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# Volumetric And Viscometric Studies Of Some Binary And Ternary Sodium Dodecyl Sulfate (SDS) Containing Alcohol System

by

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A thesis submitted in partial fulfillment of the requirements for the degree of
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This is to certify that the thesis work entitled "Volumetric And Viscometric Studies Of Some Binary And Ternary Sodium Dodecyl Sulfate (SDS) Containing Alcohol System" has been carried out by Md. Abdul Hafiz Mia in the Department of Chemistry, Khulna University of Engineering & Technology, Khulna, Bangladesh. The above thesis work or any part of this work has not been submitted anywhere for the award of any degree or diploma.

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**Md. Abdul Hafiz Mia**

# ABSTRACT

Densities and viscosities of binary mixtures of Methanol + Water, Ethanol + Water, *n*-Propanol + Water and *iso*-Propanol + Water and ternary mixtures of Methanol + 0.005M and 0.01M aqueous SDS, Ethanol + 0.005M and 0.01M aqueous SDS, *n*-Propanol + 0.005M and 0.01M aqueous SDS and *iso*-Propanol + 0.005M and 0.01M aqueous SDS have been studied over the entire range of composition ($0 < x_2 < 1$) at 298.15- 323.15K with an interval of 5K except methanol. Methanol system was studied at 298.15K, 303.15K and 308.15K 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 ~ 0.45 mole fraction of Methanol, ~ 0.4 mole fraction of Ethanol, ~ 0.25 mole fraction of *n*-Propanol and ~ 0.3 mole fraction of *iso*-Propanol. The $V^E$ values for the *n*-Propanol + Water and *iso*-Propanol + Water mixtures are sigmoids, being negative at lower mole fractions ($x_2$) and positive at higher $x_2$ of Propanols. The magnitudes of the $V^E$ values of the mixtures are in the order: *iso*-Propanol > Methanol > Ethanol > *n*-Propanol. The observed values of $V^E$ for the mixtures have been explained in terms of physical, chemical, and geometrical contributions. The physical interactions, that is, nonspecific interactions between the real species present in the mixture, involve mainly dispersion force giving a positive contribution. The chemical or specific intermolecular interactions result in a volume decrease and these interactions include formation of hydrogen bonds and other complex-forming interactions. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume.

The viscosity coefficients, $\eta$ of all the above mixtures at all the six different temperatures have also been determined. Viscosities increase rapidly with alcohol concentration and show maxima in the water and aqueous SDS rich region at 0.2 – 0.3 mole fraction of alcohols. The position of maxima virtually does not change remarkably with the variation of temperature. The viscosity coefficients of the polar-polar mixtures, quite expectedly, show considerable deviation from ideal behavior. The excess viscosities, $\eta^E$ values are found to be positive and large in magnitude, indicating that the aqueous and aqueous SDS solutions of alcohols are

highly non ideal. All the curves pass through maxima in water and aqueous SDS rich region. The heights of the maxima are in the order:
*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol + Water > Methanol + Water

The rapidly ascending part of viscosity curves in the dilute region of alcohols can be explained primarily in terms of the phenomenon called hydrophobic hydration, which assumes that, in water–rich region, the water molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. The interaction parameter, $\varepsilon$ have also been found to be positive in magnitude indicating strong solute-solvent interaction.

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

The critical micelle concentration (CMC) of sodium dodecyl sulfate (SDS) in water was determined from the conductance and viscosity measurement. They shows a sharp break in their values where micelle starts to form and is determined by extrapolating the data in pre-micellar region to intersect with a straight line drawn through the data in the post-micellar region. The estimated value of CMC was found to be 0.0085 mol.$L^{-1}$ at $29^0$C. The concentration of SDS in pre-micellar and post-micellar region of 0.005M and 0.01M were used for the volumetric, viscometric and thermodynamic measurements.

Although the value of density and viscosity of the studied systems in pre-micellar and post-micellar aqueous SDS solutions (0.005M SDS and 0.01M SDS) are higher than the pure water solutions, but no appreciable change in the volumetric and viscometric properties were observed by the addition of the surfactants.

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## Nomenclature

| | |
|---|---|
| SDS | Sodium dodecyl sulphate |
| CMC | Critical micelle concentration |
| $\varphi_v$ | The apparent molar volume |
| $\varphi_v^0$ | The limiting apparent molar volume |
| $\rho$ | Density |
| $\rho_1$ | Density of solvent |
| $\rho_2$ | Density of solute |
| $\rho_{mix}$ | Density of the mixture |
| $V^E$ | Excess molar volume |
| $V_2$ | Partial molar volume |
| $\eta$ | Viscosity |
| $\eta^E$ | Excess viscosity |
| $\eta_{expt}$ | Observed viscosity |
| $\eta_{id}$ | Ideal viscosity |
| $\sigma$ | Standard deviation |
| $\varepsilon$ | 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 ONE

# INTRODUCTION

# CHAPTER I

## Introduction

### 1.1 Properties of solutions

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

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

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

The macroscopic properties of any system have to be interdependent, since these essentially originate from the most probable distribution of energy between the constituent molecules comprising the system. There has, therefore, been interest for seeking interrelations between the macroscopic properties of any system. It should, in principle, be possible to express the value of any macroscopic property in terms of the known values of the other. Since viscosity coefficient is a macroscopic property under non equilibrium condition, there has been a considerable effort for establishing its relationship with thermodynamic properties of a system.

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

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

Physical properties like density, viscosity, surface tension, conductivity, dielectric constant, refractive index, group frequency shifts in I.R. spectra etc. give an indication about the molecular structure as well as the molecular interactions that occur when liquids are mixed together. The density and viscosity are two fundamental physico-chemical properties of which are easy, simple, inexpensive and precise tools, by which one can get the valuable information about the molecular interactions in liquids and liquid mixture correlated with equilibrium and transport properties. The thermodynamic and excess thermodynamic data are used subsequently by a variety of physical scientists including chemical kineticists and spectroscopists involved in reaction occurring in solution and by chemical engineers engaged in the operation and design of chemical reactor, distillation columns or other type of separation devices. 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 a sound information about the structure of some alcohol, 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 *iso*-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 heavier fruity odours. Some of the highly branched alcohols and many alcohols containing more than 12 carbon atoms are solids at room temperature.

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

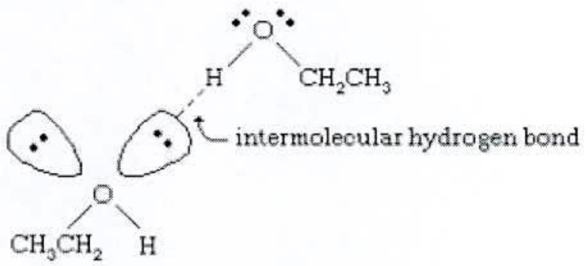

Fig. 1.1

The oxygen atom of the strongly polarized O-H bond of an alcohol pulls electron density away from the hydrogen atom. This polarized hydrogen, which bears a partial positive charge can form a hydrogen bond with a pair of nonbonding electrons on another oxygen atom (Fig. 1.1).

Water and alcohols have similar structural properties because water molecules contain hydroxyl groups that can form hydrogen bonds with other water molecules and with alcohol molecules and like wise alcohol molecules can form H-bonds with other alcohol molecules as well as with water molecules. As alcohols form hydrogen bonds with water they tend to be relatively soluble in water. The hydroxyl group is referred to as a hydrophilic group, as it forms hydrogen bonds with water and enhances the solubility of alcohol in water. Methanol, Ethanol, *n*-Propanol, *iso*-Propanol and t-Butanol are all miscible with water. Alcohols with higher molecular weights tend to be less water-soluble, as the hydrocarbon part of the molecule, which is hydrophobic ("water-hating"), in nature. Alcohols are strongly polar, so they are better solvents than alkanes for ionic and polar compounds.

### 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 an apolar hydrophobic tail group (hydrocarbon chain).

### 1.4 Classification of surfactants

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

Surfactants are classified as anionic, cationic, non-ionic or ampholytic according to the change carried by the surface-active part of the molecule. Some common examples are given in table-1.2. In addition, surfactants are often named in relation to their technological application, hence names such as detergents, wetting agent, emulsifier and dispersant.

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

Table 1.2: Surface active agents

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

### 1.5 Physical Properties of Surfactant Solutions

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

Mc-Bain(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 lyphobic hydrocarbon chains are oriented towards the interior of the micelle, leaving the hydrophilic groups in contact with the aqueous medium. The concentration above which micelle formation becomes appreciable is termed critical micelle concentration (CMC).

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

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

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

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

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

Two main approaches namely the phase-separation model and the mass-separation model to the thermodynamic analysis of the micellization process have gained wide acceptance. In the phase separation approach the micelles are considered to form a separate phase at the CMC. While in the mass-separation approach micelles and unassociated monomers are considered to be in association dissociation equilibrium. The mass action model developed by Desnoyers et al.(2) can fit the apparent molar quantities of monomeric surfactant over a wide concentration range below and above the CMC, Recently this model has been extendent by Caron et al.(3) 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 1.3), 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 1.3: 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 1.4

Table 1.4: Critical micelle concentrations of sodium dodecyl sulfate in aqueous sodium chloride solutions at $25^0$C.

| Concetration 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. Micelle 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.

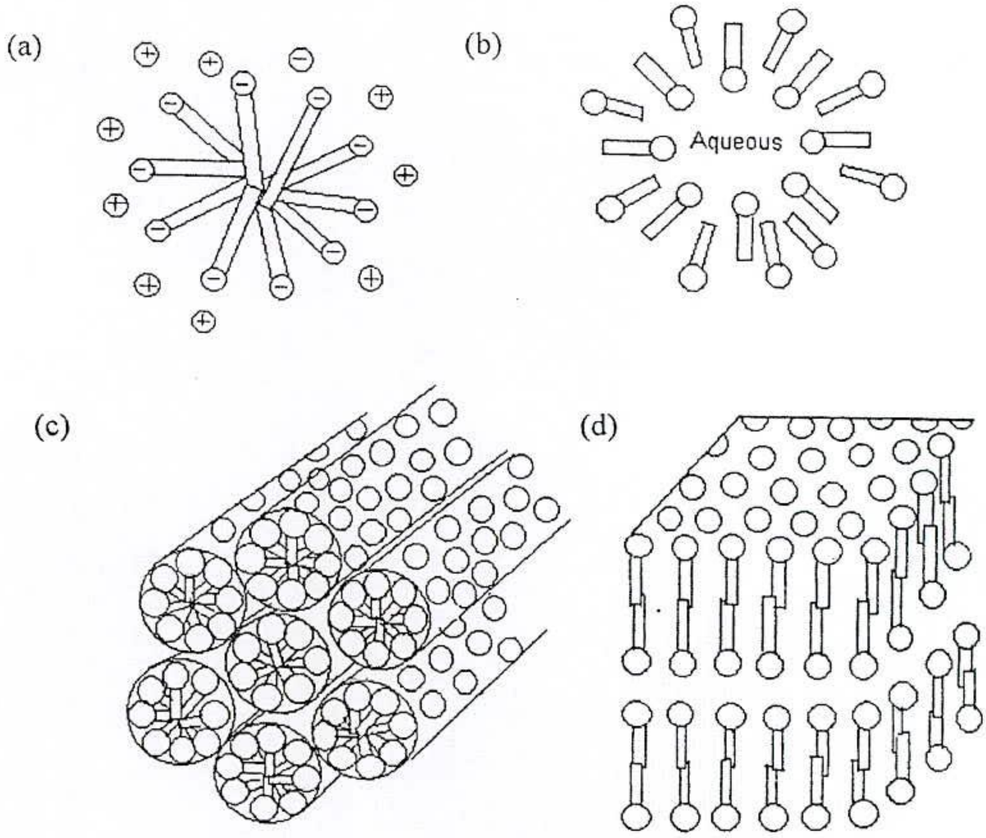

Figure 1.2: Micellar structures: (a) Spherical (anionic) micelle. This is the usual shape at surfactant concentrations below about 40 percent. (b) Spherical vesicle bilayer structures, which is representative of the living cell. (c) and (d) Hexagonal and lamellar phase formed cylindrical and lamellar 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 (4,5) did not accord with the view of spherical structure of the aggregates the results of angular light scattering studies by debye and anqcker (5) 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 (6) 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 (7,8). 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.

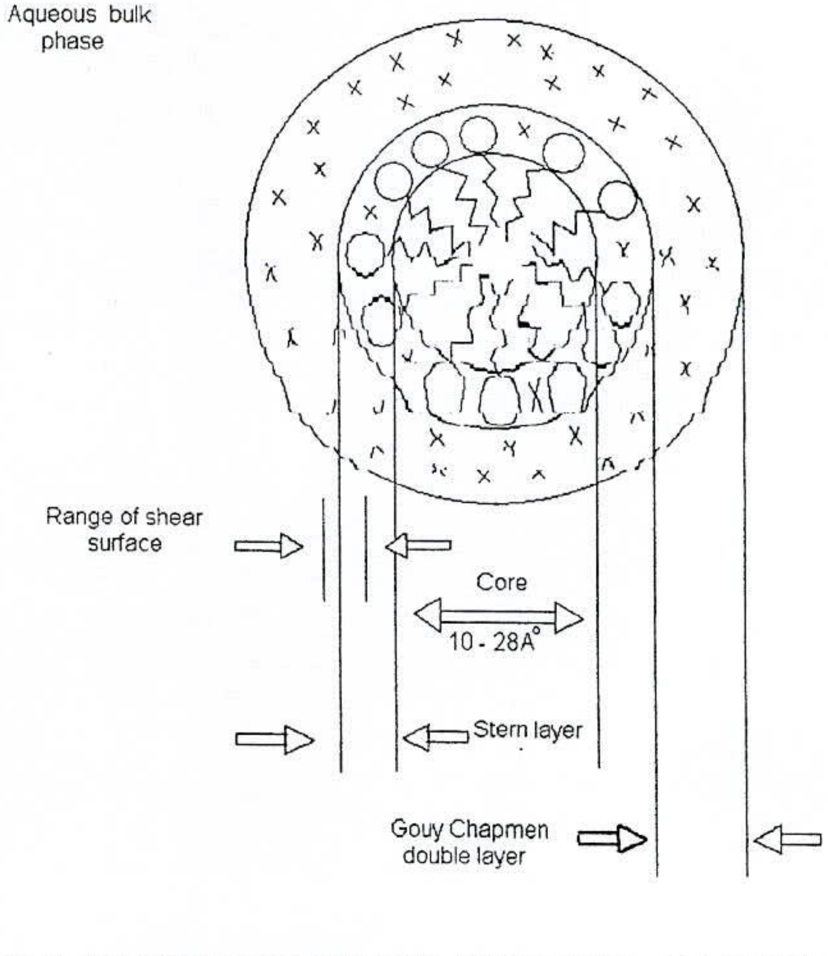

Figure 1.3: A two-dimensional schematic representation of a model of an ionic micelle, x the counter ions. (Adapted from "Solution Chemistry" Ed.K I. Mittal, Planum press, New York 1979)

In an attempt to develop a consistent interpretation of the result of a variety of experimental studies, stigter (9) introduced a rather detailed model for an ionic micelle. According to this model three regions, (Figure 1.3) can be identified; (a) a spherical micelle core (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 out side 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 (10). The deviations from regularity indicate some kind of association of water molecules. The notable unique physical properties exhibited by liquid water are (11) : 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 (12.13) 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 (14,15,16) 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 (17), latter developed by Nemethy and scherage (12), 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)

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

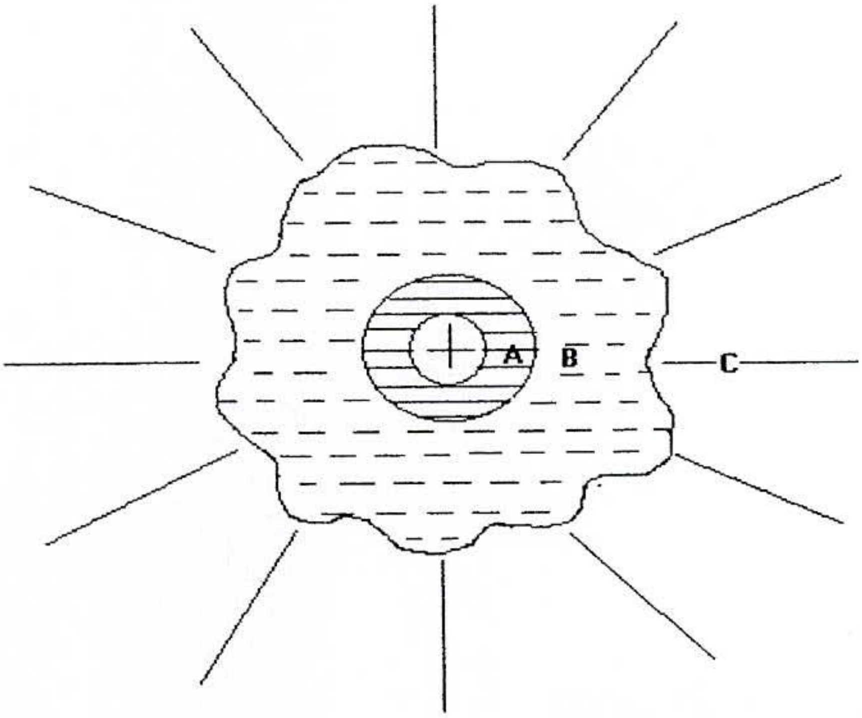

Fig 1.4: Frank and Wen model for the structure modification produce by an ion

The hydrogen bonding in the clusters is postulated (18) to be cooperative phenomenon. 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.

### 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 (20). 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 a much stronger attractive interaction energy between the nonpolar solutes merged in water than their vander waals interaction in free space (21). The tendency of relativity nonpolar molecules to "stick together" in aqueous solution is denoted as the hydrophobic interaction (22). 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 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 (18,23-26). There has also been considerable interest in the measurement of physicochemical properties, review on which are available in various complications, (27-31) of particular interest has been the determination of densities and viscosities of mixtures.

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

Besides the theoretical importance, the knowledge of 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 nine binary and ternary mixtures, viz., Mehanol + Water, Ethanol + Water, *n*-Propanol + Water, *iso*-Propanol + Water, Sodium Dodecyl Sulfate (SDS) + Water, Mehanol + SDS + Water, Ethanol + SDS + Water, *n*-Propanol + SDS + Water, *iso*-Propanol + SDS + Water at 298.15-323.15K have been determined. In order to understand the issue of solute-solvent interactions in 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 (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:

1. Interpret the experimental results and suggest the structure of the solutions,
2. Study the properties of the mixture in terms of excess properties,
3. Examine the thermodynamic properties of the solutions.

# CHAPTER TWO

## THEORITICAL BACKGROUND

# 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 (32).

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

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

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

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

## 2.2 Density

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

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

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

### 2.3 Density and temperature

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

### 2.4 Molarity

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

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

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

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$^{-1}$ (33).

### 2.5 Molar volume of Mixtures

The volume in mL occupied by one gram of any substance is called its specific volume and the volume occupied by 1 mole is called the molar volume of the substance. Therefore, if ρ is the density and M be the molar mass, we have the molality (m) of a solution is defined as the number of moles of the solute per 1000 g of solvent (33). 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

$\rho_0$ = Density of solvent in g $cm^{-3}$

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

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

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

## 2.6 Apparent/ partial molar volume

The apparent molar volume of a solute in solution, generally denoted by is defined by $\varphi_v$ the relation (34)

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

where, V is the volume of solution containing $n_1$ moles of solvent and $n_2$ moles of solute and $\overline{V}_1^0$ is the molal volume of the pure solvent at specified temperature and pressure. For binary solution, the apparent molar volume ($\varphi_v$) of an electrolyte in an aqueous solution is given by (35),

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

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

$n_1$ and $n_2$ are the number of moles, $M_1$ and $M_2$ are molar masses of the solvent and solute respectively and $\rho$ is the density of the solution. For molal concentration, $n_2 = m$, the molality and $n_1 = 55.51$, the number of moles of solvent in 1000g of solvent (water), the equation for apparent molal volume takes the form (35,36),

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

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

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

where, $\rho_o$ and $\rho$ are the densities of the solvent and solution and $W_e$, $W_0$ and W are the weight of empty bottle, weight of bottle with solvent and weight of bottle with solution respectively.

If the concentration is expressed in molarity (C), the equation 2.8 takes the form (37):

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

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

is used for inter conversion of the concentration in the two scales (37).

The partial molal property of a solute is defined as the change in property when one mole of the solute is added to an infinite amount of solvent, at constant temperature and pressure, so that the concentration of the solution remains virtually unaltered. If 'Y' represents partial molal property of a binary solution at constant temperature and pressure, Y will then be a function of two independent variables $n_1$ and $n_2$, which represent the number of moles of the two components present. The partial molar property of component one is then defined by the relation:

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

Similarly for component 2,

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

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

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

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

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

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

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

and,

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

For solutions of simple electrolytes, the apparent molar volume ($\varphi_v$) vary linearly with $\sqrt{m}$, even upto moderate concentrations. This behavior is in agreement with the prediction of the Debye-Huckel theory of dilute solutions as (34) :

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

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

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

and

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

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

When molar concentration scale is used to express $\varphi_v$ as a function of concentration, then

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

and

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

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

The concentration dependence of the apparent molar volume of electrolytes have been described by the Masson equation (38), the Redlich-Mayer equation (40) and Owen-Brinkley equation (39). Masson (38) found that the apparent molar volume of the electrolytes vary with the square root of the molar concentration as,

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

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

Redlich and Rosenfeld (40) predicated that a constant limiting slope $S_v$, should be obtained for a given electrolyte charge type if the Debye-Huckel limiting law is obeyed. By differentiating the Debye-Huckel limiting law for activity coefficients with respect to pressure, the theoretical limiting law slope $S_v$, could be calculated using the equation,

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

where, the terms K and W are given by

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

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

where, β is the compressibility of the solvent, $\gamma_i$ is the number of ions of the species i of valency $Z_i$ formed by one molecule of the electrolyte and the other symbols have their usual significance (40). For dilute solutions the limiting law for the concentration dependence of the apparent molar volume of electrolytes is given by the equation,

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

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

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

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

## 2.7 Excess molar volume

For binary systems the molar volumes of pure components, $\rho_0$ and of mixtures, $\rho_{mix}$ 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 $\rho_1$ are the mole fraction, molar mass and density of component 1(solvent); $X_2$, $M_2$, and $\rho_2$ are the corresponding values of component 2 (organic solutes); and $\rho_{mix}$ is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich Kister polynomial equation of the form,

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

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

## 2.8 Viscosity

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

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

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

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

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

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

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

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

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

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

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

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

The rate of flow of the liquid, under a given pressure will obviously be less, the smaller the radius of the tube, and the connection between these quantities was first derived by J.L.M. Poiseuille in 1844, known as the Poiseuille equation (41). 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 (41):

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

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,

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

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

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

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

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

### 2.9 Viscosity and temperature

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

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

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

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

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

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

## 2.10 Viscosity of liquid mixtures

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

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

where $\varphi$ is the fluidity of the mixture, $\varphi_1$ and $\varphi_2$ 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.

## 2.11 Excess viscosity measurements

The theoretical viscosities, $\eta_{id}$ 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, $\eta^E$ of a mixture is given by, subtracting the theoretical (ideal) viscosity from the observed (experimental) value, $\eta_{expt}$

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

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

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

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

## 2.12 Interaction parameter measurements, (ε)

Interaction parameter, ε for viscosity for all compositions of the mixtures at different temperatures have been calculated by using Grunberg-Nissan equation (42),

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

Where , ε = Interaction parameter.

$\eta_{expt.}$ = observed viscosity

$\eta_{id}$ = calculated viscosity

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

$\eta_1$ and $\eta_2$ 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.

## 2.13 Viscosity as a rate process

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

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

i) The motion of one layer with respect to another is assumed to involve the passes of a molecule from one equilibrium position to another 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 a such site requires the expenditure of energy because work must be done in pushing back the molecules.

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

Eyring and his co-workers (43) using absolute reaction rate theory and partition function. Correlated co-efficient of viscosity, $\eta$ as follows:

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

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 (44):

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

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

**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 (43):

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

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

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

Since,

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

The Eyring equation takes the form,

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

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

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

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

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

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

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

### 2.14 Different thermodynamic parameters

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

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

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

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

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

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

## 2.15 Redlich-Kister equation

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

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

Where $\mathrm{PROP}^E$ 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:

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

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

$\mathrm{PROP}^E_{calcd}$ = 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 THREE

## EXPERIMENTAL

# 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.

### 4.2 Materials

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

| Chemicals | Molecular formula | Molar mass | Reported purity | Producer |
|---|---|---|---|---|
| Methanol | $CH_3OH$ | 32.04 | 99.8% | E. MERCK Germany |
| Ethanol | $C_2H_5OH$ | 46.07 | 100.0% | E. MERCK Germany |
| n-Propanol | $CH_3CH_2CH_2OH$ | 60.10 | 99.0% | E. MERCK Germany |
| iso-Propanol | $(CH_3)_2CHOH$ | 60.10 | 99.0% | E. MERCK India |
| SDS | $C_{12}H_{25}NaO_4S$ | 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 $1\times10^{-6}$ $S.cm^{-1}$. This redistilled water was used for the preparation of 0.005M and 0.01M SDS solutions for volumetric 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 $\pm 0.0001$g was used for weighting. The flow time of liquids were recorded by a stop-watch capable to read up to 0.01 seconds. The temperature was controlled by water thermostat with an accuracy of $\pm 0.05^0$C. The experimental temperatures were 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K respectively. Both the density bottle and viscometer were calibrated with doubly distilled water at the studied temperature. Calibrated volumetric flask, pipette and burette were used for necessary volume measurement.

### 3.5 Methods (preparation of solution)

The binary solution of alcohol-water and ternary solution of alcohol-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 water and aqueous SDS solution 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 weighing a definite volume of the solution in a density bottle at specified temperature. The volumes were obtained by measuring the weight of water at that temperature and using the density of water from literature. The density of solution was determined from the relation.

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

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

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

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

### 3.8 Apparent/ Partial molar volume measurements

The apparent molar volumes of the solution for binary and ternary systems were determined from density measurement using the following equation. (34,35):

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

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

where, ρ is the density of the experimental solution, $M_2$ and m are the molar mass and molality of the electrolyte respectively and $\rho_0$ is the density of the solvent. The molality 'm' of a solution were calculated from mole fraction of solute and solvent

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

where, $M_1$ and $M_2$ = the molecular weight of solute and solvent

and also from molarity C,

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

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

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

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

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

Molar volume of solvent (pure water) at experimental temperature was calculated using the following equation (34).

$$\overline{V}_1^0 = \frac{\text{Molecular masses of solvent}}{\text{Density of solvent (at expt. temp.)}} \quad \ldots\ldots(3.5)$$

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

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

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

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

The values of $\frac{\delta\varphi_v}{\delta\sqrt{m}}$ were obtained from the slope of the plot of $\varphi_v$ against $\sqrt{C}$ by the use of Masson (38) equation and the apparent molar volume of solutes at infinite dilution ($\varphi_v{}^0 \approx \overline{V}_2{}^0$) were determined from the intercept of the plot, at C equal to zero.

### 3.9 Excess molar volume measurements

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

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

Where $X_1$, $M_1$, and $\rho_1$ are the mole fraction, molar mass and density of component 1(solvent);

$X_2$, $M_2$, and $\rho_2$ are the corresponding values of component 2(organic solutes); and $\rho_{mix}$ is the density of the mixture, respectively. The excess molar volumes were fitted to a Redlich-Kister polynomial equation of the form,

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

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

### 3.10 Viscosity measurements

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

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

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

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.

### 3.11 Excess viscosity measurements

The excess viscosities, $\eta^E$ were calculated using the following equation:

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

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

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

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

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

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

### 3.12 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 (42),

$$\varepsilon = \frac{\ln \eta_{\mathrm{expt}} - \ln \eta_{id}}{X_1X_2} \quad \text{.......} 3.14$$

Where , ε = Interaction parameter.

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

$\eta_{id}$ = calculated viscosity

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

$\eta_1$ and $\eta_2$ 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.

### 3.13 Thermodynamic parametes

The change of free energy of activation ($\Delta G^{\#}$) was calculated by the help of Nightingle and Benck (44) equation:

$$\Delta G^{\#} = RT \ln \left( \frac{\eta V_{m}}{Nh} \right) \tag{3.15}$$

Where $\eta$ = 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 = $6.023 \times 10^{23}\ mol^{-1}$

h = Plank's constant = $6.626 \times 10^{-34} Js$

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 (43):

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

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

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

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

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

$$\Delta H^{\#} = \text{slope} \times R \tag{3.18}$$

and

$$\Delta S^{\#} = -\text{intercept} \times R \tag{3.19}$$

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.

### 3.14 Coefficient Redlich-Kister equation and standard deviation

The experimentally obtained values of excess properties, i.e. excess molar volume ($V^E$), excess viscosities ($\eta^E$) 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:

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

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 FOUR

# RESULTS AND DISCUSSION

# CHAPTERE IV

## Results and Discussion

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

1. **Methanol + Water**
2. **Ethanol + Water**
3. ***n*-Propanol + Water**
4. ***iso*-Propanol + Water**
5. **Sodium Dodecyl Sulfate (SDS) + Water**
6. **Methanol + SDS + Water**
7. **Ethanol + SDS + Water**
8. ***n*-Propanol + SDS + Water**
9. ***iso*-Propanol + SDS + Water**

The above-mentioned systems were studied precisely at six equidistant temperatures ranging from 298.15K to 323.15K at interval of 5K by volumetric and viscometric methods. except methanol system. Methanol system was studied at 298.15, 303.15 and 308.15K The volumetric properties such as, partial molar volume ($\overline{V}_2$), excess molar volume $V^E$ are determined from density. Viscometric properties like excess viscosity ($\eta^E$), interaction parameter (ε) and thermodynamic properties like enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$) and free energy ($\Delta G^{\#}$) of activation for viscous flow and their excess quantities, $\Delta H^{\#E}$, $\Delta S^{\#E}$ and $\Delta G^{\#E}$ are determined from viscosity values. From these studies we obtained various information, which are presented in various section and discussed in the light of theories mentioned in the earlier chapter.

### 4.1 Conductance and viscosity studies of SDS:

The critical micelle concentration (CMC) of surfactant in water is one of the most important properties in the formation of micelle. This property has significant importance for quantitative study of the thermodynamics of interactions involved in the monomer micelle equilibrium as well as in systems involving solubilization of an additional component or its distribution between bulk solution and micelle. Among the various physical properties of solution of surfactant used for the determination of CMC, molar conductivity shows an abrupt change in their magnitude when micelle formation occurs. Therefore, CMC can be determined from the plot of molar conductivity as a function of concentration of surfactant.

In this research the CMC of sodium dodecyl sulfate (SDS) in water was determined from the conductance and viscosity measurement. The concentration dependence of molar conductivity of aqueous solutions of SDS is shown in Figure 4.1 and the data is presented in Table 4.1. The molar conductivity decreases with increasing SDS concentration and then remains unchanged 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-micellar region to intersect with a straight line drawn through the data in the post-micellar region. Viscosities vs. concentration of aqueous solution of SDS are plotted in Figure 4.2 and the data is presented in Table 4.2. The viscosities increases with increasing SDS concentration and then decreases and eventually increases again. The minima of viscosity express the CMC of SDS. The estimated value of CMC was found to be 0.0085 $mol.L^{-1}$ at 29°C. The conductance data is in good agreement with the viscosity data. The literature value also has been found to be satisfactory with this data (45). The effect of surfactant, SDS to alcohol systems has been studied in terms of volumetric, viscometric and thermodynamic properties. The concentration of SDS in pre-micellar and post-micellar region of 0.005M and 0.01M were used for these measurements.

### 4.2 **Volumetric Properties**

The densities, $\rho$ of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water systems were determined at temperatures ranging from (298.15, 303.15, 308.15, 313.15, 318.15 and 323.15)K except methanol system with an interval of 5K over the entire composition range $0 < x_2 < 1$, where $x_2$ represents the mole fraction of Alkanols. Methanol system was studied at 298.15, 303.15 and 308.15K. 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 densities of the binary systems have been shown in Table 4.4-4.7 at different temperatures. Figure 4.3- 4.6 shows the plots of densities as a function of mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water systems. It shows continuous decrease in density on addition of Methanol. For Ethanol, *n*-Propanol and *iso*-Propanol systems, it shows continuous decrease in density with different variation. In Ethanol, *n*-Propanol and *iso*-Propanol systems the decrease in density is found firstly rapidly and beyond the 0.4 mole fraction it shows slowly on addition of solute. The concave density curves for Ethanol, *n*-Propanol and *iso*-Propanol systems show that at lower mole fraction of solute, the rate of change of density with temperature appears to be much higher than the rate at higher mole fraction of solute. Density value decreases with increase in the temperature. In pure state the density of alcohol has been found to be in the order of,

Ethanol > *n*-Propanol > Methanol > *iso*-Propanol

The experimental density values in pure state of Water, Methanol, Ethanol, *n*-Propanol and *iso*-Propanol at 298.15K are 0.997130, 0.787323, 0.808867, 0.800501, 0.778306 gcm$^{-3}$, respectively. As the densities of pure Methanol, Ethanol, *n*-Propanol and *iso*-Propanol are less than that of pure water, with the increase of concentration of alcohol the density of alcohol + water system decreases and eventually proceeds towards the density of pure alcohol.

The effect of addition of surfactant, SDS to alcohol systems has also been studied. The concentration of SDS in pre-micellar and post-micellar region of 0.005M and 0.01M, respectively were used. Figures 4.7-4.14 show the plots of densities as a function of mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS solutions. The data are presented in the Table 4.8-4.15. From these Figures, it is seen that the basic pattern of density behavior of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS solution is very similar to pure water systems. In SDS systems, density increases in comparison to corresponding systems without SDS. The density of alcohol in Water and SDS systems has been found to be in the order of,

Alcohol - 0.01M SDS > Alcohol- 0.005M SDS > Alcohol - Water

The excess molar volume, $V^E$ of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water 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 4.4-4.7. For $V^E$ the fitting coefficients ($a_i$) are shown in Table 4.52-4.55 along with standard deviations. Figure 4.15 shows the plots of excess molar volume as a function of mole fraction of Methanol at different temperatures. The values have been found to be negative throughout the whole range of composition, showing minima at ~ 0.45 mole fraction of Methanol. The temperature variation of excess molar volume is not appreciable. The excess molar volumes of Ethanol, *n*-Propanol and *iso*-Propanol in water systems are shown in Figures 4.16-4.18. For Ethanol, the values of $V^E$ are negative throughout the whole range of composition. The minima appear at ~ 0.4 mole fraction of Ethanol. At low concentration of *n*-Propanol, $V^E$ are negative and with the increase of alcohol concentration, $V^E$ reaches minimum value between 0.2-0.3 mole fraction of *n*-Propanol and then increases continuously and eventually becomes positive. At lower concentration of *iso*-Propanol, $V^E$ are negative and with the increase of alcohol concentration, $V^E$ reaches minimum value at ~ 0.3 mole fraction of *iso*-Propanol and then increases continuously and finally becomes positive. In the present investigation at 298.15K, the minimum values $V^E$ have been found to be -1.1721 (at $x_2 =$ 0.30), -1.0911 (at $x_2 = 0.5$), -0.8340 (at $x_2 = 0.389$), -0.5880 (at $x_2 = 0.3$) for the Water + *iso*-Propanol, Water + Methanol, Water + Ethanol and Water + *n*-Propanol mixtures, respectively. The negative excess molar volume has been found to be in the orders:

*iso*-Propanol > Methanol > Ethanol > *n*-Propanol

Examination of the excess molar volume curves in the Figures 4.15-4.18 reveals the following characteristics:

a) The mixing of alcohols with water is accompanied by significant contractions of volume i.e $V^E$ are negative and large in magnitude.
b) All systems show well defined minima.
c) Temperature effects on $V^E$ are not much significant.
d) *n*-Propanol and *iso*-Propanol, the $V^E$ are being slightly positive at higher mole fractions.

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.

The observed $V^E$ may be discussed above which may be arbitrarily divided into physical, chemical, and geometrical contributions (46,47). The physical interactions, that is, nonspecific interactions between the real species present in the mixture, involve mainly dispersion force giving a positive contribution. The chemical or specific intermolecular interactions result in a volume decrease and these interactions include formation of hydrogen bonds and other complex-forming interactions. The structural contributions for these systems are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume. In other words, 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 (48). 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 the binary mixtures which are under investigations may be considered to be the resultant of the above-mentioned competing interactions of the component molecules. All the components are polar compounds; the value of dipole moment (μ) being 1.85, 1.7, 1.69, 1.68 and 1.66 D for Water, Methanol, Ethanol, *n*-Propanol, *iso*-Propanol, respectively. Due to dipole-dipole interactions between the components negative $V^E$ values are generally expected.

Water + *n*-Propanol and water + *iso*-Propanol mixtures have slightly positive $V^E$ values at higher mole fractions. Unfavorable packing may, however, result due to disruption of the closely associated water molecules on addition of alkanols and formation of new association between the unlike water and an alkanol molecules. Reorganization of the pure components in the mixtures due to formation of different type of weaker bond and geometrical mismatch or steric hindrence may also result unfavorable packing and lead to expansion in volume. As far the magnitude of $V^E$, it has been observed that the value of $V^E$ increases with increasing chain lengths (49) and size (50) of the components. This do not accords with the magnitude of our $V^E$ values which are in the order at 298.15K: water + *iso*-Propanol > water + Methanol> water + Ethanol > water + *n*-Propanol.

The molar volumes of Methanol, Ethanol, *n*-Propanol, and *iso*-Propanol, at 298.15K are, respectively, 40.70, 56.95, 74.96, and 77.21 $cm^3$ $mole^{-1}$. The Methanol and Ethanol molecules, being smaller there is possibility of partial accommodation of Methanol and Ethanol molecule in the interstices of the water molecules. Large and negative $V^E$ value of water + Methanol mixtures may be attributed to the occupation of void spaces of one component by other. 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, aliphatic alcohol, one can easily visualize that factors such as chemical contraction through hydrogen bonding between water and alcohol, the physical forces such as dipole-dipole interaction and the size difference between water and alcohol, the hydrophobic hydration are all the important causes for volume contraction. For these particular systems the factors causing volume expansion are of little or no significance. The contractive forces thus predominate far more than the expansive forces, if any. The overall effect 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 interactions due to H-bonds and by the hydrophobic hydration with overall economy of space. When hydrogen bonded tetrahedral structure of liquid water is formed near a hydrophobic part of the solute the inert part (alkyl group of alcohol) of the solute fills the interstitial cavities of the structures. This loss of free space 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 as has been observed in the present systems: more negative $V^E$ has been observed with Methanol+ Water and Ethanol+ Water systems than with *n*-Propanol + Water systems. In the case of *iso*-Propanol + Water systems, the $V^E$ becomes much more negative than Methanol + Water, Ethanol + Water and *n*-Propanol + Water systems. The strength of the intermolecular hydrogen bonding through in water and Alkanols, is 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. Larger the branch of alkanols, the water structure around the hydrocarbon moieties of aliphatic alcohol is highly promoted leading to the formation of cages surrounding the alcohol molecules as a result more negative $V^E$ is observed. Such results can also be seen in the work of Aminabhavi et al. (46) for methyl acetoacetate + branch-alcohol mixtures.

Examination of the results shows that the temperature effects on $V^E$ are not much significant. However, for the systems (i.e *n*-Propanol and *iso*-Propanol) $V^E$ values are being positive at higher mole fractions, $V^E$ increases with temperature and for those with negative values, $V^E$ decreases with temperature.

The values of Excess molar volume, $V^E$ for the systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS solution systems are given in the Tables 4.8-4.15. The plots of $V^E$ of alcohol + SDS water systems against mole fraction of alcohols are shown in Figures 4.19-4.26, respectively. The lines are generated by the polynomial equation 3.9. For $V^E$ the fitting coefficients ($a_i$) are shown in Table 4.52-4.55 along with standard deviations.

The values have been found to be negative throughout the whole range of composition, showing minima at ~ 0.45 mole fraction of Methanol in aqueous SDS systems. For Ethanol +SDS, the values of $V^E$ are negative throughout the whole range of composition. The minima appear at ~ 0.4 mole fraction of Ethanol. At low concentration of *n*-Propanol in aqueous SDS solutions, $V^E$ are negative and with the increase of alcohol concentration, $V^E$ reaches minimum value between 0.2 - 0.3 mole fraction of *n*-Propanol and then increases continuously and eventually becomes positive. At lower concentration of *iso*-Propanol, $V^E$ are negative and with the increase of alcohol concentration, $V^E$ reaches minimum value at ~ 0.3 mole fraction of *iso*-Propanol and then increases continuously and finally becomes positive. In the present investigation at 298.15K, the minimum values $V^E$ have been found to be -1.08 (at $x_2 = 0.30$), -1.03 (at $x_2 = 0.5$), -0.81 (at $x_2 = 0.389$), -0.63 (at $x_2 = 0.3$) for the 0.01M SDS-Water + *iso*-Propanol, 0.01M SDS -Water + Methanol, 0.01M SDS -Water + Ethanol and 0.01M SDS -Water + *n*-Propanol mixtures, respectively. The negative excess molar volume has been found to be in the orders similar to water systems:

*iso*-Propanol > Methanol > Ethanol > *n*-Propanol

In the case of aqueous SDS solution, for pre-micellar or post-micellar region there is no appreciable change of $V^E$ observed.

## 4.3 Viscometric Properties

The viscosities of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water systems at 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15K except methanol over the entire composition range are shown in Tables 4.16-4.19. Methanol system was studied at 298.15, 303.15 and 308.15K. The viscosities of the pure components are shown in Table 4.3 together with the literature values for Methanol, Ethanol, *n*-Propanol and *iso*-Propanol, wherever possible for comparison. The agreement between the measured values and literature values has been found to be almost satisfactory.

The variation of viscosities at these temperatures as a function of the mole fraction of the alcohols is shown in Figures 4.27-4.30. The following characteristic features of viscosity are observed:

a) Viscosities increase rapidly with alcohol concentration and show maxima in the water rich region at 0.2 – 0.3 mole fraction of alcohol. The position of maxima virtually does not change remarkably with the variation of temperature.

b) Viscosity decreases with rise of temperature.

c) The viscosity maxima follow the order:

*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol + Water > Methanol + Water

d) At the alcohol rich region shallow minima are observed for *iso*-Propanol at 0.9 mole fraction of alcohol. The minima seem to disappear with the rise of temperature. Such minima were also observed by Tanaka (51) for t-Butanol.

The effect of addition of surfactant, SDS to alcohol systems has also been studied. The concentration of SDS in pre-micellar and post-micellar region of 0.005M and 0.01M, respectively were used. The values of viscosity at different temperatures have been shown in Table 4.20-4.27. Figures 4.31-4.38 show the plots of viscosities as a function of mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water, 0.005M and 0.01M SDS solutions. From these Figures, it is seen that the basic pattern of viscosity behavior of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS is very similar to pure water systems. In the presence of SDS solution the viscosity of alcohol solution increases similarly of water systems, indicating that the micelle formation of SDS is not occurred in alcohol solutions. In SDS systems, viscosity increases in comparison to corresponding systems without SDS. This indicate that the SDS solution are reorganized the alcohol structure again so that the viscosity increasing are observed. The viscosity of alcohol in Water and SDS systems has been found to be in the order of,

Alcohol - 0.01M SDS > Alcohol - 0.005M SDS > Alcohol - Water.

Excess viscosities, $\eta^E$ were calculated by using equation 3.11. The $\eta^E$ values are shown in Table 4.16-4.19. The excess viscosities were fitted by least squares method to a polynomial equation 3.13. The values of the fitting parameters along with the standard deviation are presented in Table 4.56-4.59. The variation of $\eta^E$ against mole fraction of alcohol ($x_2$) is shown in Figure 4.39-4.42. The $\eta^E$ values are found to be positive and large in magnitude, indicating that the aqueous solutions of alcohols are highly non ideal. All the curves pass through maxima in water–rich region. The height of the maxima are in the order:

*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol + Water > Methanol + Water

The viscosities and excess viscosities are accounted for mainly by the following factors:

a) Strong Alcohol-water and Alcohol-Alcohol interactions,
b) Hydrophobic hydration of Alcohols.

The rapidly ascending part of viscosity curves (Figure 4.27-4.30) in the dilute region of alcohols can be explained primarily in terms of the phenomenon called hydrophobic hydration, which assumes that, in water rich region, the water molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. These are variously known as ice-bergs, clusters or cages. There is a large body of experimental evidences which suggest the existence of such cages. On addition of alcohol to water, cages are formed continuously till the water molecules necessary to form these cages are available. Simultaneously, the hydroxyl groups of alcohol form hydrogen bonds with the surrounding water molecules. The increase in viscosity with the mole fraction of alcohol in water rich region may be attributed to these two effects collectively. This evidence suggest that, at least in the case of t-Butanol and *iso*-propanol , the hydroxyl group is involved in H-bonding with water solvent (52). After attaining the state of maximum viscosity further addition of alcohol continuously breaks down both cages and alcohol-water associates, and instead, alcohol-alcohol associates are preferentially formed, which result in the regular decrease in viscosity. The appearance of viscosity maxima is therefore expected as a result of these competing processes. The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, while the hydrophilic effect is expected to be the same for all the studied alcohols.

