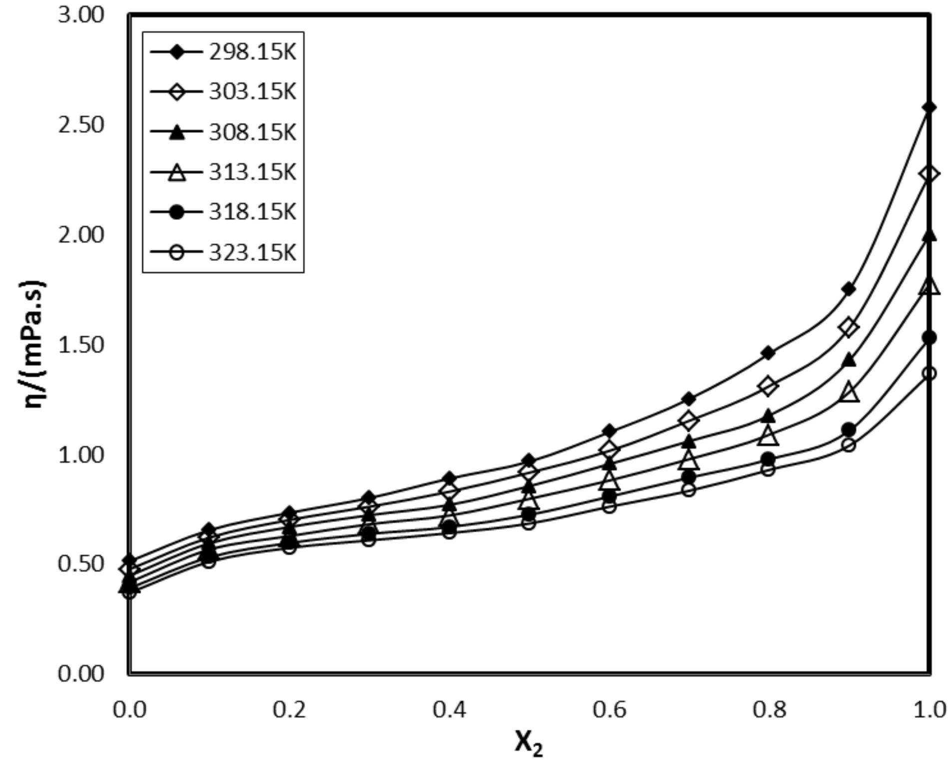

Figure 4.51: Plots of viscosity vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

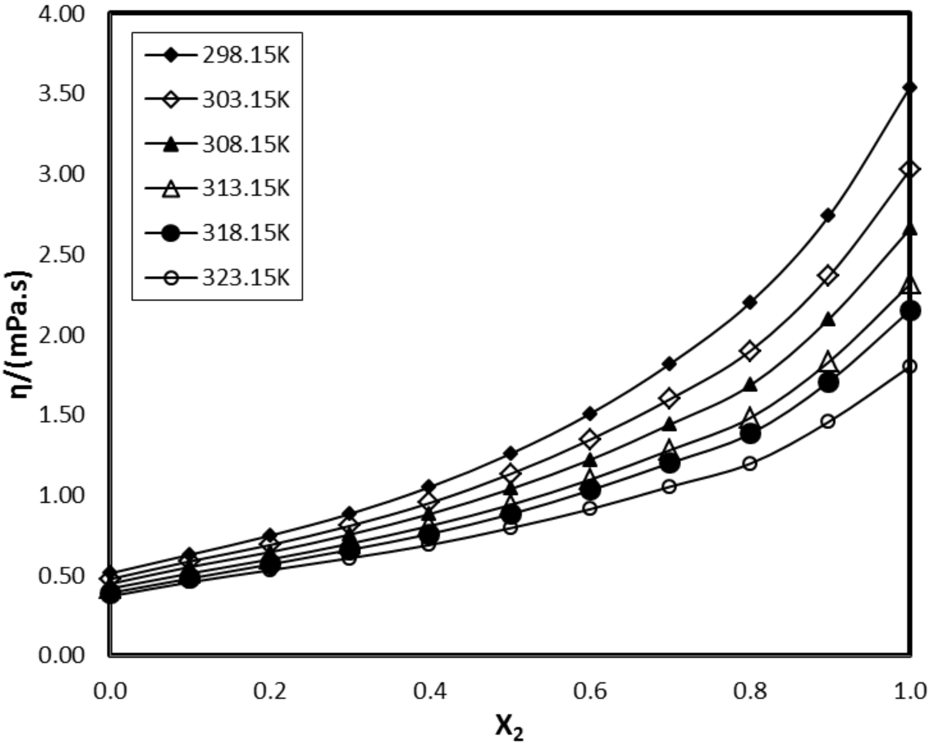

Figure 4.52: Plots of viscosity vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

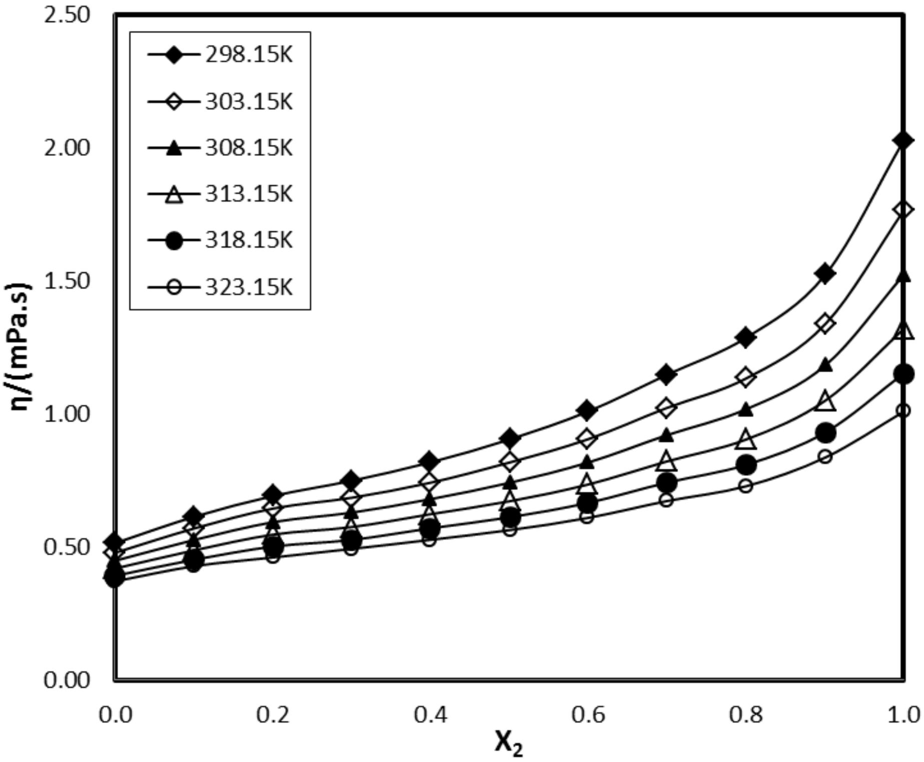

Figure 4.53: Plots of viscosity vs mole fraction of iso-propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

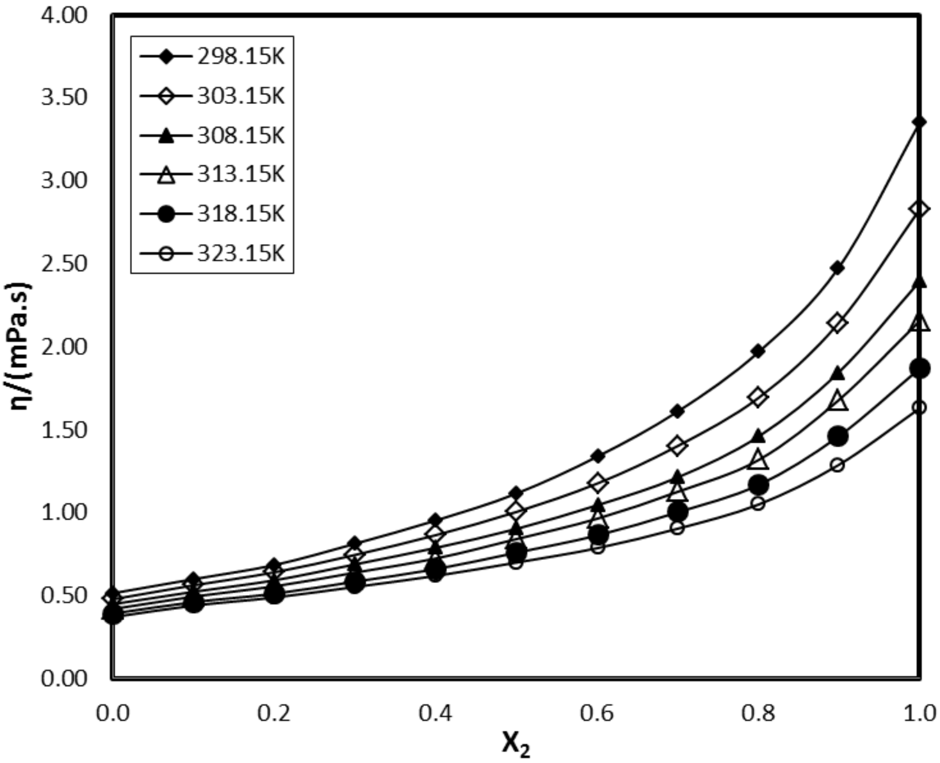

Figure 4.54: Plots of viscosity vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

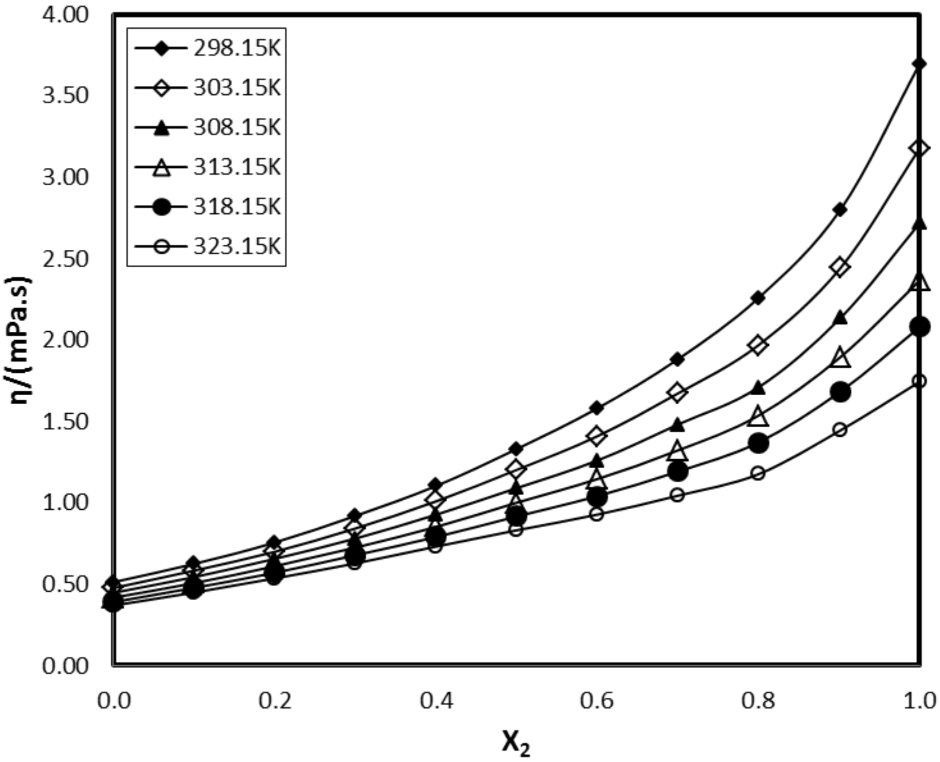

Figure 4.55: Plots of viscosity vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

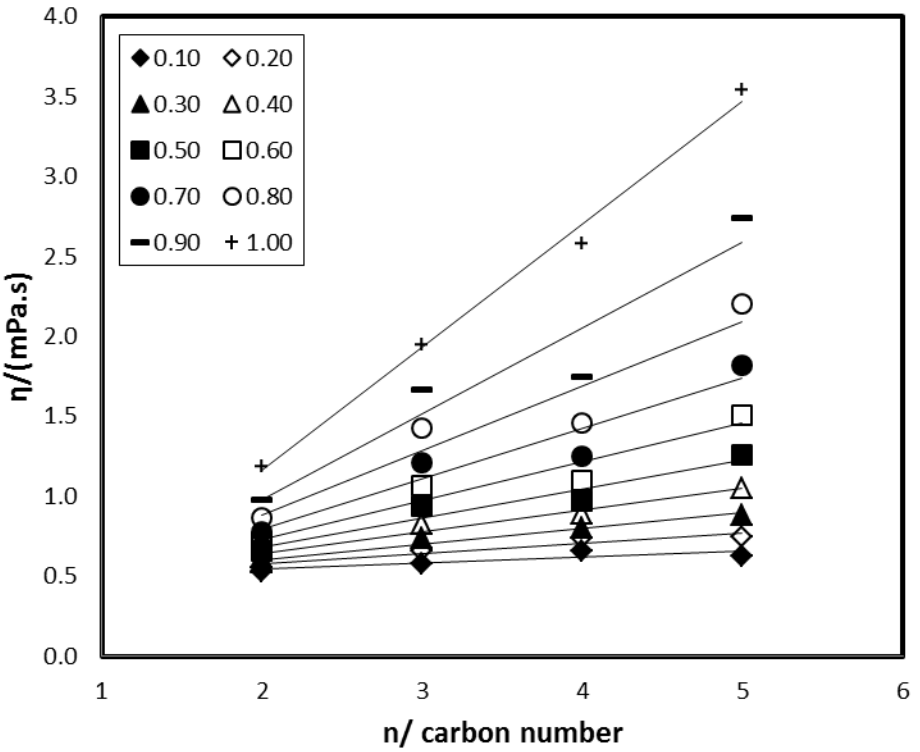

Figure 4.56: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

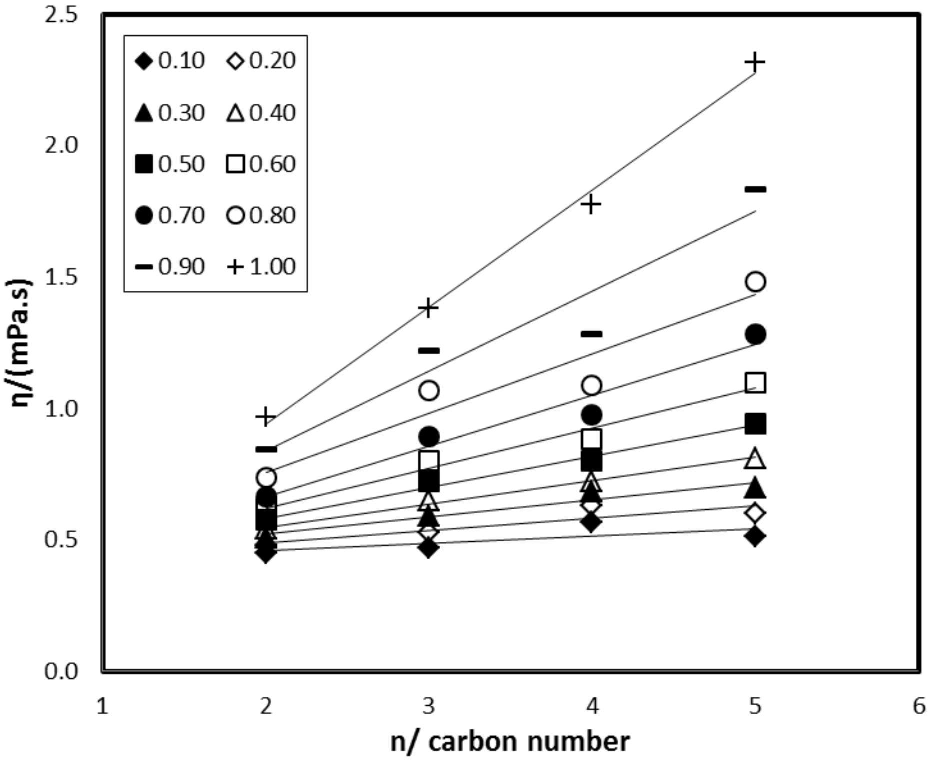

Figure 4.57: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

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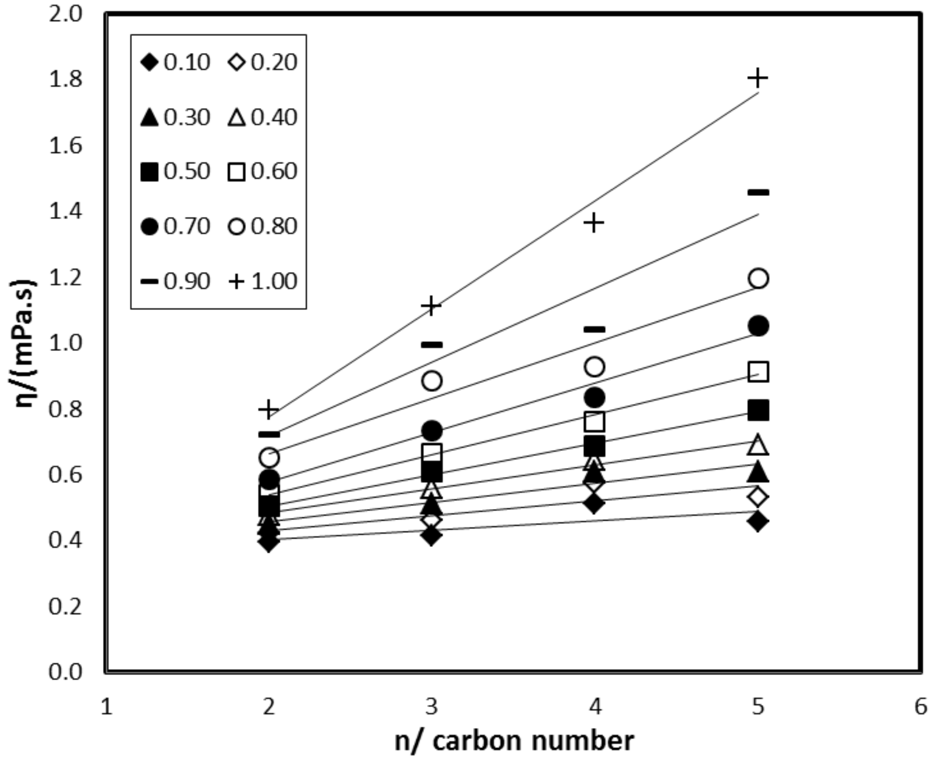