The difference in maxima of viscosity over the temperature range ($\Delta\eta_{max}$) of the different systems can be explained in terms of the thermal fragility of the cages formed. In comparison with alcohol-water association, the water-water association in the cage structure is assumed to be more fragile to heat. Examination of viscosity curves of different alcohol solutions (Figure 4.27-4.30) shows that $\Delta\eta_{max}$ varies in the order,

*iso*-Propanol (1.8 mPa.s) > *n*-Propanol (1.3 mPa.S) > Ethanol (1.1 mPa.S) > Methanol (0.75 mPa.S).

The values, therefore, indicate the extent of the destruction of the cages structures by thermal effect which, in turn, reflects the extent of cage formation. The cages formed by the water-water association around hydrocarbon tails of alcohols are also assumed to be thermally unstable than water-water association in normal water (53,54). The shallow minima occurring at ~ 0.9 mole fraction of alcohol as showed in the *iso*-Propanol (Figure 4.30) seen to be somewhat prominent at lower temperatures. This observation is in agreement with that made by Tanaka et al (51). In the study of the viscosity of aqueous solutions of isomeric butanols, Scnanayake et al (55) noticed similar minima. A work by Kipkemboi et al (56) on the viscosity aqueous mixtures of t-Butanol in the temperature range 288-318K also confirmed this phenomenon. The aqueous solutions of methanol as studied by Tanaka et al (51), however, do not show this effect. Incidentally, minima of static dielectric constants of alcohol-water mixtures occur at about the same composition where the shallow minima of viscosity are observed (57,58). Franks and Ives (58) explained these minima in terms of the formation of so called "centrosymmetric" associates which are thought to be composed of one water and four alcohol molecules.

The values of Excess viscosity, $\eta^E$ for the systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS in water systems are given in the Tables 4.20-4.27. The plots of $\eta^E$ of alcohol + SDS water systems against mole fraction of alcohols are shown in Figures 4.43-4.50, respectively. The lines are generated by the polynomial equation 3.13. For $\eta^E$ the fitting coefficients ($a_i$) are shown in Table 4.56-4.59 along with standard deviations. The $\eta^E$ values are found to be positive and large in magnitude, indicating that the aqueous SDS solutions of alcohols are also highly non ideal. All the curves pass through maxima in water SDS-rich region.

Viscosities increase rapidly with alcohol concentration, showing maxima at ≈ 0.2-0.3 mole fraction of Alcohol in aqueous SDS solution. The position of maxima virtually does not change remarkably with the variation of temperature. At the alcohol rich region shallow minima are observed for *iso*-Propanol at 0.9 mole fraction of alcohol at 0.005M SDS solutions. The minima seem to disappear at the post micellar concentration (0.01M SDS) of solutions.

In the present investigation at 298.15K, the maximum values of $\eta^E$ have been found to be 0.7 (at $x_2 = 0.30$), 1.25 (at $x_2 = 0.5$), 1.55 (at $x_2 = 0.25$), 2.2 (at $x_2 = 0.25$) for the, 0.01M SDS -Water + Methanol, 0.01M SDS -Water + Ethanol, 0.01M SDS -Water + *n*-Propanol and 0.01M SDS-Water + *iso*-Propanol mixtures, respectively. The height of the maxima are in the order has been found to be in the orders similar to water systems:

*iso*-Propanol + Water-SDS > *n*-Propanol + Water-SDS > Ethanol + Water-SDS > Methanol + Water-SDS .

In the case of aqueous SDS solution, for pre-micellar or post-micellar region, it is seen that there is no appreciable change of viscosity or excess viscosity after adding SDS to the systems observed.

### 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 Table 4.16-4.27. The values have been found to be positive and quite large in magnitude in water-rich region for all the systems. The ε values are decrease with the increase of temperature.

From the studies of ε and $\eta^E$ values of a number of binary mixtures of different polar or non-polar liquids, Fort and Moore (59) 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 our studied systems, both ε and $\eta^E$ values are positive and large in magnitude. Therefore, the positive interaction parameters indicate that strong interactions between the components of the mixtures (59) are occurred. The interaction parameters, ε increase rapidly with alcohol concentration, showing maxima at ~ 0.1-0.2 mole fraction of alcohol and then decrease continuously and finally increases again at ~ 0.8-0.9 mole fraction of alcohol solution. At the alcohol rich region small maxima are observed for all alcohol solutions. The position of maxima virtually does not change remarkably with the variation of temperature. In the present investigation at 298.15K, the maximum values of ε have been found to be 4.8 (at $x_2 = 0.1$), 6.5 (at $x_2 = 0.1$), 6.9 (at $x_2 = 0.1$), 7.9 (at $x_2 = 0.1$) for the Water + Methanol, Water + Ethanol, Water + *n*-Propanol and Water + *iso*-Propanol mixtures, respectively. The height of the maxima is in the order has been found:

*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol + Water > Methanol + Water,

From these Figures 4.17-4.28, it is seen that the basic pattern of interaction parameter viscosity behavior of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS is very similar to pure water systems. For pre-micellar or post-micellar region, it is seen that there is no appreciable change of ε after adding SDS to the systems observed.

## 4.4 Thermodynamic properties

The thermodynamic parameters such as, free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) change of activation for the viscous flow of the binary and ternary systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water, 0.005M and 0.01M SDS solutions are calculated for the entire range of composition by using equation 3.15, 3.18 and 3.19.

Free energy change ($\Delta G^{\#}$) of activation for the viscous flow of the Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water, 0.005M and 0.01M SDS solutions at the studied temperature are shown in Table 4.28-4.39. The variation of free energy ($\Delta G^{\#}$) at these temperatures as a function of the mole fraction of the alcohols is shown in Figures 4.51-4.62. The following characteristic features of free energy ($\Delta G^{\#}$) are observed:

i) The change of free energy ($\Delta G^{\#}$) increase rapidly with alcohol concentration and show maxima in the water rich region at 0.2 – 0.3 mole fraction of alcohol. The position of maxima virtually does not change remarkably with the variation of temperature.
ii) The $\Delta G^{\#}$ value is positive for all the studied systems.
iii) The change of free energy ($\Delta G^{\#}$) decreases with rise of temperature.
iv) The change of free energy ($\Delta G^{\#}$) maxima follow the order:
*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol+Water > Methanol + Water .

The positive free energy change of activation for viscous flow can be interpreted with help of the Furth model (60), which states that the kinetic species involved in forming cavities or holes in the liquid medium is given by the work required in forming the hole against surface tension of the solution. The solute-solvent interaction, interstitial incorporation, hydrophilic hydration interaction renders the binary and ternary aqueous systems more structured. This is reflected by the positive $\Delta G^{\#}$ value.

Excess free energy ($\Delta G^{\#E}$) were calculated by using equation 3.23. The $\Delta G^{\#E}$ values are shown in Table 4.28-4.39. The excess free energy ($\Delta G^{\#E}$) were fitted by least squares method to a polynomial equation 3.24. The values of the fitting parameters along with the standard deviation are presented in Table 4.60-4.63. The variation of $\Delta G^{\#E}$ against mole fraction of alcohol ($x_2$) is shown in Figure 4.63-4.74. The $\Delta G^{\#E}$ values are found to be positive and large in magnitude, indicating that the aqueous solutions of alcohols are highly non ideal. All the curves pass through maxima in water–rich region. The heights of the maxima are in the order:

*iso*-Propanol + Water > *n*-Propanol + Water > Ethanol + Water > Methanol + Water

The free energy ($\Delta G^{\#}$) and excess free energy ($\Delta G^{\#E}$) are accounted for mainly by the following factors: Hydrophobic hydration of alcohols, Strong alcohol-water and alcohol-alcohol interactions.

The ascending part of free energy ($\Delta G^{\#}$) curves (Figure 4.51-4.62) in the dilute region of alcohols can be explained in terms of hydrophobic hydration, which assumes that, in water–rich region, the water molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. On addition of alcohol to water, ordered structure are formed continuously till the water molecules necessary to form these cages are available. Simultaneously, the hydroxyl groups of alcohol form hydrogen bonds with the surrounding water molecules. The increase in viscous free energy ($\Delta G^{\#}$) with the mole fraction of alcohol in water rich region may be attributed to these effects.

After attaining the state of maximum free energy ($\Delta G^{\#}$) further addition of alcohol continuously breaks down both the ordered structure and alcohol-water association, and instead, alcohol-alcohol association are inequitably formed, which result in the continual decrease in free energy ($\Delta G^{\#}$). The appearance of free energy ($\Delta G^{\#}$) maxima is therefore expected as a result of these competing processes.

The hydrophobic effect obviously increases with the size of the hydrocarbon chain of alcohols, while the hydrophilic effect is expected to be the same for all the studied alcohols. As the saturated alcohols are more hydrophobic than unsaturated alcohols and their hydrophobicity decrease with increasing degree of unsaturation. Considering these ones it can be predicted that in water rich region the free energy ($\Delta G^{\#}$) and the maxima in viscous free energy ($\Delta G^{\#}$) should be in the order:

*iso*-Propanol > *n*-Propanol > Ethanol > Methanol .

The effect of addition of surfactant, SDS to alcohol systems has also been studied. The concentration of SDS in pre-micellar and post-micellar region of 0.005M and 0.01M, respectively were used. The values of viscous free energy ($\Delta G^{\#}$) at different temperatures have been shown in Table 4.32-4.39. Figures 4.55-4.62 show the plots of ($\Delta G^{\#}$) as a function of mole fraction of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in water, 0.005M and 0.01M SDS solutions. From these Figures, it is seen that the basic pattern of ($\Delta G^{\#}$) behavior of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS is very similar to pure water systems. The viscous free energy plot also indicating that micelle formation of SDS is not occurred in the studied alcohol solutions. In SDS systems, $\Delta G^{\#}$ increases in comparison to corresponding systems without SDS. This indicates that the SDS solution are reorganized the alcohol structure again so that the $\Delta G^{\#}$ increasing are observed. The $\Delta G^{\#}$ of alcohol in Water and SDS systems has been found to be in the order of,

Alcohol - 0.01M SDS > Alcohol - 0.005M SDS > Alcohol-Water

The values of free energy, $\Delta G^{\#}$ for the systems of Methanol, Ethanol *n*-Propanol and *iso*-Propanol are higher in post-micellar region than that of pre-micellar region. This indicates that alcohols may be more structured in post-micellar region than in the pre-micellar region. The change may be attributed to the fact that $\Delta G^{\#}$ controls the rate of flow which is governed by the slowest step in the fluid proecess.

The values of excess free energy, ($\Delta G^{\#E}$) for the systems of Methanol, Ethanol, *n*-Propanol and *iso*-Propanol in 0.005M and 0.01M SDS in water systems are given in the Tables 4.32-4.39. The plots of ($\Delta G^{\#E}$) of alcohol + SDS water systems against mole fraction of alcohols are shown in Figures 4.67-4.74, respectively. The lines are generated by the polynomial equation 3.24. For ($\Delta G^{\#E}$) the fitting coefficients ($a_i$) are shown in Table 4.60-4.63 along with standard deviations.

In the present investigation at 298.15K, the maximum values of $\Delta G^{\#E}$ have been found to be 1.6 (at $x_2 = 0.30$), 2.0 (at $x_2 = 0.5$), 2.2 (at $x_2 = 0.25$), 2.9 (at $x_2 = 0.25$) for the, 0.01M SDS - Water + Methanol, 0.01M SDS -Water + Ethanol, 0.01M SDS -Water + *n*-Propanol and

0.01M SDS-Water + *iso*-Propanol mixtures, respectively. The height of the maxima are in the order has been found to be in the orders similar to water systems:

> *iso*-Propanol + Water-SDS > *n*-Propanol + Water-SDS > Ethanol + Water-SDS > Methanol + Water-SDS .

As suggested by the author (61), a large negative excess free energy, $\Delta G^{\#E}$ indicates the presence of weak interactions, whereas a large positive excess free energy, $\Delta G^{\#E}$ suggests a specific association between the molecules in the solvent mixture. The positive $\Delta G^{\#E}$ values in our studied systems are also indicative of the strong molecular interaction among the water, SDS and alcohol systems.

The values of enthalpy of activation, $\Delta H^{\#}$ for different systems are shown in Table 4.40-4.51. Analysis of the data reveals the following order of $\Delta H^{\#}$ values for the pure liquids:

> *iso*-Propanol +Water < *n*-Propanol +Water < Ethanol +Water < Methanol +Water

An investigation of the $\Delta H^{\#}$ values of alcohols indicate that the $\Delta H^{\#}$ of Methanol is about 2.5 times larger than that of *n*-Propanol systems. It might be due to the structure of Methanol in water through H-bond, is much stronger and more rigid than that of *n*-Propanol or *iso*-Propanol requiring greater energy during the viscous flow. The $\Delta H^{\#}$ values are positive for for all the studied systems indicate that positive work has to be done to overcome the energy barrier for the flow process. That is, the viscous flow is not thermodynamically favored for the systems studied.

The value of entropy of activation, $\Delta S^{\#}$ for different systems are shown in Table 4.40-4.51. The $\Delta S^{\#}$ value is negative for all the systems studied here. The $\Delta S^{\#}$ values of the alcohols in water and in SDS solutions are in general trend of associated or weakly associated liquids showing their more orderness or structuredness as a result of the formation of activated complex than that in the initial state during the viscous flow. The $\Delta S^{\#}$ measures the randomness or dis-orderness of the systems. The $\Delta S^{\#}$ values for the flow process are negative in all cases but do not follow any specific pattern. This indicates that the entropy of mixture is less than the pure state. It is found that the $\Delta S^{\#}$ values of flow process of SDS – alcohol systems are less than for alcohol-water systems. This indicates that the environment of water-alcohol systems is more random than SDS–alcohol systems. The values of excess entropy of activation, $\Delta S^{\#E}$ for the studied systems are shown in Table 4.40-4.51. The values of excess enthalpy of activation, $\Delta H^{\#E}$ for the studied systems are shown in Table 4.40-4.51. The $\Delta S^{\#E}$ values are found to be positive and $\Delta H^{\#E}$ values are found to be negative for all the systems.

Table-4.1: Molar conductance of sodium dodecyl sulfate (SDS) in aqueous solution at 302.15K.

| Concentration (mol.L$^{-1}$) | Molar conductance ( ohm$^{-1}$cm$^{2}$mol$^{-1}$) | Concentration (mol.L$^{-1}$) | Molar conductance ( ohm$^{-1}$cm$^{2}$mol$^{-1}$) |
|---|---|---|---|
| 0.003 | 73.1 | 0.01024 | 56.7 |
| 0.004 | 70.0 | 0.01169 | 52.0 |
| 0.005 | 67.6 | 0.014 | 47.4 |
| 0.006 | 64.5 | 0.016 | 45.2 |
| 0.007 | 62.8 | 0.018 | 43.0 |
| 0.008 | 62.5 | 0.02 | 41.4 |
| 0.009 | 62.5 | | |

Table 4.2: Viscosity of sodium dodecyl sulfate (SDS) in aqueous solution at 302.15K.

| Concentration (mol.L$^{-1}$) | Viscosity (mPa.s) |
|---|---|
| 0.001 | 0.8075 |
| 0.002 | 0.8096 |
| 0.003 | 0.8129 |
| 0.004 | 0.8138 |
| 0.005 | 0.8144 |
| 0.006 | 0.8155 |
| 0.007 | 0.8120 |
| 0.008 | 0.8103 |
| 0.009 | 0.8120 |
| 0.01 | 0.8134 |
| 0.02 | 0.8385 |
| 0.03 | 0.8551 |
| 0.04 | 0.8675 |
| 0.05 | 0.8801 |

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

| Component | Temperature (K) | Density (g.cm$^{-3}$) | | Viscosity (mPa.s) | |
|---|---|---|---|---|---|
| | | $\rho_{\text{lit}}$ | $\rho_{\text{exp}}$ | $\eta_{\text{lit}}$ | $\eta_{\text{exp}}$ |
| Methanol | 298.15 | 0.787200(62) | 0.787323 | 0.553 0(67) | 0.5523 |
| | 303.15 | 0.782420(63) | 0.782764 | 0.5100(68) | 0.5108 |
| | 308.15 | 0.777100(64) | 0.777426 | 0.4837(69) | 0.4902 |
| | 313.15 | 0.772500(61) | 0.772540 | 0.4542(69) | 0.4577 |
| | 318.15 | 0.769285(53) | 0.766700 | 0.4256(69) | 0.4280 |
| | 323.15 | 0.762800(61) | 0.758600 | 0.4000(67) | 0.4055 |
| Ethanol | 298.15 | 0.801900(65) | 0.808867 | 1.0900(67) | 1.1355 |
| | 303.15 | 0.798255(53) | 0.804509 | 1.1808(69) | 1.2060 |
| | 308.15 | 0.794517(53) | 0.799029 | 1.0638(69) | 1.0871 |
| | 313.15 | 0.780157(53) | 0.793200 | 0.9646(69) | 0.9655 |
| | 318.15 | 0.785760(43) | 0.788300 | 0.8714(69) | 0.8708 |
| | 323.15 | 0.771336(53) | 0.783558 | 0.8010(69) | 0.7952 |
| n-Propanol | 298.15 | 0.799692(66) | 0.800501 | 1.9340(70) | 1.9233 |
| | 303.15 | 0.795840(63) | 0.796323 | 1.6626(63) | 1.6951 |
| | 308.15 | 0.797499(53) | 0.791910 | 1.5422(69) | 1.5234 |
| | 313.15 | 0.787500(61) | 0.787892 | 1.3000(67) | 1.3430 |
| | 318.15 | 0.789183(53) | 0.782407 | 1.2440(69) | 1.2060 |
| | 323.15 | 0.778500(61) | 0.779224 | 1.1091(69) | 1.0690 |
| iso-Propanol | 298.15 | 0.780000(71) | 0.778306 | 2.0360(74) | 2.0257 |
| | 303.15 | 0.777100(72) | 0.774467 | 1.7732(31) | 1.7639 |
| | 308.15 | 0.772460(73) | 0.771190 | 1.5420(73) | 1.5220 |
| | 313.15 | | 0.766972 | | 1.3179 |
| | 318.15 | | 0.762585 | | 1.1516 |
| | 323.15 | | 0.758129 | | 1.0075 |

Table-4.4: Density ($\rho$) and Excess molar volume ($V^E$) of Methanol + Water system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | |
|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ |
| 0.0000 | 0.997130 | 0.0000 | 0.995710 | 0.0000 | 0.994080 | 0.0000 |
| 0.1002 | 0.971000 | -0.3339 | 0.968118 | -0.3213 | 0.965754 | -0.3270 |
| 0.2000 | 0.948795 | -0.6488 | 0.946149 | -0.6555 | 0.943356 | -0.6703 |
| 0.3001 | 0.928200 | -0.8583 | 0.925400 | -0.8738 | 0.922500 | -0.9018 |
| 0.4006 | 0.905000 | -1.0173 | 0.901300 | -1.0205 | 0.898000 | -1.0546 |
| 0.5012 | 0.882212 | -1.0199 | 0.878653 | -1.0366 | 0.873940 | -1.0385 |
| 0.60056 | 0.862270 | -0.9956 | 0.858303 | -1.0065 | 0.853949 | -1.0301 |
| 0.7012 | 0.842625 | -0.8829 | 0.837975 | -0.8734 | 0.832791 | -0.8725 |
| 0.8040 | 0.823114 | -0.6677 | 0.819303 | -0.6976 | 0.814428 | -0.7152 |
| 0.8991 | 0.804735 | -0.3558 | 0.800429 | -0.3668 | 0.796307 | -0.4245 |
| 1.0000 | 0.787323 | 0.0000 | 0.782764 | 0.0000 | 0.777426 | 0.0000 |

Table-4.5: Density ($\rho$) and Excess molar volume ($V^E$) of Ethanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K .respectively

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\,mol^{-1}}$ |
| 0.0000 | 0.997130 | 0.0000 | 0.995710 | 0.0000 | 0.994080 | 0.0000 | 0.992250 | 0.0000 | 0.990220 | 0.0000 | 0.988020 | |
| 0.1005 | 0.964790 | -0.4125 | 0.963795 | -0.4454 | 0.960055 | -0.4280 | 0.956812 | -0.4257 | 0.952969 | -0.4090 | 0.949020 | -0.3921 |
| 0.1997 | 0.939743 | -0.7011 | 0.936415 | -0.6940 | 0.932453 | -0.6890 | 0.927716 | -0.6667 | 0.923498 | -0.6537 | 0.918068 | -0.6084 |
| 0.2992 | 0.916800 | -0.8217 | 0.913400 | -0.8235 | 0.908300 | -0.7983 | 0.904100 | -0.8050 | 0.899300 | -0.7842 | 0.893300 | -0.7253 |
| 0.3989 | 0.891811 | -0.8305 | 0.887877 | -0.8240 | 0.883461 | -0.8341 | 0.877800 | -0.8012 | 0.873200 | -0.7952 | 0.868522 | -0.7864 |
| 0.4988 | 0.872796 | -0.7709 | 0.868588 | -0.7598 | 0.863244 | -0.7421 | 0.858100 | -0.7366 | 0.853500 | -0.7375 | 0.849600 | -0.7688 |
| 0.6005 | 0.856200 | -0.7027 | 0.851709 | -0.6836 | 0.845222 | -0.6171 | 0.839600 | -0.5956 | 0.834331 | -0.5693 | 0.829159 | -0.5461 |
| 0.7019 | 0.842629 | -0.6142 | 0.838412 | -0.6135 | 0.831400 | -0.5186 | 0.825300 | -0.4754 | 0.820600 | -0.4832 | 0.815600 | -0.4722 |
| 0.8017 | 0.829680 | -0.4224 | 0.825498 | -0.4275 | 0.819051 | -0.3620 | 0.813700 | -0.3655 | 0.808231 | -0.3312 | 0.802420 | -0.2717 |
| 0.9002 | 0.818902 | -0.2358 | 0.815605 | -0.3026 | 0.809000 | -0.2260 | 0.803200 | -0.2047 | 0.798200 | -0.2024 | 0.792000 | -0.1138 |
| 1.0000 | 0.808867 | 0.0000 | 0.804509 | 0.0000 | 0.799029 | 0.0000 | 0.793500 | 0.0000 | 0.788500 | 0.0000 | 0.783558 | 0.0000 |

Table-4.6: Density ($\rho$)) and Excess molar volume ($V^E$) of n-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.997130 | 0.0000 | 0.995710 | 0.0000 | 0.994080 | 0.0000 | 0.992250 | 0.0000 | 0.990220 | 0.0000 | 0.988020 | |
| 0.1006 | 0.954317 | -0.4714 | 0.951246 | -0.4759 | 0.946522 | -0.4282 | 0.940076 | -0.3360 | 0.935527 | -0.3082 | 0.933842 | -0.3333 |
| 0.2005 | 0.915300 | -0.4843 | 0.910929 | -0.4768 | 0.907560 | -0.4756 | 0.903664 | -0.4534 | 0.899682 | -0.4587 | 0.895399 | -0.4134 |
| 0.2991 | 0.887907 | -0.6025 | 0.882768 | -0.5881 | 0.876400 | -0.4828 | 0.871400 | -0.4216 | 0.867883 | -0.4653 | 0.864282 | -0.4406 |
| 0.3990 | 0.867426 | -0.6204 | 0.862801 | -0.6452 | 0.856900 | -0.5530 | 0.851300 | -0.4603 | 0.846900 | -0.4836 | 0.841800 | -0.3841 |
| 0.5026 | 0.850377 | -0.5777 | 0.845022 | -0.5813 | 0.839300 | -0.4914 | 0.833238 | -0.3631 | 0.830178 | -0.4770 | 0.824453 | -0.3273 |
| 0.6011 | 0.837432 | -0.5147 | 0.833156 | -0.5975 | 0.826100 | -0.4181 | 0.820000 | -0.2740 | 0.815500 | -0.3188 | 0.811100 | -0.2355 |
| 0.7022 | 0.826107 | -0.4021 | 0.822239 | -0.5337 | 0.814800 | -0.3096 | 0.808399 | -0.1291 | 0.804100 | -0.2011 | 0.798954 | -0.0525 |
| 0.7993 | 0.817555 | -0.3208 | 0.813075 | -0.4273 | 0.806000 | -0.2117 | 0.800400 | -0.0794 | 0.794700 | -0.051 | 0.790300 | 0.0516 |
| 0.8998 | 0.808668 | -0.1088 | 0.802900 | -0.1210 | 0.798500 | -0.1188 | 0.792200 | 0.0861 | 0.786348 | 0.1263 | 0.783562 | 0.0925 |
| 1.0000 | 0.800501 | 0.0000 | 0.796323 | 0.0000 | 0.791000 | 0.0000 | 0.787892 | 0.0000 | 0.782407 | 0.0000 | 0.779224 | 0.0000 |

Table-4.7: Density ($\rho$) and Excess molar volume ($V^E$) of iso-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.997130 | 0.0000 | 0.995710 | 0.0000 | 0.994080 | 0.0000 | 0.992250 | 0.0000 | 0.990220 | 0.0000 | 0.988020 | 0.0000 |
| 0.1004 | 0.956387 | -0.7512 | 0.952306 | -0.7131 | 0.948403 | -0.6768 | 0.945115 | -0.6683 | 0.940775 | -0.6385 | 0.937294 | -0.6337 |
| 0.1988 | 0.916127 | -1.0295 | 0.911577 | -0.9825 | 0.907552 | -0.9435 | 0.903200 | -0.9154 | 0.898661 | -0.8873 | 0.894563 | -0.8774 |
| 0.3042 | 0.883300 | -1.1721 | 0.879200 | -1.1438 | 0.874400 | -1.0723 | 0.871300 | -1.1006 | 0.866100 | -1.0513 | 0.861300 | -1.0221 |
| 0.3990 | 0.859089 | -1.1525 | 0.855098 | -1.1316 | 0.849518 | -1.0136 | 0.844819 | -0.9768 | 0.840372 | -0.9610 | 0.834200 | -0.8637 |
| 0.5003 | 0.840007 | -1.1490 | 0.835820 | -1.1203 | 0.830769 | -1.0159 | 0.824900 | -0.9125 | 0.817523 | -0.7292 | 0.811200 | -0.6087 |
| 0.6000 | 0.824215 | -1.0645 | 0.819763 | -1.0194 | 0.814039 | -0.8580 | 0.807800 | -0.7180 | 0.800900 | -0.5420 | 0.794400 | -0.3941 |
| 0.7031 | 0.809966 | -0.8827 | 0.805539 | -0.8364 | 0.800159 | -0.6797 | 0.793000 | -0.4539 | 0.787200 | -0.3396 | 0.780798 | -0.1815 |
| 0.8026 | 0.799617 | -0.7708 | 0.795191 | -0.7226 | 0.790013 | -0.5662 | 0.782700 | -0.3042 | 0.777200 | -0.2052 | 0.770000 | 0.0382 |
| 0.8975 | 0.790916 | -0.6221 | 0.786626 | -0.5836 | 0.781702 | -0.4358 | 0.773290 | -0.0477 | 0.768600 | -0.0159 | 0.761618 | 0.2297 |
| 1.0000 | 0.778306 | 0.0000 | 0.774467 | 0.0000 | 0.771190 | 0.0000 | 0.766972 | 0.0000 | 0.762585 | 0.0000 | 0.758129 | 0.0000 |

Table-4.8: Density ($\rho$) and Excess molar volume ($V^E$) of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | |
|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ |
| 0.0000 | 0.998054 | 0.0000 | 0.995557 | 0.0000 | 0.993746 | 0.0000 |
| 0.1002 | 0.972061 | -0.3406 | 0.969214 | -0.3464 | 0.966452 | -0.3470 |
| 0.2000 | 0.948291 | -0.6238 | 0.946305 | -0.6613 | 0.943180 | -0.6710 |
| 0.3001 | 0.928565 | -0.8373 | 0.924581 | -0.8359 | 0.920900 | -0.8455 |
| 0.4006 | 0.905291 | -0.9754 | 0.901553 | -0.9886 | 0.897942 | -1.0145 |
| 0.5012 | 0.885412 | -1.0411 | 0.880700 | -1.0305 | 0.875419 | -1.0152 |
| 0.6006 | 0.862626 | -1.0015 | 0.858439 | -1.0125 | 0.853458 | -1.0147 |
| 0.7012 | 0.842360 | -0.8675 | 0.838024 | -0.8762 | 0.831500 | -0.8224 |
| 0.8004 | 0.823166 | -0.6528 | 0.819004 | -0.6711 | 0.813034 | -0.6405 |
| 0.8991 | 0.804963 | -0.3649 | 0.799200 | -0.3083 | 0.794828 | -0.3535 |
| 1.0000 | 0.787323 | 0.0000 | 0.782764 | 0.0000 | 0.777426 | 0.0000 |

Table-4.9: Density ($\rho$) and Excess molar volume ($V^E$) of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.998054 | 0.0000 | 0.995557 | 0.0000 | 0.993746 | 0.0000 | 0.991995 | 0.0000 | 0.989275 | 0.0000 | 0.987275 | |
| 0.1005 | 0.965109 | -0.3724 | 0.962996 | -0.3968 | 0.959083 | -0.3777 | 0.954473 | -0.3441 | 0.949621 | -0.3138 | 0.946864 | -0.3186 |
| 0.1997 | 0.941500 | -0.5605 | 0.938500 | -0.5749 | 0.934600 | -0.5706 | 0.929300 | -0.5336 | 0.925900 | -0.5484 | 0.922000 | -0.5376 |
| 0.2992 | 0.914021 | -0.7242 | 0.910064 | -0.7216 | 0.904387 | -0.6792 | 0.900500 | -0.7001 | 0.896600 | -0.7139 | 0.891700 | -0.6830 |
| 0.3989 | 0.890000 | -0.7539 | 0.885900 | -0.7523 | 0.880500 | -0.7266 | 0.874600 | -0.6911 | 0.870181 | -0.6955 | 0.865060 | -0.6601 |
| 0.4988 | 0.872335 | -0.7632 | 0.868300 | -0.7693 | 0.863400 | -0.7725 | 0.856100 | -0.6837 | 0.851700 | -0.6957 | 0.846300 | -0.6508 |
| 0.6005 | 0.855688 | -0.6717 | 0.852392 | -0.7175 | 0.848040 | -0.7567 | 0.840500 | -0.6551 | 0.835100 | -0.6236 | 0.830000 | -0.5942 |
| 0.7019 | 0.842420 | -0.5982 | 0.838211 | -0.6035 | 0.833060 | -0.6109 | 0.826800 | -0.5751 | 0.820500 | -0.4932 | 0.815100 | -0.4480 |
| 0.8017 | 0.828833 | -0.3691 | 0.824700 | -0.3806 | 0.819394 | -0.3839 | 0.813700 | -0.3840 | 0.807999 | -0.3321 | 0.802000 | -0.2480 |
| 0.9002 | 0.818119 | -0.1836 | 0.814283 | -0.2167 | 0.808507 | -0.1939 | 0.802105 | -0.1514 | 0.796600 | -0.1086 | 0.791200 | -0.0599 |
| 1.0000 | 0.808867 | 0.0000 | 0.804509 | 0.0000 | 0.799029 | 0.0000 | 0.793200 | 0.0000 | 0.788300 | 0.0000 | 0.783558 | 0.0000 |

Table-4.10: Density ($\rho$) and Excess molar volume ($V^E$) of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.998054 | 0.0000 | 0.995557 | 0.0000 | 0.993746 | 0.0000 | 0.991995 | 0.0000 | 0.989275 | 0.0000 | 0.987275 | 0.0000 |
| 0.1006 | 0.953922 | -0.4637 | 0.949285 | -0.4301 | 0.942885 | -0.3517 | 0.940208 | -0.3435 | 0.937063 | -0.3628 | 0.935426 | -0.3860 |
| 0.2005 | 0.915545 | -0.5910 | 0.910438 | -0.5441 | 0.905452 | -0.5123 | 0.903963 | -0.5498 | 0.897737 | -0.4940 | 0.894060 | -0.4652 |
| 0.2991 | 0.887183 | -0.6130 | 0.881170 | -0.5272 | 0.877300 | -0.5490 | 0.872206 | -0.4573 | 0.867700 | -0.4700 | 0.863277 | -0.4091 |
| 0.399 | 0.867580 | -0.6846 | 0.862300 | -0.6234 | 0.857000 | -0.5962 | 0.852300 | -0.5111 | 0.846300 | -0.4649 | 0.841300 | -0.3678 |
| 0.5026 | 0.850465 | -0.6588 | 0.845198 | -0.5923 | 0.839100 | -0.5272 | 0.832696 | -0.3347 | 0.827300 | -0.3215 | 0.822949 | -0.2473 |
| 0.6011 | 0.837530 | -0.6152 | 0.833034 | -0.5910 | 0.827000 | -0.5300 | 0.819500 | -0.2437 | 0.814100 | -0.2344 | 0.810900 | -0.2278 |
| 0.7022 | 0.826151 | -0.5183 | 0.821620 | -0.4909 | 0.814900 | -0.3799 | 0.808400 | -0.1306 | 0.803120 | -0.1341 | 0.799473 | -0.0952 |
| 0.7993 | 0.817189 | -0.4237 | 0.812957 | -0.4186 | 0.806300 | -0.3066 | 0.800200 | -0.0642 | 0.795200 | -0.0957 | 0.791300 | -0.0338 |
| 0.8998 | 0.808703 | -0.2617 | 0.804680 | -0.2752 | 0.797001 | -0.0663 | 0.792631 | 0.0473 | 0.787637 | 0.0083 | 0.784272 | 0.0266 |
| 1.0000 | 0.800501 | 0.0000 | 0.796323 | 0.0000 | 0.791000 | 0.0000 | 0.787892 | 0.0000 | 0.782407 | 0.0000 | 0.779224 | 0.0000 |

Table 4.11: Density ($\rho$) and Excess molar volume ($V^E$) of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.998054 | 0.0000 | 0.995557 | 0.0000 | 0.993746 | 0.0000 | 0.991995 | 0.0000 | 0.989275 | 0.0000 | 0.987275 | 0.0000 |
| 0.1004 | 0.953778 | -0.6725 | 0.950783 | -0.6782 | 0.946374 | -0.6320 | 0.940292 | -0.5518 | 0.935108 | -0.5109 | 0.930233 | -0.4659 |
| 0.1988 | 0.914588 | -0.9677 | 0.909336 | -0.9134 | 0.906140 | -0.9031 | 0.902013 | -0.8807 | 0.897623 | -0.8673 | 0.893294 | -0.8465 |
| 0.3042 | 0.883055 | -1.1508 | 0.877691 | -1.0855 | 0.870071 | -0.9012 | 0.864551 | -0.8277 | 0.861392 | -0.8689 | 0.855866 | -0.8045 |
| 0.3990 | 0.858683 | -1.1232 | 0.852634 | -1.0156 | 0.846700 | -0.8809 | 0.841200 | -0.8023 | 0.837300 | -0.8195 | 0.832300 | -0.7768 |
| 0.5003 | 0.839371 | -1.1054 | 0.834326 | -1.0380 | 0.826900 | -0.7989 | 0.820519 | -0.6619 | 0.816525 | -0.6795 | 0.810082 | -0.5491 |
| 0.6000 | 0.824531 | -1.0780 | 0.818968 | -0.9693 | 0.812100 | -0.7335 | 0.805200 | -0.5469 | 0.800200 | -0.5017 | 0.794300 | -0.3927 |
| 0.7031 | 0.810917 | -0.9467 | 0.806466 | -0.9052 | 0.798817 | -0.5816 | 0.792387 | -0.4089 | 0.786651 | -0.3026 | 0.781329 | -0.2270 |
| 0.8026 | 0.800635 | -0.8499 | 0.795996 | -0.7890 | 0.787400 | -0.3498 | 0.782000 | -0.2459 | 0.776500 | -0.1485 | 0.771600 | -0.1040 |
| 0.8975 | 0.790872 | -0.6165 | 0.786207 | -0.5461 | 0.777569 | -0.0572 | 0.772931 | -0.0146 | 0.767972 | 0.0417 | 0.763620 | 0.0362 |
| 1.0000 | 0.778306 | 0.0000 | 0.774467 | 0.0000 | 0.771190 | 0.0000 | 0.766972 | 0.0000 | 0.762585 | 0.0000 | 0.758129 | 0.0000 |

Table-4.12: Density ($\rho$) and Excess molar volume ($V^E$) of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | |
|---|---|---|---|---|---|---|
| | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ |
| 0.0000 | 1.001509 | 0.0000 | 0.999900 | 0.0000 | 0.997549 | 0.0000 |
| 0.1002 | 0.975900 | -0.3632 | 0.973200 | -0.3578 | 0.970500 | -0.3686 |
| 0.2000 | 0.951948 | -0.6583 | 0.949301 | -0.6679 | 0.946242 | -0.6872 |
| 0.3001 | 0.928919 | -0.8777 | 0.925327 | -0.8763 | 0.921195 | -0.8826 |
| 0.4006 | 0.905900 | -0.9959 | 0.901829 | -0.9905 | 0.897978 | -1.0161 |
| 0.5012 | 0.883804 | -1.0316 | 0.880161 | -1.0476 | 0.875302 | -1.0516 |
| 0.6006 | 0.863577 | -1.0104 | 0.859330 | -1.0130 | 0.855047 | -1.0447 |
| 0.7012 | 0.842487 | -0.8539 | 0.838461 | -0.8700 | 0.833234 | -0.8714 |
| 0.8004 | 0.823778 | -0.6668 | 0.819499 | -0.6770 | 0.814532 | -0.6928 |
| 0.8991 | 0.804979 | -0.3594 | 0.800732 | -0.3736 | 0.796028 | -0.4046 |
| 1.0000 | 0.787323 | 0.0000 | 0.782764 | 0.0000 | 0.777426 | 0.0000 |

Table-4.13: Density ($\rho$) and Excess molar volume ($V^E$) of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ | $\rho$ / $gcm^{-3}$ | $V^E$ / $cm^3\ mol^{-1}$ |
| 0.000 | 1.001509 | 0.0000 | 0.999900 | 0.0000 | 0.997549 | 0.0000 | 0.995318 | 0.0000 | 0.993491 | 0.0000 | 0.991432 | 0.0000 |
| 0.1005 | 0.967509 | -0.3700 | 0.966216 | -0.3982 | 0.963606 | -0.4175 | 0.959740 | -0.4035 | 0.953859 | -0.3410 | 0.948400 | -0.2854 |
| 0.1997 | 0.941630 | -0.6882 | 0.938056 | -0.6775 | 0.933945 | -0.6790 | 0.928700 | -0.6415 | 0.922850 | -0.5893 | 0.915870 | -0.4965 |
| 0.2992 | 0.913911 | -0.7504 | 0.911437 | -0.7846 | 0.907060 | -0.7921 | 0.902300 | -0.7761 | 0.896800 | -0.7432 | 0.890800 | -0.6793 |
| 0.3989 | 0.891935 | -0.7876 | 0.889039 | -0.8215 | 0.883397 | -0.7938 | 0.878500 | -0.7795 | 0.872248 | -0.7256 | 0.866616 | -0.6747 |
| 0.4988 | 0.874371 | -0.8174 | 0.869930 | -0.7989 | 0.863900 | -0.7593 | 0.859100 | -0.7547 | 0.853600 | -0.7369 | 0.847600 | -0.6704 |
| 0.6005 | 0.856899 | -0.7044 | 0.851106 | -0.6243 | 0.845600 | -0.6104 | 0.840800 | -0.6105 | 0.834638 | -0.5652 | 0.830196 | -0.5736 |
| 0.7019 | 0.843129 | -0.6172 | 0.838754 | -0.6092 | 0.832600 | -0.5652 | 0.826800 | -0.5159 | 0.821600 | -0.5265 | 0.816400 | -0.4988 |
| 0.8017 | 0.830048 | -0.4283 | 0.825634 | -0.4206 | 0.819470 | -0.3748 | 0.814000 | -0.3434 | 0.808000 | -0.3109 | 0.802871 | -0.2876 |
| 0.9002 | 0.819610 | -0.2736 | 0.815125 | -0.2638 | 0.810395 | -0.3117 | 0.804400 | -0.2466 | 0.798000 | -0.1895 | 0.793200 | -0.1901 |
| 1.0000 | 0.808867 | 0.0000 | 0.804509 | 0.0000 | 0.799029 | 0.0000 | 0.794000 | 0.0000 | 0.788400 | 0.0000 | 0.783558 | 0.0000 |

Table-4.14: Density ($\rho$) and Excess molar volume ($V^E$) of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 1.001509 | 0.0000 | 0.999900 | 0.0000 | 0.997549 | 0.0000 | 0.995318 | 0.0000 | 0.993491 | 0.0000 | 0.991432 | 0.0000 |
| 0.1006 | 0.955353 | -0.4426 | 0.951882 | -0.4233 | 0.948164 | -0.4122 | 0.945105 | -0.4301 | 0.940744 | -0.3862 | 0.939865 | -0.4295 |
| 0.2005 | 0.917694 | -0.6089 | 0.913223 | -0.5699 | 0.907800 | -0.5151 | 0.904700 | -0.5620 | 0.901576 | -0.5577 | 0.897520 | -0.5181 |
| 0.2991 | 0.888902 | -0.6360 | 0.884306 | -0.5952 | 0.877377 | -0.4775 | 0.871500 | -0.4413 | 0.867392 | -0.4034 | 0.863875 | -0.3800 |
| 0.3990 | 0.868135 | -0.6729 | 0.862923 | -0.6053 | 0.854900 | -0.4201 | 0.850000 | -0.4374 | 0.844600 | -0.3357 | 0.840400 | -0.2776 |
| 0.5026 | 0.850533 | -0.6315 | 0.844575 | -0.5190 | 0.837193 | -0.3426 | 0.832033 | -0.3594 | 0.829763 | -0.4236 | 0.824281 | -0.2862 |
| 0.6011 | 0.837747 | -0.6038 | 0.833266 | -0.5741 | 0.824900 | -0.3167 | 0.820000 | -0.3621 | 0.815500 | -0.2949 | 0.811900 | -0.2631 |
| 0.7022 | 0.826175 | -0.5015 | 0.821580 | -0.4647 | 0.813242 | -0.1790 | 0.808938 | -0.2806 | 0.803423 | -0.1334 | 0.801108 | -0.1939 |
| 0.7993 | 0.817406 | -0.4279 | 0.813000 | -0.4062 | 0.805200 | -0.1354 | 0.799000 | -0.1018 | 0.796400 | -0.1781 | 0.791700 | -0.0514 |
| 0.8998 | 0.808564 | -0.2435 | 0.803100 | -0.1307 | 0.797404 | -0.0163 | 0.791700 | -0.0289 | 0.787600 | 0.0193 | 0.784232 | 0.0378 |
| 1.0000 | 0.800501 | 0.0000 | 0.796323 | 0.0000 | 0.791910 | 0.0000 | 0.786000 | 0.0000 | 0.782407 | 0.0000 | 0.779224 | 0.0000 |

Table-4.15: Density ($\rho$) and Excess molar volume ($V^E$) of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | 303.15K | | 308.15K | | 313.15K | | 318.15K | | 323.15K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ | $\frac{\rho}{gcm^{-3}}$ | $\frac{V^E}{cm^3\ mol^{-1}}$ |
| 0.0000 | 0.998054 | 0.0000 | 0.995557 | 0.0000 | 0.993746 | 0.0000 | 0.991995 | 0.0000 | 0.989275 | 0.0000 | 0.987275 | 0.0000 |
| 0.1004 | 0.956443 | -0.7375 | 0.952396 | -0.7179 | 0.948346 | -0.6809 | 0.942400 | -0.6047 | 0.938000 | -0.5842 | 0.932805 | -0.5319 |
| 0.1988 | 0.914700 | -0.9712 | 0.910000 | -0.9346 | 0.905315 | -0.8765 | 0.901600 | -0.8673 | 0.897600 | -0.8665 | 0.893200 | -0.8434 |
| 0.3042 | 0.881500 | -1.0893 | 0.876600 | -1.0418 | 0.871100 | -0.9430 | 0.866056 | -0.8897 | 0.860291 | -0.8231 | 0.856393 | -0.8266 |
| 0.3990 | 0.859785 | -1.0801 | 0.854255 | -0.9989 | 0.850213 | -0.9565 | 0.845910 | -0.9377 | 0.840200 | -0.8684 | 0.836357 | -0.8832 |
| 0.5003 | 0.839451 | -1.1098 | 0.833500 | -0.9916 | 0.829056 | -0.9218 | 0.823880 | -0.8561 | 0.818468 | -0.7931 | 0.814430 | -0.8066 |
| 0.6000 | 0.823900 | -1.0378 | 0.819000 | -0.9713 | 0.812000 | -0.7270 | 0.806800 | -0.6535 | 0.802100 | -0.6298 | 0.797400 | -0.6045 |
| 0.7031 | 0.811045 | -0.9559 | 0.806673 | -0.9204 | 0.799200 | -0.6101 | 0.793100 | -0.4629 | 0.787500 | -0.3678 | 0.782386 | -0.3093 |
| 0.8026 | 0.800560 | -0.8439 | 0.795787 | -0.7719 | 0.788100 | -0.4082 | 0.781700 | -0.2205 | 0.776200 | -0.1227 | 0.771000 | -0.0517 |
| 0.8975 | 0.791200 | -0.6457 | 0.786698 | -0.5904 | 0.778683 | -0.1598 | 0.772700 | 0.0070 | 0.767200 | 0.1148 | 0.762112 | 0.1807 |
| 1.0000 | 0.778306 | 0.0000 | 0.774467 | 0.0000 | 0.771190 | 0.0000 | 0.766972 | 0.0000 | 0.762585 | 0.0000 | 0.758129 | 0.0000 |

Table-4.16: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Methanol + Water system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.8910 | 0.0000 | 0.0000 | 0.7890 | 0.0000 | 0.0000 | 0.7200 | 0.0000 | 0.0000 |
| 0.1002 | 1.3032 | 0.4539 | 4.7489 | 1.1316 | 0.3762 | 4.4831 | 1.0087 | 0.3159 | 4.1672 |
| 0.2000 | 1.5331 | 0.7233 | 3.9894 | 1.3108 | 0.5875 | 3.7161 | 1.1608 | 0.4941 | 3.4657 |
| 0.3001 | 1.5629 | 0.7910 | 3.3586 | 1.3555 | 0.6630 | 3.1977 | 1.1953 | 0.5537 | 2.9626 |
| 0.4006 | 1.4880 | 0.7523 | 2.9336 | 1.2870 | 0.6242 | 2.7633 | 1.1488 | 0.5316 | 2.5873 |
| 0.5012 | 1.3301 | 0.6290 | 2.5613 | 1.1737 | 0.5392 | 2.4605 | 1.0609 | 0.4671 | 2.3214 |
| 0.6006 | 1.1585 | 0.4899 | 2.2915 | 1.0221 | 0.4144 | 2.1677 | 0.9308 | 0.3611 | 2.0618 |
| 0.7012 | 1.0030 | 0.3658 | 2.1654 | 0.8943 | 0.3127 | 2.0534 | 0.8192 | 0.2670 | 1.8438 |
| 0.8040 | 0.8449 | 0.2383 | 2.1030 | 0.7601 | 0.2039 | 1.9816 | 0.7051 | 0.1766 | 1.8291 |
| 0.8991 | 0.6956 | 0.1160 | 2.0101 | 0.6404 | 0.1067 | 2.0097 | 0.5952 | 0.0856 | 1.7118 |
| 1.0000 | 0.5523 | 0.0000 | 0.0000 | 0.5108 | 0.0000 | 0.0000 | 0.4902 | 0.0000 | 0.0000 |

Table-4.17: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Ethanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.8910 | 0.0000 | 0.0000 | 0.7890 | 0.0000 | 0.0000 | 0.7200 | 0.0000 | 0.0000 | 0.6530 | 0.0000 | 0.0000 | 0.5960 | 0.0000 | 0.0000 | 0.5470 | 0.0000 | 0.0000 |
| 0.1005 | 1.7935 | 0.8656 | 7.2891 | 1.5043 | 0.6809 | 6.6666 | 1.3020 | 0.5515 | 6.0948 | 1.1348 | 0.4556 | 5.6780 | 0.9920 | 0.3728 | 5.2141 | 0.8784 | 0.3104 | 4.8235 |
| 0.1997 | 2.3177 | 1.3517 | 5.4759 | 1.8986 | 1.0399 | 4.9643 | 1.6219 | 0.8402 | 4.5667 | 1.3863 | 0.6802 | 4.2217 | 1.2015 | 0.5586 | 3.9130 | 1.0472 | 0.4577 | 3.5958 |
| 0.2992 | 2.3527 | 1.3470 | 4.0533 | 1.9764 | 1.0806 | 3.7739 | 1.7121 | 0.8977 | 3.5434 | 1.4809 | 0.7468 | 3.3470 | 1.2764 | 0.6088 | 3.0909 | 1.1176 | 0.5058 | 2.8737 |
| 0.3989 | 2.2529 | 1.2058 | 3.1954 | 1.9100 | 0.9755 | 2.9813 | 1.6760 | 0.8274 | 2.8384 | 1.4410 | 0.6778 | 2.6504 | 1.2470 | 0.5537 | 2.4481 | 1.0857 | 0.4506 | 2.2364 |
| 0.4988 | 2.1135 | 1.0232 | 2.6476 | 1.7946 | 0.8196 | 2.4405 | 1.5730 | 0.6887 | 2.3040 | 1.3656 | 0.5720 | 2.1709 | 1.1860 | 0.4659 | 1.9958 | 1.0569 | 0.3977 | 1.8881 |
| 0.6005 | 1.9440 | 0.8079 | 2.2390 | 1.6690 | 0.6510 | 2.0610 | 1.4810 | 0.5589 | 1.9751 | 1.2766 | 0.4508 | 1.8156 | 1.1330 | 0.3846 | 1.7285 | 1.0000 | 0.3152 | 1.5784 |
| 0.7019 | 1.7872 | 0.6035 | 1.9691 | 1.5458 | 0.4831 | 1.7909 | 1.3781 | 0.4167 | 1.7207 | 1.2000 | 0.3407 | 1.5963 | 1.0740 | 0.2962 | 1.5424 | 0.9585 | 0.2472 | 1.4256 |
| 0.8017 | 1.6420 | 0.4095 | 1.8046 | 1.4410 | 0.3323 | 1.6491 | 1.2800 | 0.2782 | 1.5416 | 1.1208 | 0.2274 | 1.4262 | 0.9975 | 0.1897 | 1.3271 | 0.8992 | 0.1608 | 1.2396 |
| 0.9002 | 1.4950 | 0.2124 | 1.7057 | 1.3244 | 0.1684 | 1.5139 | 1.1889 | 0.1456 | 1.4540 | 1.0390 | 0.1105 | 1.2511 | 0.9484 | 0.1099 | 1.3706 | 0.8467 | 0.0806 | 1.1141 |
| 1.0000 | 1.3355 | 0.0000 | 0.0000 | 1.2060 | 0.0000 | 0.0000 | 1.0871 | 0.0000 | 0.0000 | 0.9655 | 0.0000 | 0.0000 | 0.8708 | 0.0000 | 0.0000 | 0.7952 | 0.0000 | 0.0000 |

Table-4.18: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of n-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.8910 | 0.0000 | 0.0000 | 0.7890 | 0.0000 | 0.00000 | 0.7200 | 0.0000 | 0.0000 | 0.6530 | 0.0000 | 0.0000 | 0.5960 | 0.0000 | 0.0000 | 0.5470 | 0.0000 | 0.0000 |
| 0.1006 | 2.1021 | 1.1394 | 8.6311 | 1.7515 | 0.8994 | 7.9636 | 1.5129 | 0.7365 | 7.3733 | 1.2948 | 0.5930 | 6.7683 | 1.1304 | 0.4912 | 6.3011 | 0.9962 | 0.4120 | 5.8983 |
| 0.2005 | 2.5785 | 1.5389 | 5.6667 | 2.1625 | 1.2427 | 5.3333 | 1.8703 | 1.0335 | 5.0177 | 1.6148 | 0.8607 | 4.7507 | 1.4002 | 0.7150 | 4.4581 | 1.2317 | 0.6081 | 4.2457 |
| 0.2991 | 2.6730 | 1.5514 | 4.1427 | 2.2690 | 1.2772 | 3.9477 | 1.9640 | 1.0631 | 3.7174 | 1.7000 | 0.8907 | 3.5406 | 1.4750 | 0.7411 | 3.3300 | 1.3000 | 0.6348 | 3.1963 |
| 0.3990 | 2.6370 | 1.4259 | 3.2447 | 2.2212 | 1.1507 | 3.0439 | 1.9329 | 0.9620 | 2.8712 | 1.6671 | 0.7977 | 2.7150 | 1.4548 | 0.6681 | 2.5637 | 1.2716 | 0.5615 | 2.4298 |
| 0.5026 | 2.5150 | 1.2033 | 2.6039 | 2.1270 | 0.9682 | 2.4294 | 1.8490 | 0.7996 | 2.2659 | 1.5934 | 0.6569 | 2.1260 | 1.4110 | 0.5655 | 2.0488 | 1.2296 | 0.4697 | 1.9252 |
| 0.6011 | 2.3780 | 0.9630 | 2.1652 | 2.0240 | 0.7745 | 2.0117 | 1.7591 | 0.6293 | 1.8467 | 1.5359 | 0.5309 | 1.7688 | 1.3514 | 0.4459 | 1.6702 | 1.1917 | 0.3812 | 1.6079 |
| 0.7022 | 2.2530 | 0.7236 | 1.8525 | 1.9310 | 0.5811 | 1.7120 | 1.6960 | 0.4773 | 1.5805 | 1.4703 | 0.3896 | 1.4724 | 1.3080 | 0.3366 | 1.4228 | 1.1485 | 0.2827 | 1.3510 |
| 0.7993 | 2.1330 | 0.4849 | 1.6079 | 1.8568 | 0.4028 | 1.5245 | 1.6250 | 0.3143 | 1.3400 | 1.4210 | 0.2624 | 1.2727 | 1.2690 | 0.2297 | 1.2449 | 1.1160 | 0.1934 | 1.1864 |
| 0.8998 | 2.0184 | 0.2378 | 1.3904 | 1.7787 | 0.2086 | 1.3838 | 1.5732 | 0.1600 | 1.1899 | 1.3720 | 0.1268 | 1.0756 | 1.2250 | 0.1105 | 1.0481 | 1.0820 | 0.0967 | 1.0387 |
| 1.0000 | 1.9233 | 0.0000 | 0.0000 | 1.6951 | 0.0000 | 0.0000 | 1.5234 | 0.0000 | 0.0000 | 1.3380 | 0.0000 | 0.0000 | 1.1950 | 0.0000 | 0.0000 | 1.0520 | 0.0000 | 0.0000 |

Table-4.19: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of iso-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.8910 | 0.0000 | 0.0000 | 0.7890 | 0.0000 | 0.0000 | 0.7200 | 0.0000 | 0.0000 | 0.6530 | 0.0000 | 0.0000 | 0.5960 | 0.0000 | 0.0000 | 0.5470 | 0.0000 | 0.0000 |
| 0.1004 | 2.4034 | 1.4358 | 10.0734 | 1.9724 | 1.1170 | 9.2498 | 1.6673 | 0.8911 | 8.4652 | 1.4249 | 0.7242 | 7.8583 | 1.2196 | 0.5829 | 7.1956 | 1.0653 | 0.4837 | 6.7015 |
| 0.1988 | 3.0168 | 1.9678 | 6.6320 | 2.4691 | 1.5433 | 6.1586 | 2.0892 | 1.2537 | 5.7540 | 1.8599 | 1.1091 | 5.6951 | 1.5142 | 0.8348 | 5.0317 | 1.3131 | 0.6954 | 4.7354 |
| 0.3042 | 3.0102 | 1.8664 | 4.5714 | 2.5053 | 1.4975 | 4.3025 | 2.1421 | 1.2380 | 4.0752 | 1.8780 | 1.0695 | 3.9817 | 1.5729 | 0.8447 | 3.6382 | 1.3685 | 0.7098 | 3.4547 |
| 0.3990 | 2.8769 | 1.6404 | 3.5213 | 2.3939 | 1.3063 | 3.2900 | 2.0463 | 1.0757 | 3.1105 | 1.7515 | 0.8873 | 2.9460 | 1.5019 | 0.7267 | 2.7583 | 1.3064 | 0.6084 | 2.6142 |
| 0.5003 | 2.6332 | 1.2895 | 2.6909 | 2.1920 | 1.0120 | 2.4773 | 1.8866 | 0.8395 | 2.3551 | 1.6015 | 0.6736 | 2.1831 | 1.3811 | 0.5525 | 2.0434 | 1.1934 | 0.4509 | 1.8980 |
| 0.6000 | 2.4279 | 0.9694 | 2.1235 | 2.0400 | 0.7615 | 1.9468 | 1.7680 | 0.6398 | 1.8718 | 1.5000 | 0.5048 | 1.7096 | 1.3000 | 0.4151 | 1.6029 | 1.1150 | 0.3259 | 1.4403 |
| 0.7031 | 2.2460 | 0.6586 | 1.6627 | 1.8914 | 0.5023 | 1.4787 | 1.6446 | 0.4258 | 1.4355 | 1.4071 | 0.3372 | 1.3126 | 1.2243 | 0.2772 | 1.2299 | 1.0649 | 0.2245 | 1.1341 |
| 0.8026 | 2.1061 | 0.3836 | 1.2690 | 1.7954 | 0.2905 | 1.1141 | 1.5630 | 0.2500 | 1.1003 | 1.3430 | 0.1957 | 0.9940 | 1.1810 | 0.1698 | 0.9798 | 1.0270 | 0.1339 | 0.8819 |
| 0.8975 | 2.0233 | 0.1612 | 0.9026 | 1.7276 | 0.1033 | 0.6705 | 1.5101 | 0.1005 | 0.7486 | 1.3053 | 0.0789 | 0.6775 | 1.1382 | 0.0618 | 0.6072 | 1.0060 | 0.0596 | 0.6639 |
| 1.0000 | 2.0257 | 0.0000 | 0.0000 | 1.7639 | 0.0000 | 0.0000 | 1.5220 | 0.0000 | 0.0000 | 1.3179 | 0.0000 | 0.0000 | 1.1516 | 0.0000 | 0.0000 | 1.0075 | 0.0000 | 0.0000 |

Table-4.20: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.9044 | 0.0000 | 0.0000 | 0.7962 | 0.0000 | 0.0000 | 0.7252 | 0.0000 | 0.0000 |
| 0.1002 | 1.3167 | 0.4560 | 4.7147 | 1.1233 | 0.3618 | 4.3114 | 0.9951 | 0.2978 | 3.9445 |
| 0.2000 | 1.5410 | 0.7216 | 3.9474 | 1.3415 | 0.6130 | 3.8158 | 1.1633 | 0.4927 | 3.4432 |
| 0.3001 | 1.5767 | 0.7967 | 3.3509 | 1.3626 | 0.6657 | 3.1924 | 1.2065 | 0.5617 | 2.9831 |
| 0.4006 | 1.4921 | 0.7499 | 2.9079 | 1.2886 | 0.6221 | 2.7458 | 1.1533 | 0.5335 | 2.5858 |
| 0.5012 | 1.3388 | 0.6324 | 2.5577 | 1.1766 | 0.5392 | 2.4523 | 1.0580 | 0.4620 | 2.2960 |
| 0.6006 | 1.1671 | 0.4945 | 2.2975 | 1.0297 | 0.4199 | 2.1836 | 0.9313 | 0.3581 | 2.0234 |
| 0.7012 | 1.0074 | 0.3674 | 2.1652 | 0.8985 | 0.3153 | 2.0630 | 0.8230 | 0.2720 | 1.9150 |
| 0.8004 | 0.8406 | 0.2311 | 2.0124 | 0.7571 | 0.1990 | 1.9092 | 0.7026 | 0.1725 | 1.7640 |
| 0.8991 | 0.6969 | 0.1164 | 2.0148 | 0.6365 | 0.1024 | 1.9327 | 0.5961 | 0.0862 | 1.7221 |
| 1.0000 | 0.5523 | 0.0000 | 0.0000 | 0.5108 | 0.0000 | 0.0000 | 0.4902 | 0.0000 | 0.0000 |

Table-4.21: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.9044 | 0.0000 | 0.0000 | 0.7962 | 0.0000 | 0.0000 | 0.7252 | 0.0000 | 0.0000 | 0.6583 | 0.0000 | 0.0000 | 0.6014 | 0.0000 | 0.0000 | 0.5502 | 0.0000 | 0.0000 |
| 0.1005 | 1.8570 | 0.9165 | 7.5253 | 1.5825 | 0.7525 | 7.1377 | 1.3374 | 0.5821 | 6.3205 | 1.1544 | 0.4702 | 5.7870 | 1.0121 | 0.3879 | 5.3463 | 0.8911 | 0.3201 | 4.9233 |
| 0.1997 | 2.3268 | 1.3492 | 5.4259 | 1.9122 | 1.0472 | 4.9635 | 1.6306 | 0.8443 | 4.5641 | 1.3976 | 0.6869 | 4.2317 | 1.2109 | 0.5634 | 3.9166 | 1.0565 | 0.4643 | 3.6217 |
| 0.2992 | 2.3547 | 1.3384 | 4.0075 | 1.9741 | 1.0726 | 3.7381 | 1.7056 | 0.8870 | 3.5011 | 1.4750 | 0.7368 | 3.3010 | 1.2824 | 0.6106 | 3.0831 | 1.1236 | 0.5092 | 2.8792 |
| 0.3989 | 2.2476 | 1.1911 | 3.1482 | 1.8895 | 0.9499 | 2.9135 | 1.6490 | 0.7967 | 2.7526 | 1.4290 | 0.6620 | 2.5952 | 1.2520 | 0.5549 | 2.4421 | 1.1000 | 0.4627 | 2.2763 |
| 0.4988 | 2.1028 | 1.0043 | 2.5974 | 1.7780 | 0.7986 | 2.3852 | 1.5540 | 0.6666 | 2.2410 | 1.3630 | 0.5661 | 2.1469 | 1.1947 | 0.4713 | 2.0069 | 1.0530 | 0.3918 | 1.8616 |
| 0.6005 | 1.9360 | 0.7931 | 2.1971 | 1.6590 | 0.6374 | 2.0209 | 1.4474 | 0.5227 | 1.8675 | 1.2760 | 0.4475 | 1.8000 | 1.1280 | 0.3769 | 1.6951 | 0.9953 | 0.3088 | 1.5486 |
| 0.7019 | 1.7713 | 0.5823 | 1.9052 | 1.5345 | 0.4690 | 1.7430 | 1.3646 | 0.4012 | 1.6636 | 1.1974 | 0.3360 | 1.5743 | 1.0639 | 0.2841 | 1.4845 | 0.9431 | 0.2305 | 1.3397 |
| 0.8017 | 1.6169 | 0.3808 | 1.6892 | 1.4170 | 0.3063 | 1.5322 | 1.2635 | 0.2603 | 1.4511 | 1.1230 | 0.2281 | 1.4283 | 1.0000 | 0.1908 | 1.3317 | 0.8890 | 0.1498 | 1.1606 |
| 0.9002 | 1.4720 | 0.1875 | 1.5166 | 1.3022 | 0.1451 | 1.3153 | 1.1702 | 0.1262 | 1.2704 | 1.0457 | 0.1164 | 1.3132 | 0.9303 | 0.0911 | 1.1465 | 0.8431 | 0.0766 | 1.0600 |
| 1.0000 | 1.3355 | 0.0000 | 0.0000 | 1.2060 | 0.0000 | 0.0000 | 1.0871 | 0.0000 | 0.0000 | 0.9655 | 0.0000 | 0.0000 | 0.8708 | 0.0000 | 0.0000 | 0.7952 | 0.0000 | 0.0000 |

Table-4.22: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.9044 | 0.0000 | 0.0000 | 0.7962 | 0.0000 | 0.0000 | 0.7252 | 0.0000 | 0.0000 | 0.6583 | 0.0000 | 0.0000 | 0.6014 | 0.0000 | 0.0000 | 0.5502 | 0.0000 | 0.0000 |
| 0.1006 | 2.1557 | 1.1801 | 8.7616 | 1.7900 | 0.9309 | 8.1138 | 1.5451 | 0.7637 | 7.5345 | 1.3309 | 0.6237 | 6.9874 | 1.1614 | 0.5164 | 6.5002 | 1.0250 | 0.4367 | 6.1368 |
| 0.2005 | 2.6360 | 1.5839 | 5.7299 | 2.2003 | 1.2739 | 5.3962 | 1.8961 | 1.0546 | 5.0675 | 1.6459 | 0.8864 | 4.8247 | 1.4281 | 0.7367 | 4.5250 | 1.2584 | 0.6298 | 4.3300 |
| 0.2991 | 2.7155 | 1.5821 | 4.1681 | 2.2750 | 1.2769 | 3.9300 | 1.9655 | 1.0601 | 3.6972 | 1.7130 | 0.8982 | 3.5445 | 1.5000 | 0.7595 | 3.3670 | 1.3140 | 0.6428 | 3.2047 |
| 0.3990 | 2.6381 | 1.4160 | 3.2090 | 2.2260 | 1.1496 | 3.0301 | 1.9359 | 0.9607 | 2.8595 | 1.6744 | 0.7995 | 2.7067 | 1.4562 | 0.6623 | 2.5300 | 1.2784 | 0.5612 | 2.4104 |
| 0.5026 | 2.4770 | 1.1556 | 2.5134 | 2.1130 | 0.9490 | 2.3850 | 1.8460 | 0.7929 | 2.2452 | 1.6140 | 0.6720 | 2.1538 | 1.3970 | 0.5438 | 1.9725 | 1.2380 | 0.4697 | 1.9085 |
| 0.6011 | 2.3290 | 0.9056 | 2.0536 | 2.0190 | 0.7650 | 1.9864 | 1.7670 | 0.6340 | 1.8535 | 1.5490 | 0.5384 | 1.7812 | 1.3500 | 0.4363 | 1.6280 | 1.1975 | 0.3773 | 1.5782 |
| 0.7022 | 2.2177 | 0.6815 | 1.7558 | 1.9082 | 0.5547 | 1.6424 | 1.6950 | 0.4737 | 1.5674 | 1.4822 | 0.3962 | 1.4871 | 1.3015 | 0.3212 | 1.3554 | 1.1635 | 0.2864 | 1.3510 |
| 0.7993 | 2.1120 | 0.4590 | 1.5276 | 1.8350 | 0.3784 | 1.4396 | 1.6459 | 0.3334 | 1.4108 | 1.4381 | 0.2741 | 1.3184 | 1.2665 | 0.2176 | 1.1754 | 1.1242 | 0.1886 | 1.1446 |
| 0.8998 | 2.0125 | 0.2293 | 1.3415 | 1.7610 | 0.1895 | 1.2628 | 1.5779 | 0.1637 | 1.2146 | 1.3900 | 0.1396 | 1.1739 | 1.2317 | 0.1069 | 1.0070 | 1.0940 | 0.0938 | 0.9945 |
| 1.0000 | 1.9233 | 0.0000 | 0.0000 | 1.6951 | 0.0000 | 0.0000 | 1.5234 | 0.0000 | 0.0000 | 1.3430 | 0.0000 | 0.0000 | 1.2060 | 0.0000 | 0.0000 | 1.0690 | 0.0000 | 0.0000 |

Table-4.23: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.9044 | 0.0000 | 0.0000 | 0.7962 | 0.0000 | 0.0000 | 0.7252 | 0.0000 | 0.0000 | 0.6583 | 0.0000 | 0.0000 | 0.6014 | 0.0000 | 0.0000 | 0.5502 | 0.0000 | 0.0000 |
| 0.1004 | 2.4634 | 1.4827 | 10.1980 | 2.0193 | 1.1569 | 9.4202 | 1.7103 | 0.9290 | 8.6751 | 1.4576 | 0.7518 | 8.0291 | 1.2465 | 0.6045 | 7.3471 | 1.0960 | 0.5113 | 6.9567 |
| 0.1988 | 3.0656 | 2.0040 | 6.6578 | 2.4773 | 1.5447 | 6.1337 | 2.1164 | 1.2760 | 5.7989 | 1.7935 | 1.0377 | 5.4259 | 1.5238 | 0.8395 | 5.0261 | 1.3243 | 0.7038 | 4.7593 |
| 0.3042 | 3.0979 | 1.9421 | 4.6580 | 2.5347 | 1.5205 | 4.3278 | 2.1543 | 1.2457 | 4.0785 | 1.8193 | 1.0062 | 3.8049 | 1.5681 | 0.8353 | 3.5941 | 1.3408 | 0.6794 | 3.3386 |
| 0.3990 | 2.8941 | 1.6465 | 3.5090 | 2.4050 | 1.3114 | 3.2865 | 2.0408 | 1.0660 | 3.0812 | 1.7513 | 0.8829 | 2.9253 | 1.4985 | 0.7192 | 2.7263 | 1.3065 | 0.6061 | 2.5996 |
| 0.5003 | 2.6690 | 1.3152 | 2.7151 | 2.2336 | 1.0482 | 2.5343 | 1.9194 | 0.8686 | 2.4097 | 1.6510 | 0.7194 | 2.2887 | 1.4188 | 0.5864 | 2.1332 | 1.2308 | 0.4861 | 2.0097 |
| 0.6000 | 2.4540 | 0.9868 | 2.1433 | 2.0750 | 0.7918 | 2.0026 | 1.7856 | 0.6541 | 1.9010 | 1.5460 | 0.5476 | 1.8219 | 1.3326 | 0.4445 | 1.6909 | 1.1673 | 0.3763 | 1.6213 |
| 0.7031 | 2.2670 | 0.6726 | 1.6861 | 1.9260 | 0.5332 | 1.5526 | 1.6670 | 0.4457 | 1.4903 | 1.4360 | 0.3635 | 1.3983 | 1.2550 | 0.3054 | 1.3359 | 1.0958 | 0.2539 | 1.2624 |
| 0.8026 | 2.1072 | 0.3796 | 1.2537 | 1.7975 | 0.2899 | 1.1103 | 1.5729 | 0.2581 | 1.1312 | 1.3508 | 0.2017 | 1.0205 | 1.1922 | 0.1792 | 1.0280 | 1.0484 | 0.1542 | 1.0044 |
| 0.8975 | 2.0703 | 0.2053 | 1.1353 | 1.7732 | 0.1474 | 0.9433 | 1.5490 | 0.1383 | 1.0167 | 1.3372 | 0.1098 | 0.9314 | 1.1669 | 0.0895 | 0.8674 | 1.0219 | 0.0749 | 0.8277 |
| 1.0000 | 2.0257 | 0.0000 | 0.0000 | 1.7639 | 0.0000 | 0.0000 | 1.5220 | 0.0000 | 0.0000 | 1.3179 | 0.0000 | 0.0000 | 1.1516 | 0.0000 | 0.0000 | 1.0075 | 0.0000 | 0.0000 |

Table-4.24: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 1.0951 | 0.0000 | 0.0000 | 0.9688 | 0.0000 | 0.0000 | 0.8820 | 0.0000 | 0.0000 |
| 0.1002 | 1.5115 | 0.4889 | 4.3346 | 1.3060 | 0.3974 | 4.0243 | 1.1622 | 0.3306 | 3.7125 |
| 0.2000 | 1.7024 | 0.7474 | 3.6130 | 1.4474 | 0.5951 | 3.3095 | 1.2813 | 0.4970 | 3.0681 |
| 0.3001 | 1.6640 | 0.7722 | 2.9697 | 1.4310 | 0.6315 | 2.7717 | 1.2710 | 0.5315 | 2.5788 |
| 0.4006 | 1.5398 | 0.7073 | 2.5611 | 1.3364 | 0.5868 | 2.4077 | 1.1968 | 0.4997 | 2.2511 |
| 0.5012 | 1.3670 | 0.5899 | 2.2592 | 1.1821 | 0.4792 | 2.0793 | 1.0750 | 0.4179 | 1.9692 |
| 0.6006 | 1.1840 | 0.4580 | 2.0387 | 1.0441 | 0.3845 | 1.9145 | 0.9480 | 0.3282 | 1.7715 |
| 0.7012 | 1.0050 | 0.3273 | 1.8808 | 0.9050 | 0.2866 | 1.8172 | 0.8250 | 0.2408 | 1.6471 |
| 0.8004 | 0.8420 | 0.2088 | 1.7840 | 0.7650 | 0.1846 | 1.7288 | 0.7050 | 0.1539 | 1.5411 |
| 0.8991 | 0.6830 | 0.0912 | 1.5791 | 0.6289 | 0.0841 | 1.5822 | 0.5875 | 0.0674 | 1.3427 |
| 1.0000 | 0.5523 | 0.0000 | 0.0000 | 0.5108 | 0.0000 | 0.0000 | 0.4902 | 0.0000 | 0.0000 |

Table-4.25: Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 1.0951 | 0.0000 | 0.0000 | 0.9688 | 0.0000 | 0.0000 | 0.8820 | 0.0000 | 0.0000 | 0.7973 | 0.0000 | 0.0000 | 0.7259 | 0.0000 | 0.0000 | 0.6630 | 0.0000 | 0.0000 |
| 0.1005 | 2.0582 | 0.9411 | 6.7593 | 1.7369 | 0.7465 | 6.2144 | 1.5057 | 0.6050 | 5.6838 | 1.3051 | 0.4923 | 5.2382 | 1.1310 | 0.3917 | 4.7034 | 0.9939 | 0.3187 | 4.2770 |
| 0.1997 | 2.4527 | 1.3133 | 4.7973 | 2.0384 | 1.0263 | 4.3807 | 1.7306 | 0.8110 | 3.9563 | 1.4738 | 0.6454 | 3.6047 | 1.2731 | 0.5204 | 3.2879 | 1.1205 | 0.4330 | 3.0562 |
| 0.2992 | 2.4203 | 1.2582 | 3.4990 | 2.0352 | 1.0008 | 3.2276 | 1.7622 | 0.8232 | 3.0024 | 1.5216 | 0.6773 | 2.8091 | 1.3146 | 0.5480 | 2.5724 | 1.1545 | 0.4545 | 2.3860 |
| 0.3989 | 2.2946 | 1.1093 | 2.7548 | 1.9309 | 0.8737 | 2.5121 | 1.6839 | 0.7252 | 2.3492 | 1.4452 | 0.5846 | 2.1620 | 1.2647 | 0.4841 | 2.0125 | 1.1104 | 0.3975 | 1.8482 |
| 0.4988 | 2.1316 | 0.9225 | 2.2681 | 1.8110 | 0.7304 | 2.0654 | 1.5915 | 0.6126 | 1.9438 | 1.3828 | 0.5056 | 1.8206 | 1.2026 | 0.4077 | 1.6562 | 1.0695 | 0.3435 | 1.5498 |
| 0.6005 | 1.9577 | 0.7240 | 1.9248 | 1.6838 | 0.5788 | 1.7558 | 1.4803 | 0.4803 | 1.6351 | 1.3064 | 0.4120 | 1.5792 | 1.1493 | 0.3396 | 1.4598 | 1.0233 | 0.2838 | 1.3540 |
| 0.7019 | 1.7759 | 0.5171 | 1.6450 | 1.5359 | 0.4061 | 1.4676 | 1.3635 | 0.3421 | 1.3805 | 1.1999 | 0.2879 | 1.3114 | 1.0691 | 0.2443 | 1.2398 | 0.9533 | 0.2000 | 1.1256 |
| 0.8017 | 1.6141 | 0.3302 | 1.4396 | 1.4156 | 0.2608 | 1.2810 | 1.2614 | 0.2185 | 1.1964 | 1.1227 | 0.1932 | 1.1877 | 0.9918 | 0.1518 | 1.0453 | 0.8945 | 0.1275 | 0.9669 |
| 0.9002 | 1.5050 | 0.1958 | 1.5510 | 1.3153 | 0.1354 | 1.2094 | 1.1832 | 0.1186 | 1.1757 | 1.0542 | 0.1070 | 1.1912 | 0.9417 | 0.0865 | 1.0728 | 0.8542 | 0.0733 | 0.9991 |
| 1.0000 | 1.3355 | 0.0000 | 0.0000 | 1.2060 | 0.0000 | 0.0000 | 1.0871 | 0.0000 | 0.0000 | 0.9655 | 0.0000 | 0.0000 | 0.8708 | 0.0000 | 0.0000 | 0.7952 | 0.0000 | 0.0000 |

Table-4.26. Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 1.0951 | 0.0000 | 0.0000 | 0.9688 | 0.0000 | 0.0000 | 0.8820 | 0.0000 | 0.0000 | 0.7973 | 0.0000 | 0.0000 | 0.7259 | 0.0000 | 0.0000 | 0.6630 | 0.0000 | 0.0000 |
| 0.1006 | 2.3027 | 1.1438 | 7.5881 | 1.9310 | 0.9061 | 7.0011 | 1.6708 | 0.7389 | 6.4529 | 1.4515 | 0.6096 | 6.0198 | 1.2643 | 0.5000 | 5.5631 | 1.1218 | 0.4248 | 5.2603 |
| 0.2005 | 2.7751 | 1.5491 | 5.0962 | 2.3099 | 1.2261 | 4.7206 | 1.9957 | 1.0116 | 4.4104 | 1.7426 | 0.8540 | 4.2014 | 1.5069 | 0.7024 | 3.9155 | 1.3257 | 0.5933 | 3.7012 |
| 0.2991 | 2.8004 | 1.5043 | 3.6751 | 2.3390 | 1.1937 | 3.4062 | 2.0310 | 0.9923 | 3.1989 | 1.7570 | 0.8198 | 2.9976 | 1.5280 | 0.6819 | 2.8193 | 1.3370 | 0.5677 | 2.6368 |
| 0.3990 | 2.7025 | 1.3314 | 2.8299 | 2.2661 | 1.0550 | 2.6127 | 1.9740 | 0.8771 | 2.4502 | 1.7004 | 0.7112 | 2.2589 | 1.4886 | 0.5980 | 2.1422 | 1.3026 | 0.4942 | 1.9894 |
| 0.5026 | 2.5500 | 1.0966 | 2.2488 | 2.1629 | 0.8795 | 2.0878 | 1.8718 | 0.7109 | 1.9111 | 1.6369 | 0.5907 | 1.7905 | 1.4350 | 0.4959 | 1.6959 | 1.2675 | 0.4163 | 1.5928 |
| 0.6011 | 2.4080 | 0.8717 | 1.8743 | 2.0444 | 0.6884 | 1.7121 | 1.7985 | 0.5734 | 1.6013 | 1.5851 | 0.4817 | 1.5107 | 1.3890 | 0.4013 | 1.4218 | 1.2240 | 0.3301 | 1.3110 |
| 0.7022 | 2.2630 | 0.6367 | 1.5799 | 1.9520 | 0.5170 | 1.4714 | 1.7230 | 0.4284 | 1.3670 | 1.5178 | 0.3524 | 1.2633 | 1.3440 | 0.3037 | 1.2251 | 1.1900 | 0.2501 | 1.1281 |
| 0.7993 | 2.1550 | 0.4373 | 1.4137 | 1.8660 | 0.3509 | 1.2985 | 1.6560 | 0.2908 | 1.2039 | 1.4632 | 0.2350 | 1.0914 | 1.2968 | 0.2034 | 1.0637 | 1.1486 | 0.1622 | 0.9491 |
| 0.8998 | 2.0310 | 0.2132 | 1.2303 | 1.7799 | 0.1772 | 1.1632 | 1.5819 | 0.1397 | 1.0253 | 1.4151 | 0.1183 | 0.9686 | 1.2498 | 0.0987 | 0.9124 | 1.1239 | 0.0870 | 0.8936 |
| 1.0000 | 1.9233 | 0.0000 | 0.0000 | 1.6951 | 0.0000 | 0.0000 | 1.5234 | 0.0000 | 0.0000 | 1.3689 | 0.0000 | 0.0000 | 1.2118 | 0.0000 | 0.0000 | 1.0899 | 0.0000 | 0.0000 |

Table-4.27. Viscosity ($\eta$), Excess viscosity ($\eta^E$) and Interaction parameter ($\varepsilon$) of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | 298.15K | | | 303.15K | | | 308.15K | | | 313.15K | | | 318.15K | | | 323.15K | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ | $\frac{\eta}{mPa.s}$ | $\frac{\eta^E}{mPa.s}$ | $\varepsilon$ |
| 0.0000 | 0.9044 | 0.0000 | 0.0000 | 0.7962 | 0.0000 | 0.0000 | 0.7252 | 0.0000 | 0.0000 | 0.6583 | 0.0000 | 0.0000 | 0.6014 | 0.0000 | 0.0000 | 0.5502 | 0.0000 | 0.0000 |
| 0.1004 | 2.7183 | 1.7377 | 11.2884 | 2.1879 | 1.3255 | 10.3079 | 1.8668 | 1.0855 | 9.6446 | 1.5758 | 0.8700 | 8.8924 | 1.3545 | 0.7126 | 8.2674 | 1.1768 | 0.5921 | 7.7438 |
| 0.1988 | 3.1549 | 2.0932 | 6.8380 | 2.5590 | 1.6264 | 6.3375 | 2.1736 | 1.3333 | 5.9665 | 1.8553 | 1.0996 | 5.6386 | 1.5817 | 0.8974 | 5.2602 | 1.3860 | 0.7654 | 5.0448 |
| 0.3042 | 3.1503 | 1.9945 | 4.7374 | 2.6145 | 1.6004 | 4.4743 | 2.2323 | 1.3236 | 4.2465 | 1.9050 | 1.0919 | 4.0224 | 1.6119 | 0.8791 | 3.7242 | 1.4015 | 0.7401 | 3.5476 |
| 0.3990 | 3.0173 | 1.7697 | 3.6827 | 2.4771 | 1.3835 | 3.4097 | 2.1241 | 1.1493 | 3.2479 | 1.8061 | 0.9377 | 3.0538 | 1.5554 | 0.7761 | 2.8818 | 1.3447 | 0.6442 | 2.7198 |
| 0.5003 | 2.7680 | 1.4142 | 2.8608 | 2.2800 | 1.0946 | 2.6166 | 1.9606 | 0.9098 | 2.4947 | 1.6704 | 0.7388 | 2.3355 | 1.4490 | 0.6166 | 2.2174 | 1.2524 | 0.5077 | 2.0793 |
| 0.6000 | 2.5340 | 1.0669 | 2.2770 | 2.1140 | 0.8308 | 2.0802 | 1.8330 | 0.7016 | 2.0102 | 1.5630 | 0.5646 | 1.8675 | 1.3550 | 0.4669 | 1.7605 | 1.1740 | 0.3830 | 1.6453 |
| 0.7031 | 2.3218 | 0.7274 | 1.8004 | 1.9618 | 0.5690 | 1.6408 | 1.7035 | 0.4821 | 1.5939 | 1.4645 | 0.3920 | 1.4925 | 1.2710 | 0.3215 | 1.3967 | 1.1088 | 0.2669 | 1.3193 |
| 0.8026 | 2.1501 | 0.4225 | 1.3811 | 1.8419 | 0.3344 | 1.2644 | 1.6048 | 0.2899 | 1.2577 | 1.3969 | 0.2477 | 1.2321 | 1.2183 | 0.2053 | 1.1650 | 1.0699 | 0.1758 | 1.1331 |
| 0.8975 | 2.0820 | 0.2170 | 1.1966 | 1.7779 | 0.1521 | 0.9723 | 1.5507 | 0.1400 | 1.0285 | 1.3381 | 0.1107 | 0.9383 | 1.1668 | 0.0894 | 0.8667 | 1.0207 | 0.0737 | 0.8148 |
| 1.0000 | 2.0257 | 0.0000 | 0.0000 | 1.7639 | 0.0000 | 0.0000 | 1.5220 | 0.0000 | 0.0000 | 1.3179 | 0.0000 | 0.0000 | 1.1516 | 0.0000 | 0.0000 | 1.0075 | 0.0000 | 0.0000 |

Table 4.28: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Methanol + Water system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | |
|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K |
| 0.0000 | 10.5924 | 10.4672 | 10.4095 | 0.0000 | 0.0000 | 0.0000 |
| 0.1002 | 11.6008 | 11.4469 | 11.3475 | 1.0685 | 1.0288 | 0.9736 |
| 0.2000 | 12.0608 | 11.8753 | 11.7674 | 1.5884 | 1.5060 | 1.4289 |
| 0.3001 | 12.1629 | 12.0157 | 11.8996 | 1.7505 | 1.6954 | 1.5967 |
| 0.4006 | 12.1040 | 11.9516 | 11.8670 | 1.7519 | 1.6805 | 1.5998 |
| 0.5012 | 11.8891 | 11.7834 | 11.7327 | 1.5973 | 1.5616 | 1.5012 |
| 0.6006 | 11.6034 | 11.4939 | 11.4567 | 1.3712 | 1.3207 | 1.2606 |
| 0.7012 | 11.3032 | 11.2177 | 11.1938 | 1.1314 | 1.0938 | 1.0334 |
| 0.8040 | 10.9362 | 10.8645 | 10.8667 | 0.8261 | 0.7909 | 0.7428 |
| 0.8991 | 10.5100 | 10.4915 | 10.4900 | 0.4569 | 0.4645 | 0.3999 |
| 1.0000 | 9.9926 | 9.9776 | 10.0542 | 0.0000 | 0.0000 | 0.0000 |

Table 4.29: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Ethanol +Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 11.4927 | 11.3826 | 11.3400 | 11.2745 | 11.2183 | 11.1701 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1005 | 13.3086 | 13.0911 | 12.9469 | 12.8080 | 12.6674 | 12.5509 | 1.6630 | 1.5471 | 1.4446 | 1.3726 | 1.2877 | 1.2172 |
| 0.1997 | 14.0094 | 13.7506 | 13.5847 | 13.4096 | 13.2574 | 13.1122 | 2.2128 | 2.0472 | 1.9221 | 1.8156 | 1.7184 | 1.6169 |
| 0.2992 | 14.1078 | 13.9145 | 13.7906 | 13.6486 | 13.4875 | 13.3606 | 2.1598 | 2.0512 | 1.9673 | 1.8953 | 1.7888 | 1.7033 |
| 0.3989 | 14.0689 | 13.8998 | 13.8070 | 13.6544 | 13.5038 | 13.3582 | 1.9691 | 1.8763 | 1.8227 | 1.7416 | 1.6450 | 1.5386 |
| 0.4988 | 13.9640 | 13.7980 | 13.7038 | 13.5736 | 13.4315 | 13.3453 | 1.7122 | 1.6140 | 1.5581 | 1.5010 | 1.4123 | 1.3630 |
| 0.6005 | 13.8043 | 13.6647 | 13.6034 | 13.4549 | 13.3707 | 13.2621 | 1.3978 | 1.3172 | 1.2935 | 1.2195 | 1.1882 | 1.1143 |
| 0.7019 | 13.6355 | 13.5111 | 13.4611 | 13.3385 | 13.2731 | 13.1924 | 1.0746 | 1.0007 | 0.9875 | 0.9408 | 0.9278 | 0.8795 |
| 0.8017 | 13.4638 | 13.3732 | 13.3103 | 13.1976 | 13.1178 | 13.0646 | 0.7511 | 0.7024 | 0.6755 | 0.6403 | 0.6122 | 0.5891 |
| 0.9002 | 13.2637 | 13.1910 | 13.1527 | 13.0341 | 13.0172 | 12.9381 | 0.4011 | 0.3619 | 0.3588 | 0.3191 | 0.3535 | 0.3023 |
| 1.0000 | 13.0145 | 12.9894 | 12.9551 | 12.8747 | 12.8240 | 12.7984 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.30: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.1517 | 12.0526 | 12.0211 | 11.9667 | 11.9216 | 11.8844 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1006 | 14.3882 | 14.1778 | 14.0491 | 13.8896 | 13.7651 | 13.6466 | 1.9904 | 1.8746 | 1.7762 | 1.6747 | 1.5957 | 1.5212 |
| 0.2005 | 14.9981 | 14.8182 | 14.7002 | 14.5674 | 14.4345 | 14.3297 | 2.3560 | 2.2662 | 2.1772 | 2.1058 | 2.0190 | 1.9651 |
| 0.2991 | 15.1626 | 15.0185 | 14.9149 | 14.7960 | 14.6674 | 14.5697 | 2.2793 | 2.2209 | 2.1452 | 2.0911 | 2.0091 | 1.9690 |
| 0.3990 | 15.1869 | 15.0226 | 14.9317 | 14.8059 | 14.6956 | 14.5813 | 2.0592 | 1.9761 | 1.9120 | 1.8544 | 1.7912 | 1.7413 |
| 0.5026 | 15.1186 | 14.9658 | 14.8712 | 14.7439 | 14.6675 | 14.5469 | 1.7375 | 1.6613 | 1.5922 | 1.5367 | 1.5080 | 1.4588 |
| 0.6011 | 15.0178 | 14.8763 | 14.7840 | 14.6900 | 14.6005 | 14.5066 | 1.3957 | 1.3265 | 1.2585 | 1.2398 | 1.1983 | 1.1826 |
| 0.7022 | 14.9177 | 14.7910 | 14.7258 | 14.6134 | 14.5515 | 14.4480 | 1.0483 | 0.9894 | 0.9472 | 0.9136 | 0.9002 | 0.8818 |
| 0.7993 | 14.8078 | 14.7205 | 14.6440 | 14.5505 | 14.5025 | 14.4001 | 0.7009 | 0.6770 | 0.6225 | 0.6110 | 0.6121 | 0.6014 |
| 0.8998 | 14.6980 | 14.6440 | 14.5851 | 14.4860 | 14.4371 | 14.3400 | 0.3452 | 0.3502 | 0.3120 | 0.2984 | 0.2991 | 0.3006 |
| 1.0000 | 14.5979 | 14.5434 | 14.5238 | 14.4348 | 14.3848 | 14.2794 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.31: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Propanol + Water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.1517 | 12.0526 | 12.0211 | 11.9667 | 11.9216 | 11.8844 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1004 | 14.7149 | 14.4743 | 14.2931 | 14.1249 | 13.9511 | 13.8170 | 2.2971 | 2.1545 | 2.0141 | 1.9073 | 1.7853 | 1.6964 |
| 0.1988 | 15.3850 | 15.1506 | 14.9838 | 14.9367 | 14.6445 | 14.5041 | 2.7065 | 2.5690 | 2.4521 | 2.4733 | 2.2392 | 2.1520 |
| 0.3042 | 15.4701 | 15.2784 | 15.1432 | 15.0556 | 14.8428 | 14.7170 | 2.5122 | 2.4163 | 2.3408 | 2.3287 | 2.1811 | 2.1170 |
| 0.3990 | 15.4266 | 15.2339 | 15.1000 | 14.9543 | 14.8004 | 14.6781 | 2.2175 | 2.1195 | 2.0541 | 1.9906 | 1.9080 | 1.8550 |
| 0.5003 | 15.2630 | 15.0692 | 14.9489 | 14.7833 | 14.6515 | 14.5101 | 1.7854 | 1.6853 | 1.6429 | 1.5665 | 1.5126 | 1.4487 |
| 0.6000 | 15.1087 | 14.9370 | 14.8347 | 14.6674 | 14.5458 | 14.3838 | 1.3669 | 1.2877 | 1.2726 | 1.2015 | 1.1643 | 1.0878 |
| 0.7031 | 14.9589 | 14.7906 | 14.6933 | 14.5492 | 14.4326 | 14.3068 | 0.9439 | 0.8669 | 0.8664 | 0.8256 | 0.8003 | 0.7682 |
| 0.8026 | 14.8314 | 14.6917 | 14.5957 | 14.4618 | 14.3713 | 14.2468 | 0.5527 | 0.5033 | 0.5132 | 0.4895 | 0.4968 | 0.4741 |
| 0.8975 | 14.7591 | 14.6221 | 14.5346 | 14.4190 | 14.3032 | 14.2206 | 0.2289 | 0.1811 | 0.2084 | 0.2096 | 0.1978 | 0.2247 |
| 1.0000 | 14.8018 | 14.7137 | 14.5894 | 14.4655 | 14.3548 | 14.2371 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.32: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Methanol+0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | |
|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | | 298.15K | 303.15K | |
| 0.0000 | 10.6270 | 10.4904 | 10.4288 | 0.0000 | 0.0000 | 0.0000 |
| 0.1002 | 11.6237 | 11.4256 | 11.3108 | 1.0602 | 0.9866 | 0.9195 |
| 0.2000 | 12.0749 | 11.9333 | 11.7734 | 1.5748 | 1.5455 | 1.4195 |
| 0.3001 | 12.1838 | 12.0311 | 11.9280 | 1.7472 | 1.6946 | 1.6116 |
| 0.4006 | 12.1101 | 11.9539 | 11.8773 | 1.7372 | 1.6690 | 1.5986 |
| 0.5012 | 11.8963 | 11.7838 | 11.7212 | 1.5873 | 1.5504 | 1.4802 |
| 0.6006 | 11.6206 | 11.5122 | 11.4596 | 1.3746 | 1.3298 | 1.2558 |
| 0.7012 | 11.3149 | 11.2294 | 11.2097 | 1.1327 | 1.0986 | 1.0436 |
| 0.8004 | 10.9232 | 10.8556 | 10.8618 | 0.8040 | 0.7757 | 0.7328 |
| 0.8991 | 10.5141 | 10.4801 | 10.4990 | 0.4575 | 0.4507 | 0.4070 |
| 1.0000 | 9.9926 | 9.9776 | 10.0542 | 0.0000 | 0.0000 | 0.0000 |