Figure 4.58: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

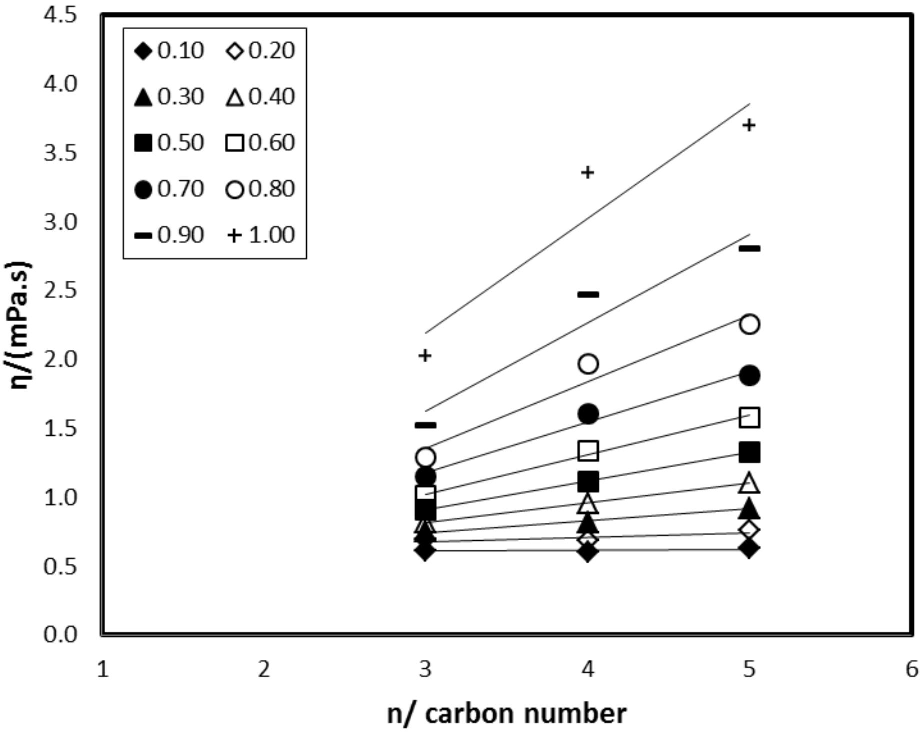

Figure 4.59: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

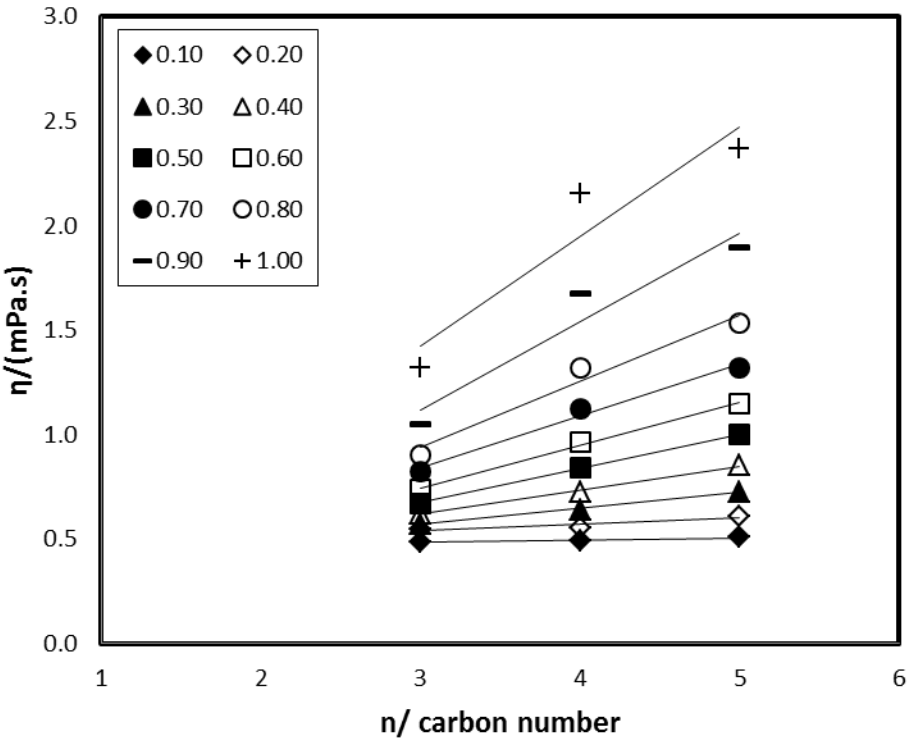

Figure 4.60: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

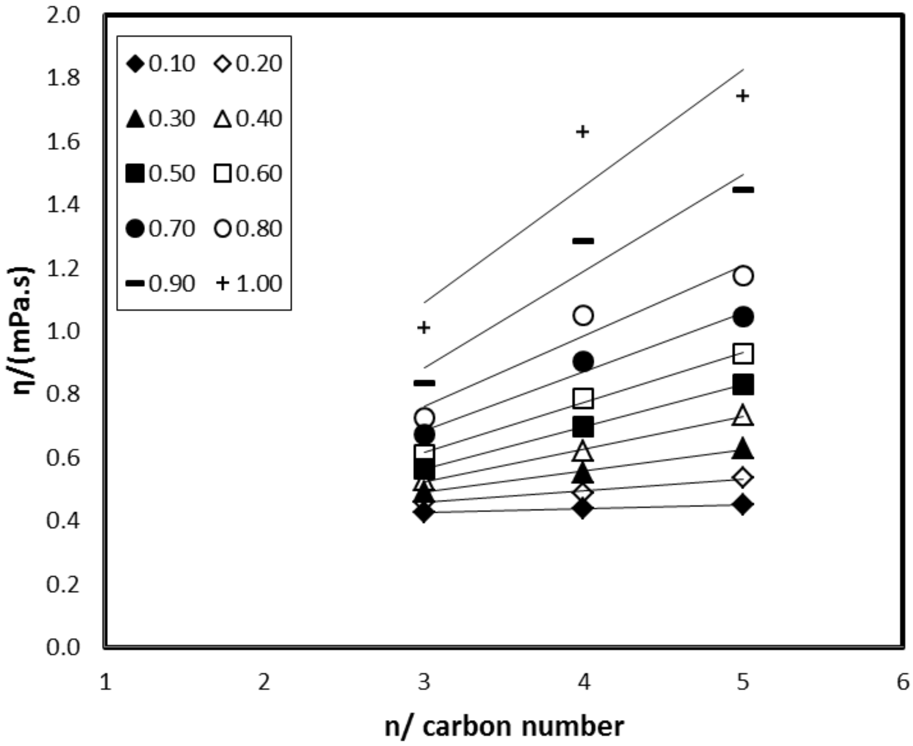

Figure 4.61: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

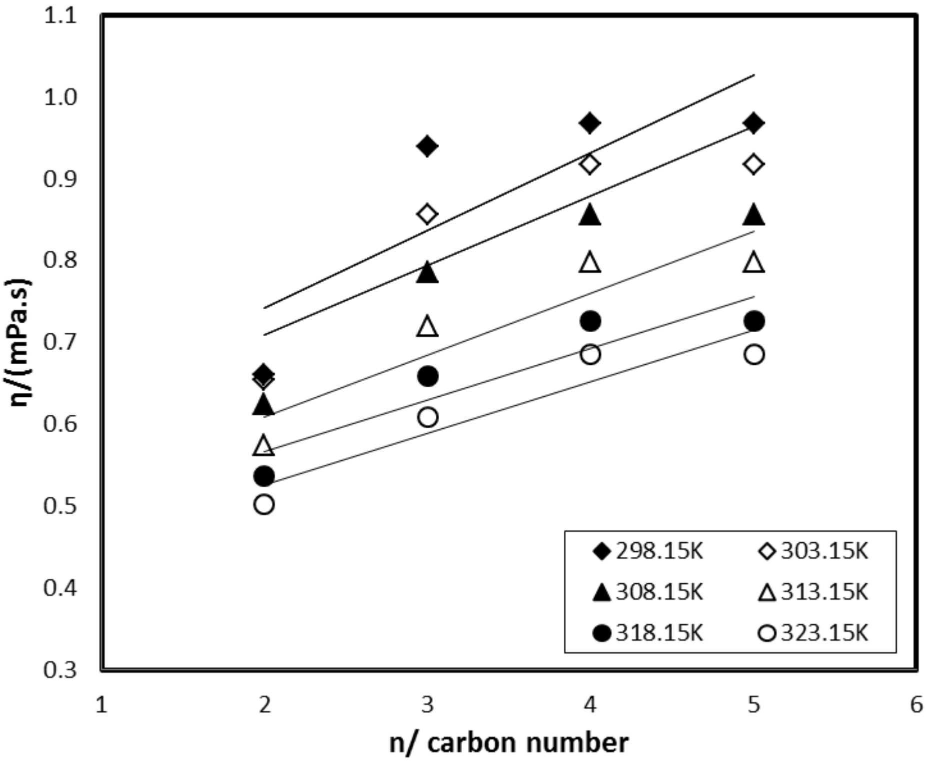

Figure 4.62: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

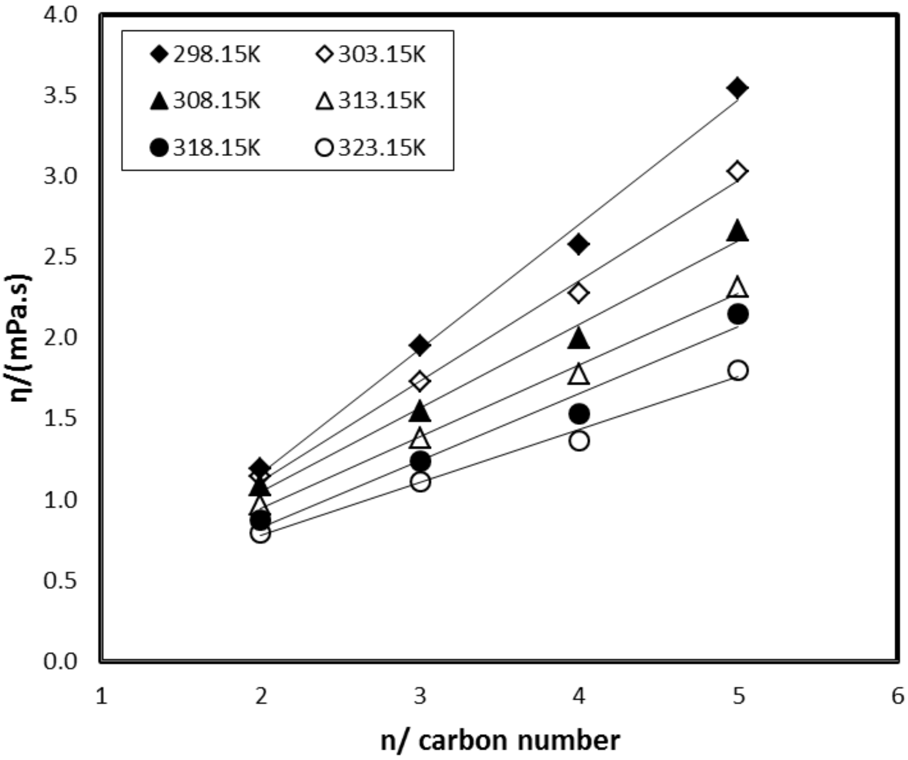

Figure 4.63: Dependence of the viscosity (η) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

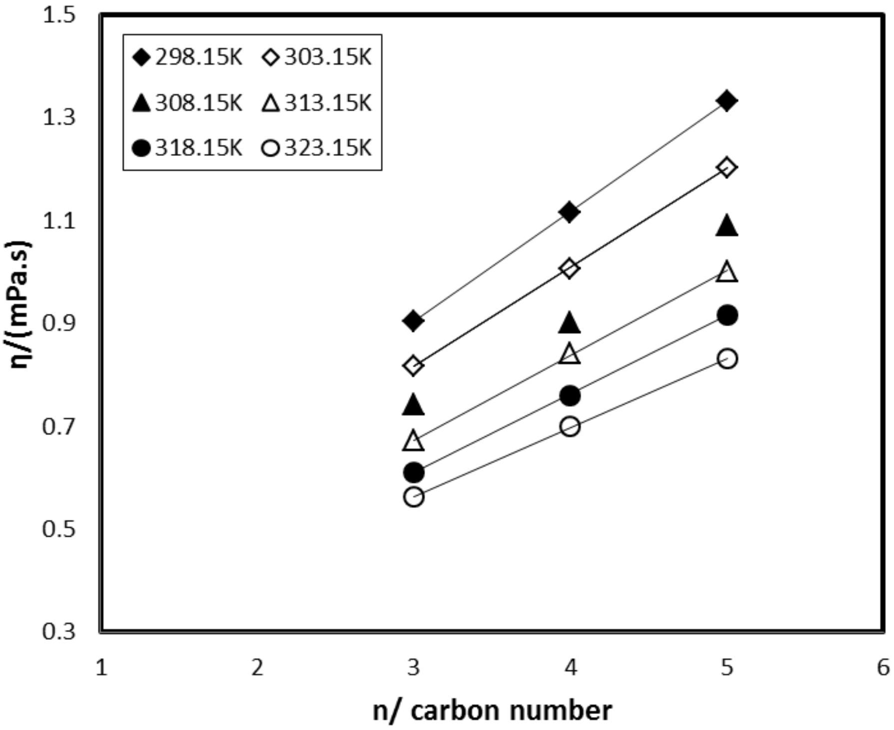

Figure 4.64: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

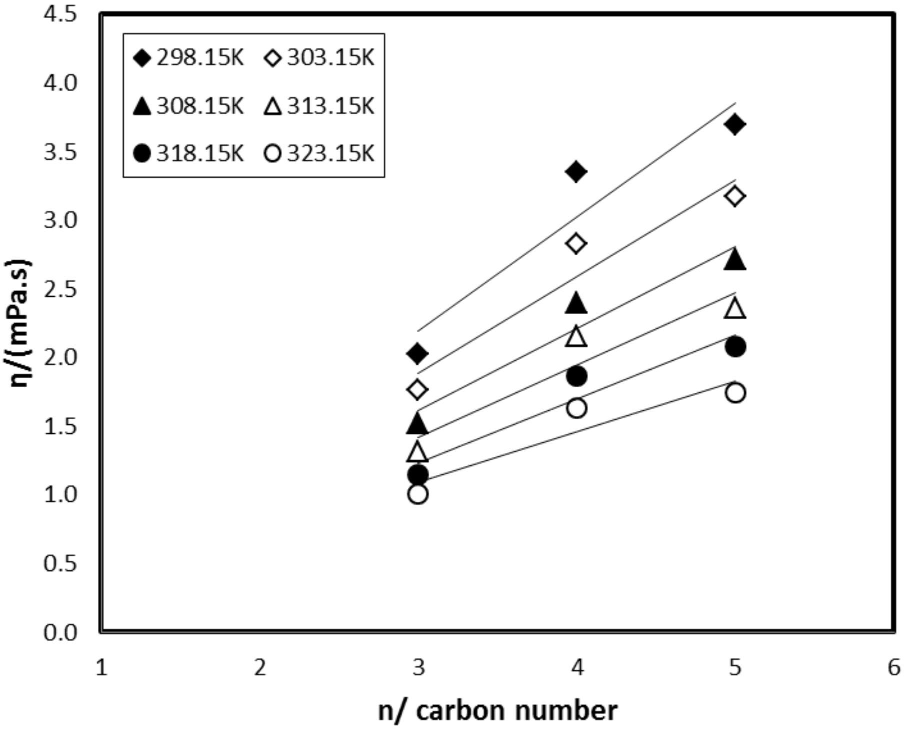

Figure 4.65: Dependence of the viscosity (η) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

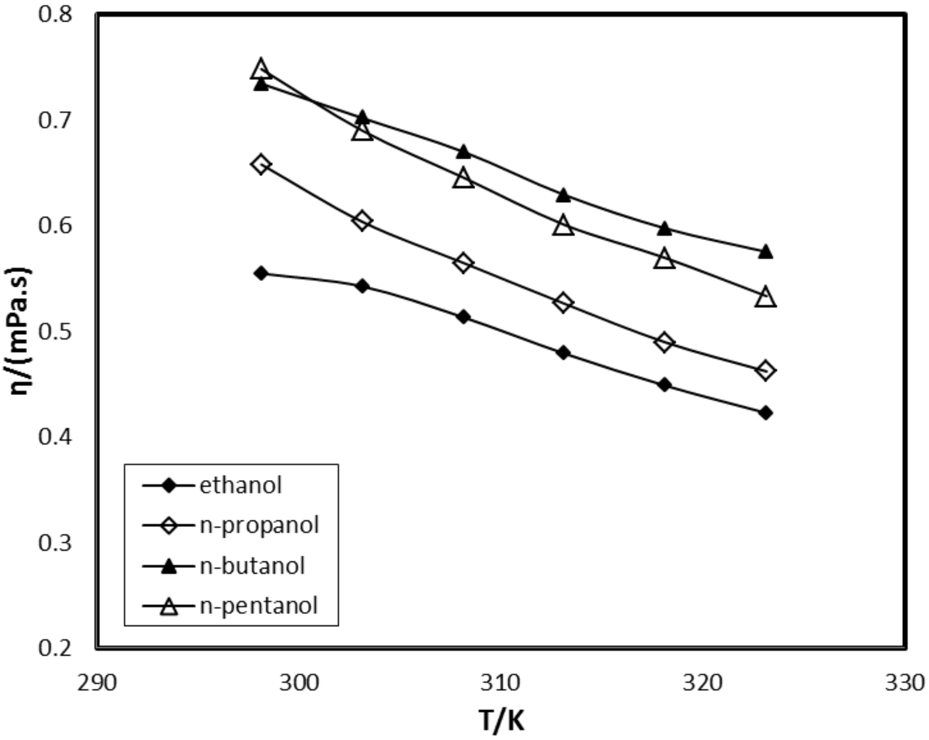

Figure 4.66: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

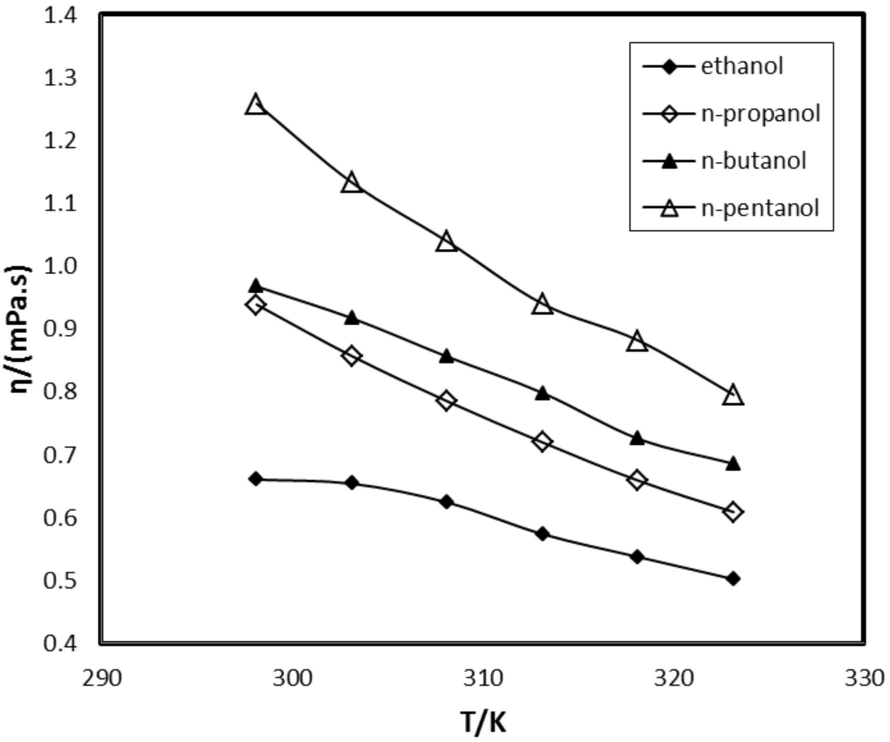

Figure 4.67: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

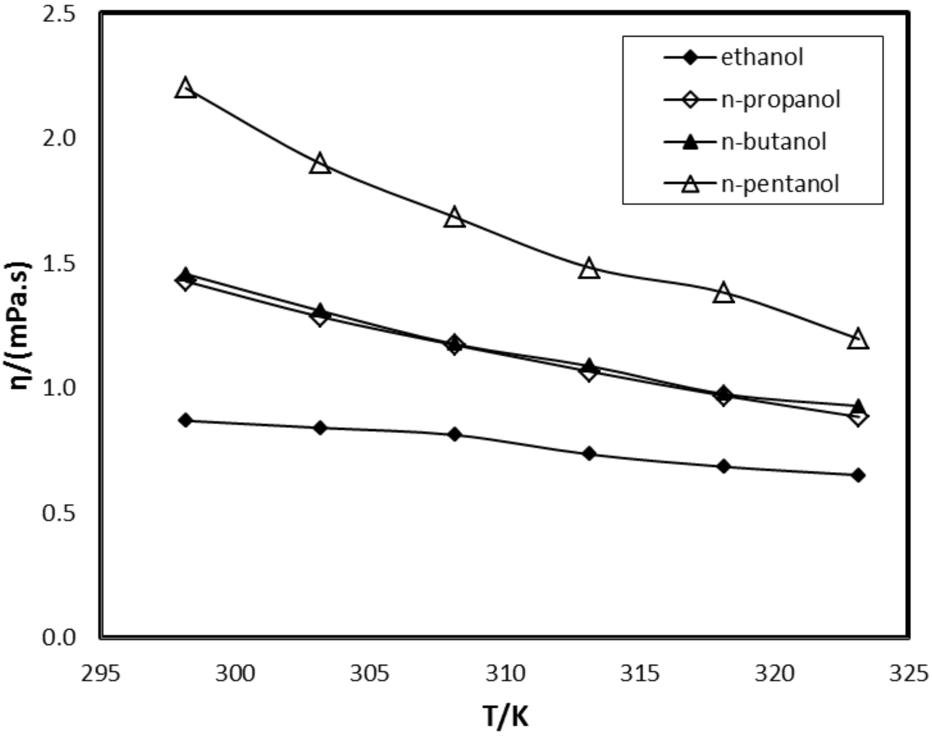

Figure 4.68: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

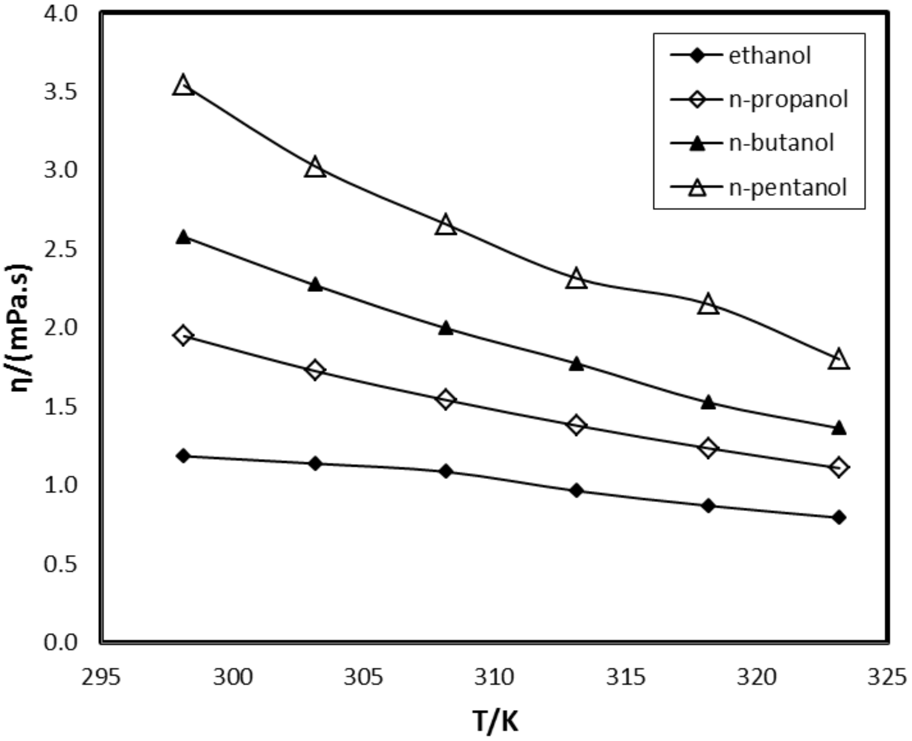

Figure 4.69: Comparison of viscosity (η) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

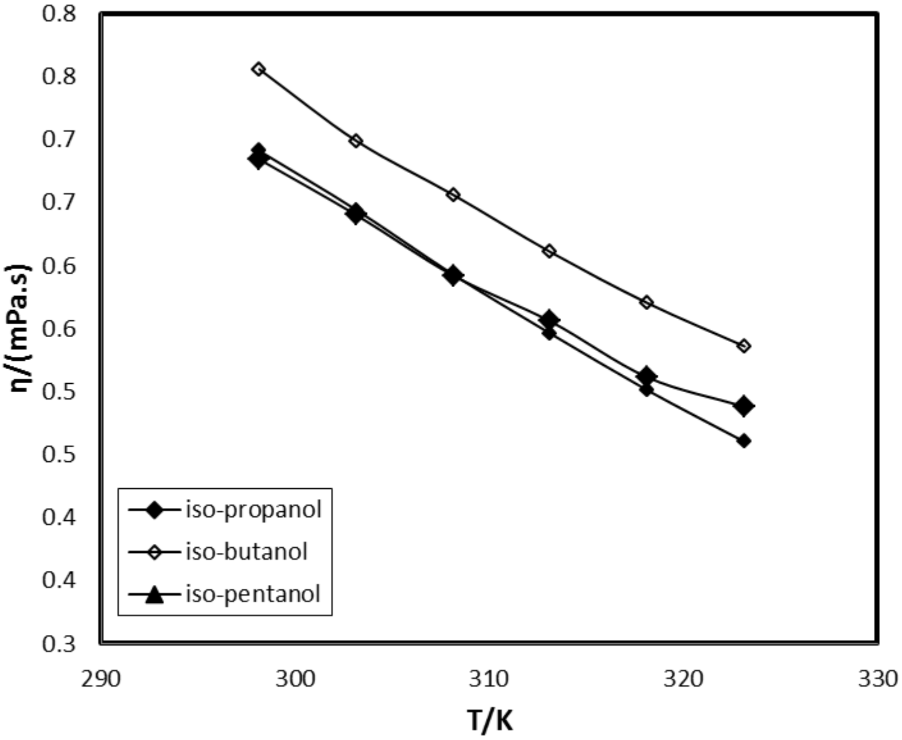

Figure 4.70: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

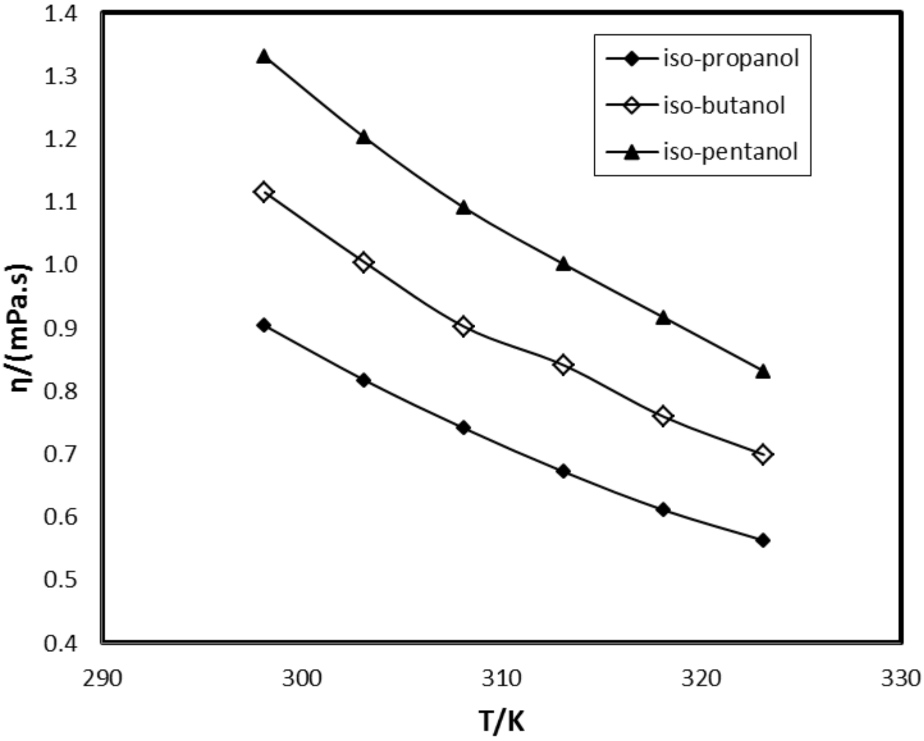

Figure 4.71: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

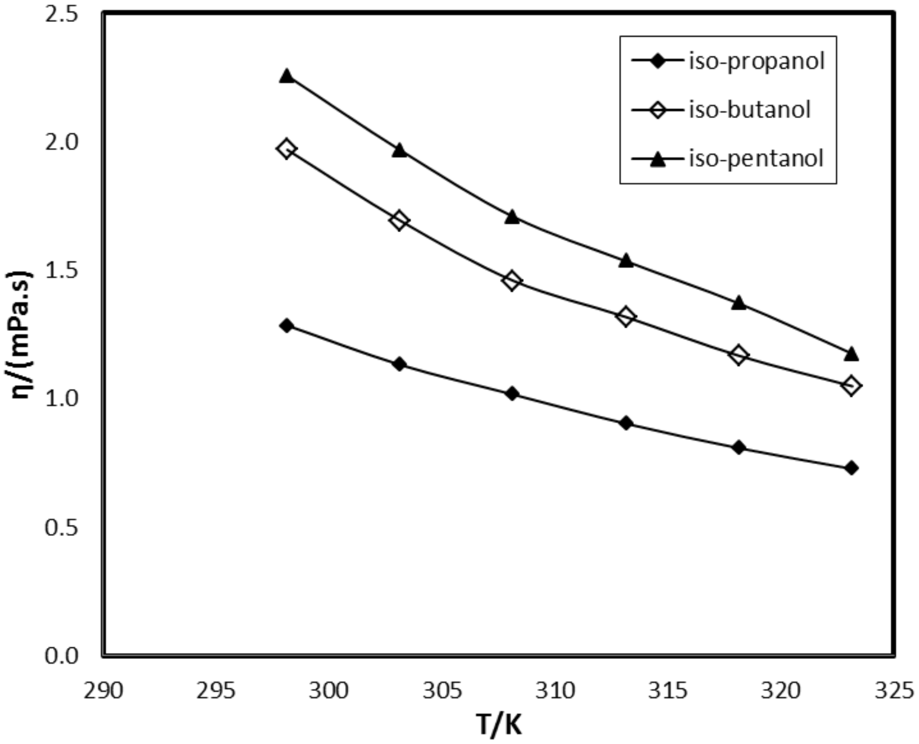

Figure 4.72: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

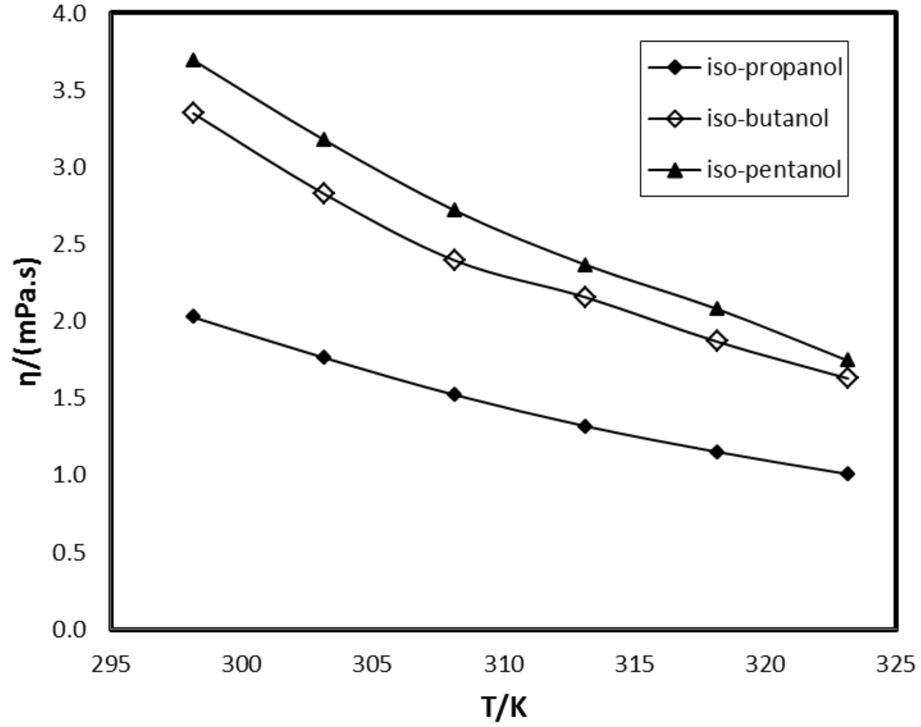

Figure 4.73: Comparison of viscosity (η) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

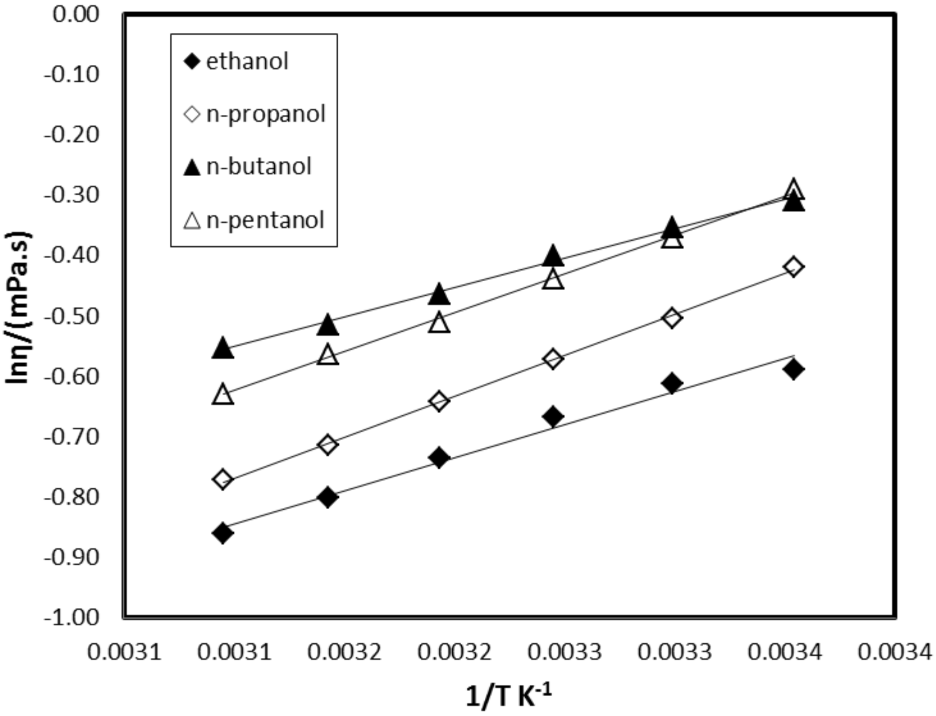

Figure 4.74: Comparison of lnη vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

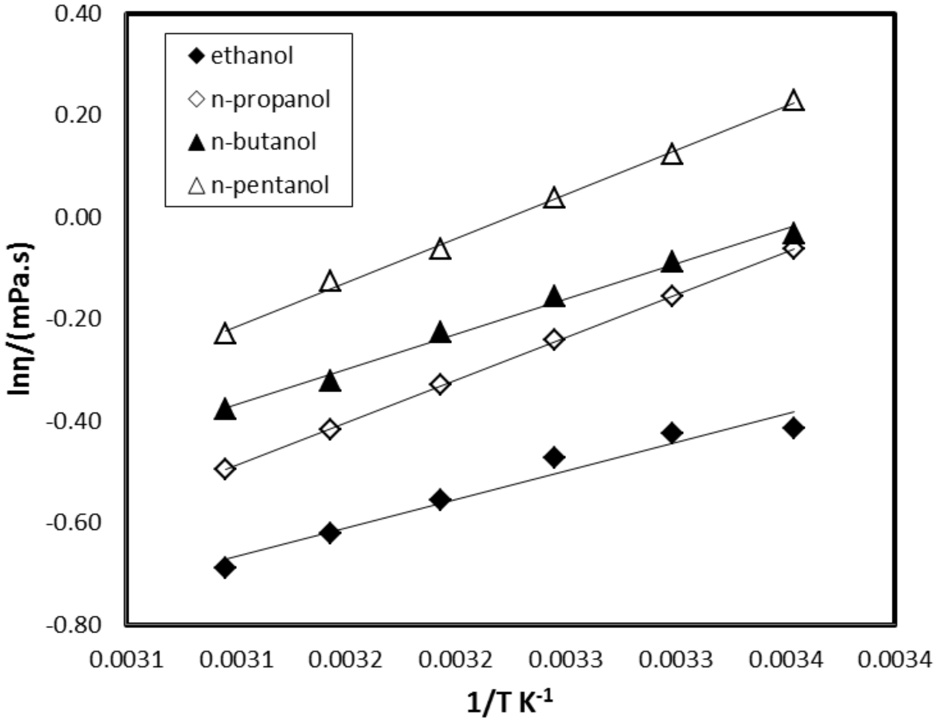

Figure 4.75: Comparison of lnη vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

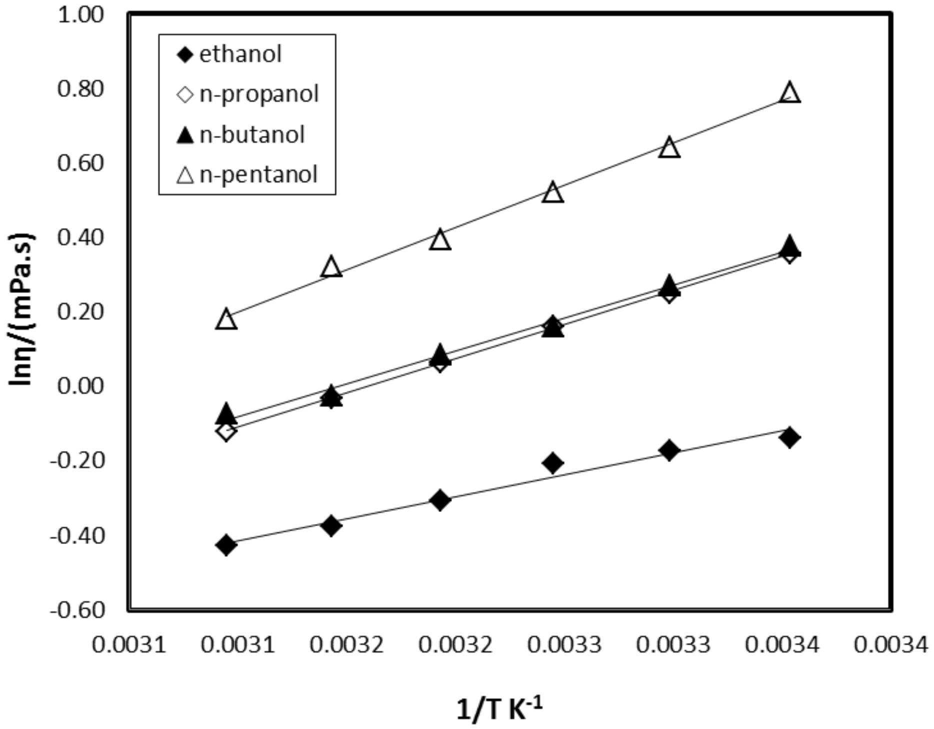

Figure 4.76: Comparison of lnη vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

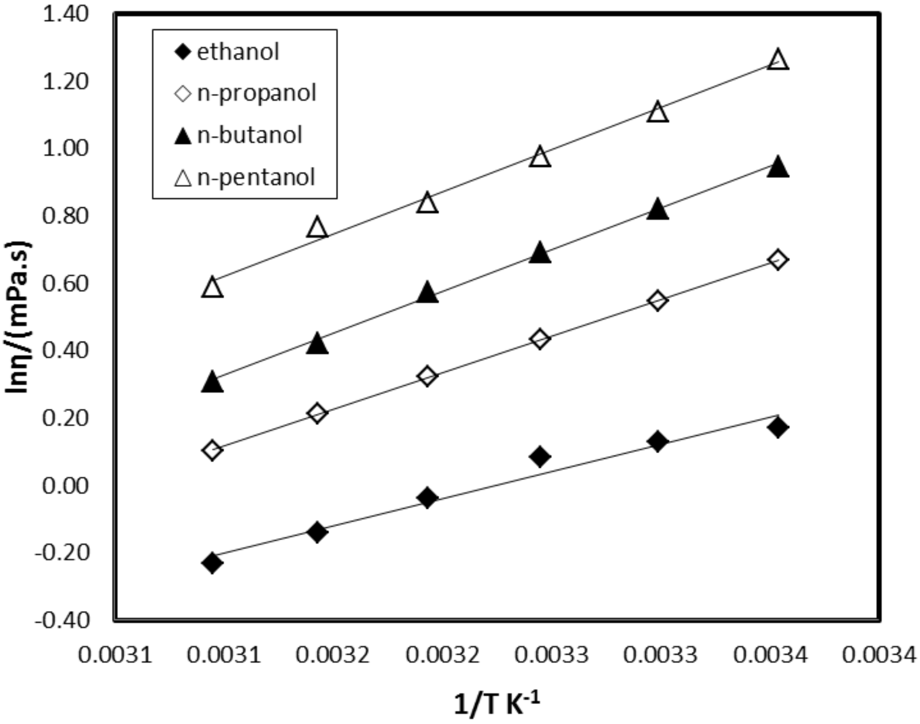

Figure 4.77: Comparison of lnη vs 1/T of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

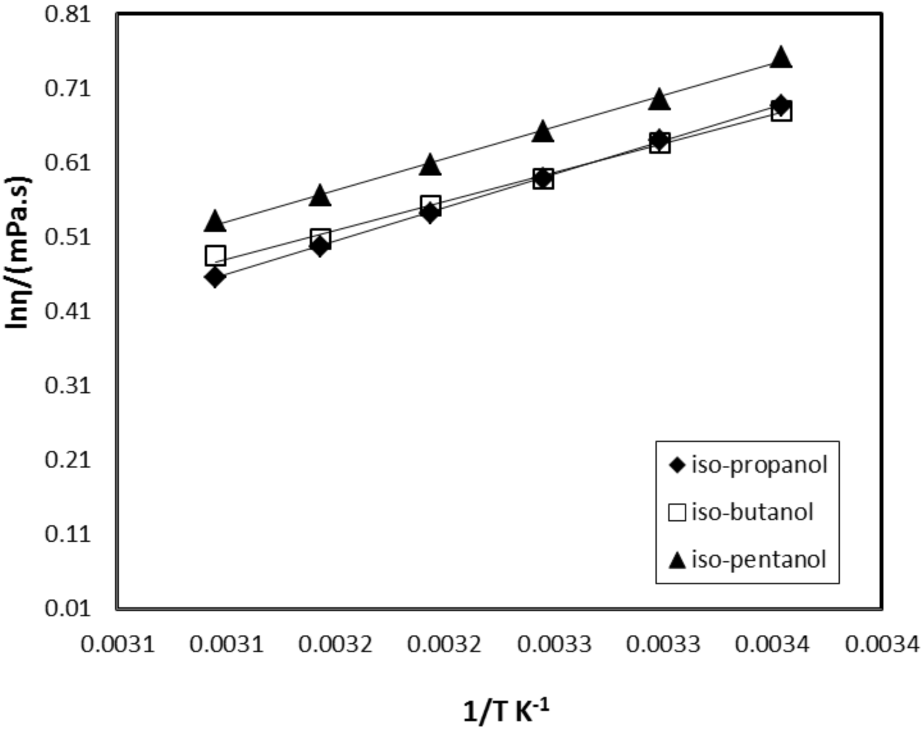

Figure 4.78: Comparison of lnη vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

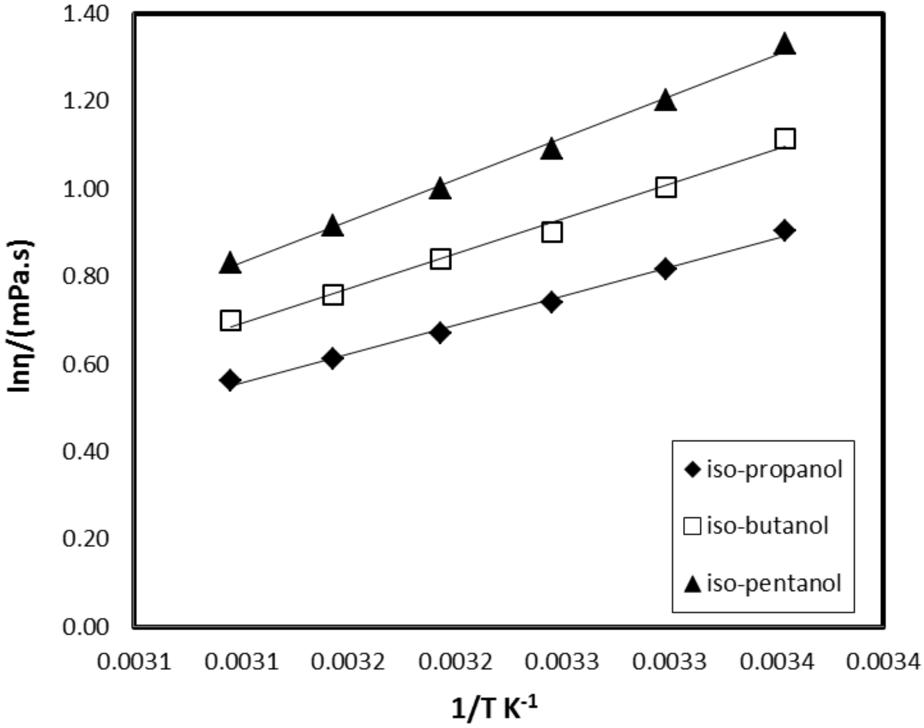

Figure 4.79: Comparison of lnη vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

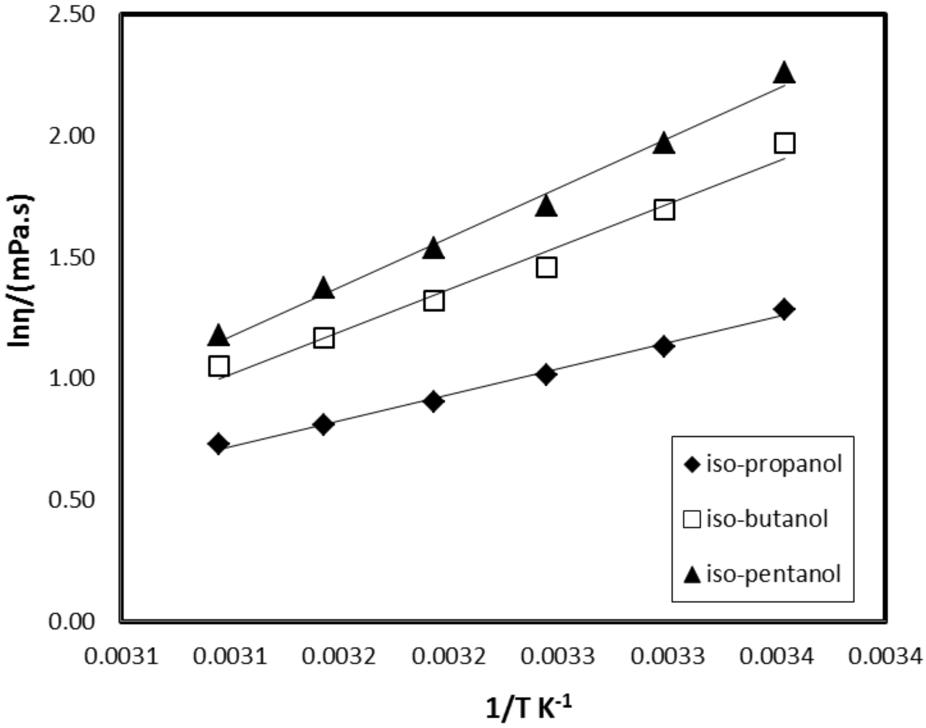

Figure 4.80: Comparison of lnη vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

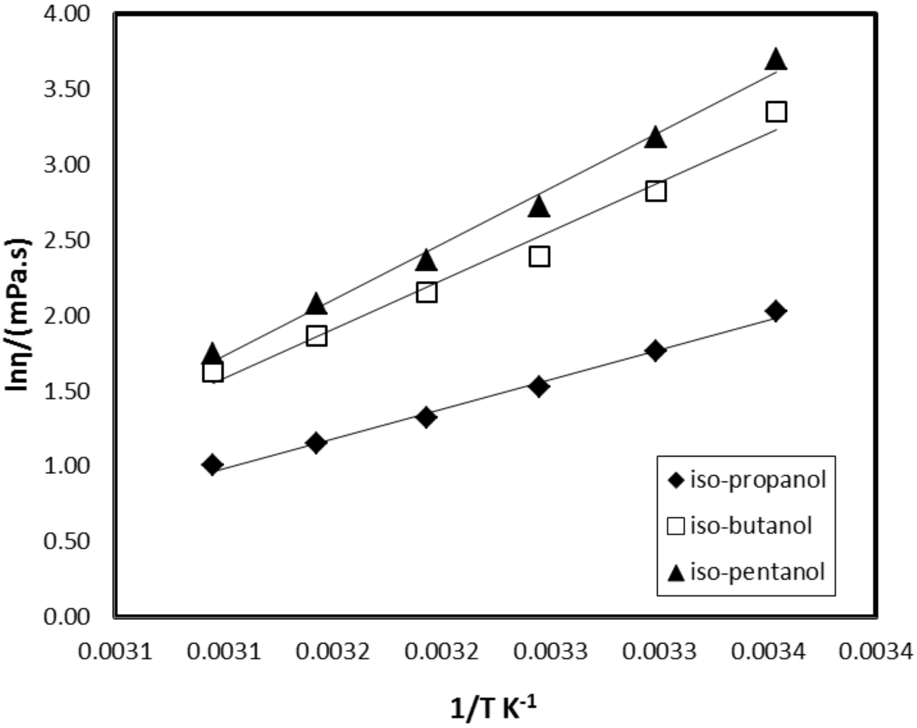

Figure 4.81: Comparison of lnη vs 1/T of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 1.0 mole fraction.