Table 4.33: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 11.5273 | 11.4057 | 11.3593 | 11.2963 | 11.2447 | 11.1881 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1005 | 13.3940 | 13.2211 | 13.0184 | 12.8590 | 12.7298 | 12.5956 | 1.7172 | 1.6562 | 1.4987 | 1.4040 | 1.3263 | 1.2457 |
| 0.1997 | 14.0144 | 13.7629 | 13.5924 | 13.4263 | 13.2712 | 13.1246 | 2.1902 | 2.0409 | 1.9145 | 1.8146 | 1.7109 | 1.6149 |
| 0.2992 | 14.1174 | 13.9208 | 13.7918 | 13.6487 | 13.5079 | 13.3797 | 2.1452 | 2.0412 | 1.9550 | 1.8799 | 1.7905 | 1.7098 |
| 0.3989 | 14.0680 | 13.8782 | 13.7740 | 13.6421 | 13.5236 | 13.4042 | 1.9475 | 1.8407 | 1.7781 | 1.7158 | 1.6486 | 1.5738 |
| 0.4988 | 13.9527 | 13.7755 | 13.6722 | 13.5747 | 13.4564 | 13.3459 | 1.6835 | 1.5798 | 1.5169 | 1.4906 | 1.4236 | 1.3546 |
| 0.6005 | 13.7956 | 13.6475 | 13.5361 | 13.4508 | 13.3566 | 13.2466 | 1.3752 | 1.2908 | 1.2185 | 1.2061 | 1.1631 | 1.0915 |
| 0.7019 | 13.6139 | 13.4932 | 13.4309 | 13.3281 | 13.2485 | 13.1505 | 1.0427 | 0.9759 | 0.9515 | 0.9232 | 0.8948 | 0.8322 |
| 0.8017 | 13.4282 | 13.3333 | 13.2760 | 13.2027 | 13.1252 | 13.0354 | 0.7086 | 0.6580 | 0.6373 | 0.6402 | 0.6139 | 0.5564 |
| 0.9002 | 13.2277 | 13.1523 | 13.1138 | 13.0543 | 12.9717 | 12.9294 | 0.3616 | 0.3210 | 0.3180 | 0.3362 | 0.3047 | 0.2917 |
| 1.0000 | 13.0145 | 12.9894 | 12.9551 | 12.8757 | 12.8246 | 12.7984 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.34: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.1863 | 12.0758 | 12.0404 | 11.9885 | 11.9479 | 11.9023 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1006 | 14.4517 | 14.2377 | 14.1129 | 13.9609 | 13.8323 | 13.7186 | 2.0223 | 1.9137 | 1.8224 | 1.7253 | 1.6367 | 1.5728 |
| 0.2005 | 15.0521 | 14.8632 | 14.7413 | 14.6163 | 14.4925 | 14.3914 | 2.3811 | 2.2927 | 2.2024 | 2.1353 | 2.0511 | 2.0038 |
| 0.2991 | 15.2037 | 15.0297 | 14.9143 | 14.8134 | 14.7124 | 14.6017 | 2.2945 | 2.2159 | 2.1302 | 2.0903 | 2.0284 | 1.9755 |
| 0.3990 | 15.1875 | 15.0294 | 14.9353 | 14.8142 | 14.7000 | 14.5972 | 2.0367 | 1.9691 | 1.9028 | 1.8458 | 1.7701 | 1.7292 |
| 0.5026 | 15.0806 | 14.9486 | 14.8676 | 14.7791 | 14.6504 | 14.5701 | 1.6795 | 1.6326 | 1.5776 | 1.5562 | 1.4655 | 1.4514 |
| 0.6011 | 14.9659 | 14.8704 | 14.7928 | 14.7137 | 14.6024 | 14.5204 | 1.3266 | 1.3114 | 1.2578 | 1.2489 | 1.1751 | 1.1633 |
| 0.7022 | 14.8785 | 14.7630 | 14.7239 | 14.6345 | 14.5416 | 14.4812 | 0.9948 | 0.9544 | 0.9376 | 0.9214 | 0.8654 | 0.8795 |
| 0.7993 | 14.7844 | 14.6911 | 14.6759 | 14.5823 | 14.4955 | 14.4164 | 0.6660 | 0.6429 | 0.6481 | 0.6307 | 0.5804 | 0.5796 |
| 0.8998 | 14.6906 | 14.6132 | 14.5974 | 14.5185 | 14.4472 | 14.3672 | 0.3293 | 0.3170 | 0.3198 | 0.3200 | 0.2847 | 0.2873 |
| 1.0000 | 14.6035 | 14.5434 | 14.5268 | 14.4445 | 14.4090 | 14.3225 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.35: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.1863 | 12.0758 | 12.0404 | 11.9885 | 11.9479 | 11.9023 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1004 | 14.7828 | 14.5376 | 14.3637 | 14.1974 | 14.0247 | 13.9136 | 2.3339 | 2.1969 | 2.0674 | 1.9602 | 1.8352 | 1.7768 |
| 0.1988 | 15.4289 | 15.1651 | 15.0208 | 14.8455 | 14.6643 | 14.5309 | 2.7227 | 2.5649 | 2.4737 | 2.3645 | 2.2379 | 2.1644 |
| 0.3042 | 15.5419 | 15.3121 | 15.1705 | 14.9931 | 14.8491 | 14.6791 | 2.5599 | 2.4339 | 2.3546 | 2.2511 | 2.1690 | 2.0665 |
| 0.3990 | 15.4426 | 15.2528 | 15.1016 | 14.9653 | 14.8041 | 14.6845 | 2.2127 | 2.1245 | 2.0441 | 1.9885 | 1.8959 | 1.8506 |
| 0.5003 | 15.2983 | 15.1211 | 15.0050 | 14.8765 | 14.7260 | 14.5968 | 1.8034 | 1.7256 | 1.6894 | 1.6487 | 1.5739 | 1.5264 |
| 0.6000 | 15.1343 | 14.9823 | 14.8661 | 14.7545 | 14.6135 | 14.5073 | 1.3787 | 1.3238 | 1.2963 | 1.2798 | 1.2215 | 1.2041 |
| 0.7031 | 14.9791 | 14.8333 | 14.7323 | 14.6041 | 14.5001 | 14.3816 | 0.9538 | 0.9028 | 0.8997 | 0.8740 | 0.8599 | 0.8377 |
| 0.8026 | 14.8295 | 14.6922 | 14.6204 | 14.4792 | 14.3986 | 14.2965 | 0.5439 | 0.4992 | 0.5341 | 0.5027 | 0.5189 | 0.5203 |
| 0.8975 | 14.8161 | 14.6890 | 14.6133 | 14.4832 | 14.3711 | 14.2557 | 0.2824 | 0.2457 | 0.2851 | 0.2716 | 0.2630 | 0.2579 |
| 1.0000 | 14.8018 | 14.7137 | 14.5894 | 14.4655 | 14.3548 | 14.2371 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.36: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | |
|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 298.15K | 303.15K | 308.15K |
| 0.0000 | 11.0929 | 10.9741 | 10.9206 | 0.0000 | 0.0000 | 0.0000 |
| 0.1002 | 11.9559 | 11.7951 | 11.6978 | 0.9732 | 0.9209 | 0.8640 |
| 0.2000 | 12.3124 | 12.1169 | 12.0126 | 1.4395 | 1.3421 | 1.2652 |
| 0.3001 | 12.3164 | 12.1525 | 12.0607 | 1.5538 | 1.4775 | 1.4000 |
| 0.4006 | 12.1863 | 12.0450 | 11.9720 | 1.5342 | 1.4702 | 1.3984 |
| 0.5012 | 11.9525 | 11.7971 | 11.7625 | 1.4111 | 1.3224 | 1.2761 |
| 0.6006 | 11.6535 | 11.5444 | 11.5004 | 1.2214 | 1.1688 | 1.1001 |
| 0.7012 | 11.3086 | 11.2461 | 11.2105 | 0.9872 | 0.9708 | 0.8974 |
| 0.8004 | 10.9256 | 10.8802 | 10.8660 | 0.7134 | 0.7037 | 0.6388 |
| 0.8991 | 10.4640 | 10.4450 | 10.4576 | 0.3603 | 0.3668 | 0.3159 |
| 1.0000 | 9.9926 | 9.9776 | 10.0542 | 0.0000 | 0.0000 | 0.0000 |

Table 4.37: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 11.9932 | 11.8894 | 11.8511 | 11.7864 | 11.7312 | 11.6775 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1005 | 13.6429 | 13.4472 | 13.3100 | 13.1642 | 13.0119 | 12.8846 | 1.5471 | 1.4472 | 1.3480 | 1.2685 | 1.1709 | 1.0945 |
| 0.1997 | 14.1448 | 13.9252 | 13.7468 | 13.5662 | 13.4124 | 13.3004 | 1.9477 | 1.8161 | 1.6752 | 1.5628 | 1.4630 | 1.3991 |
| 0.2992 | 14.1859 | 13.9938 | 13.8679 | 13.7245 | 13.5729 | 13.4554 | 1.8871 | 1.7753 | 1.6865 | 1.6130 | 1.5146 | 1.4426 |
| 0.3989 | 14.1140 | 13.9240 | 13.8192 | 13.6600 | 13.5440 | 13.4246 | 1.7134 | 1.5958 | 1.5277 | 1.4401 | 1.3768 | 1.3000 |
| 0.4988 | 13.9806 | 13.8171 | 13.7318 | 13.6032 | 13.4680 | 13.3834 | 1.4780 | 1.3790 | 1.3300 | 1.2748 | 1.1916 | 1.1468 |
| 0.6005 | 13.8197 | 13.6887 | 13.6011 | 13.5113 | 13.4075 | 13.3205 | 1.2132 | 1.1387 | 1.0870 | 1.0724 | 1.0199 | 0.9699 |
| 0.7019 | 13.6183 | 13.4938 | 13.4301 | 13.3335 | 13.2578 | 13.1751 | 0.9082 | 0.8323 | 0.8041 | 0.7844 | 0.7594 | 0.7109 |
| 0.8017 | 13.4203 | 13.3279 | 13.2715 | 13.2011 | 13.1034 | 13.0490 | 0.6083 | 0.5566 | 0.5353 | 0.5435 | 0.4959 | 0.4729 |
| 0.9002 | 13.2782 | 13.1751 | 13.1361 | 13.0681 | 12.9992 | 12.9579 | 0.3656 | 0.2955 | 0.2912 | 0.3035 | 0.2840 | 0.2714 |
| 1.0000 | 13.0145 | 12.9894 | 12.9551 | 12.8730 | 12.8243 | 12.7984 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.38: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.6522 | 12.5595 | 12.5322 | 12.4786 | 12.4344 | 12.3918 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1006 | 14.6115 | 14.4220 | 14.2990 | 14.1730 | 14.0465 | 13.9484 | 1.7630 | 1.6629 | 1.5665 | 1.4910 | 1.4122 | 1.3572 |
| 0.2005 | 15.1738 | 14.9780 | 14.8658 | 14.7628 | 14.6232 | 14.5210 | 2.1304 | 2.0208 | 1.9343 | 1.8788 | 1.7904 | 1.7317 |
| 0.2991 | 15.2753 | 15.0907 | 14.9980 | 14.8816 | 14.7623 | 14.6464 | 2.0394 | 1.9378 | 1.8701 | 1.7982 | 1.7335 | 1.6616 |
| 0.3990 | 15.2456 | 15.0726 | 14.9916 | 14.8613 | 14.7635 | 14.6504 | 1.8149 | 1.7216 | 1.6648 | 1.5760 | 1.5362 | 1.4676 |
| 0.5026 | 15.1524 | 15.0092 | 14.9090 | 14.8178 | 14.7135 | 14.6289 | 1.5195 | 1.4527 | 1.3757 | 1.3230 | 1.2803 | 1.2407 |
| 0.6011 | 15.0480 | 14.9013 | 14.8445 | 14.7721 | 14.6732 | 14.5759 | 1.2228 | 1.1493 | 1.1151 | 1.0781 | 1.0442 | 0.9923 |
| 0.7022 | 14.9285 | 14.8203 | 14.7711 | 14.6944 | 14.6255 | 14.5361 | 0.9061 | 0.8677 | 0.8404 | 0.7960 | 0.7957 | 0.7521 |
| 0.7993 | 14.8337 | 14.7332 | 14.6950 | 14.6312 | 14.5541 | 14.4728 | 0.6218 | 0.5880 | 0.5709 | 0.5365 | 0.5313 | 0.4963 |
| 0.8998 | 14.7137 | 14.6450 | 14.6027 | 14.5681 | 14.4859 | 14.4399 | 0.3058 | 0.3005 | 0.2784 | 0.2702 | 0.2634 | 0.2641 |
| 1.0000 | 14.6035 | 14.5434 | 14.5238 | 14.5006 | 14.4216 | 14.3745 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.39: Change of free energy ($\Delta G^{\#}$) and Excess free energy ($\Delta G^{\#E}$) of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

| $X_2$ | $\frac{\Delta G^{\#}}{kJ.mol^{-1}}$ | | | | | | $\frac{\Delta G^{\#E}}{kJ.mol^{-1}}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K | 298.15K | 303.15K | 308.15K | 313.15K | 318.15K | 323.15K |
| 0.0000 | 12.1863 | 12.0758 | 12.0404 | 11.9885 | 11.9479 | 11.9023 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 0.1004 | 15.0200 | 14.7354 | 14.5827 | 14.3946 | 14.2364 | 14.0972 | 2.5711 | 2.3947 | 2.2864 | 2.1574 | 2.0469 | 1.9604 |
| 0.1988 | 15.4998 | 15.2451 | 15.0916 | 14.9349 | 14.7630 | 14.6534 | 2.7935 | 2.6449 | 2.5444 | 2.4539 | 2.3366 | 2.2869 |
| 0.3042 | 15.5879 | 15.3934 | 15.2585 | 15.1084 | 14.9253 | 14.7963 | 2.6060 | 2.5152 | 2.4427 | 2.3664 | 2.2452 | 2.1837 |
| 0.3990 | 15.5428 | 15.3224 | 15.1934 | 15.0309 | 14.8936 | 14.7488 | 2.3129 | 2.1941 | 2.1359 | 2.0541 | 1.9853 | 1.9149 |
| 0.5003 | 15.3883 | 15.1754 | 15.0528 | 14.8963 | 14.7754 | 14.6291 | 1.8935 | 1.7799 | 1.7371 | 1.6685 | 1.6233 | 1.5587 |
| 0.6000 | 15.2158 | 15.0292 | 14.9336 | 14.7778 | 14.6514 | 14.5122 | 1.4601 | 1.3706 | 1.3638 | 1.3031 | 1.2594 | 1.2091 |
| 0.7031 | 15.0378 | 14.8791 | 14.7865 | 14.6529 | 14.5308 | 14.4099 | 1.0126 | 0.9486 | 0.9539 | 0.9228 | 0.8906 | 0.8660 |
| 0.8026 | 14.8797 | 14.7544 | 14.6694 | 14.5675 | 14.4570 | 14.3534 | 0.5942 | 0.5614 | 0.5832 | 0.5909 | 0.5773 | 0.5772 |
| 0.8975 | 14.8291 | 14.6941 | 14.6124 | 14.4856 | 14.3736 | 14.2578 | 0.2953 | 0.2508 | 0.2842 | 0.2740 | 0.2655 | 0.2600 |
| 1.0000 | 14.8018 | 14.7137 | 14.5894 | 14.4655 | 14.3548 | 14.2371 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

Table 4.40: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Methanol +Water 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 | 0.0045 | 0.0000 | -0.0124 | 0.0000 |
| 0.1002 | 0.0037 | -0.0011 | -0.0069 | 0.0084 |
| 0.2000 | 0.0034 | -0.0018 | -0.0048 | 0.0133 |
| 0.3001 | 0.0036 | -0.0020 | -0.0062 | 0.0147 |
| 0.4006 | 0.0037 | -0.0022 | -0.0076 | 0.0161 |
| 0.5012 | 0.0041 | -0.0021 | -0.0108 | 0.0158 |
| 0.6006 | 0.0044 | -0.0022 | -0.0126 | 0.0168 |
| 0.7012 | 0.0049 | -0.0021 | -0.0166 | 0.0157 |
| 0.8040 | 0.0052 | -0.0021 | -0.0189 | 0.0163 |
| 0.8991 | 0.0062 | -0.0014 | -0.0268 | 0.0110 |
| 1.0000 | 0.0079 | 0.0000 | -0.0407 | 0.0000 |

Table 4.41: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Ethanol + Water 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 | 0.0045 | 0.0000 | -0.0141 | 0.0000 |
| 0.1005 | 0.0031 | -0.0014 | -0.0031 | 0.0111 |
| 0.1997 | 0.0028 | -0.0017 | -0.0010 | 0.0133 |
| 0.2992 | 0.0030 | -0.0015 | -0.0032 | 0.0112 |
| 0.3989 | 0.0031 | -0.0014 | -0.0038 | 0.0107 |
| 0.4988 | 0.0032 | -0.0012 | -0.0053 | 0.0093 |
| 0.6005 | 0.0034 | -0.0010 | -0.0069 | 0.0078 |
| 0.7019 | 0.0037 | -0.0007 | -0.0092 | 0.0056 |
| 0.8017 | 0.0038 | -0.0006 | -0.0099 | 0.0050 |
| 0.9002 | 0.0040 | -0.0003 | -0.0122 | 0.0028 |
| 1.0000 | 0.0044 | 0.0000 | -0.0151 | 0.0000 |

Table 4.42: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Propanol + Water 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 | 0.0045 | 0.0000 | -0.0153 | 0.0000 |
| 0.1006 | 0.0030 | -0.0015 | -0.0032 | 0.0117 |
| 0.2005 | 0.0030 | -0.0014 | -0.0043 | 0.0103 |
| 0.2991 | 0.0031 | -0.0012 | -0.0055 | 0.0088 |
| 0.3990 | 0.0031 | -0.0011 | -0.0055 | 0.0084 |
| 0.5026 | 0.0032 | -0.0010 | -0.0061 | 0.0074 |
| 0.6011 | 0.0033 | -0.0008 | -0.0073 | 0.0059 |
| 0.7022 | 0.0034 | -0.0006 | -0.0082 | 0.0046 |
| 0.7993 | 0.0035 | -0.0004 | -0.0095 | 0.0030 |
| 0.8998 | 0.0036 | -0.0002 | -0.0105 | 0.0017 |
| 1.0000 | 0.0038 | 0.0000 | -0.0118 | 0.0000 |

Table 4.43: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Propanol + Water 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 | 0.0045 | 0.0000 | -0.0153 | 0.0000 |
| 0.1004 | 0.0027 | -0.0017 | -0.0008 | 0.0135 |
| 0.1988 | 0.0027 | -0.0016 | -0.0012 | 0.0122 |
| 0.3042 | 0.0028 | -0.0013 | -0.0030 | 0.0094 |
| 0.3990 | 0.0028 | -0.0012 | -0.0029 | 0.0086 |
| 0.5003 | 0.0029 | -0.0010 | -0.0030 | 0.0076 |
| 0.6000 | 0.0029 | -0.0008 | -0.0035 | 0.0062 |
| 0.7031 | 0.0031 | -0.0005 | -0.0046 | 0.0040 |
| 0.8026 | 0.0032 | -0.0003 | -0.0059 | 0.0019 |
| 0.8975 | 0.0033 | -0.0001 | -0.0066 | 0.0003 |
| 1.0000 | 0.0032 | 0.0000 | -0.0059 | 0.0000 |

Table 4.44: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Methanol + 0.005M 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 | 0.0045 | 0.0000 | -0.0121 | 0.0000 |
| 0.1002 | 0.0036 | -0.0012 | -0.0054 | 0.0093 |
| 0.2000 | 0.0034 | -0.0017 | -0.0044 | 0.0129 |
| 0.3001 | 0.0036 | -0.0019 | -0.0064 | 0.0137 |
| 0.4006 | 0.0037 | -0.0021 | -0.0074 | 0.0153 |
| 0.5012 | 0.0041 | -0.0020 | -0.0105 | 0.0148 |
| 0.6006 | 0.0043 | -0.0021 | -0.0122 | 0.0157 |
| 0.7012 | 0.0047 | -0.0020 | -0.0154 | 0.0152 |
| 0.8004 | 0.0053 | -0.0018 | -0.0197 | 0.0136 |
| 0.8991 | 0.0063 | -0.0011 | -0.0278 | 0.0081 |
| 1.0000 | 0.0077 | 0.0000 | -0.0386 | 0.0000 |

Table 4.45: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Ethanol + 0.005M 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 | 0.0045 | 0.0000 | -0.0137 | 0.0000 |
| 0.1005 | 0.0030 | -0.0015 | -0.0021 | 0.0117 |
| 0.1997 | 0.0028 | -0.0016 | -0.0011 | 0.0129 |
| 0.2992 | 0.0030 | -0.0014 | -0.0034 | 0.0108 |
| 0.3989 | 0.0032 | -0.0013 | -0.0047 | 0.0095 |
| 0.4988 | 0.0033 | -0.0011 | -0.0059 | 0.0085 |
| 0.6005 | 0.0034 | -0.0010 | -0.0070 | 0.0075 |
| 0.7019 | 0.0036 | -0.0008 | -0.0089 | 0.0058 |
| 0.8017 | 0.0038 | -0.0005 | -0.0107 | 0.0041 |
| 0.9002 | 0.0041 | -0.0003 | -0.0130 | 0.0019 |
| 1.0000 | 0.0044 | 0.0000 | -0.0151 | 0.0000 |

Table 4.46: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Propanol + 0.005M 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 | 0.0045 | 0.0000 | -0.0149 | 0.0000 |
| 0.1006 | 0.0030 | -0.0014 | -0.0033 | 0.0113 |
| 0.2005 | 0.0030 | -0.0013 | -0.0044 | 0.0100 |
| 0.2991 | 0.0031 | -0.0012 | -0.0056 | 0.0087 |
| 0.3990 | 0.0031 | -0.0011 | -0.0056 | 0.0084 |
| 0.5026 | 0.0033 | -0.0009 | -0.0071 | 0.0067 |
| 0.6011 | 0.0034 | -0.0007 | -0.0084 | 0.0052 |
| 0.7022 | 0.0035 | -0.0005 | -0.0096 | 0.0038 |
| 0.7993 | 0.0036 | -0.0004 | -0.0104 | 0.0028 |
| 0.8998 | 0.0037 | -0.0002 | -0.0116 | 0.0014 |
| 1.0000 | 0.0039 | 0.0000 | -0.0128 | 0.0000 |

Table 4.47: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Propanol + 0.005M 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 | 0.0045 | 0.0000 | -0.0149 | 0.0000 |
| 0.1004 | 0.0027 | -0.0016 | -0.0011 | 0.0129 |
| 0.1988 | 0.0027 | -0.0016 | -0.0009 | 0.0122 |
| 0.3042 | 0.0027 | -0.0014 | -0.0015 | 0.0107 |
| 0.3990 | 0.0028 | -0.0011 | -0.0027 | 0.0086 |
| 0.5003 | 0.0029 | -0.0009 | -0.0038 | 0.0066 |
| 0.6000 | 0.0031 | -0.0006 | -0.0049 | 0.0046 |
| 0.7031 | 0.0031 | -0.0004 | -0.0056 | 0.0030 |
| 0.8026 | 0.0033 | -0.0002 | -0.0067 | 0.0009 |
| 0.8975 | 0.0032 | -0.0001 | -0.0062 | 0.0006 |
| 1.0000 | 0.0032 | 0.0000 | -0.0059 | 0.0000 |

Table 4.48: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of Methanol + 0.01M 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 | 0.0044 | 0.0000 | -0.0123 | 0.0000 |
| 0.1002 | 0.0037 | -0.0011 | -0.0072 | 0.0081 |
| 0.2000 | 0.0034 | -0.0018 | -0.0045 | 0.0137 |
| 0.3001 | 0.0035 | -0.0020 | -0.0055 | 0.0158 |
| 0.4006 | 0.0037 | -0.0022 | -0.0074 | 0.0169 |
| 0.5012 | 0.0040 | -0.0023 | -0.0099 | 0.0174 |
| 0.6006 | 0.0044 | -0.0023 | -0.0128 | 0.0175 |
| 0.7012 | 0.0047 | -0.0023 | -0.0155 | 0.0178 |
| 0.8004 | 0.0056 | -0.0018 | -0.0225 | 0.0138 |
| 0.8991 | 0.0064 | -0.0014 | -0.0285 | 0.0107 |
| 1.0000 | 0.0081 | 0.0000 | -0.0422 | 0.0000 |

Table 4.49: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\# E}$) of Ethanol + 0.01M 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 | 0.0044 | 0.0000 | -0.0139 | 0.0000 |
| 0.1005 | 0.0031 | -0.0014 | -0.0030 | 0.0110 |
| 0.1997 | 0.0028 | -0.0016 | -0.0014 | 0.0128 |
| 0.2992 | 0.0030 | -0.0014 | -0.0034 | 0.0109 |
| 0.3989 | 0.0031 | -0.0013 | -0.0041 | 0.0102 |
| 0.4988 | 0.0033 | -0.0011 | -0.0057 | 0.0088 |
| 0.6005 | 0.0035 | -0.0009 | -0.0079 | 0.0067 |
| 0.7019 | 0.0037 | -0.0007 | -0.0093 | 0.0054 |
| 0.8017 | 0.0039 | -0.0005 | -0.0109 | 0.0039 |
| 0.9002 | 0.0041 | -0.0003 | -0.0125 | 0.0024 |
| 1.0000 | 0.0044 | 0.0000 | -0.0151 | 0.0000 |

Table 4.50: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of n-Propanol + 0.01M 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 | 0.0044 | 0.0000 | -0.0151 | 0.0000 |
| 0.1006 | 0.0031 | -0.0013 | -0.0044 | 0.0105 |
| 0.2005 | 0.0030 | -0.0013 | -0.0047 | 0.0102 |
| 0.2991 | 0.0031 | -0.0012 | -0.0051 | 0.0097 |
| 0.3990 | 0.0031 | -0.0011 | -0.0057 | 0.0091 |
| 0.5026 | 0.0032 | -0.0010 | -0.0069 | 0.0078 |
| 0.6011 | 0.0034 | -0.0008 | -0.0083 | 0.0063 |
| 0.7022 | 0.0036 | -0.0006 | -0.0100 | 0.0045 |
| 0.7993 | 0.0037 | -0.0004 | -0.0108 | 0.0036 |
| 0.8998 | 0.0039 | -0.0002 | -0.0128 | 0.0016 |
| 1.0000 | 0.0040 | 0.0000 | -0.0142 | 0.0000 |

Table 4.51: Change of Enthalpy ($\Delta H^{\#}$), Excess enthalpy ($\Delta H^{\#E}$), Entropy ($\Delta S^{\#}$) and Excess entropy ($\Delta S^{\#E}$) of iso-Propanol + 0.01M 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 | 0.0045 | 0.0000 | -0.0149 | 0.0000 |
| 0.1004 | 0.0027 | -0.0017 | -0.0006 | 0.0134 |
| 0.1988 | 0.0027 | -0.0015 | -0.0015 | 0.0116 |
| 0.3042 | 0.0028 | -0.0013 | -0.0022 | 0.0099 |
| 0.3990 | 0.0028 | -0.0012 | -0.0024 | 0.0089 |
| 0.5003 | 0.0029 | -0.0010 | -0.0030 | 0.0074 |
| 0.6000 | 0.0030 | -0.0008 | -0.0038 | 0.0057 |
| 0.7031 | 0.0031 | -0.0005 | -0.0050 | 0.0035 |
| 0.8026 | 0.0033 | -0.0002 | -0.0069 | 0.0007 |
| 0.8975 | 0.0032 | -0.0001 | -0.0061 | 0.0007 |
| 1.0000 | 0.0032 | 0.0000 | -0.0059 | 0.0000 |

Table 4.52: Coefficient, $a_i$, of Redlich-Kister Equation expressing $V^E$ and standard deviation, $\sigma$ for the Methanol+Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water + Methanol Systems | 298.15 | -4.1929 | 0.1302 | 0.4065 | -0.4674 | 0.0192 |
| | 303.15 | -4.2324 | 0.2426 | 0.3768 | -0.9389 | 0.0264 |
| | 308.15 | -4.2849 | 0.5410 | 0.0942 | -1.9024 | 0.0315 |
| 0.005M SDS + Methanol systems | 298.15 | -4.1641 | -0.1041 | 0.4248 | -0.0814 | 0.0055 |
| | 303.15 | -4.2012 | -0.2826 | 0.4906 | 0.8036 | 0.0210 |
| | 308.15 | -4.1628 | 0.2493 | 0.3634 | -0.3602 | 0.0214 |
| 0.01M SDS + Methanol Systems | 298.15 | -4.1654 | 0.0104 | 0.1681 | 0.0073 | 0.0109 |
| | 303.15 | -4.1861 | -0.0466 | 0.0965 | -0.0323 | 0.0095 |
| | 308.15 | -4.2386 | 0.0102 | -0.0778 | -0.2667 | 0.0162 |

Table 4.53: Coefficient, $a_i$, of Redlich-Kister Equation expressing $V^E$ and standard deviation, $\sigma$ for the Ethanol+Water, +0.005M SDS, +0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water + Ethanol systems | 298.15 | 3.1769 | 1.3786 | -0.8890 | -0.2060 | 0.0244 |
| | 303.15 | 3.0892 | 1.5042 | -1.4911 | -0.7648 | 0.0219 |
| | 308.15 | -2.9816 | 2.0290 | -0.9190 | -1.1051 | 0.0125 |
| | 313.15 | -2.9028 | 2.1209 | -0.8931 | -1.2150 | 0.0106 |
| | 318.15 | -2.8734 | 2.1410 | -0.6925 | -1.2982 | 0.0152 |
| | 323.15 | -2.8978 | 1.8326 | 0.3118 | -0.1526 | 0.0321 |
| 0.005M SDS + Ethanol, systems | 298.15 | -3.0357 | 0.7352 | -0.1443 | 0.9784 | 0.0200 |
| | 303.15 | -3.0677 | 0.5515 | -0.3746 | 1.3065 | 0.0178 |
| | 308.15 | -3.0850 | 0.0578 | -0.0886 | 2.2756 | 0.0214 |
| | 313.15 | -2.8403 | 0.4732 | -0.3030 | 1.3522 | 0.0296 |
| | 318.15 | -2.8209 | 1.0863 | 0.1800 | 0.6220 | 0.0309 |
| | 323.15 | -2.6724 | 1.0845 | 0.4608 | 1.3406 | 0.0287 |
| 0.01M SDS +Ethanol systems | 298.15 | -3.1525 | 1.0167 | -0.7691 | -0.1146 | 0.0314 |
| | 303.15 | -3.0838 | 1.5090 | -1.0031 | -0.8704 | 0.0322 |
| | 308.15 | -2.9376 | 1.8283 | -1.4218 | -1.4424 | 0.0316 |
| | 313.15 | -2.9193 | 1.7820 | -0.7887 | -0.9735 | 0.0211 |
| | 318.15 | -2.8321 | 1.5448 | -0.1977 | -0.6617 | 0.0342 |
| | 323.15 | -2.6784 | 1.2126 | 0.1854 | -0.7117 | 0.0280 |

Table 4.54: Coefficient, $a_i$, of Redlich-Kister Equation expressing $V^E$ and standard deviation, σ for the n-Propanol+Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+n-Propanol systems | 298.15 | -2.2886 | 0.5986 | -1.0106 | 2.2726 | 0.0431 |
| | 303.15 | -2.4632 | -0.3963 | -1.2150 | 3.5887 | 0.0502 |
| | 308.15 | -1.8926 | 0.8548 | -1.0998 | 1.7998 | 0.0397 |
| | 313.15 | -1.4652 | 1.4176 | -0.0767 | 2.0704 | 0.0330 |
| | 318.15 | -1.7893 | 1.2298 | 0.9371 | 2.6871 | 0.0274 |
| | 323.15 | -1.2756 | 1.8356 | 0.2024 | 1.7717 | 0.0199 |
| 0.005M SDS+ n-Propanol systems | 298.15 | -2.5676 | 0.3907 | -1.8172 | 1.4711 | 0.0291 |
| | 303.15 | -2.3319 | 0.0635 | -1.9717 | 1.5683 | 0.0366 |
| | 308.15 | -2.2374 | 0.5488 | -0.4359 | 1.9980 | 0.0310 |
| | 313.15 | -1.4464 | 2.1069 | -0.6756 | 0.9270 | 0.0422 |
| | 318.15 | -1.3514 | 1.9346 | -1.0881 | 0.7627 | 0.0234 |
| | 323.15 | -1.0843 | 1.4594 | -1.3054 | 2.2005 | 0.0208 |
| 0.01M SDS+ n-Propanol systems | 298.15 | -2.5253 | 0.5931 | -1.8813 | 1.1413 | 0.0173 |
| | 303.15 | -2.2867 | 0.1784 | -1.6727 | 2.5869 | 0.0380 |
| | 308.15 | -1.4121 | 1.2245 | -1.5325 | 2.3244 | 0.0195 |
| | 313.15 | -1.5254 | 0.6331 | -1.5303 | 3.8079 | 0.0329 |
| | 318.15 | -1.3542 | 0.8396 | -1.4692 | 3.1821 | 0.0696 |
| | 323.15 | -1.0921 | 0.3625 | -1.7732 | 4.9182 | 0.0253 |

Table 4.55: Coefficient, $a_i$, of Redlich-Kister Equation expressing $V^E$ and standard deviation, σ for the iso-Propanol + Water, + 0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+iso-Propanol systems | 298.15 | -4.4189 | 1.5896 | -4.0049 | -0.8252 | 0.0504 |
| | 303.15 | -4.3057 | 1.7554 | -3.5195 | -1.1513 | 0.0489 |
| | 308.15 | -3.8227 | 2.1833 | -2.9374 | -0.6360 | 0.0432 |
| | 313.15 | -3.5755 | 3.0532 | -0.6581 | 1.5339 | 0.0409 |
| | 318.15 | -3.0616 | 4.0300 | -1.0554 | -0.1232 | 0.0376 |
| | 323.15 | -2.6536 | 4.5150 | 0.0927 | 1.7579 | 0.0509 |
| 0.005M SDS+ iso-Propanol systems | 298.15 | -4.4039 | 1.0441 | -3.8803 | -0.9556 | 0.0262 |
| | 303.15 | -4.0509 | 0.7669 | -3.9299 | 0.1468 | 0.0289 |
| | 308.15 | -3.3031 | 1.2485 | -1.3066 | 4.3474 | 0.0270 |
| | 313.15 | -2.7484 | 2.3020 | -1.3839 | 2.3629 | 0.0420 |
| | 318.15 | -2.7545 | 3.2543 | -0.4498 | 1.0338 | 0.0361 |
| | 323.15 | -2.3544 | 3.7159 | -0.8823 | -0.1696 | 0.0483 |
| 0.01M SDS+ iso-Propanol systems | 298.15 | -4.2428 | 0.6301 | -4.5378 | 0.1230 | 0.0389 |
| | 303.15 | -3.9158 | 0.4913 | -4.5871 | 0.8103 | 0.0294 |
| | 308.15 | -3.5056 | 1.5925 | -1.5535 | 2.8591 | 0.0327 |
| | 313.15 | -3.3222 | 2.2287 | -0.0251 | 3.0905 | 0.0261 |
| | 318.15 | -3.1088 | 2.1093 | 0.5572 | 4.4453 | 0.0324 |
| | 323.15 | -3.1434 | 2.5570 | 1.5602 | 3.8880 | 0.0358 |

Table 4.56: Coefficient, $a_i$, of Redlich-Kister Equation express in $\eta^E$ and standard deviation, $\sigma$ for the Methanol + Water, + 0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+Methanol Systems | 298.15 | 2.5580 | -2.6793 | 1.0975 | 0.5026 | 0.0101 |
| | 303.15 | 2.1591 | -2.1832 | 0.8514 | 0.4984 | 0.0053 |
| | 308.15 | 1.8556 | -1.7617 | 0.6140 | 0.2756 | 0.0057 |
| 0.005M SDS+Methanol Systems | 298.15 | 2.5637 | -2.6548 | 1.0865 | 0.4120 | 0.0084 |
| | 303.15 | 2.1687 | -2.2101 | 0.8538 | 0.4843 | 0.0140 |
| | 308.15 | 1.8612 | -1.8300 | 0.5452 | 0.5324 | 0.0079 |
| 0.01M SDS+Methanol Systems | 298.15 | 2.3790 | -2.6260 | 1.5002 | -0.3016 | 0.0106 |
| | 303.15 | 1.9693 | -2.0447 | 1.2238 | -0.2140 | 0.0080 |
| | 308.15 | 1.6919 | -1.7245 | 0.8854 | -0.1587 | 0.0045 |

Table 4.57: Coefficient, $a_i$, of Redlich-Kister Equation express in $\eta^E$ and standard deviation, $\sigma$ for the Ethanol+Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+Ethanol systems | 298.15 | 4.0927 | -4.4024 | 3.4414 | -0.5607 | 0.0325 |
| | 303.15 | 3.3034 | -3.5127 | 2.4997 | -0.1828 | 0.0164 |
| | 308.15 | 2.8081 | -2.8588 | 1.8291 | 0.0026 | 0.0112 |
| | 313.15 | 2.3117 | -2.3767 | 1.4334 | 0.0097 | 0.0093 |
| | 318.15 | 1.9049 | -1.8454 | 1.2663 | -0.0367 | 0.0095 |
| | 323.15 | 1.5868 | -1.4675 | 0.9860 | -0.2010 | 0.0085 |
| 0.005M SDS+Ethanol systems | 298.15 | 4.0088 | -4.3022 | 3.5948 | -1.4367 | 0.0216 |
| | 303.15 | 3.1993 | -3.3029 | 2.8515 | -1.4480 | 0.0061 |
| | 308.15 | 2.6852 | -2.8052 | 2.0939 | -0.5654 | 0.0095 |
| | 313.15 | 2.2647 | -2.2956 | 1.6344 | -0.2455 | 0.0066 |
| | 318.15 | 1.9001 | -1.8578 | 1.2624 | -0.2781 | 0.0058 |
| | 323.15 | 1.5756 | -1.6125 | 0.9984 | -0.0966 | 0.0045 |
| 0.01M SDS+Ethanol systems | 298.15 | 3.6415 | -4.1716 | 4.1018 | -1.8811 | 0.0213 |
| | 303.15 | 2.8942 | -3.2282 | 3.1004 | -1.7429 | 0.0120 |
| | 308.15 | 2.4160 | -2.6152 | 2.3540 | -1.2193 | 0.0081 |
| | 313.15 | 1.9980 | -2.0056 | 1.9061 | -1.0387 | 0.0126 |
| | 318.15 | 1.6440 | -1.6106 | 1.4477 | -0.8171 | 0.0091 |
| | 323.15 | 1.3689 | -1.3445 | 1.1712 | -0.6098 | 0.0079 |

Table 4.58: Coefficient, $a_i$, of Redlich-Kister Equation expressing $\eta^E$ and standard deviation, σ for the n-Propanol+Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water + n-Propanol Systems | 298.15 | 4.7960 | -4.5301 | 4.2701 | -2.6516 | 0.0105 |
| | 303.15 | 3.8772 | -3.8667 | 3.5043 | -1.4259 | 0.0026 |
| | 308.15 | 3.2162 | -3.3427 | 2.7559 | -1.0337 | 0.0042 |
| | 313.15 | 2.6809 | -2.8407 | 2.1881 | -0.6611 | 0.0089 |
| | 318.15 | 2.2703 | -2.3083 | 1.7799 | -0.5415 | 0.0067 |
| | 323.15 | 1.9127 | -1.9935 | 1.5495 | -0.3589 | 0.0087 |
| 0.005M SDS+ n-Propanol systems | 298.15 | 4.6360 | -4.9999 | 4.8757 | -2.4223 | 0.0068 |
| | 303.15 | 3.8189 | -3.9647 | 3.6866 | -1.8654 | 0.0067 |
| | 308.15 | 3.1904 | -3.2669 | 3.0805 | -1.3687 | 0.0050 |
| | 313.15 | 2.6969 | -2.7983 | 2.4711 | -0.9431 | 0.0072 |
| | 318.15 | 2.2158 | -2.4474 | 2.0562 | -0.6507 | 0.0084 |
| | 323.15 | 1.9035 | -1.9942 | 1.7416 | -0.6792 | 0.0088 |
| 0.01M SDS+ n-Propanol systems | 298.15 | 4.3830 | -4.7069 | 4.9070 | -2.8066 | 0.0110 |
| | 303.15 | 3.4885 | -3.7034 | 3.9107 | -2.1783 | 0.0089 |
| | 308.15 | 2.8844 | -3.0894 | 3.1847 | -1.7115 | 0.0064 |
| | 313.15 | 2.3783 | -2.5270 | 2.6929 | -1.5584 | 0.0129 |
| | 318.15 | 2.0012 | -2.0713 | 2.1736 | -1.2202 | 0.0088 |
| | 323.15 | 1.6546 | -1.7513 | 1.8873 | -1.0621 | 0.0091 |

Table 4.59: Coefficient, $a_i$, of Redlich-Kister Equation expressing $\eta^E$ and standard deviation, σ for the iso-Propanol+Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+iso-Propanol systems | 298.15 | 5.1725 | -6.7861 | 5.8611 | -3.4697 | 0.0192 |
| | 303.15 | 4.1073 | -5.5798 | 4.3425 | -2.3792 | 0.0135 |
| | 308.15 | 3.4206 | -4.5860 | 3.4304 | -1.5336 | 0.0129 |
| | 313.15 | 2.7922 | -4.2886 | 3.1582 | -0.6339 | 0.0336 |
| | 318.15 | 2.2831 | -3.2584 | 2.2515 | -0.5651 | 0.0135 |
| | 323.15 | 1.8681 | -2.8903 | 1.9618 | -0.0799 | 0.0116 |
| 0.005M SDS+ iso-Propanol systems | 298.15 | 5.2424 | -7.0706 | 6.3040 | -3.1644 | 0.0192 |
| | 303.15 | 4.1890 | -5.4647 | 4.5420 | -2.6000 | 0.0127 |
| | 308.15 | 3.4445 | -4.4662 | 3.8074 | -1.8473 | 0.0137 |
| | 313.15 | 2.8536 | -3.6099 | 2.8933 | -1.5710 | 0.0139 |
| | 318.15 | 2.3404 | -2.9649 | 2.3640 | -1.0817 | 0.0074 |
| | 323.15 | 1.9466 | -2.3839 | 2.0152 | -1.1115 | 0.0071 |
| 0.01M SDS+iso-Propanol systems | 298.15 | 5.5340 | -6.6621 | 7.2449 | -5.9191 | 0.0499 |
| | 303.15 | 4.3551 | -5.4200 | 5.4539 | -4.0551 | 0.0268 |
| | 308.15 | 3.6344 | -4.4234 | 4.4663 | -3.1746 | 0.0236 |
| | 313.15 | 2.9646 | -3.7293 | 3.6763 | -2.2709 | 0.0121 |
| | 318.15 | 2.4492 | -2.9850 | 2.9173 | -1.9679 | 0.0121 |
| | 323.15 | 2.0264 | -2.5611 | 2.5561 | -1.5499 | 0.0055 |

Table 4.60: Coefficient, $a_i$, of Redlich-Kister Equation express in $\Delta G^{\#E}$ and standard deviation, σ for the Methanol + Water, + 0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+Methanol systems | 298.15 | 6.3827 | -3.6916 | 3.1902 | -0.7924 | 0.0176 |
| | 303.15 | 6.1703 | -3.5839 | 3.0129 | -0.4518 | 0.0187 |
| | 308.15 | 5.9034 | -3.2797 | 2.4991 | -0.9678 | 0.0209 |
| 0.005M SDS+Methanol systems | 298.15 | 6.3590 | -3.5816 | 3.1062 | -1.0129 | 0.0089 |
| | 303.15 | 6.1748 | -3.5875 | 2.9033 | -0.5128 | 0.0186 |
| | 308.15 | 5.9040 | -3.4129 | 2.3143 | -0.2866 | 0.0120 |
| 0.01M SDS+Methanol systems | 298.15 | 5.6344 | -3.1033 | 2.8530 | -1.8261 | 0.0093 |
| | 303.15 | 5.3624 | -2.8209 | 2.8454 | -1.5223 | 0.0120 |
| | 308.15 | 5.1170 | -2.7890 | 2.2652 | -1.4852 | 0.0093 |

Table 4.61: Coefficient, $a_i$, of Redlich-Kister Equation express in $\Delta G^{\#E}$ and standard deviation, σ for the Ethanol + Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+Ethanol systems | 298.15 | 6.7131 | -5.7306 | 7.1199 | -4.8185 | 0.0246 |
| | 303.15 | 6.3711 | -5.5576 | 6.3038 | -4.0590 | 0.0180 |
| | 308.15 | 6.2149 | -5.2485 | 5.5785 | -3.4748 | 0.0174 |
| | 313.15 | 5.9592 | -5.0897 | 5.0745 | -3.2181 | 0.0172 |
| | 318.15 | 5.6636 | -4.6488 | 4.9887 | -2.8895 | 0.0206 |
| | 323.15 | 5.3851 | -4.3042 | 4.5323 | -3.0700 | 0.0170 |
| 0.005M SDS+Ethanol systems | 298.15 | 6.5979 | -5.5982 | 7.1574 | -5.8617 | 0.0298 |
| | 303.15 | 6.2108 | -5.2615 | 6.7407 | -5.9216 | 0.0363 |
| | 308.15 | 5.9969 | -5.2642 | 5.9416 | -4.2669 | 0.0255 |
| | 313.15 | 5.8616 | -5.0179 | 5.4471 | -3.4696 | 0.0258 |
| | 318.15 | 5.6418 | -4.6676 | 4.9169 | -3.4490 | 0.0246 |
| | 323.15 | 5.3591 | -4.6927 | 4.4689 | -2.7266 | 0.0263 |
| 0.01M SDS+Ethanol systems | 298.15 | 5.7613 | -5.0345 | 6.7355 | -5.0343 | 0.0341 |
| | 303.15 | 5.3990 | -4.6805 | 6.0189 | -5.1600 | 0.0335 |
| | 308.15 | 5.1928 | -4.4223 | 5.3454 | -4.4081 | 0.0364 |
| | 313.15 | 4.9908 | -3.9815 | 5.0657 | -4.0788 | 0.0402 |
| | 318.15 | 4.7450 | -3.7424 | 4.5053 | -3.7030 | 0.0341 |
| | 323.15 | 4.5221 | -3.6469 | 4.1988 | -3.2461 | 0.0296 |

Table 4.62: Coefficient, $a_i$, of Redlich-Kister Equation expressing $\Delta G^{\#E}$ and standard deviation, σ for the n-Propanol + Water, +0.005M SDS, + 0.01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+n-Propanol systems | 298.15 | 6.7888 | -5.9970 | 8.4340 | -8.0385 | 0.0617 |
| | 303.15 | 6.5095 | -6.1621 | -6.1621 | -6.5451 | 0.0502 |
| | 308.15 | 6.2752 | -6.1331 | 7.4646 | -5.9808 | 0.0413 |
| | 313.15 | 6.1242 | -6.0422 | 6.9622 | -5.2607 | 0.0276 |
| | 318.15 | 5.9558 | -5.7360 | 6.6027 | -4.8545 | 0.0266 |
| | 323.15 | 5.8214 | -5.6509 | 6.3410 | -4.2814 | 0.0168 |
| 0.005M SDS+ n-Propanol systems | 298.15 | 6.5822 | -6.4324 | 8.9442 | -7.8140 | 0.0600 |
| | 303.15 | 6.4221 | -6.2273 | 8.2724 | -7.2324 | 0.0520 |
| | 308.15 | 6.2026 | -5.9803 | 8.0077 | -6.5625 | 0.0464 |
| | 313.15 | 6.1182 | -5.8800 | 7.4392 | -5.8441 | 0.0363 |
| | 318.15 | 5.8296 | -5.9345 | 7.0235 | -5.1918 | 0.0253 |
| | 323.15 | 5.7606 | -5.6389 | 6.7165 | -5.0527 | 0.0185 |
| 0.01M SDS+ n-Propanol systems | 298.15 | 5.9584 | -5.5798 | 7.7812 | -6.8111 | 0.0437 |
| | 303.15 | 5.6614 | -5.3626 | 7.3673 | -6.1752 | 0.0414 |
| | 308.15 | 5.4643 | -5.1947 | 6.8920 | -5.6373 | 0.0285 |
| | 313.15 | 5.2317 | -5.0300 | 6.6342 | -5.3948 | 0.0233 |
| | 318.15 | 5.1008 | -4.7892 | 6.1909 | -4.9258 | 0.0168 |
| | 323.15 | 4.8792 | -4.7119 | 5.9983 | -4.5577 | 0.0226 |

Table 4.63: Coefficient, $a_i$, of Redlich-Kister Equation expressing $\Delta G^{\#E}$ and standard deviation, σ for the iso-Propanol + Water, + 0.005M SDS, .01M SDS systems.

| Systems | $T$/ K | $a_o$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ |
|---|---|---|---|---|---|---|
| Water+iso-Propanol, systems | 298.15 | 6.9707 | -7.8338 | 9.7608 | -9.8908 | 0.0626 |
| | 303.15 | 6.6402 | -7.7964 | 8.8970 | -8.8693 | 0.0505 |
| | 308.15 | 6.5083 | -7.5228 | 8.2720 | -7.5982 | 0.0401 |
| | 313.15 | 6.2733 | -8.0259 | 8.3878 | -6.0414 | 0.0107 |
| | 318.15 | 6.0457 | -7.2442 | 7.3071 | -5.6285 | 0.0252 |
| | 323.15 | 5.7970 | -7.3898 | 7.1410 | -4.1707 | 0.0251 |
| 0.005M SDS+ iso-Propanol, systems | 298.15 | 6.9957 | -8.0204 | 10.1672 | -9.5559 | 0.0722 |
| | 303.15 | 6.7237 | -7.6558 | 9.1445 | -8.9999 | 0.0698 |
| | 308.15 | 6.5520 | -7.3754 | 8.8783 | -7.7397 | 0.0581 |
| | 313.15 | 6.4074 | -7.0103 | 8.0377 | -7.3989 | 0.0592 |
| | 318.15 | 6.1525 | -6.6780 | 7.6104 | -6.5314 | 0.0431 |
| | 323.15 | 5.9814 | -6.2485 | 7.3264 | -6.6172 | 0.0460 |
| 0.01M SDS+iso-Propanol, systems | 298.15 | 7.2583 | -7.4891 | 11.0742 | -12.3067 | 0.1197 |
| | 303.15 | 6.8988 | -7.4358 | 10.2237 | -10.9222 | 0.0968 |
| | 308.15 | 6.7701 | -7.0883 | 9.8613 | -10.0060 | 0.0911 |
| | 313.15 | 6.5264 | -6.9751 | 9.4637 | -8.9017 | 0.0731 |
| | 318.15 | 6.3152 | -6.5971 | 8.7886 | -8.3911 | 0.0731 |
| | 323.15 | 6.0901 | -6.5002 | 8.6889 | -7.7563 | 0.0570 |

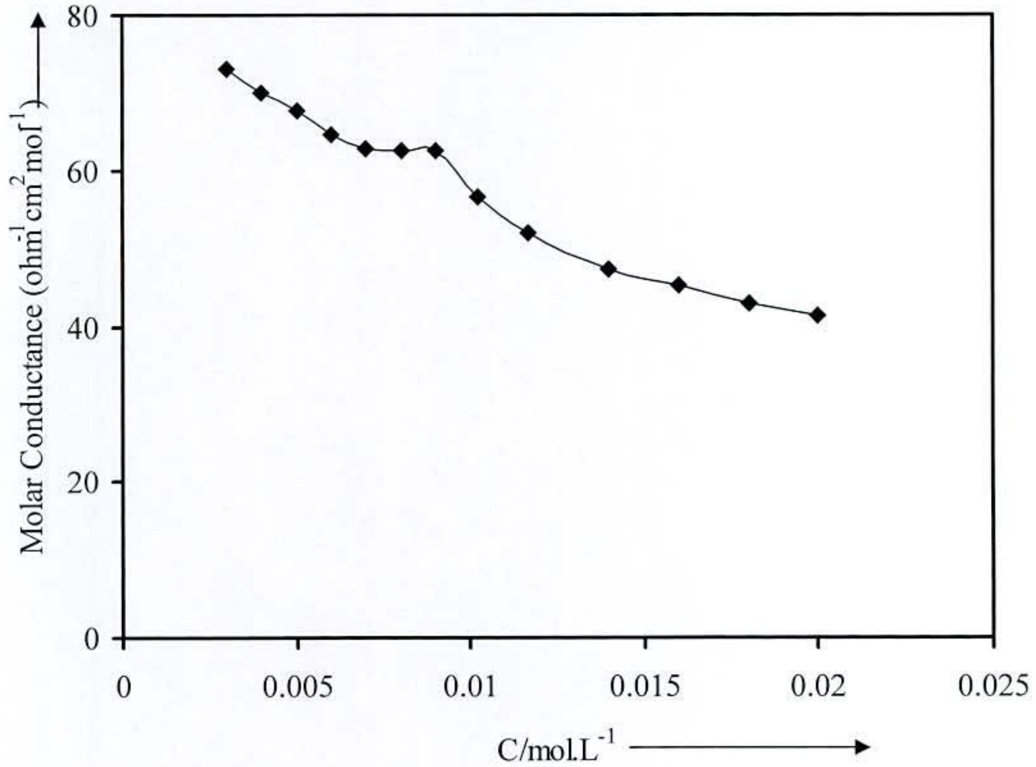

Figure 4.1: Plots of Molar conductance vs concentration of SDS in aqueous solution at 302.15K.

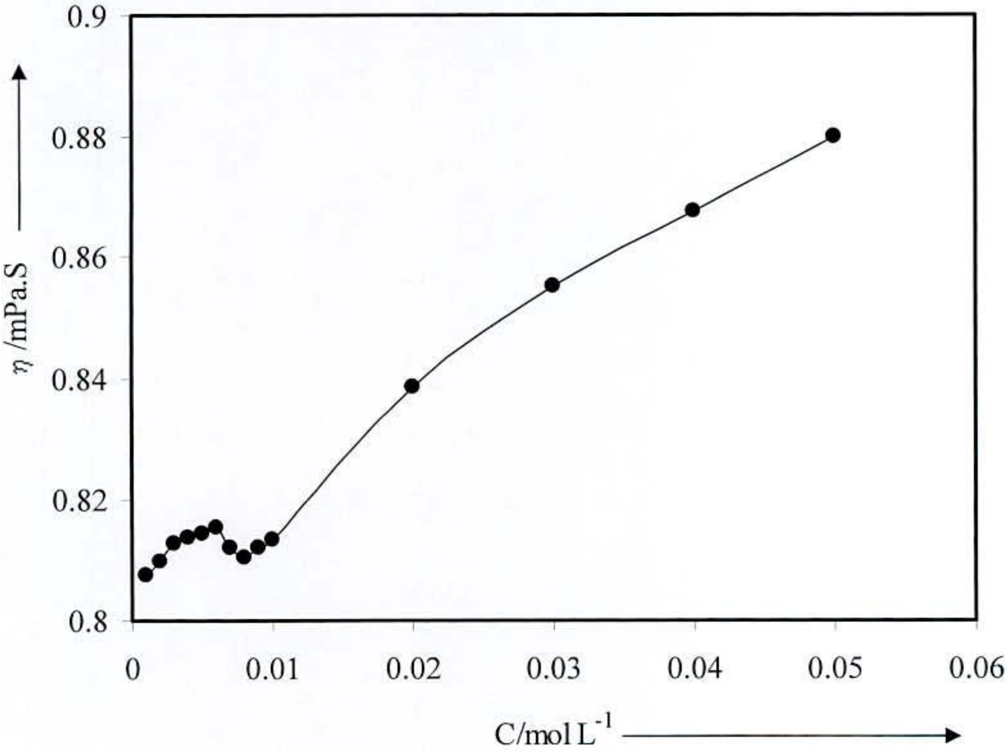

Figure 4.2: Plots of viscosity vs concentration of SDS in aqueous solution at 302.15K.

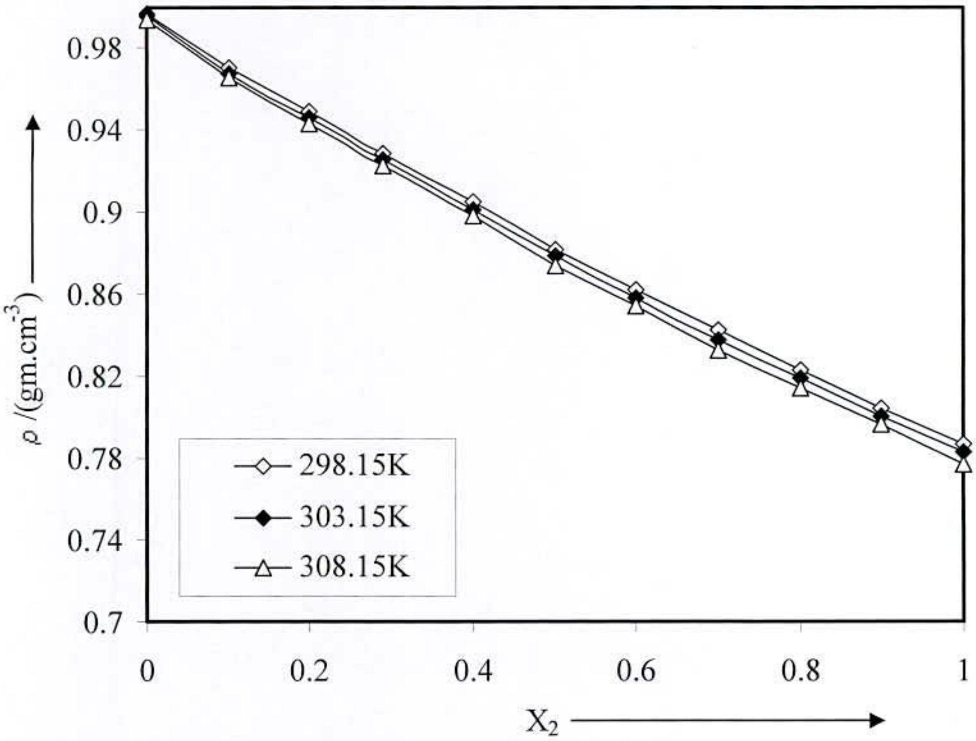

Figure 4.3: Plots of density vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively.

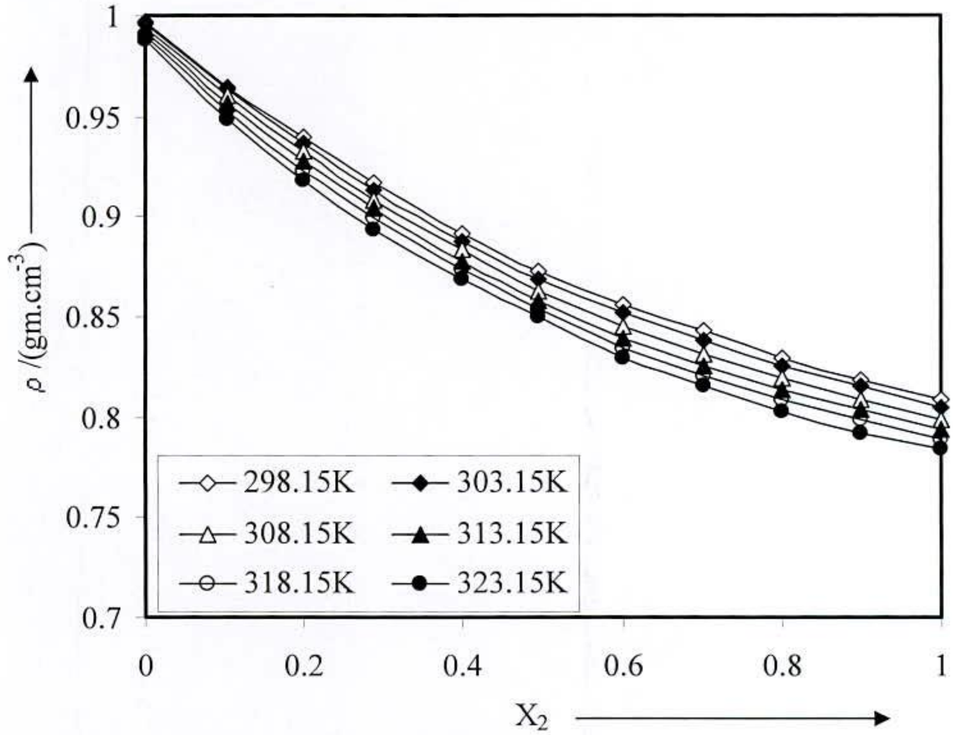

Figure 4.44: Plots of density vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

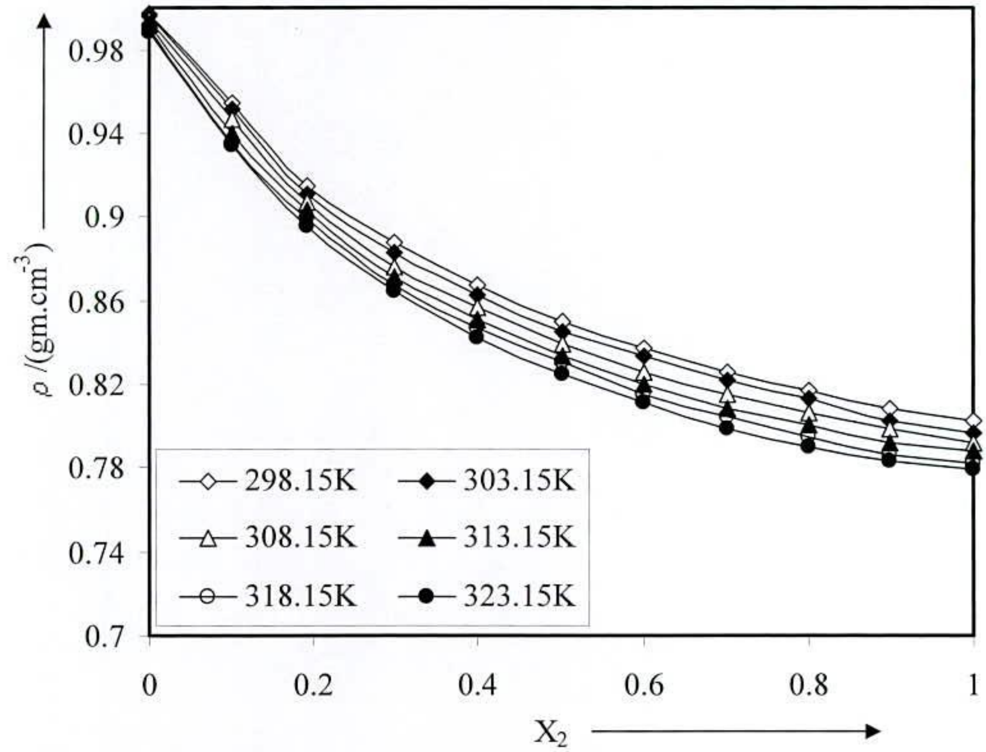

Figure 4.5: Plots of density vs mole fraction of n-Propanol+ water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

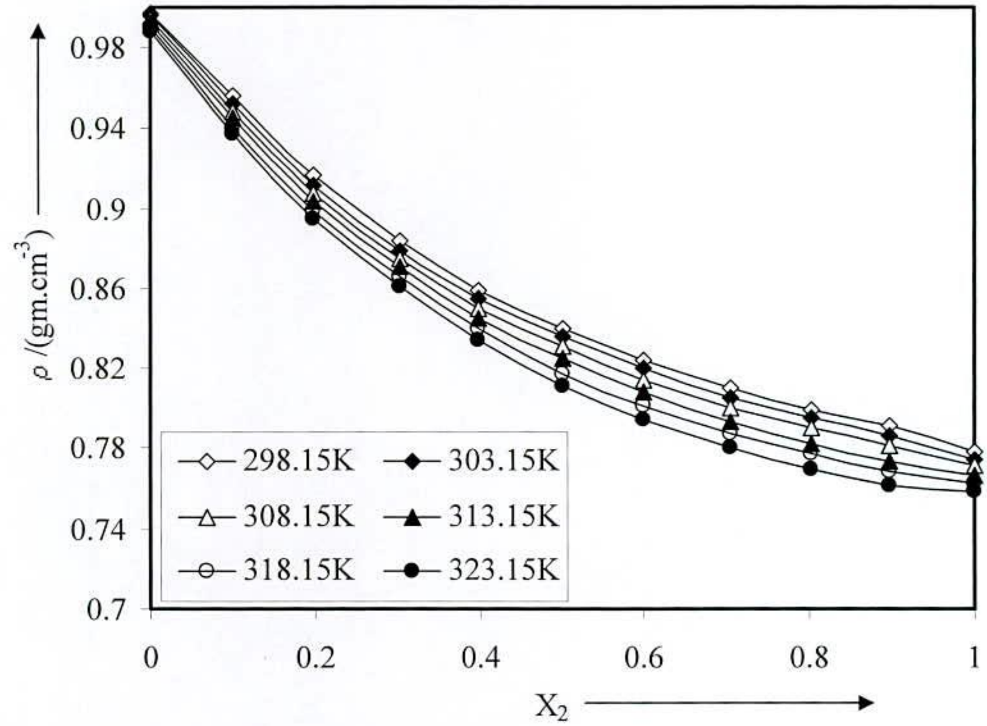

Figure 4.6: Plots of density vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

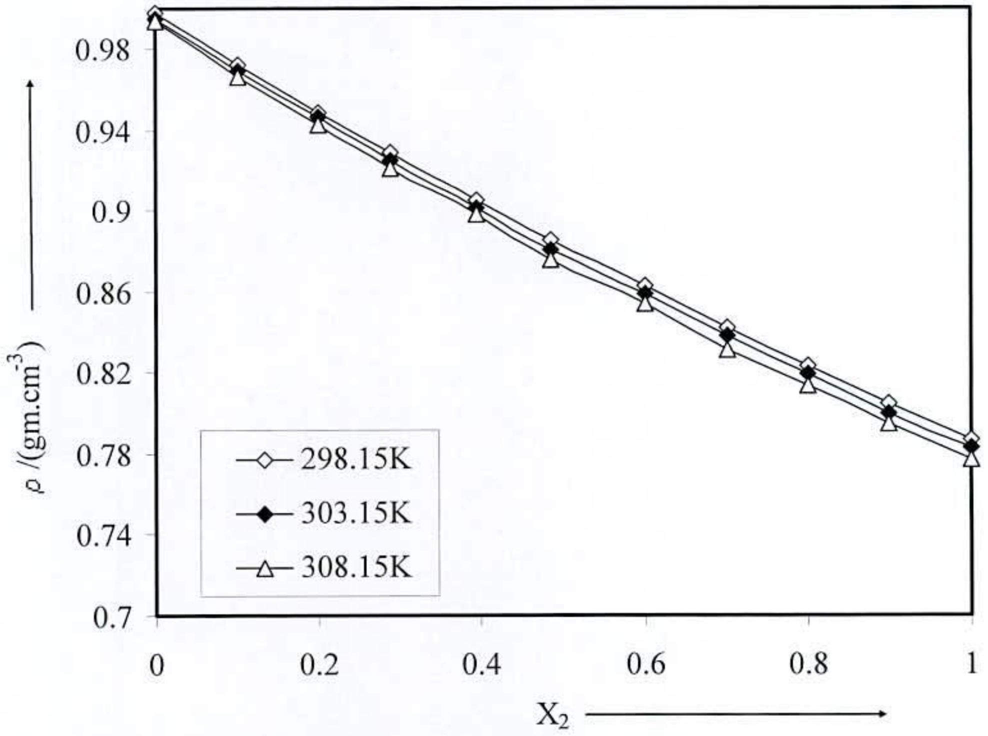

Figure 4.7: Plots of density vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

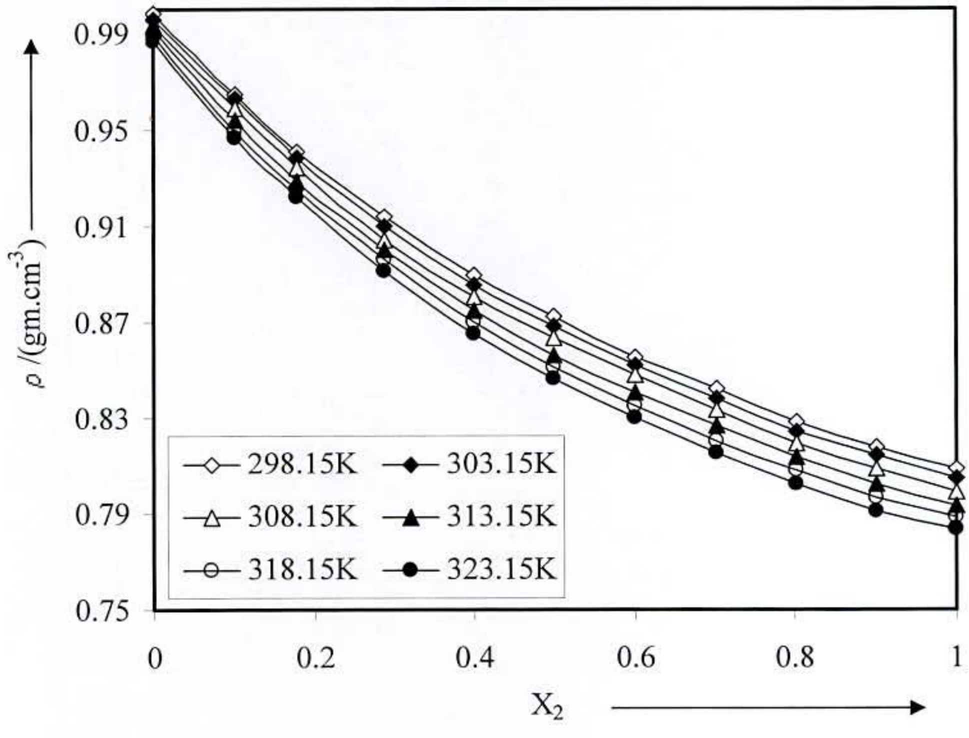

Figure 4.8: Plots of density vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

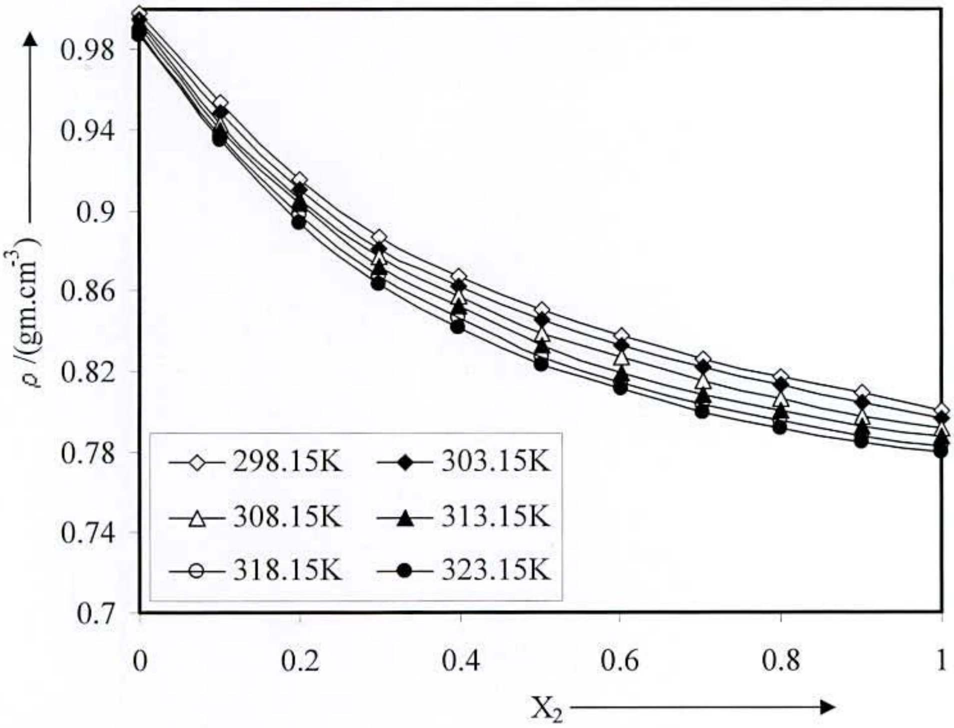

Figure 4.9: Plots of density vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

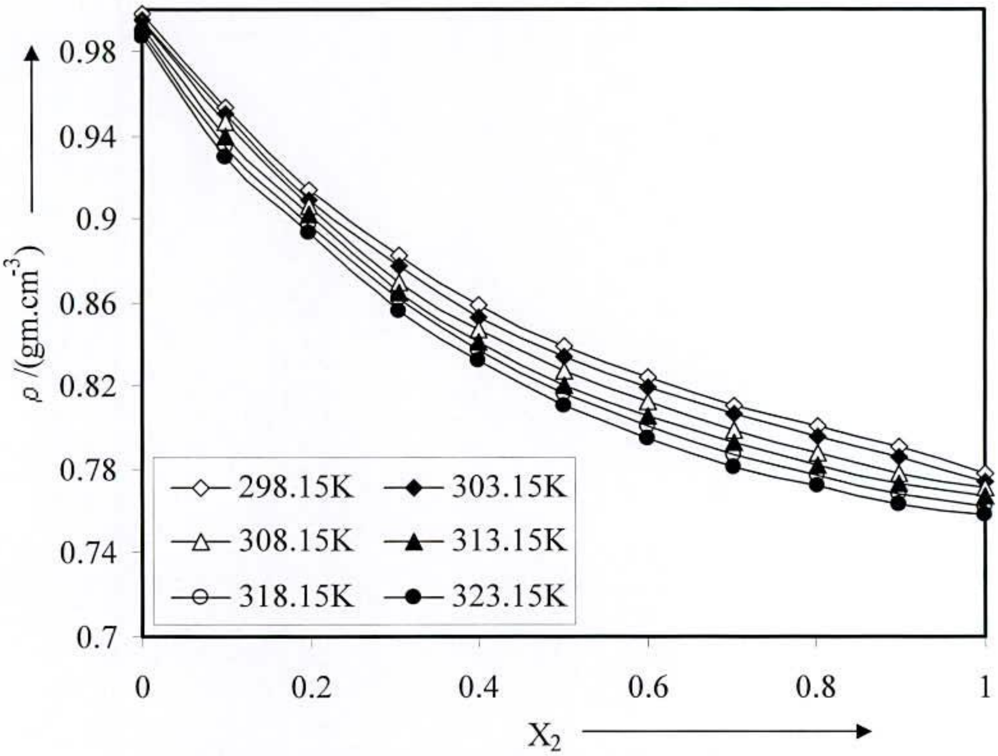

Figure 4.10: Plots of density vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

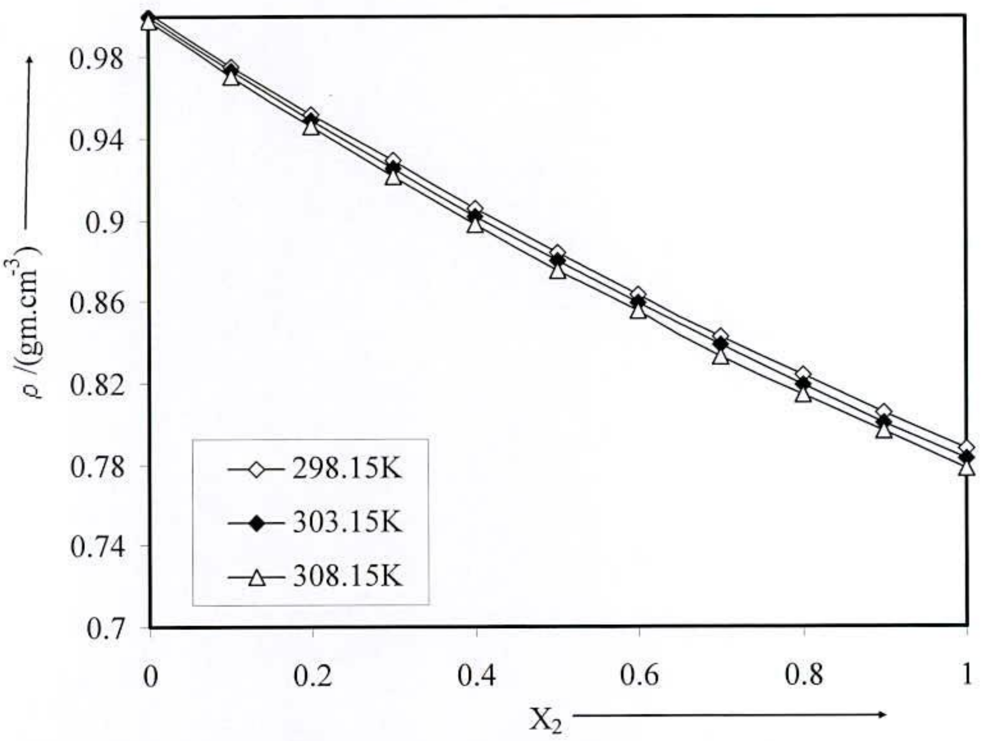

Figure 4.11: Plots of density vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

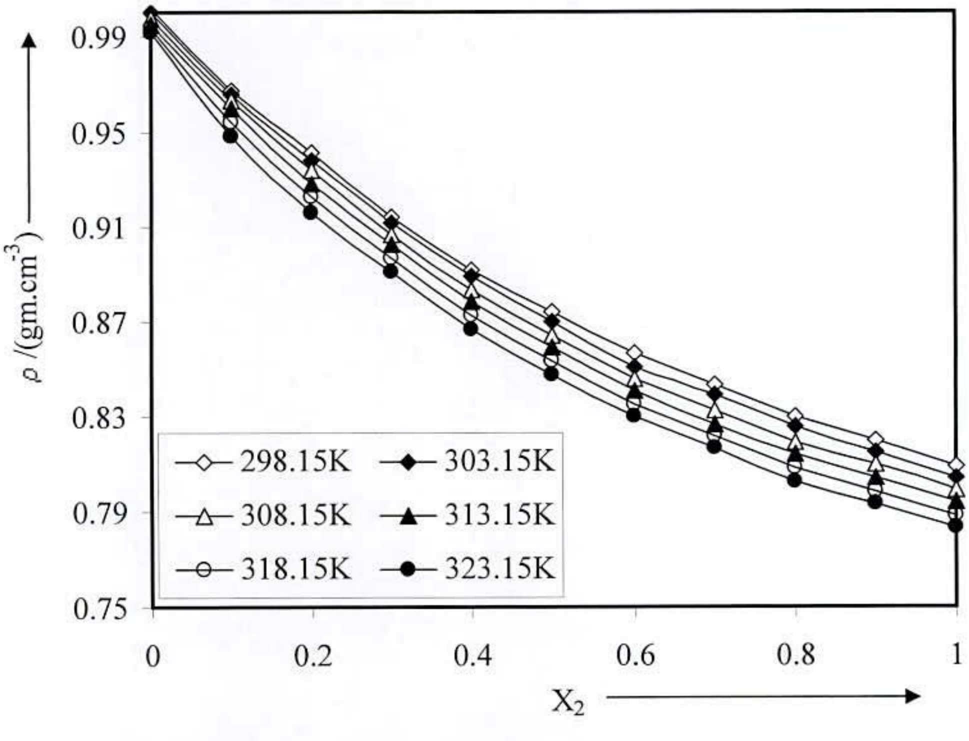

Figure 4.12: Plots of density vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

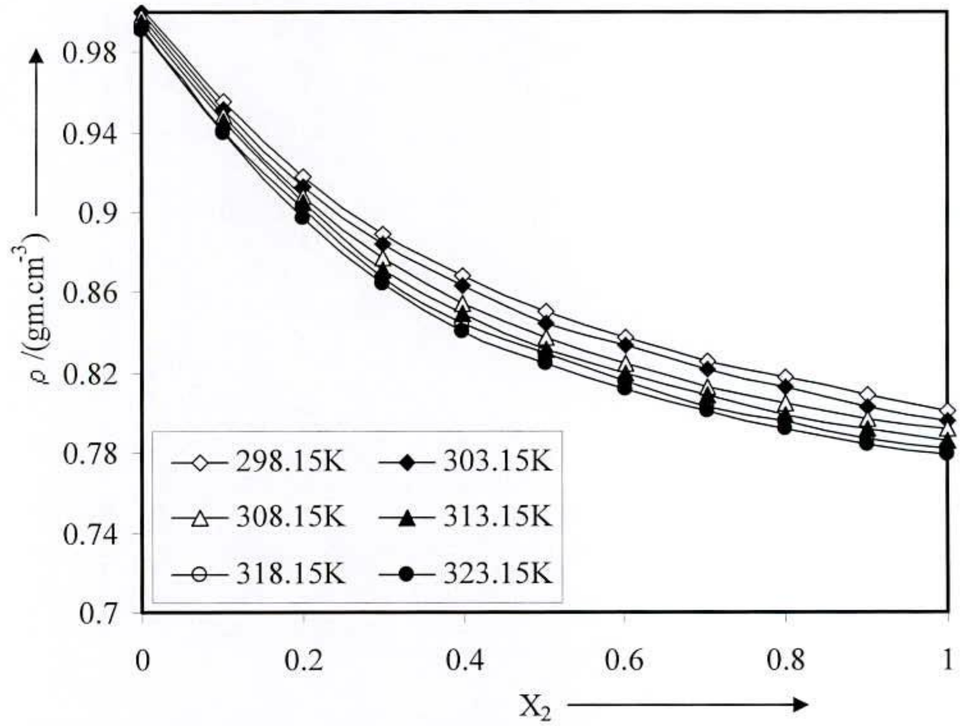

Figure 4.13: Plots of density vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

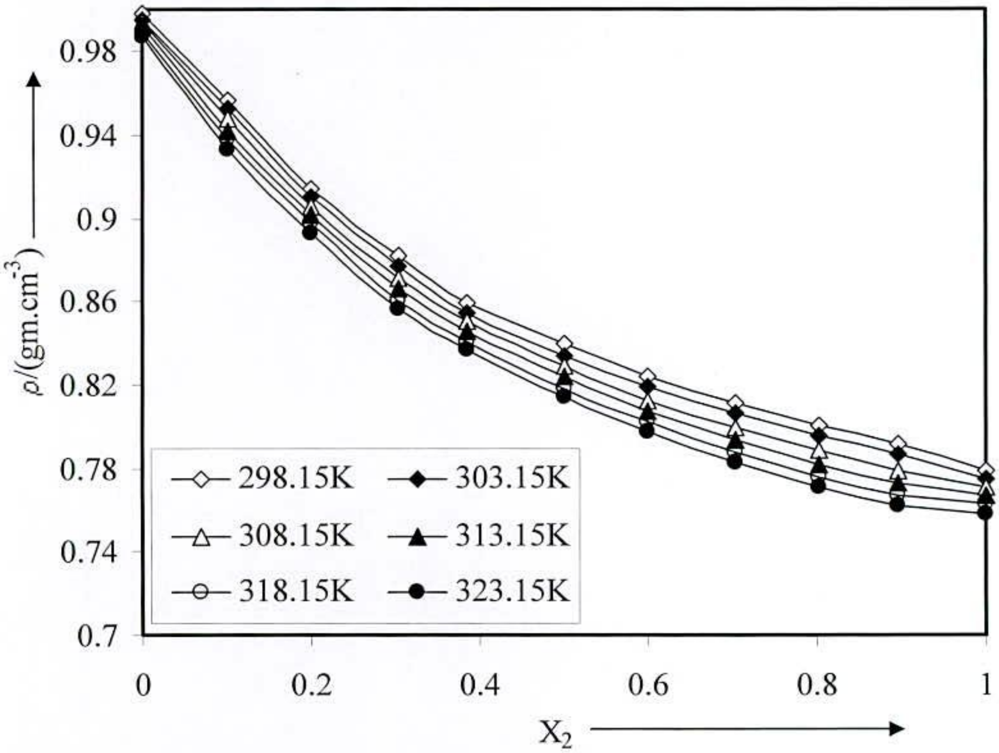

Figure 4.14: Plots of density vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

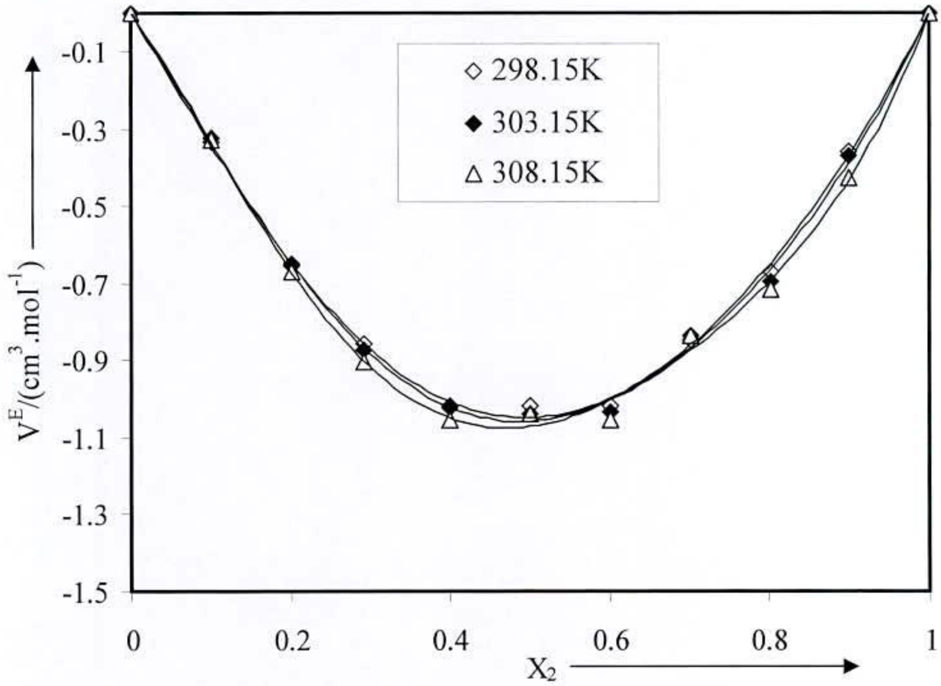

Figure 4.15: Plots of excess molar volume vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively.