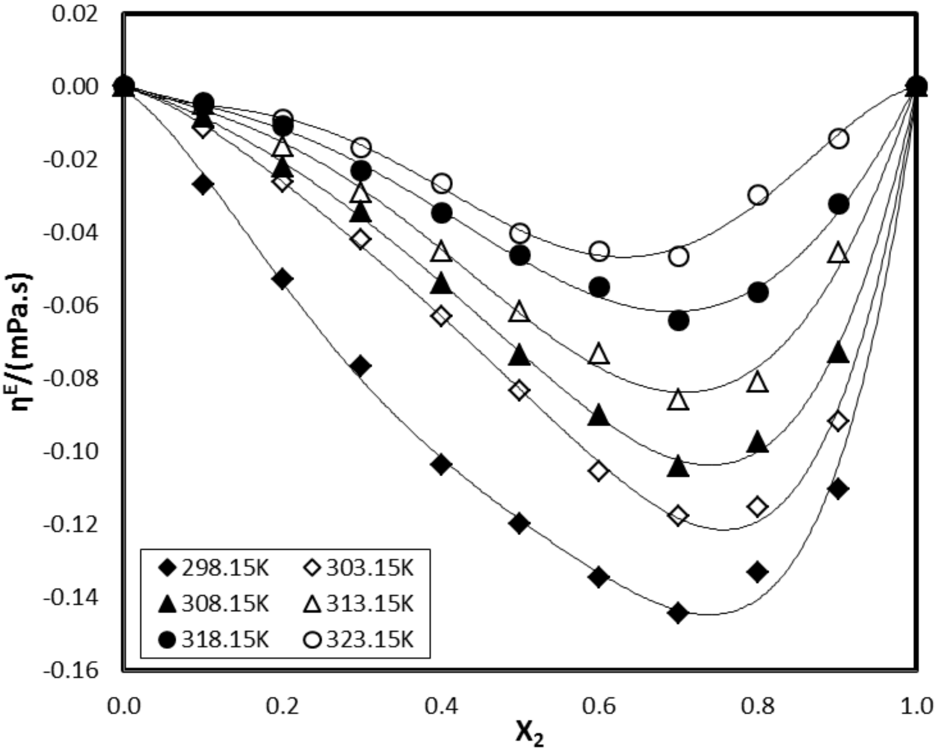

Figure 4.82: Plots of excess viscosity vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

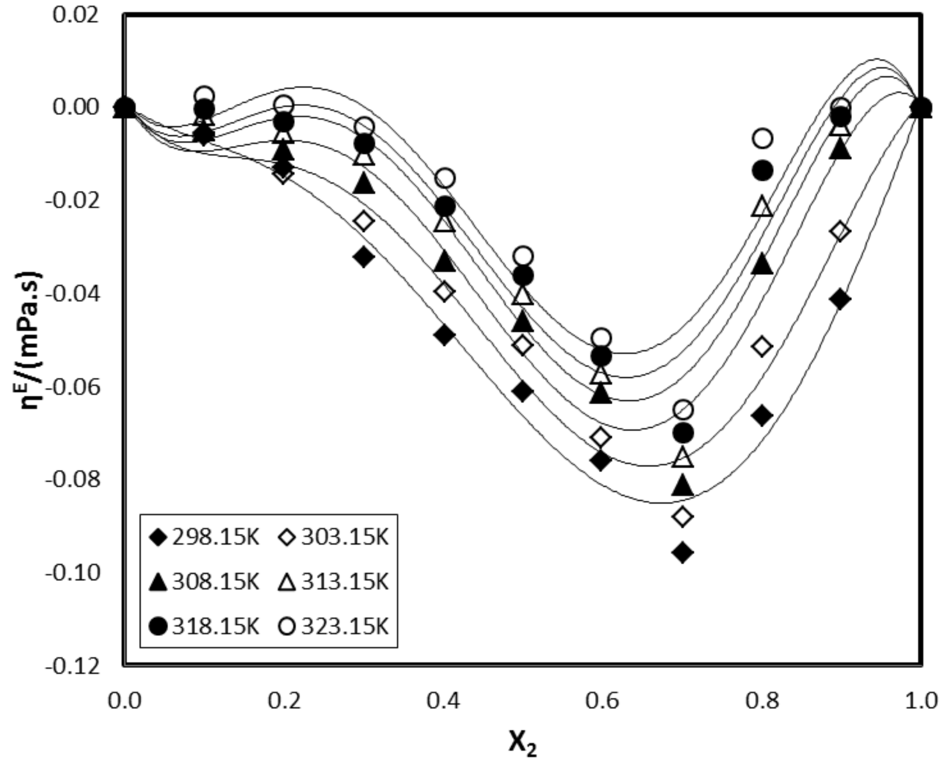

Figure 4.83: Plots of excess viscosity vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

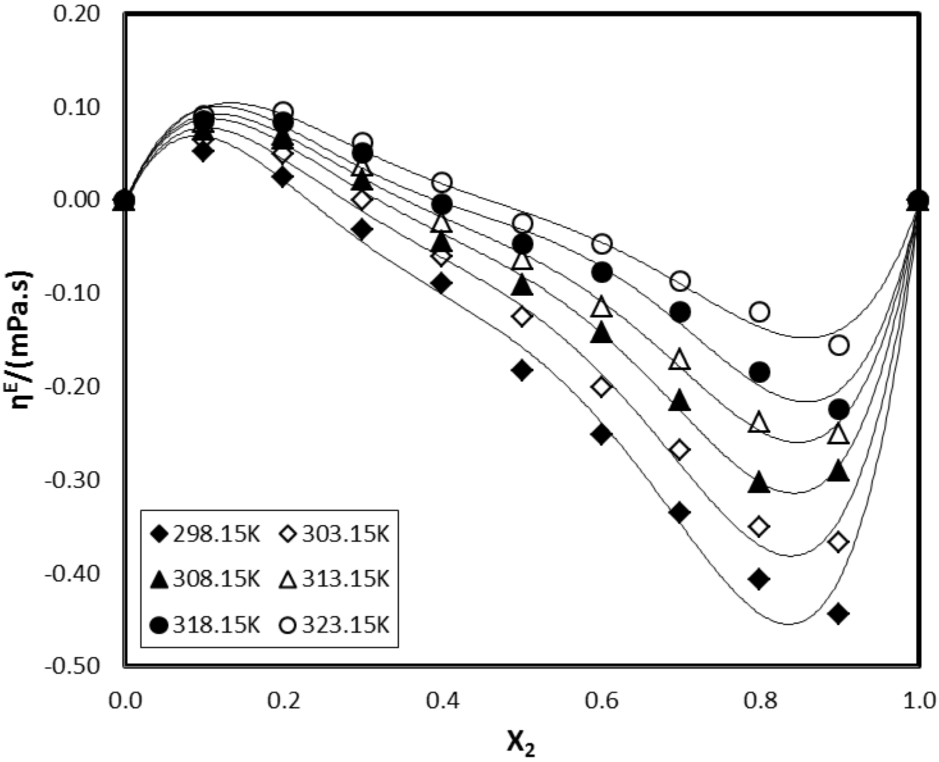

Figure 4.84: Plots of excess viscosity vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

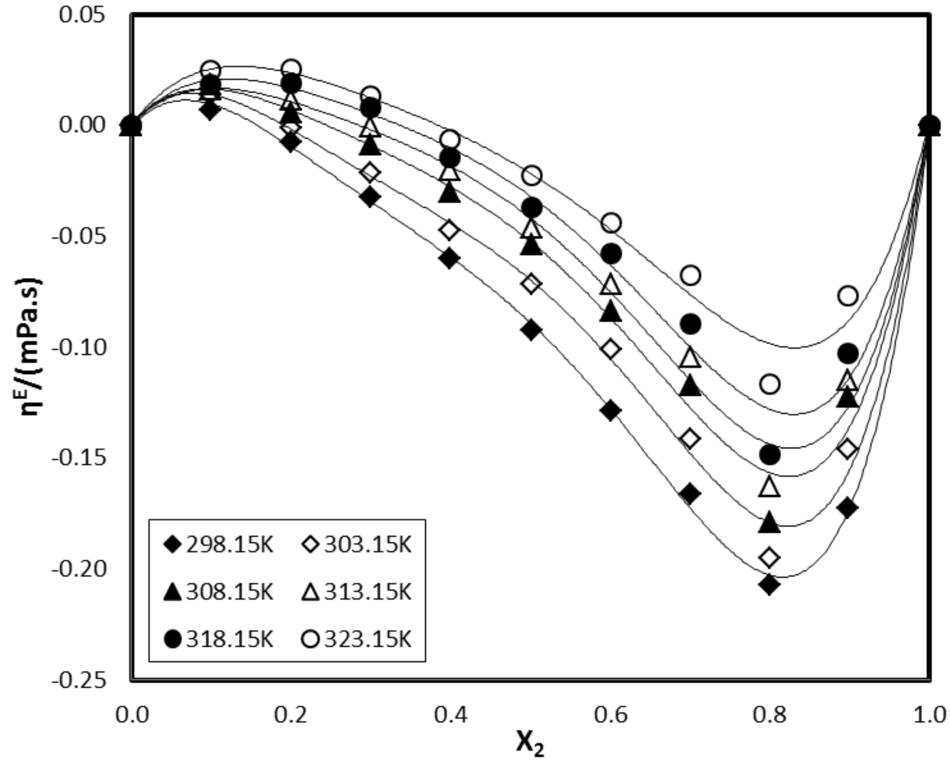

Figure 4.85: Plots of excess viscosity vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

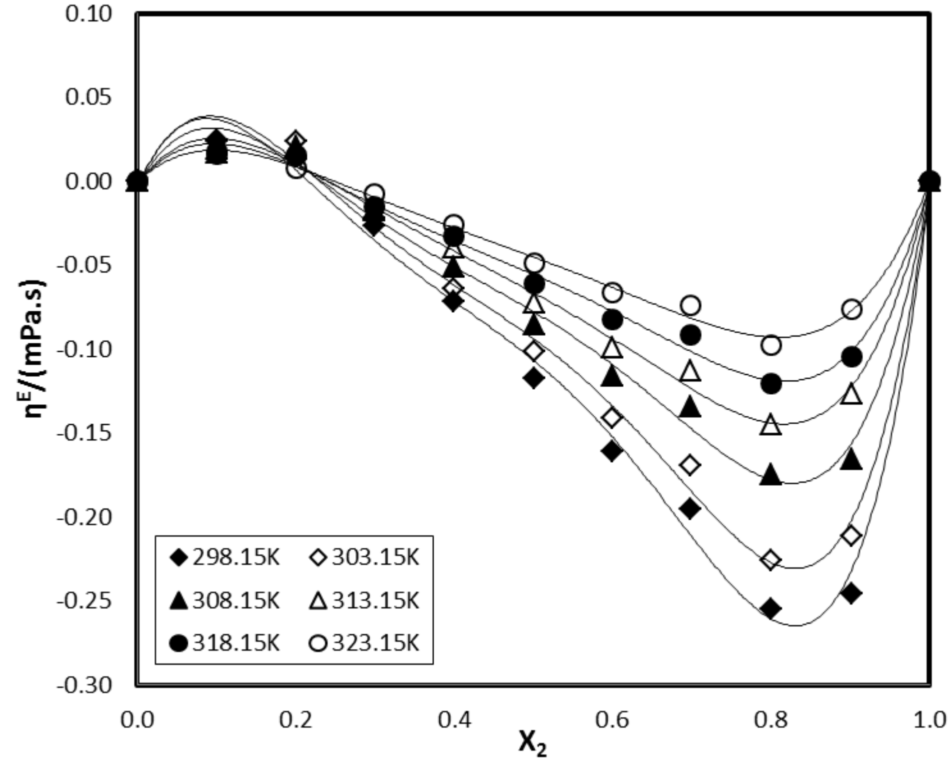

Figure 4.86: Plots of excess viscosity vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

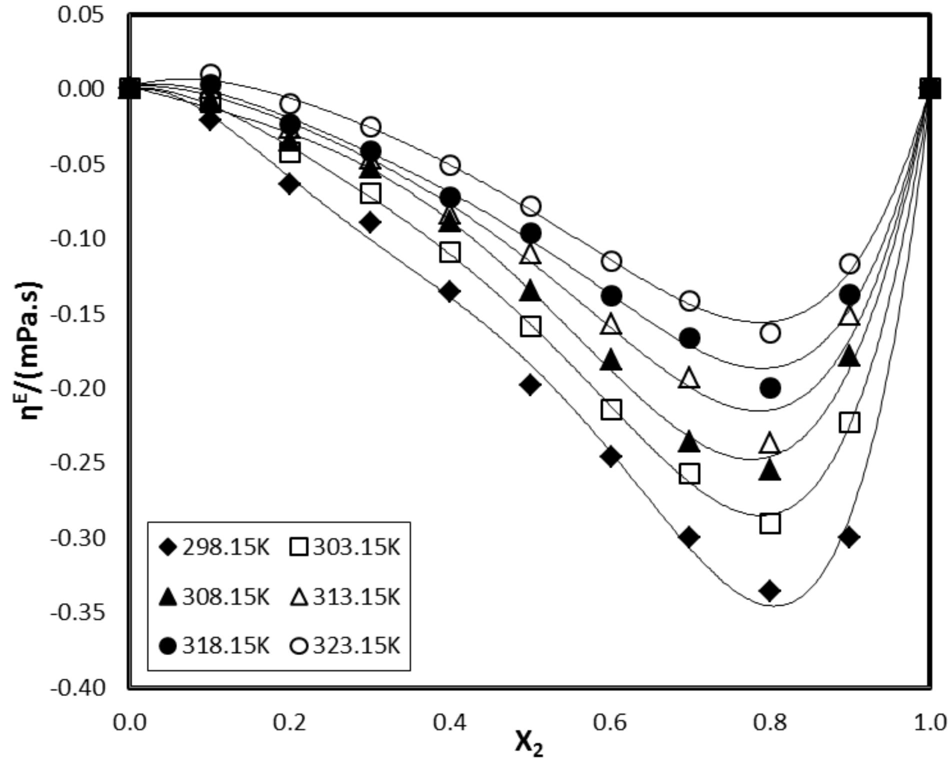

Figure 4.87: Plots of excess viscosity vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

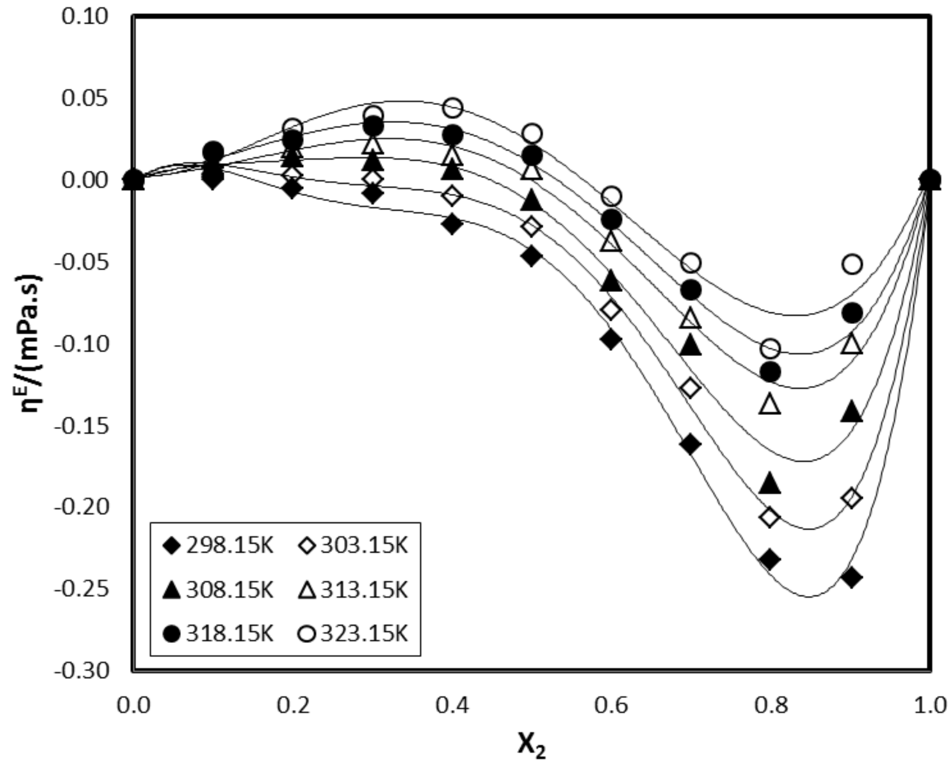

Figure 4.88: Plots of excess viscosity vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

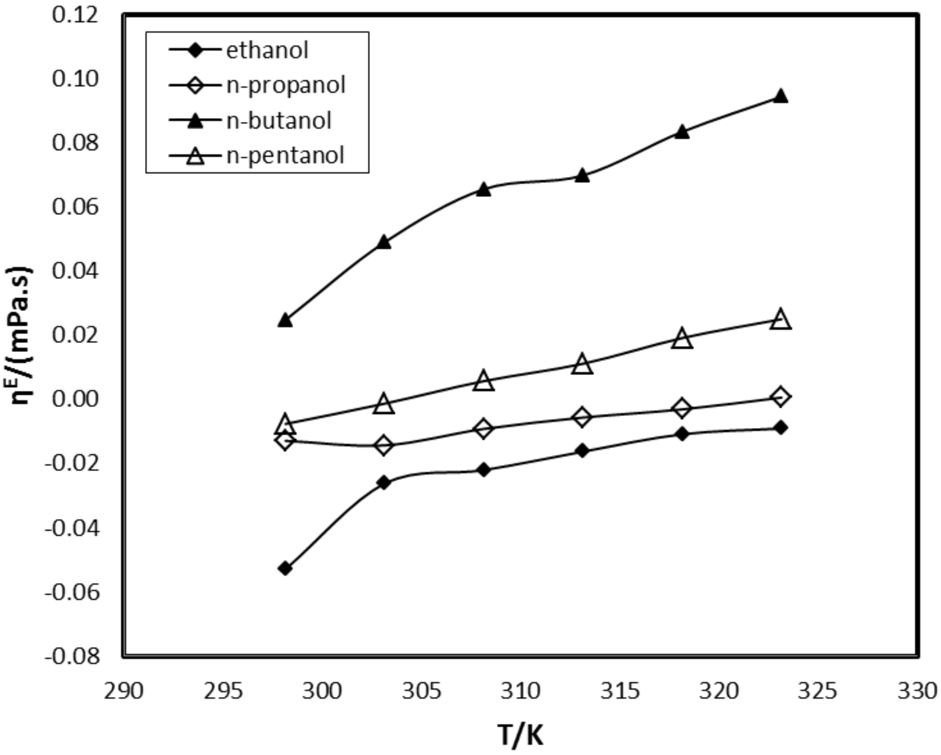

Figure 4.89: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

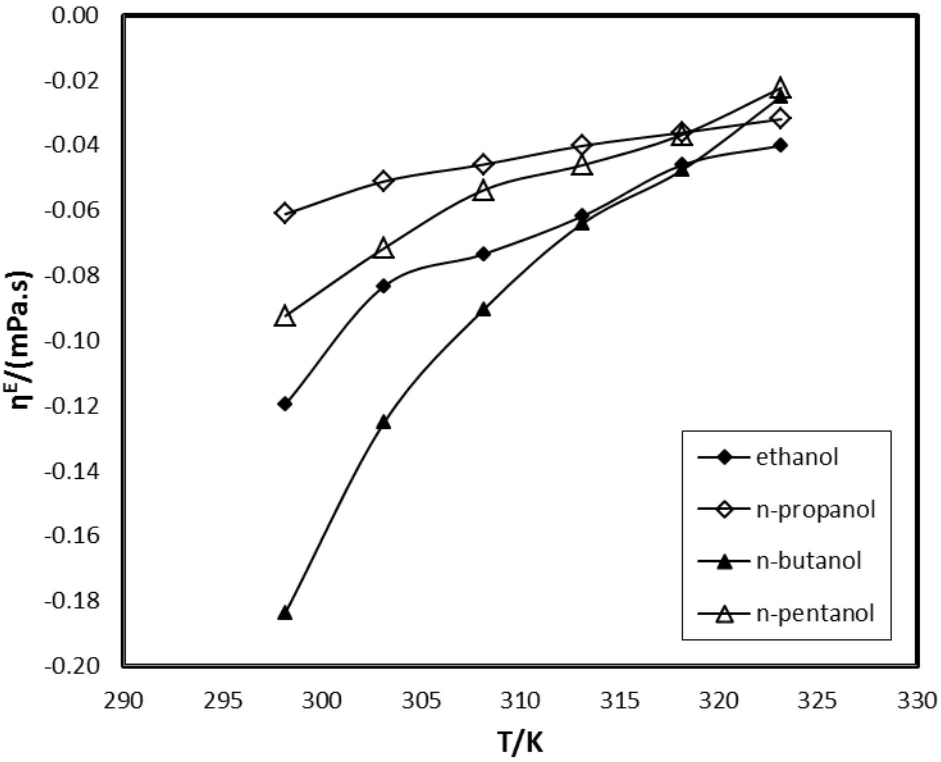

Figure 4.90: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

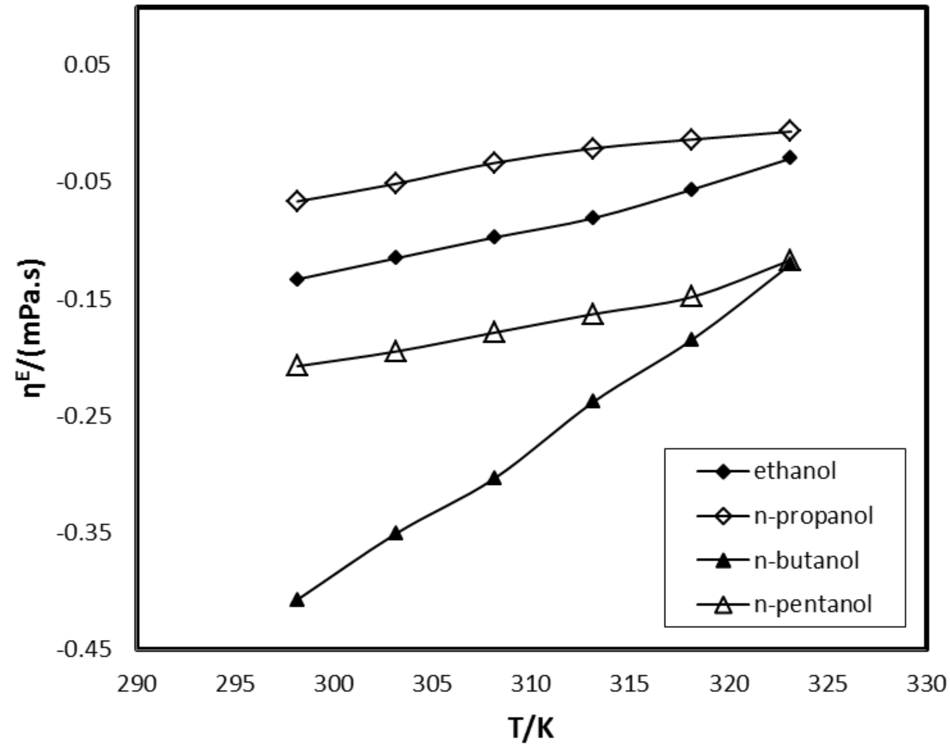

Figure 4.91: Comparison of excess viscosity (η^E) vs temperature (T) of Ethanol, n-Propanol, n-Butanol and n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

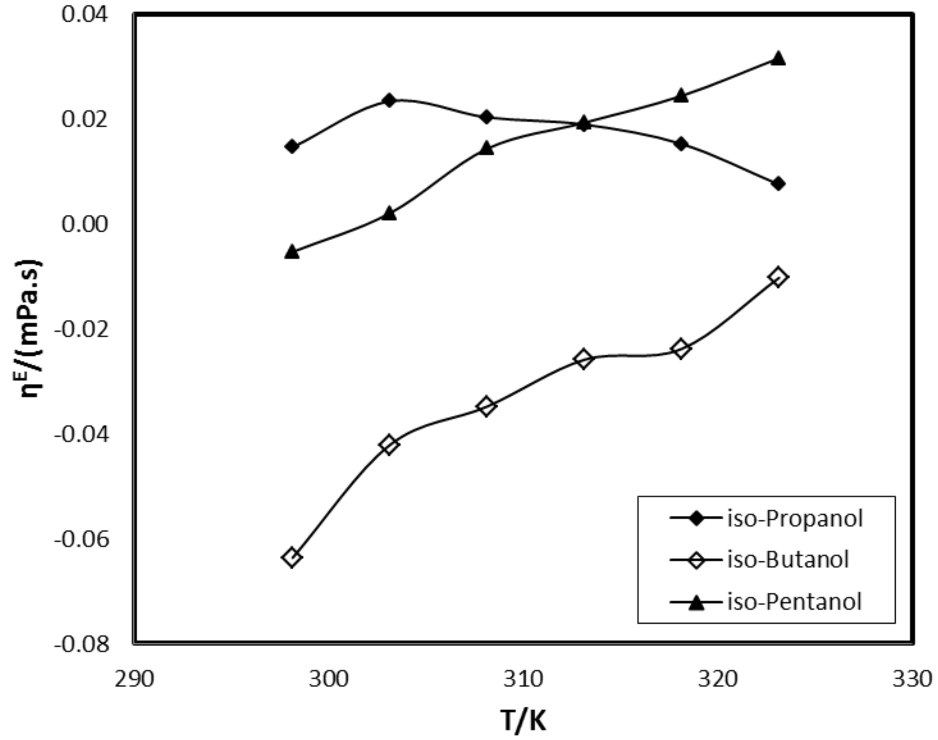

Figure 4.92: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.2 mole fraction.