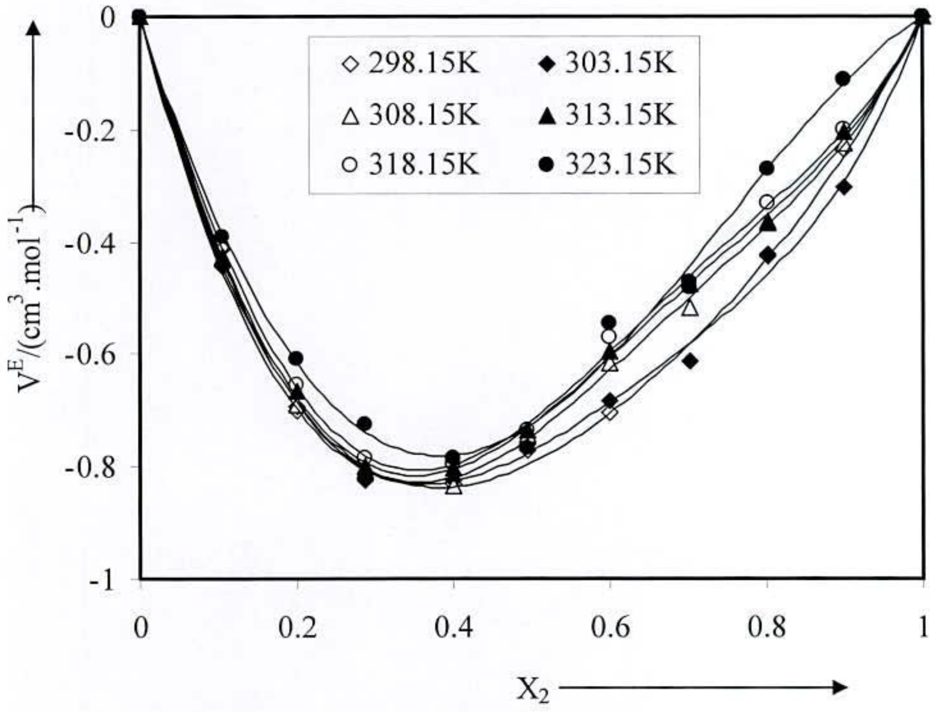

Figure 4.16: Plots of excess molar volume vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

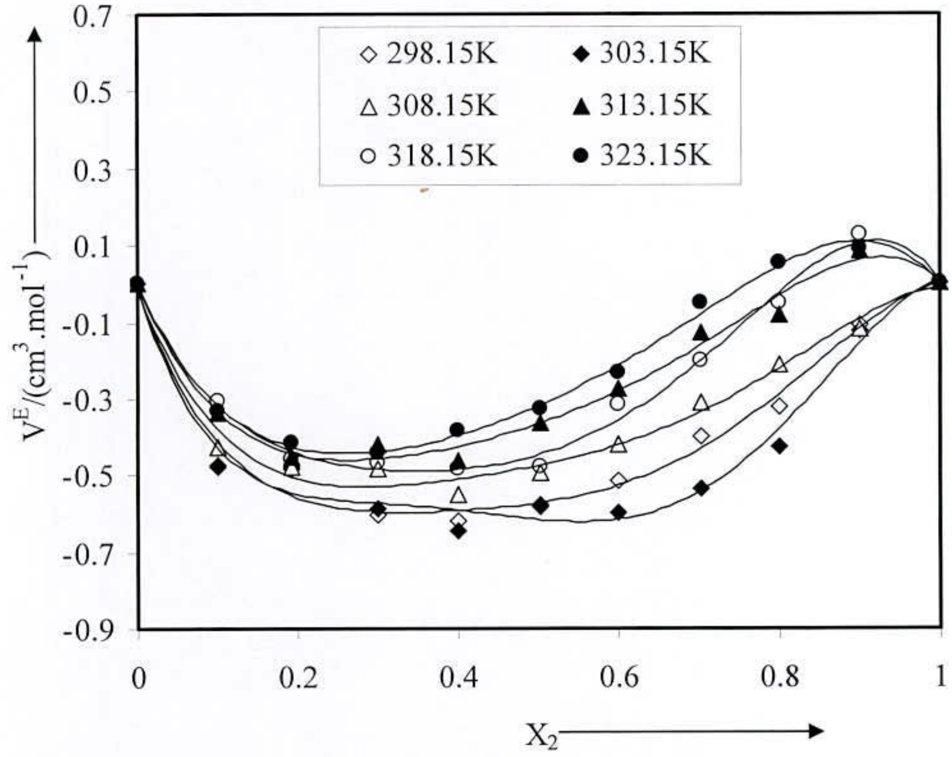

Figure 4.17: Plots of excess molar volume vs mole fraction of n-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

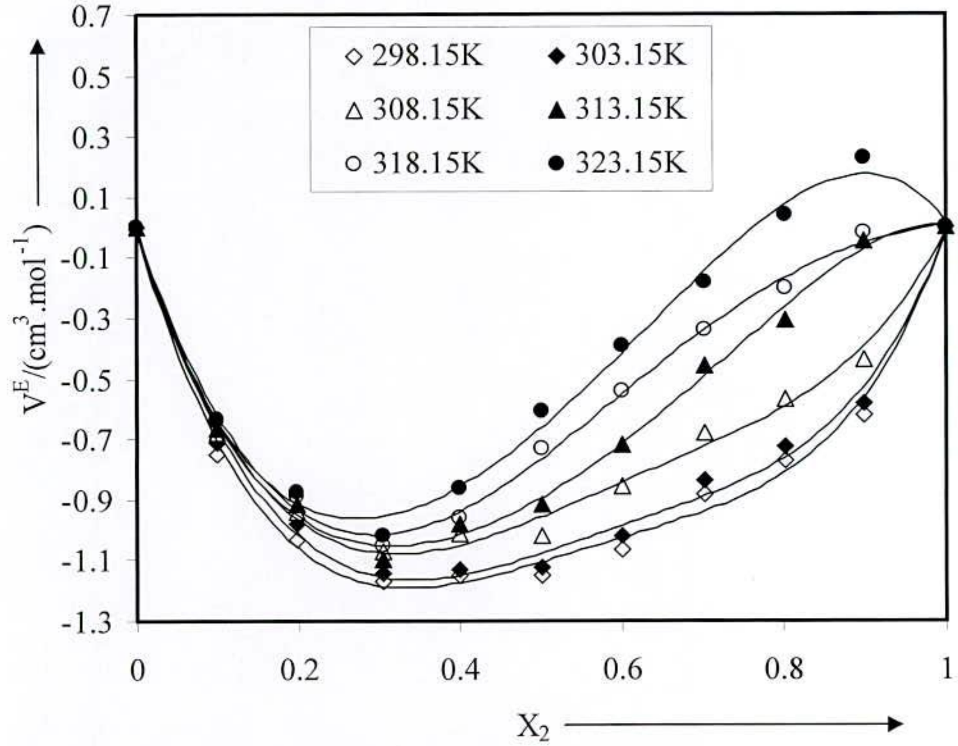

Figure 4.18: Plots of excess molar volume vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

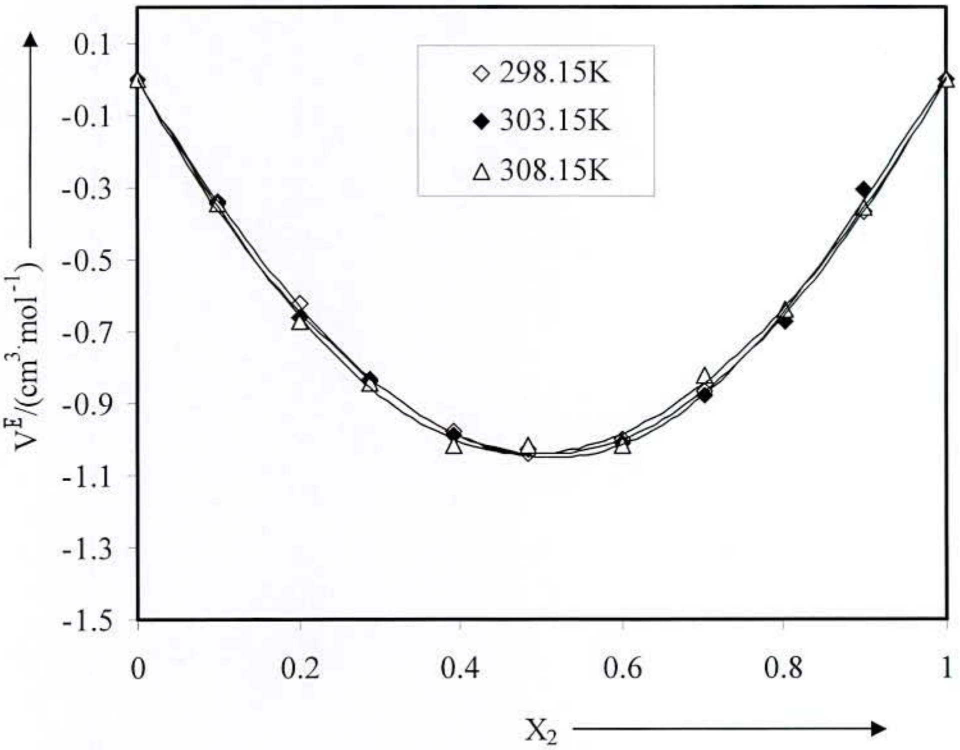

Figure 4.19: Plots of excess molar volume vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

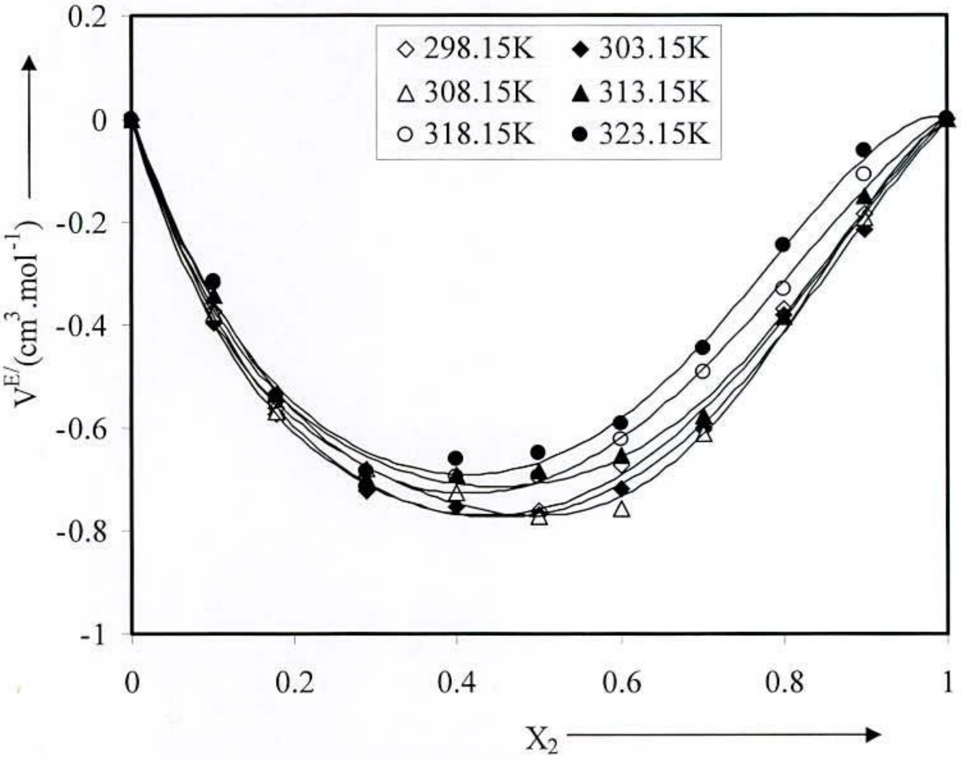

Figure 4.20: Plots of excess molar volume vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

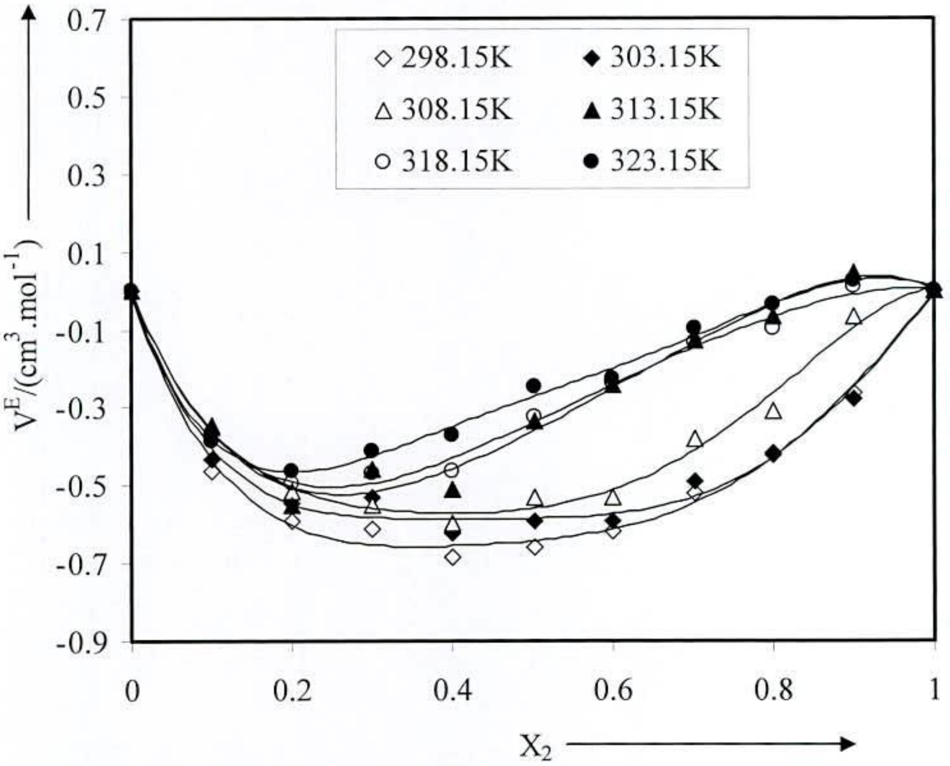

Figure 4.21: Plots of excess molar volume vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

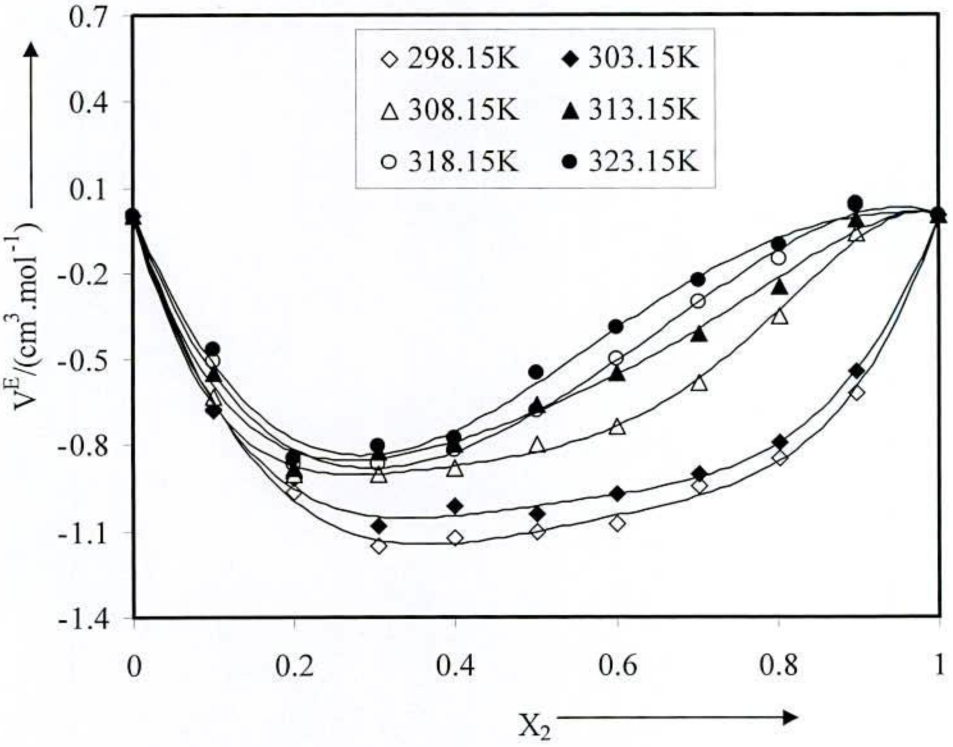

Figure 4.22: Plots of excess molar volume vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

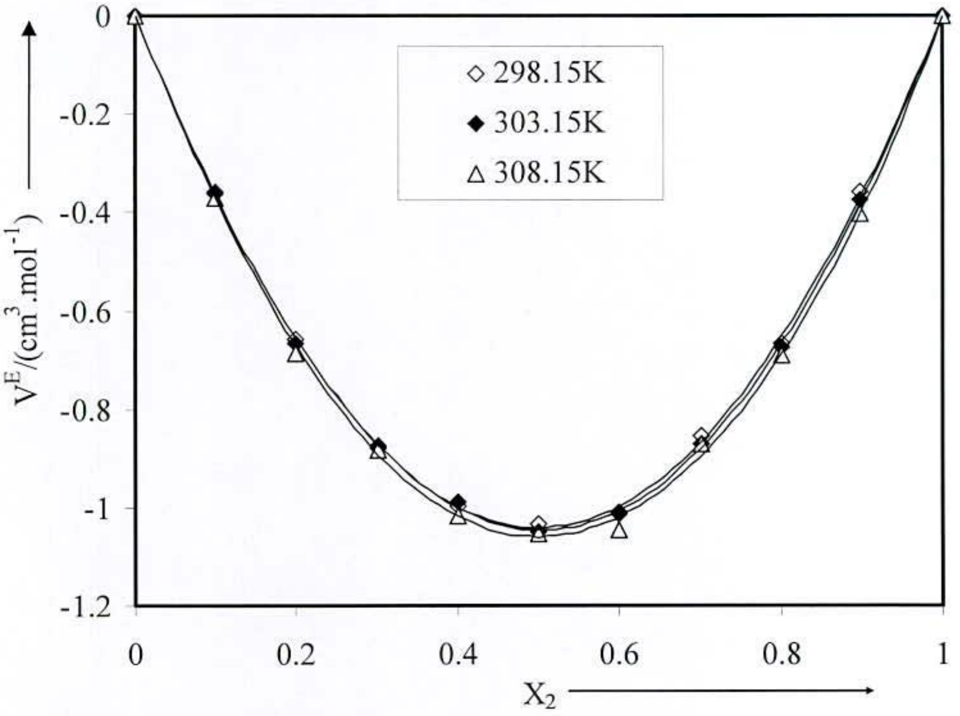

Figure 4.23: Plots of excess molar volume vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

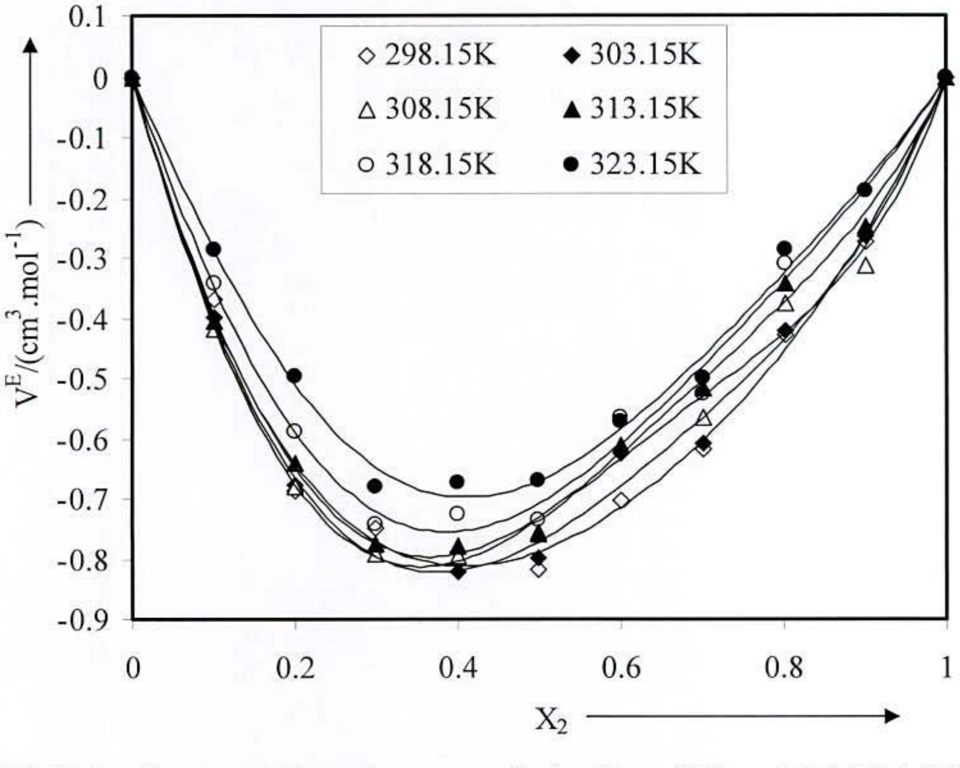

Figure 4.24: Plots of excess molar volume vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

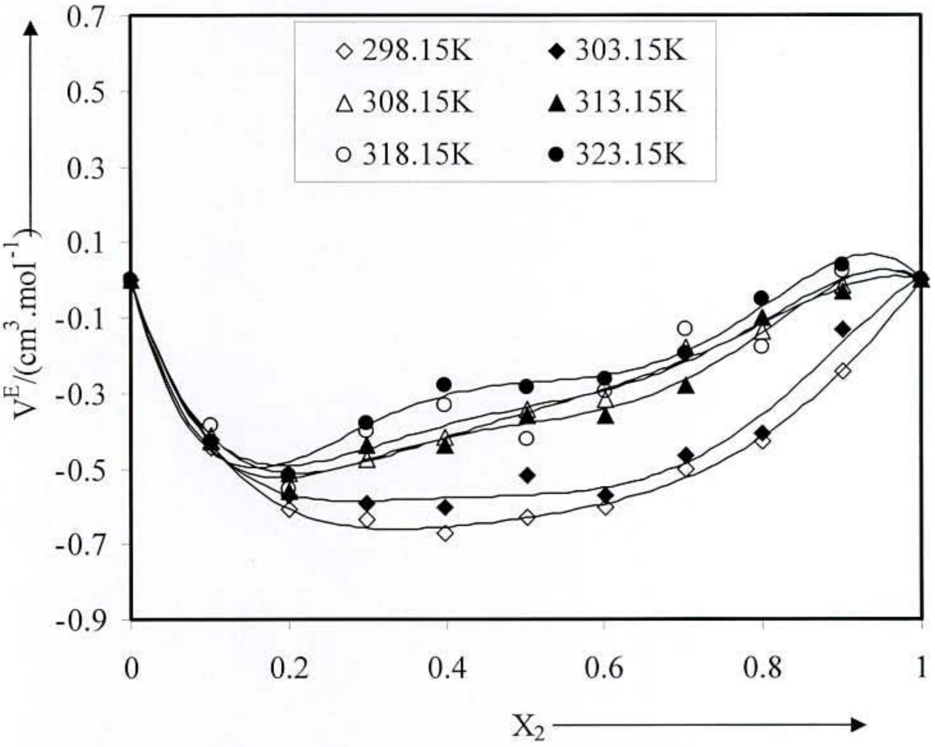

Figure 4.25: Plots of excess molar volume vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

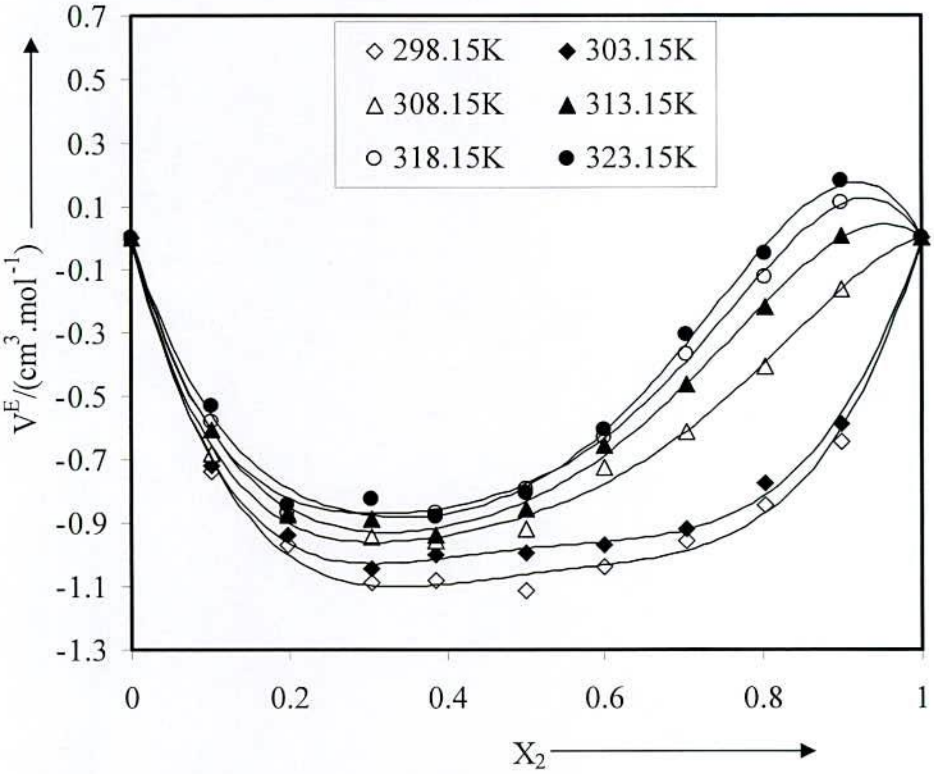

Figure 4.26: Plots of excess molar volume vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

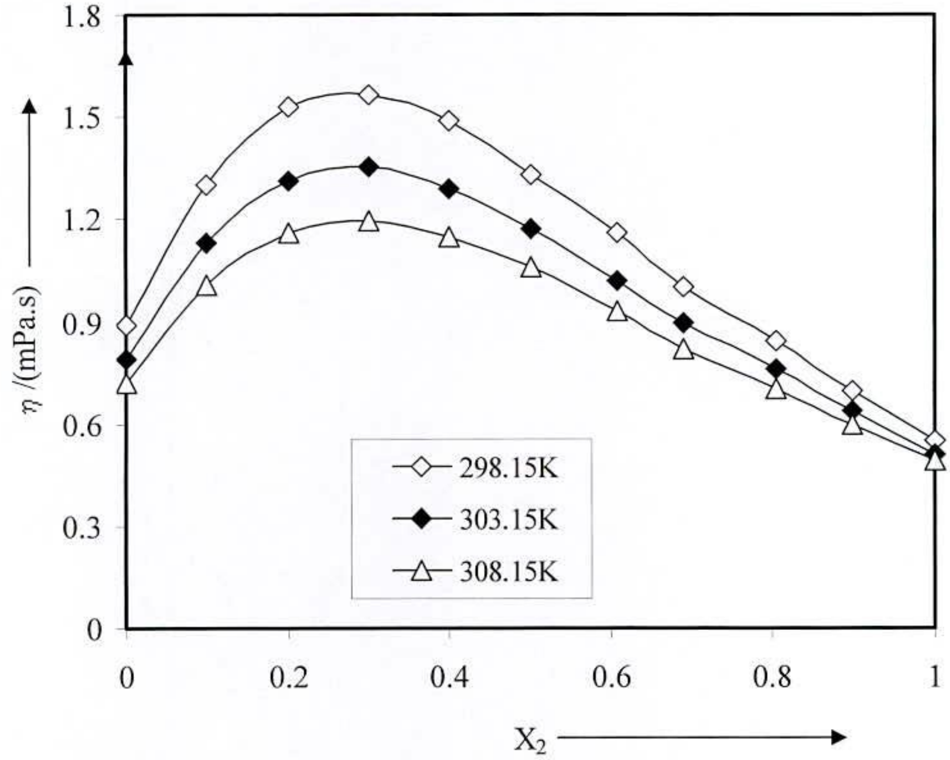

Figure 4.27: Plots of viscosity vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively .

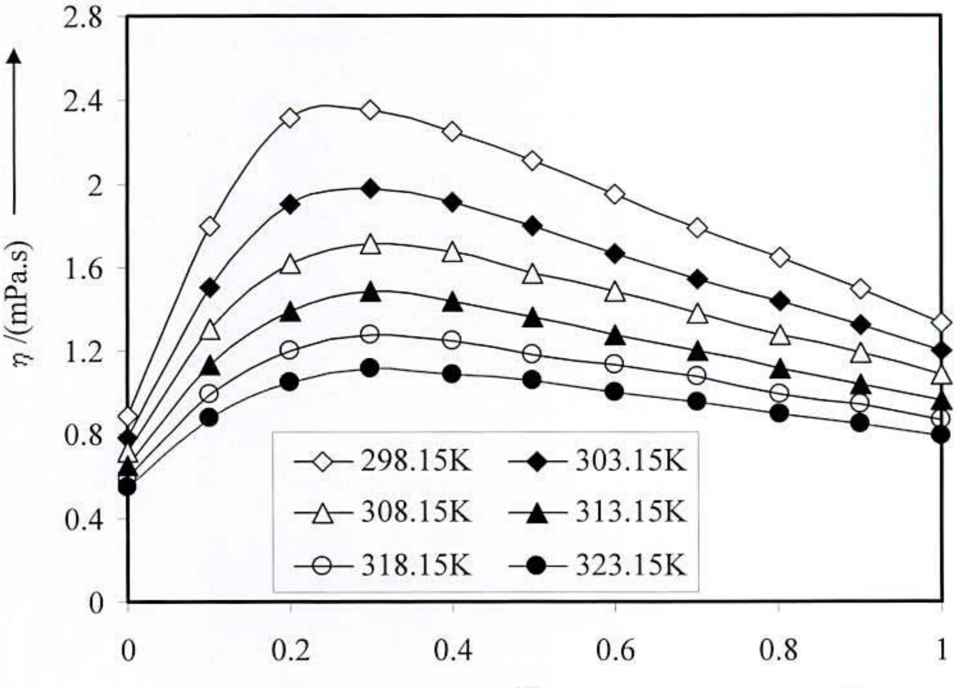

Figure 4.28: Plots of viscosity vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

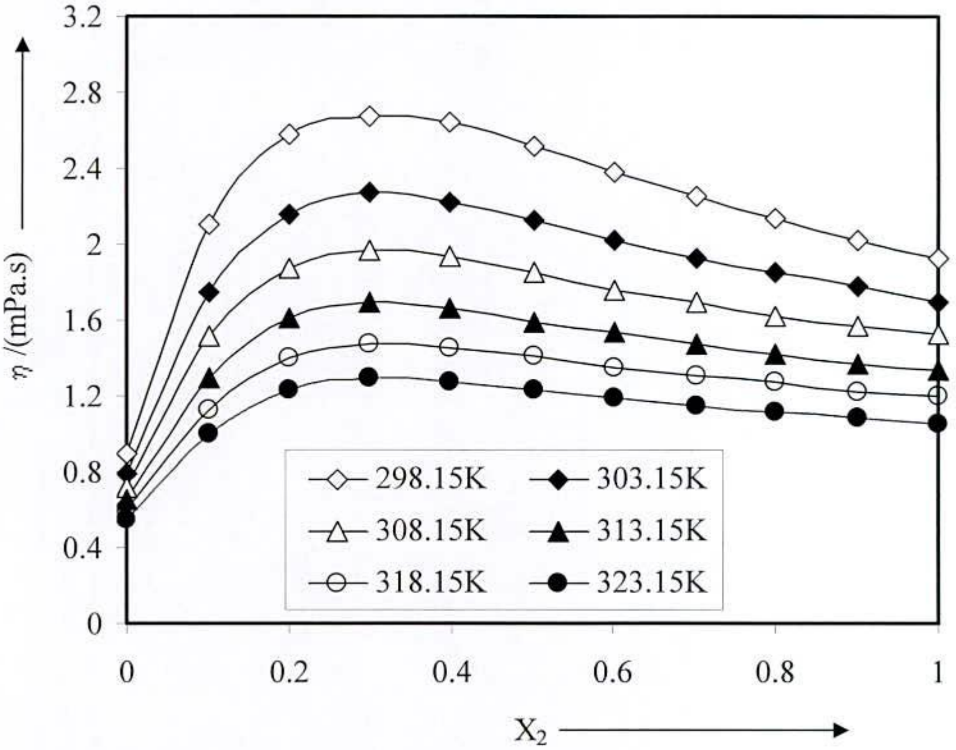

Figure 4.29: Plots of viscosity vs mole fraction of n-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K.

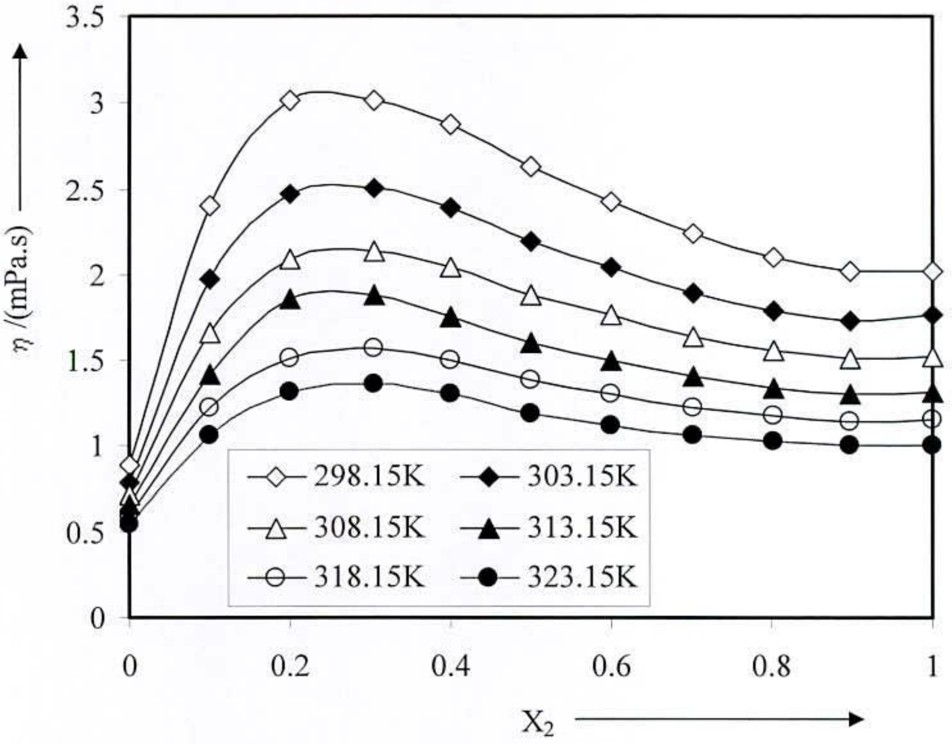

Figure 4.30: Plots of viscosty vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

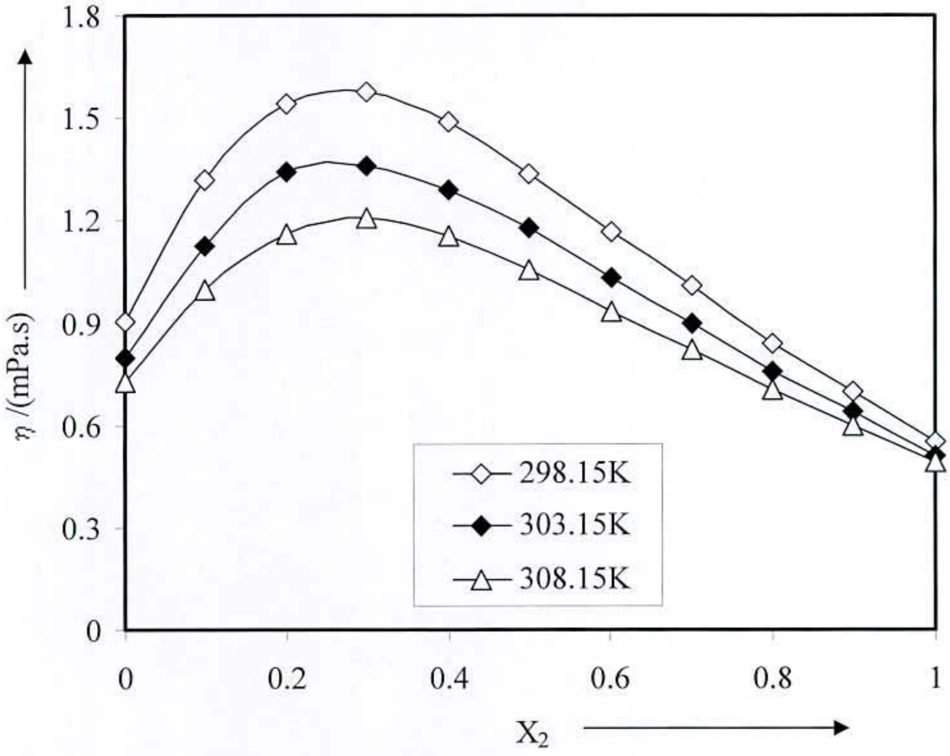

Figure 4.31: Plots of viscosity vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

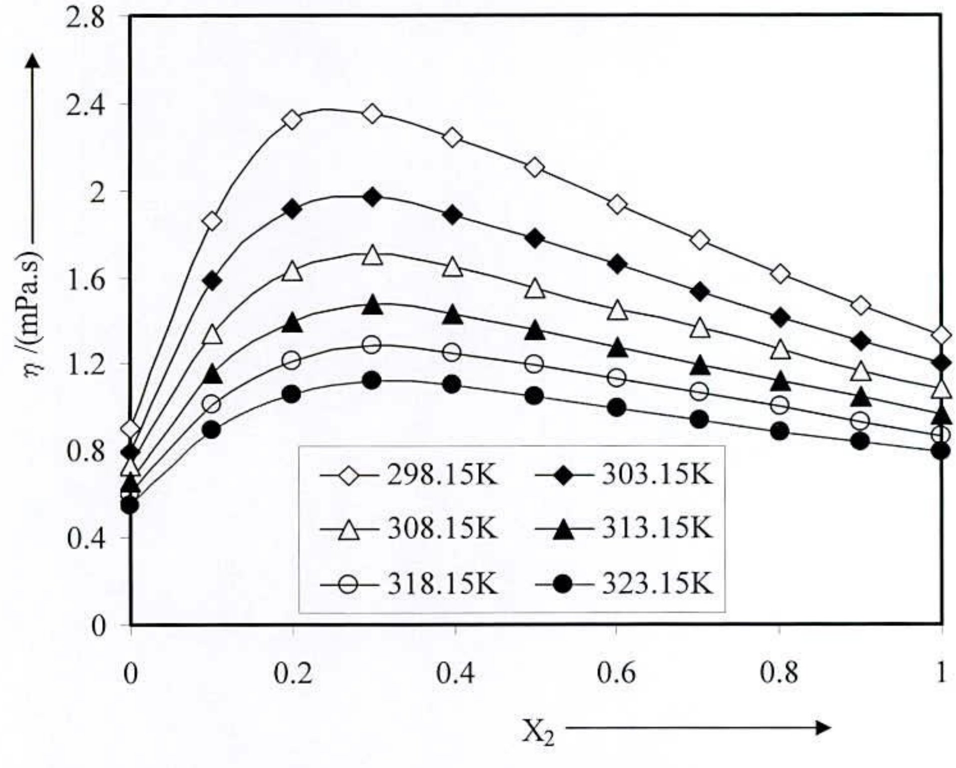

Figure 4.32: Plots of viscosity vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

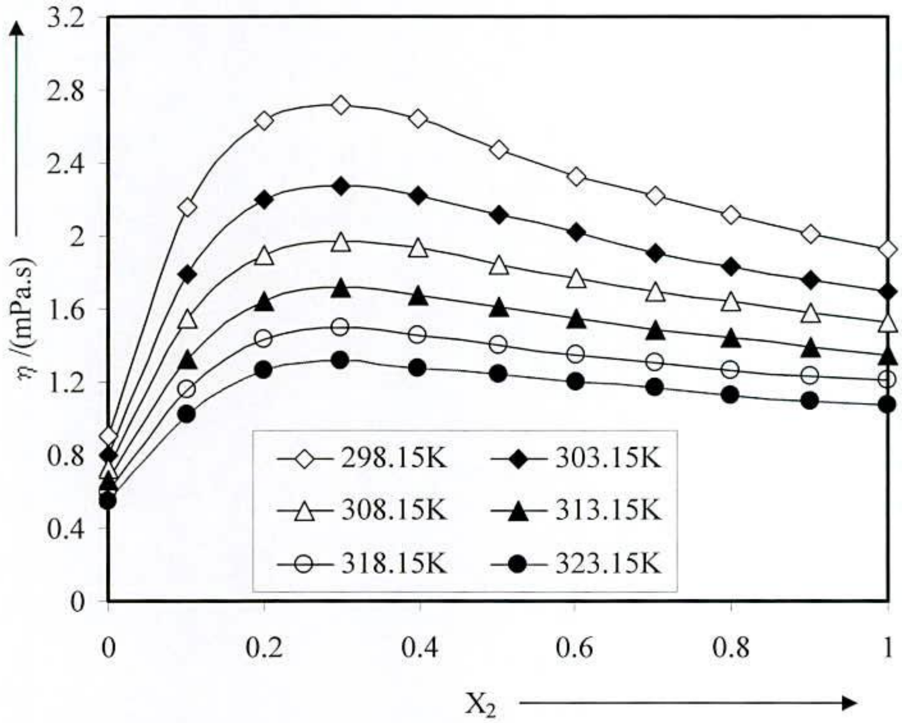

Figure 4.33: Plots of viscosity vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

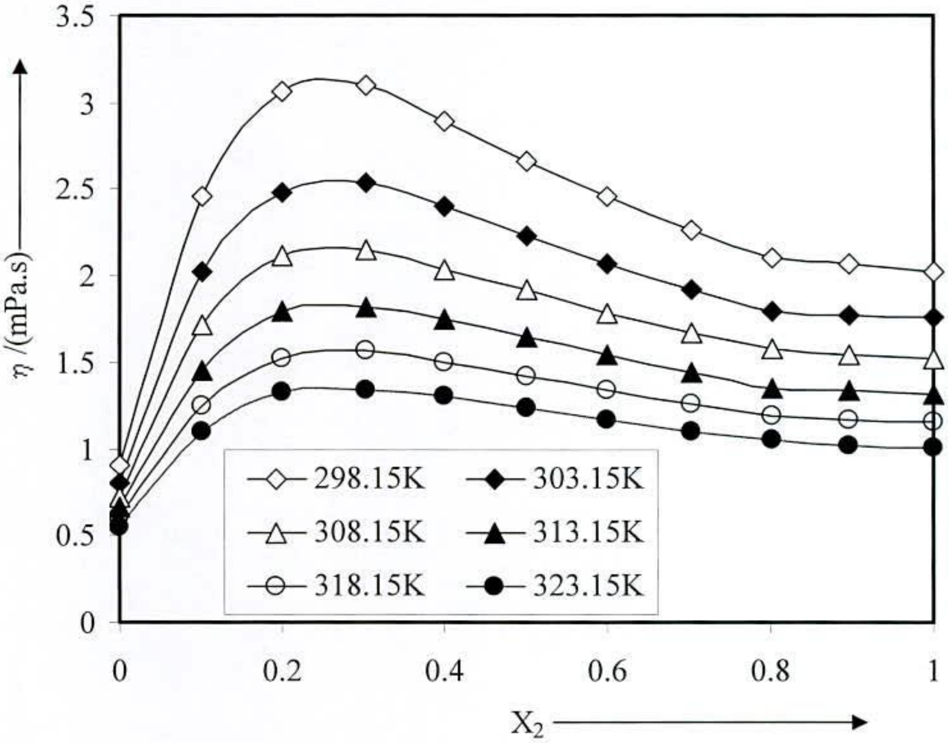

Figure 4.34: Plots of viscosity vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

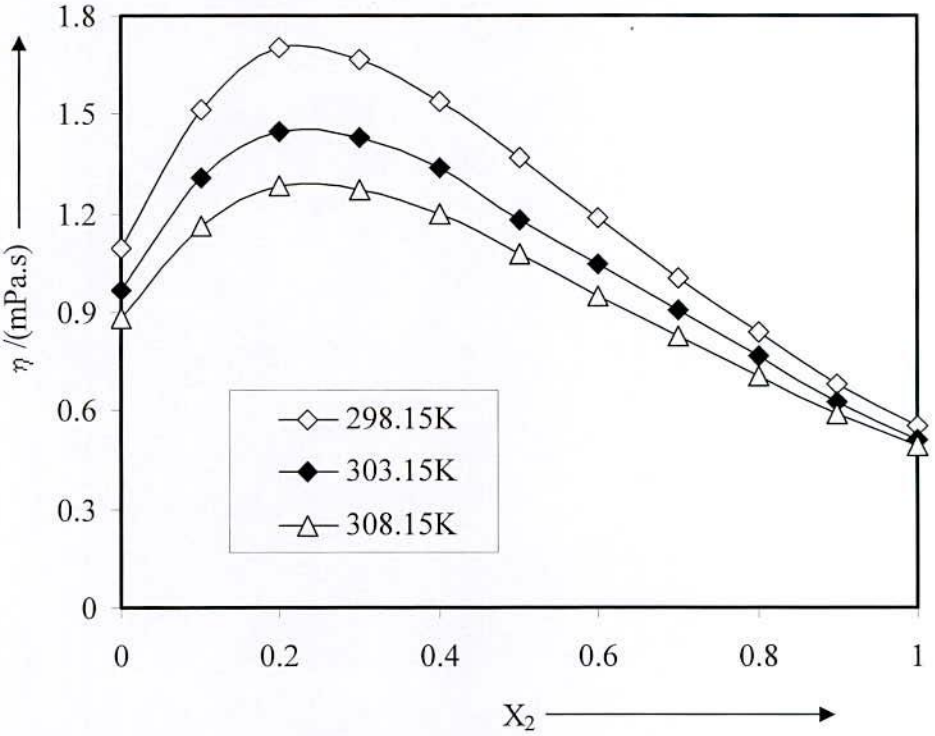

Figure 4.35: Plots of viscosity vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

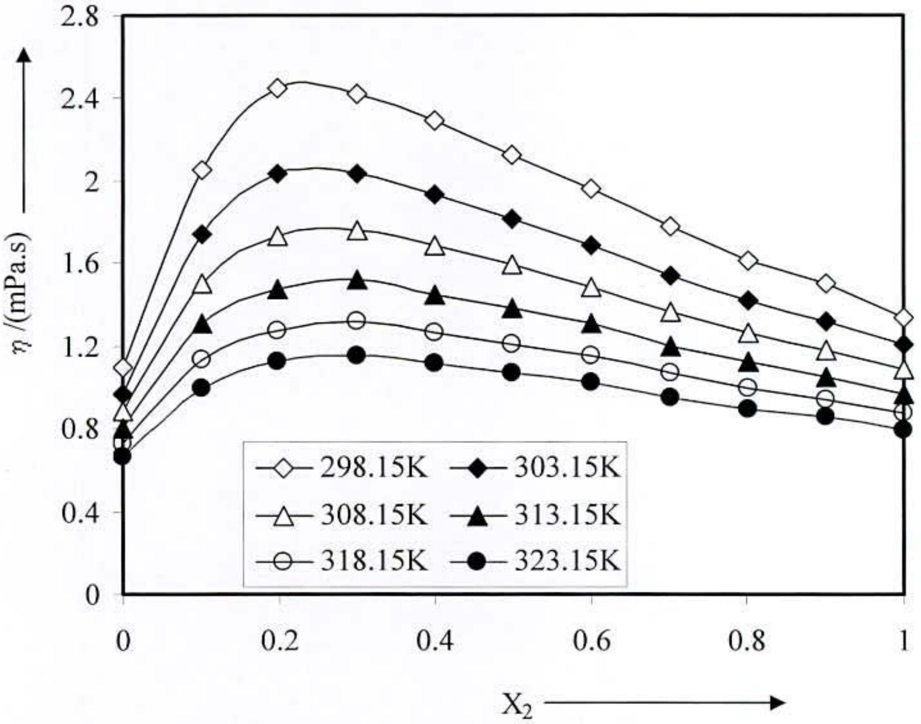

Figure 4.36: Plots of viscosity vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

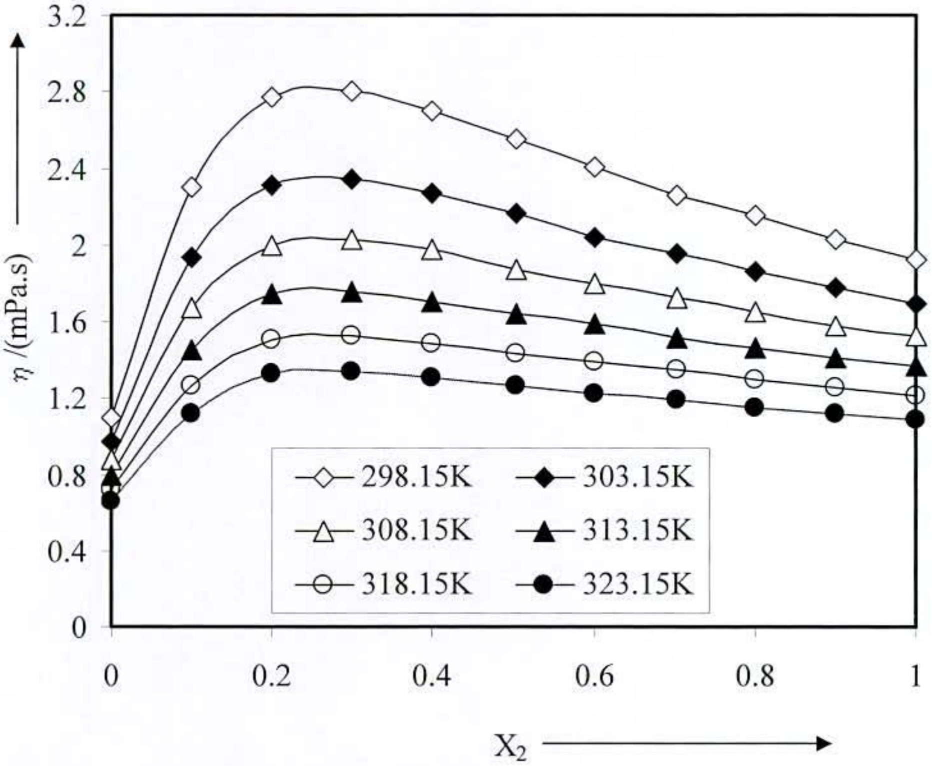

Figure 4.37: Plots of viscosity vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

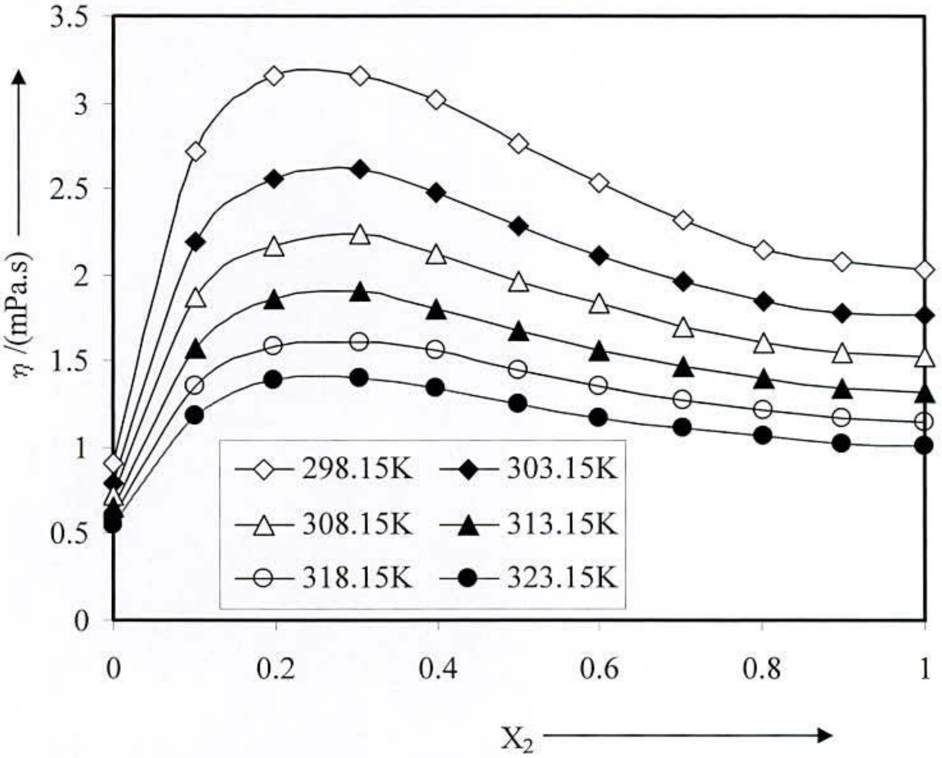

Figure 4.38: Plots of viscosity vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

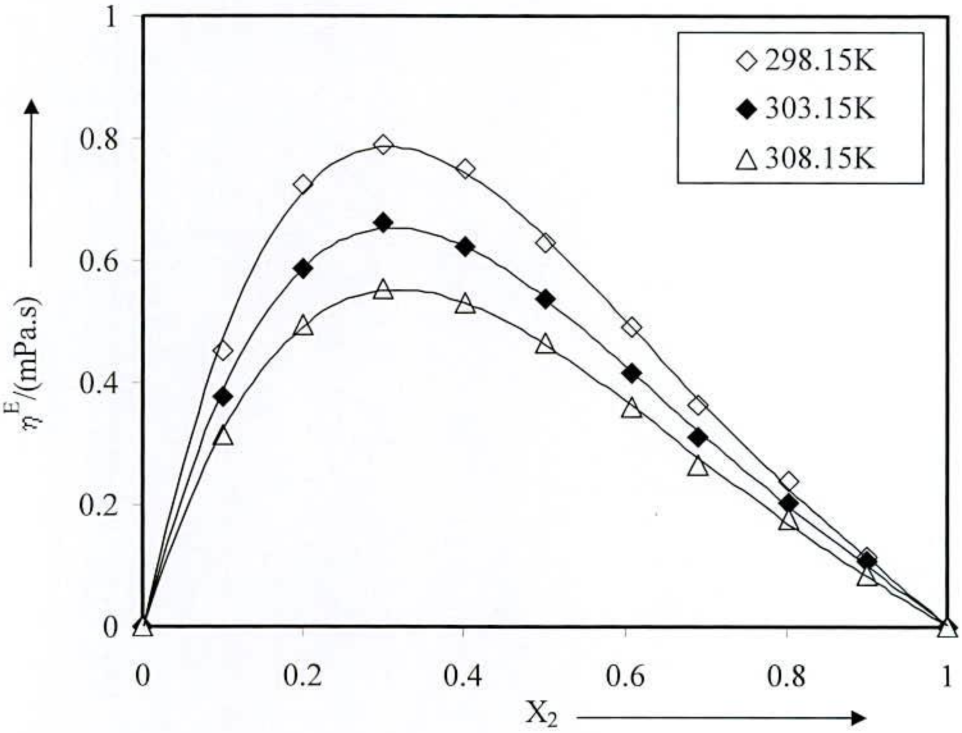

Figure 4.39: Plots of excess viscosity vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively.

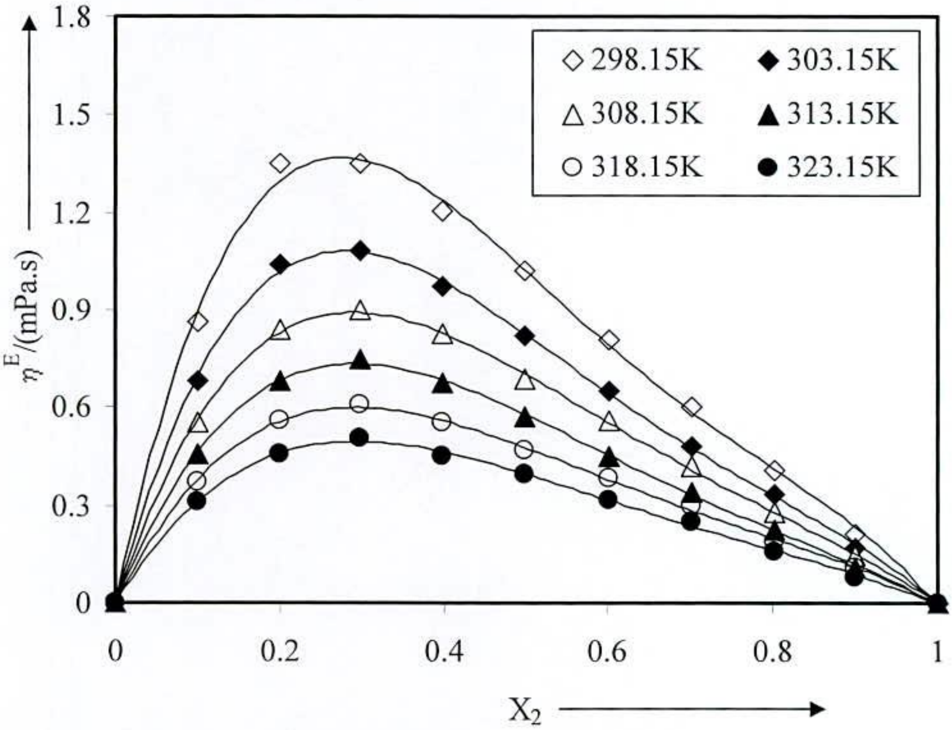

Figure 4.40: Plots of excess viscosity vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

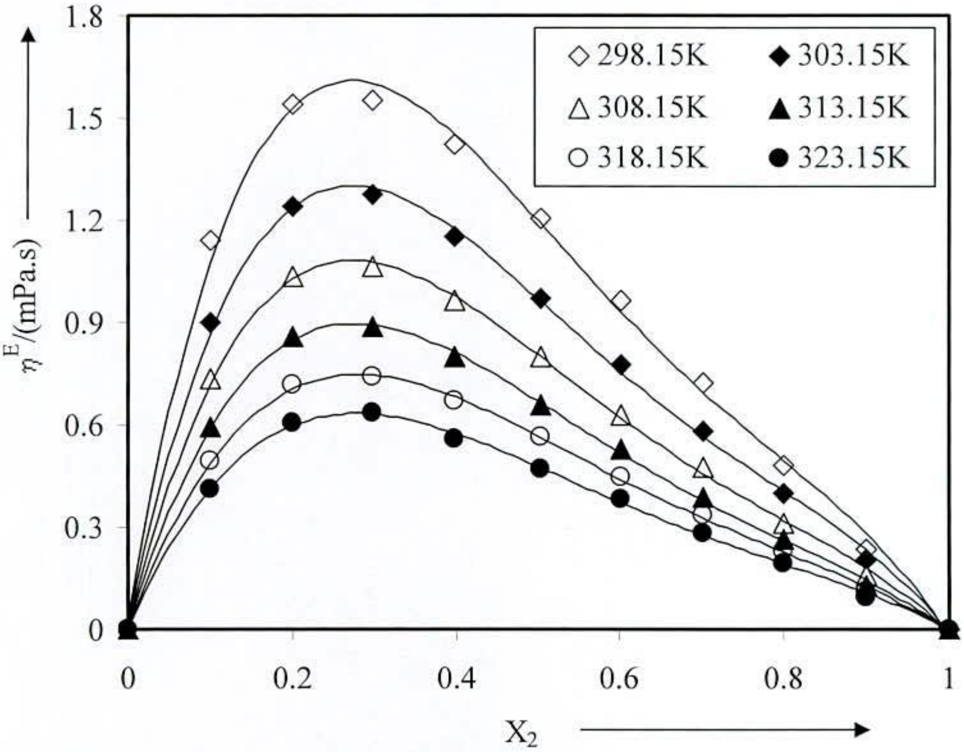

Figure 4.41: Plots of excess viscosity vs mole fraction of n-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

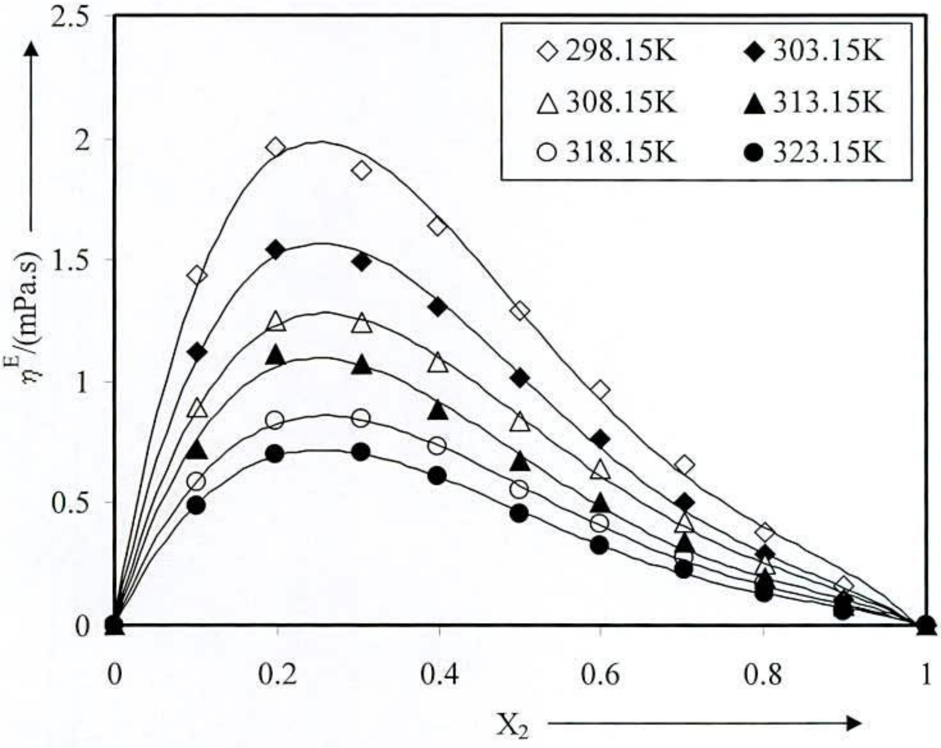

Figure 4.42: Plots of excess viscosity vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

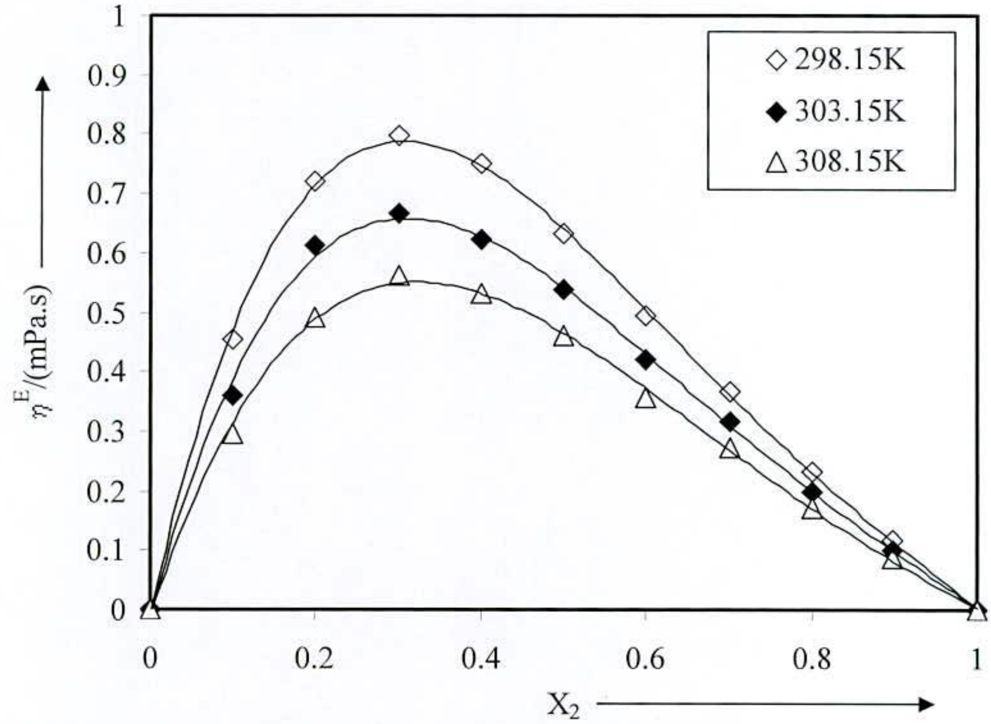

Figure 4.43: Plots of excess viscosity vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

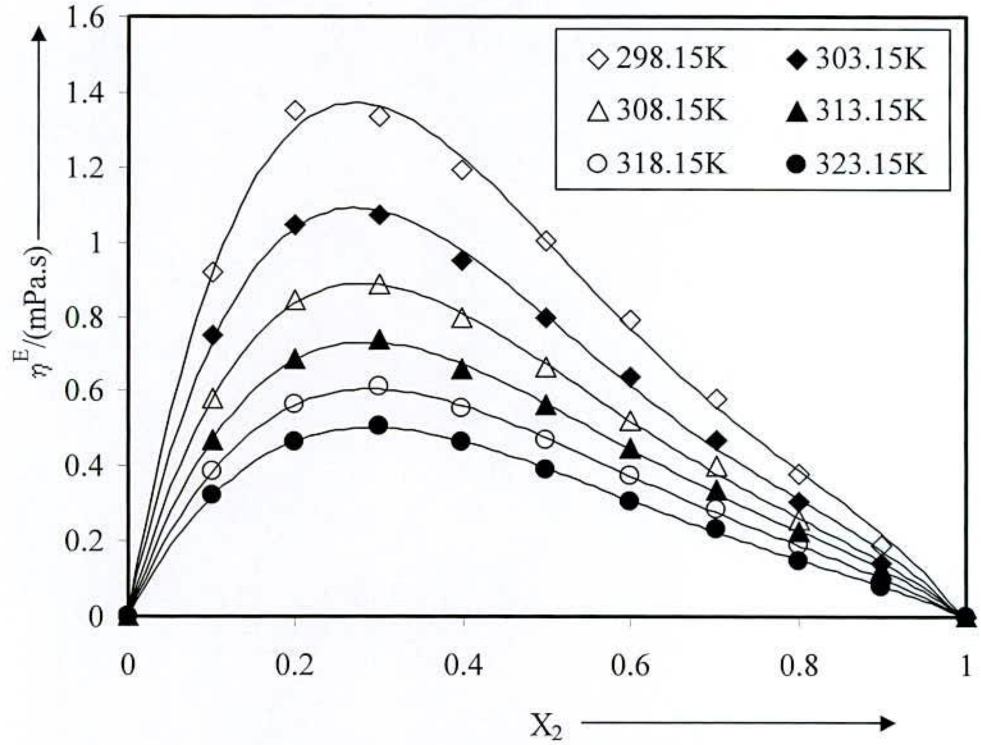

Figure 4.44: Plots of excess viscosity vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

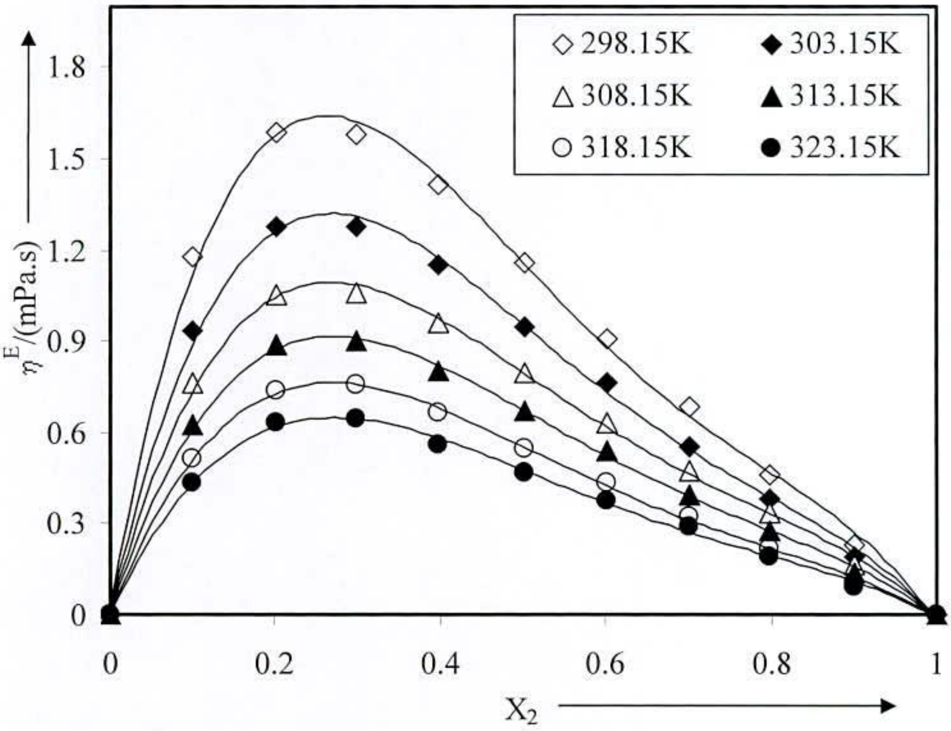

Figure 4.45: Plots of excess viscosity vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

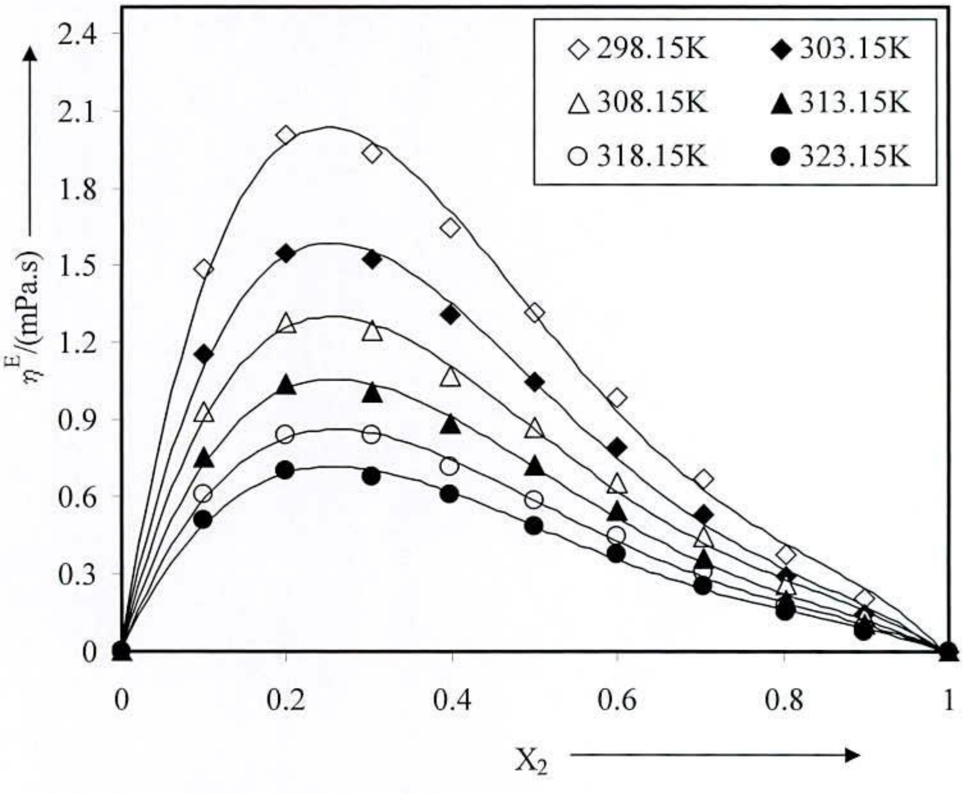

Figure 4.46: Plots of excess viscosity vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

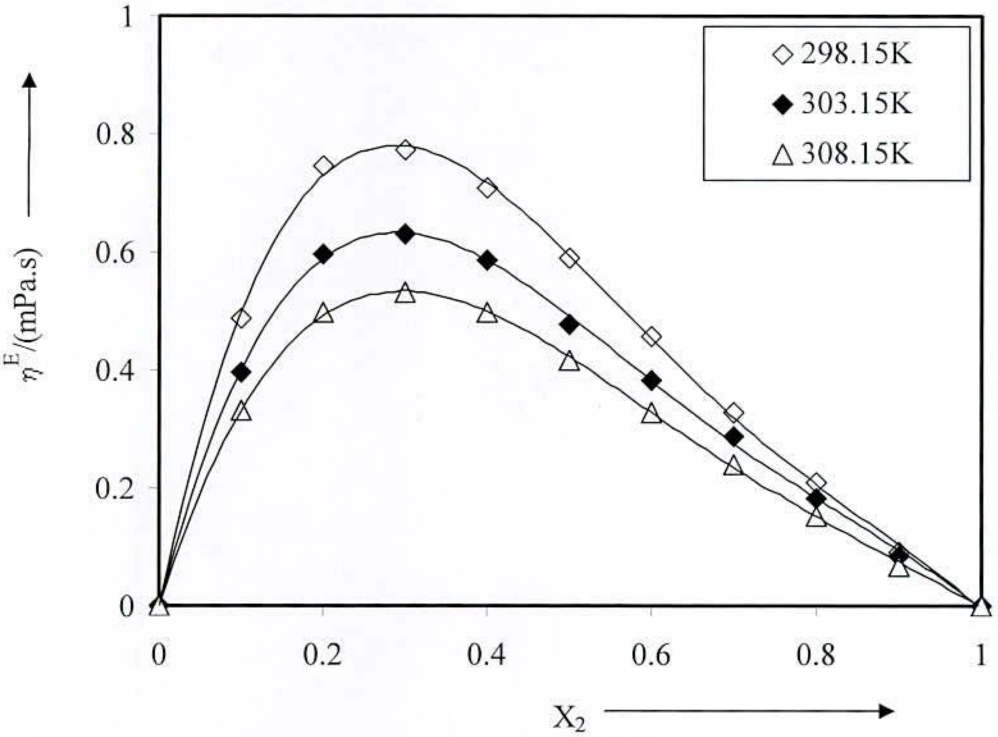

Figure 4.47: Plots of excess viscosity vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

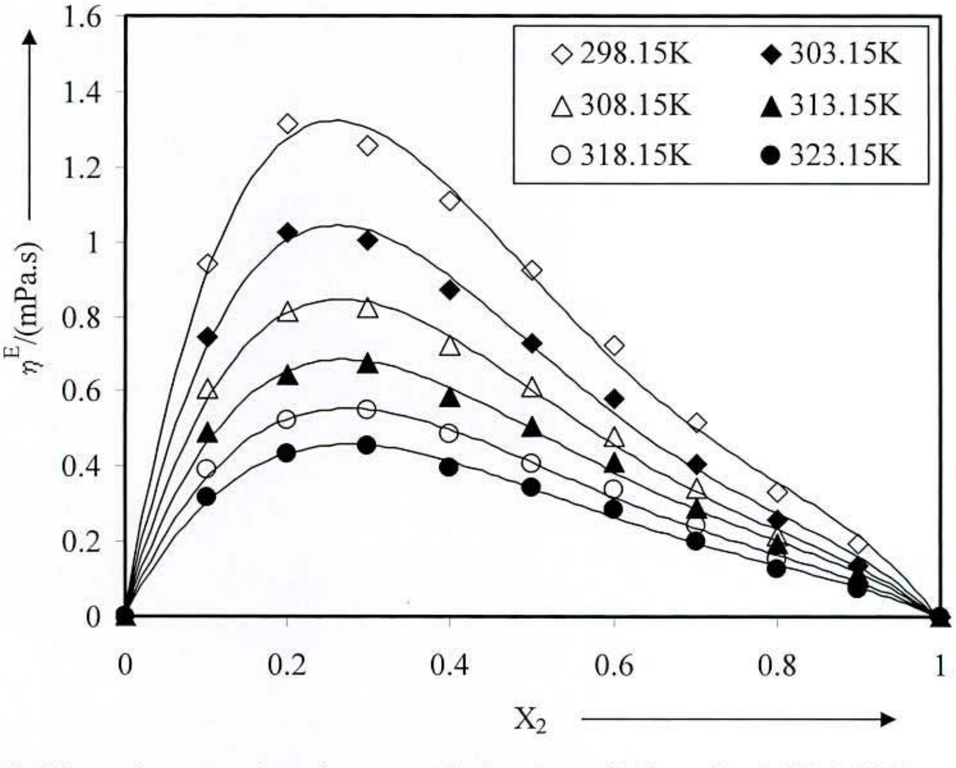

Figure4.48: Plots of excess viscosity vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

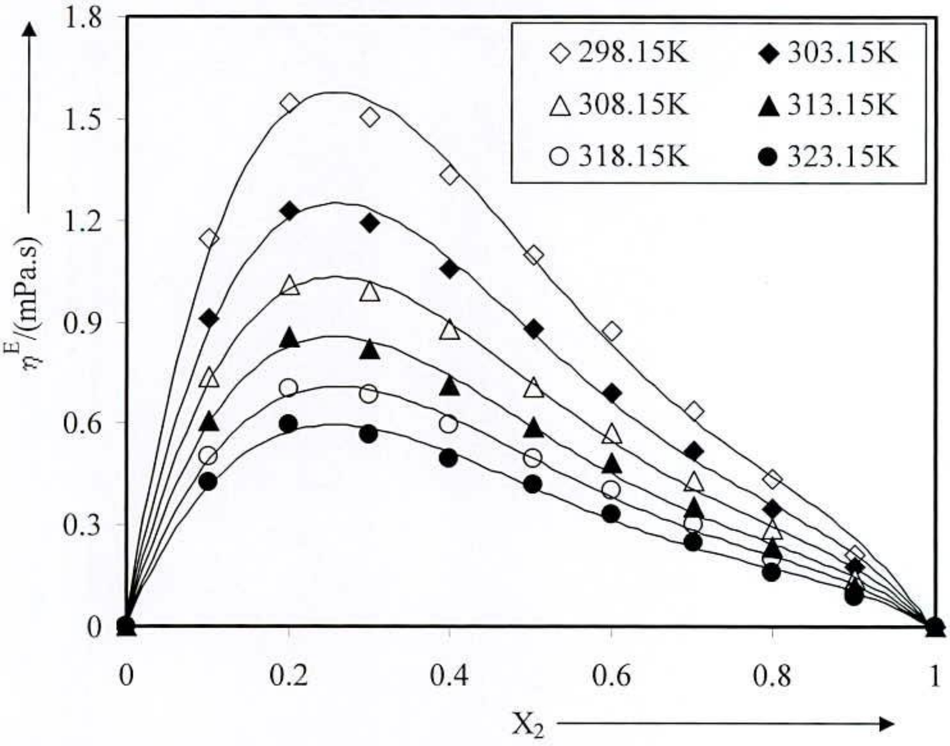

Figure 4.49: Plots of excess viscosity vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

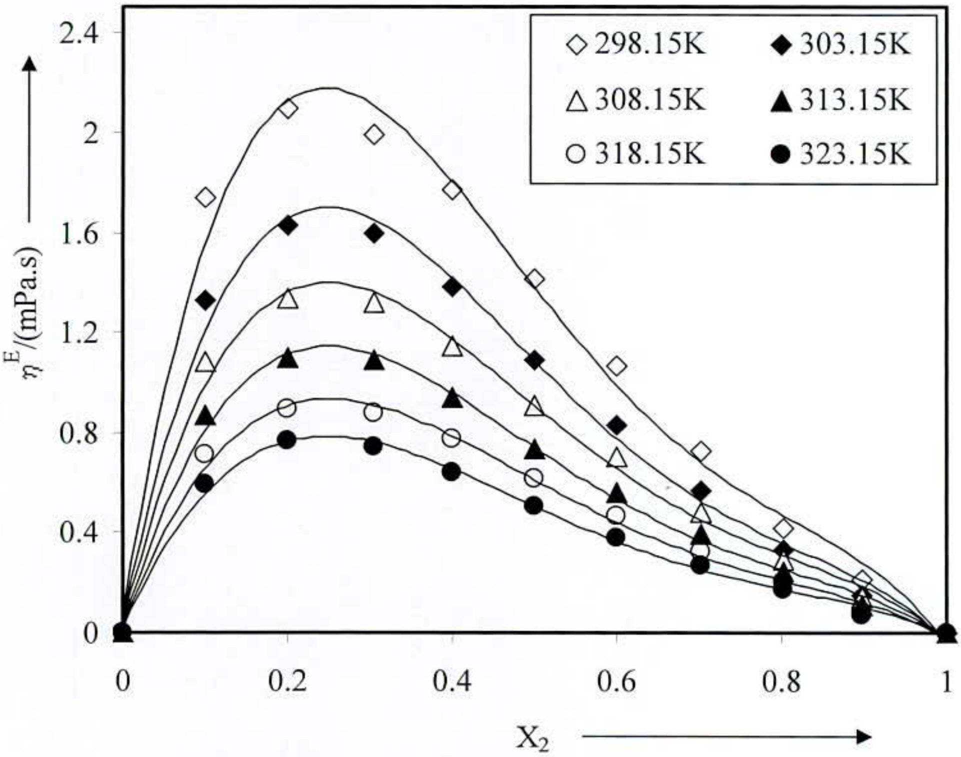

Figure 4.50: Plots of excess viscosity vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

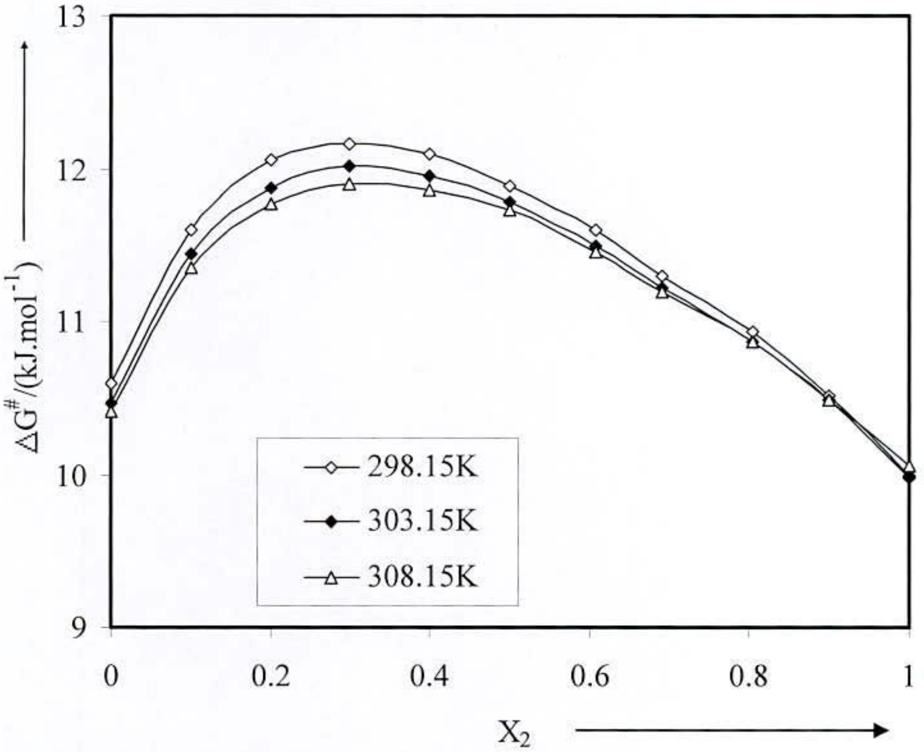

Figure 4.51: Plots of change of free energy vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively.

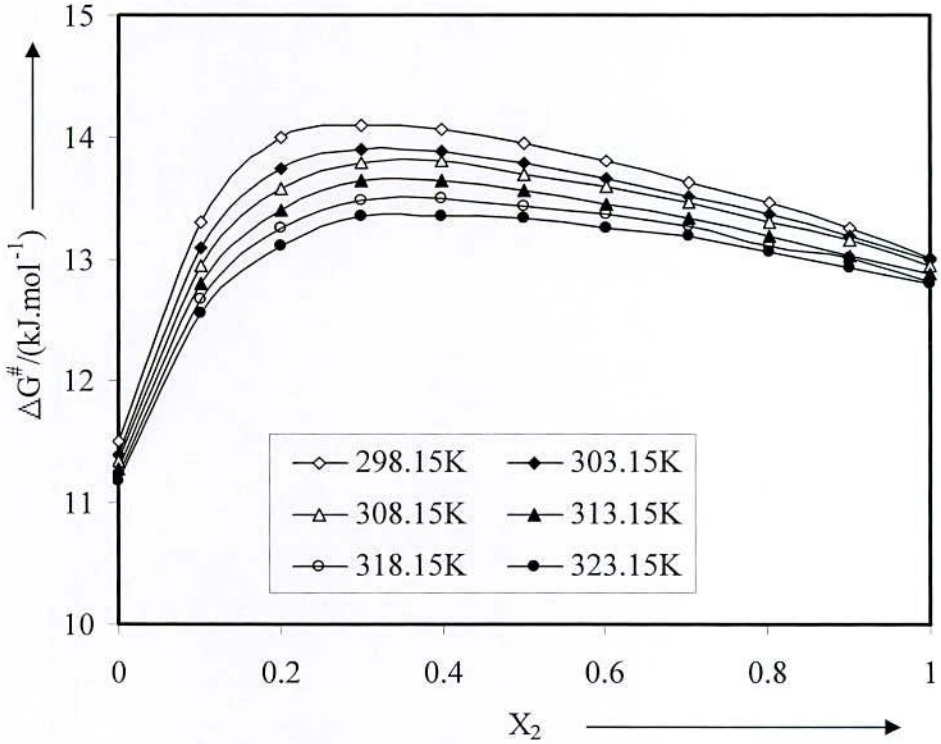

Figure 4.52: Plots of change of free energy vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

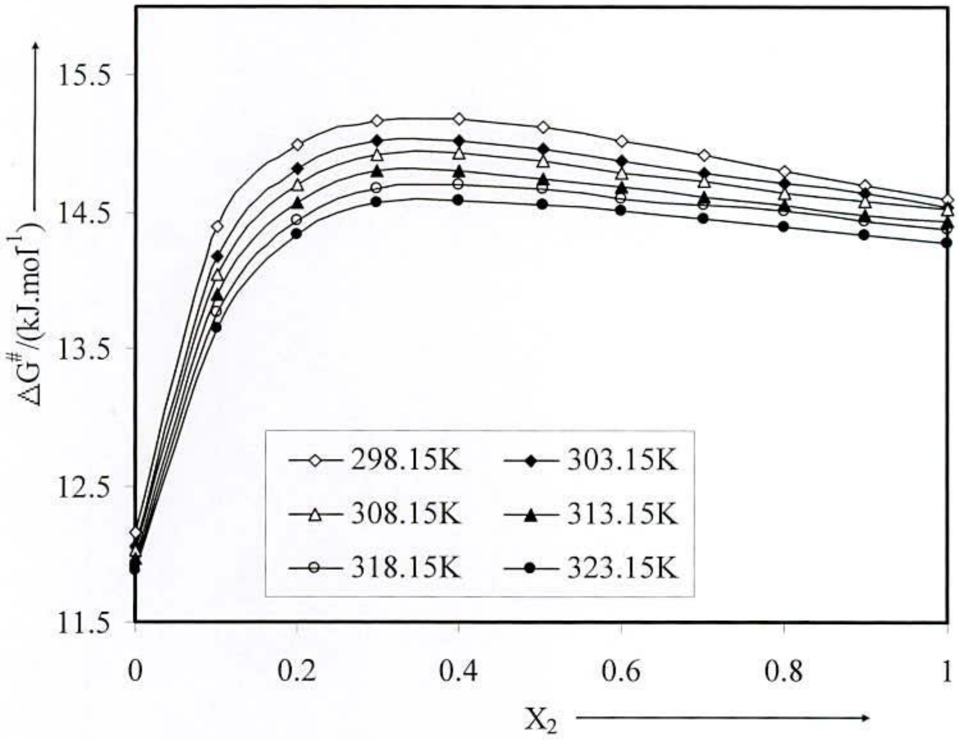

Figure 4.53: Plots of change of free energy vs mole fraction of n-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

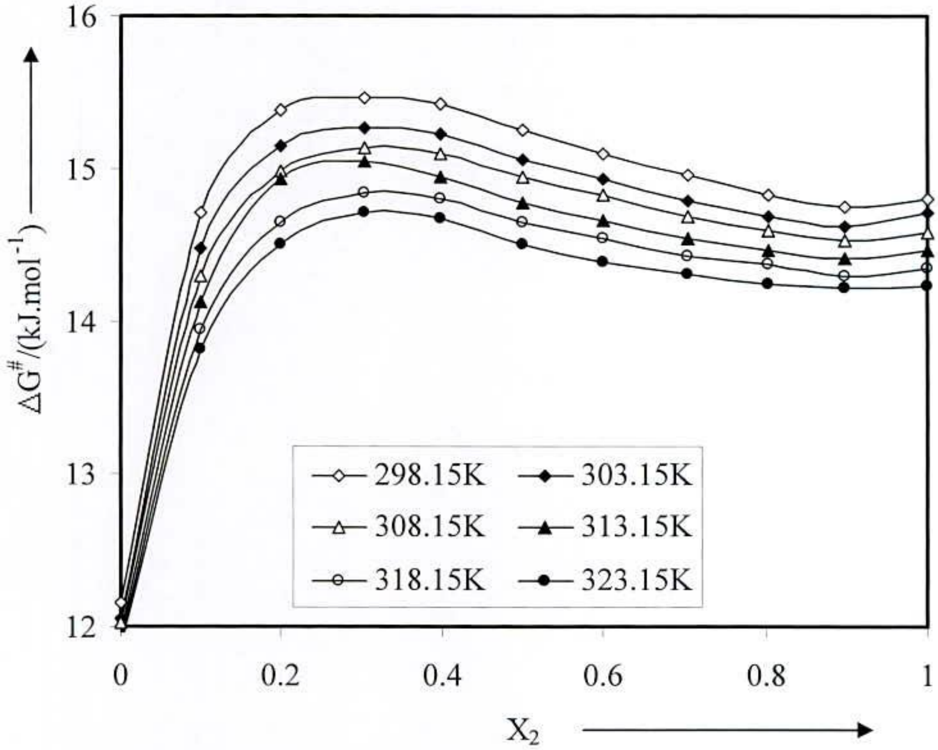

Figure 4.54: Plots of change of free energy vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

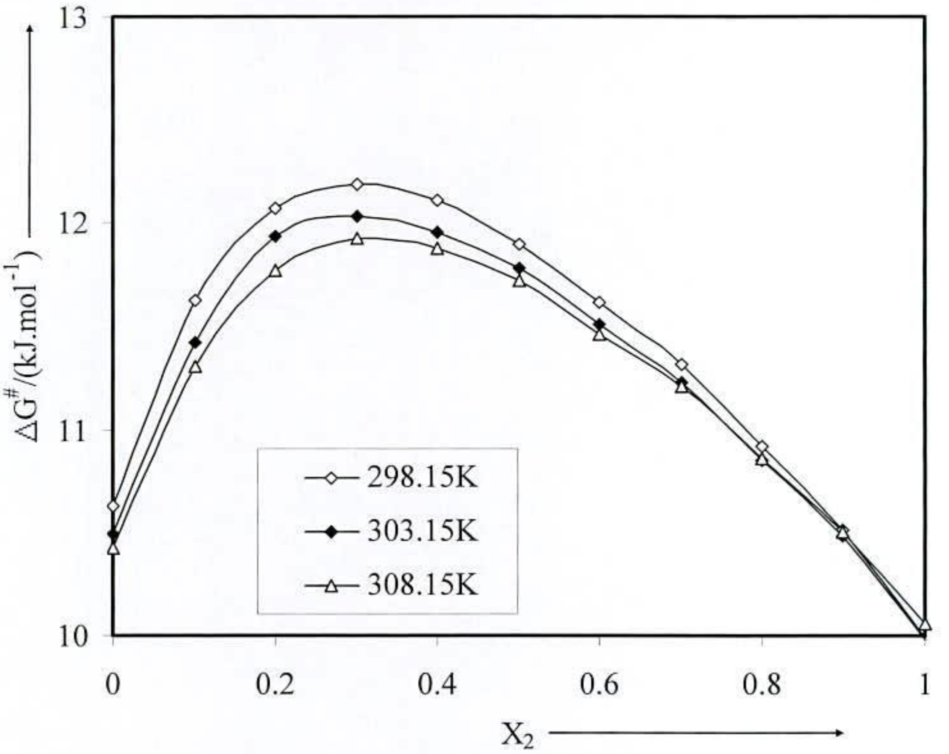

Figure 4.55: Plots of change of Free energy vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