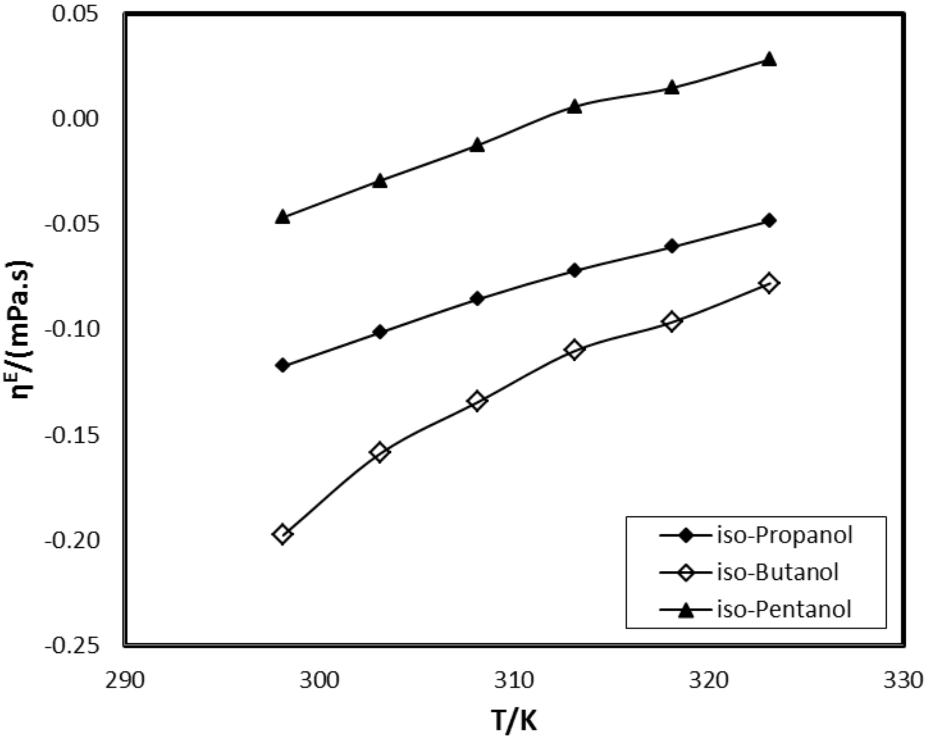

Figure 4.93: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.5 mole fraction.

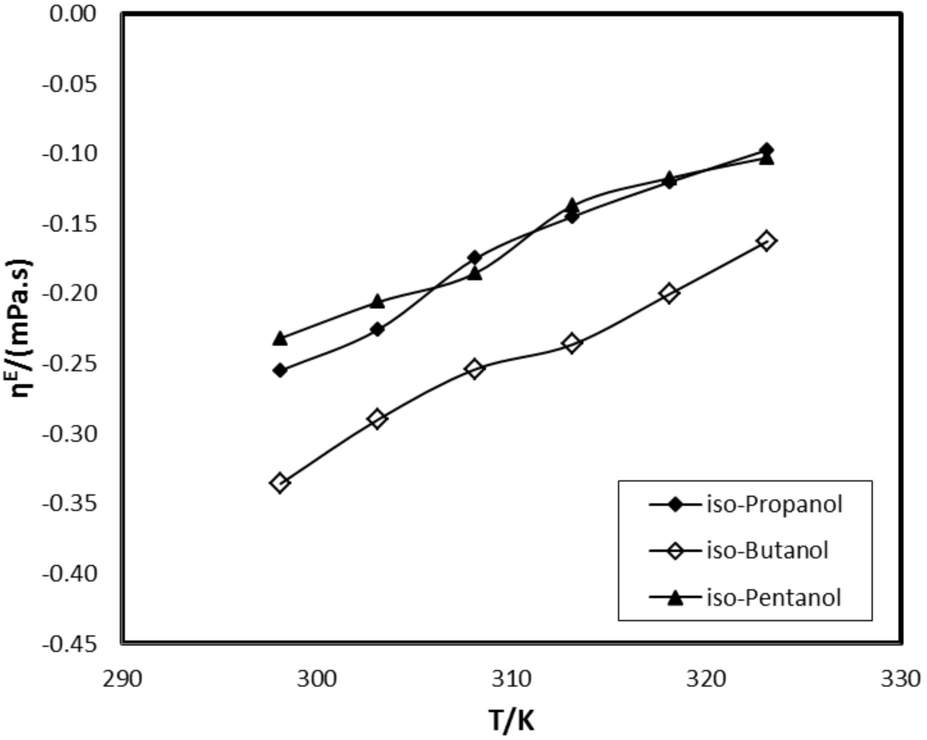

Figure 4.94: Comparison of excess viscosity (η^E) vs temperature (T) of iso-Propanol, iso-Butanol and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) at 0.8 mole fraction.

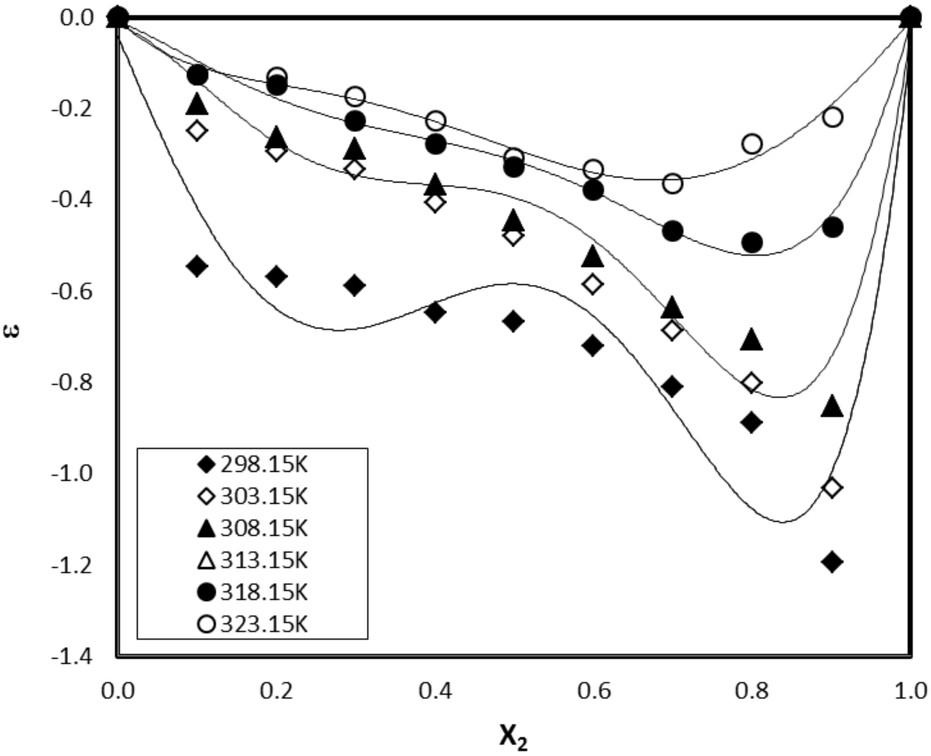

Figure 4.95: Plots of interaction parameter (ε) vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

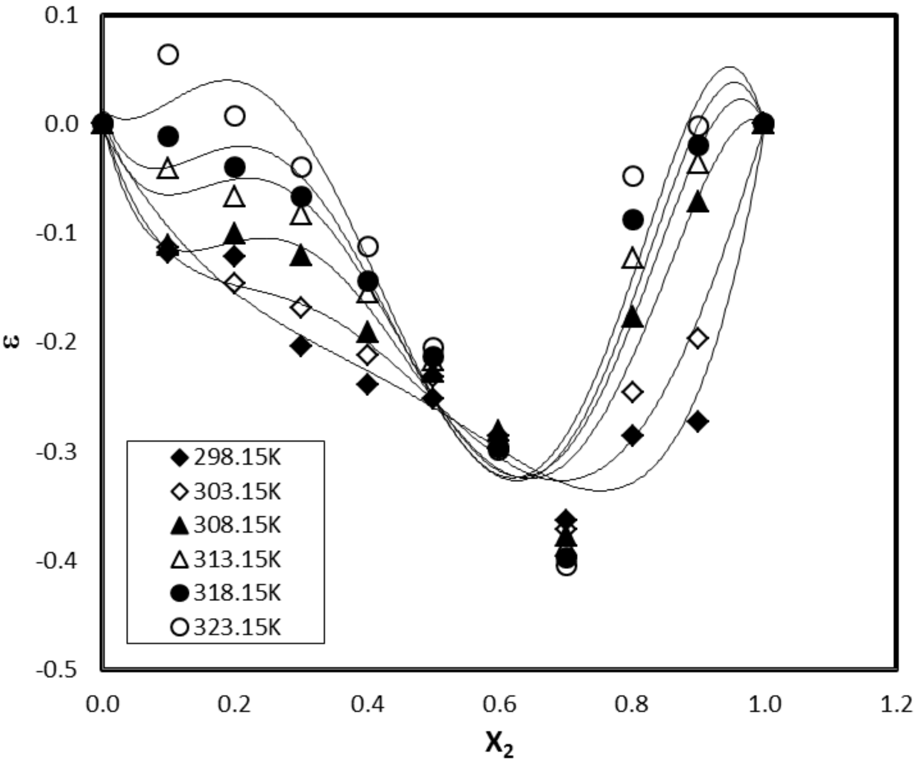

Figure 4.96: Plots of interaction parameter (ε) vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

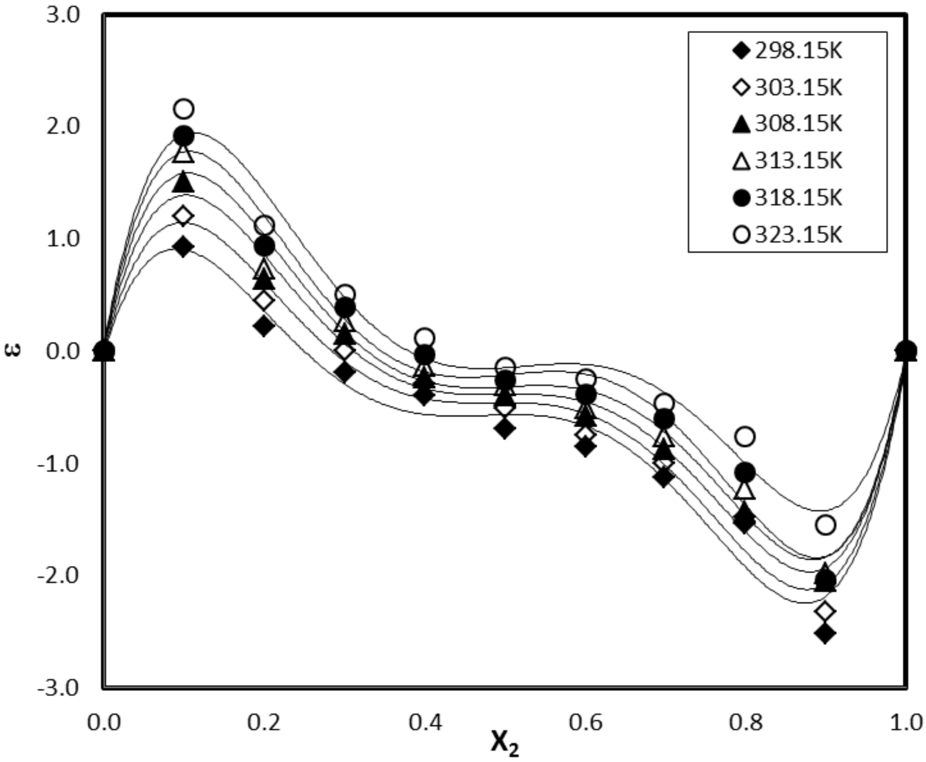

Figure 4.97: Plots of interaction parameter (ε) vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

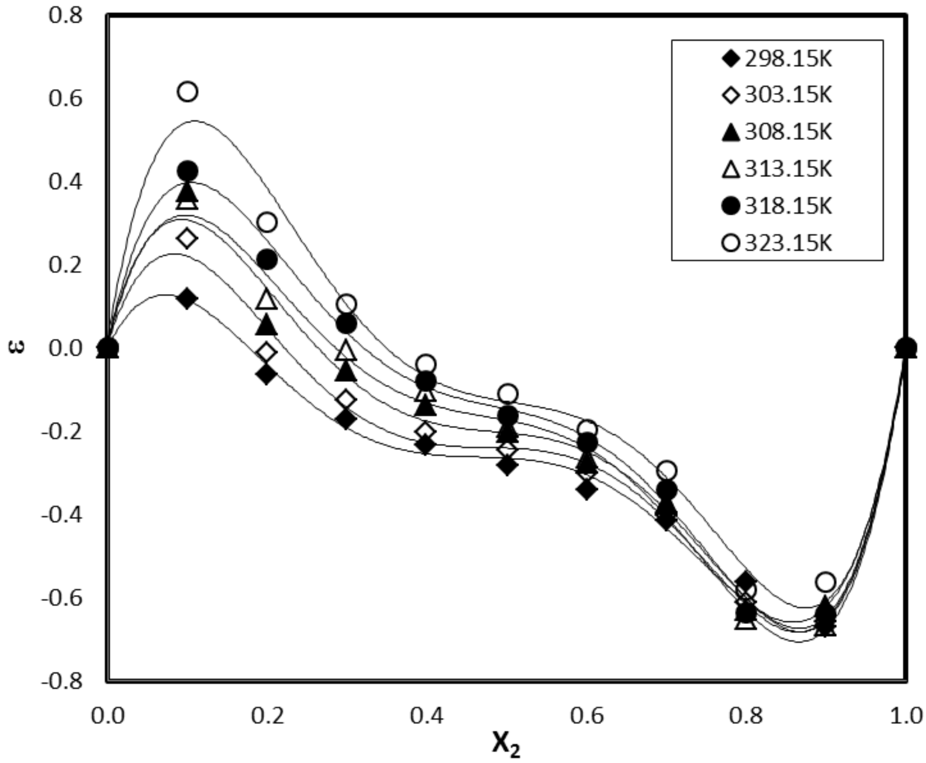

Figure 4.98: Plots of interaction parameter (ε) vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

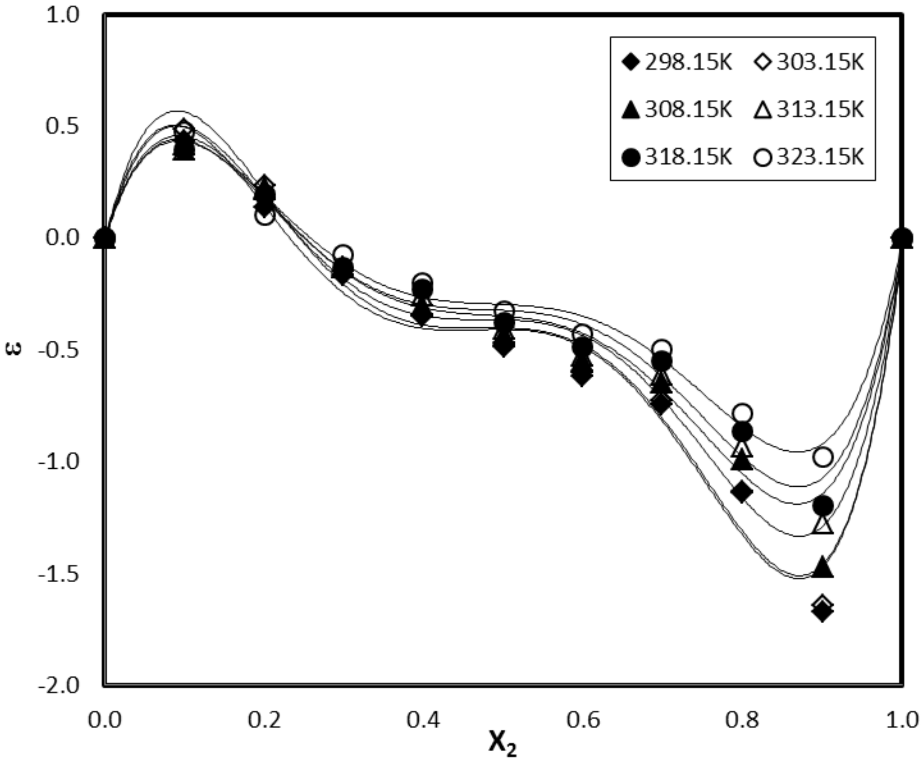

Figure 4.99: Plots of interaction parameter (ε) vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

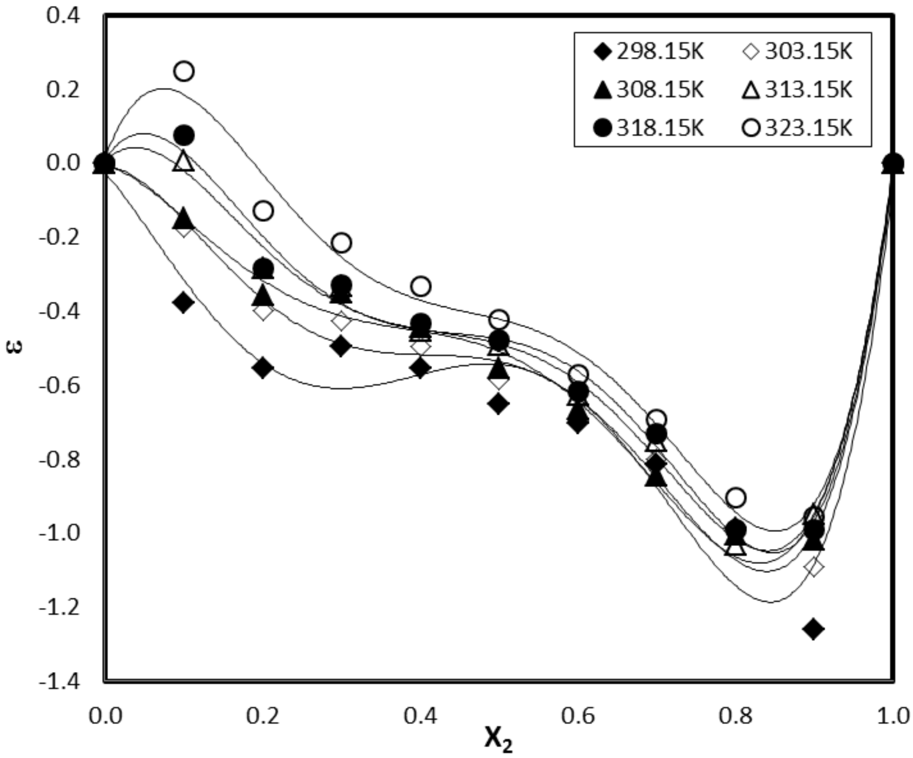

Figure 4.100: Plots of interaction parameter (ε) vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

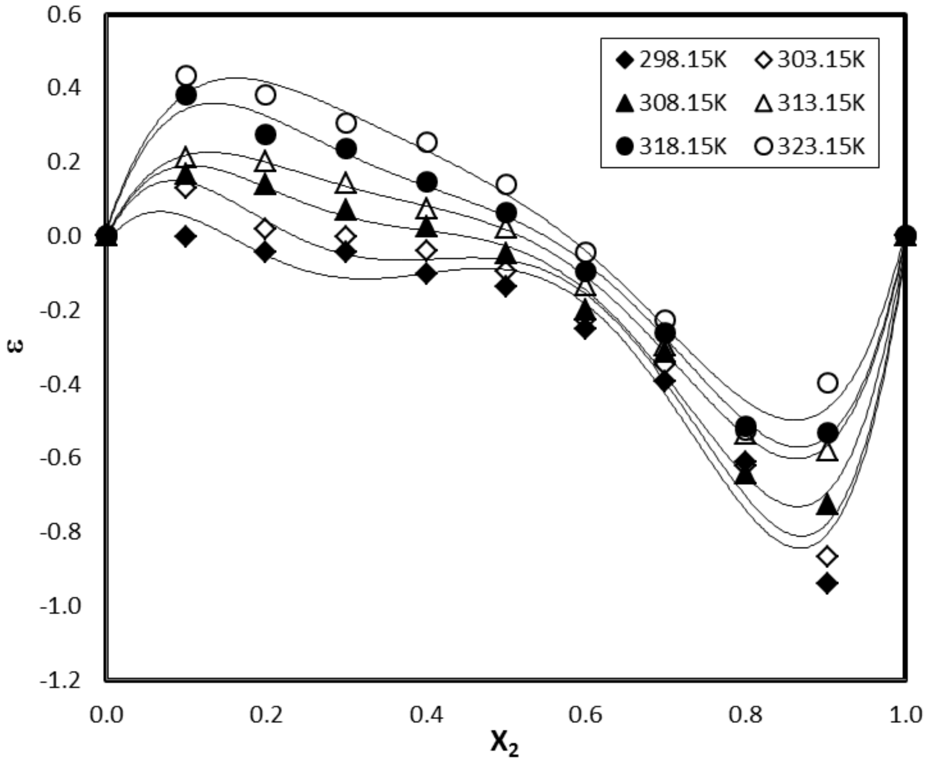

Figure 4.101: Plots of interaction parameter (ε) vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