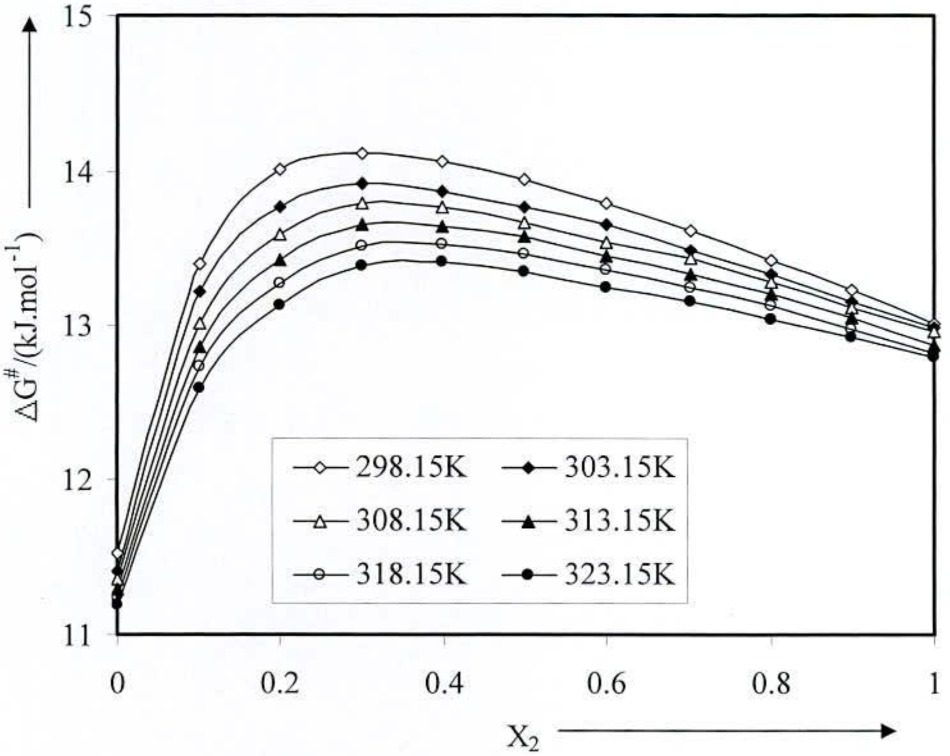

Figure 4.56: Plots of change of free energy vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

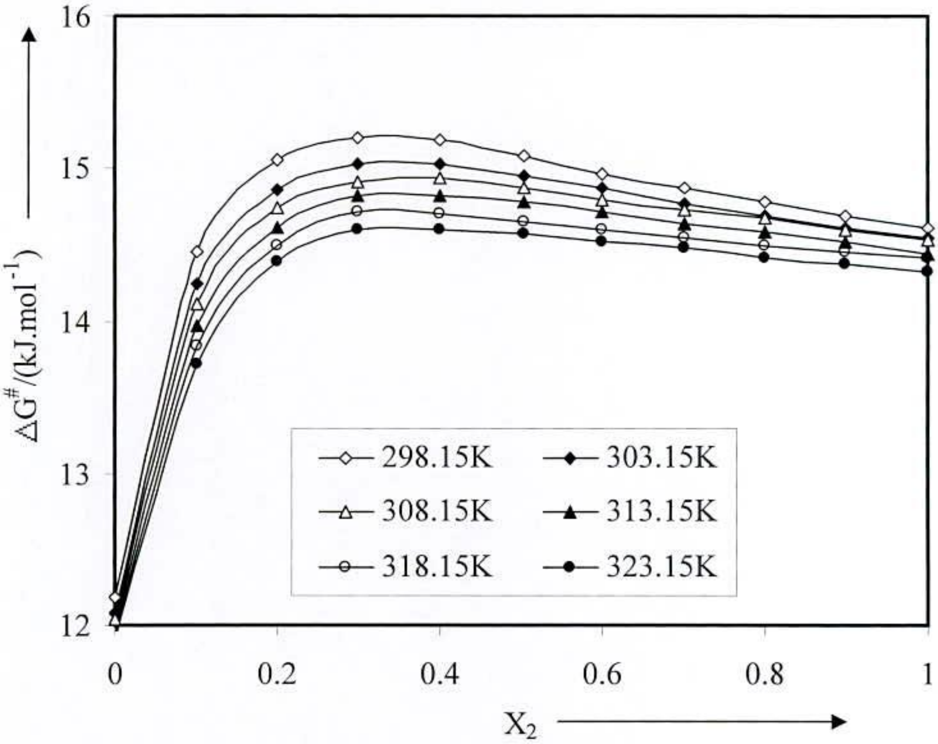

Figure 4.57: Plots of change of free energy vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

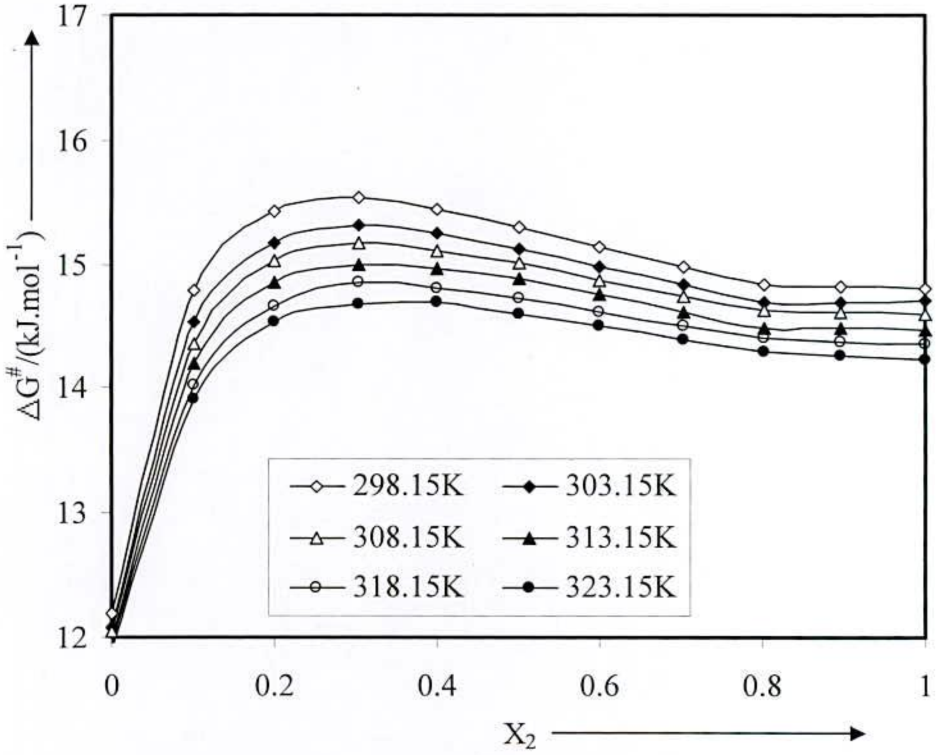

Figure 4.58: Plots of change of free energy vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

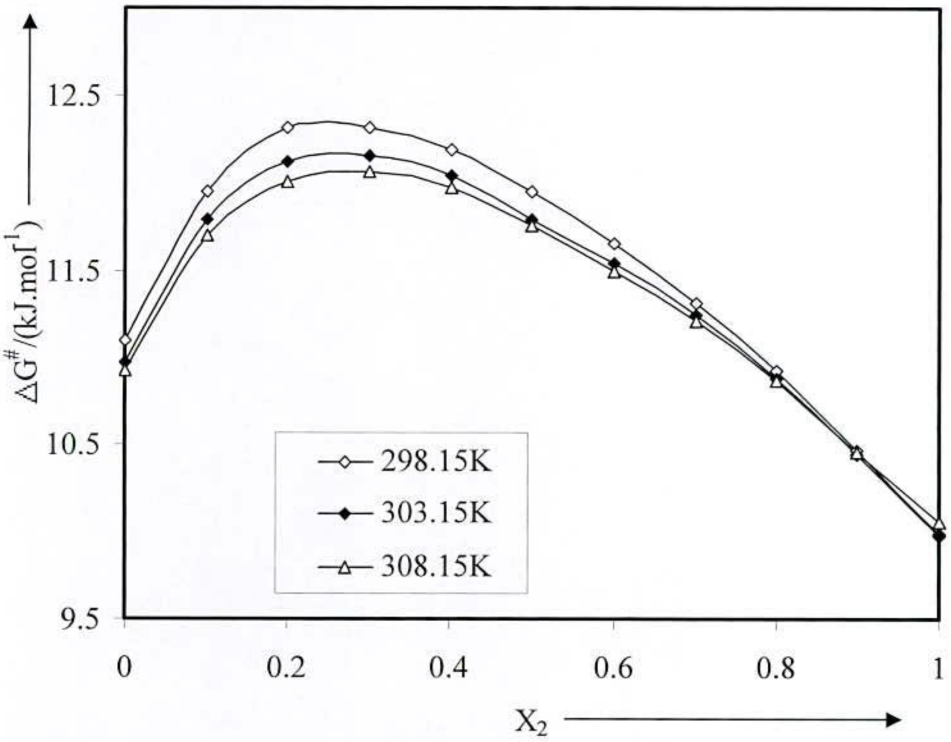

Figure 4.59: Plots of change of free energy vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

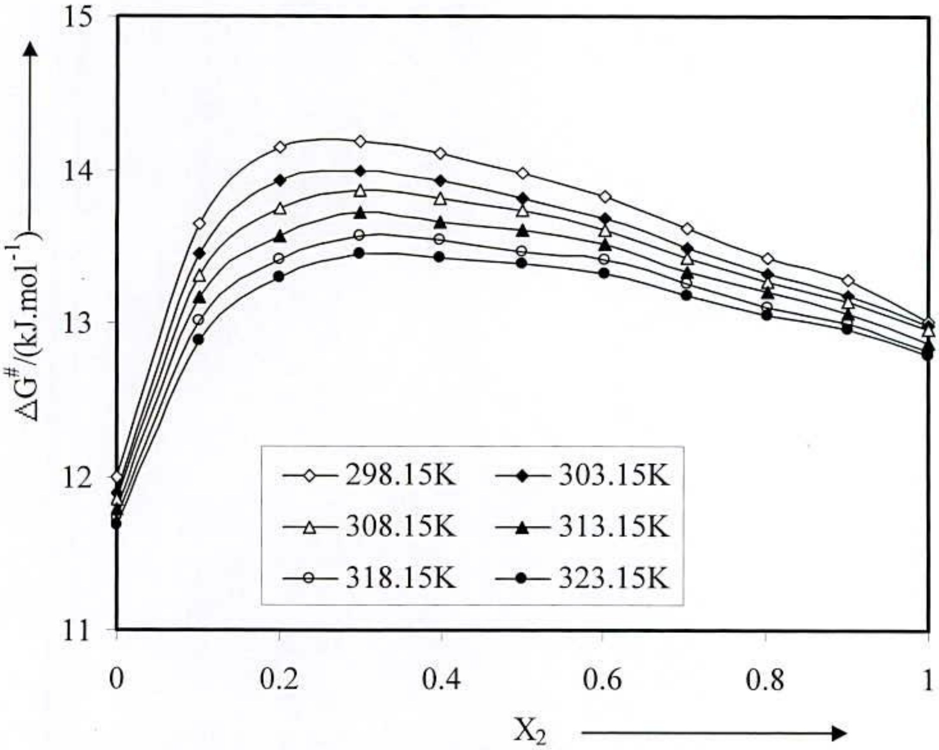

Figure 4.60: Plots of change of free energy vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

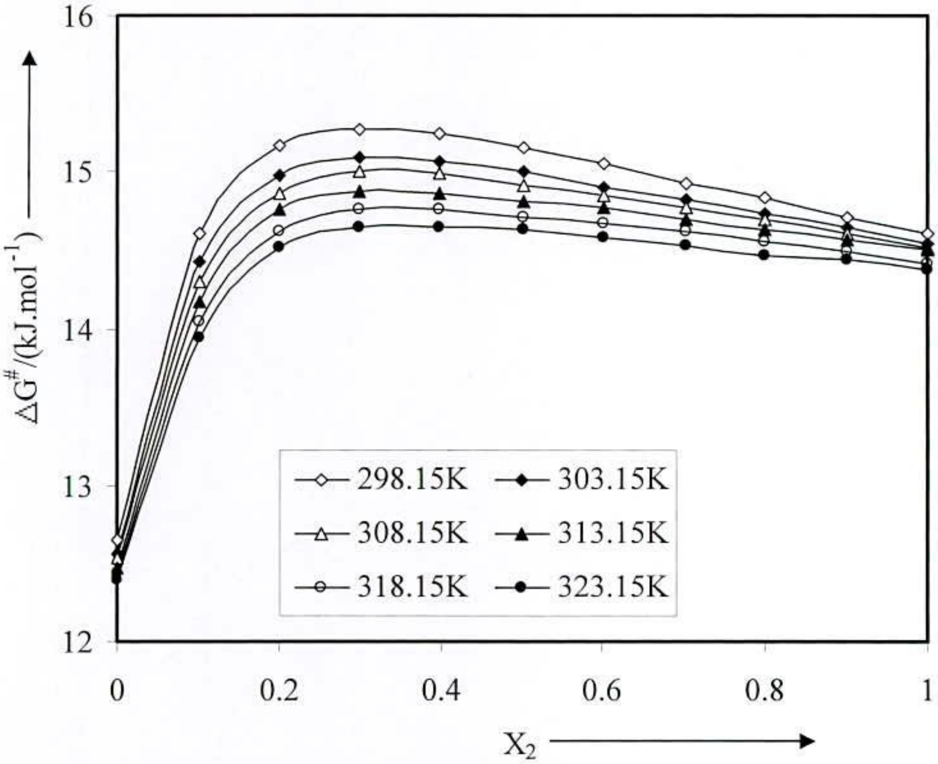

Figure 4.61: Plots of change of free energy vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

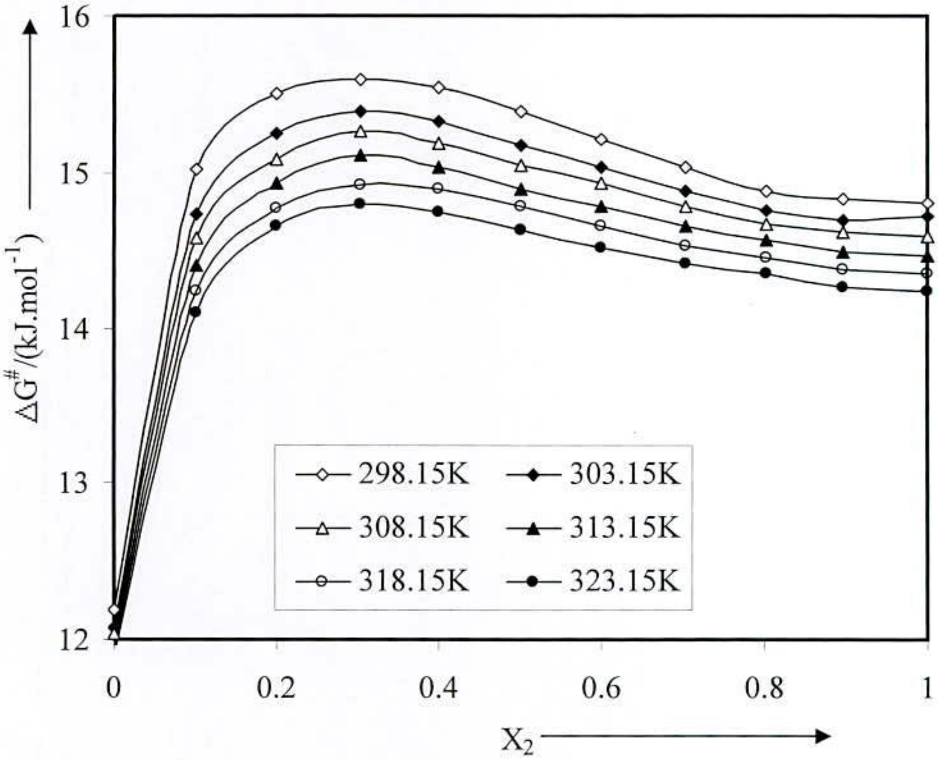

Figure 4.62: Plots of change of free energy vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

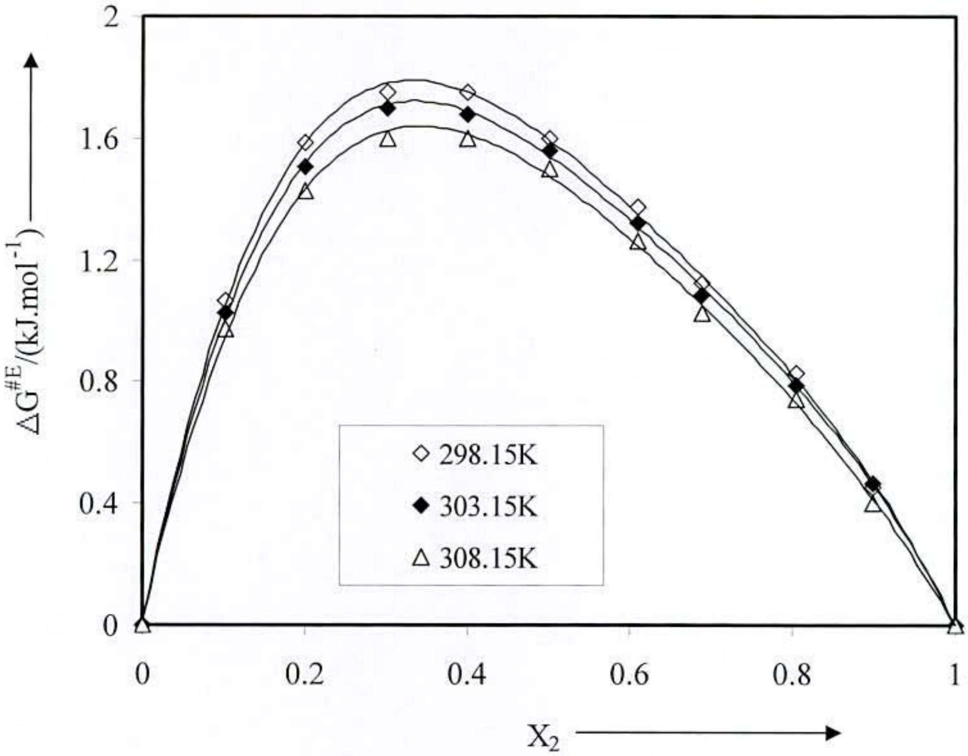

Figure 4.63: Plots of excess free energy vs mole fraction of Methanol + water system at 298.15K, 303.15K, 308.15K respectively.

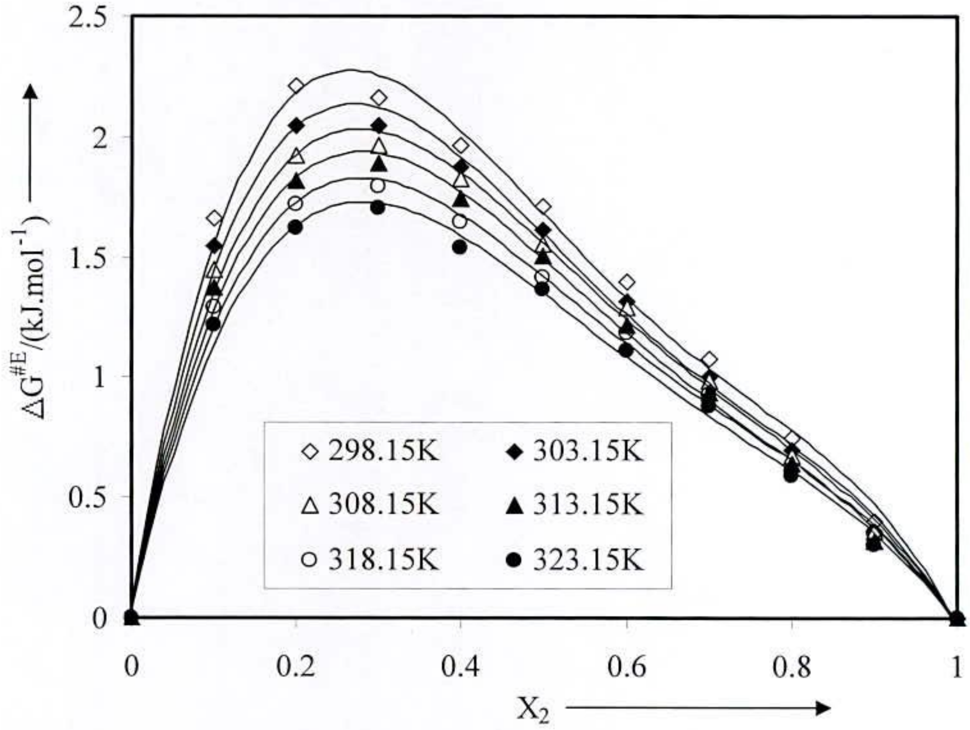

Figure 4.64: Plots of excess free energy vs mole fraction of Ethanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

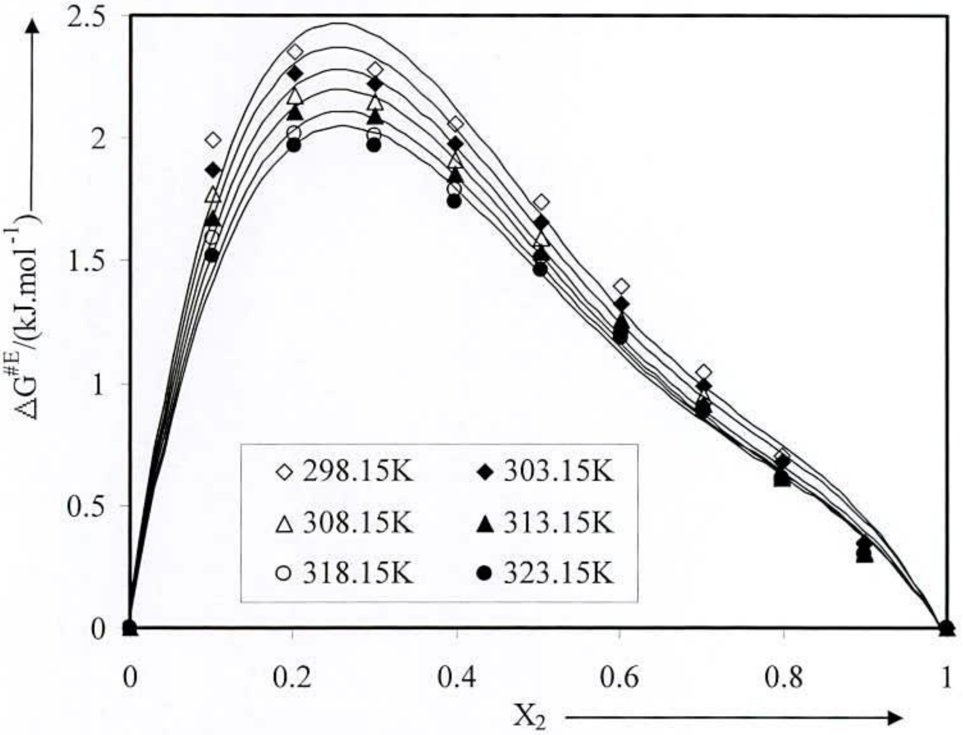

Figure 4.65: Plots of excess free energy vs mole fraction of n-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

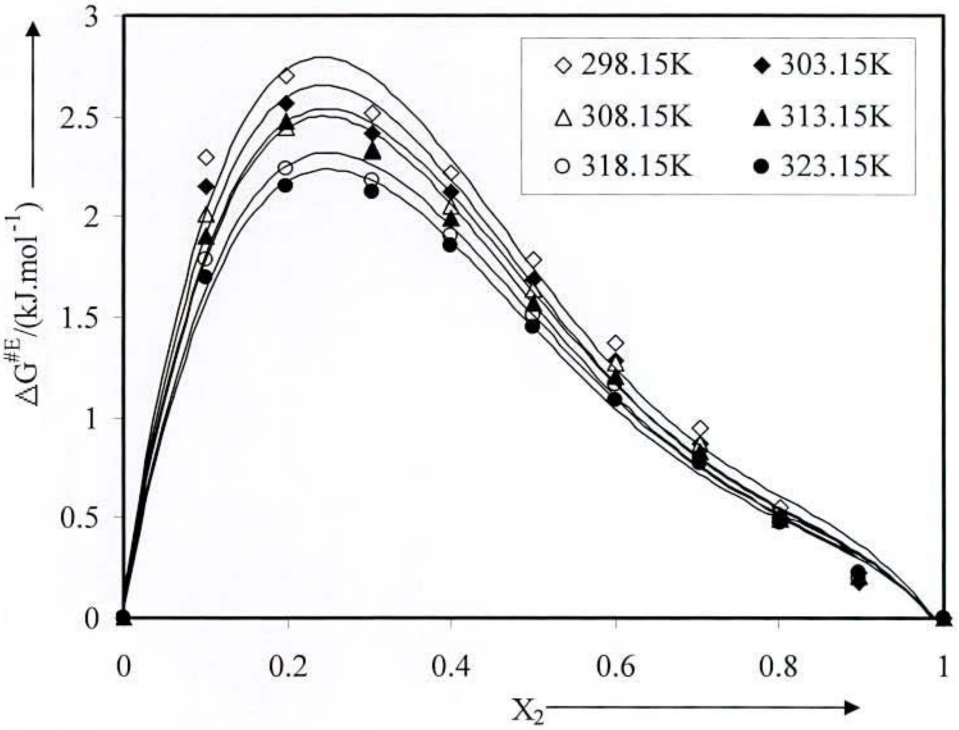

Figure 4.66: Plots of excess free energy vs mole fraction of iso-Propanol + water system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

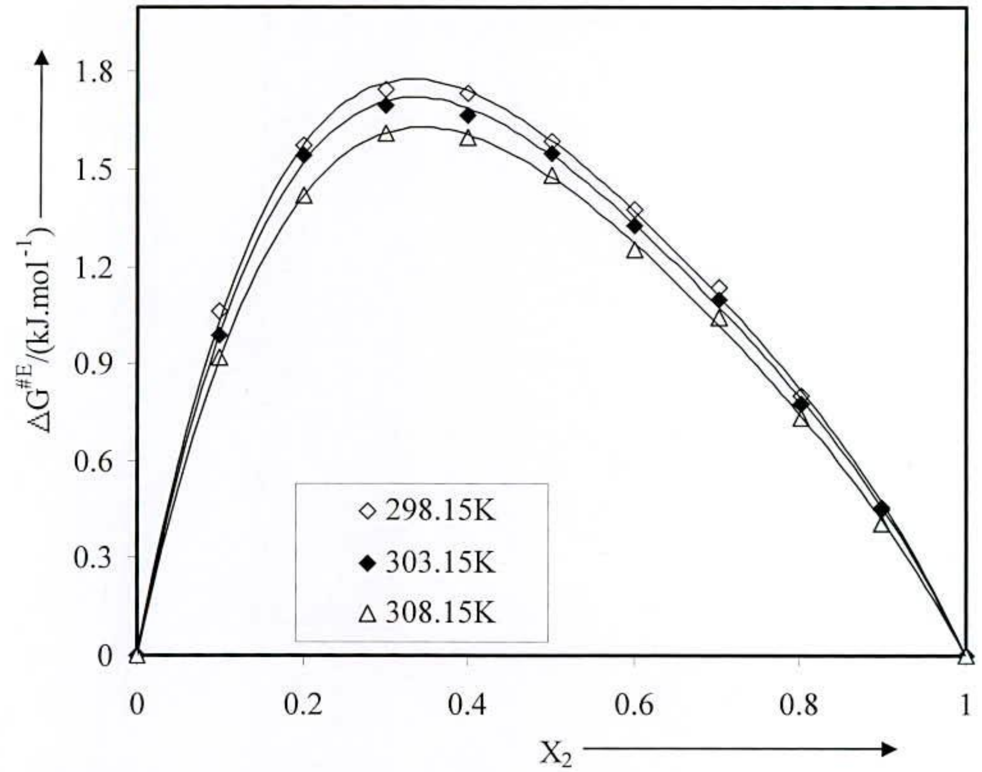

Figure 4.67: Plots of excess Free energy vs mole fraction of Methanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K respectively.

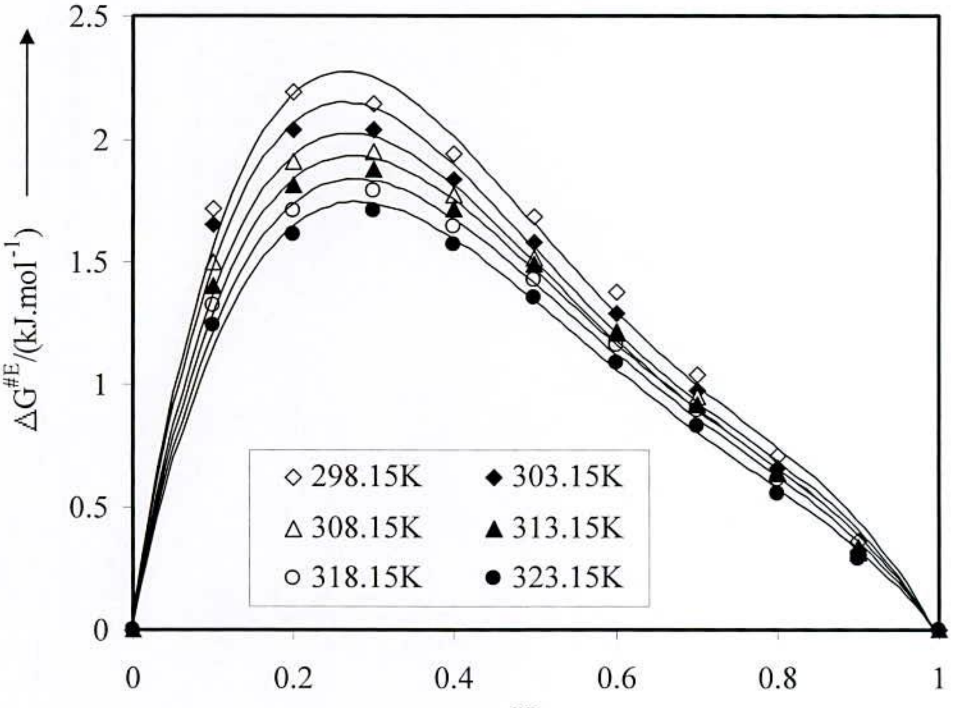

Figure 4.68: Plots of excess free energy vs mole fraction of Ethanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

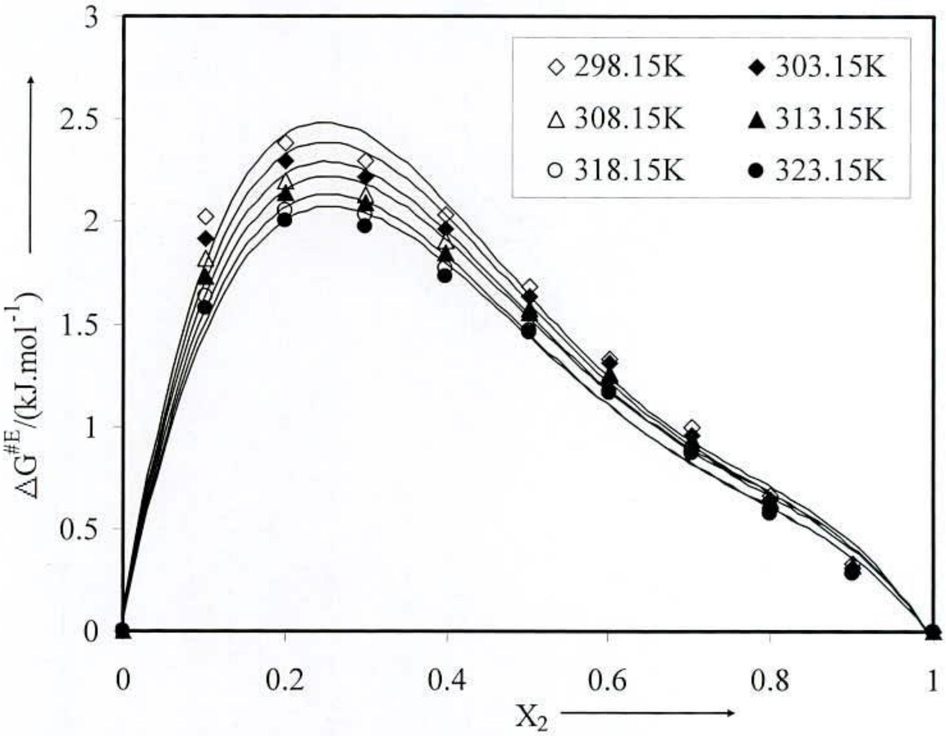

Figure 4.69: Plots of excess free energy vs mole fraction of n-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

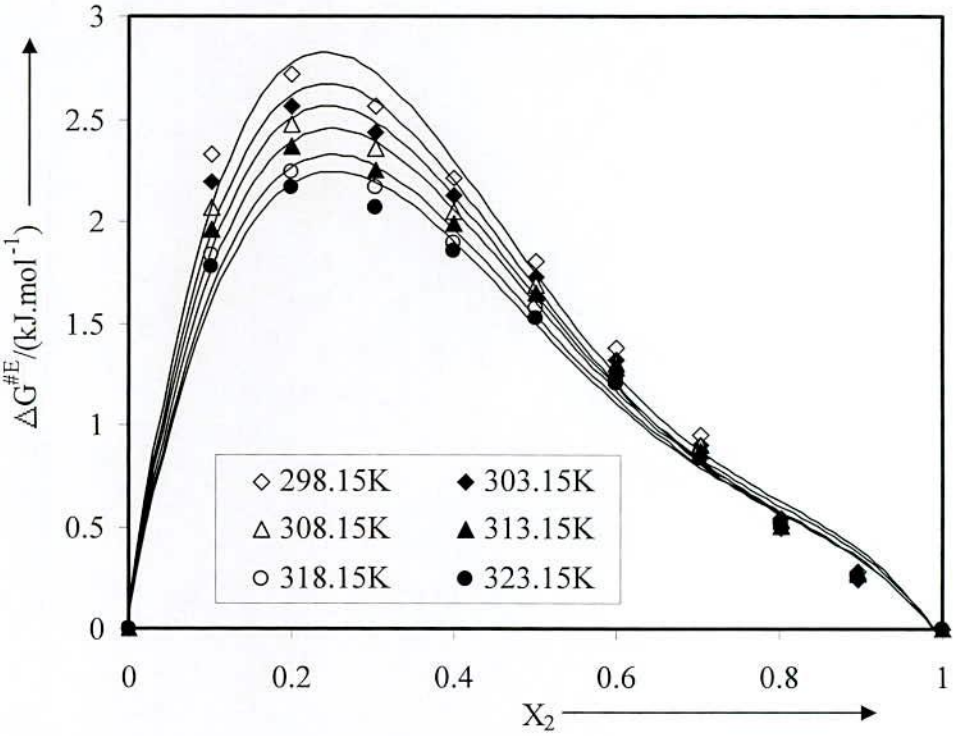

Figure 4.70: Plots of excess free energy vs mole fraction of iso-Propanol + 0.005M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

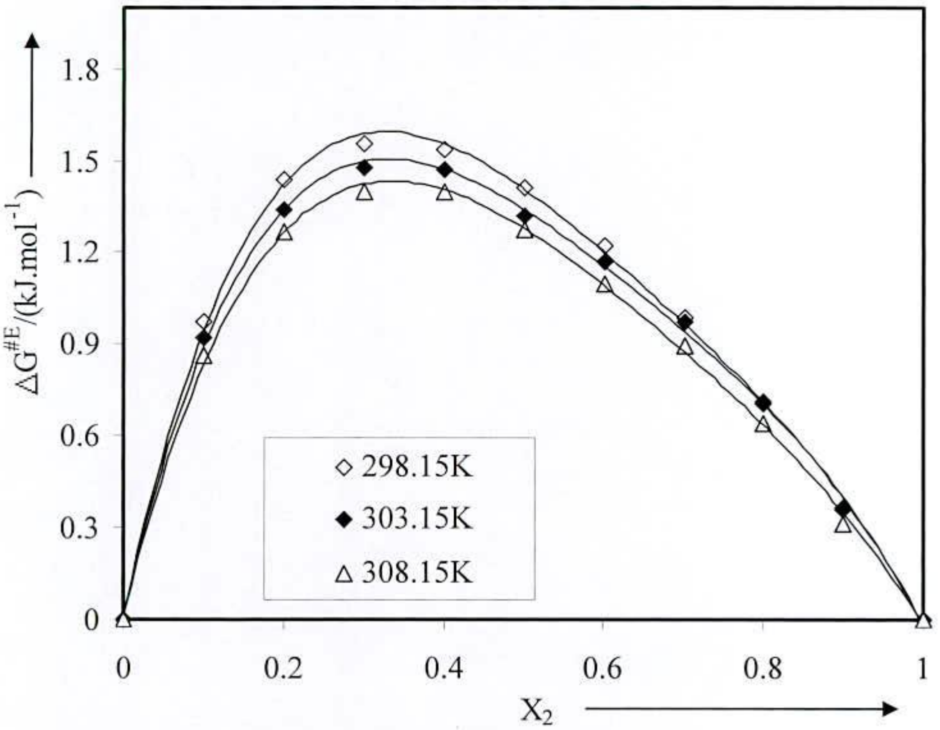

Figure 4.71: Plots of excess free energy vs mole fraction of Methanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K respectively.

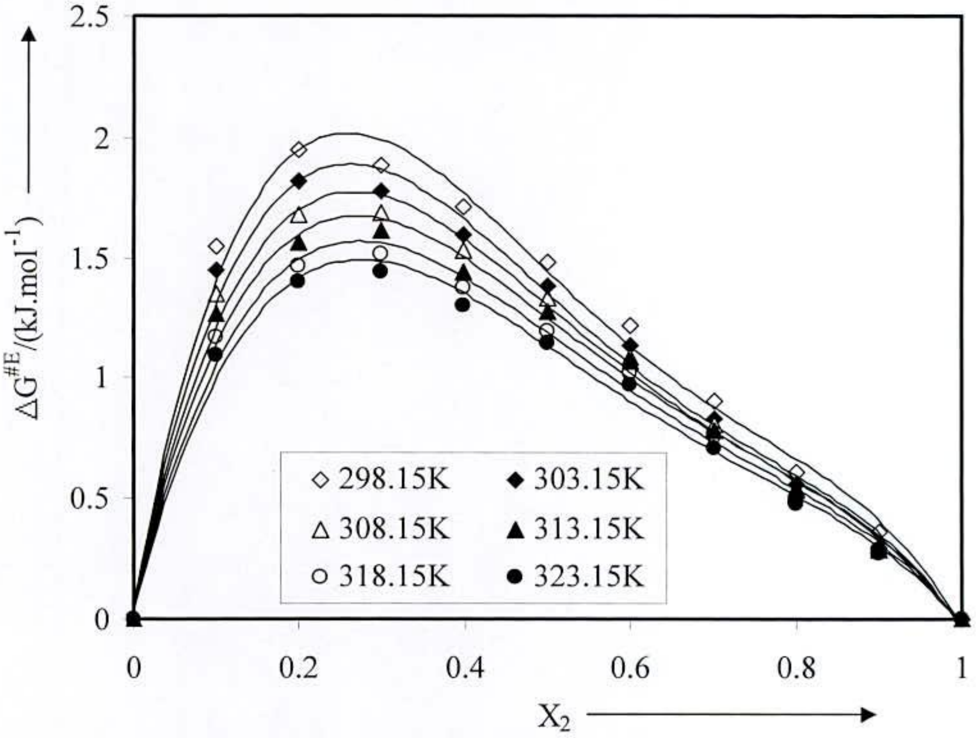

Figure 4.72: Plots of excess Free energy vs mole fraction of Ethanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

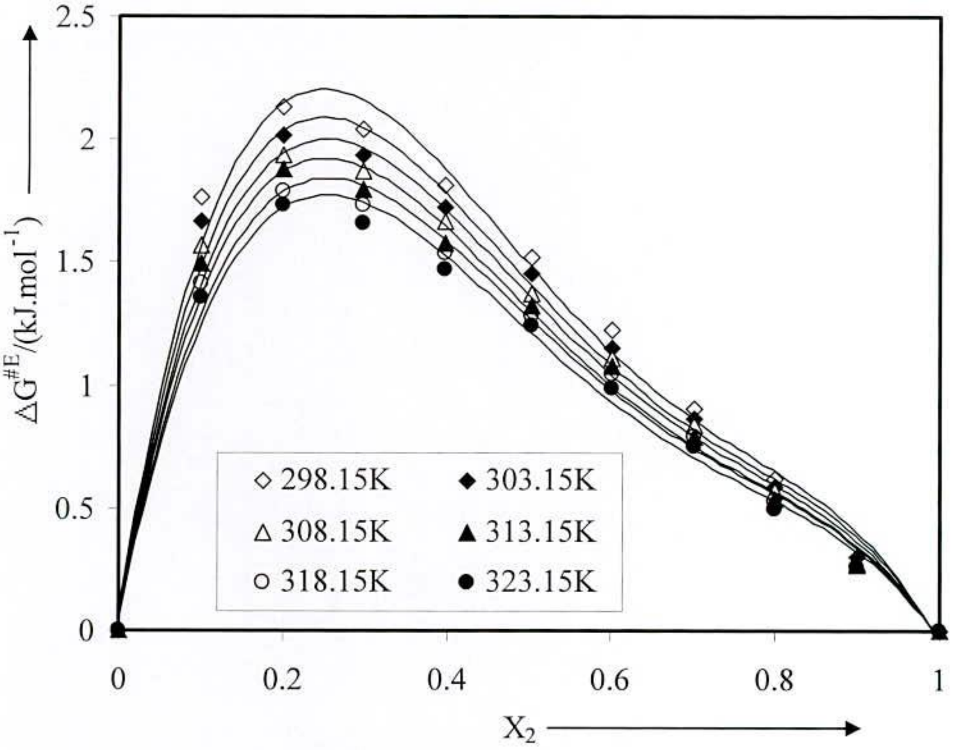

Figure 4.73: Plots of excess free energy vs mole fraction of n-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

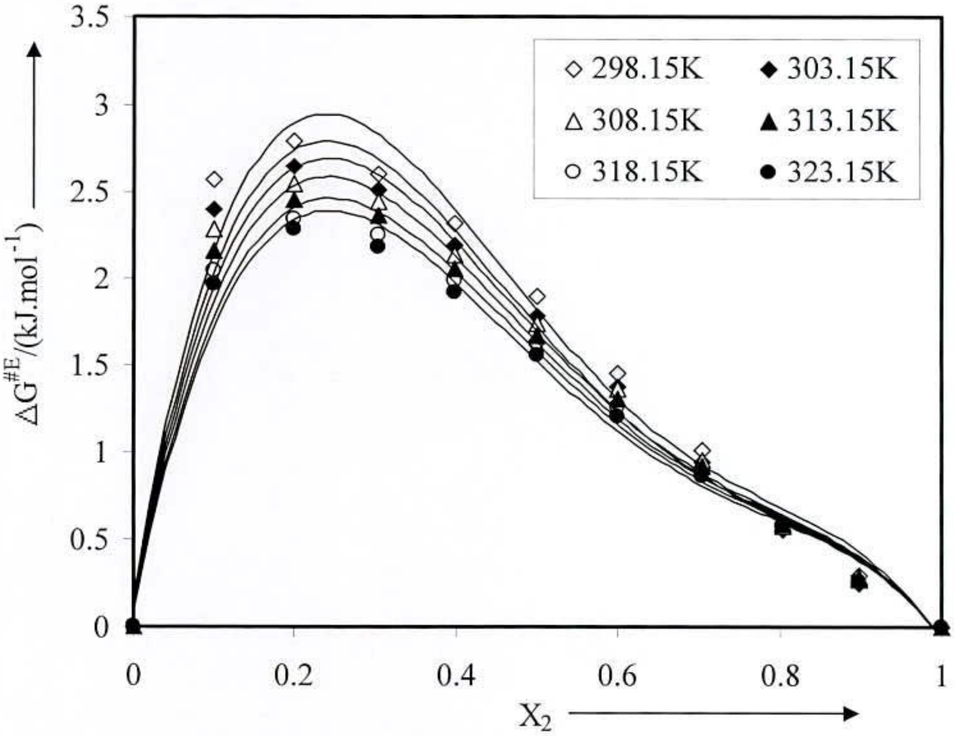

Figure 4.74: Plots of excess free energy vs mole fraction of iso-Propanol + 0.01M SDS system at 298.15K, 303.15K, 308.15K, 313.15K, 318.15K, 323.15K respectively.

# CHAPTER FIVE

## CONCLUSION

# CHAPTER V

## Conclusion

The studies presented in this thesis are based on simple binary and ternary systems. The molar conductivity and viscosity data of SDS solutions show a sharp break in its value where micelle starts to form. The estimated CMC of SDS was found to be 0.0085 mol.$L^{-1}$ at 29°C. We have considered two concentration of SDS solutions as pre-micellar region (0.005M SDS) and post-micellar (0.01M SDS) region for the volumetric, viscometric and thermodynamic properties measurements.

The studies on the solution properties of binary mixtures of Methanol + Water, Ethanol + Water, *n*-Propanol + Water and *iso*-Propanol + Water and ternary mixtures of Methanol + 0.005M SDS and 0.01M aqueous SDS, Ethanol + 0.005M SDS and 0.01M aqueous SDS, *n*-Propanol + 0.005M SDS and 0.01M aqueous SDS and *iso*-Propanol + 0.005M SDS and 0.01M aqueous SDS solutions, show strong solute–solvent interactions in water and aqueous-SDS region, the water molecules form highly ordered structures through hydrogen bonding around the hydrocarbon moieties of alcohols. The values of excess molar volumes for all the systems are negative and showing minima at water 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 the water rich region. The position of maxima does not change with the variation of temperature. The excess viscosities values are found to be positive and large in magnitude, indicating that the aqueous solutions of alcohols are highly non ideal. The viscometric data are consistent with the volumetric properties data. The interaction parameters were found to be positive in magnitude indicating strong solute-solvent interaction.

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

The shallow minima occurring at ~ 0.9 mole fraction of *iso*-Propanol, seen to be somewhat prominent at lower temperatures. This is due to the the formation of "centrosymmetric" associates.

Although the value of density and viscosity of the studied systems in pre-micellar and post-micellar aqueous SDS solutions (0.005M SDS and 0.01M SDS) are higher than the pure water solutions, but no appreciable change in the volumetric and viscometric properties are observed by the addition of the surfactants.

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