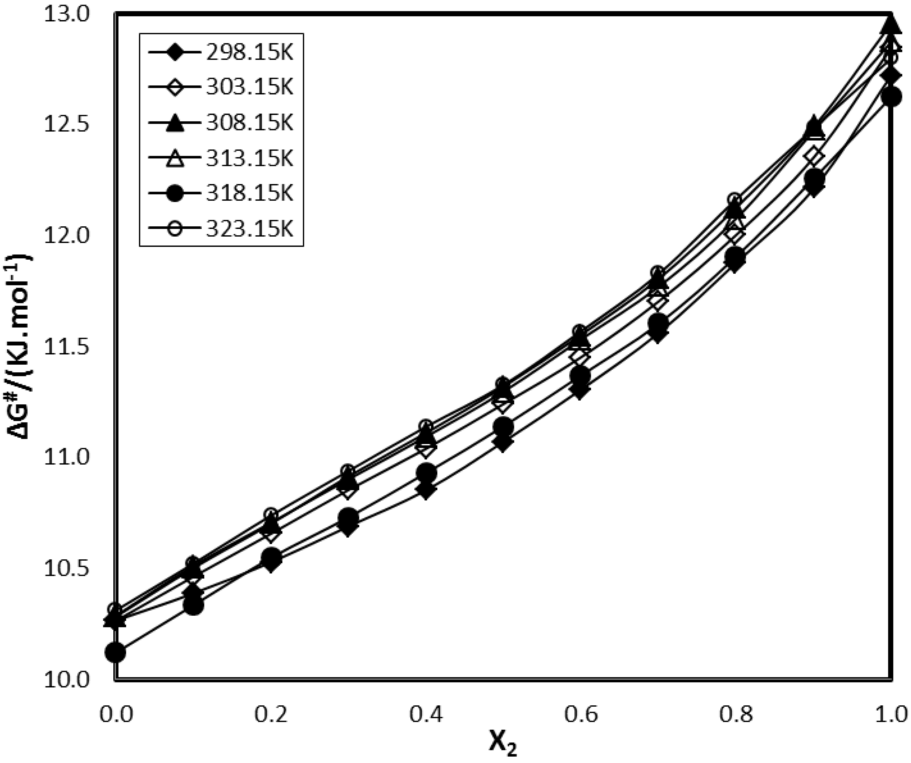

Figure 4.102: Plots of change of free energy vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

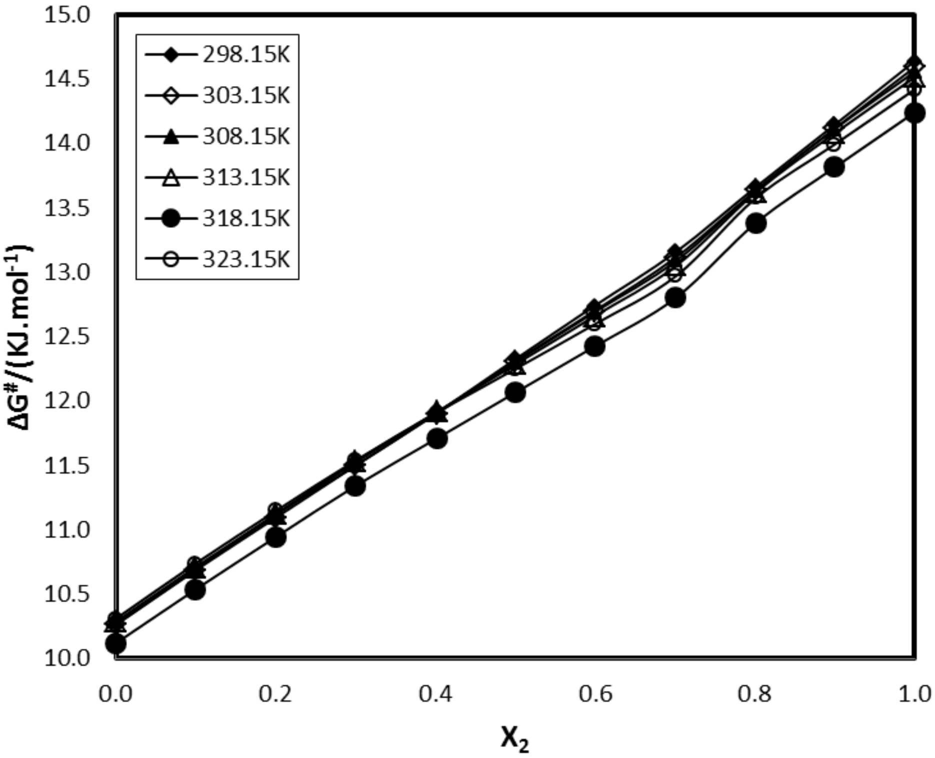

Figure 4.103: Plots of change of free energy vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

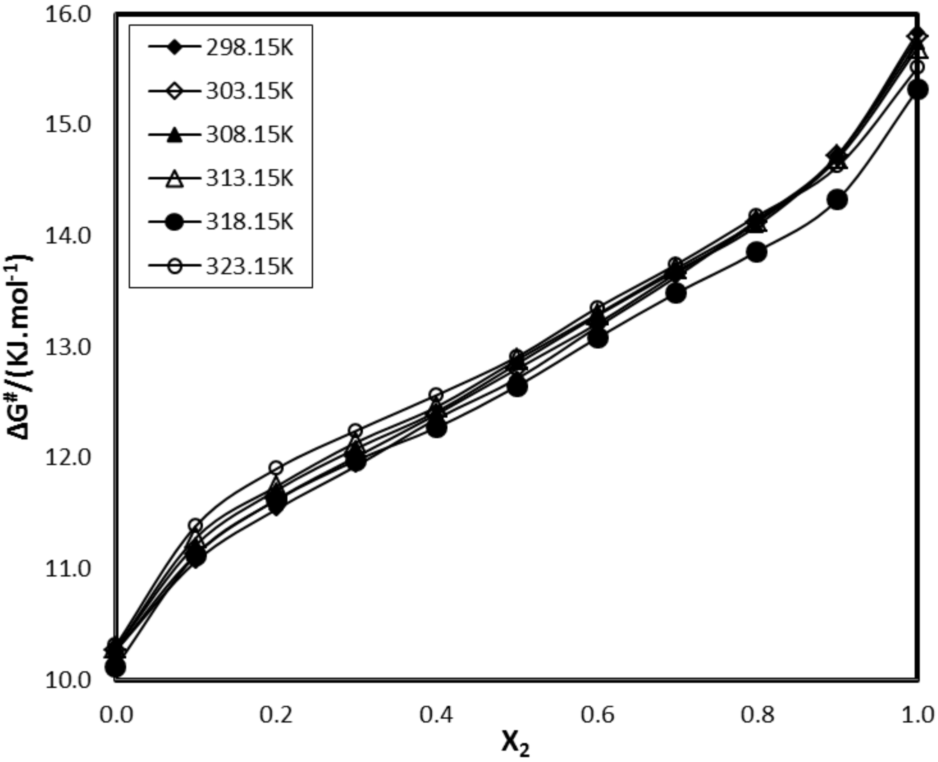

Figure 4.104: Plots of change of free energy vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

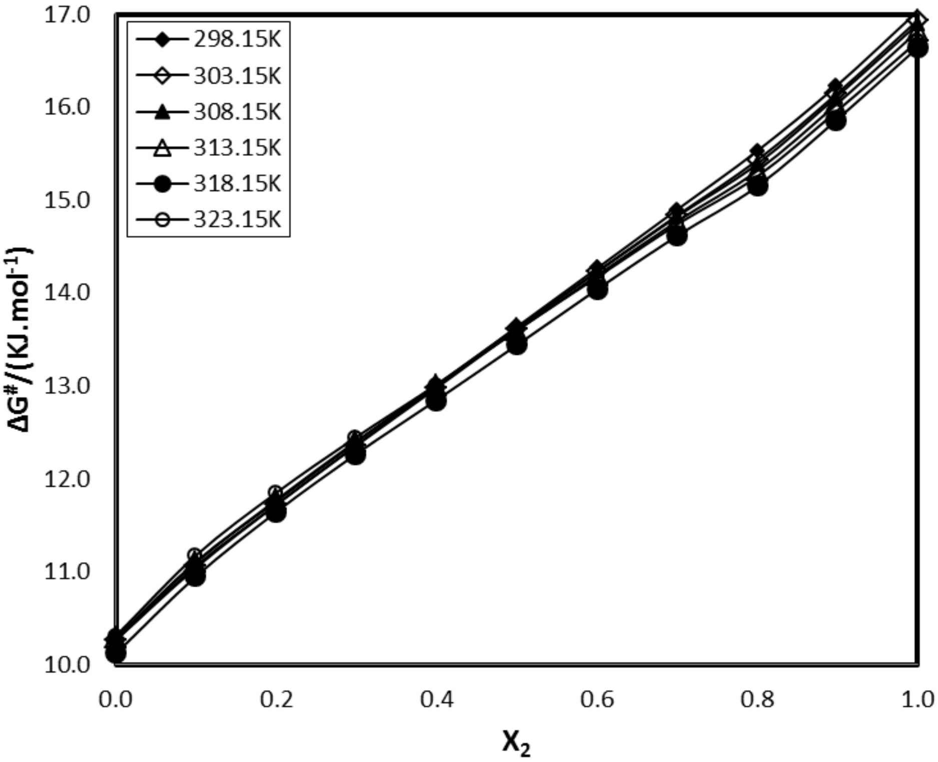

Figure 4.105: Plots of change of free energy vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

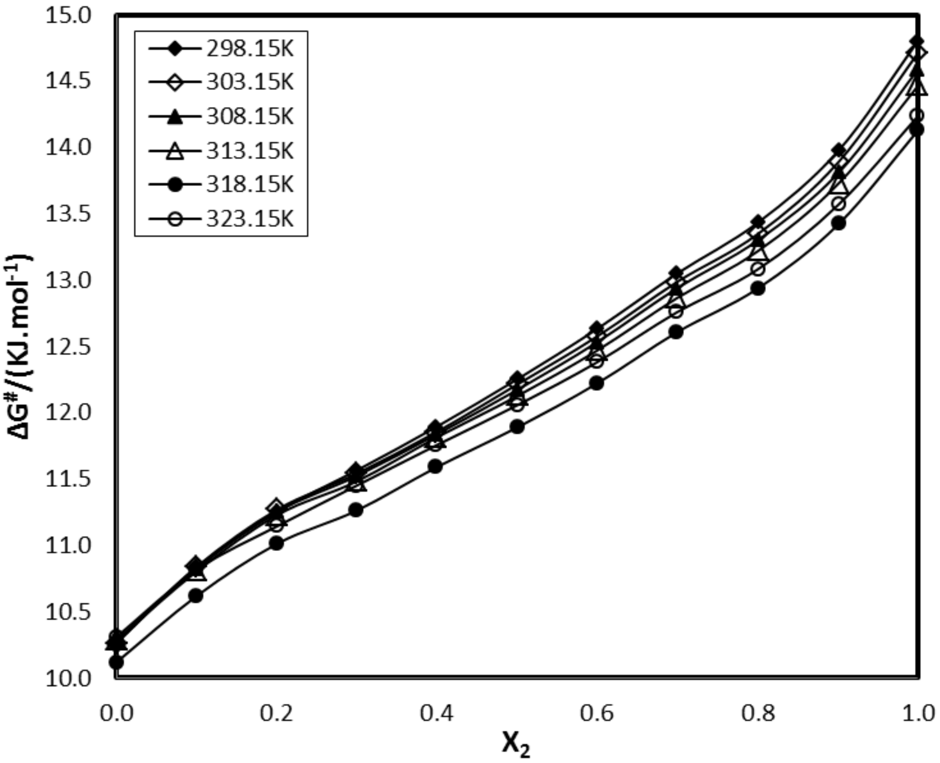

Figure 4.106: Plots of change of free energy vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

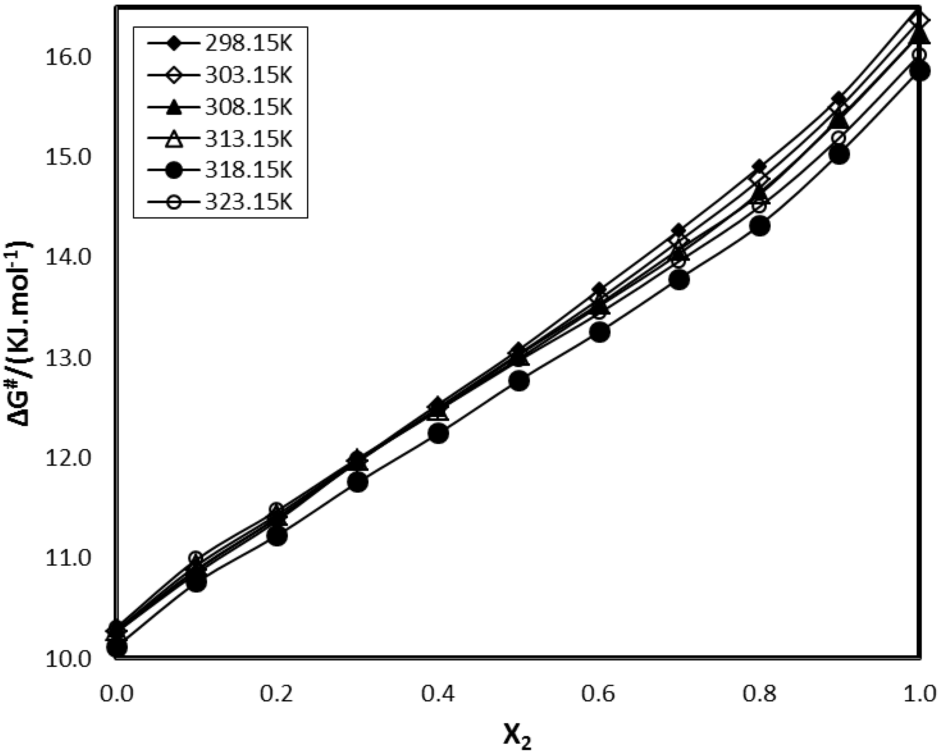

Figure 4.107: Plots of change of free energy vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

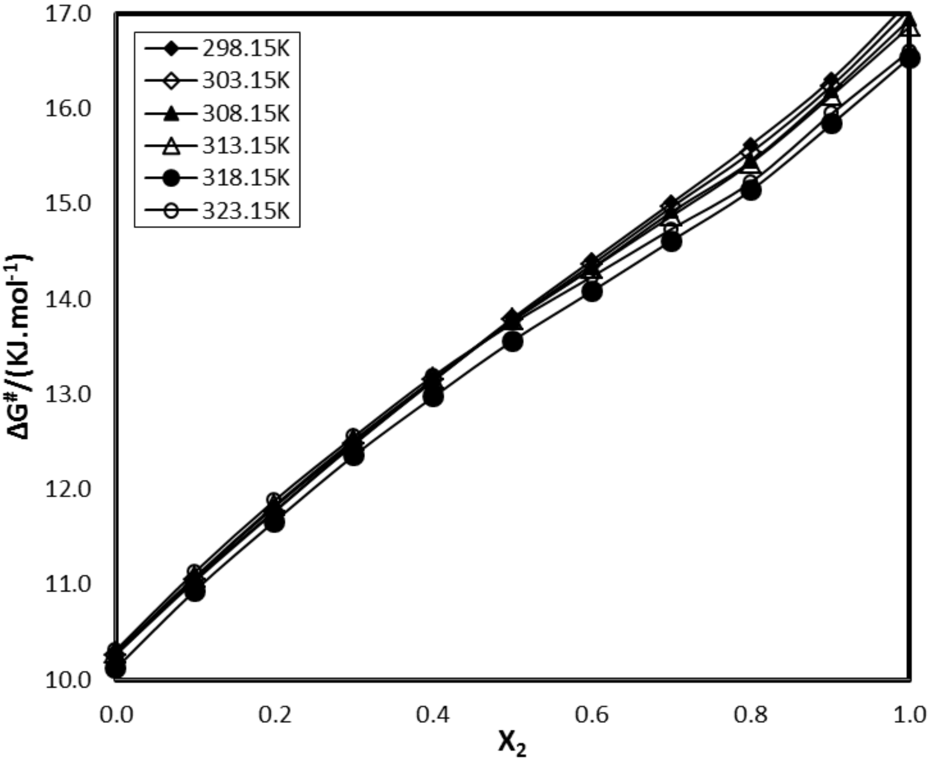

Figure 4.108: Plots of change of free energy vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

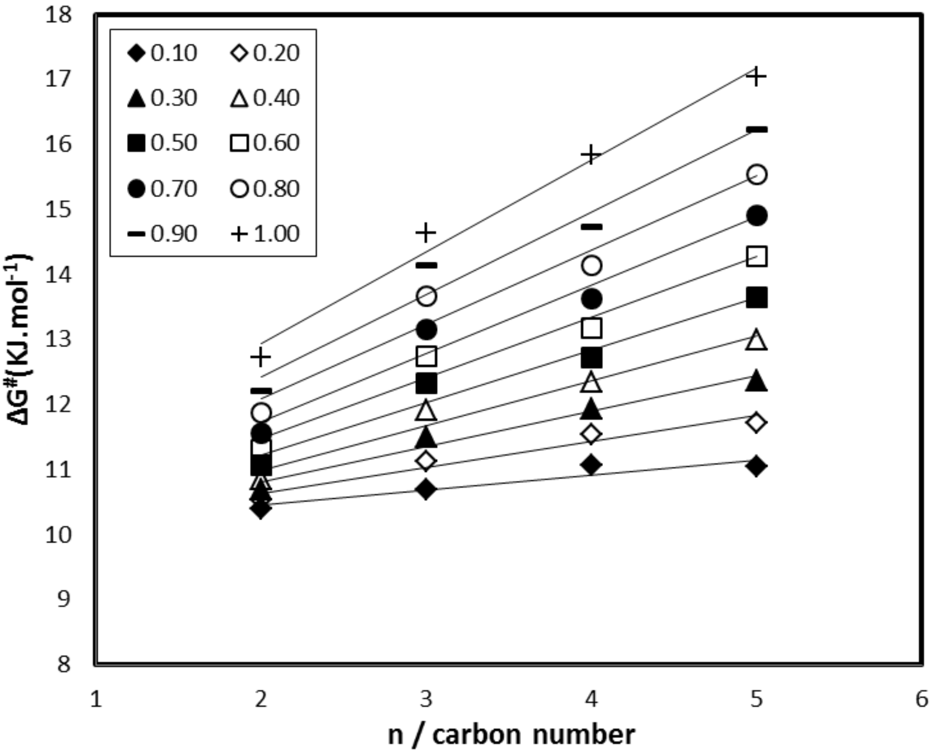

Figure 4.109: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

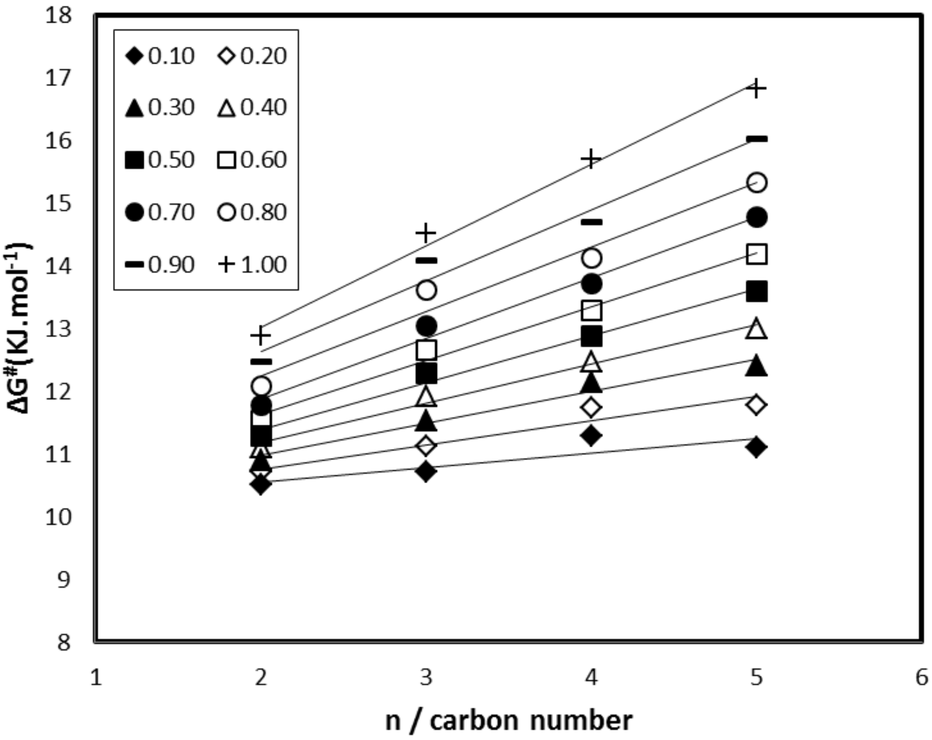

Figure 4.110: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

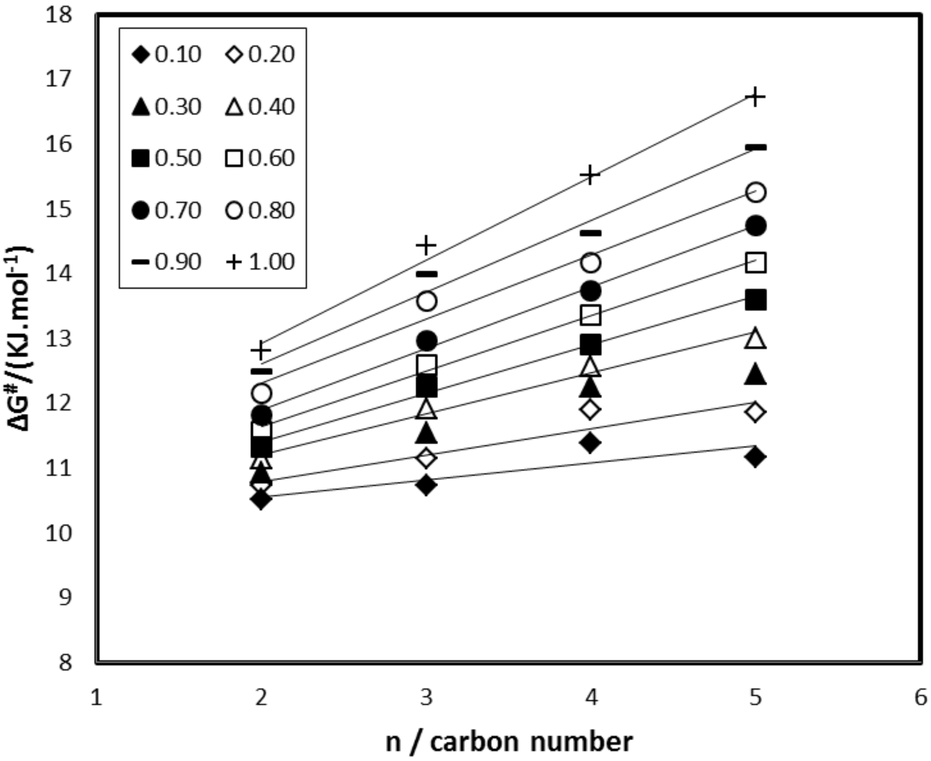

Figure 4.111: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

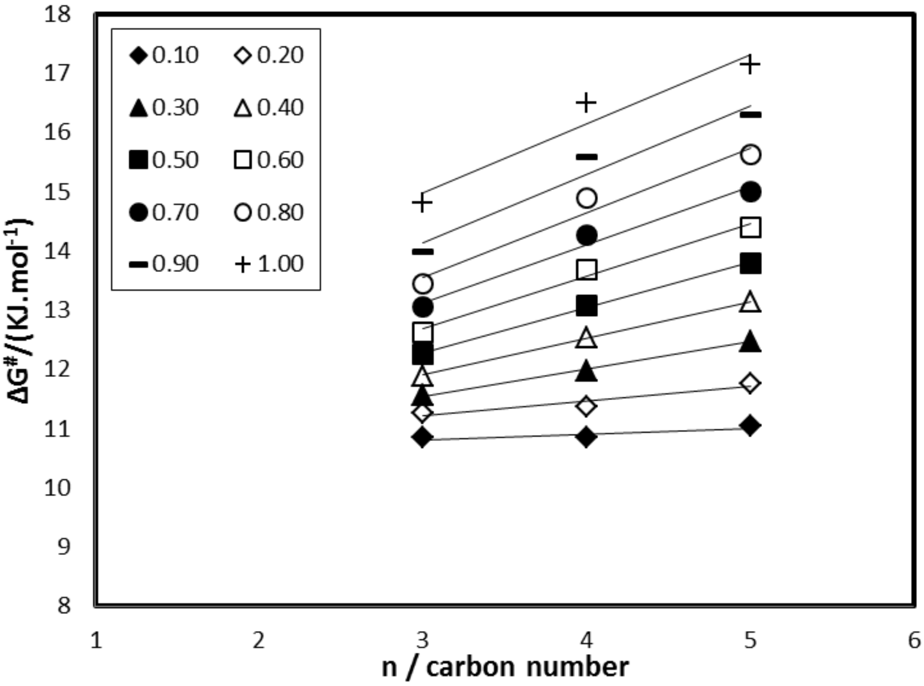

Figure 4.112: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 298.15K.

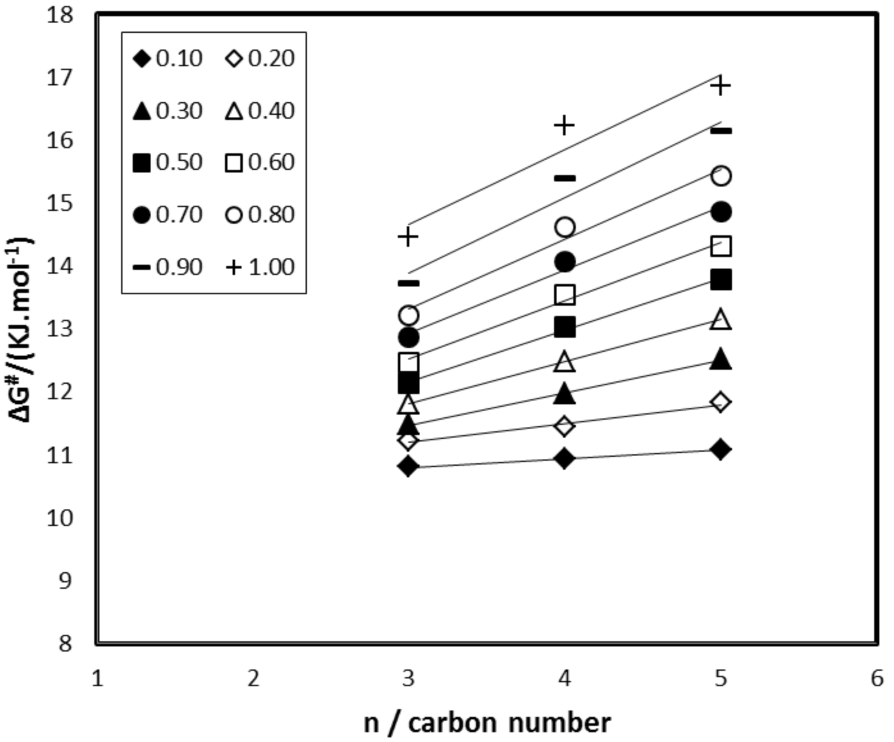

Figure 4.113: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 313.15K.

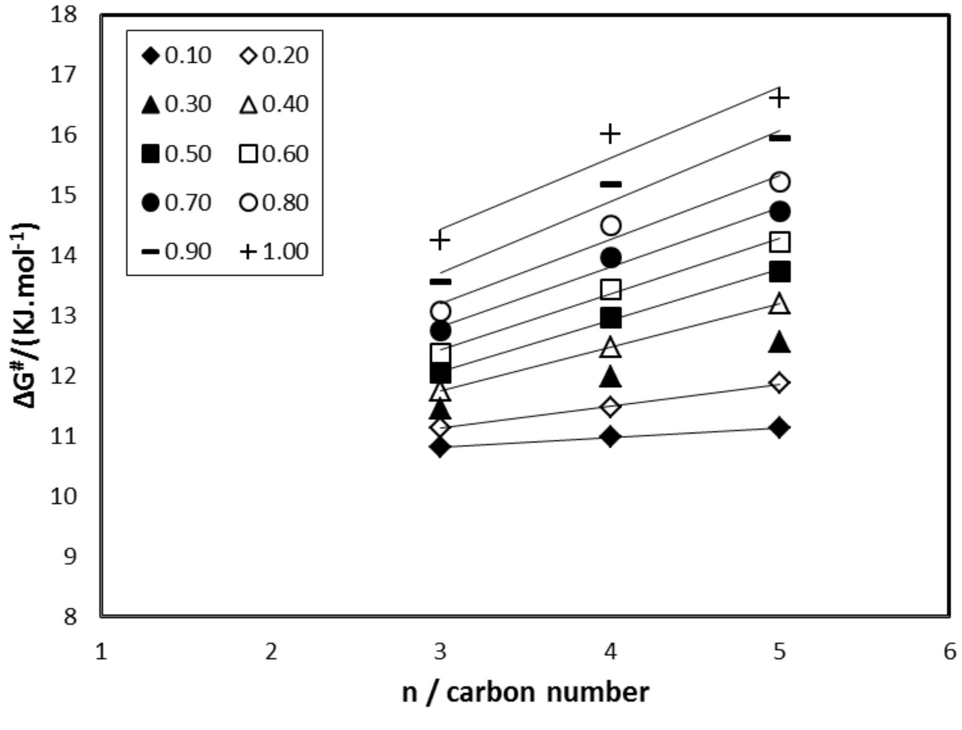

Figure 4.114: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different mole fraction at 323.15K.

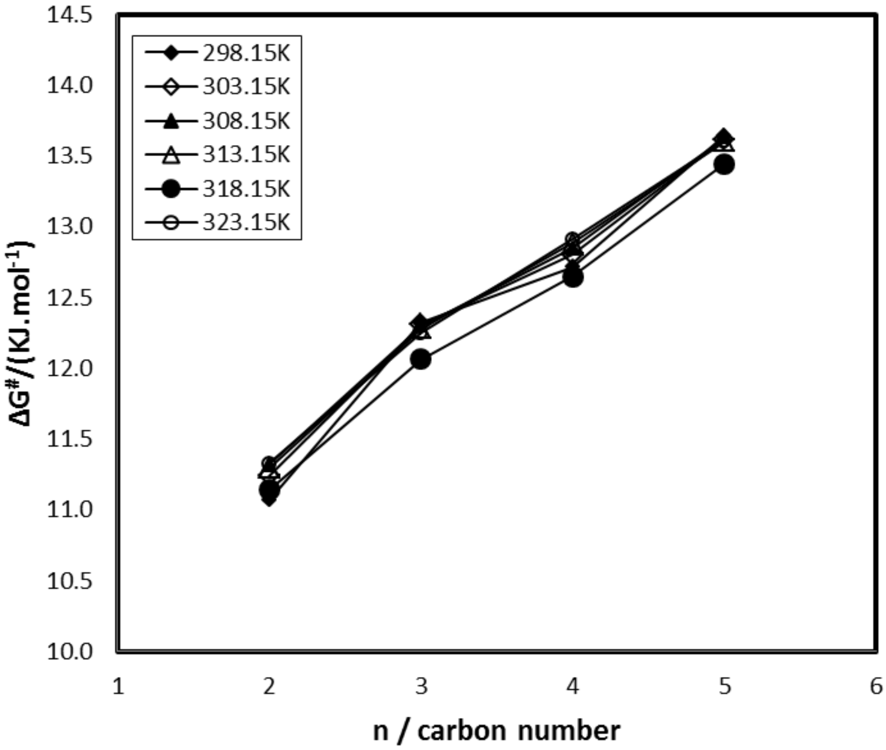

Figure 4.115: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

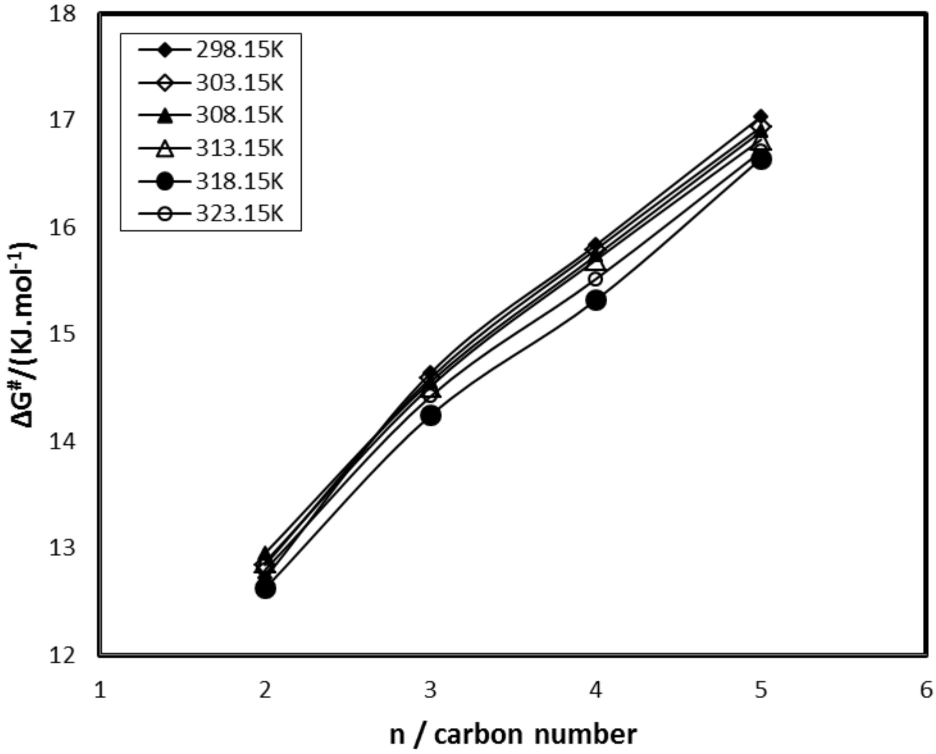

Figure 4.116: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of n-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

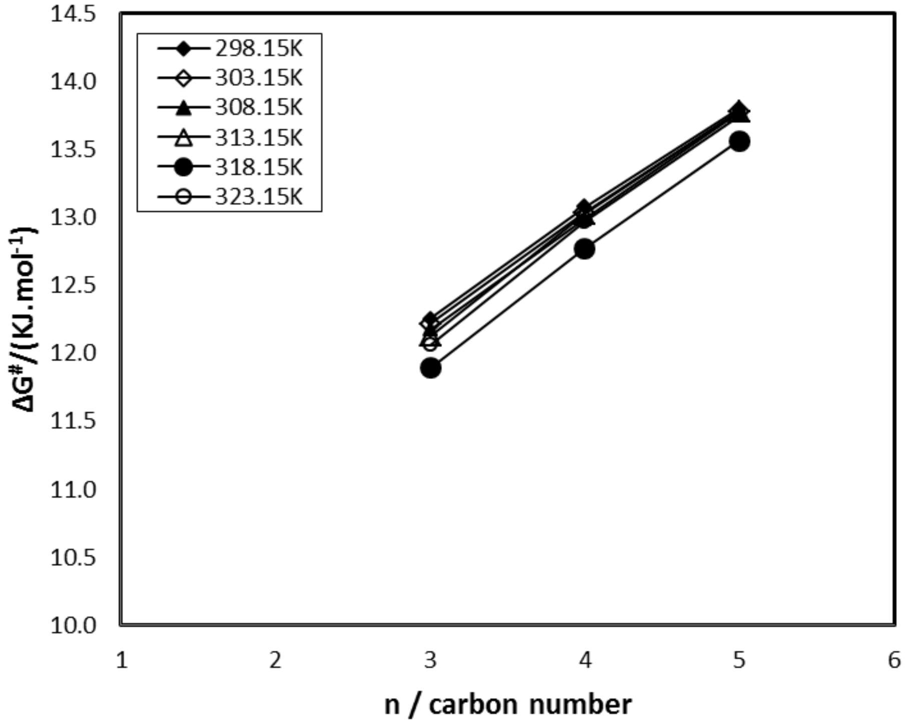

Figure 4.117: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 0.5 mole fraction.

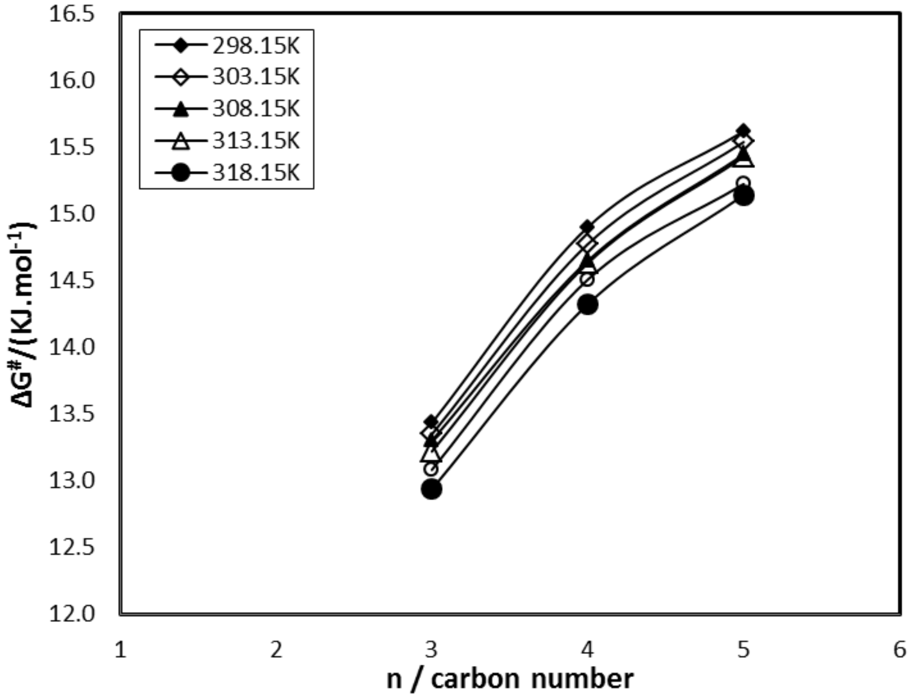

Figure 4.118: Dependence of the change of free energy ($\Delta G^{\#}$) with carbon number (n) of iso-alcohols in (80% acetonitrile + 20% water + 0.02M SDS) with different temperature at 1.0 mole fraction.

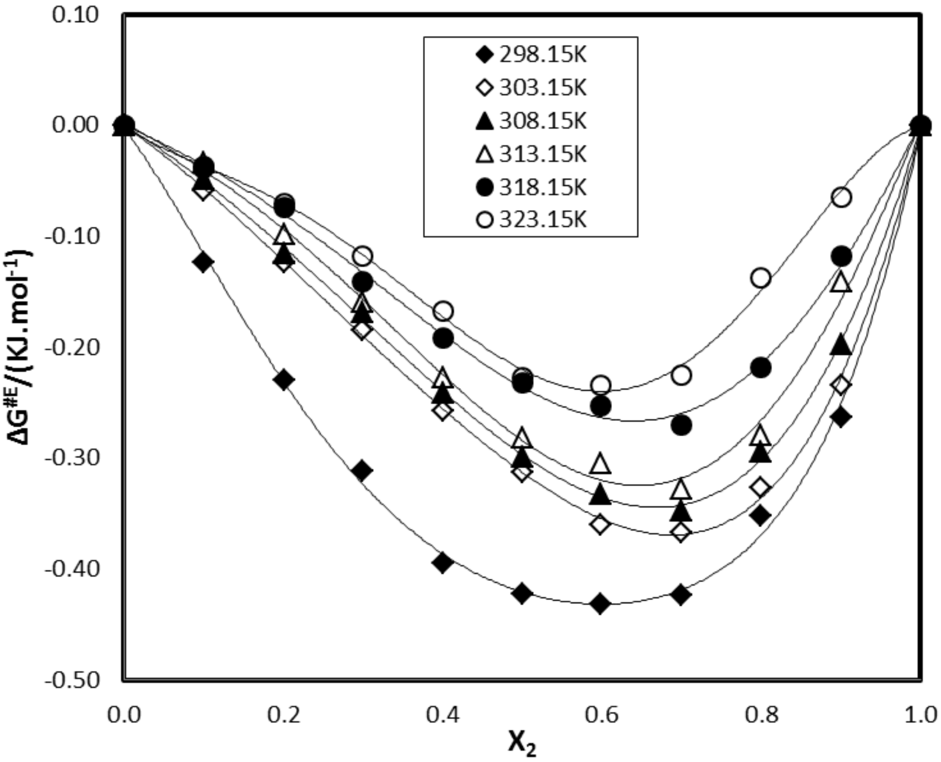

Figure 4.119: Plots of excess free energy vs mole fraction of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

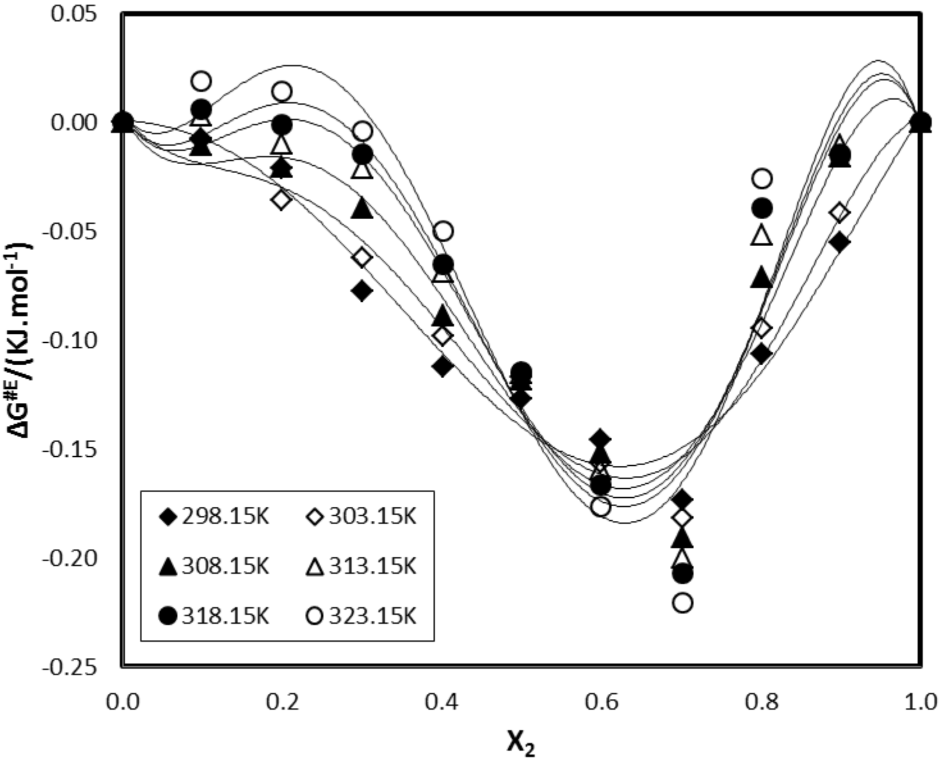

Figure 4.120: Plots of excess free energy vs mole fraction of n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

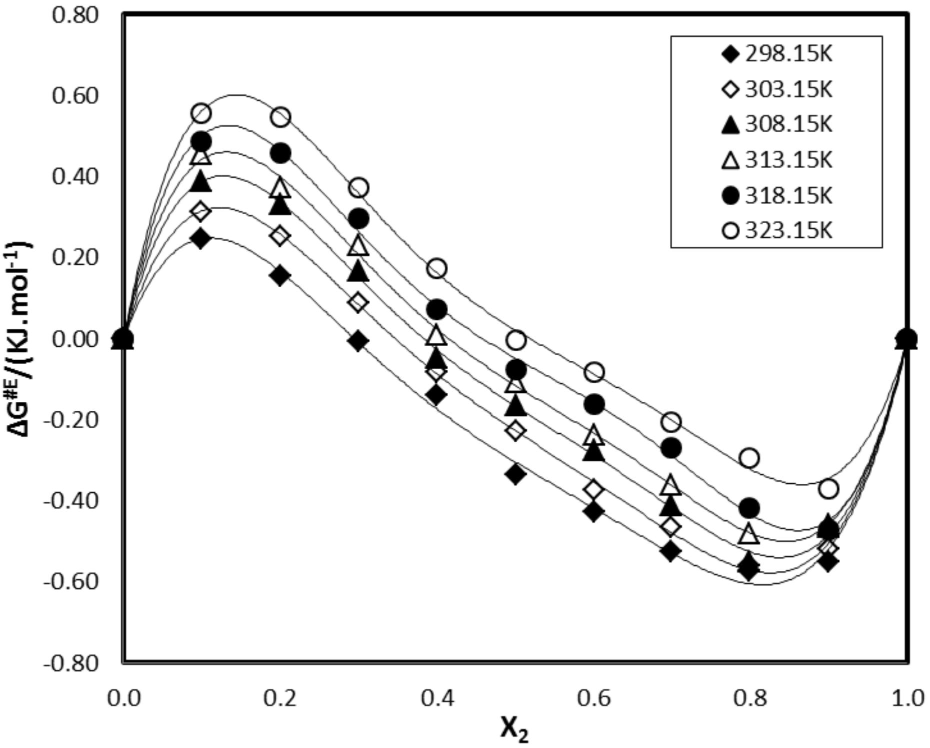

Figure 4.121: Plots of excess free energy vs mole fraction of n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

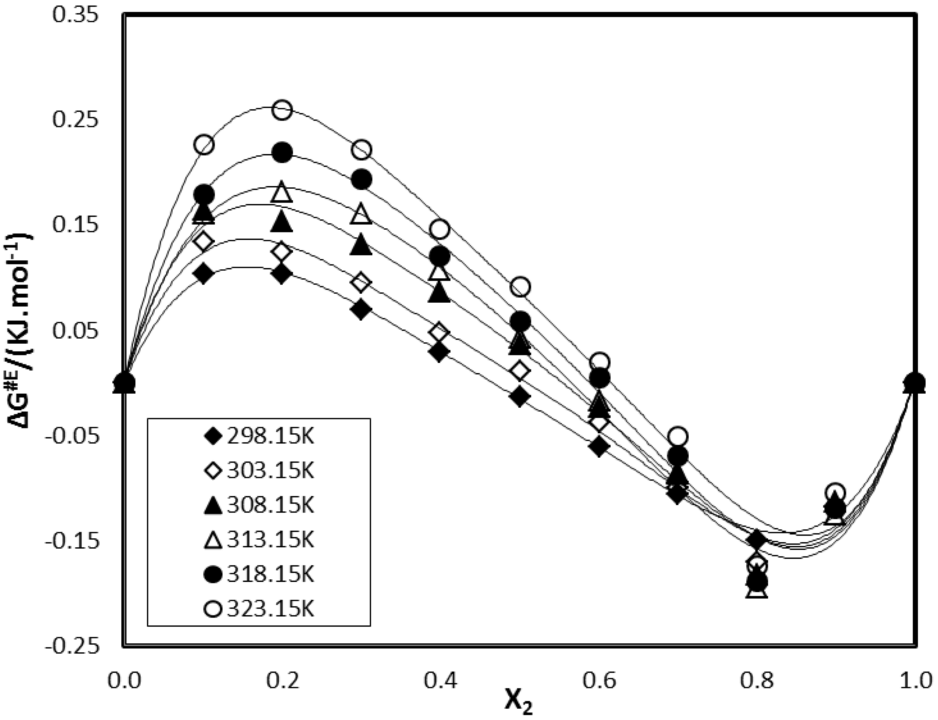

Figure 4.122: Plots of excess free energy vs mole fraction of n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

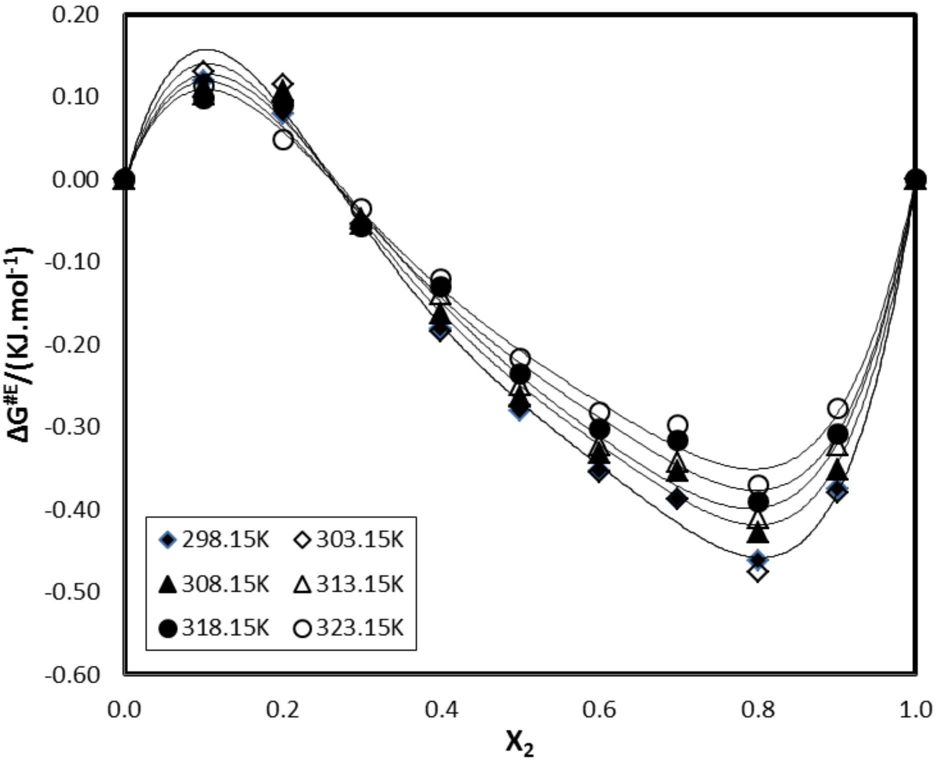

Figure 4.123: Plots of excess free energy vs mole fraction of iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

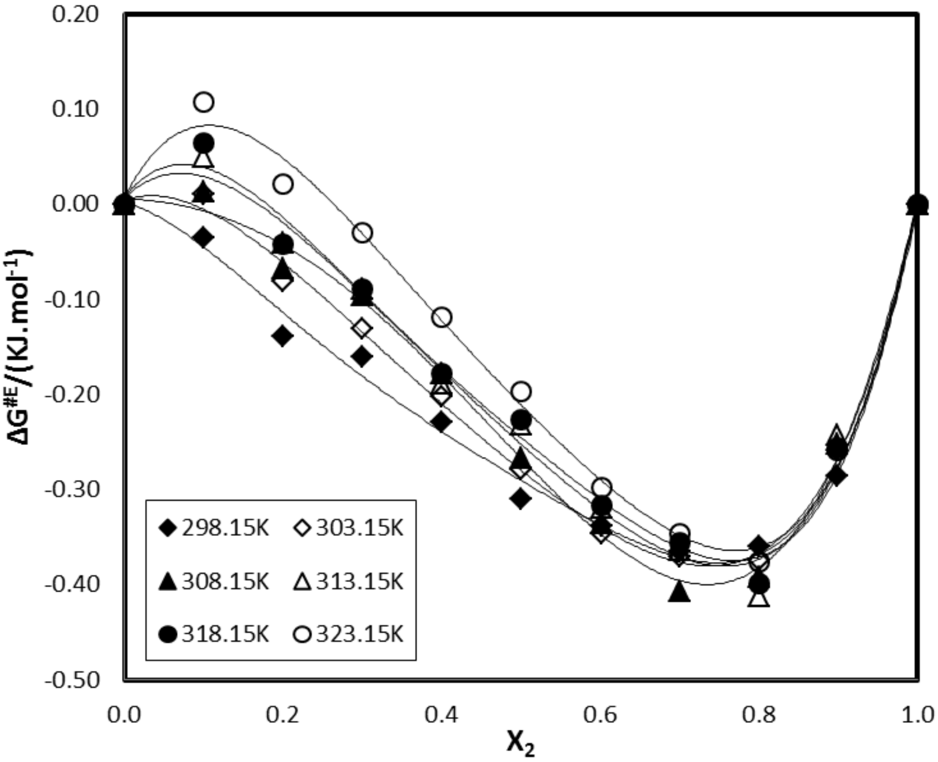

Figure 4.124: Plots of excess free energy vs mole fraction of iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

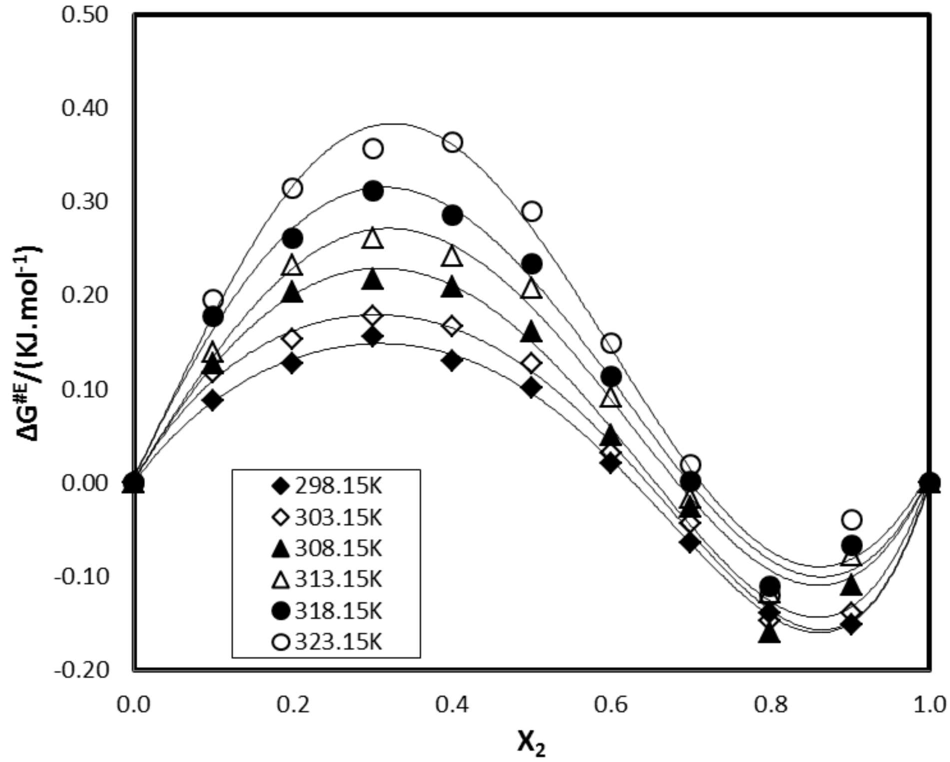

Figure 4.125: Plots of excess free energy vs mole fraction of iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K and 323.15K respectively.

CHAPTER V

Conclusions

The studies presented in this thesis are based on ternary systems. The molar conductivity and viscosity data of SDS in acetonitrile + water solutions show a sharp break in its where micelle starts to form. The estimated CMC of SDS was found to be 0.02 mol. L^{-1}. We have considered this concentration of SDS solution (0.02M) for the volumetric, viscometric and thermodynamic properties for alkanols measurements.

The studies on the solution properties of ternary mixtures of Ethanol in (80% acetonitrile + 20% water + 0.02M SDS), n-Propanol in (80% acetonitrile + 20% water + 0.02M SDS), iso-Propanol in (80% acetonitrile + 20% water + 0.02M SDS), n-Butanol in (80% acetonitrile + 20% water + 0.02M SDS), iso-Butanol in (80% acetonitrile + 20% water + 0.02M SDS), n-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) and iso-Pentanol in (80% acetonitrile + 20% water + 0.02M SDS) show the strong solute-solvent interactions. The mixtures are non-ideal. The values of excess molar volumes, V^E for all the systems are negative and showing minima at (80% acetonitrile + 20% water + 0.02M SDS) rich region. The observed values of V^E for the mixtures have been explained in terms of specific intermolecular interactions and structural contributions.

The viscosities increase with alcohol concentration and show maxima in (80% acetonitrile + 20% water + 0.02M SDS) rich region. The position of maxima does not change with the variation of temperature. At the alcohols rich region rapid change of viscosity are observed for Ethanol, n-Propanol, iso-Propanol, n-Butanol, iso-Butanol, n-Pentanol and iso-Pentanol alcohols but the change is pronounced for the branched chain alcohols systems (iso-Propanol, iso-Butanol, iso-Pentanol) than linear alcohol (Ethanol, n-Propanol, n-Butanol, n-Pentanol) systems. The increasing of viscosity with carbon number of alcohols or branched chain alcohols ascribed that the solution resistance increases with the increase of carbon chain length.

The excess viscosity, η^E values are found to be negative, indicating that maxima (80% acetonitrile + 20% water + 0.02M SDS) solutions of alcohols are non-ideal. Excess viscosities are negative at all the temperature over the entire range of composition for all the systems with minima occurring between 0.7-0.8 mole fraction of Ethanol, 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 systems.

The negative V^E, negative η^E and negative ε for the systems indicate the segmental inclusion of acetonitrile in the interstices of polymolecular alkanols aggregate, these will be fewer surfaces available for friction that may results in a reduction of viscosity. For long chain or branched chain alkanols, maximum geometrical for the steric hindrance are occurred.

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

REFERENCES

1. Timmermans, J, 1950, “Physico-Chemical Constants of pure organic compounds” Elsvelar, Publishing CO, New York, pp. 304-457.

2. Ai-Azzawl, S.F; Awwad, A.M; “Excess Molar Volumes logarithmic Viscosities and Excess Activation Energies of Viscous Flow for 2-Ethoxyethanol, 2-Butyrolactone and + Sulfolane as 303.15K” J. Chem. Eng. Data 35.

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 [BMIM][DMP] or [EMIM][MP] at atmospheric pressures in the Temperature range of (293.15 to 333.15)K; J. Chem .Eng. Data 57, pp. 33-39.

4. Awwad, M. M., Aj. Dujaili, A. H. and Salam, H.E., 2001, “Refractive Index, Relative Permittivity and Excess properties of substituted Benzene sulfonate at 303.15K” Iraqi J. Chem., Vol. 27, pp. 115-120.

5. Awwad, M. M., Aj. Dujaili, A. H. and Salam, T.A., 2001,”Excess Molar Volumes abd Viscosities of Binary and Ternary Mixtures of Sulfolanic + Benzene + 1-Alcanol at 303.15K” Iraqui l. Chem., Vol. 27, pp. 121-125.

6. Awwad, M. M., Aj. Dujaili, A. H. and Allian N. R., 2000,”Delectric Constants of the Binary Mixtures of 2- Ethoxyethanol + Butyrolactone and Sulfonate at 303.15K comparison with Theory” Iraqui J. Chem, Vol. 26, pp. 94-100.

7. Sacco, A and Rakshit, A. k., 1975, “Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfonate 111, Excess Volumes of Sulfonate with Each of Nine alcohols” J. Chem. Thermodynamic, Vol. 7, pp. 257-261.

8. Karim, M., 1980, “Thermodynamic and Physical Properties of Binary Mixtures Containing Sulfolane V. Excess Enthalpies of cyclohexane + Benzene, Cyclohexane + Toluene, Benzene + Sulfolane and Toluene + Salfolane”. J. Chem. Thermodynamic, Vol. 12, pp. 635-639.

9. Marera, I. and Natjaniec, I., 2006, “Experimental and theoretical IR, R and INS spectra of 2,2,4,4-tetramethyl-3-t-butyl-pentane-3-ol*”,* Journal of Molecular Structure 788 (1-3), pp. 93-101.

10. Adriani, John., 1962, The Chemistry and Physics of Anesthesia. Second Edition. Illinois: Thomas Books. pp. 273–274.

11. "Alcohols, Phenols, Thiols, and Ethers". Chemistry - Louisiana Tech University. Retrieved 31 December 2013.

12. Geertinger, P., Bodenhoff, J. and Helweg-Larsen, K. A., "Endogenous alcohol production by intestinal fermentation in sudden infant death". Zeitschriftfür Rechtsmedizin (Springer-Verlag) 89 (3), pp.167–172.

13. Awwad, A. M., Al-Dujaili, A. H. and Alian, N. R., 2000, Iraqi J. Chem., vol.26, p. 94.

14. Kim, E. S. and Marsh, K. N., 1988, J. Chem. Eng. Data, Vol. 33, pp. 288-292.

15. Reiss-Husson, F. and Luzzatti, V., 1968, J. Phys. Chem, Vol. 38, p. 3504.

16. Debye, P. and Anacker, E. W., 1951, J. Phys. And Colloid, Chem, Vol 55, p. 644.

17. Tartar, H. V., 1955, J. Phys, Vol. 59, p. 1195

18. Shott, H., 1971, J. Pharm. Sci., Vol. 60, p. 1594

19. Tanford, C., 1972, J. Phys. Chem.,Vol. 76, p. 3020

20. Stigter, D., 1964, J. Phys. Chem.,Vol. 68, p. 3603.

21. Sanyal, S. K., 1984, J. Chem.Educ.,p 110

22. F. Franks, 1972, “Water, A comprehensive treaties”, Vol. 1, Plenum press, NewYork, 9.

23. Nemethy, G. and Scherage, H. A., 1962, J. Chem . Phys., Vol. 36, pp. 3382 and 3401.

24. Clementy, E., 1976, “Determination of liquid water structure, co-ordination number for ions and salvation of Biological molecules”. Springer, verlag, Berlin, p.74.

25. Barnse, P., Finny, J. L., Nicoler, J. D. and Quinn, J. E., 1979, Nature.Vol. 202, p. 459.

26. Rahman, A. and Stillings, F. H., 1975, J. Chem. Phys., Vol. 55, p. 3336.

27. Rahman, A. and Stillings, F. H. and Lainberg, H. L., 1975, J. Chem. Phys. Vol. 69, p. 5223.

28. Franc, H. S. and Wen, W. Y., 1957, “Structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of eater structure” Disc. Faraday Soc., Vol. 24, p. 133.

29. Hildebrand, J. H., 1949, Chemical Reviews; Vol. 44, p. 37.

30. Gurney, R., 1954, Ionic processes in solution, McGraw Hill, New York.

31. Fuhrhop, J. and Koning, J., 1994, Membrances and Molecular Assembelies, The Synkinetic Approach, Royal Soc. Chem.

32. Israclachvili, J. N., 1985, Intermolecular and Surface Forces, Academic, London.

33. Blokzijl, W. and Engberts, J. B. F. N., 1993, Angew. Chem. Intl. Ed. Engl.Vol. 32, p. 1545.

34. WHO. World Health Organization. Internation Program on Chemical Safety (IPCS). Environment health criteria 154-acetonitrile. Geneva: World Health Organization; 1993.

35. Ashford's Dictionary of Industrial Chemicals, Third edition, 2011, p. 76.

36. Nyalala, S.O., Grout, B.W.W. and Petersen, M.A., 2011, “Acetonitrile (methyl cyanide) emitted by the African spider plant (Gynandropsisgynandra L (Briq); bioactivity against spider mite (Tetranychusurticae Koch) on roses,” Scientia Horticulture, Vol. 128, pp. 352-356.

37. Dibiase, S. A., Beadle, J. R. and Gokel, G. W., "Synthesis of α,β-Unsaturated Nitriles from Acetonitrile: Cyclohexylidene acetonitrile and Cinnamonitrile". Org. Synth. ; Coll. Vol. 7, p. 108.

38. Lewis, R. J., 1997, Hawley‘s condensed chemical dictionary. New york: Van Nosttrand Reinhold.

39. Acetonitrile - Compound Summary". Pub Chem Compound. USA: National Center for Biotechnology Information, Retrieved 5 June 2012.

40. Motin, M. A., Hafiz Mia, M. A. and 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, p. 172–180.

41. Acetonitrile - Compound Summary". PubChem Compound. USA: National Center for Biotechnology Information, Retrieved 5 June 2012.

42. Hickey, K. and Waghorne, W. E., “Viscosities and Volumes of Dilute Solutions of Formamide in Water + Acetonitrile and for Formamide and N,N-Dimethylformamide in Methanol + Acetonitrile Mixed Solvents: Viscosity B-Coefficients, Activation Free Energies for Viscous Flow, and Partial Molar Volumes” Vol. 46, pp. 851–857.

43. Tôrres, R.B., Francesconi, Z. and Volpe, A. Z. P. L. O., “Experimental study and modelling using the ERAS-Model of the excess molar volume of acetonitrile–alkanol mixtures at different temperatures and atmospheric pressure” Vol. 210, pp.287–306.

44. Nagata, I. and Tamura, K., 1985, “Excess enthalpies of binary and ternary mixtures of acetonitrile with methanol, ethanol and benzene” Vol.24, pp.289–306.

45. Nagata, S. and Kazuhiro Tamura, K., 1988, “Excess molar enthalpies of (propan-1-ol or propan-2-ol + acetonitrile), (propan-1-ol or propan-2-ol + chlorobenzene), and (propan-1-ol or propan-2-ol + acetonitrile + chlorobenzene) at 298.15 K” Vol.20, pp.287-293.

46. Tahery, R., Modarress, H. and Satherley, J., 2006 “Density and Surface Tension of Binary Mixtures of Acetonitrile + 1-Alkanol at 293.15 K” Vol.51 pp. 1039–1042.

47. Domańska, U. and Marciniak, M., 2005, “Experimental (Solid + Liquid) and (Liquid + Liquid) Equilibria and Excess Molar Volume of Alkanol + Acetonitrile, Propanenitrile, and Butanenitrile Mixtures” Vol. 50 pp. 2035–2044.

48. Galvão, A. and Francesconi, Z., 2006, “ERAS modeling of the excess molar enthalpies of binary liquid mixtures of 1-pentanol and 1-hexanol with acetonitrile at atmospheric pressure and 288, 298, 313 and 323 K” Vol. 450 pp. 81–86.

49. González, J. A., Cobos, j. c., Tristán, C. A. and Sanz, L. F., 2015, “Orientational Effects and Random Mixing in 1-Alkanol + Nitrile Mixtures” Vol.54 pp. 550–559.

50. Martínez, Santiago, Garriga, Rosa., Sánchez, Pérez, Pascual. and Gracia, Mariano (2000), “Densities and Viscosities of Binary Mixtures of Butanenitrile with Butanol Isomers at Several Temperatures” Vol.45 pp. 1182–1188.

51. Garriga, Rosa., Sánchez, Francisco., Pérez, Pascual. and Gracia, Mariano., 1997, “Excess Gibbs free energies at several temperatures and excess enthalpies and volumes at 298.15 K of butanenitrile with 2-methyl-1-propanol or 2-methyl-2-propanol” Vol. 130 pp. 195–206.

52. Garriga, Rosa., Sánchez, Francisco., Pérez, Pascual. and Gracia, Mariano., 1997,”Excess Gibbs Free Energies at Eight Temperatures and Excess Enthalpies and Volumes at T = 298.15 K for Butanenitrile + 2-Butanol” Vol. 42 pp.78-83.

53. Garriga, Rosa., Sánchez, Francisco., Pérez, Pascual. and Gracia, Mariano., 1998, Ann. N. Y. Acad. Sci, Vol.16 pp. 156-158.

54. Gurdeep, Raj. P., 1996-97, “Advanced physical chemistry” Twenty First Edition. Goel Publishing House, p. 1281.

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

56. Glasstone, S., 1948, “Text book of Physical chemistry” 2nd edition, pp. 524, 496.

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

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

59. Nightingale, E. R. and Beneck, R. F., 1969, “Viscosity of acqueous fluoride and sodium periodate solutions ionic energies and entropies of activation for viscous follow” J. Phys. Chem. Vol. 63 pp. 1777-1781.

60. Dikko, A. B. and Alkasim, A., 2015, “Some Excess Properties of Ternary Liquid Mixture of Water, Methanol, Ethanol at Several Temperatures”. J. (IJRRPCS) Vol. 1. pp. 8-12.

61. Md. Abdul Hafiz Mia, Studies on Volumetric and Viscositic Studies of Some Binary and Ternary Sodium Dodecyl Sulfate (SDS) Containing Alcohol System”. M.Pill. Thesis, December 2010.

62. Monoranjan Mondal, “Study of the Effects of Acetonitrile on the Alcohol Solutions by Volumetric and Viscometric Measurements”. M.Pill Thesis, February 2013.

63. Simth, F. and Brown, I., 1973, Aust. J. Chem. Vol.26 p. 691.

64. Franks, F. and Ives D. J. G., 1966, Q. Rev. 20.

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

66. Costas, M. and Patterson, D., 1985, J. Chem. Sci., Farady Trans., I Vol. 88. p. 635.

67. Treszcanowicz, A., 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 + n-Hexadecane. J. Chem. Thermodyn., Vol. 13, pp. 253-260.

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

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

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

71. Bhuiyan, M. M. H., Uddin H. H., 2008 Excess molar volumes and excess viscosities for mixtures of DMF with methanol, ethanol and 2-propanol at different temperatures, Journal of Molecular Liquids pp. 138-139.

72. Andini, S., Castronuovo, G., Eila, V. and Fasano, L., 1990, J. Chem. Soc. Farday.

73. Kabir, M. H., Motin, M. A. and Haque, 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.

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

75. Fort, R. J. and Moore, W.R., 1966, Tras, Farad. Soc. 62, pp. 112-119.

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

77. Timmermans, J., 1950, Physico-chemical constants of pure organic compounds, pp. 304-357.

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

79. Saleh, M. A., Habibulla, M. and Khan, N. U. A., 1995, Chittagong Uni. Stud. Part II: Soc., 19(2), p. 191.

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

81. Gojlo, M., Smiechoeski J. and Stangret J., 2005, J. mol. Structure, Vol. 744, p. 809.